

CONFIGURATION AND CONFORMATION OF HYDROXIMOYL CHLORIDES AND THEIR DERIVATIVES. O-BENZOYLBENZHYDROXIMOYL CHLORIDES

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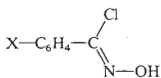
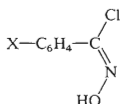
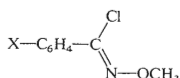
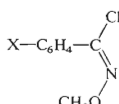
The dipole moments of O-benzoylbenzhydroximoyl chloride (*IIIa*) and its chloro derivatives *IIIb*–*IIIc* have been measured in benzene solution and interpreted by the *Z* configuration on the C=N double bond and *ap* conformation on the N—O bond (formula *A*). The comparison of the UV, NMR and IR spectra of compounds *III* with those of (*E*)-O-benzoylbenzaldoximes (*IV*) brings further evidence in favor of the *Z* configuration. A more detailed analysis of the dipole moments of compounds *III* does not show any special features which may be valuable for gaining more insight on the dipole moment analysis of the parent hydroximoyl chlorides *I*.

The configuration on the C=N double bond of imino compounds and its assignment particularly from dipole moment data, have been recently reviewed by one of us^{1,2}. A case which is still unresolved is that of aromatic hydroximoyl chlorides *I*. In fact, while the *Z* configuration of 4-nitrobenzhydroximoyl chloride (*Ib*) has been recently established in the solid state by X-ray diffractometry³, the configuration in solution deduced from dipole moment studies for compounds *I* in general, is still controversial^{4–8}. The main difficulty of the dipole moment analysis arose from the uncertainty of the conformation on the N—O bond which affects the values of the calculated dipole moments to a larger extent than the configuration on the C=N bond. Also spectroscopic studies of *I* by NMR (ref.⁵) or of their radicals by ESR (ref.⁹), lead to opposite conclusions.

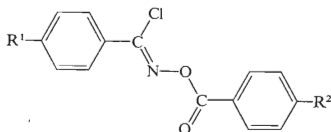
Although for hydroximoyl chlorides *I* only one of the two possible stereoisomers has been isolated¹, one cannot exclude the existence of an equilibrium in solution or a change of configuration from solution to solid state as assumed for other imino compounds¹⁰. A similar discrepancy has recently emerged for O-methylbenzhydroxi-

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moyl chlorides (*II*) which, however, exist as two isomers in solution as well as in the solid state¹¹. The X-ray study¹² of one of the two isomers of O-methyl-4-nitrobenzhydroximoyl chloride (*IIa*) has revealed the *Z* configuration which is, also in this case, the reverse to that assigned in solution from dipole moment studies¹¹.

*I Z**a*; X = H*b*; X = 4NO₂*I E**II Z**II E*

In these circumstances we feel that a fundamental reinvestigation of the subject, possibly by several approaches, is necessary. One of these may be the study of some derivatives of hydroximoyl chlorides whose configuration, established with good reliability, might serve later as model for other compounds. The present paper deals with the stereochemistry of O-benzoylbenzhydroximoyl chlorides (*III*) where the focal point concerning the conformation of the N—O bond is greatly facilitated by the possibility of introducing substituents in the two phenyl rings. Another advantage is the absence of the free hydroxyl group, this preventing intermolecular interactions in solution.

*IIIa*; R¹ = R² = H*IIIb*; R¹ = Cl, R² = H*IIIc*; R¹ = H, R² = Cl*IIId*; R¹ = R² = Cl

EXPERIMENTAL AND RESULTS

Materials

Melting points determined on a Kofler block and not corrected.

O-Benzoylbenzhydroximoyl chloride¹³ (*IIIa*), m.p. 107–108°C (literature¹³, 109°C).

