Tetrahedron, 1962, Vol 17, pp. 199 to 214. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRON DONOR AND ACCEPTOR PROPERTIES OF ALKYL SUBSTITUENTS

W. M. SCHUBERT,[1] R. B. MURPHY and J. ROBINS
Department of Chemistry of the University of Washington

(*Received 9 January 1961*)

Abstract—The polar effects of alkyl substituents in electrophilic and nucleophilic chemical and electronic transitions is discussed. The question of the importance of hyperconjugation in the electron donor properties of alkyl substituents is raised. In view of the cogent arguments of Dewar, it is doubtful whether quantum mechanical calculations embodying hyperconjugation constitute proof of this effect. That the art of quantum mechanics may not yet be sufficiently developed to be used as proof for or against secondary resonance effects also is evidenced by the calculations of Simpson, who found that an internal dispersion force model (in which conjugation was neglected) reproduced the properties of butadiene just as satisfactorily as the models embodying conjugation. The *experimental* facts do not unequivocally support the hyperconjugation hypothesis and indeed are, at least in part, contradictory to it. In particular, the demonstration that the Baker–Nathan Effect[2] may be due to the influence of alkyl substituents on the differential solvation of ground and transition states casts doubt on the interpretation that this experimental effect is due to a dominant role of C-H hyperconjugation.

In nucleophilic chemical reactions, rate or equilibrium constants for *para* (or *meta*) alkyl derivatives are somewhat smaller than those of the corresponding hydrogen compounds. A number of authors have interpreted this in terms of a permanent electron donor role of alkyl substituents (e.g. by hyperconjugation) relative to the hydrogen substituent. However, this static viewpoint of substituent effects fails to account for the finding that *p*-alkyl substituents function as apparent electron acceptors (relative to the *p*-hydrogen substituent) in appreciably lowering the energy of the nucleophilic principal electronic transition of phenol, anisole, aniline and N,N-dimethylaniline. These results are qualitatively rationalized in terms of "substituent-polarizability" and electronegativity.

The *p*-neopentyl substituent lowers the energy of both electrophilic and nucleophilic electronic transitions to an appreciably greater extent than either the *p*-methyl or *p*-*t*-butyl substituent. This extra stabilizing effect of the neopentyl substituent on both electron deficient and electron rich centers may be due to an internal dispersion force interaction, since the geometry of the neopentyl compounds is particularly favorable for such an interaction.

IN recent years the electronic effect of alkyl substituents in chemical and electronic transitions has undergone a thorough reappraisal. The role of alkyl substituents as electron donors has received by far the most study and attention, and the first part of this paper discusses the current status of the role of alkyl substituents as apparent electron donors toward electron-demanding unsaturated systems. In the second part of this paper data is presented which shows that under suitable conditions alkyl substituents may also function as apparent electron acceptors relative to the hydrogen substituent. A qualitative empirical treatment of polar effects of alkyl substituents in terms of substituent electro-negativity and "substituent-polarizability" is presented.

ALKYL GROUPS AS APPARENT ELECTRON DONORS

The many viewpoints and postulates regarding the electron donor properties of alkyl substituents seem to be roughly divisible into two categories, a "hyperconjugative

---

[1] John Simon Guggenheim Fellow at the Laboratorium für Physikalische Chemie und Elektrochemie der Technischen Hochschule, Stuttgart, Germany, 1960–1961.

category" and an "inductive effect category". However, variations of viewpoint within each of these categories are many, and all shades of meaning between the two categories can be read into the many words written about alkyl substituent effects. The founders of the hyperconjugation viewpoint are Baker and Nathan, who first postulated hyperconjugation (C—H) in 1935 to account for the Baker-Nathan Effect in chemical reactions in which the alkyl substituent is presumably strongly called upon to release electrons.[2-5] Among quantum mechanicians, the prime proponent of hyperconjugation is Mulliken, who has carried out numerous LCAO-MO calculations based on an acetylenic or ethylenic model for the alkyl group (e.g. $H_3{\equiv}C{-}X{=}Y$ or $R_3{\equiv}C{-}X{=}Y$, in which one of the bonds to the H_3 or R_3 group is considered as a pseudo σ bond, labeled $[\sigma]$, and the other two bonds are considered as pseudo-π, labeled $[\pi_x]$ and $[\pi_y]$.[6-9] A similar model is used by Coulson[10]. Other models include those in which a methyl group is treated as a single heteroatom.[11,12] Kreevoy and Eyring, in order to explain what they considered to be the particular effectiveness of α-hydrogens on the alkyl group, used an "α-hydrogen bonding" model in which is employed a non-zero resonance integral of the α-hydrogen 1s orbital with the π-orbital of the unsaturated system.[13]

The inductive viewpoint in its extreme was expressed by Burawoy, who advocated the idea that π-electron resonance is non-existent.[14] In keeping with this idea Burawoy and Spinner assumed a purely inductive mechanism for electron release by alkyl groups.[15]

Dewar considers the evidence for delocalization of bonds in polyenes (e.g. butadiene), olefins (e.g. propylene) and acetylenes (e.g. methylacetylene) to be inconclusive, and has concluded that "resonance is important only in molecules for which more than one classical (unexcited) structure can be written". All observable effects in the ground states of conjugated and hyperconjugated molecules, such as "stabilization energy",[16] shortenings of single bond distances (e.g. the carbon carbon single bond of butadiene and methylacetylene) and polarities (e.g. of propylene) are ascribed to changes in carbon carbon σ bond hybridization.[17] However, these conclusions were considered not necessarily applicable to excited electronic states or to transition states of the reactions of such molecules. Mulliken, in arguing against the Dewar proposals and

---

[2] The term Baker Nathan Effect is used here in its experimental sense; that is, it refers to a tendency for observed energies or heats of electron-demanding transitions to take the order $CH_3 < Et < iPr < tBu$, or for rate or equilibrium constants to take the order $CH_3 > Et > iPr > tBu$.

[3] The term "hyperconjugation" for the delocalization of σ-bonds to saturated carbon first appeared in a publication by Mulliken and was suggested by W. G. Brown[6,7]

[4] J. W. Baker *Hyperconjugation*, Oxford University Press, London (1953).

[5] Conference on Hyperconjugation, *Tetrahedron* 5, 105–274 (1959).

[6] R. S. Mulliken, *J. Chem. Phys.* 7, 339 (1939).

[7] R. S. Mulliken, C. A. Riecke and W. G. Brown, *J. Amer. Chem. Soc.* 63, 41 (1941).

[8] R. S. Mulliken, *Tetrahedron* 5, 253 (1959).

[9] R. S. Mulliken, *Tetrahedron* 6, 68 (1959).

