

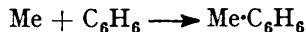
Methyl Affinities of Aromatic Compounds.

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The methyl affinity, recently introduced by Levy and Szwarc to describe reactions of the form $\text{Me} + \text{A} \longrightarrow \text{MeA}$, where A is an aromatic molecule, is shown to be closely related to both the atom-localisation energy and the appropriate free valence of A. The analysis predicts the position of addition of the methyl group, and could be used to estimate values of the methyl affinity which have not yet been measured experimentally.

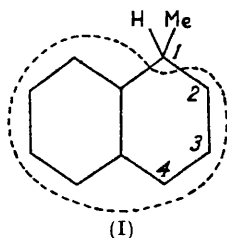
IN a preliminary note, Levy and Szwarc (*J. Chem. Phys.*, 1954, 22, 1621) have introduced the term "methyl affinity" to describe the ease of addition of a methyl group to aromatic compounds. A typical example would be the reaction:



By comparison of the rates of reaction for different molecules, these authors were able to assign a relative methyl affinity to each member of a series of aromatic compounds, most, but not all, of which were pure hydrocarbons. Numerical values for these affinities were given. It is the purpose of the present paper to show that there is a close relation between Levy and Szwarc's methyl affinity values and certain theoretical magnitudes which have already been found useful in discussions of substitution and addition reactions (see, *e.g.*, Coulson, *Research*, 1951, 4, 307; R. D. Brown, *Quart. Rev.*, 1952, 6, 63). The relationships are so close that it would seem to be possible to predict the appropriate affinity values for other aromatic hydrocarbons for which experimental results are not yet

available. At the same time the success of the theory leads to predictions concerning the positions in the aromatic molecules at which the methyl radical attaches itself. In view of the fact that no experimental indications of these positions are reported by Levy and Szwarc, these theoretical considerations may be of some value.

Let us consider the addition of a methyl group to naphthalene. A plausible assumption is that the radical attaches itself to one or other of the carbon atoms. Suppose first that this is position 1 [see (I)]. Then, following the model developed by Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) for substitution reactions, we may suppose that in the final product the bonds around carbon atom $C_{(1)}$ are tetrahedral so that the resonating part of the molecule is now reduced to the region within the dotted lines. The formation of the new bond $C_{(1)}-Me$ requires that one π -electron be removed from the conjugating system. It is a reasonable supposition that the only variable part of the energy of formation of



(I) as compared with attack at other possible positions such as $C_{(2)}$ or with attack on other hydrocarbon molecules, lies in the loss of resonance energy due to this localisation process. We may therefore expect a correlation between the ease of reaction and the localisation energy just described. It is true that this simple picture ignores both the possibility of an activation energy additional to that involved in breaking the resonance system, and also any entropy effects. It is also probable that hyperconjugation from the attached methyl group, acting as an electron donor, will tend to feed electrons into the residual resonating system and so help to stabilise this "odd-alternant" by partly completing its top half-occupied molecular orbital. But none of these complications would be expected to influence the correlation with localisation energy to any great extent.

The Figure, curve *a*, which is constructed from the data in the Table shows how closely the relative methyl affinity of an aromatic hydrocarbon is connected with the localisation energy. In this table we have chosen that particular carbon atom in each of the molecules for which the localisation energy is lowest. And we have first divided Levy and Szwarc's index by the number of equivalent positions of attack, so that the figures in the fifth column of the Table show the affinities per effective atom, scaled in such a way that benzene is unity. Curve *a* in the figure shows that there is an almost linear relation between the localisation energy (calculated in terms of the conventional resonance integral β) and the logarithm of the relative affinity per atom. A logarithmic relation of this kind is just what we should have hoped to find if our interpretation of the reaction were correct.

The second column in the Table shows which are the reactive atoms in each molecule. These are very much what we should have expected. But the agreement leaves little doubt about our conclusions. For example, in naphthalene there are three conceivable positions of attack—atoms 1, 2, and 9. The deviations of the localisation energies appropriate to these three positions from the value to be expected from the curve in the Figure are -0.01β , $+0.17\beta$, and $+0.75\beta$, respectively. If we had chosen any but the first of these three, the theoretical point would be very far off from the line which is drawn in the Figure.

There is a further numerical magnitude with which a correlation might be sought. This is the free valence of the carbon atom under attack. The relative interpretation of free valence and localisation energies has been discussed by Burkitt, Coulson, and Longuet-Higgins (*Trans. Faraday Soc.*, 1951, **47**, 553) and so need not be discussed here. The figures given in that paper being used, the values in the seventh column of the Table are obtained. Again, as curve *b* of the Figure shows, the correlation is excellent. In neither the free valence nor the localisation description is there any inversion in the sequence of values for the molecules listed.

