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THE HMO TREATMENT AND CONFIGURATION OF SOME SUBSTITUTED PHENOLS

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Abstract—Parameters have been chosen for the coulomb and resonance integrals for the HMO treatment of phenols which correctly predict values of their dipole moments. Comparison of the predicted moments with those observed permits the direction of the OH bond in relation to the other substituent groups in the benzene ring to be defined when the compound is dissolved in low concentration in benzene. Agreement is also obtained between the predicted and observed 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 hetero atoms compounds of interest in explosives technology.[1, 2] In the present work, the method has been extended to phenol and certain substituted phenols, viz: 2,3 and 4-aminophenols, 2,3 and 4-nitrophenols, 2,4,6-trinitrophenol, resorcinol, 2-nitroresorcinol, 2,4-dinitroresorcinol, 4,6-dinitroresorcinol, 2,4,6-trinitroresorcinol, phloroglucinol and trinitrophloroglucinol, by adjusting the coulomb and resonance integrals for the C—OH bond until the predicted and observed dipole moments of phenol and of 4-nitrophenol agree to within 0·2 D. The derived value for the coulomb integral $\alpha(\text{—O—})$ is $\alpha + 3{\cdot}2\,\beta$, i.e. the same as that used in previous work.[2, 3] The value chosen for the resonance integral $\beta(\text{C—OH})$ is $1{\cdot}5\,\beta$. All other parameters used in this work have been quoted in an earlier paper.[2] It has been assumed that all the molecules considered here are planar.

Following Orgel's work,[3] the dipole moment was calculated by the vector addition of the π moment divided by 1·6 and the σ moment. π moments were calculated in the usual way assuming that all the bond angles were 120° and that bond lengths for C—C, C—NO_2, C—NH_2, C—O and N—O bonds were 1·40, 1·42, 1·39, 1·32, 1·22 Å respectively. σ bond moments were estimated from individual bond moments quoted elsewhere.[3, 1] For the C—OH bonds, the COH bond angle was assumed to be 109°. Small variations in this angle will not significantly alter the total predicted moment. The OH σ bond moment was assumed to be 1·6D.

In certain substituted phenols several different planar configurations for the structure of the molecule are possible because the hydrogenatom of the OH group is subtended at an angle to the C—O bond. Each configuration has a unique predicted dipole moment. Comparison of these predicted moments with those observed experimentally allows the direction of the OH bond to be defined. It should be stressed, how-

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ever, that the configuration so defined refers to the molecule in the experimental environment, i.e. when dissolved in low concentration in benzene.

RESULTS

The results are given in Tables 1 and 2 and in Fig. 1. Table 1 lists the energies of the occupied and lowest unoccupied orbitals (in terms of $\alpha - \varepsilon/\beta$) and the delocalization energy of all the phenols considered.

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

Compound	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}	E_{11}	E_{12}	E_{13}	Delocalization Energy β
1 Phenol	3·9304	1·8681	1·0000	0·8008	−1·0000									8·4786
2 2-Aminophenol	3·9467	2·5839	1·7297	0·9089	0·6880	−1·0277								8·7944
3 3-Aminophenol	3·9352	2·6385	1·6611	0·8807	0·7452	−1·0257								8·8014
4 4-Aminophenol	3·9344	2·6470	1·6207	1·0000	0·6549	−1·0000								8·7940
5 2-Nitrophenol	3·9954	3·9234	2·0000	1·9066	1·0886	0·8370	0·5093							11·5320
6 3-Nitrophenol	3·9829	3·9330	2·0000	1·9265	1·0788	0·8175	0·5162							11·5074
7 4-Nitrophenol	3·9819	3·9301	2·0000	1·9328	1·0000	0·8975	0·5067							11·5146
8 2,4,6-Trinitrophenol	4·0077	3·9811	3·9802	3·9160	2·0000	2·0000	2·0000	1·9945	1·1574	0·9919	0·5284			17·5876
9 Resorcinol	3·9830	3·8811	1·7246	$0{\cdot}8842_5$	0·7453	−1·0341								8·9965
10 2-Nitroresorcinol	$4{\cdot}0244_5$	3·9457	3·8811	2·0000	1·7508	1·0230	0·7453	0·5041						11·9807
11 2,4-Dinitroresorcinol	4·0324	3·9827	3·9414	3·8793	2·0000	2·0000	1·8038	1·0486	0·8371	0·5072				15·1106
12 4,6-Dinitroresorcinol	4·0167	3·9862	3·9527	3·8777	2·0000	2·0000	1·8317	0·9438	0·9118	0·5225				15·1012
13 2,4,6-Trinitroresorcinol	4·0390	3·9862	3·9805	3·9371	3·8777	2·0000	2·0000	2·0000	1·8503	1·0569	0·9438	0·5269		18·1530
14 Phloroglucinol	4·0285	3·8811	3·8811	1·5463	0·7453	0·7453	−1·1064							9·4952
15 2,4,6-Trinitrophloroglucinol	4·0772	3·9862	3·9862	3·9471	3·8777	3·8777	2·0000	2·0000	2·0000	1·6747	0·9438	0·9438	0·5238	18·7188

