Tetrahedron, 1963, Vol. 19, pp. 2171 to 2175. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRIC DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF ALIPHATIC NITRO COMPOUNDS AND OXIMES

S. SOUNDARARAJAN
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore–12

(*Received* 6 *June* 1963; *in revised form* 19 *August* 1963)

Abstract—Using the treatment of Smith *et al.* charge distributions in and consequently the dipole moments of some aliphatic nitro compounds and oximes have been evaluated. The mesomeric moment derived as a difference between the calculated and the observed values gives a clear picture as to how the positive (+M) and the negative (−M) mesomeric effects operate in such systems.

INTRODUCTION

THOUGH electric moment[1–4] and other studies[5–7] have given satisfactory proof of mesomerism in nitro compounds and oximes, no attempt has so far been made to evaluate this effect with any degree of accuracy after allowing for induction in these compounds. In this paper the treatment of Smith *et al.*[8] has been used for calculating the electric moments of a number of aliphatic nitro compounds and oximes so as to evaluate the extent of mesomerism in these compounds (Tables 1–5).

TABLE 1. PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION BY THE SRME METHOD

Bond	β_{ab}	γ_{ab}	Basic molecule	Moment used to derive γ_{ab}
H—C	0·130	0·00	—	—
Cl—C	0·710	−1·49	Methyl chloride	1·86D
O_2N—C	0·243	−2·65	Nitromethane	3·54D
HON=C	0·583	−0·758	Acetaldoxime	0·75D
H_2N—C	0·243	1·100	Methylamine	1·28D
C—C	$\beta_c^c = 0·718$	$\alpha_{c\text{-}c} = 0$	—	—

DISCUSSION

Nitro compounds. In nitro compounds, the C—N and N—O valence bonds are coplanar the ONO angle being near 120°. The partial double bond character of the NO links is due to the electrons that are fed into the delocalized NO bonding molecular orbitals. Though the π electrons are fed also into an O ←→, O antibonding π^* type M.O., this does not significantly affect the π bonding effect which is shown by the

---

[1] L. G. Wesson, *Tables of Electric Dipole Moments*. The Technology Press (1948).

[2] K. E. Calderbank and R. J. W. LeFevre, *J. Chem. Soc.* 1462 (1949).

[3] A. Audsley and F. R. Goss, *J. Chem. Soc.* Supp. Issue No. **1**, 5228 (1949).

[4] R. Raman and S. Soundararajan, *Proc. Ind. Acad. Sci.* **47**, 357 (1958).

[5] N. V. Sidgewick, *The Chemical Elements and Their Compounds*, Vol. I, p. 696. Oxford (1949).

[6] J. Donohue, *J. Amer. Chem. Soc.* **78**, 4172 (1956).

[7] B. Jerslov, *Nature, Lond.* **180**, 1410 (1957).

[8] R. P. Smith, T. Ree, L. Magee and H. Eyring, *J. Amer. Chem. Soc.* **73**, 2263 (1951).

TABLE 2. FORMAL CHARGE DISTRIBUTION IN ALIPHATIC NITRO COMPOUNDS

Atom or group	Chloro-picrin	Nitro-form	Nitro-methane	Chloronitro-methane	Nitro-ethane	1-Chloro-2-nitro ethane	1-Nitro-propane	2-Nitro-propane	1-Chloro-1-nitro propane	1-Nitro-butane	2-Nitro-butane	Nitro-t butane
Halogen	0·009	—	—	−0·162	—	−0·811	—	—	−0·355	—	—	—
Nitrogroup	−2·137	−1·610	−2·256	−2·196	−2·324	−2·285	−2·330	−2·373	−2·262	−2·330	−2·376	−2·408
Carbon-1	2·111	4·277	1·623	1·871	1·341	0·956	1·318	0·389	1·599	1·316	0·384	0·996
Carbon-2	—	—	—	—	0·457	1·502	0·386	1·142	0·468	0·380	1·126	0·339
Carbon-3	—	—	—	—	—	—	0·131	0·389	0·159	0·111	0·330	—
Carbon-4	—	—	—	—	—	—	—	—	—	0·038	0·112	—
Hydrogen-1	—	0·556	0·211	0·243	0·174	0·124	0·171	0·051	0·208	0·171	0·050	0·044
Hydrogen-2	—	—	—	—	0·059	0·195	0·050	0·149	0·061	0·049	0·146	—
Hydrogen-3	—	—	—	—	—	—	0·017	0·051	0·021	0·015	0·043	—
Hydrogen-4	—	—	—	—	—	—	—	—	—	0·005	0·015	—

