# ESR Study on Molecular Alignment of Various Nitroxides in a Nematic Liquid Crystal†

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Various nitroxides with characteristic molecular shapes were studied by ESR spectroscopy to determine the relation between the molecular shape and the ordering in the nematic phase. The hyperfine splitting shifts upon going from the nematic to the isotropic phase and the relative widths of the nitroxyl nitrogen hyperfine lines were examined. Together with an estimate of the molecular dimensions, these results revealed that the ordering properties in three types of nitroxides(each of which has its elongated molecular axis along one of the three principal axes of the nitroxyl nitrogen dipolar tensor) can all be understood well in terms of the slender molecular shape. This led to the deduction that the Saupe-type anisotropic induced dipole-dipole interaction between the overall molecule of nitroxide and the nematic molecule is superior to the local interaction between the substituent moieties of nitroxide and nematic molecule. The dipolar anisotropy of the $\beta$-proton of nitroxide was evaluated to be 3 G.

In the nematic mesophase, the solvent molecules which arrange their elongated axes in parallel through the anisotropic potential presented by Maier and Saupe[1] align first in the direction of the external magnetic field; then the solute molecules dissolved in the mesophase are forced to align partially with the field due to the solute-solvent interaction.[2–4] In consequence of this partial orientation of the solute molecules, the anisotropic spin interactions cause characteristic changes of the spin coupling and relaxation in nuclear magnetic[5–8] and electron spin resonances.[9–12]

We have investigated the solute-solvent interaction in a nematic solution by an ESR technique, using nitroxides as solutes. In the course of these studies, nitroxides have shown some advantages: they are generally stable, have large anisotropies of the dipolar spin interaction of the nitroxyl nitrogen, give relatively simple ESR patterns, and also are rich in the variety of their compounds.

In present study we have examined the effect of the molecular shape of nitroxide on its ordering property in the nematic phase. Another approach to the problem has been made using the diamagnetic species as solutes.[13] We have synthesized many stable nitroxides with a variety of molecular shapes, *e.g.* small or large and spherical or slender, and have measured the hyperfine(hf) splittings in the nematic and isotropic phases together with the widths of the nitrogen hf lines. We wish to report here that a complete examination of the various nitroxides led to the idea that the molecular shape makes a major contribution to the ordering property.

## Experimental

The nematic liquid crystal *N*-(4-methoxybenzylidene)-4-butylaniline(MBBA) purchased from Fuji Color Co. was purified by a zone refining method with *ca.* 30 repetitions using Dry Ice–methanol as cooling reagent. It was dried with a mixture of molecular sieves 3A and 5A, followed by distillation under vacuum. The melting point of the purified material and its nematic-isotropic transition point were 20 and 43 °C, respectively, as found from differential thermal analysis(DTA).

The nitroxides studied are shown in Fig. 1. 2,2,6,6-Tetramethyl-4-oxo-1-piperidinyloxyl (Tanone; **6**) and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (Tanol; **4**) were obtained from Frinton Laboratories Co. The hydrazone derivatives of Tanone,**1**, **2**, and **3**, were synthesized by condensation[14] of the corresponding hydrazine and Tanone in water–methanol solvent. The five-membered nitroxides **5** and **7** were produced[15] by the respective 1-pyrroline *N*-oxides and hydrogen atoms which were generated by a microwave discharge in hydrogen gas. The nitroxides **8** and **9** were synthesized through reactions[16] of *N*-*t*-butyl-$\alpha$-phenylmethanimine *N*-oxide with phenyllithium and with butyllithium, respectively, followed by air oxidation.

The ESR samples were prepared as a nematic solution containing *ca.* $10^{-3}$ mol/dm$^3$ of nitroxide in MBBA and were degassed by several repetitions of a freezing and thawing cycle under vacuum. The ESR spectra were recorded using a home-made X-band spectrometer with a JEOL 30 cm magnet under 455 kHz field modulation at the low limits of microwave and modulation powers. The temperature of a given sample was regurated by controlling the flow rate and temperature of dry nitrogen gas which first passed over a heater and then went around a sample tube set in a double-walled quartz tube inside a cavity. The temperature was read from an Ohkura AM-1001 microvoltmeter by placing

