CONFIGURATION AND CONFORMATION OF AMIDOXIMES.
N,N-DIALKYL DERIVATIVES*

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Dipole moments of N,N-dialkylamidoximes *Ia—Ie* and of substituted O-benzoyl-N,N-dimethyl-benzamidoximes *IIa—IIe* were measured in benzene or dioxan, respectively. The results with the latter set of compounds allow to assign in an independent and unambiguous way the E-configuration which was found previously for all N,N-dialkylamidoximes investigated in the crystalline state; our reasoning does not involve bond moment values within the amidoxime functional group. The fundamental difference in the stereochemistry between unsubstituted amidoximes and their N,N-dialkyl derivatives has thus been confirmed. On the other hand, the configuration of simple N,N-dialkylamidoximes (*e.g. Ia—Ie*) cannot be deduced from their dipole moments in a straightforward manner. The reason is that the conjugation within the N═C—N chain requires a mesomeric correction term which cannot be neglected and is not equal in either configuration. The example shows very clearly limitations of the bond moment approach if applied to conjugated molecules.
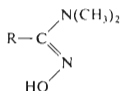
The configurational equilibrium of amidoximes is rather sensitive to substitution. The observed regularities may be rationalized in terms of our original proposal[1,2] distinguishing N,N-disubstituted amidoximes and those bearing at last one hydrogen atom on the amino nitrogen. In the latter case the stereoisomers *A* and *B* can interconvert in a protomeric reaction *via* the imino form *C*; the Z-configuration (*A*) is thermodynamically stable as evidenced by X-ray crystallography[3-7], in solution mainly from dipole moment measurement[1,2,8] and by some supporting arguments from IR, ^{1}H NMR, and UV spectroscopies[2]. On the contrary, the two stereoisomeric N,N-disubstituted amidoximes are kinetically stable since any protomerism is excluded; they were also actually isolated in some cases[9,10]. As a rule, it is the E-configuration (*F*) which is thermodynamically stable. It was found in crystals of the more stable isomers of compounds *Ia, Ic, Id, If,* and *Ig* (refs[11,7,12,9,13], respectively); the assignment in solution was based mainly on ^{1}H NMR spectroscopy[9,13], while the dipole moment results were not unequivocal[13]. The reversed stability as com-
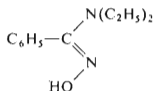
pared with unsubstituted derivatives was explained by steric hindrance[11] in the form D, or by a hydrogen bond[4,13] in A.
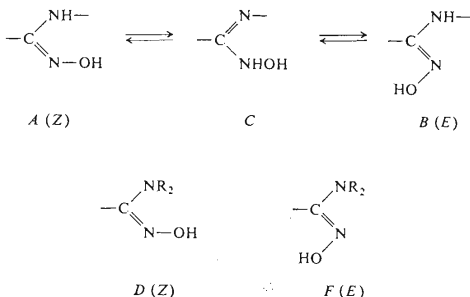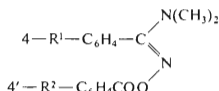

In the present paper our previous investigation of dipole moments[2] is extended from unsubstituted to N,N-dialkylated amidoximes. Since the interconversion of stereoisomers is virtually impossible and the configuration in crystal beyond doubts, its new independent proof is not so desirable as it was in the previous case[2]. A more important task was to verify the dipole moment approach on an oximino compound with authentic E-configuration. In the course of our investigations, configuration of several types of compounds with the functional group X—C=N—O— was assigned[1,2,8,14−17], using a graphical comparison[18] of experimental dipole moments with those calculated by the bond moment scheme. Most of these compounds, however, were actually in the Z-configuration: the originally assumed[1] E-configuration of hydroximoyl chlorides (X = Cl) was later reassigned[17] and that of S,S-dioxo-S-alkyl-thiohydroximic acids[14] (X = SO_2R) is not known with certainty. There remain the higher melting isomers of O-alkylhydroximic acids[1] (X = = OR) and stable isomers of N-morpholino- and N-pyrrolidino-amidoximes[13] (X = NC_4H_8O and NC_4H_8) as the only known cases of indisputable E-forms, but the agreement of calculated and experimental dipole moments was not very good and might by partly fortuitous; in addition the free rotation of the OR or NC_4H_8O groups prevented a more exact comparison. Besides its very approximate character, the bond moment principle is in fact not valid for conjugated systems[19] and special correction terms may appear necessary. Concerning oximino compounds the formal moments of the C=N, N—O, and C—X bonds might already involve some allowance for the conjugation within the functional group. Nevertheless, additional correcting terms were still found necessary in the case of amidoximes[2] and hydroximoyl chlorides[17]. One can envisage that these corrections need not be necessarily equal in either configuration.
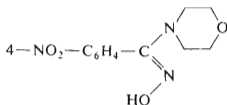
$$R-C\begin{array}{c}\diagup N(CH_3)_2\\\diagdown N\end{array}$$
$$\quad\diagdown HO$$

