Organic and Biological Chemistry

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. III.[1,2] Further Monosubstituted Benzenes and Monosubstituted Durenes

R. T. C. Brownlee,[3] R. E. J. Hutchinson,[4] A. R. Katritzky,[3] T. T. Tidwell,[3] and R. D. Topsom[5]

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England, the School of Physical Sciences, La Trobe University, Melbourne, Australia, and the Department of Chemistry, University of Canterbury, Christchurch, New Zealand. *Received September 5, 1967*

Abstract: Integrated intensities for the ν_{16} mode of 110 monosubstituted benzenes (with the substituent ring linked by halogen, oxygen, sulfur, nitrogen, or carbon) are tabulated together with $\sigma_R°$ values for the substituents derived by a refined relation. Little variation of $\sigma_R°$ occurs with solvent, but results for 11 monosubstituted durenes show that twisting of a noncylindrically symmetrical substituent decreases mesomeric interaction markedly. The $\sigma_R°$ values generally compare well with those found by other methods and discrepancies can be explained. The nature of substituent–ring interactions is discussed. Consideration of the $\sigma_R°$ values by compound classes *inter alia* provides evidence for significant conjugative interactions in cyclopropylbenzene, and confirms recent conclusions on the variation of nitrogen–ring interaction in N-phenyl cyclic imines.

Previous work indicated that a precise correlation, formulated initially as eq 1[1] and later as eq 2,[2] existed between $A^{1/2}$, the square root of the integrated absorbance of the ν_{16} ring bands[6] in monosubstituted benzenes, and $\sigma_R°$ for the substituents. The measurement of infrared intensities promised[2] to be a convenient and reliable method for the determination of $\sigma_R°$ values, which are of great importance in the correlation and prediction of physicochemical properties. We have therefore extended our work on monosubstituted benzenes with the following main aims: (a) to further test the validity of, and if possible to further refine, eq 2; (b) to investigate the variation of $\sigma_R°$ values with solvent and with steric hindrance; (c) to elucidate the nature of substituent–benzene ring interactions; (d) to make available a wide range of $\sigma_R°$ values; (e) to illustrate the use of infrared intensity measurements in the clarification of specific problems involving substituent–ring interactions.

$$\sigma_R° = 0.0075A^{1/2} \tag{1}$$

$$\sigma_R° = 0.0079A^{1/2} - 0.027 \tag{2}$$

There have been many indications that the quantitative failure of the Hammett relation to correlate precisely all types of reactions is a result of the differences in resonance demands of various reaction types and sites (for reviews see ref 7 and 8). Many multiparameter equations have been postulated to account for this behavior; these equations can usually be written in a form equivalent to eq 3 (for recent explicit examples see ref 9). Accurate values for σ_I are available for many substituents (see ref 10 and references contained therein); we believe that a large collection of reliable $\sigma_R°$ values will be useful in further correlation work.

$$\log (k/k_0) = \rho_I\sigma_I + \rho_R\sigma_R° \tag{3}$$

For the estimation of the effects of steric hindrance we have investigated monosubstituted durenes. As regards specific problems, we have chosen (i) the interaction of a benzene ring with cyclopropyl rings compared with other benzene–cycloalkyl group interactions, and (ii) the variation of the interaction of a benzene ring with a lone pair located on a nitrogen atom forming part of a saturated heterocyclic ring with the size of this ring.

We also recorded the intensities of the ν_{13} bands near 1500 cm^{-1}; these correlate[2] with $\sigma_R°$, but we defer further discussion until analogous work in progress on disubstituted benzenes is complete. Other workers have considered the intensities of other vibrations in monosubstituted benzenes; the intensity of the C–H aromatic stretching modes is directly related[11–13] to the σ_I value of the substituent. However, the intensities of the C–H out-of-plane bending modes for monosubstituted alkyl-[14] and halobenzenes[15] show no simple

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(5) La Trobe University, Melbourne, Australia.

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Table I. Spectral Data and Calculated and Literature $\sigma_R°$ values for Monosubstituted Benzenes

Compd	Infrared solvent	$\pm\sigma_R°$, calcd	Lit. $\sigma_R°$			1600 band		1585 band		A[d]	5100 band		
			^{19}F[a]	React.[b]	Other	ν	ϵ_A[c]	ν	ϵ_A[c]		ν	ϵ_A[c]	$\epsilon^{1/2}$[e]
PhH	CCl_4	0.00	0.00	0.00[f]			0		0	0	1480	53	17.7
PhD	CCl_4	0.00				1594	1			30	1479	43	18.8
PhF	CCl_4	0.341	−0.32	−0.35	−0.34[f]	1597	213			2153	1497	375	32.3
PhCl	CCl_4	0.217	−0.18	−0.20	−0.20[f]	1585	68	1567	11	930	1489	226	33.7
PhBr	CCl_4	0.231	−0.16	−0.19	−0.14[f]	1580	84			1044	1476	226	43.2
PhI	CCl_4	0.221	−0.14	−0.12	−0.08[f]	1574	139	1560	11	961	1474	152	27.7
$PhICl_2$	$CHCl_3$	0.118	0.00		0.0[h]	1564	41			348	1469	191	30.9
Ph_2I^+	DMSO	0.281				1566	45			1492	1474	122	36.8
PhOH	CCl_4	0.402	−0.43	−0.40	−0.45[h]	1607	145	1598	201	2940	1499	268	38.5
PhOMe	CCl_4	0.428	−0.43	−0.41	−0.38[f]	1603	208	1590	96	3330	1498	304	44.4
PhOEt	CCl_4	0.439				1603.	233	1588	124	3500	1499	312	48.4
$PhOPr^i$	CCl_4	0.428				1602	174	1589	169	3334	1495	392	50.5
Ph_2O	CCl_4	0.364	−0.31		−0.32[h]	1592	114	1586	168	2421	1488	459	47.9
PhOCOMe	CCl_4	0.235	−0.21			1596	114			1075	1493	236	37.6
$PhOCOCF_3$	CCl_4	0.234	−0.20			1593	78			1067	1493	268	34.8
$PhOSO_2Me$	CCl_4	0.264				1591	85			1326	1489	399	40.0
$PhOCF_3$	CCl_4	0.250	−0.18	−0.17	−0.04[h]	1594	71			1205	1492	256	39.1
PhOH	D_2O	0.424	−0.43	−0.40	−0.38[f]	1603	284	1585	91	3268	1493	207	41.9
PhO^-Na^+	D_2O	0.593	−0.60	−0.66	−0.60[f]	1588	324			6290	1482	669	79.6
PhSH	CCl_4	0.195	−0.15			1586	47			764	1481	135	27.6
PhSMe	CCl_4	0.250	−0.17	−0.24	−0.16[h]	1585	62			1193	1482	143	26.8
PhSEt	CCl_4	0.192				1587	46			750	1482	120	26.8
Ph_2S	CCl_4	0.189			−0.07[h]	1582	60			728	1476	116	20.9
PhSCOMe	CCl_4	0.081				1586	17			215	1499	112	22.4
$PhSCF_3$	CCl_4	0.00			+0.06[i]	1584	9			89	1477	38	15.7
PhS^-Na^+	D_2O	0.334				1579	115			2065	1474	102	26.7
$PhSO_3^-Na^+$	D_2O	0.00	+0.07		+0.07[h]	1610	3	1590	3	100	1482	20	15.4
Ph_2SO_2	$CHCl_3$	0.064				1585	13			172	1480	16	7.4
$PhSO_2Me$	$CHCl_3$	0.069	+0.16	+0.08[f]	+0.16[h]	1589	20		0	185	1482	25	11.2
$PhSO_3Me$	CCl_4	0.087				1598	12	1575	3	233	1481	24	10.9
$PhSO_2Cl$	CCl_4	0.108				1585	21			304	1479	26	12.0
$PhSO_2^-Na^+$	D_2O	0.00				1610	2	1582	3	80	1478	25	14.1
Ph_2SO	CCl_4	0.065				1583	13			178	1478	39	12.6
$PhND_2$	CCl_4	0.467	−0.48	−0.48	−0.48[f]	1607	359	1585	23	3950	1501	336	46.7
PhNHMe	CCl_4	0.522				1607	338			4897	1509		
PhNDMe	CCl_4	0.523				1607	351	1582	38	4922	1505	474	51.0
$PhNMe_2$	CCl_4	0.533	−0.54	−0.52	−0.50[f]	1604	346	1578	45	5098	1508	262	50.0
PhNHEt	CCl_4	0.520				1605	308			4865	1506	376	60.6
$PhNHBu^n$	CCl_4	0.536				1604	344			5170	1506	360	65.7
$PhNHPr^i$	CCl_4	0.533				1603	346			5104	1505	392	59.2
$PhNEt_2$	CCl_4	0.571				1607	293	1582	59	5852	1513	370	63.9
$PhN(CH_2)_2$	CCl_4	0.382				1600	305	1584		2663			
$PhN(CH_2)_3$	CCl_4	0.552				1601	540	1579		5461			
$PhN(CH_2)_4$	CCl_4	0.628				1596, 1601		1569		7039			
$PhN(CH_2)_5$	CCl_4	0.474				1599	320	1579		4045			
Ph_2NH	CCl_4	0.504				1594	531	1566	26	4576	1495		
Ph_3N	CCl_4	0.438				1589	191			3489	1495	338	32.2
$PhN(CF_3)_2$	CCl_4	0.132	0.00		0.0[h,i]	1599	23	1592	22	405	1492	200	31.8
$PhNHNH_2$	C_6H_{12}	0.487	−0.43		−0.40[h]	1505	325			4259	1497	342	50.6
$Ph_2(NH)_2$	CCl_4	0.441				1602	399			3523			
PhNHOH	$CHCl_3$	0.222				1605	71			963	1494	107	23.1
PhNMeCOMe	$CHCl_3$	0.408				1599	373			3040	1499	358	42.3
PhNHCOMe	$CHCl_3$	0.413	−0.30	−0.20	−0.21[h]	1602	234			3115	1499		
PhNO	CCl_4	0.071	+0.33		+0.32[i]	1595	13			189			
Ph_2N_2	CCl_4	0.056	+0.02		+0.08[h]	1586	26			155	1485	107	23.1
PhNCO	CCl_4	0.403			−0.17[g]	1601	290	1587	64	2957	1513	145	42.4
PhNCS	CCl_4	0.354	−0.06		−0.07[g]	1595	200			2182	1491	300	31.9
PhNSO	CCl_4	0.087			+0.13[h]	1600	3	1575	21	235	1484	131	21.2
PhNCNPh	CCl_4	0.461				1595	461			3856	1489	523	58.3
$PhNO_2$	CCl_4	0.174	+0.19	+0.16[f]	+0.20[g]	1608	42	1591	13	634			
$PhN_2^+BF_4^-$	D_2O	0.304			+0.65[h]	1591	128			1726			
$PhND_3^+Cl^-$	D_2O	0.183			−0.05[h]	1605	77			689	1500	130	30.2
$PhND_2Me^+Cl^-$	D_2O	0.149				1602	31			492	1498		
$PhNDMe_2^+Cl^-$	D_2O	0.136				1601	23			428	1498		
$PhNMe_3^+Cl^-$	D_2O	0.149			−0.09[h]	1599	28			490	1495	165	51.5
$PhNDCMeNDPh^+Cl^-$	D_2O	0.585				1590	396			6104			
PhMe	CCl_4	0.099	−0.15	−0.10	−0.06[f]	1605	27			275	1496	70	19.6
PhEt	CCl_4	0.103	−0.14	−0.09		1602	24	1584	4	289	1496	69	19.5
$PhPr^n$	CCl_4	0.109				1605	24	1586	7	310	1497	68	20.2
$PhPr^i$	CCl_4	0.115				1605	20	1583	4	332	1494	63	20.0
$PhBu^s$	CCl_4	0.115				1604	19	1585	5	330	1494	66	19.7
$PhBu^t$	CCl_4	0.125			−0.17[h]	1602	25	1584	5	377	1498		
$PhCH(CH_2)_2$	CCl_4	0.175				1604	61	1581		645			
$PhCH(CH_2)_3$	CCl_4	0.124				1602	33	1579		369			
$PhCH(CH_2)_4$	CCl_4	0.136				1603	33	1581		438			

