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THE HMO TREATMENT OF THE $O—NO_2$, $N—NO_2$ AND $C—NO_2$ GROUPS

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Abstract—Parameters have been chosen for the coulomb and resonance integrals for the HMO treatment of the $O—NO_2$, $N—NO_2$ and $C—NO_2$ groups, which correctly predict values of the dipole moments of nitric esters, nitramines and aromatic C-nitro compounds. In most cases good agreement is also obtained between the theoretical and experimental bond lengths.

INTRODUCTION

The HMO method has been shown to be a useful means of predicting the electric dipole moments, bond lengths and chemical reactivity of some conjugated heteroatom compounds.[1,2] Calculations made in an attempt to extend the method to diaminotrinitrobenzene (DATB) and triaminotrinitrobenzene (TATB) showed that the parameters did not adequately account for the appreciable differences observed between the $C—NO_2$ and $C—NH_2$ bond lengths derived from X-ray data.[3,4] Since no difficulty had previously been experienced in predicted $C—NH_2$ bond lengths, attention was focussed on the $C—NO_2$ group. A survey of $C—NO_2$, $N—NO_2$ and $O—NO_2$ experimental bond lengths showed that these bonds were much longer than had previously been appreciated, being about 0·07 Å longer than those predicted from simple HMO theory. Clearly the coulomb and resonance integrals for these bonds needed refining. Streitwieser[5] had already pointed out that the couloumb integral of a nitrogen atom in a nitro group should be different to that for an amine nitrogen since the former has a formal positive charge. Calculations on the nitramine group, however, soon indicated that both bond orders and dipole moments were virtually insensitive to changes in $\alpha(\overset{+}{N})$; in contrast, they were sensitive to changes in the resonance integral. In the present work, the coulomb integral $\alpha(\overset{+}{N})$ was put equal to $\alpha + 2{\cdot}5\,\beta$, and the resonance integrals for the $N—\overset{+}{N}$, $—O—\overset{+}{N}$ and $C—\overset{+}{N}$ bonds adjust until the predicted and experimental dipole moments of nitroamine, alkyl nitrates and nitrobenzene agreed to within 0·2D. The final choice of parameters together with the ancillary parameters, based on Orgel's original paper[1] and subsequent refinements,[2] are listed below.

$$\alpha(C) = \alpha;\ \alpha(—\overset{|}{N}—) = \alpha + 2\beta;\ \alpha(—N{=}) = \alpha + \beta;\ \alpha(—\overset{+}{N}) = \alpha + 2{\cdot}5\beta$$
$$\alpha({=}O) = \alpha + 2\beta;\ \alpha(—O—) = \alpha + 3{\cdot}2\,\beta;\ \alpha[C(X)] = \alpha + 0{\cdot}1\,\delta X$$
$$\beta(CC) = \beta;\ \beta(CN) = \beta;\ \beta(NO) = 1{\cdot}2\,\beta;$$
$$\beta(C\overset{+}{N}) = 0{\cdot}3\beta;\ \beta(N\overset{+}{N}) = 0{\cdot}4\,\beta;\ \beta(—O\overset{+}{N}) = 0{\cdot}7\,\beta$$

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[1] L. E. Orgel, T. L. Correll, W. Dick and L. E. Sutton. *Trans. Far. Soc.* **47**, 113 (1951).

[2] A. J. Owen, *Tetrahedron* **14**, 237 (1961).

[3] J. R. Holden, Naval Ordnance Laboratory Report NOLTR 62–64, 1962 (1963. *Chem. Abstr.* **59**, 13417L).

[4] H. H. Cady and A. C. Larson, *Acta. Cryst.* **18**, 485 (1965).

[5] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists.* Wiley, New York (1961).

Follow Orgel's work, the dipole moment was calculated by the vector addition of the π moment divided by 1·6 and the σ moment. σ bond moments were estimated using the individual bond moments quoted elsewhere.[2]

These parameters were chosen in preference to those recommended by Streitwieser,[5] because (a) the latter set did not predict correctly dipole moments for many conjugated heteroatom compounds and (b) in order to adjust them very low numerical values would have been required for the resonance integrals.

RESULTS

The results are given in Tables 1 and 2 and in Fig. 1. Table 1 lists the energies of the occupied and the lowest unoccupied orbitals (in terms of $\alpha - \varepsilon/\beta$) for each compound, together with the delocalisation energy.

TABLE 1. ENERGIES OF THE OCCUPIED AND LOWEST UNOCCUPIED MOLECULAR ORBITALS (E_1, E_2 . . .)

