

**CONJUGATION WITHIN THE OXIMINO GROUP:
A SEMIQUANTITATIVE ESTIMATION***Otto EXNER^a and Václav JEHLIČKA^b^a *Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6 and*^b *Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

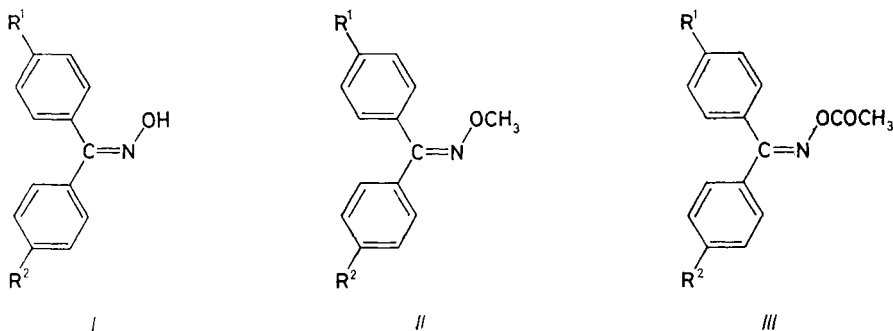
Received September 3rd, 1987

The $n-\pi$ conjugation within the oximino group was estimated on the basis of dipole moments and of bond lengths. The dipole moments were measured on oximes *I* and O-methyloximes *II* in benzene solution, the C=N and N—O bond lengths were retrieved from the Cambridge Structural Database for all available derivatives. The results differ somewhat in the quantitative sense but can be always interpreted in terms of the classical mesomeric formulae $IV \leftrightarrow V$. This formalism postulates — in agreement with experiments — a lowered C=N bond order, some double bond character of the N—O bond, planarity of the C=NOR group, and an excess dipole moment (μ_m) oriented in the sense of a charge transfer from O toward C. Quite different results were obtained for O-acetyloximes *III*. While their bond lengths could agree with a weakened conjugation, the excess dipole moment is oriented from C towards O and cannot be expressed by any simple formula. Hence the mesomeric formulae may represent an acceptable description of the actual charge distribution in many cases but not in all.

Conjugation of a double bond with a lone electron pair has been studied mostly on the systems X=C—Y like esters¹⁻³, amides⁴⁻⁶, thioamides^{4,7,8}, amidines⁹, or amidoximes¹⁰. In several papers to follow we shall give attention to systems X=N—Y, i.e. with nitrogen instead of carbon in the central position. This communication is devoted to oximes (*I*) and some of their simple functional derivatives (*II* and *III*).

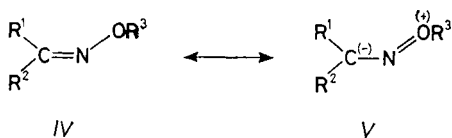
The experimental proofs of the $n-\pi$ conjugation are mostly based on the decreased bond order of the double bond to X and increased order of the single bond to Y, as manifested in bond lengths^{1,4,6,9}, infrared frequencies², or rotational barriers around the formally single bond^{4,7,11}. In the case of oximes this means a lowered C=N bond order and higher N—O bond order as expressed by the formulae $IV \leftrightarrow V$. Another line of evidence was obtained from dipole moments^{3,5,8-10}: a contribution from the strongly polar form (e.g. *V*) enhances the experimental moment over

* Part XI in the series Oxime Derivatives; Part X: Collect. Czech. Chem. Commun. **44**, 2221 (1979); simultaneously Part IX in the series Mesomeric Dipole Moments; Part VIII: J. Mol. Struct., in press.



In formulae I-III: *a*, $R^1 = R^2 = H$ *b*, $R^1 = Br$; $R^2 = H$ *c*, $R^1 = H$; $R^2 = Br$ *d*, $R^1 = NO_2$; $R^2 = H$
e, $R^1 = H$; $R^2 = NO_2$

that expected for the classical formula (e.g. IV). This approach has not yet been applied to oximes.



In this work we have tried all the mentioned physical properties but no significant results were obtained from IR spectra since the shifts of the C=N stretching frequency were either too small (e.g. no difference between 4-nitrobenzaldoxime and 4-hydroxybenzaldoxime), or an unambiguous assignment of the N—O stretching frequency was not feasible. For this reason we report here on the results from dipole moments and from molecular geometry. The experimental dipole moments were used first to determine the direction of the group moment. This was done by comparing the values of several *para*-substituted derivatives (e.g. Ia–Ie). Then the calculated dipole moment, anticipated for the non-polar formula, was subtracted vectorially as described in our previous work^{3,5,8–10}. The vector difference, μ_m , indicates the charge transfer due to conjugation (Eq. (1))

$$\mu_m = \mu_{\text{exp}} - \mu_{\text{calc}} \quad (1)$$

The bond lengths C=N and N—O were obtained from the Cambridge Structural Database¹² and compared within various classes of compounds and between these classes. Some indirect evidence concerning the barriers to rotation was obtained from the dihedral angles taken from the same source¹².

EXPERIMENTAL AND RESULTS

Materials. Benzophenone oxime (*Ia*), m.p. 140°C; benzophenone O-methyloxime¹³ (*IIa*), m.p. 61°C (ethanol); benzophenone O-acetyloxime¹⁴ (*IIIa*), m.p. 73°C (chloroform), in agreement with literature data.