Ia; R = CH₃
Ib; R = C₆H₅
Id; R = 4-ClC₆H₄
Ie; R = 4-NO₂C₆H₄
If; R = 4-CH₃C₆H₄

$$C_6H_5-C\begin{array}{c}\diagup N(C_2H_5)_2\\\diagdown N\end{array}$$
$$\qquad\diagdown HO$$

Ic

$$4-R^1-C_6H_4-C\begin{array}{c}\diagup N(CH_3)_2\\\diagdown N\end{array}$$
$$4'-R^2-C_6H_4COO$$

IIa; R¹ = R² = H
IIb; R¹ = Cl, R² = H
IIc; R¹ = H, R² = Cl
IId; R¹ = R² = Cl
IIe; R¹ = H; R² = OCH₃

$$4-NO_2-C_6H_4-C\begin{array}{c}\diagup N\diagdown O\\\diagdown N\end{array}$$
$$\qquad\qquad\diagdown HO$$

Ig

For the reasons outlined we investigated dipole moments of dialkylated benzamid-oximes *Ia—Ie*, and by their resolution into bond moments sought for the contribution due to conjugation. In order to get still an independent proof of the *E*-configuration we had recourse to benzoyl derivatives *IIa—IIe*. The merit of these compounds is in the possibility of introducing polar substituents (chlorine) in two directions. Hence the configuration can be solved without referring to bond moments within the functional group, only the C—Cl moment is needed. Similar derivatives were already used with the same intention in the case of amidoximes[2] unsubstituted on N, and of hydroximoyl chlorides[16].

EXPERIMENTAL

Melting points determined on a Kofler block and not corrected.

The N,N-dialkylamidoximes

Were prepared from the corresponding hydroximoyl chloride (obtained freshly by chlorinating the aldoxime) and dimethylamine or diethylamine in slight excess (2·2 mol). The solutions in methanol were mixed at 0°C, set aside overnight filtered and evaporated *in vacuo*. The product was separated from hydrochloride of the amine by washing with ice-cold water. The procedure differs from that in ref.[9] mainly by using methanol as solvent. Under these conditions we obtained only *E*-isomers, while following strictly the conditions in the literature[9], we were not able to prepare *Z*-isomers in a sufficient purity for physical measurements.

N,N-Dimethylacetamidoxime (Ia), yield 15%, m.p. 58°C (cyclohexane); for C₄H₁₀N₂O (102·1) calculated: 47·03% C, 9·87% H, 27·43% N; found: 47·25% C, 10·06% H, 27·16% N. (The sample used in an X-ray study[11] was not characterized, according to a personal communication[20] it was prepared in a similar way, yield 30%, m.p. 55·5°C.). IR spectrum in CCl₄ (cm⁻¹): 991

(N—O), 1 643 (C=N), 3 620 (O—H); in KBr 3 180 infl., 3 280. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2·04 (s, 3 H, CH$_3$), 2·80 (s, 6 H, NCH$_3$), 8·30 (broad, 1 H, OH).

N,N-*Dimethylbenzamidoxime* (Ib), yield 86%, m.p. 125°C (cyclohexane), literature[9] 132°C. IR spectrum in CHCl$_3$ (cm^{-1}): 703 (δ CH), 962 (N—O), 1 625 (C=N), 3 598 (O—H); in KBr 3 140, 3 240 infl., 3 275. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2·60 (s, 6 H, CH$_3$), ~7·34 (m, 5 H, C$_6$H$_5$), 9·09 (broad, 1 H, OH); in fair agreement with ref.[9]. UV spectrum in ethanol (λ nm, log ε): 217 (3·98), 260 (3·43).