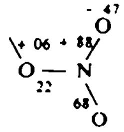
	E_1	E_2	E_3	E_4	E_5	E_6	E_7
Compound							
Nitric Esters	4·2483	2·9956	2·0000	0·45605			
Nitramines	4·0114	2·0000	2·0000	0·4886			
Nitorguanidine	4·0007	2·9651	2·0000	2·0000	1·3142	0·4783	
Nitrobenzene	3·9816	2·0469	2·0000	1·1008	1·0000	0·5169	
β.Nitroaniline	3·9816	2·6601	2·0000	1·8593	1·0000	0·8911	0·5082
DATB	3·9854	3·9805	3·9803	2·7887	2·5284	2·0000	2·0000
TATB	3·9859	3·9805	3·9805	2·8661	2·5284	2·5284	2·0000

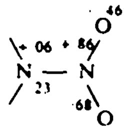
	E_8	E_9	E_{10}	E_{11}	E_{12}	E_{13}	Delocalisation Energy
Compound							
Nitric Esters							3·0878
Nitramines							3·0228
Nitroguanidine							6·0600
Nitrobenzene							11·0086
β.Nitroaniline							11·3342
DATB	2·0000	1·7096	1·0415	0·9305	0·5271		17·7398
TATB	2·0000	2·0000	1·4934	0·9305	0·9305	0·5242	18·0984

TABLE 2. PREDICTED AND EXPERIMENTAL DIPOLE MOMENTS

Compound	Moment calculated D.	Moment predicted D.	Total Moment predicted D.	Total Moment observed D.
Nitric Esters				
e.g. Alkyl Nitrates	3·2	1·2	2·7	2·9
		$\theta = -70°$	$\theta = -25°$	
Nitramines	3·0	1·8	3·7	3·8
Nitroguanidine	8·2	1·8	6·8	7·0
	$\theta = -24·5°$	$\theta = -14°$	$\theta = -21·5°$	
Nitrobenzene	4·1	1·35	3·9	3·9
p.Nitroaniline	6·7	1·8	6·0	6·2
DATB	1·8	0·45	1·5	—

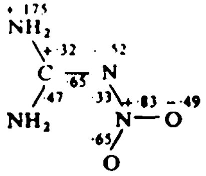
θ is measured anticlockwise relative to a L → R horizontal axis in the charge diagrams.





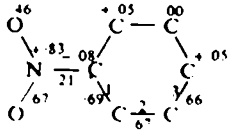
Bond length Å	—O—N	N—O	N—N	N—O
theory	1·30	1·31	1·38	1·21
expt.	1·36	1·26–1·28	1·36–1·40	1·18–1·22

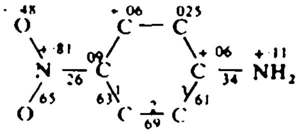
Nitric esters Nitramines



Bond length Å	C—NH_2	C—N	N—N	N—O
theory	1·35	1·32	1·35	1·21
expt.	1·36	1·34	1·35	1·22

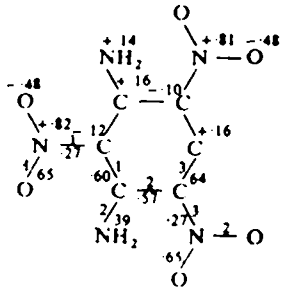
Nitroguanidine

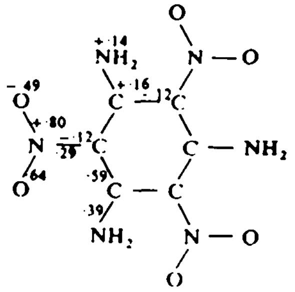




Bond length Å	N—O	N—C	C′—C	C^2—C	C^3—C	N—O	N—C	C′—C	C^2—C	C^3—C	C—NH_2
theory	1·21	1·42	1·38	1·38	1·38	1·21	1·41	1·38	1·37	1·38	1·37
expt.	1·21	1·49	1·37	1·43	1·36	1·25–9	1·41	1·34–9	1·36–40	1·37–40	1·37

Nitro benzene P.Nitro aniline





Bond length Å	N′—O	C′—N	C′—C	C^6—N	C^6—C	C^6—N	N^3—O	C^6—C	N—O	N—C	C—C	C—NH_2
theory	1·21	1·40	1·39	1·36	1·40	1·40	1·21	1·38	1·21	1·40	1·40	1·36
expt.	1·24	1·42	1·45	1·33	1·40	1·44–9	1·22	1·37	1·24–5	1·42	1·44	1·31-2

DATB TATB

FIG. 1

Figure 1 contains diagrams of the charge distribution for each molecule and the mobile bond orders for each bond. Comparison of the predicted and experimental bond lengths[6,7] is given underneath the diagram of each molecule, the theoretical bond lengths being interpolated from graphs of single, double and triple bond lengths[8] against mobile bond order. Comparison of the predicted and observed[9] dipole moments is given in Table 2.

