

ELECTRON DISTRIBUTION IN THE MOLECULE OF NITRONES*

OTTO EXNER

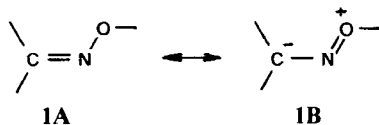
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Vector analysis of dipole moments of two series of nitrones revealed a mesomeric dipole moment compatible with a relatively great contribution of a zwitterionic structure and possibly some contribution from a hypervalent structure. The latter was also suggested from a detailed comparison of bond lengths among several classes of compounds, involving the CNO grouping. Since both the C=N and N-O bonds seem to possess an appreciable double bond character, it is suggested that the N atom might be allocated more than eight valence electrons.

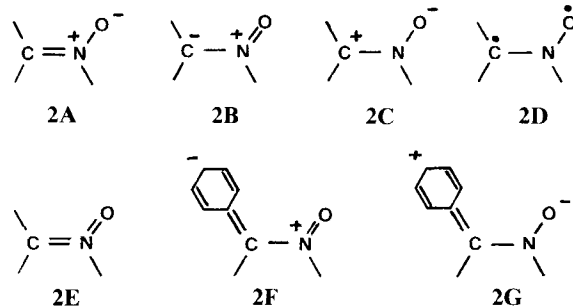
Conjugation of a double bond with a lone electron pair has been investigated mostly on the systems X=C-Y, e.g. esters,¹⁻³ amides,⁴⁻⁶ thioamides,⁷ amidines^{8,9} and amidoximes.¹⁰ The most important experimental proofs established were bond lengths^{2,4,5,8,9} of the formally double bond C=X and formally single bond C-Y, the rotational barrier about the latter⁵ resulting in a fixed conformation^{1,2,5} and stretching vibrations³ of these two bonds. In previous papers^{6-8,10} we followed another line of evidence based on dipole moments. In this approach the vector difference μ_m (sometimes called the mesomeric dipole moment) is obtained from the experimental dipole moment and that calculated for the simple classical formula. It is considered to be a symbolic representation of an electron redistribution due to conjugation and correlated with possible polar mesomeric formula:

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

In the previous paper in this series¹¹ we extended the above reasoning to systems X=N-Y with nitrogen as the central atom. Analysis of the dipole moments of oximes revealed a mesomeric contribution μ_m , oriented approximately from O towards C, in agreement with the electron transfer shown in formula **1B**, contributing ca 10%. Bond lengths obtained from the Cambridge Structural Database¹² (CSD) showed a decreased C=N bond order and increased N-O bond order.

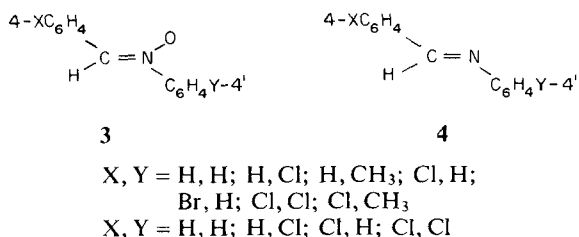


Since all previous investigations^{6-8,10,11} afforded reasonable results, we felt ourselves justified in extending them to further classes of compounds, possibly more problematic. This paper deals with imine N-oxides (nitrones) (**2**) which possess the same conjugated system as oximes but differ by the presence of formula charges even in the basic formula **2A**. Of the other formulae,¹³⁻¹⁶ **2B** was generally considered to be the most important¹⁶ or even the only one of importance.¹³ Exceptionally, **2C** (with an electron sextet on C) was preferred since it expresses the similarity to ketones.¹⁴ According to the presence of formal charges, one would expect **2B** to contribute more to the actual structure than does **1B** in the case of oximes. The 'diradical' formula **2D** was introduced recently on the basis of quantum chemical calculations,¹⁷ although it violates the classical condition for resonance (the same number of unpaired electrons¹⁸). The hypervalent formula **2E** was rejected for nitrones, although a similar formulation was suggested for nitro compounds.¹⁷



* Part XII in the series Oxime Derivatives, simultaneously Part XI in the series Mesomeric Dipole Moments. For preceding parts, see Refs 11 and 49.

