The transmission of polar effects. Part VII.[1] A proton magnetic resonance spectra study of substituted mesitylenes, durenes, anthracenes, and triptycenes

KEITH BOWDEN, J. G. IRVING, AND M. J. PRICE
Department of Chemistry, The University of Essex, Wivenhoe Park, Colchester, Essex, England

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The chemical shifts of the ring protons in a series of monosubstituted mesitylenes and durenes, and of the 10-protons of a series of 9-substituted triptycenes and anthracenes have been measured in dimethyl sulfoxide, acetone, 2-methoxyethanol, and carbon tetrachloride. The solvent dependence of the substituent chemical shifts has been analyzed by linear free energy relations. The systems all show similar dependence which increases with increasing dielectric constant of the solvent. This does not result from the field effect being transmitted through the medium, but appears to arise from the formation of a hydrogen-bonded interaction between the solvent and the hydrogen of the solute. The substituent chemical shifts appear to arise from contributions from substituent field, resonance, magnetic anisotropy, and solvent effects.

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Introduction

Recently, many studies have attempted to relate the chemical shifts to properties of the substituents causing them (1–4). The chemical shift, δ, of a proton, relative to that in the unsubstituted compound, can be considered to consist of several additive factors, as shown below

$$[1] \qquad \delta = \delta_I + \delta_R + \delta_F + \delta_M + \delta_{\text{solv.}}$$

The factors are those due to the inductive (δ_I), resonance (δ_R), electric field (δ_F), magnetic (δ_M), and solvent ($\delta_{\text{solv.}}$) effects. Particular theories of the substituent chemical shift have been advanced in terms of the electric field (5, 6) and magnetic anisotropy (7, 8) effects. For an electric field, the substituent field effect at the proton, E, is a function of the substituent dipole, μ, the distance between the dipole and the proton, r, and the angle, θ, between the dipole and r, as shown in eq. [2].

$$[2] \qquad E = \frac{\mu(1 + 3\cos^2\theta)^{\frac{1}{2}}}{r^3}$$

The shielding, σ_E, arising from this field has been related by Buckingham (5) to the electric field by the eq. [3], where ϕ is the angle between the C—H bond and the vector E.

$$[3] \qquad \sigma_E = -10^{-12}E(2\cos\phi + 10^{-6}E)$$

A similar relation has been suggested by Musher (6). An anisotropic magnetic field has been shown by McConnell (7) to be approximated by the eq. [4], where the shielding, σ_M, is related to the anisotropy in the magnetic susceptibility of the g^{th} bond, $\Delta\chi_g$, the distance between the proton and that bond, r_g, and the angle between r_g and the bond axis, θ_g.

$$[4] \qquad \sigma_M = \Sigma_g\left[\Delta\chi_g \frac{(1 - 3\cos\theta_g)}{3r_g^{\,3}}\right]$$

Solvent effects on the chemical shifts have contributions (9–14) from the bulk magnetic susceptibility of the medium (δ_B), the van der Waals interactions (δ_W), the magnetic anisotropy of the solvent (δ_A), and the solvent reaction field effect (δ_{ES}), as shown in eq. [5]

$$[5] \qquad \delta_{\text{solv.}} = \delta_B + \delta_W + \delta_A + \delta_{ES}$$

Specific local effects such as hydrogen-bonding to the solvent will strongly influence the chemical shift (14). In considering the substituent chemical shifts in large molecules at non-proximate positions only δ_{ES} and specific local effects can be considered to be important. The local solvent reaction field treatment of Buckingham (5) implicitly includes dependence on the medium as shown in eq. [6]

$$[6] \qquad R \propto \frac{\varepsilon - 1}{2\varepsilon + 2.5}$$

where ε represents the dielectric constant of the medium and R the reaction field.

Recent studies of solvent induced chemical shift (15) have shown the limitations of the reaction field theory. Specific solvent–solute complex formation has been suggested as being particularly suitable for aromatic solvents but has an analogy in hydrogen-bonding for non-aromatic solvents.

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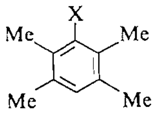
[1] For Part VI, see ref. 62.

