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MOLECULAR ORBITAL CALCULATIONS ON ORGANIC MOLECULES—II

CNDO SOLUTIONS FOR POLYMETHYLBENZENES AND BENZENONIUM IONS

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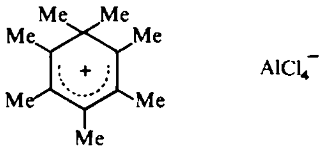
Abstract—Binding energies, charge distributions and orbital energies have been calculated for the series of polymethylbenzenes and all the benzenonium ions derived from them by protonation, using the CNDO method. Reactivities correlate well with calculated energies of protonation; charge-transfer excitation energies correlate best with energies of the highest filled MOs.

In continuation of our programme[1] of applying the CNDO (Complete Neglect of Differential Overlap) method[2] in the study of chemical reactivity we now report solutions for the series of polymethylbenzenes and for the benzenonium ions derived from them by protonation at all available positions. Most applications of molecular orbital theory to aromatic reactivity have, perforce, been used to examine polycyclic molecules since this type of structural variation is amenable to Hückel and related calculations.[3] In this field it has recently been shown that the CNDO method is superior to less sophisticated approaches[4] for the correlation of reactivity. A further advantage prompted the present work namely that formally non-conjugated groups (e.g. methyl) may be incorporated in the calculations without recourse to semi-empirical parameters; the coordinates of the system alone provide the basis of the computation. The polymethylbenzenes are, furthermore, a convenient series of compounds for study since ample rate data is available for comparison. The most familiar type of reaction, electrophilic substitution, is generally believed to proceed via a benzenonium ion for which MO solutions may also be obtained. One may therefore attempt to answer the question from a theoretical viewpoint, as to whether the transition state for electrophilic substitution most resembles the aromatic species or the benzenonium ion, according to whether experimental rates correlate with energies of the former or the latter. This question will now be examined.

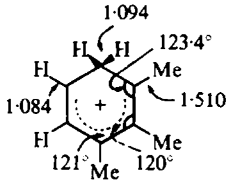
CALCULATIONS AND RESULTS

The method of calculation was as discussed previously.[1] Bond lengths and angles of the aromatic species were taken where possible from available results of X-ray diffraction and electron diffraction studies. The only benzenonium ion for which a full structure is known is heptamethylbenzenonium tetrachloroaluminate, I.[5] whose geometry formed the basis of the coordinates used for all the benzenonium ions. The energies were further minimised with respect to the internal bond angles assuming a planar conformation and the values, as shown in II used throughout. The calculated binding energies are shown in Table 1 and dipole moments in Table 3. In Table 2 is given the computed charge distribution on each carbon atom.

