Title	Analysis of ESR Spectrum of UV Irradiated Azobisisobutyronitrile in Polycrystalline State
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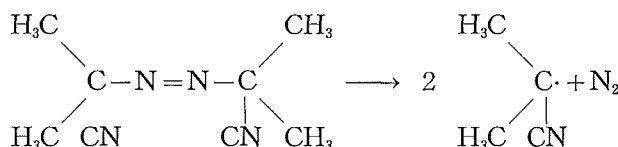# Analysis of ESR Spectrum of UV Irradiated Azobisisobutyronitrile in Polycrystalline State

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Abstract

A radical which was produced by UV irradiation in solid Azobisisobutyronitrile was identified as $(CH_3)_2\dot{C}CN$ by the simulation method. The coupling constant with the methyl hydrogen was 21.3 gauss. The coupling with the nitrogen of the radical has an axial symmetry and it was determined by the simulation that the axial and perpendicular components $A_{\parallel}$ and $A_{\perp}$ were 13.4 gauss and 2 gauss, respectively. A theoretical consideration leads to the conclusion that the sign was positive for the $A_{\parallel}$ but negative for the $A_{\perp}$. The spin density on the nitrogen atom in the radical was estimated as 0.3 which is compatible with the theoretical density estimated by McLachlan's procedure if the effect of the methyl groups to the spin density on the nitrogen in the radical was taken into account as the induction effect.

1. Introduction

Azobisisobutyronitrile (ABIN) is one of the common compounds which initiate radical polymerization. It has not been established as yet, however, what species of radical is produced from the mother molecule in a solid state. For example, Ayscough and his collaborators[1] reported on the ESR spectrum observed from irradiated ABIN and they attributed the spectrum to the radical $(CH_3)_2C(CN)N_2\cdot$ existing during the reaction. But a detailed analysis of the spectrum has not been performed. On the other hand it is generally accepted among workers who study the initiation mechanism with ABIN that the radical is produced thermally by a homolytic cleavage described as follows:

$$
\begin{array}{ccc}
H_3C & CH_3 & H_3C \\
\diagdown & \diagup & \diagdown \\
C-N=N-C & \longrightarrow \quad 2 & C\cdot +N_2 \\
\diagup \qquad | \diagdown & & \diagup \; | \\
H_3C \; CN \quad CN \; CH_3 & & H_3C \; CN
\end{array}
$$

The ESR of the radicals containing the nitrile groups have been extensively studied in liquid phase by Fraenkel and his collaborators[2],[3]. ESR studies of ABIN radical produced by UV irradiation in liquid phase were reported by Weiner and Hammond[4], Livingston and Zeldes[5] and Yoshida and Warashina[6]. Only a few works on the ABIN radicals in solid state have been reported the best of author's knowledge[1]. Reports hitherto on ESR studies were carried out on the radical in the liquid phases and therefore information on the anisotropy of the coupling

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constants related to the nitrile group is lacking. It is of interest to identify unambiguously the radical species from the observed ESR spectrum from the radical trapped in a solid state and to determine the anisotropic coupling constant of the nitrogen in order to obtain information on the electronic state of the radical. Since a single crystal of ABIN can hardly be obtained, all of the available samples of solid state were polycrystalline. Although ESR spectra obtained from the polycrystalline samples were rather complicated, the spectra could be analysed by a computer simulation method based on tne Blinder theory on the line shape of ESR spectrum from a polycrystalline sample[7].

2. Experimental

The samples used in the experiment were commercial reagent grade without further purification. The samples were UV irradiated at 77°K for six hours using a 400 W Toshiba High Pressure Mercury Lamp (HP-400) without a filter. ESR spectrum was observed at 77°K with a JEOL X band spectrometer with 100 KHz field modulation.

