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NMR MEASUREMENTS OF THE ANISOTROPY EFFECT OF THE PHENYLIMINO GROUP[1]

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Abstract—Two peaks due to α-methylene protons adjacent to the phenylimino group are observed in NMR spectra of phenyliminocyclohexane, phenyliminocyclopentane and 2-phenyliminotetrahydrofuran. In order to assign these two peaks, conformation of the phenylimino group is discussed in relation to the IR, UV and NMR spectra. It is concluded that the $>C{=}N$ plane is nearly perpendicular to the phenyl plane and that hybridization of the nitrogen atom is of sp^2 type. Thus the higher field signal is assigned to the *syn* proton and the lower field signal to the *anti* proton.

IT HAS been reported,[2,3] that splitting of two NMR peaks due to α methylene protons adjacent to a hydroxyimino group may be interpreted in terms of the local paramagnetic current and the dipolar field effect due to lone pair electrons of the nitrogen atom. The anisotropy effect of the phenylimino group (I), in which the hydroxyl group is replaced by a phenyl group, should be more complicated than that of the hydroxyimino group, because a ring current effect of the phenyl group exists in addition to the anisotropy effect of the nitrogen atom. Benzalaniline (II),[4-6] which is a typical phenylimine, is not coplanar and π electrons in $>C{=}N$ and a benzene ring in the phenylimino group do not conjugate with each other. The benzene ring plane of the aniline moiety (the right side ring in II) is believed to be nearly perpendicular relative to the rest of the molecular plane in this compound. Furthermore, it was proposed[5] by taking into account of the electronic energy of this compound that the hybridization of the nitrogen atom is close to sp type.

In this paper, phenyliminocyclohexane (III), phenyliminocyclopentane (IV) and 2-phenyliminotetrahydrofuran (V) studied by IR, UV and NMR spectroscopy are reported. The first two compounds correspond to cyclohexanone oxime and cyclopentanone oxime, respectively, the NMR spectra of the latter having been analysed.[2,3] In the NMR spectra of these phenylimines, two peaks due to α-methylene protons adjacent to the phenylimino group were observed. In order to assign these two peaks, an alternative conformation of the phenylimino group in which the hybridization of the nitrogen atom is of sp^2 type is proposed. The result of the IR and UV studies also supports the conclusion.

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[1] Part of this paper was presented at the *International Symposium on Nuclear Magnetic Resonance*. Tokyo, September (1965).

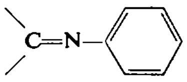
[2] H. Saitô, K. Nukada and M. Ohno, *Tetrahedron Letters* 2124 (1964).

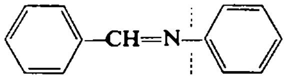
[3] H. Saitô and K. Nukada, *J. Mol. Spectroscopy* **18**, 1 (1965).

[4] V. A. Ismaliski and E. A. Smirnov, *J. Gen. Chem., U.S.S.R.* **26**, 3389 (1956).

[5] N. Ebara, *Bull. Chem. Soc. Japan* **33**, 534 (1960).

[6] P. Brocklehurst, *Tetrahedron* **18**, 299 (1962).


(I)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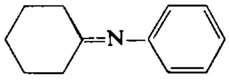
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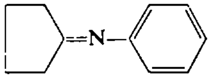
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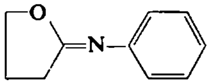
(V)

EXPERIMENTAL

Compounds III and IV were synthesized by the method of Hoch[7] in which diethyl ketals of the corresponding cyclic ketones were condensed with aniline in the presence of a trace of acid. III b.p. 156°/30 mm (lit.[7] 157°/30 mm); IV b.p. 86–88°/3 mm. V was kindly supplied by Mr. H. Takahashi of our laboratories. NMR spectra (Varian HR-100 (100 Mc) in a neat state and in CCl_4 soln, TMS as an internal standard). IR and UV spectra (Perkin-Elmer 125 and a Cary 14 spectrometer, respectively).

