

DIPOLE MOMENTS OF HYDROXAMIC ACIDS AND N,O-DIACYLHYDROXYLAMINES*

Aleksandr I. ARTEMENKO^a, Inga V. TIKUNOVA^a, Evgenii K. ANUFRIEV^a,
Václav JEHLIČKA^b and Otto EXNER^c

^a Department of Organic and Analytical Chemistry,

Belgorod Technological Institute of Building Materials, Belgorod, 308 600 U.S.S.R.,

^b Department of Physical Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6 and

^c Institute of Organic Chemistry and Biochemistry,

Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia

Received July 27th, 1980

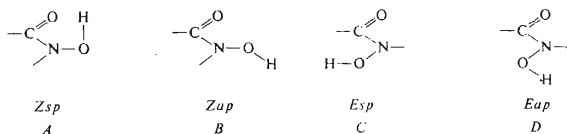
Dipole moments of nine aromatic hydroxamic acids *Ia—Ii* and of nine N,O-diacylhydroxylamines *Ila—IIIi* were measured in dioxan solution. The results for hydroxamic acids are interpreted in terms of the *Zsp* conformation (*A*) with an intramolecular hydrogen bond contributing considerably to the total dipole moment; the conformation is similar to that of peroxy acids but the hydrogen bond is weaker. A similar interpretation is possible for N-phenylbenzhydroxamic acids using the dipole moment data from the literature. New data for N,O-diacylhydroxylamine agree with the previously established nonplanar conformation (*L*). If axially unsymmetrical aryl groups are present, they take one of the two coplanar positions independently of the other moiety; hence the effective dipole moments do not differ too much from the assumption of a statistical population of all conformations.

Within a broader programme^{1,2} devoted to synthesis and physical properties of hydroxamic acids *I* and their O-acyl derivatives *II*, we have proceeded to reinvestigating and extending the dipole moment data. Previous studies on hydroxamic acids^{3,4} need a reexamination for several reasons. The experimental data are scanty and the original value for benzhydroxamic acid³ was in error⁴. This is why even the interpretations in terms of conformation were inexact: Either a nonplanar conformation³ intermediate between *B* and *A*, or the hydrogen bonded form *A* with strong librations around the N—O bond⁴ were preferred. However, the mesomeric moment within the O=C—N grouping was not properly accounted for in the calculations, and a possible moment originating in the hydrogen bond was completely neglected. Therefore, the agreement of experimental and calculated values was only fair^{3,4}. We are now able to resume these calculations since the mesomeric moment has been studied in more detail on amides and N,N-dimethylamides⁵,

* Part XXIII in the series Acyl Derivatives of Hydroxylamine; Part XXII: J. Chem. Soc. Perkin Trans. 2, 1980, 1051.

RESULTS AND DISCUSSION

The dipole moments of hydroxamic acids (Table I) can firstly serve to determine the group moment of the —CONHOH grouping by means of axially symmetrical substituents with known moments. In geometrical terms it means to construe a triangle given its three sides, this is done for each substituent separately. We obtained a good coincidence with substituents H, 4-Cl, 4-Br, 4-NO₂ (compounds *Ia–Id*), the resulting vector amounted to 12.1 at an angle of 67° to the C₍₁₁₎—C bond. (All the dipole moment values are given in units 10⁻³⁰ C m.). The remaining derivatives *Ie, Ih, Ii* are less important for determining the group moment since the substituent dipoles are not known with a sufficient reliability. In addition, the unsymmetrical substitution in *Ie* and *Ii* gives rise to two conformations the population of which must be estimated. On the whole, the compounds *Ie, Ih, Ii* are only in rough agreement with the above group moment.



