

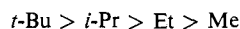
Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. XII.¹ π Distortions in the Ground States of Some *p*-Alkylbenzenes

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Abstract: Integrated intensities for the ν_{16} mode of alkyl- and *para*-substituted alkylbenzenes are reported and used to assess the relative π -electron distortions in these molecules. The results show that the order of π -electron disturbance found in alkylbenzenes (*t*-Bu > *i*-Pr > Et > Me) is maintained under conditions of strong electron demand but is reversed when strongly π -electron donating substituents are in the *para* position. These findings are discussed in relation to recent work on hyperconjugation.

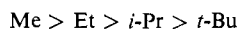
Recent interest in the relative electron releasing or attracting powers of alkyl substituents continues unabated. There has been considerable discussion about the relative magnitude and direction of their electronic effects when attached to sp^3 -hybridized carbon atoms, but it would seem³ that the "inductive order" of relative electron release is followed.



The position of H as a substituent in the series appears to depend³ on steric factors, and it has been claimed³ to be unwise to assume that the methyl group, in particular, even acts as an electron-withdrawing substituent relative to hydrogen.

When the above "big four"⁴ alkyl groups are connected to an sp^2 -hybridized carbon atom, as in alkylbenzenes, two general orders of behavior are found depending on the method of observation employed. The inductive order above, with methyl being electron donating relative to hydrogen, is observed in many reactions⁵ of alkylbenzenes. The π -electron component of the total effect of alkyl substituents joined to a benzene ring would also seem to follow this order as measured by σ_{R} values obtained from ¹⁹F resonance experiments⁶ or infrared intensities.⁷

Experimental results,⁵ however, frequently indicate the opposite order of total electron effect by alkyl groups, the so-called Baker-Nathan⁸ order.



Various hypotheses have been advanced to explain the Baker-Nathan order, including hyperconjugation,^{8,9} steric inhibition of solvation of the developing positive charge at the adjacent trigonal carbon atom,¹⁰ and

steric inhibition of the tendency of a carbon atom with a formal positive charge to shrink its orbitals and hence shorten its bonds.¹¹ Recent papers^{4,12-15} provide much relevant discussion.

Another possible mechanism of electron release by alkyl groups attached to conjugated systems is the π -inductive effect,¹⁶ although recent studies suggest that this effect is negligible in systems analogous to those under discussion here.^{7,17} Repulsive interactions between direct filled orbitals on the substituent and the π system (orbital penetration effects¹⁸) or polarization through space¹⁹ are other possible causes of electron disturbance in alkylbenzenes.

Measurements made on equilibria or reactions involve energy differences between pairs of ground states or a ground and transition state, respectively. This, together with solvation effects, makes it very difficult to draw firm conclusions especially since the relative energy differences are usually very small.⁴ Furthermore, the benzene nucleus to which the alkyl group is attached may carry varying amounts of excess negative or positive charge during the equilibrium or reaction. The relative electric effects of the alkyl groups may well be affected by these changes.

We therefore wished to measure the relative effect of alkyl groups on the π -electron framework of benzene under varying conditions of electron demand but in the ground state. As far as we know our previously developed²⁰ infrared intensity method is uniquely suited to this purpose.

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Previous papers in this series have shown that the total integrated area of the bands near 1600 and 1585 cm^{-1} for mono-²⁰ and *para*-disubstituted benzenes²¹ are related by eq 1 and 2, respectively, to the $\sigma_{\text{R}}^{\circ}$ value(s) of the substituent(s).

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

$$A_{\text{para}} = 11,800(\sigma_{\text{R}}^{\circ 1} - \sigma_{\text{R}}^{\circ 2})^2 + 170 \quad (2)$$

Equation 2 is based on the assumption that there is no direct interaction between the *para* substituents. The presence of any interaction results in a difference between the $(A_{\text{para}} - 170)/11,800$ value obtained experimentally and the calculated $(\sigma_{\text{R}}^{\circ 1} - \sigma_{\text{R}}^{\circ 2})^2$ value obtained using $\sigma_{\text{R}}^{\circ}$ values derived from the corresponding monosubstituted benzenes. This may be expressed in terms of eq 3. This provides us with a method for

$$A_{\text{para}} = 11,800(\sigma_{\text{R}}^{\circ 1} - \sigma_{\text{R}}^{\circ 2} + \lambda)^2 + 170 \quad (3)$$

studying the effects of alkyl groups in the ground states of *para*-substituted alkylbenzenes. We have measured intensity values for a series of *para*-substituted alkylbenzenes in which the *para* substituent varies from the relatively strongly electron-releasing dimethylamino and methoxy substituents, through the weakly electron-withdrawing aldehyde, aza (*N*- in pyridines), and quaternary nitrogen ($\text{N}^+ - \text{CH}_3$ in 1-methylpyridinium salts) substituents, to the strongly electron withdrawing carbonium ion substituent.

