Acyl Derivatives of Hydroxylamine. Part XVII.[1] Dipole Moments, Configuration, and Conformation of Benzohydroxamoyl Chlorides

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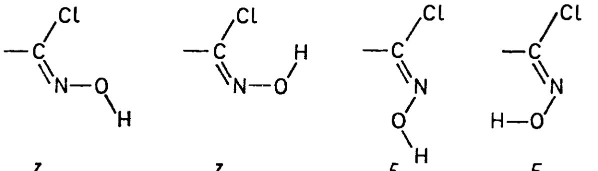
The dipole-moment data of eleven aromatic hydroxamoyl chlorides, measured in benzene, have been analysed in terms of the configuration of the C=N bond and conformation on the N–O bond. The total group moment of the –C(Cl)=NOH grouping amounts to 1·65 D and lies at the angle of 49° to the C_{ar}–C bond. Although the reasoning is more complex and agreement of computed and experimental values somewhat worse than in similar cases, it is concluded that the most probable form is E_{ap} (*anti*-periplanar). Hence the stable configuration is different from that of oximes and seems to be controlled by other factors than purely steric ones.

Configuration of the C=N double bond of the oximino-group is a classical stereochemical problem, definitely settled in the case of oximes and alkyl hydroximates.[1] Other types of hydroximic acid derivative were isolated only in one form whose configuration was deduced with more or less reliability.[2,3] The isolation of stereoisomeric hydroxamoyl chlorides claimed in one case[4] has not been confirmed since; from the two stereoisomeric aldoximes only one hydroxamoyl chloride of undefined configuration is always produced. On the basis of dipole-moment measurements on two compounds we preferred the *E*-configuration,[3] whereas Barassin, Armand, and Lumbroso deduced[5] the *Z*-configuration by comparing the dipole moments of hydroxamoyl chlorides with those of *syn*- and *anti*-benzaldoximes and with that of a rigid model molecule, as well as by n.m.r. spectroscopic data.

The aim of this paper is to provide more extensive dipole-moment data, and to draw conclusions from this single experimental approach. The problem is more complicated than, for example, the case of imidoyl chlorides,[6] since in addition to the configuration on the C=N bond (*E* or *Z*), we have to determine the conformation on the N–O bond. Even when planar forms only, *viz. syn*-periplanar (sp) or *anti*-periplanar (ap), are considered,[3,5] four possibilities have to be examined: Z_{ap}, Z_{sp}, E_{ap}, and E_{sp}. From these only the last one (E_{sp}) can be rejected *a priori* for steric reasons.



Z_{ap} (*syn*,*trans*[5]) Z_{sp} (*syn*,*cis*[5]) E_{ap} (*anti*,*trans*[5]) E_{sp} (*anti*,*cis*[5])

An additional complication arises from the uncertainty of the N–O and C=N bond moments, whose values can be affected by polarization induced by the other bonds.[3,7] The preceding study[6] has revealed that the C=N bond moment is not so variable as was expected, but the uncertainty of the N–O bond moment remains.

Results and Discussion

The dipole moments of benzohydroxamoyl chlorides (1)—(11) are shown in the Table; the polarization data are also included. The accuracy of dipole moments can be estimated as ±0·05 D in addition to the uncertainty due to correction for atomic polarization which is represented by the differences between the last two columns. The results of the Table are internally consistent (see

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[1] Part XVI, I. K. Larsen and O. Exner, *Chem. Comm.*, 1970, 254.

[2] (*a*) Part XV, D. Šnobl and O. Exner, *Coll. Czech. Chem. Comm.*, 1969, **34**, 3325; (*b*) O. Exner, M. H. Benn, and F. Willis, *Canad. J. Chem.*, 1968, **46**, 1873.

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

[4] A. Werner, *Ber.*, 1892, **25**, 27; A. Werner and H. Buss, *ibid.*, 1894, **27**, 2193.

[5] J. Barassin, J. Armand, and H. Lumbroso, *Bull. Soc. chim. France*, 1969, 3409.

[6] A. Dondoni and O. Exner, *J.C.S. Perkin II*, preceding paper.