I



II

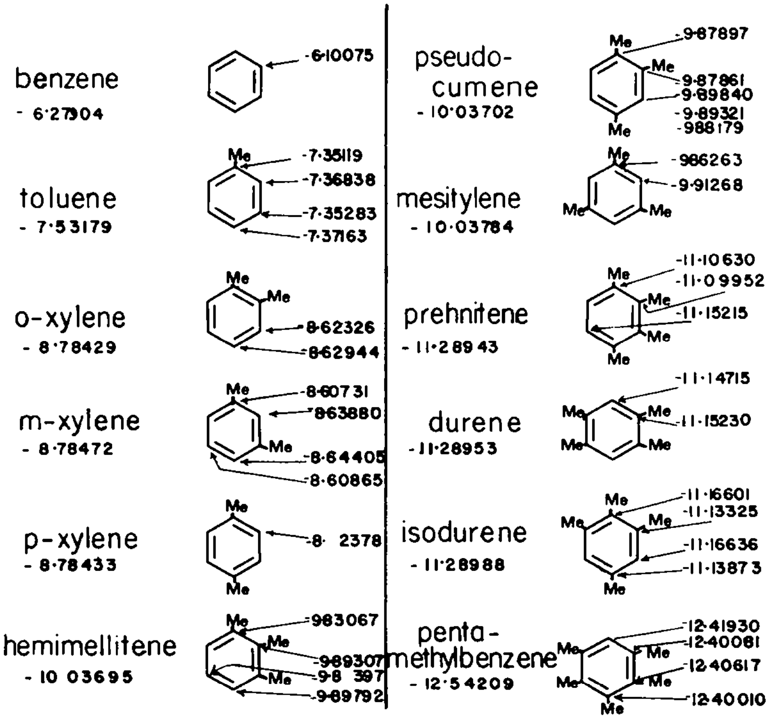


DISCUSSION

Binding energies

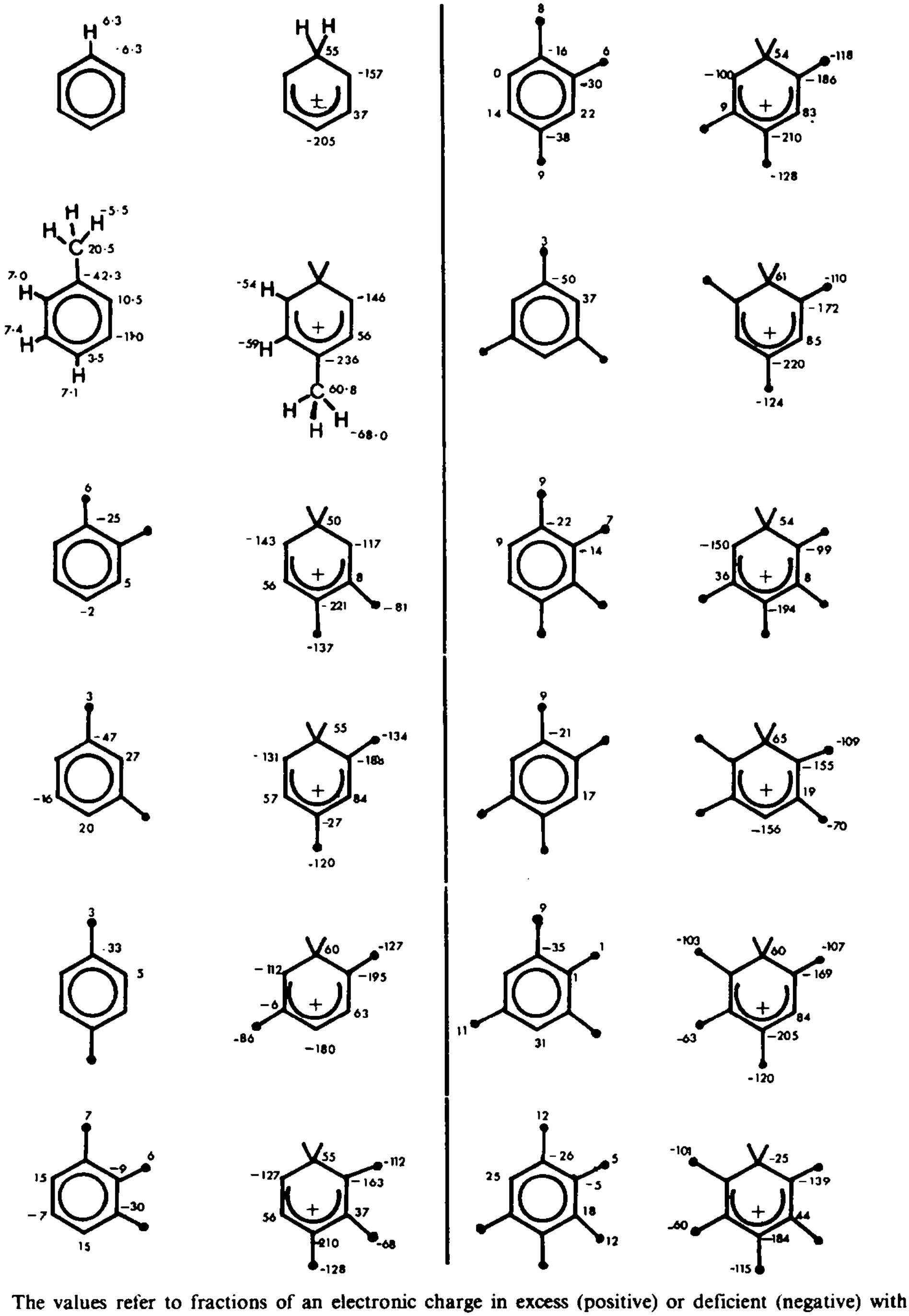
The correlation between calculated binding energies and experimental heats of formation of the aromatic molecules is shown in Fig. 1. Since both are, to a first approximation a linear function of the numbers and types of atoms present this is not a very sensitive test. It is seen that, whereas there is agreement on the stability orders for the dimethyl- and trimethylbenzenes, for instance, the experimental energy