Experimental Section

The structures of all compounds were confirmed by their physical constants and infrared and nmr spectra. Commercially available compounds were distilled before use and purity was confirmed by vapor phase chromatography.

***p*-Alkyl-N,N-dimethylanilines.** N,N-Dimethyl-*p*-toluidine, bp 210° (lit.²² 210–211°), and *p*-ethyl-N,N-dimethylaniline, bp 220–230° (lit.²³ 104° (16 mm)), were prepared by methylation of the corresponding *p*-alkylanilines with dimethyl sulfate.²³ Primary and secondary amines were removed by standard methods. The infrared spectra of the products showed no N–H absorptions. N,N-Dimethyl-*p*-cumidine, bp 220° (lit.²³ 111–112° (16 mm)), and *p*-*t*-butyl-N,N-dimethylaniline, bp 220° (lit.²³ 124–126° (16 mm)), were prepared by nitration of cumene²⁴ and *t*-butylbenzene,²⁵ respectively, followed by reduction with Sn–HCl,²⁶ to the corresponding alkylianilines. *p*-Cumidine was purified by recrystallization of the ionic oxalate salt from water²³ while *p*-*t*-butylaniline was purified by recrystallization of the acetyl derivative from ethanol²³ and subsequent hydrolysis. Methylation of the purified *p*-alkylanilines with dimethyl sulfate²³ gave the required products.

***p*-Alkylanisoles.** *p*-Methyl-, *p*-ethyl-, *p*-isopropyl-, and *p*-*t*-butylanisole were prepared by methylation of the corresponding commercially available phenols.^{27a} *p*-Cyclopropylanisole, bp 118–119° (35 mm) (lit.²⁸ bp 81–83° (8 mm); 232–234° (745 mm)), was prepared from *p*-methoxystyrene by carbene addition using the

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technique developed for phenylcyclopropane.²⁹ Reaction of anisaldehyde with malonic acid gave *p*-methoxycinnamic acid.³⁰ Decarboxylation³¹ gave *p*-methoxystyrene which was allowed to react with dichlorocarbene²⁹ to give *p*-dichlorocyclopropylanisole. Reduction²⁹ with sodium in methanol gave *p*-cyclopropylanisole.

***p*-Alkylbenzaldehydes.** *p*-Tolualdehyde and *p*-cuminaldehyde were commercially available. *p*-*t*-Butylbenzaldehyde, bp 81° (3 mm) (lit.³² 130° (25 mm)), was prepared in two steps by LiAlH_4 reduction of *p*-*t*-butylbenzoic acid to *p*-*t*-butylbenzyl alcohol,³³ which was then oxidized to the aldehyde using the method of Smith and coworkers³⁴ for oxidation of 3,6-dimethoxy-2,4,5-trimethylbenzyl alcohol. *p*-*t*-Butylbenzaldehyde was purified *via* the bisulfite compound and was distilled. *p*-Cyclopropylacetophenone, mp 32° (lit.³⁵ 35–36°), was prepared by acetylation³⁵ of phenylcyclopropane obtained by reaction of cinnamaldehyde with hydrazine hydrate.³⁶

***p*-Alkylpyridines and Pyridinium Salts.** γ -Picoline and 4-*t*-butylpyridine were commercially available. 1-Methylpyridinium iodide, mp 118–119° (ethanol–ether) (lit.³⁷ 116–117°), 1,4-dimethylpyridinium iodide, mp 153–154° (ethanol–ether) (lit.³⁸ 153–153.8°), and 1-methyl-4-*t*-butylpyridinium iodide, mp 122–123° (ethanol) (lit.³⁸ 124–125°), were prepared by the reaction of pyridine, γ -picoline, and 4-*t*-butylpyridine, respectively, with methyl iodide.³⁸

Carbonium Ion Salts. The triarylmethyl fluoroborates were prepared from the corresponding triarylcarbinols by reaction with fluoroboric acid (42%) in acetic anhydride.³⁹ If after about 15 min the carbonium ion salt had not been precipitated, dry ether was added to reduce the solubility. The salts were filtered in the drybox and were washed with dry ether. They were dried under vacuum and stored under nitrogen.

