Substituent Effects on the Ring Proton Splitting in the Electron Spin Resonance Spectra of Some Tetrasubstituted Benzenes

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Abstract: The signs of the proton splitting constants ($a_{CH}{}^{H}$) in 18 previously reported radicals derived from 1,4(R)-2,5(R')-tetrasubstituted benzenes have been assigned by comparison with the known signs of 12 other similarly substituted radicals. The magnitudes of $a_{CH}{}^{H}$ from all 30 compounds have been correlated with the substituent constant $\sigma_p{}^+$ values, the only exception being for the 2,5-difluorobenzosemiquinone radical. When R and R′ are not too unequal in electron donating ability, $a_{CH}{}^{H}$ is shown to be sensitive to effects of solvent and/or temperature; this fact explains the previously reported solvent effects on several of the radicals. Predictions have also been made of $a_{CH}{}^{H}$ for a number of unreported radicals.

In a recent paper[1] the signs and magnitudes of the ring proton splittings in a series of 1,2,4,5-tetrasubstituted benzene cation radicals were investigated. It was noted that the sign and magnitude of this splitting should be sensitive to the electronic effects of the substituents. There are several other reports in the literature involving tetrasubstituted benzene radical ions, all of which have left the sign of the proton splittings undetermined. It is the purpose of this paper to show that when an appropriate sign is given to these splittings all of the results fall into a coherent pattern which is related to the electronic effects of the substituents. The results are then able to explain the fact that certain radicals show large solvent effects whereas others do not. They are also able to rationalize the large spin density changes which occur with certain substituents.

Previous treatments of substituent effects on ESR spectra have been recently reviewed[2] and in only one case[3] (that of the substituted N,N-dimethylanilinium cation radicals) has a substantial change in spin density distribution been observed in the aromatic portion of the radical.

General Considerations

The effect of substituents on the spin density distribution in tetrasubstituted benzene cation radicals can be most simply visualized in terms of the Hückel molecular orbitals of benzene. For 1,4-disubstituted benzene cation radicals containing two equally electron-donating substituents the unpaired electron is found in the highest occupied symmetric molecular orbital (Figure 1) which has a spin density of $\frac{1}{12}$ at the unsubstituted positions. This corresponds roughly to a splitting for the ring protons of ca. −2.25 G ($Q_{CH}{}^{H} = -27$ G) which is very close to that observed for a number of disubstituted benzenes (see the far right hand column of Table I). On the other hand for a 1,2,4,5-tetrasubstituted benzene cation radical containing four equally electron-donating substituents the unpaired electron is found in the highest occupied antisymmetric orbital containing a node (in the Hückel approximation) at the unsubstituted position, thereby predicting zero splitting for the ring protons. However, it is anticipated that electron correlation effects will result in a small negative spin density at the unsubstituted position, hence giving rise to a small positive splitting constant of ca. 0.70 to 0.96 for the ring proton. (See the entries on the diagonal of Table I.) For a 1,2,4,5-tetrasubstituted benzene cation radical containing different substituents in 1,4 and 2,5 positions, the orbital containing the unpaired electron may have a spin density distribution somewhere in between the two extremes given above. For a situation in which one pair of substituents are much more electron donating than the other the spin density distribution will tend toward that in the symmetric orbital, whereas when the substituents become more nearly equal in electron-donating ability the spin density distribution will tend toward that in the antisymmetric orbital. The ring proton splitting may therefore vary between −2.25 and +0.80 G depending on the relative electron-donating abilities of the two substituents. These considerations only strictly apply to substituents which act as small perturbations on the benzene-like orbitals; however, the results which follow illustrate the utility of this approach.

Results

A major difficulty in applying these considerations is that one normally cannot directly determine the sign of ring proton splitting constants from the ESR spectrum. However, in a recent paper[1] we have shown that the sign can be obtained indirectly from observations of the temperature coefficients and line width asymmetries of the proton splitting constant and from the proton–deuterium splitting constant ratio. Thus the sign of the splitting was obtained for the 12 compounds shown without parentheses in Table I.

The other entries in Table I have been obtained from the literature.[4-16] The arrangement of the table is such that the 1,4 substituents are shown in the left-hand column and the 2,5 substituents in the top row. The substituents are arranged in order of decreasing electron-donating ability as measured by $\sigma_p{}^+$ parameters.[17] This arrangement itself is one factor in the assignment of a sign to the ring proton splitting constant.