In the case of aromatic derivatives, one must still consider conjugation with the benzene ring. The weights of the two structures **2F** and **2G** may change according to the substitution on the benzene ring.¹⁹ From electronic spectra, **2F** was preferred in the case of unsubstituted phenyl,²⁰ this referring mainly to the excited state. In the ground state, both **2F** and **2G** were found to be necessary to interpret the dipole moments.^{19,21} For the dissociation constants, conjugation as in **2G** was important, whereas **2F** was not important even in the presence of a *para*-nitro group.²²



Analysis of dipole moments may be based on several sets of good experimental data.^{19,21,23} Those on substituted *N*-benzylideneaniline *N*-oxides (**3**) may be immediately compared with substituted *N*-benzylideneanilines²³ (**4**), which have the same configuration (the two phenyl groups *trans*) and similar bond angles.^{24,25} We determined first the direction of the dipole moment of **3** by triangulation (Figure 1) as in our previous study.¹¹ The bond angles C—C=N = 123°, C=N—C = 120° and C=N—O = 123° were adopted from a heterocyclic *N*-phenyl nitrone,²⁴ the bond and group moments of the substituents were standard values.²⁶ The resulting vector of 11.3 (all dipole moments in 10⁻³⁰ C m) was situated at an angle of 52° to the C=N bond. In the next step, it was simulated by the group moment of **4** plus the contribution of the N⁺—O⁻ bond as in **2A**. The direction of the group moment of **4** was determined in the same way as above with angles²⁵ of C—C=N = 122° and C=N—C = 120° and a resulting vector of 5.0 at an angle of 12° to the C=N bond. The N⁺—O⁻ bond moment was estimated to be 13.33 from the difference in dipole moments²⁷ of trimethylamine *N*-oxide and trimethylamine, thus corresponding to replacing a lone electron pair on N by a single bonded O atom (more recent measurements,²⁸ but in different solvents, yielded 14.27). According to equation (1) we obtained the mesomeric dipole moment $\mu_m = 6.2$, which should express the charge redistribution when proceeding from the formula **2A** to the actual structure. Its direction is 211° to the C=N bond, i.e. 3° to the direction from O to C.

Further, the above result is not changed when the C=N and C—N standard bond moments²⁶ are used instead of the experimental dipole moments of **4** (Figure 1), or if another set of experimental data¹⁹ is chosen for

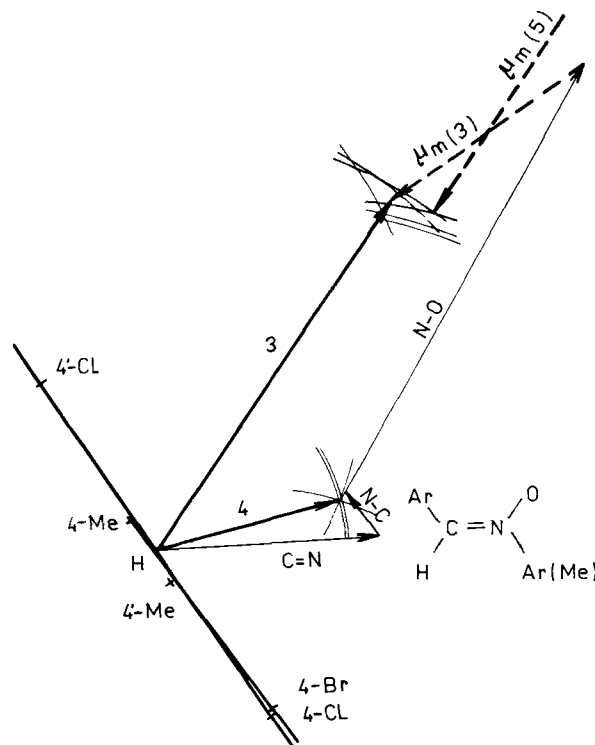
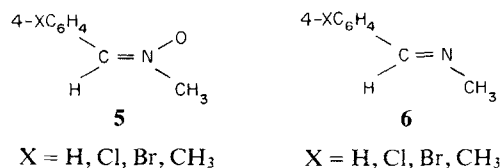


Figure 1. Analysis of dipole moments of nitrones **3** and **5** and reference compounds **4** and **6**. Heavy arrows, group moments of the functional groups of **3** and **4**; light arrows, bond moments; broken arrows, mesomeric dipole moments

3 (not shown). A similar result is obtained also for *N*-benzylidenemethylamine *N*-oxides (**5**). The experimental data²¹ were processed using the bond angles measured on 4-chloro derivative:²⁹ C—C=N = 125°, C=N—C = 119°, C=N—O = 125°. The resulting group moment of 11.7 (47° to the C=N bond) is lower than calculated by semi-empirical methods.^{21,30} The dipole moments³¹ of reference compounds (**6**) were processed with the same angles: group moment 4.8 (31° to the C=N bond). Finally, μ_m of the same absolute value was obtained as for **3** (6.2) but differing in its direction: 233° to the C=N bond. Only this vector is shown in Figure 1. The calculation is slightly less dependable than for **3** owing to the smaller number of compounds.



