

## PRINCIPLE OF ADDITIVITY OF DIPOLE MOMENTS: 1,3- AND 1,3,5-DERIVATIVES OF BENZENE

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Dipole moments of fourteen 1,3-derivatives and thirteen 1,3,5-derivatives of benzene, with axially symmetrical substituents only, were measured in two solvents. After excluding the compounds forming the donor-acceptor complexes with benzene, the experimental values are well reproduced by the vector addition of group moments, *i.e.* the accuracy achieved is sufficient for practical purposes. Nevertheless, small systematic deviations were observed: the experimental moments were as a rule less than additive in the case of 1,3-derivatives but greater in the case of 1,3,5-derivatives. These deviations cannot be accounted for by deformation of bond angles from the hexagonal geometry but they can be semiquantitatively interpreted by mutual inductive interaction of dipoles. The latter interpretation was supported by CNDO/2 calculations.

The vector addition of bond moments has been extensively used as a method for predicting dipole moment of a given structure<sup>1</sup>. While only approximative, this approach may still work well provided that the bond moments have been determined on molecules similar to those to which they are applied. The relevant approximation is in fact not the additivity within one molecule but rather the transferability from one molecule to another. In the present state of development the additivity scheme attains certainly better accuracy than available by common quantum chemical methods<sup>1,2</sup>. Its most popular application has been in stereochemistry where usually several calculated values are confronted with the experiment in order to take a decision about the actual structure<sup>1,3</sup>. Another possibility is comparison of the measured dipole moment of a real molecule with that calculated for an idealized structure; the differences are assigned to features neglected in the idealized model, *e.g.* to mesomeric interaction<sup>1,4</sup> or to the intramolecular hydrogen bond<sup>5</sup>. For this reason many molecules with strong interaction between functional groups were thoroughly investigated and significant deviations from additivity were found and interpreted. Much less attention has been given to checking the precision of the additivity principle in the case of simple molecules in which strong interactions are excluded. Such studies require a high experimental accuracy on the one hand and a systematic choice of compounds on the other.

With the aforementioned idea in mind we investigated the polyhalogen derivatives of adamantane as described in the preceding communication<sup>6</sup>. Although the bond

moment approach was shown to be sufficiently precised for any practical purpose, minute but real deviations were observed. Their explanation is more probably in the mutual inductive interaction of dipoles than in a deformation of bond angles, although both effects may be operative. In the present communication we deal with benzene derivatives. Since they are the most easily available compounds with known molecular geometry, they served always as a popular example to demonstrate the additivity of bond moments. For instance the isomeric dichlorobenzenes are quoted in many textbooks. When a model compound is to be constructed bearing a substituent with a known dipole moment, substitution on an aromatic nucleus is always the most natural choice<sup>7</sup>. Nevertheless, the interpretation of results may be less straightforward than in the case of adamantane derivatives since the following effects have to be taken into account: *a*) Steric hindrance and/or short-range electrostatic action, together called *ortho*-effect, may be operative in *ortho* derivatives; see *e.g.* the lowered dipole moment of 1,2-dichlorobenzene<sup>8</sup>. *b*) Conjugation of functional groups ("through-resonance") may raise the dipole moment of *para* (or even *ortho*) derivatives if one substituent can act as acceptor and the other as donor, *e.g.* in 4-nitroaniline<sup>1</sup>. *c*) Axially unsymmetrical substituents may give rise to several conformations, see *e.g.* the non-zero dipole moment of 1,4-dimethoxybenzene<sup>8</sup>. *d*) Benzene as solvent may form donor-acceptor complexes with aromatic derivatives bearing several acceptor substituents<sup>1</sup>. For instance the apparent dipole moment of 1,3,5-trinitrobenzene in benzene belongs to a complex with coplanar rings<sup>9</sup>, the orientation of the moment is perpendicular to the ring plane. *e*) Dipole moments of some benzene monoderivatives (*e.g.* halogenobenzenes) involve a contribution from the conjugation of the substituent with the benzene nucleus<sup>1</sup>. Then the additivity of bond moments would call even for the additivity of these mesomeric contributions.