RESULTS AND DISCUSSION

IR spectra

The C=N stretching vibration (ν(C=N)) characteristic of a phenylimino group (liquid film) are listed in Table 1. The degree of conjugation between π electrons of C=N bond and phenyl group was determined qualitatively with the IR data. First, a slight difference between ν(C=N) of III and IV was observed and the same tendency was recognized in the spectra of five- and six-membered ring monoximes (1690 and 1669 cm^{-1}, respectively).[8] It has been suggested that the effect in the latter case is due to the ring strain.[8] Secondly, ν(C=N) is generally shifted to a lower wave number region by conjugation with the aromatic ring.[9] For instance, that of acetophenone oxime[10] and benzalaniline[11] is found at 1630 cm^{-1}. In III and IV, ν(C=N) is shifted to a somewhat lower wave number (10 and 21 cm^{-1}, respectively) as compared with the corresponding oximes. From these observations, we can conclude that, in III and IV, the degree of conjugation between C=N and phenyl group is decreased as compared with that of acetophenone oxime or benzalaniline.

This conclusion will be checked with the NMR data in the following section. The reason why the C=N stretching frequency of V is higher than that of IV, the ring size of which being the same as the former, is due to the effect of oxygen atom adjacent to the phenylimino group. The same tendency was observed in the case of ph—CH=N—ph(1630 cm^{-1}) and ph—C(OCH_3)=N—ph (1665 cm^{-1}) but not in the case of —CH=N and —C(CH_3)=N.[11]

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[7] J. Hoch, *C.R. Acad. Sci. Paris* **199**, 1428 (1934).

[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* p. 269. Methuen, (1958).

[9] Ref. 8, p. 270.

[10] A. Palm and H. Werbin, *Canad. J. Chem.* **31**, 1005 (1953).

[11] J. Fabian and M. Legrand, *Bull. Soc. Chim. Fr.* 1461 (1956).

TABLE 1. C=N STRETCHING FREQUENCIES OF PHENYLIMINO GROUP

	ν(C=N) (cm^{-1})
Phenyliminocyclohexane (III)	1658
Phenyliminocyclopentane (IV)	1669
2-Phenyliminotetrahydrofuran (V)	1687

UV spectra

The results of UV measurement of phenylimines (isooctane) are given in Table 2. In III and IV, two bands appear in the UV spectra. The low-wavelength band is more intense than the high-wavelength one. Only the former band appears in the case of V and is shifted to the high-wavelength region as compared with other phenylimines. This shift is interpreted in terms of the conjugation and inductive effect of the oxygen atom adjacent to the phenylimino group. The low-wavelength and the high-wavelength band are called the primary ($^1A \rightarrow {}^1L_b$) and secondary band ($^1A \rightarrow {}^1L_a$), respectively.[12]

TABLE 2. UV SPECTRA OF PHENYLIMINO GROUP

	λ(mμ)	ε
Phenyliminocyclohexane (III)	225·1	6500
	281·0	1240
Phenyliminocyclopentane (IV)	229·4	*ca.* 6000
	272·4	*ca.* 2000
2-Phenyliminotetrahydrofuran (V)	238·4	3400

In benzene the secondary band is very weak, since this band is due to the forbidden transition because of its symmetry. If the C=N bond does not conjugate with the phenyl group perfectly as described in the preceding section, the lone pair electrons of the nitrogen atom conjugate with π electrons of the phenyl ring to some extent. As is described later, hybridization of the nitrogen should be of sp^2 type. It is then expected that UV spectra in this model are similar to those of aniline. The primary and the secondary band of aniline are 230 mμ (ε = 8600) and 280 mμ (ε = 1430), respectively,[13] and these values and their extinction coefficients are similar to those of III and IV. The band shape and position of the primary band of aniline also resemble those of maximum peak of V. The result of UV spectra thus supports the conclusion deduced from the analysis of IR spectra.

NMR *spectra*

There is a specific solvent effect in phenylimines because of the ring current effect characteristic of the phenyl group. The proton signals in the neat state or concentrated solution are shifted to a higher field. In order to discuss the anisotropy effect of the phenylimino group, intermolecular (solvent) effect must therefore be eliminated by extrapolating the observed signals to infinite dilution. Proton shifts at infinite dilution are given in Table 3 and NMR spectra in the neat state of phenylimines are illustrated in Fig. 1.[14] As we can see in Table 3, no signal other than α methylene proton signals

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[13] H. H. Jaffé and Milton Orchin, *Theory and Applications of Ultraviolet Spectroscopy* p. 243. Wiley, New York (1962).

