are located at ν_0 = 964 and 1138 c./s., and δ_c = 123.6 p.p.m. and J = 174 c./s. For $\Delta\delta_c/\Delta q_r$ = 200, the shift relative to benzene corresponds to a q_r of about 1.3, or a total of 1.5 electrons per ring. This is not significantly different from the 1.0 electrons per ring and q_r of 1.2 of the $C_5H_5^-$ ion. The involvement of the π-orbitals of the ring with the iron may have an important effect on the shifts; measurements on the spectra of the $C_5H_5^-$ ion itself (and on $C_7H_7^+$) would be most interesting.
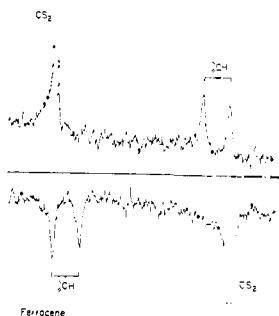

Fig. 18.—The 8.50 Mc./s. C^{13} n.m.r. spectrum of ferrocene.

Carbon–Hydrogen Spin–Spin Coupling Constants.—A relationship between the s characters of carbon–hydrogen bonds and the carbon–hydrogen spin–spin couplings has been proposed by several authors.[15,33,34] For non-equivalent hy-brids, the s character can be calculated from the orthogonality conditions.[35] A set of plane trigonal hybrids with one angle of 108° requires about 53% s character in the opposite bond and a coupling constant of about 250 c./s. if the value for 120° and 33% s character is taken as 159 c./s. from benzene. The 174 c./s. coupling in ferrocene, in which the C–C–C angles are 108°, requires that the bonds be strongly bent, with only a slight disturbance of the sp^2 hybridization of the carbons. It might be argued that ferrocene is unusual, but couplings of about 175 c./s. have also been found for the β-carbons in pyrolle, furan and thiophene.[36] The couplings in the five-membered ring of azulene also appear to be larger than those in benzene. Couplings of about 110 c./s. might be expected for seven-membered rings; although none of the experimental couplings for the large ring in azulene are believed to be very accurate, they are all slightly less than the benzene value and imply that there has been little change in the hybridization. Table II shows that methyl substitution changes the benzene couplings. Hybridization changes might be responsible, but there is no good independent way of estimating them.

(33) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).

(34) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(35) C. A. Coulson, "Valence," Oxford University Press, London, 1953, pp. 193–195.

(36) P. C. Lauterbur, to be published in later papers of this series.

C^{13} Nuclear Magnetic Resonance Spectroscopy. II. Phenols, Anisole and Dimethoxybenzenes

BY PAUL C. LAUTERBUR[1]

The C^{13} n.m.r. spectra of phenol and five methylphenols and of anisole, the three dimethoxybenzenes and 3,4-dimethoxy toluene have been obtained and complete assignments have been made. The effects of methyl groups on the spectra of methylphenols have been analyzed in detail, and the ring C^{13} chemical shifts caused by OH, OCH_3 and CH_3 are compared with other n.m.r. data, calculated charge distributions and substituent constants. The effects of the methoxy groups in the dimethoxybenzenes are found to be nearly additive when they are *meta* or *para* to one another but not when they are *ortho*.

Introduction

The F^{19} chemical shifts in substituted fluorobenzenes have been correlated with Hammett σ constants[2] and with separated inductive and resonance substituent constants.[3-5] Proton chemical shifts in substituted benzenes appear to be related to substituent constants in much the same way,[3,4,6,7] even to having about the same ratio of susceptibilities to inductive and resonance parameters.[4] Methyl C^{13} shifts in substituted toluenes have also

been studied,[8] but the shifts found for *meta* and *para* methyl groups were so small compared to the experimental uncertainties that no firm conclusions could be reached. The shifts of *ortho* methyl groups were found to be proportional to those of *ortho* fluorines after adjustment by an empirical factor meant to compensate for the different susceptibilities of methyl groups and fluorine atoms to resonance interactions. The chemical shifts of the ring carbon atoms themselves might be expected to reflect substituent effects more clearly than those of any substituent. The shifts are large[8] and the effects are not complicated by interactions with substituents other than that being studied. The proton shifts share the latter advantage but are small and subject to long range shielding and to solvent effects,[9] to which C^{13} shifts appear to be nearly inert.[8] There is also

(1) Multiple Fellowship on Silicones sustained by the Dow Corning Corporation and Corning Glass Works.

(2) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952). (b) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(3) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(4) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis and R. E. Glick, *ibid.*, **81**, 5352 (1959).

(5) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(6) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).

(7) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(8) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, (4), 841 (1958).

