TABLE VI

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR COMPOUNDS 5[a]

Compd	δ values in DMSO-d_6
5a	10.42 (s, 1, NH), 2.68 (s, 3, SCH_3), 2.04 (br, 4, $C(2', 6')H_2$), 1.62 (br, 6, $C(3', 4', 5')H_2$)
5b	10.48 (s, 1, NH), 2.68 (s, 3, SCH_3), 1.70 (s, 6, $2CH_3$)
5c	10.47 (br, 1, NH), 5.10 (m, 1, CH), 2.68 (s, 3, SCH_3), 1.60 (d, 3, CH_3, $J = 5$ Hz)
5e	10.86 (br, 1, NH), 7.75 (s, 1, CH), 6.48 (s, 3, C_4H_3O), 2.66 (s, 3, SCH_3)
5f	10.68 (s, 1, NH), 3.18 (q, 2, CH_2CH_3, $J = 6$ Hz), 2.12 (br, 4, $C(3', 4')H_2$), 1.76 (br, 4, $C(2', 5')H_2$), 1.32 (t, 3, CH_2CH_3, $J = 6$ Hz)
5g	10.52 (s, 1, NH), 3.20 (q, 2, SCH_2CH_3, $J = 6$ Hz), 1.98 (q, 2, CH_2CH_3, $J = 6$ Hz), 1.62 (s, 3, CH_3), 1.32 (t, 3, SCH_2CH_3, $J = 6$ Hz), 0.92 (t, 3, CH_2CH_3, $J = 6$ Hz)
5h	10.83 (br, 1, NH), 6.96 (d, 3, C_6H_3), 6.22 (d, 1, CH, $J = 4$ Hz), 6.06 (s, 2, CH_2), 3.14 (q, 2, SCH_2CH_3, $J = 6$ Hz), 1.26 (t, 3, SCH_2CH_3, $J = 6$ Hz)
5i	10.70 (s, 1, NH), 4.20 (s, 2, CH_2), 4.10 (q, 2, CH_2CH_3, $J = 6$ Hz), 1.65 (s, 6, $2CH_3$), 1.20 (t, 3, CH_3CH_3, $J = 6$ Hz)

[a] Recorded on a JNM-C-60 high-resolution nmr spectometer operating at 60 MHz using tetramethylsilane as an internal standard.

Registry No.—**3a**, 29082-78-8; **3b**, 29082-79-9; **3c**, 29082-80-2; **5a**, 29082-81-3; **5b**, 29082-82-4; **5c**, 29082-83-5; **5d**, 29082-84-6; **5e**, 29082-85-7; **5f**, 29082-86-8; **5g**, 29082-87-9; **5h**, 39082-88-0; **5i**, 29082-89-1.

Acknowledgment.—The author wishes to express his thanks to Professor Dr. Tatsuo Takeshima and Dr. Hiroshi Midorikawa for their helpful discussion and encouragement throughout the course of this work.

The Conformation of 1,4-Dihydro-1-naphthoic Acid from the Nuclear Magnetic Resonance Spectrum

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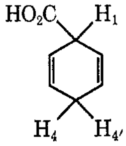
Received August 31, 1970

We recently discussed the long-range splitting between the 1 and 4 protons in 1,4-dihydrobenzoic acid (**1**).[1] This extremely large value of $J_{1,4}$ (8–9 Hz)[2] is somewhat surprising when compared with the negligibly small $J_{9,10}$ values of 9,10-dihydroanthracenes.[3,4] To explain the difference between $J_{1,4}$ in **1** and $J_{9,10}$ in **2**, we considered two possibilities: (1) **1** is flat and **2** is not, and the angular dependence of $J_{1,4}$ is such that the 1 and 4 protons couple when the dihydrobenzene ring is flat, but do not couple when the ring is in the boat conformation;[5] (2) the spin–spin interaction between the 1 and 4 protons is conveyed by an olefin, but not by an aromatic, π system.[6] To decide which explanation is correct, it is necessary to know whether 1,4-dihydrobenzenes and 9,10-dihydroanthracenes are flat. It is known that dihydroanthracenes are not flat (by the nmr chemical nonequivalence of the two 10 protons),[3,4] but, unfortunately, it is not known whether the dihydrobenzene system is relatively flat.[7,8]