N,N-*Diethylbenzamidoxime* (Ic), yield 85%, m.p. 79°C (methylcyclohexane), literature[21] m.p. 81°C; m.p. 176°C given in ref.[22] is possibly a misprint. For C$_{11}$H$_{16}$N$_2$O (192·2) calculated: 68·72% C, 8·39% H, 14·57% N; found: 68·95% C, 8·38% H, 14·48% N. IR spectrum in CHCl$_3$ (cm^{-1}): 704 (δ CH), 958 (N—O), 1 619 (C=N), 3 594 (O—H); in KBr 3 140 infl., 3 215, 3 280. ^{1}H NMR spectrum in CDCl$_3$ (δ): 1·04 (t, $J = 8$ Hz, 6 H, CH$_3$), 3·08 (q, $J = 8$ Hz, 4 H, CH$_2$), ~7·42 (m, 5 H, C$_6$H$_5$), 9·15 (broad, 1 H, OH), corresponding well to the data of ref.[23] in CS$_2$.

N,N-*Dimethyl-4-chlorobenzamidoxime* (Id), yield 74%, m.p. 142°C (cyclohexane), literature[9] 150°C. IR spectrum in CHCl$_3$ (cm^{-1}): 834 (δ CH), 963 (N—O), 1 628 (C=N), 3 591 (O—H); in KBr 3 150 infl., 3 240 infl., 3 275. ^{1}H NMR spectrum in CD$_3$SOCD$_3$ (δ): 2·55 (s, 6 H, CH$_3$), 7·26 (d, $J = 8·5$ Hz, 2 H, 3—5), 7·49 (d, $J = 8·5$ Hz, 2 H, 2—6), 9·23 (s, 1 H, OH); in fair agreement with ref.[9]. UV spectrum in ethanol (λ nm, log ε): 225 (4·15), 274 infl. (3·32).

N,N-*Dimethyl-4-nitrobenzamidoxime* (Ie), m.p. 167°C (aqueous methanol), literature[9] 180°C. IR spectrum in KBr (cm^{-1}): 3 110, 2 210, 3 265. ^{1}H NMR spectrum in CD$_3$SOCD$_3$ (δ): 2·56 (s, 6 H, CH$_3$), 7·59 (d, $J = 9$ Hz, 2 H, 2—6), 8·29 (d, $J = 9$ Hz, 2 H, 3—5), 9·45 (s, 1 H, OH); in ref.[9] the signals of aromatic protons are evidently misassigned.

O-Aroyl Derivatives of Substituted N,N-Dimethylbenzamidoximes

Were prepared by acylation with the appropriate aroyl chloride (20% excess) in pyridine at 0°C. After standing 2 h at laboratory temperature the mixture was poured on ice and the product collected.

O-*Benzoyl*-N,N-*dimethylbenzamidoxime* (IIa), yield 80%, m.p. 126°C (aqueous ethanol), For C$_{16}$H$_{16}$N$_2$O$_2$ (268·3) calculated: 71·61% C, 6·01% H, 10·44% N; found: 71·82% C, 6·02% H, 10·55% N. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2·89 (s, 6 H, CH$_3$), 7·3—7·7 (m, 10 H, C$_6$H$_5$).

O-*Benzoyl*-N,N-*dimethyl-4-chlorobenzamidoxime* (IIb), yield 64%, m.p. 109°C (aqueous ethanol). For C$_{16}$H$_{15}$ClN$_2$O$_2$ (302·8) calculated: 63·47% C, 4·99% H, 11·70% Cl, 9·25% N; found: 63·17% C, 4·94% H, 11·84% Cl, 9·36% N. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2·88 (s, 6 H, CH$_3$), 7·23 (d, $J = 9$ Hz, 2 H, 3—5), 7·25—7·40 (m, 3 H, 3'—4'—5'), 7·47 (d, $J = 9$ Hz, 2 H, 2—6), 7·71 (m, 2 H, 2'—6').

O-(4'-*Chlorobenzoyl*)-N,N-*dimethylbenzamidoxime* (IIc), yield 85%, m.p. 129°C (aqueous ethanol). For C$_{16}$H$_{15}$ClN$_2$O$_2$ (302·8) calculated: 63·47% C, 4·99% H, 11·70% Cl, 9·25% N; found: 63·58% C, 4·93% H, 11·76% Cl, 9·42% N. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2·89 (s, 6 H, CH$_3$), 7·18 (d, $J = 8·5$ Hz, 2 H, 3'—5'), 7·30—7·55 (m, 5 H, C$_6$H$_5$), 7·51 (d, $J = 8·5$ Hz, 2 H, 2'—6').