(9) T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218, 1224 (1960).

Figs. 1-7.—8.50 Mc./s. C^{13} n.m.r. spectra of phenols and anisole.

Figs. 9-12.—8.50 Mc./s. C^{13} n.m.r. spectra of dimethoxybenzenes.

evidence that ring C^{13} shifts in aromatic hydrocarbons are closely related to π-electron densities,[10] and it should be enlightening to compare the shifts in substituted benzene and in heterocyclics with calculated charge distributions and with the closely related substituent constants.

This paper includes data on phenol, methylphenols, anisole, the three dimethoxybenzenes and a dimethoxytoluene. The spectra are well resolved and can be completely analyzed. The effects of methyl substituents can be obtained from the shifts in the spectra of the several methyl phenols and are consistent with the qualitative observations made on methylbenzenes.[10] These shifts, and those caused by OH and OCH_3 groups, appear to be correlated well by Taft's σ_I and σ_R^0 parameters[4] and to be closely related to the fluorine shifts in the corresponding *meta* and *para* derivatives of fluorobenzene, although *ortho* shifts are somewhat anomalous. In the dimethoxybenzene spectra, the ring shifts produced by two methoxy groups *ortho* to one another are larger than those

(10) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

calculated from the anisole spectrum; when the methoxy groups are *meta* or *para* to one another their effects are almost exactly additive.

Experimental

N.m.r. Spectra.—The spectra were measured at 8.50 Mc./s., using a small tube of saturated $K_2C^{13}O_3$ solution as an external secondary reference, and the primary reference was CS_2. The charts were calibrated by modulating a CS_2 spectrum at 720 c./s. All samples were deoxygenated by bubbling with nitrogen. Additional experimental details will be found in the first paper of this series.[10]

Samples.—Phenol, 2,6-dimethylphenol, 3,5-dimethylphenol and 1,4-dimethoxybenzene were run as saturated $CHCl_3$ solutions, all others as neat liquids.

Phenol was reagent grade from J. B. Baker Chemical Co. and the cresols were Eastman "Practical" grade. Purification of the *o*-cresol to a colorless sharply-melting solid did not produce any measurable changes in its spectrum. Anisole was reagent grade from Fisher Scientific Co., the dimethoxybenzenes were from Bios Laboratories and the 1,2-dimethoxy-4-methylbenzene (3,4-dimethoxytoluene) was purchased from K. & K. Laboratories.

Results and Discussion

Spectra of Phenol, Methylphenols and Anisole.—The spectra of phenol, the five methylphenols and anisole are shown in Figs. 1-7, and the

peak positions and heights are given in Table I. Most peaks are resolved, and the assignments, based upon the fact that the methyl effects on shifts and couplings are small[10] and upon relative peak heights, are straightforward in most cases. In the o- and m-cresol spectra the assignments CH-3 vs. CH-5 and CH-2 vs. CH-6, respectively, are based upon the *ortho* and *para* shifts produced by a methyl group and are confirmed by the consistency of such shifts in the various methyl derivatives, as will be discussed in detail below.