3. Analysis of the spectrum

Fig. 1 shows a spectrum observed from the UV irradiated ABIN. The spectrum is mainly septet with satellites and the pattern of the spectrum indicates that the radical species responsible for the spectrum are not species of $(CH_3)_2C(CH)N_2\cdot$. Because an unpaired electron should exist in the σ orbital of nitrogen and the expected spectrum would be made up with nine main peaks due to unequal couplings with the two nitrogens, if the responsible radical was $(CH_3)_2C(CN)N_2\cdot$. The observed spectrum is completely different from the spectrum anticipated from the above
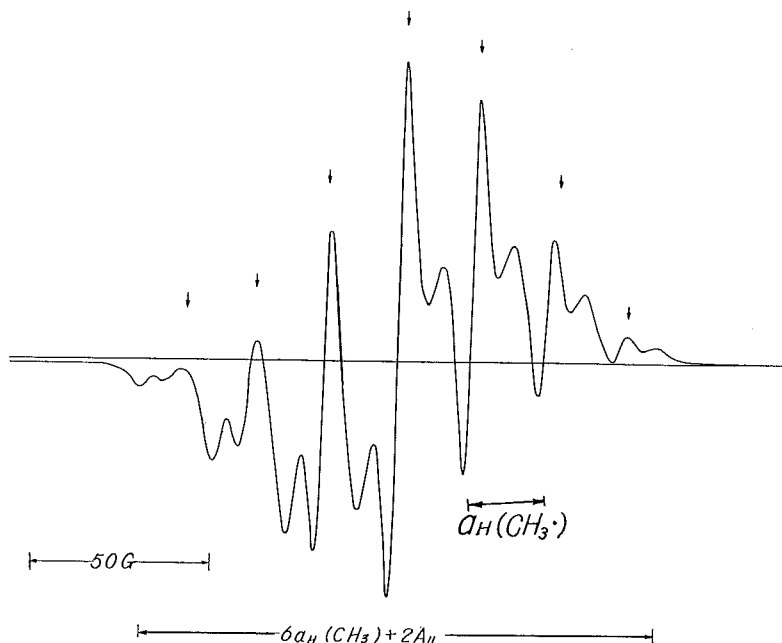

Fig. 1.   Spectrum observed at 77°K from the ABIN UV irradiated at 77°K.

assumed radical. Thus, it is alternatively assumed that the responsible species was $(CH_3)_2\overset{\text{CN}}{\underset{}{C}}\cdot$. The detailed and quantitative analysis described in the following sections will support this assumption.

In order to analyse the spectrum quantitatively three additional assumptions were made on the nature of the proposed radical, $(CH_3)_2C(CN)$; 1) free rotation of the methyl groups at 77°K. 2) an axial symmetry in the hyperfine coupling of the unpaired electron with the nitrogen atom. 3) no anisotropy of the g factor. Assumption (3) is verified by the observed symmetry of the spectrum, as shown in Fig. 1. The observed spectrum consists of the seven main peaks (marked with the arrows in Fig. 1) with satellites and their relative intensities are nearly of the binominal distribution. The assumed free rotation of the two methyl groups results in the septet, relative intensities of which appear as the binominal distribution. Thus, one can attribute these main seven peaks to the coupling of the unpaired electron with the protons in the two rotating methyl groups, and a separation between the two adjacent peaks of the main septet gives the experimental coupling constant of the hydrogen in the methyl groups. As shown in Fig. 1 the coupling with the methyl proton was obtained as $a_H(CH)_3 = 21.3$ gauss. It is apparent, especially in central part of the spectrum, that each peak of the septet shows a characteristic line shape to the spectrum observed from a polycrystalline matrix[7]. This characteristic pattern, the so-called the polycrystalline pattern, is observable if the responsible radicals have an anisotropy and are trapped in a polycrystalline matrix. The anisotropic hyperfine coupling should be ascribed not to the hydrogen in the methyl group but to the nitrogen atom at the α position in a resonance structure of the radical. A theoretical representation of the line shape $g_M(\nu)$ was given by Blinder[7] with an assumption of random distribution of the orientation as follows,

$$g_M(\nu) = g_{-M}(\nu) = \frac{1}{2}d(\cos\phi)/d\nu$$

$$= \frac{\nu/M}{(M)\left[\frac{2}{3}(A_{\parallel} + 2A_{\perp})^2 + \frac{1}{3}(A_{\parallel} - A_{\perp})^2\right]^{1/2}\left[(\nu/M)^2 - A_{\perp}^2\right]^{1/2}} \qquad (1)$$

