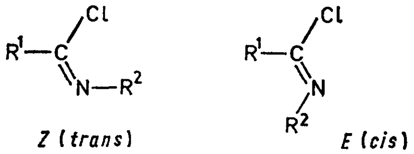
Dipole Moments and Configuration of Imidoyl Chlorides

By **A. Dondoni**, Laboratorio dei Composti del Carbonio contenenti Eteroatomi del C.N.R., Ozzano E., and Istituto di Chimica Organica e Industriale dell'Università, Bologna, Italy
O. Exner * J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Academy of Sciences, Prague 011, Czechoslovakia

The electric dipole moments of six aromatic imidoyl chlorides have been measured in benzene solution. The results allow the *Z*-configuration to be confirmed unambiguously by a graphical method, irrespective of possible variations of the bond moments used. A more exact determination of these bond moments from experimental data is not feasible, the common values hitherto used being however, quite acceptable. Hence the C=N bond may not be as highly polarizable as was expected.

CONFIGURATIONS of the C=N double bond have been determined for many classes of compound even when the two stereoisomers could not be isolated.[1–3] This is also the case with imidoyl chlorides; for example, Greenberg and Aston failed to separate isomers but were able to prove the *Z*-configuration from the dipole moment of 4-nitro-*N*-(4-nitrophenyl)benzimidoyl chloride.[2] Even though rough measurements were carried out,[2] the method of introducing *para*-substituents is so sensitive that the result is, in our opinion, dependable.



Z (*trans*) *E* (*cis*)

This paper aims to confirm the configuration of imidoyl chlorides by dipole moment measurements of standard accuracy on several derivatives (1a—c) and (2a—c) (Table 1). The results are evaluated by comparing calculated and experimental μ^2 values of *para*-substituted and unsubstituted compounds in a simple graph[4] (Figures 1—3). The main advantage of this method is the low sensitivity of the final results to small variations of bond moments used. In our case it is particularly the value of the C=N bond moment which may be influenced by polarization; this was therefore discussed.[3,5,6] Our second aim was to deduce more reliable values of bond moments (or group moment) in order to apply them subsequently to hydroxamoyl chlorides[7] where the problem of configuration is more delicate.

RESULTS AND DISCUSSION

The experimental values of polarization and dipole moments listed in the Table are in our opinion internally consistent. Only the dipole moments of compounds (1b) and (2a) which fall below 1 D are less reliable because of the uncertainties in correction for atomic polarization and in the value of molar refraction. This peculiarity of error distribution of dipole moment data has been discussed in some detail.[8]

Polarization data and dipole moments of some imidoyl chlorides in benzene at 25 °C

	Compound	R_D[a]/cm³	P_2/cm³	μ(5%)[b]/D	μ(15%)[b]/D	μ(calc.)/D	
						Z	*E*
(1a)	Ph·C(Cl)=NPh	66·2	103·7	1·29	1·16	1·19	1·95
(1b)	*p*-Cl·C_6H_4·C(Cl)=NPh	71·1	83·7	0·64	0·25	0·41	0·62
(1c)	*p*-NO_2·C_6H_4·C(Cl)=NPh	73·0	311·4	3·39	3·34	3·31	2·68
(2a)	Ph·C(Cl)=NBu^n	58·9	73·7	0·76	0·54	0·89	2·18
(2b)	*p*-Cl·C_6H_4·C(Cl)=NBu^n	63·8	92·2	1·11	0·96	0·70	0·92
(2c)	*p*-NO_2·C_6H_4·C(Cl)=NBu^n	65·8	361·3	3·74	3·78	3·61	2·60

[a] Calculated from Vogel's increments (*J. Chem. Soc.*, 1948, 1833) and the value 8·11 cm³ for the C=N group bound on a benzene ring; the latter has been derived from the experimental refraction of ethyl benzimidate.[6] [b] Correction for the atomic polarization 5 or 15% of the R_D value, respectively. The latter values were used in the discussion and graphs.

In the analysis of the data from the Table, two kinds

---

[1] C. G. McCarty in 'The Chemistry of the Carbon–Nitrogen Double Bond,' ed. S. Patai, Wiley, New York, 1970.

[2] B. Greenberg and J. G. Aston, *J. Org. Chem.*, 1960, **25**, 1894.

[3] O. Exner, *Coll. Czech. Chem. Comm.*, 1965, **30**, 652.

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

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

[6] O. Exner, V. Jehlička, and A. Reiser, *Coll. Czech. Chem. Comm.*, 1959, **24**, 3207.

[7] A. Battaglia, A. Dondoni, and O. Exner, *J.C.S. Perkin II*, following paper.