Table 1. Calculated binding energies (A.U.) of polymethylbenzenes and benzenonium ions. The values to the right of the formulae refer to the benzenonium ions protonation being at the position indicated by the arrow



benzene	- 6·27304	-6·10075
toluene	- 7·53179	-7·35119 -7·36838 -7·35283 -7·37163
o-xylene	- 8·78429	-8·62326 -8·62944
m-xylene	- 8·78472	-8·60731 -863880 -8·64405 -8·60865
p-xylene	- 8·78433	-8· 2378
hemimellitene	- 10 03695	-983067 -9·89307 -9·8 397 -9·89792
pseudo-cumene	- 10·03702	-9·87897 -9·87861 -9·89840 -9·89321 -988179
mesitylene	- 10·03784	-986263 -9·91268
prehnitene	- 11·28943	-11·10630 -11·09952 -11·15215
durene	- 11·28953	-11·14715 -11·15230
isodurene	- 11·28988	-11·16601 -11·13325 -11·16636 -11·13873
penta-methylbenzene	- 12·54209	-12·41930 -12·40081 -12·40617 -12·40010

TABLE 2. CALCULATED EXCESS ELECTRON DENSITIES ON POLYMETHYLBENZENES AND BENZENONIUM IONS. (10^3 ELECTRONIC UNITS).



The values refer to fractions of an electronic charge in excess (positive) or deficient (negative) with respect to the normal complement of valence electrons (carbon, four; hydrogen, one). The charge densities apply to carbon atoms except where hydrogen atoms are explicitly marked, and to methyl groups as a whole (denoted —●).

TABLE 3. CALCULATED AND OBSERVED DIPOLE MOMENTS OF POLYMETHYLBENZENES.

Polymethyl-benzene	dipole moment (D) calculated	dipole moment (D) observed
—	0	0
1	0·194	0·43
1.2	0·308	0·50–0·58
1.3	0·197	0·30–0·36
1.4	0	0
1.2.3	0·347	0·56
1.2.4	0·161	0·30
1.3.5	0	0
1.2.3.4	0·296	—
1.2.4.5	0	0
1.2.3.5	0·147	—
1.2.3.4.5	0·155	—

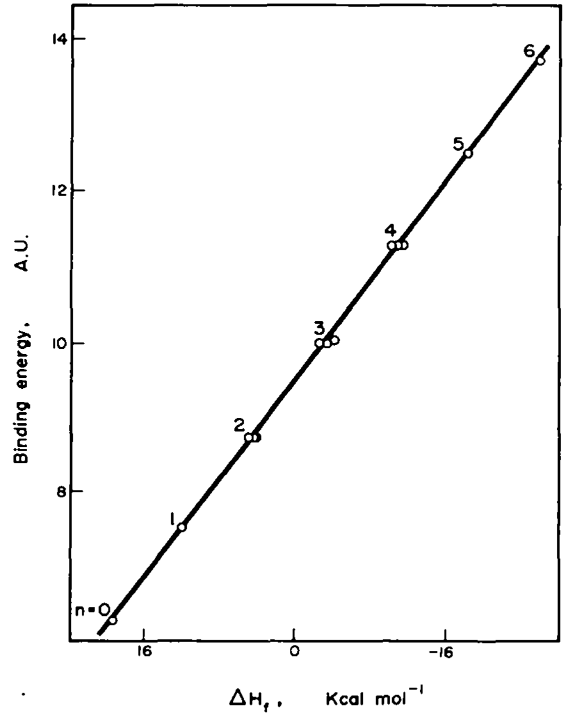


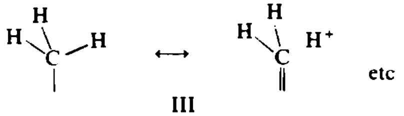
FIG. 1. Relation between experimental heats of formation and calculated binding energies for polymethylbenzenes, $C_6Me_nH_{(6-n)}$

differences are underestimated[6] by the calculations, probably due to neglect of nonbonding interactions between neighbouring methyls to some extent. It is predicted that protonation at carbon bearing hydrogen is energetically more favourable than at one bearing methyl, attesting to the charge-stabilising effect of the methyl group on the pentadiene cation residue.

Charge densities

Dipole moments are, on the whole, predicted in the correct order for isomeric molecules[7] and are zero for all centrosymmetric species. The magnitudes of the calculated moments are underestimated by a reasonably constant factor, 0·63. Those of the benzenonium ions (not shown) fall within the range 5–7 D which seems not unreasonable though cannot be checked against experimental data.

