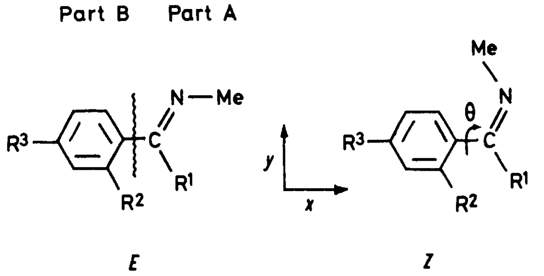
Molecular Conformation and Electronic Structure of Azomethines. Part 5.[1a] Determination of the Conformation of Some *N*-Methylimine Derivatives of Aldehydes and Ketones from Dipole Moment Data

By **Demetrio Pitea,* Giorgio Favini, and Gianpaolo Capietti,** Institute of Physical Chemistry, University of Milan, Milan, Italy

The dipole moments of some *N*-methylimine derivatives of aldehydes and ketones have been measured in benzene and analysed in terms of the configuration of the C=N bond and the conformation on the Ph–C bond. The evidence presented here suggests that a σ–π approximation is sufficient for dipole moment calculations as far as conformational assignments are concerned. The dipole moment analysis yields unambiguous conformational assignments in the presence of a single configuration. When a configurational equilibrium is present, an additional molecular property, *e.g.* n.m.r., must be employed; this additional datum on the isomer ratio allows the most probable conformation to be selected by the dipole moment analysis.

In spite of the large number of experimental[1] and theoretical[2] studies on Schiff's bases, the configurations and the conformations of these derivatives have not been unequivocally defined. Experimental evidence[1a,b,i,3] indicates that unsubstituted and *para*-substituted aldimines exist completely in the planar *E*-configuration (see Scheme). When α-methyl and/or *ortho*-substituents are present, the n.m.r. spectra[1i] revealed an equilibrium between the *E*- and *Z*-forms; the ratio of isomers was determined without a detailed conformational assignment.



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^2 = H$, $R^3 = Me$
(3) $R^1 = R^3 = H$, $R^2 = Me$
(4) $R^1 = H$, $R^2 = R^3 = Me$
(5) $R^1 = Me$, $R^2 = R^3 = H$
(6) $R^1 = R^3 = Me$, $R^2 = H$
(7) $R^1 = Me$, $R^2 = H$, $R^3 = Cl$
(8) $R^1 = R^2 = Me$, $R^3 = H$
(9) $R^1 = R^2 = R^3 = Me$

SCHEME

We report here the determination of the conformation of compounds (3)—(9) carried out by comparison of the dipole moments of the *para*-substituted and unsubstituted compounds.

EXPERIMENTAL

Preparation and Purification of Compounds.—The imines (3)—(9) were synthesized from the corresponding aldehyde or ketone and methylamine by a standard literature method;[4] each compound was purified by fractionation or by preparative g.l.c. Its purity was checked by analytical g.l.c. (SE 30 column; flame ionization detector) and by i.r. spectroscopy (Perkin-Elmer 21 instrument). The imines, which were purified immediately before use, showed no i.r.

TABLE 1

Polarization data and electric dipole moments at 25.0 °C in benzene solution *

Compound	α	β	$_{\mu}P_2$/cm^3	μ/D
(3)	2.11 ± 0.02	0.437 ± 0.006	41.98	1.43 ± 0.01
(4)	1.99 ± 0.06	0.409 ± 0.017	43.82	1.46 ± 0.03
(5)	2.91 ± 0.03	0.191 ± 0.006	68.16	1.83 ± 0.01
(6)	3.24 ± 0.05	0.589 ± 0.022	73.43	1.89 ± 0.02
(7)	3.99 ± 0.06	0.203 ± 0.002	120.0	2.42 ± 0.02
(8)	2.63 ± 0.02	0.347 ± 0.023	63.28	1.76 ± 0.01
(9)	2.98 ± 0.03	0.185 ± 0.007	84.66	2.04 ± 0.01

* Errors in α and β are quoted as ± probable errors and based on the least-squares plot. These errors are combined to give the quoted error in μ.