[8] O. Exner, *Chem. Listy*, 1966, **60**, 1047.

of approach are followed. In the first, the dipole moments for the *Z*- and *E*-configurations of each compound have been calculated by vector addition of bond moments. The standard values, well tried in our previous studies,[3,6] were used: $H{-}C_{al}$, 0·3 D; $H{-}C_{ar}$, 0·0 D; C=N, 1·8 D; C–N, 0·45 D; $C_{al}{-}Cl$, 1·75 D; $C_{ar}{-}Cl$, 1·60 D; for the aromatic nitro-group an enhanced moment of 4·5 D had to be used, as found for other compounds where the nitro-group and a C=N double bond are conjugated.[3,6] The bond angles used in computation were: $\angle C{-}C{=}N = \angle Cl{-}C{=}N = 125°$, $\angle C{=}N{-}C = 114°$.

The calculated moments listed in the two last columns of the Table are, on first inspection, consistent with the *Z*-configuration. This was made more evident by the graphical method[4] (Figure 1), which not only allows us to decide in favour of the *Z*-configuration, but also gives an idea about the accuracy of this decision. This result is further confirmed by the moments of *N*-butyl derivatives (2a—c) (Figure 2) and by that of 4-nitro-*N*-(4-nitrophenyl)benzimidoyl chloride, as measured by Greenberg and Aston,[2] * combined with our measurements of compound (1a) (Figure 3).

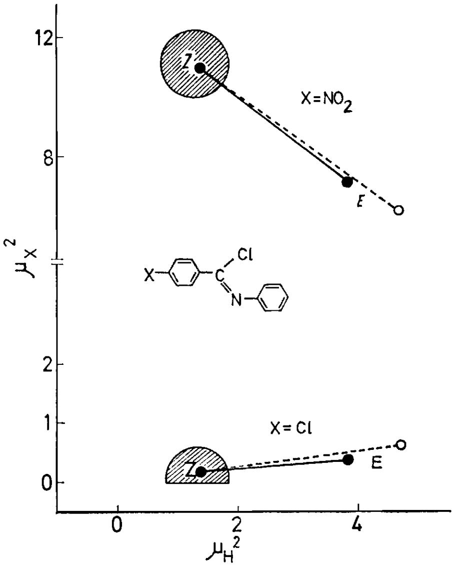


FIGURE 1 Graphical comparison of dipole moments (plotted as μ^2) of *N*-phenylbenzimidoyl chloride (1a) (*x*-axis) and its derivatives (1b) and (1c) (*y*-axis). Calculated (full and empty points) and experimental values (hatched circles) for *E*- and *Z*-configurations are shown; the lines represent various mixtures

Hence the *Z*-configuration is proved at least for chlorides of aromatic amidic acids, and probably is a general feature, since aliphatic and aromatic aldimines also possess the same configuration.[9] The stability of this form seems to be controlled by strong steric effects which disfavour the *E*-form.

The second kind of analysis of dipole-moment data deals with the determination of the moment of the whole functional group by the graphical method of van Woerden and Havinga.[10] Figure 4 shows that the analysis was not completely successful in our case since

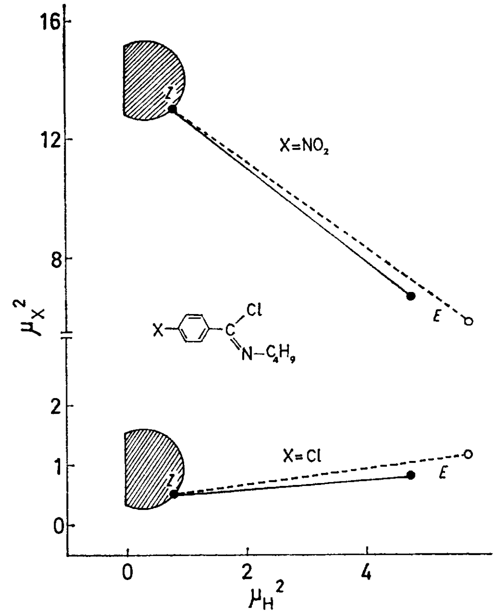


FIGURE 2 Graphical comparison of calculated and experimental dipole moments (plotted as μ^2) of *N*-butylbenzimidoyl chloride (2a) and its derivatives (2b) and (2c)

