Mesomeric Dipole Moments. Part 6.[1] Steric Inhibition of Conjugation in 2,4,6-Trimethylphenyl Derivatives

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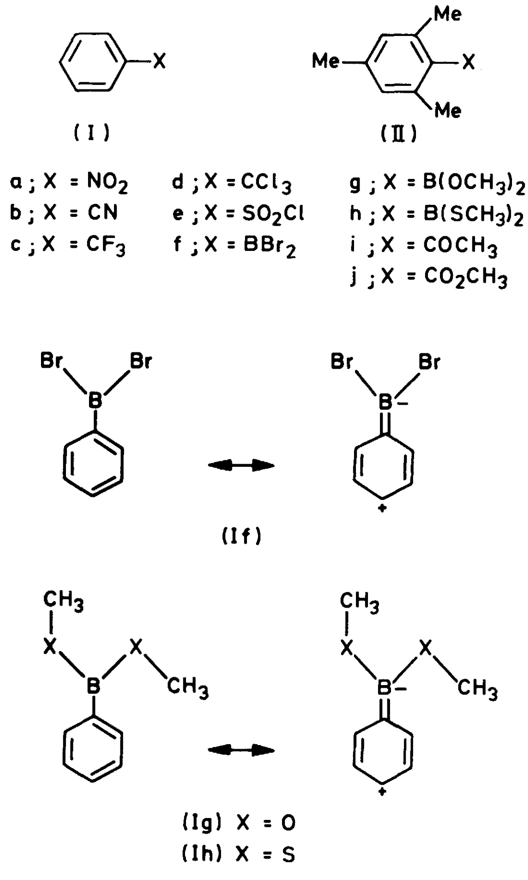
The dipole moments of 2,4,6-trimethylphenyl derivatives (IIb—h) measured in benzene solution were compared to those of simple phenyl derivatives (Ib—h) in order to evaluate the steric inhibition of mesomerism of individual substituents. The best example of this phenomenon was found in the case of the BBr_2 substituent [(If) and (IIf)], and it is demonstrable for $B(OMe)_2$, $B(SMe)_2$, $COCH_3$, and CO_2CH_3; conjugation of these substituents with the benzene nucleus is also proved by results from other areas. In contrast, conjugation in aromatic nitro-compounds, often quoted as a classical example, is certainly very weak and can hardly be proven. The relatively small changes in the dipole moments of compounds (Ia) and (IIa) may originate for the most part in the strong inductive effect of the nitro-group combined with the anisotropic polarizability of the benzene nucleus. Also, analysis of other experimental data concerning nitro-compounds revealed a strong inductive effect and negligible conjugation with the benzene nucleus unless a donor substituent is present.

According to the classical theory of substituent effects,[2] functional groups on a benzene ring exert their influence essentially by two mechanisms, induction and mesomerism (conjugative), although a more detailed classification has been elaborated.[3] Attempts to separate these two effects quantitatively were either based on quantum chemical calculations of charges [4] and energies,[5] or on experimental rate and equilibrium constants, using a saturated compound as reference.[6,7] The results obtained were more convincing for donor groups than for acceptors since, in the latter case, the two effects are of the same direction and the inductive effect usually much stronger. Therefore, the possible conjugation of typical acceptors, like NO_2, CN, and SO_2X, was sometimes appreciated cautiously [2c,8] and the opinion was offered by us [9] that their mesomeric effect had been overestimated and could become virtually zero unless a donor substituent capable of conjugation is also present. This view was supported by further experiments [10] and *ab initio* calculations;[5,10e] it also conforms with the concept of ' isovalent ' and ' sacrificial ' conjugation.[11]

However, apparently contradictory evidence derives from dipole moments.[12,13] Particularly impressive are the reduced dipole moments [2b,13] of 2,4,6-trimethylnitrobenzene and 2,3,5,6-tetramethylnitrobenzene in which the nitro-group is forced out of the ring plane. Even in this case, however, the reasoning based on steric inhibition of mesomerism was questioned in view of the fact that dipole moments of 2,4,6-tricyclohexylnitrobenzene and 2,4,6-triphenylnitrobenzene are further lowered,[14] although the distorsion of planarity cannot proceed further than up to 90°. Nevertheless, it is rather difficult to explain all this evidence without taking into account the concept of mesomerism. We suggested [14] tentatively electrostatic induction [15] and/or anisotropic polarizability for the benzene nucleus but a comparison with further acceptor groups is of the utmost importance.