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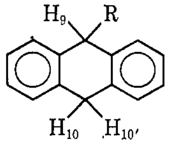
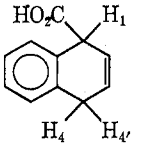


2

It was thought that a good test molecule to help resolve these difficulties would be 1,4-dihydro-1-naphthoic acid (**3**). This molecule possesses both an aromatic ring, whose ring currents would cause the two 4 protons to be chemically nonequivalent and would thus demonstrate the molecule to be nonplanar if it indeed were so, and also an olefin to transmit the spin–spin interaction if explanation 2 were operative. Therefore, **3** was synthesized by the Birch reduction[9] of 1-naphthoic acid and an nmr study of **3** was undertaken.



3

The 60-MHz nmr spectrum of **3** showed five regions of signals centered at δ 11.5, 7.3, 6.2, 4.6, and 3.6 that integrated in the respective ratio of 1, 4, 2, 1, and 2. Unlike the case of 1,4-dihydrobenzoic acid,[1] the spectral pattern of **3** was so complex that a complete 60-MHz analysis was impossible. Therefore, the 100-MHz spectrum was taken and studied. Decoupling experiments and use of the LAOCOON III nmr computer program[10] led to a set of parameters for the protons 1, 2, 3, 4, and 4′. These parameters are given in Table I.

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[1] J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

[2] For other examples of large homoallylic couplings in 1,4-dihydrobenzenes, see E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968); D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969); L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965).

[3] D. Nicholls and M. Szwarc, *J. Amer. Chem. Soc.*, **88**, 5757 (1966); R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

[4] A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *ibid.*, **92**, 5912 (1970).

[5] Theory predicts that the size of the homoallylic coupling constant varies as $\cos^2 \phi \cdot \cos^2 \phi'$ with the two angles ϕ and ϕ' each being the dihedral angle between each C–H bond and the intervening p orbitals of the π system: M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960); M. Barfield, *ibid.*, **48**, 4463 (1968).

[6] There is a theoretical basis for this explanation. If one assumes that the proton–proton coupling is dominated by a (nuclear-spin)–(electron-spin)–(electron-spin)–(nuclear-spin) coupling mechanism, then coupling *via* olefin bonds can be calculated to rather large and *via* aromatic bonds to be rather small: H. M. McConnell, *ibid.*, **30**, 126 (1959).

[7] See ref 2. See also B. A. Shoulders, R. M. Gipson, R. J. Jandacek, S. H. Simonsen, and W. Shive, *J. Amer. Chem. Soc.*, **90**, 2992 (1968); F. H. Herbstein, *J. Chem. Soc.*, 2292 (1959).

[8] The conformation of 1,4-dihydrobenzene itself is known to be very slightly puckered: H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

[9] M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963). For the synthesis of **3**, see the Experimental Section.

[10] A. A. Bothner-By and S. M. Castellano, "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.

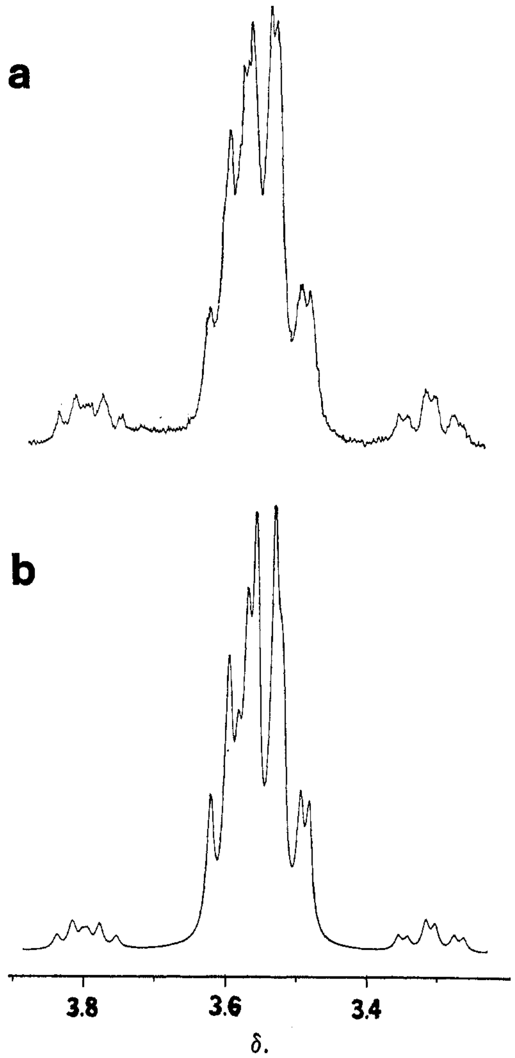

Figure 1.—(a) Observed and (b) computer-simulated spectral regions for methylene protons (H_4, $H_{4'}$) of 1,4-dihydro-1-naphthoic acid.