---

[1] (*a*) Part 4, D. Pitea, D. Grasso, and G. Favini, *J. Chem. Soc.* (*B*), 1971, 2290; (*b*) D. Pitea, D. Grasso, and G. Favini, *J. Mol. Structure*, 1971, **10**, 101 and references cited therein; (*c*) M. Ashraf El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, 1971, **93**, 586, 590; (*d*) V. M. S. Gil and M. E. L. Saraiva, *Tetrahedron*, 1971, **27**, 1309; (*e*) A. Van Putten and J. W. Pavlik, *ibid.*, pp. 3007, 3301; (*f*) P. Grammaticakis and H. Texier, *Bull. Soc. chim. France*, 1971, 1323; (*g*) J. Bernstein and G. M. T. Schmidt, *J.C.S. Perkin II*, 1972, 951; (*h*) E. P. Kyba, *Tetrahedron Letters*, 1973, 5117; (*i*) J. Bjørgo, D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J.C.S. Perkin II*, 1974, 757, 1081, and preceding papers; (*j*) P. Skrabal, J. Steiger, and H. Zollinger, *Helv. Chim. Acta*, 1975, **58**, 800; (*k*) A. S. Al-Tai, D. M. Hall, and A. R. Mears, *J.C.S. Perkin II*, 1976, 133.

[2] (*a*) G. Favini, D. Pitea, and F. Zuccarello, *J. Chim. Phys.* 1972, **69**, 9 and references cited therein; (*b*) C. H. Warren, G Wettermark, and K. Weiss, *J. Amer. Chem. Soc.*, 1971, **93**, 4658; (*c*) R. S. Tsekhanskii, S. N. Nikolaev, and L. T. Vinogradov, *Russ. J. Phys. Chem.*, 1971, **45**, 1001; (*d*) H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 1255; (*e*) M. Shanshal, *Tetrahedron*, 1972, **28**, 61; (*f*) J. Berges, H. Perrin, and M. Jaffrain, *Compt. rend. C*, 1975, 441; (*g*) T. Bally, E. Haselbach, S. Lanyiova, F. Marschner, and M. Rossi, *Helv. Chim. Acta*, 1976, **59**, 486; (*h*) G. Leroy, G. Louterman-Leloup, and B. Scheuer-Lamalle, personal communication.

[3] H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1970, **52**, 1747.

[4] H. Weingarten, J. P. Chupp, and W. A. White, *J. Org. Chem.*, 1967, **32**, 3246.

carbonyl absorption. Physical properties were in good agreement with literature data.

Dipole Moments.—The dipole moments were determined as described previously.[1a] The measured properties of the solutions at 25.0 °C are collected in Supplementary Publication No. SUP 22112 (6 pp.).* The polarization data together with the dipole moments are given in Table 1; the symbols have their usual meanings.

CALCULATIONS

The co-ordinate system is shown in the Scheme.

Direction of the Experimental Dipole Moments.—The direction of the dipole moment of *N*-benzylidenemethylamine (1) has been previously established[1a] but a more reliable value may be determined by a statistical treatment[5] of experimental moment of (1) and its *p*-methyl, *p*-chloro-, *p*-bromo-, and *p*-nitro-derivatives.[1a] Graphical resolution gives $\mu\ (E)\text{-}(1) = 0.12i + 1.40j$.

Derivatives (3)—(9) exist in solution as a mixture of two forms at equilibrium: therefore, the direction of their experimental dipole moments cannot be determined.

Moment of the Methyl Group.—The methyl group moment for substitution in the ring can be obtained from the equation $(0.12 + \mu_{\text{Me}})^2 + 1.40^2 = \mu^2(2)$. Substituting $\mu(2) = 1.53$ D,[1a] gives μ_{Me} 0.50 D. This value, considering the electronic effects of the *p*-methyl group on conjugation, is quite reasonable.

Vector Addition Scheme.—The dipole moments may be considered as the vector resultant of components μ_A and μ_B (see Scheme); if μ_A is rotated around the x axis by an angle θ, a straight line for the plot of μ_S^2 *versus* μ_H^2 is obtained.[6]

Theoretical π-Moments.—The π-components (μ_π) of the total dipole moment were calculated using the SCF-MO technique in the Pople approximation[7] by taking n electrons of the heteroatom into account as long as the molecule under investigation is non-planar.[8] The two electrons for each methyl group which interact with the π-electron system are treated by the heteroatom model with Roos parametrization.[9] The parameters adopted are given in SUP 22112. The results for *N*-benzylidenemethylamine are reported in Table 2.

TABLE 2

Theoretical π-dipole moments of *N*-benzylidenemethylamine[a]

	Unit vectors for *E*-configuration			Unit vectors for *Z*-configuration		
θ(°)	*i*	*j*	*k*	*i*	*j*	*k*
0	0.834	0.901		1.20	0.695	
30	0.714	0.895	−0.031	1.08	0.692	−0.023
60	0.472	0.886	−0.029	0.832	0.680	−0.021
90	0.346	0.878		0.706	0.672	

[a] For the axis and the definition of the angle θ see Scheme.