where ϕ is the angle between the applied magnetic field and the orientation of a molecule, M is the magnetic quantum number and the $A_{\parallel}$ and the $A_{\perp}$ mean either the parallel component or the perpendicular one of the hyperfine coupling with the nitrogen, respectively. In the derivation of Eq. (1) each line of the spectrum was assumed to have no broadening. But the theoretical line shape, $g(\nu)$, compared with the experimental one should be derived with a finite width of a spectral line, inasmuch as a real spectral line is always broadened. By the convolution technique a theoretical line shape with a finite line width is represented as an integral transform of Eq. (1)

$$g(\nu) = \int d\nu' G(\nu - \nu')g_M(\nu') \qquad (2)$$

where $G(\nu - \nu')$ is taken as a normalized Gaussian expressing the shape of each line. Using equations (1) and (2) simulation operations were carried out by a NEAC 2203 G computer with the various sets of adjustable parameters of the $A_{\parallel}$, the

$A_\perp$ and the line width. Since the separation of the two outermost peaks in the observed spectrum was equal to $6a_H(CH_3)+2A_{/\!/}$, as shown in Fig. 1, and $a_H(CH_3)$ was previously determined experimentally, $A_{/\!/}$ was roughly estimated as 11.4 gauss, which was chosen as the initial trial value of $A_{/\!/}$ in the simulation. And the main adjustable parameters were the $A_\perp$ and the line width which give separate effects to the line shape. The increased line width reduces the resolution of the spectrum. On the other hand the satellites in the spectrum were enhanced if the $A_\perp$ was taken closer to the $A_{/\!/}$. The examples of the line shape variation caused by variations of the adjustable parameters are illustrated in Fig. 3. A set which gives the best simulated pattern to the observed is determined as

$$A_{/\!/} = 13.4 \text{ gauss}, \qquad A_\perp = 2 \text{ gauss},$$
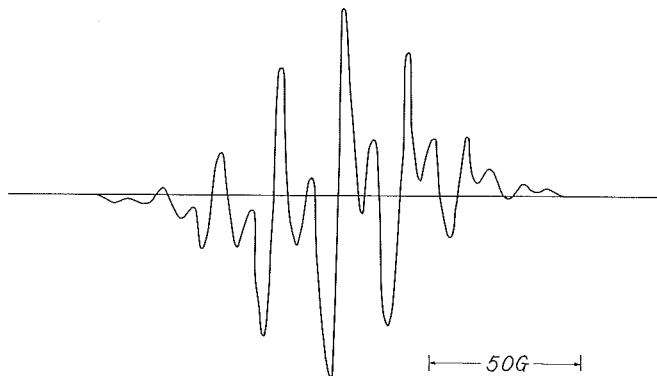
and

$$\Delta H_{msl} = 6 \text{ gauss},$$

Fig. 2. Simulated spectrum with the chosen parameters of $A_{/\!/}=13.4$ gauss, $A_\perp=2$ gauss and $\Delta H_{msl}=6$ gauss.

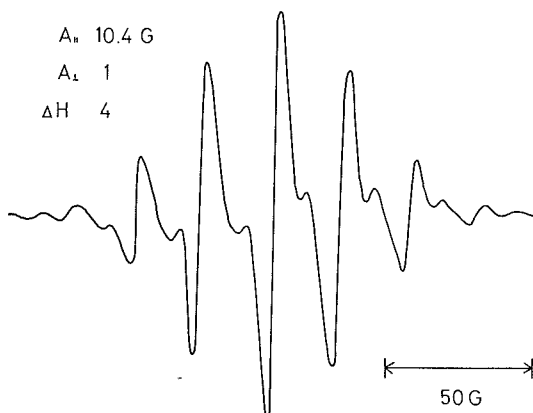**Fig. 3.** Simulated spectrum with the broadened line width, $\Delta H_{msl}=9$ gauss. The other parameters are $A_{/\!/}=13.4$ gauss and $A_\perp=8.9$ gauss.

(a) Simulated spectrum with the narrowed line width. $\Delta H_{msl}= 4$ gauss. The difference of the two components of hfs is almost similar to the best simulated pattern; $A_{/\!/}=10.4$ gauss, $A_\perp=1$ gauss.