[10] C. A. Coulson, *Valence*, pp. 307–317. Oxford University Press, London (1952).

[11] F. A. Matsen, *J. Amer. Chem. Soc.* 72, 5243 (1950).

[12] A. Streitwieser, Jr. and P. M. Nair, *Tetrahedron* 5, 149 (1959).

[13] M. M. Kreevoy and H. Eyring, *J. Amer. Chem. Soc.* 79, 5121 (1957); M. M. Kreevoy, *Tetrahedron* 5, 233 (1959).

[14] A. Burawoy, *Trans. Faraday Soc.* 40, 537 (1944); *Victor Henri Memorial Volume*. Desoer, Liége (1948).

[15] A. Burawoy and E. Spinner, *J. Chem. Soc.* 3752 (1954)

[16] Dewar has suggested the term "stabilization energy" to be used in place of "resonance energy" for the observed extra thermodynamic stability of conjugated molecules compared with unconjugated analogues.[17]

[17] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* 5, 166 (1959); *Ibid.* 11, 96 (1960).

for an important role of π-electron delocalization in "ordinary" conjugated or hyperconjugated molecules seems to rely mainly on the fairly consistent agreement of a number of quantum mechanical calculations.[8,9] However, he concedes that "Dewar's challenge has in any event made clear the importance of a careful re-examination of the theoretical basis of conjugation, hyperconjugation and related phenomena".[9]

Simpson also has raised the question of the relative importance of conjugative interaction in butadiene and higher polyenes. Neglecting resonance interaction altogether, he carried out quantum mechanical calculations based on a dispersion force model for butadiene which satisfactorily reproduced the stabilization energy and positions of singlet singlet absorption bands and accounted for bond length alternations.[18] Internal dispersion force interactions also are given considerable weight in the calculations of Berry[19].

The experimental chemist finds himself somewhat at a loss to evaluate to what extent the necessarily approximate quantum mechanical calculations based on various models can alone be used as arguments for or against specific effects such as hyperconjugation. However, the viewpoints expressed by Dewar and the calculations of Simpson have at least given cause for reflection as to whether the quantum-mechanical "evidence" for hyperconjugation is sufficiently convincing. The need of a theory of hyperconjugation to explain certain *experimental observations* seems to be no longer as urgent as once thought to be since these observations are now also subject to different interpretations.

Chief among the experimental observations cited in support of the theory of hyperconjugation has been the Baker-Nathan Effect.[2] This effect, which is usually found in chemical transitions that call strongly upon the substituent for electron release, has until recently been universally interpreted as showing net electron release in the order Me > Et > iPr > tBu and hence as meaning that C–H hyperconjugation is the main mechanism of electron release in these instances.[20] However, this interpretation has been seriously questioned.[22–26]

By and large there has been a tendency to take experimental results such as orders of rate constants or equilibrium constants at face value; that is, to view transitions in solution as if they were taking place in the gas phase. The possible effect of alkyl substituents on the solvent stabilization of the states in a transition usually has been omitted altogether from consideration, and in other instances dismissed with varying degrees of arbitrariness as being of secondary importance.[8,21,26] However, the research groups of Shiner[27] and Schubert[22–25] have found the Baker-Nathan Effect to be solvent dependent, in a manner not explainable by the original theory of Baker and

---

[18] W. T. Simpson, *J. Amer. Chem. Soc.* 73, 5363 (1951).

[19] R. S. Berry, *J. Chem. Phys.* **26**, 1660 (1957); *Ibid.* **30**, 936 (1959).

[20] Berliner has listed some forty reactions in which the Baker-Nathan Effect is found and has concluded primarily from the mere persistence of this effect that "hyperconjugation of C—H bonds provides the most consistent and satisfactory explanation".[21]

[21] E. Berliner, *Tetrahedron* 5, 202 (1959).

[22] W. M. Schubert and W. A. Sweeney, *J. Org. Chem.* **21**, 119 (1956); *J. Amer. Chem. Soc.* **76**, 4625 (1954).

[23] [a] W. M. Schubert, J. Robins and J. L. Haun, *J. Amer. Chem. Soc.* **79**, 910 (1957); [b] W. M. Schubert and J. Robins, *Ibid.*, **80**, 559 (1958); [c] W. M. Schubert, J. Robins and J. M. Craven, *J. Org. Chem.* **24**, 943 (1959)

[24] W. M. Schubert, J. M. Craven, R. Minton and R. B. Murphy, *Tetrahedron* **5**, 194 (1959).

[25] W. M. Schubert and R. Minton, *J. Amer. Chem. Soc.* **82**, 6188 (1960).

[26] R. W. Taft, Jr. and Irwin C. Lewis, *Tetrahedron* **5**, 210 (1959).

[27a] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **76**, 1603 (1954); [b] *Tetrahedron*, **5**, 243 (1959), [c] V. J. Shiner, Jr. and C. J. Verbanic, *J. Amer. Chem. Soc.* **79**, 369 (1957).

Nathan, and have suggested specific roles of the solvent. These groups were led independently to a consideration of the solvent role through a recognition of the fact that the Baker-Nathan Effect, though often observed in electron-demanding chemical reactions, is rarely encountered in measurements on other electron-demanding transitions, e.g., in the ionization potentials and "principal" electronic excitation energies of alkyl-unsaturated compounds.[22] [25,28] The Baker-Nathan Effect also is not found in ground state measurements such as dipole moments,[31] bond lengths[32] and heats of hydrogenation.[33] This inconsistency between the Baker-Nathan Theory and experimental fact also was recognized by Burawoy and Spinner.[15] They neglected the possible role of the solvent, however, and attributed the Baker Nathan Effect to "steric hindrance to bond shortening" in purely inductive electron release by alkyl substituents. The absence of the Baker Nathan Effect in highly electron demanding electron transitions was explained in terms of the Franck-Condon Principle; that is, in the short time of the electronic excitation process there is practically no movement of atomic nuclei, hence practically no bond shortening.[15] However, the hypothesis of Burawoy and Spinner does not satisfactorily account for the solvent dependence of the Baker-Nathan Effect in both chemical and electronic transitions.