Table I (*Continued*)

Compd	Infrared solvent	$\pm\sigma_R°$, calcd	Lit. $\sigma_R°$			1600 band		1585 band		A[d]	5100 band		
			^{19}F[a]	React.[b]	Other	ν	ϵ_A[c]	ν	ϵ_A[c]		ν	ϵ_A[c]	$\epsilon^{1/2}$[e]
$PhCH(CH_2)_5$	CCl_4	0.128				1601	33	1581		392			
$PhCH_2CHO$	CCl_4	0.110				1603	18	1587	7	314	1499	56	20.5
$PhCH_2CN$	CCl_4	0.090	−0.08			1605	16	1589	5	241	1498	113	18.4
Ph_2CH_2	CCl_4	0.117			−0.08[h]	1602	51	1586	12	339	1496	130	31.2
$PhCH_2OH$	CCl_4	0.00	−0.07		−0.06[h]	1608	4	1587	3	95	1497	36	14.0
$PhCH_2OMe$	CCl_4	0.054				1603	5	1587	4	150	1497	40	15.3
$PhCHBr_2$	CCl_4	0.00				1603	3	1586	5	99	1495	47	13.8
$PhCH_2Cl$	CCl_4	0.00	−0.03			1604	3	1587	3	90	1497	46	14.3
Ph_3CH	CCl_4	0.113			−0.12[h]	1599	82	1583	17	324	1496	270	32.8
$PhCH(OCH_2)_2$	CCl_4	0.00				1610	2	1590	2	55	1494	17	
$PhCH_2Br$	CCl_4	0.00				1602	3	1587	3	100	1497	49	15.5
$PhCHCl_2$	CCl_4	0.00			+0.02[h]	1598	3	1586	3	80	1499	25	13.1
Ph_4C	C_6H_6	0.130				1597	23			398	1494		
$PhCH_2ND_3^+Cl^-$	D_2O	0.00	0.00		0.0[h]	1607	1	1599	2	60	1501		
$PhCCl_3$	CCl_4	0.00	0.00		+0.02[h]	1584	1			15	1499		
$PhCBr_3$	CCl_4	0.00			+0.03[h]	1602	2	1584	2	61	1492	65	15.1
$PhCF_3$	CCl_4	0.111	+0.10	+0.08[f]	+0.10[g]	1611	33			317			
PhC_2F_5	CCl_4	0.075	0.11[g]			1610	15			198	1502	18	9.5
Ph_2	CCl_4	0.096	−0.09	−0.10	−0.09[f]	1598	22	1582	4	260	1484	104	20.4
$PhCHCH_2$	CCl_4	0.050	−0.03		−0.03	1602	7	1576	13	144	1496	98	16.2
$PhCHCHCOOEt$	CCl_4	0.100				1580	39			277	1498	54	17.2
$PhCHCHNO_2$	CCl_4	0.127	+0.16			1604	15	1580	45	387	1497		
$PhCHCHN(CH_2)_5$	C_6H_{12}	0.311				1600	213	1575	28	1800	1499	48	16.7
$PhCHO$	CCl_4	0.244	+0.27			1598	81	1586	71	1150	1480	2	3.0
$PhCOMe$	CCl_4	0.219	+0.19	+0.18[f]		1601	77	1581	38	940	1491	4	5.1
Ph_2CO	CCl_4	0.190			+0.17[h]	1602	111	1580	61	746	1488	0	0
$PhCOOH$	CCl_4	0.292			+0.21[h]	1607	101	1586	98	1598	1496	33	11.6
$PhCOOMe$	CCl_4	0.155				1603	55	1583	15	526	1493	144	29.4
$PhCOOEt$	CCl_4	0.180	+0.19	+0.12[f]		1603	45	1585	32	670	1491	11	8.1
$PhCOCl$	CCl_4	0.213	+0.30		+0.32[h]	1598	70	1585	47	899	1487	7	6.6
Ph_2C_2	CCl_4	0.152				1605	42	1575	7	509	1501	126	25.0
$PhCCH$	CCl_4	0.072			+0.08[h]	1599	11	1575	10	190	1489	118	20.3
$PhCN$	CCl_4	0.085	+0.21	+0.10[f]	+0.22[h]	1600	12	1583	6	228	1492	74	17.7
$PhCF(CF_3)_2$	CCl_4	0.023	0.04[g]		+0.06[h]	1605	4	1593	3	109	1502	38	18.3
$PhCOH(CF_3)_2$	CCl_4	0.110	0.02[g]	+0.02		1605	12			313	1504	36	18.6
$PhSF_5$	CCl_4	0.000			+0.07[h]	1597	3			85	1488	71	19.8
$PhC(OMe)_3$	CCl_4	0.000			−0.01[h]	1620	3	1604	1	77			