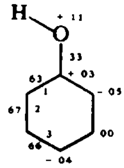
TABLE 2. PREDICTED AND EXPERIMENTAL DIPOLE MOMENTS

Compound	π Moment ÷ 1·6 calculated D	α Moment predicted D	Total moment predicted D	Total moment observed D
Phenol	0·89 $\theta = 180^\circ$	1·65 $\theta = -66^\circ$	1·5 $\theta = -97^\circ$	1·55
2-Aminophenol (H left)	1·45 $\theta = -153^\circ$	1·955 $\theta = -77^\circ$	2·7 $\theta = -108^\circ$	
(H right)		1·12 $\theta = 68^\circ$	1·0 $\theta = 15^\circ$	
3-Aminophenol (H left)	0·88 $\theta = -40\cdot5^\circ$	2·10 $\theta = -64^\circ$	2·9 $\theta = -58^\circ$	
(H right)		1·24 $\theta = 51^\circ$	1·7 $\theta = 19^\circ$	1·85
4-Aminophenol	0·23 $\theta = -180^\circ$	1·92 $\theta = -52^\circ$	1·8 $\theta = -58^\circ$	
2-Nitrophenol (H left)	2·74 $\theta = 80^\circ$	1·39 $\theta = -14^\circ$	3·0 $\theta = 52^\circ$	3·1–3·2
(H right)		2·70 $\theta = 60^\circ$	5·3 $\theta = 70^\circ$	
3-Nitrophenol (H left)	2·02 $\theta = 139^\circ$	0·34 $\theta = 89^\circ$	1·8 $\theta = 147^\circ$	
(H right)		2·68 $\theta = 90^\circ$	4·2 $\theta = 111^\circ$	3·9
4-Nitrophenol	4·46 $\theta = 180^\circ$	1·65 $\theta = -114^\circ$	5·3 $\theta = -164^\circ$	5·1
2,4,6-Trinitrophenol	1·38 $\theta = 180^\circ$	1·62 $\theta = 65^\circ$	1·7 $\theta = 108^\circ$	1·51
Resorcinol				
(both H's up)	0·97 $\theta = 180^\circ$	1·94 $\theta = 180^\circ$	2·9 $\theta = 180^\circ$	
(both H's down)		3·30 $\theta = 0^\circ$	2·3 $\theta = 0^\circ$	2·10
(one H up, one H down)		1·65 $\theta = 66^\circ$	1·5 $\theta = 101^\circ$	
2-Nitroresorcinol				
(both H's up)	2·15 $\theta = 0^\circ$	0·59 $\theta = 180^\circ$	1·5 $\theta = 0^\circ$	
(both H's down)		4·65 $\theta = 0^\circ$	6·8 $\theta = 0^\circ$	
(one H up, one H down)		2·53 $\theta = 36^\circ$	4·5 $\theta = 20^\circ$	
2,4-Dinitroresorcinol				
(both H's up)	3·11 $\theta = -94^\circ$	3·1 $\theta = -63^\circ$	5·9 $\theta = -79^\circ$	
(both H's down)		1·06 $\theta = 8^\circ$	3·1 $\theta = -74^\circ$	