Schubert and Sweeney maintained that alkyl substituents stabilize electron-demanding unsaturated systems in the inductive order, regardless of whether the substituent is faced with a large or small electron deficiency. They postulated that the Baker-Nathan Effect is due to steric hindrance to solvation near bulky alkyl groups; that is, that the solvent stabilization of alkyl unsaturated compounds is significantly decreased with increasing ability of the alkyl substituent to shield electron deficient sites in its vicinity.[22] This hypothesis leads to many of the same qualitative predictions for chemical reactions in solution as the hypothesis of Baker and Nathan, e.g. that the Baker Nathan Effect should be observed when the electron deficiency (and hence the requirement for solvation) created in that part of the reacting molecule containing the substituent is large.[34] On the other hand, observations made on electronic transitions,[22,24] such as the inductive order of the principal electronic transition energies of p-alkyl nitrobenzenes and acetophenones in the gas phase and, the partial inversion of this order in polar basic solvents,[23a] are consistent with the hypothesis of Schubert and Sweeney and inconsistent with the hypothesis of Baker and Nathan. The fact that the solvent molecules are not fully oriented to the electronic excited states (Franck-Condon Principle) accounts for the mildness of the Baker Nathan Effect in this particular instance and for its rare appearance in electron-demanding electronic transitions in

---

[28] A hyperconjugative order of excitation energies in the gas phase has been found only for the low intensity "B-band" of alkyl benzenes at ca. 2600 Å (but not for the intense polar "principal" or "E-band" transition at ca. 2100 Å).[29] What the substituent is called upon to do in this "almost non-polar transition"[30a] is not entirely clear. The interpretation that the energy order is due to predominant C—H hyperconjugation in the excited state[29] has been questioned and other explanations have been advanced.[30]

[29] F. A. Matsen, W. W. Robertson and R. L. Choake, *Chem. Rev.* 41, 273 (1947).

[30a] K. Bowden and E. A. Braude, *J. Chem. Soc.* 1068 (1952), [b] V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Disc. Faraday Soc.* 9, 53 (1950).

[31] C. P. Smyth, *Dielectric Behavior and Structure* Chaps. IX and X. McGraw-Hill, New York (1955).

[32] Sutton has concluded that "hyperconjugation is not clearly and ambiguously proved by bond length anomalies to exist in the ground state of molecules, although on the other hand its existence is not certainly disproved". L. E. Sutton, *Tetrahedron* 5, 118 (1959).

[33] Turner has concluded that thermochemical results do not provide significant information on the nature of the stabilization of unsaturated systems by alkyl groups (see, however, ref. 26); R. B. Turner, *Tetrahedron* 5, 141 (1959).

[34] A typical example is the solvolysis of p-alkyl benzhydryl chlorides, for which the latter hypothesis, however, accounts more satisfactorily for the order of observed activation entropies.[22,26]

solution in general.[23–24] Qualitatively considered, these results also are consistent with Shiner's suggestion that the solvent, through incipient hydrogen bonding with the α-hydrogens of the alkyl substituent, may function to enhance C—H over C–C hyperconjugation.[27] Quantitatively considered, the solution data for the *p*-alkyl nitro-benzenes and acetophenones were better accomodated by the hypothesis of steric hindrance to solvation near bulky alkyl groups.[23a]

Most recently it has been found that the kinetic parameters (k, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the solvolysis of 3-R- and 3,5-diR-benzhydryl chlorides (R = H, CH_3, and t-Bu) vary with solvent composition and substituent in a manner consistent with the hypothesis of Schubert and Sweeney, and inconsistent with the Baker–Nathan hypothesis, either as originally enunciated or as modified by Shiner.[25] Support for the steric hindrance to solvation argument was also found by Clement and co-workers in the solvation energies of benzyl, *p*-methylbenzyl and *p*-t-butylbenzyl chlorides in methanol, determined from vapor pressures of the pure chlorides and the Henry's law constants in solution.[36] Earlier, Shiner had found that the Baker–Nathan Effect in the solvolysis of *p*-alkylbenzhydryl chlorides is solvent dependent and concluded that the variations in relative rates with solvent composition could be explained in terms of solvent assistance to hyperconjugation or steric hindrance to solvation, or both.[27c]

In view of the above considerations it is the contention of the authors that the appearance of the Baker–Nathan Effect in transitions in solution does not constitute evidence for a C—H hyperconjugative order of electron release by alkyl substituents. If this contention is correct, then C—H hyperconjugation would have to yield in importance to stabilization mechanisms in the inductive order, such as the inductive effect itself, or internal dispersion forces,[18] or C–C hyperconjugation. It is a moot question whether hyperconjugation in general (both C–C and C–H) is important, although the postulate that it is a major factor seems now to offer no special advantage.

In connection with the question of the total electron donor effect of alkyl substituents, it is interesting to note that there has been a recent tendency among those favoring the hyperconjugation viewpoint to de-emphasize the relative importance of C—H hyperconjugation and to assign to C–C hyperconjugation an important, though generally lesser role. Thus Mulliken, who suggests the term "differential hyperconjugation" for use in discussions of the Baker–Nathan Effect, sees "no obvious reason" why C–C hyperconjugation "should be radically different in its effectiveness" than C–H hyperconjugation.[8] In fact, Mulliken early made no distinction between C—H and C–C hyperconjugation.[6,7] Perhaps the first to explicitly apply C–C hyperconjugation, in a qualitative way, are Berliner and Bondhus, who held that the rate of molecular bromination of t-butyl benzene relative to benzene ($k_{\mathrm{tBu}}/k_{\mathrm{H}}$ = 115 for "total" bromination at 25°) is too great to be attributable to the inductive effect alone and hence must be determined considerably by C–C hyperconjugation.[36] However, as de la Mare has pointed out, this is still a matter of opinion.[37] Recently, varying degrees of effectiveness have been assigned to C–C hyperconjugation, up to a ratio of C–C to C—H hyperconjugation of about 0·8.[28,38] It is to be emphasized that

---

[36] R. A. Clement, J. N. Naghizadeh and M. R. Rice, *J. Amer. Chem. Soc.* **82**, 2449 (1960). R. A. Clement and J. N. Naghizadeh, *Ibid.* **81**, 3154 (1959)

[36] E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.* **70**, 854 (1948).

[37] P. B. D. de la Mare, *Tetrahedron* **5**, 107 (1959)

[38a] P. D. Bartlett, *J. Chem. Educ.* **30**, 29 (1953); N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.* **70**, 854 (1948); [b] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

these "quantitative" estimations are based on rate constants in solution and neglect the possible effect of differential solvation on k_{CH_3}/k_{tBu} ratios.

