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Molecular structure of *trans*-cinnamaldehyde as determined by gas electron diffraction aided by DFT calculations

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Abstract

The molecular structure of *trans*-cinnamaldehyde ((E)-3-phenyl-2-propenal) was determined by means of gas electron diffraction. The nozzle temperature was 165 °C. The results of B3LYP calculations with the 6-31G** basis set were used as supporting information. It was found that this molecule has two stable conformers, s-*cis* and s-*trans*, which differ in the orientation of the -CH=O group. Their abundances at 165 °C were determined to be 25±19% and 75%, for the s-*cis* and s-*trans*, respectively. This conformational composition is consistent with the prediction by the theoretical calculations. The determined structural parameters (r_g and $\angle_\alpha$) of the more abundant conformer, s-*trans*, of *trans*-cinnamaldehyde are as follows: $<r(C–C)_{ring}> = 1.398(1)$ Å; $r(C=C) = 1.348$ Å ($\leftarrow$); $r(C_1–C) = 1.470(8)$ Å; $r(C–C(=O)) = 1.473(\leftarrow)$ Å; $r(C=O) = 1.225(6)$ Å; $<r(C–H)> = 1.116(6)$ Å; $\angle C_6–C_1–C_2 = 118.6(3)°$; $\angle C_1–C_2–C = 121.0(\leftarrow)°$; $\angle C–C_6–C_1 = 121.4(\leftarrow)°$; $\angle C_2–C_1–C(=C) = 122.0(26)°$; $\angle C_1–C=C = 128.3(26)°$; $\angle C=C–CO = 115.3(27)°$; $\angle C–C=O = 126.6(19)°$. The C_1, C_2 and C_6 atoms are on the ring with the C_1 attached to the -CH=CH–CHO group, and the C_2 and C_6 are on the *cis* and *trans* sides to the C=C bond, respectively. Angle brackets denote average values; parenthesized values are the estimated

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limits of error (3σ) referring to the last significant digit; left arrows in the parentheses mean that the differences to the preceding parameters are fixed.

1. Introduction

The geometrical structure of odorant molecule is one of the essential factors in the molecular recognition by olfactory receptors. However, the majority of studies on the structure-odor relationship of molecules are not based on the experimentally determined geometrical structures, and it is expected that the reliable molecular structures of odorant molecules will contribute to the investigation of the molecular recognition by the receptors.

Recently we have succeeded in the structural determination of some compounds with characteristic odors such as menthol [1], isomenthol [1], carvone [2], vanillin [3], isovanillin [3] and ethylvanillin [3], by means of gas electron diffraction (GED). In the present study, *trans*-cinnamaldehyde ((*E*)-3-phenyl-2-propenal) has been chosen as the target.

This compound is the main constituent of cinnamon oil and has a strong smell of cinnamon. In addition, it has been found recently that *trans*-cinnamaldehyde activates the transient receptor potential (TRP) ion channel, TRPA1, that is activated also by noxious cold [4]. In spite of the physiological importance of *trans*-cinnamaldehyde, its geometrical structure has not been thoroughly studied. As in the case of vanillin and isovanillin [3], *trans*-cinnamaldehyde is expected to have two conformers, s-*cis* and s-*trans*, which are different from each other in the orientation of the aldehyde group (see Fig. 1). In the present study, the molecular structure and conformational property of *trans*-cinnamaldehyde have been investigated by means of GED aided by the density functional theory (DFT) calculations.

2. Experimental

A commercial sample (Aldrich Chemical Co.) with purity of 99% was used after vacuum distillation. Electron diffraction patterns were recorded on 8 in × 8 in Kodak projector slide plates with an apparatus equipped with an r^3-sector [5]. The camera distance was 244.3 mm to cover the s-range of 4.5 – 33.9 Å^{-1}, which is sufficient for molecules of this size. Although the sample is liquid at room temperature with a strong smell of cinnamon, its vapor pressure is not high enough for the GED experiment and the sample was heated to 165 °C by using the nozzle system reported in Ref. [6]. The acceleration voltage of incident electrons was about 38 kV and the electron wavelength calibrated to the r_a (C=S) distance of CS_2 (1.5570 Å) [7] was 0.06319 Å. The photographic plates were developed for 4.5 min in a Dektol developer diluted 1:1. The photometry process was described in detail elsewhere [8]. Other experimental conditions are as follows: beam current, 1.0 – 1.1 µA; background pressure during exposure, 2.7 × 10^{-6} Torr; uncertainty in the scale factor (3 σ), 0.05%; exposure time, 108 – 163 s; number of plates used, 3. The experimental intensities and backgrounds are available as supplementary information (Table S1).