Charge density distributions on carbon atoms and on methyl groups as a whole for the aromatic molecules and for the most stable of the benzenonium ions derived from each are shown in Table 2. It emerges from these figures that methyl-bearing carbons in the aromatic hydrocarbons tend to be slightly electron-deficient; hydrogen-bearing carbon *ortho-* and *para-* to them and methyl groups are of rather high electron density and those *meta-*, slightly low. It is predicted that the methyl group is the negative end of the local dipole. A very different pattern of electron distribution emerges upon protonation of an aromatic molecule. Much larger disparities of charge are found, a considerable amount of charge being transferred from a methyl group to the conjugated part of the ring. This amounts to 100–140 × 10^{-3} electronic units from a 2- or 4-methyl and 60–80 × 10^{-3} units from a 3-methyl group. These figures are obtained by summation of the charges on carbon and hydrogen atoms of the methyl group. As found for simple cations,[1] the positive charge is resident mainly on the hydrogen. These figures are in accordance with chemical experience and with the valence bond formulation of hyperconjugation, III, by the methyl group. The



III

centres of electron deficiency in the benzenonium ions are at 2,4 and 6 as indicated, though in more extreme form, by Hückel MO theory.

Reactivity correlation

Three distinct approaches have been used to correlate the reactivities of aromatic molecules with molecular orbital parameters at various levels of sophistication.[3,9] The Isolated Molecule approach seeks a correlation between rates of attack of an electrophilic reagent and centres of high electron density in the aromatic molecules. The Frontier Orbital treatment emphasises the importance of the energies of the highest filled orbitals of the aromatic molecules (with which the reagent interacts). The Localization Energy method employs the change in π-energy between the aromatic molecule and the benzenonium ion. The present data enables all three to be compared. The best rate data for comparative purposes would be of a reaction in which steric interactions between the reagents are relatively unimportant. It is probable that acid-catalysed proton exchange (e.g. in CF_3COOH) comes closest to this ideal.[10] It would be desirable to have individual rates or partial rate factors for

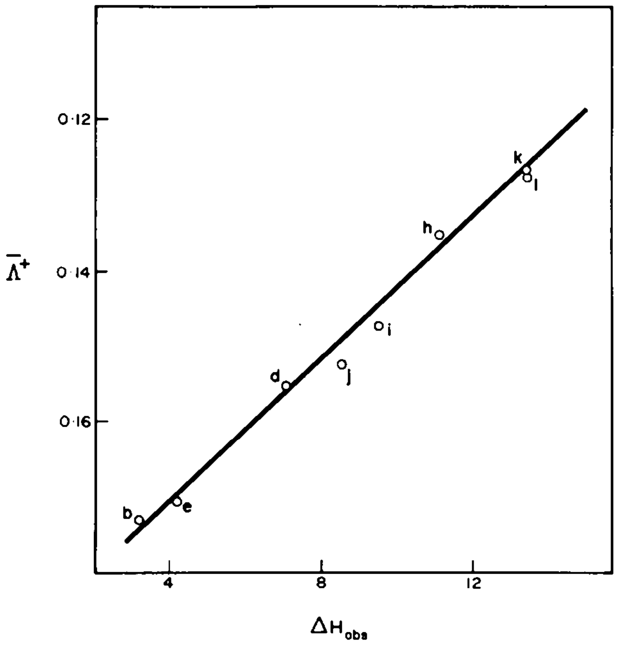


FIG 2. Relation between experimental and calculated heats of protonation of polymethylbenzenes

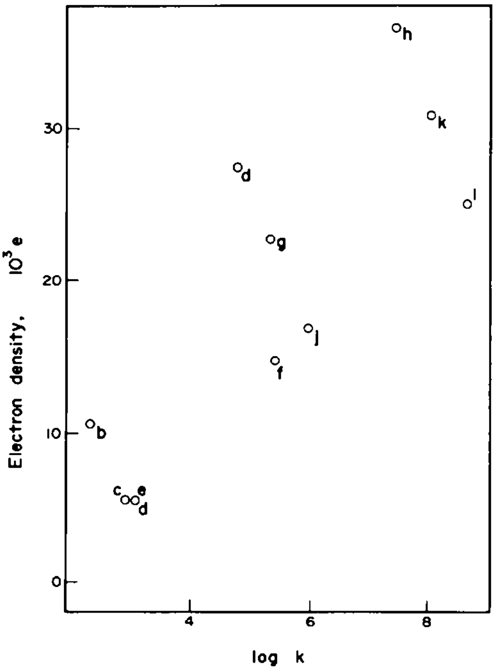
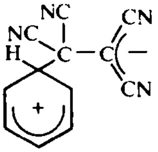