TABLE 3. FORMAL CHARGE DISTRIBUTION IN OXIMES

Atom or group	Glyoxime	Methylglyoxime	Dimethylglyoxime	Methyl propyl-glyoxime	Methyl ethyl-glyoxime	Formamidoxime	Acetoxime
NOH group-1	−0·500	−0·535	−0·543	−0·546	−0·547	−0·860	−0·583
NOH group-1′	−0·500	−0·510	−0·543	−0·544	−0·546	—	—
Glyoxime carbon-1	0·443	0·383	0·369	0·363	0·363	−0·175	0·300
carbon-2	—	0·131	0·126	0·105	0·106	—	0·102
carbon-3	—	—	—	0·031	0·036	—	—
carbon-4	—	—	—	0·010	—	—	—
Glyoxime carbon-1′	0·443	0·425	0·369	0·367	0·364	—	—
carbon-2′	—	—	0·126	0·125	0·113	—	0·102
Hydrogen-1′	0·057	—	—	—	—	−0·023	—
Hydrogen-2	—	0·017	0·016	0·014	0·014	—	0·013
Hydrogen-3	—	—	—	0·004	0·005	—	—
Hydrogen-4	—	—	—	0·001	—	—	—
Hydrogen-1′	0·057	0·055	—	—	—	—	—
Hydrogen-2′	—	—	0·016	0·016	0·015	—	0·013
Amino group	—	—	—	—	—	1·058	—

TABLE 4. BOND ANGLES AND BOND DISTANCES USED FOR CALCULATING MOMENT

Molecule	Bond angle in degrees		Bond distance in Å	
Chloronitromethane	$\widehat{\text{Cl—C—N}}$	110°	C—H	1·09Å
	$\widehat{\text{H—C—H}}$	109·5°	C—Cl	1·77
			C—N	1·49
Chloropicrin	$\widehat{\text{Cl—C—Cl}}$	110·8°	C—Cl	1·75
			C—N	1·59
Glyoxime	$\widehat{\text{C—C=N}}$	120°	C—H	1·073
	$\widehat{\text{H—C—C}}$	120°	C=N	1·27
	$\widehat{\text{H—C=N}}$	120°		
Formamidoxime	$\widehat{\text{H—C=N}}$	130°	C—N	1·47
	$\widehat{\text{N—C—H}}$	110°	C—H	1·07
	$\widehat{\text{N—C=N}}$	120°	C=N	1·29
Acetoxime	$\widehat{\text{C—C=N}}$	120°	C=N	1·29
	$\widehat{\text{C—C—C}}$	120°	C—H	1·07

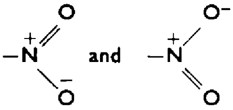
TABLE 5. CALCULATED AND OBSERVED ELECTRIC MOMENTS OF ALIPHATIC NITRO COMPOUNDS AND OXIMES

Molecule	Dipole moment in Debyes		Difference in Debyes	
	Calculated	Observed		
Nitro Compounds				
Chloropicrin	3·41	1·80(B)	−1·61	
		1·88(G)		
Nitroform	3·01	2·71	−0·30	
		2·61	−0·40	
Chloronitromethane	3·39	2·91(G)	−0·48	
Nitroethane	3·61	3·58(G)	−0·03	
1-Chloro-2-nitroethane	2·02(Z)	3·33(G)	—	
	4·92(U)			
1-Nitropropane	3·58(Z)	3·57(G)	−0·01[*]	−0·07[a]
	3·64(U)	3·70(G)	0·12[*]	0·06[a]
		3·72(G)	0·14[*]	0·08[a]
2-Nitropropane	3·63	3·73(G)	0·10	
Nitro t-butane	4·07	3·71	−0·36	
Oximes				
Glyoxime	1·21	1·22(D)	0·01	
Methylglyoxime	1·22	0·88(D)	−0·34	
Dimethylglyoxime	1·23	1·38(D)	0·17	
Acetoxime	0·77	0·88(D)	0·11	
Formamidoxime	2·27	2·24(D)	−0·03	

