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MESOMERIC MOMENTS AND STRUCTURE OF SOME ORGANIC MOLECULES

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Abstract

Mesomeric moments have been derived for a number of simple aromatic molecules, as a difference between the moment calculated for the corresponding aliphatic analogue, using the method of Smith, Ree, Magee and Erying and the observed moment of the phenyl or diphenyl derivative. The structure of the aromatic molecules have been discussed in terms of the positive and negative mesomeric effects that operate in such systems.

Introduction

It is well-known that a conjugated system tends to planarity due to its maximal mesomeric interaction and minimal potential energy in that configuration and that any factors which prevent a group from becoming almost coplanar with the aromatic ring should diminish its mesomeric effect and this diminution should be reflected in the dipole moment. Involving as they do, the electron displacements away from and towards the substituents respectively, the + M and − M interaction effects have been shown by Sutton[12] to be reflected in the magnitude and direction of the algebraic difference between the moments of an aromatic molecule and that of its aliphatic analogue. Sutton allowed as far as possible for inductive effects by comparing the aromatic compounds with the corresponding tert-butyl compounds but induction in conjugated system is rather different from that in saturated compounds. The additional inductive effect term which arises on account of the highly polarizable character of the π electron system cannot be separated completely from the mesomeric effect.[5]

Recently it has been shown by the author that the magnitude and direction of the effect could be adequately predicted on the basis of simple considerations of kernal charges and the screening effect[10] in aliphatic compounds with conjugated system. The difference between the calculated values for aliphatic molecules and the observed values for the aromatic analogues is a measure of the mesomeric moment and accordingly the values have been derived for a few simple aromatic molecules. Measurements on a few simple aromatic compounds which pertain to the present discussion have also been included.

EXPERIMENTAL

Materials. Benzanilide was prepared by the method of Webb.[13] The product was twice crystallised from hot alcohol using decolorizing carbon. M. Pt. 160°—161° C. Benzyl aniline an Eastman Kodak Product was twice recrystalised from ligroin. M. Pt. 37°-38° C.

Apparatus and Method: The apparatus and method of measurement and calculation of results were as described earlier.[9] The molar refractions were calculated from the bond refractions given by Denbigh.[4] The data and calculated moments are presented in Tables I and II. Though the experimental measurements of dielectric constants, densities, etc., correspond to a precision of the order of 0.01 D in observed moments, the uncertainty in molar refraction and the well recognised solvent effect suggest that a margin of 0.1 to 0.2 D in benzene and up to 0.5 D in dioxan should be allowed in considering their interpretation.

Theoretical calculation. Following Smith, Ree, Magee and Erying[8] the charges on each atom or group in the molecule and from these charges the bond moments have been evaluated and consequently the resultant moment is obtained from the vector sum of these moments. The values of β and γ are given in Table III for a number of bonds and the appropriate bond angles and distances used to calculate the resultant moments have been taken from the Tables of interatomic distances and configurations in molecules and ions, compiled by Sutton *et al.*[16] Table IV contains values of formal charges for each atom or group calculated using parameters of Table III and Table V gives values of the calculated moments for the aliphatic molecules and of the observed moments for the aliphatic and the corresponding phenyl and diphenyl derivatives, as also the difference in moment between those observed and the calculated S. R. M. E. value for the corresponding aliphatic molecule. Table VI contains values of the observed moments and also the difference in moment between those observed and the basic observed value, for some amines.

TABLE I

Dielectric Constants and Densities at 35° ± 0.005° C

Concentration In Mole Fraction	Dielectric Constant	Density
Benzanilide in Dioxan		
0.00153_8	2.2410	1.01716
0.00254_4	2.2607	1.01748
0.00404_9	2.2946	1.01800
0.00610_4	2.3357	1.01864
Benzyl aniline in Benzene		
0.00354_7	2.2710	0.86425
0.00514_2	2.2779	0.86485
0.00981_3	2.2945	0.86670
0.01156_5	2.3041	0.86738
0.01464_5	2.3170	0.86860

TABLE II

	Benzanilide in dioxan	Benzylaniline in benzene
Hedestrand α	10.072	1.838
Hedestrand β	0.342	0.450
Molar Refraction (cm^3) (calculated)	59.07	55.75
Total Polarization (cm^3)	373.66	112.87
Orientation Polarization (cm^3)	314.59	57.82
Dipole Moment (D)	4.00	1.70

TABLE III

Parameters used in calculating the charge distribution by the Smith, Ree, Magee, Eyring method