O-Benzoyl-4-chlorobenzhydroximoyl chloride (IIIb): To a solution of 4-chlorobenzhydroximoyl chloride⁷ (0.02 mol) and benzoyl chloride (0.04 mol) in benzene (50 ml), 15 ml of pyridine was added dropwise under cooling. The mixture was allowed to stand for one hour, poured into ice water and the product filtered, yield 65%, m.p. 83–84°C (ethanol); for $C_{14}H_9Cl_2NO_2$ (294.1) calculated: 57.16% C, 3.08% H, 4.76% N; found 57.18% C, 3.04% H, 4.69% N. IR spectrum in KBr disc (cm^{-1}): 457, 488, 594, 614, 620, 688, 706, 733, 800, (826), 835, (855), 867, 920, 984, 1016, 1029, 1061, 1080, 1098, 1178, 1238, 1262, 1283, 1402, 1452, 1491, 1564, 1590, 1760, 3075, 3100; ¹H-NMR spectrum in $CDCl_3$ (δ): 7.35–7.65 (m, 3 H), 7.43 (d, 2 H, $J = 8.5$ Hz), 7.99 (d, 2 H, $J = 8.5$ Hz), 8.18 (m, 2 H); UV spectrum in ethanol (λ nm, log ϵ): 214 inf. (4.32), 267 (4.51).

O-(4-Chlorobenzoyl)benzhydroximoyl chloride (IIIc) was prepared in the same way as above, yield 67%, m.p. 114–115°C (ethanol); for $C_{14}H_9Cl_2NO_2$ (294.1) calculated: 57.16% C, 3.08% H, 4.76% N; found: 57.15% C, 3.10% H, 4.73% N; IR spectrum in KBr disc (cm^{-1}): 463, 481, 528, 603, 614, 681, 691, 737, 750, 767, 846, 868, 916, 928, 977, 982, 1012, 1031, 1071, 1092, 1114, 1178, (1238), 1252, 1269, 1287, 1314, 1367, 1402, 1446, 1488, 1568, 1591, 1756, 3067, 3100; ¹H-NMR spectrum in $CDCl_3$ (δ): 7.45–7.60 (m, 3 H), 7.50 (d, 2 H, $J = 8.5$ Hz), 8.06 (m, 2 H), 8.15 (d, 2 H, $J = 8$ Hz); UV spectrum in ethanol λ 263 nm, log ϵ 4.54.

O-(4-Chlorobenzoyl)-4-chlorobenzhydroximoyl chloride (IIIId) was prepared in the same way, yield 65%, m.p. 150–151°C (ethanol) literature¹⁴ m.p. 147–148°C; ¹H-NMR spectrum in $CDCl_3$ (δ): 7.45 (d, 2 H, $J = 9$ Hz), 7.50 (d, 2 H, $J = 9$ Hz), 8.01 (d, 2 H, $J = 8.5$ Hz), 8.14 (d, 2 H, $J = 8.5$ Hz).

O-Benzoyl-4-chlorobenzaldoxime (IVb) was prepared previously¹⁵, m.p. 145°C; IR spectrum in KBr disc (cm^{-1}): 428, 482, 516, 683, 702, (797), 820, 834, 878, 938, 983, 1016, 1031, 1066, 1087, 1186, 1216, 1258, 1286, 1316, 1350, 1406, 1450, 1494, 1597, 1604, 1747, 3035, 3065, 3097; ¹H-NMR spectrum in $CDCl_3$ (δ): 7.38–7.58 (m, 3 H), 7.43 (d, 2 H, $J = 9$ Hz), 7.76 (d, 2 H, $J = 8.5$ Hz), 8.12 (m, 2 H), 8.52 (s, 1 H); UV spectrum in ethanol (λ nm, log ϵ): 214 (4.40), 220 inf. (4.34), 267 (4.59), 288 inf. (4.22), 295 (3.87).