Our problem requires to deal with minute differences. Therefore we have to combine results on many compounds, in order to obtain statistically significant conclusions. Simultaneously the aforementioned effects are to be excluded. We thus restricted our study to 1,3- and 1,3,5-derivatives of benzene with the axially symmetrical substituents Cl, Br, CN, CF<sub>3</sub>, and NO<sub>2</sub>. In this way the effects *a*)–*c*) were eliminated. The problems with the mesomeric contributions, see *e*), are at least minimized for substituents CN, CF<sub>3</sub>, and NO<sub>2</sub> the conjugation of which is negligible<sup>1,10</sup>. Complex formation, see *d*), cannot be eliminated completely but can be revealed by comparing the experimental dipole moments measured in tetrachloromethane and in benzene. Compounds insufficiently soluble in the former were measured in dioxan instead. Altogether we investigated 27 compounds in two solvents (Table I). This set should represent compounds for which the preconditions for the additive behaviour are relatively best fulfilled. Among them there are many whose dipole moments were measured already several times. Our values need not be better than previous ones but we considered necessary to compare results obtained by the same method and in the same laboratory. Our experimental results were compared

TABLE I  
Dipole moment data of substituted benzenes (25°C)

	Substituents	Solvent	$\alpha^a$	$\gamma^a$	$\mu^b$	$\mu^{b,c}$	$\mu$ lit. values <sup>b,d</sup>
1	Cl, Cl	CCl <sub>4</sub>	3.12	0.148	5.0	5.2	4.7
		C <sub>6</sub> H <sub>6</sub>	1.88	0.077	5.2	5.3	4.6—5.2
2	Br, Br	CCl <sub>4</sub>	1.95	0.375	4.6	5.1	
		C <sub>6</sub> H <sub>6</sub>	1.10	0.145	4.8	5.2	4.9, 5.2
3	NO <sub>2</sub> , NO <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	9.30	0.070	12.5	13.3	12.8 <sup>e</sup>
		C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	12.75	0.260	13.8		
4	CN, CN	C <sub>6</sub> H <sub>6</sub>	12.80	0.188	12.9	13.2	12.6
		C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	16.48	0.275	13.6		
5	CF <sub>3</sub> , CF <sub>3</sub>	CCl <sub>4</sub>	5.19	—0.372	8.3	8.4	
		C <sub>6</sub> H <sub>6</sub>	3.00	—0.300	8.5	8.5	7.0, 8.1
6	Cl, NO <sub>2</sub>	CCl <sub>4</sub>	14.69	0.315	11.4	11.5	
		C <sub>6</sub> H <sub>6</sub>	8.40	0.111	11.6	11.6	11.4 <sup>e</sup>
7	Cl, CN	CCl <sub>4</sub>	16.60	0.370	11.3	11.4	
		C <sub>6</sub> H <sub>6</sub>	9.73	0.152	11.6	11.5	11.4, 11.6
8	Cl, CF <sub>3</sub>	CCl <sub>4</sub>	5.28	—0.065	7.4	7.4	
		C <sub>6</sub> H <sub>6</sub>	2.99	—0.148	7.6	7.5	7.1, 7.4
9	Br, NO <sub>2</sub>	CCl <sub>4</sub>	11.70	0.480	11.4	11.5	
		C <sub>6</sub> H <sub>6</sub>	6.45	0.135	11.4	11.6	10.7—11.5
10	Br, CN	CCl <sub>4</sub>	13.40	0.410	11.6	11.4	
		C <sub>6</sub> H <sub>6</sub>	7.80	0.105	11.7	11.5	
11	Br, CF <sub>3</sub>	CCl <sub>4</sub>	4.48	0.068	7.3	7.4	
		C <sub>6</sub> H <sub>6</sub>	2.24	—0.095	7.3	7.4	
12	NO <sub>2</sub> , CN	CCl <sub>4</sub>	19.75	0.400	12.8	13.2	
		C <sub>6</sub> H <sub>6</sub>	10.80	0.135	12.7	13.3	12.7
13	NO <sub>2</sub> , CF <sub>3</sub>	CCl <sub>4</sub>	11.20	—0.047	11.1	11.6	
		C <sub>6</sub> H <sub>6</sub>	6.57	0.107	11.2	11.7	
14	CN, CF <sub>3</sub>	CCl <sub>4</sub>	12.60	—0.450	11.3	11.5	
		C <sub>6</sub> H <sub>6</sub>	7.40	—0.156	11.5	11.6	
15	Cl, Cl, NO <sub>2</sub>	CCl <sub>4</sub>	6.60	0.422	8.2	8.0	
		C <sub>6</sub> H <sub>6</sub>	3.79	0.113	8.5	8.0	8.3, 8.9
16	Cl, Cl, CN	CCl <sub>4</sub>	7.15	0.370	8.2	7.9	
		C <sub>6</sub> H <sub>6</sub>	4.21	0.196	8.4	7.9	8.4
17	Br, Br, NO <sub>2</sub>	CCl <sub>4</sub>	4.95	0.410	8.5	8.1	
		C <sub>6</sub> H <sub>6</sub>	2.70	0.136	8.6	8.1	
18	Br, Br, CN	CCl <sub>4</sub>	5.60	0.440	8.8	8.0	
		C <sub>6</sub> H <sub>6</sub>	3.10	0.196	8.8	8.0	

