Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXVI.[1] Variable Resonance Behaviour by Alkyl and Substituted Alkyl Groups

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It is shown that long chain and some bridgehead alkyl substituents (such as adamantan-1-yl and bicyclo[2.2.2]-octan-1-yl) have greater resonance interaction with a benzene ring than methyl groups. Such substituents are also shown to be more polarisable as the electron demand of the π-system is changed. The neopentyl group shows different behaviour. The failure of adamantanyl and bicyclo-octanyl substituents to show significant enhancement of donation in the solvolysis of alkyl-substituted cumyl chlorides is thus ascribed to solvation. Studies on the resonance interaction and polarisability of some halogeno-substituted alkyl groups provide clarification of the present controversy as to their mode of action.

INTEREST continues in the electronic effects of alkyl groups. Since our previous work,[2] a short review [3] has appeared covering recent gas phase and theoretical results. Measurements on the gas phase acidity and basicity of alcohols,[4,5] amines,[6] and toluenes [7] suggest that the order of stabilisation of both positive and negative charge follows the order neopentyl $> \mathrm{Bu^t} \sim$ n-pentyl $\sim \mathrm{Bu^n} > \mathrm{Pr^i} > \mathrm{Pr^n} > \mathrm{Et} > \mathrm{Me} > \mathrm{H}$. Calculations have suggested a similar effect in the stabilisation of benzenium ions, although this is apparently not observed experimentally.[8] Other calculations [9,10] supported the order cited above, except [9] that n-butyl and n-pentyl were close to n-propyl rather than to t-butyl. Various explanations have been proposed for these orders, and solvation effects have been suggested [11] to be the main factor affecting the order for reactions in solution.

However little work has been done on the longer straight-chain alkyl groups to see if they are indeed more polarisable than methyl or ethyl groups. Some years ago Berliner [12] investigated the rates of bromination of various alkyl benzenes and suggested the possibility of some additional effect involving bending the alkyl substituent back and through-space interaction with the benzene ring.

The neopentyl group has long been regarded as having anomalous properties.[13] It has been suggested [14] that part of its enhanced effectiveness in electronic transitions results from a polarisation across space of the terminal methyl group which overhangs the side of the benzene ring, but this explanation is difficult to reconcile with recent u.v. work [15] on the deuteriated substituent.

Interest also continues [16] in the adamantane system, and its reactivity at the bridgehead position has been the subject of experimental work [17] and theoretical [18] calculations. The adamantan-1-yl group has been claimed [19] to be a relatively strong electron donor. Its size should effectively prevent solvation near the attachment site in 1-phenyladamantane. The bicyclo[2.2.2]-octan-1-yl substituent is similar. It has been much used as an aliphatic model for a benzene ring in both theoretical [20] and experimental studies,[21] and the possibility of the transfer of electrons though the octyl cage has been examined [22] in 1,4-diphenylbicyclo[2.2.2]octane radicals. We recently reported [23] that the σ values for the adamantan-1-yl and bicyclo[2.2.2]octan-1-yl substituents are virtually unaffected by electron demand and suggested that this observation was related to steric inhibition of solvation.

We have earlier shown [24] that the resonance interaction

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of a substituent with a benzene ring, as measured by its σ°_{R} constant, could be ascertained through measurements of the intensity of the ν_8 (ν_{16} in Herzberg's notation) absorption of the appropriate monosubstituted benzene. The appropriate equation is (1), and the resonance interaction in *para*-disubstituted benzenes is

$$A_{\text{mono}} = 17{,}600(\sigma^{\circ}_{R})^2 + 100 \qquad (1)$$

described by equation (2), where λ is indicative of any

$$A_{para} = 15{,}000[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2) + \lambda]^2 + 170 \qquad (2)$$

change of interaction of the substituents resulting from the presence of the second group. This formula represents an improvement [1] over an earlier one which used [25] a constant of 11,800 rather than 15,000.

We have therefore prepared a series of alkylbenzenes, *p*-methoxyalkylbenzenes, and *p*-acetylalkylbenzenes and measured the intensities of their ν_8 bands in order to study the interaction of the alkyl groups with the π-system under various conditions of electron demand. At the same time we show that our previous conclusions,[2] derived from a study of a restricted range of these compounds with the earlier equation, are still justified. We extended the study to include series of *para*-substituted benzylidyne trifluorides and trichlorides because of the considerable recent interest in such groups (see later).