Elastic atomic scattering factors were calculated as described in Ref. [9], and inelastic ones were taken from Ref. [10]. The experimental molecular scattering intensities are shown in Fig. 2 with the final calculated intensities. A diagonal weight matrix was used in the least-squares analysis on the molecular scattering intensities.

3. Theoretical calculations

Geometry optimizations and vibrational calculations of the two conformers of *trans*-cinnamaldehyde were carried out by using the B3LYP method with the 6-31G** basis set. Program GAUSSIAN 03 [11] was used. The obtained geometrical parameters for the s-*cis* and s-*trans* conformers are listed in Table 1. No imaginary frequency was yielded

from the vibrational calculations showing that these planar forms with the C_s symmetry correspond to the local minima of the potential surface. As shown in Table 1, the obtained energy difference between the two conformers, ΔE, is about 4.69 kJ/mol with the *s-trans* conformer being more stable. The s-*cis* conformer has a larger C_8–C_9 distance and C_8–C_9=O_{10} angle than the s-*trans* by 0.008 Å and 0.4°, respectively. The conformational dependence of these parameters seems to be caused by the steric repulsion between the C_7 and O_{10} atoms of the s-*cis* conformer, and the energy difference between the conformers can be attributed to this steric repulsion. In order to predict the relative abundance of the conformers at 438 K, at which the GED intensity was measured, the free energy difference, ΔG, was calculated by using the ΔE, the theoretical rotational constants and the scaled force constants (see the Analyses section for the scaling of the force constants). The obtained ΔG value of 4.68 kJ/mol corresponds to the relative abundance of 22% (s-*cis*) vs. 78% (s-*trans*).

The potential function for the C_8–C_9 internal rotation was obtained by a series of geometry optimizations where only the internal rotation angle, $\phi_1 = \phi(C_7{=}C_8{-}C_9{=}O_{10})$, was fixed at 0 to 180° with an interval of 30°. The potential functions for the C_1–C_7 internal rotation were also obtained similarly, where the internal rotation angle is defined as $\phi_2 = \phi(C_2{=}C_1{-}C_7{=}C_8)$. The obtained potential functions are shown in Figs. 3 and 4. The minima at $\phi_1 = 0°$ and 180° shown in Fig. 3 correspond to the s-*cis* and s-*trans* conformers, respectively. Figures 3 and 4 rule out the possibility of the conformer other than the s-*cis* and s-*trans*.

4. Analyses

Normal vibration analysis. The Cartesian force constants obtained from the B3LYP/6-31G** calculations were transformed into the force constants, f_{ij}, for the internal coordinates. The theoretical f_{ij}'s were modified by the scaling method so as to reproduce the observed vibrational wavenumbers [12]. The linear scaling formula, f_{ij} (scaled) = (c_i

$c_j)^{1/2}$ f_{ij} (unscaled), was used where c_i is a scale factor [13]. An agreement between the observed and calculated vibrational wavenumbers within $\pm 2\%$ was obtained by assuming that the observed wavenumbers are those of the more stable s-*trans* conformer and that all the c_i's are 0.924. This value is consistent with the frequency scaling factor of 0.9614 recommended for B3LYP/6-31G* calculations [14]. The observed and calculated vibrational wavenumbers are listed in Table S2 of Supplementary Information.

Analysis of electron diffraction data. The following treatment was adopted using the results of the B3LYP/6-31G** geometry optimizations: (1) the molecule was assumed to be planar with C_s symmetry; (2) the differences among the C–C bond lengths in the ring and the $C_7=C_8$ double bond length were set equal to their theoretical values; (3) the difference between the two C–C single bond lengths, $r(C_1–C_7)$ and $r(C_8–C_9)$, was set equal to its theoretical value; (4) the differences among all the C–H bond lengths were set equal to their theoretical values; (5) the differences among the $C_6–C_1–C_2$, $C_1–C_2–C_3$ and $C_5–C_6–C_1$ angles were set equal to their theoretical values; (6) all the C–H bonds in the ring bisect the C–C–C angles; (7) the difference between the $C_1–C_7–H_{16}$ and $C_8=C_7–H_{16}$ angles was set equal to its theoretical value, and the bond angles, $C_7=C_8–H_{17}/C_9–C_8–H_{17}$ and $C_8–C_9–H_{18}/O_{10}=C_9–H_{18}$, were treated similarly; (8) the parameter differences between the s-*cis* and s-*trans* conformers were set equal to their theoretical values. The relative abundance of the s-*cis* and s-*trans* conformers was refined as an independent parameter in the analysis. The $C_7=C_8$ bond length had to be treated as a dependent parameter (assumption (2)) because a preliminary analysis in which the $C_7=C_8$ bond length was refined as an independent parameter resulted in an unreasonably small value for it. The independent parameters and the constraints are summarized in Table 2.