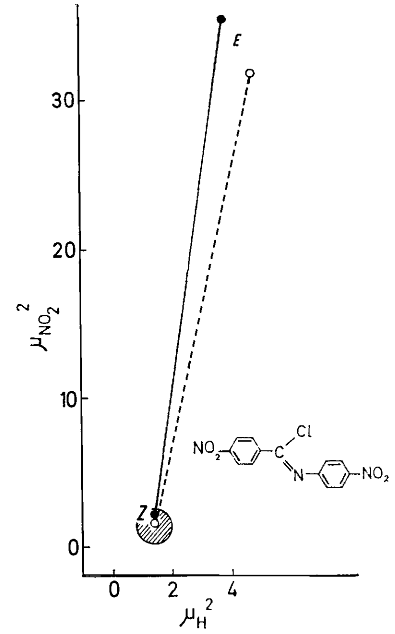


FIGURE 3 Graphical comparison of calculated and experimental dipole moments (plotted as μ^2) of *N*-phenylbenzimidoyl chloride (1a) and its 4,4′-dinitro-derivative (see ref. 2)

---

* The value of μ = 1·2 D, as given originally[2] can be corrected for atomic polarization (15% R_D) and a more reliable value of R_D = 78·6 cm^3 introduced. The resulting value is μ = 0·93. In view of the large experimental error (±0·5 D) the correction seems not to be essential.

[9] G. J. Karabatsos and S. S. Lande, *Tetrahedron*, 1968, **24**, 3907; D. Pitea, D. Grasso, and G. Favini, *J. Chem. Soc.* (*B*), 1971, 2290.

[10] H. F. van Woerden and E. Havinga, *Rec. Trav. chim.*, 1967, **24**, 3907.

the circles, drawn with radius equal to the experimental moments of the compounds,* do not intersect exactly in one point, determining the desired group moment, but in the hatched area. Consequently, a moment of *ca.* 1·1 D can be estimated for the group –C(Cl)=N–, but its direction remains uncertain within the angles +20° to –15°.

An attempt to analyse this group moment into its components is also shown in Figure 4 by drawing the standard values of bond moments in their proper directions. The comparison confirms the *Z*-configuration of the compounds studied since the *E*-configuration would require an almost opposite direction of the C–N vector.

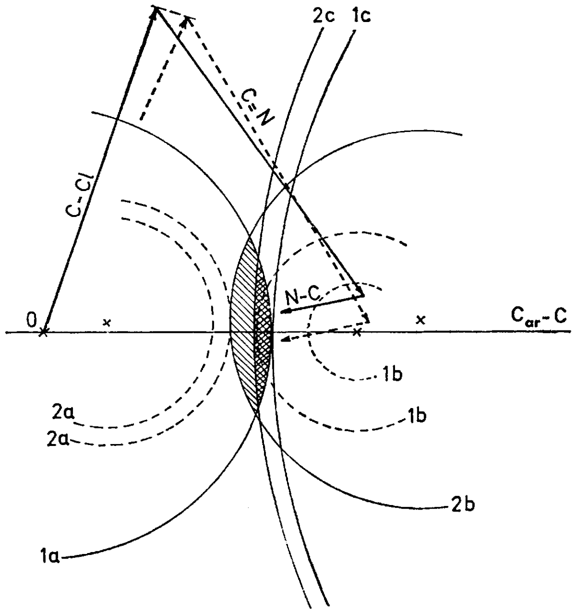


FIGURE 4 Determination of the –C(Cl)=N– group moment and its analysis into components. Broken circles correspond to low, less reliable dipole moments, and show possible limits or accuracy

In order to obtain better agreement of experiment with theory, the bond angles used were also re-examined. Since *X*-ray studies[11] have shown that bond angles are not equal in stereoisomeric oximino-compounds with substituents of unequal size, the following values were used: in *Z*-configuration, $\angle$C–C=N = 120°, $\angle$Cl–C=N = 125°; in *E*-configuration, $\angle$C–C=N = 130°, $\angle$Cl–C=N = 115°. Moments computed with these values are plotted in Figures 1—3 (empty points, broken lines). They differ significantly only for the *E*-configuration so that they cannot be directly proved or disproved by experiment. This example shows nicely the relative insensitivity of this graphical method to small variations of parameters. Figure 4 shows the corresponding vectors by broken lines for the *Z*-configuration only. The change of bond angles has a greater influence in this case than in Figures 1—3, but a definite experimental decision is not possible, either, from this graph.

In general the accuracy attained does not allow us to compute more precise values for any bond involved. Particularly, the proper moment of the C=N bond has been discussed for several classes of compound,[3,5,6] and the value of 1·8 D was finally preferred. On the basis of a few data on hydroxamoyl chlorides, it was suggested[3] that this bond is relatively highly polarizable and its effective moment can be lowered in the neighbourhood of a C–Cl bond to 1·4 D. The evidence presented here suggests that the C=N bond moment can be given a constant value (1·8 D) with the same standard accuracy and range of validity as for other bonds. Hence its polarizability might have been somewhat overestimated.