Triphenylcarbinol was commercially available. Tri-*p*-tolylcarbinol, mp 91–93° (petroleum ether 60–80°) (lit.⁴⁰ 93.4–94°), was prepared by reaction of *p*-tolylmagnesium bromide with methyl *p*-toluate.^{27b} Tri-*p*-*t*-butylphenylcarbinol, mp 212–213° (CCl_4) (lit.⁴¹ 215–216°), was prepared by reaction of *p*-*t*-butylphenylmagnesium bromide with methyl *p*-*t*-butylbenzoate.^{27b}

Spectroscopy. The infrared spectra were recorded on a Perkin-Elmer Model 225 infrared spectrophotometer. Carbon tetrachloride was spectroscopic grade solvent. Acetonitrile (BDH, laboratory reagent) was purified by distillation from phosphorus pentoxide. The fraction boiling at 82° was collected.

1,1,2,2-Tetrachloroethane (A.R. reagent) was fractionally distilled and the fraction bp 145–147° was collected and stored over activated molecular sieves.

The spectroscopic technique for the nonpolar solvents in sodium chloride cells and the integration procedure for the 1600- and 1585- cm^{-1} bands were as previously reported.²⁰

The spectra of the carbonium ions were measured in a Teflon-coated cell⁴² in which the solution to be measured did not come in contact with the sodium chloride plates. The absorbance due to the Teflon was approximately balanced by the introduction of an equivalent amount of Teflon in the reference beam. There was still a slight residual absorbance, but this was constant throughout and was subtracted from all the intensity measurements.

The integrated intensity of the 1600- and 1585- cm^{-1} bands of standard compounds (*e.g.*, fluorobenzene and anisole) was within 3% of that obtained by the standard procedure in a sodium chloride cell.²⁰

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Table I. Spectral Data and σ_R° Values for Alkylbenzenes^a

Subst	1600-cm ⁻¹ region cm ⁻¹	A	σ_R°
Me	1605	275	-0.099
Et	1602, 1584	289	-0.103
<i>i</i> -Pr	1605, 1583	332	-0.115
<i>t</i> -Bu	1602, 1584	377	-0.125
CH(CH ₂) ₂	1604, 1581	645	-0.175

^a In CCl₄ solvent.Table II. Spectral Data for *p*-Alkylanisoles and Dimethylanilines^a

Subst	1600-cm ⁻¹ region cm ⁻¹	A	($\sigma_R^\circ 1 - \sigma_R^\circ 2$)	$\left[\frac{A - 170}{11,800}\right]^{1/2}$	λ	$\bar{\sigma}_R^\circ$
OMe, H	1603, 1590	3330	-0.428			
Me	1613, 1586	1530	-0.329	-0.339	-0.010	-0.089
Et	1611, 1584	1743	-0.325	-0.365	-0.040	-0.063
<i>i</i> -Pr	1614, 1584	1738	-0.313	-0.363	-0.050	-0.065
<i>t</i> -Bu	1613, 1581	1798	-0.303	-0.372	-0.069	-0.056
CH(CH ₂) ₂	1614, 1538	1405	-0.253	-0.323	-0.070	-0.105
NMe ₂ , H	1604, 1578	5098	-0.533			
Me	1618, 1570	2200	-0.434	-0.416	+0.018	-0.117
Et	1616, 1567	2947	-0.430	-0.485	-0.055	-0.048
<i>i</i> -Pr	1617, 1567	2650	-0.418	-0.460	-0.042	-0.073
<i>t</i> -Bu	1615, 1564	2999	-0.408	-0.490	-0.082	-0.043

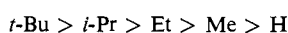
^a In CCl₄ solvent.

For the carbonium ions, the *A* values have been divided by the number of benzene rings (*i.e.*, 3).

The $[(A - 170)/11,800]^{1/2}$ values listed for the *para*-substituted alkylbenzenes are in the range 0.34–0.73. Errors resulting from uncertainty in the overtone correction (± 50) are therefore small here and the values are readily reproducible to well within ± 0.01 . The values are given to three figures in Tables II and III to avoid introducing additional error in taking differences but the arguments presented below are not dependent on this third figure.

