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Title	Structural studies of 2-, 3- and 4-pyridinecarboxylic acid methyl esters by gas-phase electron diffraction and ¹ H-NMR using a liquid crystal solvent
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Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第4006号
Issue Date	1997-03-25
DOI	https://doi.org/10.11501/3122164
Doc URL	https://hdl.handle.net/2115/32569
Type	doctoral thesis
File Information	4006.pdf



**Structural studies of 2-, 3- and 4-pyridinecarboxylic
acid methyl esters by gas-phase electron diffraction
and ^1H -NMR using a liquid crystal solvent**

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Hokkaido University

1997

Acknowledgments

The author is greatly indebted to Professor Shigehiro Konaka for his advice and encouragement on both experimental and theoretical aspects.

The author is indebted to Professor Fukashi Sasaki, Professor Tamotsu Inabe and Professor Shun-ich Ikawa for their valuable suggestions and critical reading of the manuscript.

The author wishes to acknowledge Dr. Toru Egawa for his technical assistance in the experiments and valuable advice in the analyses of gas electron diffraction data, Dr. Hiroshi Takeuchi for his valuable advice for the data analyses of gas electron diffraction and NMR.

The author thanks all members of Professor Konaka's laboratory, especially Dr. Hideo Fujiwara, Dr. Nobuhiko Kuze for their valuable advice for experiments and data analysis of gas electron diffraction, Mr. Jun-ichiro Enmi for valuable and interesting discussion in NMR data analysis, Mr. Kenji Tonan for his valuable advice in the discussion of the molecular structures, Mr. Ryousuke Tatsunami and Mrs. Teruyo Kurai for gas electron diffraction experiments.

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Chapter 1

General introduction

1-1 Purpose of this study

In the gas phase, structural data are scarce for a series of ring compounds consisting of three or more structural isomers which are only different in the positions of substituents [1-3]. It is interesting to study the structural similarity of these isomers. 2-, 3- and 4-Pyridinecarboxylic acid methyl esters, which are also called as methyl picolinate, methyl nicotinate and methyl isonicotinate, respectively, have flexible and asymmetric structures as shown in Fig. 1-1. A few conformational studies have been reported [4, 5] but no experimental data are available for the bond lengths and angles of these isomers. In methyl isonicotinate (MI), methyl nicotinate (MN) and methyl picolinate (MP), the molecular structure should change with the position of nitrogen atom. It is interesting to observe the differences in the bond lengths and angles. The difference in the conformational compositions is also interesting, for both MN and MP are expected to have two different conformers due to the internal rotation of the C-C bond connecting the pyridine ring and the COOCH₃ group. These isomers are biochemically interesting substances. Especially, the structural study of MN is considered to be important in biochemistry because nicotinic acid is an anti-pellagra factor as well as a component of the vitamine B complex.

The molecular structure of a free molecule can be determined precisely by gas-phase electron diffraction. On the other hand, molecular structure and conformation can be studied by NMR using nematic liquid crystals as solvents (LCNMR) [6, 7]. The structure of a solute molecule generally differs from that of a free molecule. This is due to the solute-solvent interaction

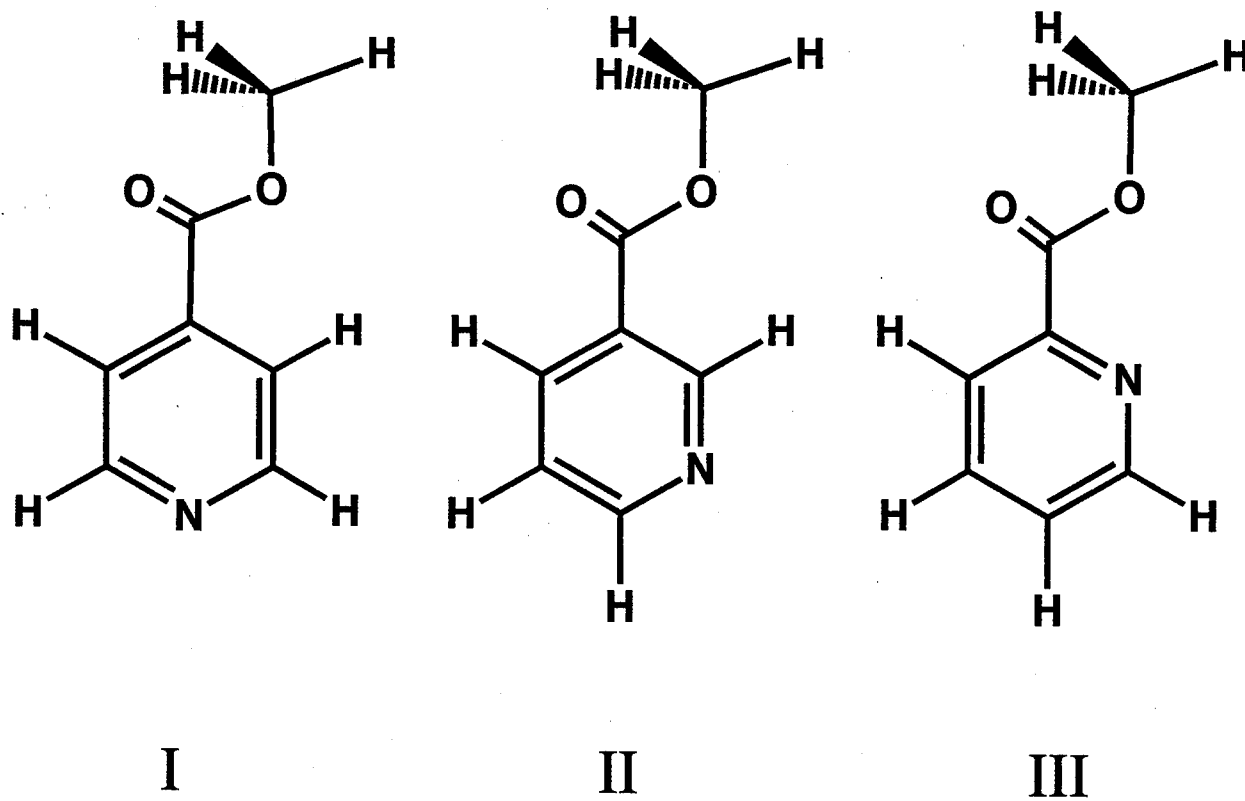


Fig. 1-2. Molecular models of methyl isonicotinate (I), methyl nicotinate (II) and methyl picolinate (III).

but its nature is not yet well understood [8-13]. If the solute molecule has degrees of freedom for internal rotation, it is expected that its conformation is liable to be influenced by the interaction, but little is known about the conformational change. Comparison of the conformation in the gas phase with that in a liquid crystal solvent will provide us with the information on the solute-solvent interaction.

The principal purpose of this thesis is to determine the molecular structures of 2-, 3- and 4-pyridinecarboxylic acid methyl esters by gas-phase electron diffraction (GED) and to determine the conformational compositions of these compounds in the gas-phase and the meso-phase by GED and LCNMR, respectively.

GED is a powerful method to determine the structures of free molecules [14, 15]. However, the molecular structures of MI, MN and MP are difficult to be determined by GED alone because each molecule has many closely spaced interatomic distances. Precise determination of conformational compositions is also difficult because the atomic scattering factors of carbon and nitrogen are similar. For this reason, vibrational spectroscopic data and ab initio calculations are combined with the data of GED in the present study. Accurate mean amplitudes and shrinkage corrections must be used for resolving similar distances. Therefore normal coordinate analyses have been performed on the gas-phase vibrational frequencies to derive harmonic force constants, which are used to calculate mean amplitudes and shrinkage corrections. In addition, ab initio calculations have been performed to obtain structural constraints in the data analyses of GED [16].

Molecular structures can also be determined precisely by LCNMR. Distances between any nuclei with spin 1/2 can be determined precisely by LCNMR. Especially interproton distances can be obtained easily by this method [6, 7].

In the present study, the conformational analyses of MI, MN and MP are carried out by ^1H -NMR using liquid crystal solvent, ZLI 1167. Two different analyses are performed. In the first one, the correlation between reorientational motion and internal rotation is neglected (effective order method). In the second the correlation is taken into account according to the theory of Emsley, Luckhurst and Stockley (ELS) [8, 17, 18]. In the present study, the skeletal structures determined by GED are used in conformational analyses. Furthermore, vibrational corrections are calculated from harmonic force constants. Determined conformational compositions are compared with those in the gas phase.

The principles of GED and LCNMR are outlined in the following two sections.

1-2 Gas-phase electron diffraction

In usual experiments, the incident electrons of about 40 keV energy are scattered by sample gas and diffraction patterns are recorded on photographic plates. Molecular scattering intensities, $sM(s)$, are derived from the electron diffraction patterns as follows,

$$sM(s)^{\text{obs.}} = s(I_T / I_B - 1). \quad (1-1)$$

In this equation, I_T is the total scattering intensity, I_B is the background and s is defined by

$$s = (4\pi/\lambda) \sin(\theta/2) \quad (1-2)$$

where λ is the wavelength of electrons and θ is the scattering angle. Theoretical molecular scattering intensities are given by

$$sM(s)^{\text{theor.}} = k \sum_{i \neq j} C_{ij} \mu_{ij} \cos \Delta \eta_{ij} \frac{\sin s(r_{aij} - \kappa_{ij}s^2)}{s r_{aij}} \exp(-\frac{1}{2} l_{ij}^2 s^2) \quad (1-3)$$

where r_{aij} is the distance between i th and j th atoms, l_{ij} is the vibrational mean amplitude of r_{aij} , k is the index of resolution and κ is the asymmetry parameter due to vibrational anharmonicity. C_{ij} and μ_{ij} are defined as,

$$C_{ij} = Z_i Z_j / \sum_k (Z_k^2 + Z_k) \quad (1-4)$$

and

$$\mu_{ij} = \frac{\sum_k (Z_k^2 + Z_k)}{Z_i Z_j} \frac{|f_i(s)| |f_j(s)|}{\sum_k \left\{ |f_k(s)|^2 + \left(\frac{2}{as^2} \right)^2 S_k(s) \right\}} \quad (1-5)$$

where Z_i is the atomic number, a is the relativistic Bohr radius, f_i is the complex atomic scattering factor for elastic electron scattering and S_k is the atomic scattering factor for inelastic X-ray scattering. Structural parameters are

determined by least-squares calculations on observed $SM(s)$. The r_a distances directly derived from $SM(s)$ have no physical meaning but they can easily be converted to thermal average distances, r_g :

$$r_g = r_a + l^2/r_a \quad (1-6)$$

Radial distribution function, $f(r)$, is given by

$$f(r) = \int_0^{s_{\max}} SM(s) \exp(-bs^2) \sin(sr) ds \quad (1-7)$$

Here an artificial damping factor, $\exp(-bs^2)$, is introduced to reduce the truncation effect, for no experimental $SM(s)$ is available for s -values larger than $s_{\max}$. In the present study, the value of b is chosen so as to satisfy the following condition [15]:

$$\exp(-bs_{\max}^2) = 0.1 \quad (1-8)$$

1-3 NMR using liquid crystal solvents

Nuclear magnetic resonance (NMR) using nematic liquid crystals as solvents has been used to study the molecular structure and the conformation of solute molecules [6, 7]. Orientational order parameters can also be determined. The molecules forming nematic liquid crystals align in a strong magnetic field because of the diamagnetic anisotropy of molecules. When a solute is dissolved in a nematic liquid crystal solvent, solute molecules interact with the ordered

nematogens and the solute molecules become partially oriented. The NMR spectrum of the solute dissolved in a liquid crystal solvent is generally very complex because of direct coupling constants. Direct coupling constants represent the through-space interaction between nuclear magnetic moments.

Direct coupling constant, D_{ij} , is related to internuclear vector and orientational order parameters as follows;

$$D_{ij} = -\gamma_i \gamma_j h \left\{ S_{zz} (3l_{ijz}^2 - 1) + (S_{xx} - S_{yy}) (l_{ijx}^2 - l_{ijy}^2) + S_{xy} l_{ijx} l_{ijy} + S_{yz} l_{ijy} l_{ijz} + S_{xz} l_{ijx} l_{ijz} \right\} / 8\pi^2 r_{ij}^3 \quad (1-9)$$

where r_{ij} is the distance between i th and j th nuclei, $l_{ij\alpha}$ is the direction cosine of the vector r_{ij} with respect to the α axis of the molecular fixed coordinate and γ is the gyromagnetic ratio. Order parameter, $S_{\alpha\beta}$, is defined by

$$S_{\alpha\beta} = (1/2) \left(3 \cos\theta_{\alpha Z} \cos\theta_{\beta Z} - \delta_{\alpha\beta} \right) \quad (1-10)$$

where $\theta_{\alpha Z}$ is the angle between the α axis of molecular fixed coordinate and the direction of applied magnetic field, Z , and $\delta_{\alpha\beta}$ is Kronecker's delta. Therefore the direct coupling constant gives the molecular structure and order parameters. The spectrum complexity increases with the number of interacting nuclei. It is difficult to analyse the spectrum of the solute molecule with more than 8 or 9 interacting nuclei.

Molecular vibration affects direct coupling constants [6],

$$D_{ij}^{\text{obs}} = D_{ij}^{\alpha} + \Delta D_{ij} \quad (1-11)$$

where D_{ij}^{obs} denotes the observed value, D_{ij}^{α} the direct coupling constant in the r_{α} structure and ΔD_{ij} vibrational correction. Vibrational corrections can be calculated from harmonic force constants. Vibrational corrections have been neglected not only in early reports but also in recent publications [9, 19-21].

The rapid internal rotation compared with the NMR time scale causes the averaging of dipolar couplings. The observed direct coupling constant of the solute molecule with an internal rotor is averaged with respect to the angle of internal rotation, ϕ . In the semiclassical treatment of large-amplitude torsional motion, D_{ij} can be written as

$$D_{ij} = \int p(\phi) D_{ij}(\phi) d\phi \quad (1-12)$$

where

$$p(\phi) = \frac{\exp(-V(\phi)/RT)}{\int \exp(-V(\phi)/RT) d\phi} \quad (1-13)$$

and $V(\phi)$ is the potential energy function for internal rotation. the data analysis is simple if the correlation between orientational motion and internal rotation is negligible. However, the correlation must be taken into account according to the studies of Emsley, Luckhurst and Stockley [8, 17, 18] and Diehl et al. [9].

1-4 Chapters of this thesis

This thesis consists of six chapters. Following the general introduction written in this chapter, Chapters 2, 3 and 4 describe the gas-phase electron diffraction studies of MI, MN, and MP, respectively. In Chapter 4, the gas-phase molecular structures of MI, MN and MP are compared with one other. The origin of the differences in the molecular structures of the three compounds is discussed. Chapter 5 describes the measurement and analyses of the ^1H -NMR spectra of MI, MN and MP dissolved in a liquid crystal, ZLI 1167. Conformational analyses are carried out and resultant conformational compositions are compared with the experimental values in the gas phase. Chapter 6 is a summary of this thesis.

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Chapter 2

**Structural study of methyl isonicotinate by gas
electron diffraction combined with ab initio
calculations**

2-1 Introduction

The conformational study of methyl isonicotinate (MI) in a liquid crystal solvent was performed by using NMR spectroscopy combined with ab initio calculations [1]. In this study, the molecular structure was estimated from the RHF/4-21G ab initio calculations and it was concluded that the planar form as shown in Fig. 2-1 was a single stable conformer. However, no experimental data is available for the bond lengths and angles of MI.

We have examined the gas-phase molecular structures of some esters of carboxylic acids, i.e., ethyl acetate [2], isopropyl acetate [3], t-butyl acetate [4] and methyl acrylate [5]. It has been found that the geometry of the COO moiety of the ester group is very sensitive to substituents through steric and electronic effects. Therefore the present study has been undertaken to determine the molecular structure of MI by gas electron diffraction (GED).

Since there are many bonded atomic pairs with similar distances in MI, structure determination is not straightforward. In the present study, ab initio calculations have been performed by using 4-21G and 6-31G* basis sets and the results are used in diffraction data analysis.

2-2 Experimental

A commercial sample with a purity of better than 99% (Tokyo Chemical Industry Co., Ltd.) was used with no further purification. A high-temperature nozzle was used [6] to obtain vapor pressure enough for the experiment. The temperature of

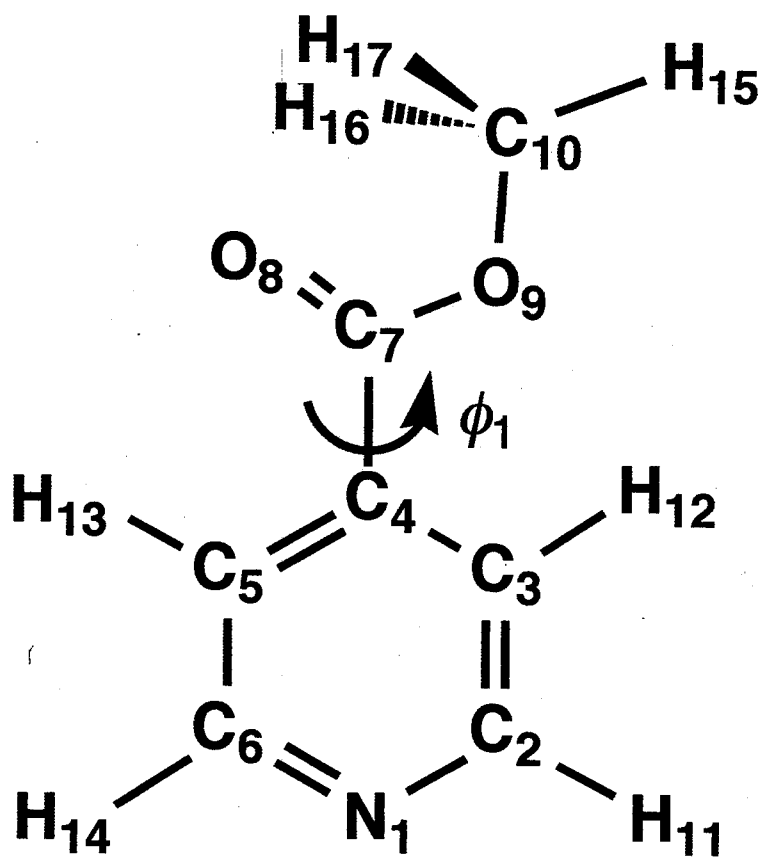


Fig. 2-1. Atom numbering of a conformer of methyl isonicotinate. ϕ_1 denotes the C₃C₄C₇O₉ torsional angle.

nozzle tip was measured to be 367 K. Electron diffraction patterns were recorded on 8 × 8 inch Kodak projector slide plates by using an apparatus equipped with an r^3 -sector [7]. The acceleration voltage of electrons was about 37 kV. Diffraction patterns of carbon disulfide were recorded at room temperature in the same sequence of exposures using another nozzle and the electron wavelength was calibrated to $r_a(\text{C-S})$ distance (1.5570 Å) [8]. Other experimental conditions were as follows: camera distance, 244.4 mm; electron wavelength, 0.06351 Å; beam current, 2.7 μA ; background pressure during exposure, 1.9×10^{-6} Torr; exposure time, 40 ~ 45 s; range of s -value, 4.2 ~ 33.7 Å⁻¹; uncertainty in the scale factor (3σ), 0.1 %.

Optical densities were measured by using a microphotometer of a double-beam autobalanced type at intervals of 100 μm along the diameter. Five optical densities were averaged and thus the densities taken at intervals of 500 μm were converted to intensities. The intensities obtained for four plates were averaged. Elastic and inelastic scattering factors were taken from refs. [9] and [10], respectively.

A vapor-phase IR spectrum between 600 ~ 3600 cm^{-1} was measured at room temperature on a BOMEM DA3.16 Fourier transform spectrometer with a resolution of 0.5 cm^{-1} . Sample pressure was about 0.4 Torr. An absorption cell with a 10 m path length and KBr windows was used. Observed vibrational frequencies are listed in Table 2-1.

Table 2-1

Observed and calculated vibrational wavenumbers (cm^{-1}) and assignment of methyl isonicotinate

$\nu_{\text{obs}}^{\text{a}}$	ν_{calc}	Assignments ^b	
3098vw	3096	A'	C-Hring str.(99)
3079vw	3079	A'	C-Hring str.(99)
3048sh	3054	A'	C-Hring str.(103)
3041w	3049	A'	C-Hring str.(99)
3007w	3006	A'	CH ₃ asym. str.(99)
2965m	2979	A''	CH ₃ asym. str.(100)
2857w	2904	A'	CH ₃ sym. str.(101)
1759vs	1753	A'	C=O str.(92)
1601w	1605	A'	C-Cring str.(68) + C-Hring in-plane bend.(27)
1571w	1573	A'	C-Cring str.(57) + C-N str.(26)
1566w			
1495vw	1499	A'	C-Hring in-plane bend.(73) + C-N str.(19) + C-C(in ring) str.(15)
1462vw	1469	A'	CH ₃ asym. def.(89)
1446m	1458	A'	CH ₃ asym. def.(95)
1413m	1425	A'	CH ₃ sym. def.(81)
1406m	1414	A'	C-Hring in-plane bend.(59)
1326m	1347	A'	C-Hring in-plane bend.(80)
1287vs	1301	A'	Cring-C str.(32) + ring def.(26) + C-O str.(22) + CH ₃ sym. def.(12)
1249m	1233	A'	C-Hring in-plane bend.(44) + ring

			def.(15) + C-N str.(12)
1214w	1191	A'	C-O str.(29) + CH ₃ rock.(26) + ring def.(18)
1198w	1176	A'	CH ₃ rock.(50) + ring def.(19)
1123s	1143	A'	CH ₃ rock.(92)
	1108	A'	C-N str.(57) + C _{ring} -C str.(31) + C-H _{ring} in-plane bend.(44)
	1106	A'	C-C(in ring) str.(28) + C-H _{ring} in- plane bend.(25) + C-N str.(19) + O-C _{Me} str.(17)
1069w	1073	A'	C-C(in ring) str.(123) + C-N str.(32)
993w	1011	A'	C-N str.(50) + ring def.(12)
981w	986	A''	C-H out-of-plane bend.(126)
979w	975	A''	C-H out-of-plane bend.(112) + ring tor.(33)
	971	A'	O-C _{Me} str.(64) + C-C(in ring) str.(23)
851vw	870	A''	C-H _{ring} out-of-plane bend.(108)
832vw	839	A''	C-H _{ring} out-of-plane bend.(59) + C _{ring} -C out-of-plane bend.(20) + C=O out-of-plane bend.(21)
824vw	809	A'	C-O str.(25)+ O-C=O def.(22) + C-O-C _{Me} bend.(18)
759m	739	A''	ring tor.(52) + C-H _{ring} out-of- plane bend.(50) + C=O out-of-plane bend.(30)
707m	686	A''	ring tor.(109)+ C=O out-of-plane

			bend.(26)
677m	661	A'	ring def.(57) + O-C=O def.(18)
	640	A'	ring def.(88)
	493	A'	O-C=O rock.(48) + C _{ring} -C in-plane bend.(14) + C-C(in ring) str.(11)
	450	A"	ring tor.(103) + C _{ring} -C out-of- plane bend.(55)
	386	A"	ring tor.(142) + C-Hring out-of- plane bend.(21)
	346	A'	ring def.(33) + C _{ring} -C str.(26) + C-O-C _{Me} bend.(14)
	311	A'	C-O-C _{Me} bend.(45) + O=C-O def.(30) + C _{ring} -C in-plane bend.(26)
	207	A"	C-O tor.(50)+ ring tor.(29) + C- Hring out-of-plane bend.(13)
	160	A'	C _{ring} -C in-plane bend.(43) + O=C-O rock.(27) + C-O-C _{Me} bend.(15)
	126	A"	O-C _{Me} tor.(65)
	104	A"	C-O tor.(32) + O-C _{Me} tor.(30) + C _{ring} -C out-of-plane bend.(23)
	74	A"	C _{ring} -C tor.(82)

^a Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

^b Numbers in parentheses denote potential energy distribution(%).

2-3 Ab initio calculations

Ab initio calculations were performed for the planar form shown in Fig. 2-1 with the program GAUSSIAN 92 [11]. Molecular structure was optimized at the RHF/6-31G* level [12] and the result is listed in Table 2-2. We examined the differences in similar bond lengths and angles. In the 6-31G* structure, the values of $|r(N_1-C_2) - r(N_1-C_6)|$, $|r(C_2-C_3) - r(C_6-C_5)|$, $|r(C_3-C_4) - r(C_5-C_4)|$ and $|r(C_2-C_3) - r(C_3-C_4)|$ are below 0.002 Å and those of $|\angle N_1C_2C_3 - \angle N_1C_6C_5|$ and $|\angle C_2C_3C_4 - \angle C_6C_5C_4|$ are below 0.2°. Such small differences are usually undetectable by GED. Therefore it is a reasonable assumption in GED data analysis that the pyridine ring has C_{2v} symmetry and that $r(C_2-C_3)$ equals $r(C_3-C_4)$.

Cartesian force constants were calculated at the optimized RHF/4-21G structure [1].

2-4 Normal coordinate analysis

The Cartesian force constants given by the 4-21G ab initio calculations were transformed to internal force constants, which were then scaled to reproduce the observed vibrational frequencies. We used the linear scaling formula [13]: $f_{ij}(\text{scaled}) = (c_i c_j)^{1/2} f_{ij}(\text{unscaled})$, where c_i 's are the scale factors. Definition of the internal coordinates, quadratic force constants and scale factors for calculated force constants are listed in Tables A2-1, A2-2 and A2-3, respectively, in Appendix. Mean amplitudes and shrinkage corrections were calculated from the scaled force constants. Calculated mean amplitudes are listed in Table 2-3.

Table 2-2

Optimized r_e structures of methyl isonicotinate^a

	6-31G* ^b	4-21G ^c
Bond lengths(Å)		
$r(N_1-C_2)$	1.320	1.333
$r(N_1-C_6)$	1.321	1.333
$r(C_2-C_3)$	1.386	1.382
$r(C_6-C_5)$	1.384	1.381
$r(C_3-C_4)$	1.385	1.383
$r(C_5-C_4)$	1.386	1.383
$r(C_4-C_7)$	1.497	1.487
$r(C_7=O_8)$	1.189	1.207
$r(C_7-O_9)$	1.320	1.351
$r(O_9-C_{10})$	1.419	1.460
$\langle r(C-H_{ring}) \rangle^d$	1.074	1.069
$\langle r(C-H_{Me}) \rangle^d$	1.080	1.077
Bond angles(°)		
$\angle C_2N_1C_6$	118.0	119.0
$\angle N_1C_2C_3$	123.6	122.6
$\angle N_1C_6C_5$	123.4	122.4
$\angle C_2C_3C_4$	118.2	118.1
$\angle C_6C_5C_4$	118.2	118.3
$\angle C_3C_4C_5$	118.7	119.7
$\angle C_3C_4C_7$	122.7	122.1
$\angle C_4C_7O_8$	123.5	124.7

$\angle C_4C_7O_9$	112.8	112.5
$\angle C_7O_9C_{10}$	116.9	117.7
$\angle C_3C_2H_{11}$	120.2	120.9
$\angle C_5C_6H_{14}$	120.3	121.0
$\angle C_4C_3H_{12}$	121.3	120.4
$\angle C_4C_5H_{13}$	120.5	120.0
$\angle O_9C_{10}H_{15}$	105.7	105.3
$\angle O_9C_{10}H_{16,17}$	110.4	109.9

^a See Fig. 2-1 for the atom numbering.

^b $E = -473.3408$ Eh (hartree) (present work).

^c $E = -472.2772$ Eh (hartree) [1].

^d $\langle \rangle$ denotes averaged values.

