SECONDARY STERIC EFFECTS
IN 2,4,6-TRIALKYLATED ACETOPHENONES AND NITROBENZENES:
DIPOLE MOMENTS AND ^{13}C NMR SPECTRA*

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Dipole moments of 2,4,6-trialkylated acetophenones (*II*) and bromobenzenes (*III*) with variable size of the alkyl groups were measured in two solvents. The main intention was to shed more light on the previous results with similarly substituted nitrobenzenes (*I*). The comparison reveals a steady decrease of the dipole moment with the increasing size of the alkyl group in all three series. In addition, there is a stronger effect of steric inhibition of mesomerism in the series *II* and a comparably strong effect of the anisotropic polarizability in *I*; the two cannot be distinguished on the basis of dipole moments. Similarly an analysis of ^{13}C NMR shifts reveals at least two effects. In one of them the series *I* behaves like *III*, in the other like *II*. Summarizing, our results are in agreement with the conception of negligible conjugation of the nitro group but they do not contribute significantly to its evidence which is based mainly on other physical quantities.

The dipole moment of 2,4,6-trimethylnitrobenzene (*Ib*) is distinctly reduced compared to nitrobenzene (*Ia*). This secondary steric effect was considered a long time as a classical proof of the conjugation of the nitro group with the benzene nucleus[1,2]. Similar reasoning was applied[2,3] to 2,4,6-trimethylacetophenone (*IIb*). We challenged this explanation in the former case[4] and brought some evidence that the nitro group is actually conjugated in a negligible degree. This view is now supported by findings from other areas[5-8]. In the field of dipole moments our main argument was[4] that the substitution by bulkier alkyl groups results in further reduction of dipole moments of compounds *Ic−Ie*, although the distortion of the nitro group cannot evidently proceed further than up to the dihedral angle of 90°. It follows that the simple dipole moment difference of *Ib* and *Ia* cannot serve as a quantitative measure of conjugation[4,9]. The latter statement applies even to the acetyl group in *IIa* and *IIb*, although its conjugation itself is unquestionable. The successive decrease of dipole moments when going from *Ib* to *Ie*, has remained in fact unexplained; as a tentative possibility we considered electrostatic induction in the *ortho*-standing alkyl groups[4]. The drop of dipole moments from *Ia* to *Ib* can be understood[4] in terms of dif-

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ferent polarizability of benzene π-electrons within the ring plane and perpendicularly to it[10].

a: R = H d: R = t-C_4H_9
b: R = CH_3 e: R = C_6H_5
c: R = cyclo-C_6H_{11}
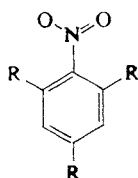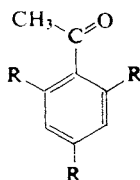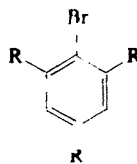
In this note we report on the dipole moments of compounds *IIc−IIe* and *IIIc− IIIe*. Our idea was to compare three series of compounds: bromo derivatives *III* in which any rotation of the substituent is meaningless, acetyl derivatives *II* in which the distortion of planarity supresses the conjugation, and nitro derivatives *I* in which distortion of planarity occurs but in our view does not affect the conjugation. We wanted to explore whether the individual effects can be separated: general steric effect present in all three series, steric inhibition of conjugation in *II*, and effect of the differential polarizability in *I*. In addition, we compared the steric effect on dipole moments to the effect on ^{13}C NMR shifts.

EXPERIMENTAL

Materials. Nitro compounds *I* were described[4]. 2,4,6-Trimethylacetophenone (*IIb*) and 2,4,6-tricyclohexylacetophenone (*IIc*) were prepared by Friedl–Crafts acylation of the respective hydrocarbons[11], 2,4,6-tri-tert-butylacetophenone (*IId*) by the reaction of 2,4,6-tri-tert-butyl-benzoyl chloride with dimethyllithiumcuprate[12], 2,4,6-triphenylacetophenone (*IIe*) from 2,4,6-tri-phenylmagnesium bromide by the reaction with acetyl chloride[11]. 2,4,6-Trimethylbromobenzene (*IIIb*), 2,4,6-tri-tert-butylbromobenzene[12] (*IIId*), and 2,4,6-triphenylbromobenzene[13] (*IIIe*) were prepared by bromination of the parent hydrocarbons.

2,4,6-*Tricyclohexylbromobenzene* (IIIc) was obtained by bromination of 1,3,5-tricyclohexyl-benzene under the same conditions as in the case of compound *IIId*, yield 40% m.p. 165°C (etha-nol). For $C_{24}H_{35}Br$ (403·4) calculated 71·45% C, 8·74% H, 19·81% Br; found: 71·72% C, 8·41% H, 20·34% Br. Mass spectrum: 404/402 (M$^+$).

The purity of compounds was checked by melting point determination, TLC, and the ^{13}C NMR spectra.