ALKYL GROUPS AS APPARENT ELECTRON ACCEPTORS

1. *Introduction*

The amount of theorizing and experimental study that has been devoted to the influence of alkyl substituents on nucleophilic, i.e. electron rich, centers is much less than that given to the influence of alkyl substituents on electrophilic, i.e. electron deficient, centers. Nevertheless, rate or equilibrium constants have been determined for *p*-alkyl compounds in a number of nucleophilic chemical reactions in which negative charge is fed toward the substituent. Most of the reactions in which *para* hydrogen, methyl and t-butyl compounds have been compared are listed in Table 1. These reactions have a positive value of the Hammett reaction constant, ρ. The rate constants are somewhat smaller for the *p*-alkyl derivatives than for the corresponding *p*-hydrogen compounds, in agreement with the negative sign of the substituent constants, σ, assigned to alkyl substituents.[39,40]

TABLE 1. NUCLEOPHILIC REACTIONS OF *p*-ALKYL COMPOUNDS

Ref.	Reaction	Solvent	Temp.	Relative rate constants H	Me	t-Bu	ρ Values[a]
41a	Ethylbenzoates + OH^-	85%, EtOH[b]	25°	1	0·44	0·56	2·5
41a	Ethylbenzoates + OH^-	56%, Acetone[b]	25°	1	0·41	0·31	2·3
42[c]	*l*-menthylbenzoates + OCH_3^-	CH_3OH	40°	1	0·48	0·59	2·6
41b	Neutral hydrolysis of benzoic anhydrides	75%, Dioxane[b]	58°	1	0·35	0·39	1·6
43	Ethanolysis of benzoyl chlorides	EtOH	0°	1	0·57	0·67	1·5
43	Benzylpyridinium ions + OEt	EtOH	20	1	0·50	0·69	
43	2-Cl-5-alkyl-3,5-dinitrobenzenes + piperidine	Piperidine	50	1	0·18	0·31	
41c[d]	2-Bromo-5-alkylnitrobenzenes + piperidine	Piperidine	25°	1	0·15	0·17	4·9

[a] Values of the reaction constant, ρ, are taken either from the original reference or from ref. 40.

[b] Given as percentage by weight of aqueous solution.

[c] Activation energies obtained from rate constants at two temperature are 17·6, 18·0 and 18·1 for *p*-H, *p*-CH_3 and *p*-t-Bu compounds respectively. It was cautioned that these values may be somewhat in error.[42]

[d] Activation energies obtained from rate constants at two temperatures are 12·1 ± 0·8, 13·2 ± 0·6 and 12·9 ± 0·4 for *p*-H, *p*-CH_3 and *p*-t-Bu compounds respectively.

---

[39] L. P. Hammett, *Physical Organic Chemistry* Chap. VII. McGraw-Hill, New York (1940).

[40] H. H. Jaffé, *Chem. Rev.* 53, 191 (1953).

In the discussions of the deactivating effect of alkyl substituents relative to the hydrogen substituent in nucleophilic reactions, a static viewpoint has been taken. That is, the alkyl group is treated as a permanent electron donor relative to hydrogen, i.e. it is considered as resisting negative charge, and the usual discussions of hyperconjugative vs. inductive electron release are applied.[41–43] In most of these nucleophilic reactions, the rate or equilibrium constant is slightly smaller for the *p*-methyl than for the *p*-t-butyl derivative. This has been attributed to hyperconjugation, that is to an electron release order governed by C—H hyperconjugative electron release.[41–43] There is a certain inconsistency between this argument and that applied to electrophilic reactions. For electrophilic reactions, it is maintained that C—H hyperconjugative electron release should predominate over inductive electron release only when the electron *demand* placed upon the substituent is high. Why C—H hyperconjugative electron *release* should predominate in nucleophilic reactions, in which the electron demand placed upon the substituent is negative, is not altogether clear. Actually, there is no assurance that the very small differences between the rate or equilibrium constants of the methyl and t-butyl compounds reflect differences in the direct potential energy effects of the methyl and t-butyl substituents, or indeed, that these rate or equilibrium constant differences are due to differences in heats of activation or entropies of reaction. Heats and entropies of activation were determined for but two of the reactions of Table 1, but in these instances the values obtained are not reliable enough to permit a definite conclusion to be made. Furthermore, it is not known to what extent differential solvation of ground and excited states may influence the relative rates of the compounds of Table 1. That differential solvation may be a factor is evidenced by the inversion of the rate order for *p*-methyl and *p*-t-butyl compounds in the basic hydrolysis of ethyl benzoates in "56%" acetone as compared to "85%" alcohol.[44] In the absence of accurate heat and entropy data for the reactions of Table 1 it may be premature to attribute the small rate or equilibrium constant differences between the *p*-methyl and *p*-t-butyl compounds to differences in the direct polar effects of the substituents. Presumably, the larger rate or equilibrium constant differences between the *p*-alkyl and *p*-hydrogen compounds do qualitatively follow the differences in the polar effects of *p*-alkyl and *p*-hydrogen substituents in these instances, although this is not altogether certain.

The consideration of alkyl substituents as permanent electron donors relative to hydrogen is a manifestation of a prevalent static viewpoint of substituent effects in general; i.e. the electrical influence of substituents are treated in terms of mesomeric and inductive effects in fixed directions. Contributing toward the crystallization of a static viewpoint of substituent electronic effects has been the assignment to substituents of σ-values of constant sign, if not of constant magnitude. Thus, a negative σ is taken as implying permanent net electron release relative to hydrogen and a positive σ is taken as implying permanent electron acceptance to hydrogen. Both Burawoy and

---

[41a] F. Berliner, M. C. Beckett, E. A. Blommers and B. Newman, *J. Amer. Chem. Soc.* 74, 4940 (1952); [b] F. Berliner and L. H. Altschul, *Ibid.* 74, 4110 (1952); [c] E. Berliner and L. C. Monack, *Ibid.* 74, 1574 (1952).

[42] M. S. Newman and E. K. Easterbrook, *J. Amer. Chem. Soc.* 77, 3763 (1955)

[43] C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature, Lond.* 171, 301 (1953).

[44] This has been commented upon by Price and Lincoln, who attributed the smaller rate constant for the *p*-t-Bu compound in "56%" acetone to steric hindrance by the large *p*-alkyl group to solvation of the direct reaction site (i.e. the ester group) in the transition state; C. C. Price and D. C. Lincoln, *J. Amer. Chem. Soc.* 73, 5836 (1951)

Schubert have questioned such a static viewpoint of substituent effects. They have presented evidence that certain substituents may function as either apparent electron donors or as apparent electron acceptors relative to hydrogen, at least in certain electronic transitions, and were led independently to a consideration of substituent effects in terms of the "polarizability" of the substituent. Burawoy and Thompson proposed that the apparent electron release by *p*-halogen substituents in electron demanding electronic transitions and the apparent electron acceptance by *p*-halogen substituents in electron donating electronic transitions is determined by the polarizability of the σ-electrons to the substituent.[45] Schubert and co-workers suggested that the extent of electron "release" or "acceptance" by a substituent in a given state can be considered to be a function of both the magnitude of the electronegativity difference between the substituent and the site to which it is bonded and what will here be labeled as "substituent-polarizability".[46] They applied this viewpoint to a consideration of the effect of *para* alkyl, halogen and other substituents on electron demanding transitions and to the effect of *p*-halogen substituents on electron donating transitions.[23,48] The substituent is viewed upon as being capable of being polarized with roughly equal ease in either a positive sense (electron "release" by the substituent) or a negative sense (electron "acceptance" by the substituent) depending on whether the site to which the substituent is attached is more or less electronegative than the substituent. The vague term "substituent-polarizability" skirts the question of the exact manner in which the substituent is polarized but is considered to include either or both direct polarization of the bonding electrons to the substituent (σ and also π-bonds, if any) and possible internal dispersion force polarization.[48,49]