Many attempts have been made to correlate chemical shifts of protons with Hammett substituent constants σ (16–20), with varying degrees of success. These constants express the polar effect of the substituent relative to hydrogen and are the sum of the "inductive" and resonance effects (21). The "inductive" effect probably originates from a field effect (22). A recent study (23) of substituted styrenes and ethylbenzenes has concluded that inductive and resonance effects are of greatest importance.

It was considered that a study of the substituent chemical shifts in model systems, and their solvent dependence, would give important information about the factors which control chemical shifts. This would then enable an evaluation of their use in assessing the transmission of polar substituent effects. The model systems selected for this study are those of fixed and known geometry, together with simplicity of spectra. These are the ring protons of substituted durenes (**1**) and mesitylenes (**2**), the 10-proton of 9-substituted anthracenes (**3**), and the 10-proton of 9-substituted triptycenes (**4**).



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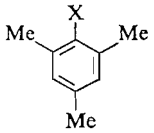

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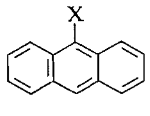

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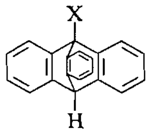

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Previously, very complete studies have been made of substituted mesitylenes in cyclohexane (24), together with very limited studies of durenes and mesitylenes in carbon tetrachloride (25), and of triptycenes in tetrahydrofuran (26).

Experimental

Materials

Mesitylene, 1,2,3,5-tetramethylbenzene, 2,4,6-trimethylacetophenone, 2,4,6-trimethylaniline, 2,4,6-trimethylphenol, 2,4,6-trimethylbenzaldehyde, and 2,4,6-trimethylbenzoic acid were obtained commercially. Nitromesitylene was prepared by nitration of mesitylene by fuming nitric acid in acetic acid (27). Mesitylene was chlorinated, using an anhydrous ferric chloride catalyst, to give chloromesitylene (28). Bromomesitylene was synthesized by bromination of mesitylene in carbon tetrachloride (29). Esterification of 2,4,6-trimethylbenzoic acid with diazomethane in ether gave the methyl ester (30).

Durene, pentamethylbenzene, and 2,3,5,6-tetramethylphenol were obtained commercially. Durene was nitrated to give dinitrodurene (31), which was reduced with sodium sulfide to nitroaminodurene (32). The diazonium salt, prepared from nitroaminodurene, was reduced with hypophosphorus acid to give nitrodurene (33). Aminodurene was prepared by the reduction of nitrodurene with zinc and acetic acid (34). Friedel–Craft acylation of durene gave 2,3,5,6-tetramethylacetophenone (35). Bromodurene was prepared by bromination of durene with bromine in carbon tetrachloride (36). The chlorination of durene using an iodine catalyst gave chlorodurene (37). The carboxylation of the Grignard compound obtained from bromodurene gave 2,3,5,6-tetramethylbenzoic acid, which was esterified with diazomethane in ether to form the methyl ester (38).

Anthracene, 9-methylanthracene, 9-acetylanthracene, and 9-anthraldehyde were obtained commercially. Nitration of anthracene with concentrated nitric acid in acetic acid gave 9-nitroanthracene (39). 9-Bromoanthracene was prepared by bromination of anthracene (40) and gave, on treatment with phenyl lithium and carboxylation, 9-anthroic acid (41). Methyl 9-anthroate was obtained by esterification of the acid by the action of trifluoroacetic anhydride and methanol (42). The reaction of anthrone with phenyl magnesium bromide gave 9-phenylanthracene (43).