The two stereoisomeric 4-bromobenzophenone oximes were prepared according to the literature¹⁵. Their partial separation by fractional crystallization¹⁵ was proved to be still more effective than by fractional extraction with alkali¹⁶. The *Z* isomer *Ib* (called α) crystallizes from ethanol spontaneously in a relatively pure form, yield 24%, m.p. 170–173°C after several recrystallizations (literature^{15,16} m.p. 165 and 168–170°C, respectively). The *E* isomer *Ic* (called β) was obtained from the mother liquors: After evaporation the mixture of oximes was acetylated with acetanhydride and (*E*)-4-bromobenzophenone O-acetyloxime isolated by crystallization from cyclohexane, m.p. 125°C. Its hydrolysis to (*E*)-4-bromobenzophenone oxime (*Ic*) was accomplished with 10% potassium hydroxide. Pure product was obtained by chromatography on silica, elution with benzene, and by recrystallization from diethyl ether. Heating in ethanol is better avoided. Yield of the pure product was 12%, m.p. 105–112°C (literature^{14,15} m.p. 107–110 and 109–110°C). The configuration of *Ia* and *Ib* is unambiguously determined by the Beckmann rearrangement of *Ib* to 4-bromobenzanilide.¹⁵

(*Z*)-4-Bromobenzophenone O-acetyloxime (*IIIb*) was prepared from pure *Ib* by boiling with acetic anhydride for 10 minutes. m.p. 160°C (ethanol) in agreement with the literature¹⁵. (*E*)-4-Bromobenzophenone O-acetyloxime (*IIIc*) was obtained as described above, m.p. 125°C (cyclohexane), literature¹⁵ m.p., 121°C.

(*Z*)-4-Bromobenzophenone O-methyloxime (*IIb*) was prepared from pure (*Z*)-4-bromobenzophenone oxime (*Ib*) by methylation with dimethyl sulphate as described for unsubstituted benzophenone oxime¹³. Since the separation from the simultaneously formed 4-bromobenzophenone imine-N-oxide could not be accomplished in this case by simple extraction, the latter was removed by hydrolysis with 1% hydrochloric acid to 4-bromobenzophenone and separated by column chromatography on silica, elution with benzene-hexane 3 : 7. Yield of *IIb* was 35%, m.p. 79°C (ethanol). For C₁₄H₁₂BrNO (290.2) calculated: 57.94% C, 4.17% H, 27.54% Br, 4.82% N; found: 58.40% C, 4.15% H, 27.45% Br, 4.94% N.

(*E*)-4-Bromobenzophenone O-methyloxime (*IIc*) was prepared in the same way as its stereoisomer, yield 40%, b.p. 156–158°C/27 Pa. For C₁₄H₁₂BrNO (290.2) calculated: 57.94% C, 4.17% H, 27.54% Br, 4.82% N; found: 57.79% C, 4.27% H, 28.23% Br, 4.77% N.

The identity and purity of all compounds was checked in a mass spectrometric study, carried out simultaneously. All samples were carefully dried in vacuum (6 Pa) and kept in a desiccator at –70°C until measured (at most several days). This precaution is necessary particularly for bromobenzophenone derivatives of the *E* series (*Ic*, *IIc*, *IIIc*) which can rearrange under non specified condition into *Z* isomers. In addition all benzophenone oxime derivatives, in particular benzophenone oxime itself, decompose slowly under evolution of dinitrogen tetroxide which acts autocatalytically.

Physical measurements. The dipole moments were measured in benzene solution using the method of Halverstadt and Kumler¹⁷. Some details of the technique were given previously⁹. With respect to possible association of oximes the concentration range was restricted to the weight fraction $w_2 < 2 \cdot 10^{-3}$ in the case of compounds *Ia*–*Ic*. At this concentration the association of various oximes is less than 5% (ref.¹⁸). The remaining compounds were used in the concentrations up to $w_2 = 4 \cdot 10^{-3}$.

Molar refractions were calculated from increments¹⁹, using the value of 9.91 cm³ for the C=NOH group adjacent to an aromatic nucleus, i.e. 7.36 cm³ for the C=N group⁹. Conjugation of the bromine atom with the benzene nucleus was accounted for by an increment of 0.1 cm³, while the conjugation is already included in the value for nitro group (7.36 cm³). Polarization data are listed in Table I. Those for compounds *IId*, *IIf* were obtained by recalculating original experimental data of Taylor and Sutton²⁰ according to the Halverstadt-Kumler method¹⁷, including the conversion of mole fractions to weight fractions and a correction of 5% for the atomic polarization. Similarly, the dipole moment of *IIf* was recalculated from the literature data²¹ and in addition redetermined experimentally. Fair agreement was obtained (Table I) but the difference against the originally reported²¹ value is significant. Since even recalculation according to the originally outlined method gave a similar result, the literature value²¹ is probably loaded with a computational error.

Calculations. The dipole moments anticipated for individual structures were calculated by vector addition of standard bond moments²² (in 10⁻³⁰ C m): H_{al}-C 1.0, H_{ar}-C 0, C-O 2.47, C=O 8.33, C=N 6.0, N-O 1.0 (concerning this value see Discussion), H-O 5.03, C_{ar}-Br 5.23. The standard group moment of C_{ar}-NO₂ (13.33) was enhanced to 15 in the case of compounds *IId*, *IIf* to account for the extra conjugation of the two functional groups through the benzene nucleus.