In this paper we report the dipole moment of seven pairs of benzene (Ib—h) and 1,3,5-trimethylbenzene derivatives (IIb—h). The experimental results are assembled in the Table together with the literature data for compounds (Ia, i, j) and (IIa, i, j). Of the substituents investigated CN is not capable of rotating, while rotation of CCl_3, CF_3, and SO_2Cl should exhibit negligible effect on their conjugation if there is any. The borine-containing groups BBr_2, $B(OCH_3)_2$, and $B(SCH_3)_2$ were chosen as substituents certainly [5a,16–19] strongly conjugated with the benzene nucleus as shown in the Scheme. Besides the nitro-group, a similar comparison has been carried out [20] for the substituents COR, CO_2R, and SO_2CH_3.



(I) (II)

a ; X = NO_2
b ; X = CN
c ; X = CF_3
d ; X = CCl_3
e ; X = SO_2Cl
f ; X = BBr_2
g ; X = $B(OCH_3)_2$
h ; X = $B(SCH_3)_2$
i ; X = $COCH_3$
j ; X = CO_2CH_3

(If)

(Ig) X = O
(Ih) X = S

Scheme.

Discussion

We have started with the assumption that the extent of conjugation of various substituents with the benzene nucleus is

Polarization and dipole moments of monosubstituted benzenes (I) and their 2,4,6-trimethyl derivatives (II) in benzene at 25 °C

Compound	Substituent	α [a]	β [a]	P_2^0 [b] (cm^3)	R_D (cm^3)	μ(5) [c] (10^{-30} cm)	μ(15) [c] (10^{-3} cm)	Δμ [d]
(Ia)	NO_2					13.3 [e]	13.2	
(IIa)	NO_2					12.3 [e]	12.0	1.0
(Ib)	CN	14.72	−0.172	315.0	31.58	12.4 [f]	12.3	
(IIb)	CN	11.38	−0.124	354.5	45.5	12.9 [g]	12.8	−0.5
(Ic)	CF_3	4.27	−0.256	155.9	30.70	8.2 [h]	8.1	
(IIc)	CF_3	3.84	−0.214	188.0	44.6	8.8	8.6	−0.5
(Id)	CCl_3	2.40	−0.466	127.7	45.87	6.6 [i]	6.4	
(IId)	CCl_3	2.84	−0.358	182.4	59.8	8.1	7.9	−1.5
(Ie)	SO_2Cl	12.72	−0.455	458.2	41.03	15.1 [j]	15.0	
(IIe)	SO_2Cl	10.32	−0.338	476.4	55.0	15.1	15.0	0.0
(If)	BBr_2	2.23	−0.488	152.3	46.8	7.5	7.3	
(IIf)	BBr_2	1.02	−0.438	116.6	60.7	5.3	5.0	2.3
(Ig)	$B(OCH_3)_2$	1.52	−0.140	87.8	43.46	4.8	4.5	
(IIg)	$B(OCH_3)_2$	1.34	−0.062	110.4	57.4	5.2	4.9	1.0
(Ih)	$B(SCH_3)_2$	1.19	−0.230	90.4	55.8	4.2	3.8	
(IIh)	$B(SCH_3)_2$	1.50	−0.150	129.2	69.7	5.5	5.1	~2
(Ii)	$COCH_3$					10.2 [k]		
(IIi)	$COCH_3$					9.4 [k]		1.4
(Ij)	CO_2CH_3					6.4 [k]		
(IIj)	CO_2CH_3					6.0 [k]		1.0

[a] Slopes of the plots ε_{12} and d_{12}^{-1}, respectively, *versus* the weight fraction w_2. [b] Molar polarization of the solute. [c] Correction for the atomic polarization, 5% or 15% of the R_D value. [d] Vector difference of dipole moments of compounds (II) and (I). [e] Median value of those listed in ref. 19. [f] Ref. 19 gives values between 12.6 and 13.5. [g] G. Speroni, *Ric. Sci.*, 1957, **27**, 1199, gives a value of 13.8 but the difference with (Ib) is exactly the same as in this paper. [h] Ref. 19 gives values between 8.4 and 8.7. [i] Ref. 19 gives 6.8—7.2. [j] Ref. 19 gives 15.0—15.3. [k] Refs. 20*b*, *c*.