O-(4'-*Chlorobenzoyl*)-N,N-*dimethyl-4-chlorobenzamidoxime* (IId), yield 60%, m.p. 116°C (aqueous ethanol). For C$_{16}$H$_{14}$Cl$_2$N$_2$O$_2$ (337·2) calculated: 56·98% C, 4·18% H, 21·02% Cl, 8·30% N; found: 56·93% C, 4·06% H, 20·88% Cl, 8·34% N. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2·88 (s, 6 H, CH$_3$), 7·23 (d, $J = 8·5$ Hz, 2 H, 3'—5'), 7·25 (d, $J = 8·5$ Hz, 2 H, 3—5), 7·46 (d, $J = 8·5$ Hz, 2 H, 2—6), 7·54 (d, $J = 8·5$ Hz, 2 H, 2'—6').

O-(4′-*Methoxybenzoyl*)-N,N-*dimethylbenzamidoxime* (IIe), yield 86%, m.p. 96°C (aqueous ethanol). For $C_{17}H_{18}N_2O_3$ (298.3) calculated: 68.43% C, 6.08% H, 9.39% N; found: 68.39% C, 5.98% H, 9.42% N. ^{1}H NMR spectrum in CDCl$_3$ (δ): 2.88 (s, 6 H, NCH$_3$), 3.75 (s, 3 H, OCH$_3$), 6.72 (d, $J = 9$ Hz, 2 H, 3′–5′), 7.30–7.55 (m, 5 H, C$_6$H$_5$), 7.53 (d, $J = 9$ Hz, 2 H, 2′–6′); the spectrum was not changed up to 350 K (in CD$_3$SOCD$_3$) or down to 215 K (in CD$_3$COCD$_3$).

Physical Measurements

The dipole moment measurement was carried out as in the previous communication[2], this concerns also calculation of molar refraction from increments. The dipole moment data are listed in Table I.

The IR absorption spectra were registered on a Zeiss, Model UR 20 spectrometer, concentration of chloroform solutions c. 0.2 mol l^{-1}, cell thickness 0.01 cm, calibration with polystyrene foil. The ^{1}H NMR spectra were registered on a TESLA BS-497 instrument (60 MHz) at 30°C, concentration c. 0.1 mol l^{-1}, tetramethylsilane as internal reference. The UV absorption spectra were recorded on a Specord UV-VIS spectrophotometer (Zeiss, Jena), concentrations c. 10^{-4} mol l^{-1}.

Calculations

Calculations of expected dipole moments of compounds *I* and *II* were carried out by vector addition of standard bond moments[19] (in 10^{-30} C m): H—C$_{al}$ 1, H—C$_{ar}$ 0, C=N 6.0, C—N 1.5, C=O 8.33, C—O 2.47, N—O 1, H—O 5.03, C$_{ar}$—Cl 5.33, C$_{ar}$—NO$_2$ 13.33. In the last value no contribution of the conjugation through the benzene ring is involved, in contradistinction to a higher value (14.33) used previously[2] for amidoximes with a free NH$_2$ group. This distinction is substantiated by the suppressed conjugation in compounds *II* (see later the discussion of UV spectra), at any rate it is without influence on the final conclusions. In addition a mesomeric moment (m_1) of 0.83 expressing the conjugation C$_6$H$_5$—CO was applied, while the mesomeric moment m_2 corresponding to the conjugation in the N=C—N chain of the functional group is discussed in the next section. The bond angles within the oximino group were adopted with respect to the configuration, viz. N=C—N 118° and C—C=N 124° for *E*-configuration according to X-ray results on (*E*)-N,N-dialkylamidoximes[7,9,11–13], N=C—N 124° and C—C=N 117° for *Z*-configuration according to X-ray results on (*Z*)-amidoximes[4–7]; these values do not differ significantly from those recently recommended[13] but are somewhat amended as compared to our early studies[1,16]. The remaining angles were C=N—O 112°, N—O—H 105°, N—O—C 113°C, O=C—O 124°, O=C—C 125°, angles on amino nitrogen 120°. The calculated dipole moments are partly listed in Table I, partly shown in Fig. 3.