TABLE I
Polarization data of oxime derivatives (benzene, 25°C)

Compound	α^a	β^a	P_2^0, cm^3	R_D, cm^3	μ^b	μ_{calc}^c
<i>Ia</i>	0.86	-0.18	87.9	60.6	3.6	3.4
<i>Ib</i>	1.01	-0.23	127.7	68.4	5.5	5.6
<i>Ic</i>	2.60	-0.35	200.3	68.4	8.4	8.5
<i>IIf</i>	0.60	-0.28	78.3	65.5	2.2	1.5
	0.59 ^d	-0.22 ^d	81.8 ^d	65.5	2.7 ^d	1.5
<i>IIf</i>	0.85	-0.465	105.2	73.3	3.9	3.8
<i>IIf</i>	1.50	-0.455	141.4	73.3	5.9	5.8
<i>IId</i>	6.62 ^e	-0.345 ^e	379.8 ^e	71.8	12.9 ^e	12.9 ^f
<i>IIf</i>	8.50 ^e	-0.34 ^e	256.2 ^e	71.8	14.6 ^e	14.8 ^f
<i>IIIa</i>	6.62	-0.29	358.6	70.0	12.5	12.4
<i>IIIb</i>	2.34	-0.415	209.2	77.8	8.3	8.3
<i>IIIc</i>	5.90	-0.56	407.8	77.8	13.3	13.3

^a Slopes of the plots $\epsilon_{1,2}$ and $d_{1,2}^{-1}$, respectively, versus the weight fraction w_2 ; ^b dipole moments in units 10⁻³⁰ C m, calculated with a 5% correction for the atomic polarization; ^c calculated from the average group moment of the respective functional group, the agreement with the preceding column expresses just the vector additivity of substituents moments; ^d obtained by recalculating the original experimental data of ref.²¹ by the Halverstadt-Kumler method, in the original paper the dipole moment 1.30 is reported; ^e obtained by recalculating the original experimental data of ref.²⁰ by the Halverstadt-Kumler method, the originally reported dipole moments are 12.5 and 14.2, respectively; ^f calculated with the group moment 15.0 for the NO₂ group.

The bond angles were adopted mostly from recent X-ray work, using for each structural fragment the values from the most similar available compound. The angles within the benzophenone moiety, C—C=N (*Z*) 125°, C—C=N (*E*) 115°, C=N—O 108° were those found in (*E*)-4-bromobenzophenone O-picryloxime²³. The angle N—O—H 103° was preferred for oximes in the gas phase²⁴, N—O—CH₃ 109° was found recently in two O-methyloximes^{25,26}. All the estimated angles differ insignificantly from the mean values for the C=NO group as given later. The angles within the ester moiety, O—C=O 123°, O=C—C 126°, and N—O—C(O) 117° are the mean values for aliphatic esters.¹

The Cambridge Structural Database¹² (CSD) search was carried out with the May 1986 version (55 265 entries). Retrieved were compounds containing the structural fragment C=NO— without any other heteroatom on the carbon atom (excluding thus e.g. amidoximes and hydroxamic acid derivatives). Compounds which contained heavy atoms or cycles including the C=N bond, further disordered crystal structures, or those with the *R* factor ≥ 0.1 were also discarded. Compounds investigated several times were included only once. If several non identical molecules were present in the cell of several equivalent functional groups in one molecule, only average values were taken for further processing. With all these restrictions the number of retrieved compounds was reduced considerably, up to 121 items. When these were divided into four main groups (oximes, O-alkyloximes, O-acyloximes, and oximate anions) and further subgroups, some of them were too small to estimate average values. Hence, some of the subgroups were again united or even certain discarded compounds taken into account for special purposes. These exceptions are mentioned in the Discussion.

DISCUSSION

Dipole Moments of Oximes and O-Methyloximes

The dipole moments of these compounds have been discussed almost exclusively in terms of the configuration on the C=N bond^{20,27-31}. O-Methyloximes were usually found to be more suitable^{20,28} since oximes associate in nonpolar solutions. Dipole moment measurement was extended to further classes of compounds with the C=NO group and exploited as a method for assigning configuration^{10,32-36}. In spite of many correct assignments, the method is not particularly suitable for this purpose due to several unknown factors¹⁰: *a*) The unknown conformation around the N—O bond must be solved simultaneously^{30,33}. *b*) The N—O bond moment is small and difficult to obtain reliably^{32,33,37}, but just this moment is deciding for the difference between stereoisomers. *c*) The *n*- π conjugation within the C=N—O group modifies the resulting dipole moment and makes additive calculations inaccurate^{10,36}. *d*) In the case of more complex derivatives even the conformation of the adjoining groups is of importance³²⁻³⁵. Nowadays, the configuration is mostly known from the X-ray work. Concerning the conformation around the N—O bond, ample evidence has accumulated that it is *ap* with few exceptions caused by hydrogen bonds³⁸ (see also the next section). It follows that the unknown factors *a*) and *b*) are eliminated and the problem statement can be now reversed: Provided the configuration is known, one can use the experimental dipole moments

to estimate quantitatively the conjugation within the C=NO group. Note that the two applications have different requirements on the precision of experiments. Assignment of configuration means only to decide between two possibilities, minor differences between theory and experiment do not count. On the contrary, when exploring the conjugation, we focus attention just to these differences.

The experimental dipole moments were processed in the same way as in preceding papers^{3,5,8,10}. First the direction of the group moment of the functional group was determined graphically, using the *para* substituents (Fig. 1). For one substituent this means in geometrical terms to construct a triangle given its three sides: the dipole moments of the substituted compound, of the unsubstituted compound, and of the substituent itself. When this procedure is repeated for various substituents, all points should coincide within the experimental accuracy. For compounds *Ila–Ile* good agreement was obtained: point for R=CH₃ in Fig. 1 gives the C=NOCH₃ group moment of 1.5 (all dipole moments in 10⁻³⁰ C m) at an angle of -39° to the C=N bond. A certain deviation of the circle for the unsubstituted compound *Ila* is understandable since its dipole moment is too small and sensitive to the correction for atomic polarization (Table I). Note that the vectors of substituents themselves must be plotted in proper directions (axes *Z* and *E* in Fig. 1). However, just this possibility to introduce substituents from two sides is of advantage as compared