Table 2-3

Calculated mean amplitudes, l , and interatomic distances, r_a , for methyl isonicotinate ($\text{\AA}$)^a

Atom pair	l	r_a
N ₁ - C ₂	0.047	1.341
N ₁ ... C ₃	0.054	2.415
N ₁ ... C ₄	0.064	2.800
N ₁ ... C ₇	0.071	4.289
N ₁ ... O ₈	0.087	5.036
N ₁ ... O ₉	0.089	4.952
N ₁ ... C ₁₀	0.091	6.337
C ₂ - C ₃	0.047	1.399
C ₂ ... C ₄	0.054	2.397
C ₂ ... C ₅	0.062	2.730
C ₂ ... C ₆	0.053	2.293
C ₂ ... C ₇	0.065	3.757
C ₂ ... O ₈	0.068	4.735
C ₂ ... O ₉	0.101	4.098
C ₂ ... C ₁₀	0.110	5.506
C ₂ - H ₁₁	0.077	1.096
C ₃ - C ₄	0.047	1.399
C ₃ ... C ₅	0.056	2.408
C ₃ ... C ₆	0.062	2.735
C ₃ ... C ₇	0.062	2.485
C ₃ ... O ₈	0.064	3.575
C ₃ ... O ₉	0.098	2.708
C ₃ ... C ₁₀	0.107	4.118

C ₄ - C ₅	0.047	1.399
C ₄ ... C ₆	0.054	2.401
C ₄ - C ₇	0.050	1.497
C ₄ ... O ₈	0.058	2.356
C ₄ ... O ₉	0.062	2.370
C ₄ ... C ₁₀	0.068	3.668
C ₅ ... O ₈	0.097	2.884
C ₅ ... O ₉	0.067	3.665
C ₅ ... C ₁₀	0.081	4.841
C ₆ ... O ₈	0.099	4.266
C ₆ ... O ₉	0.071	4.754
C ₆ ... C ₁₀	0.077	6.043
C ₇ = O ₈	0.038	1.204
C ₇ - O ₉	0.047	1.330
C ₇ ... C ₁₀	0.065	2.322
O ₈ ... O ₉	0.053	2.242
O ₈ ... C ₁₀	0.102	2.631
O ₉ - C ₁₀	0.050	1.429
C ₁₀ - H ₁₅	0.078	1.101

^a See Fig. 2-1 for the atom numbering. Non-bonded C ... H, N ... H, O ... H and H ... H pairs are not listed although they were included in the data analysis.

2-5 Analysis of electron diffraction data

In order to reduce the number of independent structure parameters, the following assumptions were imposed:

(1) each of the pyridine ring and the skeleton of the COOCH₃ group is planar as shown in Fig. 2-1; (2) the pyridine ring has local C_{2v} symmetry; (3) $r(\text{C}_2\text{-C}_3)$ is equal to $r(\text{C}_3\text{-C}_4)$; (4) the difference between $r(\text{C}_7\text{-O}_9)$ and $r(\text{O}_9\text{-C}_{10})$ is equal to 0.099 Å (the 6-31G* value); (5) the methyl group has local C_{3v} symmetry; (6) the C-H bond lengths of the ring are the same; (7) the difference between $r(\text{C-H}_{\text{Me}})$ and $r(\text{C-H}_{\text{ring}})$ is 0.006 Å (the 6-31G* value); (8) the C₄C₃H and C₃C₂H bond angles are equal to 120.6° (the averaged 6-31G* value); (9) the OCH bond angles are equal to 108.8° (the averaged 6-31G* value).

Assumptions (2) and (3) are based on the 6-31G* calculations as described previously. Thus adjustable structure parameters were taken to be; $r(\text{N}_1\text{-C}_2)$, $r(\text{C}_2\text{-C}_3)$, $r(\text{C}_4\text{-C}_7)$, $r(\text{C}_7=\text{O}_8)$, $r(\text{C}_7\text{-O}_9)$, $r(\text{C-H}_{\text{ring}})$, $\angle\text{C}_2\text{N}_1\text{C}_6$, $\angle\text{C}_3\text{C}_4\text{C}_5$, $\angle\text{C}_3\text{C}_4\text{C}_7$, $\angle\text{C}_4\text{C}_7\text{O}_8$, $\angle\text{C}_4\text{C}_7\text{O}_9$, $\angle\text{C}_7\text{O}_9\text{C}_{10}$ and $\phi_1^\circ(\text{C}_3\text{C}_4\text{C}_7\text{O}_9)$. Two ring bond angles, $\angle\text{N}_1\text{C}_2\text{C}_3$ and $\angle\text{C}_2\text{C}_3\text{C}_4$, depend on $r(\text{N}_1\text{-C}_2)$, $r(\text{C}_2\text{-C}_3)$, $\angle\text{C}_2\text{N}_1\text{C}_6$ and $\angle\text{C}_3\text{C}_4\text{C}_5$. Notation ϕ_1° was used for the equilibrium torsional angle.

Vibrational amplitudes and shrinkage corrections were fixed at calculated values. Asymmetry parameters were estimated by the same method as described in refs. [14, 15]. The torsion around the C₄-C₇ bond was treated as a large amplitude motion. Adjustable structure parameters and the index of resolution were determined by least-squares calculations on molecular scattering intensities for various fixed values of ϕ_1° .

2-6 Results and discussion

The molecular scattering intensities and radial distribution curves are shown in Figs. 2-2 and 2-3, respectively. Figure 2-4 shows the R-factors against the torsional angles. The torsional angle ϕ_1° was determined to be nearly zero from Fig. 2-4. It is unnatural for ϕ_1° to take a small finite value. Thus the value of ϕ_1° was concluded to be zero, which means that the molecular skeleton is planar.

Table 2-4 lists the determined molecular structure. The absolute values of correlation coefficients are less than 0.7 except for $\angle C_4C_7O_8 / \angle C_4C_7O_9 = -0.74$. A correlation matrix is listed in Table A2-4 in Appendix.

It is known that the geometries of the aromatic rings in mono-substituted benzene depend on substituents [16]. However, no systematic investigations have been made for pyridine derivatives. The $r_g(N_1-C_2)$, $r_g(C_2-C_3)$ and $r_g(C_3-C_4)$ values of pyridine are 1.344(1) Å, 1.399 Å (d.p.) and 1.398 Å (d.p.), and the $\angle_z C_2N_1C_6$, $\angle_z N_1C_2C_3$, $\angle_z C_2C_3C_4$ and $\angle_z C_3C_4C_5$ values are 116.1(2)°, 124.6° (d.p.), 117.8° (d.p.) and 119.1° (d.p.), respectively, where d.p. means a dependent parameter [17]. These values agree with the corresponding values of MI except for $\angle_z C_2N_1C_6$ within experimental errors. Therefore the effect of the substituent, $COOCH_3$, on the ring structure is generally small.

$R = \{ \sum_i W_i (\Delta SM(s)_i)^2 / \sum_i W_i (SM(s)_{obs_i}^2) \}^{1/2}$, where $\Delta SM(s)_i = SM(s)_{obs_i} - SM(s)_{calc_i}$ and W_i is a diagonal element of the weight matrix.

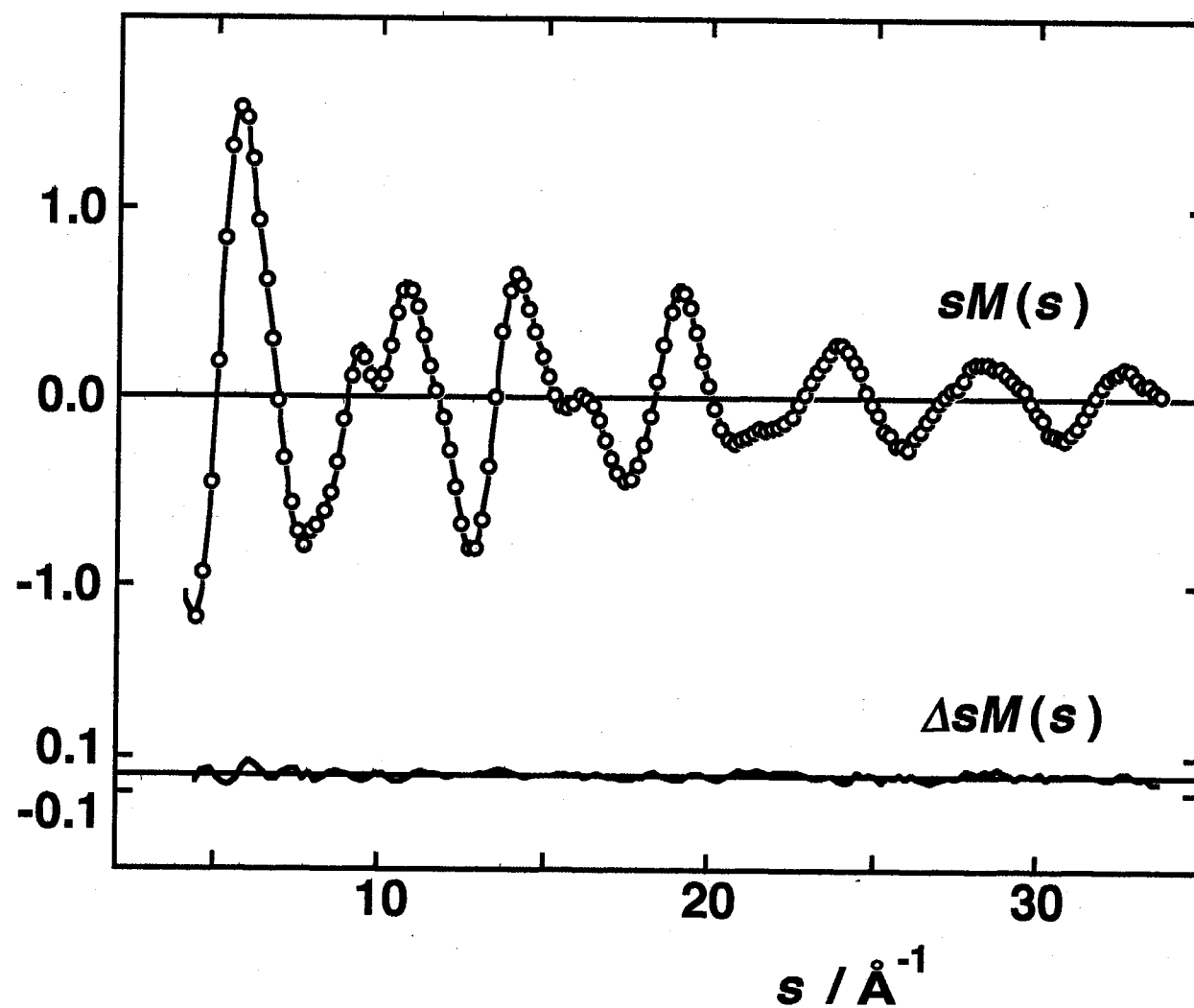


Fig. 2-2. Experimental (o) and theoretical (-) molecular scattering intensities for methyl isonicotinate; $\Delta sM(s) = sM(s)^{\text{obs}} - sM(s)^{\text{calc}}$.

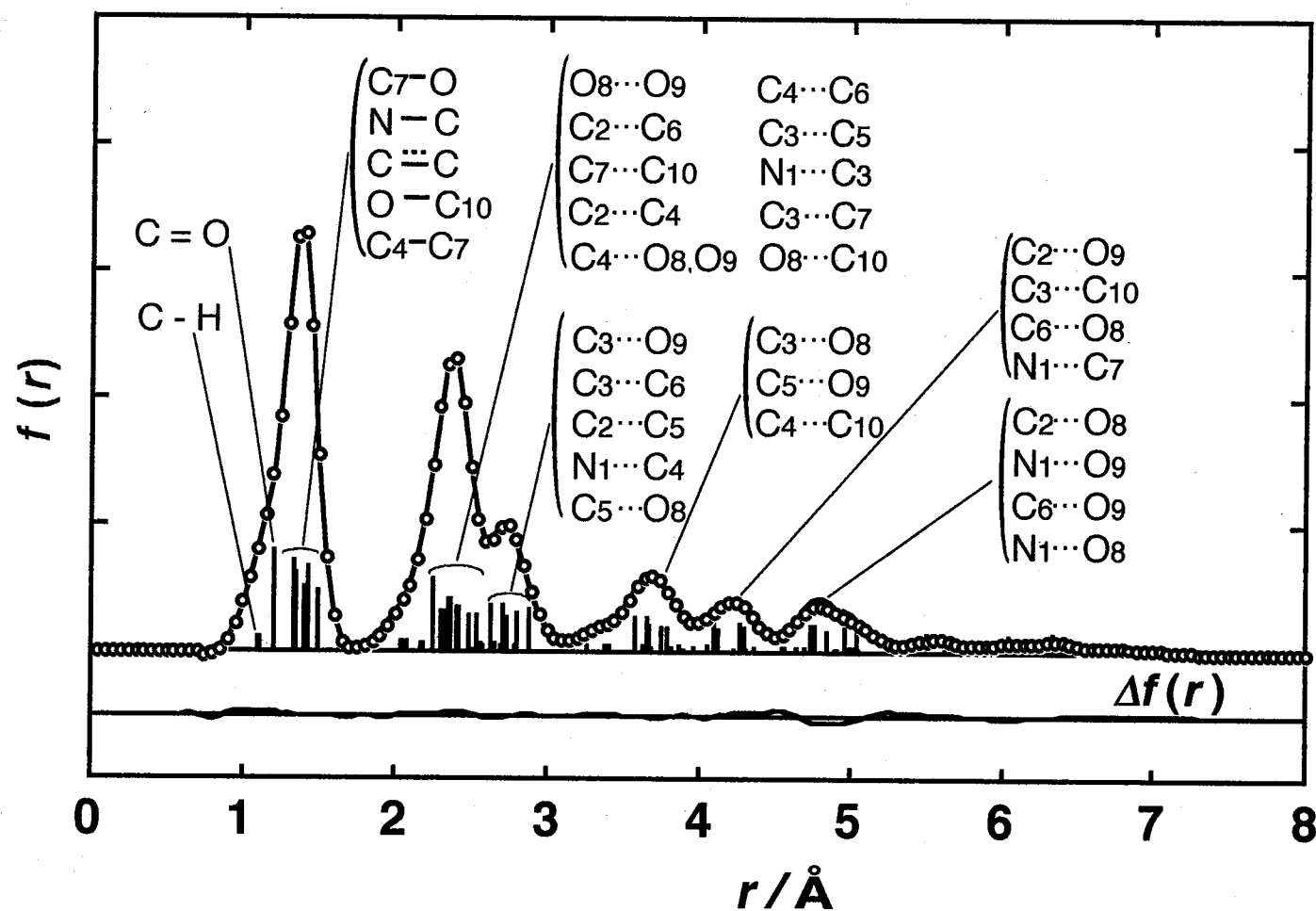


Fig. 2-3. Experimental (o) and theoretical (-) radial distribution curves for methyl isonicotinate; $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$. Vertical bars indicate atom pairs.

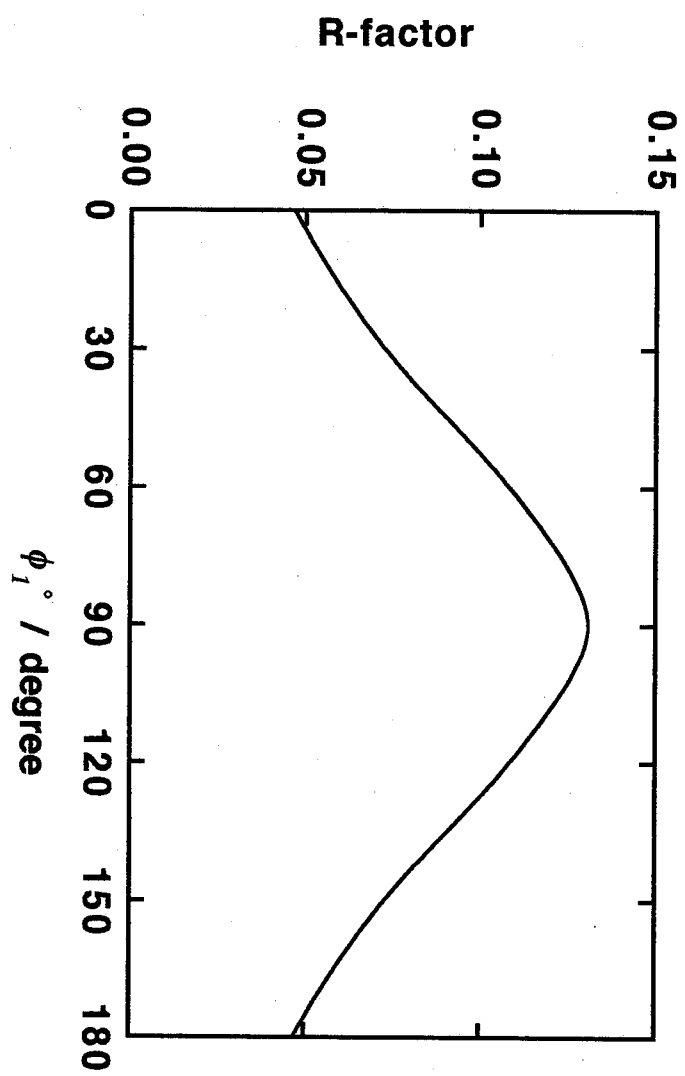


Fig. 2-4. R-factor versus ϕ_1 .

The structures of the COOCH_3 group of MI, methyl acetate [18] and methyl acrylate [5] are compared in Table 2-5. There is no significant difference in the $\text{C}=\text{O}$ bond length between MI and the others. On the other hand, the $(\text{O}=\text{C})\text{-O}$ bond length of MI is about 0.02 and 0.03 Å shorter than the corresponding bond lengths of methyl acrylate and methyl acetate, respectively. This shortening can be ascribed to conjugation of the COO moiety and the pyridine ring. The $\text{C}_7\text{-O}_9$ and $\text{C}_7=\text{O}_8$ bonds are conjugated according to the literature [5, 19, 20]. The COO moiety and the pyridine ring of MI are conjugated because the skeletal structure of MI is planar. Thus the electron delocalization in the COO moiety of MI is considered to be large compared with the case of methyl acetate. This increases the double bond character of $\text{C}_7\text{-O}_9$ bond of MI and explains the $\text{C}-\text{O}$ bond of MI is shorter than that of methyl acetate.

The $\text{CC}=\text{O}$ angle is about 4° smaller and the $\text{CC}-\text{O}$ about 3° larger than the corresponding angles of methyl acrylate and methyl acetate. This shows that the COOCH_3 tilts away from the H_{12} atom. The $\text{O}_9\cdots\text{H}_{12}$ distance, 2.36 Å, is much shorter than the $\text{O}_8\cdots\text{H}_{13}$ distance, 2.64 Å. The latter is comparable to the sum of the van der Waals radii of O and H atoms, which are 1.4 and 1.2 Å, respectively. Therefore the tilt of the COOCH_3 group can be ascribed to the steric repulsion between O_9 and H_{12} . This interpretation is consistent with the fact that the $\text{C}-\text{C}(=\text{O})$ bond distance of MI is larger than the corresponding distance of methyl acrylate.

Table 2-4

Structure parameter values for methyl isonicotinate^a

Bond lengths (Å)		Bond angles (°)	
$r_g(\text{N}_1\text{-C}_2)$	1.343 (5)	$\angle_{\alpha}\text{C}_2\text{N}_1\text{C}_6$	117.6 (9)
$r_g(\text{C}_2\text{-C}_3)$	1.401 (3)	$\angle_{\alpha}\text{N}_1\text{C}_2\text{C}_3$	123.6 ^b
$r_g(\text{C}_4\text{-C}_7)$	1.499 (9)	$\angle_{\alpha}\text{C}_2\text{C}_3\text{C}_4$	118.2 ^b
$r_g(\text{C}_7=\text{O}_8)$	1.205 (5)	$\angle_{\alpha}\text{C}_3\text{C}_4\text{C}_5$	118.7 (9)
$r_g(\text{C}_7\text{-O}_9)$	1.331	$\angle_{\alpha}\text{C}_3\text{C}_4\text{C}_7$	118.6 (12)
$r_g(\text{O}_9\text{-C}_{10})$	1.430	$\angle_{\alpha}\text{C}_4\text{C}_7\text{O}_8$	121.4 (12)
$r_g(\text{C}_2\text{-H})$	1.101	$\angle_{\alpha}\text{C}_4\text{C}_7\text{O}_9$	114.2 (10)
$r_g(\text{C}_{14}\text{-H})$	1.107	$\angle_{\alpha}\text{C}_7\text{O}_9\text{C}_{10}$	115.4 (15)
		$\angle_{\alpha}\text{C}_3\text{C}_2\text{H}$	120.6 ^c
		$\angle_{\alpha}\text{O}_9\text{C}_{10}\text{H}$	108.8 ^c
		$\phi_1^\circ(\text{C}_3\text{C}_4\text{C}_7\text{O}_9)$	0.0

^a See Fig. 2-1 for the atom numbering. Numbers in parentheses are the estimated limit of error (3σ) referring to the last significant digit. The index of resolution is 0.97(2).

^b Dependent parameter.

^c Fixed at the 6-31G* value.

Table 2-5

Molecular structures of R-COOCH₃

R	C ₅ H ₄ N ^a	H ₂ C=CH ^b	H ₃ C ^c
	$r_g / \angle_\alpha$	$r_g / \angle_z$	$r_g / \angle_z$
Bond lengths(Å)			
$r(\text{C}-\text{C})$	1.499 (9)	1.480 (6)	1.496 (7)
$r(\text{C}=\text{O})$	1.205 (5)	1.211 (2)	1.209 (6)
$r(\text{C}-\text{O})$	1.331	1.349	1.360 (6)
$r(\text{O}-\text{C}_{\text{Me}})$	1.430 } (8)	1.439 } (3)	1.442 (7)
Bond angles(°)			
$\angle \text{CC}=\text{O}$	121.4 (12)	126.1 (5)	125.5 ^d
$\angle \text{CC}-\text{O}$	114.2 (10)	110.3 (3)	111.4 (9)
$\angle \text{COC}$	115.4 (15)	116.4 (5)	116.4 (9)

^a Present work.^b The structure of the s-cis conformer determined by a joint analysis of GED data and rotational constants [5].^c Determined by a joint analysis of GED data and rotational constants [18].^d Dependent parameter.

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Appendix

Table A2-1	Definition of the internal coordinates of methyl isonicotinate.
Table A2-2	Scale factors of the force constants in the internal coordinates for methyl isonicotinate.
Table A2-3	Valence force constants of methyl isonicotinate.
Table A2-4	The correlation matrix for methyl isonicotinate.

Table A2-1

Definition of the internal coordinates of methyl isonicotinate

Coordinates		Definitions ^a
s ₁	N-C ₂ str.	r ₁ 2
s ₂	C ₂ -C ₃ str.	r ₂ 3
s ₃	C ₃ -C ₄ str.	r ₃ 4
s ₄	C ₄ -C ₅ str.	r ₄ 5
s ₅	C ₅ -C ₆ str.	r ₅ 6
s ₆	N-C ₆ str.	r ₆ 1
s ₇	C _{ring} -C str.	r ₄ 7
s ₈	C=O str.	r ₇ 8
s ₉	C-O str.	r ₇ 9
s ₁₀	O-C _{Me} str.	r ₉ 10
s ₁₁	C ₂ -H str.	r ₂ 11
s ₁₂	C ₃ -H str.	r ₃ 12
s ₁₃	C ₅ -H str.	r ₅ 13
s ₁₄	C ₆ -H str.	r ₆ 14
s ₁₅	CH ₃ sym. str.	(r ₁₀ 15 + r ₁₀ 16 + r ₁₀ 17) / √3
s ₁₆	CH ₃ asym. str.	(2r ₁₀ 15 - r ₁₀ 16 - r ₁₀ 17) / √6
s ₁₇	C ₂ -H in-plane bend.	(δ ₁ 2 11 - δ ₃ 2 11) / √2
s ₁₈	C ₃ -H in-plane bend.	(δ ₂ 3 12 - δ ₄ 3 12) / √2
s ₁₉	C _{ring} -C in-plane bend.	(δ ₃ 4 7 - δ ₅ 4 7) / √2
s ₂₀	C ₅ -H in-plane bend.	(δ ₆ 5 13 - δ ₄ 5 13) / √2

s21	C ₆ -H out-of-plane bend.	$(\delta_1 6 14 - \delta_5 6 14) / \sqrt{2}$
s22	ring def.	$(\delta_2 1 6 - \delta_3 2 1 + \delta_4 3 2 - \delta_5 4 3 + \delta_6 5 4 - \delta_1 6 5) / \sqrt{6}$
s23	ring def.	$(2\delta_2 1 6 - \delta_3 2 1 - \delta_4 3 2 + 2\delta_5 4 3 - \delta_6 5 4 - \delta_1 6 5) / \sqrt{12}$
s24	ring def.	$(\delta_3 2 1 - \delta_4 3 2 + \delta_6 5 4 - \delta_1 6 5) / 2$
s25	O-C=O def.	$(-\delta_4 7 8 - \delta_4 7 9 + 2\delta_8 7 9) / \sqrt{6}$
s26	O-C=O rock.	$(\delta_4 7 8 - \delta_4 7 9) / \sqrt{2}$
s27	C-O-C _{Me} bend.	$\delta_7 9 10$
s28	CH ₃ sym. def.	$(\delta_9 10 15 + \delta_9 10 16 + \delta_9 10 17 - \delta_{15} 10 16 - \delta_{15} 10 17 - \delta_{16} 10 17) / \sqrt{6}$
s29	CH ₃ asym. def.	$(2\delta_{16} 10 17 - \delta_{15} 10 16 - \delta_{15} 10 17) / \sqrt{6}$
s30	CH ₃ rock.	$(2\delta_9 10 15 - \delta_9 10 16 - \delta_9 10 17) / \sqrt{6}$
s31	CH ₃ asym. str.	$(r_{10 16} - r_{10 17}) / \sqrt{2}$
s32	CH ₃ sym. def.	$(\delta_{15} 10 16 - \delta_{15} 10 17) / \sqrt{2}$
s33	CH ₃ rock.	$(\delta_9 10 16 - \delta_9 10 17) / \sqrt{2}$
s34	ring tor.	$(\tau_1 2 - \tau_2 3 + \tau_3 4 - \tau_4 5 + \tau_5 6 - \tau_6 1) / \sqrt{6}$
s35	ring tor.	$(\tau_1 2 + \tau_3 4 - \tau_4 5 - \tau_6 1) / 2$
s36	ring tor.	$(-\tau_1 2 + 2\tau_2 3 - \tau_3 4 - \tau_4 5 + 2\tau_5 6 - \tau_6 1) / \sqrt{12}$

s37	C _{ring} -C tor.	τ_4 7
s38	C-O tor.	τ_7 9
s39	O-C _{Me} tor.	τ_9 10
s40	C ₂ -H out-of-plane bend.	w ₁₁
s41	C ₃ -H out-of-plane bend.	w ₁₂
s42	C _{ring} -C out-of-plane bend.	w ₇
s43	C ₅ -H out-of-plane bend.	w ₁₃
s44	C ₆ -H out-of-plane bend.	w ₁₄
s45	C=O out-of-plane bend.	w ₈

^a Abbreviations used: *r*, stretching; δ , in-plane bending; τ , torsion; *w*, out-of-plane bending. See Fig. 2-1 for the atom numbering.

Table A2-2

Scale factors of the force constants in the internal coordinates
for methyl isonicotinate

Values	Coordinates s_i ^a
0.851	1, 2, 3, 4, 5, 6
0.820	11, 12, 13, 14
0.800	18, 20
1.050	22, 26, 27, 37, 38, 39
0.815	17, 21
0.785	19
0.705	23, 24, 34, 35, 36, 40, 41, 43, 44
0.715	42
0.810	15, 16, 31, 25, 30, 33, 45
0.870	10
0.767	28, 29, 32
0.864	7, 8, 9

^a See Table A2-1 for the definition of the coordinates.