TABLE 2—*continued*

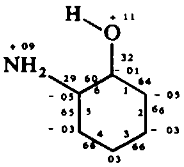
Compound	π Moment ÷ 1·6 calculated D	α Moment predicted D	Total moment predicted D	Total moment observed D
(left H up, right H down)		3·905	5·6	
		$\theta = -20°$	$\theta = -52°$	
(left H down, right H up)		1·71	4·5	
		$\theta = -137°$	$\theta = -109°$	
4,6-Dinitroresorcinol				
(both H's up)	3·50	3·29	6·8	
	$\theta = 180°$	$\theta = 180°$	$\theta = 180°$	
(both H's down)		1·95	1·6	
		$\theta = 0°$	$\theta = 180°$	
(one H up, one H down)		1·65	4·4	
		$\theta = 114°$	$\theta = 160°$	
2,4,6-Trinitroresorcinol				
(both H's up)	1·32	1·94	3·3	
	$\theta = 180°$	$\theta = 180°$	$\theta = 180°$	
(both H's down)		3·30	2·0	
		$\theta = 0°$	$\theta = 0°$	
(one H up, one H down)		1·65	1·6	1·50 ± 0·03
		$\theta = 66°$	$\theta = 133°$	

The direction of the O—H bond is defined relative to the geometry of the molecule illustrated in Fig. 1. θ is measured anticlockwise relative to the upward vertical axis in the charge diagram.



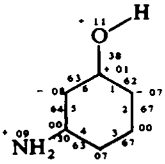
Phenol

Bond lengths Å		
	theory	expt
C—O	1·33	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·38	
$C\overset{3}{-}C$	1·38	



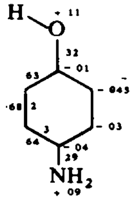
2-Aminophenol

Bond lengths Å		
	theory	expt
C—O	1·33	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·38	
$C\overset{3}{-}C$	1·38	
$C\overset{4}{-}C$	1·38	
$C\overset{5}{-}C$	1·38	
$C\overset{6}{-}C$	1·39	
C—N	1·39	



3-Aminophenol

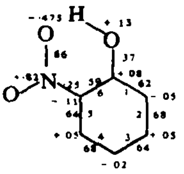
C—O	1·32
$C\overset{1}{-}C$	1·39
$C\overset{2}{-}C$	1·38
$C\overset{3}{-}C$	1·38
$C\overset{4}{-}C$	1·39
$C\overset{5}{-}C$	1·38
$C\overset{6}{-}C$	1·39
C—N	1·39



4-Aminophenol

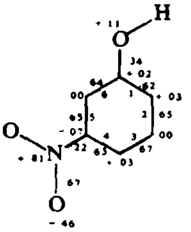
C—O	1·33	1·33	1·47
$C\overset{1}{-}C$	1·39	1·39	1·36—1·37
$C\overset{2}{-}C$	1·38	1·38	1·37—1·39
$C\overset{3}{-}C$	1·38	1·38	1·39—1·40
C—N	1·39	1·39	1·47

FIG. 1.



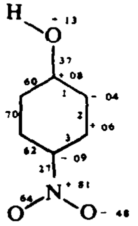
2-Nitrophenol

Bond lengths Å	theory	expt.
C—O	1·32	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·38	
$C\overset{3}{-}C$	1·38	
$C\overset{4}{-}C$	1·38	
$C\overset{5}{-}C$	1·38	
$C\overset{6}{-}C$	1·39	
C—N	1·40	
N—O	1·21	



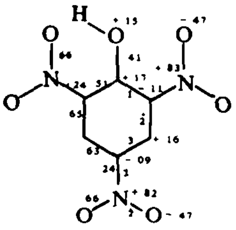
3-Nitrophenol

Bond lengths Å	theory	expt.
C—O	1·33	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·38	
$C\overset{3}{-}C$	1·38	
$C\overset{4}{-}C$	1·39	
$C\overset{5}{-}C$	1·38	
$C\overset{6}{-}C$	1·38	
C—N	1·41	
N—O	1·21	