RESULTS AND DISCUSSION

In the previous communication[2] we inferred from infrared spectra and from dielectric measurements that association in solution does not impair the dipole moment values of unsubstituted amidoximes. This statement is *a fortiori* valid for their N,N-dialkyl derivatives *I* and even for acyl derivatives *II*. With this provision the dipole moments of Table I can be discussed in terms of steric arrangement of the isolated molecule. In addition to two possible configurations (*E* or *Z*) on the C=N double bond it is possible to consider two planar conformations around the N—O

bond, *ap* or *sp*. This gives altogether four planar forms, $G-K$, for N,N-dialkyl-benzamidoximes *I*. Heavy deviations from planarity can be excluded; in addition to the reasoning given previously[2] also all the X-ray studies on N,N-dialkylamid-

TABLE I

Polarization and dipole moments of N,N-dialkylamidoxime derivatives (25°C)

Compound	R^1 R^2	α^a β^b	P_2^0, cm^3 R_D^b, cm^3	μ (5)^c μ (15)^c	μ_{calc}^d
	N,N-Dialkylamidoximes $R^1C(=NOH)NR_2^2$ in benzene				
Ia	CH_3 CH_3	2·92 −0·151	86·3 29·7	5·5 5·3	6·3
Ib	C_6H_5 CH_3	2·26 −0·265	112·8 49·4	5·8 5·5	5·9
Ic	C_6H_5 C_2H_5	2·36 −0·216	138·5 58·7	6·5 6·2	5·9
Id	$4\text{-}ClC_6H_4$ CH_3	2·50 −0·360	139·8 54·3	6·7 6·5	6·3
Ie	$4\text{-}NO_2C_6H_4$ CH_3	7·54 −0·406	342·3 55·7	12·4 12·3	12·4
	O-Benzoyl-N,N-dimethylbenzamidoximes $R^1C_6H_4C(=NOC_6H_4R^2)N(CH_3)_2$ in dioxane				
IIa	H H	9·23 −0·102	475·2 79·1	14·6 14·5	14·6
IIb	4-Cl H	4·58 −0·183	297·2 84·0	10·6 10·4	10·2
IIc	H 4-Cl	9·42 −0·194	537·6 84·0	15·6 15·5	14·8
IId	4-Cl 4-Cl	5·53 −0·201	382·0 88·9	12·5 12·3	11·9
IIe	H 4-OCH₃	8·90 −0·121	510·5 86·0	15·1 14·9	14·6^e

^{a} Slopes of the plots ε_{12} vs w_2 and d_{12}^{-1} vs w_2, respectively; ^{b} calculated from increments like in the previous communication[2]; ^{c} units 10^{-30} C m, correction for the atomic polarization 5% or 15% of the R_D values, respectively; ^{d} calculated for configuration E and conformation *ap* (formulae J and N), the mesomeric moment $m_2 = 4·0$ (16° to the $C=N$ bond) as derived from compounds *Ib*, *Id*, *Ie* was applied also to the remaining compounds; ^{e} assuming equal population of the two planar conformations of the methoxy group.

oximes themselves confirmed a planar structure[7,9,11-13]. Slight deviations from planarity have negligible effect on dipole moments.
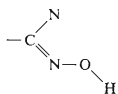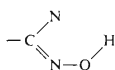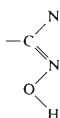

G (Z ap)   H (Z sp)   J (E ap)   K (E sp)

In the molecule of acyl derivatives *II* there is one axis of rotation more (the C—O bond) but a convincing evidence exists that all similar ester-like compounds possess the *Z* conformation on this partial double bond[24], see particularly the very similar molecules of O-benzoylhydroximoyl chloride[16], O-benzoylbenzaldoxime[25], and O-benzoylbenzamidoxime[2] (*IIIa*). Hence the number of possible forms is again only four, *L — O*; in addition *M* and *O* are very improbable for steric reasons.
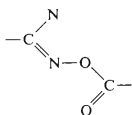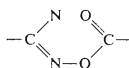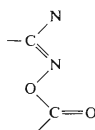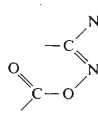
L(Z ap)   M (Z sp)   N (E ap)   O (E sp)