The $C_1–C_7$ internal rotation (*i.e.*, the ϕ_2 rotation) was treated as a large amplitude motion because the vibrational wavenumber of the $C_1–C_7$ torsional mode was estimated to be only about 55 cm^{-1} for both conformers. First, eigenfunctions and energy levels were calculated from the potential function shown in Fig. 4 according to the method described in

ref. [15]. Then the thermal-averaged probability distribution of the angle ϕ_2 was estimated from the obtained eigenfunctions and energy levels. Finally, mean amplitudes, l, shrinkage corrections, $r_a - r_\alpha$ [16], and the anharmonic parameters, κ [17], were estimated by using the probability distribution based on the method described in ref. [18]. The contribution of the small-amplitude vibrational modes to the l, $r_a - r_\alpha$ and κ was calculated by using the above-mentioned scaled force constants, where the contribution from the C_1–C_7 torsion was omitted. The κ's for the bonded atom pairs were calculated in a diatomic approximation, $\kappa = (a/6)l^4$ [19], where the Morse parameter, a, was assumed to be 2.0 Å^{-1}. The mean amplitudes were adjusted in groups. The groups were separated according to the r_a distances of the atomic pairs. The differences among the mean amplitudes in each group were fixed at the calculated values. Table S3 of Supplementary Information lists the mean amplitudes, shrinkage corrections and κ's with the corresponding r_a distances. Structural parameters, mean amplitudes, the relative abundance of the s-*cis* and s-*trans* conformers and the index resolution, k,[1] were determined by least-square analysis on molecular scattering intensities.

5. Results and discussions

Table 3 lists the obtained structural parameters for the s-*trans* conformer of *trans*-cinnamaldehyde. The experimental radial distribution curve with residuals is shown in Fig. 5. The resultant R-factor[2] was 0.040 and the index of resolution, k, was 0.89±0.02. From this fitting quality, it can be concluded that the assumption of the conformational composition (s-*cis* and s-*trans* only) is correct. The correlation matrix is listed in Table S4 of Supplementary Information. No off-diagonal element of the correlation matrix has an absolute value larger than 0.87.

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[1] k is defined as $sM(s)^{\text{obs}} = k\, sM(s)^{\text{calc}}$.

[2] R-factor is defined as $R = [\, \sum_i W_i\,(\Delta sM(s)_i)^2 \,/\, \sum_i W_i\,(sM(s)_i^{\text{obs}})^2 \,]^{1/2}$, where $\Delta sM(s)_i = sM(s)_i^{\text{obs}} - sM(s)_i^{\text{calc}}$ and W_i is a diagonal element of the weight matrix.

The conformational composition of *trans*-cinnamaldehyde at 438 K was determined to be 25% (s-*cis*) vs. 75% (s-*trans*) with the estimated error limit (3σ) of $\pm$ 19%. This result is consistent with the estimation obtained from the B3LYP/6-31G** calculations (22% vs. 78%). The conformational composition of *trans*-cinnamaldehyde at room temperature (298 K) was calculated by using the observed relative abundance and the temperature dependence of the ΔG, that was derived from the theoretical rotational constants and the scaled force constants, to be 22% (s-*cis*) vs. 78% (s-*trans*) with the estimated error limit of $\pm$ 20%. Therefore, it can be concluded that *trans*-cinnamaldehyde exists mostly as the s-*trans* conformer, although the existence of the minor conformer, s-*cis*, cannot be ruled out. As mentioned in the Theoretical calculations section, the steric repulsion between the C_7 and O_{10} atoms of the s-*cis* seems to make this conformer unstable compared with the s-*trans*, for which such an interaction is absent.