TABLE 1

Intensities (A/l mol^{-1} cm^{-2}) for the ν_8 vibrations of some *para*-disubstituted benzenes (dilute solutions in carbon tetrachloride)

Substituents		ν/cm^{-1}	$A - 170$	M.p. [B.p.] (°C)	Lit. m.p. [b.p.] (°C)	Ref. to prep.
OMe	Bu	1613, 1584	1598	[220—224]	[120 at 19 mmHg] [a]	Text
	Pentyl	1613, 1584	1510	[240—244]	[124 at 14 mmHg] [b]	Text
	Neopentyl	1611, 1582	1722	[220—230]	[103—104 at 9 mmHg] [c]	*d*
	Bicyclo-octan-1-yl	1621, 1580	1820	86—87		Text
	Adamantan-1-yl	1613, 1607, 1580	1743	76—77		Text
COMe	Me	1608, 1588, 1574	2626	[226—227]	[225 at 736 mmHg] [e]	*f*
	Et	1608, 1571	2728	[230—235]	[236] [g]	*f*
	Bu	1607, 1572	2631	[266—270]	[100—103 at 3 mmHg] [h]	*j*
	Pentyl	1607, 1573	2642	[282—286]	[121—123 at 3 mmHg] [h]	*j*
	Neopentyl	1608, 1570	2180	[240—250]	[105—106 at 10 mmHg] [k]	*j*
	Pr^i	1608, 1573, 1596	2615	[234—238]	[252—254] [l]	*j*
	Bu^t	1607, 1576, 1564	2805	[258—262]	[136—138 at 20 mmHg] [m]	*j*
	Bicyclo-octan-1-yl	1604, 1562	4041	88—90	88—90 [j]	*j*
	Adamantan-1-yl	1607, 1573	3402	105—107	105—107 [j]	*j*
CF_3	NMe_2	1619, 1572	8339	69—70	70·5 [n]	*n*
	OMe	1617, 1591	4880	[166—168]	[168·6] [o]	Text
	F	1615, 1607	3110			*p*
	Cl	1611, 1584	2040			*p*
	Br	1603, 1587	1980			*p*
CCl_3	OMe	1606, 1582	4335	[88 at 0·1 mmHg]	[98 at 1 mmHg] [q]	*q, r*
	F	1602, 1590, 1574	2123	[100—102 at 20 mmHg]	[93·7 at 14 mmHg] [s]	*q*
	Cl	1594, 1575	758			*f*
	Br		783	35—36	39—40 [t]	*u*
	Me	1613, 1588	364	43	46 [q]	*q, v*
	CO_2Me	1609, 1577	602	55	59—60 [w]	*w, x*
	NO_2	1608, 1600	930	41—42	46—47 [y]	*y*
CH_2Cl	OMe	1611, 1586	2590			*z*
	Me	1618, 1580	87	[80—90 at 20 mmHg]	[92—94 at 20 mmHg] [aa]	*bb*
	CO_2Me	1615, 1578	1156	33	39 [cc]	Text
$CHCl_2$	OMe	1611, 1588	4470	26—27	[120—121 at 8 mmHg] [dd]	*e*

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EXPERIMENTAL

Table 1 lists the ν_8 intensity values for *p*-substituted alkylbenzenes, determined for the first time or redetermined in this work. New values for certain monosubstituted compounds are given in Table 2. *m*-Chlorobenzylidyne trichloride (ν 1601 and 1578 cm^{-1}; A 1357 l mol^{-1} cm^{-2}) and *m*-chlorobenzyl chloride (ν 1592 cm^{-1}; A 1050 l mol^{-1} cm^{-2}), were purified from commercial samples.

p-n-Butyl- and *p*-n-pentyl-anisoles were prepared *via* the reactions of anisaldehyde with the appropriate alkylmagnesium bromides followed by replacement of the

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[25] P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767.

hydroxy-group with a chlorine atom and subsequent reduction with lithium aluminium hydride. They were purified by preparative g.l.c. (5 ft × ½ in 10% Carbowax 20 M on Chromosorb W; 190°).

p-(*Bicyclo*[2.2.2]*octan*-1-*yl*)*anisole*, m.p. 86—87° (Found: C, 83·1; H, 9·5. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%), was prepared by the reaction[26] of anisole with 1-bromobicyclo-[2.2.2]octane[27] in the presence of anhydrous zinc chloride. The product was sublimed at 120° and 10 mmHg; p-(*adamantan*-1-*yl*)*anisole*, m.p. 76—77° (Found: C, 84·1; H, 9·2. $C_{17}H_{22}O$ requires C, 84·3; H, 9·1%), was similarly prepared from anisole and 1-bromoadamantane.