*O-(4-Chlorobenzoyl)benzaldoxime*¹⁵ (IVc), m.p. 116°C; IR spectrum in KBr disc (cm^{-1}): 462, 482, 493, 514, 536, 628, 648, 679, 695, 730, 749, 760, 834, 846, 876, 925, 989, 1018, 1074, 1080, 1094, 1174, 1217, 1259, 1297, 1322, 1343, 1359, 1401, 1448, 1490, 1576, 1593, 1614, 1746, 3020, 3060, 3070, 3085; ¹H-NMR spectrum in $CDCl_3$ (δ): 7.42–7.56 (m, 3 H), 7.48 (d, 2 H, $J = 8$ Hz), 7.82 (m, 2 H), 8.09 (d, 2 H, $J = 8$ Hz) 8.56 (s, 1 H); UV spectrum in ethanol: λ 263 nm, log ϵ 4.57.

Physical Measurements

Dielectric constants and densities of benzene solutions were determined at 25°C, usually at five concentrations within the range 0.005–0.05M. A heterodyne apparatus with frequency 1.2 MHz was used. The dipole moments were evaluated according to Halverstadt and Kumler¹⁶. The molar refractions were calculated from Vogel's increments¹⁷ valid for 20°C and from the exaltations of 0.5 and 0.7 cm^3 for the conjugation $Ar-C=N$ and $Ar-C=O$, respectively. Correction for the atomic polarization, 5 or 15% of the R_D value, was applied. The results are listed in Table I.

The IR spectra were measured on a Zeiss UR 20 spectrometer, the ¹H-NMR spectra on a VARIAN HA-100 spectrometer with tetramethylsilane as internal standard, the UV spectra were measured on a Jasco spectrometer model ORD/UV-5 at the concentrations 10^{-5} – 10^{-3} M.

Calculations: The dipole moments expected for the conformations A–D were calculated using the same bond moments as previously^{7,15,18}: $H-C_{ar}$ 0 D, $C=N$ 1.8 D, $C_{ar}-Cl$ 1.75 D, $N=O$

0.3 D, $C_{ar}-Cl$ 1.6 D; in addition $C=O$ 2.5 D, $C-O$ 0.74 D and a mesomeric moment of 0.25 D for the conjugation $Ar-C=O$. The bond angles used previously⁷ were partly replaced by new crystallographic values³: $\angle C_{ar}-C_{a1}-Cl$ 118°, $C-C=N$ 122°, $C=N-O$ 115°, but the changes are not important; the remaining angles were $N-O-C$ 113°, $O-C_{a1}-C_{ar}$ 111°, $O=C-C$ 125°.

TABLE I

Polarization Data and Dipole Moments of O-Benzoylbenzhydroximoyl Chloride and its Derivatives (benzene, 25°C)

Compound Substituent	<i>IIIa</i> H	<i>IIIb</i> 4-Cl	<i>IIIc</i> 4'-Cl	<i>IIId</i> 4,4'-Cl ₂
α^a	2.12	2.92	2.62	1.42
β^a	-0.365	-0.360	-0.402	-0.439
P_2^0, cm^3	163.8	231.0	204.4	150.0
R_D^b, cm^3	70.6	75.5	75.5	80.4
μ (5%) ^c , D	2.09	2.72	2.47	1.79
μ (15%) ^c , D	2.00	2.65	2.40	1.68
μ calc.	$\left\{ \begin{array}{l} C-Cl \\ 1.75^d \\ C-Cl \end{array} \right.$	$\left\{ \begin{array}{l} 1.71 \\ 2.01 \end{array} \right.$	$\left\{ \begin{array}{l} 2.43 \\ 2.48 \end{array} \right.$	$\left\{ \begin{array}{l} 1.41 \\ 1.71 \end{array} \right.$
	$\left\{ \begin{array}{l} 1.75^d \\ C-Cl \end{array} \right.$	$\left\{ \begin{array}{l} 1.98 \\ 2.40 \end{array} \right.$	$\left\{ \begin{array}{l} 2.48 \\ 2.48 \end{array} \right.$	$\left\{ \begin{array}{l} 1.71 \\ 1.71 \end{array} \right.$
	$\left\{ \begin{array}{l} 1.4^d \\ C-Cl \end{array} \right.$	$\left\{ \begin{array}{l} 1.98 \\ 2.40 \end{array} \right.$	$\left\{ \begin{array}{l} 2.48 \\ 2.48 \end{array} \right.$	$\left\{ \begin{array}{l} 1.71 \\ 1.71 \end{array} \right.$

^a Slopes of the Halverstadt-Kumler plots¹⁶, ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively; ^b calculated from increments¹⁷ as given in the experimental section; ^c correction for the atomic polarization 5%, or 15% of the R_D value, respectively; ^d calculated for the configuration *Z* and conformation *ap* (*A*) with the $C_\alpha-Cl$ bond moment of 1.75 or 1.4 D, respectively.