According to the treatment of substituent effects in terms of "substituent-polarizability" and electronegativity, alkyl substituents would be expected to lower the energy of transitions in which a sufficiently strong migration of negative charge toward the substituent occurs. The authors therefore undertook to measure the effect of *p*-alkyl substituents on the energy and intensity of the principal electronic transitions of phenol, anisole, aniline, and N,N-dimethylaniline.[51] These transitions, in which the interaction with the electric vector of the light is in the long axis of the molecule,[52] can

---

[45] A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).

[46] This is equivalent to postulating that the energy, Δ, released in the hypothetical reaction, A:B (ideal covalent) $\rightarrow$ A·B (actual molecule), is empirically a function not only of the electronegativity difference between A and B but also of the ease with which interacting electrons between A and B are polarized, this depending on the nature of both A and B. Pauling, in setting up an empirical scale of electronegativities, assumed that Δ is a function of only the electronegativity difference, specifically that Δ = const. $(x_A - x_B)^2$;[47]

[47] L. Pauling, *The Nature of the Chemical Bond* Chap. II. Cornell University Press, New York, (1944).

[48a] W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.* 22, 1285 (1957); [b] W. M. Schubert, J. M. Craven and H. Steadly, *J. Amer. Chem. Soc.* 81, 2695 (1959); [c] W. M. Schubert, H. Steadly and J. M. Craven, *Ibid.* 82, 1353 (1960); [d] W. M. Schubert and J. M. Craven, *Ibid.* 82, 1357 (1960).

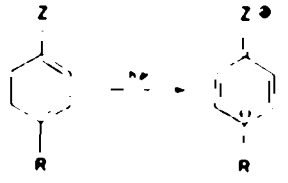
[49] The term "substituent-polarizability" is not to be confused with polarizability as determined from molar refractions. The "bond" or group refraction of a substituent is a measure of the ease with which the electrons are polarized by an external electro-magnetic field,[50] and thus is not necessarily a measure of the ability of the substituent to undergo internal polarization in an electronic transition. However, a parallelism between the two types of polarization may exist, as evidenced, e.g., by the correlation between the energies of the principal electronic transitions and the molar refractions of *p*-halo anisoles, nitrobenzenes and acetophenones.[48a]

[50] K. Fajans in Physical Methods of Organic Chemistry (Edited by A. Weissburger) Part II p. 1163. Interscience, New York, (1949).

[51] Preliminary results were reported in reference 24.

[52] W. T. Simpson, *J. Amer. Chem. Soc.* 75, 597 (1953). W. T. Simpson and C. W. Looney, *Ibid.* 76, 6293 (1954).

be crudely represented by equation (1) (see e.g. refs. 52, 53).[54] That the electron migration in these transitions is indeed away from the functional group and toward the substituent is amply verified by the effects of solvents on the principal electronic transition energies of such compounds.[48d,53]



I II (1)

Z = OH, OCH$_3$, NH$_2$, N(CH$_3$)$_2$

II. *Results*

Gas phase spectral measurements on carefully purified compounds were made in 20 cm Aminco quartz cells at elevated temperature with a Beckman DU instrument as previously described.[23,48] Measurements in heptane were made in 1 cm stoppered quartz cells at 25 ± 1°. Absorption maxima were located as previously described. Values of the transition moment length,[55] q, in heptane were calculated according to equation (2) from spectra measured in a Cary Model 14 instrument.

$$q^2 = 1{\cdot}09 \times 10^{-19} \int \epsilon \, d \ln \lambda \tag{2}$$

Representative of the principal band spectra of the members of each of the series are those of the p-methyl compounds in heptane, shown in Fig. 1. Each compound also exhibits a low intensity band ($\epsilon < 1000$) which has considerable fine structure and appears around 280 mμ. This evidently is the so-called B band, corresponding to the 260 mμ band of benzene. The principal band of the anilines and dimethylanilines is quite symmetrical, though overlapped slightly by a lower wave length band, and ν_{max} is probably a fairly accurate measure of the transition energy. The principal band of the phenols is considerably distorted through overlap by an intense lower wave length band. This is also true for the anisoles, but to a lesser extent. Thus, although the values of ν_{max} are precise to ± 20–30 cm^{-1}, the limits of accuracy of ν_{max} for the phenols and the anisoles are probably much higher than this. Table 2 lists the ν_{max} values found in the gas phase. Table 3 lists values obtained in heptane of ν_{max}, ϵ_{max}, and q. For comparative purposes, values for p-alkylnitrobenzenes are included.

III. *Discussion*

p-*Alkyl vs.* p-*hydrogen.* Consider first the observation that p-alkyl substituents lower the principal electronic transition energy of phenol, anisole, aniline and dimethylaniline (Tables 2 and 3). The lower excitation energy for the p-alkyl compounds means that the quantity, $E_H^* - E_R^*$, is greater than the quantity $E_H - E_R$, where

---

[53] N. S. Bayliss and L. Hulme, *Aust. Chem. J.* 6, 257 (1953); N. S. Bayliss and F. G. McRae, *J. Phys. Chem.* 58, 1002 (1954); K. Bowden and E. A. Braude, *J. Chem. Soc.* 1068 (1952).

[54] Obviously the use of single valence bond depictions for ground and excited states is merely for convenience, and the depictions I and II are arbitrarily chosen as perhaps the single best *representative* structures. It is understood that polar structures such as II *may* also contribute to the ground state, but certainly not to the extent as to the excited state.

[55] G. S. Levinson, W. T. Simpson and W. Curtis, *J. Amer. Chem. Soc.* 79, 4314 (1957); G. Herzberg, *Molecular Spectra and Molecular Structure* pp. 381–383. Van Nostrand, New York (1950).