EXPERIMENTAL

Materials.—The starting benzanilides and *N*-butylbenzamides were prepared by the Shotten–Baumann procedure.[12] Their m.p.s (uncorr.) agreed with literature data.[12-14]

Benzimidoyl chlorides (1a) and (2a) were prepared by refluxing the respective benzamides with excess of thionyl chloride,[15,16] whereas (1b, c) and (2b, c) were prepared by the phosphorus pentachloride procedure.[16,17] The products were purified by fractional vacuum distillation except for (1c) which was crystallized from benzene–light petroleum. All the products, even when not specified, gave satisfactory elemental analyses. Yields were *ca.* 70%. *N*-Phenylbenzimidoyl chloride (1a) had m.p. 38—39 °C, b.p. 139—140 °C/0·8 mmHg (lit.,[15] m.p. 40 °C, b.p. 174—176 °C/12 mmHg); *N*-phenyl-*p*-chlorobenzimidoyl chloride (1b) had m.p. 68—69 °C, b.p. 154—155 °C/0·3 mmHg (lit.,[18] m.p. 66—67 °C); *N*-phenyl-*p*-nitrobenzimidoyl chloride (1c) had m.p. 119—120 °C (lit.,[16] 137—138 °C) (Found: C, 60·0; H, 3·6; Cl, 13·5; N, 10·6. Calc. for $C_{13}H_9ClN_2O_2$: C, 59·9; H, 3·5; Cl, 13·6; N, 10·7%); *N*-butylbenzimidoyl chloride (2a) had b.p. 77—79 °C/0·5 mmHg (lit.,[16] b.p. 85—86 °C/1 mmHg); *N*-butyl-*p*-chlorobenzimidoyl chloride (2b) had b.p. 92—93 °C/0·3 mmHg (lit.,[14] 135—136 °C/3 mmHg); N-*butyl*-p-*nitrobenzimidoyl chloride* (2c) had b.p. 146—147 °C/0·5 mmHg (Found: C, 54·8; H, 5·39; Cl, 14·9; N, 11·3. $C_{11}H_{13}ClN_2O_2$ requires C, 54·9; H, 5·44; Cl, 14·7; N, 11·6%).

The n.m.r. spectra (in $[^2H_6]$acetone with Me_4Si as internal standard) were consistent with the structures of all the

---

* The centres of the circles (crosses in Figure 4) were obtained by plotting the substituent moments from the origin of coordinates O in proper directions but in the opposite sense. The correction, accounting for the moment of the n-butyl group in order to allow the comparison of butyl derivatives (2a—c) with phenyl derivatives (1a—c), was unimportant when the *Z*-configuration was assumed.

[11] K. Folting, W. N. Lipscomb, and B. Jerslev, *Acta Cryst.*, 1964, **17**, 1263; G. K. Jensen, *Acta Chem. Scand.*, 1970, **24**, 3293; K. A. Kerr, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.* (*B*), 1967, 1305.

[12] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1961, p. 582.

[13] G. H. Coleman and H. P. Howells, *J. Amer. Chem. Soc.*, 1923, **45**, 3088.

[14] Fr.P. M2868/1964 (*Chem. Abs.*, 1965, **62**, 9072c).

[15] J. v. Braun and W. Pinkernelle, *Ber.*, 1934, **67**, 1218.

[16] I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, 1962, **95**, 126, and references therein.

[17] A. J. Hill and M. V. Cox, *J. Amer. Chem. Soc.*, 1926, **48**, 3214.

[18] G. H. Coleman and R. E. Pyle, *J. Amer. Chem. Soc.*, 1946, **68**, 2007.

compounds: (1) showed the resonance in the τ 1·80—3·00 region (ArH), (2) in addition, showed multiplets at τ 6·25 (NCH_2), τ 8·40 (CH_2–CH_2), and at τ 1·0 (CH_3).

Physical Measurements.—Dielectric constants and densities were determined at 25 °C, usually on five solutions in the concentration range 0·005—0·05M. A heterodyne apparatus with frequency 1·2 MHz was used. Results were evaluated according to Halverstadt and Kumler.[19]

The theoretical dipole moments of individual configurations were determined graphically with an accuracy of ±0·03 D.

Dielectric constants and densities were measured by Mrs. M. Kuthanovà, Department of Physical Chemistry, Institute of Chemical Technology, Prague, under the supervision of Dr. V. Jehlička; their aid is gratefully acknowledged.

[2/831 *Received*, 13*th April*, 1972]

---

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