Evaluation of Small Gaussian Basis Sets and Analysis of Substituent Effects in Monosubstituted Benzenes and Phenols

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Abstract: Ab initio, molecular orbital calculations on a series of monosubstituted benzenes and phenols are reported. These calculations were carried out with minimum basis (MB) sets constructed from small Gaussian atomic basis sets parametrized to mimic the valence shell description of larger basis sets. Total energies, reaction energies, dipole moments, ionization potentials, and charge distributions are presented, and with the help of a statistical analysis the reliability of the calculated results has been assessed and compared with STO-3G and CNDO/2 values. Reactivity indices obtained with these minimum bases are discussed with the help of a linear regression analysis of the highest orbital energy and net π-charge distributions with the Taft substituent parameters, σ_I and σ_R^0. Finally, the applicability of substituent parameters in ortho-substituted phenols is considered, a unified dual regression equation for the HOMO orbital energy is derived which includes all para, meta, and ortho isomers, and for the monosubstituted phenols considered in this work it is shown that proximity effects arising between ortho substituents involve primarily σ-electrons.

Molecular orbital (MO) theory has played a fundamental role in the study of the relationships between electronic structure and reactivity. This has been especially true for organic reactivity where both perturbational methods[1] and stastistical approaches such as the Hammett equation and its extensions[2] have been used. The latter methods have also seen application to biological problems,[3] and the direct utilization of reactivity indices obtained from MO calculations is also finding important applications.[4]

When MO indices are to be used directly in the study of biological effects, it is usually not possible to determine a priori which properties will be significant. Thus, all properties to be considered have to be calculated to a given level of reliability. This requirement makes the use of ab initio methods essential in most cases. At the same time, limitations on computing resources require that the calculations be performed at the minimum basis (MB) set level using small Gaussian atomic basis sets. Both of these factors can present considerable problems in obtaining qualitatively reliable MO properties because of the limited flexibility of the wave functions.

Recently one of us (E.L.M.) reported new sets of small Gaussian atomic basis sets (GABS) for most first-row (5s, 2p) and second-row (7s, 4p) atoms important in biologically active molecules. These basis sets were specially constructed to preserve the valence shell character of larger basis sets and avoid the overemphasis on the inner shell which is characteristic of fully energy optimized small basis sets.[5] Subsequently they were refined and tested on a number of small molecules, and the results showed that they yielded qualitatively reliable values for a number of properties such as the dipole moment, ionization potential (IP), and proton affinity, but consistently overestimated bond lengths.[6]

These small GABS require about 25–30% of the computing time needed for (6s, 3p) or (7s, 3p) GABS which is particularly advantageous for biological applications. At the same time it has

been shown that "core-deficient" basis sets may give unreliable results,[7] so that it seems appropriate to augment the previous tests with additional comparisons.

During the last few years we have applied these basis sets to a large number of multiply substituted benzenes in connection with studies on nonsteroidal antiinflammatory drugs.[8] The monosubstituted benzenes and phenols appear to have been the most extensively studied, both theoretically and experimentally, and therefore seem to be the most suitable for a comparative study. Statistical analysis has been used to assess the reliability of the calculated properties and to compare them with the results of STO-3G[9] calculations. The properties of all systems reported here have also been recalculated with the CNDO formalism[10] to obtain some additional insight into the relative reliability of this semiempirical method. In a later paper we will report the results of calculations on substituted benzoic and salicyclic acids.

The influence of substituents as a determinant of difference in biological activity observed in a set of congeners is of major importance. It is therefore of interest to study the extent to which the MO parameters calculated with these basis sets can describe empirically observed substituent effects. However, in order to be generally useful in these types of applications, it is important that ortho-substituted systems can be treated as well as meta and para substituents. In this work we have analyzed the orbital energies and charge distributions of the ortho-, meta-, and para-substituted phenols for their correlation with the Taft substituent parameters σ_I and σ_R^0.[11] The applicability of substituent parameters to polysubstituted benzenes is in part dependent on the additivity of substituent effects. To gain some insight into the extent and character of nonadditivity effects, we have analyzed the additivity of charge contributions of substituents to the ring in the phenols. This analysis indicates that for the molecules studied here special proximity effects[12] arising from ortho sub-

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Table I. Total Energies and Dipole Moments of Monosubstituted Benzenes

R	total energy (au)		dipole moment (D)			
	MB	STO-3G[a]	MB	STO-3G[a]	CNDO/2	exp[b]
NH_2 (Pl)	-282.6599	-282.2046	1.62	1.30	1.14	
NH_2 (Py)	-282.6592	-282.2089	1.87	1.44	1.54	1.49
OH	-302.1777	-301.7286	1.85	1.22	1.73	1.36
CH_3	-266.8991	-266.4738	0.66	0.25	0.20	0.38
C_2H_5	-305.5322	-305.0539	0.76	0.28	0.17	0.58
$CH(CH_3)_2$	-344.1682		0.83		0.30	0.65
H	-228.2581	-227.8901	0.00	0.00	0.00	0.00
F	-325.7737	-325.3494	2.14	0.93	1.66	1.60
Cl	-683.0072	-681.8936[c]	2.13		2.22	1.72
COOH	-413.5647	-412.9735	2.04	1.08	1.46	

[a] Reference 18. [b] A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco: Vol 1, 1963; Vol 2, 1974. Only dipole moments explicitly obtained from the gas phase are included. [c] Reference 34.

stituents involve primarily the σ-electrons, and that the deviations from additivity of the π-electrons are small for all isomers.

Details of the Calculations and Molecular Geometries

The calculations were carried out using (5s, 2p) and (7s, 4p) Gaussian atomic basis sets for the first- and second-row atoms, respectively, and Huzinaga's (3s) basis[13] for hydrogen. These bases were contracted to the MB level, and the parameters have been reported previously.[6] The one- and two-electron integrals were evaluated using a modified version of the Meyer–Pulay Gaussian lobe program,[14] and the SCF calculations were performed with programs developed in this laboratory.[15] The CNDO/2 program was obtained from the QCPE and has been modified for use on a UNIVAC 1100/61.

Molecular geometries were obtained from standard bond lengths and angles[16] with the exception of the amino group. Aniline was calculated in both the planar and pyramidal conformation where the out-of-plane bending angle was taken from the microwave determination.[17] Only the pyramidal conformation of the aminophenols was calculated. With the exception of the amino and isopropyl substituents, geometries conserving σ–π symmetry were assumed. For isopropyl a staggered conformation was used.