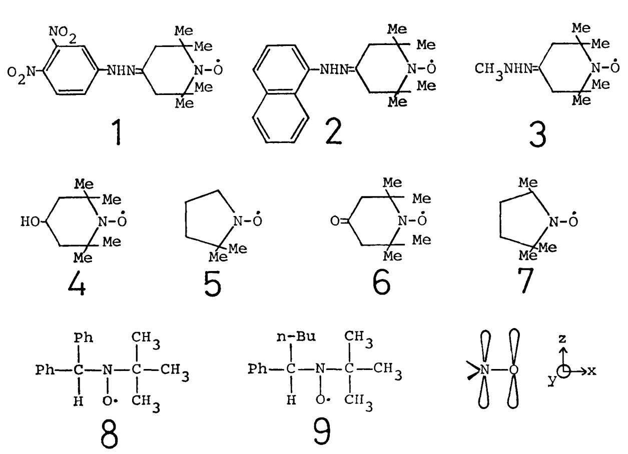

Fig. 1. The nitroxides in present study and the dipolar axes system of nitroxyl nitrogen.

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a copper-constantan thermocouple near the sample tube and was constant to within ±1 °C.

## Results

For the nitroxides **1**—**4** and **6**, the ESR spectrum consisted of only three hf absorptions due to the coupling of the nitroxyl nitrogen. For **5**, **7**, **8**, and **9** each of these three was further split into a doublet or triplet due to the couplings of one or two protons in $\beta$-position to the nitroxyl group. The nitrogen hf splitting $a_N^{nem}$ and proton hf splitting $a_H^{nem}$ measured in the nematic phase of MBBA at 25 °C, together with the $a_N^{iso}$ and $a_H^{iso}$ values in its isotropic phase at 50 °C, are given in Tables 1 and 2. For some nitroxides the temperature dependence of the nitrogen hf splitting in both nematic and isotropic phases is shown in Fig. 2.

TABLE 1. NITROGEN hf SPLITTING $a_N^{nem}$ IN THE NEMATIC PHASE OF MBBA AT 25 °C, $a_N^{iso}$ IN ITS ISOTROPIC PHASE AT 50 °C, SHIFT $a_N^{nem}-a_N^{iso}$, AND ORDERING PARAMETER $\theta_{zz}$ (1G=$10^{-4}$ T)

| Nitroxide | $a_N^{nem}$/G | $a_N^{iso}$/G | ($a_N^{nem}-a_N^{iso}$)/G | $\theta_{zz}$ |
|---|---|---|---|---|
| **1** | 12.35 | 14.56 | −2.21 | −0.135 |
| **2** | 12.98 | 14.69 | −1.71 | −0.104 |
| **3** | 13.74 | 14.64 | −0.90 | −0.055 |
| **4** | 15.49 | 15.51 | −0.02[a)] | — |
| **5** | 13.55 | 13.55 | 0.00[a)] | — |
| **6** | 13.41 | 14.61 | −1.20 | −0.073 |
| **7** | 13.54 | 14.90 | −1.36 | −0.083 |
| **8** | 16.71 | 14.93 | +1.78 | +0.110 |
| **9** | 16.02 | 14.73 | +1.26 | +0.079 |

a) These are zero within an experimental error of ±0.05 G.

TABLE 2. PROTON hf SPLITTING $a_H^{nem}$ IN THE NEMATIC PHASE OF MBBA AT 25 °C, $a_H^{iso}$ IN ITS ISOTROPIC PHASE AT 50 °C, AND SHIFT $a_H^{nem}-a_H^{iso}$ FOR THE NITROXIDES WITH $\beta$-PROTONS (1G=$10^{-4}$ T)

| Nitroxide | $a_H^{nem}$/G | $a_H^{iso}$/G | ($a_H^{nem}-a_H^{iso}$)/G |
|---|---|---|---|
| **5** | 19.17 | 19.18 | −0.01 |
| **7** | 20.35 | 20.74 | −0.39 |
| **8** | 3.16 | 3.36 | −0.20 |
| **9** | 2.33 | 2.49 | −0.16 |

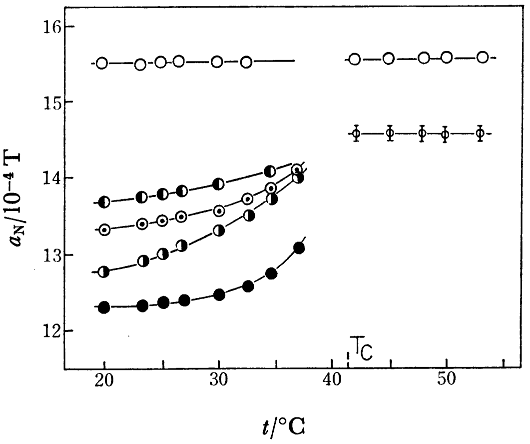


Fig. 2. Temperature dependence of the nitrogen hf splitting for some nitroxides measured above and below the nematic-isotropic transition point of MBBA ($T_c$): ●: **1**, ◑: **2**, ◐: **3**, ○: **4**, ⊙: **6**, and Φ; **1**—**3** and **6** in the isotropic range.