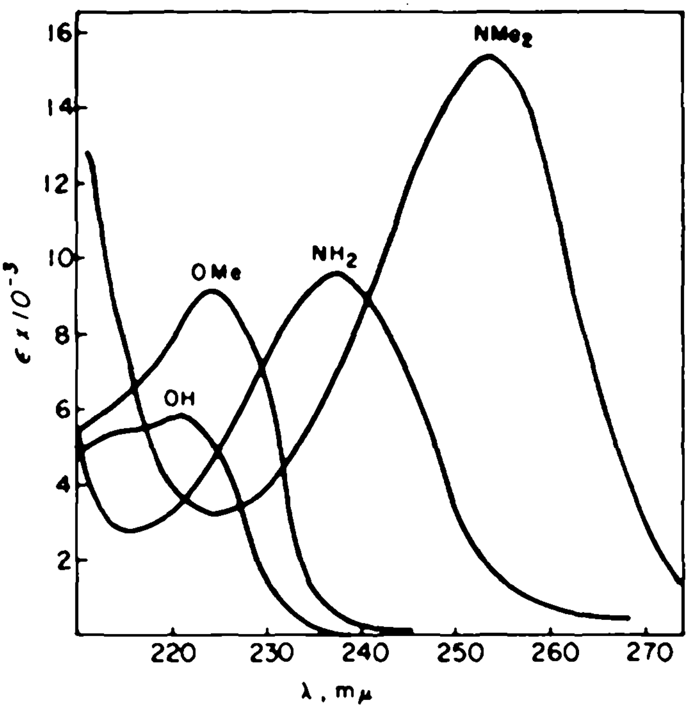


FIG. 1. Plot of the principal band spectra in heptane of the *p*-methyl derivatives of phenol, anisole, aniline and N,N-dimethylaniline.

TABLE 2 VALUES OF ν_{max} (cm^{-1}) FOR p-RC$_6$H$_4$Z IN THE GAS PHASE[a]

Z	H	Me	t-Bu	NeoP
OH	48470[c]	46280[c]	46300[c]	45480
OCH$_3$[b]	46510	45500	45470	44880
NH$_2$	43590	42790	42970	42280
NMe$_2$	41360	(41070)[d]	(40900)[d]	·
NO$_2$[e]	41820	39970	39760	39490

[a] Average of three determinations at 150°, duplicable to ± 20–30 cm^{-1}. A temperature of 150° was used to insure the absence of adsorption of the less volatile compounds on the cell windows.[illegible]

[b] Also determined at 80°, with results within experimental error of those at 150°.

[c] Spectral peak highly unsymmetrical due to strong overlap by a lower wave length band.

[d] Of doubtful accuracy due to slow change of spectrum with time and temperature.

[e] Previously reported.[illegible]

TABLE 3. VALUES OF ν_{max} (cm^{-1}), $\epsilon_{max} \times 10^{-3}$ AND TRANSITION MOMENT LENGTH, q(Å), FOR p-RC$_6$H$_4$Z AT 25° IN HEPTANE[a,b,c,d]

Anisoles

	H	Me	t-Bu	NeoP
ν_{max}	45330	44750	44810	44270
$\epsilon \times 10^{-3}$	7·6	9·1	10·1	11·3
q^e	0·50	0·56	0·62	0·64

Anilines

	H	Me	t-Bu	NeoP
ν_{max}	42740	42230	42320	41770
$\epsilon \times 10^{-3}$	9·0	9·5	10·7	11·6
q	0·66	0·69	0·74	0·77

N,N-Dimethylanilines

	H	Me	t-Bu	NeoP
ν_{max}	39830	39490	39600	—
$\epsilon \times 10^{-3}$	14·9	15·7	16·3	—
q	0·87	0·91	0·94	—

Phenols[f]

	H	Me	t-Bu	NeoP
ν_{max}	47430	45420	45500	44900
$\epsilon \times 10^{-3}$	5·7	5·9	6·8	8·0
q	—	—	—	0·55

Nitrobenzenes

	H	Me	t-Bu	NeoP
$\nu_{max}{}^g$	39700	37870	37670	37410
$\epsilon \times 10^{-3}$	8·7	10·0	11·0	11·7
q	0·80	0·86	0·90	0·95

[a] Values of ν_{max} are averages of three determinations, duplicable to ± 20 cm^{-1}.

[b] Values of ν_{max} also were determined for some of the compounds on the Cary Model 14 spectrophotometer. The differences in ν_{max} values obtained this way were within experimental error of those obtained on the Beckman DU.

[c] Values of $\epsilon_{max} \times 10^{-3}$ are averages of two determinations, duplicable to ± 2%.

[d] Values of q, equation (2), are averages of two determinations, duplicable to ± 1%, except where noted.

[e] Duplicable to ± 2%. Choice of area under principal band arbitrary due to overlap by lower wave length band.

[f] Except for the p-neopentyl derivative, the spectral band of the phenols was quite unsymmetrical due to strong overlap of the principal band by a lower wave length band. This prevented q from being accurately determined

[g] Previously reported[13a,b]

E_H^* and E_R^* are the energies of the excited states of the *p*-hydrogen and *p*-alkyl compounds, respectively; and E_H and E_R are the energies of the corresponding ground states. This implies that the excited state is *stabilized* through *p*-alkyl substitution, i.e. $E_H^* \quad E_R^*$ positive and $E_H - E_R$ less positive, zero, or negative; for if one assumes that the excited state is destabilized by *p*-alkyl substitution, i.e. $E_H^* - E_R^*$ negative, then one is forced to the unlikely conclusion that the much less polar ground state is destabilized even more by *p*-alkyl substitution, i.e. $E_H - E_R$ more negative than $E_H^* \quad E_R^*$. Since the electron migration in the principal electronic transitions of phenol, anisole, aniline and dimethylaniline is *away* from the functional group and *toward* the substituent, i.e. the excited state is electron rich in the region of the *p*-substituent, the results imply further that the *p*-alkyl substituents are functioning as apparent electron *acceptors* relative to the *p*-hydrogen substituent in the excited state of these transitions.[44]

The "activating" effect of *p*-alkyl substituents in the principal electronic transition of phenol, anisole, aniline and dimethylaniline is inconsistent with the current static viewpoint of the electronic effects of alkyl substituents, in which alkyl groups are considered as permanent electron donors relative to hydrogen and are pictured as resisting negative charge, e.g. by hyperconjugation (see e.g. refs. 41 43). A possible role of alkyl substituents as electron *acceptors* relative to hydrogen also seems nowhere to have received specific theoretical treatment, although Mulliken in a recent paper has written: "It seems to the writer that the customary use of a symbolism such as $H{\cdot}CH_2 \quad CH - CH_2$ and corresponding emphasis on electron release, without any mention of an oppositely polarized ionic structure and, especially of the long bond structure $H_3 \quad C \quad CH \quad \dot{C}H_2$, may be seriously misleading".[illegible]