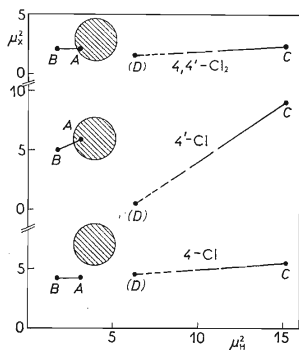


FIG. 1

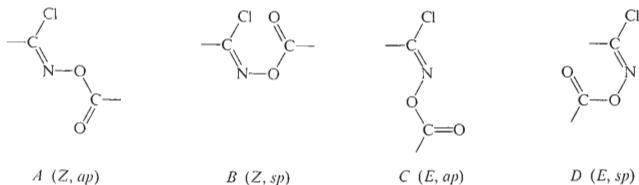
Graphical Comparison of Squared Dipole Moments of O-Benzoylbenzhydroximoyl Chloride *IIIa* (*x*-axis) and Its Derivatives *IIIb*–*IIId* (*y*-axis)

Calculated values for the conformation *A*–*D* (full points) and experimental values (hatched circles) are shown.

The calculated dipole moments are partly listed in Table I, the remaining ones are only plotted in Fig. 1.

DISCUSSION

Similarly as for the parent hydroximoyl chlorides⁷ we have to consider for our compounds four planar forms *A–D*, differing in the configuration on the C=N double bond on the one hand and in the conformation on the bond N–O on the other hand. The partial double bond character of the latter is well established on many examples²; in all cases it was sufficient to force planarity. The *Z* conformation on the C–O bond of esters and similar derivatives is so general and so rigid² that other conformations need not be considered. From the four conformations, *D* is virtually impossible to be planar, even if the upper benzene nucleus were twisted from the Cl–C–N plane.



Standard graphical method¹⁹ was employed for the comparison of calculated and experimental dipole moments (Fig. 1). Although the agreement is not perfect, the *Z* form *A* can be preferred with good reliability. Even though the form *B* can be a possible alternative to *A* if very large errors in calculations and experiments are assumed, the *Z* configuration on C=N bond appears to be well established since the form *C* is excluded in any case.

Due to the systematic substitution another simple proof of the configuration is possible, without resorting to the bond moments within the functional group. From the experimental dipole moments of *IIIa* and *IIIb* their directions can be determined by solving the triangle ABC (Fig. 2), the same for *IIIc* and *IIId* (the triangle ABD). Since there are two solutions in each case, one of the four vectors $D_1 - C_1$, $D_2 - C_2$, $D_2 - C_1$, $D_1 - C_2$ can represent the contribution of the $C_{(4)'} - Cl$ bond, but the third or fourth would be impossibly large. It follows that the $C_{(4)'} - Cl$ bond (whether represented by $D_1 - C_1$ or by $D_2 - C_2$) is approximately parallel with the $Cl - C_{(4)}$ bond; this is only compatible with the conformation *A* or *B*.