[a] ^{19}F values from ref 34, or calculated from figures for dilute solution in cyclohexane using the formulas therein, and ref 10. Zero values are taken from ref 32. [b] Reactivity values collected in ref 34, and taken from J. Hine, *J. Amer. Chem. Soc.*, **82**, 4877 (1960). [c] ϵ_A is the peak extinction coefficient; $\epsilon_A = A_{max}/cl$. [d] A is the integrated intensity of the 1600- and 1585-cm^{-1} band; $A = \Sigma A/cl$. [e] ϵ is an estimate of the integrated intensity given by $\epsilon = \epsilon_A \Delta\nu^{1/2}$. [f] Reactivity value from R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, **81**, 5352 (1959); values are 2.0 σ_R^m. [g] Reference 63 ^{19}F value. [h] Private communication by R. W. Taft and W. A. Sheppard giving ^{19}F values. [i] ^{19}F values from F. S. Fawcett and W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 4341 (1965).

variation with the usual substituent parameters although a limited correlation with dipole moments has been reported[16] (see also ref 17). Russian workers[18,19] have correlated the logarithms of the intensities of the Raman bands near 1600 cm^{-1} for monosubstituted benzenes with Hammett σ constants; however, we found no precise relation between the reported Raman and our measured infrared intensities.

It is of interest that the effect of substituents on the integrated intensity of the ν_{CN} in substituted phenyl cyanides is better correlated by reactivity parameters than the effect of substituents on the ν_{CN} frequency.[20]

Experimental Section

Vapor phase chromatography and/or melting points were used as criteria for purity throughout. The monosubstituted benzenes were mainly commercial samples or simple derivatives of them. The fluorinated compounds were kindly supplied by Dr. W. A. Sheppard, Experimental Station, Du Pont. Benzene iodine dichloride[21a] and N-β-phenylvinylpiperidine[22] were made by literature methods. Amino compounds were deuterated on nitrogen by shaking twice with excess deuterium oxide, and the purity of the distilled products was checked by the absence of N–H bands. N-Phenylazetidine was prepared[23] by the aluminium chloride catalyzed decomposition of 3-amino-1-phenoxy-N-phenylpropane using the general method[24] employed for the preparation of chromans from the corresponding diphenoxypropanes. The other N-phenylimines were prepared by standard methods.

Hydroxy-, methoxy-, nitro-, chloro-, bromo-, iodo-, and cyanodurenes were kindly donated by Professor G. Illuminati, University of Rome, and were used as supplied. Commercial pentamethylbenzene was found to be pure by vpc. Aminodurene was obtained from dinitrodurene[25] by reduction to aminonitrodurene,[26] deamination, and further reduction;[27] it was purified by recrystallization, fractional sublimation up to 80° (0.2 mm), and further recrystallization from 80% ethanol, to mp 65–72° (lit.[28] 74–74.5°); nmr ex-

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amination then showed approximately 5% impurity. Dimethylaminodurene was prepared from the primary amine by reaction with trimethyl phosphate;[21b] the product was steam distilled directly from the basified reaction mixture; nmr and infrared spectra showed no N-H absorption. Purification by sublimation (0.5 mm, 100°) and then recrystallization from 50% ethanol gave white plates, mp 45-51° (lit.[28] 52-53°), with no impurities visible in the nmr. Fluorodurene was obtained *via* the Schiemann reaction[29] on aminonitrodurene followed by reduction and deamination[29] and purification by chromatography on alumina, sublimation (0.2 mm, 60°), and finally recrystallization from 50% ethanol, to mp 55-58° (lit.[29] 54.5-55°); it showed no impurities in the nmr. For some durenes, the lower band appeared as a shoulder on other bands at lower wave number, and large base-line corrections were needed. For many of the durenes insufficient material was available for more than a single solution, although duplicate determinations were made on this solution ($A^{1/2}$ reproducible to ±1 unit); where duplicate solutions were available the $A^{1/2}$ values were also reproducible within ±1 unit.

Carbon tetrachloride, cyclohexane, and 2-propanol were spectroscopic grade solvents. Chloroform was purified by passing it through alumina immediately prior to use; dimethyl sulfoxide was dried over CaH_2. Deuterium oxide (Imperial Chemical Industries Ltd.) was used without further purification. The spectroscopic technique for the nonpolar solvents in the sodium chloride cells and the integration procedure for the 1600- and 1500-cm^{-1} bands were as previously reported.[2]

The spectra of solutions in deuterium oxide or dimethyl sulfoxide were recorded using a balanced pair of Irtran II cells (~0.05 mm). Spectra when recorded in these cells were superimposed upon the interference pattern which altered in position as the cell heated in the spectrometer. Previous workers[30] have subtracted such interference patterns, but we did not find this procedure satisfactory. The interference pattern can be removed by grinding one plate in each cell to a mat surface using fine carborundum powder. The cells then have a constant base line, even when the cell heats up; however, the cell length can still be measured in air using the interference method. The reproducibility of $A^{1/2}$ is ±1 for most cases in nonpolar solvents, except that where the compound was sparingly soluble or there were interfering bands (*e.g.*, $PhICl_2$, $PhNO_2$, and compounds containing the groups C=C or C=O) the reproducibility fell to ±4 in $A^{1/2}$. For the polar solvents, balancing is not possible, and the error is ±4 in $A^{1/2}$.

For compounds having more than one benzene ring, the A, ϵ_A, and $\epsilon^{1/2}$ values have been divided by the number of benzene rings.

Results

Table I collects the data for the 1600- and 1500-cm^{-1} bands for the monosubstituted benzenes now reported, and includes values from the previous paper:[2] it records band positions, extinction coefficients, and integrated intensities together with literature and calculated $\sigma_R°$ values. Table II gives the experimental data for the durenes. Table III records the solvent dependence for the 1600-cm^{-1} band intensities of selected compounds.

Table II. A Values for Monosubstituted Durenes Compared with $\sigma_R°$ Values for Corresponding Benzenes

Substituent	Solvent	Frequency, cm^{-1}	A (durene)	$\sigma_R°$ (benzene)
F	CCl_4	1634, 1572	1063	0.341
	C_6H_{12}	1634, 1572	984	0.341
Cl	C_6H_{12}	1612, 1560	472	0.217
Br	CCl_4	1607, 1548	738	0.231
	C_6H_{12}	1608, 1550	655	0.231
I	C_6H_{12}	1604, 1538	576	0.221
NO_2	CCl_4	1624	87	0.174
OMe	C_6H_{12}	1616, 1566	875	0.428
OH	CCl_4	1626, 1574	1940	0.402
Me_2N	CCl_4	1604, 1566	540	0.533
Me	C_6H_{12}	1608, 1570	147	0.099
CN	C_6H_{12}	1606	84	0.085

Table III. Variation of Integrated Intensities ($A^{1/2}$ Values) with Solvent

Substituent	C_6H_{12}	CCl_4	$CHCl_3$	$(CH_3)_2CHOH$
NMe_2	69.0	71.4	70.3	68.7
OMe	58.3	57.7	55.8	57.7
OH	52.3	54.2	55.9	60.1
F	47.4	46.4	45.7	46.6
Br	31.7	32.3	31.2	31.2
Cl	29.5	30.5	30.2	29.3
NO_2	22.2	25.2	22.8	21.7
Me	16.0	16.6	18.6	16.7
CN	15.9	15.1	15.4	14.2

Few precise intensity data for these bands have been reported in the literature. Wexler[14] measured the integrated intensities of alkylbenzenes; his values (Me, 280; Et, 280; *i*-Pr, 310; *sec*-Bu, 340; *t*-Bu, 430) agree to within *ca.* 5% with our values except for *t*-butyl. Earlier measurements of ϵ_A values,[31] made on a prism instrument, are generally about 70% of the ϵ_A values now reported in Table I. The ± $\sigma_R°$ values given in this table are those calculated using eq 5.

Discussion

Comparison of Measured with Previous $\sigma_R°$ Values and Refinement of $\sigma_R°$ Intensity Relationship. A detailed comparison of $\sigma_R°$ values derived from our previous[2] eq 2 with all the literature values available discloses the following results.

(i) Agreement within $0.03\sigma_R°$ unit with both fluorine nmr and reactivity values where these are available for following substituents: NMe_2, ND_2 (NH_2), OMe, OH, F, Ph, OAc, CF_3, CH_2Cl, CCl_3, CHO, COMe, CO_2Me, NO_2. The $\sigma_R°$ from eq 2 for the substituent O^- agrees excellently with the fluorine nmr value, but shows a discrepancy of 0.05 with the reactivity value. Slightly greater discrepancies (up to 0.05 units) are shown between the infrared and the fluorine nmr values for the substituents OPh, Me, Et.