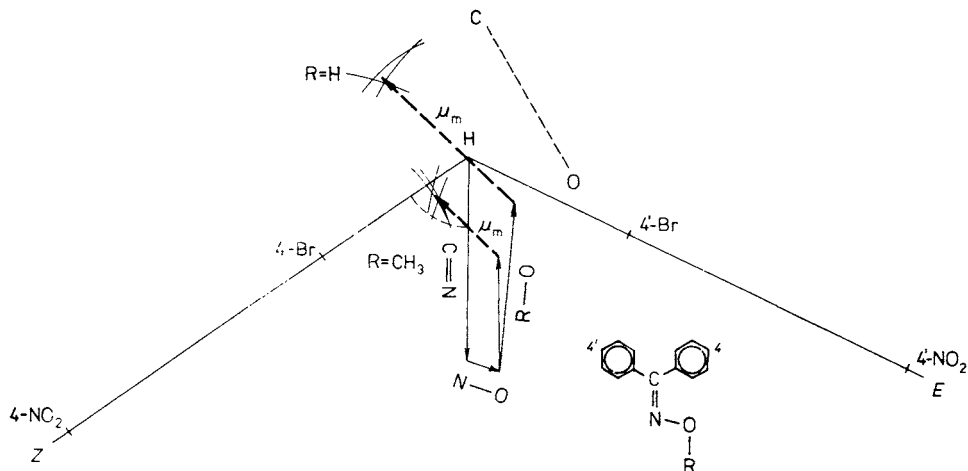


FIG. 1

Determination of the group moments of the C=NOH and C=NOCH₃ groups and their resolution into components. Shown are the component bond moments (light arrows) and the mesomeric moments μ_m expressing the conjugation (broken arrows), the group moments (not shown by arrows) are given by the origin H and end-points coinciding with the end-points of broken arrows

e.g. to esters³, amides⁵, or amidoximes¹⁰. In these compounds substituents could be introduced effectively only in the symmetrical position and two in principle possible solutions were obtained. In our case the solution is unambiguous. On the other hand the choice of proper substitution is in our case somewhat limited since the 4- and 4'-nitro substituents (compounds *IId*, *IIf*) are evidently conjugated and the necessary correction of their group moments is somewhat arbitrary. It follows that the two bromo derivatives, *IIf* and *IIf*, are of decisive importance for the results.

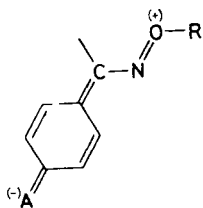
In the next step of the analysis the experimental dipole moment is decomposed vectorially into components. When all the bond moments are plotted in proper directions (light arrows in Fig. 1), their vectorial sum represent the dipole moment expected for the basic nonpolar formula *IV*. The vector difference μ_m toward the experimental value (broken arrow) then represents charge reorganization when proceeding from formula *IV* to formula *V*. The result confirms expectation: The vector obtained is almost exactly in the direction from oxygen to carbon as required by formula *V*. Its angle with the N=C bond is 47°, with the direction O...C 15°. Its absolute value of 2.5 is well outside the possible error and of similar magnitude as in amides⁵, imidates⁹, or amidines⁹. Comparison with N-methylimidates⁹ is particularly interesting: it suggests that conjugation in the systems C=N—OCH₃ and N=C—OCH₃ is equally developed although it involves a negative charge either on carbon or on nitrogen. In a semiquantitative manner one can estimate that in O-methyloximes about 7 per cent of the electron charge is transferred, or that contribution of the mesomeric form *V* is 7 per cent. We are aware that estimations of this kind are both imprecise and questionable in principle.

When the complete procedure was repeated for unsubstituted oximes, *Ia*–*Ic*, a reasonable agreement was obtained in the first step (Fig. 1). The C=NOH group moment is 3.5 at –132° to the C=N bond. Good fit obtained confirms a posteriori that the association of these compounds is not so extensive to prevent the measurement. Note that the concentration in this work was three to ten times lower than in previous studies^{28,29,31}. In addition, our derivatives of benzophenone are bulkier and probably less associated than the derivatives of benzaldehyde³¹. The equilibrium constant of dimerization, as determined for several oximes in benzene¹⁸, would imply a content of less than 5% dimer under the conditions of our measurements, but the compounds investigated were smaller molecules than benzophenone oxime.

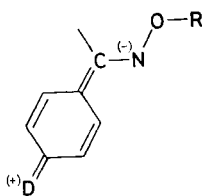
The resulting mesomeric dipole moment of free oximes agrees in its direction exactly with that for oxime methyl ethers (Fig. 1), showing unambiguously electron transfer from oxygen to carbon. However, rather strange is the absolute value of 5.4, corresponding to a transfer of 16 per cent of the electron charge, approximately twice more than in the case of O-methyloximes. In the compounds investigated so far, alkylation on the donor end of the conjugated system enhanced its basicity and hence also the mesomeric dipole moment: in N,N-dimethylamides compared to amides⁵, N,N-dimethylthioamides compared to thioamides⁸, in t-butyl esters

compared to methyl esters³. From analogy or from the dipole moment of formaldoxime, μ_m in oximes was estimated^{30,31} only to 2.7 or more than 3, respectively. In any case we can conclude that the mesomeric dipole moments found here agree very well with the classical representation through the mesomeric formulae $IV \leftrightarrow V$.