[14] Ref. 12, p. 257.

TABLE 3. NMR SPECTRA OF PHENYLIMINO COMPOUNDS AT INFINITE DILUTION (ppm)

	α-CH$_2$		β-CH$_2$	β'-CH$_2$[a]	γ-CH$_2$
Phenyliminocyclohexane (III)	−2·41	−2·13	−1·67[b]	—	−1·67[b]
Phenyliminocyclopentane (IV)	−2·53	−2·15	−1·90	—	—
2-Phenyliminotetrahydrofuran (V)	−2·68	−2·36	−2·24	−4·25	—

[a] β' denotes methylene proton adjacent to oxygen atom.
[b] β and γ proton signal are not resolved.

is split into two peaks. Splitting of α methylene proton signal can be interpreted in terms of the anisotropy effect of the phenylimino group. Separations of two α-methylene protons are 0·28, 0·38 and 0·32 ppm for III, IV and V, respectively. Those of the corresponding cyclic oximes in which skeletons of methylene protons are the same as in the phenylimines are 0·26 and 0·11 ppm for cyclohexanone oxime and cyclopentanone oxime, respectively.[3] A slight increase of separation between two α-methylene protons on passing from a six-membered to a five-membered ring in phenyliminocycloalkanes is inverted in the case of the oximes. This result shows that the ring current effect of the phenyl group is the predominant cause of the anisotropy effect of the phenylimino group, while the effect of the lone pair electrons of the nitrogen atom is predominant in the oximes. The effect of the ring current can be estimated by assuming the conformation of the phenylimino group.

Firstly, a model is considered where the $>$C=N plane is perpendicular to the benzene ring, and the hybridization of the nitrogen atom is of sp type (Fig. 2). It is not expected that there exists a separation of two α-methylene protons due to the ring current effect, because this effect is equivalent with respect to both sides of α-methylene protons. The anisotropy effect of the lone pair electrons of the nitrogen atom is considered as superposition of two contributions, a local paramagnetic field induced by the $n \rightarrow \pi^*$ transition and a dipolar field effect of the lone pair electrons.[8] The dipolar field does not occur when the lone pair electrons are in p orbital as in this model.[15]

Furthermore, $n \rightarrow \pi^*$ transition does not exist, because the lone pair electrons conjugate with the phenyl group. Thus the separation between two α-methylene protons is not expected in this model. Actually the separation is about 0·3 ppm and this model is not correct. Secondly, an alternative model is considered, in which the $>$C=N plane is perpendicular to the phenyl plane and the hybridization of the nitrogen atom is of sp^2 type as illustrated in Fig. 3. The effect of the ring current induced by the phenyl group is calculated by the equation based on the double doughnut model proposed by Johnson and Bovey[16] assuming that the amount of the effect of the phenyl group is the same as that of benzene. Calculation was performed by assuming that an internal conversion between two chair conformations occurs in

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[14] In Fig. 1A, shapes of two α-methylene proton signals are different from each other. This is attributed to the difference of the relaxation mechanism and/or of mobilities between two types of methylene protons, because an interaction between methylene protons and the phenyl protons will occur in the case of *syn*-methylene protons. (This notation is given later.)

[15] C. A. Coulson, *Valence* (2nd Ed.) p. 218. Oxford Univ. Press.

[16] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.* **29**, 1012 (1958).