An independent and unambiguous proof of the *E* configuration can be obtained as follows. From experimental dipole moments of *IIa* and *IIb* their direction can be inferred since the bond moment C—Cl is well documented[19]; the solution means to construe a triangle given its three sides (Fig. 1, triangle *XYZ*). The same is possible for the couple *IIc* and *IId* (triangle *XYU*). The vector connecting points *Z* and *U* then represents the contribution of the second chlorine atom in position 4′. Its absolute value should be equal to the C—Cl bond moment and its direction is rather different for configurations *E* or *Z*, respectively, while it is virtually independent on the conformation around the N—O bond. (The reasoning only assumes that this conformation is the same for compounds *IIa—IId*.) Note that there are two solutions of either triangle, *viz.* on either side of the C—Cl bond. However, these two solutions can be combined only in such a manner that the distance *ZU* equals actually the C—Cl bond moment. Alternatively, the decision between the two solutions could be reached considering that the most important bond moments are those of the C=O and C=N bonds, hence the total dipole moment of *IIa* should roughly parallel the C=N direction. In practice one has still to take into account

the experimental errors and/or inaccuracy of the additivity principle of partial moments. In Fig. 1 the errors were staggered among the experimental quantities while the direction and magnitude of C—Cl vectors are as theoretically expected. For comparison the same treatment is reproduced in Fig. 1 for (Z)-O-benzoylbenz-amidoxime *IIIa* and its derivatives *IIIb*—*IIId*, as carried out in our previous paper[2]. The different configuration is evident.

$$4-R^1-C_6H_4-C\begin{array}{c} NH_2 \\ \diagdown \\ N-OCOC_6H_4-R^2-4' \end{array}$$
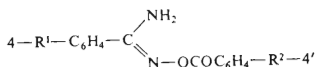
IIIa: $R^1 = R^2 = H$ *IIIc*; $R^1 = H$, $R^2 = Cl$
IIIb; $R^1 = Cl$, $R^2 = H$ *IIId*; $R^1 = R^2 = Cl$

A similar analysis as above is not possible in the case of simpler compounds *I* since substituents can be introduced from one side only. Hence the configuration could be determined only in such a way that the expected dipole moments would be put together from bond moments (including a mesomeric moment allowing for the
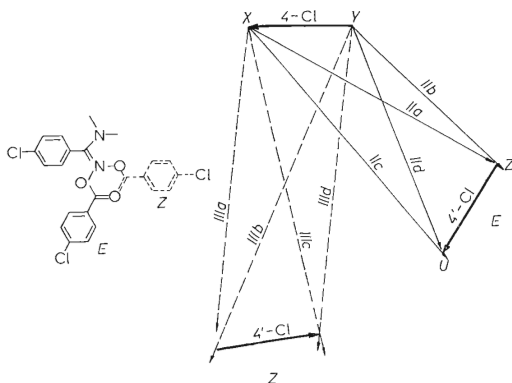

FIG. 1

Analysis of experimental dipole moments of O-benzoylderivatives of amidoximes. Substituted O-benzoyl-N,N-dimethylbenzamidoximes *IIa*—*IId* in the configuration *E*, substituted O-benzoyl-benzamidoximes *IIIa*—*IIId* in the configuration *Z*; heavy arrows show the bond moments C—Cl

conjugation within the $N=C-N$ chain) and compared with experiments. We shall proceed in the reverse way: from experimental results the mesomeric moment will be inferred assuming that the E configuration is established. In the first step of the analysis we determined the direction of the moment of the $(CH_3)_2NC=NOH$ group, (*i.e.* of the compound *Ib*), referring to compounds *Id* and *Ie*, and to the known bond moments[19] $C-Cl$ and $C-NO_2$ (Fig. 2). The result amounts 5·87 at an angle of $-13°$ to the $C=N$ bond. Note again that the second solution, symmetrical to the $C-C$ bond, is in principle possible but would be incompatible with any reasonable bond moment values. In the next step the group moment is resolved into individual bond moments, the rest representing the mesomeric moment of the $N=C-N$ group (m_2). Assuming the E configuration and *ap* conformation around $N-O$, we obtain $m_2 = 4·0$ at an angle of $16°$ to the $C=N$ bond. This finding is rather different from that for unsubstituted amidoximes[2] in the Z configuration, *viz.* 2·6, $-31°$. It is well evidenced that similar mesomeric moments are sensitive to substitution, compare *e.g.* amides and N,N-dimethylamides[26]. Nevertheless, the above difference is so striking, particularly as far as the direction is concerned, that it is probably controlled by the configuration, too. Then the determination of configuration may become problematic. For instance, if we assumed Z configuration for *Ib* and adopted m_2 as for unsubstituted Z-amidoximes[2], the resulting vector would be rather close to the experiment. Actually, the configuration of *Ic* and its 4-nitro derivative was mis-assigned in our earlier study[1] while that of benzamidoxime and 4-nitrobenzamido-xime was correct; the two couples of compounds have very similar dipole moments and the mesomeric correction m_2 was originally neglected.*