Table I

Nmr Parameters for 1,4-Dihydro-1-naphthoic Acid (**3**)[a]

Proton	Chemical shift, δ	$J_{A,B}$ A	B	Hz
1	4.55	1	2	4.59
2	6.07	1	3	−1.22
3	6.25	1	4	3.93
4	3.47	1	4′	3.93
4′	3.63	2	3	9.62
		2	4	−1.24
		2	4′	−2.97
		3	4	4.60
		3	4′	2.44
		4	4′	−21.92

[a] These final values were obtained by using the iterative subroutine of the LAOCOON III nmr computer program[10] to obtain the best fit of the data. The rms error was 0.07 Hz.

Figures 1, 2, and 3 show the observed and computer-simulated patterns of the methylene region (H_4, $H_{4'}$), the methine region (H_1), and the olefin region (H_2, H_3), respectively.

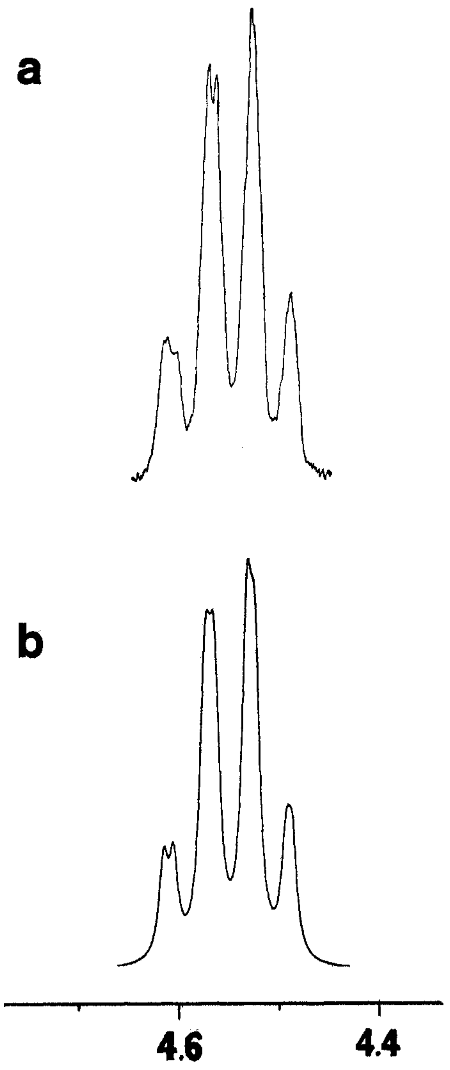

Figure 2.—(a) Observed and (b) computer-simulated spectral regions for the methine proton (H_1) of 1,4-dihydro-1-naphthoic acid.

Two notable differences exist between the spectral patterns for 1,4-dihydrobenzoic acid[1] and for 1,4-dihydro-1-naphthoic acid. First, the two methylene protons (H_4 and $H_{4'}$) in **3** now have different chemical shifts. This can be explained by the nonplanarity of the dihydro ring which places the methylene protons in different chemical environments (pseudoaxial and pseudoequatorial).

Second, the olefin protons in **3** now couple significantly with the methine (H_1) and the methylene (H_4, $H_{4'}$) protons. This again suggests nonplanarity of the ring in **3**, because calculations[11] indicate that this coupling decreases as the ring becomes more planar. 1,4-Dihydrobenzoic acid, which has negligible olefin–methylene and olefin–methine coupling,[1] is thus indicated to be more nearly flat.