The triptycenes were synthesized from the corresponding 9-substituted anthracenes by the addition of benzyne. The benzyne was generated by a modification of the method of Friedman and Logullo (44). A solution of anthranilic acid (15 g, 0.109 mole) in acetone (50 ml) was added over a period of 1 to 4 h to a refluxing mixture of the substituted anthracene (e.g. 9-nitroanthracene; 6.5 g, 0.0292 mole) in dichloromethane (50 ml) and isoamyl nitrite (13.5 g, 0.115 mole). The solution was then evaporated in a rotary evaporator to form a dark oil. This oil was dissolved in a minimum amount of dry benzene and eluted on an alumina chromatographic column with benzene. The first fraction was, in all cases, the triptycene and the second fraction was the unreacted anthracene. The triptycene could be purified by treatment with maleic anhydride and then a base, or by N-ethylmaleimide and

TABLE I

Physical properties of triptycenes

9-Substituent	Melting points (°C) This study	Melting points (°C) Literature	Reference
H	249–250	247–248	45
Me	255–257	253–254	45
Ph*	274–275	—	
Br	246–247	246–248	45
COMe†	210–211	—	
NO_2	244	241–243	45

*Anal. Calcd. for $C_{26}H_{18}$: C, 94.55; H, 5.55. Found: C, 94.99; H, 5.54.

†Anal. Calcd. for $C_{22}H_{16}O$: C, 89.17; H, 5.42; O, 5.41. Found: C, 89.36; H, 5.49; O, 5.43.

TABLE II

Chemical shifts of proton in substituted mesitylenes, durenes, and anthracenes

	Chemical shifts* of											
	Mesitylenes in				Durenes in				Anthracenes in			
Substituent	DMSO	MCS	Acetone	CTC	DMSO	MCS	Acetone	CTC	DMSO	MCS	Acetone	CTC
H	6.78	6.73	6.77	6.68	6.89	6.84	6.88	6.77	8.58	8.48	8.52	8.39
Me	6.78	6.74	6.79	6.69	6.79	6.74	6.79	6.68	8.49	8.35	8.42	8.23
NH_2	6.64	6.66	6.65	6.61	6.33	6.31	6.32	6.29	—	—	—	—
OH	6.71	6.70	6.73	6.66	6.50	6.48	6.50	6.46	—	—	—	—
Cl	6.99	6.86	6.91	6.80	6.95	6.90	6.93	6.78	—	—	—	—
Br	7.01	6.88	6.93	6.82	6.98	6.92	6.94	6.83	8.74	8.58	8.59	8.40
CHO	6.96	6.91	6.92	6.81	—	—	—	—	9.03	8.85	8.82	8.58
CO_2Me	6.90	6.85	6.89	6.76	7.05	6.98	7.00	6.88	8.81	8.68	8.70	8.46
COMe	6.86	6.80	6.85	6.73	7.00	6.95	6.98	6.85	8.73	8.61	8.63	8.42
NO_2	7.11	7.04	7.08	6.88	7.21	7.13	7.16	6.98	9.04	8.85	8.89	8.59
Ph	—	—	—	—	—	—	—	—	8.70	8.58	8.59	8.41

*Chemical shifts are accurate to ±0.01 p.p.m. relative to TMS.
Solvents: DMSO, dimethyl sulfoxide; MCS, 2-methoxyethanol; CTC, carbon tetrachloride.

then chromatography over alumina. After recrystallization from methylcyclohexane, the triptycenes were obtained as colorless solids whose physical properties are shown in Table I. The yields of triptycenes varied from between 25 to 50%, and the recovery of unreacted anthracenes between 60 to 30%.

The samples used for measurements were fractionally distilled or recrystallized to constant melting points. The physical constants of these samples were identical or close to those in the literature, except 9-methyltriptycene whose calculated and found elemental analyses were in good agreement. The elemental analysis for 9-phenyltriptycene was rather less satisfactory. The solvents, dimethyl sulfoxide and 2-methoxyethanol, were purified in the manner previously described (46). Acetone and carbon tetrachloride were "Analar" grade and were dried over 5 Å molecular sieves before use.

Nuclear Magnetic Resonance Measurements

A Varian A60-A nuclear magnetic resonance (n.m.r.) spectrometer operating at 60 Mc/s was used to obtain the spectra. These were measured as 0.1 *M* solutions in dimethyl sulfoxide, 2-methoxyethanol, acetone, and carbon tetrachloride containing 2% tetramethylsilane (TMS) as an internal standard. No significant shifts were noted on further dilution. A number of duplicate runs were made for each measurement. The uncertainty in peak position was considered to be ±0.5 c.p.s., relative to TMS. The spectra were calibrated by means of a Varian Associates standard and the calibration was checked at convenient and regular intervals. Standard instrument conditions were used throughout the measurements.