[7] H. Lumbroso and G. Pifferi, *Bull. Soc. chim. France*, 1969, 3401; H. Lumbroso, D. M. Bertin, and G. P. Cum, *Compt. rend.*, 1969, **269**, 5.

TABLE

Polarization data and dipole moments of benzohydroxamoyl chlorides [X–Ar–C(Cl)=NOH] (1)—(11) in benzene at 25 °C

	X	R_D[a]/cm^3	P_2/cm^3	μ(5%)[b]/D	μ(15%)[b]/D
(1)	H	41·1	94·4	1·58[c]	1·52[c]
(2)	4-Me	45·9	152·6	2·26	2·21
(3)	2-Cl	46·0	184·4	2·58	2·54
(4)	3-Cl	46·0	117·8	1·84	1·78
(5)	4-Cl	46·0	97·4	1·55[d]	1·48
(6)	2,4-Cl$_2$	50·9	106·6	1·61	1·54
(7)	2-Br	48·9	153·7	2·24	2·18
(8)	2-NO$_2$	47·9	383·1	4·04	4·00
(9)	3-NO$_2$	47·9	343·8	3·79	3·76
(10)	4-NO$_2$	47·9	307·4	3·55[e]	3·51[e]
(11)	4-OMe	48·1	169·4	2·41	2·36

[a] Calculated from Vogel's increments (*J. Chem. Soc.*, 1948, 1833) and the value of 9·91 cm^3 for the C=NOH-group, including conjugation (see ref. 3). [b] Correction for the atomic polarization 5 or 15% of the R_D value, respectively; the latter values were used in discussion and graphs. [c] Our previous [3] values were 1·63 D (5%) and 1·57 D (15%) while ref. 5 reports 1·87 D in dioxan. [d] Ref. 5 gives 1·92 D in dioxan. [e] These values were confirmed by repeated experiments and are preferred to 4·08 and 4·05 D respectively, previously reported.[3]

below) and agree reasonably with previous determinations,[3,5] except for compound (10) to which was formerly attributed [3] a higher dipole moment.

The results were first interpreted by the graphical method of comparison of dipole moments of the parent compound with those of *para*-substituted derivatives.[8] Expected dipole moments were computed for the forms Z_{ap}, Z_{sp}, E_{ap}, and E_{sp} of compounds (1), (2), (5), and (10); the common bond moments, verified in the preceding study,[6] and in addition, the values 1·51 D for the H–O bond and 0·3 D for the N–O bond were used; [2,3] the bond angles employed were the same as previously: [6] $\angle$C–C=N = $\angle$Cl–C=N = 125°, $\angle$C=N–O = 114°, $\angle$N–O–H = 105°. In Figure 1 each 'calculated' form is represented by a full point and the tie-line connecting two points of the same configuration can correspond either to mixtures of both forms or, more probably in this case, to non-planar conformations arising from rotation around the N–O bond. Since such a rotation cannot be excluded *a priori*, we should consider it as a proof of a certain configuration when the experimental values (hatched circles) are situated on one of these lines. Figure 1 reveals that the resulting moment is much more sensitive to the conformation of the N–O bond than to the configuration of C=N. While the forms E_{sp} and Z_{sp} are safely disproved, a decision between the forms E_{ap} and Z_{ap}, both not strictly planar, cannot be made reliably.

Since the imperfect agreement between theory and experiment can also be due to incorrect values of bond moments or angles used in calculation, the approach of the preceding paper [6] was followed. In Figure 2, circles (not shown) have been drawn with radius equal to the experimental moments of (1), (2), (4), (5), (9), (10), and (11) from appropriate centres, obtained by plotting the substituent moments from the origin of co-ordinates O in the opposite sense.* All the circles should intersect in one point determining the moment of the –C(Cl)=NOH group. In the present case, however, the intersection is not sharply defined by a point but rather spread out in a small area (shaded in Figure 2) so that only a 'mean' group moment of 1·65 D with the angle of 49° to the C$_{ar}$–C bond can be deduced. Although the sign of this angle remains undetermined, the agreement is satisfactory with the values of 1·87 D and 69° derived by