The width of the low field nitrogen hf line, $\Delta H_1$, was slightly but apparently different from the width of the central line, $\Delta H_0$, although the linewidth on the high field side, $\Delta H_{-1}$, was greatly broadened for all the nitroxides in the nematic phase. The relative widths $\Delta H_1/\Delta H_0$ and $\Delta H_{-1}/\Delta H_0$ which were estimated from the relation[17)] $\Delta H_M/\Delta H_0=\sqrt{h_0/h_M}$ ($h$; peak to peak height) are listed in Table 3.

TABLE 3. RELATIVE WIDTHS $\Delta H_1/\Delta H_0$ AND $\Delta H_{-1}/\Delta H_0$ AMONG THREE NITROGEN hf LINES, MEASURED IN THE NEMATIC PHASE OF MBBA AT 25 °C

| Nitroxide | $\Delta H_1/\Delta H_0$ | $\Delta H_{-1}/\Delta H_0$ |
|---|---|---|
| **1** | 0.94 | 1.83 |
| **2** | 0.96 | 1.62 |
| **3** | 0.96 | 1.55 |
| **6** | 1.04 | 1.45 |
| **7** | 1.03 | 1.42 |
| **8** | 1.04 | 1.85 |
| **9** | 1.04 | 1.75 |

As seen in Table 1, the coupling shift $a_N^{nem}-a_N^{iso}$ upon going from the nematic to the isotropic phase is a negative value for the nitroxides **1**—**3**, **6**, and **7**, is zero within experimental error for **4** and **5**, and is a positive value for **8** and **9**. The five nitroxieds with a negative shift are divided into two groups with respect to $\Delta H_1/\Delta H_0$: the three nitroxides **1**—**3** with $\Delta H_1/\Delta H_0$ less than 1.00 and the two **6** and **7** with $\Delta H_1/\Delta H_0$ more than 1.00. Thus, from the viewpoints of both splitting shift and relative width, the present nitroxides can be classified into four groups: **1**—**3**, **4** and **5**, **6** and **7**, and **8** and **9**.

## Discussion

*Nitroxides **1**—**3**.* The principal axes system of the nitroxyl nitrogen dipolar tensor in nitroxides is shown in Fig. 1: here the z-axis is along the nitrogen $\pi$-orbital, the x-axis is extended along the N–O bond, and the y-axis is perpendicular to both the x- and the z-axes. We adopt the principal values[18)] of the tensor of Tanone, *i.e.* $A_{Nzz}=16.4$ and $A_{Nxx}=A_{Nyy}=-8.2$ G for all the nitroxides studied here. Then, taking into account the axial symmetry of the dipolar tensor, the ordering element[19)] about the z-axis, $\theta_{zz}$ can be simply related to the observed shift $a_N^{nem}-a_N^{iso}$, as in Eq. 1.[20)]

$$a_N^{nem}-a_N^{iso}=\theta_{zz}A_{Nzz} \tag{1}$$

The parameter $\theta_{zz}$ takes a positive value between 0 and 1 when the z-axis is preferentially along the external magnetic field. It takes a negative value between 0 and −1/2 when the z-axis is preferentially across the field, in correspondence to a partial orientation of the solute molecules in the nematic phase. In the extremes of alignment of the z-axis with respect to the field, the $\theta_{zz}$ value ideally reaches 1 or $-1/2$. Of course in the isotropic phase it is 0.

The $\theta_{zz}$ values at 25 °C are estimated from Eq. 1 and the $a_N^{nem}-a_N^{iso}$ values and are shown in Table 1. In this table we find that the $\theta_{zz}$ values in nitroxides **1**—**3** are all negative, while the absolute values are in the increasing order from **3** to **1**, indicating that the most preferential alignment of the z-axis across the field is in **1**. This order was conserved at all the other temperatures measured in the nematic phase, as shown in Fig. 3.