reflected in the effect of steric hindrance on dipole moments, *i.e.* in the variable magnitudes of Δμ (Table). On the other hand, these values could result from other effects. Let us consider first the substituents the conjugation of which cannot be influenced by the steric effect of *ortho*-methyl groups. Among them, there is only one which provides equal dipole moments for compounds (I) and (II), *viz.* SO_2Cl, while the results with SO_2CH_3 were ambiguous.[20d,e] In the remaining cases methyl substitution raises the dipole moment, although with CN and CF_3 the effect need not be significant. As a possible explanation we could advance the moments induced in *ortho*-methyl groups [14] and/or the deflection of these methyl groups from the plane of the benzene nucleus, as supported by the much larger effect in the sterically overcrowded compound (IId). Regardless of the explanation the important feature emerges that in no case was a reduction of dipole moment by methyl substitution observed.

The essential point of the discussion is a comparison of BBr_2, strongly conjugated with the benzene ring, and NO_2 the conjugation of which has been questioned.[9,10,14] In both cases the methyl substitution causes a reduction of the dipole moment but this effect is much greater for BBr_2, 31% against 7%. This difference is overemphasized by STO-3G calculations.[5b]

Strong conjugation with the benzene nucleus has been inferred for various borine-containing groups,[5a,9a,16,17a] sometimes in sharp distinction to the non-conjugated nitro-group.[5a,9a] Even the so-called resonance constants [21] are greater for borine substituents than for NO_2, CN, or SO_2X. The conjugation of borine is classified [11] as ' isovalent ' (the number of bonds in the polar formula is unchanged) and hence much more efficient than the ' sacrificial ' conjugation of NO_2. Returning to the nitro-group we have to explain the origin of the Δμ value if the conjugation is almost negligible. Complex formation with benzene is excluded since the dipole moments in other solvents are unchanged.[19] Electrostatic induction within the *ortho*-methyl groups could not be estimated in a quantitative manner; [14] our results with CN, CF_3, and CCl_3 suggest that this effect can even be of opposite sign.

In our opinion the rotation of the nitro-group affects the π-electron distribution and the effect can be described in terms of unequal polarizabilities [22] of the benzene nucleus in the horizontal and perpendicular directions. This picture differs from the classical resonance formula in that the C−N bond does not acquire double-bond character.[10e,14] If we accept this explanation, the same phenomenon must come into existence even with the BBr_2 group and constitute less than half of the observed Δμ.

The remaining substituents gave less telling results mainly because of their unsymmetrical structure. The borine substituents $B(OCH_3)_2$ and $B(SCH_3)_2$ are certainly strongly conjugated; the observed Δμ is of the right sign but lower than for BBr_2.* A possible reason might be in the steric requirement of these groups [see formulae (Ig and h) in the Scheme] which causes a distortion of planarity even in simple benzene derivatives. In addition, the values of Δμ are obtained with a low accuracy due to the unfavourable orientation of the vectors. As regards the substituents $COCH_3$ and CO_2CH_3, previous analysis of the reactivity data [9a] uncovered a mesomeric effect, even if smaller than that expressed by common resonance constants.[6,21] In fact, the conjugation of carbonyl substituents has never been doubted.[20,23] The values of Δμ listed in the Table are qualitatively consistent with the previous analysis in terms of inhibition of resonance [20] which, however, treated dipole moments in an oversimplified manner as scalar quantities.

We conclude that the classical concept [2b,13] of steric inhibition of resonance (conjugation) retains its validity, but the most quoted example of 2,4,6-trimethylnitrobenzene (IIa) is not justified from the quantitative point of view. The main problem is that the strong inductive effect of the nitro-group does not allow an estimate of the effect of conjugation which may be either weak or even effectively zero. More convincing examples are (IIf), more strongly compounds (IIg—j), or, *e.g.*,

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* Note that the direction of the dipole moment is reversed in compounds (Ig and h) compared to (If), but the direction of Δμ is the same.