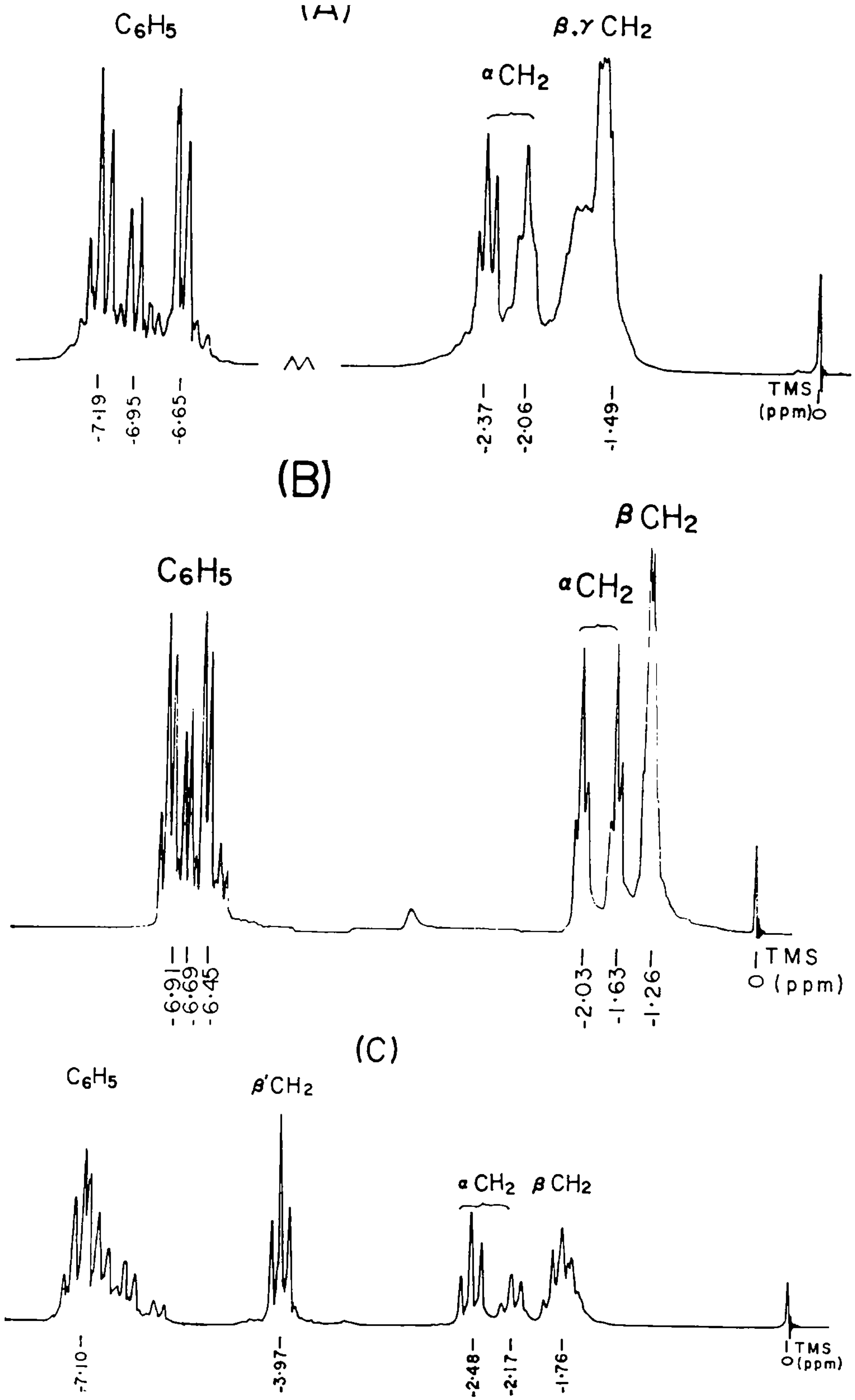

FIG. 1. 100 Mc NMR spectra of phenylimines (neat).
A: Phenyliminocyclohexane (III)

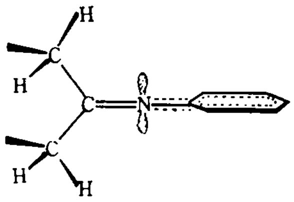

Fig. 2. A perpendicular model of the phenylimino group. (sp hybridization of the nitrogen atom)

cyclohexane part of III.[17] Bond lengths and bond angles are obtained from the Dreiding molecular model. Here we define two types of α methylene protons as *syn* and *anti* with respect to the phenyl group as shown in Fig. 3. The results of calculation based upon this model are listed in Table 4. Here it is assumed that the conformations of methylene protons in tetrahydrofuran ring are the same as in cyclopentane ring. The separation of *syn* and *anti* α-methylene proton signals in phenyliminocycloalkanes other than III can be explained in terms of the ring current effect as shown in Table 4. The calculated value is about three times as large as the observed