TABLE 2

Intensities (A/l mol^{-1} cm^{-2}) for the ν_8 vibration of some monosubstituted benzenes

Substituent	ν	$A - 100$	σ°_R	M.p. [B.p.] (°C)	Lit. m.p. [b.p.] (°C)	Ref. to prep.
Bu	1603, 1584	248	−0·119			*a*
Pentyl	1604, 1584	268	−0·123	[196—200]	[198—202] [b]	*c*
Octyl	1604, 1584	355	−0·141	[149—151 at 20 mmHg]	[95—97 at 0·5 mmHg] [d]	*d*
Neopentyl	1609, 1601, 1584	134	−0·087	[180—182]	[185—186] [e]	*e*
Bicyclo-octan-1-yl	1611, 1598, 1580	504	−0·169	78—79	78—80 [f]	*f*
Adamantan-1-yl	1603, 1598, 1580	382	−0·147	78—80	82 [f]	*f*
$CH_2{\cdot}CHMe_2$	1604, 1595, 1584	237	−0·116	[168—170]	[172] [g]	*c*
$CH_2{\cdot}CH[CH_2]_2$	1605, 1584	261	−0·122			*a*

[a] Commercial sample checked for purity by g.l.c., i.r., and n.m.r. [b] H. Gilman and J. Robinson, *Org. Synth.*, Coll. Vol. 11, 1943, p. 47. [c] H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, 1944, **66**, 1515. [d] F. W. Gray, J. F. Gerecht, and I. J. Krems, *J. Org. Chem.*, 1955, **20**, 511. [e] A. Bygden, *Ber.*, 1912, **45**, 3479. [f] Ref. 23. [g] I. Ramadane, *Uch. Rizhsk. Pditekhn. Inst. Khim. Fah.*, 1959, **2**, 49.

TABLE 3

Effective σ values for *para*-substituted alkylbenzenes

	p-RC_6H_4OMe			p-RC_6H_4COMe				
R	σ°_R	$\left(\frac{A - 170}{15,000}\right)^{\frac{1}{2}}$	$[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$	Δ	$\left(\frac{A - 170}{15,000}\right)^{\frac{1}{2}}$	$[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$	Δ	ΣΔ
Me	0·10	0·30 [a]	0·33	−0·03	0·42 [b]	0·32	0·10	0·07
Et	0·10	0·33 [a]	0·32	0·01	0·43 [b]	0·32	0·11	0·12
Bu	0·12	0·33 [b]	0·31	0·02	0·42 [b]	0·33	0·09	0·11
Pentyl	0·125	0·32 [b]	0·31	0·01	0·44 [b]	0·33	0·11	0·12
Neopentyl	0·085	0·34 [b]	0·34	0·00	0·38 [b]	0·31	0·07	0·07
Pr^i	0·115	0·33 [a]	0·31	0·02	0·42 [b]	0·33	0·09	0·11
Cyclopropyl	0·175	0·29 [a]	0·25	0·04	0·52 [b]	0·39	0·13	0·17
Bu^t	0·125	0·33 [a]	0·30	0·30	0·44 [b]	0·34	0·10	0·13
Bicyclo-octan-1-yl	0·17	0·35 [b]	0·26	0·09	0·52 [b]	0·39	0·13	0·22
Adamantan-1-yl	0·145	0·34 [b]	0·28	0·06	0·48 [b]	0·37	0·11	0·17

[a] Value from ref. 2. [b] This paper.

p-Trifluoromethylanisole was prepared from p-trifluoromethyl chlorobenzene by treatment for 5 h with sodium methoxide in 4 : 1 (v/v) dimethyl sulphoxide–methanol at 100°.

The i.r. intensities (A in l mol^{-1} cm^{-2}) were measured for dilute solutions in carbon tetrachloride as previously described.[24] The reproducibility in $(A - 170)^{\frac{1}{2}}$ values was ±1 for A values greater than 400 l mol^{-1} cm^{-2}, but greater for smaller intensities; in such cases the actual values are also less accurate because of uncertainty in the value of the overtone correction.

DISCUSSION

In Table 2 we report new σ°_R values obtained for alkyl substituents. Comparison with σ°_R values previously obtained for other alkyl groups (Table 3) shows that there is some evidence for greater resonance donation by the longer straight-chain alkyl groups such as pentyl and octyl than by methyl and ethyl groups. The adamantanyl and bicyclo-octanyl groups are also significantly stronger donors than the simpler alkyl groups, a result earlier[24] noted for the cyclopropyl substituent. At the other extreme the neopentyl group appears to be the weakest resonance donor of all alkyl groups so far investigated.