The $r_g(C_8-C_9)$ of *trans*-cinnamaldehyde (1.473$\pm$0.008 Å) is shorter and the $r_g(C_9=O_{10})$ (1.225$\pm$0.006 Å) is slightly longer than the corresponding values of acrolein ($CH_2=CH-CHO$, 1.484$\pm$0.004 and 1.217$\pm$0.003 Å, respectively [20]) suggesting a stronger conjugation for *trans*-cinnamaldehyde caused by the aromatic ring. On the other hand, the average of the $r_g(C-C)_{ring}$ of *trans*-cinnamaldehyde (1.398$\pm$0.001 Å) is very close to that of benzene (1.399$\pm$0.001 Å [21]).

In Table 3, the optimized structural parameters of the B3LYP/6-31G** calculation are also listed for comparison. In order to compare the experimental r_g distances with the theoretical r_e distances, the differences between them were estimated to be, $r_g - r_e \approx (3/2)al^2$ [15], by using the diatomic approximation [22] and by neglecting the centrifugal distortion term. By assuming the Morse parameter, a, to be 2.0 Å^{-1}, the term, $r_g - r_e$, is estimated to be around 0.006 Å for the C–C bonds in the ring, 0.007 Å for the C–C single bonds, 0.005 Å for the C=C bond, 0.004 Å for the C=O bond and 0.016 – 0.018 Å for the C–H bonds. As compared with the experimental result, the B3LYP/6-31G** calculation overestimates the C–C distances in the ring and underestimates the C–H distances. As for

the bond angles, the theoretical values reproduce the experimental values with a moderate accuracy except for the $C_7=C_8-C_9$ angle.

In some cases, DFT and MP2 methods provide significantly different results especially for the conformational stability of benzene derivatives (*e.g.*, refs. [23, 24]). Therefore, a similar comparison has been made with the theoretical geometries of the MP2 calculations. First, the MP2/6-31G** calculations have been carried out, from which the non-planar structures were obtained for both conformers. However, the application of the cc-pVTZ basis set has provided planar structures in accordance with the experiment. From Table 3 it can be seen that both theoretical methods provide almost the same results, which justifies the application of the B3LYP/6-31** calculations as constraints in our structural analysis.

6. Supplementary information

Tables of the leveled total intensities and the backgrounds, observed and calculated vibrational wavenumbers, mean amplitudes, and the correlation matrix are deposited.

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Table 1

Geometrical parameters and energies of s-*cis* and s-*trans* conformers of

trans-cinnamaldehyde obtained from the B3LYP/6-31G** calculations

Parameters [a]	s-*cis*	s-*trans*
Bond lengths / Å		
$C_1–C_2$	1.409	1.409
$C_2–C_3$	1.390	1.390
$C_3–C_4$	1.399	1.399
$C_4–C_5$	1.395	1.395
$C_5–C_6$	1.393	1.393
$C_6–C_1$	1.407	1.407
$C_1–C_7$	1.460	1.462
$C_7=C_8$	1.350	1.349
$C_8–C_9$	1.473	1.465
$C_9=O_{10}$	1.221	1.219
$C_2–H_{11}$	1.085	1.085
$C_3–H_{12}$	1.086	1.086
$C_4–H_{13}$	1.086	1.086
$C_5–H_{14}$	1.086	1.086
$C_6–H_{15}$	1.087	1.087
$C_7–H_{16}$	1.089	1.091
$C_8–H_{17}$	1.087	1.087
$C_9–H_{18}$	1.111	1.114
Bond angles / °		
$C_2–C_1–C_6$	118.2	118.3
$C_1–C_2–C_3$	120.7	120.7

C$_2$–C$_3$–C$_4$	120.3	120.3
C$_3$–C$_4$–C$_5$	119.8	119.8
C$_4$–C$_5$–C$_6$	119.9	119.9
C$_5$–C$_6$–C$_1$	121.1	121.1
C$_2$–C$_1$–C$_7$	123.2	123.0
C$_6$–C$_1$–C$_7$	118.5	118.8
C$_1$–C$_7$=C$_8$	128.3	128.3
C$_7$=C$_8$–C$_9$	120.7	120.7
C$_8$–C$_9$=O$_{10}$	124.9	124.5
C$_1$–C$_2$–H$_{11}$	119.9	119.9
C$_3$–C$_2$–H$_{11}$	119.4	119.5
C$_2$–C$_3$–H$_{12}$	119.7	119.7
C$_4$–C$_3$–H$_{12}$	120.0	120.0
C$_3$–C$_4$–H$_{13}$	120.0	120.1
C$_5$–C$_4$–H$_{13}$	120.2	120.2
C$_4$–C$_5$–H$_{14}$	120.2	120.2
C$_6$–C$_5$–H$_{14}$	119.9	119.9
C$_5$–C$_6$–H$_{15}$	119.9	119.8
C$_1$–C$_6$–H$_{15}$	119.0	119.1
C$_1$–C$_7$–H$_{16}$	116.0	114.8
C$_8$=C$_7$–H$_{16}$	115.7	116.9
C$_7$=C$_8$–H$_{17}$	122.4	123.1
C$_9$–C$_8$–H$_{17}$	116.9	116.2
C$_8$–C$_9$–H$_{18}$	114.9	114.6
O$_{10}$=C$_9$–H$_{18}$	120.3	120.9