Bond	β_{ab}	γ_{ab}	Basic molecule	Moment used to derive γ_{ab}	
H – C (methyl)	0.130	0.00			
O = C (carbonyl)	0.450	-2.33	Formaldehyde	2.27	
Cl – C	0.710	-1.49	Methl chloride	1.86	
Br – C	0.906	-1.44	Methyl bromide	1.78	
X – C where X equals NH_2	0.243	$+1.10$	Methyl amine	1.28	(14)
N ≡ C	0.627	-3.573	Hydrogen cyanide	2.93	
Y – C where Y equals NO_2	0.243	$-2\ 650$	Nitro methane	3.54	
Z – C where Z equals $-NHNH_2$	0.243	$+1.44$	Methyl hydrazine	1.68	
C – C	$\beta_c^c = 0.718$;	$\alpha_{cc} = 0$			
C = C	$\beta_c^c = 1.700$;	$\alpha_{cc} = 0$			

DISCUSSION

In benzonitrile the higher mesomeric moment (1.41 D) is the result of the overlap of the P_π orbital of nitrile carbon with that of the ring carbon to which it is linked. But in nitrobenzene, benzaldehyde and benzoyl chloride, where the bonding orbitals of the atom linked to the aromatic ring are sp^2 hybridized, the mesomeric moment is due to the maximum overlap. In benzoyl halides, the phenyl group is responsible for the higher mesomeric moment derived than in acetyl halides. The net mesomeric moment decreases in the order of the electro-negativity of the halogen. The introduction of a CH_2 group in between the substituent and the phenyl radical brings about non-planarity, thereby inhibiting mesomeric interaction which is reflected in the mesomeric moments of benzyl cyanide (0.49 D), phenyl nitromethane ($-0\ 31$ D) and phenyl acetyl chloride (0.75 D).

TABLE IV

Formal Charge Distribution

Molecule	Carbon	Hydrogen	Carbon (methyl)	Hydrogen (methyl)	Oxygen	Group x
Acetonitrile	1.7020 (nitrile)	......	0.579	0 075		– 2.506 (nitrile nitrogen)
Nitroethane	......	......	1.341 C_1	0.174 H_1	......	– 2.324 (nitro group)
			0.457 C_2	0.059 H_2		
Acetyl chloride	1.447 (carbonyl)	......	0.492	0 064	– 1.669	– 0 462 (chlorine)
Acetyl bromide	1.329 ,,	......	0 452	0.059	– 1.772	– 0.235 (bromine)
Acetaldehyde	1.131 ,,	0.147	0.384	0.050	– 1.811	......
Acraldehyde	1.111 ,,	0.144	0.310 C_2	0 040 H_2	– 1.830	......
			0.178 C_3	0.023 H_3		
Acetone	0.986 ,,	......	0.329	0 043	– 1 885	......
			0 330	0.043		
Divinyl ketone	0.938 ,,	......	0.262 C_2, C_4	0.195 H_2, H_4	– 1.908	......
			0 150 C_1, C_5	0.034 H_1, H_5		
Glyoxal	1.474 ,,	0.192	......	......	– 1.666	......
Diacetyl	1.212 ,,	......	0 413	0.054	– 1.785	
Formamide	0.669 ,,	0.087	......	......	– 2.019	1.263 (amino group)
Acetamide	0 564 ,,	......	0.192	0.025	– 2.066	1.237 ,,
Urea	0 062 ,,	......	......	......	– 2.292	1.115 ,,
Formhydrazide	0.484 ,,	0 063	......	......	– 2.100	1.557 (hydrazyl group)
Carbohydrazide	– 0.289 ,,	......	......	......	– 2.450	1.370 ,,