TABLE I  
(Continued)

	Substituents	Solvent	$\alpha^a$	$\gamma^a$	$\mu^b$	$\mu^{b,c}$	$\mu$ lit. values <sup>b,d</sup>
19	NO <sub>2</sub> , NO <sub>2</sub> , Cl	C <sub>6</sub> H <sub>6</sub> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	3.71 6.20	0.280 0.300	8.4 10.3	8.0	
20	NO <sub>2</sub> , NO <sub>2</sub> , Br	C <sub>6</sub> H <sub>6</sub>	3.04	0.128	8.6	8.1	7.7
21	NO <sub>2</sub> , NO <sub>2</sub> , CN	C <sub>6</sub> H <sub>6</sub> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.85 0.54	0.162 0.315	3.7 1.8	0.1	5.3 <sup>f</sup>
22	NO <sub>2</sub> , NO <sub>2</sub> , CF <sub>3</sub>	CCl <sub>4</sub> C <sub>6</sub> H <sub>6</sub>	1.47 1.11	0.070 -0.044	4.3 5.3	4.8 4.8	
23	CN, CN, NO <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	1.16 1.50	0.162 0.280	4.2 4.3	0.1	
24	Cl, CF <sub>3</sub> , CF <sub>3</sub>	CCl <sub>4</sub> C <sub>6</sub> H <sub>6</sub>	1.18 0.77	-0.209 -0.200	4.5 5.0	3.2 3.2	4.3, 4.5
25	Br, CF <sub>3</sub> , CF <sub>3</sub>	CCl <sub>4</sub> C <sub>6</sub> H <sub>6</sub>	0.78 0.43	-0.145 -0.357	4.0 4.9	3.4 3.4	4.8
26	CF <sub>3</sub> , CF <sub>3</sub> , NO <sub>2</sub>	CCl <sub>4</sub> C <sub>6</sub> H <sub>6</sub>	1.17 0.64	-0.223 -0.207	4.6 4.7	4.8 4.8	
27	CN, CF <sub>3</sub> , CF <sub>3</sub>	CCl <sub>4</sub> C <sub>6</sub> H <sub>6</sub>	1.48 0.78	-0.234 -0.215	4.9 4.9	4.7 4.7	

<sup>a</sup> Slopes of the plots  $\epsilon_{12}$  vs  $w_2$  and  $n_{12}^2$  vs  $w_2$ , respectively; <sup>b</sup> units  $10^{-30}$  C m; <sup>c</sup> calculated by vector addition of bond moments with the hexagonal geometry, see Experimental; <sup>d</sup> ref.<sup>8</sup> unless otherwise noted; <sup>e</sup> median values from 13 or 7 measurements<sup>8</sup>, respectively; <sup>f</sup> ref.<sup>14</sup>.

with the prediction based on the additivity of bond moments and with the CNDO/2 calculations as well.

## EXPERIMENTAL AND RESULTS

**Materials.** All compounds investigated (Table I) were either commercially available or were prepared by well-known methods. They were purified by repeated crystallization, at least the last one was carried out from a non-polar solvent, usually from benzene. The purity of samples was checked by melting point determination, GLC and TLC.

**Physical measurements.** The method of measuring dipole moments was described previously<sup>5,6</sup>. The results are listed in Table I. The references to previous work were restricted to more important cases, they are given in footnotes to Table I.