A collection of sorting programs has been developed for manipulating the two-electron integral lists. These programs can rearrange, expand, or contract a given list of integrals so that for successive calculations only those integrals which actually change have to be recalculated. For example, from the triply substituted benzene $XYZC_6H_3$ the list corresponding to XYC_6H_4 can be constructed, and only the integrals which include basis functions from the proton or any other group replacing Z have to be computed. Thus, once $XYZC_6H_3$ has been determined, the wave functions of the three disubstituted and three monosubstituted benzenes which can be derived from it can be calculated at very little extra cost. These features save substantial amounts of computing time in evaluating two-electron integrals when ab initio wave functions for a large number of related molecules have to be determined.

Monosubstituted Benzenes

Energies and Dipole Moments. Energetic and dipole moment results for the monosubstituted benzenes are given in Table I. The STO-3G values are taken from Hehre et al.,[18] and the CNDO calculations were carried out as described above. Consistent with previous reports,[6] the MB total energies lie slightly below the STO-3G values. It is noted, however, that the energy surface of aniline is too shallow with respect to the amino out-of-plane bending angle. The optimum value is about 15° whereas the experimental value is 37.5°,[17] and STO-3G gives 45°.[18]

The MB dipole moments are all greater than the experimental values which was also found in the calculations of smaller molecules.[6] Linear regressions 1–3 in Table II give the statistics for the monosubstituted benzenes. The stability of these results can

Table II. Linear Regressions of Theoretical vs. Experimental Dipole Moments and Ionization Potentials[a]

no.	Y	X	A	B	r	F	n
1[b]	μ	(MB)	-0.040	0.791	0.995	605.2	8
2[b]	μ	(STO-3G)	0.177	1.056	0.932	26.3	6
3[b]	μ	(CNDO)	0.287	0.705	0.965	81.5	8
4[c]	μ	(STO-3G)	0.310	1.038	0.958	123.5	13
5[d]	μ	(MB)	-0.177	0.848	0.976	245.4	14
6[d]	μ	(STO-3G)	0.081	1.147	0.915	61.5	14
7[e]	IP	(MB)	0.848	0.798	0.991	377.1	9
8[e]	IP	(CNDO)	0.412	0.663	0.839	16.6	9
9[f]	IP	(MB)	2.170	0.674	0.922	107.0	21
10[f]	IP	(CNDO)	2.818	0.483	0.758	26.6	21

[a] The linear regression equation has the form $Y = A + BX$ where Y is the experimental and X the calculated value, r is the correlation coefficient, F is the F-test, and n is the sample size. μ values are in Debyes and IP's in eV. [b] Monosubstituted benzenes calculated in this work. [c] All monosubstituted benzenes from ref 18 for which gas-phase dipole moments are given. [d] Monosubstituted benzenes from this work and small molecules from ref 6; STO-3G results from ref 18 and J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980). [e] Monosubstituted benzenes from this work. [f] Monosubstituted benzenes and phenols from this work.

be evaluated by increasing the sample size. A sample comprising all the monosubstituted benzenes reported by Hehre et al.,[18] for which gas-phase dipole moments are given, yields a correlation coefficient slightly better than the smaller sample, but a large increase in the confidence level (no. 4, Table II). A final comparison is based on a sample constructed from six monosubstituted benzenes of the present work and eight small molecules from previous calculations.[6] Regressions 5 and 6 indicate that for this sample dipole moments calculated with the MB are statistically somewhat more significant than those obtained with STO-3G bases.

Ionization Potentials. The orbital energies of the four highest valence shell orbitals and their assignments (σ–π only) are given in Table III from the MB and CNDO calculations. In a series of interesting papers, Palmer et al.[19] have determined photoelectron spectra and ab initio energy levels for a large number of substituted benzenes which are also listed in Table III. Their assignments are in close agreement with an earlier study,[20] but where there are disagreements the earlier assignments have also been included. It is seen that the MB level assignments are in quite good agreement with experiment. Only the HOMO-2 and HOMO-3 orbitals of phenol are reversed from Palmer et al.'s assignments. These two orbitals are separated by only 0.2 eV in the MB calculation so that the reversal may be due to using standard bond lengths instead of the optimal separations. This type of distortion had already been noticed earlier in a study of formamide using the MB's.[5]

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Table III. Ionization Potentials, Orbital Energies, and Assignments of Monosubstituted Benzenes

R	IP(eV)	assignment	MB $-\epsilon$ (eV)	MB symm	CNDO/2 $-\epsilon$ (eV)	CNDO/2 symm
H	9.25[a]	π	10.51	π	13.85	π
	11.55	σ	14.10	σ	14.06	σ
	11.8	π	15.04	π	18.97	σ
	14.1	σ	17.20	σ	19.64	σ
NH$_2$	8.05[b]	π	8.90	π	11.63	π
	9.23	π	10.42	π	13.71	σ
	10.84	LPN[c](π)[d]	13.02	π	13.86	π
	11.82	σ	14.01	σ	14.24	σ
OH	8.56[e]	π	9.72	π	12.40	π
	9.28	π	10.76	π	13.76	σ
	11.52	π(n)[d]	14.00	σ	14.03	π
	11.93	σ	14.20	π	14.63	σ
CH$_3$	8.80[a]	π	10.03	π	12.87	π
	9.25	π	10.34	π	13.77	σ
	11.40	σ	13.62	σ	13.83	σ
	11.40	$\sigma(\pi)$[d]	13.86	σ	13.85	π
F	9.31[a]	π	10.61	π	13.28	π
	9.88	π	11.11	π	14.05	σ
	12.33	σ	14.40	σ	14.31	π
	13.0	$\pi, \sigma(\pi)$[d]	15.19[g]	π	15.18	σ
Cl	9.05[f]		10.35	π	12.75	π
			11.04	π	13.56	σ
			12.71	σ	13.84	σ
			13.68	π	14.34	π
COOH	9.73[f]		10.99	π	13.18	σ
			11.13	π	13.24	π
			12.67	σ	14.23	π
			13.37	π	14.24	σ
C$_2$H$_5$	8.76[f]		9.98	π	12.86	π
			10.27	π	13.61	σ
			13.24	σ	13.66	σ
			13.37	σ	13.83	π
CH(CH$_3$)$_2$	8.69[f]		9.87	π	12.60	π
			10.27	π	13.18	σ
			12.77	σ	13.66	σ
			13.02	π	13.83	π

[a] Reference 19a. [b] Reference 19c. [c] Lone pair at nitrogen. [d] Assignments in parentheses from ref 20 when they differ from ref 19. [e] Reference 19b. [f] H.M. Rosenstck, K. Drexl, B.W.Steiner, and J.T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Suppl. 1 (1977). [g] Close lying σ orbital, $\epsilon = 15.34$ eV.

With the exception of the π-HOMO, the energy level ordering resulting from the CNDO calculations is usually incorrect. This has already been observed earlier,[20] and an attempt at scaling the σ and π levels did not alleviate the uncertainties in the ordering.