The above conclusion is based on comparison of an experimental value with a theoretical construction. Its validity depends rather sensitively on the values of standard bond moments²². Of these the C=N bond moment makes the greatest contribution, but its value seems to be rather well supported, particularly by measurements on aldimines³⁷ and ketimines³⁹. The moments C—O and H—O have been tested on a number of oxygen compounds. Most critical is the N—O bond moment which cannot be determined directly due to lack of suitable model compounds with fixed conformation. The value in use in our work^{9,10,32-36} (1.0) was listed by Smyth as approximate⁴⁰, but agrees with more recent values⁴¹ (1.33 or 1.1). A much higher value (3.33) was calculated on the basis of several more complex compounds³⁷, taking into account their supposed conformations or conformational equilibria. The main reason why we prefer the former value is the relation to other bond moments: even when considering the lone electron pairs it should be certainly smaller than the C—O bond moment (2.47, ref.²²) and of the same order of magnitude as the P—O or S—O moments²². For these reasons we believe that the N—O bond moment should not be greater than 2, but it seems hardly possible to obtain a quite dependable value by conventional means. Note that even a value as high as 3 would not invalidate our results in a qualitative sense. Even a negative value was reported⁴² (−0.67, in the direction from O towards N) but it includes the conjugation and agrees rather roughly with our results.



VI



VII

Another general problem is that the above results have been obtained exclusively on aromatic derivatives and may be affected by the conjugation with the benzene ring. It was concluded from ultraviolet spectra⁴³ and from dipole moments²¹ that the oximino group is operating toward a benzene ring as donor (formula VI). An additional proof is given by the dipole moments of *Id*, *Ie* which are by 1.7 greater than expected from the assumption of non-interacting *para* substituents. (This extra conjugation was corrected for, in order to bring the dipole moments in agreement with those of compounds *Ia*–*Ic*, see Experimental – Calculations.). An interaction

in the opposite sense would come into consideration only if the phenyl ring bore a donor substituent (VII). A contribution from the formula VI to the structure of compounds I and II would result in a slightly overestimated value of μ_m while its direction would not be perceptibly changed. Attempts to separate the two kinds of mesomeric moments (conjugation with the benzene ring and conjugation within the functional group itself) were made e.g. in the case of amides^{5,37}. They seem somewhat oversophisticated since the first term is rather small. In the case of amidines⁹ and amidoximes¹⁰ we were unable to obtain any finite value, a possible explanation⁹ could be that the bond moment C=N itself has been derived on aromatic compounds. In the case of oximes the first term was estimated³⁰ to 0.7 but direct comparison of dipole moments of benzaldoxime and acetaldoxime⁴⁴ does not provide a convincing support. There is a larger difference between the dipole moments of acetone O-methyloxime and acetophenone O-methyloxime²¹ but even these values are too low to be completely reliable (cf. the recalculation in Table I, footnote d). We conclude that our values of mesomeric moments within the oximino group might be but slightly overestimated due to the presence of aromatic rings in our model compounds. The main results are not affected by this inaccuracy.

Bond Lengths and Angles

An independent quantitative measure of the conjugation within the oximino group can be obtained from geometrical parameters. Formula V requires lengthening of the C=N and shortening of the N—O bond as compared to the standard values expected for formula IV. Some double-bond character of the N—O bond should be also manifested in the planar arrangement of the C=NOX group. The effect on bond angles should be probably less evident, except possible widening of the N—O—C angle in the case of alkyl oximes. The above predictions can be verified either on the mean values of geometrical parameters or on their mutual dependence.

The mean geometry of the oximino group was examined separately on several groups of related structures. When no differences were found, some subgroups were again united. The results listed in Table II reveal minute differences between oximes of aldehydes and ketones, aliphatic and aromatic, or their O-alkyl derivatives. There is also a reasonable agreement with the gas phase data for formaldoxime⁴⁵. According to two conventional scales^{48,50} the bond order of the C=N bond would be estimated to 1.8–1.9 or to 1.9–2. Such figures are very inaccurate and formal since there is no agreement in the standard bond lengths of pure C=N and C—N bonds^{48–50}. The bond order of N—O would be⁵⁰ 1–1.03.

When comparing the extent of conjugation in individual structures, including anions and derivatives with polar substituents, we expect that the longer the C=N bond the shorter the N—O bond. For instance, in aromatic derivatives VI (with a phenyl ring either unsubstituted or substituted with an acceptor group) the C=N

bond should be longer and N—O shorter as compared to aliphatic derivatives. This effect is confirmed in Table II for ketoximes just at the limits of the attainable accuracy, but it escaped detection in the case of aldoximes. When we wanted to find such a regularity by plotting the bond lengths C=N and N—O against each other, we obtained always great scatter due to several disturbing effects. For instance, a conjugation with the benzene ring and a donor substituent may contribute to lengthening the C=N bond without affecting N—O (formula VII). More important are certainly purely crystallographic effects due to incomplete compensation of thermal motions. They tend to affect all bond lengths in the same sense⁵¹ producing a just opposite trend to that due to conjugation. Also the structures with strong hydrogen bonds gave sometimes quite irregular bond lengths. Relatively best results were obtained for the subgroup of O-alkyloximes which is more homogeneous than the others, but Fig. 2 reveals nothing more than a trend. However, a very significant relationship was observed for oximate anions the structure of which can vary from VIII to IX, representing O-anion and C-anion, respectively. The variation in Fig. 2 is so great that even certain less accurate data could be included (with $R > 0.1$), without disturbing the relationship. Some points are almost approaching the limiting values, corresponding to a single bond C—N and double bond N=O