Discussion

Alkylbenzenes. The previously reported²⁰ σ_R° values for the monoalkylbenzenes are listed in Table I. These values represent the relative π -electron disturbances in the aromatic nucleus and therefore show that the order of decreasing effect is



Since this order is the same as observed in σ frameworks,³ the total electric effect of the alkyl group in these systems should be similar.

There is little other evidence in the literature on these substituent effects in the absence of a perturbing influence such as found in the presence of a second substituent acting as a probe or in equilibria or reaction studies. The *p*-hydrogen shifts⁴³ at 200 MHz have been shown to be in the same order suggesting greater electron donation by the *t*-butyl group but the evidence is not clear-cut since ring-current corrections may be necessary.⁴⁴ The σ_R° values determined⁶ by ¹⁹F shifts of *p*-alkylfluorobenzenes (*t*-Bu, 0.173, Et, 0.144, Me, 0.143 in carbon tetrachloride) could be somewhat dependent on the influence of the π electron donating fluorine atom in the *para* position (see below).

On the Baker–Nathan hypothesis,^{8,9} this order requires either that the inductive effect of the alkyl groups is more important than C–H hyperconjugative release at low electron demand or that C–C hyper-

conjugation is more important than C–H hyperconjugation.⁴⁵ The latter possibility is discussed further below.

The Schubert–Sweeney hypothesis¹⁰ does not directly concern itself with the nature of the electronic interactions but does assume^{12,13} that the net intrinsic electronic effect of alkyl groups is in the inductive order regardless of large or small electron deficiency in electron-demanding systems. The order observed

is therefore that required on their hypothesis since solvation effects will be of little importance in our measurements.

Electron-Rich Systems. Table II lists our results for *p*-alkylanisoles and -dimethylanilines. In the absence of any interaction between the *para* substituents, eq 2 indicates that the values of $(A_{para} - 170/11,800)^{1/2}$ given should correspond to the difference of σ_R° values of each pair. This is approximately true for the *p*-methyl substituent but increasing deviations (λ values) are observed with the other alkyl substituents. The last column of the table indicates the effective σ_R° value ($\bar{\sigma}_R^\circ$) that the alkyl group is exerting in each compound. It can be seen that the order of overall effect of the alkyl groups has been almost inverted in the anisoles and dimethylanilines. Clearly, therefore, the measured effect of an alkyl substituent depends quite sensitively on the electron density already present in the benzene ring. In the absence of solvent effects we would therefore suggest that the order Me > *t*-Bu would be followed in electron-rich systems and in substituted alkylbenzenes where an equilibrium or reaction led to an increasing negative state or transition state as predicted by Schubert and coworkers.¹²

Previous evidence appears to agree with this. It has been shown^{12,46} that in systems such as *p*-alkylphenols, anisoles, anilines, or dimethylanilines, where the alkyl substituent is called upon strongly to accept electrons, the principal electronic transition indicates that alkyl groups can act as acceptors relative to hydrogen. Recent experimental⁴⁷ and theoretical^{48,49} studies of the stabilization of negative charge in gaseous

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





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Table III. Spectral Data for *p*-Alkylbenzaldehydes,^a Acetophenones,^a Pyridines,^a and N-Methylpyridinium Salts^b

Subst	1600-cm ⁻¹ region cm ⁻¹	A	(σ _R [°] 1 - σ _R [°] 2)	$\left[\frac{A - 170}{11,800}\right]^{1/2}$	λ	σ _R [°]
CHO, H	1598, 1586	1308	0.262			
COMe, H	1601, 1581	940	0.219			
CHO, Me	1606, 1579	3549	0.361	0.535	0.174	-0.273
CHO, <i>i</i> -Pr	1608, 1577	3585	0.377	0.538	0.161	-0.276
CHO, <i>t</i> -Bu	1608, 1575	3722	0.387	0.549	0.162	-0.287
COMe, CH(CH ₂) ₂	1607, 1570	4157	0.394	0.582	0.188	-0.363
 N, H	1598, 1582	1360	0.268			
 Me	1606, 1565	2555	0.367	0.450	0.083	-0.182
 <i>t</i> -Bu	1597, 1555	2900	0.393	0.481	0.088	-0.213
 N ⁺ -Me, H	1637, 1587	1821	0.313			
 Me	1645, 1580	4150	0.412	0.581	0.169	-0.269
 <i>t</i> -Bu	1645, 1571	4723	0.438	0.621	0.183	-0.305

^a In CCl₄. ^b In MeCN.