The results of a statistical analysis of the π-HOMO Koopman's theorem IP's with the experimental values is given in Table II. For the nine monosubstituted benzenes the correlation coefficient and F-test is substantially better for the MB calculations than for the CNDO results. Indeed, the MB correlation coefficient of 0.99 cannot be improved, so that increasing the sample size will probably lower the correlation coefficient as shown by augmenting the sample with monosubstituted phenols.

Recently Brown and Simas[21] have studied the use of CNDO indices for predicting chemical reactivity. They found no simple relationship between the π-HOMO energy and the Hammett σ_p and σ_m parameters.[11] We have carried out a regression analysis of the π-HOMO energy with Taft's parameters (see Table IV) and also found no significant correlation between ϵ_{HOMO} and either σ_1 of σ_R^0 separately. However, we obtained quite a good relationship from the combined regression of the form

$$\epsilon_{HOMO} = -1.634\sigma_1 - 2.418\sigma_R^0 - 10.240$$
$$r = 0.92, F = 15.4, n = 9, SD = 0.28 \tag{1}$$

where ϵ is given in eV, r is the correlation coefficient, F is the F-test, n is the number of cases in the sample, and SD is the standard deviation.

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Table IV. Net Mulliken Charge Populations in Monosubstituted Benzenes

R	$q_\sigma(R)$[a] MB	$q_\sigma(R)$[a] STO-3G[c]	$q_\pi(R)$[a] MB	$q_\pi(R)$[a] STO-3G[c]	σ_1[b]	σ_R^0[b]
NH$_2$(Pl)	-0.209	-0.159	0.143	0.120		
NH$_2$ (Py)	-0.196	-0.140	0.128	0.095	0.12	-0.47
OH	-0.320	-0.185	0.108	0.102	0.25	-0.40
CH$_3$	0.083	0.007	0.016	0.008	-0.04	-0.10
C$_2$H$_5$	0.074	0.013	0.016	0.005	-0.05	-0.10
IPR	0.064		0.016		-0.06	-0.12
H	0.313	0.063	0.0	0.0	0.0	0.0
F	-0.442	-0.215	0.072	0.080	0.50	-0.34
Cl	-0.054		0.057		0.46	-0.22
COOH	-0.033	-0.029	-0.052	-0.034	0.32	0.21

[a] q_σ and q_π are the net charge populations of the substituents. [b] Taft induction and resonance parameters from ref 11. [c] STO-3G values from ref 18.

Table V. Simple and Dual Parameter Regressions between Empirical Substituent Constants, σ_R^0 and σ_1, and π-Charge Populations[a]

Y	C_R^0	C_1	r	F	SD
$q(R)$	-0.2507	0.0	0.991	448.4	0.009
	-0.2519	-0.0021	0.991	196.8	0.010
$q(C_2)$	0.1490	0.0	0.912	39.5	0.019
	0.1879	0.0705	0.984	107.6	0.009
$q(C_3)$	-0.0565	0.0	0.978	172.2	0.003
	-0.0608	-0.0079	0.985	110.6	0.003
$q(C_4)$	0.1021	0.0	0.876	26.3	0.016
	0.1380	0.0649	0.997	664.7	0.003

[a] The regression equation has the form $Y = C_R^0\sigma_R^0 + C_1\sigma_1$, where Y is the net π population, σ_R^0 and σ_1 are the Taft resonance and induction parameters, respectively (ref 11), r is the correlation coefficient, F is the F-test, SD is the standard deviation, and the sample comprises the nine monosubstituted benzenes of this work.

Charge Distributions. A Mulliken population analysis[22] has been carried out and the results are reported in Table IV as the σ and π charges on the substituents. Similar values from STO-3G calculations[18] are also listed, as well as the Taft σ_1 and σ_R^0 substituent parameters.[11] The two sets of net charges are highly correlated: $q_\pi(r = 0.98, F = 166, n = 8)$ and $q_\sigma(r = 0.98, F = 127, n = 8)$ showing that they are qualitatively identical. The correlations remain virtually unchanged when the sample is augmented with the substituted phenols so that the qualitative similarity of the population analysis is probably quite general for first-row substituents. Hehre et al.[23] have studied the correlation between σ and π net charges at various ring positions using STO-3G bases. As suggested by the high correlations between the two basis sets, similar results are found with the MB net populations.

The σ-charge population of chlorine is considerably less than that of fluorine, leading to a total population of only 0.003 e in contrast to -0.37 e on fluorine. Bernardi et al.[24] reported STO-3G calculations on fluoro- and chlorobenzene where the C–X distance was optimized and standard values were used for the remaining geometric parameters. They reported a total net charge of -0.13 and -0.15 e on the fluoro and chloro compounds, respectively, whereas using standard geometries throughout Dietrich et al.[25] obtained -0.130 and -0.117 e. Finally, in a calculation using double-zeta (ζ) basis sets Binning and Sando[26] obtained -0.407 (0.053 e) and -0.133 e (0.060 e) for the $\sigma(\pi)$ net charges of fluoro- and chlorobenzene. Thus, it seems that our net charges for these two molecules follow the double-ζ results more closely than the STO-3G results.

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Table VI. Total Energies, Dipole Moments, and Reaction Energies of Substituted Phenols

	total energy (au)		dipole moment (D)			ΔE (kcal/mol)[b]	
R	MB	STO-3G[a]	MB	STO-3G[a]	CNDO/2	MB	STO-3G[a]
o-NH$_2$	−356.5781	−356.0450	1.69	1.57	0.79	−0.43	−1.6
m-NH$_2$	−356.5797	−356.0488	2.02	1.57	2.02	0.53	0.8
p-NH$_2$	−356.5748	−356.0450	2.84	1.93	2.45	−2.54	−1.5
o-OH	−376.0999	−375.5661	3.20	2.15	3.02	1.62	−0.7
m-OH	−376.0981	−375.5685	1.83	1.22	1.73	0.49	0.8
p-OH	−376.0940	−375.5649	0.00	0.00	0.00	−2.09	−1.4
o-CH$_3$	−340.8212	−340.3122	1.17	1.00	1.58	1.53	−0.1
m-CH$_3$	−340.8190	−340.3128	2.15	1.29	1.83	0.16	0.3
p-CH$_3$	−340.8176	−340.3118	2.15	1.29	1.83	−0.70	−0.4
o-IPR	−418.0899		1.00		1.48	1.29	
m-IPR	−418.0884		1.25		1.53	0.35	
p-IPR	−418.0867		1.84		2.34	−0.72	
H	−302.1777	−301.7286	1.85	1.22	1.73		
o-F (t)	−399.6855	−399.1830	3.90	2.11	3.41	−4.88	−3.1
o-F (c)	−399.6921	−399.1857	1.48	0.75	1.43	−0.78	−1.4
m-F (t)	−399.6921	−399.1884	3.67	2.04	3.07	−0.78	
m-F (c)	−399.6926	−399.1886	0.63	0.52	0.32	−0.46	0.4
p-F	−399.6908	−399.1865	2.43	1.42	1.94	−1.58	−0.9
o-Cl (t)	−756.9246		3.80		3.98	−1.43	
o-Cl (c)	−756.9275		1.52		1.73	0.42	
m-Cl (t)	−756.9255		3.59		3.54	−0.82	
m-Cl (c)	−756.9259		0.58		0.56	−0.55	
p-Cl	−756.9258		2.46		2.40	−0.62	
o-COOH	−487.4965		2.68		2.26	7.64	
m-COOH	−487.4835		0.79		0.81	−0.51	
p-COOH	−487.4866		1.47		1.07	1.44	

^{a} Reference 28. ^{b} Isodesmic reaction energy for the reaction $C_6H_4(OH)(R) + C_6H_6 \rightleftharpoons C_6H_5OH + C_6H_5R$.