Identical stereochemistry as shown by formula *A* has been established for O-benzoylbenzaldoxime (*IVa*) and derivatives *IVb, c* from dipole moments¹⁵ and from the

chemical reactivity²⁰. Comparison of spectroscopic characteristics of compounds *III* and *IV* confirm that their configuration is the same. First of all they have similar UV spectra (Fig. 3), whereas the differences between stereoisomers are much more pro-

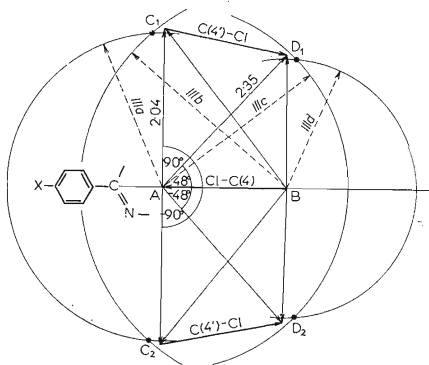


FIG. 2

Analysis of the Experimental Dipole Moments of Substituted O-Benzoylbenzhydroximoyl Chlorides *IIIa–III d*

The directions of the vectors are obtained by solving the triangles ABC and ABD.

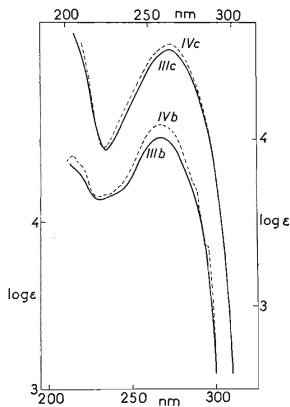
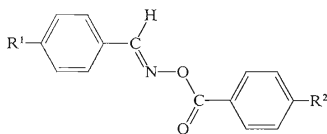


FIG. 3

Ultraviolet Absorption Spectra of Substituted O-Benzoylbenzhydroximoyl Chlorides *IIIb, c* and O-Benzoylbenzaldoximes *IVb, c* (ethanol)

nounced in a similar case²¹. In the ¹H NMR spectra, the chemical shifts of the phenyl protons *ortho* to the —C(Cl)=N grouping are instructive. When compounds *IIIb, c* are compared with the corresponding benzaldoxime derivative *IVb, c*, it appears that the substitution of H for Cl entails a $\Delta\delta$ of 0.23 and 0.24 units, respectively (Table II). Similar changes occur for simple model compounds 4-chlorobenzoyl chloride and 4-chlorobenzaldehyde or benzoyl chloride and benzaldehyde²². On the other hand, differences as much as 0.4 δ are found for stereoisomeric benzaldoximes²³.



IVa; R¹ = R² = H

IVb; R¹ = Cl, R² = H

IVc; R¹ = H, R² = Cl

TABLE II

The ¹H-NMR Chemical Shifts (δ in CDCl₃) in Substituted O-Benzoylbenzhydroximoyl Chlorides and in the Model Compounds

Compound	Position			
	2	3	2'	3'
<i>IVb</i>	7.76	7.43	8.12	—
<i>IIIb</i>	7.99	7.43	8.18	—
$\Delta\delta(\text{H} \rightarrow \text{Cl})$	0.23	0	0.06	—
4-Chlorobenzaldehyde ^a	7.74	7.44	—	—
4-Chlorobenzoyl chloride ^a	8.03	7.42	—	—
$\Delta\delta(\text{H} \rightarrow \text{Cl})$	0.29	—0.02	—	—
<i>IVc</i>	7.82	—	8.09	7.48
<i>IIIc</i>	8.06	—	8.15	7.50
$\Delta\delta(\text{H} \rightarrow \text{Cl})$	0.24	—	0.06	0.02
Benzaldehyde ^b	7.81	7.45	—	—
Benzoyl chloride ^b	8.07	7.47	—	—
$\Delta\text{H} \rightarrow \text{Cl}$	0.26	0.02	—	—
<i>III d</i>	8.01	7.45	8.14	7.50

^a In tetrachloromethane²²; ^b ref.²².