Table A2-3

Force constants in the internal coordinates for methyl isonicotinate^a

A'-block

s_i^b	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9	s_{10}	s_{11}	s_{12}	s_{13}	s_{14}	s_{15}
s_1	6.745														
s_2	1.004	6.479													
s_3	-0.602	0.784	6.625												
s_4	0.696	-0.568	0.814	6.622											
s_5	-0.666	0.568	-0.577	0.769	6.521										
s_6	0.939	-0.669	0.702	-0.604	1.011	6.761									
s_7	-0.076	-0.012	0.308	0.336	-0.027	-0.072	4.569								
s_8	-0.026	0.023	-0.028	-0.017	0.003	-0.017	0.498	12.146							
s_9	-0.013	0.001	0.012	-0.018	0.015	-0.018	0.337	1.135	5.892						
s_{10}	0.001	-0.002	0.003	0.004	-0.002	0.000	-0.068	-0.131	0.187	4.735					
s_{11}	0.185	0.072	-0.006	-0.026	-0.018	-0.017	-0.001	0.006	0.007	-0.002	5.107				
s_{12}	-0.002	0.041	0.042	-0.018	-0.013	-0.018	-0.049	-0.004	0.009	0.001	0.012	5.245			
s_{13}	-0.023	-0.016	-0.013	0.063	0.042	-0.005	-0.036	0.016	-0.002	0.001	0.001	0.000	5.185		
s_{14}	-0.018	-0.018	-0.026	-0.005	0.073	0.184	-0.001	0.007	0.006	-0.002	0.004	0.001	0.011	5.114	

s15	0.001	0.000	-0.002	0.000	0.001	-0.000	0.006	0.031	-0.068	0.194	0.000	-0.001	0.000	0.000	4.915
s16	-0.001	0.000	0.002	0.000	0.000	-0.000	0.006	-0.027	0.010	-0.028	0.000	-0.000	-0.000	0.000	0.042
s17	0.312	-0.158	-0.010	-0.000	-0.025	0.021	-0.006	-0.006	-0.003	0.001	-0.015	0.003	0.000	0.005	-0.000
s18	0.007	0.137	-0.176	-0.006	0.026	-0.021	-0.003	0.010	-0.025	-0.005	-0.001	-0.007	-0.005	0.001	0.001
s19	-0.023	0.034	0.225	-0.219	-0.031	0.012	0.009	0.027	0.001	-0.007	0.006	-0.069	0.047	-0.006	-0.002
s20	-0.023	0.026	-0.003	-0.167	0.136	0.006	0.010	-0.029	0.016	-0.005	0.001	-0.006	-0.021	-0.000	0.000
s21	0.021	-0.025	-0.001	-0.010	-0.158	0.311	-0.006	-0.003	-0.006	0.000	0.005	0.000	0.004	-0.016	-0.000
s22	0.229	0.015	0.023	0.034	0.011	0.228	0.259	0.033	0.038	-0.002	0.089	-0.116	-0.114	0.088	0.001
s23	0.369	-0.245	0.071	0.060	-0.244	0.367	-0.241	-0.053	-0.053	0.008	0.027	0.057	0.051	0.027	-0.001
s24	0.238	-0.066	-0.257	0.264	0.067	-0.247	0.007	-0.010	0.011	0.001	-0.073	0.067	-0.072	0.073	0.001
s25	0.029	-0.012	-0.062	-0.039	-0.003	0.028	-0.436	0.341	0.248	-0.132	-0.005	0.031	0.016	-0.004	-0.019
s26	-0.026	0.004	-0.026	-0.064	-0.009	0.061	-0.088	0.434	-0.517	0.012	0.003	0.070	-0.042	-0.003	-0.010
s27	0.001	0.001	0.010	0.014	-0.001	0.001	0.015	0.001	0.560	0.521	-0.001	0.012	0.001	0.000	-0.042
s28	0.001	-0.000	-0.003	0.001	0.001	-0.001	0.009	0.051	-0.078	0.566	0.001	-0.001	0.000	0.001	-0.098
s29	0.000	-0.000	-0.001	0.000	0.000	-0.000	-0.002	0.016	-0.029	-0.007	-0.000	-0.000	0.000	-0.000	0.011
s30	-0.002	0.000	0.004	0.003	-0.000	-0.000	0.005	-0.026	0.080	0.014	0.000	0.001	-0.000	0.000	0.006

A'-block(continued)

	s16	s17	s18	s19	s20	s21	s22	s23	s24	s25	s26	s27	s28	s29	s30
s16	4.842														
s17	-0.000	0.570													
s18	-0.001	0.007	0.493												
s19	0.001	-0.011	-0.005	0.915											
s20	0.000	0.001	0.012	-0.008	0.493										
s21	-0.000	0.008	0.002	0.010	0.007	0.569									
s22	0.001	0.013	0.003	-0.003	0.008	0.013	1.714								
s23	-0.002	0.065	-0.063	-0.004	-0.070	0.064	-0.040	1.124							
s24	-0.000	0.004	0.036	-0.044	-0.037	-0.003	0.001	-0.003	1.244						
s25	0.016	0.003	0.012	-0.053	-0.000	0.002	-0.054	0.080	-0.005	1.295					
s26	-0.001	-0.005	0.011	-0.094	0.010	0.006	-0.029	0.034	-0.079	0.084	1.318				
s27	0.060	0.001	-0.005	-0.029	-0.002	-0.001	0.004	0.002	0.003	-0.023	-0.066	1.347			
s28	0.004	-0.000	0.002	-0.004	0.000	-0.000	0.002	-0.003	0.001	-0.016	-0.018	0.024	0.646		
s29	-0.150	0.000	-0.000	-0.000	-0.000	0.000	-0.000	0.000	0.000	-0.017	-0.002	-0.015	-0.001	0.523	
s30	0.071	-0.000	-0.003	-0.002	0.000	-0.000	0.004	-0.003	0.000	-0.030	-0.014	0.049	-0.014	-0.036	0.815

A"-block

	s31	s32	s33	s34	s35	s36	s37	s38	s39	s40	s41	s42	s43	s44	s45
s31	4.764														
s32	0.142	0.522													
s33	0.062	0.017	0.791												
s34	-0.000	-0.000	0.000	0.320											
s35	0.001	0.000	0.000	-0.042	0.260										
s36	0.000	0.000	0.001	0.001	-0.002	0.262									
s37	-0.002	-0.001	-0.006	0.005	-0.005	-0.020	0.129								
s38	-0.021	0.005	0.020	0.004	-0.005	0.002	-0.012	0.177							
s39	-0.014	0.015	0.020	-0.000	0.000	0.000	-0.001	0.008	0.025						
s40	0.000	0.000	-0.000	0.125	0.064	-0.105	0.003	-0.001	-0.000	0.439					
s41	0.001	0.001	0.002	-0.141	0.078	0.109	-0.017	-0.002	0.000	-0.057	0.439				
s42	-0.001	-0.001	0.002	0.143	-0.153	0.003	0.026	0.012	0.001	-0.008	-0.080	0.473			
s43	0.000	0.000	-0.000	-0.144	0.083	-0.111	0.014	-0.003	0.000	-0.024	0.004	-0.089	0.446		
s44	0.000	0.000	0.000	0.124	0.064	0.104	-0.004	0.000	0.000	-0.002	-0.025	-0.008	-0.057	0.438	
s45	0.007	-0.005	0.019	0.018	-0.018	0.000	0.002	-0.000	0.003	-0.000	-0.003	0.048	-0.002	0.000	0.578

^a Units are mdyne Å⁻¹ for the stretching-stretching constants, mdyne rad⁻¹ for the stretching-bending constants and mdyne Å rad⁻² for the bending-bending and torsional-torsional constants.

^b See Table S2 for the numbering of the definition of the coordinates.

Table A2-4

Correlation matrix of methyl isonicotinate^a

	1	2	3	4	5	6	7	8	9	10	11	12	13
k^b	$r(N_1-C_2)$	$r(C_2-C_3)$	$r(C_4-C_7)$	$r(C_7=O_8)$	$r(C_7-O_9)$	$r(C_2-H_{11})$	$\angle C_2N_1C_6$	$\angle C_3C_4C_5$	$\angle C_3C_4C_7$	$\angle C_4C_7O_8$	$\angle C_4C_7O_9$	$\angle C_7O_9C_{10}$	
1	1.00												
2	-0.43	1.00											
3	0.62	-0.21	1.00										
4	0.49	0.14	0.35	1.00									
5	-0.59	0.59	-0.43	-0.19	1.00								
6	-0.31	-0.40	-0.62	-0.36	0.14	1.00							
7	-0.59	0.34	-0.48	-0.21	0.54	0.33	1.00						
8	0.09	-0.04	0.42	0.08	-0.17	-0.34	-0.14	1.00					
9	0.05	0.16	0.07	0.45	0.06	-0.10	0.00	0.04	1.00				
10	-0.10	-0.31	-0.28	-0.34	-0.09	0.40	0.10	-0.10	-0.60	1.00			
11	-0.12	-0.40	-0.28	-0.37	-0.12	0.50	0.11	0.00	-0.14	0.66	1.00		
12	-0.20	0.29	-0.07	-0.11	0.27	-0.17	0.06	0.12	0.05	-0.56	-0.74	1.00	
13	0.14	-0.03	0.26	-0.13	-0.21	-0.34	-0.10	-0.14	-0.15	0.17	0.21	-0.42	1.00

^a See Fig. 2-1 for the atom numbering.^b Index of resolution.

Chapter 3

**Structural study of methyl nicotinate by gas
electron diffraction combined with ab initio
calculations**

3-1 Introduction

The conformation of methyl nicotinate (MN) in a liquid crystal solvent has been studied by NMR spectroscopy using the molecular structure estimated from RHF/4-21G *ab initio* calculations [1]. The *s-trans* conformer has been found to be more stable than the *s-cis* conformer (see Fig. 3-1) by 0.075 kcal mol⁻¹. No experimental data, however, is available for MN in the gas phase.

We have examined the gas-phase molecular structures of some esters of carboxylic acids, i.e., ethyl acetate [2], isopropyl acetate [3], *t*-butyl acetate [4] and methyl acrylate [5]. It has been found that the geometry of the COO moiety of the ester group is very sensitive to substituents. In order to extend this series of studies to aromatic compounds, the molecular structure of methyl isonicotinate has been determined by gas electron diffraction (GED) combined with *ab initio* calculations in Chapter 2. It has been found that the (O=)C-O bond length of methyl isonicotinate is considerably shorter than the corresponding ones of methyl acetate [6] and methyl acrylate [5]. The present study has been undertaken to determine the molecular structure of MN by GED and to compare the structural parameters of MN with those of methyl isonicotinate and other related molecules.

Since there are many closely spaced interatomic distances in MN, structure determination is not straightforward. In the present study, *ab initio* calculations have been performed by using 4-21G and 6-31G* basis sets and the results are used in data analysis.

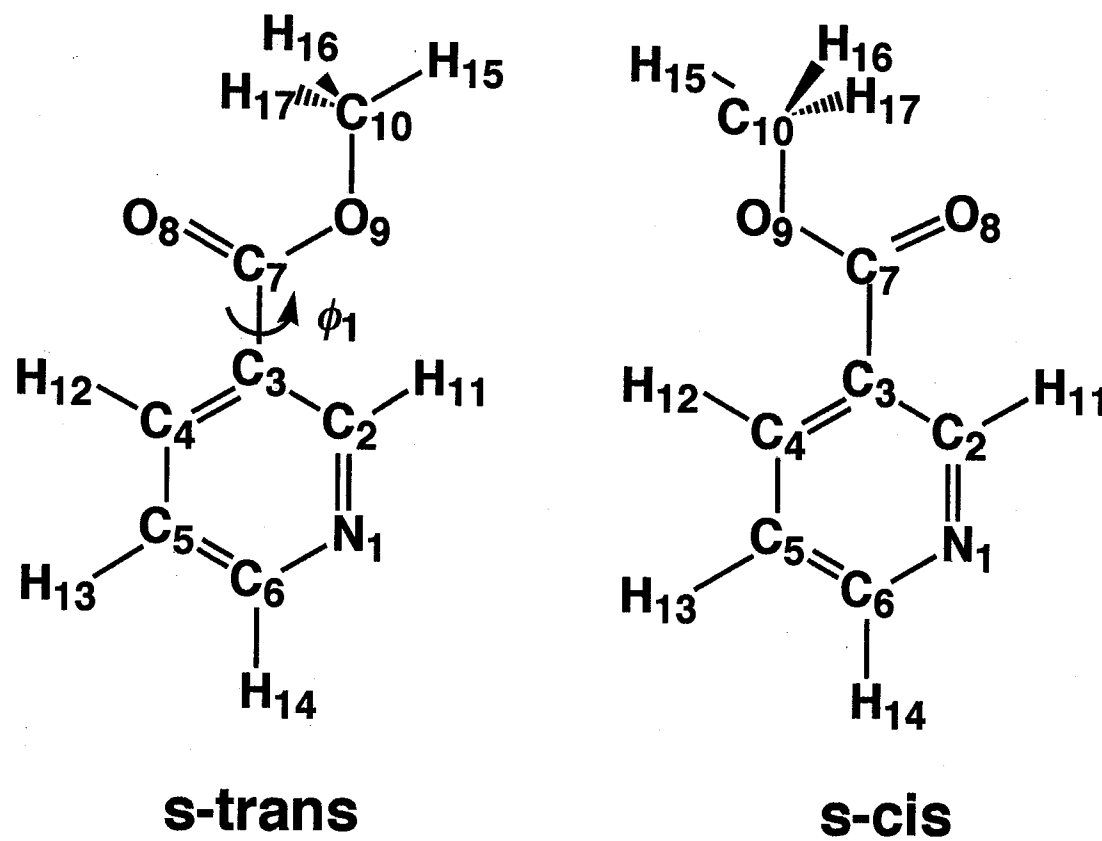


Fig. 3-1. Atom numbering of the s-trans and s-cis conformers of methyl nicotinate, where ϕ_1 denotes the C₂C₃C₇O₉ torsional angle.

3-2 Experimental

A commercial sample with a purity of better than 99% (Tokyo Chemical Industry Co., Ltd.) was used with no further purification. A high-temperature nozzle was used [7] to obtain vapor pressure enough for GED experiment. The temperature of the nozzle tip was 341 K. Electron diffraction patterns were recorded on 8 × 8 inch Kodak projector slide plates by using an apparatus equipped with an r^3 -sector [8]. The acceleration voltage of electrons was about 37 kV. Diffraction patterns of carbon disulfide were recorded at room temperature (297 K) in the same sequence of exposures using another nozzle and the electron wavelength was calibrated to $r_a(\text{C-S})$ distance (1.5570 Å) [9]. Other experimental conditions were as follows: camera distance, 244.5 mm; electron wavelength, 0.06348 Å; beam current, 2.1 μA ; background pressure during exposure, $(2.4 \sim 3.6) \times 10^{-6}$ Torr; exposure time, 51 ~ 58 s; range of s -value, $4.2 \sim 33.7 \text{ \AA}^{-1}$; uncertainty in the scale factor (3σ), 0.04%.

Optical densities were measured by using a microphotometer of a double-beam autobalanced type at intervals of 100 μm along the diameter. Five optical densities were averaged and thus the densities taken at intervals of 500 μm were converted to intensities. The intensities obtained for four plates were averaged and divided by a theoretical background. Elastic and inelastic scattering factors were taken from refs. [9] and [10], respectively.

A vapor-phase IR spectrum between $100 \sim 3500 \text{ cm}^{-1}$ was measured at the saturated vapor pressure at 320 K on a BOMEM DA3.16 Fourier transform spectrometer with a resolution of 0.5

cm^{-1} . An absorption cell with a 7 cm path length and KBr windows was used. Table 3-1 lists observed vibrational wavenumbers.

3-3 Ab initio calculations

As shown later, the molecule has a planar skeleton in gas phase. Fig. 3-1 shows the s-trans and s-cis conformers of MN and the atom numbering. Ab initio calculations were performed with the GAUSSIAN 92 program [11] at the RHF/6-31G* level [12]. The molecular structures of both conformers were optimized and the results are given in Table 3-2. The results show that the s-trans form is more stable than the s-cis form by 0.29 kcal mol^{-1} . From the energy difference, the populations of the s-trans and s-cis conformers at 341 K were evaluated to be 60 and 40%, respectively, by assuming Boltzmann distribution.

Quadratic Cartesian force constants were calculated at the RHF/4-21G level [1] to calculate mean amplitudes and shrinkage corrections.

3-4 Normal coordinate analysis

The Cartesian force constants given by the 4-21G ab initio calculations were transformed to valence force constants f_{ij} .

They were modified by using scale factors, c_i , as:

$f_{ij}(\text{scaled}) = (c_i c_j)^{1/2} f_{ij}(\text{unscaled})$ [13]. The scale factors of the two conformers were assumed to be the same. The scale factors were determined so as to reproduce the observed vibrational wavenumbers. Definition of the internal coordinates, quadratic force constants for the s-trans conformer

Table 3-1

Observed and calculated vibrational wavenumbers (cm^{-1}) and assignments of methyl nicotinate

ν_{obs}^a	ν_{calc}		S^b	Assignment ^c
	s-trans	s-cis		
3056 sh	3060	3056	A'	C-Hring str.(99)
3043 m	3043	3042	A'	C-Hring str.(98)
3025 w	3029	3034	A'	C-Hring str.(101)
3006 w	3013	3013	A'	C-Hring str.(101)
2982 w	2987	2986	A'	CH ₃ asym. str.(101)
2957 m	2959	2959	A''	CH ₃ asym. str.(100)
2907 w	2885	2885	A'	CH ₃ asym. str.(101)
1728 vs	1734	1736	A'	C=O str.(87)
1592 s	1597	1595	A'	C-Cring str.(51) + C-Hring in-plane bend.(33)
1574 m	1576	1577	A'	C-Cring str.(65) + C-Hring in-plane bend.(29)
1480 m	1487	1488	A'	C-Hring in-plane bend.(67)
1476 m	1472	1472	A'	CH ₃ asym. def.(99)
1461 sh	1461	1461	A''	CH ₃ asym. def.(95)
1438 s	1431	1436	A'	CH ₃ sym. def.(31) + C-Hring in-plane bend.(27)
1420 s	1422	1422	A'	CH ₃ sym. def.(58)
1328 m	1336	1331	A'	C-Hring in-plane bend.(81)
1288 vs	1277	1273	A'	C-O str.(30) + C _{ring} -C str.(29)
1238 sh	1219	1220	A'	C-Hring in-plane bend.(74)

1193	m	1184	1183	A'	CH ₃ asym. def.(72)
1131	sh	1144	1144	A"	CH ₃ rock.(93)
		1131	1140	A'	C-Cring str.(42) + C-N str.(31) + C-Hring in-plane bend.(22)
1113	s	1124	1118	A'	O-C _{Me} str.(29)
1089	sh	1084	1084	A'	C-Cring str.(103) + C-N str.(72)
1038	w	1031	1032	A'	C-Cring str.(35) + C-N str.(30)
1025	s	1027	1025	A"	C-H out-of-plane bend.(80)+ C _{ring} -C out- of-plane bend.(50)
1013	sh	1001	1001	A"	C-H out-of-plane bend.(85) + C _{ring} -C out- of-plane bend.(36)
994	vw	988	991	A'	ring def.(46) + C-Cring str.(30)
961	m	966	968	A"	C-Hring out-of-plane bend.(114) + ring tor.(20)
938	sh	957	949	A'	O-C _{Me} str.(45) + ring def.(31)
826	m	837	834	A"	C-H out-of-plane bend.(78) + ring tor.(25)
		802	803	A'	C-O str.(24) + O-C=O def.(21)
741	s	735	735	A"	C=O out-of-plane bend.(55) + C-H out-of- plane bend.(43)
702	m	698	697	A"	ring tor.(134) + C-Hring out-of-plane bend.(29)
		697	697	A'	ring def.(60)
620	w	611	613	A'	ring def.(90)
501	vw	511	512	A'	O-C=O rock.(40)
465	vw	440	440	A"	ring tor.(113) + C-Hring out-of-plane bend.(58)
406	vw	407	406	A"	ring tor.(131) + C-Hring out-of-plane

				bend.(22)
	355	356	A'	C _{ring} -C str.(29) + ring def.(27)
331 m	329	327	A'	C-O-C _{Me} bend.(40) + O=C-O def.(30) + C _{ring} -C in-plane bend.(27)
212 w	211	211	A''	C-O tor.(49) + ring tor.(30)
	172	174	A'	C _{ring} -C in-plane bend.(33) + O=C-O rock.(32)
	129	130	A''	O-C _{Me} tor.(64)
	107	108	A''	C-O tor.(33) + O-C _{Me} tor.(31) + C _{ring} -C out-of-plane bend.(25)
	80	78	A''	C _{ring} -C tor.(77)

^a Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

^b Symmetry of vibrational modes.

^c Assignments for s-trans conformer. Numbers in parentheses denote potential energy distribution(%). Contributions less than 20% are not shown.

Table 3-2

Results of the RHF/6-31G* calculations on methyl nicotinate^a

Parameter	s-trans ^b	s-cis ^c
Bond length (Å)		
$r(\text{N}_1\text{-C}_2)$	1.320	1.318
$r(\text{N}_1\text{-C}_6)$	1.321	1.322
$r(\text{C}_2\text{-C}_3)$	1.389	1.390
$r(\text{C}_5\text{-C}_6)$	1.386	1.385
$r(\text{C}_3\text{-C}_4)$	1.389	1.388
$r(\text{C}_4\text{-C}_5)$	1.380	1.382
$r(\text{C}_3\text{-C}_7)$	1.487	1.487
$r(\text{C}_7\text{=O}_8)$	1.191	1.190
$r(\text{C}_7\text{-O}_9)$	1.322	1.324
$r(\text{O}_9\text{-C}_{10})$	1.418	1.418
$\langle r(\text{C-H}_{\text{ring}}) \rangle^{\text{d}}$	1.074	1.074
$\langle r(\text{C-H}_{\text{Me}}) \rangle^{\text{d}}$	1.080	1.080
Bond angle(°)		
$\angle \text{C}_2\text{N}_1\text{C}_6$	117.8	117.7
$\angle \text{N}_1\text{C}_2\text{C}_3$	123.3	123.5
$\angle \text{N}_1\text{C}_6\text{C}_5$	123.8	123.8
$\angle \text{C}_2\text{C}_3\text{C}_4$	118.2	118.2
$\angle \text{C}_6\text{C}_5\text{C}_4$	118.1	118.2
$\angle \text{C}_3\text{C}_4\text{C}_5$	118.7	118.6
$\angle \text{C}_2\text{C}_3\text{C}_7$	122.8	118.7
$\angle \text{C}_3\text{C}_7\text{O}_8$	123.6	124.0
$\angle \text{C}_3\text{C}_7\text{O}_9$	113.0	112.7
$\angle \text{C}_7\text{O}_9\text{C}_{10}$	117.0	116.9

$\angle C_3C_2H_{11}$	120.3	119.5
$\angle C_3C_4H_{12}$	119.6	120.4
$\angle C_4C_5H_{13}$	121.5	121.3
$\angle C_5C_6H_{14}$	120.2	120.2
$\angle O_9C_{10}H_{15}$	105.7	105.8
$\angle O_9C_{10}H_{16}$	110.4	110.4
$\angle O_9C_{10}H_{17}$	110.4	110.4
ΔE^e	0.0	0.29

^a See Fig. 3-1 for the atom numbering.

^b $E = -473.34380$ Eh (hartree).

^c $E = -473.34335$ Eh (hartree).

^d Angled brackets denote averaged values.

^e Relative energy in kcal mol⁻¹.

and scale factors for modified force constants are listed in Tables A3-1, A3-2 and A3-3, respectively, in Appendix. The calculated wavenumbers of the s-trans conformers are not much different from those of s-cis conformer (see Table 3-1).

Mean amplitudes and shrinkage corrections were calculated from the modified force constants. Calculated mean amplitudes are listed in Table 3-3.

3-5 Analysis of electron diffraction data

In order to reduce the number of adjustable structure parameters, data analysis was performed under the following assumptions: (1) the pyridine ring and the skeleton of COOCH₃ group are planar as shown in Fig. 3-1; (2) the methyl group has local C_{3v} symmetry; (3) the C-H bond lengths in the pyridine ring are the same; (4) the C₃C₂H, C₃C₄H, C₄C₅H and C₅C₆H bond angles are equal to the 6-31G* values and the OCH bond angles are equal to the average of 6-31G* values; (5) the differences between similar parameters in each conformer are equal to the values given by the 6-31G* calculations; (6) the differences between the corresponding structural parameters of s-trans and s-cis conformers are equal to the 6-31G* values; (7) the OCH bond angles are equal to the average of 6-31G* values; (8) The C₇O₈C₁₀ bond angle of major conformer is 115.4°. The constraints on the structural parameter are summarized in Table 3-4.

In a preliminary data analysis, least squares calculations were carried out for the various values of the C₃-C₇ torsion angles and molecule is found to have a planar skeleton.

Table 3-3

Calculated mean amplitudes, l , and interatomic distances, r_a , for methyl nicotinate ($\text{\AA}$)^a

Atom pair	s-trans		s-cis	
	l	r_a	l	r_a
N1 - C2	0.046	1.332	0.046	1.330
N1 - C3	0.055	2.394	0.055	2.397
N1 - C4	0.063	2.785	0.063	2.788
N1 - C5	0.055	2.397	0.055	2.396
N1 - C6	0.047	1.333	0.047	1.334
N1 - C7	0.064	3.707	0.064	3.755
N1 - O8	0.066	4.703	0.093	4.210
N1 - O9	0.094	4.036	0.069	4.752
N1 - C10	0.104	5.441	0.075	6.017
C2 - C3	0.047	1.402	0.047	1.403
C2 - C4	0.056	2.409	0.056	2.406
C2 - C5	0.061	2.736	0.061	2.729
C2 - C6	0.054	2.294	0.054	2.290
C2 - C7	0.062	2.466	0.063	2.536
C2 - H	0.077	1.084	0.077	1.084
C2 - O8	0.062	3.554	0.090	2.889
C2 - O9	0.091	2.712	0.065	3.672
C2 - C10	0.100	4.120	0.078	4.838
C3 - C4	0.047	1.402	0.047	1.401
C3 - C5	0.056	2.400	0.056	2.399
C3 - C6	0.060	2.726	0.060	2.727
C3 - C7	0.050	1.475	0.050	1.475
C3 - O8	0.057	2.332	0.057	2.335

C3	-	O9	0.060	2.370	0.060	2.368
C3	-	C10	0.067	3.657	0.067	3.655
C4	-	C5	0.047	1.393	0.047	1.395
C4	-	C6	0.055	2.396	0.055	2.397
C4	-	C7	0.063	2.528	0.062	2.461
C4	-	O8	0.090	2.870	0.062	3.552
C4	-	O9	0.064	3.669	0.090	2.698
C4	-	C10	0.077	4.831	0.099	4.107
C5	-	C6	0.047	1.398	0.047	1.394
C5	-	C7	0.065	3.775	0.064	3.733
C5	-	O8	0.092	4.247	0.068	4.717
C5	-	O9	0.071	4.756	0.093	4.085
C5	-	C10	0.076	6.030	0.102	5.491
C6	-	C7	0.067	4.193	0.067	4.196
C6	-	O8	0.080	4.961	0.083	4.935
C6	-	O9	0.084	4.855	0.082	4.898
C6	-	C10	0.087	6.237	0.085	6.273
C7	-	O8	0.038	1.195	0.038	1.194
C7	-	O9	0.047	1.328	0.047	1.330
C7	-	C10	0.063	2.318	0.063	2.319
O8	-	O9	0.053	2.217	0.053	2.217
O8	-	C10	0.099	2.596	0.098	2.594
O9	-	C10	0.050	1.424	0.050	1.424
C10	-	H	0.079	1.090	0.079	1.090

^a See Fig. 3-1 for the atom numbering. Non-bonded C - H, N - H, O - H and H - H pairs are not listed although they were included in the data analysis.