**Calculations.** The bond moments calculations were based on the bond and group moments, derived from measurements on monosubstituted benzenes and valid essentially for benzene

derivatives only. For benzene solution the standard values<sup>1</sup> were adopted without a significant change (all dipole moments in  $10^{-30}$  C m): C—Cl 5.33, C—Br 5.17, C—NO<sub>2</sub> 13.30, C—CN 13.20, C—CF<sub>3</sub> 8.53. These values are based always on several accordant measurements in benzene solution<sup>8</sup>. In tetrachloromethane solution several measured values are available only for monoderivatives with substituents Cl, Br, and NO<sub>2</sub>; at least in two cases they are by *ca.* 0.1 lower than in benzene. Also the plot of our experimental dipole moments of polyderivatives in benzene *vs* in tetrachloromethane (Fig. 1) reveals a systematic difference of the same order. Therefore, we adopted for tetrachloromethane the bond moments by 0.1 less than in benzene: C—Cl 5.23, C—Br 5.07, C—NO<sub>2</sub> 13.20, C—CN 13.10, C—CF<sub>3</sub> 8.43. These values should be considered as mere estimates, but their uncertainty is of the same order as is the experimental error. As regards the molecular geometry, we assumed bond angles of 120° throughout as the first possibility (hexagonal geometry). The calculated dipole moments are listed in Table I. As a possible improvement, small deviations from 120° were considered, calculated as a sum of empirical increments due to individual substituents. The numerical values of these were derived by Domenicano and his collaborators<sup>11</sup> by a statistical analysis of carefully selected X-ray data of many benzene derivatives. For substituents Cl, CN, NO<sub>2</sub> we used the increments of ref.<sup>11</sup>, for Br the same values as for Cl, and for CF<sub>3</sub> the following values<sup>12</sup>:  $\Delta\alpha$  0.9,  $\Delta\beta$  -0.8,  $\Delta\gamma$  0.1,  $\Delta\delta$  0.4. (They mean the angle deformations raised in the positions 1, 2, 3, and 4, respectively, by the substituent in the

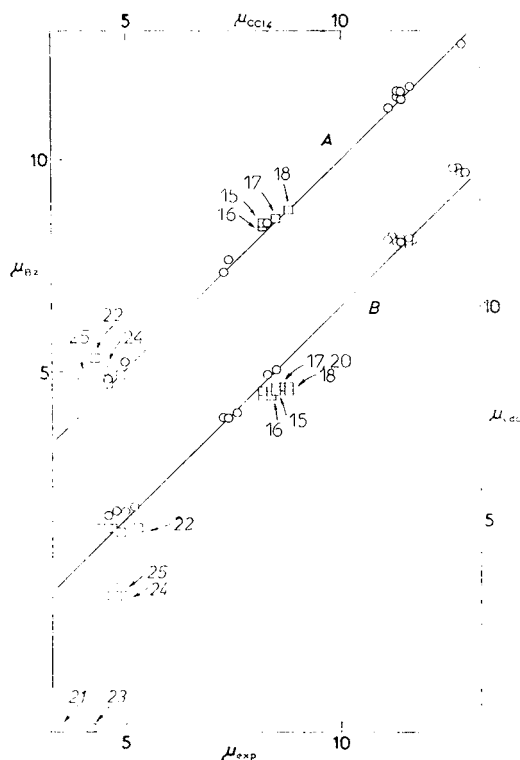


FIG. 1

Comparison of dipole moments of benzene derivatives: *A* experimental values in benzene solution *vs* tetrachloromethane solution, *B* additive values *vs* experimental; ○ 1,3-derivatives, □ 1,3,5-derivatives; compounds forming complexes with benzene are marked by arrows. The straight lines have unity slope

position 1.) The dipole moments calculated with this improvement ("Domenicano geometry") are not tabulated since they differ but slightly from the previous ones.

The CNDO/2 calculations were carried out with the standard parametrization<sup>13</sup>. The hexagonal geometry of the benzene ring was not optimized. The relevant results are listed in Table II, they were restricted to derivatives not containing bromine.