Physical measurements. The method of dipole moment measurement was described pre-viously[14,15]. The results are listed in Table I. The ^{13}C NMR spectra were recorded at 23°C on a Varian XL-200 instrument (operating at the frequency 200 MHz for ^{1}H and 50·3 MHz for ^{13}C) in a 5 mm cell with C^2HCl_3 as internal standard. Chemical shift of C^2HCl_3 was taken

as 77·0 ppm. Concentration of the solutions was 20 mg of the substance in 0·3 ml of the solvent. Assignment was made on the basis of intensities of signals in the ^{1}H-decoupled ^{13}C NMR spectra (without NOE), and using the chemical shifts expected according to the additivity rules[16]. The chemical shifts are given in Table II, accuracy ±0·1 ppm.

DISCUSSION

In order to facilitate the comparison of the series *I*−*III*, we recalculated our experimental dipole moments together with those[17] of *Ib*−*IIIb* in percent of the dipole moment[17] of the parent compound *Ia*−*IIIa*. The results are plotted in Fig. 1. As the abscissae the steric constants[18] *v* of the group R were used but the choice is immaterial since we shall deal merely with the order of values. Fig. 1 reveals firstly the completely irregular behaviour of the triphenyl derivatives *Ie*−*IIIe*. We can advance an *ad hoc* explanation in terms of charge transfer from the phenyl groups and/or their variable conformation. In any case the compounds *Ie*−*IIIe* must be excluded from further considerations. The remaining compounds reveal at least two separate effects:

a) A slight gradual decrease of the dipole moment with increasing size of the substituent R is observable in all three series. It may be classified as steric effect without attempting an actual explanation, or may be interpreted tentatively in terms

TABLE I

Dipole moment data of substituted acetophenones *II* and bromobenzenes *III* (25°C)

Compound	Solvent	α^a	γ^a	$10^{-30}\,\dfrac{\mu}{\text{C m}}$
IIc	CCl_4	4·10	0·418	8·8
	C_6H_6	2·05	0·090	8·6
IId	CCl_4	4·39	0·250	8·3
	C_6H_6	2·42	0·036	8·4
IIe	CCl_4	4·70	0·920	8·6
	C_6H_6	2·80	0·388	9·3
IIIc	CCl_4	1·59	0·410	5·2
	C_6H_6	0·74	0·126	5·0
IIId	CCl_4	1·52	0·240	4·9
	C_6H_6	0·78	0·050	5·0
IIIe	CCl_4	1·25	0·860	2·7
	C_6H_6	0·80	0·400	3·9

^{a} Slopes of the plots ε_{12} *vs* w_2 and n^2_{12} *vs* w_2, respectively.

of electrostatic induction within the *ortho*-standing alkyl groups[4]. In fact, any presently available theory can hardly account for such a small effect.

b) In addition, a much greater reduction of the dipole moment is observed in the series *I* and *II* between the first and second member, possibly also between the second and third to a lesser extent. This reduction is evidently due to forcing out the substi-

TABLE II

^{13}C-NMR shifts in substituted nitrobenzenes *I*, acetophenones *II*, and bromobenzenes *III* (in C^2HCl_3 solution)

Compound	Chemical shift, ppm[a]					
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	CO	CH_3
Ia[b]	147·2	122·5	128·6	133·9	—	—
	(−0·9)	(−0·7)	(−0·7)	(−0·6)	—	—
Ib	149·1	129·0	129·0	139·9	—	—
	(2·9)	(−3·5)	(1·6)	(−3·9)	—	—
Ic	148·7	137·8	123·1	149·8	—	—
	(7·1)	(−5·5)	(0·3)	(−4·8)	—	—
Id	147·0	140·1	123·5	151·3	—	—
	(8·8)	(−4·4)	(4·1)	(−4·5)	—	—
IIa	137·5	128·6	128·4	132·9	196·8	26·2
	(−0·3)	(−0·1)	(−0·3)	(0·2)	—	—
IIb	140·6	132·3	128·7	137·9	206·6	31·7
	(4·7)	(−5·7)	(1·9)	(−4·1)	—	—
IIc	139·9	142·6	122·7	148·4	207·3	33·8
	(8·6)	(−6·2)	(0·5)	(−4·4)	—	—
IId	137·5	144·6	122·7	149·3	211·6	38·4
	(9·6)	(−5·4)	(3·9)	(−4·7)	—	—
IIIa[b]	122·4	131·2	129·8	126·6	—	—
	(−0·7)	(−0·6)	(−0·9)	(−0·9)	—	—
IIIb	124·1	137·7	128·9	136·0	—	—
	(2·9)	(−3·4)	(0·1)	(−0·8)	—	—
IIIc	124·0	146·3	123·3	146·8	—	—
	(7·4)	(−5·6)	(−0·9)	(−0·8)	—	—
IIId	121·7	148·6	123·7	148·4	—	—
	(8·5)	(−4·5)	(2·9)	(−0·4)	—	—

[a] In parentheses: difference between the experimental values and those calculated from group contributions[16]; [b] ref.[19].

tuent of the plane of the benzene ring. Since the resulting dihedral angle is approximately[3,4] 70° in *Ib* or *IIb*, and virtually 90° in *Ic* or *IIc*, the effect cannot be further enhanced by a still greater steric hindrance. On the other hand, we are unable to find any qualitative or quantitative difference in the behaviour of the series *I* and *II*, although we attribute the decrease of dipole moments to two different causes: steric inhibition of conjugation in *II* and anisotropic polarizability in *I*. A decision is not possible on the basis of dipole moments alone.