TABLE I

THE 8.50 Mc./s. C^{13} N.M.R. SPECTRA OF PHENOL, METHYLPHENOLS AND ANISOLE

Compound	Peak no.	ν_c, c./s.	Height obsd.	Height calcd.	Assignments
Phenol[a]	1	317	0.66	1.00	C-1
	2	450	1.18	1.00	CH-3,5(1)
	3	523	0.57	0.50	CH-4(1)
	4	572	0.97	1.00	CH-2,6(1)
	5	611	1.09	1.00	CH-3,5(2)
	6	685	0.57	0.50	CH-4(2)
	7	733	0.97	1.00	CH-2,6(2)
o-Cresol[b]	1	331	0.73	1.00	C-1
	2	443	.57	0.50	CH-3(1)
	3	469	.57	.50	CH-5(1)
	4	525	.76	.50	CH-4(1)
	5	582	1.20	2.00	C-2 + CH-6(1) + CH-3(2)
	6	633	0.63	0.50	CH-5(2)
	7	683	.57	.50	CH-4(2)
	8	731	.60	.50	CH-6(2)
	9	1313	.16	.12	$CH_3(1)$
	10	1433	.48	.38	$CH_3(2)$
	11	1557	.54	.38	$CH_3(3)$
	12	1704	.19	.12	$CH_3(4)$
m-Cresol	1	319	0.87	1.00	C-1
	2	452	1.39	1.50	C-3 + CH-5(1)
	3	517	0.44	0.50	CH-4(1)
	4	570	.50	0.50	CH-2(1)
	5	606	.99	1.00	CH-6(1) + CH-5(2)
	6	677	.53	0.50	CH-4(2)
	7	728	.51	.50	CH-2(2)
	8	758	.59	.50	CH-6(2)
	9	1271	.12	.12	$CH_3(1)$
	10	1395	.48	.38	$CH_3(2)$
	11	1523	.51	.38	$CH_3(3)$
	12	1655	.08	.12	$CH_3(4)$
p-Cresol[b]	1	339	0.81	1.00	C-1
	2	451	.98	1.00	CH-3,5(1)
	3	527	.72	1.00	C-4
	4	577	1.05	1.00	CH-2,6(1)
	5	607	1.05	1.00	CH-3,5(2)
	6	735	1.20	1.00	CH-2,6(2)
	7	1271	0.17	0.12	$CH_3(1)$
	8	1398	.41	.38	$CH_3(2)$
	9	1525	.45	.38	$CH_3(3)$
	10	1659	.17	.12	$CH_3(4)$
2,6-Dimethylphenol[a]	1	342	0.76	1.00	C-1
	2	463	.99	1.00	CH-3,5(1)
	3	532	.83	0.50	CH-4(1)
	4	585	1.06	2.00	C-2,6
	5	619	1.19	1.00	CH-3,5(2)
	6	691	0.89	0.50	CH-4(2)
	7	1314	.20	.25	$CH_3(1)$
	8	1442	.91	.75	$CH_3(2)$
	9	1567	.83	.75	$CH_3(3)$
	10	1696	.33	.25	$CH_3(4)$
3,5-Dimethylphenol[a,c]	1	323	0.96	1.00	C-1
	2	455	1.81	2.00	C-3,5
	3	521	0.48	0.50	CH-4(1)
	4	600	1.04	1.00	CH-2,6(1)
	5	679	0.48	0.50	CH-4(2)
	6	755	1.15	1.00	CH-2,6(2)
	7	0		0.25	$CH_3(1)$
	8	1398	0.89	.75	$CH_3(2)$
	9	1527	.89	.75	$CH_3(3)$
	10	1666	.30	.25	$CH_3(4)$
Anisole	1	278	0.62	1.00	C-1
	2	457	.92	1.00	CH-3,5(1)
	3	531	.57	0.50	CH-4(1)
	4	593	1.05	1.00	CH-2,6(1)
	5	614	1.10	1.00	CH-35(2)
	6	693	0.45	0.50	CH-4(2)
	7	749	.80	1.00	CH-2,6(2)
	8	959	.20	0.12	$OCH_3(1)$
	9	1104	.52	.38	$OCH_3(2)$
	10	1249	.52	.38	$OCH_3(3)$
	11	1391	.25	.12	$OCH_3(4)$

[a] Run as a saturated $CHCl_3$ solution. [b] Supercooled. [c] Two weak peaks were observed at $\nu_c = 875$ and 1074 and ascribed to the $CHCl_3$ solvent; $\delta_c = 114.7$ p.p.m., $J = 198$ c./s.

Most of the observed peak heights (normalized to a total equal to the number of carbon atoms in the molecule) are in excellent agreement with the calculated ones. Those of the oxygen-substituted ring carbons, however, are significantly smaller and the peaks are noticeably broadened. A detailed study of the effects of methyl substitution upon the broadening of the resonances of ring carbons bearing oxygen and nitrogen atoms suggests that it is the result of small spin–spin couplings with protons on the ring, primarily those in the *meta* and *para* positions.[11] Such long-range carbon–hydrogen couplings have been observed by Karabatsos,[12] who found couplings in the proton spectrum of 2,4-dimethyl-3-pentanone-3-C^{13}[13] of about 3 c./s. between the C^{13}—O and the tertiary hydrogens and about 6 c./s. with the methyl hydrogens.

Chemical Shifts and Spin–Spin Couplings.— Table II contains the chemical shifts and spin–spin couplings calculated from the data in Table I. In three cases, o-cresol (CH-3 and CH-6) and m-cresol (CH-6), one component of a doublet could not be measured accurately because of overlap with another peak and a coupling of 160 c./s. was assumed for the shift calculation. Fig. 8, a chart of the ring carbon shifts, shows very clearly the similarity of the phenol and anisole spectra and how unambiguous assignments are made possible by the fact that the methyl effects are consistent, additive and relatively small.

Direct Methyl Effects.—It was noted in I[10] that the replacement of H by CH_3 on a benzene ring shifted the resonance of the substituted ring carbon to low field (the "direct methyl effect") but that at 8.50 Mc./s. this brought it into near coincidence

(11) P. C. Lauterbur, unpublished work.
(12) G. J. Karabatsos, J. Org. Chem., **25**, 315 (1960).