With the derivative *Ig* and its stereoisomer[13] the situation was more advantageous since both isomers were available for measurement. However, the calculations reported[13] neglect not only the mesomeric correction but also the unknown orientation of the morpholine residue. The rather rough agreement with experiment might be to a certain extent fortuitous and the example shows little efficiency of the approach if proper substitution is not exploited. Besides the problem of conjugation another complicating factor is the conformation around the $N-O$ bond which affects the final dipole moment more than the configuration on $C=N$, like in the case of hydro-ximoyl chlorides[17]. Therefore, the *ap* conformation can be inferred with certainty in agreement with the experience on other oximino compounds[24]; this result is more straightforward and more reliable than the assignment of configuration.

With the results obtained on N,N-dialkylamidoximes *I* we can now analyse the dipole moments of their O-benzoylderivatives *II* in more detail. Resolution of the gross group moment yielded a similar mesomeric term m_2 as in the case of compounds

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* Figs 2 and 3 of ref.[1] are interchanged but their description is correct. Note still that the actual configuration and/or identity of our original sample[1,27] of *Ic* is somewhat in doubt, see the discrepancy in melting points[21,22] as given in Experimental.

I (Fig. 2). Considering the larger uncertainty due to unfavourable angle of vectors, we may rather adopt the value of m_2 as determined on compounds *I*, also for *II*. Then the calculated and experimental dipole moments can be confronted in a conventional graphical representation[18] (Fig. 3) in which the values for the unsubstituted and substituted compound are plotted on the *x*- and *y*-axis, respectively. The agreement is quite good and the decision in favour of the *E* configuration and *ap* conformation cannot be doubted. Fig. 3 shows also the calculated dipole moments which would be obtained with the mesomeric term m_2 as determined[2] on Z-amidoximes. A dependable determination of configuration would not be possible, although *E* would appear still more probable.

The configuration of compounds *I* and *II* can be supported by some additional proofs which, however, do not exceed too much those already given in the literature[9,13] for derivatives of this type. In ¹H NMR spectra of *I* the signals of OH, 2 H in C_6H_5, and C—H adjoining to N are sensitive to configuration[9,13]; their relative shifts together with lathanide induced shifts and especially the Nuclear Overhauser Effect[9] constitute the most relevant proof of the configuration in solution. If we compare our compounds *IIb−IId* to *IIIb−IIId*, the reversal of configuration and methylation cause an upfield shift (*c.* 0·33) of the hydrogens in position 2, this is comparable to the shift between stereoisomers[9] of *Ib, Id, Ie, If* (*c.* 0·25). Still more marked is the shift in the position 2′ of the second nucleus, in *II c.* 0·65 upfield as
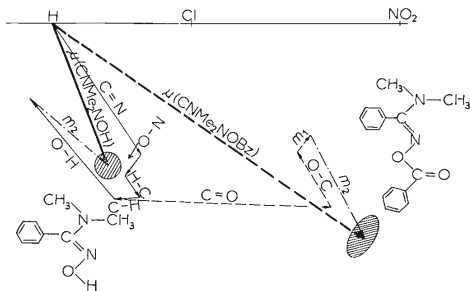