$A_{\shortparallel}$ 13.4 G
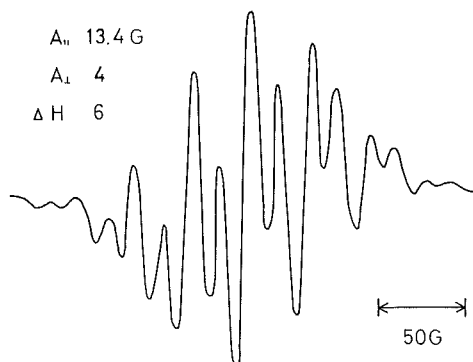
$A_{\perp}$ 4

ΔH 6

50G

Fig. 3. (b)   Simulated spectrum with the less asymmetric hfs constants and the same line width to the best simulated pattern; $A_{\perp}$ = 13.4 gauss, $A_{\perp}$ = 4 gauss and H_{msl} = 6 gauss.
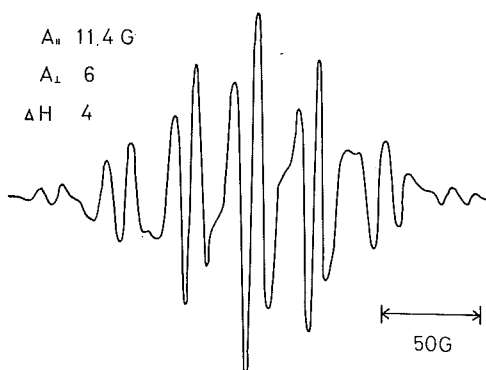
$A_{\shortparallel}$ 11.4 G

$A_{\perp}$ 6

ΔH 4

50G

Fig. 3. (c)   Simulated spectrum with the less asymmetric hfs components and the narrowed line width; A_{ℓ} = 11.4 gauss, $A_{\perp}$ = 6 gauss and ΔH_{msl} = 4 gauss.

$A_{\shortparallel}$ 13.4 G

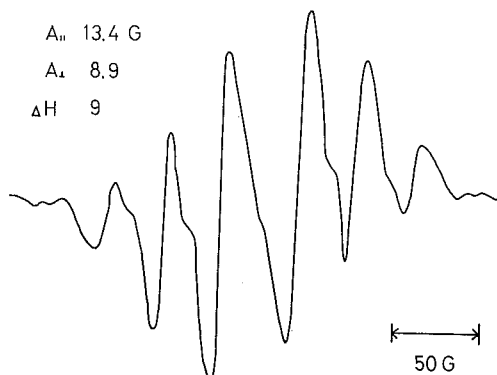$A_{\perp}$ 8.9

ΔH 9

50 G

Fig. 3. (d)   Simulated spectrum with the broadened line width, ΔH_{msl} = 9 gauss and the less asymmetric hfs components; A_{ℓ} = 13.4 gauss. $A_{\perp}$ = 8.9 gauss.
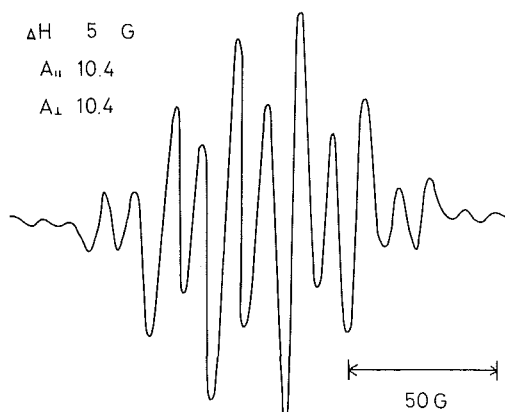
Fig. 3. (e)   Simulated spectrum with symmetric hfs components $\Delta A_{\ell} = \Delta A_{\perp} = 10.4$
gauss and the similar line width to the best simulated pattern.

where ΔH_{ms1} is the line width expressed by the separation between the maximum
slopes. The pattern obtained with the above chosen parameters is reproduced as
Fig. 2. Comparing Fig. 1 with Fig. 2 one can find that agreement between these
two patterns is satisfactory. It should be remembered that the experimental value
of the coupling constants are absolute values and no information on the sign of the
coupling constants are obtainable from an experimental method such as a simulation.