TABLE II

C[13] Chemical Shifts and Spin-Spin Couplings in Phenol, Methylphenols and Anisole

Compound	Group	δc, p.p.m.	J,[a] c./s.
Phenol	C-1	37.4	..
	CH-2,6	76.8	161
	CH-3,5	62.4	159
	CH-4	71.1	162
o-Cresol	C-1	39.0	..
	C-2	68.5	..
	CH-3	61.5	(160)[b]
	CH-4	71.1	158
	CH-5	64.8	163
	CH-6	76.6	(160)[b]
	CH₃	175.8	124
m-Cresol	C-1	37.6	..
	CH-2	76.4	158
	C-3	53.2	..
	CH-4	70.3	159
	CH-5	62.2	154
	CH-6	79.8	(160)[c]
	CH₃	171.6	128
p-Cresol	C-1	39.9	..
	CH-2,6	77.2	158
	CH-3,5	62.3	156
	C-4	62.0	..
	CH₃	171.9	126
2,6-Dimethylphenol	C-1	40.2	..
	C-2,6	68.9	..
	CH-3,5	63.7	156
	CH-4	71.9	158
	CH₃	177.1	126
3,5-Dimethylphenol	C-1	38.0	..
	CH-2,6	79.7	156
	C-3,5	53.6	..
	CH-4	70.6	158
	CH₃	172.1	129
Anisole	C-1	32.7	..
	CH-2,6	79.0	156
	CH-3,5	63.0	158
	CH-4	72.0	162
	OCH₃	138.4	145[d]

[a] Values in parentheses were assumed for calculation of the corresponding δc. [b] CH-1,3(2) and CH-6(1) merged with C-2 in peak 5. [c] CH-6(1) merged with CH-5(2) in peak 5. [d] N. Muller and D. C. Pritchard, J. Chem. Phys., 31, 1471 (1959), find 143 c./s. from the proton spectrum.

with the low-field components of the CH doublets, so that accurate measurements could not be made on toluene and o- and m-xylene. Somewhat more reliable measurements may be made on the methylphenols, and the results are shown in Table III.

TABLE III

The Direct Effect of Methyl Substitution on Ring C[13] Shifts in Phenols

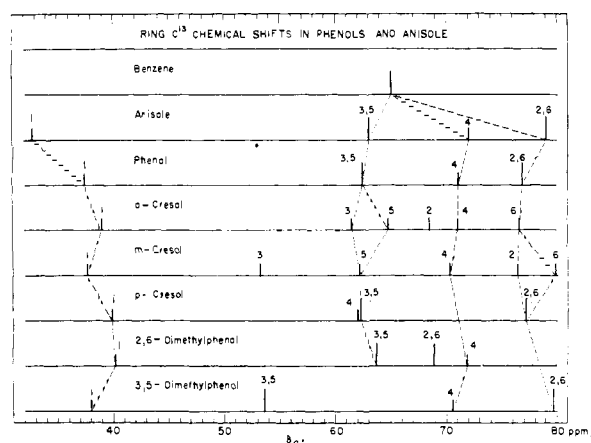| CH	C*-Me	δc(*-Me) − δc(CH), p.p.m.
Phenol	o-Cresol	−8.3
Phenol	m-Cresol	−9.2
Phenol	p-Cresol	−9.1
o-Cresol	2,6-Dimethylphenol	−7.7
m-Cresol	3,5-Dimethylphenol	−8.6

Fig. 8.—C[13] shift diagrams for phenols and anisole.

The direct methyl effect meta or para to the hydroxyl group is about −9.0 p.p.m. and that for an o-methyl group is −8.0 p.p.m.

Indirect Methyl Effects.—The effects of methyl groups on the shifts of other ring carbons have been classified in Table IV according to type (ortho,

TABLE IV

The Indirect Effect of Methyl Substitution of Ring C[13] Shifts in Phenols

Type of inter-action	Methyl position[a]	Methyl effect on ring C[13] shift[b] (p.p.m.)				Methyl derivative
		s[c]	o	m	p	
o	o	1.6	...	−0.9	...	o-Cresol
		1.2		−1.1		2,6-Dimethylphenol
	m	..	−0.4	...	−0.8	m-Cresol
			−0.1		0.3	3,5-Dimethylphenol
	p	..	...	−0.1	...	p-Cresol
m	o	..	−0.2	...	0	o-Cresol
			(0.4)		0.8	2,6-Dimethylphenol
	m	0.2	...	−0.2	...	m-Cresol
		0.4		(0.4)		3,5-Dimethylphenol
	p	..	0.4	...	...	p-Cresol
p	o	..	...	2.4	...	o-Cresol
				2.2		2,6-Dimethylphenol
	m	..	3.0	...	...	m-Cresol
			3.3			3,5-Dimethylphenol
	p	2.5	...	...	...	p-Cresol