Dihedral angles / °

C$_2$–C$_1$–C$_7$=C$_8$	0.0	0.0

C_6–C_1–C_7=C_8	180.0	180.0
C_1–C_7=C_8–C_9	180.0	180.0
C_7=C_8–C_9=O_{10}	0.0	180.0
Energy / E_h	-422.9865223	-422.9883084
ΔE / kJ mol^{-1}	4.690	0.000

[a] See Fig. 1 for the atom numbering.

Table 2

Structural constraints and independent parameters of *trans*-cinnamaldehyde [a]

Parameters [a]	s-*cis*	s-*trans*
Bond lengths (Å)		
C_1–C_2	$r_1 + 0.001$	r_1
C_2–C_3	$r_1 - 0.019$	$r_1 - 0.019$
C_3–C_4	$r_1 - 0.010$	$r_1 - 0.010$
C_4–C_5	$r_1 - 0.013$	$r_1 - 0.014$
C_5–C_6	$r_1 - 0.016$	$r_1 - 0.016$
C_6–C_1	$r_1 - 0.001$	$r_1 - 0.002$
C_1–C_7	$r_2 - 0.002$	r_2
C_7=C_8	$r_1 - 0.059$	$r_1 - 0.060$
C_8–C_9	$r_2 + 0.011$	$r_2 + 0.003$
C_9=O_{10}	$r_3 + 0.002$	r_3
C_2–H_{11}	$r_4 + 0.000$	r_4
C_3–H_{12}	$r_4 + 0.001$	$r_4 + 0.001$
C_4–H_{13}	$r_4 + 0.001$	$r_4 + 0.001$
C_5–H_{14}	$r_4 + 0.001$	$r_4 + 0.001$
C_6–H_{15}	$r_4 + 0.002$	$r_4 + 0.002$
C_7–H_{16}	$r_4 + 0.004$	$r_4 + 0.006$
C_8–H_{17}	$r_4 + 0.002$	$r_4 + 0.001$
C_9–H_{18}	$r_4 + 0.026$	$r_4 + 0.029$
Bond angles (°)		
C_2–C_1–C_6	$\theta_1 - 0.0$	θ_1
C_1–C_2–C_3	$\theta_1 + 2.4$	$\theta_1 + 2.4$
C_5–C_6–C_1	$\theta_1 + 2.8$	$\theta_1 + 2.8$

C_2–C_1–C_7	$\theta_2 + 0.3$	θ_2
C_1–C_7=C_8	$\theta_3 + 0.0$	θ_3
C_7=C_8–C_9	$\theta_4 + 0.1$	θ_4
C_8–C_9=O_{10}	$\theta_5 + 0.4$	θ_5
C_1–C_2–H_{11}	$180 - 0.5\,(C_1$–C_2–$C_3)$	$180 - 0.5\,(C_1$–C_2–$C_3)$
C_2–C_3–H_{12}	$180 - 0.5\,(C_2$–C_3–$C_4)$	$180 - 0.5\,(C_2$–C_3–$C_4)$
C_3–C_4–H_{13}	$180 - 0.5\,(C_3$–C_4–$C_5)$	$180 - 0.5\,(C_3$–C_4–$C_5)$
C_4–C_5–H_{14}	$180 - 0.5\,(C_4$–C_5–$C_6)$	$180 - 0.5\,(C_4$–C_5–$C_6)$
C_5–C_6–H_{15}	$180 - 0.5\,(C_5$–C_6–$C_1)$	$180 - 0.5\,(C_5$–C_6–$C_1)$
C_1–C_7–H_{16}	$180 - 0.5\,(C_1$–C_7=$C_8) + 0.1$	$180 - 0.5\,(C_1$–C_7=$C_8) - 1.1$
C_7=C_8–H_{17}	$180 - 0.5\,(C_7$=C_8–$C_9) + 2.8$	$180 - 0.5\,(C_7$=C_8–$C_9) + 3.5$
C_8–C_9–H_{18}	$180 - 0.5\,(C_8$–C_9=$O_{10}) - 2.7$	$180 - 0.5\,(C_8$–C_9=$O_{10}) - 3.2$

Dihedral angles (°)

C_7=C_8–C_9=O_{10}	0.0	180.0

[a] See Fig. 1 for the atom numbering.