Table 3-4

Structural parameters and constraints of methyl nicotinate^a

Parameter	s-trans	s-cis
Bond length (Å)		
$r(\text{N}_1\text{-C}_2)$	r_1	$r_1 - 0.002$
$r(\text{N}_1\text{-C}_6)$	$r_1 + 0.001$	$r_1 + 0.002$
$r(\text{C}_2\text{-C}_3)$	r_2	$r_2 + 0.001$
$r(\text{C}_3\text{-C}_4)$	r_2	$r_2 - 0.001$
$r(\text{C}_4\text{-C}_5)$	$r_2 - 0.009$	$r_2 - 0.007$
$r(\text{C}_3\text{-C}_7)$	r_3	r_3
$r(\text{C}_7\text{=O}_8)$	r_4	$r_4 - 0.001$
$r(\text{C}_7\text{-O}_9)$	r_5	$r_5 + 0.002$
$r(\text{O}_9\text{-C}_{10})$	$r_5 + 0.096$	$r_5 + 0.096$
$r(\text{C}_2\text{-H}_{11})$	r_6	r_6
$r(\text{C}_{14}\text{-H}_{15})$	$r_6 + 0.006$	$r_6 + 0.006$
Bond angle(°)		
$\angle\text{C}_6\text{N}_1\text{C}_2$	θ_1	$\theta_1 - 0.1$
$\angle\text{N}_1\text{C}_2\text{C}_3$	θ_2	$\theta_2 + 0.2$
$\angle\text{C}_5\text{C}_6\text{N}_1$	$\theta_2 + 0.5$	$\theta_2 + 0.5$
$\angle\text{C}_2\text{C}_3\text{C}_7$	θ_3	$360 - \theta_3 - \angle\text{C}_2\text{C}_3\text{C}_4$
$\angle\text{C}_3\text{C}_7\text{O}_8$	θ_4	$\theta_4 + 0.4$
$\angle\text{C}_3\text{C}_7\text{O}_9$	θ_5	$\theta_5 - 0.3$
$\angle\text{C}_7\text{O}_9\text{C}_{10}$	115.4^b	115.3^b
$\angle\text{C}_3\text{C}_2\text{H}_{11}^c$	120.3	119.5
$\angle\text{C}_3\text{C}_4\text{H}_9^c$	119.6	120.4
$\angle\text{C}_4\text{C}_5\text{H}_{10}^c$	121.5	121.3

$\angle C_5C_6H_{11}$ ^c	120.2	120.2
$\angle O_9C_{10}H$ ^d	108.8	108.8

^a See Fig. 3-1 for the atom numbering.

^b Assumed.

^c Assumed at the 6-31G* values.

^d Assumed at the average of 6-31G* values.

In the calculations, the C7O9C10 bond angle was assumed to be 115.4° because this angle considerably depends on the relative abundance of s-trans conformer. Therefore assumption (8) was introduced. The assumed value of the C7O9C10 angle was taken from the correspond bond angle of methyl isonicotinate (see Chapter 2). The C7O9C10 angle of methyl isonicotinate has been determined rather precisely, for it is essentially independent of conformation in the data analysis of GED. Adjustable structure parameters are as follows: $r(N_1-C_2)$, $r(C_2-C_3)$, $r(C_3-C_7)$, $r(C_7=O_8)$, $r(C_7-O_9)$, $r(C-H_{ring})$, $\angle C_2N_1C_6$, $\angle N_1C_2C_3$, $\angle C_2C_3C_7$, $\angle C_3C_7O_8$ and $\angle C_3C_7O_9$. Three bond angles $\angle C_2C_3C_4$, $\angle C_3C_4C_5$ and $\angle C_4C_5C_6$ depend on $r(N_1-C_2)$, $r(C_2-C_3)$, $\angle C_2N_1C_6$ and $\angle N_1C_6C_3$.

To determine the molecular skeleton of the equilibrium state, least squares calculations were performed on $SM(s)$ for various values of ϕ_1 . The best fitting was obtained for ϕ_1 values of nearly 0° and 180°. Thus the molecular skeleton was determined to be planar in the equilibrium state.

Vibrational mean amplitudes and shrinkage corrections were fixed at calculated values. Asymmetry parameters were estimated in the same way as described in refs. [14, 15]. Adjustable structure parameters and the index of resolution were determined by least-squares calculations on molecular scattering intensities.

3-6 Results and discussion

The molecular scattering intensities and radial distribution curves are shown in Figs. 3-2 and 3-3, respectively. Figure 3-4

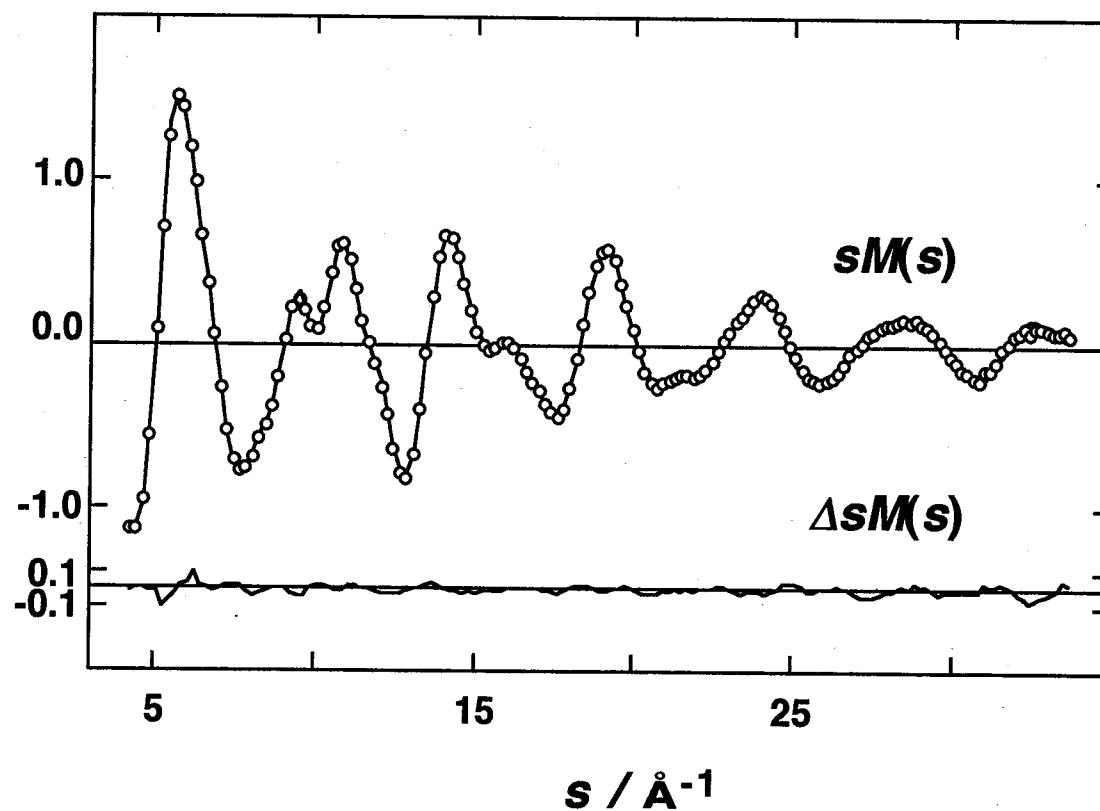


Fig. 3-2. Experimental (o) and theoretical (—) molecular scattering intensities for methyl nicotinate; $\Delta sM(s) = sM(s)_{\text{obs}} - sM(s)_{\text{calc}}$.

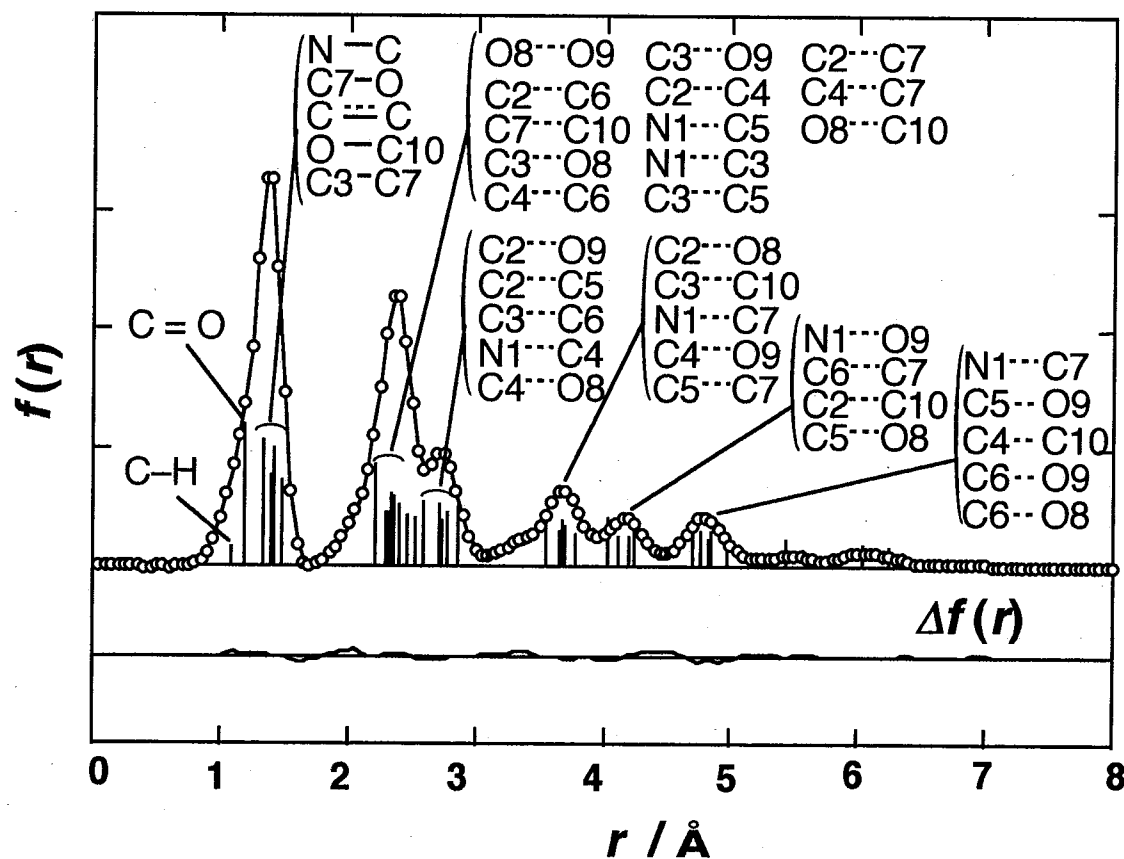


Fig. 3-3. Experimental (o) and theoretical (-) radial distribution curves for methyl nicotinate; $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$. Vertical bars indicate relatively important atom pairs of the s-trans conformer.

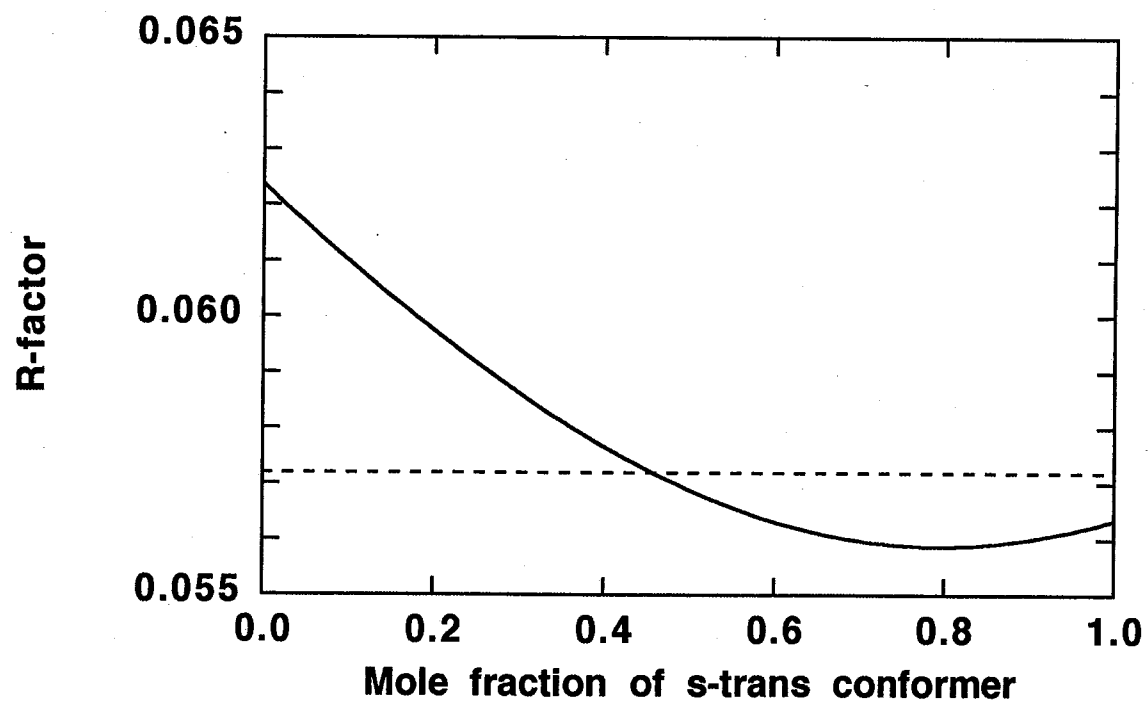


Fig. 3-4. R-factors versus the mole fraction of the s-trans conformer. Dashed line shows the 99% significant level.

shows the R-factors¹ against the mole fraction of s-trans conformer. The relative abundance of s-trans conformer was determined to be 75(25)%, which is consistent with 6-31G* calculations (60%).

Table 3-5 lists the determined structure parameters. The absolute values of correlation coefficients are less than 0.7 except for $\angle C_2N_1C_6 / \angle N_1C_2C_3$ (-0.89) and $\angle C_2C_3C_7 / \angle C_3C_7C_8$ (0.79). A correlation matrix is listed in Table A3-4 in Appendix.

The structures of the pyridine rings of MN, methyl isonicotinate (Chapter 2), and pyridine [16] are compared in Table 3-6. Estimated errors include the uncertainties due to the estimated errors $\pm 1.5^\circ$ of the $C_7O_9C_{10}$ bond. No obvious difference is found in the structures of the rings of MN and methyl isonicotinate. However some differences are found between those of MN and pyridine. The C_2-C_3 and C_3-C_4 bond length of MN are longer than corresponding bond length of pyridine.

The C_3-C_7 bond length of MN are shorter than those of methyl nicotinate. This shows that the electron more delocalize in MN than in methyl isonicotinate.

As for the structure of the $COOCH_3$ group, there is no significant difference between MN and methyl isonicotinate. The C_7-O_9 bond length of MN (1.332 Å) and that of methyl isonicotinate (1.331 Å) are considerably shorter than the corresponding bond length of methyl acetate (1.360 Å) [6].

The C_7-O_9 and $C_7=O_8$ bonds are conjugated [17, 18]. The COO moiety and pyridine ring of MN are also conjugated because MN

¹ $R = \{ \sum_i W_i (\Delta SM(s)_i)^2 / \sum_i W_i (SM(s)_{i}^{obs})^2 \}^{1/2}$, where $\Delta SM(s)_i = SM(s)_{i}^{obs} - SM(s)_{i}^{calc}$ and W_i is a diagonal element of the weight matrix.

Table 3-5

Observed structural parameters of methyl nicotinate^a

Parameter	s-trans	s-cis
Bond length (Å)		
$r_g(\text{N}_1\text{-C}_2)$	1.336	1.334
$r_g(\text{N}_1\text{-C}_6)$	1.337	1.338
	} (4)	
$r_g(\text{C}_2\text{-C}_3)$	1.405	1.406
$r_g(\text{C}_5\text{-C}_6)$	1.401	1.400
$r_g(\text{C}_3\text{-C}_4)$	1.405	1.404
$r_g(\text{C}_4\text{-C}_5)$	1.396	1.398
	} (3)	
$r_g(\text{C}_3\text{-C}_7)$	1.480 (12)	1.480 (12)
$r_g(\text{C}_7\text{=O}_8)$	1.199 (7)	1.198 (7)
$r_g(\text{C}_7\text{-O}_9)$	1.332	1.334
$r_g(\text{O}_9\text{-C}_{10})$	1.428	1.428
	} (9)	
$r_g(\text{C}_2\text{-H})$	1.092	1.092
$r_g(\text{C}_{14}\text{-H})$	1.098	1.098
	} (12)	
Bond angle (°)		
$\angle_{\alpha}\text{C}_2\text{N}_1\text{C}_6$	119.0 (12)	119.0 (12)
$\angle_{\alpha}\text{N}_1\text{C}_2\text{C}_3$	122.5	122.7
$\angle_{\alpha}\text{N}_1\text{C}_6\text{C}_5$	123.0	123.0
	} (10)	
$\angle_{\alpha}\text{C}_2\text{C}_3\text{C}_4^b$	118.5	118.4
$\angle_{\alpha}\text{C}_6\text{C}_5\text{C}_4^b$	118.6	118.6
$\angle_{\alpha}\text{C}_3\text{C}_4\text{C}_5^b$	118.5	118.5
$\angle_{\alpha}\text{C}_2\text{C}_3\text{C}_7$	118.3 (12)	123.8 (12)
$\angle_{\alpha}\text{C}_3\text{C}_7\text{O}_8$	121.5 (11)	121.9 (11)

$\angle_{\alpha}C_3C_7O_9$	115.6 (10)	115.3 (10)
$\angle_{\alpha}C_7O_9C_{10}$	115.4 ^c	115.3 ^c

^a See Fig. 3-1 for the atom numbering. The index of resolution is 0.96 (5). Parenthesized numbers are the estimated limits of error (3 σ) referring to the last significant digit. The structures of s-trans and s-cis forms are not independent (see Table 3-4).

^b Dependent parameter.

^c Assumed.

Table 3-6

Molecular structures of methyl nicotinate and related molecules^a

Parameter	Methyl nicotinate ^b	Methyl isonicotinate ^c	Pyridine ^d
	$r_g/\angle\alpha$	$r_g/\angle\alpha$	$r_g/\angle_z$
Bond lengths(Å)			
$r(N_1-C_2)$	1.336	1.343	1.344
$r(N_1-C_6)$	1.337	1.343	1.344
$r(C_2-C_3)$	1.405	1.401	1.399
$r(C_6-C_5)$	1.401	1.401	1.399
$r(C_3-C_4)$	1.405	1.401	1.398
$r(C_5-C_4)$	1.396	1.401	1.398
$r(C_3-C_7)$	1.480 (12)	1.499 (9)	
$r(C_7=O_8)$	1.199 (7)	1.205 (5)	
$r(C_7-O_9)$	1.332	1.331	
$r(O_9-C_{10})$	1.428	1.430	
Bond angles(°)			
$\angle C_6N_1C_2$	119.0 (11)	117.6 (9)	116.1
$\angle N_1C_2C_3$	122.5	123.6 ^e	124.6
$\angle N_1C_6C_5$	123.0	123.6 ^e	124.6
$\angle C_2C_3C_4$	118.5 ^e	118.2 ^e	117.8
$\angle C_6C_5C_4$	118.6 ^e	118.2 ^e	117.8
$\angle C_3C_4C_5$	118.5 ^e	118.7 (9)	119.1
$\angle C_2C_3C_7$	118.3 (11)	118.6 (12)	
$\angle C_3C_7=O_8$	121.5 (13)	121.4 (12)	

$\angle C_3C_7-O_9$	115.6 (13)	114.2 (10)
$\angle C_7O_9C_{10}$	115.4 ^f	115.4 (15)

^a Atom numbering is shown in Fig. 3-1. Parenthesized numbers are the estimated limit of error (3 σ) referring to the last significant digit.

^b The structure of s-trans conformer (present work).

^c Determined by GED combined with ab initio calculations. The pyridine ring was assumed to be C_{2v} symmetry (Chapter 2).

^d Determined by a joint analysis of GED data and rotational constants [15]. The ring structure was assumed to be C_{2v} symmetry.

^e Dependent parameter.

^f Assumed.

has a planar skeleton. Therefore the electron delocalization in the COO moiety of MN is considered to be larger than that of methyl acetate [6]. This increases the double bond character of the C₇-O₉ bond and explains that the (O=)C-O bond of MN is shorter than that of methyl acetate.

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Appendix

Table A3-1	Definition of the internal coordinates of methyl nicotinate.
Table A3-2	Scale factors of the force constants in the internal coordinates for methyl nicotinate.
Table A3-3	Valence force constants of methyl nicotinate.
Table A3-4	The correlation matrix for methyl nicotinate.

Table A3-1

Definition of the internal coordinates of methyl nicotinate

Coordinates		Definitions ^a
s ₁	N-C ₂ str.	r ₁ 2
s ₂	C ₂ -C ₃ str.	r ₂ 3
s ₃	C ₃ -C ₄ str.	r ₃ 4
s ₄	C ₄ -C ₅ str.	r ₄ 5
s ₅	C ₅ -C ₆ str.	r ₅ 6
s ₆	N-C ₆ str.	r ₆ 1
s ₇	C _{ring} -C str.	r ₃ 7
s ₈	C=O str.	r ₇ 8
s ₉	C-O str.	r ₇ 9
s ₁₀	O-C _{Me} str.	r ₉ 10
s ₁₁	C ₂ -H str.	r ₂ 11
s ₁₂	C ₄ -H str.	r ₄ 12
s ₁₃	C ₅ -H str.	r ₅ 13
s ₁₄	C ₆ -H str.	r ₆ 14
s ₁₅	CH ₃ sym. str.	(r ₁₀ 15 + r ₁₀ 16 + r ₁₀ 17) / $\sqrt{3}$
s ₁₆	CH ₃ asym. str.	(2r ₁₀ 15 - r ₁₀ 16 - r ₁₀ 17) / $\sqrt{6}$
s ₁₇	C ₂ -H in-plane bend.	(δ_1 2 11 - δ_3 2 11) / $\sqrt{2}$
s ₁₈	C _{ring} -C in-plane bend.	(δ_2 3 7 - δ_4 3 7) / $\sqrt{2}$
s ₁₉	C ₄ -H in-plane bend.	(δ_3 4 12 - δ_5 4 12) / $\sqrt{2}$
s ₂₀	C ₅ -H in-plane bend.	(δ_4 5 13 - δ_6 5 13) / $\sqrt{2}$
s ₂₁	C ₆ -H in-plane bend.	(δ_1 6 14 - δ_5 6 14) / $\sqrt{2}$
s ₂₂	ring def.	(δ_2 1 6 - δ_3 2 1 + δ_4 3 2 - δ_5 4 3

	$+ \delta_6 5 4 - \delta_1 6 5) / \sqrt{6}$
s23 ring def.	$(2\delta_2 1 6 - \delta_3 2 1 - \delta_4 3 2 + 2\delta_5 4 3 - \delta_6 5 4 - \delta_1 6 5) / \sqrt{12}$
s24 ring def.	$(\delta_3 2 1 - \delta_4 3 2 + \delta_6 5 4 - \delta_1 6 5) / 2$
s25 O-C=O def.	$(- \delta_3 7 8 - \delta_3 7 9 + 2\delta_8 7 9) / \sqrt{6}$
s26 O-C=O rock.	$(\delta_3 7 8 - \delta_3 7 9) / \sqrt{2}$
s27 C-O-C _{Me} bend.	$\delta_7 9 10$
s28 CH ₃ sym. def.	$(\delta_9 10 15 + \delta_9 10 16 + \delta_9 10 17 - \delta_{15} 10 16 - \delta_{15} 10 17 - \delta_{16} 10 17) / \sqrt{6}$
s29 CH ₃ asym. def.	$(2\delta_{16} 10 17 - \delta_{15} 10 16 - \delta_{15} 10 17) / \sqrt{6}$
s30 CH ₃ rock.	$(2\delta_9 10 15 - \delta_9 10 16 - \delta_9 10 17) / \sqrt{6}$
s31 CH ₃ asym. str.	$(r_{10} 16 - r_{10} 17) / \sqrt{2}$
s32 CH ₃ sym. def.	$(\delta_{15} 10 16 - \delta_{15} 10 17) / \sqrt{2}$
s33 CH ₃ rock.	$(\delta_9 10 16 - \delta_9 10 17) / \sqrt{2}$
s34 ring tor.	$(\tau_1 2 - \tau_2 3 + \tau_3 4 - \tau_4 5 + \tau_5 6 - \tau_6 1) / \sqrt{6}$
s35 ring tor.	$(\tau_1 2 + \tau_3 4 - \tau_4 5 - \tau_6 1) / 2$
s36 ring tor.	$(-\tau_1 2 + 2\tau_2 3 - \tau_3 4 - \tau_4 5 + 2\tau_5 6 - \tau_6 1) / \sqrt{12}$
s37 C _{ring} -C tor.	$\tau_3 7$
s38 C-O tor.	$\tau_7 9$
s39 O-C _{Me} tor.	$\tau_9 10$
s40 C ₂ -H out-of-plane bend.	w_{11}

s ₄₁	C _{ring} -C out-of-plane bend.	w ₇
s ₄₂	C ₄ -H out-of-plane bend.	w ₁₂
s ₄₃	C ₅ -H out-of-plane bend.	w ₁₃
s ₄₄	C ₆ -H out-of-plane bend.	w ₁₄
s ₄₅	C=O out-of-plane bend.	w ₈

^a Abbreviations used: *r*, stretching; δ , in-plane bending; τ , torsion; *w*, out-of-plane bending. See Fig. 3-1 for the atom numbering.

Table A3-2

Scale factors of the force constants in the internal coordinates for methyl nicotinate

Values	Coordinates s_i^a
0.830	1, 2, 3, 4, 5, 6,
0.805	11, 12, 13, 14,
0.870	19, 20,
0.760	17, 21,
1.100	18,
0.710	22,
0.750	23, 24, 34, 35, 36, 40, 41, 42, 43, 44,
0.800	15, 16, 31,
0.810	25, 30, 33, 45,
0.870	10,
0.770	28, 29, 32,
1.100	26, 27, 37, 38, 39,
0.840	7, 8, 9,

^a See Table A3-1 for the definition of the coordinates.

