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

OTTO EXNER*

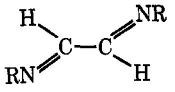
J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague 1, Czechoslovakia

JONATHAN M. KLIEGMAN

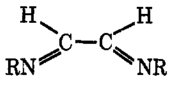
Research and Development Department, Chemicals and Plastics Division, Union Carbide Corporation, South Charleston, West Virginia 25303

Received September 15, 1970

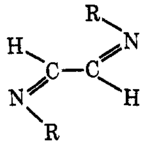
Studies on the reaction of glyoxal with aliphatic[1] and aromatic[2] amines have led, in certain cases, to the isolation of N,N′-substituted 1,2-diimines. Their configuration was shown to be *E* (anti) at both C=N double bonds by analysis of their nmr spectra, the course of protonization, and by analogy 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



B



C

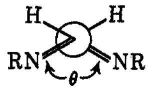
From *a priori* considerations, it follows that both planar forms are stabilized by mesomerism, the s-trans form A being more favored than s-cis B. However, the double bond character of the central bond cannot be very accurately expressed since the corresponding mesomeric formula is destabilized by charge 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-



$\theta = 90\text{–}140°$

---

[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 Fèvre, *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).

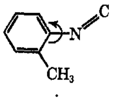
[6] P. H. Cureton, C. G. Le Fèvre, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 4447 (1961).

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

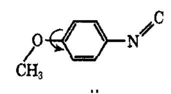
[8] A nonplanar conformation with a dihedral angle N-C-C-N *ca.* 120–140° has been also preferred for glyoximes. A more exact determination is, in this case, prevented by possible distortion of the O-N bonds: C. Pigenet, J. Armand, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 2124 (1970).

[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.



i



ii

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

TABLE I

POLARIZATION DATA OF 1,2-DIIMINES $RN{=}CHCH{=}NR$ AT 25°

No.	Registry no.	R	Mp, °C	Solvent[a]	$_{\infty}P_2$,[b] cm³	R_D[c] (calcd), cm³	μ (5%),[d] D	μ (15%),[a] D
1	28387-17-9	C_4H_9	1.4548[e]	B	80.8	53.7	1.09	0.96
2	28227-40-9	i-C_4H_9	1.4518[e]	B	85.3	53.7	1.28	1.27
3	28227-38-5	c-C_6H_{11}	145–147	B	123.0	67.8	1.59	1.48
4	24978-40-3	2-$CH_3C_6H_4$	122–124	B	106.6	77.4	1.11	1.93
5	24978-41-4	4-$CH_3C_6H_4$	164–165	B	113.9	77.4	1.26	1.10
				D	160.2	77.4	1.96	1.87
6	24978-44-7	4-ClC_6H_4	107–110	B	183.0	78.0	2.22	2.14
				D	241.3	78.0	2.79	2.72
7	24978-42-5	4-$CH_3OC_6H_4$	153–154	B	196.7	81.9	2.32	2.24

[a] B, benzene; D, dioxane. [b] Overall polarization. [c] Molar refraction. [d] Correction for the atomic polarization, 5 or 15% of the R_D value, respectively. [e] $n^{25}D$.

tive **5** than for the 4-chloro derivative **6**. Quite on the contrary, the experimental value is significantly smaller showing that either the C–N–C angle is larger or the C–C–N angle smaller, or more probably that the conformation of both compounds **5** and **6** is somewhat different. The situation is pictured by a graphical representation used in our previous papers[7,9] (Figure 1). Computed moments for various dihedral angles are shown by straight lines, the full line corresponding to angles C–N–C = C–C–N = 120°, the broken one to a change of one of them by 5°. From the experimental point it can be concluded that the conformations of both compounds **5** and **6** may differ.[12] A more exact determination of dihedral angles from our data is not possible.

It should be stressed once more that all the results were obtained with a precondition of the *E* configuration on the C=N double bond. For the *Z* configuration the theoretical dipole moments can also be computed. The results in that case are still dependent on the value for the C—N bond, whereas the mesomeric moment can be neglected since the benzene rings are not coplanar with the C=N bonds.[13] It is, however, not possible to distinguish between all various possibilities from the values of dipole moments alone.