## DISCUSSION

In contradistinction to the previously investigated adamantane derivatives<sup>6</sup>, benzene derivatives represent a sample of merely practical importance. Therefore, the discussion should accentuate the question whether the vector addition of bond and group

TABLE II  
Main results of CNDO/2 calculations on benzene derivatives

Compound <sup>a</sup>	$\mu_{\text{calc}}$		$\mu_{\text{add}}^c$		$\sum q_C^d$
	CNDO/2	(STO-3G) <sup>b</sup>	CNDO/2	(STO-3G) <sup>b</sup>	
1	8.9		8.4		-0.2435
3	16.1		16.5		-0.1848
5	8.4		8.6		-0.0389
6	15.1		14.3		-0.2116
7	9.2		9.2		-0.1879
8	7.9		8.5		-0.1407
12	14.4	(12.8)	14.4	(13.3)	-0.1588
13	14.1		14.3		-0.1120
14	9.3		9.5		-0.0858
15	9.5		8.1		-0.3014
16	3.2		1.5		-0.2835
19	9.5		8.1		-0.2735
21	6.2		6.6		-0.2267
22	7.7		7.9		-0.1776
23	6.3		6.6		-0.2004
24	1.6		0.2		-0.1324
26	7.7		7.9		-0.1049
Chlorobenzene	8.4		—		-0.1367
Benzonitrile	9.9	(12.2)	—		-0.0373
Trifluoro-					
methylbenzene	8.6	(5.6)	—		-0.0421
Nitrobenzene	16.5	(14.2)	—		-0.1163

<sup>a</sup> Numbering as in Table I; <sup>b</sup> ref.<sup>15</sup>; <sup>c</sup> calculated as the vector sum of dipole moments calculated by CNDO/2 for the respective monoderivatives; <sup>d</sup> sum of net charges on the six carbon atoms of the nucleus.

moments is sufficiently precise for concrete problems, say in stereochemistry. Due to the greater diversity of substituents and their greater group moments, we expect also greater deviations from additivity than in the case of adamantane derivatives.

Before discussing the additivity problem we have to estimate reliability of our results and to reveal compounds forming complexes with benzene. The reliability can be appreciated both according to the inner consistency of our data and according to the agreement with the literature. When we compare the measurements on the same compound in benzene and in tetrachloromethane, the average difference 0.13 is probably real (see also Fig. 1), although the standard deviation from this average is 0.11. Compounds forming complexes (see later) were dropped from this comparison. Comparison of corresponding chloro and bromo derivatives reveals an almost zero average difference and a standard deviation of 0.32. However, this value is evidently greater than the experimental error since the bond moments C—Cl and C—Br are not equal and the difference affects different derivatives the opposite sense. Comparison to literature values is impaired by the discrepancies among these values themselves: standard deviation 0.32 for the compounds of Table I. In cases when more literature data were available, our measurements differ by at most 0.2 from their average (Table I). We conclude that our experimental error does not exceed this value.

The existence of donor-acceptor complexes with benzene and their approximate structure have been proven<sup>9</sup>. Nevertheless these complexes have not always received proper attention in the discussions of experimental dipole moments. Sometimes they served to explain apparent non-zero moments of symmetrical molecules<sup>1</sup>, like 1,4-dinitrobenzene or 1,3,5-trinitrobenzene, but the possibility has been neglected that they can affect in some degree even the measured moments of unsymmetrical molecules. The necessary condition is only the lowered  $\pi$ -electron density giving the molecule an electron acceptor character. Since the planes of the two benzene rings are parallel in the complex<sup>9</sup>, the charge-transfer moment is perpendicular to them and makes the total observed dipole moment greater. Among our compounds the donor-acceptor complexes might be encountered relatively often due to the presence of strongly electron attracting substituents. We believe that their existence is proven if the three following conditions are met simultaneously: *a*) There is a significant positive difference between the experimental dipole moments measured in benzene and in tetrachloromethane, respectively, see Fig. 1A. (For compounds insufficiently soluble in tetrachloromethane we can observe a difference between the measurements in benzene and dioxane but we cannot safely predict its sign.) *b*) The experimental dipole moment in benzene is significantly higher than calculated from the additivity of bond moments, see Fig. 1B. *c*) The electron density on the benzene nucleus is lowered by the presence of strongly electron attracting substituents.