4. Nitrogen coupling

The agreement between the observed spectrum and the simulated one supports
the assumption of the axial symmetry of the coupling constant of the nitrogen in
the proposed radical. The hyperfine coupling constant experimentally obtained
from the observed spectrum is separated into the two components, the anisotropic
A_a, and the isotropic, a_N. Thus,

$$(A_{\ell})_{\mathrm{obs}} = (A_a)_{\ell} + a_N \tag{3}$$

$$(A_{\perp})_{\mathrm{obs}} = (A_a)_{\perp} + a_N \tag{4}$$

The isotropic coupling of the nitrogen, a_N, originates from the s-electron, which
is induced by spin polarization of the unpaired electron since it is mainly in the
$2p$ orbital of the radical. The sign of the isotropic coupling can be deduced
theoretically to be positive[8]. It was also experimentally determined that signs of
the isotropic couplings were positive for the nitrogen atom[9] or the nitrogen either
in the hydrazyl cation[10] or in the other nitrogen compounds[11],[12]. Thus, it is safe to
assume that the sign of the isotropic coupling is positive for the nitrogen of $C \equiv N$
bond in the ABIN radical likewise. It is well known that the anisotropic hyperfine
coupling results from the dipole-dipole coupling and is formulated as follows,

$$A_a = A_0(3\cos^2\theta - 1) \tag{5}$$

$$A_0 = \left\langle \phi_{2p} \frac{(3\cos^2\alpha - 1)}{r^3} \phi_{2p} \right\rangle \tag{6}$$

where θ stands for the angle between the applied magnetic field and the p_π orbital,

r for the distance between the nucleus and the unpaired electron, ϕ_{2p} for the $2p$ wave function.   Since $(A_a)_{\!/\!/}$ is defined as the component when the field is applied in parallel to the p_π orbit and $(A_a)_{\!/\!/}$ as the component when the field is perpendicular to the p_π, one can obtain $(A_a)_{\!/\!/} = 2A_0$ and $(A_a)_\perp = -A_0$ by inserting $\theta = 0°$ and $\theta = 90°$ into Eq. (5), respectively.   Combining the above relations with Eqs. (3) and (4), the following equations are derived.

$$(A_{\!/\!/})_{\text{obs}} = 2A_0 + a_N \tag{7}$$

$$(A_\perp)_{\text{obs}} = a_N - A_0 \tag{8}$$

$$a_N = \frac{1}{3}\Big[(A_{\!/\!/})_{\text{obs}} + 2(A_\perp)_{\text{obs}}\Big] \tag{9}$$

The signs of both of the A_0 and the a_N are positive, therefore the $(A_{\!/\!/})_{\text{obs}}$ invariably has the positive sign.   But the sign of the $(A_\perp)_{\text{obs}}$ is undetermined, because there is no information as to which one of the two quantities, a_N and A_0, is larger. There are two possibilities for the sign of the $(A_\perp)_{\text{obs}}$:   Case I; both $(A_{\!/\!/})_{\text{obs}}$ and $(A_\perp)_{\text{obs}}$ are positive, Case II; $(A_{\!/\!/})_{\text{obs}}$ are positive but $(A_\perp)_{\text{obs}}$ is negative.   In case I the a_N and the A_0 are determined as 5.8 gauss and 3.8 gauss, respectively, from the observed values of $(A_{\!/\!/})_{\text{obs}} = +13.4$ gauss, $(A_\perp)_{\text{obs}} = +2$ gauss and Eqs. (7), (8) and (9).   In case II the $(A_\perp)_{\text{obs}}$ is assumed to be negative thus $(A_\perp)_{\text{obs}}$ should be taken as -2 gauss and the a_N and the A_0 are deduced to be 3.1 gauss, and 5.2 gauss, respectively.   Symons reported that the anisotropic coupling constant A_0 of the $2p_z$ unpaired electron with the nitrogen is 34.1 gauss when the unpaired electron is exclusively limited to the $2p_\pi$ orbital[13].   Using this value the spin density ρ_N on the nitrogen atom can be evaluated as 0.22 in case I, and as 0.3 in case II.