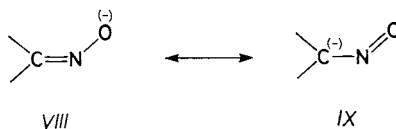
TABLE II

Mean geometrical parameters of the oximino group from X-ray data

Compound	Bond length, pm		Bond or dihedral angle, °			Number of compounds
	C=N	N—O	CNO	NOC	τ CNOC	
Aldoximes ^a	127	139	112	—	—	39
Aliphatic ketoximes	128	141	113	—	—	60
Aromatic ketoximes	130	139	~113	—	—	13
O-Alkyloximes ^b	128	141	111	109	176	27
O-Acyloximes ^c	127	141	112	112	165	4
Oximate anions ^d	134	130	117	—	—	5
Formaldoxime (gas) ^{4,5}	127.6	140.8	110.2	(102.7) ^e	(180) ^e	1
Formaldoxime (4-31G) ^{4,6}	125.4	142.0	111.4	(106.3) ^e	(180) ^e	—
Formaldoxime (6-31G**) ^{4,7}	124.9	136.7	112.0	(104.5) ^e	(180) ^e	—

^a No difference between aliphatic and aromatic aldoximes; ^b mainly aliphatic and aromatic ketoximes, the number of compounds does not allow reliable evaluation in subgroups; ^c essentially aromatic ketoximes; ^d only α -substituted derivatives (keto, cyano), but α -dioximes discarded due to strongly deviating values; ^e concerns the angles NOH and CNOH, respectively.

which, however, are given differently in the literature.^{49,50} The mean values for oximate anions as given in Table II could be calculated only for a subgroup of five compounds, after eliminating derivatives of α -diketones and those containing heavy metals. The mean bond length $C=N$ would correspond^{48,50} to the bond order of 1.4. The classical resonance theory predicts that the conjugation $VIII \leftrightarrow IX$ is much stronger than $IV \leftrightarrow V$ due to the destabilizing effect of two charges in V .



Certain double-bond character of the N—O bond is evidenced very clearly by the planarity of the C=NOR group. Most remarkably, this group is almost invariantly in the ap conformation. This applies to O-alkyloximes and O-acyloximes both in solution³⁸ and in the crystalline state. Among twenty-seven examples of Table II there is no exception as far as the conformation is concerned, and the deviations from planarity are negligible. Additional six examples may be found in the compounds previously eliminated from the final set. Unsubstituted simple oximes are in the ap conformation both in the gas phase⁴⁵ and in solution³⁸, in qualitative agreement with *ab initio* calculations^{46,47} which predict this form to be more stable by 102 or 23 kJ mol⁻¹, respectively. More complex oximes, containing another functional group, may appear in the sp conformation if it is stabilized by a hydrogen

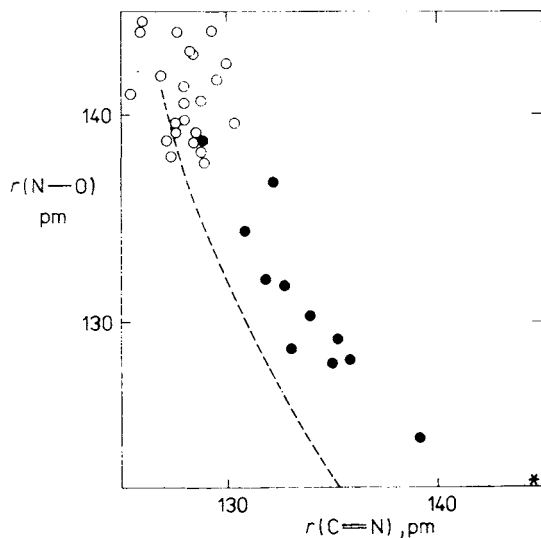


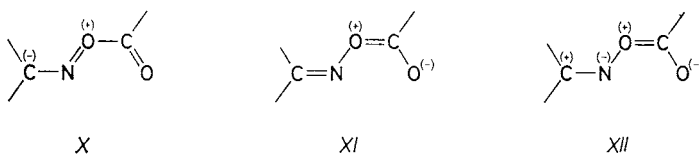
FIG. 2

Scatter-plot of the bond lengths $C=N$ and $N-O$ in some oximino derivatives: \circ O-alkyloximes, \bullet oximates with different substitution and different counterions, broken line — standard bond lengths for decreasing $C=N$ and increasing $N-O$ bond order⁵⁰, * limiting values for the standard $C-N$ and $N=O$ bond lengths⁴⁹

bond³⁸. On the other hand, the *ap* conformation was found even in amidoximes¹⁰ and various hydroximoyl derivatives³⁸ and seems to be one of the most general features in the stereochemistry of functional groups.

O-Acyloximes

This class of compounds will be discussed separately since the results are quite different. A priori, the mesomeric formula *X* is anticipated to have less weight, than *V* in the case of free oximes since it is destabilized by partial positive charges on adjoining atoms. Formula *XI*, expressing the conjugation present in all esters, may acquire somewhat more weight in acyloximes for just opposite reasons. This is expressed formally by the somewhat oversophisticated formula *XII*.



The experimental dipole moments of *IIIa–IIIc* were processed in Fig. 3 in the same way as described above in detail (Fig. 1). The $\text{C}=\text{NOCOCOCH}_3$ group moment (12.4, -24° to the $\text{C}=\text{N}$ bond) is determined reliably: there are only three compounds but the fit is very good. For the next step – decomposition into bond moments – the steric arrangement must be known. The configuration of *IIIb*, *IIIc* is certain due to the relationship to the parent oximes *Ib*, *Ic*. The conformations