(ii) The infrared-derived $\sigma_R°$ values are larger than the fluorine nmr $\sigma_R°$ values by 0.04-0.09 unit for the substituents Cl, Br, SH, and SMe. We believe that this discrepancy is due to interactions involving d orbitals in the corresponding *para*-substituted fluorobenzenes used for the nmr determinations; previous evidence for such interactions[32] is confirmed by work presented in an accompanying paper.[33] For the substituents Cl and SMe, our $\sigma_R°$ values are in good agreement with reactivity values; unfortunately, no such data are available for SH, and alternative reactivity values for Br are widely divergent (0.14, 0.19; see ref 34 and Table I).

(iii) Significant overlap of the ν_{16} ring mode with the substituent vibration at 1631 cm^{-1} for styrene may invalidate the infrared-derived $\sigma_R°$ value for the group

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(29) G. Grassini, G. Illuminati, and G. Marino, *Gazz. Chim. Ital.*, **86**, 1138 (1956); *Chem. Abstr.*, **52**, 1937*a* (1958).

(30) C. A. Swenson, *Spectrochim. Acta*, **21**, 987 (1965).

(31) A. R. Katritzky and J. M. Lagowski, *J. Chem. Soc.*, 4155 (1958).

(32) R. W. Taft and J. W. Rakshys, Jr., *J. Amer. Chem. Soc.*, **87**, 4387 (1965).

(33) P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topson, *J. Amer. Chem. Soc.*, **90**, 1767 (1968).

(34) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

$CH{=}CH_2$. The infrared-derived $\sigma_R°$ values are considerably lower than the fluorine nmr values for the CN and SO_2Cl substituents. For the former, the infrared and reactivity values agree; no reactivity data are available for SO_2Cl. The discrepancies with the fluorine nmr results could be due to mutual conjugation in the *para*-substituted fluorobenzenes; however, the fluorine nmr measurements were made in the nonpolar solvent CCl_4 where no large interaction is expected (this is underlined by our own results with the *para*-disubstituted fluorobenzenes[33]) and, significantly, no such discrepancies were found for the substituents CO_2Me, CHO, COMe, NO_2.

(iv) The substituents NCS, OCF_3, SCF_3, and $N(CF_3)_2$ are discussed later.

We previously[2] justified the nonzero intercept at zero $\sigma_R°$ in eq 2 on the grounds that monosubstituted benzenes should have a combination band at about 1600 cm^{-1} arising from C–H out-of-plane bending fundamentals. However the correction for the intensity of this combination band should more correctly be made before taking the square root of the total intensity, since a dependence between the former and $\sigma_R°$ is otherwise implied. We have therefore plotted *A* values against $(\sigma_R°)^2$ (Figure 1) for all the substituents in group i above using both nmr and reactivity values, and additionally, for the substituents Cl and SMe from group ii using only reactivity values. The results were treated statistically using a least-squares procedure and the equation derived was

$$(\sigma_R°)^2 = 6.10A \times 10^{-5} - 0.0136 \qquad (4)$$

(correlation coefficient 0.998)

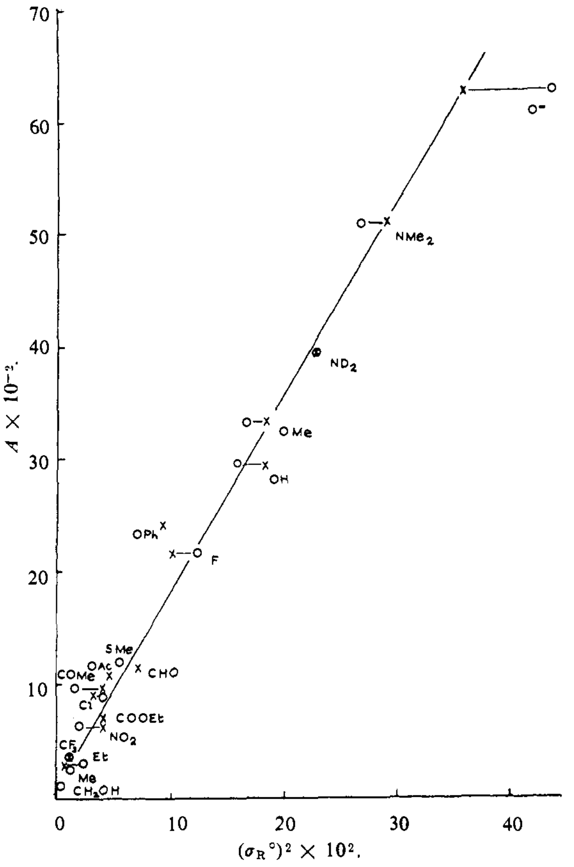

Figure 1. Plot of *A* for monosubstituted benzenes against the squares of the literature $\sigma_R°$ values: O, reactiviy; ×, fluorine nmr.

Equation 4 implies that the combination band has a constant intensity of 220; we believe this to be too high, since a considerable number of monosubstituted benzenes have a total intensity of less than 100. We have therefore chosen to assign a value of 100 to the intensity of the combination band in this region and to define our value of $\sigma_R°$ by eq 5 which is derived by a least-squares plot for the line passing through the point (0, 100). We believe that the likely range of error in the value of the combination band is ±50 (*cf.* Figure 1).

$$A_{\text{mono}} = 17{,}600(\sigma_R°)^2 + 100 \qquad (5)$$

The uncertainty in the intensity of the combination band clearly has a much greater effect on small values of $\sigma_R°$ than on large. The percentage error in $\sigma_R°$ thus caused is 56% at $\sigma_R° = 0.05$, 14% at $\sigma_R° = 0.1$, 6% at $\sigma_R° = 0.15$, and 3% at $\sigma_R° = 0.2$. We plan in later work to check all the values of $\sigma_R°$ less than 0.15 by measurements on polysubstituted compounds.

Solvent Variation of $\sigma_R°$. Few experimental data are available concerning the effect of substituents on single reactions over a range of solvents,[7] and thus it is at the moment difficult to assess the solvent variation of $\sigma_R°$ from the reactivity standpoint.

The difference between the fluorine chemical shift of a *meta*-substituted fluorobenzene and that of internal fluorobenzene, which is proportional to the inductive σ parameter (σ_I) for the substituent, shows little variation with solvent except when the substituent is subject to specific solvent interactions such as hydrogen bonding.[10] A strongly solvent-complexed substituent should have a different electronic configuration from one not so complexed, so that these exceptions are not surprising. The chemical shift difference between *para*- and *meta*-substituted isomeric fluorobenzenes, which can be used for calculating $\sigma_R°$ values, also shows[34] little solvent variation, provided the substituent in question is of the electron donor or weakly interacting type, unless specific solvent–substitutent interactions occur. However, for electron acceptor substituents, these *para*/*meta* differences show[34] variations which correspond to variations of the order of 0.1 in $\sigma_R°$; we discuss this matter further in our consideration of *para*-disubstituted benzenes.[33]

Deviations from linear correlations of acidities with σ constants were also found for 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids in different solvents.[35] However, most of the substituents investigated could be subject to specific solvent–substituent interactions and it is not clear whether "normal" solvent effects would affect the linear correlation of these substituent effects. A reported[36] dependence of infrared intensities on the σ_I value of the group R in solvents RH appears to be of doubtful general validity.

We have examined the solvent effects on the intensity of the ring-stretching mode for a variety of substituents (Table III). Except for phenol, where the intensity shows a marked increase from cyclohexane through 2-propanol presumably due to specific hydrogen bonding, the variations in intensity are small and apparently

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(35) C. D. Ritchie and E. S. Lewis, *J. Amer. Chem. Soc.*, **84**, 591 (1962).

(36) S. Tanaka, K. Tanabe, and H. Kamada, *Spectrochim. Acta*, **23a**, 209 (1967).