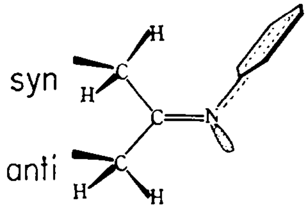

Fig. 3. An alternative perpendicular model of the phenylimino group (sp^2 hybridization of the nitrogen atom)

Table 4. Proton shifts due to the ring current effect of phenyl ring (ppm)

	calc.			obs.
	syn	*anti*	separation	separation
Phenyliminocyclohexane (III)	+0·83	−0·18	+1·01	0·28
Phenyliminocyclopentane (IV)	+0·33	−0·17	+0·50	0·38
2-Phenyliminotetrahydrofuran (V)	+0·33	−0·17	+0·50	0·32

one for III. The anisotropy effect of the phenylimino group due to the lone pair electrons can be neglected considering a model in which the lone pair electrons participate in the π conjugation with the phenyl group. Then the high field signal is assigned to the *syn* protons and the low field one to the *anti* protons, if we accept the above model. The observed intensity ratio of *syn* to *anti* protons is 1:1 for III and IV because of the symmetry of α methylene protons with respect to C=N group. The intensity ratio for V is observed to be 1:2·3 and the *anti* proton signal is more intense than the *syn* proton. Therefore the amount of VI is twice as much as that of VII.

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[17] This assumption is justified by the observation that separated axial and equatorial methylene protons cannot be distinguished in NMR spectra measured at room temperature.

This observation can be explained by comparing the Van der Waals' radius of oxygen atom (1·4 Å) with that of methylene group (2·0 Å),[18] i.e. VI is more stable because the repulsive interaction with the phenyl group is smaller in the case of oxygen atom.

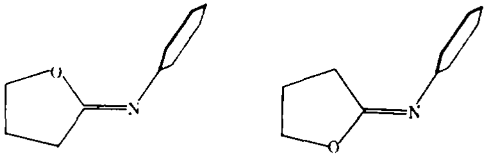
VI VII

FIG. 4. Two isomers of 2-phenyliminotetrahydrofuran (V)

While the above discussion is restricted to the case where dihedral angle between the $>C{=}N$ and the phenyl planes is 90°, the other possible conformations such that the hybridization of the nitrogen atom is of sp^2 type and the dihedral angle is smaller than 90° will be discussed. Now the observed separation between *syn* and *anti* proton signal, δ_{obs}, is expressed as follows;

$$\delta_{obs} = \delta_N(\theta) + \delta_{ring}(\theta) \qquad (1)$$

where $\delta_N(\theta)$ and $\delta_{ring}(\theta)$ are separations due to the anisotropy effect of the lone pair electrons in the nitrogen atom and due to the ring current effect, respectively. θ is the dihedral angle. Here we should mention that θ cannot be smaller than about 60° in order to keep a separation of 2 Å between methylene and phenyl protons, considering the Van der Waals' radius of hydrogen atom to be 1·2 Å.[18] A plot of $\delta_{ring}(\theta)$ is illustrated in Fig. 5. When θ is decreased from 90°, $\delta_{ring}(\theta)$ is decreased to some extent. The analytical expression of $\delta_N(\theta)$ is not determined but is zero at 90° and is equal to $\delta_{hydroxyimino}$ at 0°. $\delta_{hydroxyimino}$ is the separation observed in the corresponding oximes which differ from the phenylimino compounds only in that a phenyl group is replaced by a hydroxyl group. Combining the IR and NMR results, we can suggest that the twisted angle between $>C{=}N$ and phenyl group is a little smaller than 90°, that the chemical shift between *syn* and *anti* proton is mainly due to the