In Fig. 1 the experimental moment of the CONHOH group is compared with those anticipated for the individual conformations. Like in previous studies^{3,4} we took into consideration first only planar forms *A–D* which differ in the conformation around the partial double bond C—N (*Z* or *E*) and in the conformation around the N—O bond (*sp* or *ap*). In the calculations according to the bond moment scheme¹⁵ two mesomeric moments were included: one (m_1) representing the conjugation C₆H₅—CONH, the other (m_2) the conjugation N—CO within the functional group. The same value of m_1 (0.83) was used as previously^{3,5}; it is substantiated by comparison⁵ of aliphatic and aromatic amides. For final conclusions this small value is not significant. Much more critical is the mesomeric moment m_2 since it is by far not constant in differently substituted amides⁵. Regarding the electron attracting substitution on N, we used tentatively the value $m_2 = 1$, lower than in unsubstituted amides⁵ and much lower than in N,N-dimethylamides⁵. Inspection of Fig. 1 reveals a marked divergence between the experimental point and all the calculated points, which cannot be remedied by modifying the value of m_2 . There is only one solution *viz.* the *Zsp*-conformation (*A*) with a significant supplementary moment (h) arising from the intramolecular hydrogen bond.

In two similar molecules with a five-membered chelate ring, significant but variable contributions of the hydrogen bond to the gross dipole moment were found, *viz.* 4.5 in α -hydroxyacetophenone⁶ and 8.3 in peroxybenzoic acid⁷. However, the direction

TABLE I
Polarization and Dipole Moments of Hydroxamic Acids *I* and N,O-Diacylhydroxylamines *II*
(Dioxan, 25°C)

No Substituents		α^a β^a	$\frac{P_2^0}{R_D^b}$ cm ³ mol ⁻¹	μ (5) ^c μ (15) ^c 10 ⁻³⁰ C m
Hydroxamic acids X—C ₆ H ₄ CONHOH				
<i>Ia</i>	H	12.45 -0.202	312 36.6	12.2 ^d 12.1
<i>Ib</i>	4-Cl	8.60 -0.15	284 41.5	11.4 11.3
<i>Ic</i>	4-Br	6.62 -0.398	271 44.4	11.1 11.0
<i>Id</i>	4-NO ₂	12.56 -0.316	411 42.9	14.1 ^e 14.1
<i>Ie</i>	4-OCH ₃	11.56 -0.26	353 43.5	12.9 12.8
<i>If</i>	2-OH	15.56 -0.24	425 38.3	14.5 14.4
<i>Ig</i>	2-OCH ₃	17.30 -0.272	510 43.5	15.9 15.8
<i>Ih</i>	4-(C ₅ H ₄ N)CONHOH	7.70 -0.202	206 34.6	9.6 9.5
<i>Ii</i>	2-(C ₄ H ₃ O)CONHOH	12.42 -0.504	277 28.7	11.6 11.5
N,O-Diacylhydroxylamines X—C ₆ H ₄ CONHOCOC ₆ H ₄ —Y				
<i>IIa</i>	H 3'-NO ₂	13.5 -0.31	691 72.6	18.3 18.2
<i>IIb</i>	H 4'-OCH ₃	5.70 -0.194	316 73.2	11.4 11.2
<i>IIc</i>	3-NO ₂ H	7.10 -0.29	391 72.6	13.1 13.0
<i>IId</i>	4-OCH ₃ H	5.98 -0.388	313 73.2	11.4 11.2
<i>IIe</i>	3-NO ₂ 4'-Cl	8.36 -0.21	512 77.5	15.3 15.2
<i>IIf</i>	3-NO ₂ 3'-NO ₂	20.3 -0.49	1 153 78.9	24.2 24.1

TABLE I
 (Continued)

No Substituents	α^a β^a	P_D^0 R_D^b cm ³ mol ⁻¹	μ (5) ^c μ (15) ^c 10 ⁻³⁰ C m
<i>Ilg</i> 4-NO ₂	5.04	312	11.2
4'-NO ₂	-0.59	78.9	11.0
<i>Ihh</i> 4-NO ₂	13.30	760	19.2
4'-CH ₃	-0.23	79.5	19.1
<i>Ili</i> C ₆ H ₅ CH ₂ CONH C ₆ H ₅ COO	5.26	264	10.2
	-0.394	70.2	10.0