We made measurements on the series of p-methoxy- and p-acetyl-alkylbenzenes in order to look at the effect on typical alkyl groups of changing the electron demand of the attached system. Our earlier work[2] showed that alkyl groups are polarisable in this respect, a result supported by other recent work mentioned above. Table 3 lists values of $[(A - 170)/15,000]^{\frac{1}{2}}$, $[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$ and the difference (Δ) between these quantities.

There are small but definite trends. In the *para*-alkylanisoles there is greater resonance interaction for the bridgehead and cyclopropyl groups than for tertiary and secondary alkyl groups, which in turn show slightly greater interaction than primary alkyl groups.* The same is true for the *para*-alkylacetophenones and this is clearly indicated by comparing the ΣΔ values of the series. The order of polarisability is Me, neopentyl < Et, Bu, pentyl, Pr^i < Bu^t < cyclopropyl, adamantan-1-yl < bicyclo-octan-1-yl, confirming and extending our previous[2] conclusions on some of these substituents. This change of polarisability is unlikely to result from

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* A similar trend is found in the result reported in ref. 2 for p-alkyl-NN-dimethylanilines.

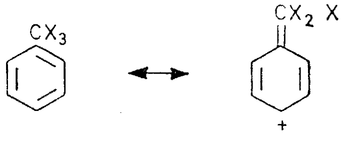
[26] H. F. Reinhardt, *J. Org. Chem.*, 1962, **27**, 3258.

[27] Z. Suzuki and K. Morita, *J. Org. Chem.*, 1967, **32**, 31.

changes in the interaction of the OMe or COMe groups with the π-system since the alkyl groups all have similar electronic effects of the same direction. It must therefore indicate changes in alkyl group–π-system interaction brought about by the electron-donating and electron-demanding nature of the π-system in the anisoles and acetophenones, respectively. This tendency for greater polarisability in the order shown fits in with the theoretical results discussed in the introduction and with other recent evidence.[28] The low polarisability of the neopentyl group remains a puzzle.

These results also confirm that the failure [23] of adamantan-1-yl and bicyclo-octan-1-yl substituents to show significantly enhanced σ values in the solvolysis of the corresponding 2-aryl-2-chloropropanes is a result of steric inhibition of solvation rather than of any inherent electronic feature.

Halogeno-substituted Methyl Groups.—The electronic effects of such substituents, particularly the trifluoromethyl group, have recently attracted considerable attention. There has been controversy [29,30] as to their mode of interaction and suggestions have been advanced for halogen hyperconjugation,[31] p–π interaction [32] and π-electron induction.[30,33] The first of these possibilities involves the movement of electron density from the π-orbitals of, say, a benzene ring into the σ-orbitals of the carbon–halogen bond. In valence-bond terminology we can write canonical forms of type (A). The second possibility allows for interaction of the unshared p-electrons of the halogen atoms with the π-system of the ring; the third considers the movement of π-electron density in the ring caused by the polar nature of the σ-electron system of the substituent. (It is, however, not always clear what is meant by π-inductive effects.) [34]



(A)

Investigation of the ^{19}F shifts in *meta*- and *para*-fluoro-substituted halogenotoluenes has given [32,35,36] the following σ°_{R} values: CF_3, +0·10; CCl_3, +0·03; $CHCl_2$, +0·02; CH_2Cl, −0·03. We earlier reported [24] a value of 0·11 for CF_3. The use of i.r. intensities for *meta*-substituted derivatives allows [37] a more accurate estimation of low σ°_{R} values than can be obtained from monosubstituted benzenes. The appropriate formula [37] is (3).

$$A = 19{,}000[\sigma^{\circ}_{R}(1)^2 + \sigma^{\circ}_{R}(2)^2 + \sigma^{\circ}_{R}(1)\sigma^{\circ}_{R}(2)] + 340 \quad (3)$$

Use of this formula for *meta*-substituted chlorobenzenes gives * values of 0·065 for CCl_3 and −0·026 for CH_2Cl, in good agreement with the above. Theoretical studies of electron densities in halogenomethylbenzenes have been interpreted [35] as evidence for important hyperconjugative contributions. However, measurement of dipole moments of substituted benzylidyne trifluorides led to the recent conclusion [38] that π-electron induction was the major factor (but see also ref. 39).