Table A3-3

Force constants in the internal coordinates for methyl nicotinate^a

A'-block															
s_i^b	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9	s_{10}	s_{11}	s_{12}	s_{13}	s_{14}	s_{15}
s_1	6.714														
s_2	0.956	6.332													
s_3	-0.525	0.764	6.404												
s_4	0.703	-0.543	0.748	6.504											
s_5	-0.632	0.487	-0.578	0.788	6.307										
s_6	0.882	-0.649	0.649	-0.553	0.951	6.565									
s_7	-0.032	0.316	0.351	-0.044	-0.072	-0.068	4.583								
s_8	0.052	-0.038	-0.047	0.024	-0.017	-0.047	0.530	11.666							
s_9	0.014	-0.017	-0.025	0.031	-0.027	-0.017	0.354	1.086	5.702						
s_{10}	-0.009	0.005	0.008	-0.007	0.003	0.003	-0.070	-0.127	0.183	4.754					
s_{11}	0.145	0.036	-0.015	-0.019	-0.006	-0.007	-0.044	-0.003	0.011	0.001	5.131				
s_{12}	-0.015	-0.013	0.064	0.053	0.000	-0.016	-0.036	0.016	-0.002	0.001	0.001	5.045			
s_{13}	-0.028	-0.018	-0.006	0.071	0.058	-0.011	-0.001	0.006	0.005	-0.002	0.001	0.010	5.038		
s_{14}	-0.015	-0.017	-0.027	-0.003	0.068	0.179	0.004	0.002	0.003	-0.002	0.003	0.001	0.013	4.994	
s_{15}	0.001	-0.002	-0.000	0.002	-0.001	0.000	0.006	0.031	-0.068	0.195	-0.001	0.000	0.000	0.000	4.852

S16	-0.000	0.000	0.000	0.001	-0.000	-0.001	0.007	-0.027	0.010	-0.028	0.000	-0.000	0.000	0.000	0.043
S17	0.273	-0.163	-0.010	-0.001	-0.018	0.026	-0.009	0.008	-0.024	-0.005	-0.021	-0.006	0.000	0.004	0.001
S18	0.068	0.284	-0.283	-0.033	0.027	-0.045	0.010	0.021	0.002	-0.009	-0.078	0.056	-0.006	0.002	-0.003
S19	-0.021	0.006	0.168	-0.153	-0.009	0.017	-0.013	0.032	-0.016	0.005	0.006	0.027	0.006	-0.006	-0.000
S20	0.027	-0.027	0.002	0.176	-0.156	-0.002	0.005	0.003	0.006	-0.000	-0.001	-0.006	-0.004	0.000	0.000
S21	-0.026	0.025	0.001	0.015	0.142	-0.292	-0.000	-0.003	0.001	0.000	-0.003	0.005	-0.003	0.015	-0.000
S22	0.197	-0.025	-0.026	-0.002	0.025	0.230	-0.206	-0.035	-0.038	0.004	0.076	0.088	-0.090	0.072	-0.001
S23	0.379	-0.214	0.169	0.126	-0.249	0.348	0.127	0.014	0.031	-0.001	0.008	-0.086	0.038	0.027	0.001
S24	0.254	-0.018	-0.201	0.267	0.057	-0.249	0.203	0.054	0.044	-0.005	-0.082	-0.013	-0.081	0.076	0.001
S25	-0.031	-0.060	-0.031	-0.012	0.033	0.032	-0.428	0.329	0.235	-0.132	0.030	0.016	-0.004	-0.003	-0.019
S26	-0.009	-0.064	-0.067	-0.002	0.058	-0.025	-0.075	0.449	-0.536	0.012	0.074	-0.042	-0.003	-0.000	-0.010
S27	-0.004	0.010	0.017	-0.002	0.001	0.001	0.016	0.003	0.564	0.533	0.012	0.001	0.000	-0.001	-0.043
S28	0.002	-0.004	0.000	0.003	-0.001	0.000	0.010	0.050	-0.076	0.566	-0.002	0.000	0.001	0.000	-0.098
S29	-0.001	-0.000	0.000	-0.000	-0.000	0.000	-0.002	0.016	-0.029	-0.007	-0.000	0.000	-0.000	-0.000	0.010
S30	-0.001	0.002	0.003	-0.000	-0.000	-0.002	0.005	-0.025	0.077	0.014	0.001	-0.000	0.000	-0.000	0.006

A'-block(continued)

	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	S28	S29	S30
S16	4.781														
S17	-0.001	0.524													
S18	0.001	-0.013	1.271												
S19	-0.000	-0.012	0.012	0.546											
S20	0.000	-0.002	-0.013	0.009	0.548										
S21	0.000	-0.008	-0.006	-0.010	0.007	0.533									
S22	-0.001	0.013	0.006	0.006	-0.000	-0.010	1.161								
S23	0.000	0.062	-0.048	-0.006	0.070	-0.067	-0.022	1.166							
S24	0.002	0.001	0.026	-0.085	0.042	0.005	-0.016	0.022	1.347						
S25	0.016	0.013	-0.061	0.001	-0.003	0.001	0.049	-0.039	-0.063	1.295					
S26	-0.001	0.012	-0.101	-0.013	-0.006	0.003	0.020	-0.093	0.019	0.079	1.373				
S27	0.062	-0.005	-0.031	0.002	0.001	0.000	-0.002	0.004	-0.002	-0.027	-0.075	1.408			
S28	0.004	0.001	-0.006	-0.000	0.000	-0.000	-0.002	0.002	0.002	-0.016	-0.018	0.024	0.648		
S29	-0.149	-0.000	-0.001	0.000	0.000	0.000	0.000	0.000	-0.000	-0.017	-0.003	-0.015	-0.001	0.526	
S30	0.071	-0.002	-0.002	-0.001	0.000	0.000	-0.003	0.002	0.003	-0.031	-0.015	0.050	-0.014	-0.036	0.816

A"-block

	s31	s32	s33	s34	s35	s36	s37	s38	s39	s40	s41	s42	s43	s44	s45
s31	4.701														
s32	0.142	0.525													
s33	0.062	0.017	0.791												
s34	0.000	0.000	0.000	0.334											
s35	0.000	-0.000	0.001	-0.043	0.271										
s36	-0.001	-0.000	-0.001	-0.008	0.000	0.267									
s37	-0.002	-0.001	-0.007	-0.004	-0.018	0.011	0.155								
s38	-0.022	0.005	0.019	-0.005	0.004	0.003	-0.018	0.182							
s39	-0.015	0.015	0.020	0.000	0.000	-0.000	-0.001	0.009	0.026						
s40	0.001	0.001	0.002	0.132	0.066	-0.109	-0.011	-0.001	0.001	0.483					
s41	0.000	0.000	-0.000	0.142	-0.155	-0.008	0.014	-0.003	0.000	-0.005	0.492				
s42	0.000	0.000	0.000	-0.147	0.080	-0.114	-0.004	0.001	0.000	-0.026	-0.074	0.447			
s43	0.000	0.000	0.000	0.125	0.068	0.102	-0.004	-0.000	0.000	-0.003	-0.015	-0.058	0.471		
s44	-0.001	-0.001	0.003	-0.158	0.084	0.122	0.027	0.012	0.001	-0.069	-0.092	0.001	-0.028	0.479	
s45	0.007	-0.005	0.019	-0.020	0.012	0.012	0.001	0.001	0.003	0.000	-0.002	0.003	-0.005	0.048	0.590

^a Units are m dyn Å⁻¹ for the stretching-stretching constants, m dyn rad⁻¹ for the stretching-bending constants and m dyn Å rad⁻² for the bending-bending and torsional-torsional constants.

^b See Table A3-1 for the numbering of the definition of the coordinates.

Table A3-4

Correlation matrix for methyl nicotinate^a

	1	2	3	4	5	6	7	8	9	10	11	12
k^b	$r(N_1-C_2)$	$r(C_2-C_3)$	$r(C_3-C_7)$	$r(C_7-O_8)$	$r(C_7-O_9)$	$r(C_2-H)$	$\angle C_2N_1C_6$	$\angle N_1C_2C_3$	$\angle C_2C_3C_7$	$\angle C_3C_7O_8$	$\angle C_3C_7O_9$	
1	1.00											
2	-0.33	1.00										
3	0.55	-0.00	1.00									
4	0.48	0.37	0.39	1.00								
5	-0.59	0.54	-0.34	-0.19	1.00							
6	-0.35	-0.51	-0.66	-0.61	0.12	1.00						
7	-0.57	0.32	-0.42	-0.18	0.55	0.29	1.00					
8	0.28	0.08	0.69	0.31	-0.25	-0.60	-0.29	1.00				
9	-0.16	-0.38	-0.59	-0.50	0.08	0.69	0.17	-0.89	1.00			
10	-0.12	-0.42	-0.43	-0.36	-0.08	0.58	0.12	-0.47	0.64	1.00		
11	-0.17	-0.48	-0.42	-0.48	-0.08	0.66	0.13	-0.41	0.57	0.79	1.00	
12	-0.14	0.13	0.07	-0.19	0.19	-0.20	0.01	0.27	-0.30	-0.62	-0.63	1.00

^a See Fig. 3-1 for the atom numbering.^b Index of resolution.

Chapter 4

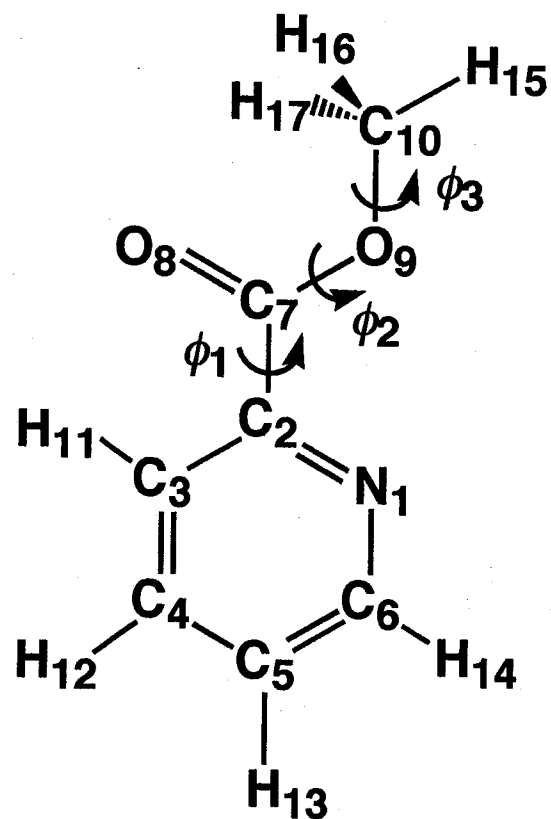
**Structural study of methyl picolinate by gas
electron diffraction combined with ab initio
calculations**

4-1 Introduction

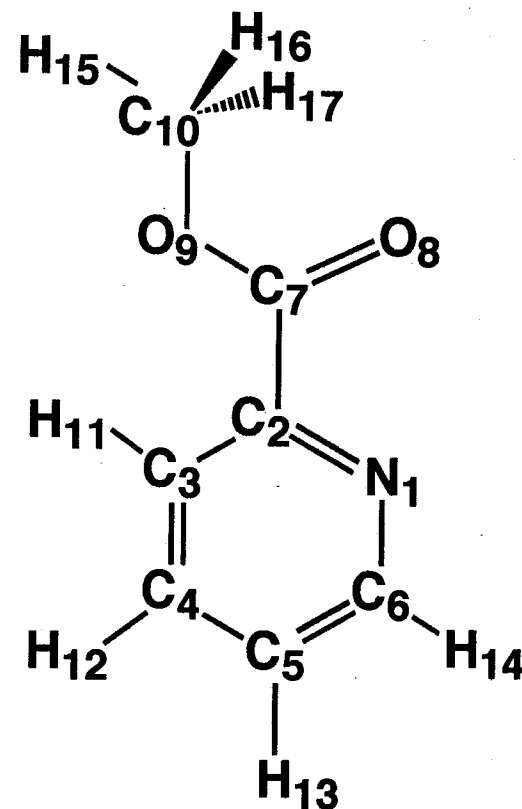
The molecular structures of carbonic acid esters, RCOOR' , are sensitive to substituents, R and R' . We have determined the molecular structures of ethyl acetate ($\text{R} = \text{Me}$, $\text{R}' = \text{Et}$) [1], isopropyl acetate ($\text{R} = \text{Me}$, $\text{R}' = i\text{-Pr}$) [2], *t*-butyl acetate ($\text{R} = \text{Me}$, $\text{R}' = t\text{-Bu}$) [3] and methyl acrylate ($\text{R} = \text{CH}_2=\text{CH}$, $\text{R}' = \text{Me}$) [4]. In the case of alkyl acetates the $(\text{O}=\text{C})\text{-O}$ bond lengths are considerably influenced by the electronic effects of R' [3].

In Chapters 2 and 3, the molecular structures of methyl isonicotinate and methyl nicotinate ($\text{R} = \text{C}_5\text{H}_4\text{N}$, $\text{R}' = \text{CH}_3$) have been determined by gas electron diffraction (GED) combined with *ab initio* calculations. The $(\text{O}=\text{C})\text{-O}$ bond lengths of methyl isonicotinate (1.331 Å) and methyl nicotinate (1.332 Å) are considerably shorter than those of methyl acetate (1.360 Å) [5] and methyl acrylate (1.349 Å) [4]. It is interesting to investigate the effect of R on the COO moiety. The present study aims to determine the molecular structure of methyl picolinate (MP) as shown in Fig. 4-1 by GED combined with *ab initio* calculations.

It is very difficult to determine the molecular structure of MP by GED alone because there are many closely spaced interatomic distances. In the present study, *ab initio* calculations have been performed by using 4-21G and 6-31G* basis sets and the results are used in the data analysis of GED.



s-trans



s-cis

Fig. 4-1. Atom numbering of the s-trans and s-cis conformers of methyl picolinate. The skeletons of the pyridine ring and the methoxy carbonyl group are assumed to be planar. ϕ_1 , ϕ_2 and ϕ_3 represent dihedral angles $N_1C_2C_7O_8$, $O_8C_7O_9C_{10}$ and $C_7O_9C_{10}H_{15}$, respectively.

4-2 Experimental

A commercial sample with a purity of better than 99% (Tokyo Chemical Industry Co., Ltd.) was used with no further purification. Electron diffraction patterns were recorded on 8 × 8 inch Kodak projector slide plates by using an apparatus equipped with an r^3 -sector [6] and a high temperature nozzle [7]. The temperature of the nozzle tip was 343 K. The acceleration voltage of electrons was about 37 kV. Diffraction patterns of carbon disulfide were recorded at room temperature (298 K) in the same sequence of exposures using a sub-nozzle and the electron wavelength was calibrated to the $r_a(\text{C-S})$ distance (1.5570 Å) [8]. Other experimental conditions are as follows: camera distance for the main nozzle and sub-nozzle, 249.1 mm; electron wavelength, 0.06363 Å; beam current, 3.6 μA ; background pressure during exposure, $(2.5 \sim 4.5) \times 10^{-6}$ Torr; exposure time, 30 ~ 45 s; range of s -value, $4.2 \sim 33.6 \text{ \AA}^{-1}$; uncertainty in the scale factor (3σ), 0.1%.

Optical densities were measured by using a microphotometer of a double-beam autobalanced type at intervals of 100 μm along the diameter. Five optical densities were averaged and thus the densities taken at intervals of 500 μm were converted to intensities. The intensities obtained for three plates were averaged and divided by a theoretical background. Elastic and inelastic atomic scattering factors were taken from refs [8] and [9], respectively.

A vapor-phase IR spectrum between $30 \sim 3500 \text{ cm}^{-1}$ was measured at 296 K on a BOMEM DA3.16 Fourier transform spectrometer with a resolution of 0.5 cm^{-1} . Sample pressure was

about 0.2 Torr. An absorption cell with a 10 m path length and KBr windows was used. Observed vibrational wavenumbers are listed in Table 4-1.

4-3 Ab initio calculations

As shown later, the molecule has a planar skeleton in the gas phase. Figure 4-1 shows the s-trans and s-cis conformers of MP and the numbering of atoms. Ab initio calculations were performed with the program GAUSSIAN 92 [10]. Preliminary geometry optimization was carried out for each conformer at the RHF/4-21G [11] level. Next, the potential energy function for internal rotation $V(\phi_1, \phi_2, \phi_3)$ was calculated by using the optimized bond lengths and angles of the s-trans form (see Fig. 4-1). The potential function is approximately represented as $V(\phi_1, \phi_2, \phi_3) = V(\phi_1, 0, 0) + V(0, \phi_2, 0) + V(0, 0, \phi_3)$. The results are shown in Table 4-2. The 4-21G calculations indicate that the s-trans and s-cis forms correspond to energy minima. Harmonic force constants were calculated in the Cartesian coordinates for both forms.

To obtain more reliable information, the structures of the s-trans and s-cis conformers were optimized at the RHF/6-31G* [12] level and the results are listed in Table 4-3. The s-trans conformer is more stable than the s-cis conformer by about $1.65 \text{ kcal mol}^{-1}$, which is considerably larger than the 4-21G value, $0.18 \text{ kcal mol}^{-1}$. According to the 6-31G*

Table 4-1

Observed and calculated vibrational wavenumbers (cm^{-1}) and assignments for methyl picolinate

ν_{obs}^a	ν_{calc}		S^b	Assignment ^b
	s-trans	s-cis		
		3085		
3075 m	3068		A'	C-Hring str.(99)
3060 m	3047	3047	A'	C-Hring str.(99)
3028 w	3030	3030	A'	C-Hring str.(101)
	3020	3019	A'	C-Hring str.(101)
3001 w	2989	2983	A'	CH ₃ asym. str.(98)
2962 m	2956	2956	A"	CH ₃ asym. str.(100)
2914 vw				
2887 sh	2884	2883	A'	CH ₃ sym. str.(98)
2856 w				
1777 m		1788		
1744 vs	1739		A'	C=O str.(92)
1701 w				
1603 sh	1607	1603	A'	C-Cring str.(61) + C-Hring in-plane bend.(38)
1581 m	1591	1593	A'	C-Cring str.(47) + C-Hring in-plane bend.(34)+ C-N str.(21)
1575 sh				
1503 m	1508	1506	A'	C-Hring in-plane bend.(61) + Cring-C str.(21)

	1495	1494	A'	C-Hring in-plane bend.(73)
1476 m	1480	1482	A'	CH ₃ asym. def.(98)
1470 m	1471	1471	A"	CH ₃ asym. def.(96)
1446 s	1437	1434	A'	CH ₃ sym. def.(81)
1430 sh				
1335 sh	1338	1331	A'	C-Hring in-plane bend.(40)
1315 vs	1310		A'	C-O str.(21)
1298 sh				
1282 s		1276		
1247 s	1242	1244	A'	C-Hring in-plane bend.(83) + C-N str.(22)
1219 m				
1199 m	1187	1187	A'	CH ₃ asym. def.(73)
1134 vs	1144	1146	A'	O-C _{Me} str.(22) + C-Cring str.(21)
	1144	1145	A"	CH ₃ rock.(93)
	1117	1112	A'	C-Cring str.(45) + C-Hring in-plane bend.(27)
1094 m				
1084 sh	1083	1084	A'	C-Cring str.(107) + C-N str.(79)
1050 m				
1046 m	1046	1044	A"	C-Hring out-of-plane bend.(133)
	1037	1039	A'	C-Cring str.(62)
1000 vw	1010	1007	A"	C-Hring out-of-plane bend.(123)
980 w	971	977	A'	O-C _{Me} str.(66) + C-Cring str.(23)
	949	945	A'	ring def.(74) + C-N str.(20)
927 vw	939	936	A"	C-Hring out-of-plane bend.(111)
828 w	836	835	A"	C-Hring out-of-plane bend.(41) + ring tor.(35) + Cring-C out-of-plane

				bend.(34) + C=O out-of-plane
				bend.(26)
816 w	818	811 A'		O=C-O def.(23) + C-O str.(21) + C-O-C _{Me} bend.(20)
775 s	755	755 A"		C-Hring out-of-plane bend.(89) + ring tor.(62)
752 m				
706 m	704	702 A"		ring tor.(65)
	702	701 A'		ring def.(62)
	620	620 A'		ring def.(90)
	513	499 A'		O=C-O rock.(45)
	460	457 A"		ring tor.(102) + C _{ring} -C out-of-plane bend.(48)
	421	421 A"		ring tor.(134)
	358	364 A'		C _{ring} -C str.(30) + ring def.(22)
	327	323 A'		C-O-C _{Me} bend.(40) + O=C-O def.(28) + C _{ring} -C in-plane bend.(27)
	211	211 A"		C-O tor.(51) + ring tor.(37)
	168	175 A'		C _{ring} -C in-plane bend.(39) + O=C-O rock.(28)
	136	133 A"		O-C _{Me} tor.(85)
	111	109 A"		C-O tor.(40) + C _{ring} -C out-of-plane bend.(26)
56 vw	69	68 A"		C _{ring} -C tor.(92)

^a Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

^b Symmetry of vibrational modes.

^c Assignments for the s-trans conformer. Numbers in parentheses denote potential energy distribution(%). Contributions of less than 20% are not shown.

Table 4-2

Potential energy functions for internal rotation given by
RHF/4-21G ab initio calculations (kcal mol⁻¹)

ϕ_i (°)	$V(\phi_1, 0, 0)$	$V(0, \phi_2, 0,)$	$V(0, 0, \phi_3)$
0	0.0	0.0	0.0
30	1.86	2.82	0.35
60	6.27	7.91	1.09
90	9.04	9.63	
120	6.93	11.13	
150	3.03	32.37	
180	1.47	42.38	

Table 4-3

Optimized 6-31G* structures of methyl picolinate^a

Parameter	s-trans	s-cis
Bond length(Å)		
$r(\text{N}_1\text{-C}_2)$	1.321	1.322
$r(\text{N}_1\text{-C}_6)$	1.317	1.314
$r(\text{C}_2\text{-C}_3)$	1.386	1.386
$r(\text{C}_5\text{-C}_6)$	1.388	1.389
$r(\text{C}_3\text{-C}_4)$	1.384	1.386
$r(\text{C}_4\text{-C}_5)$	1.382	1.380
$r(\text{C}_2\text{-C}_7)$	1.503	1.506
$r(\text{C}_7\text{=O}_8)$	1.192	1.184
$r(\text{C}_7\text{-O}_9)$	1.313	1.327
$r(\text{O}_9\text{-C}_{10})$	1.416	1.417
$\langle r(\text{C-H}_{\text{ring}}) \rangle^b$	1.074	1.074
$\langle r(\text{C-H}_{\text{Me}}) \rangle^b$	1.080	1.080
Bond angle(°)		
$\angle \text{C}_2\text{N}_1\text{C}_6$	118.0	118.3
$\angle \text{N}_1\text{C}_2\text{C}_3$	123.5	123.2
$\angle \text{N}_1\text{C}_6\text{C}_5$	123.3	123.3
$\angle \text{C}_2\text{C}_3\text{C}_4$	118.1	118.2
$\angle \text{C}_6\text{C}_5\text{C}_4$	118.4	118.2
$\angle \text{C}_3\text{C}_4\text{C}_5$	118.7	118.8
$\angle \text{N}_1\text{C}_2\text{C}_7$	118.6.	115.3
$\angle \text{C}_2\text{C}_7\text{O}_8$	122.3	124.7

$\angle C_2C_7O_9$	113.8	111.8
$\angle C_7O_9C_{10}$	116.8	116.6
$\angle N_1C_6H$	116.2	116.3
$\angle C_2C_3H$	119.8	120.5
$\angle C_3C_4H$	120.5	120.4
$\angle C_4C_5H$	121.4	121.5
$\angle O_8C_9H_{15}$	105.7	105.9
$\angle O_8C_9H_{16,17}$	110.5	110.5
ΔE (s-trans - s-cis) ^c	0.0 ^d	1.65

^a See Fig. 4-1 for the atom numbering.

^b Angle bracket denotes averaged values.

^c Conformational energy (kcal mol⁻¹).

^d Total energy is -473.33935 Eh (hartree).

calculations, the mole functions of the s-trans and s-cis conformers at 343 K are estimated to be 92 and 8%.

4-4 Normal coordinate analysis

The Cartesian force constants given by the 4-21G ab initio calculations were transformed to the force constants in internal coordinates, f_{ij} . They were modified by using scale factors, c_i [13] as $f_{ij}(\text{scaled}) = (c_i c_j)^{1/2} f_{ij}(\text{unscaled})$. The scale factors for the s-trans and s-cis conformers were assumed to be the same. The scale factors were divided into several groups and were determined so as to reproduce the observed vibrational wavenumbers. Definition of the internal coordinates, the scale factors and the modified force constants in internal coordinates are listed in Tables A4-1, A4-2 and A4-3, respectively, in Appendix. Table 4-1 lists the wavenumbers calculated from the modified force constants.

Mean amplitudes and shrinkage corrections were calculated from the modified force constants. Table 4-4 lists calculated mean amplitudes.

4-5 Analysis of electron diffraction data

Data analysis was performed under the following assumptions : (1) the pyridine ring and the skeleton of the COOCH₃ group are planar; (2) the methyl group has local C_{3v} symmetry; (3) the C-H bond lengths of the pyridine ring are the same; (4) the differences between similar bond lengths and bond angles in each conformer are equal to the values given by 6-31G* calculations; (5) $r(\text{C-H}_{\text{Me}})$ is larger than $r(\text{C-H}_{\text{ring}})$ by 0.006 Å, a value

Table 4-4

Calculated mean amplitudes, l , and interatomic distances, r_a , for the s-trans and s-cis conformer of methyl picolinate ($\text{\AA}$)^a

Atom pair	s-trans		s-cis	
	l	r_a	l	r_a
N ₁ - C ₂	0.046	1.342	0.046	1.343
N ₁ - C ₃	0.055	2.416	0.055	2.414
N ₁ - C ₄	0.063	2.788	0.063	2.779
N ₁ - C ₅	0.055	2.411	0.055	2.407
N ₁ - C ₆	0.046	1.338	0.046	1.335
N ₁ - C ₇	0.062	2.389	0.063	2.441
N ₁ - O ₈	0.061	3.486	0.090	2.810
N ₁ - O ₉	0.093	2.632	0.064	3.580
N ₁ - C ₁₀	0.101	4.041	0.076	4.748
C ₂ - C ₃	0.047	1.395	0.047	1.395
C ₂ - C ₄	0.055	2.379	0.055	2.378
C ₂ - C ₅	0.060	2.723	0.060	2.728
C ₂ - C ₆	0.053	2.283	0.053	2.287
C ₂ - C ₇	0.050	1.492	0.050	1.495
C ₂ - O ₈	0.057	2.349	0.057	2.375
C ₂ - O ₉	0.061	2.378	0.060	2.365
C ₂ - C ₁₀	0.067	3.669	0.067	3.664
C ₃ - C ₄	0.047	1.393	0.047	1.395
C ₃ - C ₅	0.056	2.407	0.056	2.411
C ₃ - C ₆	0.061	2.730	0.061	2.734
C ₃ - C ₇	0.064	2.509	0.063	2.466

C ₃ - H	0.077	1.085	0.077	1.085
C ₃ - O ₈	0.090	2.835	0.062	3.570
C ₃ - O ₉	0.065	3.648	0.090	2.672
C ₃ - C ₁₀	0.078	4.807	0.099	4.082
C ₄ - C ₅	0.047	1.391	0.047	1.389
C ₄ - C ₆	0.055	2.384	0.055	2.381
C ₄ - C ₇	0.065	3.759	0.064	3.733
C ₄ - H	0.077	1.085	0.077	1.085
C ₄ - O ₈	0.092	4.212	0.067	4.731
C ₄ - O ₉	0.070	4.742	0.093	4.058
C ₄ - C ₁₀	0.075	6.013	0.102	5.467
C ₅ - C ₆	0.047	1.397	0.047	1.398
C ₅ - C ₇	0.067	4.208	0.067	4.216
C ₅ - H	0.077	1.085	0.077	1.085
C ₅ - O ₈	0.081	4.960	0.082	4.978
C ₅ - O ₉	0.085	4.884	0.082	4.891
C ₅ - C ₁₀	0.087	6.266	0.085	6.275
C ₆ - C ₇	0.064	3.617	0.064	3.654
C ₆ - H	0.077	1.088	0.077	1.085
C ₆ - O ₈	0.065	4.610	0.094	4.133
C ₆ - O ₉	0.097	3.960	0.068	4.640
C ₆ - C ₁₀	0.105	5.368	0.074	5.914
C ₇ - O ₈	0.038	1.205	0.038	1.201
C ₇ - O ₉	0.046	1.323	0.047	1.337
C ₇ - C ₁₀	0.062	2.315	0.063	2.325
O ₈ - C ₁₀	0.097	2.608	0.097	2.609
O ₉ - C ₁₀	0.050	1.426	0.050	1.427
C ₁₀ - H	0.078	1.091	0.078	1.091

^a See Fig. 4-1 for the atom numbering. Non-bonded C - H, N - H, O - H and H - H pairs are not listed although they were included in the data analysis.

given by the 6-31G* calculations; (6) the $N_1C_6H_{14}$, $C_2C_3H_{11}$, $C_3C_4H_{12}$ and $C_4C_5H_{13}$ bond angles are equal to the 6-31G* values; (7) the OCH bond angles are equal to the average of 6-31G* values; (8) the $C_7O_9C_{10}$ angle of major conformer is 115.4° . Assumption (8) was required because of the strong correlation between the $C_7O_9C_{10}$ bond angle and the relative abundance of s-trans conformer. The value of this bond angle was assumed to be the same as that of methyl isonicotinate, $115.4 (15)^\circ$. The constraints are summarized in Table 4-5. Three ring bond angles, $\angle C_2C_3C_4$, $\angle C_3C_4C_5$ and $\angle C_4C_5C_6$ depend on $r(N_1-C_2)$, $r(C_2-C_3)$, $\angle C_2N_1C_6$ and $\angle N_1C_2C_3$. Adjustable structure parameters are $r(N_1-C_2)$, $r(C_2-C_3)$, $r(C_2-C_7)$, $r(C_7=O_8)$, $r(C_7-O_9)$, $r(C-H_{ring})$, $\angle C_2N_1C_6$, $\angle N_1C_2C_3$, $\angle N_1C_2C_7$, $\angle C_2C_7O_8$ and $\angle C_2C_7O_9$.