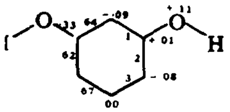
4-Nitrophenol

	theory	expt.
C—O	1·32	1·36
$C\overset{1}{-}C$	1·39	1·39
$C\overset{2}{-}C$	1·38	1·38
$C\overset{3}{-}C$	1·39	1·39
C—N	1·40	1·44
N—O	1·21	1·24



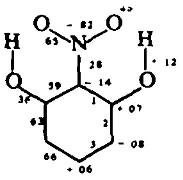
2,4,6-Trinitrophenol

	theory	expt.
C—O	1·32	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·38	
$C\overset{3}{-}C$	1·39	
$C\overset{1}{-}C$	1·40	
$N\overset{1}{-}O$	1·21	



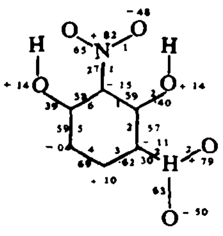
Resorcinol

	theory	expt.
C—O	1·33	1·34–1·36
$C\overset{1}{-}C$	1·38	1·38
$C\overset{2}{-}C$	1·39	1·34–1·38
$C\overset{3}{-}C$	1·38	1·40



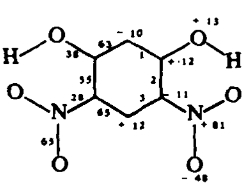
2-nitroresorcinol

	theory	expt.
C—O	1·32	
C—N	1·40	
N—O	1·21	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·38	
$C\overset{3}{-}C$	1·38	



	theory	expt.
$C\overset{1}{-}O$	1·32	
$C\overset{2}{-}O$	1·32	
$C\overset{1}{-}N$	1·40	
$C\overset{2}{-}N$	1·40	
$N\overset{1}{-}O$	1·21	
$N\overset{2}{-}O$	1·21	
$C\overset{1}{-}C$	1·39	
$C\overset{2}{-}C$	1·39	
$C\overset{3}{-}C$	1·39	
$C\overset{4}{-}C$	1·38	
$C\overset{5}{-}C$	1·39	
$C\overset{6}{-}C$	1·39	

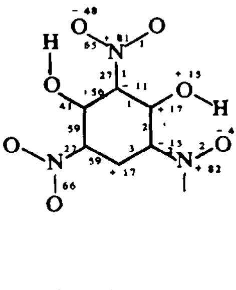
2,4-Dinitroresorcinol



4,6-Dinitroresorcinol

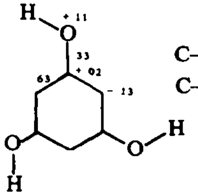
	theory	expt.
C—O	1·32	
C—N	1·40	
N—O	1·21	
$C\overset{1}{-}C$	1·38	
$C\overset{2}{-}C$	1·40	
$C\overset{3}{-}C$	1·38	

Fig. 1—*continued*



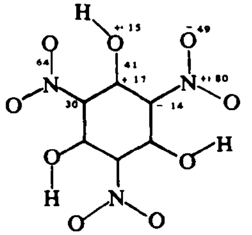
2,4,6-Trinitroresorcinol

C—O 1·32
$\mathrm{C}\overset{1}{—}\mathrm{N}$ 1·40
$\mathrm{C}\overset{2}{—}\mathrm{N}$ 1·40
$\mathrm{N}\overset{1}{—}\mathrm{O}$ 1·21
$\mathrm{N}\overset{2}{—}\mathrm{O}$ 1·21
$\mathrm{C}\,^{1}\,\mathrm{C}$ 1·40
$\mathrm{C}\overset{1}{—}\mathrm{C}$ 1·40
$\mathrm{C}\overset{2}{—}\mathrm{C}$ 1·39
$\mathrm{C}\overset{3}{—}\mathrm{C}$ 1·39



Phloroglucinol

C—O 1·33 1·33–1·37
C—C 1·38 1·38–1·44



Trinitrophloroglucinol

C—O 1·34
C—N 1·39
N—O 1·21
C—C 1·40

FIG. 1—*continued*

Fig. 1 contains diagrams of the charge distribution for each molecule and the mobile bond orders for each bond. The predicted and experimental[4, 5] bond lengths are also listed in Fig. 1, the theoretical bond length being interpolated from graphs of single, double and triple bond lengths[6] against mobile bond order.