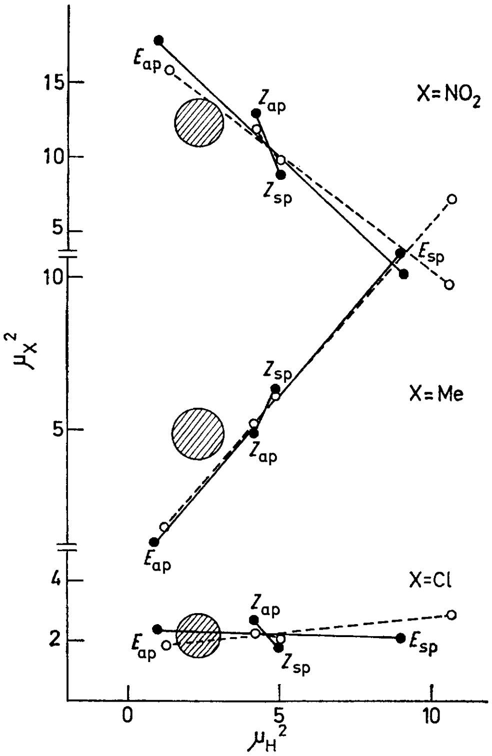

FIGURE 1 Graphical comparison of dipole moments (plotted as μ^2) of benzohydroxamoyl chloride (1) (*x*-axis) and its *para*-derivatives (2), (5), and (10) (*y*-axis). Calculated (full and empty points) and experimental values (hatched circles) for various conformations are shown

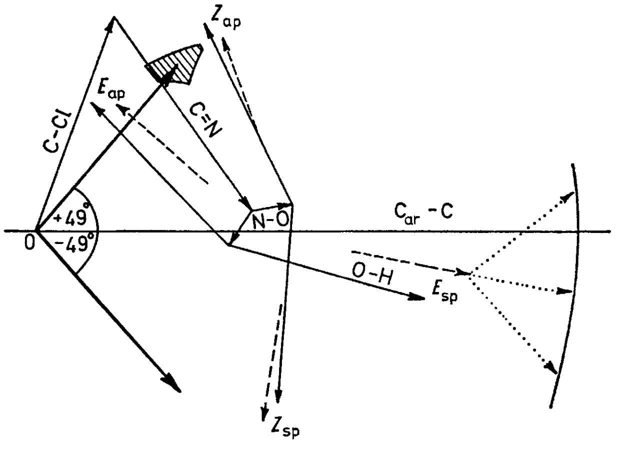

FIGURE 2 Determination of the –C(Cl)=NOH group moment (heavy arrows) and its analysis into components (light and broken arrows)

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* It was assumed that the two possible positions of the substituent are equally represented in the unsymmetrical compounds (4), (9), and (11).

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

Lumbroso and his associates from measurements in dioxan.[5,9]

In Figure 2 the components of the group moment are also shown in their proper directions for the four forms Z_{ap}, Z_{sp}, E_{ap}, and E_{sp}. Since no one of the end points coincides exactly with the end point of the group moment in one of the two possible directions, the values of bond moments and angles were reconsidered. While the C=N moment was re-examined in the preceding paper [6] and previous estimates [3,7] confirmed, the N–O moment was given [7] a much larger value than ours. However, Figure 2 shows that no change of any of these bond moments improves the agreement with experiment; enhancement of the N–O moment makes the situation even worse. Moreover, as in the preceding paper,[6] the values of bond angles obtained from recent *X*-ray studies were used, *viz.*, ∠C–C=N = 130°, ∠Cl–C=N = 115° for the *E*-configuration, and ∠C–C=N = 120°, ∠Cl–C=N = 125° for the *Z*-configuration (broken arrows in Figure 2 and broken lines in Figure 1). Also in this case there is no essential improvement and neither is a clear decision achieved; however, the probability is shifted in favour of the E_{ap} form.