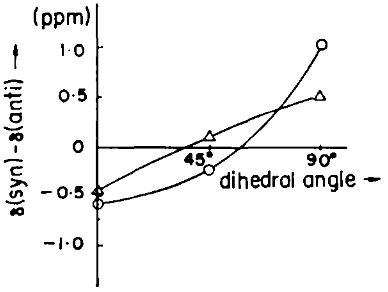

FIG. 5. A plot of separation between *syn* and *anti* proton signals due to the ring current effect against the dihedral angle.
○: phenyliminocyclohexane
△: phenyliminocyclopentane

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[18] L. Pauling, *The Nature of the Chemical Bond* (3rd Ed.) pp. 261–262. Cornell Univ. Press. (1960).

ring current effect of the phenyl group, and that *syn* proton signal appears at higher field.

The patterns of phenyl proton signals are more complicated than aliphatic ones, although they are symmetrical with respect to the axis between carbons 1 and 4. The signals of III and IV can be treated as A_2B_2C spin system, because these signals are very similar to those of aniline which are considered to be of the same spin system (Fig. 6). If the phenyl protons of the phenylimines are affected by the anisotropy effect of the lone pair electrons of the nitrogen atom adjacent to the phenyl ring, the spin system must be more complicated (as, e.g., ABCDE system). In fact, the anisotropy effect of the nitrogen atom is negligible in the case of III and IV. Such situation occurs when the dihedral angle between the C=N plane and the phenyl ring is nearly 90° or rapid torsional oscillation of phenyl ring occurs around nearly the right angle. It cannot be determined at present which model is plausible.

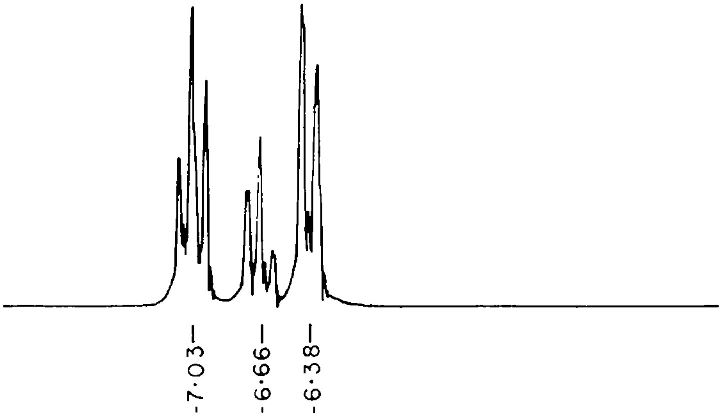

FIG. 6. 100 Mc NMR spectrum of aniline (neat).

Finally, another alternative possibility that the angle between the N=C and N-phenyl bond is different from that corresponding to exact sp^2 hybridization is discussed. It is sufficient to consider the case where this angle becomes larger than 120° to prevent repulsion between α methylene and phenyl protons, and at the same time the C=N double bond is conjugated with phenyl group. Then the ring current effect of the phenyl group causes the *anti* proton to shift to a high field as compared with the *syn* proton as shown in Fig. 5.[19] The effect of the lone pair electrons also causes the *anti* proton to shift to a high field.[20] In this assignment, the amount of VII is twice as much as that of VI, since the *syn* proton signal is more intense than the *anti* proton (see Fig. 1(C)). This conclusion, however, is inconsistent with the consideration that VI should be more stable because the repulsive interaction of the methylene protons with the phenyl group is larger than that of the oxygen atom. Accordingly this model is excluded.

Acknowledgements—The authors are grateful to Mr. H. Takahashi for supplying us with 2-phenyliminotetrahydrofuran and to Mr. A. Abe for his technical assistance.

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[19] Fig. 5 is based on the sp^2 hybridization model of the nitrogen atom. However, this figure is reasonable qualitatively even when the angle between N=C and N-phenyl is greater than 120°.

[20] W. D. Phillips, *Ann. N.Y. Acad. Sci.* **70**, 817 (1958); E. Lustig, *J. Phys. Chem.* **65**, 491 (1961). Further discussion of this assignment will be published elsewhere.