The largest body of data in the literature is found for the p-benzosemiquinone anion radicals (first row of data). It should be pointed out, however, that the orbital containing the unpaired electron is the same as that for the cation radicals in the table. This can be rationalized by thinking of a benzosemiquinone as a benzene cation radical substituted by two O⁻ substituents (i.e., structure I). Since the O⁻ substituent is very sensitive to solvent effects (see later), the results in Table I, row 1, are all given for the similar solvent systems H_2O, aq EtOH, or aq MeOH. All the other results for the cation radicals in Table I are given for nitrometh-

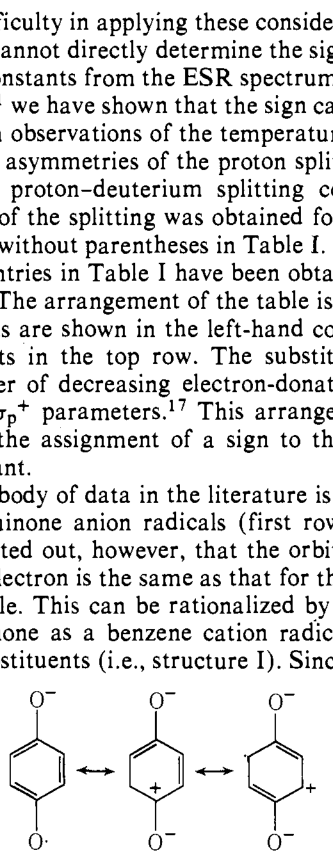

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Table I. The Ring Proton Splitting Constants for Some Tetrasubstituted Benzene Cation Radicals[a]

1,4 substituents	2,5 substituents														
	O^-	$N(Me)_2$	NH_2	NHMe	OH	OMe	OEt	O-*i*-Pr	SMe	SEt	Me	*t*-Bu	F	Cl	None
O^{-b}	(+)0.79		(+)0.75	(+)0.77		(−)0.26	(−)0.35		(−)0.87	(−)0.95	(−)1.80	(−)2.13	(−)1.41	(−)2.16	(−)2.35
$N(Me)_2$											(−)1.38				(−)1.98
NH_2											(−)1.71	(−)2.10			(−)2.13
NHMe															
OH					+0.95	+0.90					−0.91	−1.43			(−)2.25
OMe						+0.85					−0.57	−1.02			(−)2.26
OEt							+0.86		+0.79	+0.77	−0.60	−1.05			(−)2.27
O-*i*-Pr								(+)0.70				−1.06			
SMe									(+)0.71						(−)1.41
SEt															(−)1.40
Me											(+)0.80				
t-Bu															(−)2.10
F															
Cl															
σ_p	−1.00	−0.70	−0.07		−0.36	−0.27	−0.24		−0.05		−0.17	−0.20	0.06	0.23	
σ_p^+		−1.70	−1.30		−0.92	−0.78	−0.73		−0.60		−0.31	−0.26	−0.07	0.11	
σ_R^+		−1.97	−1.67		−1.17	−1.03			−0.75		−0.26		−0.59		

[a] Data taken from ref 1 and 4−16, See text, splitting constants in gauss. [b] In H_2O, aq EtOH or aq MeOH.

ane, nitroethane, or acetonitrile as solvent.

Assignment of the Sign to the Proton Splitting Constants. 2,5-Dihydroxy-1,4-benzosemiquinone Trianion[4] (Tetra O^-). The four equally strong substituents should result in a small positive splitting constant.

2,5-Diamino-1,4-benzosemiquinone.[5] The NH_2 and O^- substituents are believed to be about equal in electron-donating ability as shown by their similar σ_p values and by comparison of the ring proton splittings of 2,5-dimethyl-1,4-benzosemiquinone (−1.80) and 2,5-dimethyl-1,4-diaminobenzene (−1.71). The almost equal effect of the methyl substitution in these two compounds indicates that O^- is slightly more electron donating than NH_2 in these systems. These criteria suggest that the appropriate sign for the ring proton splitting is positive. Since NHMe is of similar strength to NH_2 the sign of the proton splitting is also believed positive in *N,N'*-dimethyl-2,5-diamino-1,4-benzosemiquinone.[6]

2,5-Dimethoxy- and 2,5-Diethoxy-1,4-benzoquinone.[5,7] The small splitting in these two compounds (0.25 and 0.35 G, respectively) might be either positive or negative. The primary reason for assigning a negative sign to the splitting arises from the effect of solvent on the splitting constant (see later).