Finally, we attempted to relate the calculated π-charge shifts to the Taft substituent parameters by a single and dual linear regression. The results of this analysis are given in Table V and are comparable with STO-3G[23] and CNDO[27] calculations which also give an interpretation of the charge shifts in terms of substituent parameters. Thus the relative dependence of $q_\pi(R)$, $q_\pi(C_3)$, and $q_\pi(C_4)$ on π-delocalization and the π-inductive effect is similar to what was found from the STO-3G calculations. The relative dependence on the π-inductive effect at the ortho, meta, and para positions is $f^p > f^o > f^m$, where $f = C_1/C_R^0$. However, since $f^m/f^p = 0.28$ whereas $f^p/f^p = 0.79$, the origin of the π-charge shifts in the ortho and para positions seem much more closely related than with the meta position. The differences between the ortho and para π-charge populations appear to arise almost exclusively from differences in resonance effects, i.e., $C_1(o)/C_1(p) \sim 1$, but $C_R^0(o)/C_R^0(p) \sim 1.4$.

Monosubstituted Phenols

Total Energies, Dipole Moments, and Reaction Energies. In Table VI the total energies, dipole moments, and reaction energies are reported for the ortho, meta, and para isomers of seven monosubstituted phenols. In most cases the lowest energy conformation is given, but for fluorine and chlorine both nonequivalent ortho and meta conformers were calculated. The isopropyl and amino substituent geometries were as given above. The STO-3G results have been taken primarily from Pross and Radom's thorough discussion of substituted aromatics.[28] The stabilization energies of the intramolecular hydrogen bonds calculated for the o-fluorophenol and o-chlorophenol are 4.1 and 1.8 kcal/mol, respectively. The experimental results are 1.63 kcal/mol for both species obtained from torsional frequency spectra[29] and 3.41 kcal/mol for o-chlorophenol measured from the spectra of the O–H stretching frequency.[30] The cis conformer of o-fluorophenol was not clearly observed in the stretching frequency spectra. Dietrich et al.[25] have reported STO-3G calculations on some halophenols and obtained 1.7 and 1.8 kcal/mol for the o-fluoro-

and o-chlorophenols, respectively, in good agreement with the torsional vibration results.

One of the sources of error in calculating intermolecular H-bonding interaction energies with small basis sets is due to the artificial energy lowering arising from the increased basis set size in the interacting system relative to the separated monomers. The counterpoise method[31] has been used to estimate this superposition effect, and in various applications it has been observed that correcting interaction energies and other properties by this estimate tends to improve the predicted values and stabilize them with respect to basis set variation.[32] Such artificial basis set effects may also be operative in intramolecular H-bonding of the type discussed here, and we have tried to estimate it by a modified counterpoise method. The superposition effect of the proton's basis set on the proton acceptor can be calculated by placing the hydrogen atomic basis of the phenolic proton in the cis and trans positions in the halobenzene. Upon taking the difference between the cis and trans total energies, the effect of the H-basis set on the rest of the molecule will cancel. Similarly, the superposition effect due to the halogen basis can be estimated by including it at the appropriate position in phenol and evaluating the energy for the proton cis and trans positions. Here too, the difference between the two energies will cancel out all the effects except on the proton.

For o-fluorophenol we have found that the hydrogen basis set effect, $E_{cis} - E_{trans}$, is −0.50 kcal/mol, whereas for o-chlorophenol it is 0.09 kcal/mol. The effect of the halogen basis set is 0.26 kcal/mol for o-fluorophenol and 0.73 kcal/mol for o-chlorophenol. Combining the two estimates for each molecule yields a basis set superposition error of −0.24 kcal/mol for o-fluorophenol and 0.82 kcal/mol for o-chlorophenol. It is of interest to note that in contrast to superposition effects in the intermolecular case, where they must lead to overestimation of the interaction energy, this is not so in the intramolecular case as the result for the chloro substituent shows. Corrected estimates for the interaction energies are then 3.9 and 2.6 kcal/mol for the fluoro and chloro systems, respectively, which are considerably closer together than the uncorrected values. Nevertheless, they are still in contradiction

(27) R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, **90**, 6537 (1968).
(28) A. Pross and L. Radom, *Prog. Phys. Org. Chem.*, **13**, 1 (1981).
(29) G. L. Carlson, W. G. Fately, A. S. Manocha, and F. F. Bentley, *J. Phys. Chem.*, **76**, 1553 (1972).
(30) T. S. Lin and E. Fishman, *Spectrochim. Acta, Part A*, **23**, 491 (1967).

(31) S. F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 558 (1970).
(32) G. F. H. Diercksen, W. P. Kraemer, and B. O. Roos, *Theor. Chim. Acta*, **36**, 249 (1975); B. Jeziorski and M. van Hemert, *Mol. Phys.*, **31**, 713 (1976); E. L. Mehler, *J. Chem. Phys.*, **74**, 6298 (1981).