The flexible behavior of the *p*-alkyl substituents in functioning as apparent electron acceptors in the nucleophilic principal electronic transition of phenols, etc. and as apparent electron donors in electrophilic electronic transitions such as the principal electronic transition of nitrobenzene or acetophenone is qualitatively consistent with the treatment of substituent effects in terms of "substituent polarizability" and substituent electronegativity. This treatment can be graphically illustrated as in Fig. 2. The ordinate labeled *D*, the "demand for electrons", represents the electronegativity of A in the molecule A:X, where X is the substituent. Stabilization energy (positive) resulting from "electron release" by the substituent is given to the right on the *x*-axis. Stabilization energy (also positive) resulting from "electron acceptance" by the substituent is given to the left on the *x*-axis. The plot for two substituents of differing electronegativity and differing "substituent-polarizability", say H and CH_3, has been arbitrarily made linear. The origin of this plot is placed at the point of intersection of the *D*-axis with the line for the hydrogen substituent. At this value of *D* the hydrogen would neither release nor accept electrons, i.e. the electronegativity of A and H in A:H equal. For positive values of *D*, i.e. A in A:H more electronegative than H, H would "release" to A. For negative values of *D*, i.e. A less electronegative than H, H would "accept" from A. The slope of the arbitrary line is inversely related to the "substituent-polarizability".

---

[44] The term "apparent" electron acceptor is used here in recognition of the possibility that the stabilizing effect of the *p*-alkyl substituent on the excited state conceivably may be due at least in part to an internal dispersion force,[18] a type of interaction that does not involve a direct electron exchange between the substituent and the rest of the molecule.

The line for methyl has been given a smaller slope than that for hydrogen since methyl presumably has the greater "substituent-polarizability". In placing the intersection of the methyl line below the origin, the methyl substituent has been assumed to be less electronegative than the hydrogen substituent. This is in accord with the electronegativity order assigned by Walsh[57], Moffitt[58] and Bent[59]. It should be pointed out, however, that in the electronegativity tables of Pauling[47] and of Mulliken[60], tetrahedral carbon is assigned a greater electronegativity than hydrogen, and that this order has found more widespread use in the literature.

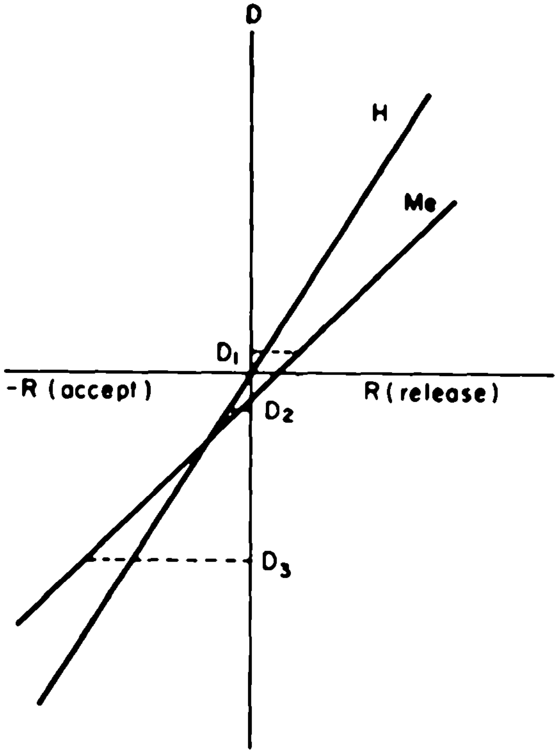


Fig. 2. Arbitrary electron demand–electron release plot for the H and CH_3 substituents. The D axis represents the electron demand placed on the substituent, X, by the varying group A in the ideal covalent molecule A : X. On the x-axis R represents positive stabilization energy resulting from electron release by the substituent and —R represents stabilization energy (also positive) resulting from electron acceptance by the substituent.

Consider now the principal electronic transitions of the phenols, etc. in terms of Fig. 2. In the ground state, the demand, D, placed on the p-substituent is neither very high nor very low. If, e.g. the demand is at D_1[61] the ground state would be stabilized through electron release in the order $CH_3 > H$. In the excited state the value of D is

---

[57] A. D. Walsh, *Proc. Roy. Soc.* A 207, 13 (1951).

[58] W. Moffitt, *Proc. Roy. Soc.* A 207, 74 (1951); *ibid.* A 202, 534, 548 (1950).

[59] H. A. Bent, *J. Chem. Phys.* 32, 1382 (1960).

[60] R. S. Mulliken, *J. Chem. Phys.* 2, 782 (1934); *Ibid.* 3, 573, 586 (1935).

[61] This is in accordance with an electronegativity order; $C^{sp^2} > H > C^{sp^3}$, for neutral atoms.[57,58]

probably quite low; i.e. the *p*-substituent is attached to a highly electron rich, electropositive center.[62] If D is sufficiently low, e.g. at D_3, the excited state of the *p*-methyl compound would be stabilized sufficiently over that of the *p*-hydrogen compound to insure a qualitative order of excitation energies $CH_3 < H$, even *if* the hydrogen substituent were more electronegative than the methyl substituent. Similarly, for the principal electronic transition of nitrobenzene or acetophenone, the very high D in the excited state (i.e. the *p*-substituent attached to a highly electron deficient, electronegative center)[62] would also insure an excitation energy order $CH_3 < H$, even if the hydrogen substituent were less electronegative than the methyl substituent.

With this treatment one could also rationalize why a *p*-alkyl substituent is "deactivating" in ordinary nucleophilic chemical transitions although "activating" in the nucleophilic electronic transitions, *provided* the hydrogen substituent is indeeed more electronegative than the alkyl substituent. In other words, a higher D value (i.e. smaller electron deficiency at the *p*-position in the transition state of the nucleophilic chemical transition as compared to the nucleophilic electronic transitions)[62] could result in the order, $H < CH_3$, for the activation energies. For example, if D in the transition state is only at D_2 the transition state would be stabilized in the electronegativity order. If D in the transition state is below the intersection of the hydrogen and methyl lines, the transition state would be stabilized in the substituent polarizability order. However, unless D is sufficiently low, the transition state would be stabilized less by the *p*-methyl relative to the *p*-hydrogen substituent than the ground state (ground state D say at D_1) and the activation energies would still be in the electronegativity order.[64] A greater electronegativity for the hydrogen than the alkyl substituent would also be consistent with the fact that alkyl substituents are activating even in mildly electrophilic transitions.

Effect of changing p-*alkyl substituent.* The energy order for the nucleophilic electronic transitions is neoP $<$ CH_3, t-Bu $<$ H, with the *p*-methyl and *p*-t-butyl groups having comparable effects. In heptane (Table 3), the ν_{max} values of the *p*-methly and *p*-t-butyl compounds lie within experimental error of each other in the phenol and anisole series and in the order $CH_3 <$ t-Bu in the aniline and N,N-dimethylaniline series. In the gas phase (Table 2) the *p*-methyl-*p*-t-butyl ν_{max} order is clearly established only in the aniline series, it also being $CH_3 <$ t-Bu.