The results for the dipole moment analysis were thus represented by either of the two vectors, which differ

slightly (Figure 1). Whereas for compounds **3** the vector would be compatible with a contribution from **2B** (approximately 17%), for **5** it would suggest some contributions from both **2B** and **2C**, or alternatively it could be explained by either **2D** or **2E** (but a 30% contribution would be necessary). We are aware that these vectors are difference values between incompatible quantities [equation (1)]: the real dipole moment of an existing molecule and an approximate dipole moment anticipated for the classical formula. The most important imperfection of the bond moment scheme is probably the neglect of the moments of lone electron pairs,³² which are only partly incorporated into the bond moments.¹¹ However, there is ample evidence³³ that this scheme works for non-adjacent and non-conjugated bonds; see also the good fit in Figure 1 for compounds **3** and **4** with variable substituents. Even the accuracy of the scheme was approximately estimated:³⁴ our values of μ_m exceed it at least 10-fold. Moments of lone electron pairs are actually not involved in our calculations since the situation is the same in nitrones (with respect to alkylideneamines) as in amine *N*-oxides (with respect to amines). Therefore, we believe that the values of μ_m have real significance and represent the difference in electron distribution between these two classes of compounds. In other words, they show the difference between the real molecule and its classical structure, and hence they may be interpreted in terms of mesomeric formulae. Of course, this interpretation may become ambiguous when several formulae are taken into consideration.

In order to obtain additional information we carried out a CSD¹² search with the same restrictions as

previously.¹¹ Eleven true nitrones were retrieved.^{24,29,35-42} The mean geometric parameters differ slightly in aliphatic and aromatic derivatives as far as substitution on C is concerned, but there was no difference between *N*-alkyl and *N*-aryl derivatives except for the C—N bond length (Table 1). Aliphatic and aromatic derivatives are distinguished more clearly in the plot of the C=N and N—O bond lengths against each other (Figure 2). Whereas the experimental values are similar, the calculated values^{17,43} disagree both with the experiments and with each other. In the plot a certain reversed relationship between the two bond lengths can be traced. However, most striking is the shortening of the N—O bond in comparison with oximes,¹¹ which is not accompanied by corresponding lengthening of the C=N bond. This fact is more clearly evident from the relationship to all compounds involving a C=N—O grouping (Figure 2). The double bond character of N—O increases simultaneously with the decrease in C=N and this trend is roughly followed by the theoretical bond lengths.^{44,45} Nitrones deviate from both the trend of experimental values and theoretical curve. One must accept that their N—O bond has achieved some double bond character while this character of the C=N bond was retained, as pictured in the hypervalent structure **2E**. This formula was already rejected as an inappropriate description of the real structure,¹⁷ but our more detailed comparison suggests its contribution. This conclusion agrees also with the CNO angle of nitrones, which is abnormally widened compared with both oximes and aromatic nitroso compounds (113° and 114°, respectively). Shortening of the N—O bond cannot be caused by electrostatic attraction

Table 1. Mean geometric parameters of nitrones

Parameter	Aliphatic nitrones	Aromatic nitrones	Calculated for CH ₂ NHO	
			4-31G	UHF/6-31G
Bond lengths (Å):				
C=N	1.29	1.30	1.263	1.334
N—O	1.28	1.29	1.334	1.245
C—N	1.51	1.50 (1.45) ^a	—	—
Bond angles:				
C=N—O	124	125	126.2	125.4
C=N—C	121	121	(119.3) ^b	—
Dihedral angles:				
τ^c	—	15, 21, 32(58)	—	—
φ^d	—	35, 68, 88	—	—
References	35–39	24, 29, 40–42	43	17

^a In *N*-phenyl derivatives.

^b Angle C=N—H.

^c Angle of the C-phenyl group plane with the CNO plane.

^d Angle of the *N*-phenyl group plane with the CNO plane.