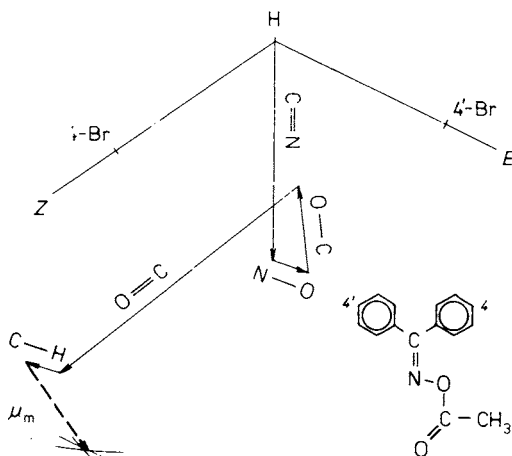


FIG. 3

Determination of the group moment of the $\text{C}=\text{NOCOCOCH}_3$ group in oxime acetates and its resolution into components. The same symbols are used as in Fig. 1

around the N—O and C—O bonds were determined for O-acyloximes generally³⁵ and are confirmed also by the results in the crystalline phase without exception (Table II). The *ap* conformation on N—O accords with all other oxime derivatives (Table II and the pertinent discussion), while the *sp* conformation on C—O is typical for esters¹ and all derivatives with a COO grouping.³⁸ With the known geometry one gets the mesomeric dipole moment $\mu_m = 2.3$ (38° to the C=N bond). While the absolute value is well outside the experimental error, the direction, approximately from C to O, seems rather strange and is just opposite to free oximes. In terms of conventional mesomeric formulae this direction could be compatible with some contribution of *XII*, but it is just opposite to that postulated by *X*.

A similar, but less accurate result may be obtained from our previous measurements on O-benzoyloximes³⁵. From the dipole moments of O-benzoylbenzaldoxime, O-benzoyl-4-chlorobenzaldoxime, and O-(4-chlorobenzoyl)benzaldoxime³⁵ we obtained the mesomeric moment of 1.2 (32° to the C=N bond). Due to a much worse fit, this value approaches the possible experimental uncertainty but the direction is the same as above. Note that the same experimental dipole moments were used previously³⁵ to determine steric arrangement of O-acyloximes, assuming that the electron distribution (i.e. bond moments) is known. The two approaches and their relationship can be shown very well just on this example. In Fig. 4 the squared dipole moments of *IIIb* and *IIIc* are plotted against each other to compare the calculated and experimental values according to our graphical method⁵². Determining the steric arrangement means to decide in favour of the right hypothesis (point 1) against the alternatives (points 2–4), small disagreement with experiment can be

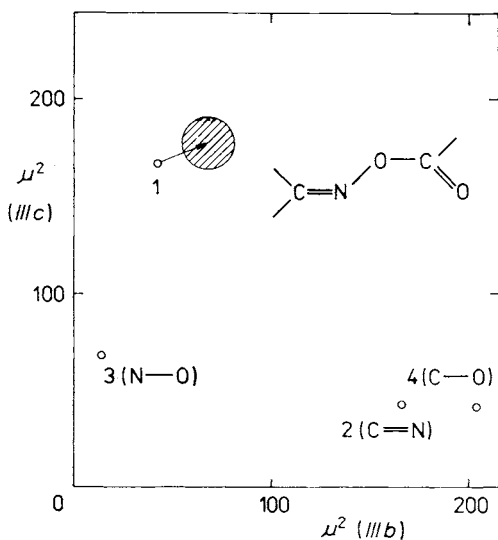


FIG. 4

Interpretation of the dipole moments of O-acyloximes in terms of stereochemistry or of the electron distribution: *x*-axis (*Z*)-4-bromobenzophenone O-acetyloxime (*IIIb*), *y*-axis (*E*)-4-bromobenzophenone O-acetyloxime (*IIIc*), 1 calculated from bond moments for the correct steric arrangement, 2–4 calculated for the other alternatives (with wrong configuration on C=N, wrong conformation on N—O, and wrong conformation on C—O, respectively), experimental point shadowed

neglected. The second task, determining the electron distribution on the functional group, means to state and interpret just this small disagreement. In some favourable cases only, the two problems can be solved on the basis of the same data. However, when the differences between theory and experiment became comparable to the differences between alternative hypotheses, a simple solution would be impossible and it would be necessary to determine the steric arrangement from another source.

The evidence from bond lengths of O-acyloximes is not at variance with dipole moments but is not much telling in itself. The C=N and N—O bond lengths (Table II) can be interpreted as a weakened conjugation compared to free aromatic ketoximes, but they do not point out to any different kind of electron distribution. We conclude that the electron distribution in O-acyloximes reveals some interaction between individual bonds but it can be hardly described in terms of conventional mesomeric formulae.

Our thanks belong to Mrs P. Marešová for skilful preparative work, Mrs M. Kuthanová for measuring permittivities and densities, Dr P. Fiedler for infrared spectra, and Dr B. Tinant for making available the Cambridge Structural Database.