The geometry of the carbon skeleton assumed to arrive at the alternative values of calculated moments is indicated by capital letters in brackets thus: (U) conforms to structure  and (Z) to structure 

[*] Difference from the calculated value of 3·58. [a] Difference from the calculated value of 3·64.

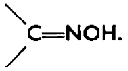
experimental data on bond lengths and vibrational frequencies of nitro compounds. In valence bond terms the groups may be represented by two equally stable resonating structures



the nitro group moment lying along the axis of the group bond which bisects the ONO angle.

The close accord between the values of resultant moment using the method of Smith *et al.*[8] and the observed moments, in the cases of nitroethane and 1 and 2 nitropropanes shows that the effects other than that of induction in these compounds are negligible. In nitro-butane, the calculated value is slightly higher than the observed value, a trend which is significant when the substituent is an electronegative halogen as in the cases of chloronitro methane and chloropicrin, of which the latter has the lowest observed moment. The presence of three nitro groups has a similar effect in nitro form. It has recently been shown that the high negative potentials of lone pairs of first row elements are reduced by delocalization towards nearby nuclei, e.g., double bonding.[9,10] Thus in a molecule like chloropicrin since the carbon chlorine bond is unequally shared, an increase occurs in the numerical coefficient of the local electron denuded carbon atom with the result the local antibonding orbitals at the carbon atom are greatly stabilized by electron withdrawal from nitrogen, owing to increased effective nuclear charge, i.e., the reactive lone pair on nitrogen then overlaps with the electron deficient antibonding orbital of another C—Cl bond, the ability of utilizing the antibonding orbitals being maximum in the case of carbon, whereas the tendency to release electrons being maximum in the case of nitrogen. Such a M.O. description explains the net mesomeric moments which decrease in the order chloropicrin > chloronitromethane > nitroform > nitrotertbutane. In the case of 1 chloro 2 nitro ethane the possibility of rotation of groups precludes the assessment of the mesomeric moment.

Oximes. The structure of oximes corresponds closely with the classical formula[6]



The agreement between the calculated value using Smith *et al.* scheme and the observed value for acetoxime clearly reveals its covalent structure which is confirmed by X-ray,[11] infrared[12] and Raman spectrum[13] studies. From the planar structure of formamidoxime as shown by precise structure analysis,[14] it was indicated that it is best represented as a resonance hybrid, the predominant forms being

$$\underset{\text{I}}{H_2N-CH{=}NOH} \quad \text{and} \quad \underset{\text{II}}{H_2\overset{+}{N}{=}CH-\overset{-}{N}OH}$$

---

[9] E. A. C. Luken, *J. Chem. Soc.* 2954 (1959).

[10] J. F. A. Williams, *Trans. Faraday Soc.* **57**, 2089 (1961).

[11] J. D. Dunitz and J. H. Robertson, *Ann. Repts.* **49**, 378 (1952).

[12] A. M. Buswell, W. H. Rodebush and M. F. Roy, *J. Amer. Chem. Soc.* **60**, 2239, 2444, 2528 (1938).

[13] H. J. Bernstein and W. H. Martin, *Trans. Roy. Soc., Canada* III **31**, 95 (1937).

[14] D. Hall and F. S. Llewellyn, *Acta Cryst.* **9**, 108 (1950).

It is clear however from the close accord between the calculated and the observed values that formamidoxime is best represented by structure I. The same is true of glyoxime and a negative mesomeric moment in the case of methyl glyoxime is anomalous though stabilization of antibonding orbitals by double bonding is not ruled out as in the case of halonitromethanes.

Acknowledgement—The author thanks Professor M. R. A. Rao for his kind interest and encouragement in this work.