FIG 3. Relation between proton exchange rates and maximum charge densities on polymethylbenzenes

Table 4 CNDO Localization energies (Λ^+) and mean localization energies ($\bar{\Lambda}^+$) for polymethylbenzenes.

Polymethylbenzene	Position	Λ^+	$\bar{\Lambda}^+$
None	all	0·1782	
1	1	0·1806	
	2	0·1634	
	3	0·1790	0·1633
	4	0·1602	
1.2	1 (2)		
	3 (6)	0·1610	0·1577
	4 (5)	0·1548	
1.3	1 (3)	0·1774	
	2	0·1459	01·454
	4 (6)	0·1407	
	5	0·1761	
1.4	2 (3.5.6)	0·1605	0·1605
1.2.3	1 (3)	0·2063	
	2	0·1439	
	4 (6)	0·1390	0·1426
	5	0·1530	
1.2.4	3	0·1438	
	5	0·1386	0·1458
	6	0·1584	
1.3.5	1 (3.5)	0·1752	
	2 (4.6)	0·1252	0·1252
1.2.3.4	1 (4)	0·1831	
	2 (3)	0·1899	
	5 (6)	0·1374	0·1374
1.2.4.5	1 (2.4.5)	0·1372	
	3 (6)	0·1424	0·1424
1.2.3.5	1 (3)	0·1566	
	2	0·1229	
	4 (6)	0·1235	0·1235
	5	0·1512	
1.2.3.4.5	1 (5)	0·1359	
	2 (4)	0·1359	
	3	0·1463	
	5	0·1228	0·1228
1.2.3.4.5.6	all	0·1522	0·1522

each position of each methylbenzene. This is only available for toluene and one or two of the xylenes under different conditions.[11] Total rates are, however, known for the whole series of polymethylbenzenes.[12]



IV

Isolated molecule method. The relation between total rates of proton exchange and electron densities at the position of highest electron density, corrected statistically, are shown in Fig. 3. The correlation is extremely bad and is not significantly improved if contributions due to other, less reactive positions are weighed in. There is none the less a tendency for the more reactive aromatic molecules to possess a position which bears a high electron density and this may have a secondary influence on rates.

Frontal orbital treatment. A plot of log k for proton exchange against energies of the highest filled MO is equally poor and shows no more than a trend in the positive direction. The apparently more satisfactory relationship of the highest filled orbitals with charge-transfer phenomena (charge transfer spectra) lends confidence to the conclusion that the frontier orbital is not the major influence on rates.

Localization energy method. We define the CNDO proton affinity, Λ^+, as

$$\Lambda^+ = (E_{\mathrm{ArH}} - E_{\mathrm{ArH_2^+}})$$

where E_{ArH} and $E_{\mathrm{ArH_2^+}}$ are the calculated binding energies of the aromatic species and the derived benzenonium ion, respectively. Using the binding energies in Table 1 we calculated values of Λ^+ appropriate to each position of each of the polymethylbenzenes (Table 4). The values are positive, the smaller the magnitude the more reactive the position denoted. From these figures, a moderately good correlation exists between proton exchange rates (all positions) and the value of for the most reactive position which is expressed by eq. 1.

$$\log k = 26{\cdot}9 - (150{\cdot}0\,\Lambda^+_{\mathrm{min}}) \tag{1}$$

This would be appropriate if only the most reactive positions were undergoing reaction, which is obviously not the case with some of the aromatic molecules e.g. toluene in which reaction at positions 2,4 and 6 are contributing to the measured rate. A significantly improved correlation is achieved by using weighted mean proton affinities, $\bar{\Lambda}^+$, obtained by summation of the rates at every hydrogen-bearing carbon in the aromatic molecule obtained by application of eq. 1 and reiteration (twice) until no further change in values occurred. Values of $\bar{\Lambda}^+$ are given in Table 4 and the correlation with rate data shown in Fig. 4. The best linear fit is expressed by eq. 2.