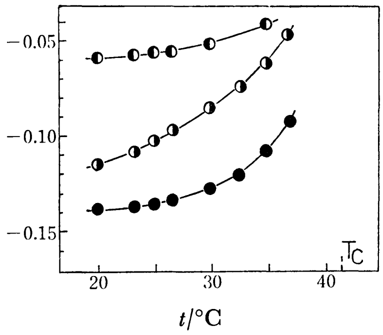


Fig. 3. Temperature dependence of the ordering parameter $\theta_{zz}$ for some nitroxides in the nematic phase of MBBA: ●: **1**, ◑: **2**, and ◐: **3**.

From the relative width $\Delta H_1/\Delta H_0$ we can determine the molecular axis directed preferentially to the field, according to the theoretical results[12,21-23] on the anisotropic spin relaxation in a low region of the solute alignment, such as present cases: the molecular axis with the maximum Brownian rotation is near the x-axis of nitroxide when $\Delta H_1/\Delta H_0<1$, while it is near the y- or z-axis when $\Delta H_1/\Delta H_0>1$. In addition, if the molecular shape of the present nitroxide is approximated as an ellipsoid,[13] the axis with the maximum Brownian rotation corresponds to the elongated molecular axis and hence the axis directed along the field.

Thus we can deduce that, for the nitroxides **1**—**3** with $\Delta H_1$ smaller than $\Delta H_0$, the x-axis represents the alignment axis along the field. Supporting this deduction, the Dreiding model for these radicals showed the elongated molecular axis closest to the x-axis. The alignment degrees of the x-axis, $\theta_{xx}$, are calculated from the $\theta_{zz}$ values and the relation $\theta_{xx}=-2\theta_{zz}$, which is derived from the assumption of the traceless property of the ordering matrix $(\theta_{xx}+\theta_{yy}+\theta_{zz}=0)$ and its axial symmetry in the ellipsoidal molecule $(\theta_{yy}=\theta_{zz})$; they are 0.27. 0.21, and 0.11 for the nitroxides **1**, **2**, and **3**, respectively. These values mean that the nitroxide **1** aligns along the field most preferentially, while **3** aligns the least.[24]

From a glance of Fig. 1, it can be seen that the above order in the alignment degrees is related to the difference in the molecular shapes. Indeed, the Dreiding model allows us to estimate rough molecular dimensions of the nitroxides and to give the $L_x/L_\perp$ values of 1.9, 1.5, and 1.2 for the nitroxides **1**, **2**, and **3**, respectively, where $L_x$ is the molecular length along the x-axis and $L_\perp$ is the larger one of $L_y$ and $L_z$.

A good agreement between the order of $L_x/L_\perp$ values and that of the $\theta_{xx}$ values indicates that the more slender the molecular shape of the nitroxide is, the higher its alignment degree becomes. The bulkiness of the molecule and the properties of the substituent moieties do not seem to exert a primary effect on the molecular ordering of the nitroxides.

*Nitroxides 4 and 5.* These species showed no appreciable shift in the splitting constants (Table 1 and Fig. 2). An absence of the solute alignment can be explained in terms of the spherical property but not in terms of the smallness.

*Nitroxides 6 and 7.* Interestingly, these small radicals can align in the nematic phase, giving negative splitting shifts, although the six-membered nitroxides **4** and **6**, as well as the five-membered nitroxides **5** and **7**, are similar to each other in molecular structure and in mass. In the latter two the introduction of the third methyl group into the $\beta$-position of the five-membered ring of **7** may lead to a slight extention of the molecular dimension along the y-axis of the dipolar principal axes in **7**. In fact, the $L_\perp/L_y$ value (where $L_\perp$ is the larger one of $L_x$ and $L_z$) is 0.7 for **7** while it is 0.9 for **5**. This small difference in the molecular shape allows the y-axis of **7** to orient along the external field and prevents **5** from such an alignment. The observation of the relative width $(\Delta H_1/\Delta H_0>1)$ could also support the alignment of the y-axis along the field in **7**, in contrast to the alignment of the x-axis along the field in **1**—**3**.