TABLE V

Molecule	Moment by S.R.M.E. method	Observed value	Difference from S.R.M.E. value	Phenyl compound	Observed value	Difference from S.R.M.E. value	Diphenyl compound	Observed value	Difference from S.R.M.E. value
1 Acetonitrile	2.98	3.94 G	0.96	Benzonitrile	4.39 G	1.41			
					4.02 B	1.04			
				Cinnamic acid nitrile	4.14 D	1.16			
				Benzyl cyanide	3.47 B	0.49			
				Penyl propiol nitrile	4.50 B	1.52			
				Nitrobenzene	4 23 G	0.62			
2 Nitroethane	3.61	3.58 G	—0.03	Phenyl nitro methane	3.30 B	−0.31			
		3.70 G	0.09						
3 Acetyl chloride	1.79	2.45 B	0.66	Benzoyl chloride	3.33 B	1.54			
		2.68 G	0.89						
				Phenyl acetyl chloride	2.54 B	0.75			
4 Acetyl bromide	1.92	2.43 B	0.51	Benzoyl bromide	3.37 B	1.45			
				Benzaldehyde	2.77 B	0.45			
5 Acetaldehyde	2.32	2 69 G	0.37	Phenyl acetaldehyde	2.48 B	0.16			
		2.72 G	0 40						
6 Acraldehyde	2.31 Z	3.04 G	0.73	Cinnamaldehyde (2)	3.71 B	1.39			
			0.67		3.63 B	1.31			
	2.37 U	2 90 B	0.59						
			0.53						
7 Acetone	2.35	2.85 G	0.50	Acetophenone (2)	3 00 G	0.68	Benzophenone	2.95 B	0.63
		2 98 B	0.63		2 96 B	0.64			
8 Divinyl ketone	2.33 U	...	...	Benzalacetone	3.31 B	0.99	Dibenzyl ketone	2.65 B	0.33
	2.36 V								
	2.36 W						Benzylidene acetophenone	3.00 B	0.68
9 Glyoxal	3.74	...	...				Dibenzal acetone	2.28 B	0.96
10 Diacetyl	3.70	1.22 G Free rotation	...				Benzil	3.76 B	0.02
11 Formamide (1)	3.78	3.22 G	−0.56	Benzamide	3.77 D	−0.01	Benzanilide (15)	4.00 D*	0.22
					3.84 D	0.06		3.38 B	—0.40
12 Acetamide (1)	3.78	3.44 B	−0.34	Acetanilide	4.01 B	0.23			
		3.90 D	0.12						
13 Urea	4.43	4.56 D	0.13	Phenyl urea	3.60 D	−0.83	Diphenyl urea (symm)	4.60 D	0.17
14 Formhydrazide(8)	2.30	2.24 D	0.06	Benzoic hydrazide	2.70 B	0.40	Diphenyl urea (unsymm)	2.70 D	− 1.73
15 Carbohydrazide (hypothetical(11))	4.99	...	...				Diphenyl carbohydrazide(11)	3.77 D	−1.22

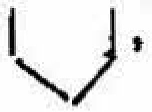
* Observed value in this work: The geometry of the carbon skeleton used to calculate the particular S.R.M.E. value is indicated by capital letters thus: U conforms to structure , V to , W to  and Z to .

TABLE VI

	Melecule	Observed value	Difference from observed basic value	Phenyl compound	Observed value	Difference from observed basic value	Diphenyl compound	Observed value	Difference from observed basic value
1.	Methyl amine (Basic)	1.28 G	...	Aniline	1.48 G	0.20	Diphenyl amine (3)	1.08 B	—0.20
					1.54 B	0.26		0.95 B	—0.33
2.	Dimethyl amine	1.02 G	—0.16	Methyl aniline (3)	1.64 B	0.36	Benzyl aniline *	1.70 B	0.42
3.	Allyl amine (7)	1.31 B	0.03	Dimethyl aniline	1.61 G	0.33	N Benzylidine aniline	1.55 B	0.27
					1.58 B	0.30			
				Benzyl amine (7)	1.38 B	0.10			
					1.30 B	0.02			

* Observed value in this work

In benzaldehyde and acetophenone, the dipole resides primarily in the carbonyl group, so that the mesomeric moment which is directed away from the ring augments the primary moment. Hence the mesomeric moments (0.45 and 0.68D) of both the molecules are appreciably higher than those of aliphatic aldehydes and ketones. In benzophenone, the effect is much more pronounced due to the higher + M effect of the phenyl group. An extension of the unsaturated system in benzal acetone and cinnamaldehyde increases the mesomeric moment (0.99 and 1.39 D respectively). With the postulate of a large contribution from conjugation of the ring with the dienoid system, it can be seen that the contribution is almost the same in cinnamaldehyde, benzylidine, acetone and dibenzylidine acetone.

Whereas in formamide and acetamide the net mesomeric moment is in the negative direction, with the introduction of a phenyl group in place of hydrogen in formamide, the net mesomeric moment has a positive direction. In trans benzanilide the two phenyl groups act to nullify the effect of each other with the result the net mesomeric moment retains the same direction as in formamide. In acetanilide two paths are available for the migration of the lone pair of the nitrogen atom with the result that the + M effect of the methyl group reinforces the + M mesomeric interaction from nitrogen to the phenyl ring.

In phenyl urea, the net mesomeric moment has a reverse direction to that in urea and is much more enhanced in the unsymmetrical diphenyl urea, whereas the introduction of the two phenyl groups symmetrically, act to nullify each other's effect. The net negative mesomeric moment between the calculated value for carbohydrazide and the observed value for diphenyl carbohydrazide is quite anamalous. This may be due to the fact that the benzene ring does not lie in the plane of the conjugated chain system.

That the lone pair orbital has more p character in aromatic amine compounds, than in aliphatic amine compounds is shown by the mesomeric moments of aniline, dimethyl aniline, benzylamine and N benzylidene aniline. The case of diphenyl amine and dibenzyl amine are analogous to dimethyl amine in that the two phenyl groups exactly cancel each other's effect. In benzyl aniline, the benzyl group reinforces the + M mesomeric effect of the amino group with the result a higher mesomeric moment is obtained.

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