^a Slopes of the plots ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively; ^b calculated from increments, see Experimental; ^c correction for the atomic polarization 5%, or 15%, of the R_D value; ^d previously we reported³ an erroneous value of 15.1, the new determination agrees with ref.⁴; ^e in ref.^{3,4} the values 14.4 and 13.3, respectively, are given.

of the vector was the same in either compound (-164° with respect to the H—O bond). A vector of this direction and of an intermediate absolute value (6.4) has been plotted in Fig. 1 (denoted h') and bears near to the experimental point. An acceptable hypothesis would be that the hydrogen bond contribution has actually a similar value ($h = 6.1$, Fig. 1) but a somewhat divergent direction at an angle of -140° to the H—O bond. This interpretation seems rather arbitrary but we believe that it is the only possibility how the agreement with experimental results can be reached. Note that two assumptions were necessary concerning the values of m_2 and h which are known to vary considerably with the structure. By a lucky chance, however, these two vectors are almost of the same direction giving the result some reliability. Actually, the mesomeric moment m_2 might be somewhat higher than our first estimate, say 2–2.5 and the hydrogen bond term h accordingly lower, viz. 5.1–4.6. Similar values are quite approximate, nevertheless, the conclusion seems warranted that the hydrogen bond in hydroxamic acids is weaker than in peroxy acids⁷.

Previously we discussed³ the dipole moments of hydroxamic acids in terms of an equilibrium $A \rightleftharpoons B$, or of nonplanar conformations, transitory between A and B . Besides smaller variations in calculation and in experimental values, the fundamental difference compared to the present work was neglecting of a possible effect of the hydrogen bond. Barassin, Armand, and Lumbroso⁴ neglected this effect, too, and calculated the anticipated dipole moment by an alternative formal procedure based on model compounds instead on bond moments. They preferred the form A

with librations around the equilibrium position, but the agreement with experiment was very bad. In fact a decision is relatively difficult on the basis of dipole moments alone. In a conventional graph²⁰ (Fig. 2) are plotted the squared dipole moments of compounds *Ia*–*Id*, calculated and found. Evidently the experimental points do not match any of the calculated ones. An equilibrium of the forms *A* (*Zsp*) and *B* (*Zap*) would require the experimental point lying on the connecting line; this hypothesis cannot be rejected with an absolute certainty, taking into account the inaccuracy of the calculation and several assumptions made. The theoretical values based on model compounds⁴ do not work better and in fact suggest a conformation between *Esp* and *Eap*, rather than *Zsp*. If the possibility of an intramolecular hydro-

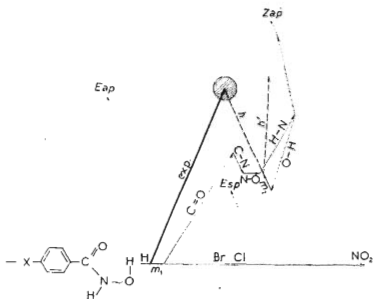


FIG. 1

The Dipole Moment of the $-CONHOH$ Group and its Analysis in Terms of Conformation

Shown are the experimental group moment (hatched circle), moments calculated for the conformations *Zsp*, *Zap*, *Esp*, and *Eap* (*A*–*D*), the bond moments including the mesomeric moments (m_1 , m_2) and contribution of the hydrogen bond (h — actual, h' — anticipated with respect to perbenzoic acid).

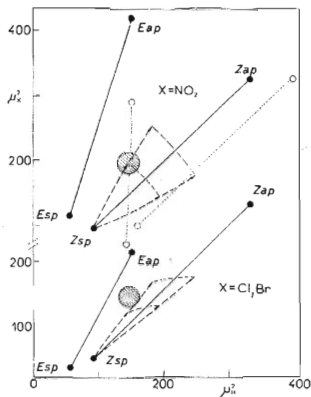


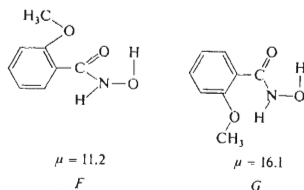
FIG. 2

Comparison of Squared Dipole Moments of Hydroxamic Acids *Ia*–*Id*, Calculated and Experimental