Table 3

Experimental and theoretical structural parameters of the s-*trans* conformer of

trans-cinnamaldehyde

Parameters [a]	GED (r_g and $\angle_\alpha$) [b]	B3LYP/6-31G** (r_e)	MP2/cc-pVTZ (r_e)
Bond lengths / Å			
C_1–C_2	1.408 ⎰	1.409	1.403
C_2–C_3	1.390 ⎟	1.390	1.389
C_3–C_4	1.398 ⎟	1.399	1.396
C_4–C_5	1.395 ⎬ (1)	1.395	1.393
C_5–C_6	1.392 ⎟	1.393	1.391
C_6–C_1	1.406 ⎟	1.407	1.402
$< C–C_{ring} >$ [c]	1.398 ⎟	1.399	1.396
C_7=C_8	1.348 ⎱	1.349	1.347
C_1–C_7	1.470 ⎰	1.462	1.458
C_8–C_9	1.473 ⎭ (8)	1.465	1.463
C_9=O_{10}	1.225 (6)	1.219	1.219
$< C–H >$ [c]	1.116 (6)	1.090	1.085
Bond angles / °			
C_6–C_1–C_2	118.6 ⎰	118.3	118.6
C_1–C_2–C_3	121.0 ⎬ (3)	120.7	120.5
C_5–C_6–C_1	121.4 ⎱	121.1	120.9
C_2–C_3–C_4	118.7 —[d]	120.3	120.4
C_3–C_4–C_5	122.1 —[d]	119.8	119.7

C_4–C_5–C_6	118.3	—[d]	119.9	119.9
C_2–C_1–C_7	122.0	(26)	123.0	122.6
C_1–C_7=C_8	128.3	(26)	128.3	127.4
C_7=C_8–C_9	115.3	(27)	120.7	119.7
C_8–C_9=O_{10}	126.6	(19)	124.5	124.4
Abundance / %				
c (s-*trans*)	75	(19)	78	90

[a] See Fig. 1 for the atom numbering.

[b] Values in parentheses are estimated error limits (3σ) referring to the last significant digit.

[c] Average value.

[d] Dependent parameter.

Figure captions

Fig. 1 Molecular models and atom numberings of the s-*cis* and s-*trans* conformers of *trans*-cinnamaldehyde. The internal rotation angles, ϕ_1 and ϕ_2, are defined as $\phi_1 = \phi(C_7=C_8-C_9=O_{10})$ and $\phi_2 = \phi(C_2=C_1-C_7=C_8)$.

Fig. 2 Experimental (open circles) and theoretical (solid curve) molecular scattering intensities of *trans*-cinnamaldehyde; $\Delta sM(s) = sM(s)^{obs} - sM(s)^{calc}$. The theoretical curve was calculated from the best-fit parameters.

Fig. 3 Theoretical potential function for the internal rotation of the aldehyde group of *trans*-cinnamaldehyde obtained by the B3LYP/6-31G** calculations. See Fig. 1 for the definition of ϕ_1. The potential minima at $\phi_1 = 0°$ and $180°$ correspond to the s-*cis* and s-*trans* conformers, respectively.

Fig. 4 Theoretical potential functions for the ring internal rotation of the s –*cis* and s-*trans* conformers of *trans*-cinnamaldehyde obtained by the B3LYP/6-31G** calculations. See Fig. 1 for the definition of ϕ_2.

Fig. 5 Experimental radial distribution curve of *trans*-cinnamaldehyde; $\Delta f(r) = f(r)^{obs} - f(r)^{calc}$. Distance distribution is indicated by vertical bars.