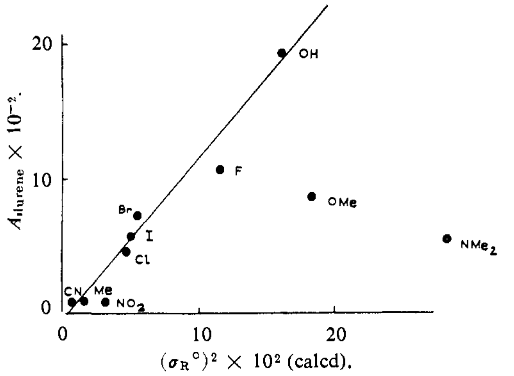

Figure 2. Plot of A for durenes against the squares of the $\sigma_R°$ values for the corresponding monosubstituted benzenes.

random. We conclude that unless strong specific solvent–substituent interactions occur, the ring–substituent interactions are little affected. This conclusion is in good agreement with the results found for the nmr of the *meta*-substituted fluorobenzenes.[10]

Steric Effects. Durene Results. Fundamental to present theories on conjugation is the concept of the reduction of mesomeric interaction between ring and substituent by twisting. For example, from the fluorine nmr of 3-methyl-4-dimethylaminofluorobenzene, Taft, *et al.*,[34] found the value $\sigma_R° = -0.24$ for the twisted NMe_2 group, a reduction of 56% by the steric effects of one *o*-methyl group. To test the effect of steric hindrance on infrared intensities we have utilized substituted durenes (I). The infrared spectrum of durene (I, Y = H) shows no band near 1600 cm^{-1}; the ν_{16} mode is forbidden because of the D_{2h} symmetry of the molecule. Although a normal coordinate analysis has apparently not been carried out for durene, the form of the modes for 1,2,4,5-tetrachlorobenzene[37] suggests that the ν_{16a} mode will not be very different from that in benzene. Steric hindrance in durenes has been the subject of considerable earlier work, and decrease in conjugation of substituents compared with that in phenyl derivatives has been demonstrated by uv spectra,[38] dipole moments,[39] nmr shielding,[40] and chemical reactivity.[41]

In Figure 2 the A values for the durenes (Table II) are plotted against $(\sigma_R°)^2$ for the corresponding substituent. Substituents with cylindrical symmetry (CN, CH_3, halogens, and possibly OH) show a linear relation found by the least-squares procedure to be as in eq 6; the small nonzero intercept is probably not significant. The lower over-all values for the durenes for the symmetrical substituents may be a result of a decreased contribution of CH wagging mode to the ν_{16} for durene as compared with benzene.[42]

Equation 6 implies that in the durene system, the substituents of low symmetry, NMe_2, OMe, NO_2, exhibit effective $\sigma_R°$ values of 0.225, 0.280, and 0.102, respectively. This indicates steric inhibition of respectively 58, 35, and 41% of the resonance interaction. If the angle of twist is related to the resonance interaction by an equation of the type $\sigma_R{}^t = \sigma_R° \cos\phi$, where $\sigma_R{}^t$ indicates the value for the twisted substituent, then this corresponds to angles of twisting as follows: NMe_2, 65°; OMe, 49°; NO_2, 54°. (Such treatment assumes

$$A_{durene} = 11{,}300(\sigma_R°)^2 - 30 \qquad (6)$$
$$\text{(correlation coefficient} = 0.976)$$

implicitly that π-inductive effects are completely absent *cf.* ref 43.)

Available data from the literature suggest considerable twisting of the methoxy group out of the plane of the ring and significantly less twisting for the hydroxy group. The classification of the hydroxy group with the non-twisted substituents for the purpose of determining the least-squares plot may not be justified; indeed the angles of twist calculated from the uv data[44a] for hydroxy- and methoxybenzene and -durene by the relation[44b] $\epsilon/\epsilon_0 = \cos^2\phi$ yield values of 37 and 63° for OH and OMe, respectively. However, other measurements suggest considerably less twisting for the hydroxy group. Molecular polarizabilities indicate an angle of twist of 14° for a hydroxy flanked by two *o-t*-butyl groups, whereas two *o*-methyl groups on this criterion apparently cause an angle of twist for the methoxy group[45] of 90°; such data are of limited reliability. There is only a small change in dipole moment due to twisting in the hydroxy compound (μ for phenol is 1.61 D, and for hydroxydurene, 1.68 D);[26] the dipole moment for methoxydurene is unfortunately not recorded. The OH stretching frequency for hydroxydurene also indicates essential coplanarity of the O–H and the ring.[46] Yukawa, *et al.*,[47] concluded that there is no steric interference with resonance stabilization by the hydroxy group in the bromination of hydroxydurene, but there is substantial retardation due to twisting in the bromination of methoxydurene and methylthiodurene.

Ultraviolet spectral comparisons with nitrobenzene indicate an angle of twist of 71° for nitrodurene (nitrobenzene, ϵ_{max} 8900; nitrodurene, ϵ_{max} 990)[38] by the equation given above. These ϵ_{max} values and those for other nitrobenzene derivatives with varying degrees of twist are linearly related to other data such as molecular refractions, and also to the base strengths and deacylation rate constants for the corresponding amino-substituted compounds.[38] The effect of twist is also shown in the dipole moments (nitrobenzene, 4.01 D; nitrodurene, 3.62 D) but these moments are not linearly related to the other properties.[47] Baciocchi and Illuminati[41] conclude from reactivity data that the nitro group in nitrodurene has lost *ca.* 50% of its resonance compared with nitrobenzene. An angle of twist of 69° is indicated for N,N-dimethylaminodurene by uv extinction coefficients (N,N-dimethylaminodurene, ϵ_{max}

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(37) J. R. Scherer, "Planar Vibrations of Chlorinated Benzenes," The Dow Chemical Co., Midland, Mich., 1963.

(38) B. M. Wepster, *Rec. Trav. Chim.*, **76**, 355 (1957).

(39) H. Kofod, L. E. Sutton, P. E. Verkade, and B. M. Wepster, *ibid.*, **78**, 790 (1959); R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1937).

(40) P. Diehl and G. Svegliado, *Helv. Chim. Acta*, **46**, 461 (1963).

(41) E. Baciocchi and G. Illuminati, *J. Amer. Chem. Soc.*, **86**, 2677 (1964).

(42) D. H. Whiffen, *Spectrochim. Acta*, **7**, 253 (1965).

(43) M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, **89**, 390 (1967).

(44) (a) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952); these data on the methoxy compounds are confirmed by L. J. Frolen and L. Goodman, *J. Amer. Chem. Soc.*, **83**, 3405 (1961). (b) This equation is used, for example, in ref 38.

(45) M. J. Aroney, M. G. Cornfield, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 2954 (1964).

(46) N. A. Puttnam, *ibid.*, 5100 (1960).

(47) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Japan*, **39**, 2274 (1966).

2090; N,N-dimethylaniline, ϵ_{max} 5500). For a summary of literature data on reactivities of durenes see also ref 48. We conclude that there is over-all qualitative, and indeed reasonable quantitative, agreement between the infrared results and reactivity data which strongly supports the view that $\sigma_R{}^\circ$ values derived from infrared intensities are indeed a measure of mesomeric interaction.

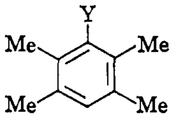
Nature of the Interaction. Infrared Aspects. The normal coordinates of the vibrations ν_{16a} and ν_{16b} for benzene itself have been shown[37] to be as in II and III. Calculations for a variety of monosubstituted benzenes[49] have indicated that the form is but little altered. Evidently, little mixing normally occurs between ν_{16} and substituent modes in monosubstituted benzenes. The frequency of ν_{16} is known to be remarkably insensitive to substituent type in monosubstituted benzenes except that a significant effect of mass is noticed for substituents linked by an element not in the first row of the periodic table.

Some insight into the nature of the substituent–ring interaction may be obtained by a valence bond treatment. In a monosubstituted benzene, during the vibration ν_{16a} there is a distortion of the molecule in the sense of IV $\rightleftharpoons$ V (where the effect is much exaggerated). The shorter bonds will have greater double bond character and the longer bonds greater single bond character, as shown. If the substituent Y is capable of resonance interaction with the ring, then canonical forms of types either VI or VII (whether VI or VII will depend on whether Y is an electron donor or acceptor) will be of greater importance for IV than for V. This will lead to an oscillating dipole during the vibration and hence to intensity in the infrared spectrum. The π-dipole moment change with respect to the normal coordinate of the vibration is evidently directly proportional to $\sigma_R{}^\circ$, for together with eq 7, this leads to the

$$A = \frac{N\pi}{3c^2}\left(\frac{\partial\mu}{\partial Q}\right)^2 \qquad (7)$$

observed relation 5 (the second term in eq 5 is due to a combination band[42]).

We are at present investigating possible quantitative relations between MO parameters, A, and $\sigma_R{}^\circ$ (*cf.* ref 50).