Finally the analysis of the data was checked by considering 4-chloro-1*H*-2,3-benzoxazine, which represents a rigid model of the E_{sp} form. In Figure 2 the calculated dipole moment of this compound is approximately represented by the point denoted E_{sp}. However, the experimental value [7] of 4·01 D is too high.* It may be suggested that the enhancement of the moment, as expressed by any of the dotted arrows, arises from an additional effect of unknown nature. Formally this could be accounted for by enhancing the C–Cl moment, but such a tendency was not detected [6] in structurally similar imidoyl chlorides. If we assume that a similar additional effect is operating in open-chain hydroxamoyl chlorides and the appropriate vector is included in the calculation, the only possible form is E_{ap}. Moreover, it follows that the more probable position of the –C(Cl)=NOH group moment is that at the angle +49° to the C_{ar}–C bond, *i.e.*, approximately in the direction of the C–Cl bond. Lumbroso and his associates assumed [9] it to lie in the mirror position and suggested the *Z*-configuration without deciding the conformation on the N–O bond.[5,9] Figure 2 reveals that in this case the only possibility is the Z_{sp} form which by contrast is in poor agreement with experiment according to Figure 1.

An additional argument can be forwarded in the behaviour of *ortho*-derivatives (3), (6), (7), and (8). These compounds can possess either a non-planar conformation with the phenyl ring almost perpendicular to the Cl–C=N plane, or a planar conformation in which a less hindered position of the *ortho*-group would be preferred, *viz.*, on the side of N in Z_{ap} or Z_{sp}, and on the side of Cl in E_{ap} or E_{sp} forms.

We have calculated the expected dipole moments for all the eight possibilities † (four forms, Z_{ap}, Z_{sp}, E_{ap}, and E_{sp}, each either planar or non-planar) and compared them with the experimental values in a graphical representation (Figure 3) similar to Figure 1. When only non-planar conformations are considered, the analysis is clearly in favour of the E_{ap} form in which the OH-group may lie somewhat outside the Cl–C=N plane. This result is in agreement with that from Figure 1. When, however, planar conformations are admitted as well, the Z_{ap} form could be the second possibility, the Z_{sp} being excluded in any case.

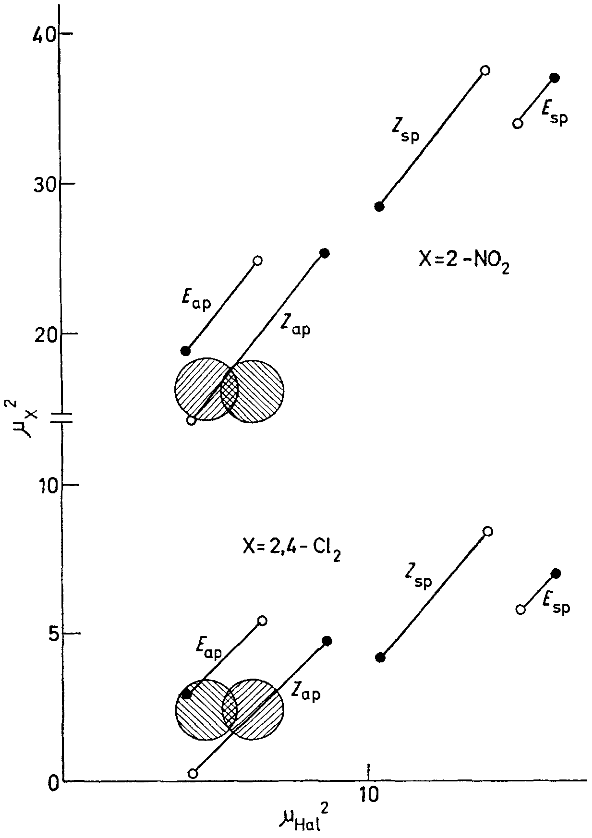

FIGURE 3 Graphical comparison of dipole moments (plotted as μ^2) of *ortho*-substituted benzohydroxamoyl chlorides (3), (7) (*x*-axis) and (6), (8) (*y*-axis). Experimental (hatched circles) and calculated values for various conformations with a coplanar (○) or perpendicular (●) position of the phenyl ring, are shown

We conclude that the form E_{ap} is, with a high probability, the correct one for hydroxamoyl chlorides; at least it is in agreement with the evidence from the method of dipole moments alone. We are aware that the argument was more sophisticated and the agreement with experiment somewhat worse than in similar

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* The conclusion is not affected by a small impurity in the sample examined,[7] nor by differences of bond angles in cyclic and open-chain compounds. On the contrary the effect must be even larger owing to the difference between H–O and C–O moments.