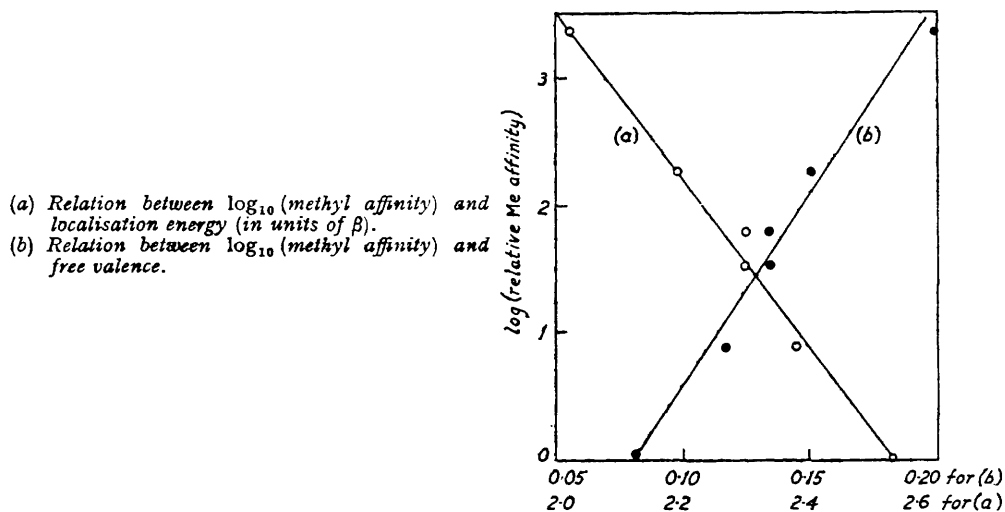
The excellent fit in curves *a* and *b* suggests that calculated localisation energies or free valences could be used to predict methyl affinities for other molecules for which experimental values are not yet available. The equations of the best straight lines in the Figure are :

$$\text{curve } a : \log_{10} r = 16.66 - 6.57 E_a \text{ and curve } b : \log_{10} r = 29.44 F - 2.40$$

where r = relative methyl affinity per effective atom, E_a = localisation energy in units of

β , and F = free valence at the point of addition. It is a simple matter to use these equations to predict methyl affinities, though since the calculation of localisation energies for large molecules soon becomes exceedingly tedious, it might be necessary to resort to the simplified calculations of Dewar (*J. Amer. Chem. Soc.*, 1952, **74**, 3357) and Gore (*J.*, 1954, 3166).

In the above discussion no reference has been made to molecules other than hydrocarbons, but there is no reason in principle why the method should not be extended to cover such heterocyclic molecules as pyridine and quinoline, studied by Levy and Szwarc. The best approach would be along the lines laid down in a similar type of discussion by Longuet-Higgins (*J. Chem. Phys.*, 1950, **18**, 283). We have not reported any such calculations here because they require a knowledge of the correct Coulomb terms for the heteroatom and its neighbours, such as we do not yet possess. The free valence correlation, if



still applicable, would, however, lead us to expect a small, but definite, increase in methyl affinity on passing from a hydrocarbon (*e.g.*, naphthalene) to a related heterocyclic molecule (*e.g.*, quinolone). This is precisely what Levy and Szwarc have found; and a comparison of the localisation energies for benzene and pyridine (Wheland, *loc. cit.*) suggests a similar conclusion. On this basis we should not expect a great difference between the heterocyclic molecule and its related hydrocarbon.

Molecule	Position of attack	No. of equiv. positions	Observed methyl affinity	Relative methyl affinity per atom	Localisation energy (units of β)	Free valence
Benzene	1-6	6	1	1.0	2.54	0.081
Diphenyl	2	4	5	7.5	2.38	0.118
Naphthalene ...	1	4	22	33	2.30	0.134
Phenanthrene ...	1, 9	4	42	63	2.30	0.134 (9, 10) 0.133 (1, 8)
Pyrene	1, 3	4	125	187	2.19	0.151
Anthracene	9	2	820	2460	2.01	0.202

Observed methyl affinities are due to Levy and Szwarc (*J. Chem. Phys.*, 1954, **22**, 1621). Localisation energies and free valences are taken from the list in Burkitt, Coulson, and Longuet-Higgins (*Trans. Faraday Soc.*, 1951, **47**, 553), except for pyrene, the free valence of which is given by Berthier, Coulson, Greenwood, and Pullman (*Compt. rend.*, 1948, **236**, 1906) and the localisation energy is newly calculated, by the method recently proposed (Coulson, *J.*, 1954, 3111). The author is indebted to Mr. V. W. Maslen for making these calculations.