We attempted to discuss the ^{13}C NMR shifts in the same empirical way as dipole moments, *i.e.* only on the basis of similarities and differences among the series *I—III*. The data of Table II reveal similar trends in the three series: All signals are shifted upfield by methyl substitution, larger alkyls produce further upfield shifts of signals $C_{(2)}$ and $C_{(4)}$ but reverse shifts on $C_{(1)}$ and $C_{(3)}$). A graphical comparison of the three series is carried out in Fig. 2 for two positions on the benzene nucleus. In the case of atoms $C_{(1)}$ or $C_{(2)}$ the behaviour of the series *I* and *III* is more similar to each other than to series *II*. On the other hand, the shifts on $C_{(3)}$ and $C_{(4)}$) show virtually the same pattern in the series *I* and *II*, but different from *III*. With the intention to obtain a more sensitive test, we calculated the expected chemical shifts by the additive scheme, using the group contributions derived for aromatic substituents[16].
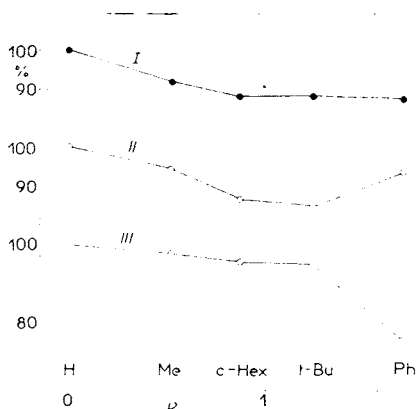

FIG. 1

Comparison of dipole moments of alkyl substituted nitrobenzenes *I*, acetophenones *II*, and bromobenzenes *III*. The relative values in percent, related to the parent compound, are plotted *vs* the steric constants *v* of the alkyl groups
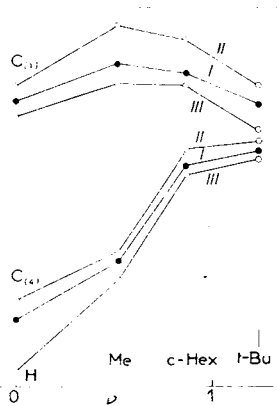
FIG. 2

Comparison of ^{13}C NMR shifts of the same compounds as in Fig. 1. The chemical shifts are plotted *vs* the steric constants *v* of the alkyl groups, the individual curves are arbitrarily shifted along the *y*-axis.

(For c-C_6H_{11} we used the value for i-C_3H_7). The differences of experimental and calculated values are listed in Table II. In the case of compounds *Ia − IIIa* they represent the combined error of the experiment and of the additive scheme but for other compounds they have a physical meaning and may be interpreted as general steric effect. Most significant differences are observed on $C_{(1)}$. In this position and also on $C_{(2)}$, series *I* and *III* show exactly the same pattern. This may be understood as a manifestation of steric hindrance in the overcrowded part of the molecule. In the steric inhibition of conjugation, on the other hand, the deviations on $C_{(4)}$ are similar in the series *I* and *II* but negligible in *III*. They may be understood in terms of π-electron withdrawal from the *para* position, inhibited by rotating out the functional group. For the latter effect the methyl groups are sufficient and the different mechanism in the series *I* and *II* is not evident. Hence the non-conjugated nitro group behaves once similarly to the conjugated and sterically hindered acetyl group, once to the bromine atom, which is insensitive to steric hindrance.

In conclusion, our experimental results are compatible with the advanced different mechanism of substituent effects in the compounds *I* and *II*, but they cannot confirm it against some possible alternatives. Generally, it does not seem feasible to differentiate various mechanisms of substituent effects in benzene derivatives on the basis of observable quantities like dipole moments of NMR shifts which essentially reflect the electron density. A recent classification, possibly oversophisticated, distinguished not less than ten effects which may be operative in benzene derivatives[20]. Of them particularly the mesomeric effect (conjugation), direct π-polarization, and the so-called inductomesomeric effect[20] can affect quite similarly both the total dipole moment and the electron density in the *para* position. In our opinion, characteristic features of the conjugation are a certain double bond character of the bond to the substituent and a π-electron transfer from the whole benzene nucleus toward the substituent. Our statement that the acetyl group in acetophenone is significantly conjugated while the nitro group in nitrobenzene only negligibly is thus supported mainly by geometrical factors (bond length of the C—N bond[4], deformation of ring angles[8]) and by quantum chemical calculations[6,7] of π-electron densities. Much telling is also systematic comparison of the substituent effects in *meta* and *para* positions[5]. The present results confirm our previous view[4] that dipole moments of benzene derivatives cannot serve as a direct measure of conjugation of substituents, and have not the relevance attributed to them formerly.

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