DISCUSSION

The agreement between the predicted and experimental dipole moments for compounds which were not used to adjust the parameters, i.e. nitroguanidine and *p*-nitroaniline, is good, being within 0·2D. Similarly, the predicted and experimental bond lengths for most compounds are also in good agreement. The exceptions are the $O—NO_2$ and $C—NO_2$ bonds in nitric esters and nitrobenzene. No explanation can readily be put forward for nitric esters. For nitrobenzene, the experimental bond length of 1·49 Å[10] is longer than the usually accepted value of a pure single C—N bond. The survey of $C—NO_2$ bond lengths in planar aromatic nitro compounds shows that most of them have $C—NO_2$ bond lengths between 1·39 and 1·46 Å. Since the formal positive charge on the nitrogen atom should reduce its covalent radius and not increase it, it is not at all clear why nitrobenzene should exhibit this abnormally long bond length. Other workers have carried out calculations on this type of molecule. Murto[11] using Streitwieser's parameters, obtained a mobile bond order of 0·41. Magnoli *et al.*[12] predicted short C—N bond lengths in *p*-nitro phenyl azide. Similarly Basu,[13] in an attempt to predict electronic transitions, used $\beta(C\overset{+}{N}) = 0{\cdot}7$ in a HMO treatment of nitrobenzene and obtained a mobile bond order of 0·38: a SCF treatment gave a more realistic result of 0·17, but the charges on the o, m and p ring positions were all negative, predicting, contrary to experiment, nitrobenzene to be more reactive to electrophilic attack than benzene. Trotter[14] attempted to account for the long bond length by assuming that the nitro group was tilted at an angle of 60° from planarity with the ring i.e. $\beta(C—NO_2) = \beta \cos 60°$. This gave 1·45 Å for the C—N bonds in 9,10-dinitroanthracene and nitrobenzene. Subsequently he showed by X-ray methods[10] that nitrobenzene was planar. Although we have not been able to predict the bond length in nitrobenzene accurately, the trend to longer $C—NO_2$ bond lengths is clearly shown. The excellent agreements obtained with *p*-nitroaniline however, illustrates the correctness of the present treatment.

DATB and TATB have been shown to be planar[3,4] In the present work fair agreement has been obtained between the predicted and experimental bond lengths. Differences between the $C—NO_2$ and $C—NH_2$ bond lengths, however, are still larger

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[6] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Special Publication No. 11 of the Chemical Society, London (1958).

[7] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement 1956–1959, Special Publication No. 18 of the Chemical Society, London (1964).

[8] G. W. Wheland, *Resonance in Organic Chemistry* p. 172. Wiley, New York (1955).

[9] A. L. McClellan. *Tables of Experimental Dipole Moments.* Freeman, San Francisco (1963).

[10] J. Trotter. *Acta. Cryst.* **11**, 884 (1959).

[11] J. Murto. *Suomen Kemistilenti* **38B**, 246 (1965).

[12] A. Mugnoli, C. Mariani and M. Simonetta, *Acta. Cryst.* **19**, 367 (1965).

[13] R. Basu. *Theoretica Chim. Acta.* **2**, 87 (1964).

[14] J. Trotter, *Canad. J. Chem.* **37**, 905 (1959).

than those predicted, and in both molecules the experimental N—O bond lengths are larger than those predicted. Intramolecular hydrogen bonding occurs to an appreciable extent in both cases. This phenomenon is not considered in the present simple HMO treatment, and it may well account for these discrepancies.

The results obtained for nitroguanidines are particularly encouraging. In many nitramines e.g. ethylene dinitramine, RDX[15] and HMX,[16,17] the nitramine group is unable to conjugate with the rest of the molecule: consequently the HMO treatment is confined exclusively to that group. With nitroguanidine, however, delocalization of the π electrons occurs over the entire molecule. The change in experimental N—N bond lengths from 1·38 A in the localized nitramine group to 1·35 A in the delocalized nitroguanidine molecule is completely paralleled by the theoretical values obtained here. These results confirm the conclusion reached previously concerning the structure of nitroguanidine,[2] when unrefined parameters lead to a predicted dipole moment of 8·3D and a short N—N bond length of 1·29 A.

The low values of the resonance integrals required by these groups to account for the physical properties of molecules containing them imply that the O—NO_2, C—NO_2 and N—NO_2 bonds are weaker than has generally been thought.

The parameters adopted in this paper should not be used to calculate electronic transitions even though the predicted UV max in nitramines is fortuitously close to the experimental value (β assumed $= 30{,}000\ \text{cm}^{-1}$).[18]

CONCLUSIONS

Values of the coulomb and resonance integrals quoted here may be used in HMO calculation to predict the dipole moments, and chemical reactivity of a number of conjugated nitro compounds. Bond lengths may also be predicted, but in some cases only qualitative agreement is obtained. The parameter values must always be used as a set. Other sets, e.g. those recommended by Streitwiesser, may be adjusted for qualitative work by arranging the ratio $\beta(\text{NO})$: $\beta(\text{—O}\overset{+}{\text{N}})$: $\beta(\text{N—}\overset{+}{\text{N}})$: $\beta(\text{C—}\overset{+}{\text{N}})$ to be 1:0·6:0·35:0·25.

Acknowledgements—A number of the calculations were carried out by Mrs. J. Hingston on a Mercury Computer.

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[15] P. M. Harris, *Structures of Trinitro-aromatic Crystals and Related Substances*, Ohio State University Research Foundation Report, AFOSR-TR-59, 165. Sept. (1959).

[16] P. F. Eiland and R. Pepinsky. *Z. Krist.* **106**, 273 (1955).

[17] H. H. Cady, A. C. Larson, and D. T. Cromer, *Acta Cryst.* **16**, 617 (1963).

[18] Z. Simon and A. T. Balaban, *Revue de Chimie* **8**, 199 (1963).