The nitroxide **6** has the carbonyl group in the $\gamma$-position of the six-membered ring and **4** has the hydroxyl group in the same position. In addition, as has been previously suggested,[25] **6** prefers a twisted form and **4** prefers a chair form in the ring conformation. Both these facts tend to shorten slightly the molecular dimension of the x-axis in **6**, while keeping the length of the y-axis in both nitroxides constant ($L_\perp/L_y$; 0.8 for **6** and 0.9 for **4**). This allows the y-axis of **6** to orient along the field as in the case of **7**. The relative width $\Delta H_1/\Delta H_0$ of 1.04 does not conflict with the above view.

From the results in the relatively small nitroxides **4**—**7** we recognize that the major factor in determining the solute alignment in the nematic phase is not the mass of the nitroxide but rather its slenderness. The effect of the local interaction between the polar group (hydroxyl in **4** or carbonyl in **6**) and the solvent molecule does not affect primarily the molecular ordering, as shown by the fact that the nitroxide **4** or **6** is analogous to **5** or **7**, respectively, in the ordering property.

*Nitroxides 8 and 9.* These are unique nitroxides which provide positive splitting shifts and hence have their z-axes in the direction along the external field in the nematic phase. A possible explanation of the preferential alignment of the z-axis along the field is given on the basis of a special configuration: the elongated molecular axis linking the two phenyl moieties in **8** and that linking the phenyl and butyl moieties in **9** are nearly parallel to the respective z-axes; the free rotation around the bond between nitrogen and the carbon attached by those substituents is also restricted.

The above picture could be supported by estimating the dihedral angle of the $\beta$-H–C bond to the $\pi$-orbital of the nitroxyl nitrogen in both nitroxides. The observed Fermi coupling of the $\beta$-proton, $a_H^{iso}$, is related to the dihedral angle $\phi_H$ in the McConnell Eq. 2,[26] where the negligible term independent of $\phi_H$ is excluded.

$$a_H^{iso} = B\rho_N \cos^2 \phi_H \tag{2}$$

The product $B\rho_N$, where $B$ is a constant and $\rho_N$ is the unpaired electron density on the nitrogen atom, is usually taken for nitroxide as 25 G ($B \simeq 50$G and $\rho_N \simeq 0.5$).[27] Then, from the $a_H^{iso}$ values in Table 2, we can obtain *ca.* 70 ° for $\phi_H$ in both **8** and **9**. Hence, as seen in the Neumann projection (Fig. 4), the axis linking the two bulky groups which attach to the carbon which is bonded to the $\beta$-proton is approximately parallel to the z-axis.

Now we can conclude as follows, summarizing the results of the ordering preferences in all the nitroxides: with respect to the principal axes of the nitroxyl nitrogen dipolar tensor, the nitroxides **1**—**3** orient their elongated x-axes along the field, **6** and **7** orient their elongated y-axes along the field, and **8** and **9** orient their elongated z-axes along the field (Table 4). The nearly spherical nitroxides **4** and **5** do not show any appreciable orientation. The alignment degree becomes higher for the more slender ellipsoid in the molecular shape of the solute, as can be seen from the comparison among **1**—**3**. The substituent groups of the nitroxide mainly act on the ordering property through the effect of their shapes on the overall molecular shape. These results taken together lead us to consider that the major interaction between nitroxide and nematic molecules is the Saupe-typed anisotropic dispersion interaction[1—4] which is most stabilized when the long axes of both solute and solvent molecules, along which the induced dipoles are distributed uniformly over the molecules, are arranged in parallel to each other. Then the slender shape of the nitroxide molecule, corresponding to the high anisotropy of the induced dipole, causes its high ordering in the nematie phase through the effective solute-solvent interaction. These results correspond to the results[13] in the case of the use of diamagnetic species as solutes.

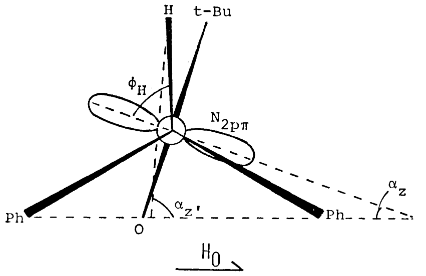
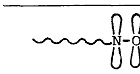
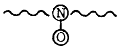
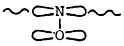


Fig. 4. Neumann projection of nitroxide **8** oriented to the external field in the nematic phase. In nitroxide **9** whether of the two phenyl moieties is only replaced by a butyl moiety. The $\phi_H$, $\alpha_z$, and $\alpha_{z'}$ are defined in the text.