In a preliminary analysis, least squares calculations were performed on $SM(s)$ for various values of ϕ_1 . The best fitting was obtained for ϕ_1 values of nearly 0° and 180° . Thus the molecular skeleton was determined to be planar in the equilibrium state.

Vibrational amplitudes and shrinkage corrections were fixed at calculated values. Asymmetry parameters were estimated by the conventional method [14, 15]. Adjustable structure parameters including $\phi_1^\circ(N_1C_2C_7O_8)$ and the index of resolution were determined by least-squares calculations on molecular scattering intensities.

The mole fraction of the s-trans conformer was determined from the R-factor¹ for molecular scattering intensities.

¹ $R = \{ \sum_i W_i (\Delta SM(s)_i)^2 / \sum_i W_i (SM(s)_{obs_i}^2) \}^{1/2}$, where $\Delta SM(s)_i = SM(s)_{obs_i} - SM(s)_{calc_i}$ and W_i is a diagonal element of the weight matrix.

Table 4-5

Structural parameters and constraints of methyl picolinate^a

parameters	s-trans	s-cis
Bond lengths (Å)		
$r(\text{N}_1\text{-C}_2)$	r_1	$r_1 + 0.001$
$r(\text{N}_1\text{-C}_6)$	$r_1 - 0.004$	$r_1 - 0.007$
$r(\text{C}_2\text{-C}_3)$	r_2	r_2
$r(\text{C}_5\text{-C}_6)$	$r_2 + 0.002$	$r_2 + 0.003$
$r(\text{C}_3\text{-C}_4)$	$r_2 - 0.002$	r_2
$r(\text{C}_4\text{-C}_5)$	$r_2 - 0.004$	$r_2 - 0.006$
$r(\text{C}_2\text{-C}_7)$	r_3	$r_3 + 0.003$
$r(\text{C}_7\text{=O}_8)$	r_4	$r_4 - 0.004$
$r(\text{C}_7\text{-O}_9)$	r_5	$r_5 + 0.014$
$r(\text{O}_9\text{-C}_{10})$	$r_5 + 0.103$	$r_5 + 0.104$
$r(\text{C}_2\text{-H}_{11})$	r_7	r_7
$r(\text{C}_{14}\text{-H}_{15})$	$r_7 + 0.006$	$r_7 + 0.006$
Bond angles(°)		
$\angle\text{C}_2\text{N}_1\text{C}_6$	θ_1	$\theta_1 - 0.3$
$\angle\text{N}_1\text{C}_2\text{C}_3$	θ_2	$\theta_2 - 0.3$
$\angle\text{N}_1\text{C}_6\text{C}_5$	$\theta_2 - 0.2$	$\theta_2 - 0.2$
$\angle\text{N}_1\text{C}_2\text{C}_7$	θ_3	$-\theta_3 + 118.6^{\text{c}} + 115.3^{\text{d}}$
$\angle\text{C}_2\text{C}_7\text{O}_8$	θ_4	$\theta_4 + 2.4$
$\angle\text{C}_2\text{C}_7\text{O}_9$	θ_5	$\theta_5 - 2.0$
$\angle\text{C}_7\text{O}_9\text{C}_{10}$	θ_6^{e}	$\theta_6 - 0.2$
$\angle\text{N}_1\text{C}_6\text{H}_{11}$	116.2	116.3
$\angle\text{C}_2\text{C}_3\text{H}_8^{\text{f}}$	119.8	120.5

$\angle C_3C_4H_9^f$	120.5	120.4
$\angle C_4C_5H_{10}^f$	121.4	121.5
$\angle O_9C_{10}H^g$	108.9	109.0

^a See Fig. 4-1 for atom numbering.

^b Differences were fixed at the 6-31G* values.

^c The 6-31G* value of $\angle N_1C_2C_7$ for s-trans conformer (see Table 4-2).

^d The 6-31G* value of $\angle N_1C_2C_7$ for s-cis conformer (see Table 4-2).

^e θ_6 is assumed to be 115.4° for the major conformer..

^f Assumed at the 6-31G* values.

^g Assumed at the average of the 6-31G* values.

4-6 Results and discussion

The molecular scattering intensities and radial distribution curves are shown in Figs. 4-2 and 4-3, respectively. Figure 4-4 shows the R-factor against the relative abundance of s-trans conformer. The mole fraction of s-trans conformer was determined to be 77(23)%, which is consistent with the 6-31G* calculations (92%). The relative abundances for the C₇O₉C₁₀ angles of 114° and 117° of s-trans conformer were also estimated from R-factors. The estimated relative abundances of s-trans conformer are not significantly different from the result for the C₇O₉C₁₀ angle of 115.4°.

Table 4-6 lists the determined molecular structure. The limits of error were estimated from three times standard deviations and systematic errors accompanied with the estimated uncertainty ($\pm 1.5^\circ$) of $\angle \text{C}_7\text{O}_9\text{C}_{10}$. The absolute values of correlation coefficients are greater than 0.7 are $r(\text{C}_2-\text{C}_3) / r(\text{C}_7-\text{O}_9)$ (-0.73), $r(\text{C}_7-\text{O}_9) / \angle \text{N}_1\text{C}_2\text{C}_3$ (0.76) and $\angle \text{C}_2\text{N}_1\text{C}_6 / \angle \text{N}_1\text{C}_2\text{C}_3$ (-0.84). A correlation matrix is listed in Table A4-4 in Appendix.

Table 4-7 compares the structures of MP, methyl nicotinate and methyl isonicotinate. There is no significant difference between the structures of pyridine rings. That is, the structure of the pyridine ring is not significantly depend of the position of the substituent. On the other hand, there are some differences between the ring structure of the three compounds and pyridine [16].

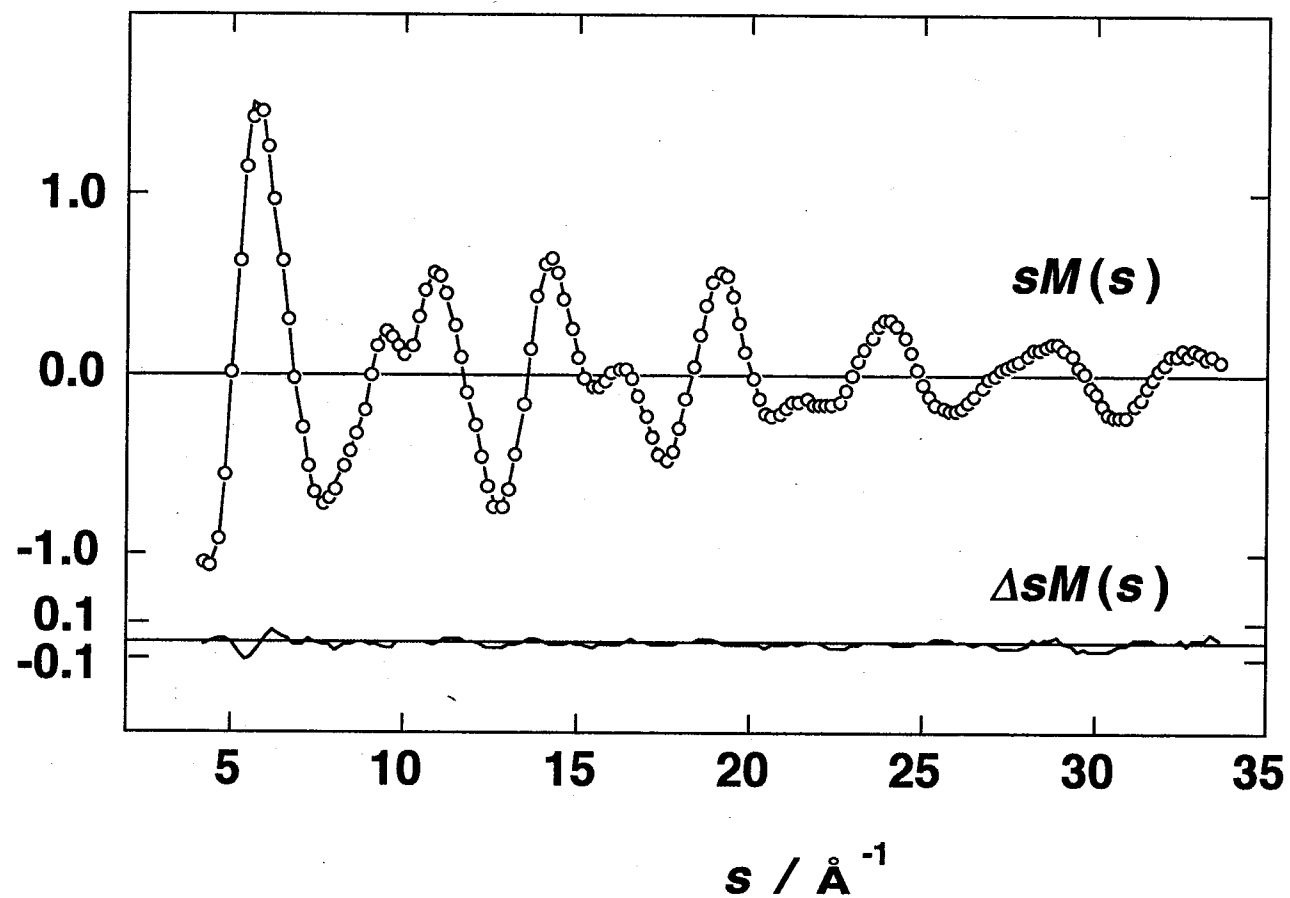


Fig. 4-2. Experimental (o) and theoretical (—) molecular scattering intensities for methyl picolinate; $\Delta sM(s) = sM(s)^{\text{obs}} - sM(s)^{\text{calc}}$.

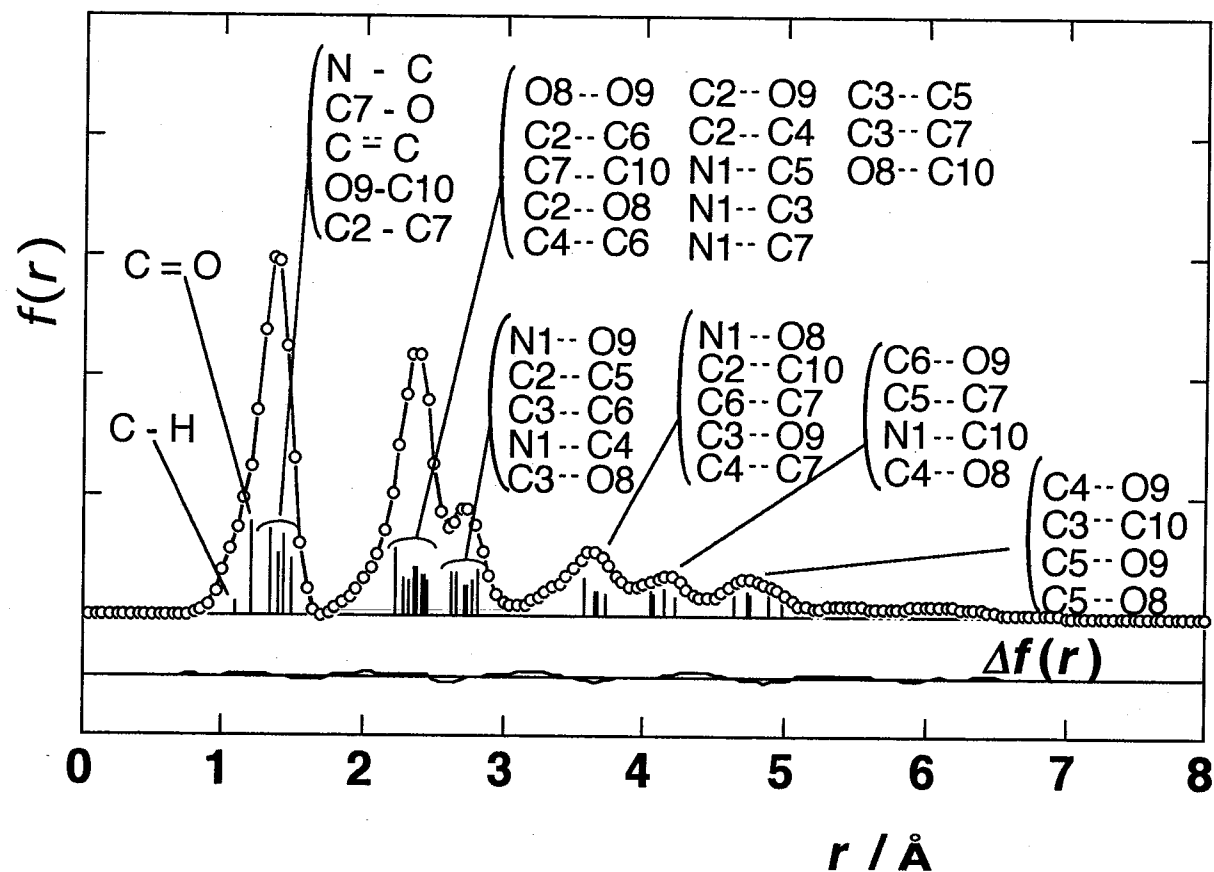


Fig. 4-3. Experimental (o) and theoretical (—) radial distribution curves for methyl picolinate; $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$. Vertical bars indicate relatively important atom pairs of the s-trans conformer.

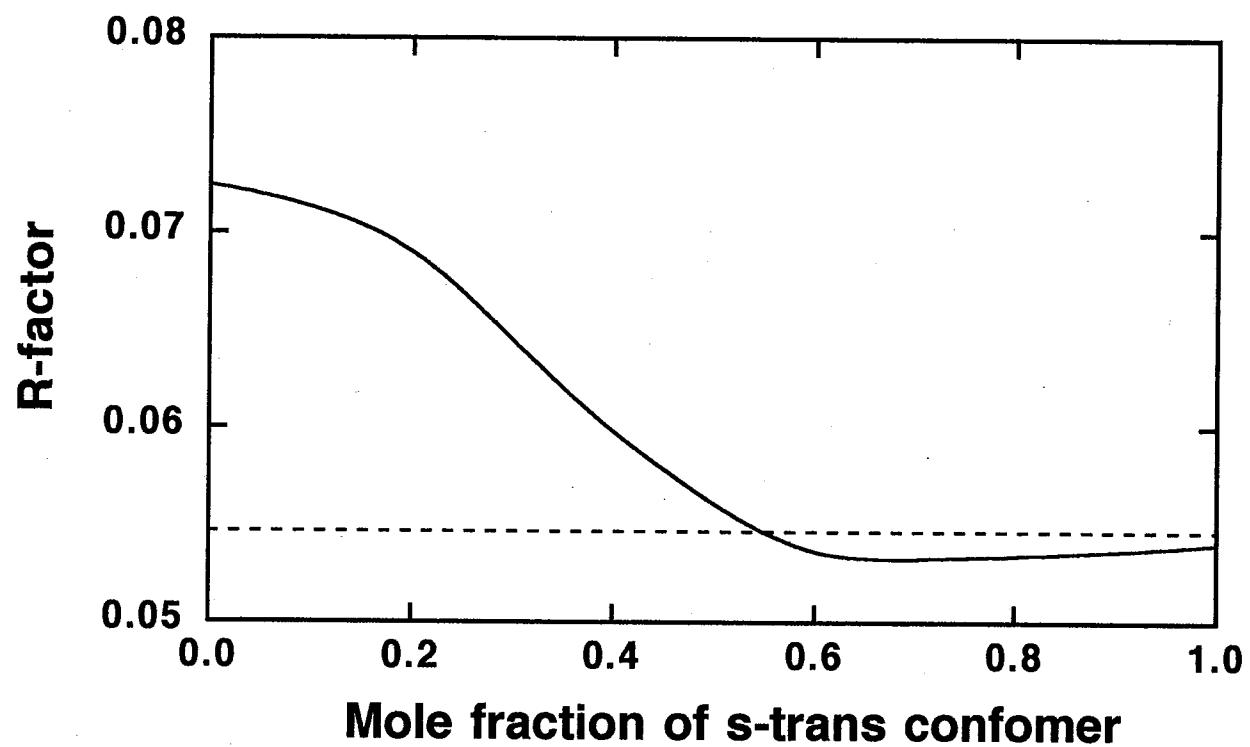


Fig. 4-4. R-factors versus the mole fraction of the s-trans conformer. Dashed line shows the 99% significance level.

Table 4-6

Structure parameter values of methyl picolinate^a

Parameter	s-trans	s-cis
Bond lengths (Å)		
$r_g(\text{N}_1\text{-C}_2)$	1.346	1.347
$r_g(\text{N}_1\text{-C}_6)$	1.342	1.339
$r_g(\text{C}_2\text{-C}_3)$	1.399	1.399
$r_g(\text{C}_5\text{-C}_6)$	1.401	1.402
$r_g(\text{C}_3\text{-C}_4)$	1.397	1.399
$r_g(\text{C}_4\text{-C}_5)$	1.396	1.394
$r_g(\text{C}_2\text{-C}_7)$	1.497 (14)	1.500 (14)
$r_g(\text{C}_7\text{=O}_8)$	1.209 (7)	1.205 (7)
$r_g(\text{C}_7\text{-O}_9)$	1.328	1.342
$r_g(\text{O}_9\text{-C}_{10})$	1.431	1.432
$r_g(\text{C}_2\text{-H})$	1.093	1.093
$r_g(\text{C}_{14}\text{-H})$	1.099	1.099
Bond angles (°)		
$\angle_{\alpha}\text{C}_2\text{N}_1\text{C}_6$	117.2 (14)	117.5 (14)
$\angle_{\alpha}\text{N}_1\text{C}_2\text{C}_3$	124.0	123.7
$\angle_{\alpha}\text{N}_1\text{C}_6\text{C}_5$	123.8	123.8
$\angle_{\alpha}\text{C}_2\text{C}_3\text{C}_4^b$	117.3	117.3
$\angle_{\alpha}\text{C}_6\text{C}_5\text{C}_4^b$	117.7	117.5
$\angle_{\alpha}\text{C}_3\text{C}_4\text{C}_5^b$	120.0	120.2
$\angle_{\alpha}\text{N}_1\text{C}_2\text{C}_7$	115.1 (9)	118.8 (9)
$\angle_{\alpha}\text{C}_2\text{C}_7\text{O}_8$	121.0 (12)	123.8 (12)

$\angle_{\alpha}C_2C_7O_9$	115.1 (12)	113.5 (12)
$\angle_{\alpha}C_7O_9C_{10}^c$	115.4	115.2
$\phi_1^\circ(N_1C_2C_7O_9)$	0.0	180.0

^a See Fig. 4-1 for the atom numbering. The index of resolution is 0.90 (5). Numbers in parentheses are the estimated limits of error (3σ) referring to the last significant digit.

^b Dependent parameter.

^c Assumed parameter.

Table 4-7

Molecular structures of methyl picolinate and related molecules^a

Methyl picolinate ^b Methyl nicotinate ^c Methyl isonicotinate ^d			
Bond length(Å)			
$r_g(\text{N}_1\text{-C}_2)$	1.346	1.334	1.343
$r_g(\text{N}_1\text{-C}_6)$	1.342	1.335	1.343
$r_g(\text{C}_2\text{-C}_3)$	1.399	1.405	1.401
$r_g(\text{C}_5\text{-C}_6)$	1.401	1.401	1.401
$r_g(\text{C}_3\text{-C}_4)$	1.397	1.405	1.401
$r_g(\text{C}_4\text{-C}_5)$	1.396	1.396	1.401
$r_g(\text{C}_2\text{-C}_7)$	1.497 (11)	1.480 (12)	1.499 (9)
$r_g(\text{C}_7\text{=O}_8)$	1.209 (8)	1.199 (7)	1.205 (5)
$r_g(\text{C}_7\text{-O}_9)$	1.328	1.332	1.331
$r_g(\text{O}_9\text{-C}_{10})$	1.431	1.428	1.430
Bond angle(°)			
$\angle_{\alpha}\text{C}_6\text{N}_1\text{C}_2$	117.2 (10)	119.0 (12)	117.6 (9)
$\angle_{\alpha}\text{N}_1\text{C}_2\text{C}_3$	124.0	122.5	123.6 ^g
$\angle_{\alpha}\text{N}_1\text{C}_6\text{C}_5$	123.8	123.0	123.6 ^g
$\angle_{\alpha}\text{C}_2\text{C}_3\text{C}_4$	117.3 ^g	118.5 ^g	118.2 ^g
$\angle_{\alpha}\text{C}_6\text{C}_5\text{C}_4$	117.7 ^g	118.6 ^g	118.2 ^g
$\angle_{\alpha}\text{C}_3\text{C}_4\text{C}_5$	120.0 ^g	118.5 ^g	118.7 (9)
$\angle_{\alpha}\text{C}_2\text{C}_7\text{=O}_8$	121.0 (12)	121.5 (12)	121.4 (12)

$\angle_{\alpha}C_2C_7-O_9$	115.1(11)	115.6 (10)	114.2 (10)
$\angle_{\alpha}C_7O_9C_{10}$	115.4 ^h	115.4 ^h	115.4 (15)

^a Atom numbering is shown in Fig. 4-1. Parenthesized numbers are the estimated limits of error (3σ) referring to the last significant digits except pyridine.

^b Present work. The structure of s-trans conformer.

^c The structure of s-trans conformer. Determined by GED combined with ab initio calculations (see Chapter 3).

^d Determined by GED combined with ab initio calculations. The symmetry of the pyridine ring was assumed to be C_{2v} (see Chapter 2).

^g Dependent parameter.

^h Assumed parameter.

Both the $\text{CC}_7=\text{O}_8$ and CC_7-O_9 angles are in agreement with the corresponding angles of methyl nicotinate and methyl isonicotinate. However, the $\text{CC}_7=\text{O}_8$ angle is about 4° smaller than the corresponding angles of methyl acetate (125.5°) [5] and methyl acrylate (126.1°) [4]. The CC_7-O_9 angle is about 3° larger than the corresponding angles of methyl acetate (111.4°) [5] and methyl acrylate (110.3°) [4].

The $(\text{O}=\text{C})-\text{O}$ distances in MP ($1.328 \text{ \AA}$), methyl nicotinate ($1.331 \text{ \AA}$) and methyl isonicotinate ($1.330 \text{ \AA}$) are considerably shorter than the corresponding distances in methyl acetate ($1.360 \text{ \AA}$) [5] and methyl acrylate ($1.349 \text{ \AA}$) [4].

The C_7-O_9 and $\text{C}_7=\text{O}_8$ bonds are conjugated [17, 18]. The COO moiety and pyridine ring of MP are also conjugated because MP has a planar skeleton. Therefore the electron delocalization in the COO moiety of MP is considered to be larger than that of methyl acetate [5]. This increases the double bond character of the C_7-O_9 bond and explains the fact that the $(\text{O}=\text{C})-\text{O}$ bond of MP is shorter than that of methyl acetate.

The C_2-C_7 bond length of methyl nicotinate ($1.480 (12) \text{ \AA}$) is significantly shorter than those of MP ($1.497 (11) \text{ \AA}$) and methyl isonicotinate ($1.499 (9) \text{ \AA}$) for the difference between the C_2-C_7 bond lengths of methyl nicotinate and MP is $0.017 (16) \text{ \AA}$ and the corresponding difference between methyl isonicotinate and MP is $0.019 (15) \text{ \AA}$. The RHF/6-31G* calculations show the similar tendency: the $r(\text{C}_2-\text{C}_7)$ of methyl nicotinate MP and methyl isonicotinate are 1.477 , 1.503 and $1.497 \text{ \AA}$, respectively (see Table 4-2, Chapters 2, 3).

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Appendix

Table A4-1 Definition of the internal coordinates of methyl picolinate.

Table A4-2 Scale factors of the force constants in the internal coordinates for methyl picolinate.

Table A4-3 Force constants in the internal coordinates for methyl picolinate.

Table A4-4 The correlation matrix of methyl picolinate.

Table A4-1

Definition of the internal coordinates of methyl picolinate

Coordinates		Definitions ^a
s ₁	N-C ₂ str.	r ₁ 2
s ₂	C ₂ -C ₃ str.	r ₂ 3
s ₃	C ₃ -C ₄ str.	r ₃ 4
s ₄	C ₄ -C ₅ str.	r ₄ 5
s ₅	C ₅ -C ₆ str.	r ₅ 6
s ₆	N-C ₆ str.	r ₆ 1
s ₇	C _{ring} -C str.	r ₂ 7
s ₈	C=O str.	r ₇ 8
s ₉	C-O str.	r ₇ 9
s ₁₀	O-C _{Me} str.	r ₉ 10
s ₁₁	C ₃ -H str.	r ₃ 11
s ₁₂	C ₄ -H str.	r ₄ 12
s ₁₃	C ₅ -H str.	r ₅ 13
s ₁₄	C ₆ -H str.	r ₆ 14
s ₁₅	CH ₃ sym. str.	(r ₁₀ 15 + r ₁₀ 16 + r ₁₀ 17) / √3
s ₁₆	CH ₃ asym. str.	(2r ₁₀ 15 - r ₁₀ 16 - r ₁₀ 17) / √6
s ₁₇	C _{ring} -C in-plane bend.	(δ ₁ 2 7 - δ ₃ 2 7) / √2
s ₁₈	C ₂ -H in-plane bend.	(δ ₂ 3 11 - δ ₄ 3 11) / √2
s ₁₉	C ₄ -H in-plane bend.	(δ ₃ 4 12 - δ ₅ 4 12) / √2
s ₂₀	C ₅ -H in-plane bend.	(δ ₄ 5 13 - δ ₆ 5 13) / √2
s ₂₁	C ₆ -H in-plane bend.	(δ ₁ 6 14 - δ ₅ 6 14) / √2
s ₂₂	ring def.	(δ ₂ 1 6 - δ ₃ 2 1 + δ ₄ 3 2 - δ ₅ 4 3

		$+ \delta_6 5 4 - \delta_1 6 5) / \sqrt{6}$
s23	ring def.	$(2\delta_2 1 6 - \delta_3 2 1 - \delta_4 3 2 + 2\delta_5 4 3$ $- \delta_6 5 4 - \delta_1 6 5) / \sqrt{12}$
s24	ring def.	$(\delta_3 2 1 - \delta_4 3 2 + \delta_6 5 4$ $- \delta_1 6 5) / 2$
s25	O-C=O def.	$(- \delta_3 7 8 - \delta_3 7 9 + 2\delta_8 7 9) / \sqrt{6}$
s26	O-C=O rock.	$(\delta_3 7 8 - \delta_3 7 9) / \sqrt{2}$
s27	C-O-C _{Me} bend.	$\delta_7 9 10$
s28	CH ₃ sym. def.	$(\delta_9 10 15 + \delta_9 10 16 + \delta_9 10 17$ $- \delta_{15} 10 16 - \delta_{15} 10 17 - \delta_{16} 10 17)$ $/ \sqrt{6}$
s29	CH ₃ asym. def.	$(2\delta_{16} 10 17 - \delta_{15} 10 16$ $- \delta_{15} 10 17) / \sqrt{6}$
s30	CH ₃ rock.	$(2\delta_9 10 15 - \delta_9 10 16$ $- \delta_9 10 17) / \sqrt{6}$
s31	CH ₃ asym. str.	$(r_{10} 16 - r_{10} 17) / \sqrt{2}$
s32	CH ₃ sym. def.	$(\delta_{15} 10 16 - \delta_{15} 10 17) / \sqrt{2}$
s33	CH ₃ rock.	$(\delta_9 10 16 - \delta_9 10 17) / \sqrt{2}$
s34	ring tor.	$(\tau_1 2 - \tau_2 3 + \tau_3 4 - \tau_4 5$ $+ \tau_5 6 - \tau_6 1) / \sqrt{6}$
s35	ring tor.	$(\tau_1 2 + \tau_3 4 - \tau_4 5 - \tau_6 1) / 2$
s36	ring tor.	$(-\tau_1 2 + 2\tau_2 3 - \tau_3 4 - \tau_4 5$ $+ 2\tau_5 6 - \tau_6 1) / \sqrt{12}$
s37	C _{ring} -C tor.	$\tau_2 7$
s38	C-O tor.	$\tau_7 9$
s39	O-C _{Me} tor.	$\tau_9 10$
s40	C _{ring} -C out-of-plane bend.	w ₇

s ₄₁	C ₃ -H out-of-plane bend.	w ₁₁
s ₄₂	C ₄ -H out-of-plane bend.	w ₁₂
s ₄₃	C ₅ -H out-of-plane bend	w ₁₃
s ₄₄	C ₆ -H out-of-plane bend	w ₁₄
s ₄₅	C=O out-of-plane bend	w ₈

^a Abbreviations used: *r*, stretching; δ , in-plane bending; τ , torsion; *w*, out-of-plane bending. See Fig. 4-1 for atom numbering.