Figure 1
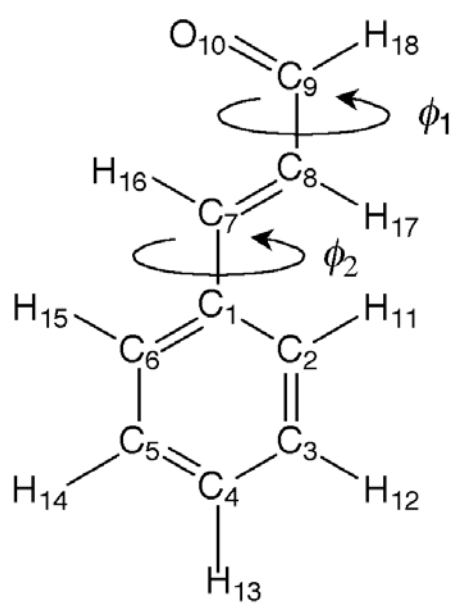
s-*cis*

$(\phi_1, \phi_2) = (\ 0°, 0°)$
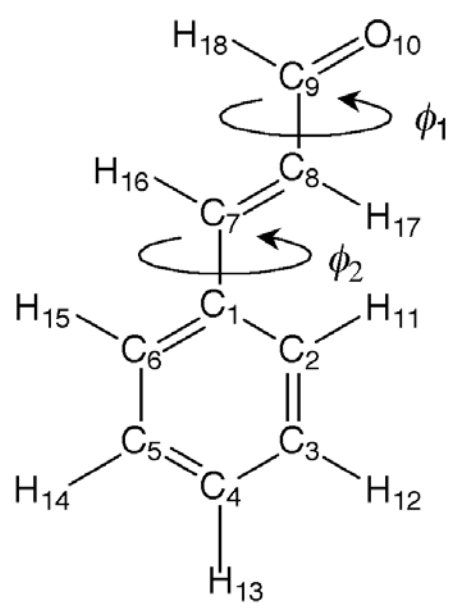
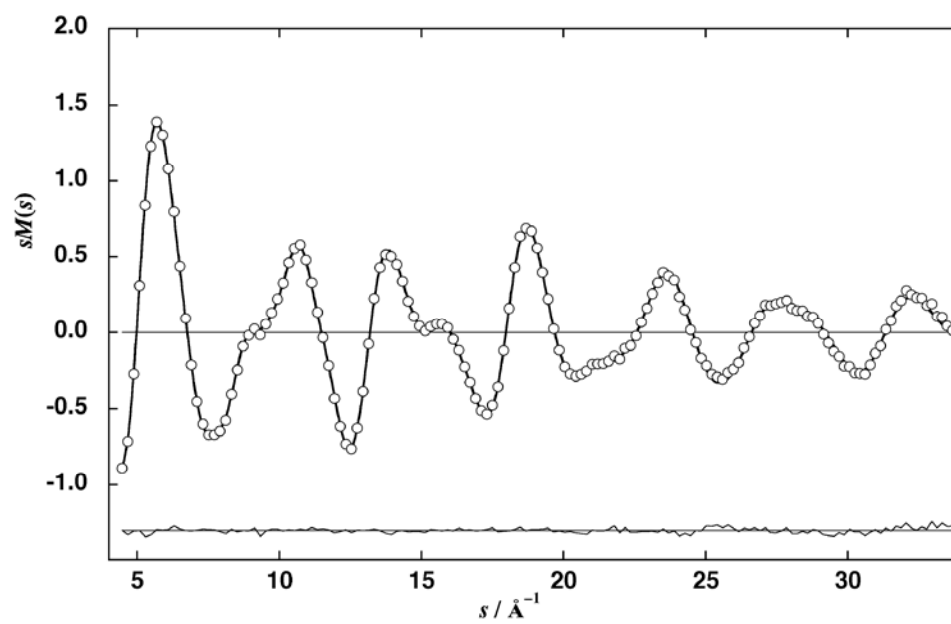**s-*trans***