3,5-dimethyl-4-nitroaniline[13a] in which the conjugative ability of the nitro-group is promoted by the donor group in the *para*-position. Our results thus fit into the general pattern[9,10,14] that the conjugation of some typical acceptor groups (NO_2, CN, SO_2X) with the benzene nucleus has been commonly overestimated, particularly in the values of resonance constants[6,21] and of mesomeric dipole moments.[12]

Experimental

Materials.—Benzonitrile (Ib), trifluoromethylbenzene (Ic), trichloromethylbenzene (Id), benzenesulphonyl chloride (Ie), and 2,4,6-trimethylbenzenesulphonyl chloride (IIe) were commercial products (Fluka; purity >99%) and were further purified by distillation. 2,4,6-Trimethylbenzonitrile[24] (IIb), 2,4,6-trimethylbenzotrifluoride[25] (IIc), 2,4,6-trimethylbenzotrichloride[26] (IId), dibromophenylborane[17a] (If), dimethoxyphenylborane[27] (Ig), dimethoxy-(2,4,6-trimethylphenyl)borane[28] (IIg), bismethylthiophenylborane[29] (Ih), and bismethylthio-(2,4,6-trimethylphenyl)borane[30] (IIh) were prepared by established procedures.

Dibromo-(2,4,6-*trimethylphenyl*)*borane* (IIf) was prepared by reaction of 2,4,6-trimethylphenylmercury bromide with boron tribromide in dry benzene following a general method of syntheses of arylboron dihalides.[31] Compound (IIf) was twice distilled and had b.p. 71 °C at 0.15 mmHg (yield 48%) (Found: C, 37.0; H, 3.7; Br, 54.9. $C_9H_{11}BBr_2$ requires C, 37.3; H, 3.8; Br, 55.1%).

2,4,6-*Trimethylphenylmercury bromide*. Mesitylmagnesium bromide was prepared[32] from bromomesitylene (19.9 g, 100 mmol) and magnesium (3.16 g) in dry tetrahydrofuran (THF) (20 ml) under nitrogen. The mixture was diluted with THF (40 ml) and filtered under nitrogen through a glass wool plug into a dropping funnel. The filtrate was gradually added (1 h) under stirring to a suspension of mercury(II) bromide (36 g, 100 mmol) in THF (100 ml). The mixture was stirred overnight at room temperature and hydrolysed with 200 ml of 5% aqueous hydrogen bromide. Most of the THF was removed under vacuum and the solid material left was filtered, washed with hot water, and dried. This yielded the product (19.5 g, 49%), m.p. 191—194 °C. Recrystallization from acetonitrile gave m.p. 194—196 °C (Found: C, 27.3; H, 2.9; Br, 19.8. $C_9H_{11}BrHg$ requires C, 27.0; H, 2.8; Br, 20.0%).

Physical Measurements.—The dipole moment measurements were carried out as previously described.[33] The manipulation with moisture-sensitive compounds (If—h) and (IIf—h) was carried out under dry nitrogen. Molar refractions (R_D) of compounds (Ib),[34] (Ic), (Id), (Ie),[34] and (Ig)[27] were experimental values, mostly determined at 20 °C. The molar refraction of (Ih) was calculated from (Ig) using the increments[34] for oxygen and sulphur, and that of (If) was calculated solely from increments[34] with the value[27] of 3.94 cm^3 for borine conjugated with the benzene nucleus. The molar refractions of (II) were calculated from (I) by adding increments[34] of three methylene groups. The accuracy of the whole procedure is adequate since only dipole moment differences between compounds (I) and (II) need to be known accurately. The effect of methyl substitution, denoted $\Delta\mu$, is defined as the vector difference between the dipole moments of (II) and (I). In the case of substituents a—d, it reduces to a simple algebraic difference, whereas for the remaining compounds (I) the direction of the dipole moments was approximately estimated by summing up the standard bond moments,[16b,35] or by comparison with *para*-substituted derivatives.[35] The following angles of the C(1)–X bond were obtained: (Ig), 141°; (Ih), *ca.* 120°; (Ii), 54°; (Ij), 64°. The inaccuracy of these values is not critical, except in the case of (Ih), the main problem being the unknown moment of the B–S bond. The values of $\Delta\mu$ were then calculated assuming that their direction is along the C(1)–X bond.

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