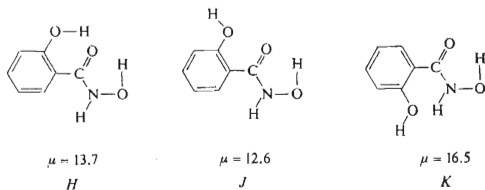
Full points calculated (this work), empty points calculated (ref.⁴), hatched circle experimental, dashed arrows—effect of the hydrogen bond; on the *x*-axis benzhydroxamic acids *Ia*, on the *y*-axis substituted benzhydroxamic acids *Ib*–*Id*.

gen bond is considered, an additional uncertainty enters the calculation. The supposed effect within the limits of values $4.5-6.3$ ($-164 \pm 25^\circ$ to the H—O bond) is shown in Fig. 2 by broken arrows. A coincidence with the experimental can be reached but the arbitrariness is of consequence. Therefore, an independent proof of the hydrogen bond would be advisable. The infrared spectra of benzhydroxamic acid are difficult to study in less polar solutions^{21,22} but evidence was obtained with dodecanhydroxamic acid in tetrachloromethane solution²¹. The spectrum of benzhydroxamic acid in dioxan²² suggests that the intramolecular hydrogen bond could persist even in this solvent; this view is corroborated by the behaviour of peroxybenzoic acid in benzene and in dioxan⁷. In conclusion, there is at least an important supporting evidence of the hydrogen bond.

Comparison to peroxy acids enables us to deal with the effect of solvent even on the dipole moment values themselves. Barassin, Armand, and Lumbroso⁴ applied a correction of $2 \cdot 10^{-30}$ C m to account for the effect of dioxan. This is not warranted in our opinion since substituted peroxybenzoic acids show equal dipole moments in dioxan as in benzene⁷. Even with *N*-phenylhydroxamic acids²³ the solvent effect is negligible in most cases. Hence we used the system of bond moments¹⁵, derived essentially from measurements in benzene, without any particular correction. It is true that this reasoning assumes the presence of an intramolecular hydrogen bond in all the compounds considered.



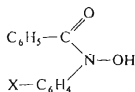
The two *ortho*-substituted benzhydroxamic acids, *If* and *Ig*, present additional problems concerning the conformation of the substituent. It follows that their dipole moments are com-



patible with the conformation *A*, but add only little evidence in its favour. In *Ig* two coplanar positions of the methoxy group are sterically admissible: *F* or *G*. The experimental data favour clearly *G*, stabilized possibly by another hydrogen bond which, however, does not make itself

felt in the dipole moment value. The hydroxyl group of *If* can take three coplanar positions *H—K*. Again the form with the second hydrogen bond (*H*) seems most probable. The agreement with experiment is not perfect and we can hardly estimate to which extent one hydrogen bond weakens another one on the same acceptor atom²⁴.

In the light of the results obtained we can attempt a reinterpretation of the dipole moments of substituted N-phenylbenzhydroxamic acids²³ (*III*). The merit of these compounds is their better solubility allowing the measurement in benzene. An intramolecular hydrogen bond has been well evidenced by IR spectroscopy in the case of N-phenylacethydroxamic acid in tetrachloromethane²⁵ and can be reasonably assumed in other N-phenyl derivatives in benzene. Note that the hydrogen bond of N-methylformhydroxamic acid is partly broken already in chloroform²⁶. Four substituents (H , $4'$ - CH_3 , $4'$ - Cl , $4'$ - Br) in the molecule of *III* allowed us to construe a graph (Fig. 3). The experimental group moment (11.5 at an angle of 35° to the $C_{(1)}-C$ bond) differs mainly in direction from that of the unsubstituted $-CONHOH$ group). When calculating the dipole moments of individual conformations, the mesomeric moment m_2 is to be further reduced with respect to the crossed conjugation on nitrogen. We believe that it can be taken as zero. Similarly as in Fig. 1, none of the calculated vectors matches the experimental result. This finding again does not depend on a particular value of m_2 and allows the only explanation: the form *A* with an extra dipole moment (h) of the intramolecular hydrogen bond. Even the absolute value of the latter moment (5.7) is similar as in Fig. 1 but differs in the direction (163° to the $H-O$ bond). Regarding the inherent inaccuracy we do not give too much credit to similar differences. We can only conclude that the intramolecular hydrogen bond in hydroxamic acids and N-phenylhydroxamic acids as well as in α -hydroxy ketones⁶ and peroxy acids⁷ gives rise to a dipole moment oriented roughly in the $O-H$ direction, with the negative end toward hydrogen. The disagreement of this orientation with current theoretical concepts was already noticed^{6,7}.