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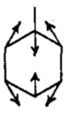
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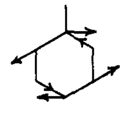
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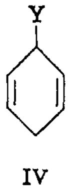

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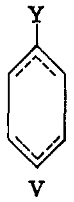

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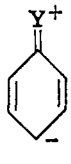

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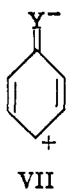

VII

Nature of the Interaction. Physical-Organic Aspects. The detailed interpretation of substituent effects is presently in a state of flux. Exner claims[51] that classical electron-accepting substituents, such as nitro, interact effectively only by the inductive effect, whereas Fueno, *et al.*,[52] believe that the π effects are dominant and inductive effects can be allowed for in calculations by correction terms. The importance of direct field effects has been emphasized.[53] Dewar has recently questioned[54,55] the whole basis of Taft's conclusions from fluorine nmr; he also now concludes that π-inductive effects are relatively unimportant.[43] One of the objects of the present study, together with cognate work on polysubstituted compounds, was to illuminate the origins and methods of propagation of substituent effects.

Exner[51] (*cf.* also ref 56 and 57) has shown that for the p*K* of $XC_6H_4CO_2H$ in 80% methyl Cellosolve, and for a large number of other ionization processes and reactions, the effective σ values for many substituents are related by eq 8. He assumes that substituents such as CH_2X are not conjugated with the benzene nucleus (our results[33] with *para*-disubstituted benzenes indicate that CH_2Cl, for example, is a donor substituent), and concludes that many of the usual resonance acceptor

$$\sigma_p = (1.14 \pm 0.05)\sigma_m \qquad (8)$$

substituents (NO_2, CF_3, CN, SO_2Me) also have negligible resonance interaction with the benzene ring as measured by their effect on substituent reactions. However, as Exner himself indicates, his results can also be explained if the CO_2H group in benzoic acids with a *para*-electron-acceptor substituent strongly impedes the mesomeric interaction of the acceptor substituent and the ring. As Exner points out, the simple electrostatic I effect, either by transmission through σ bonds or directly through space, cannot explain $\sigma_{I(p)} > \sigma_{I(m)}$. He therefore interprets his results in terms of the π-inductive effect, *i.e.*, alternating polarity in the π system due to the inductive effect of the ring-substituent σ bond. We previously[1] concluded that the contribution of this effect is small because some substituents have a large resonance effect relative to the inductive effect (for carbethoxyl $\sigma_R{}^\circ = 0.180$ and $\sigma_I = 0.21$), whereas other substituents make a very small resonance contribution and a large inductive one (for trichloromethyl $\sigma_R{}^\circ = 0.00$ and $\sigma_I = 0.42$).[1] Our further results substantiate this conclusion. Pertinently, for $NMe_3{}^+$, $\sigma_I = 0.92$[58] whereas $\sigma_R{}^\circ = -0.150$ (see below and ref 33 for a discussion of the sign of this latter number); the results for the substituent SO_2Me and SO_2Cl are also significant. Another example from the recent literature is the tricyanomethyl group, which has $\sigma_I = 0.47$ and $\sigma_R{}^\circ = -0.01$.[33] Trimethoxymethyl and $CH_2NH_3{}^+$, which presumably have significant inductive effects, have also $\sigma_R{}^\circ = 0$ by the ^{19}F nmr criterion.[59] Dewar[60] has also now adduced evidence that the group CF_3 acts mainly by

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(48) E. Baciocchi and G. Illuminati, submitted for publication.

(49) J. R. Scherer, *Spectrochim. Acta*, **21**, 321 (1965).

(50) T. L. Brown, *J. Chem. Phys.*, **43**, 2780 (1965).

(51) O. Exner, *Collection Czech. Chem. Commun.*, **31**, 65 (1966).

(52) T. Fueno, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **39**, 569 (1966).

(53) R. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, **88**, 5928 (1966).

(54) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966).

(55) W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967).

(56) A. Talvik, P. Zuman, and O. Exner, *Collection Czech. Chem. Commun.*, **29**, 1266 (1964).

(57) O. Exner, *Tetrahedron Letters*, 815 (1963).

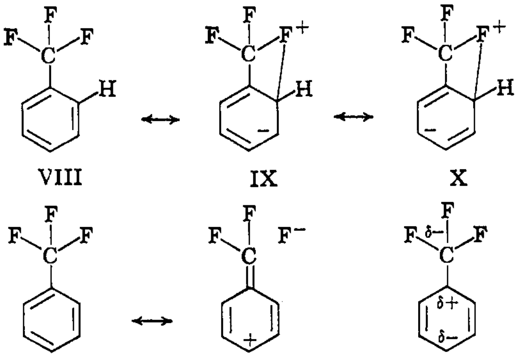
(58) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 335 (1964).

(59) J. K. Williams, E. L. Martin, and W. A. Sheppard, *J. Org. Chem.*, **31**, 919 (1966).

(60) M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 354 (1966).

field rather than a π-inductive effect. Hence we feel that Exner's results[51] must have some other explanation: conjugation of a resonance-acceptor substituent Y may not be very different for $YC_6H_4CO_2H$ and $YC_6H_4CO_2^-$ in the polar and hydrogen-bonding media in which the reactions were investigated; the group X could also affect the conjugation of the group CH_2X with a benzene ring.

The transmission of substituent effects through nonbonded repulsions of the π electrons of the ring away from free electron pairs on the substituent is interpreted by some authors[61] as being related to the π-inductive effect. Recently it was suggested[61,62] that most of the interactions of the substituent in aniline and related compounds with the benzene ring arise from this effect. The present work could be interpreted on this concept as regards amino, alkoxyl, and halogen substituents. It is not clear how such an effect would act from the trifluoromethyl substituent; the free electrons on the fluorines are comparatively close to the π system of the ring and hence might repel the ring π electrons; alternatively, an attraction of the π electron by the fluorine atoms could be postulated which would be more in accord with the experimental findings.



VIII IX X

XI XII XIII

Sheppard[63] has proposed that fluorinated substituents donate electrons specifically to the *meta* positions in substituted benzenes by means of a bonding interaction with the adjacent *ortho* ring atoms (VIII–X). This type of interaction would explain the high electron density at the *meta* relative to the *ortho* and *para* positions in such compounds and is supported by other data advanced by Sheppard.[63] The alternative formulations are fluorine hyperconjugation (XI ↔ XII) and the π-inductive effect (XIII). Dewar and Marchand[60] have criticized Sheppard's proposal for three reasons: (i) no analogy for direct electron delocalization by a side chain, (ii) no analogy for a resonance effect specifically directed to the *meta* position, and (iii) the data can be satisfactorily explained by the π-inductive effect. Sheppard[63] has presented his reasons for considering the π-inductive explanation inadequate; it is argued above that in general the π-inductive effect does not make a large contribution in these systems, and Dewar in his own latest work[43] has abandoned the concept of the dominant π-inductive effect. Our studies with polysubstituted benzenes[33,64] have not revealed any systematic deviation with trifluoromethyl substituents that might be attributed to these specific substituent–ring interactions. However, in the monosubstituted series there are several substituents, mostly fluorinated ones, that give finite $\sigma_R°$ values as determined by our method, whereas these values determined by other techniques are zero. The reasons for this behavior are not yet clear. Recent work involving bridgehead fluorine atoms does not support the concept of fluorine "no-bond" resonance.[65]

Dewar and Marchand[54] suggest that fluorine chemical shifts of benzene derivatives are not suitable for the determination of σ parameters because the chemical shifts are primarily determined by the electrostatic polarization of the C–F σ bond, in contrast to the effect of charge distribution on chemical reactivities and other physical properties. However, our infrared results, the ^{19}F chemical shift parameters, and chemical reactivities all have much the same dependence on structure.

The origin of the resonance component of the substituent effects of saturated alkyl groups is of great interest, and hyperconjugation is a popularly assumed source. Additional methyl groups on carbon or uncharged nitrogen increase the effectiveness of electron donation (see Table I) (the opposite trend is noted for substituents on charged nitrogen, probably due to solvation effects). These findings would indicate that the C–C bond is able to enter into hyperconjugation at least as easily as the C–H bond. Nonbonded repulsion of the ring π electron by the σ electrons in the C–H or C–C bonds, similar to the nonbonded repulsions discussed above, provides an alternative explanation to hyperconjugation.

Discussion of Substituent Effects by Classes.