REFERENCES

1. Schweizer W. B., Dunitz J. D.: *Helv. Chim. Acta* **65**, 1547 (1982).
2. Varetto E. L., Aymonino P. J.: *Spectrochim. Acta*, A **27**, 183 (1971).
3. Plesničar B., Exner O.: *Collect. Czech. Chem. Commun.* **46**, 490 (1981).
4. Smolíková J., Bláha K.: *Chem. Listy* **69**, 1009 (1975).
5. Exner O., Papoušková Z.: *Collect. Czech. Chem. Commun.* **45**, 2410 (1980).
6. Chakrabarti P., Dunitz J. D.: *Helv. Chim. Acta* **65**, 1555 (1982).
7. Walter W., Schaumann E.: *Chem. Ber.* **104**, 3361 (1971).
8. Exner O., Waisser K.: *Collect. Czech. Chem. Commun.* **47**, 828 (1982).
9. Exner O., Buděšínský M., Hnyk D., Všetečka V., Raczynska E. D.: *J. Mol. Struct.*, in press.
10. Exner O., Motekov N.: *Collect. Czech. Chem. Commun.* **43**, 2740 (1978); **47**, 814 (1982).
11. Gilli G., Bertolasi V., Bellucci F., Ferretti V.: *J. Am. Chem. Soc.* **108**, 2420 (1986).
12. Allen F. H., Bellard S., Brice M. D., Cartwright B. A., Doubleday A., Higgs H., Hummelink T., Hummelink-Peters B. G., Kennard O., Motherwell W. D. S., Rogers J. R., Watson D. G.: *Acta Crystallogr.*, B **35**, 2331 (1979).
13. Semper L., Lichtenstadt L.: *Ber. Dtsch. Chem. Ges.* **51**, 928 (1918).
14. Meisenheimer J., Mahler E.: *Justus Liebigs Ann. Chem.* **508**, 185 (1934).
15. Schäfer A.: *Justus Liebigs Ann. Chem.* **264**, 152 (1891).
16. Johnson R. W., Golenternek J.: *J. Am. Chem. Soc.* **59**, 365 (1937).
17. Halverstadt I. F., Kumler W. D.: *J. Am. Chem. Soc.* **64**, 2988 (1942).
18. Reiser A.: *Chem. Listy* **52**, 397 (1958).
19. Vogel A. I.: *J. Chem. Soc.* **1948**, 1833.
20. Taylor T. W. J., Sutton L. E.: *J. Chem. Soc.* **1933**, 63.
21. Reiser A., Jehlička V., Dvořák K.: *Collect. Czech. Chem. Commun.* **16**, 13 (1951).
22. Exner O.: *Dipole Moments in Organic Chemistry*, p. 33. Thieme, Stuttgart 1975.
23. McCullough J. D., Paul I. C., Curtin D. Y.: *J. Am. Chem. Soc.* **94**, 883 (1972).
24. Yoshida K., Sakaizumi T., Ohashi O., Yamaguchi I.: *Bull. Chem. Soc. Jpn.* **59**, 1620 (1986).

25. Cromer R. D. T., Ryan R. R., Wilbur D. S.: *Acta Crystallogr.*, C 40, 301 (1984).
26. Jerslev B., Lerche J., Larsen I. K.: *Acta Crystallogr.*, C 39, 1134 (1983).
27. Parsons G. S., Porter C. W.: *J. Am. Chem. Soc.* 55, 4745 (1933).
28. Calderbank K. E., Le Fèvre R. J. W.: *J. Chem. Soc.* 1949, 1462.
29. Le Fèvre R. J. W., Pierens R. K., Steel K. D.: *Aust. J. Chem.* 19, 1769 (1966).
30. Barassin J., Lumbroso H.: *Bull. Soc. Chim. Fr.* 1961, 492.
31. Barassin J., Armand J., Lumbroso H.: *Bull. Soc. Chim. Fr.* 1969, 3409.
32. Exner O., Jehlička V., Reiser A.: *Collect. Czech. Chem. Commun.* 24, 3207 (1959).
33. Exner O.: *Collect. Czech. Chem. Commun.* 30, 652 (1965).
34. Exner O., Benn M. H., Willis F.: *Can. J. Chem.* 46, 1873 (1968).
35. Exner O., Hollerová J., Jehlička V.: *Collect. Czech. Chem. Commun.* 32, 2096 (1967).
36. Smolíková J., Exner O., Barbaro G., Macciantelli D., Dondoni A.: *J. Chem. Soc., Perkin Trans. 2*, 1980, 1051.
37. H. Lumbroso, G. Pifferi: *Bull. Soc. Chim. Fr.* 1969, 3401.
38. Exner O. in the book: *The Chemistry of Double-Bonded Functional Groups* (S. Patai, Ed.), p. 1. Interscience, London, 1977.
39. Exner O., Jehlička V., Mahaffy R., Boyd D. R.: *Collect. Czech. Chem. Commun.* 42, 1636 (1977).
40. Smyth C. P.: *Dielectric Behavior and Structure*, p. 244. McGraw-Hill, New York 1955.
41. Vereshchagin A. N., Artsybasheva Yu. P., Kamalyutdinova A. M., Ioffe B. V.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1978, 470.
42. Basu S., Cumper C. W. N.: *J. Chem. Soc., Perkin Trans. 2*, 1974, 325.
43. Exner O.: *Collect. Czech. Chem. Commun.* 21, 1500 (1956).
44. McClellan A. L.: *Tables of Experimental Dipole Moments*, Vols 1 and 2. Freeman, San Francisco 1963 and Raha Enterprises, El Cerrito 1974.
45. Harmony M. D., Laurie V. W., Kuczkowski R. L., Schwendeman R. H., Ramsay D. A., Lovas F. J., Lafferty W. J., Maki A. G.: *J. Phys. Chem. Ref. Data* 8, 619 (1979).
46. Adeney P. D., Bouma W. J., Radom L., Rodwell W. R.: *J. Am. Chem. Soc.* 102, 4069 (1980).
47. Armstrong D. R., Walker G. T.: *J. Mol. Struct.* 149, 369 (1987).
48. Burke-Laing M., Laing H.: *Acta Crystallogr.*, B 27, 1635 (1971).
49. Stull D. R., Westrum E. F., Sinke G. C.: *The Chemical Thermodynamics of Organic Compounds*, p. 96. Wiley, New York 1969.
50. Allmann R. in the book: *The Chemistry of Hydrazo, Azo and Azoxy Groups* (S. Patai Ed.), p. 23. Wiley, London 1975.
51. Domenicano A., Murray-Rust P., Vaciano A.: *Acta Crystallogr.*, B 39, 457 (1983).
52. Exner O., Jehlička V.: *Collect. Czech. Chem. Commun.* 30, 639 (1965).

Translated by the author (O.E.).