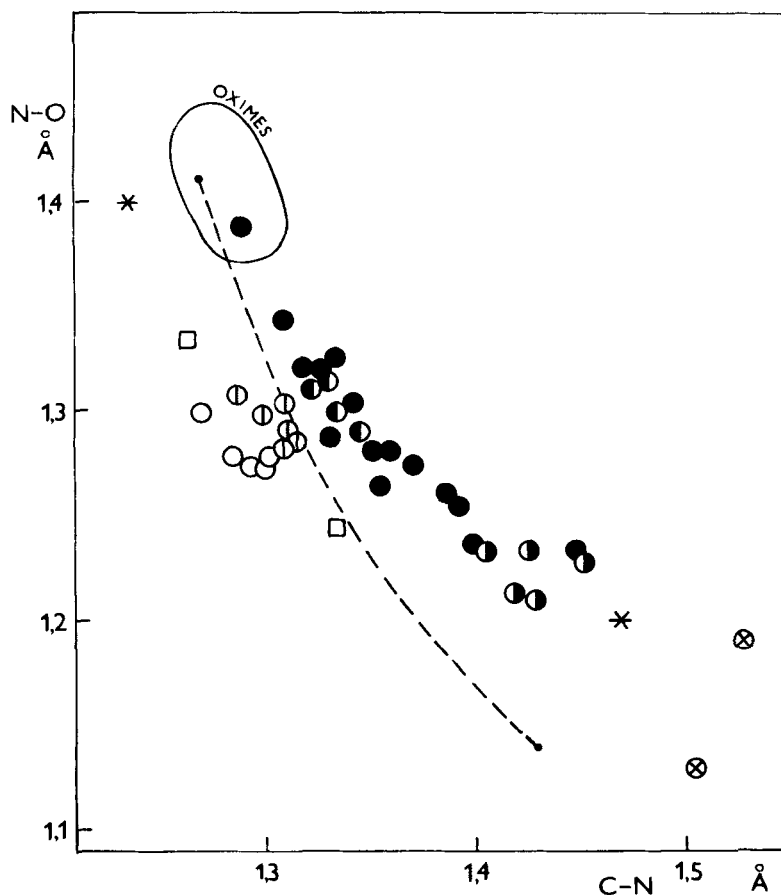


Figure 2. Dependence of the C-N and N-O bond lengths in compounds involving the $C=N\cdots O$ group. \circ , Aliphatic nitrones; \odot , aromatic nitrones; \square , calculated for $CH_2=NH-O$; \bullet , anions (oximates and nitrosolates); \ominus , aromatic nitroso compounds; $\omin�$, olefinic nitroso compounds; \otimes , aliphatic *gem*-chloronitroso compounds; *, standard values for pure single and double bonds.⁴⁴ Broken line, standard values⁴⁵ for simultaneously decreasing C=N bond order and increasing N-O bond order

since this bond is normal in trimethylamine *N*-oxide⁴⁶ (1.404 Å). An additional piece of evidence comes from the IR spectra, although we were not able to construct a graph as in Figure 2 for the stretching frequencies C-N and N-O: the end points are well defined⁴⁷ [for $CH_2=NOH$, $\nu(C=N) = 1642$, $\nu(N-O) = 888\text{ cm}^{-1}$; for CH_3NO , $\nu(C-N) = 842$, $\nu(N=O) = 1566\text{ cm}^{-1}$], but there are no certain points between. Even so, it is evident that the N-O stretching frequency of nitrones¹³ is strongly enhanced (1155–1280 cm^{-1}) compared with oximes, while C=N is little affected (1565–1610 cm^{-1}).

The conjugation with the benzene ring as expressed by the formula **2F** or **2G** can be estimated according to the conformation of the aromatic nitrones. The dihedral angles τ in Table 1 are high and hardly compatible with

strong conjugation. Still weaker (almost absent) is the conjugation of the *N*-phenyl ring (dihedral angle φ).

In conclusion, the structure of nitrones cannot be described adequately either by a single conventional formula or by resonance of just two structures. In addition to the basic formula **2A**, there is certainly a significant contribution^{17,48} from the closed-shell zwitterionic structure **2B**, greater than, e.g., in oximes. In addition, we have suggested some contribution of the hypervalent structure **2E**. The admissibility of such a structure depends on what exactly is meant by the double bond symbol. If it should express only observable quantities (such as bond length, stretching frequency, bond energy) and a high electron density, a contribution of formula **2E** can be seriously taken into consideration. It means that the N atom allocates more than its normal comple-

ment of valence electrons.¹⁷ Problems arise if the double bond symbol should be connected with orbitals of a certain type. Since we are of the opinion that the concept of a double bond is simpler and more general than a particular quantum chemical description, we consider the formula **2E** to be admissible in principle. On the other hand, we have not found any experimental support for the open-shell zwitterionic structure **2C** or the 'diradical' structure **2D**, the latter advanced from unrestricted Hartree-Fock¹⁷ or VB 4-31G⁴⁸ calculations. These two structures would in fact require more single character of both the C-N and N-O bonds, the opposite of what has been found.

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