Table VII. Ionization Potentials, Orbital Energies and Assignments of Substituted Phenols

R	IP (eV)	assignment	MB $-\epsilon$ (eV)	MB symm	CNDO/2 $-\epsilon$ (eV)	CNDO/2 symm
o-NH$_2$			8.59	π	10.90	π
			10.05	π	12.96	π
			13.04	π	13.51	σ
			14.14	σ	14.34	σ
m-NH$_2$			8.99	π	11.55	π
			9.86	π	12.80	π
			12.72	σ	13.67	σ
			13.99	σ	14.56	σ
p-NH$_2$	7.83[a]	π	8.40	π	10.82	π
	9.34	π	10.68	π	13.49	π
	10.38	π	12.31	π	14.04	π
	11.78		13.91	σ	14.85	σ
o-OH	8.56[b]	π	9.38	π	11.72	π
	9.25	π	10.46	π	13.34	π
	11.60	π	14.01	π	13.79	σ
	12.21	σ	14.25	σ	14.59	σ
m-OH	8.63[b]	π	9.62	π	12.10	π
	9.15	π	10.40	π	13.19	π
	11.25	π	13.60	π	13.92	σ
	12.14	σ	14.35	σ	14.66	σ
p-OH	8.44[b]	π	9.10	π	11.41	π
	9.66	π	11.02	π	13.54	σ
	11.21	π	13.36	π	14.21	π
	11.98	σ	14.02	σ	15.37	σ
o-CH$_3$	8.50[b]	π	9.45	π	12.02	π
	9.12	π	10.34	π	13.39	π
	11.38	σ	13.53	σ	13.49	σ
	11.76	π	13.93	π	14.25	σ
m-CH$_3$	8.41[b]	π	9.53	π	12.24	π
	9.14	π	10.33	π	13.30	π
	11.18	σ	13.68	σ	13.51	σ
	11.31	π	13.74	π	14.39	σ
p-CH$_3$	8.35[b]	π	9.32	π	11.75	π
	9.24	π	10.60	π	13.58	σ
	11.12	π	13.65	π	14.05	π
	11.24	σ	13.76	σ	14.31	σ
o-IPR			9.35	π	11.88	π
			10.22	π	12.97	σ
			12.79	π	13.24	π
			12.82	π	13.92	σ
m-IPR			9.45	π	12.17	π
			10.17	π	13.02	σ
			12.89	π	13.12	π
			12.89	π	14.07	σ

R	IP (eV)	assignment	MB $-\epsilon$ (eV)	MB symm	CNDO/2 $-\epsilon$ (eV)	CNDO/2 symm
p-IPR			9.19	π	11.57	π
			10.54	π	13.29	σ
			12.82	π	13.66	σ
			12.95	σ	14.02	π
o-F (c)	8.95[b]	π	10.09	π	12.37	π
	9.60	π	11.00	π	13.83	π
	11.86	π	14.48	σ	14.00	σ
	12.40	σ	14.56	π	15.21	σ
m-F (c)	8.99[b]	π	10.15	π	12.61	π
	9.52	π	11.04	π	13.78	π
	11.62	π	14.38	σ	14.38	σ
	12.5	σ	14.89	σ	14.94	σ
p-F	8.77[b]	π	9.87	π	12.08	π
	9.75	π	11.35	π	13.83	σ
	11.57	π	14.28	π	14.48	π
	12.25	σ	14.43	σ	15.94	σ
o-Cl (c)	9.28[c]		10.05	π	12.31	π
			10.85	π	13.52	π
			13.40	σ	13.61	σ
			14.00	π	13.85	σ
m-Cl (c)			10.04	π	12.50	π
			10.83	π	13.35	π
			12.89	σ	13.63	σ
			13.40	π	13.77	σ
p-Cl	9.07[b]		9.75	π	12.03	π
			11.29	π	13.46	σ
			12.72	σ	14.13	σ
			13.09	π	14.53	π
o-COOH			10.11	π	12.43	π
			11.46	π	12.73	σ
			13.01	σ	13.77	π
			14.09	π	14.37	σ
m-COOH			10.20	π	12.61	π
			11.27	π	13.13	σ
			12.84	σ	13.58	π
			13.44	π	14.57	σ
p-COOH			10.37	π	12.30	π
			11.25	π	13.22	σ
			12.62	σ	14.00	σ
			13.23	π	14.43	π

[a] H. Goetz, H. Hartam, H. Juds, F. Marschner, and H. Pohle, *Justus Liebigs Ann. Chem.*, 556 (1977). [b] Reference 19b. [c] See Table III, footnote f.

with the available experimental results which indicate ΔE(Cl) $\simeq$ ΔE(F). An additional source of error is, as pointed out above, that the MB's used in these calculations overestimate bond lengths and, in fact, somewhat more in bonds including second-row atoms than in bonds between only first-row atoms.[6] Thus, the use of standard geometries may distort the wave functions enough to give the present incorrect ordering.

The reaction energies for the isodesmic reaction (eq 2) are listed
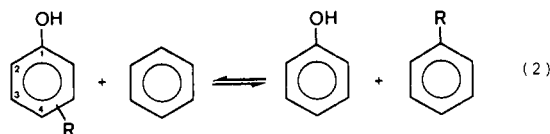
in Table VI. Isodesmic reactions are characterized by the fact that the formal bond types are conserved on both sides of the reaction, which has the advantage that systematic basis set errors tend to cancel. However, the regression between MB and STO-3G values has a correlation of only 0.58, and it appears therefore that the basis set errors are not cancelled as completely as might be hoped. The basis set dependence of isodesmic reaction energies has also been discussed in a recent paper by Dixon et al.[33]

The main sources of the remaining error probably are the one- and two-electron interaction integrals between the two substituents in the doubly substituted benzenes which are not cancelled by any of the other molecular species appearing in reaction 2.

Further insight into this problem can be gained by considering reaction 2 with R a positive or negative unit charge. In that case no new two-electron interaction terms appear. Calculations of this type have been performed for meta and para isomers by Vorpagel et al.[34] using STO-3G basis sets, and we have repeated them with our MB's. Because of the nonequivalence of the meta positions in phenol, four meta and two para isomers arise. Adding the six calculated reaction energies to the sample in Table VI increases the correlation between MB and STO-3G values to 0.74.[35] Although this test is too limited to draw definite conclusions, the increase in r does suggest that the instability in the reaction energies is mainly due to the two-electron terms.

Since gas-phase dipole moments are not available for the substituents reported here, we compared the calculated results with each other including both the monosubstituted benzenes and phenols in the samples. The regression of the MB with the

(33) D. A. Dixon, R. A. Eades, R. Frey, P. G. Gassman, M. L. Hendewerk, M. N. Paddon-Row, and K. N. Houk, *J. Am. Chem. Soc.* **106**, 3885 (1984).

(34) E. R. Vorpagel, A. Streitwieser, Jr., and S. D. Alexandratos, *J. Am. Chem. Soc.* **103**, 3777 (1981).

(35) The correlation for the six point charge isomers is 0.84. It should also be noted that the geometries used by Vorpagel et al.[34] are not exactly identical with ours.

MO Studies of Monosubstituted Benzenes and Phenols

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STO-3G dipole moments yielded $r = 0.94$, $F = 145$ for $n = 23$ and a slope of 0.58, and between the MB and CNDO/2 dipole moments gave $r = 0.95$, $F = 287$ for $n = 36$ and a slope of 0.94. These results suggest that the trends in the reliability of the dipole moments observed for the monosubstituted benzenes will be similar in the substituted phenols.