2,5-Dimethylthio- and 2,5-Diethylthio-1,4-benzoquinone.[6] The magnitude of the splitting (0.87 and 0.95) indicates that if positive the O^- and SMe or SEt substituents are of equal electron-donating ability. This is clearly unlikely so that a negative sign may be assigned.

2,5-Dimethyl- and 2,5-Di-*tert*-butyl-1,4-benzosemiquinone.[6] The weaker electron-donating ability of methyl and *tert*-butyl groups in addition to the magnitude of the splitting strongly indicates that the sign of the proton interaction is negative.

2,5-Difluoro- and 2,5-Dichloro-1,4-benzosemiquinone.[8] The magnitude of the splitting and the σ^+ values of F and Cl indicate that a negative sign is appropriate.

2,5-Dimethyl-*N,N,N',N'*-tetramethyl-*p*-phenylenediamine.[9] Again the magnitude of the splitting implies a negative sign.

2,5-Dimethyl- and 2,5-Di-*tert*-butyl-*p*-phenylenediamine.[9] The magnitude of the splittings and the similarity with those of the benzosemiquinones indicates a negative sign.

1,2,4,5-Tetrahydroxybenzene,[10] 1,2,4,5-Tetraisopropoxybenzene,[13] and 1,2,4,5-Tetramethylbenzene.[16] The magnitudes of the splittings 0.95, 0.71, and 0.80 and the four equal substituents indicate that a positive sign should be assigned in these cases.

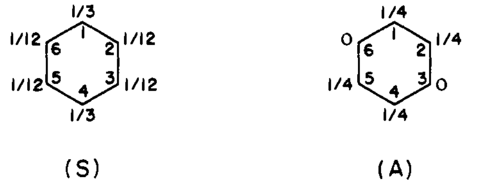

Figure 1.

1,4-Di-*tert*-butyl-2,5-diisopropoxybenzene.[14] By analogy with other di-*tert*-butyldialkoxybenzenes a negative sign is thought to be correct.

1,4-Disubstituted Benzenes. In each case it is predicted that the symmetric orbital is the one occupied by the unpaired electron and this would lead to a negative splitting constant.

Correlations with Substituent Constants

The substituent constants σ_p, σ_p^+, and σ_R^+ are given,[3,17,18] where available, at the bottom of Table I. Good agreement is found between the relative electron-donating abilities of the substituents as predicted from the signs and magnitudes of the splitting constants,[19] and the order predicted from σ^+ values. Thus one finds $O^- \approx NH_2 > OH >$ OMe ≈ OEt ≈ O-*i*-Pr > SMe ≈ SEt > Me > *t*-Bu > Cl. The only major exception to the agreement occurs for fluorine. From the ESR data one predicts that fluorine should fall between SMe and Me in electron-donating ability. Interestingly when one considers the σ_R^+ values of Taft,[3] fluorine is indeed found to fall between SMe and Me, suggesting that in the case of 2,5-difluorobenzosemiquinone resonance interactions play an important part in the structure of this radical.

Plots of σ^+ vs. a_{CH}^H can be constructed for the different series of radicals, the *p*-benzosemiquinones, the 1,4-diethoxybenzenes, and the 1,4-dimethylbenzenes (see Figure 2). The three plots are representative of those expected for strong, intermediate, and weak electron donors. Thus for the strong and weak cases the a_{CH}^H value steadily increases or decreases with increasing σ^+ value of the 2,5 substituent. For the 1,4-diethoxy compounds a_{CH}^H increases, reaches a maximum, and then decreases with increasing σ^+ values.