Table IV. Spectral Data for Tris(*p*-alkylphenyl)carbonium Tetrafluoroborates^a

Subst	1600-cm ⁻¹ region cm ⁻¹	A/3	(σ _R [°] 1 - σ _R [°] 2)	$\left[\frac{A/3 - 170}{11,800}\right]^{1/2}$	λ	σ _R [°]
H	1582	6336	0.60			
Me	1592	14280	0.699	1.09	-0.39	-0.49
<i>t</i> -Bu	1584	17315	0.725	1.21	-0.485	-0.61

^a Measured in tetrachloroethane in a Teflon-coated cell.

alkoxide ions also show that the acidity order is *t*-butyl alcohol > isopropyl alcohol > ethanol > methanol >> water. Calculations⁴⁹ (CNDO/2) on acidities of alkanes have also indicated that alkyl groups can stabilize negative charge and that the larger or more complex the alkyl group, the greater the negative charge stabilization. The stabilization is suggested⁴⁹ to proceed through the increase in alkyl group polarizability with increasing size or complexity. There is, however, some disagreement between workers^{50,51} as to the relative stability of alkylbenzene radical anions. In chemical reactions or equilibria leading to increasingly negative states, the order Me > *t*-Bu is usually observed⁵¹ as anticipated.

It should be noted that many of the examples above represent highly electron-rich systems compared to our results and evidently under these conditions the alkyl groups can actually stabilize negative charge relative to hydrogen.

Electron-Deficient Systems. Table III lists our results for *p*-alkylbenzaldehydes, acetophenones, pyridines, and pyridinium iodides. The observed λ values (or σ_R[°]) indicate increasing electron donation by the alkyl substituents as the demand is increased but the order observed in the unsubstituted alkylbenzenes is maintained. To increase the demand to a maximum we also synthesized tritylcarbonium ions containing *p*-methyl or *p*-*t*-butyl substituents, but the inductive order is still observed (Table IV). In fact, as the demand for electrons is increased (*i.e.*, in the order aldehyde ≈ acetophenone ≈ pyridine < N-methylpyridinium salt < carbonium ions) the difference between the *t*-butyl and methyl substituents is increased. The tritylcarbonium ion is not planar,⁵² but any con-

jugation between a *para* substituent and the positive center will increase the tendency for planarity. Thus, while the order of electron release is definitely *t*-butyl > methyl, the magnitude of this difference may be enhanced slightly by this factor.

We predict therefore that in the absence of solvent effects, alkyl groups should show order *t*-Bu > Me when attached to electron deficient aromatic nuclei or in equilibria or reactions leading to more positive states.

This order is hard to explain on the Baker-Nathan hypothesis since it requires that C-C hyperconjugation is more important than C-H hyperconjugation. However, electron paramagnetic resonance spectral data of semiquinones and empirical analyses of reaction data suggest⁵³ that the difference in relative importance of the two forms of hyperconjugation may only be nominal. Dewar¹⁶ has also shown that on a theoretical basis the hyperconjugative ability of CR₁R₂R₃ should be almost independent of whether R is H or an alkyl group. It is of interest that C-C hyperconjugation has been suggested¹⁵ to predominate when certain conformations lead to reasonable overlap although these seem unlikely in simple alkylbenzenes. The order is that expected by the Schubert-Sweeney hypothesis as mentioned above.

Dipole moment studies⁵⁴ of *p*-alkylnitrobenzenes and *p*-alkylbenzonitriles in nonpolar solvents do indicate that the *t*-butyl group is more strongly electron releasing than methyl and furthermore that this difference is increased when an electron-demanding group is located *para* to the alkyl group in accord with our results. In more polar solvents, such as dioxane, the same worker⁵⁴ observed the opposite (Baker-Nathan)

(52) See, for example, (a) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); (b) I. I. Shuster, A. K. Colter, and R. J. Kurland, *ibid.*, **90**, 4679 (1968).

(53) L. M. Stock and J. Suzuki, *ibid.*, **87**, 3909 (1965).

(54) T. L. Brown, *ibid.*, **81**, 3232 (1959).

(50) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

(51) R. G. Lawler and C. T. Tabit, *J. Amer. Chem. Soc.*, **91**, 5671 (1969); but see a possible exception in ref 12.

order suggesting that solvation was responsible in accord with the Schubert-Sweeney hypothesis.

Rather analogous results^{13,14} seem to be obtained in electrophilic aromatic substitution. Thus the partial rate factors for the *para* positions in electrophilic bromination¹³ or chlorination¹⁴ of alkylbenzenes are in the order *t*-Bu > Me in poorly solvating media but are reversed when nucleophilic solvation of the transition state is more important. It has also been suggested⁵⁵ that electrophilic nitration of the highly deactivated *p*-alkylphenyltrimethylammonium ions follows the inductive order.