Ionization Potentials. The four highest energy levels of the monosubstituted phenols calculated with MB's and with CNDO/2 are reported in Table VII. The observed IP's are listed where available. Comparison of the level assignments obtained from the MB calculations with Palmer et al.'s[19] assignments shows good agreement. In contrast, the CNDO/2 energy levels are again in a substantially different ordering, and only the HOMO is consistently of the correct symmetry. A statistical analysis of the π-HOMO energies with the observed IP's is reported in Table II for the combined sample. Comparison of the ab initio (no. 9) with the CNDO (no. 10) regression shows the former to have a considerably higher correlation and F-test with the observed IP's than the CNDO/2 results.

A statistical analysis of the π-HOMO energies with Taft's substituent parameters indicated no significant correlations with σ_I and σ_R^0 taken separately. Combining the substituent parameters in a dual regression yielded

$$\epsilon = -1.670\sigma_I - 2.250\sigma_R^0 - 9.543$$
$$r = 0.95, F = 24.5, n = 8, \text{SD} = 0.21 \tag{3}$$

for the para substituents, and

$$\epsilon = -1.511\sigma_I - 1.174\sigma_R^0 - 9.630$$
$$r = 0.93, F = 17.2, n = 8, \text{SD} = 0.17 \tag{4}$$

for the meta substituents. Comparison of eq 3 with eq 1 shows that the regression of the para-substituted phenols is approximately the same as the monosubstituted benzenes. It is also noted that the regression coefficient C_I of σ_I is the same in eq 1, 3, and 4 but that the regression cooefficient C_R^0 of σ_R^0 is about half as large in magnitude in eq 4 as in eq 3. If one defines $\sigma_R^\phi(\text{para}) = \sigma_R^0$ and $\sigma_R^\phi(\text{meta}) = \sigma_R^0/2$, eq 3 and 4 can be combined to give

$$\epsilon = -1.630\sigma_I - 2.264\sigma_R^\phi - 9.567$$
$$r = 0.95, F = 56.7, n = 15, \text{SD} = 0.18 \tag{5}$$

The correlation coefficient of this relation is the same as for eq 3, but the significance as expressed by the F-test has increased substantially. Moreover, it is seen that eq 5 is still similar to eq 1.

If one tries to correlate the π-HOMO energies of the ortho-substituted phenols with the Taft parameters, one finds

$$\epsilon = -1.731\sigma_I - 1.617\sigma_R^0 - 9.555$$
$$r = 0.89, F = 9.86, n = 8, \text{SD} = 0.28 \tag{6}$$

As expected, the correlation coefficient and F-test have decreased and the standard deviation is considerably greater than in eq 3 or 4. C_I, however, has remained essentially the same, and the ratio of C_R^0 from eq 6 with C_R^0 from eq 3 is 0.718 or approximately $1/\sqrt{2}$.

Defining $\sigma_R^\phi(\text{ortho}) = \sigma_R^0/\sqrt{2}$ and collecting all the σ-HOMO energies into a unified dual regression with σ_I and σ_R^ϕ yields

$$\epsilon = -1.696\sigma_I - 2.237\sigma_R^\phi - 9.544$$
$$r = 0.93, F = 65.4, n = 22, \text{SD} = 0.20 \tag{7}$$

Equation 7 exhibits an additional increase in F, a standard deviation in the same range as eq 3, 4, and 5, and its regression coefficients still are essentially the same as eq 1. By way of comparison, the result of the regression using unmodified σ_R^0's for the ortho, meta, and para isomers yields a dual regression with $r = 0.90$, $F = 39.6$, and SD $= 0.24$. The regression coefficient, C_R^0, is of course, quite different from eq 1.

This rather unexpected result that the ortho substituents can be combined with the para and meta substituents without additional factors[12] to yield one regression equation may, in part, be due to the limited sample or to possible instabilities in the orbital energies inherent in small basis sets.[36] Whether or not such instabilities affect the reliability of a given property calculated with a fixed basis set applied to a set of molecules is not clear. The results in Table II demonstrate a reasonable qualitative agreement between calculated and experimental values of the dipole moment and ionization potential, but do not give much insight into the reliability of relationships like eq 1 and 3-7. However, for the monosubstituted benzenes considered here the experimental IP's are all available (Table III) and can be used in a dual regression with σ_I and σ_R^0. The result is

$$\text{IP} = 1.34\sigma_I + 2.00\sigma_R^0 + 9.03$$
$$r = 0.94, F = 23.1, n = 9, \text{SD} = 0.19 \tag{1'}$$

The statistics of this dual regression are the same or better than eq 1, and the regression coefficients are also not very different. This result and the fact that by introducing the resonance factors[2] 1, 1/2, and $1/\sqrt{2}$ for the para, meta, and ortho isomers, respectively, one obtains a relation for the substituted phenols which is essentially identical with that for the monosubstituted benzenes suggests that eq 7 may have some generality. It indicates that the ortho substituents do not interact with each other in such a way as to distort the π-HOMO from pair-additive effects between the substituents and the benzene ring. We will return to this point below.

Finally, the statistical analysis of the HOMO energies of the CNDO/2 calculations with the observed IP's given in Table II (no. 10) yielded a lower correlation coefficient than with the MB-HOMO energies ($r = 0.92$). This difference is not surprising, since the parametrization of the CNDO/2 method is calibrated to reproduce ab initio calculations using a minimal basis set.[10]

Charge Distributions. The results of the population analysis are reported in Table VIII. The net σ and π charge on the phenolic group and substituent is given, as well as the total contribution to the ring. Statistical analysis with the STO-3G net charges[28] for a sample of 20 molecules comprising monosubstituted benzenes and phenols yields q_π ($r = 0.99$, $F = 699$) and q_σ ($r = 0.99$, $F = 708$). The sample excludes the chloro and isopropyl substituents and the carboxyl phenols. The correlation and F-test for both σ and π populations are high so that previous observations obtained from STO-3G calculations will also be valid for the MB results.

The statistical analysis of the π populations with the Taft substituent parameters has been carried out for the total contribution to the ring. As in the case of the monosubstituted benzenes, σ_I made only a very small contribution to the regression so that a simple regression with σ_R^0 was sufficient. For the para substituents one obtains

$$q_\pi = -0.240\sigma_R^0 \qquad r = 0.99, F = 348, \text{SD} = 0.010, n = 8 \tag{8}$$

The meta isomers gave similar results with $r = 0.99$, $F = 425$, and SD $= 0.010$, and the ortho substituents gave $r = 0.97$, $F = 134$, and SD $= 0.017$. Comparison of eq 8 with the first equation in Table V shows them to have similar slopes, and for the meta and ortho isomers the slopes were −0.259 and −0.256, respectively. As for the orbital energies, one could derive a single regression equation for all three types of isomers relating q_π and σ_R^0 with high r and F values. This, however, would not be very meaningful as we now show.