Table I and Figure 2 enable one to make predictions with

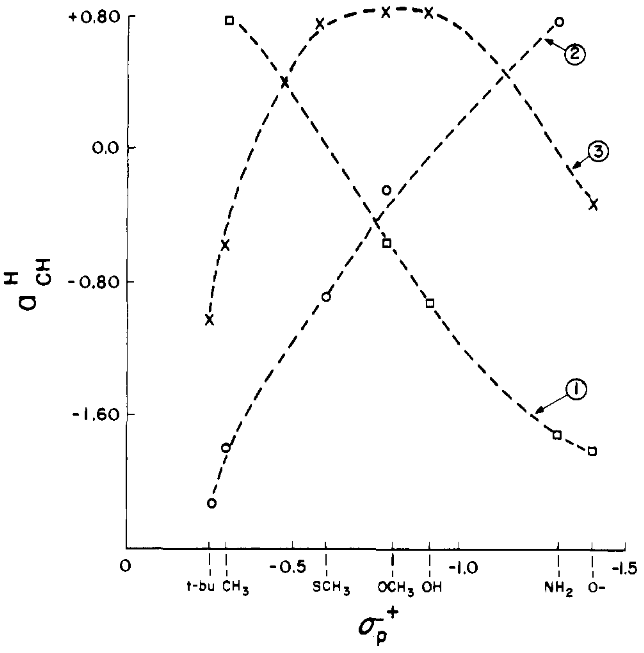

Figure 2. Plots of $a_{\mathrm{CH}}^{\mathrm{H}}$ vs. σ_p^+ for (1) the 2,5-disubstituted 1,4-dimethylbenzenes, (2) the 2,5-disubstituted *p*-benzosemiquinones, and (3) the 2,5-disubstituted 1,4-diethoxybenzenes.

regard to the magnitude of $a_{\mathrm{CH}}^{\mathrm{H}}$ for some missing compounds. In particular one predicts that $a_{\mathrm{CH}}^{\mathrm{H}}$ for 1,4-diamino-2,5-dimethoxybenzene and for 1,4-dimethyl-2,5-dimethylthiobenzene should both be very close to zero. It will be interesting to see if these predictions are realized. In addition from Figure 2 it is indicated that $a_{\mathrm{CH}}^{\mathrm{H}}$ is most sensitive to small changes in electronic efforts (such as might be caused by solvent, temperature, or steric interactions) at intermediate splitting constant values, i.e., between 0.00 and −1.20 G.

Steric Effects. A possible criticism of the above results may be made in terms of the steric interactions in a tetrasubstituted benzene. Specifically one needs to question whether the electronic effects of the substituent, in the radical form, are being altered by such multiple substitution. Fortunately the ESR analysis of the spectra of many of the compounds enables one to investigate this possibility. Considering first the alkoxy and alkylthio groups, it is known from investigations of the disubstituted compounds that in the radical cations the alkoxy and alkylthio groups are in or very close to the plane of the benzene ring as evidenced by the existence of cis and trans isomers.[11,12] Out-of-plane movements of these groups in the tetrasubstituted benzenes would manifest themselves in greatly reduced splitting constants and large temperature variations. For those compounds previously investigated in detail[1] these effects were not observed and the alkoxy and alkylthio groups are apparently still in the plane of the benzene ring. In many instances this may be achieved by a rotation of the group away from the additional substituents, so that for example in the 2,5-dimethoxy-1,4-dimethylbenzene a trans conformation is preferred. Deviations from coplanarity are more likely to occur for the alkoxy and alkylthiobenzosemiquinones. Comparing the methoxyl splitting constants of 3.35, 2.25, and 0.99 G for dimethoxybenzene (DMB), tetramethoxybenzene (TMB), and 2,5-dimethoxybenzosemiquinone, assuming a relationship of the form $a_{\mathrm{OCH_3}}^{\mathrm{H}} = Q_{\mathrm{OCH_3}}^{\mathrm{H}} \rho_{\mathrm{O}}^{\pi}$ and using the spin densities from the simple Hückel MO's, one determines $Q_{\mathrm{OCH_3}}^{\mathrm{H}}$ for DMB and TMB to be 10.15 and 9.00, respectively. This then requires