According to the above criteria the measured dipole moments of 3,5-dinitrobenzonitrile (21) and 3,5-dicyanonitrobenzene (23) in benzene are due essentially to the

complex, those of several other compounds (19, 20, 22, 24, 25) may involve a contribution up to say 0.5 from the complex formation. Some complex formation with benzene is in fact possible for all 1,3,5-derivatives of Table I. A fundamental question is now to what extent the complex formation may affect the observed dipole moments of 1,3-derivatives. We attacked this problem by calculating the CNDO/2 electron densities on the carbon atoms of the benzene nucleus (Table II). The results are impaired by systematic overestimating the electron attracting power of chlorine in chlorobenzene itself and in all other chloro derivatives as well. If the latter are neglected, the remaining results reveal that the sum of net charges for all the ring atoms is of the order  $-0.2$  or at least  $-0.15$  when the molecule forms sufficiently strong complexes. It follows that of our 1,3-derivatives only 1,3-dinitrobenzene (3) could show a charge-transfer moment of the order of 0.5; a somewhat less effect is possible in the case of 3-nitrobenzonitrile (12) and possibly still 1,3-dicyanobenzene (4). A direct comparison of the experimental values in benzene and tetrachloromethane was possible only in the last case; the difference is insignificant. More important, the dipole moments calculated additively are greater than experimental for all three compounds, the opposite of the expected effect of the complex.

From the preceding paragraph we conclude that complex formation is not consequential for 1,3-derivatives. Hence the test of additivity can be based on 1,3-derivatives measured in either solvent and on 1,3,5-derivatives in tetrachloromethane only. Considering the insufficient solubility of some compounds we have altogether 35 experimental values for the test. The salient result is now that the experimental values are lower than additive for practically all 1,3-derivatives (in average by 0.18) while they are greater for most 1,3,5-derivatives (in average by 0.35), see Fig. 1B. The deviations do not depend on solvent and in one case (compound 1) they can be confirmed even on the gas phase values<sup>8</sup>. Similarly as in the case of substituted adamantanes<sup>6</sup> the explanation may be sought either in the distortion of bond angles from the ideal hexagonal geometry, or in the mutual induction of substituents. The actual deviations from the hexagonal symmetry can be relatively reliably estimated from the incremental perturbations raised by individual substituents as reported by Domenicano<sup>11,12</sup> (see Experimental). Since every substituent exerts the greatest effect just on C—C—C angle in the *ipso* position, the angles between bond moments are less affected. The greatest deviations among our compounds were found for the angle between the bond moments C—Cl and C—NO<sub>2</sub> in the compound 6 ( $+1.1^\circ$ ), further between the two C—Br bond moments in the compound 18 ( $-0.9^\circ$ ). These deviations correspond to a difference of 0.1 in the calculated dipole moments. In other cases the dipole moments anticipated for the Domenicano geometry are either equal as for the hexagonal geometry or differ just in the rounding off the last decimal. The predicted effect of angle distortion is thus mostly in the right direction for 1,3-derivatives but from the quantitative point of view it is insufficient to explain the observed effects. For 1,3,5-derivatives the geometrical correction would make the



agreement with experiment only insignificantly worse. More important, the deformation of geometry has almost constant effect on all derivatives while the observed non-additivity tends to be greater with greater dipole moments (Fig. 1B).

The aforementioned facts are better explained in terms of mutual induction of the functional groups<sup>15</sup>. The schematic representation in Fig. 2A shows that the induced dipole moments are almost of opposite direction to the original ones, reducing the resulting dipole moment of 1,3-derivatives. There are individual differences in the group polarizabilities and in the position of the dipoles, even the approximation of point dipole is rather crude and may be more or less appropriate for different substituents. For these reasons we abandoned any more quantitative estimation and were satisfied with the qualitative statement that greater bond moments are more reduced by induction. In 1,3,5-derivatives with two equal substituents the six induced moments add vectorially in such a way that the final dipole moment is always greater than the additive value (Fig. 2B or 2C). The increase is the greater the more different are the substituent group moments. These predictions are roughly fulfilled by the data of Table I, see also Fig. 1B. There are some exceptions but their attempted explanation would not be warranted with respect to the experimental accuracy on the one hand and to the oversimplified theory on the other. Even a more detailed calculation of the induced moments in terms of the Smith-Eyring theory<sup>16</sup> is not feasible for aromatic derivatives, in addition some parameters are unknown, particularly for the nitro group. Note still that for halogen substituents the expected