The total σ- and π-charge contributions to the ring for the monosubstituted phenols is the sum of the contributions from each substituent, i.e., $q_\sigma(\text{OH}) + q_\sigma(\text{R})$ and $q_\pi(\text{OH}) + q_\pi(\text{R})$. Comparison of the individual q_π contributions in each molecule with the values given in Table IV shows that the net charges in the phenols deviate slightly from the monosubstituted benzenes. These deviations are due to the interactions between the two substituents and the higher order deformations transmitted via the ring. If there were no such additional interactions, the net charges in the phenols would be given by

$$\tilde{q}(\text{R-PHNL}) = q(\text{PHNL}) + q(\phi\text{-R}) \tag{9}$$

(36) P. G. Mezey and E. C. Haas, *J. Chem. Phys.*, **77**, 870 (1982).

Table VIII. Net Mulliken Charge Populations in Substituted Phenols

R	$q_\sigma(\text{OH})$	$q_\sigma(\text{R})$	$q_\sigma(\phi)^a$	$q_\pi(\text{OH})$	$q_\pi(\text{R})$	$q_\pi(\phi)^a$
o-NH$_2$	−0.319	−0.179	0.499	0.098	0.128	−0.226
m-NH$_2$	−0.322	−0.192	0.514	0.110	0.132	−0.242
p-NH$_2$	−0.320	−0.194	0.514	0.098	0.120	−0.218
o-OH	−0.318	−0.302	0.620	0.095	0.107	−0.202
m-OH	−0.318	−0.315	0.633	0.111	0.112	−0.223
p-OH	−0.317	−0.317	0.634	0.101	0.101	−0.203
o-CH$_3$	−0.323	0.102	0.221	0.104	0.016	−0.120
m-CH$_3$	−0.323	0.090	0.232	0.108	0.017	−0.124
p-CH$_3$	−0.321	0.082	0.239	0.105	0.014	−0.119
o-IPR	−0.324	0.082	0.242	0.103	0.017	−0.120
m-IPR	−0.324	0.073	0.251	0.107	0.018	−0.125
p-IPR	−0.322	0.063	0.259	0.104	0.015	−0.119
H	−0.321	0.313	0.007	0.108	0.000	−0.108
o-F (c)	−0.299	−0.442	0.741	0.109	0.062	−0.171
o-F (t)	−0.301	−0.428	0.729	0.108	0.069	−0.177
m-F (c)	−0.310	−0.440	0.750	0.112	0.074	−0.186
m-F (t)	−0.312	−0.438	0.750	0.112	0.074	−0.186
p-F	−0.314	−0.439	0.753	0.107	0.067	−0.175
o-Cl (c)	−0.308	−0.059	0.368	0.115	0.049	−0.164
o-Cl (t)	−0.306	−0.033	0.339	0.112	0.056	−0.168
m-Cl (c)	−0.311	−0.049	0.361	0.111	0.059	−0.170
m-Cl (t)	−0.313	−0.046	0.358	0.111	0.059	−0.170
p-Cl	−0.315	−0.053	0.368	0.111	0.052	−0.163
o-COOH	−0.309	−0.022	0.331	0.149	−0.083	−0.066
m-COOH	−0.310	−0.029	0.340	0.108	−0.050	−0.059
p-COOH	−0.317	−0.032	0.349	0.122	−0.061	−0.061

$^a q_\sigma(\phi)$ and $q_\pi(\phi)$ are the net σ and π charges donated by the substituents to the ring.
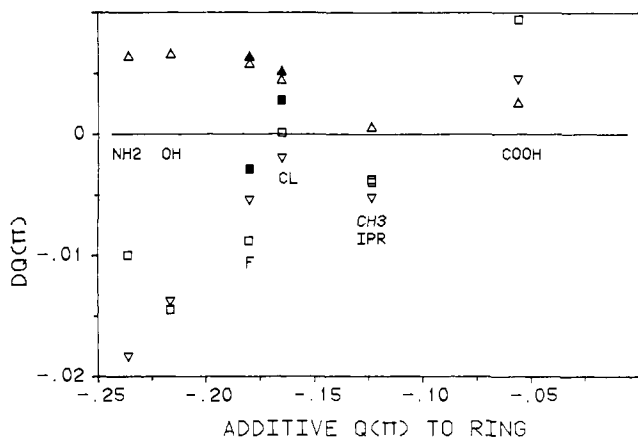

Figure 1. Deviation from additivity of π-charge contributions to the ring in monosubstituted phenols: □, ortho substituent; △, meta substituent; ▽, para substituent; ■, ortho halo substituent, trans conformation; ▲, meta halo substituent, trans conformation. $DQ = Q(\text{additive}) - Q(\text{calculated})$; see text.

Figure 2. Deviation from additivity of σ-charge contributions to the ring in monosubstituted phenols. See legend to Figure 1 for explanation of symbols.

i.e., they would be purely additive. In Figure 1 the deviations from additivity of the actual π charges are plotted against $\tilde{q}_\pi$.

The deviation from additivity is defined as $Dq = \tilde{q} - q$ so that in Figure 1 a negative Dq means diminution, while a positive Dq indicates enhancement of charge shift. It is seen that Dq_π is less than 0.02 e in magnitude, and most cases lie between ±0.01 e. From eq 8 SD = 0.010, and for the meta and ortho isomers it is 0.010 and 0.017, respectively. Since the SD's are of the same magnitude as the Dq's, we have to conclude that eq 8 merely repeats the first equation in Table V. In contrast, the changes in π-HOMO energies discussed above are two to five standard deviations.

All the substituents except carboxyl donate π charge to the ring, and, indeed, only the carboxyl group exhibits enhanced net charge in all three isomers, which is large relative to $\tilde{q}_\pi$. For the remaining substituents the charge shift tends to be diminished although in several cases a small enhancement is observed. In all but three cases Dq_π is less than 0.01 charge unit in magnitude. A change in net charge of 0.01 e corresponds to a change in electrostatic energy of about 1 kcal/mol at a unit point charge 3 Å away. In addition to being small, the ordering of the magnitude of Dq_π is not systematic with respect to isomer type. In only three of the
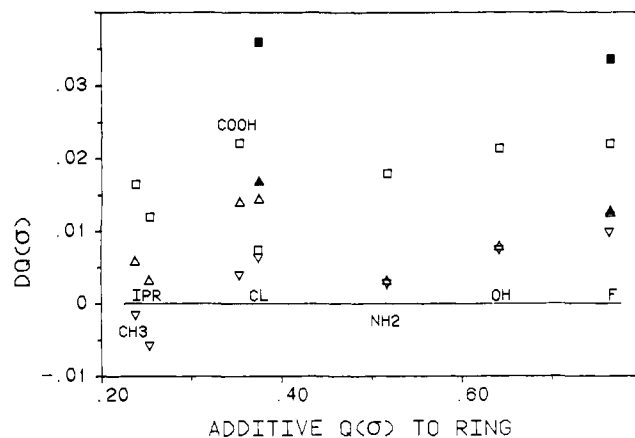
seven substituents considered does the ortho isomer exhibit the largest deviation. It is seen, therefore, that nonadditivities in the π populations are small and irregular, and for these reasons the π-HOMO energies of the ortho substituents could be combined with the meta and para isomers to obtain eq 7.