Recently the experimental values of the nitrogen coupling constants, a_N, were reported by Livingston and Zeldes[5] and Yoshida and Warashina[6].   3.4 gauss was obtained by the formers and (3.3 ± 0.1) gauss by the latter workers.   It may be reasonably assumed that the coupling constant of the radical is not affected by the phase in which the radical exists.   Then the a_N is taken as 3 gauss for the ABIN radicals trapped in the solid state.   This value coincides with the expected value for the a_N in the case II.   The arguments presented in the preceding paragraphs lead one to conclude that the sign of the $(A_a)_{\!/\!/}$ is negative and the components of the hyperfine coupling constant and the spin density ρ_N were experimentally determined as follows;

$$\left.\begin{array}{ll} (A_a)_{\!/\!/} = +13.4 \text{ gauss}, & (A_a)_\perp = -2 \text{ gauss}, \\ a_N = +3.1 \text{ gauss}, & \rho_N = 0.3 \end{array}\right\} \tag{10}$$

5. Discussion

As a first approximation the spin density, ρ_N can be evaluated by the simple Hückel theory based on a model, $C-C \equiv N$, with the parameters of $\alpha_N = \alpha + \beta$, $\beta_{C-N} = 0.9\,\beta$, $\beta_{NC} = 2\,\beta$.   However, the Hückel theory is too simple to be compared with the experimental data and some correction is required.   Following McLachlan's procedure[14] a perturbation due to the electron polarization was introduced and a spin density ρ_r at an atom r of a radical can be expressed with the following equation

$$\rho_r = C_{or}{}^2 + \lambda \sum \pi_{r,s} C_{os}{}^2 \tag{11}$$

with

$$\pi_{r,s} \equiv \left(\frac{\partial q_r}{\partial \alpha_s}\right) = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{C_{jk}C_{kr}C_{js}C_{ks}}{\varepsilon_j - \varepsilon_k} \tag{12}$$

where the subscript o means the orbital occupied with the unpaired electron, π_{rs} stands for the polarizability of the r atom due to the s atom, C for the coefficient of an atomic orbital, α_s for the coulomb energy of the s atom, q_r for the electron density on the r atom, C_{ir} for the coefficient of the atomic orbital ϕ_r consisting in the molecular orbital i, the sum of the subscript j should be taken over the occupied orbitals and the sum of the subscript k over the nonoccupied orbitals. The coefficient λ in Eq. (9) is an adjustable parameter, which is taken to be consistent with the semiempirical S.C.F. theory. The values evaluated by the simple Hückel theory were used for the C's in the equations. Through the McLachlan correction represented by Eqs. (11) and (12) the ρ_N is theoretically estimated as 0.22, which is in a not so good agreement with the experimental values, 0.3, of the ρ_N derived in case II in the last section.

In the above estimation of the ρ_N the effect of the methyl group to the density on the nitrogen was disregarded for simplicity, but it is necessary to generalize the treatment to include the effect in the calculation. For the quantitative estimation of the effect of the methyl group several models were presented[15], such as an inductive model, a heteroatom model and a conjugation model. In the inductive model the effect of the methyl group to the π orbital of the carbon with an unpaired electron is considered mainly as an induction effect and the coulomb energy of the

TABLE 1.   The parameters used for the estimation
of the methyl effect to the ρ_N

Inductive Model $C-Me$	$k_c = -0.5$	$k_{c-Me} = 0$
Heteroatom Model $C-X$	$k_x = 2$	$k_{c-x} = 0.7$
Conjugation Model $C_\alpha - Y - Z$	$k_c = -0.1$ $k_z = -0.5$	$k_{c-y} = 0.8$ $k_{y-z} = 3$

TABLE 2.   The ρ_N theoretically evaluated based on the
three different models for the methyl effect

Model	Simple Hückel Theory	McLauchlan's Method
Inductive	0.22	0.34
Heteroatom	0.15	0.21
Canjugation	0.14	0.22

carbon is represented with an equation $\alpha = \alpha_0 + h_x \beta_0$ with the negative h_x. In the heteroatom model the methyl group is taken as a pseudo-heteroatom and the electron in the methyl group is assumed to be a paired electron in a single atom having different values of the coulombic and the resonance energies. In the conjugated model the π orbital occupied with the unpaired electron is assumed to be conjugated with the hydrogens of the methyl groups. Thus, the electron density C_α of the π orbital at the carbon with the unpaired electron is reduced by the amount of the increased density at the tetrahedral carbon Y and at the hydrogens Z of the methyl group. The parameters used for the calculation are listed in the Table I for each of the three models[15]. The spin densities on the nitrogen were calculated for the three different models and the results are tabulated in the Table II. The theoretical ρ_N derived through McLachlan's procedure is compatible with the experimental value if the methyl effect is taken as the induction.

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