Calculation of σ-Moments.—*N*-Benzylidenemethylamine (1) exists exclusively as the *E*-isomer; the σ-component of the total dipole moment [$\mu_\sigma(E)$-(1)] is then the vector difference between the total dipole moment and the calculated μ_π component: $\mu_\sigma(E)\text{-}(1) = -0.71i + 0.50j$.

This procedure affords a μ_σ value independent of the nitrogen lone pair moment which is included in the π-skeleton. Moreover, this approach allows the determination of a set of internally consistent bond moment values. If it is assumed that the H–C (sp^2) bond moment is zero,† the comparison of $\mu_\sigma(E)\text{-}(1) = \{M[\text{C}(sp_2)\text{–N}] \cos 60° - M(\text{Me–N})\}i + \{M[\text{C}(sp_2)\text{–N}] \sin 60°\}j$ with the previous calculated value gives $M[\text{C}(sp_2)\text{–N}]$ 0.57 D together with M(Me–N) 1.00 D; these bond moments are in very good agreement with literature data.[10,11] The calculation of μ_σ for the coplanar conformation of the (Z)-(1) isomer gives $\mu_\sigma(Z)\text{-}(1) = 0.78i - 0.37j$.

Correlation between Experimental and Calculated Dipole Moments.—A graphical representation was used:[12] the values of μ^2 were plotted on the x-axis for the unsubstituted compound (μ_H^2) and on the y-axis for the *para*-derivative (μ_S^2); each presumed conformation is represented by a point. The diagrams were obtained as follows: for the *E*- and *Z*-configurations of each compound, the dipole moments at θ values between 0 and 180° were calculated; the relation between the variables which gives the best fit was determined. The equations for the lines referring to the *E*- or *Z*-forms of each H–S pair were obtained from these empirical relations; Figures 1 and 2 show these

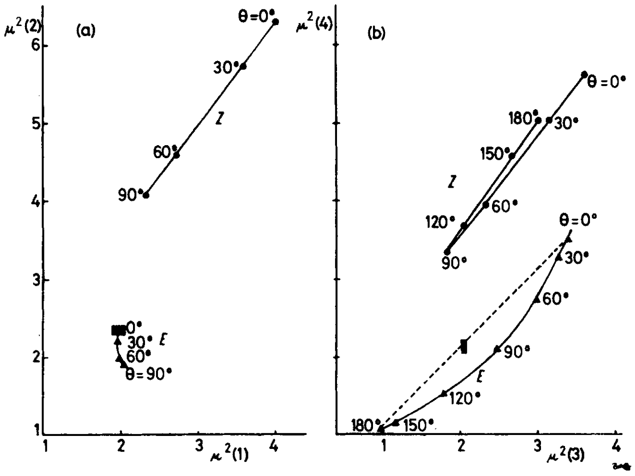


FIGURE 1 Comparison of squared dipole moments of: (a) *N*-benzylidenemethylamine (1) and its *p*-methyl derivative (2); (b) *N*-(*o*-methylbenzylidene)methylamine (3) and its *p*-methyl derivative (4). ●, Theoretical for *Z*-configuration; ▲, theoretical for *E*-configuration; ■, experimental. The dashed line refers to the vector addition calculation. The full lines refer to σ–π calculations

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue. Items less than 10 pp. are supplied as full-size copies.

† The convention used here to define bond moment takes A as the positive end of the dipole in *M*(A–B).

[5] B. Eda and K. Ito, *Bull. Chem. Soc. Japan*, (*a*) 1956, **29**, 524; (*b*) 1957, **30**, 164.

[6] O. Exner and V. Jehlicka, *Coll. Czech. Chem. Comm.*, 1965, **30**, 639.

[7] J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

[8] T. Anno, I. Matubara, and A. Sadô, *Bull. Chem. Soc. Japan*, 1957, **29**, 168.

[9] B. Roos, *Acta Chem. Scand.*, 1967, **21**, 2318.

[10] K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 1949, 2318.

[11] H. Lumbroso and G. Pifferi, *Bull. Soc. chim. France*, 1969, 3401.

[12] O. Exner, ' Dipole Moments in Organic Chemistry,' Thieme Verlag, Stuttgart, 1975.

functions as *Z*- or *E*-lines. Following the lever rule, the family of straight lines centred about the experimental point and intersecting the *E*- and *Z*-lines yields all the possible solutions. These were found by a computer program.