$(\phi_1, \phi_2) = (\ 180°, 0°)$
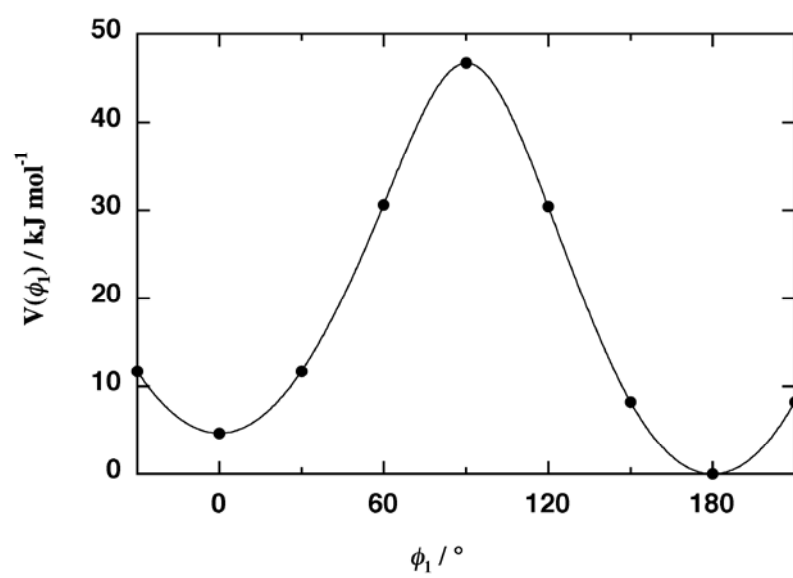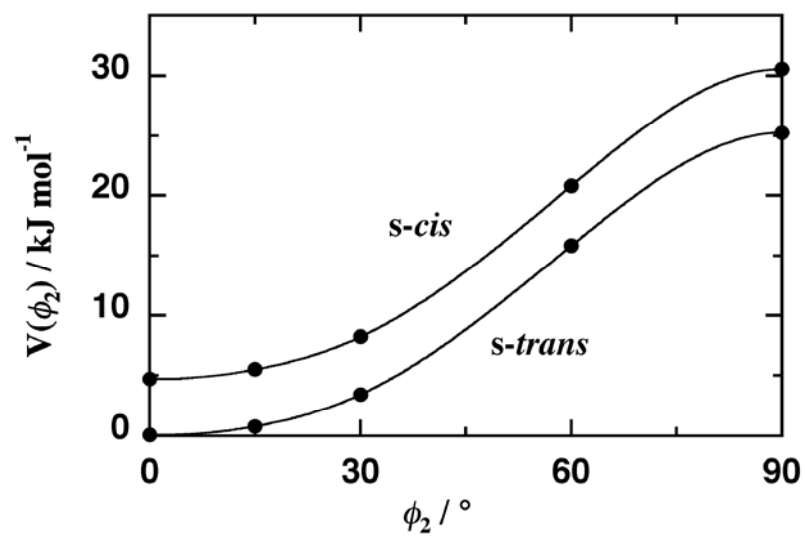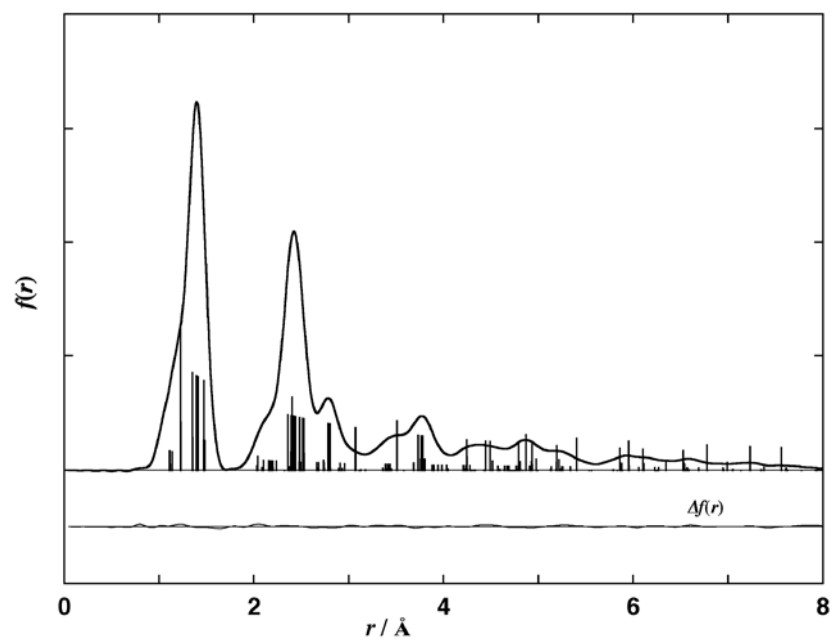
Figure 2

Figure 3

Figure 4

Figure 5

Erratum to "Molecular structure of trans-cinnamaldehyde as determined by gas electron diffraction aided by DFT calculations" [Journal of Molecular Structure 892 (1-3) (2008) 158-162]

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