Finally also the IR spectra of compounds *III* and *IV* display similar features, in particular in the region of the C—H deformation frequencies which were suggested for empirical assignment of configuration^{10,24}. In the case of the monosubstituted benzene nucleus a band appears at 698–702 cm⁻¹ in the *cis*-C₆H₅ configuration and at 692–694 cm⁻¹ in the *trans*-C₆H₅ configuration; the values found for *IIIc* and *IVc* are 691 and 695 cm⁻¹, respectively. In the case of 4-chloro derivatives the corresponding values are 824–829 cm⁻¹ (*cis*-C₆H₄Cl), 833–839 cm⁻¹ (*trans*-C₆H₄Cl), 835 cm⁻¹ (*IIIb*), 834 cm⁻¹ (*IVb*). Although the assignment of these bands^{10,24} is in our opinion problematic, the empirical correlation seems to work.

Accepting the assignment of the *Z* configuration for O-benzoylbezhydroximoyl chlorides *III*, we will shortly examine the consequence which may be brought forth on the configurational problem of their parent compounds, benzhydroximoyl chlorides *I*. Unfortunately, no direct correlations can be safely applied because of the possibility of rearrangement during the benzylation process. For instance, both stereoisomeric benzaldoximes give the same (*E*)-O-benzoylbenzaldoxime^{15,20} (*IVa*) (*i.e.* *trans*-phenyl) and the two O-ethylbenzhydroximic acids give the same *E* benzoyl derivative²¹ (*i.e.* *cis*-phenyl).

On the other hand, the benzoyl derivatives *IIIa*–*IIIc* may be used for a more detailed analysis of bond moments and the results may be transferred to the parent compounds *I*. The direction of the total dipole moments can be read from Fig. 2: if the experimental values are smoothed out to comply with the C_{ar}—Cl bond moment of 1.6 D, one gets the vectors of 2.04 D for *IIIa* and 2.35 for *IIIc* under the angles of 90° and 48°, respectively, to the C_{ar}—C_{a1} bond. In Fig. 4 these values are compared to the vectorial sum of bond moments. This test is more sensitive than Fig. 1 and the fit is worse although it is of the same order of precision as in the case of model

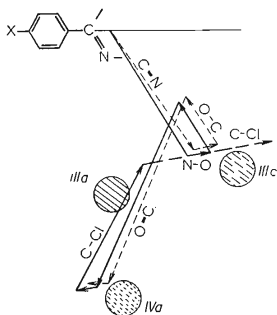


FIG. 4

Resolution of the Dipole Moments of O-Benzoylbenzhydroximoyl Chlorides *IIIa, c* and O-Benzoylbenzaldoxime¹⁵ (*IVa*) into Components

The experimental values are represented by the hatched circles in the proper positions.

molecules *IVa*, *b*. No specific features common to compounds *III* and *IV* or characteristic of one of these could be evidenced. The only change in the hydroximoyl group which could improve the fit significantly is the reduction of the $C_{a1}-Cl$ bond moment; for instance, adopting the value of 1.4 D the standard deviation drops from 0.38 to 0.13 D (Table I the last two lines). If this correction is applied to hydroximoyl chlorides (see Fig. 2 of ref.⁷), the configuration *Z* and conformation *ap* (like in *A*) would be deduced in agreement with the X-ray result³ and with the dipole moment analysis by Lumbroso and coworkers^{5,6,8}. We do not, however, believe that this *ad hoc* correction is sufficient to solve the problem. For instance, the moment of 4-chloro-1*H*-2,3-benzoxazine²⁵, a rigid model of the *E*, *sp* form (like in *D*), would remain unexplained. Another discrepancy concerns the vector difference between the dipole moments of hydroximoyl chlorides *I* and aldoximes, which should be the same as between the derivatives *III* and *IV*; this difference represents the replacement of hydrogen by chlorine on the azomethine carbon. With standard bond moments its value is expected to be 1.75 D, with the mentioned correction 1.4 D. The experimental value derived from compounds *IIIa* and *IVa* is 1.30 D (with a somewhat divergent direction) whereas Lumbroso's analysis⁸ — although leading to the right configuration — requires 2.0 D. We conclude that specific factors influencing dipole moments of hydroximoyl chlorides were not disclosed and it is uncertain whether they exist, or whether there is only a fortuitous coincidence of individual components which prevents a reliable configuration assignment. Hence this assignment will require another approach.

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