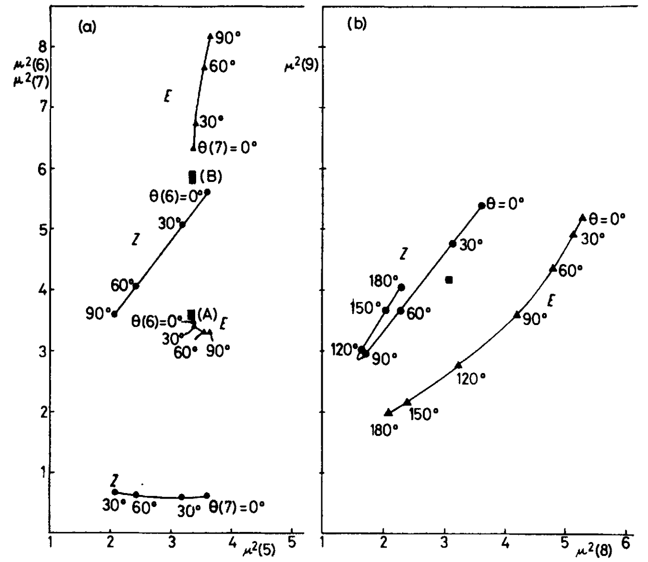


FIGURE 2 Comparison of squared dipole moments of: (a) acetophenone *N*-methylimine (5) and its *p*-methyl-derivative (6) and *p*-chloro-derivative (7), respectively; (b) *o*-methylacetophenone *N*-methylimine (8) and its *p*-methyl derivative (9). ●, Theoretical for *Z* configuration; ▲, theoretical for *E*-configurations; ■, experimental: (A) for the (5)–(6) pair, (B) for the (5)–(7) pair

RESULTS AND DISCUSSION

The two main approaches to the quantitative evaluation of the dipole moments are empirical and quantum chemical calculations.

The vector addition scheme has been critically discussed and methods for its improvement have been proposed.[13] There are at least two factors that the vector addition scheme is not able to take into account. They are (*a*) the variation of the π-component of the overall moment with the angle of rotation θ and (*b*) the different electronic effect to which the same substituent, in different positions of the ring, gives rise. Owing to rotation, such effects will be θ dependent.

Among the quantum chemical calculations, the semi-empirical method based on σ–π separation was selected. To take into account effects (*a*) and (*b*) calculations should be made as follows: estimation of $\mu_\sigma(E)$ and $\mu_\sigma(Z)$ for all compounds and computation of $\mu_\pi(E)$ and $\mu_\pi(Z)$ for each compound as functions of the dihedral angle θ. The latter calculations would be very tedious and expensive; moreover, the uncertainty due to computing approximations would probably exceed the error which is made by neglecting factor (*b*).

Thus, as a first approximation, factor (*b*) was neglected and the scheme of calculation of the overall moments was made up of three stages: (1) calculation of $\mu_\pi = \mu_\pi(\theta)$ for *N*-benzylidenemethylamine; (2) calculation of $\mu_\sigma = \mu_\sigma(\theta)$, including the methyl group moment as σ-component; (3) calculation of the dependence of the total dipole moment by the angle of rotation θ. The results of calculations in stage (1) are reported in Table 2. The values of stage (2) may be found with the proper vector addition of μ_{Me} and $\mu_\sigma(E)$–(1) or $\mu_\sigma(Z)$–(1). The total dipole moments are computed and plotted as the *E* and *Z* full lines in Figures 1 and 2.

From the graph of Figure 1a, it is evident that the experimental values for the pair of compounds (1) and (2) are in a very good agreement with the calculated values for the coplanar *E*-configuration and, hence, with the conclusions of previously reported analyses.[1a,b,i]

In the more complex cases, dipole moment data alone may be insufficient for conformational studies and other physical methods must be used. Among these, n.m.r. spectroscopy allows the detection of less populated configurations and enables their abundance to be calculated.[11]

The imines (3) and (4) show n.m.r. signals which have been attributed to a single *E*-isomer.[1i] From the full *E*-line in Figure 1b,* the conformational assignments are as given in Table 3.

TABLE 3

Dihedral angle θ (°)	*w* (%)	$\mu_{E,\theta}(3)$/D	$\mu_{E,\theta}(4)$/D
0	45	1.84	1.87
180	55	0.97	1.03