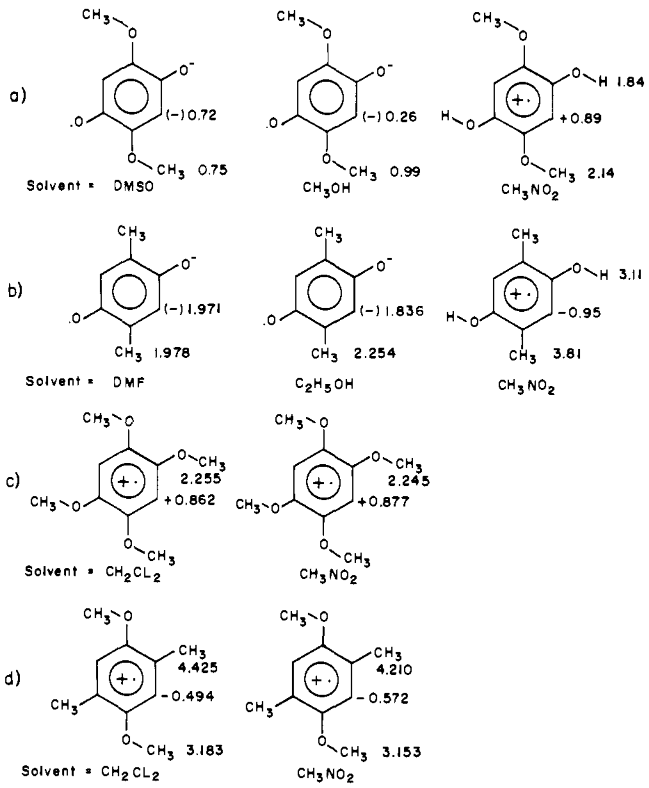

Figure 3. The effect of solvent on the ESR splitting constants of (a) 2,5-dimethoxy-*p*-benzosemiquinone and hydroquinone, (b) 2,5-dimethylbenzosemiquinone and hydroquinone, (c) 1,2,4,5-tetramethoxybenzene, and (d) 1,4-dimethyl-2,5-dimethoxybenzene.

$a_{\mathrm{OCH_3}}^{\mathrm{H}}$ for 2,5-dimethoxybenzosemiquinone to fall somewhere between 0.75 and 2.25, which it apparently does; one therefore concludes that the configuration of the methoxyl group in this compound is not much different from the other methoxyl compounds studied. Similar arguments can be made for the alkylthiobenzosemiquinones.

Steric effects of methyl and *tert*-butyl groups again appear minimal when the other substituents are OR, SR, or O^-, the OR and SR groups simply rotating away from the alkyl group.

Steric effects do appear to be important in the *N*,*N*-dialkyl- and diamino-substituted compounds, since in this case on the introduction of additional substituents the only way the steric strain can be reduced is by rotation of the *N*-alkyl or amino groups out of the plane of the benzene ring. This is manifested by a change in the splitting constants of the nitrogen and the NH or NCH_3 protons. The effects are not too large in the 2,5-dimethyl- and 2,5-di-*tert*-butyl-*p*-phenylenediamine[9] the nitrogen splitting constant being 4.88 and 4.99 G, respectively, as compared with 5.29 G in the unsubstituted compound. A somewhat larger drop occurs from *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (a_{N} = 7.02 G) to 2,5-dimethyl-*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (a_{N} = 6.44 G). The nitrogen splitting for 2,5-diamino-*p*-benzosemiquinone in aq EtOH[5] of 2.6 G is in the right range for a planar NH_2 group. It therefore appears that while steric effects are perhaps somewhat more important for diamino substituents, the results are not substantially affected by these effects and our general observations are therefore unaffected.