Table A4-2

Scale factors of the force constants in the internal coordinates for methyl picolinate

Values	Coordinates s_i ^a
0.830	1, 2, 3, 4, 5, 6
0.810	11, 12, 13, 14
0.890	18, 19, 20
0.840	21
0.900	17
0.710	22
0.770	23, 24, 34, 35, 36, 40, 41, 42, 43, 44
0.800	15, 16, 31
0.810	25, 30, 33, 45
0.870	10
0.780	28, 29, 32
1.150	26, 27, 37, 38, 39
0.863	7, 8, 9

^a See Table A4-1 for the definition of the coordinates.

Table A4-3

Force constants in the internal coordinates for methyl picolinate^a

A'-block															
s_i^b	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9	s_{10}	s_{11}	s_{12}	s_{13}	s_{14}	s_{15}
s_1	6.644														
s_2	0.916	6.435													
s_3	-0.547	0.748	6.416												
s_4	0.710	-0.568	0.787	6.443											
s_5	-0.653	0.483	-0.555	0.784	6.232										
s_6	0.853	-0.611	0.712	-0.560	0.978	6.749									
s_7	0.441	0.348	-0.007	-0.110	-0.054	-0.078	4.477								
s_8	0.024	0.014	0.000	-0.014	-0.054	0.056	0.507	11.933							
s_9	-0.005	-0.011	0.009	0.003	-0.021	0.031	0.253	1.152	6.159						
s_{10}	-0.010	-0.002	0.000	0.001	0.006	-0.007	-0.069	-0.135	0.181	4.748					
s_{11}	-0.023	0.045	0.050	0.002	-0.013	-0.021	-0.044	0.012	-0.004	0.002	5.153				
s_{12}	-0.018	-0.008	0.073	0.073	-0.007	-0.020	0.000	0.006	0.006	-0.002	0.010	5.027			
s_{13}	-0.029	-0.020	-0.003	0.068	0.055	-0.008	0.004	0.001	0.003	-0.001	0.001	0.011	5.050		
s_{14}	-0.016	-0.015	-0.028	-0.004	0.069	0.185	0.001	0.006	0.008	-0.001	0.001	0.002	0.013	5.041	
s_{15}	0.002	0.001	0.000	-0.001	-0.001	0.001	0.007	0.033	-0.072	0.196	0.000	0.000	0.000	0.000	4.850

s16	0.002	0.001	0.000	0.001	-0.001	0.001	0.003	-0.028	0.013	-0.030	0.000	0.000	0.000	0.000	0.052
s17	0.308	-0.277	-0.034	0.012	-0.019	0.038	-0.064	0.053	-0.057	-0.018	0.061	-0.007	0.000	0.004	0.001
s18	0.009	0.162	-0.163	-0.005	0.023	-0.032	0.001	0.035	-0.016	0.006	0.026	0.007	-0.006	0.001	-0.001
s19	-0.021	0.007	0.171	-0.169	-0.008	0.019	0.006	0.003	0.006	-0.001	-0.006	0.000	0.006	-0.007	0.000
s20	0.031	-0.026	0.007	0.169	-0.152	-0.010	-0.001	-0.003	0.001	0.000	0.005	-0.006	-0.005	0.000	0.000
s21	-0.024	0.027	0.003	0.010	0.156	-0.317	-0.004	-0.005	-0.004	0.001	-0.001	0.007	-0.003	0.015	0.000
s22	0.217	0.021	0.010	-0.016	-0.018	0.209	0.206	0.036	0.015	-0.003	-0.092	0.086	-0.091	0.073	0.001
s23	0.413	-0.219	0.132	0.110	-0.251	0.361	0.114	0.038	0.004	-0.002	0.027	-0.086	0.041	0.026	0.000
s24	0.265	-0.126	-0.272	0.273	0.092	-0.259	-0.240	-0.062	-0.030	0.009	0.089	0.002	-0.083	0.077	-0.003
s25	-0.052	-0.061	-0.005	0.021	0.036	-0.019	-0.416	0.331	0.289	-0.132	0.023	-0.004	-0.003	-0.005	-0.019
s26	0.052	-0.020	-0.009	0.043	-0.034	0.018	-0.033	0.452	-0.448	0.022	-0.056	-0.004	0.000	0.003	-0.011
s27	-0.011	0.009	0.003	0.004	0.004	-0.006	0.002	-0.010	0.643	0.571	0.001	0.000	-0.001	-0.001	-0.043
s28	-0.002	-0.003	-0.001	0.001	0.001	-0.002	-0.011	-0.053	0.083	-0.567	0.000	-0.001	0.000	-0.001	0.098
s29	-0.002	0.000	0.000	0.000	0.000	-0.001	-0.002	0.016	-0.031	-0.009	0.000	0.000	0.000	0.000	0.012
s30	0.002	0.002	0.000	0.001	0.000	0.000	-0.001	-0.029	0.092	0.021	0.000	0.000	0.000	0.000	0.007

A'-block(continued)

	s16	s17	s18	s19	s20	s21	s22	s23	s24	s25	s26	s27	s28	s29	s30
s16	4.785														
s16	-0.002	1.095													
s16	0.000	-0.003	0.553												
s16	0.000	-0.011	0.009	0.572											
s20	0.000	-0.005	-0.011	0.009	0.561										
s20	0.000	-0.010	-0.001	-0.011	0.008	0.589									
s20	0.000	-0.001	-0.005	-0.001	-0.001	-0.010	1.158								
s20	0.001	0.041	-0.072	-0.001	0.075	-0.069	-0.003	1.189							
s20	0.000	0.012	0.051	-0.083	0.045	0.002	-0.022	-0.026	1.392						
s20	0.018	0.000	-0.003	-0.003	0.000	0.004	-0.042	-0.038	0.067	1.282					
s20	0.003	-0.105	-0.003	-0.007	0.004	-0.004	-0.018	0.060	0.053	0.008	1.407				
s20	0.067	-0.050	0.003	0.001	0.001	0.001	0.003	0.000	0.006	-0.018	-0.066	1.479			
s20	-0.006	0.000	0.001	-0.001	0.000	0.000	-0.002	0.000	0.005	0.017	0.018	-0.029	0.655		
s20	-0.150	-0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.001	-0.017	-0.001	-0.015	0.001	0.532	
s30	0.071	-0.010	0.000	0.000	0.000	0.000	0.001	0.000	0.000	-0.026	-0.009	0.051	0.015	-0.038	0.814

A"-block

	s ₃₁	s ₃₂	s ₃₃	s ₃₄	s ₃₅	s ₃₆	s ₃₇	s ₃₈	s ₃₉	s ₄₀	s ₄₁	s ₄₂	s ₄₃	s ₄₄	s ₄₅
s ₃₁	4.691														
s ₃₂	0.143	0.532													
s ₃₃	0.063	0.016	0.788												
s ₃₄	0.000	0.000	0.001	0.346											
s ₃₅	0.000	0.000	0.000	-0.034	0.275										
s ₃₆	0.000	0.000	-0.001	-0.007	0.004	0.287									
s ₃₇	0.002	0.001	-0.001	-0.003	0.013	0.015	0.113								
s ₃₈	-0.020	0.007	0.026	0.004	0.000	-0.004	-0.022	0.198							
s ₃₉	-0.014	0.018	0.026	0.000	0.000	0.000	0.000	0.012	0.031						
s ₄₀	0.000	0.000	0.000	-0.157	0.077	0.132	0.021	-0.004	0.000	0.495					
s ₄₁	0.000	0.000	0.000	0.141	-0.150	-0.001	-0.004	0.000	0.000	-0.074	0.476				
s ₄₂	0.000	0.000	0.000	-0.147	0.078	-0.115	-0.002	0.000	0.000	-0.003	-0.074	0.467			
s ₄₃	0.000	0.000	0.000	0.135	0.074	0.111	0.005	0.000	0.000	-0.026	-0.009	-0.059	0.480		
s ₄₄	-0.001	0.000	0.003	0.145	0.067	-0.125	0.015	0.015	0.001	-0.086	-0.008	-0.031	-0.003	0.523	
s ₄₅	0.007	-0.005	0.019	0.022	0.017	-0.017	0.039	0.001	0.003	0.002	-0.001	-0.005	0.000	0.051	0.559

^a Units are mdyn Å⁻¹ for the stretching-stretching constants, mdyn rad⁻¹ for the stretching-bending constants and mydn Å rad⁻² for the bending-bending and torsional-torsional constants.

^b See Table A4-1 for the numbering of the definition of the coordinates.

Table A4-4

Correlation matrix of methyl picolinate^a

	1	2	3	4	5	6	7	8	9	10	11	12
k^b	$r(N_1-C_2)$	$r(C_2-C_3)$	$r(C_2-C_7)$	$r(C_7=O_8)$	$r(C_7-O_9)$	$r(C_2-H_{11})$	$\angle C_2N_1C_6$	$\angle N_1C_2C_3$	$\angle N_1C_2C_7$	$\angle C_2C_7O_8$	$\angle C_2C_7O_9$	
1	1.00											
2	-0.50	1.00										
3	0.63	-0.28	1.00									
4	0.59	-0.07	0.46	1.00								
5	-0.66	0.54	-0.55	-0.45	1.00							
6	-0.38	-0.26	-0.71	-0.46	0.37	1.00						
7	-0.63	0.44	-0.52	-0.32	0.65	0.38	1.00					
8	0.36	-0.18	0.67	0.24	-0.43	-0.59	-0.35	1.00				
9	-0.19	-0.22	-0.58	-0.27	0.27	0.76	0.21	-0.84	1.00			
10	0.07	0.01	0.21	0.27	-0.24	-0.24	-0.12	0.19	-0.29	1.00		
11	-0.20	-0.31	-0.41	-0.32	0.06	0.60	0.14	-0.16	0.38	0.28	1.00	
12	-0.28	0.16	-0.23	-0.50	0.37	0.10	0.22	-0.10	0.09	-0.68	-0.44	1.00

^a See Fig. 4-1 for the atom numbering.^b Index of resolution.

Chapter 5

**Conformational studies by liquid crystal ^1H -NMR:
methyl isonicotinate, methyl nicotinate and methyl
picolinate**

5-1 Introduction

Some time ago ^1H -NMR spectra of methyl isonicotinate and methyl nicotinate dissolved in a mixture of nematic liquid crystals 80 mol% EBBA + 20 mol% MBBA were measured in order to make conformational analyses [1]. In the study, the direct coupling constants determined by ^1H -NMR were used to determine the potential energy for internal rotation. However, molecular structures were estimated on the basis of ab initio calculations at the 4-21G level and direct coupling constants were not corrected for molecular vibrations [2]. It was stated that the discrepancies between observed and calculated direct coupling constants were possibly due to the neglected vibrational corrections and the solvent effect on the structures which was difficult to estimate.

The principal purpose of the present study is to determine the conformational compositions of methyl isonicotinate (MI), methyl nicotinate (MN) and methyl picolinate (MP) in nematic liquid crystal ZLI 1167 in details. The positions of the ring protons of MI are determined in the present study. The results are compared with those in the gas phase.

The molecular structures of MI, MN and MP have been determined by gas electron diffraction (GED) combined with ab initio calculations (see Chapters 2, 3 and 4). In the studies of GED, harmonic force constants were obtained from vibrational spectra with the help of ab initio calculations at the 4-21G level. Thus, it is possible to calculate vibrational corrections to direct coupling constants in the present study.

Figure 5-1 shows the molecular models of the three

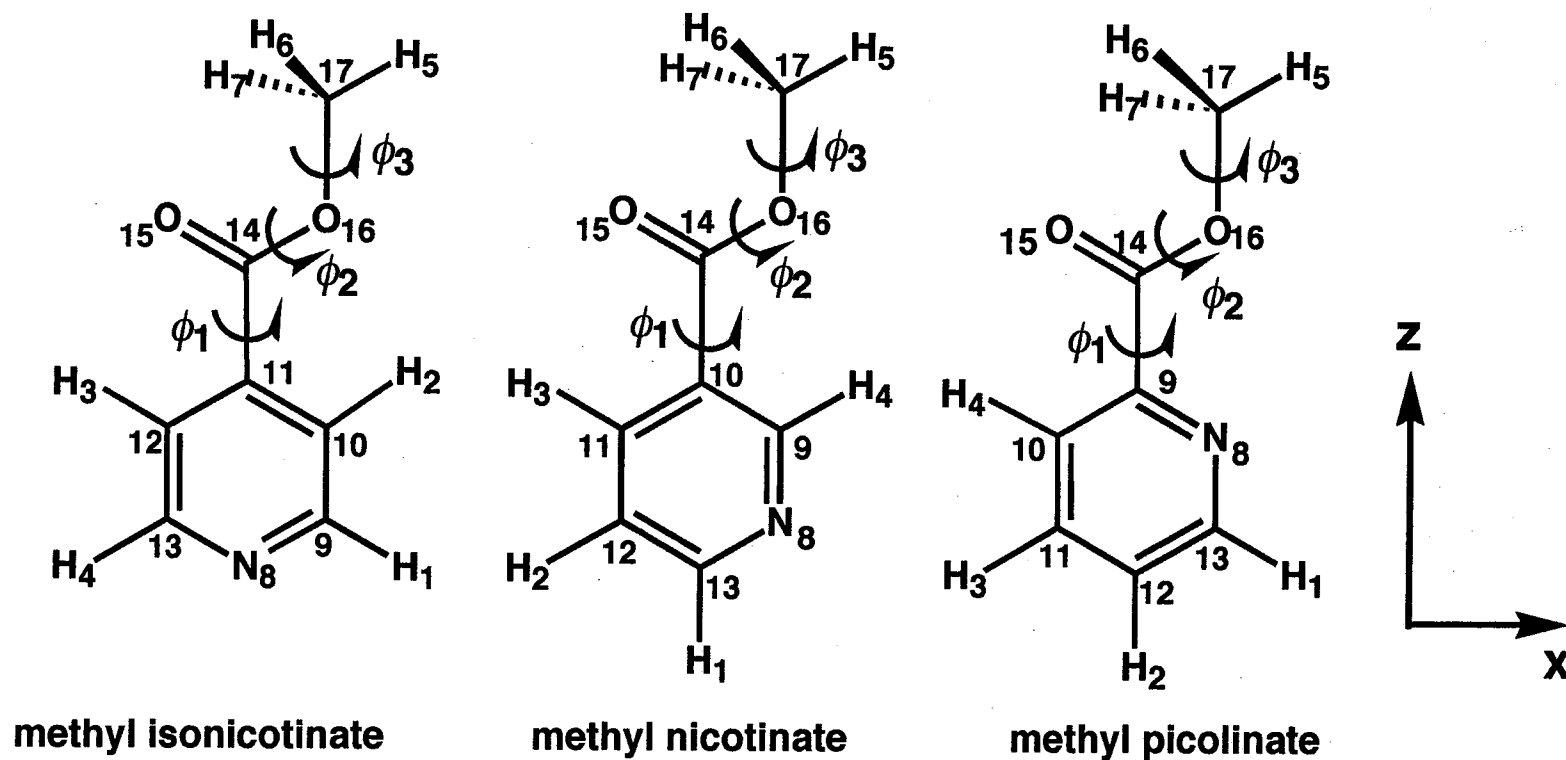


Fig. 5-1. Numbering of nuclei, dihedral angles and molecular fixed coordinates for methyl isonicotinate, and the s-trans forms of methyl nicotinate and methyl picolinate. Dihedral angles, ϕ_1 , ϕ_2 and ϕ_3 are defined to be zero in the given molecular models.

compounds. Dihedral angles $\text{CCC}_{14}\text{O}_{16}$, $\text{O}_{15}\text{C}_{14}\text{O}_{16}\text{C}_{17}$ and $\text{C}_{14}\text{O}_{16}\text{C}_{17}\text{H}_5$ are denoted by ϕ_1 , ϕ_2 and ϕ_3 , respectively. The potential energy for internal rotation is approximately represented as $V(\phi_1, \phi_2, \phi_3) = V_1(\phi_1, 0, 0) + V_2(0, \phi_2, 0) + V_3(0, 0, \phi_3)$. Because the internal rotation about the C-C₁₄ bond in the three compounds is rapid in the time scale of NMR, only the direct coupling constants averaged over internal rotation are observed. This has been confirmed by the experimental ^1H -NMR spectra of MN and MP.

Therefore the direct coupling constants D_{ij} of the molecule with internal rotors are expressed as [3, 4].

$$D_{ij} = \frac{2}{3} \sum_n p_n \sum_{\alpha, \beta} D_{ij\alpha\beta}^n S_{\alpha\beta}^n \quad (5-1)$$

where p_n and $S_{\alpha\beta}^n$ are the statistical weight and the order parameter of the n th pseudo-conformer, respectively. The direct coupling constant of the n th pseudo-conformer, $D_{ij\alpha\beta}^n$, is written as

$$D_{ij\alpha\beta}^n = -\gamma_i \gamma_j h (3 l_{ij\alpha}^n l_{ij\beta}^n - \delta_{\alpha\beta}) / 8\pi^2 r_{ij}^3 \quad (5-2)$$

where r_{ij} is the distance between nuclei i and j , $l_{ij\alpha}$ is a direction cosine of the vector r_{ij} with respect to the α axis of the molecular fixed coordinates and γ is the gyromagnetic ratio.

In the present study, the correlation between internal rotation and reorientational motion is taken into account according to the theory of Emsley, Luckhurst and Stockley (ELS)

[4-6]. In this theory, $S^n_{\alpha\beta}$ is assumed to be given by a mean external potential $U_{\text{ext}}(n, \omega)$:

$$S^n_{\alpha\beta} = Q_n^{-1} \int (1/2) (3l_\alpha l_\beta - \delta_{\alpha\beta}) \exp \{-U_{\text{ext}}(n, \omega) / RT\} d\omega \quad (5-3)$$

Here ω represents the direction of applied magnetic field in the molecular fixed coordinates and l_α denotes the direction cosine of applied magnetic field with respect to α axis of molecular fixed coordinates .

The orientational partition function Q_n is given by

$$Q_n = \int \exp \{-U_{\text{ext}}(n, \omega) / RT\} d\omega . \quad (5-4)$$

The statistical weight p_n is calculated as

$$p_n = Q_n \exp \{-U_{\text{int}}(n) / RT\} / Z \quad (5-5)$$

where $U_{\text{int}}(n)$ is the internal potential energy which is the sum of the potential energy functions for internal rotation and Z is the total partition function given by

$$Z = \sum_n \int \exp \{-(U_{\text{ext}}(n, \omega) + U_{\text{int}}(n)) / RT\} d\omega . \quad (5-6)$$

The mean external potential energy is expressed in terms of modified spherical harmonics $C_{2,m}(\omega)$ as

$$U_{\text{ext}}(n, \omega) = \sum_{m=-2}^{+2} (-1)^m \epsilon_{2,m}^n C_{2,-m}(\omega) \quad (5-7)$$

$$U_{\text{ext}}(n, \omega) = \sum_{m=-2}^{+2} (-1)^m \epsilon_{2,m}^n C_{2,-m}(\omega) \quad (5-7)$$

where $\epsilon_{2,m}^n$ is the interaction tensor of the n th pseudo-conformer in the molecular fixed coordinates and reduced spherical harmonics is expressed in terms of spherical harmonics as

$$C_{l,m}(\omega) = \left(\frac{4\pi}{2l+1} \right)^{\frac{1}{2}} Y_{l,m}(\omega). \quad (5-8)$$

It is assumed that interaction tensors $\epsilon_{2,m}^n$ are constructed from the interaction tensors of rigid sub-units, that is

$$\epsilon_{2,m}^n = \sum_j \epsilon_{2,m}^j(n). \quad (5-9)$$

The interaction tensor of the j -th rigid sub-unit in the molecular fixed coordinates, $\epsilon_{2,m}^j(n)$, is related to the interaction tensor in the local frame of each segment, $\epsilon_{2,p}^j$, by using the Wigner rotational matrix $D_{m,p}^2(\Omega_j^n)$

$$\epsilon_{2,m}^j(n) = \sum_p \epsilon_{2,p}^j D_{m,p}^2(\Omega_j^n). \quad (5-10)$$

Here Ω_j^n represents the Euler angles of the local coordinates of the j -th sub-unit with respect to the molecular fixed coordinates. Thus $U_{\text{ext}}(n, \omega)$ can be expressed in terms of the interaction parameters of rigid sub-units in the local coordinates.

5-2 Experimental

Commercial samples of MI, MN and MP with a purity of better than 99% (Tokyo Chemical Industry Co., Ltd.) were used. These compounds were dissolved in liquid crystal, Merck ZLI 1167. The concentration of each sample was 9.2 mol%. ^1H -NMR spectra were recorded on a JMN EX400 spectrometer at 400 MHz and at a constant temperature of 296 K. External D_2O was used for lock. Figure 5-2 shows observed spectra. The errors of line positions [2] were estimated to be 0.5, 0.6 and 0.7 Hz for MI, MN and MP spectra, respectively, from spectral line widths, digital resolutions and signal to noise ratios of spectra.

5-3 Analyses of the NMR spectra

The NMR spectra were analyzed by using program LCNMR [1]. Direct coupling constants and chemical shifts were determined by least-squares calculations on frequencies. The numbers of assigned absorption lines are 200, 145 and 164 for MI, MN and MP, respectively. Table 5-1 lists determined direct coupling constants and chemical shifts. The root-mean-square errors of spectral fittings for MI, MN and MP are 0.7, 0.8 and 0.7 Hz, respectively. They are consistent with the estimated errors of line positions. The indirect coupling constants (J_{ij}) in ZLI 1167 were assumed to be the same as those in CDCl_3 [1, 7] and they are listed in Table 5-2.

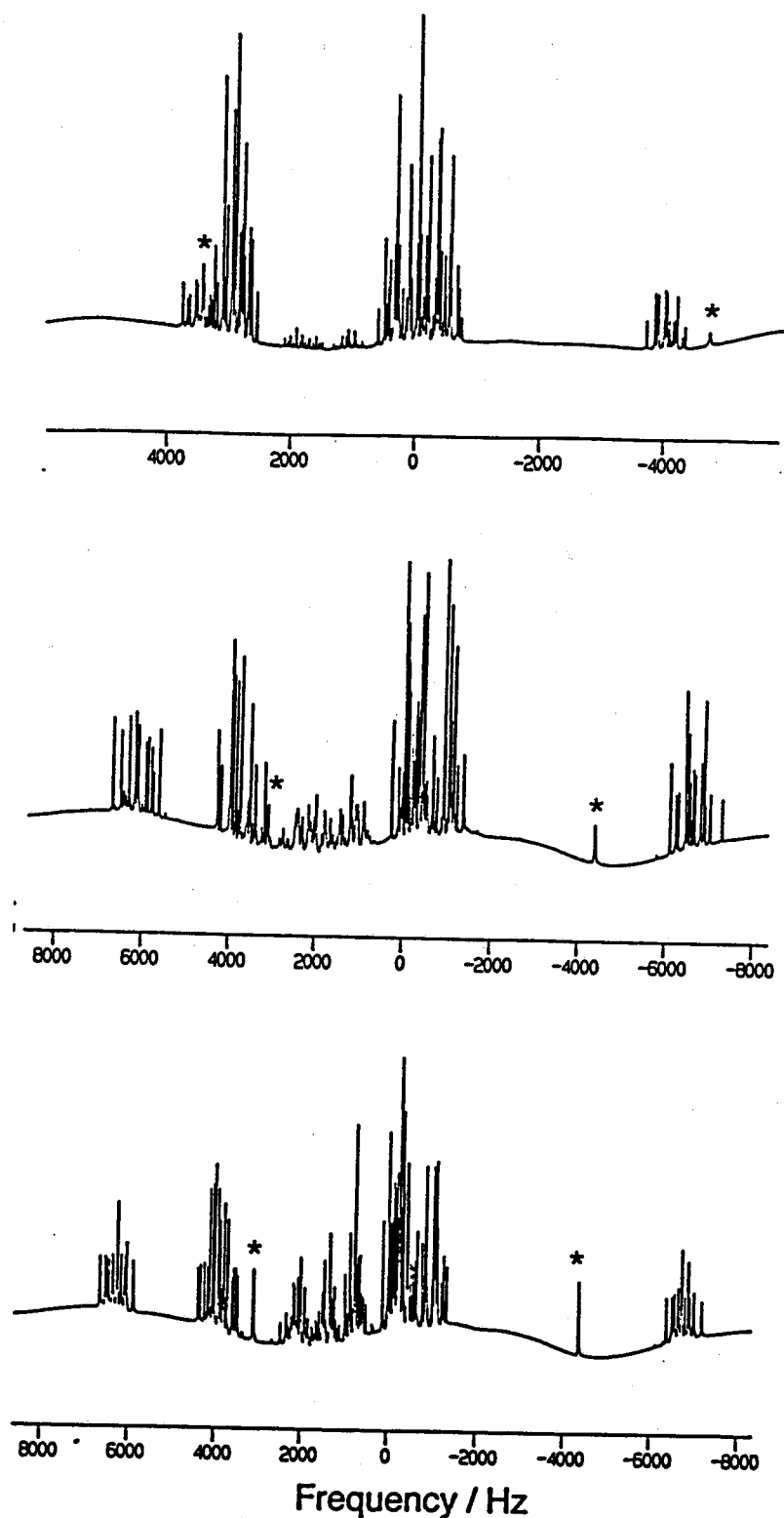


Fig. 5-2. Observed ^1H -NMR spectra of methyl isonicotinate (top), methyl nicotinate (middle), methyl picolinate (bottom) dissolved in ZLI 1167. The peaks with asterisk are due to an impurity, possibly water.