Results and Discussion

The chemical shifts of the selected protons of the durenes, mesitylenes, anthracenes, and triptycenes in the four solvents are shown in Tables II and III.

As stated previously, many attempts have been made to correlate substituent chemical shifts using linear free energy relations, especially the Hammett equation (16–20). Fair correlations have been made between substituent chemical shifts for the proton para to the substituent in benzene (16), while the correlation fails badly for the protons meta to the substituent in benzene (19). However, for mesitylenes, durenes, and anthracenes, substituents such as the nitro group will be extensively deconjugated with the aromatic ring. Studies on 4-substituted 3,5-dimethylbenzoic acids (47) and 9-substituted 10-anthroic acids (48, 49) enable the calculation of "effective" σ values which should be applicable to studies of substituted durenes and anthracenes. These "effective" σ values are calculated by dividing the observed ΔpK_a values for substituents such as the nitro group by the reaction constant obtained

TABLE III

Chemical shifts of proton in substituted triptycenes

	Chemical shifts* in			
Substituent	DMSO	MCS	Acetone	CTC
H	5.63	5.50	5.61	5.29
Me	5.64	5.50	5.59	5.29
Br	5.78	5.60	5.75	5.31
CO_2Me	5.69	5.52	5.64	5.29
COMe	5.67	5.51	5.61	5.24
NO_2	5.82	5.64	5.76	5.29
Ph	5.72	5.56	5.64	5.29

*Chemical shifts are accurate to ±0.01 p.p.m. relative to TMS. For abbreviations of solvents, see footnote of Table II.

from the unaffected substituents such as the halogeno groups. These values are shown in Table IV and the correlations for the chemical shifts in dimethyl sulfoxide in Table V. The correlations are only fair. In particular the chemical shift for the acetyl group appears to be too low and for the phenyl group appears to be too high to have resulted from the polar effect of the substituent as measured by the σ value. The failure of the correlation of the chemical shift of mesitylenes with meta-σ values has been ascribed to magnetic anisotropy effects at these positions (50). The acetyl and phenyl groups could have significant magnetic anisotropy effects also at the paraposition.

TABLE IV
Substituent constants

Substituent (R)	σ	σ_I (RCH_2)†
H	0.0	0.0
Me	−0.170	−0.03
NH_2	−0.63*	—
OH	−0.37	—
Cl	0.227	—
Br	0.232	0.47
CHO	0.19*	—
CO_2Me	0.32*	0.35_5
COMe	0.36*	0.29_5
NO_2	0.67*	0.73
Ph	0.00*	0.11_5

*"Effective" σ value (47–49).
†σ_I values used are those previously used (46) or those derived from reliable pK_a values of substituted acetic acids in water at 25° (51, 49).

Aliphatic substituent constants are required to correlate the effect of 9-substituents for triptycenes, where both proton and substituent are bonded to saturated carbon atoms. The parallel constants σ_I (46, 51) and σ^* (52) are available. The correlation with σ_I is shown in Table V for dimethyl sulfoxide as solvent and is only fair. The acetyl and phenyl groups show the same divergencies as shown in the durene and anthracene series. Both of these substituents have substantial magnetic anisotropy contributions (53, 54). It is very likely that this effect opposes the polar contribution for the acetyl group and augments that of the phenyl group.

Specific interactions between the substituents and solvents must be considered. The substituents and solvents have been chosen to avoid this. However, the hydroxy and amino groups are prone to this behavior (55) and the results for these groups must be treated with reserve.

TABLE V
Linear free energy correlations for chemical shifts in dimethyl sulfoxide

System	Reaction constants	δ_0* (p.p.m.)	r†	n‡
1,4-Durene	0.67 (ρ)	6.81	0.975	9
9,10-Anthracene	0.58 (ρ)	8.65	0.778	8
9,10-Triptycene	0.23 (ρ_I)	5.64	0.888	7

*δ_0 is the calculated chemical shift for hydrogen.
†r is the correlation coefficient.
‡n is the number of substituents studied.