$$\log k = 25{\cdot}61 - (140{\cdot}3\,\bar{\Lambda}^+) \tag{2}$$

which is a linear free energy equation. The correlation is very satisfactory, correct orders of reactivity of isomers is predicted and the exceptional reactivity of *m*-xylene and of mesitylene is in agreement with theory. This approach is clearly superior to the other methods for correlating rates from which we conclude that the transition state for electrophilic substitution closely resembles a benzenonium ion. Equally satisfactory correlations between rates of bromination[13] and mercuration[14] (Fig. 5) are also obtained. It will be noticed that the experimental rates for mesitylene (h), isodurene (k) and pentamethylbenzene (l) fall somewhat short of predicted values. These would be species in which steric hindrance to a bulky reagent would be expected to be most severe since their reactive positions are flanked by two methyl groups.

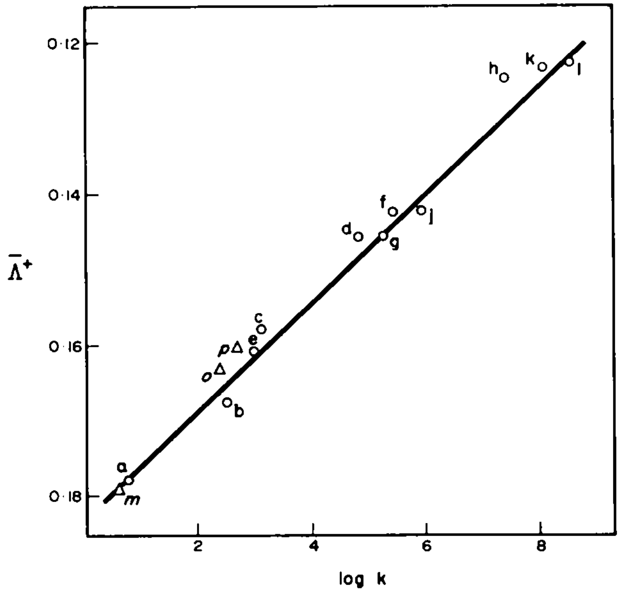


FIG 4. Relation between mean localization energies. $\overline{\Lambda}^+$, and rates of proton exchange for polymethylbenzenes

(Letters refer to the following methylbenzenes; a —; b. 1; c. 1.2; d. 1,3; e. 1,4; f. 1.2.3; g. 1.2.4; h. 1.3.5; i. 1.2.3.4; j. 1.2.4.5; k. 1.2.3.5; l. 1,2,3,4,5; n. 1.2.3.4.5.6; *m. o* and *p* refer to the *meta. ortho* and *para* positions of toluene. correlated with the appropriate values of Λ^+.)

The parameter, $\overline{\Lambda}^+$ is a measure of the energy of protonation; Arnett[8] has recently reported enthalpies of protonation for many of the polymethylbenzenes and a good agreement between theory and experimental values is observed (Fig. 2).

Proton affinities for hydrocarbons and some methylated derivatives have also been calculated by the CNDO method by Streitweiser *et al.*[4] and generally found to be in agreement with the present values for the two comparable cases (toluene and *o*-xylene). These workers reported different correlations for a series of aromatic hydrocarbons and for methylated derivatives which may well be a limitation of the calculations. In our case, however, benzene fits well on the correlation for the series of methylated compounds.

The positions of protonation of the di- tri- and tetramethylbenzenes have been determined by direct observations of the benzenonium ions in SbF_5-HF by NMR spectroscopy[19] and in all cases agree with the most stable isomers as predicted by the present calculations.