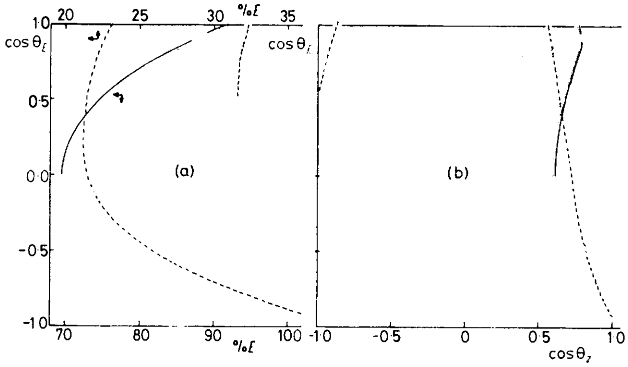


FIGURE 3 Correlation between the dihedral angle θ in the *E*-configuration and (a) the equilibrium distribution, (b) the dihedral angle θ in the *Z*-configuration. Imines (5) and (6) (full lines); (5) and (7) (dotted lines); (8) and (9) (dashed lines)

For the imines (5)—(7), an n.m.r. study revealed the presence of the *E*- and *Z*-isomers in the ratio 93 : 7, without permitting an assignment of their conform-

---

[13] V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, ' Dipole Moments in Organic Chemistry,' Plenum Press, New York, 1970, ch. 3.

* Calculations with the vector scheme are indicated as a dashed line in Figure 1b. This result may be interpreted either as a single non-planar conformation with a dihedral angle of *ca.* 90° or as a mixture of the two limiting forms in a ratio of *ca.* 1 : 1; the two possibilities are indistinguishable.

ations.[1i] The results from the dipole moment analysis are reported in Figure 2a and the entire set of possible solutions is shown in Figure 3. It must be noted that two strictly corresponding sets of solutions are obtained for the (5)–(6) and (5)–(7) pairs. It can be seen that for an isomer ratio of 92 : 8, cos $\theta_E = 1.0$ (solid and dotted lines in Figure 3a) and cos $\theta_Z = 0.765$ (Figure 3b). The dipole moments of the conformations ($\mu_{I,\theta}$) are reported in Table 4.

The imines (8) and (9) exist as a mixture of *E*- and *Z*-isomers in the ratio 24 : 76, determined from n.m.r. spectra.[1i] From the values reported in Figure 2b, the set of solution in Figure 3 was obtained (dashed line). From Figures 3a and b, cos $\theta_E = -0.371$ and cos $\theta_Z = 0.782$. The $\mu_{I,\theta}$ values are reported in Table 4.*

TABLE 4

Conformational results from dipole moment analysis

Compounds	Configuration (I)	w (%)	Conformation (θ)	$\mu_{I,\theta}$/D
(5); (6); (7)	*E*	92	0°	1.84; 1.87; 2.51
(5); (6); (7)	*Z*	8	40°	1.71; 2.17; 0.76
(8); (9)	*E*	24	110°	1.91; 1.75
(8); (9)	*Z*	76	40°	1.71; 2.12

To check the approximation used, calculations have been performed for the most probable conformations following the exact scheme. The results obtained are in good agreement with those of Table 4: the new $\mu_{I,\theta}$ values are generally higher, with a mean deviation of 5%.

The calculations show that the steric interactions between the *ortho*-hydrogen atom of the phenyl ring and the *cis*-*N*-methyl group in a *Z*-isomer may be relieved by twisting of the aryl ring from the C=N–C molecular plane of *ca.* 40°. In imines (1)—(4) the exclusive preference for the nearly coplanar *E*-isomer indicates that the energy gap between this form and the twisted *Z*-isomer is high enough. In imines (5)—(7), this energy difference should be lower owing to a little destabilization of the *E*-isomer due to steric interactions between the *ortho*-hydrogen atom and the *C*-methyl group.

In the *E*-conformation of imines (8) and (9), non-bonded interactions between the *ortho*-methyl substituent and the *C*-methyl group will tend to force the aromatic ring to twist out of the imine molecular plane. This will be opposed by the conjugative stabilization of the coplanar *E*-conformation; the net result seems to be a nearly orthogonal conformation. Thus, the significant increase in the proportion of *Z*-isomer should be attributed to a remarkable decrease in the π-energy of the *E*-isomer with θ *ca.* 90°. Among possible additional factors which may lead to an inversion in stability of the *E*- and *Z*-configurations, an increase in n–π repulsive interactions for the *E*-isomer[1i] and attractive non-bonded interactions for the *Z*-isomer[14] have been suggested.

Financial support from the Italian C.N.R. is acknowledged.

[7/456 *Received*, 14*th March*, 1977]

* From pairs of μ_{π} values such as $\mu_{E,0°}$ (2) − $\mu_{E,0°}$ (1) calculation of μ_{Me} is possible. The mean value deduced from all the available cases is $\bar{\mu}_{Me} \pm$ a standard error (0.51 ± 0.03), in good agreement with the previous estimate.

[14] N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *J. Amer. Chem. Soc.*, 1973, **95**, 7559.