III

As mentioned in the introduction, the conformation *L* of aromatic N,O-diacylhydroxylamines is well established^{3,10,11}. The dihedral angle τ has a value of $70^\circ \pm \pm 10^\circ$ according to our treatment of dipole moment data³ (in dioxan) while the X-ray analysis¹⁰ of three derivatives revealed 80° , 79° , and 88° , respectively. Therefore, our new results (Table I) will be discussed in terms of this conformation and attention will be only paid to the independence, or possible dependence of groups attached to each benzene nucleus. We can assume as a reasonable approximation that each benzene ring is coplanar with the adjoining $C=O$ bond. The deviations from planarity are small even in the crystalline state unless an *ortho* substituent is present¹⁰. Hence there are two possible conformations of a *meta* derivative (e.g. *IIc*, *IIe*) viz. with the substituent in the position 3 or 5, respectively; similarly the substituent in the second moiety (e.g. in *IIa*) can take the position 3' or 5'.

If *meta* substituents are present in either nucleus (*II*f), the number of possible conformations is four. A methoxy group in the *para* position is assumed coplanar with the ring and in this case gives rise to the same number of conformations as a

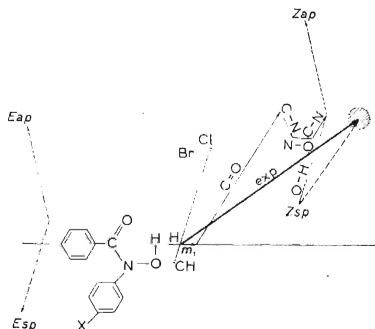


FIG. 3

The Dipole Moment of the $-\text{CON}(\text{C}_6\text{H}_6)\text{.OH}$ Group and its Analysis in Terms of Conformation
See Fig. 1 for descriptive details.

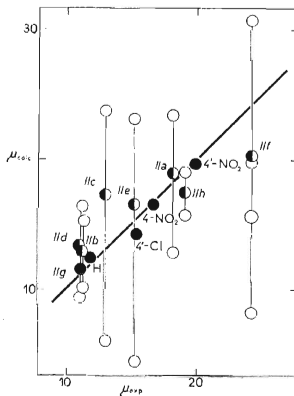
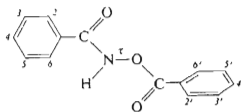


FIG. 4

Comparison of Experimental and Calculated Dipole Moments of N,O-Diacylhydroxylamines

● Axially symmetrical substituents with one conformation only, ○ angular substituents, statistical populations of conformations, ○ angular substituents, individual conformations. The straight line has unity slope, the dihedral angle $\tau = 70^\circ$ assumed always.

meta substituent. In all the cases the rotating groups are rather apart and their electrostatic interaction²⁷ is negligible. Hence one can anticipate that their conformations are populated almost equally.