[a] Relative to OH group. [b] Shifts of methyl-substituted carbons are in parentheses. [c] The symbol s is used for the carbon bearing the functional group.

meta or para) and the location of the methyl group and the carbon in question relative to the hydroxyl group. The ortho effect of a methyl group on the s (substituted) carbon, +1.4 p.p.m. average, is different from that on the o-, m- and p-carbons. The latter are all the same within experimental error, with the possible exception of the o, o, m shift. The average is −0.4 p.p.m. The meta effects are all the same within the experimental uncertainty, including those on methyl-substituted carbons (enclosed in parentheses in the table). The average meta effect is +0.2 p.p.m. The para effect is the greatest, with an average value of +2.7 p.p.m., and is the same everywhere, with the possible exception of the ortho position. The consistency of all of these shifts confirms the assignments and allows us to

use the average values as the characteristic effects of a methyl substituent.[13]

The calculated shifts in the methylbenzenes are given in Table V and compared with the experimental values taken from I.[10] The agreement is generally rather good, but there is some evidence for non-additivity of the effects of methyl groups *ortho* to one another, just as there was in Tables III and IV for adjacent methyl and hydroxyl groups. This interference is partially taken into account in the calculated values, as noted in the table, but it is unlikely that the mutual perturbation of two methyl groups is exactly the same as that of a methyl and a hydroxyl group. An attempt to apply such corrections to the hexamethylbenzene shift would give worse agreement with experiment. It is likely that steric interactions are much more important for compounds with three or more adjacent methyl groups, but measurements on other methylbenzenes, and more accurate data on several of those already studied, will be needed to evaluate them.

TABLE V

CALCULATED AND OBSERVED CHEMICAL SHIFTS OF RING CARBONS IN METHYLBENZENES

| | | δ_c | |
Compound	Group	obsd.	calcd.
o-Xylene	C-1,2	56.6	56.6[a]
	CH-3,6	63.6	64.8[b]
	CH-4,5	67.2	67.5
p-Xylene	C-1,4	58.0	58.7
	CH-2,3,5,6	64.5	64.8
Mesitylene	C-1,3,5	56.4	56.4
	CH-2,4,6	66.1	66.9
Durene	C-1,2,4,5	59.6	59.5[a]
	CH-3,6	62.0	64.4[b]
Hexamethylbenzene	C-1,2,3,4,5,6	60.4	59.3[a]

[a] Using the direct methyl effect of -8.0 p.p.m. found for *o*-methyl groups in the phenols. [b] Using the average value for the *o*-methyl effect. If the value -1.0 p.p.m. characteristic of a methyl group *ortho* to a hydroxyl group (o,o,m) were used, the calculated shifts would be in better agreement with those observed.

Correlation of Ring C[13] Shifts with Other Parameters.—It was shown in I[10] that ring C[13] chemical shifts are closely related to the calculated π-electron densities on each carbon in non-alternate hydrocarbons. Such a correlation is also apparent in phenol, although very few serious attempts have been made to calculate the charge distribution, and all of them are crude and uncertain by comparison with the work done on azulene and on heterocyclic aromatics. The best available calculations are probably those of Jaffé,[14] and a plot of the charge densities q_r against the ring C[13] shifts in phenol is a straight line with a slope δ/q_r of about 300 p.p.m./electron. This is probably not significantly larger than the slope of about 200 found for azulene and is in quantitative agreement, within the rather large uncertainty imposed by the poorly known q_r values, with the theoretical calculations in I.[10]

The halogen nuclear quadrupole coupling constants in many substituted halobenzenes have been measured, and it has been suggested that they are proportional to the charge densities on the corresponding ring carbons. The actual correlations made[15] have been with Hammet σ-values[16] and have been moderately successful for a wide variety of substituted benzenes. The effects of intermolecular forces and of double bond formation by the halogen are large, however, and intramolecular hydrogen-bond formation in the *o*-halophenols appears to perturb the spectra considerably. For these reasons, it seems unlikely that any useful detailed comparisons can be made between chemical shifts and quadrupole coupling constants, even though there is a rough correspondence between the two sets of data.