Deuteriobenzene

We ascribe the small band at 1594 cm^{-1} to the f + g combination[42] believing that deuterium has a $\sigma_R°$ not significantly different from zero. Previous work on secondary deuterium isotope effects[66,67] suggests that any difference between resonance interactions of hydrogen and deuterium is indeed minute.

Halogens. As previous workers,[59] we find similar $\sigma_R°$ values for chlorine, bromine, and iodine, but a considerably more negative value for fluorine. The effects of the widely different electronegativities,[68] polarizabilities, bond distances, masses, and d-orbital acceptor properties[32] of the heavier halogens evidently partly cancel. We discuss such effects later in connection with *para*-disubstituted derivatives.[33]

Polyvalent iodine compounds show the qualitative electron-withdrawing character expected; for the substituent ICl_2, a $\sigma_R°$ of zero was found by the nmr method.[69] Unfortunately PhIO and $PhIO_2$ were insoluble in all the available solvents and could not be investigated. Interactions between the phenyl rings and the I^+ in diphenyliodonium salts were discussed by Beringer and Galton.[70]

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Oxygen Linked. As expected, little variation is found for the σ_R° values of substituents OR where R is hydrogen or various alkyl groups. Oxygen-linked substituents carrying groups capable of conjugative electron withdrawal from the oxygen have less negative σ_R° values in the order OPh > OSO_2Me > OAc ⩾ $OCOCF_3$. Evidently, inductive withdrawal is of lesser importance than π overlap in hindering the mesomeric donor properties of oxygen because COR (σ_R° of OCOMe = 0.235) is more effective than SO_2R (σ_R° of OSO_2Me = 0.264) in reducing the σ_R° of OH (0.402); however, OCF_3 also has a low value (0.250). The O^- substituent shows a value of σ_R° considerably enhanced compared with that for OH (O^-, 0.593; OH, 0.424 for D_2O solution), as expected from the great conjugative ability of anionic oxygen.

Sulfur Linked. The divalent sulfur compounds show values which are smaller than those of the analogous oxygen derivatives by 0.18–0.26σ_R° unit. The smaller conjugative effect of sulfur is in contrast to its superior nucleophilicity over oxygen; however, when acting as nucleophiles, it is the σ electrons which are involved. The poorer availability of the sulfur π electrons compared with oxygen is due partly to less overlap resulting from the large size of the 3p orbitals, but there is also some cancellation due to acceptance of electrons by the sulfur atom into its d orbitals, as will be discussed later.[33]

Among oxygenated sulfur-linked substituents, the groups SO_2O^-, SO_2Ph, SO_2Me, SO_2OMe, SO_2Cl represent a series of groups of increasing electron-attracting power (σ_R° = 0.00 [D_2O], 0.064, 0.069, 0.087, 0.108), as would be predicted; the relative positions of Me and Ph in this series confirm that electron withdrawal from the benzene ring is now occurring. In the lower oxygenated state only SOO^- (σ_R° = 0.00) and SOPh (0.065) are available; there are no significant differences between these values and those in the higher oxidation state.

Nitrogen Linked. (i) Alkylanilines. Alkylation of aniline causes an interesting variation in σ_R° values, which probably reflects both electronic and steric influences. There is no significant effect due to deuterium substitution on nitrogen (NHMe and NDMe have σ_R° = 0.522 and 0.523, respectively), but alkyl substitution gives more complex behavior (ND_2, 0.467; NDMe, 0.523; NMe_2, 0.533) in which the difference between NDMe and NMe_2 is surprisingly small and may represent a conformational preference. Increasing the size of the alkyl group in the secondary amines has but little effect (NHEt, 0.520; NH-*n*-Bu, 0.536; NH-*i*-Pr, 0.533), but diethylaniline shows a significantly higher value (0.571) than that of the dimethyl analog (see below).

Nitrogen Linked. (ii) Cyclic Imines. We studied N-phenyl-substituted cyclic imines because of recent interest.[71,72] Comparison of the oscillator strengths of the two readily accessible absorption bands in the ultraviolet spectra suggested[71] that the nitrogen–phenyl ring interaction increased as the size of the imine ring was varied in the order three < six < four < five, and that the resonance interaction for N,N-dimethylaniline was similar to that for N-phenylazetidine. Since the nitrogen configuration in an azetidine cannot be trigonal, this result was interpreted[71] as evidence for an essentially tetrahedral configuration about the nitrogen atom in N,N-dimethylaniline and related amines. Carbon-13 magnetic shielding results[72] confirmed the relative order of resonance interactions for the three-, five-, and six-membered ring imines measured, and N,N-diethylaniline also showed a marked increase in interaction over N,N-dimethylaniline, near to that for N-phenylpyrrolidine. The relative basicities of dimethyl- and diethylaniline are in the opposite sense, probably due to steric inhibition to hydrogen bonding in the free diethyl compound. The ionization potentials[73] and rates of electrophilic substitution[74a] also indicate enhanced electron availability in the diethylaniline ring, and results mentioned above confirm this.

We now find that the carbon-13 magnetic shielding results, the *f* sums, and the exhaltations of molar refraction (Table IV) all correlate reasonably well with the infrared-derived σ_R° values, indicating a compound dependence on resonance interactions. The σ_R° value for N-phenylpyrrolidine is still higher than that for N,N-diethylaniline. Steric interactions between the α-hydrogens on the imine ring and *o*-hydrogens on the phenyl group[71] probably cause a preferred conformation in N-phenylpyrrolidine favorable for interaction of the nitrogen lone pair with the aromatic nucleus.[74b] The increase in interaction in N-phenylpyrrolidine over N,N-diethylaniline may thus result from a steric enhancement and be broadly analogous to the increased interaction between alkyl groups and the nucleus in acenaphthene compared to 1,8-dimethylnaphthalene where the substituents are free to rotate.[75] α-Hydrogen–*o*-hydrogen interactions in N-phenylpiperidine should result in a preferred conformation less favorable for interaction[71] and the lower σ_R° value found confirms

Table IV. σ_R° Values from the Integrated Intensities (*A*) of the ν_{16} Bands in Monosubstituted Benzenes[a]

Substituent	*A*	$\pm\sigma_R^\circ$	$C_{para}-C_{meta}$	*f* sum	ΔR_D
$-NMe_2$	5098	0.53	12.5[c]	0.33	1.49
$-NEt_2$	5852[b]	0.57	13.6	0.34	1.58
$-N(CH_2)_2$	2663	0.38	7.4	0.20	0.43
$-N(CH_2)_3$	5461	0.55		0.33	1.60
$-N(CH_2)_4$	7039[b]	0.63	13.9	0.37	1.64
$-N(CH_2)_5$	3919[b]	0.47	10.3	0.26	0.96

[a] ^{13}C chemical shift differences, the sum of the oscillator strengths (*f* sum), and the exhaltation in molar refraction are also listed (from ref 71 and 72). [b] An additional peak in the spectrum of N-phenylpyrrolidine and shoulders in the other two spectra occurred at 1600–1605 cm^{-1}. The intensities were included in the total since they will be almost entirely derived from the ν_{16} absorptions by Fermi resonance. [c] In parts per million with reference to benzene.

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(73) P. G. Farrell and J. Newton, *ibid.*, **69**, 3506 (1965).

(74) (a) R. P. Bell and E. N. Ramsden, *J. Chem. Soc.*, 161 (1958). (b) Recent works, *e.g.*, ref 61 and 62, have suggested that most of the interaction in aniline and related compounds arises from repulsion between the unshared electrons on the nitrogen atom and the π system of the ring rather than from delocalization. The present work measures the actual electronic disturbance in the ring and can be interpreted equally well by either concept.

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this (*cf.* the cyclopentyl- and cyclohexylbenzene comparison; see later). The sterically preferred conformation in N-phenylazetidine and N-phenylaziridine should again be the most suited for electronic interaction, and here the smaller effects observed probably result from the increased s character of the lone-pair orbitals.

We conclude that the similar electronic interactions found for N-phenylazetidine and N,N-dimethylaniline are not unambiguous evidence for similar configurations about the nitrogen atoms, and that dissimilar configurations are favored by the infrared data.

Nitrogen Linked. (iii) Further Tricoordinated Nitrogen. Phenylation at the nitrogen causes irregular behavior (NH_2, 0.467; NHPh, 0.504; NPh_2, 0.438), but trifluoromethylation results in a large reduction in σ_R° [to 0.132 for $N(CF_3)_2$]. The groups $NHNH_2$, NHOH, and NHNHPh show δ_R° values of 0.487, 0.222, and 0.441, respectively, which indicate that whereas substitution in the amino group of NH_2 and NHPh causes small variation only, hydroxylation has a large effect. Acylation also reduces the ring conjugation of amines, but the groups NHAc and NMeAc are still powerful electron donors with σ_R° values of 0.413 and 0.408, respectively. Sulfonamido derivatives were unfortunately insufficiently soluble for determination.