Table 5-1

Observed and calculated direct coupling constants (D_{ij}) and observed chemical shifts (ν_i) of methyl isonicotinate, methyl nicotinate and methyl picolinate dissolved in ZLI 1167 (Hz)^a

Parameter	Methyl isonicotinate			Methyl nicotinate			Methyl picolinate		
	Observed	Calc. I ^b	Calc. II ^c	Observed	Calc. I ^b	Calc. II ^c	Observed	Calc. I ^b	Calc. II ^c
D_{12}	876.3(2)	901.2	876.5	-311.1(7)	-325.3	-311.3	296.4(13)	300.7	297.8
D_{13}	52.3(2)	61.0	52.3	126.1(10)	122.1	126.5	-82.8(9)	-82.0	-83.3
D_{14}	49.0(4)	66.4	48.8	324.4(4)	309.9	325.4	-11.6(9)	-13.4	-13.7
D_{15}	42.2(2)	38.4	43.2	55.5(3)	48.7	55.8	79.3(2)	74.3	79.6
D_{23}	42.9(4)	58.4	42.8	1493.5(4)	1444.5	1493.9	-106.8(6)	-116.1	-116.9
D_{24}	52.3(2)	61.0	52.3	67.0(7)	59.4	67.3	185.3(6)	197.6	202.4
D_{25}	120.4(4)	116.6	119.6	73.1(5)	66.5	73.7	56.0(2)	52.1	56.6
D_{34}	876.3(2)	901.2	876.5	-72.4(6)	-77.8	-72.0	1577.7(3)	1546.2	1574.2
D_{35}	120.4(4)	116.7	119.6	204.0(5)	190.0	202.3	65.5(5)	63.0	66.8
D_{45}	42.2(2)	38.4	43.2	185.2(3)	171.0	183.7	169.7(5)	165.7	168.1
D_{56}	-1240.1(1)	-1236.3	-1240.0	-2122.0(2)	-2134.7	-2122.4	-2163.9(1)	-2170.2	-2163.1

$\nu_1-\nu_5$	2071.9(5)	1800.8(8)	1998.7(5)
$\nu_2-\nu_5$	1627.4(5)	1476.6(16)	1307.0(5)
$\nu_3-\nu_5$	1627.4(5)	1887.9(15)	1653.8(11)
$\nu_4-\nu_5$	2071.9(5)	2080.5(9)	1827.8(11)
RMS error ^d	0.74	1.06	0.70

^a See Fig. 5-1 for the atom numbering. Numbers in parentheses are the limits of error (3σ) referring to the last significant digits.

^b Values calculated by neglecting the correlation between internal rotation and reorientational motion.

^c Calculated values based on the ELS theory.

^d Root-mean-square errors of the spectral fitting.

Table 5-2

Observed indirect coupling constants (J_{ij}) of methyl isonicotinate, methyl nicotinate and methyl picolinate (Hz)

J_{ij}	Methyl isonicotinate ^a	Methyl nicotinate ^a	Methyl picolinate ^b
J_{12}	5.1	4.9	4.8
J_{13}	1.1	1.9	1.9
J_{14}	0.0	0.0	0.9
J_{15}	0.0	0.0	0.0
J_{23}	1.8	7.8	7.7
J_{24}	1.1	0.8	1.1
J_{25}	0.0	0.0	0.0
J_{34}	5.1	2.1	7.8
J_{35}	0.0	0.0	0.0
J_{45}	0.0	0.0	0.0

^a Taken from ref. [1].

^b Taken from ref. [7].

5-4 Vibrational corrections

Vibrational corrections ΔD_{ij} were calculated using the r_α structures determined by GED (see Table 5-3), and the valence force constants obtained in Chapters 2, 3 and 4. Vibrational corrections were calculated according to the following equation,

$$\Delta D_{ij} = \sum_n p_n \Delta D_{ij}^n \quad (5-11)$$

where p_n and ΔD_{ij}^n are the statistical weight and the vibrational correction for the n -th pseudo-conformer, respectively. Table 5-4 lists the calculated values of vibrational corrections. According to the 4-21G ab initio calculations on MI, MN and MP described in ref. 1 and Chapter 4, the potential barriers with respect to ϕ_2 are much higher than the barriers with respect to ϕ_1 and ϕ_3 . Therefore the torsional vibration related to ϕ_2 was treated as a small amplitude motion. The torsional vibrations related to ϕ_1 and ϕ_3 were treated as large amplitude motions.

5-5 Structural analyses

Structures of the pyridine rings

The direct coupling constants between the i th and j th protons in the pyridine ring are given by [3],

$$D_{ij} = -\gamma_i \gamma_j h \left\{ S_{zz}^R (3l_{ijz}^2 - 1) + (S_{xx}^R - S_{yy}^R) (l_{ijx}^2 - l_{ijy}^2) + S_{xz}^R l_{ijx} l_{ijz} \right\} / 8\pi^2 r_{ij}^3 \quad (5-12)$$

where $S_{\alpha\beta}^R$ ($\alpha, \beta = x, y, z$) are the local order parameters

Table 5-3

Assumed structural parameter values of methyl isonicotinate, methyl nicotinate and methyl picolinate^a

Parameter	Methyl isonicotinate ^b	Methyl nicotinate ^c	Methyl picolinate ^d
Bond lengths (Å)			
$r_{\alpha}(\text{C-H}_1)$	1.084	1.077	1.070
$r_{\alpha}(\text{C-H}_2)$	1.084	1.077	1.070
$r_{\alpha}(\text{C-H}_3)$	1.084	1.077	1.070
$r_{\alpha}(\text{C-H}_4)$	1.084	1.077	1.070
$r_{\alpha}(\text{C-H})_{\text{Me}}$	1.093	1.082	1.084
$r_{\alpha}(\text{N}_8\text{-C}_9)$	1.339	1.332	1.338
$r_{\alpha}(\text{N}_8\text{-C}_{13})$	1.339	1.334	1.332
$r_{\alpha}(\text{C}_9\text{-C}_{10})$	1.397	1.403	1.390
$r_{\alpha}(\text{C}_{12}\text{-C}_{13})$	1.397	1.399	1.392
$r_{\alpha}(\text{C}_{10}\text{-C}_{11})$	1.397	1.403	1.387
$r_{\alpha}(\text{C}_{11}\text{-C}_{12})$	1.397	1.393	1.383
$r_{\alpha}(\text{C}_{\text{ring}}\text{-C}_{14})$	1.497	1.488	1.490
$r_{\alpha}(\text{C}_{14}=\text{O}_{15})$	1.201	1.194	1.198
$r_{\alpha}(\text{C}_{14}\text{-O}_{16})$	1.328	1.322	1.312
$r_{\alpha}(\text{O}_{16}\text{-C}_{17})$	1.424	1.415	1.415
Bond angles (°)			
$\angle_{\alpha}\text{C}_{13}\text{N}_8\text{C}_9$	117.6	119.0	117.0
$\angle_{\alpha}\text{N}_8\text{C}_9\text{C}_{10}$	123.6	122.1	124.2
$\angle_{\alpha}\text{N}_8\text{C}_{13}\text{C}_{12}$	123.6	122.6	124.0
$\angle_{\alpha}\text{C}_9\text{C}_{10}\text{C}_{11}$	118.2	119.5	117.1
$\angle_{\alpha}\text{C}_{13}\text{C}_{12}\text{C}_{11}$	118.2	119.5	117.5

$\angle_{\alpha}C_{10}C_{11}C_{12}$	118.7	117.3	120.2
$\angle_{\alpha}C_{10}C_{11}C_{14}$	120.6		
$\angle_{\alpha}C_9C_{10}C_{14}$		118.1	
$\angle_{\alpha}N_8C_9C_{14}$			115.1
$\angle_{\alpha}CC_{14}O_{15}$	121.4	121.3	121.1
$\angle_{\alpha}CC_{14}O_{16}$	114.2	114.7	115.2
$\angle_{\alpha}C_{14}O_{16}C_{17}$	115.4	115.4	115.4
$\angle_{\alpha}H_1C_9C_{10}$	120.6		
$\angle_{\alpha}H_2C_{10}C_{11}$	120.6		
$\angle_{\alpha}H_3C_{12}C_{11}$	120.6		
$\angle_{\alpha}H_4C_{13}C_{12}$	120.6		
$\angle_{\alpha}H_1C_{13}C_{12}$		120.2	
$\angle_{\alpha}H_2C_{12}C_{11}$		121.5	
$\angle_{\alpha}H_3C_{11}C_{10}$		119.6	
$\angle_{\alpha}H_4C_9C_{10}$		120.3	
$\angle_{\alpha}H_1C_{13}N_8$			116.2
$\angle_{\alpha}H_2C_{12}C_{11}$			121.4
$\angle_{\alpha}H_3C_{11}C_{10}$			120.5
$\angle_{\alpha}H_4C_{10}C_9$			119.8
$\angle_{\alpha}HC_{17}O_{16}$	108.8	108.8	108.8

^a See Fig. 5-1 for the atom numbering.

Table 5-4

Calculated vibrational corrections ($\Delta D_{ij}^{\text{vib}}$) to observed direct coupling constants (Hz)

$i\ j$	Methyl isonicotinate	Methyl nicotinate	Methyl picolinate
1 2	-20.4	-7.7	-11.3
1 3	-0.5	-3.1	-0.6
1 4	-0.5	-4.6	-0.1
1 5	-0.2	-0.3	0.2
2 3	-0.4	-27.6	-5.6
2 4	-0.5	-0.3	-3.5
2 5	-0.8	-0.4	-0.2
3 4	-20.4	0.4	-33.4
3 5	-0.8	-2.1	-0.1
4 5	-0.2	-0.7	-1.3
5 6	19.2	31.1	27.9

for the pyridine ring and $l_{ij\alpha}$ is the direction cosine of the internuclear vector r_{ij} with respect to the α - axis of the molecular fixed coordinates.

Since the pyridine ring of MI is assumed to have C_{2v} symmetry, the local order parameters of the ring are represented by S^R_{zz} and $S^R_{xx} - S^R_{yy}$. Therefore the positions of protons and the local order parameters were determined from observed D_{ij} . Table 5-5 lists the local order parameters of pyridine rings and the positions of ring protons. As shown in Table 5-5, the positions of ring protons agree with those determined by GED within experimental errors.

Since the pyridine rings of MN and MP have C_s symmetry, the local order parameters of the rings are S^R_{zz} , $S^R_{xx} - S^R_{yy}$ and S^R_{xz} . Therefore the number of observed direct coupling constants in the pyridine ring is insufficient to determine the local order parameters and the positions of protons. The positions of protons determined by GED in Chapters 3 and 4 were not exactly consistent with the observed D_{ij} . Therefore the positions of ring protons were adjusted so as to be consistent with the observed D_{ij} . Table 5-5 lists the resultant positions of protons and the local order parameters of pyridine rings. Conformational analyses were performed by using the assumed positions of ring protons.

Conformational analyses

The potential function for methyl torsion was approximated by

$$V(0, 0, \phi_3) = (1/2)V_3(1 - \cos 3\phi_3) \quad (5-13)$$

Table 5-5

Local order parameters of the pyridine ring and the positions of ring protons^a

Parameter	Methyl isonicotinate ^b	Methyl nicotinate	Methyl picolinate			
Local order parameters						
S^R_{zz}	-0.1166 (7)	-0.2062 (1)	-0.214 (1)			
$S^R_{xx} - S^R_{yy}$	-0.173 (1)	-0.1081 (2)	-0.098 (3)			
S^R_{xz}		-0.0474 (2)	-0.010 (1)			
Positions of ring protons different from those determined by GED(Å) ^c						
	x	z	x	z	x	z
H ₁	-	-	0.171	-3.795	-	-
H ₂	2.151 (14)	-0.199 (15)	-2.033	-2.687	0.150	-3.760
H ₃	-2.151 (14)	-0.199 (15)	-	-	-	-

^a See Fig. 5-1 for the atom numbering. Numbers in parentheses are the estimated limits of error referring to the last significant digits.

^b The distance between H₁ and H₄ is assumed to be the same as a gas-phase value, 4.117 Å (see Chapter 2).

^c Cartesian coordinates are shown in Fig. 5-1 where the C(-C₁₄) atom of the ring is placed at (0, 0, 0). Assumed positions are listed for MN and MP. The positions of ring protons determined by GED are as follows; H₂ (2.152 (25), 0.0, -0.191 (25)) and H₃ (2.152 (25), 0.0, -0.191 (25)) for methyl isonicotinate, H₁

(0.198 (30), 0.0, -3.797 (10)) and H₂ (-2.016 (22), 0.0, -2.717 (30)) for methyl nicotinate and H₂ (0.109 (40) , 0.0, -3.787 (10)) for methyl picolinate.

where ϕ_3 is defined to be zero when the methyl group takes a staggered configuration. Since the value of V_3 was not sensitive to dipolar coupling constants, V_3 was assumed to be 1.0, 1.3 and 1.1 kcal mol⁻¹ (4-21G values) for MI, MN [1] and MP (see Chapter 4), respectively.

Potential function $V(\phi_1, 0, 0)$ was approximated by

$$V(\phi_1, 0, 0) = (1/2) \{ V_1(1 - \cos\phi_1) + V_2(1 - \cos 2\phi_1) \}. \quad (5-14)$$

Potential parameter V_1 was taken as an adjustable parameter for MN and MP. Potential parameter V_2 could not be determined simultaneously. Conformational analysis was carried out for fixed values of V_2 . The r.m.s. errors of spectral fittings took minimum values at $V_2 = 12, 15$ and 12 kcal mol⁻¹ for MI, MN and MP, respectively.

In preliminary analyses, it was assumed that order parameters are independent of internal rotation. In this case, the orientation of solute molecules is described by effective order parameters and so eq. (5-1) is written as [3]

$$D_{ij} = \frac{2}{3} \sum_{\alpha, \beta} S_{\alpha\beta} \sum_n p_n D_{ij\alpha\beta}^n \quad (5-15)$$

where α and β refer to the molecular fixed coordinates, $S_{\alpha\beta}$ the effective order parameter and $D_{ij\alpha\beta}^n$ is the dipolar coupling constant of the n th pseudo-conformer defined by eq. (5-2). Here the n th pseudo-conformer is defined to take the dihedral angle, ϕ_1 , of $n \times 10^\circ$.

Table 5-1 lists the calculated direct coupling constants. Table 5-6 shows the effective order parameters and potential parameters. The r.m.s. errors of the spectral fitting are 30, 48 and 25 Hz for MI, MN and MP, respectively. The large r.m.s errors and large discrepancies between observed and calculated coupling constants show that the correlation of internal rotation and reorientational motion should be taken into account in the conformational analysis of these compounds.

In the conformational analysis based on the ELS theory, each molecule was divided into four rigid sub-units, i.e., ring (C_5H_4N), $C=O$, $C-O$, and $O-Me$. Figure 5-3 shows the sub-units of MI and their local coordinates. The interaction parameters to describe U_{ext} are $\epsilon_{2,0}^R$, $\epsilon_{2,2}^R$, $\epsilon_{2,1}^R$, $\epsilon_{2,0}^{C=O}$, $\epsilon_{2,0}^{C-O}$ and $\epsilon_{2,0}^{O-Me}$. In the case of MI, $\epsilon_{2,1}^R$ is zero because the ring has C_{2v} symmetry.

In the case of MI, MN and MP, eq. (5-7) is expressed as follows:

Table 5-6

Potential parameters for the internal rotation with respect to ϕ_1 and effective order parameters for methyl isonicotinate, methyl nicotinate and methyl picolinate

Parameter	Methyl isonicotinate	Methyl nicotinate	Methyl picolinate
V_1^a	-	0.3 (1) ^b	0.5 (1) ^c
V_2^a	12.0 ^d	12.0 ^d	12.0 ^d
S_{zz}	-0.1197 (3)	-0.199 (1)	-0.2112 (3)
$S_{xx} - S_{yy}$	-0.180 (6)	-0.097 (12)	-0.105 (2)
S_{xz}	-	-0.049 (6)	-0.020 (1)

^a Potential parameter for internal rotation in kcal mol⁻¹ (see eq. (5-14)).

^b This value means that the population of s-trans conformer is 63(3)%.

^c It means that the population of s-trans conformer is 70(3)%

^d Assumed.

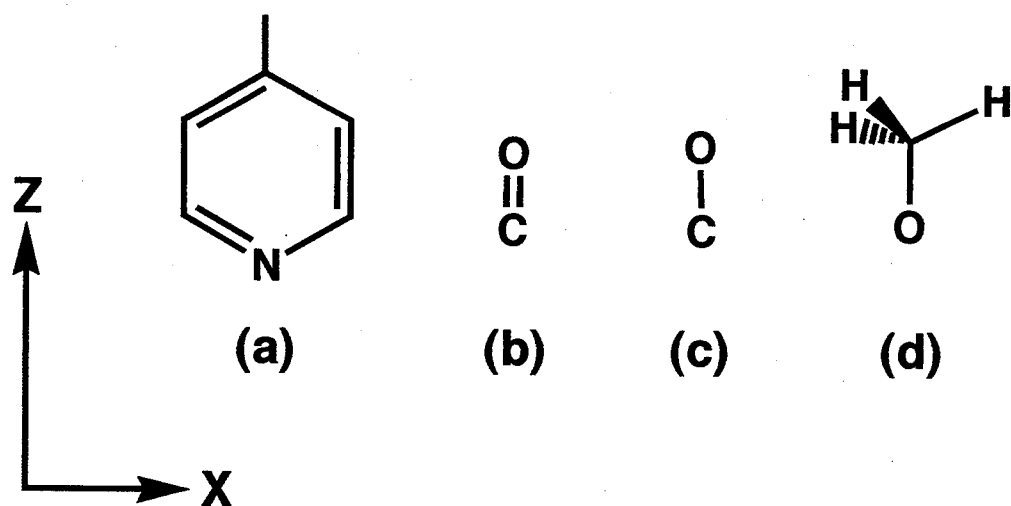


Fig. 5-3. Sub-units of methyl isonicotinate and the local coordinates of sub-units: (a)ring (b)C=O (c)C-O (d)O-CH₃.

$$\begin{aligned}
U_{\text{ext}}(n, \omega) &= \varepsilon_{2,0}^n C_{2,0}(\omega) + \varepsilon_{2,1}^n C_{2,-1}(\omega) + \varepsilon_{2,-1}^n C_{2,1}(\omega) + \varepsilon_{2,2}^n C_{2,-2}(\omega) + \varepsilon_{2,-2}^n C_{2,2}(\omega) \\
&= - \left\{ \varepsilon_{2,0}^R + \varepsilon_{2,0}^{\text{C=O}} P_2(\cos \theta^{\text{C=O}}) + \varepsilon_{2,0}^{\text{C-O}} P_2(\cos \theta^{\text{C-O}}) + \varepsilon_{2,0}^{\text{O-Me}} P_2(\cos \theta^{\text{O-Me}}) \right\} C_{2,0}(\omega) \\
&\quad + \left\{ \varepsilon_{2,1}^R - \sqrt{\frac{3}{8}} e^{-i\phi^n} \left(-\varepsilon_{2,0}^{\text{C=O}} \sin 2\theta^{\text{C=O}} + \varepsilon_{2,0}^{\text{C-O}} \sin 2\theta^{\text{C-O}} + \varepsilon_{2,0}^{\text{O-Me}} \sin 2\theta^{\text{O-Me}} \right) \right\} C_{2,-1}(\omega) \\
&\quad + \left\{ -\varepsilon_{2,1}^R - \sqrt{\frac{3}{8}} e^{i\phi^n} \left(-\varepsilon_{2,0}^{\text{C=O}} \sin 2\theta^{\text{C=O}} + \varepsilon_{2,0}^{\text{C-O}} \sin 2\theta^{\text{C-O}} + \varepsilon_{2,0}^{\text{O-Me}} \sin 2\theta^{\text{O-Me}} \right) \right\} C_{2,1}(\omega) \\
&\quad - \left\{ -\varepsilon_{2,2}^R - \sqrt{\frac{3}{8}} e^{-2i\phi^n} \left(\varepsilon_{2,0}^{\text{C=O}} \sin^2 \theta^{\text{C=O}} + \varepsilon_{2,0}^{\text{C-O}} \sin^2 \theta^{\text{C-O}} + \varepsilon_{2,0}^{\text{O-Me}} \sin^2 \theta^{\text{O-Me}} \right) \right\} C_{2,-2}(\omega) \\
&\quad - \left\{ -\varepsilon_{2,2}^R - \sqrt{\frac{3}{8}} e^{2i\phi^n} \left(\varepsilon_{2,0}^{\text{C=O}} \sin^2 \theta^{\text{C=O}} + \varepsilon_{2,0}^{\text{C-O}} \sin^2 \theta^{\text{C-O}} + \varepsilon_{2,0}^{\text{O-Me}} \sin^2 \theta^{\text{O-Me}} \right) \right\} C_{2,2}(\omega)
\end{aligned}
\tag{5-16}$$

where $P_2(\cos \theta^j)$ is the second Legendre polynomial and θ^j is the angle between the z axis of the local coordinates of the jth sub-unit and the z axis of molecular fixed coordinates.

Since the z axis in the local coordinates of C-C₅H₄N is nearly parallel to the z axis in the local coordinates of the O-Me sub-unit, it is quite difficult to determine $\varepsilon_{2,0}^R$ and $\varepsilon_{2,0}^{\text{O-Me}}$ independently. Thus the sum of $\varepsilon_{2,0}^R$ and $\varepsilon_{2,0}^{\text{O-Me}}$ was treated as a parameter. Because the remaining interaction parameters could not be determined independently, the interaction parameter $\varepsilon_{2,0}^{\text{C=O}}$ was assumed to be 0.2 kcal mol⁻¹ by referring to the NMR study of phenyl acetate dissolved in ZLI 1167 [8].

In the conformational analyses, the skeleton of the COOCH₃ group was assumed to be the same as the result of GED. The calculated D_{ij} were, however, in poor agreement with observed D_{ij} . In order to consider the possibility of the deformation

parameters of COOCH₃ group were adjusted within the experimental errors of GED results. In MI and MN, calculated D_{ij} are in good agreement with observed one when the r_α (C-H) of methyl group is assumed to be 1.091 Å and 1.079 Å for MI and MN, respectively. The calculated D_{ij} of MP agree with observed one when the r_α (C-H) of methyl group, $\angle C_2C_7O_9$ and $\angle C_7O_9C_{10}$ are assumed to be 1.091 Å, 116.3° and 113.9°, respectively.

5-6 Results and discussion

As shown in Table 5-1, calculated direct coupling constants are in good agreement with the observed ones. The r.m.s. errors of the spectral fitting are 1.2, 1.2 and 5.4 Hz for MI, MN and MP, respectively. Table 5-7 shows the interaction parameters and potential parameters.

The order parameters of pseudo-conformers were calculated by using eq. (5-3). Table 5-8 lists only the order parameters for $\phi_1 = 0^\circ$ and 180° , for the order parameters around $\phi_1 = 90^\circ$ and 270° considerably depend on the assumed value of $\epsilon^{C=O}_{2,0}$. According to the previous studies of MI and MN in 80 mol% EBBA + 20 mol% MBBA based on the ELS model [1], the differences in the order parameters are within 0.04. In ZLI 1167, however, the order parameters of the pseudo-conformers considerably change with internal rotation.

The ratio of the vibrational correction to the direct coupling constant between a proton of the pyridine ring and a methyl proton is less than 2% (see Table 5-1 and Table 5-4), which corresponds to 0.7% in the interatomic distance [2].

Table 5-7

Potential parameters for the internal rotation with respect to ϕ_1 and interaction parameters obtained on the basis of the ELS theory for methyl isonicotinate, methyl nicotinate and methyl picolinate^a

Parameter	Methyl isonicotinate	Methyl nicotinate	Methyl picolinate
V_1^b	-	0.33 (2)	0.45 (2)
V_2^b	12 (5)	15 (5)	12 (5)
$\epsilon^R_{2,0}^c$	-0.13 (1)	-0.58 (2)	-0.65 (1)
$\epsilon^R_{2,1}^c$	-	-0.10 (2)	0.04 (2)
$\epsilon^R_{2,2}^c$	-0.72 (1)	-0.59 (1)	-0.51 (1)
$\epsilon^{C=O}_{2,0}^c$	0.20 ^d	0.20 ^d	0.20 ^d
$\epsilon^{C-O}_{2,0}^c$	0.90 (3)	0.80 (5)	0.70 (5)

^a Numbers in parentheses are the estimated limits of error referring to the last significant digits.

^b Potential parameter in kcal mol⁻¹.

^c Interaction parameters in kcal mol⁻¹

^d Assumed.

Table 5-8

Calculated order parameters of the pseudo-conformers with $\phi_1 = 0^\circ$ and 180° based on the ELS theory for methyl isonicotinate, methyl nicotinate and methyl picolinate

Parameter	Methyl isonicotinate		Methyl nicotinate		Methyl picolinate	
	ϕ_1	0° 180°	0°	180°	0°	180°
S_{zz}		-0.110	-0.199	-0.208	-0.213	-0.212
$S_{xx} - S_{yy}$		-0.141	-0.070	-0.094	-0.076	-0.066
S_{xz}		-0.100 0.100	-0.110	0.050	-0.056	0.085

The experimental errors of $r_{\alpha}(\text{C-H})$ in the GED analyses are about 1% as described in Chapters 2, 3 and 4. The effect of vibrational corrections on the structure is comparable to the errors of $r_{\alpha}(\text{C-H})$ determined by GED. Therefore the results of conformational analyses are insensitive to vibrational corrections.

The positions of the ring protons of MI in ZLI 1167 agree with those determined by GED within experimental errors. Therefore the pyridine ring of MI is not significantly deformed by liquid crystal solvent ZLI 1167. In the case of MN and MP, some structural parameters must be adjusted beyond the error limits of the values determined by GED. This means the molecular structures are significantly different from those in ZLI 1167.

The population of the s-trans form in ZLI 1167 was obtained by using eq. (5-5). The population is 64 (1)% and 68 (1)% for MN and MP, respectively. It is noted that the populations could be determined very precisely by the present NMR study. The population of MN is larger than the population of 53 (1)% observed in 80 mol% EBBA + 20 mol% MBBA. Difference is much larger than the estimated limits of error. This suggests that conformation is liable to change with liquid crystals. According to the data analyses of GED, the population of the s-trans form is 75 (25)% and 77 (23)% for MN and MP, respectively (see Chapters 3 and 4). Therefore in each of MN and MP, the population of the s-trans form in ZLI 1167 is in qualitative agreement with that in the gas phase.

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Chapter 6

Summary

The molecular structures of methoxy carbonyl pyridines have been studied by gas-phase electron diffraction and liquid crystal NMR. No structural data were available for these isomers.

The molecular structures of methyl isonicotinate (MI) methyl nicotinate (MN) and methyl picolinate (MP) have been determined by gas-phase electron diffraction combined with ab initio calculations. It has been determined that the skeleton of each molecule is planar, showing the presence of the conjugation between the COOCH₃ group and the pyridine ring. Both MN and MP have s-trans and s-cis conformers. The mole fraction of the s-trans conformer is 75(25)% and 77(23)% for MN and MP, respectively. Determined structures have been compared with those of related molecules.

The (O=)C-O distances in MI (1.331 Å), MN (1.325 Å) and MP (1.325 Å) are considerably shorter than the corresponding distances in methyl acrylate (1.349 Å) [1] and methyl acetate (1.360 Å) [2]. This shortening is ascribed to the delocalization of electrons. The ring structures of MN, MI and MP are essentially in agreement with those of pyridine [3].

The C-C7 distance of MN is significantly shorter than those of MI and MP. This shows that electrons more delocalize in MN than in MI and MP.

The structures of MI, MN and MP have been studied from ¹H-NMR spectra using liquid crystal ZLI 1167 as a solvent.

Conformational analyses were carried out by using the effective order method and the ELS model. The results support the ELS model, showing the existence of the considerable correlation between the reorientational motion and the internal rotation of solute molecules.

The molecular skeletons of MI, MN and MP are planar in ZLI 1167. Both MN and MP have s-trans and s-cis conformers in ZLI 1167. The determined mole fraction of the s-trans conformer is 64(1)% and 68(1)% for MN and MP, respectively. No significant differences have been found in the mole fractions between in the gas phase and the mesophase. The mole fraction of the s-trans form of MN is about 10% larger than that in 80% EBBA + 20% MBBA. The positions of the ring protons of MI agree with those in the gas phase within experimental uncertainties.

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