TABLE 4

Resonance interactions in *para*-substituted halogenoalkylbenzenes (A − 170 in l mol^{-1} cm^{-2}; measured in carbon tetrachloride)

Substituent		$A - 170$ [a]	$\left(\frac{A - 170}{15{,}000}\right)^{\frac{1}{2}}$	$[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2)]$	Δ [b]
CF_3	NMe_2	8339	0·75	0·65	0·11
	OMe	4880	0·57	0·53	0·05
	F	3110	0·46	0·45	0·01
	Cl	2040	0·37	0·33	0·04
	Br	1980	0·36	0·34	0·03
	CN	180 [c]	0·11	0·02	−0·09
	COMe	263 [c]	0·13	−0·11	−0·02
	SOM_2e	145 [c]	0·10	0·04	−0·06
	NO_2	440 [d,e]	0·17	−0·06	−0·11
CCl_3	OMe	4335	0·54	0·46	0·08
	F	2123	0·38	0·37	0·01
	Cl	758	0·22	0·25	−0·02
	Br	783	0·23	0·26	−0·03
	Me	364	0·16	0·13	0·03
	CO_2Me	602	0·20	−0·13	−0·07
	NO_2	930 [e]	0·25	−0·14	−0·11
CH_2Cl	OMe	2590	0·42	0·40	0·02
	Cl	310 [d]	0·14	0·19	−0·05
	Me	87	0·08	0·07	0·01
	CO_2Me	1156	0·28	−0·19	−0·09
$CHCl_2$	OMe	4470	0·55	0·45	0·10

[a] This paper unless otherwise specified. [b] Defined as positive if electron movement is towards halogenoalkyl substituent. [c] Ref. 35. [d] Ref. 1. [e] These results may be subject to some error arising from interaction with the nearby ν_{NO_2} band but this should be limited with the substituents involved; see ref. 1.

Table 4 shows that considerable changes in polarisation occur in series of *para*-substituted benzylidyne trifluorides, benzylidyne trichlorides, and benzyl chlorides as the electronic nature of the *para*-substituent is changed. There are sufficient results to allow the determination of a K_A value of 0·08 ± 0·01 for the CF_3 substituent by [1] plotting $[(A - 170)/15{,}000]^{\frac{1}{2}} - [\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2)]$ values against

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[*] A Values determined by T. J. Broxton as m-$ClC_6H_4CH_2Cl$, A 1357; m-$ClC_6H_4CCl_3$, A 1050 l mol^{-1} cm^{-2}, for dilute solutions in carbon tetrachloride.

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$(\sigma^+ - \sigma^\circ)$ for the second substituent. A statistical analysis of i.r. results from *para*-disubstituted benzenes showed [1] that a satisfactory treatment is obtained if the resonance interaction of each group is allowed to be affected by the total (inductive and resonance) electronic effects of the other group. The effect could thus be made up of (*a*) a change in the halogenomethyl–π-system interaction (hyperconjugation) caused by the second substituent; (*b*) a change in the interaction between the π-system of the ring and the second substituent caused by the overall electron-withdrawing nature of the halogenomethyl substituent.

The first effect is important since the results for compounds with strongly electron-withdrawing substituents can only be explained if the CF_3 and CCl_3 groups are induced to become virtual resonance-electron donors. This effect must also be significantly greater than effect (*b*), which would tend to reduce the electron-withdrawing ability of the second substituent. The results for the two series do not allow us to establish whether effect (*b*) is of significance; it could be a minor contributor to the results. Possible evidence for this second effect is, however, available from dipole moment results [38] which were otherwise explained by the authors. Thus it is known that the dipole moment in *para*-dimethylaminobenzylidyne trifluoride is 0·65 D greater than expected from vector addition of the results from the corresponding monosubstituted compounds. The finding that the interaction moment in *meta*-dimethylaminobenzylidyne trifluoride was 0·30 D greater than calculated led to the suggestion [38] that π-induction was the major mechanism of electron interaction in both compounds. This π-induction was apparently visualised in the sense of a polarisation of the ring π-system caused by the polar nature of the CF_3 group, leading, in turn, to an increased interaction between the NMe_2 group and the π-system. However, we feel that the effect in the *meta*-compound is probably an induced increase in the interaction between the dimethylamino-group and the π-system caused directly through space by the polar nature of the CF_3 substituent. The dimethylamino-group is the most polarisable of the common substituents [1] and we will shortly publish [40] results on model systems to establish this field-induced resonance interaction of a remote substituent.

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