Comparison of the predicted dipole moments for the various configurations of each molecule with those observed[7] is given in Table 2. In this Table the conformation of the H atoms is defined relative to the geometry of molecule illustrated in Fig. 1.

DISCUSSION

Dipole moments. In previous work,[1–3] the predicted and measured dipole moments have agreed to within 0·3D. This has also been achieved in the present work.

The agreement between the predicted and observed dipole moment for 2,4,6-trinitrophenol, the only molecule with a unique configuration and which was not used to adjust the parameters, is within 0·2D. With 2-nitrophenol the configuration is known because intramolecular H-bonding fixes the position of the H-atom. In this case the predicted dipole moment of 3·0D agrees well with the observed values of 3·1 to 3·2D. It may be argued that intramolecular H-bonding influences the π electron distribution and the σ bond moments in the region of the H-bond. This does not appear to be significant since the predicted dipole moment of 2-nitroaniline (3·9D) agrees with the observed value of 4·2D.

With those molecules where ambiguity of the conformation of the OH bond exist, comparison of the predicted dipole moments with the observed value (where this is known) enables the direction of the OH bond to be determined unequivocably. The predicted dipole moments for 3-aminophenol are 2·9D if the H atom is pointing to the left of the vertical axis in the charge diagram in Fig. 1, and 1·7D if it is pointing to the right. The observed dipole moment is 1·85D, showing that the OH bond is directed away from that side of the benzene ring on which the amino group is substituted. Similarly the predicted dipole moments for 3-nitrophenol are 1·8D and 4·2D respectively as compared with the observed value of 3·9D. Clearly the OH bond is again directed to the right of the vertical axis in the charge diagram in Fig. 1. With both these molecules the predicted dipole moment for the preferred configuration is so close to the observed value that tautomerism between the two configurations is ruled out.

Three configurations are possible for resorcinol; in one, both OH bonds are pointing upwards; in the second both are pointing downwards; and in the third one is pointing upwards and the other downwards. The predicted dipole moments of these three configurations are 2·9D, 2·3D and 1·5D respectively. Since the observed dipole moment is 2·09D, the most probable configuration is that in which both OH bonds are pointing downwards. In this case, however, another interpretation is possible because tautomerism between the forms could lead to the same result.

The only other compound for which experimental data is available to enable a comparison to be made is 2,4,6-trinitroresorcinol (styphnic acid). The observed dipole moment of 1·5 ± 0·3D is close to the predicted moment of 1·6D for the configuration in which one hydrogen is pointing upwards and one downwards. Since the the other two configurations lead to much higher values for the predicted moments there is no possibility of tautomerism occurring.

Bond lengths. The experimental bond lengths are only available for four of the molecules considered in the present work. Good agreement is obtained between the predicted and experimental bond lengths (Fig. 1) for the C—O and C—C, bonds in resorcinol, phloroglucinol and for the C—O, C—C and N—O bonds in 4-nitrophenol.[8] In the latter case, the predicted C—NO_2 bond length is shorter by 0·04 Å than that observed; these bonds have been discussed previously.[2]

In the case of 4-aminophenol, the predicted C—O bond lengths of 1·33 Å is considerably shorter than the value of 1·47 Å determined by Brown.[9] In his paper he commented on the fact that this bond was longer than that generally accepted for a pure C—O bond; it is unusually long when compared with those observed in other phenols, e.g. quinol, 3·6 Å; 4-isopropylideneaminophenol, 1·38 Å, 3,3′-dichloro-4,4′-dihydroxydiphenylmethane, 1·38 Å; and tropolone; 1·34 Å. A re-examination of the X-ray diffraction pattern of crystals of 4-aminophenol would appear to be necessary.

The HMO calculations of the mobile bond orders and electron densities were carried out on an Elliott 503 computer.

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