A clue to which methylene proton is pseudoequatorial and which is pseudoaxial is given by the vicinal coupling constants $J_{3,4}$ and $J_{3,4'}$. The dihedral angle involving H_3 and the pseudoaxial proton is more nearly 90° than that involving H_3 and the pseudoequatorial proton (see **4**). Since J_{vic} decreases as the dihedral angle approaches 90°[11-13] and since $J_{3,4}$ (4.60 Hz) is greater

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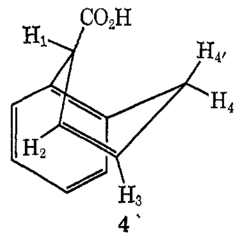
(11) K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, **83**, 4623 (1961); M, Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(12) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

(13) A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Gunther, *J. Amer. Chem. Soc.*, **88**, 2466 (1966).

than $J_{3,4'}$ (2.44 Hz), then $J_{3,4}$ must involve the pseudoequatorial proton. Thus, H_4 must be pseduoequatorial and $H_{4'}$ must be pseudoaxial, as indicated in **4**.[14]



4

The J_{vic} values can also place the position of the carboxylate group. $J_{1,2}$ (4.59 Hz) is virtually equal to $J_{3,4}$ (4.60 Hz). Since H_4 is pseudoequatorial, H_1 must also be pseudoequatorial.[15] Structure **4** thus represents the correct conformation of **3** with the carboxylate group in the pseudoaxial position.[16] Apparently the group prefers this position because of interactions with the aromatic ortho proton when in the pseudoequatorial position.

A check on the above assignments can be made by means of the allylic coupling constants. Calculations[12,17] indicate that, when a C–H bond (of an sp^3 carbon atom) is parallel to the adjacent p orbital of a π bond, the allylic coupling constant is maximum (around 3.0 Hz), and, when perpendicular, more nearly zero. Therefore, from **4** one would predict $J_{2,4'}$ to be about 3 Hz and $J_{1,3}$ and $J_{2,4}$ to be smaller and approximately equal to one another. Precisely as predicted, $J_{2,4'}$ = 2.97 Hz, $J_{1,3}$ = 1.22 Hz, and $J_{2,4}$ = 1.24 Hz. Thus, from an analysis of the vicinal and allylic coupling constants, **4** seems to be the correct conformation of 1,4-dihydro-1-naphthoic acid.

The homoallylic coupling $J_{1,4}$ and $J_{1,4'}$ is significant in **3** as in the case of **1**. In view of the present indications that **1** is more nearly planar than **3**,[18] this homoallylic coupling apparently does not depend upon the planarity of the ring (although its magnitude might). Thus, from the first paragraph above it follows that the homoallylic spin–spin interaction is transmitted through the olefin bond but cannot be transmitted significantly through an aromatic bond.

It would be of interest to determine the J_{cis}/J_{trans} ratio in **3** to see if this ratio reflects the degree of puckering in the dihydro ring.[1] Unfortunately, all of the parameters of Table I are definite *except* $J_{1,4}$ and $J_{1,4'}$; small changes in all parameters (~0.1 Hz) except $J_{1,4}$ and $J_{1,4'}$ caused significant changes in the appearance of the simulated[10] nmr spectrum. To obtain this ratio directly, we are currently investigating the nmr spectra of the deuterated analogs of 1,4-dihydro-1-naphthoic acid.

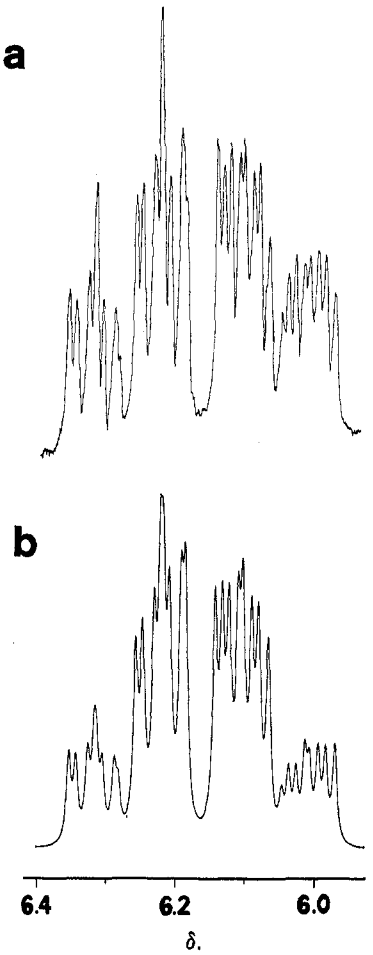


Figure 3.—(a) Observed and (b) computer-simulated spectral regions for olefin protons (H_2, H_3) of 1,4-dihydro-1-naphthoic acid.