Nitrogen Linked. (iv) Multiply Bonded and Cationic Substituents. The $N{=}O$ and $N{=}NPh$ groups both have rather small σ_R° values (0.071 and 0.056, respectively). The direction of the effect is not defined by the results for the monosubstituted compounds; we intend to deduce this from suitable polysubstituted derivatives. The substituents with cumulated double bonds $N{=}C{=}O$, $N{=}C{=}NPh$, and $N{=}C{=}S$ show comparatively large effects (σ_R° = 0.403, 0.461, 0.354, respectively); we believe that these substituents are resonance donors, as indicated by previous workers,[76] but plan to investigate polysubstituted compounds to confirm this (*cf.* ref 33). However, in thionylaniline, the substituent NSO has σ_R° of only 0.087. The triply bonded diazonium group $N^+{\equiv}N$ has the high σ_R° of 0.304; resonance withdrawal by this group is considerably greater than by NO_2 (σ_R° = 0.174).

Among cationic nitrogen derivatives, we have measured ND_3^+, $NMeD_2^+$, NMe_2D^+, and NMe_3^+ which show values of 0.183, 0.149, 0.136, and 0.149, respectively. These groups are electron donors by the resonance effect as is indicated by results for *para*-[33] and *meta*-disubstituted[64] compounds. This evidence and the implication of these results are discussed later.[33] The smaller magnitude of the effect when H is replaced by Me is probably a result of solvation being most effective in dispersing charge in the NH_3^+ compound.

The amidinium group $N^+D{=}CMe{-}NDPh$ shows a strong effect (σ_R° = 0.585), indicating considerable electron donation to the ring.

Carbon Linked. (i) Alkyl and Cycloalkyl Groups. The small increase in electron donor ability in series Me < Et < *i*-Pr < *t*-Bu indicates that any hyperconjugative release from a C–C bond is at least as important as that from a C–H bond.

The electronic interaction of a cyclopropane ring with adjacent unsaturated groups has attracted much attention[77] including theoretical,[78] spectral,[79] and reactivity[80] studies. Recent interest[81,82] has centered on the preferred conformations of such molecules; phenylcyclopropane exists[82] preferentially with the plane of the aromatic nucleus bisecting that of the three-membered ring, despite the resultant nonbonded interactions.

Cyclopentyl and cyclohexyl groups are usually assumed to have electronic effects similar to acyclic alkyl substituents, but some doubt exists regarding the cyclobutyl group.[83] Thus ultraviolet spectra suggest the absence of any special electronic interactions with unsaturated groups, but the Raman spectra of arylcyclobutanes have been interpreted in an opposite sense.

The present σ_R° values show clearly that the cyclopropyl group interacts more strongly with the aromatic nucleus than do acyclic substituents such as the isopropyl group. Published σ values (cyclopropyl, 0.22;[84] isopropyl, 0.15[85]) show a corresponding increase in magnitude supporting the assumption that this results from a change in the resonance contribution. The cyclopropyl group is usually considered[77,86,87] to act only as an electron donor and we shall later report results on *para*-substituted cyclopropylbenzenes to confirm this. We are currently investigating the temperature dependence of resonance interactions in this and other alkylbenzenes to provide direct evidence on conformational preferences.

There seems to be no significant increase in electronic interaction in cyclobutylbenzene over acyclic alkylbenzenes. A higher σ_R° value was found for cyclopentyl (0.136) than either cyclobutyl (0.124) or cyclohexyl (0.128) substituents. This may reflect that the conformation with the lowest nonbonded interactions in cyclopentylbenzene is also the most favorable for hyperconjugation of the α-hydrogen with the aromatic ring (molecular models). Ultraviolet results suggest[88] greater interaction in cyclopentyl- than cyclohexylbenzene.

(ii) Substituted Methyl Groups. A single inductive-withdrawing substituent in a methyl group reduces the Me σ_R° value of 0.099 to 0.090 (CH_2CN), to 0.054 (CH_2OMe), and essentially to 0 (CH_2OH, CH_2Cl, $CH_2ND_3^+$). Benzyl alcohol and chloride and the trimethyl-

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benzylammonium cation all show total intensities below 100 but above 50, and this was used in setting the intensity of the combination band (eq 5) as 100 ± 50.

Two or more inductive-withdrawing substituents in a methyl group also effectively reduce the $\sigma_R{}^\circ$ value to zero as is found for the groups $CHBr_2$, $CHCl_2$, $CH(OMe)_2$, and for CCl_3, CBr_3, and $C(OMe)_3$; all these compounds show total intensities in the range 50–100. However, polyfluoro substitution, as in CF_3, C_2F_5, yields electron-acceptor values of $\sigma_R{}^\circ$ of 0.111 and 0.075.

Phenyl substituents increase somewhat the $\sigma_R{}^\circ$ value of methyl to 0.117 (CH_2Ph) and 0.113 ($CHPh_2$).

(iii) CC Multiple Bonds. We have recorded values for several vinyl derivatives PhCH=CHX where X = H, CO_2Me, NO_2, and $N(CH_2CH_2)_2CH_2$. These results are less reliable than most because the compounds show the $\nu_{C=C}$ mode at *ca.* 1630 cm^{-1} and intensity sharing could occur between the two modes. We plan to study polysubstituted analogs, both to test the validity of the $\sigma_R{}^\circ$ values found and to determine their sign.

The acetylenic substituents C≡CH and C≡CPh show $\sigma_R{}^\circ$ values of 0.072 and 0.152, respectively: again the study of polysubstituted compounds is needed to confirm the direction of the effect.

(iv) Other Unsaturated Compounds. The carbonyl derivatives COY are all strongly electron withdrawing; the effect varies in the series: COOMe (0.155) $\leqslant$ COOEt (0.180) < COPh (0.190) < COCl (0.213) $\leqslant$ COMe (0.219) < CHO (0.244) < COOH (0.291). The position of OH in this series is undoubtedly affected by the association of benzoic acid to hydrogen-bonded dimers in $CHCl_3$ solution. However, without considering OH, the order in this series is in marked contrast to the corresponding SO_2Y series (see above). Comparison shows that the two series reflect the strong mesomeric interaction of Y with CO, while Y and SO_2 have mainly an inductive interaction.

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Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. IV.[1] *para*-Disubstituted Benzenes. The ν_{16} Band near 1600 cm^{-1}

P. J. Q. English,[2] A. R. Katritzky,[2] T. T. Tidwell,[2,3] and R. D. Topsom[4]

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England, and the School of Physical Sciences, La Trobe University, Melbourne, Australia. Received September 5, 1967

Abstract: The integrated intensities of the ν_{16} vibration for many *para*-disubstituted benzenes are correlated by the relation $A_{para} = 11{,}800\,(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)^2 + 170$. Discrepancies from this relation are interpreted as due to direct interactions between the substituents; such interactions between acceptor and donor substituents are proportional to $(\sigma^+ - \sigma)$ values. Halogens other than F act as d-orbital acceptors, and NO_2 is found to interact with strong acceptor groups. The relation enables the sign of the resonance effect to be directly determined; $ND_3{}^+$ and $NMe_3{}^+$ groups are shown to be resonance donors.

Previous papers in this series[1,5] have been concerned with the quantitative significance of the infrared intensities of the ring-stretching bands of monosubstituted benzenes. In particular a quantitative relation (eq 1) was found between the integrated area, *A*, of the bands near 1600 and 1585 cm^{-1} and $\sigma_R{}^\circ$ for the substituent. We have now extended this work to polysubstituted analogs, and the present paper records and discusses the results for *para*-disubstituted benzenes.

$$A_{mono} = 17{,}600(\sigma_R{}^\circ)^2 + 100 \qquad (1)$$

Some years ago, one of us, in connection with a wider investigation into the infrared spectra of heteroaromatic compounds,[6] measured the frequencies and apparent extinction coefficients for the characteristic vibrations of many *para*-disubstituted benzenes.[7] At that time it was pointed out that the intensity variations of the 1600-cm^{-1} band could be qualitatively explained on the basis of the theory earlier developed[8] for monosubstituted

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(3) Department of Chemistry, University of South Carolina, Columbia, S. C.

(4) School of Physical Sciences, La Trobe University, Melbourne, Australia.

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