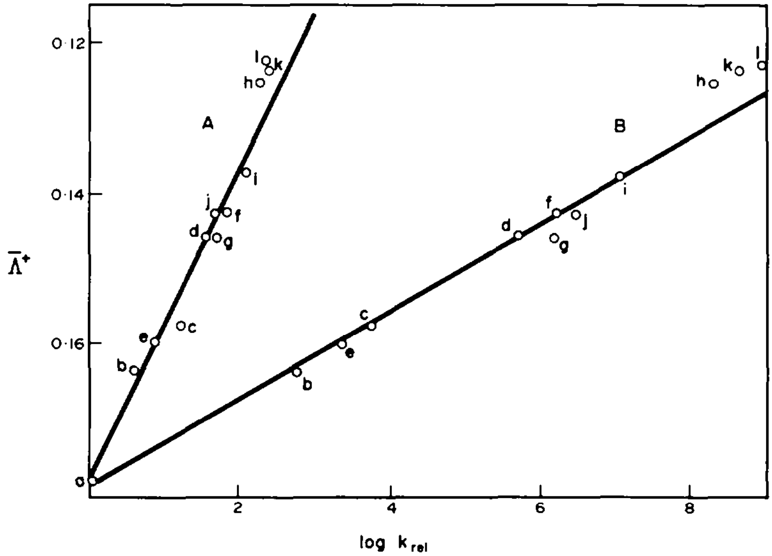


Fig 5. Relation between mean localization energy and rate of mercuration (A) and bromination (B) of polymethylbenzenes. (for key, see Fig. 4.)

Orientation of further substitution

Considerable information is available on the preferred orientation of further substitution in the polymethylbenzenes which, although of a qualitative nature may be used to test reactivity predictions in the absence of more exact data. From eq. 2 and substituting Λ^+ for $\bar{\Lambda}^+$ partial rate factors k_{rel} may be calculated and compared with experimental values. In Table 5 it is shown that remarkably good agreement is obtained bearing in mind that the experimental ratios may not always be determined with accuracy and in any case are known to vary somewhat with conditions.

Methyl migration in benzenonium ions

Migration of methyl groups around the ring during electrophilic substitution (Jacobson Rearrangement) has been known for many years.[15] Recently, Brouwer[16] has observed such processes occurring in long-lived benzenonium ions in a superacid medium using NMR spectroscopy to measure the rates. We may assume that the rearrangements occur to form a more stable benzenonium ion in each case (thermodynamic control) and may therefore predict which rearrangements are feasible by reference to the energies of the most stable benzenonium ions produced from isomeric aromatic molecules. Table 6 sets out examples of predicted and experimental data. The positions at which protonation occur do not seem to have been distinguished; the theory will permit a prediction to be made in each case.

Charge-transfer spectra

The excitation of an electron from a donor molecule such as an aromatic hydrocarbon to an acceptor such as tetracyanoethylene (TCNE) has been shown to be related to the ionisation potential of the donor.[17] There is no evidence that the excited

TABLE 5. ORIENTATION OF FURTHER ELECTROPHILIC SUBSTITUTION IN POLYMETHYLBENZENES

substrate	orientation predicted*	 observed
1	$2 \sim 4 \gg 3$ (40:57:3)	$2 \sim 4 \gg 3$ (42–45:53–56:1)[a]
1.2	$4 > 3$ (88:12)	$4 > 3$[b,c,d,k]
1.3	$4(6) > 2 \gg 5$ $(88:12:10^{-4})$	$4(6) > 2 \gg 5$[f] (77:23:0·002[e])
1.2.3	$4(6) \gg 5$ (99:1)	$4(6) \gg 5$[g]
1.2.4	$5 > 3 \gg 6$ (84:16:0·001)	$5 > 3 \gg 6$[h,i] (75:22:3)

[a] many reactions; R. O. C. Norman and R. Taylor. '*Electrophilic Substitution in Benzenoid Compounds*'. Elsevier, Amsterdam (1965)

[b] chlorination; C. Boyers. *J. Am. Chem. Soc.* **75**. 1989 (1953)

[c] alkylation; O. E. Emerson and L. I. Smith, *Ibid.*, **62**, 141 (1940)

[d] bromination; W. A. Wisansky and J. H. Saunders. *Org. Synth.* **28**, 31 (1948)

[e] chlorination; H. C. Brown and L. M. Stock. *J. Am. Chem. Soc.* **79**. 5175 (1957)

[f] acetylation; R. C. Fuson and H. O. House. *J. Org. Chem.* **18**, 496 (1953)

[g] R. H. Martin, *J. Chem. Soc.* 239 (1943)

[h] chloromethylation; R. D. Lake and B. B. Corson, *J. Org. Chem.* **24**. 1823 (1959)

[i] chloromethylation; C. D. Shacklett and H. A. Smith, *J. Am. Chem. Soc.* **73**. 766 (1951)

[j] bromination; L. I. Smith and O. W. Cass. *Ibid.*. **54**. 1606 (1932)

[k] nitration; K. A. Kobe and P. W. Pritchett. *Ind. Eng. Chem.* **44**, 1398 (1952)

* calculated relative rates in brackets.