The most interesting comparisons are those between the ring carbon shifts, the fluorine shifts in substituted fluorobenzenes[1,2] and the separated σ-constants of Taft.[3-5,17] The *meta* C[13] shifts caused by CH_3, OH and OCH_3 are inversely proportional to their σ_I-values, as are the F[19] shifts in the corresponding fluorobenzenes (Table VI). The Hammett σ-constants themselves do not correlate as well with either the C[13] or F[19] shifts, as can be seen in the table. The differences between the *para* and *meta* shifts are compared with the σ_R^0 values in Table VII. The excellent

TABLE VI

COMPARISON OF RING C[13] CHEMICAL SHIFTS WITH OTHER CHEMICAL SHIFTS AND SUBSTITUENT CONSTANTS

Substituent	Position	$\Delta\delta$-(CH), p.p.m.	$\Delta\delta$-(CH_3),[a] p.p.m.	$\Delta\delta$-(F),[b] p.p.m.	σ[c]	σ_I[d]
OH	*o*	11.8	4.0	25.0		
	m	-2.6	-0.2	-0.9	0.00	0.25
	p	6.1	0.1	10.8	-0.36	
OCH_3	*o*	14.0		22.4		
	m	-2.0		-1.1	0.12	0.23
	p	7.0		11.5	-0.27	
CH_3	*o*	-0.4	1.8	5.0		
	m	0.2	0.8	1.2	-0.07	-0.05
	p	2.7	0.3	5.4	-0.17	

[a] Taken from Table II and ref. 10; the data in ref. 8 are similar. [b] Ref. 1. [c] Ref. 17. [d] Ref. 3.

TABLE VII

CORRELATION OF RING C[13] CHEMICAL SHIFTS WITH σ_R^0

Substituent	$\delta_{para} - \delta_{meta}$, p.p.m.	σ_R^0
OH	8.7	-0.40
OCH_3	9.0	-0.41
CH_3	2.4	-0.10
H	0	0

correlation found for the methyl, hydroxyl and methoxy substituents should extend also to $+R$ substituents, for which the correlation with fluorine shifts begins to break down because of conjugation between fluorine and the other substituent.[4,5]

(13) The methyl shifts in other substituted benzenes, to be reported in later papers of this series, are almost exactly the same.

(14) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

(15) For a general discussion and references to earlier work, see P. J. Bray and R. G. Barnes, *ibid.*, **27**, 551 (1957).

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, Chapter VII.

(17) For a general discussion and review, see R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

The *ortho* effects are of some interest. On a plot of ring C^{13} shifts against F^{19} shifts in the corresponding fluorobenzenes the points for *meta* and *para* substituents fall fairly well on a single straight line, as might be expected because of their similar dependence on the σ-parameters.[18] The points for *ortho* substituents are displaced, however, probably because of direct interactions between the fluorine atom and the substituents, and the C^{13} shifts probably provide a better comparison of the *ortho*-effects of various substituents.

More detailed discussions of the C^{13} shifts will be deferred until the effects of a wider variety of substituents have been presented in later papers of this series. It should be especially interesting to study both C^{13} and F^{19} shifts in substituted fluorobenzenes, since such effects as conjugation should be revealed by deviations from additivity of the substituent effects.

Dimethoxybenzenes.—The large shifts in the methoxybenzenes provide a stringent test of the additivity of the shifts by identical groups. The spectra of the three dimethoxybenzenes and of 1,2-dimethoxy-4-methylbenzene are shown in Figs. 9–12 and peak positions and heights are listed in Table VIII. The assignments in the spectrum of

TABLE VIII

THE 8.50 Mc./s. C^{13} N.M.R. SPECTRA OF DIMETHOXYBEN-ZENES

Compound	Peak no.	ν_e c./s.	Height, obsd.	Height, calcd.	Assignments
1,2-Dimethoxy-benzene	1	361	1.26	2.00	C-1,2
	2	531	0.96	1.00	CH-4,5(1)
	3	605	0.83	1.00	CH-3,6(1)
	4	691	1.01	1.00	CH-4,5(2)
	5	763	1.03	1.00	CH-3,6(2)
	6	953	0.38	0.25	OCH₃(1)
	7	1096	1.11	.75	OCH₃(2)
	8	1240	1.11	.75	OCH₃(3)
	9	1385	0.40	.25	OCH₃(4)
1,3-Dimethoxy-benzene	1	269	1.36	2.00	C-1,3
	2	454	0.64	0.50	CH-5(1)
	3	614	0.69	0.50	CH-5(2)
	4	657	1.00	1.00	CH-4,6(1)
	5	704	0.62	0.50	CH-2(1)
	6	817	.93	1.00	CH-4,6(2)
	7	861	.50	0.50	CH-2(2)
	8	956	.28	.25	OCH₃(1)
	9	1101	.83	.75	OCH₃(2)
	10	1245	.84	.75	OCH₃(3)
	11	1387	.31	.25	OCH₃(4)
1,4-Dimethoxy-benzene	1	329	1.19	2.00	C-1,4
	2	585	1.80	2.00	CH-2,3,5,6(1)
	3	743	1.91	2.00	CH-2,3,5,6(2)
	4	952	0.36	0.25	OCH₃(1)
	5	1093	1.26	.75	OCH₃(2)
	6	1239	1.08	.75	OCH₃(3)
	7	1385	0.40	.25	OCH₃(4)
1,2-Dimethoxy-4-methylbenzene	1	372	1.28	2.00	C-1 + C-2
	2	529	1.23	1.50	C-4 + CH-5 (1)
	3	601	1.01	1.00	CH-3(1) + CH-6(1)
	4	687	0.69	0.50	CH-5(2)