The degree of success obtained for the durenes and anthracenes seems to indicate that, like para-substituted benzenes (16), the electron densities at these positions are more directly affected by the substituent polar effect (50). The mesitylenes and meta-substituted benzenes are less strongly affected by the substituent polar effect and magnetic anisotropy effects intervene (50). The partial success of the triptycene correlation indicates a small and not very significant substituent polar effect through systems not directly π-bonded. This is in accord with the recent studies of substituent effects on fluorine chemical shifts in saturated systems (56).

In the absence of very satisfactory correlations with substituent constants, it is necessary to suggest another method of analyzing the results in different solvents. Thus, the results have been analyzed by taking the chemical shift in dimethyl sulfoxide (DMSO), δ^{DMSO}, as a standard *for each system.* The chemical shifts in the other solvents have been correlated with these values, as shown in Table VI. The correlations are very good[2] and give the susceptibilities, γ, of these systems to the solvent effect, relative to that in dimethyl sulfoxide. However, the significance of these linear free energy relations is limited by their derivation and their scope. In spite of this, consideration of these γ values shows that the effect of the solvents for each series is almost the same and falls in the order:

$$\text{dimethyl sulfoxide} > \text{acetone} \approx \text{2-methoxyethanol} > \text{carbon tetrachloride}$$

This is the opposite order to that expected if the effect was due to the field effect of the substituents (see Table VII). The transmission of the substituent field effect would increase as the di-

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[2] The sole exception is the triptycene series in carbon tetrachloride where the shifts were very small.

TABLE VI

γ values for various systems*

System	Solvent	γ	δ_0 (p.p.m.)	r	n
Durene	DMSO	1.00	—	—	9
	Acetone	0.94	−0.01	0.999	9
	MCS	0.92	0.00	1.000	9
	CTC	0.79	−0.02	0.997	9
Mesitylene	DMSO	1.00	—	—	10
	Acetone	0.80	0.01	0.983	10
	MCS	0.73	0.02	0.969	10
	CTC	0.58	0.01	0.994	10
Anthracene	DMSO	1.00	—	—	8
	Acetone	0.78	−0.02	0.985	8
	MCS	0.87	−0.02	0.992	8
	CTC	0.56	−0.06	0.959	8
Triptycene	DMSO	1.00	—	—	7
	Acetone	0.93	−0.02	0.962	7
	MCS	0.77	−0.01	0.988	7
	CTC	0.61	−0.01	0.452	7

*δ_0 is the calculated chemical shift for hydrogen; r is the correlation coefficient; n is the number of substituents studied. For abbreviations of solvents, see footnote of Table II.

TABLE VII

Solvent parameters

Solvent	ε*	$\frac{\varepsilon - 1}{2\varepsilon + 2.5}$
Dimethyl sulfoxide	48.9†	0.177
Acetone	20.5‡	0.435
2-Methoxyethanol	15.95§	0.448
Carbon tetrachloride	2.23‡	0.478

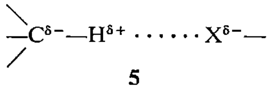
*Literature values (61), ε = dielectric constant.
†Value at 20°.
‡Value at 25°.
§Value at 30°.

electric constant of the medium falls. The dielectric constants, as shown in Table VII, decrease as γ decreases. The function proposed by Buckingham (5) does not account for the results found in this study.

The order of the susceptibility of the systems to substituent effects can be understood if the protons are interacting with the solvent by means of hydrogen-bonded interactions (14). These will vary in strength with the ability of the hydrogen-bond acceptor and will decrease in strength in the order (57):

$$\text{dimethyl sulfoxide} \gg \text{acetone} > \text{2-methoxyethanol} \gg \text{carbon tetrachloride}$$

The carbon–hydrogen bond will be polarized in accord with the strength of the hydrogen bond (**5**).



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The chemical shift of the hydrogen will have increased susceptibility to the polar effect of the substituent as the carbon–hydrogen bond becomes more polarized.