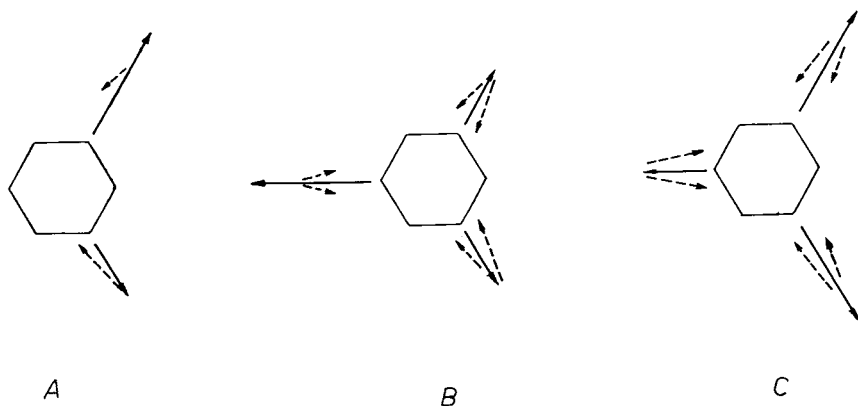


FIG. 2

Mutual induction within the functional groups: *A* benzene 1,3-derivatives, *B* 1,3,5-derivatives like 3,5-dichloronitrobenzene, *C* 1,3,5-derivatives like 3,5-dinitrochlorobenzene. Full arrows — original dipole moments, broken arrows — induced moments

deviations from additivity are of the same order as in the case of halogenated adamantanes<sup>6</sup>; the distance of the interacting dipoles is almost equal.

We attempted to support the above conclusions by CNDO/2 calculations. With standard hexagonal geometry the calculated dipole moments disagree considerably with the experiment even for monoderivatives (Table II). We have omitted all bromo derivatives from the calculations but even for chlorobenzene the disagreement is sensible. Particularly striking is further the difference between calculated values for nitrobenzene and benzonitrile, while the experimental values are virtually equal, both in solution and in the gas phase<sup>8</sup>. Just this difference was but slightly improved by optimization of geometry and required an *ad hoc* correction for the nitro group<sup>2</sup>. Note also that the optimized bond angles<sup>2</sup> are quite unrealistic, often with just opposite trends than in Domenicano's values<sup>11</sup>. Therefore, we were satisfied with the non-optimized geometry and introduced no special corrections. Our intention was not to obtain a good fit for monoderivatives but only to reproduce by the calculation the trend in the experimental values, when going from monoderivatives to polyderivatives. To this purpose we calculated also the additive dipole moments by vector addition of the CNDO/2 moments of monoderivatives (Table II). The deviations from additivity calculated within the framework of CNDO/2 are plotted in Fig. 3 vs the deviations based on the experimental values. The figure reveals a general trend: at least the greatest positive deviations for 1,3-derivatives and greatest negative deviations for 1,3,5-derivatives are reflected in the calculated values. There are some notable exceptions, particularly among trifluoromethyl derivatives, but we will not attempt their discussion. The results would not be significantly improved even on the

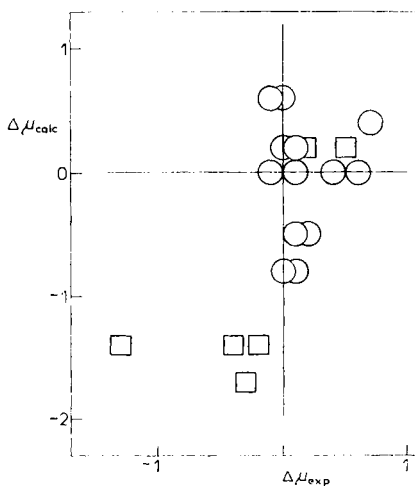


FIG. 3

Comparison of experimental and calculated deviations from the bond moment scheme. x-Axis  $\Delta\mu_{\text{exp}} = \mu_{\text{additive}} - \mu_{\text{experimental}}$ , y-axis  $\Delta\mu_{\text{calc}} = \mu_{\text{additive CNDO}} - \mu_{\text{CNDO}}$ ;  $\circ$  1,3-derivatives,  $\square$  1,3,5-derivatives

STO-3G level. From several data available<sup>17</sup> we can calculate the deviation from additivity for 3-nitrobenzonitrile (12) in excellent agreement with the observation (Tables II and I, respectively) but this agreement is probably fortuitous. The difference between nitrobenzene and benzonitrile is somewhat reduced on the STO-3G level, on the contrary the value calculated for trifluoromethylbenzene is much worse than in CNDO/2. We conclude that quantum chemical calculations reproduce the general pattern of approximate additivity of dipole moments and the principal deviations. Since the calculations relate to fixed hexagonal geometry, the calculated deviations from additivity cannot originate in angle deformation and their interpretation by dipole induction is thus strongly supported.