TABLE 4. PREFERENTIAL ALIGNMENT TO THE EXTERNAL FIELD $H_0$ IN THE PRESENT NITROXIDES

| $H_0$[a) ] $\longrightarrow$ | Sign of $\theta_{zz}$ | Relative width | Preferential axis along $H_0$[b)] | Nitroxides |
|---|---|---|---|---|
|  | $-$ | $\Delta H_0 > \Delta H_1$ | x | 1, 2, 3 |
|  | $-$ | $\Delta H_0 < \Delta H_1$ | y | 6, 7 |
|  | $+$ | $\Delta H_0 < \Delta H_1$ | z | 8, 9 |

a) ∼∼; the elongated molecular axis. b) x, y, and z; the principal axes of the nitrogen dipolar tensor.

We show an interesting application of the above treatment in the next section.

*Hf Anisotropy of β-Proton in Nitroxide.* As shown in Table 2, the splitting shifts of the $\beta$-proton, $a_H^{nem} - a_H^{iso}$, in the nitroxides **7**—**9** are rather small compared with the respective splitting shifts of the nitroxyl nitrogen, indicating the small hf anisotropy of the $\beta$-proton. We can estimate the amount of the anisotropy from the example of nitroxide **8**: under a point dipole approximation[28] for the N–O group, the maximal principal value $A_{Hz'z'} (= -2A_{H\perp'})$ of the dipolar spin interaction is found along the axis directed from the $\beta$-proton towards the point dipole located in the center of the N–O bond. Then with respect to this axis(z') a relation similar to Eq. 1 exists also in the case of the $\beta$-proton ($a_H^{nem} - a_H^{iso} = \theta_{z'z'} A_{Hz'z'}$). From both equations the $A_{Hz'z'}$ is given by

$$A_{Hz'z'} = \frac{\theta_{zz} A_{Nzz} (a_H^{nem} - a_H^{iso})}{\theta_{z'z'} (a_N^{nem} - a_N^{iso})}. \tag{3}$$

The $\theta_{ii}$ is written as follows, assuming an ellipsoidal molecular shape:

$$\theta_{ii} = \theta_{mol} (3\cos^2 \alpha_i - 1)/2, \tag{4}$$

where $\theta_{mol}$ is the alignment degree of the elongated molecular axis and $\alpha_i$ the angle which this makes with the i-axis.

We can take the elongated axis of the nitroxide **8** along the axis linking the centers of the phenyl groups, according to the previous result, and then find the $\alpha_z$ of 20° and $\alpha_{z'}$ of 86° by using the dihedral angle of 70° and the standard bond lengths and angles[29] (Fig. 4). Substituting the $A_{Nzz}$ of Tanone and the $a_N^{nem} - a_N^{iso}$, $a_H^{nem} - a_H^{iso}$, $\theta_{zz}$, and $\theta_{z'z'}$ of **8** into Eq. 3, we obtain 3.1 G for the $A_{Hz'z'}$. This value of the dipolar anisotropy is as small as expected and corresponds to the small splitting shifts in the nematic phase.

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24) Such a comparison among the radicals **1**—**3** is justified by the following reasoning: with an ellipsoidal approximation of molecular shape the alignment degree of the molecular i-axis, $\theta_{\mathrm{ii}}$, can be written as $\theta_{\mathrm{ii}}=\theta_{\mathrm{mol}}\,(3\cos^2\alpha-1)$, where $\theta_{\mathrm{mol}}$ is the alignment degree of the elongated molecular axis and $\alpha$ the angle both axes make. The radicals **1**—**3**, all hydrazone derivatives of Tanone, have approximately the same angle of $\alpha$. Then the structural difference in **1**—**3** changes the $\theta_{\mathrm{ii}}$ value only through the difference of $\theta_{\mathrm{mol}}$.

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28) Generally, this is recognized as a fairly good approximation for the $\beta$- or $\gamma$-proton.

29) J. A. Pople and D. L. Beveridge, "Approximete Molecular Orbital Theory," McGraw-Hill, New York (1970), p. 110. For the bond lengths and angles concerned here: N–O, 1.24; N–C, 1.47; C–C(phenyl), 1.52; C(phenyl)–C(phenyl), 1.39; and C–H, 1.09 Å; sp$^2$ angle, 120°, and sp$^3$ angle, 109.5°.