A number of fluorine n.m.r. studies of substituted fluoroaromatics have been made in a number of solvents (55, 58–60). Considerable differences occur in the interpretation of these results. It would appear that the effect of solvents on the fluorine chemical shifts are not interpretable in terms of a field effect (60), but are better expressed in terms of specific interactions between solute and solvent (55). The results of Wittstruck and Trachtenberg (23) are in general agreement with those presented here. The latter workers have deduced that the "net effect of field effects is insignificantly small". The possibility that electric and magnetic field effects cancel in their system remains. The present study has shown that the magnetic field effect of some substituents persists at remote positions. Wittstruck and Trachtenberg emphasize that chemical shifts can be used to evaluate conjugation. Our study shows that difficulties may arise from the intervention of other effects and stresses the importance of considering specific solvent interactions in elucidating the origin of chemical shifts. The conclusion of Dewar and Takeuchi (50) that "proton chemical shifts cannot be interpreted in terms of 'normal' substituent theory" seems amply justified.

Our conclusion from this study is that hydrogen n.m.r. shifts are not a good probe for studying the polar effects of substituents. Chemical shifts arise from complex causes. These causes are not always the same or are not governed in the same way as those affecting substituent effects on chemical reactivity.

1. J. N. Shoolery. J. Chem. Phys. **21**, 1899 (1953).
2. B. P. Dailey and J. N. Shoolery. J. Am. Chem. Soc. **77**, 3977 (1955).
3. A. A. Bothner-By and C. Naar-Colin. J. Am. Chem. Soc. **80**, 1728 (1958).
4. S. Reddy, J. H. Goldstein, and L. Mandell. J. Am. Chem. Soc. **83**, 1300 (1961).
5. A. D. Buckingham. Can. J. Chem. **38**, 300 (1960).
6. J. I. Musher. J. Chem. Phys. **37**, 34 (1962).
7. H. M. McConnell. J. Chem. Phys. **27**, 226 (1957).
8. J. A. Pople. Proc. Roy. Soc. London, Ser. A, **239**, 541, 550 (1957).
9. A. D. Buckingham, T. Schaefer, and W. G. Schneider. J. Chem. Phys. **32**, 1227 (1960).