---

[62] Application of the Hammett equation,[39,40] $\log k_X - \log k_H = \frac{1}{2 \cdot 3RT} (\Delta F_H^{\ddagger} - \Delta F_X^{\ddagger}) = \sigma_X \rho$, to the principal electronic transition of nitrobenzene substituted in the *p*-position with substituents, X, having a negative substituent constant, σ_X, gives a ρ value for this reaction of $-13 \cdot 0 \pm 1 \cdot 2$. Preliminary estimates of the ρ values for the nucleophilic principal electronic transitions of *p*-substituted phenols, anisoles and anilines are 14·5, 9·8, and 7·0 respectively.[63] Applying the criterion that the magnitude of the ρ values is a measure of the nucleophilic demand placed on the substituent, it is clear that the *p*-substituent is called upon much more strongly to "accept" electrons in the principal electronic transitions of phenol, etc., than in the chemical reactions of Table 1. A large increase in polarity in the excited state is also reflected in the large degree to which the excitation energy is lowered in heptane relative to the gas phase (of the order of 3 kcal/mole), despite the unfavorable partial orientation of the solvent to the Franck-Condon excited state.[46a] The large negative ρ values for the principal electronic transition of nitrobenzenes and acetophenones also have a much greater magnitude than the ρ values found for electrophilic chemical transitions and are indicative of a stronger electron demand on the substituent.

[63] James M. Craven, Ph.D. Thesis, University of Washington (1959).

[64] Those who have maintained that alkyl groups function as permanent electron donors relative to hydrogen in nucleophilic reaction generally have neglected to consider the ground states,[41-43] i.e. they have failed to take cognizance of the possibility that the (presumably) greater activation energy for the *p*-alkyl compounds could be the qualitative result of the greater ground state stability of the alkyl compound.

The energy order in electrophilic principal electronic transitions is neoP < t-Bu < CH_3 < H (see Tables 2 and 3 for the previously determined ν_{max} values for the nitrobenzenes). Thus, except for an inversion of the methyl-t-butyl order in some instances, the effect of *p*-alkyl substituents on the energies of the nucleophilic electronic transitions are qualitatively the same as their effect on the energies of the electrophilic electronic transitions. The qualitatively comparable effects of the *p*-alkyl substituents in the two types of transitions is consistent with the naive consideration of substituent effects in terms of "substituent-polarizability" and electronegativity, and indeed, the instances of the inversion of the methyl-t-butyl order could be rationalized in terms of a slightly greater electronegativity for the *p*-methyl substituent coupled with a slightly greater "substituent-polarizability" for the *p*-t-butyl substituent.[65] The values in heptane of the transition moment length *q*, a quantity determined from the area of the absorption band (equation 2) and considered to measure the extent of *oscillation* of the solute dipole *during* the interaction with the electric vector of the light being absorbed[56] take exactly the same order for the nucleophilic electronic transitions as for the electrophilic excitation of nitrobenzene (Table 3). The order of *q* is neoP > t-Bu > CH_3 > H, and is considered to correspond to the order of "substituent-polarizability".

It is a matter of conjecture as to just what specific mechanisms are operative in the stabilization by *p*-alkyl substituents of the attached electron rich site in the excited state of phenol, etc. One question that can be asked is whether substituent polarization occurs through space (internal dispersion force)[18] or the bonding electrons, or whether both modes of polarization are important. Polarization of the bonding electrons to the substituent *might* include hyperconjugative electron acceptance[66] (both C—H and C—C) in addition to including inductomeric electron acceptance (i.e. polarization of the σ-bonding electrons between the substituent and the ring).

The fact that the *p*-neopentyl substituent lowers the excitation energy, and increases the transition moment length, of both nucleophilic and electrophilic electronic transitions to a greater extent than either the *p*-methyl or *p*-t-butyl substituent is difficult to explain solely in terms of either an inductomeric or hyperconjugative effect, or both. An internal dispersion force interaction may be of importance in the total effect of the neopentyl substituent. In molecular models a terminal portion of the *p*-neopentyl group is held in close juxtaposition to one side of the aromatic ring in the neighborhood of the *p*-position, in a particularly favorable position for polarization through space. That is, the terminal portion of the neopentyl group "may be acting in much the same way as would an adhering hydrocarbon solvent molecule",[23a] thus helping to stabilize either an electron rich or electron deficient aromatic ring in the excited state.

The neopentyl group also appears to be exerting an exceptional stabilizing effect on the ground state of ethylene. Whereas the heats of hydrogenation of propylene, 1-butene, isopropylethylene and t-butylethylene are identical within experimental error (the values are −30·1, −30·3, −30·3, and −30·3 kcal/mole, respectively, compared with −32·8 for ethylene), the heat of hydrogenation of neopentylethylene is significantly greater (−29·5 kcal/mole).[53]

---

[65] *If* CH_3 is less electronegative than H, then the t-Bu group (having three α-methyl groups) probably should be less electronegative than the CH_3 group (having three α-hydrogens).

[66] Hyperconjugative electron acceptance could be labeled "anionoid" hyperconjugation; see, e.g. F. H. Siebold, Jr., *J. Org. Chem.* 21, 156 (1956), for the use of this term.

Effect of changing functional group. In Tables 2 and 3 it is seen that for the parent compounds of each series, or for the derivatives substituted with any particular *p*-alkyl substituent, the excitation energies decrease and the transition moment lengths increase in the order OH, OCH_3, NH_2, $N(CH_3)_2$. The functional group effect is rather large. For example, the difference in excitation energy between phenol and N,N-dimethylaniline in the gas phase is 7110 cm^{-1}, or 20·3 kcal/mole. Accompanying a decrease in excitation energy with functional group change is a decrease in the excitation energy spread between the *p*-hydrogen and the *p*-alkyl derivatives. For example, $\nu_H - \nu_{CH_3}$ in heptane has the value 2010 cm^{-1} (5·8 kcal/mole) for the phenols and decreases to only 340 cm^{-1} (1·0 kcal/mole) for the N,N-dimethylanilines. A similar parallelism between decreasing excitation energy of the parent compound and a decreased sensitivity of the excitation energy to the *p*-substituent has been noted previously for *p*-halo phenols, anisoles and anilines, and is reflected in the order of the Hammett "reaction" constants, ρ.[42]

Acknowledgements The authors wish to thank the Office of Ordnance Research, United States Army, for partial financial support of this research The hospitality extended to one of us (W. M. S.) by Prof. Th. Förster of the Laboratorium für Physikalische Chemie und Elektrochemie der Technischen Hochschule, Stuttgart, Germany, also is gratefully acknowledged.