Let us revert to the question to what extent the deviations from additivity can affect the practical importance of the bond moment scheme. The mean deviation for 1,3-derivatives, 0.18, is of the same order as the usual experimental error. To attain this accuracy, the hexagonal geometry is completely sufficient. However, the deviation from additivity may attain even 0.7 in the case of greater dipoles (compound 3) and may be thus of some consequence in determining conformation or rotamer population. Note that for these purposes substitution in the *para* position was recommended<sup>7</sup> and systematically applied<sup>1</sup>; then the induction is further reduced compared to *meta* derivatives. If compounds with several substituents on one benzene nucleus are to be used in such studies, the group moment for the polysubstitution is best derived directly from the corresponding polyderivative. This is necessary particularly if two substituents are in the *ortho* position to each other<sup>18</sup>. The overall accuracy of the bond moment scheme can be evaluated by means of the statistic<sup>19</sup>  $\psi = s/s_0$ , where  $s$  is the standard error of the additive calculation and  $s_0$  is the standard deviation of all possible dipole moment values from their mean. Like in the preceding paper<sup>6</sup> we may adopt the approximate value  $s_0 = 3$ . Then  $\psi = 0.06$  for 1,3-derivatives or 0.12 for 1,3,5-derivatives. The former estimate is more favourable than the previous one<sup>6</sup> and represents an empirical relationship of a predictive power comparable *e.g.* to the Hammett equation. Benzene derivatives are evidently a class of compounds where the bond moment principle is particularly useful. Even in other classes of compounds it works well except for conjugated systems and directly adjoining polar bonds. We conclude that the deviations from this principal are merely of theoretical interest but do not impair its practical usefulness which can be always improved by choosing proper derivatives and introducing group moments.

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#### REFERENCES

1. Exner O.: *Dipole Moments in Organic Chemistry*. Thieme, Stuttgart 1975.
2. Catalán J., Macías A.: *J. Mol. Struct.* 38, 209 (1977).

3. Exner O. in the book: *The Chemistry of Double-Bonded Functional Groups* (S. Patai, Ed.), p. 1. Wiley-Interscience, London 1977.
4. Exner O., Waisser K.: This Journal **47**, 828 (1982).
5. Exner O., Koudelka J., Vašíčková S.: This Journal **48**, 735 (1983).
6. Exner O., Koudelka J.: This Journal **50**, 200 (1985).
7. Exner O., Jehlička V.: This Journal **30**, 639 (1965).
8. McClellan A. L.: *Tables of Experimental Dipole Moments*, Vol. 1/2. Freeman, San Francisco 1963 and Rahara Enterprises, El Cerrito 1974.
9. Briegleb G., Czekalla J.: *Z. Elektrochem.* **58**, 249 (1954); **59**, 184 (1955).
10. Exner O., Folli U., Marcaccioli S., Vivarelli P.: *J. Chem. Soc., Perkin Trans. 2* **1983**, 757.
11. Domenicano A., Murray-Rust P.: *Tetrahedron Lett.* **1979**, 2283.
12. Domenicano A.: Personal communication.
13. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*, p. 163. McGraw-Hill, New York 1970.
14. Lehman F. P. A., McEachern B. D. M.: *J. Mol. Struct.* **18**, 63 (1973).
15. Smyth C. P.: *Dielectric Behavior and Structure*, Chapter VIII. 3. McGraw-Hill, New York 1955.
16. Smith R. P., Ree T., Magee J. L., Eyring H.: *J. Amer. Chem. Soc.* **73**, 2263 (1951).
17. Pross A., Radom L.: *Progr. Phys. Org. Chem.* **13**, 1 (1981).
18. Exner O., Jehlička V.: This Journal **48**, 1030 (1983).
19. Exner O.: This Journal **31**, 3222 (1966).

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