(18) The ratio of the inductive and resonance susceptibility factors is about the same for ring C^{13}, fluorine[4] and hydrogen.[4]

	5	758	1.03	1.00	CH-3(2) + CH-6(2)
	6	956	0.34	0.25	OCH₃(1)
	7	1097	1.13	.75	OCH₃(2)
	8	1239	1.10	.75	OCH₃(3)
	9		0	.12	CH₃(1)
	10	1387	0.44	.25	OCH₃(4)
	11	1404	.42	.38	CH₃(2)
	12	1523	.34	.38	CH₃(3)
	13		0	.12	CH₃(4)

ᵃ Run as a saturated CHCl₃ solution.

1,2-dimethoxybenzene are based upon the spectrum of the 4-methyl derivative. The assignments previously given[8] were erroneous. The spin-spin couplings and intensities in the spectrum of 1,3-dimethoxybenzene permit the assignment of all peaks except those of the 2 and 5 carbons, which have been given the assignments shown on the basis of the resulting agreement with calculation. The shifts and couplings are given in Table IX, along with the differences between the shifts calculated from those of anisole on the assumption of simple additivity. The agreement is almost within experimental error for the *meta* and *para* compounds, but two *ortho* methoxy groups appear to enhance the effects. Figure 13 is a
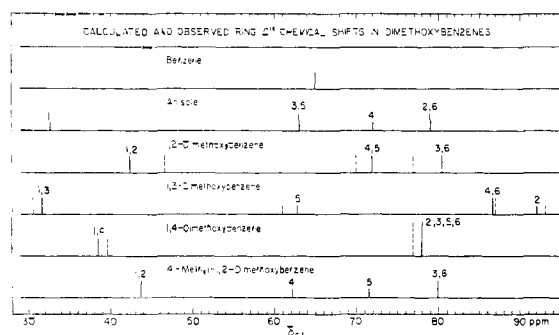

Fig. 13.—C^{13} shift diagrams for dimethoxybenzenes; the dashed lines represent the calculated shifts.

graphic comparison of the calculated and observed shifts and shows that the *ortho* groups seem to have a larger effect on the ring carbons than they would separately, so that the shifts relative to benzene are increased.[19]

Methyl C^{13} Shifts.—Comparison of the methyl C^{13} shifts with those given earlier,[8] after applying the corrections mentioned in **I**,[10] shows that the differences are about those to be expected from the stated standard deviations. The earlier results may be slightly more reliable because they were measured with an internal standard, eliminating bulk susceptibility effects, and because the reference peak (of dioxane) was closer to the methyl peaks than was that of the carbonate solution used in the present study, reducing errors caused by calibration uncertainties.

Methoxy C^{13} Shifts.—The methoxy resonances are sharp and are reasonably strong in the dimethoxybenzenes. No two measurements on any one differed by more than 0.3 p.p.m., and it seems

(19) An unpublished measurement on hydroquinone in ethanol solution, made several years ago, gave a shift in exact agreement with that calculated from the spectrum of phenol.