L

We have calculated the expected dipole moments for the molecules *Ia–Iii*, with the dihedral angle $\tau = 70^\circ$ and in the respective conformations, in addition also for the four derivatives studied previously³ (N,O-dibenzoylhydroxylamine and its 4-nitro, 4'-nitro and 4'-chloro derivatives). The results are compared with the experimental values in Fig. 4. Good agreement is found for the five *para* derivatives (full points) which do not allow any conformational equilibrium. For the remaining compounds the assumption of equally populated conformations (halved points) is not far from the reality but is mostly not fulfilled exactly; the agreement is worse than in structurally similar dibenzoylperoxides²⁸. Nevertheless, the experimental value in Fig. 4 is always situated between the limits for the possible conformations. In addition to many inaccuracies inherent in the whole procedure, one can admit that even the dihedral angle τ need not be quite constant in all the derivatives. This is particularly probable in the case of the compound *Iii* not included into Fig. 4, but a more exact determination would require still further arylaliphatic derivatives. We conclude that the principle of conformational independency of remote groups can be confirmed only roughly on the basis of compounds *II*.

Thanks are due to Mrs M. Kuthanová for skilful technical assistance.

REFERENCES

1. Artemenko A. I.: Zh. Org. Khim. 7, 714 (1971).
2. Artemenko A. I., Tikunova I. V., Anufriev E. K., Zh. Prikl. Spektrosk. 24, 487, 939 (1976).
3. Exner O.: This Journal 30, 652 (1965).
4. Barassin J., Armand J., Lumbroso H.: Bull. Soc. Chim. Fr. 1969, 3409.
5. Exner O., Papoušková Z.: This Journal 45, 2410 (1980).
6. Plesničar B., Smolíková J., Jehlička V., Exner O.: This Journal 43, 2754 (1978).
7. Exner O., Plesničar B.: This Journal 43, 3079 (1978).
8. Baker R. W., Jones G. P., Pauling P.: Nature (London) 242, 326 (1973).
9. Exner O., Dembech P., Seconi G., Vivarelli P.: J. Chem. Soc., Perkin Trans. 2, 1973, 1870.
10. Göttlicher S., Ochsenreiter P.: Chem. Ber. 107, 398 (1974).
11. Price B. J., Sutherland O. I.: Chem. Commun. 1967, 1070.

12. Sorkin E., Roth W., Erlenmeyer H.: *Helv. Chim. Acta* **35**, 1736 (1952).
13. Jones L. W., Hurd C. D.: *J. Amer. Chem. Soc.* **43**, 2422 (1921).
14. Vogel A. I.: *J. Chem. Soc.* **1948**, 1842.
15. Exner O.: *Dipole Moments in Organic Chemistry*, p. 33. Thieme, Stuttgart 1975.
16. McClellan A. L.: *Tables of Experimental Dipole Moments*, Vol. 1 and 2. W. H. Freeman, San Francisco 1963 and Rahara Enterprises, El Cerrito 1973).
17. Exner O., Jehlička V., Dondoni A.: *This Journal* **41**, 562 (1976).
18. Eda B., Ito K.: *Bull. Chem. Soc. Jap.* **29**, 524 (1956).
19. Bracher B. H., Small R. W. H.: *Acta Crystallogr., Sect. B* **26**, 1705 (1970).
20. Exner O., Jehlička V.: *This Journal* **30**, 639 (1965).
21. Hadži D., Prevoršek D.: *Spectrochim. Acta* **10**, 38 (1957).
22. Exner O.: *This Journal* **29**, 1337 (1964).
23. Granzhan V. A., Manole S. F., Barba N. A., Laktionova S. K.: *Izv. Akad. Nauk Mold. S. S.R. Ser. Biol. Khim. Nauk* **1971**, No 2, 71.
24. Huyskens P. L.: *J. Amer. Chem. Soc.* **99**, 2578 (1977).
25. Mollin J., Fiedler P., Jehlička V., Exner O.: *This Journal* **44**, 895 (1979).
26. Walter W., Schaumann E.: *Justus Liebigs Ann. Chem.* **743**, 154 (1971).
27. Exner O., Friedl Z.: *This Journal* **42**, 3030 (1977).
28. Jehlička V., Plesničar B., Exner O.: *This Journal* **40**, 3004 (1975).

Translated by the author (O. E.).