The observed ionization potentials⁵⁶ of alkylbenzenes also reflect the inductive order but the Baker-Nathan order is observed for the heats of formation of the corresponding benzenonium ions,⁴ and for certain solvolyses of aryl dimethylcarbinyl chlorides.⁵ These, we suggest, reflect solvation effects as suggested by Schubert^{10,12,13} although the promised⁴ measurement of free energy and entropy quantities in the formation of the benzenonium ions will be of great interest.

It has been shown^{52a} that the ¹³C shift of the carbonium ions, RC⁺Me₂, is in the order Et > Me > H suggesting the same order of electron donation by these substituents. The ¹⁹F shifts of various *p*-FC₆H₄C⁺YR derivatives also indicate⁵ a greater compensation of the positive charge by R = *t*-Bu than R = Me and this effect is accentuated where Y is CF₃ compared to OH.

The Cyclopropyl Group. We also report (Tables II and III) some measurements on the $\sigma_{\text{R}}^{\circ}$ values for the cyclopropyl substituent when attached *para* to variously substituted benzenes. The $\sigma_{\text{R}}^{\circ}$ value found in cyclopropylbenzene (Table I) is much larger than for acyclic alkyl groups, and this has been previously discussed in this series.²⁰ Considerable evidence^{15,57} suggests that the maximum interaction between the cyclopropyl group and an adjacent electron-deficient system occurs when the plane of the ring is perpendicular to that of the adjacent system. In the electron-deficient *p*-cyclopropylacetophenone, the cyclopropyl substituent maintains a greater electron-releasing power than the other alkyl groups but in *p*-cyclopropylanisole its electron release is reduced by the greatest amount of the alkyl groups measured.

Conclusions

Our results and discussion suggest that the order of π -electron donation *t*-Bu > Me is followed in unsubstituted alkylbenzenes and for their derivatives or

(55) J. H. P. Utley and T. A. Vaughan, *J. Chem. Soc. B*, 196 (1968).

(56) H. Bock, H. Seidl, and M. Fochler, *Chem. Ber.*, 101, 2815 (1968).

(57) H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, 88, 2051 (1966), and references given therein.

transition states having a reduced electron charge density in the aromatic nucleus. The opposite order of effect is found in alkylbenzene derivatives or transition states which have increased electron charge density in the aromatic nucleus. This change apparently outweighs any inductive contribution since the order Me > *t*-Bu seems to be invariably followed in such cases. We suggest that the occurrence of the order Me > *t*-Bu in some reactions involving electron-deficient alkylbenzenes is a solvation phenomena explicable in terms of the Schubert-Sweeney hypothesis.

The mechanism by which alkyl substituents affect the π -charge distribution in the benzene ring is of interest. We do not consider that any important contribution is made by σ -charge effects relayed by the bond connecting the alkyl group to the nucleus for reasons already^{7,20} discussed. The two primary alternatives are charge transfer between the σ orbitals of the substituent and the π orbitals of the ring (hyperconjugation) or repulsion effects (orbital penetration¹⁵) between these orbitals. The latter effect results in a redistribution of the π -charge density in the aromatic nucleus without any charge transfer between it and the substituent. Some authors consider the repulsion effect to be the predominant influence on the π -electron densities in toluene with respect to ultraviolet spectra^{18,58} or the ground state.^{18a} Recent all-valence electron calculations^{59,60} (CNDO) indicate excess π -electron densities in toluene to be α , 0.0282, *ortho*, -0.0243, *meta*, 0.0117, *para*, -0.0151, in electron units with a total resulting electron transfer from the methyl substituent of 0.0125 electron. These figures suggest that both effects above are important.

When the π -electron density at an *ortho* or *para* position in an alkylbenzene is reduced in a chemical process, the molecule can partially compensate for this either by increasing the charge transfer from the alkyl group or by redistributing the π -electron density from other ring carbons. The evidence in our paper does not allow any decision as to the relative magnitude of these effects but further all-valence electron calculations may assist. Changes in the relative importance of the two terms may explain in part the reversal of the relative effects of *t*-Bu and Me groups under differing conditions.

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(60) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, 72, 716 (1968), have published similar figures for the excess π -electron densities at the α , *ortho*, and *para* positions in toluene.