Experimental Section

Melting points were determined by a Thomas-Hoover melting point apparatus. Nuclear magnetic resonance spectra were recorded on a Jeolco MH-60 spectrometer and a Jeolco PS-100 spectrometer, using tetramethylsilane as the internal standard and deuteriochloroform as the solvent.

1,4-Dihydro-1-naphthoic Acid (3).—Into a 1000-ml three-necked flask equipped with a mechanical stirrer and a Dry Ice condenser was distilled 300 ml of ammonia under an argon atmosphere. To the stirring contents was added 5.0 g of 1-naphthoic acid (Aldrich Chemical Co.), 50 ml of dry ethanol (distilled from calcium), and then 2.2 g of sodium metal in small pieces. After 30 min of stirring, 5.4 g of ammonium chloride was added cautiously. After 1 hr of stirring, the ammonia was evaporated and 150 ml of water was added. Sufficient hydrochloric acid (6 *N*) was added to bring the pH to 8. The solution was filtered, made acidic with 6 *N* hydrochloric acid, and extracted with four 60-ml portions of ether. The combined ethereal extracts were dried (anhydrous magnesium sulfate) and concentrated under reduced pressure to give a brown solid. Recrystallization from 60–90° petroleum ether gave 3.10 g of **3** (61%), mp 87–89° (lit.[19] mp 86°). The mother liquor was concentrated to give 1.22 g of a brown solid, mp 69–76°, whose nmr analysis indicated it to be a 1:1 ratio of **3** and the isomeric 3,4-dihydro-1-naphthoic acid. Recrystallization of the 87–89° material gave a pure nmr sample, mp 88.5–90.5°.

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(14) These values of J_{vic} are consistent with previous examples: $J_{2,3}$ in cyclohexene (a flexible system where $J_{2,3} = J_{2,3'}$) is 3.1 Hz [C. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963)].

(15) The electronegative effect of the carboxylate substituent upon $J_{1,2}$ would probably be negligible and in any case should decrease the value of $J_{1,2}$ (see ref 11). Thus, in the absence of the electronegative effect ,the value of $J_{1,2}$ represents a minimal value and $J_{1,2}$ certainly corresponds with $J_{3,4}$.

(16) The 9 substituent in 9-alkyl-9,10-dihydroanthracenes is also pseudoaxial [see ref 4].

(17) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

(18) Aa a referee pointed out, theory[5] predicts that $J_{1,4} \simeq J_{1',4'}$ is only consistent with a planar molecule for **3**. Previous work [D. W. Cameron, D. G. I. Kingston, N. Sheppard, and L. Todd, *J. Chem. Soc.*, 98 (1964); J. T. Pinhey and S. Sternhell, *Tetrahedron Lett.*, 275 (1963); H. H. Appel, R. P. M. Bond, and K. H. Overton, *Tetrahedron*, **19**, 635 (1963)] indicates that (pseudoequatorial)–(pseudoequatorial) coupling should be very small. However, the conformation of the rings described in these references was not always independently definable, and in those examples involving fixed geometries at least some probably involve half chairs. Hence, the utility of the homoallylic coupling as a tool for conformational analysis has not been established.

(19) K. von Auwers and K. Moller, *J. Prakt. Chem.*, **109**, 144 (1925).

Registry No.—**3,** 5111-73-9.

Acknowledgment.—Acknowledgment is made to the Research Corporation (Frederick Gardner Cottrell Grant-in-Aid), to the Robert A. Welch Foundation (Grant No. B-325), and to North Texas State University for a Faculty Research Grant for support of this work.

The Dipole Moments and Conformations of 1,2-Diimines

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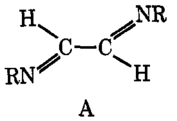
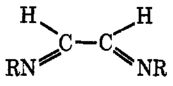
Studies on the reaction of glyoxal with aliphatic[1] and aromatic[2] amines have led, in certain cases, to the isolation of N,N′-substituted 1,2-diimines. Their configuration was shown to be *E* (anti) at both C=N double bonds by analysis of their nmr spectra, the course of protonization, and by analogy with other aldimines,[3–5] whereas the conformation of the central C—C bond was only tentatively attributed to be s-trans A rather than s-cis B. A more detailed study of this conformation is the aim of the present paper.