Solvent Effects. The results in Table I for the *p*-benzosemiquinones are those reported in aqueous or aqueous-alcohol mixtures. Changing solvent for these radicals can sometimes result in large changes in the splitting constants. The compounds which have been studied in detail by other workers include 2,5-diamino-,[5] 2,5-*N*-methylamino-,[7] 2,5-dimethoxy-,[5] and 2,5-dimethyl-*p*-benzosemiquinone.[20] The changes which occur seem to parallel the protic nature of the solvent. We have previously noted in our studies of the ^{17}O and ^{13}C splitting constants in hydroquinone[21] that the splittings vary smoothly from *p*-benzosemiquinone in dimethyl sulfoxide to *p*-benzosemiquinone in H_2O, to hydroquinone in nitromethane. A similar trend is to be expected for the substituted *p*-benzosemiquinones. For example, the results for 2,5-dimethoxy-*p*-benzosemiquinone should show a smooth behavior on comparing the splittings in DMSO and methanol with those of 2,5-dimethoxyhydroquinone. Figure 3 shows the experimental results.[1,5] The sign of $a_{CH}{}^{H}$ for 2,5-dimethoxyhydroquinone is known to be positive;[1] the sign for 2,5-dimethoxybenzosemiquinone is unknown. However, in DMSO for $a_{CH}{}^{H}$ to be positive would imply almost equal electron-donating abilities of O^- and OCH_3 and in addition the magnitude of $a_{CH}{}^{H}$ would not be expected to change on going to methanol. Clearly the sign in DMSO must be negative. In methanol the sign could be positive or negative without disturbing our previous statements. However, Ackermann[5] has measured $a_{CH}{}^{H}$ in mixed solvents. If the sign of $a_{CH}{}^{H}$ were different in DMSO and CH_3OH, then one would expect in mixed solutions that $a_{CH}{}^{H}$ would decrease to zero and then increase as the fraction of DMSO were increased. According to Ackermann's results this is not the case; $a_{CH}{}^{H}$ increases smoothly from 0.22 G in H_2O to 0.72 G in DMSO as the fraction of DMSO is increased.[5] This confirms that the sign of $a_{CH}{}^{H}$ is the same in both solvents and should therefore be negative. In addition as the value of $a_{CH}{}^{H}$ becomes more positive, the value of the methoxyl splitting constant also increases. This corresponds to a greater contribution of the antisymmetric orbital to the electronic structure.

Similar trends have also been noted for the 2,5-dimethylbenzosemiquinone and 2,5-dimethylhydroquinone radicals[22] (Figure 3b). In this case $a_{CH}{}^{H}$ is known to be negative for 2,5-dimethylhydroquinone[1] and therefore must also be negative for 2,5-dimethylbenzosemiquinone. The change in the splitting constants for 2,5-dimethylbenzosemiquinone in DMF and CH_3CH_2OH is much smaller than for 2,5-dimethoxybenzosemiquinone due to the large difference in electron-donating ability between O^- and CH_3 groups. A large change in the splitting constant is noted for the hydroquinone since OH and CH_3 are now much closer in electron-donating ability. Again $a_{CH}{}^{H}$ becomes more positive along the series as $a_{CH_3}{}^{H}$ also becomes more positive, indicating the larger contribution of the antisymmetric orbital.

These results indicate that $a_{CH}{}^{H}$ is most sensitive to small changes in electronic substituent effects when the two substituent groups are sufficiently different in electron-donating ability so that $a_{CH}{}^{H}$ falls somewhere in the range +0.20 to −1.00 G. To further test this proposal the solvent effects on the splitting constants of 1,2,4,5-tetramethoxybenzene and 1,4-dimethyl-2,5-dimethoxybenzene were measured in methylene chloride and nitromethene (Figures 3c and 3d). The results in fact substantiate the proposal since 1,2,4,5-tetramethoxybenzene is relatively insensitive to the changes in solvent whereas the 1,4-dimethyl-2,5-dimethoxybenzene shows a 4.8% decrease in the methyl splitting constant and a 16% increase in the ring proton splitting constant.

The results also indicate that our previous observations[1] on the effect of deuterium substitution for the CH protons in 1,4-dimethyl-2,5-dimethoxybenzene may have to be slightly modified. Thus the measured $a_{CH}{}^{H}/a_{CD}{}^{D}$ ratio of 6.21 ± 0.05 may not agree with the calculated ratio of 6.00 ± 0.06 due to the different electronic effect of a deuterium atom as opposed to a proton.

Conclusions

The assignment of signs to the CH-proton splitting constants of a number of tetrasubstituted benzenes by comparison with the known signs in some other similarly substituted radicals enables one to correlate the magnitude of the CH-splitting constant to the known substituent constants. Steric effects are shown to be unimportant for most of the compounds studied. However, solvent effects are important particularly for those compounds with ring-splitting constants between +0.20 and −1.00 G. This fact suggests that the study of solvent effects on $a_{CH}{}^{H}$ may be a useful method of ascertaining the effect of solvent on the substituent parameter σ^+ for certain groups. Predictions have also been made with regard to the value $a_{CH}{}^{H}$ for other unreported tetrasubstituted benzenes.

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