10. J. K. Becconsall and P. Hampson. Mol. Phys. **10**, 21 (1965).
11. P. de Montgolfier. J. Chim. Phys. **64**, 639 (1967).
12. N. Lumbroso, T. K. Wu, and B. P. Dailey. J. Phys. Chem. **67**, 2469 (1963).
13. G. Katowycz and T. Schaefer. Can. J. Chem. **45**, 1093 (1967).
14. T. Schaefer and W. G. Schneider. J. Chem. Phys. **32**, 1218 (1960).
15. I. D. Kuntz and M. D. Johnston. J. Am. Chem. Soc. **89**, 6008 (1967).
16. H. Spiesecke and W. G. Schneider. J. Chem. Phys. **35**, 731 (1961).
17. T. Schaefer and W. G. Schneider. Can. J. Chem. **41**, 966 (1963).
18. P. Diehl. Helv. Chim. Acta, **44**, 829 (1961).
19. F. Langenbucher, E. D. Schmid, and R. Mecke. J. Chem. Phys. **39**, 1901 (1963).
20. S. H. Marcus, W. F. Reynolds, and S. I. Miller. J. Org. Chem. **31**, 1872 (1966).
21. R. W. Taft and I. C. Lewis. J. Am. Chem. Soc. **80**, 2436 (1958); **81**, 5343 (1959).
22. M. J. S. Dewar and P. J. Grisdale. J. Am. Chem. Soc. **84**, 3539, 3548 (1962).
23. T. A. Wittstruck and E. N. Trachtenberg. J. Am. Chem. Soc. **89**, 3803 (1967).
24. W. A. Gibbons and V. M. S. Gil. Mol. Phys. **9**, 167 (1965).
25. E. Bullock. Can. J. Chem. **41**, 711 (1963).
26. W. Theilacker, K. Albrecht, and H. Uffmann. Chem. Ber. **98**, 428 (1965).
27. G. Powell and F. R. Johnson. Org. Syn. **14**, 68 (1934).
28. *cf.* F. Brown, J. M. A. de Bryne, and P. Gross. J. Am. Chem. Soc. **56**, 1291 (1934).
29. L. I. Smith. Org. Syn. **11**, 24 (1931).
30. H. Peckmann. Ber. **31**, 501 (1898).
31. R. H. Birtles and G. C. Hampson. J. Chem. Soc. 10 (1937).
32. C. E. Ingham and G. C. Hampson. J. Chem. Soc. 981 (1939).
33. G. Illuminati. J. Am. Chem. Soc. **74**, 4951 (1952).
34. R. Willstatter and H. Kubli. Ber. **42**, 4159 (1909).
35. L. I. Smith and C. Guss. J. Am. Chem. Soc. **59**, 804 (1937).
36. L. I. Smith and C. L. Moyle. J. Am. Chem. Soc. **55**, 1676 (1933).
37. A. Tohl. Ber. **25**, 1523 (1892).
38. L. I. Smith and J. J. Rosenbaum. J. Am. Chem. Soc. **73**, 3843 (1951).
39. C. E. Braun, C. D. Cook, C. Merritt, and J. E. Rousseau. Org. Syn. **31**, 77 (1951).
40. O. L. Wright and L. E. Mura. J. Chem. Ed. **43**, 150 (1966).
41. B. M. Mikhailov and V. P. Bronovitskaya. J. Gen. Chem. USSR, Eng. Transl. **22**, 195 (1952).
42. R. C. Parish and L. M. Stock. J. Org. Chem. **30**, 927 (1965).
43. J. W. Cook. J. Chem. Soc. 2160 (1926).
44. L. Friedman and F. M. Logullo. J. Am. Chem. Soc. **85**, 1549 (1963).
45. W. Theilacker, U. Berger-Brose, and K. H. Beyer. Chem. Ber. **93**, 1658 (1960).
46. K. Bowden, M. Hardy, and D. C. Parkin. Can. J. Chem. **46**, 2929 (1968).
47. J. P. Schaefer and T. J. Miraglia. J. Am. Chem. Soc. **86**, 64 (1964).
48. R. O. C. Norman and P. D. Ralph. J. Chem. Soc. 2221 (1961).
49. K. Bowden and D. C. Parkin. Can. J. Chem., in press, and some unpublished studies.
50. M. J. S. Dewar and Y. Takeuchi. J. Am. Chem. Soc. **89**, 390 (1967).
51. M. Charton. J. Org. Chem. **29**, 1222 (1964).
52. R. W. Taft. *In* Steric effects in organic chemistry. *Edited by* M. S. Newman. John Wiley and Sons, Inc., New York. 1956. Chap. 13.
53. R. F. Zurcher. *In* Progress in nuclear magnetic resonance spectroscopy. *Edited by* J. W. Emsley, J. Feeney, and L. H. Sutcliffe. The Pergamon Press, Ltd., Oxford. 1967. p. 259.
54. G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio. J. Am. Chem. Soc. **89**, 5067 (1967).
55. R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis. J. Am. Chem. Soc. **85**, 709 (1963); **85**, 3146 (1963).
56. M. J. S. Dewar and T. G. Squires. J. Am. Chem. Soc. **90**, 210 (1968). G. L. Anderson and L. M. Stock. J. Am. Chem. Soc. **90**, 212 (1968).
57. F. Takahashi and N. C. Li. J. Am. Chem. Soc. **88**, 117 (1966); and references therein.
58. R. W. Taft and L. D. McKeever. J. Am. Chem. Soc. **87**, 2489 (1965).
59. M. J. S. Dewar and A. P. Marchand. J. Am. Chem. Soc. **88**, 3318 (1966).
60. W. Adcock and M. J. S. Dewar. J. Am. Chem. Soc. **89**, 379 (1967).
61. C. Reichardt. Angew. Chem. Intern. Ed. Engl. **4**, 29 (1965).
62. K. Bowden and G. E. Manser. Can. J. Chem. **46**, 2941 (1968).