It is also of interest to examine the deviations from additivity of the net σ charges which are plotted in Figure 2. All the substituents except the alkyl groups, which are weakly σ-electron donating, are σ-electron withdrawing, resulting in a decrease in total electron withdrawal compared to the $\tilde{q}_\sigma$. The σ-charge shifts are more systematic: the meta and para isomers tend to exhibit small Dq's of the same magnitude as the π-electron deviations. The stable conformation of the ortho-substituted congener has the largest deviation from additivity in all cases except chlorine.

In the trans conformation of o-fluorophenol the hydroxy and fluoro group's σ net charges have lost 0.020 and 0.014 electron, respectively, compared with their values in the monosubstituted benzenes. This loss of charge is due to the proximity of two electron-withdrawing substituents in ortho isomers and is related to the ortho proximity effect discussed by Charton.[12] However, in the cis conformation fluorine gains enough charge to just compensate the loss in the trans conformation. At the same time the oxygen also gains about 0.01 e in net charge whereas the proton loses this amount of charge, leaving the hydroxy group unchanged

from the trans conformation. This movement of charge is typical for hydrogen bonding. Finally, these charge shifts are balanced by a loss of 0.02 e on the hydrogen bonded to C_6 and a small gain on the ortho carbon.

The charge shifts in *o*-chlorophenol are similar, but chlorine gains more charge than fluorine in the cis conformation. This extra charge comes from the ortho carbon which loses charge in the H-bonded conformation. Whether this reversal in movement of charge is characteristic or an artifact of the basis set is not clear at present.

It appears, therefore, that the trans conformers exhibit the full proximity effect and hence a larger Dq, whereas in the cis conformers the effect is partially compensated owing to H-bonding which allows charge to be transferred from the proton to the proton acceptor. In fluorophenol the charge gained by the proton acceptor just compensates the charge lost in the trans conformation so that $Dq_\sigma(\text{cis})$ is still large. In contrast, $Dq_\sigma(\text{cis})$ for chlorophenol is less because the charge gained overcompensates the loss of charge in the trans conformation.

Conclusions

Ab initio calculations have been carried out on monosubstituted benzenes and phenols using small Gaussian atomic basis sets constructed to preserve the valence-shell description of larger bases.[5] On the basis of statistical analyses it was shown that these MB's give qualitatively stable values of properties such as the dipole moment and Koopmans' theorem ionization potentials. Such statistical predictability allows the calculated values of a particular property to be scaled to give improved estimates of the observed values. For example, the scaled values of the dipole moment of phenol obtained from the calculated MB and STO-3G values using eq 5 and 6 of Table II, respectively, are 1.39 and 1.48 D, and for benzoic acid they are predicted to be 1.55 and 1.32

D. Naturally the calculated dipole moments of the substituted phenols given in Table VI could also be scaled with these equations. In addition, it is clear that when a given molecular property for a series of molecules is correlated with another observed property, statistical stability is essential if such correlations are to be meaningful. Mulliken charge populations calculated with the MB's or with STO-3G basis sets were found to be qualitatively identical although the atomic net charges differ considerably in absolute value. In contrast to one-electron properties, it was found that isodesmic reaction energies for reactions involving bond breakage on the ring seem to be very basis-set dependent.

A more detailed study of substituent effects was carried out allowing a unified Taft-type dual regression equation to be obtained for the π-HOMO energy which included para, meta, and ortho isomers. An analysis of the additivity of net charge donations by the substituents to the ring showed that the larger deviations from additivity characteristic of ortho substituents are found primarily in the σ-charge distribution, and that deviations were small and not dependent on isomer type for the π electrons. This suggests it should be possible to find unified regression equations for properties which derive primarily from the π-electron charge distribution. It should be noted, however, that most of the substituents studied in this work are σ-electron withdrawing so that the nonadditivity effects arise from the mutual repulsion of excess negative charge on the substituents when bound to the ring. Moreover, since the substituents are relatively small, steric effects are probably not very important.

Structural Analysis of Methyltin(IV) Polymers by Solid-State ¹³C NMR Spectroscopy

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Abstract: High-resolution solid-state ¹³C NMR analysis of 11 crystalline and amorphous polymeric methyltin(IV)s is described. Multiple Sn–methyl resonances observed for linear polymeric trimethyltin acetate and trimethylstannol indicate hindered rotation of the trigonal-planar Me_3Sn group in the crystal lattice. $|^1J(^{119}Sn,^{13}C)|$ values ranging from 470 to 1160 Hz were observed for most of the polymers examined. The magnitude of J of the amorphous polymers methylstannonic acid and bis(trimethyltin) carbonate provides new insight into their bonding and structure. Using an empirical relationship of $|^1J(^{119}Sn,^{13}C)|$ to the Me–Sn–Me angle, an angle of 135° is estimated for microcrystalline, intractable dimethyltin oxide. Chemically bound abundant NMR-active nuclei (^{19}F, $^{35,37}Cl$, ^{14}N) in the methyltin(IV) solids cause substantial line-broadening that may obscure the $^{117,119}Sn$ satellites.

Recently we described[2] the narrow lines that can be obtained in routine cross-polarization magic angle spinning (CPMAS) ¹³C NMR experiments with crystalline methyltin(IV) solids. For example, methyltin(IV) resonances less than 0.5 ppm apart have been resolved at 15.08 MHz, and the ^{117}Sn and ^{119}Sn satellites (both spin-$^1/_2$, natural abundances 7.6, 8.6%, respectively) are also evident in most spectra. We have investigated the dependence

of these NMR parameters on molecular structure by systematically examining X-ray characterized methyltin(IV) solids and found[2] that slight differences in the environment of methyls bonded to the same Sn can give rise to multiple, well-separated resonances. Further, the magnitude of $^1J(^{119}Sn,^{13}C)$, $|J|$, is linearly related[3] to the Me–Sn–Me bond angle, θ, in tetra-, penta-, and hexacoordinated di-, tri-, and tetramethyltin(IV)s: $|J|/\text{Hz} = 11.4(\theta) - 875$. This empirical relationship provides a sensitive probe of the structure of uncharacterized methyltin(IV) solids and of methyltin(IV)s in solution.

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