We conclude that nonplanar stable conformations are typical for the atom grouping X=CC=X; evidently the mesomerism is not strong enough to overcome the bond and atom repulsion. The conformation is not very rigid and differs somewhat in vapor and in the crystalline state, in various solvents, and at different temperatures.[6] This behavior is contrasted by that of 1,3-butadiene which has two energetical minima in its two planar conformations, differing by 2.3 kcal mol^{-1} and separated by a barrier of 2.6 kcal mol^{-1} (*cf.* ref 14). For 1,2 diketones, theoretical calculations which furnished the energy difference between the two planar forms, however, did not reveal the existence of an energetical minimum.[15] Similarly, in the case of 1,2-diimines no more quantitative discussion is possible at the present time.[8]

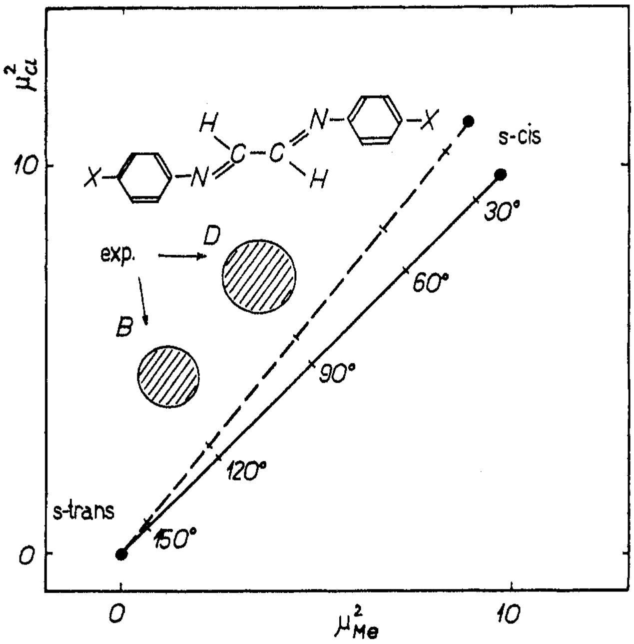


Figure 1.—Comparison of computed (straight lines) and experimental dipole moments (circles) of compounds **5** and **6** in benzene (B) and dioxane (D) over a range of bond angles.

Experimental Section

The preparation of compounds **1–7** has been previously described.[1,2] Dipole moments were determined by the method of Halverstadt and Kumler.[16] Dielectric constants of benzene or dioxane solutions were measured at 25° using a heterodyne apparatus at a frequency of 1.2 Mcps. Usually five measurements were carried out in the concentration range 5×10^{-3}–5×10^{-2} *M*. The molar refractions were calculated from Vogel's increments[17] and suitable additive corrections (exaltations) applied in order to account for the conjugation, *viz.*, 0.4 cm³ for the conjugation of two C=N bonds and 1.5 cm³ for the conjugation of one C=N bond with a benzene nucleus. The inaccuracy in this procedure does not influence the final values of dipole moments significantly.

Acknowledgment.—The measurement of dielectric constants and densities was carried out by Mrs. M. Kuthanová, Department of Physical Chemistry, Institute of Chemical Technology, Prague, under the supervision of Dr. V. Jehlička. The aid of both is gratefully acknowledged.

---

[12] A rough estimate of the dihedral angles for compounds **1–3**, and **5** and **6** would be 135–145°, 130–140°, 120–130°, 130–140°, and 90–100°, respectively.

[13] V. I. Minkin, Y. A. Zhdanov, E. A. Medyantzeva, and Y. A. Ostroumov, *Tetrahedron*, **23**, 3651 (1967).

[14] J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

[15] L. V. Vilkov, N. I. Sadova, and N. A. Tarasenko, *Zh. Strukt. Khim.*, **10**, 403 (1969).

[16] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

[17] A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).