TABLE IX

CHEMICAL SHIFTS AND SPIN–SPIN COUPLINGS IN DIMETH-
OXYBENZENES

Compound	Group	δ_c, p.p.m.	δ(obsd.) − δ(calcd.), p.p.m.	J, c./s.
1,2-Dimethoxy-	C-1,2	42.4	−4.3	..
benzene	CH-3,6	80.5	3.5	158
	CH-4,5	71.9	1.9	160
	OCH$_3$	137.5		144
1,3-Dimethoxy-	C-1,3	31.7	1.0	..
benzene	CH-2	92.0	−1.0	158
	CH-4,6	86.7	0.7	161
	CH-5	62.8	1.8	160
	OCH$_3$	138.0		145
1,4-Dimethoxy-	C-1,4	38.6	−1.1	..
benzene	CH-2,3,5,6	78.1	1.1	158
	OCH$_3$	137.2		146
1,2-Dimethoxy-4-	C-1 + C-2	43.8		..
methylbenzene	CH-3 + CH-6	80.0		156

C-4	62.3	..
CH-5	71.6	158
OCH$_3$	137.4	142
CH$_3$	172.2	120

likely that the small differences observed between the different compounds are real. The order anisole, 1,3-dimethoxybenzene, 1,2-dimethoxybenzene (and the 4-methyl derivative), 1,4-dimethoxybenzene is that expected if the interactions take place through the ring and are somewhat altered in the *ortho* compounds.

Spin–Spin Coupling Constants.—All ring CH coupling constants in the phenols and methoxybenzenes are the same as that in benzene (159 c./s.) within the experimental uncertainties, and the CH$_3$ couplings are the same as those in the methylbenzenes.[10] The OCH$_3$ couplings are all within the range 144 ± 2 c./s.

Electron Spin Resonance and Polarographic Investigation of Substituted Nitrobenzene Negative Ions

BY AUGUST H. MAKI AND DAVID H. GESKE

Electron spin resonance spectra have been obtained for 14 *para* substituted nitrobenzene mononegative ions that were generated in acetonitrile solution by electrochemical reduction within a microwave cavity. Polarographic data were also obtained for these *para* substituents and for 8 *meta* substituents. An excellent linear correlation was found between the half-wave potentials for the *meta* substituents and σ^n and σ^0 values. From gross deviation of *p*-nitro and *p*-amino substituents from the *meta* correlation line, *para* resonance energies are estimated. The N^{14} coupling constant of the nitro group is found to decrease as the ease of reducing the parent molecule is increased by the *para* substitution and *vice versa*. Measurement of ring proton coupling constants leads to the conclusion that the total electron spin magnetization in the four central ring π-orbitals is approximately constant. The *para* substituent merely effects a redistribution of the magnetization among these ring positions. Evidence based on hyperfine structure is presented for hindered rotation of the aldehyde group of *para* nitrobenzaldehyde anion, and a maximum rotational frequency of 2.8×10^8 c.p.s. is estimated. Comparison of the F^{19} hyperfine coupling constant of *p*-fluoronitrobenzene with the *para* proton coupling constant of nitrobenzene leads to the ratio $a_F/a_H = 2.12$; from this ratio is estimated that $Q_F = -47.5$.

Introduction

In recent years numerous electron spin resonance (e.s.r.) studies have been made of organic free radicals, particularly *anion* free radicals prepared by one-electron reduction of the neutral parent molecule.[1] While a variety of anion radicals have been studied, no attempt has been made to examine a related series in which a single substituent is varied. Such a project is of particular interest in view of the possibility of estimates of odd-electron distribution derived from examination of the hyperfine structure of the e.s.r. absorption spectrum.

We have chosen to examine a series of *para* substituted nitrobenzene anion free radicals (·RAr-NO$_2^-$). The interaction of the odd electron with the nitrogen nucleus is expected to depend on the nature of the substituent, R. The experimental approach is the same as that presented previously[2,3]; the anion radical is generated by electrochemical

reduction of the parent molecule

$$RArNO_2 + e \rightleftarrows \cdot RArNO_2^- \qquad (1)$$
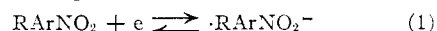
using acetonitrile as the solvent medium. An earlier study,[2] which demonstrated the experimental method, dealt with nitrobenzene anion radical, and a subsequent investigation[3] was concerned with the three dinitrobenzene anion radicals. The experimental simplicity and convenience of the electrogeneration technique have greatly facilitated the present extensive study.

Although a polarographic study of the series of *para* substituted nitrobenzenes was not the primary objective of this study, half-wave potential and current constant data were obtained. Availability of *both* e.s.r. and polarographic data provides an opportunity to relate the two quantitatively.

Experimental

Reagents.—Source and purification of the solvent, acetonitrile and supporting electrolyte, tetra-*n*-propylammonium perchlorate, were previously given.[2] Unless otherwise noted organic compounds were secured from Distillation Product Industries, Eastman Kodak Co. or K. & K. Laboratories (4-nitrobiphenyl and *p*-nitroacetophenone). Melting points agreed with literature values. Preparation

(1) (a) J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955); (b) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Academic Press, Inc., New York, N. Y., 1958, pp. 135–169.

(2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(3) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).