† For the NO_2-group in the *ortho*-position, the normal value of 4·0 D was used but, according to Figure 3, this is still somewhat high. The calculated values for compound (3; X = 2-Cl) and (7; X = 2-Br) are practically identical, but the experimental values differ from one another (hatched circles in Figure 3).

[9] C. Pigenet, J. Armand, and H. Lumbroso, *Bull. Soc. chim. France*, 1970, 2124.

cases,[2,3,6,8] hence a confirmation by a different experimental method would still be desirable. Recently we have studied[10] the e.s.r. spectra of iminoxyl radicals derived from the hydroxamoyl chlorides reported here and have found that they are consistent with the configuration in which the aromatic ring is *cis* to the iminoxy-oxygen. This may support the *E*-configuration of the hydroxamoyl chlorides as deduced from the dipole-moment data, if it is admitted that the geometry of the precursors is retained in the radicals. This has in fact been observed for other oximino-compounds.[11]

The *E*-configuration of hydroxamoyl chlorides would confirm the statement that different oximino-compounds can be more stable in different configurations on the C=N bond.[2b] The factors controlling this stability are not yet well understood but are certainly not only of steric character; it seems that electron-attracting groups X in –CX=NOH force the hydroxy-group into the corresponding *trans*-position.

EXPERIMENTAL

Materials.—Benzohydroxamoyl chlorides (1)—(11) were obtained by chlorination[12,13] of the appropriate oximes (5 g) (prepared by the hydroxylamine hydrochloride–sodium hydroxide method[14]) with three equivalents of nitrosyl chloride in anhydrous ethyl ether (50—60 ml). After being allowed to stand in an ice–water bath for 10 min with occasional shaking, the reaction mixture was left at room temperature until the green colour and the white precipitate disappeared (1—24 h). The excess of nitrosyl chloride and ether were evaporated at room temperature and the product crystallized from a suitable solvent. When an oily residue was obtained, it was first treated with light petroleum. The i.r. spectra (*sym*-C_2Cl_4–CS_2) of all hydroxamoyl chlorides showed absorption at 3580, *ca.* 3350br (OH), and 1620 (C=N) cm^{-1}. Benzohydroxamoyl chloride (1) had m.p. 51—52 °C (from ligroin) (lit.,[12] 49—50 °C); *p*-toluohydroxamoyl chloride (2) had m.p. 71·5—72·5 °C (from ligroin) (lit.,[12] 69—70 °C); *o*-chlorobenzohydroxamoyl chloride (3) had m.p. 57—58 °C (from ligroin) (lit.,[12] 56 °C); *m*-chlorobenzohydroxamoyl chloride (4) had m.p. 72—73 °C (from ligroin) (lit.,[15] 75—80 °C); *p*-chlorobenzohydroxamoyl chloride (5) had m.p. 88·5—89·5 °C (from benzene–light petroleum) (lit.,[15] 82—86 °C); 2,4-dichlorobenzohydroxamoyl chloride (6) had m.p. 98—99 °C (from benzene–light petroleum) (lit.,[15] 100—105 °C); o-*bromobenzohydroxamoyl chloride* (7) had m.p. 67—68 °C (from ligroin) (Found: C, 36·0; H, 2·1; N, 5·7. $C_7H_5BrClNO$ requires C, 35·9; H, 2·15; N, 6·0%); *o*-nitrobenzohydroxamoyl chloride (8) had m.p. 100—101 °C (from benzene–light petroleum) (lit.,[12] 99—100 °C); *m*-nitrobenzohydroxamoyl chloride (9) had m.p. 100—102 °C (from carbon tetrachloride) (lit.,[12] 99·5—100 °C); *p*-nitrobenzohydroxamoyl chloride (10) had m.p. 124—125 °C (from carbon tetrachloride) (lit.,[12] 123·5—124 °C); *p*-anisohydroxamoyl chloride (11) had m.p. 87·5—88·5 °C (from ligroin) (lit.,[13] 88—89 °C).

Physical Measurements.—The same methods were used as previously.[6] Dielectric constants and densities were measured by Mrs. Kuthanovà under the supervision of Dr. V. Jehlička; their aid is gratefully acknowledged.

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