Fig. 2

Resolution of dipole moments of N,N-dimethylbenzamidoximes and O-benzoyl-N,N-dimethyl-benzamidoximes into components. Heavy arrow — group moment of C(=NOH)N(CH₃)₂, broken arrow — group moment of C(=NOBz)N(CH₃)₂, m_2 = mesomeric corrections

compared to *III*. The temperature dependence of ^{1}H NMR spectra was followed on *IIe* within the interval of 135 K. No signs of a conformational equilibrium were detected, nor the restricted rotation of the two methyl groups around the C—N bond was observed at the temperatures down to 215 K. The assignment of configuration based on IR bands[28,29] near to 700 cm^{-1} (in the case of phenyl derivatives) or 830 cm^{-1} (in the case of 4-chlorophenyl derivatives) was already criticized in our previous papers[2,17]. The configuration of *Ib* and *Ic* would be predicted correctly but that of *Id* wrongly, confirming our evaluation of this method. The OH frequency in the crystalline state has been used as a stereochemical probe of aromatic *E*- and *Z*-aldoximes[30]. Applied to N,N-dialkylbenzamidoximes *I* this criterion fails since two bands are observed, corresponding to either category. The electronic spectra of aromatic oximino compounds show sometimes marked dependence on configuration[17,29,31] due to the distortion of coplanarity in the *cis*-phenyl isomer. The spectra

Fig. 3

Comparison of squared dipole moments[18] of O-benzoyl-N,N-dimethylbenzamidoximes *IIa—IId*, calculated and experimental. Full points — calculated with a mesomeric correction derived from (*E*)-N,N-dimethylamidoximes, broken points — with a correction derived from (*Z*)-aminoximes, shadowed circles — experimental values; the straight lines represent rotation around the N—O bond

Fig. 4

Ultraviolet absorption spectra of derivatives of amidoximes in ethanol. Full lines — N,N-dimethylbenzamidoxime *Ib* and its 4-chloroderivative *Id* (*E* configuration), broken lines — benzamidoxime and its 4-chloro derivative (*Z* configuration)

of *Ib* or of *Id* are, however, too different from possible model compounds, say from stereoisomeric benzaldoximes or 4-chlorobenzaldoximes. The only meaningful comparison we have found is to the corresponding Z-benzamidoximes[2]. Fig. 4 reveals that in the *E*-configuration the conjugation with the benzene ring is more suppressed. This effect was anticipated[11] but cannot be proven from the C—C bond lengths of *E* and *Z* benzamidoximes[4,5,7,9,13]. Similarly, the C=N and C—N bond lengths give no evidence that conjugation in the N=C—N chain should depend on configuration.

Dipole Moments and Configuration of Oximino Compounds

In this section the experience with the assignment of configuration of oximino compounds on the basis of dipole moments[1,2,8,13-17,32-34] will be summarized. In general, the merit of this approach is a simple theoretical concept and independency of special model compounds, the main drawback being the small amount of information. The latter is underlined in the case of oximino compounds by the necessity to determine simultaneously the conformation around the N—O bond[1,32]. There is, however, ample experimental evidence[24,33] corroborated by quantum chemical calculations[35] that the *ap* conformation can be considered a rule; scarce exceptions are explicable by intramolecular hydrogen bonds[24]. The most important bond moments, those of C=N and N—O bonds seem to have been estimated relatively well[36,37], they agree *e.g.* reasonably with recent measurement on (*E*) and (*Z*)-acetaldoximes in the gas phase[38,39]. (In the first paper[38] the direction of the moment is reversed in the Figure.) Thus the main difficulty arises when the C=NOH grouping is conjugated with a donor as in amidoximes[1,2,8,13], O-alkyl hydroximic acids[1] and their esters[15], S-alkyl thiohydroximic acids[14], or hydroximoyl chlorides[1,17,34]. In principle the bond moment scheme does not work for conjugated systems[19] unless special corrections are applied, expressed formally either as additional vector terms (m_2 in this paper) or as modified bond moments, *e.g.* for the C=N bond[14,16,17]. The kind of formal expression is irrelevant, but without these corrections an error in calculation arises which is the greater the stronger is the conjugation. The data presented in this and in the previous papers[2,26] show conclusively that the mesomeric moments are of importance and can depend on substitution and on configuration as well. Their neglecting was probably the main reason of wrong assignments[2,34] (for the revision see[17,40,41]) or of bad agreement between theory and experiments[1,13-15]. Of course, with the mesomeric moments the whole approach becomes more empirical in character and the original simplicity and independence of model compounds is gradually lost. Essential for the success is the possibility of introducing suitable polar substituents[18]. In this way the amount of information increases and convincing results can be obtained using minimum of empirical constants, see the example of O-benzoyl derivatives in this paper and

in ref.[2,16]. In any case, most dependable proof of configuration is an X-ray analysis, complemented by some spectroscopic evidence that there is no rearrangement in solution, even if cases when it happens[28] are rather rare among C=N compounds.

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