TABLE 6. PREDICTED AND OBSERVED METHYL MIGRATIONS IN BENZENONIUM IONS

predicted	observed
1.2 → 1.4 → 1.3	1.2 → 1.3 1.4 → 1.3
1.2.3 → 1.2.4 → 1.3.5	1.2.3 → 1.2.4 → 1.3.5 1.2.3 → 1.3.5
1.2.3.4 → 1.2.4.5 → 1.2.3.5	1.2.3.4 → 1.2.3.5

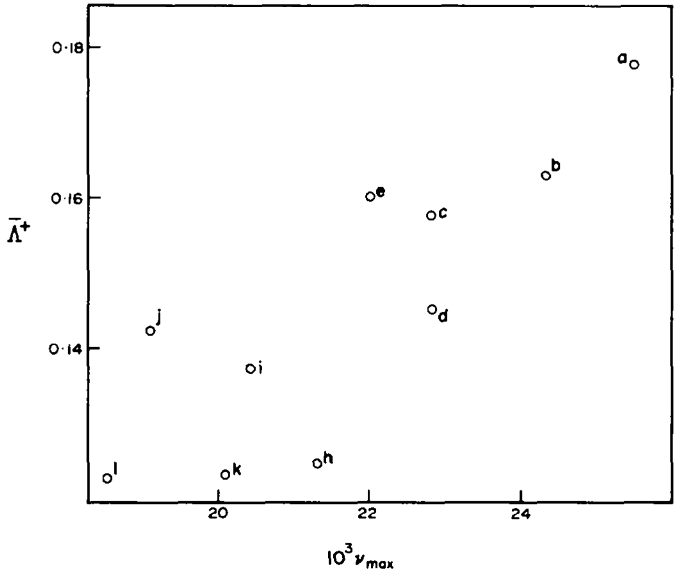


FIG 6. Relation between charge-transfer excitation energies and CNDO localization energies for polymethylbenzenes with TCNE

state of the charge-transfer complex resembles a benzenonium ion (i.e. has a significant amount of character due to IV) and, indeed, the excitation energies for polymethylbenzene-TCNE complexes correlate very poorly with values of $\bar{\Lambda}^+$ or with total charge-densities on the aromatic rings (Fig 6). With the present programme it is not possible to calculate energies of open-shell cation radicals but the loss of an electron from the polymethylbenzene will occur from the highest filled orbital which should be an index of the ease of excitation. Fig. 7 shows that a sensible trend, though

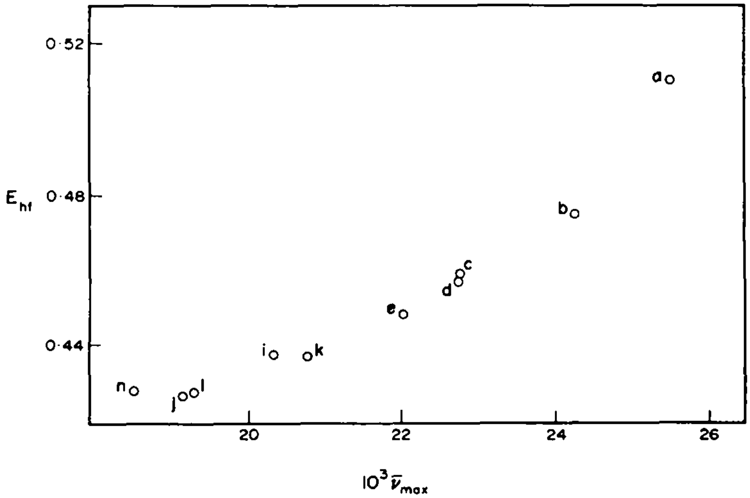


FIG 7. Relation between charge-transfer excitation energies (TCNE) and highest filled orbital energies for polymethylbenzenes

not a linear one, results from a plot of the energies of the highest filled orbitals against the excitation energy for charge-transfer. The correlation is distinctly better than a similar approach, using Hückel orbitals, with polycyclic hydrocarbons.[18]

We conclude that the CNDO method may be used with advantage for the prediction and correlation of reactivity and other physical properties of the polymethylbenzenes. The calculations clearly point to a transition state for electrophilic substitution which resembles a benzenonium ion and point to the importance of the frontier orbitals in charge-transfer excitation. Values of calculated localization energies should prove a useful index of reactivity and may be used to predict for instance, positions of protonation and partial rate factors which are not yet available from experiment.

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