A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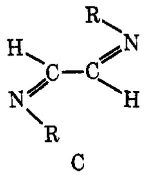
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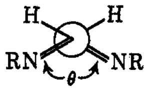
From *a priori* considerations, it follows that both planar forms are stabilized by mesomerism, the s-trans form A being more favored than s-cis B. However, the double bond character of the central bond cannot be very accurately expressed since the corresponding mesomeric formula is destabilized by charge separation and by a sextet on the nitrogen atoms. Hence, the planarity can easily be distorted by nonbonded interactions. For the same reasons the conformation of 1,2 diketones is nonplanar.[6]

Our experimental method of choice was dipole moment measurement in solution. Admittedly, this approach is of limited accuracy; however, because the results are extrapolated to zero concentration, it has the advantage that a practically isolated molecule is studied in a nonpolar medium. The accuracy can be improved by measuring several substituted derivatives and comparing experimental and computed moments graphically.[7]

The experimentally measured dipole moments are given in Table I and can be considered internally consistent, especially the values for compounds **1**, **2**, and **5**, which should be equal according to the simple method of vector addition, and, in fact, are reasonably close to each other. In general, the measurements are not very precise because of association in solution, thus making extrapolation difficult. However, the situation is much improved for the measurements taken on compounds **5** and **6**. Therefore, our discussion is mainly based on these compounds for which the standard accuracy was attained, limited ultimately by the correction for atomic polarization (compare columns 7 and 8 in Table I). When the compounds are measured in two solvents, the differences are significant.

Without any computation, one can conclude from the nonzero experimental moments that a strictly planar conformation *E*-s-trans-*E*, A, is not possible, neither is the *Z*-s-trans-*Z* one, C. When the *E* configuration is taken for granted, the experimental results can be interpreted either as a mixture of both forms A and B or as a nonplanar conformation of the C_2 symmetry. On the basis of dipole moment data, one cannot discern between these two possibilities. However, on the basis of the results on 1,2 diketones[6] and glyoximes[8] we prefer the latter.

In order to get a more quantitative picture it is necessary to compute theoretical moments for individual compounds in conformation B. Starting from trigonal valence angles and the C=N bond moment of 1.8 D[9] we get the same value, 3.12 D, for compounds **1**, **2**, **3**, **5**, and **6**, indicating the dihedral angle N–C–C–N in the real conformation to be between 90 and 140°.[10] The computation is rather sensitive to the valence angles used. A smaller C-N-C angle, *e.g.*, 117°, as found in *N*-methylmethyleneimine,[11] or a larger C–C–N angle would lead to a greater moment for the methyl deriva-


$\theta = 90–140°$

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[1] J. M. Kliegman and R. K. Barnes, *Tetrahedron*, **26**, 2555 (1970); *Tetrahedron Lett.*, 1953 (1969).

[2] J. M. Kliegman and R. K. Barnes, *J. Org. Chem.*, **35**, 3140 (1970).

[3] V. de Gaouck and R. J. W. Le Févre, *J. Chem. Soc.*, 741 (1938).

[4] G. J. Karabatsos and S. S. Lande, *Tetrahedron*, **24**, 3907 (1968).

[5] J. Hine and C. Y. Yeh, *J. Amer. Chem. Soc.*, **89**, 2269 (1967).

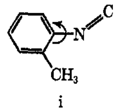
[6] P. H. Cureton, C. G. Le Févre, and R. J. W. Le Févre, *J. Chem. Soc.*, 4447 (1961).

[7] O. Exner and V. Jehlička, *Collect. Czech. Chem. Commun.*, **30**, 639 (1965).

[8] A nonplanar conformation with a dihedral angle N–C–C–N *ca.* 120–140° has been also preferred for glyoximes. A more exact determination is, in this case, prevented by possible distortion of the O–N bonds: C. Pigenet, J. Armand, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 2124 (1970).

[9] O. Exner, *Collect. Czech. Chem. Commun.*, **30**, 652 (1965).

[10] Compounds **4** and **7** are complicated by additional rotations such as those shown in i and ii. Thus our data does not allow us to make any comparison of computed and measured values.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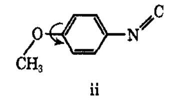
ii

[11] K. V. L. N. Sastry and R. F. Curl, *J. Chem. Phys.*, **41**, 77 (1964).