692. *A Theoretical Treatment of the Diels–Alder Reaction. Part IV.* The Significance of Free-valence Numbers.*

By R. D. Brown.

By using the para-localization energy as a standard for comparison, the possibility of employing other theoretical quantities as criteria of Diels–Alder reactivity is examined. It is shown that the sum of the appropriate free-valence numbers provides an alternative index of reactivity, probably not quite as reliable as the localization energy.

It has been shown in previous papers of this series (*J.*, 1950, 691, 2730; 1951, 1612) that a molecular-orbital energy quantity termed the para-localization energy provides a very satisfactory interpretation of the Diels–Alder properties of hydrocarbons, particularly in the polycyclic series. In the present paper the possibility of using other molecular-orbital quantities as criteria of Diels–Alder reactivity is considered. The discussion is analogous to that recently given for bond reactivity (Brown, *J.*, 1951, 1950).

The formation of the Diels–Alder activated complex is accompanied by a partial localization of the π-electrons at a pair of *para*-orientated positions. If it is supposed that the effect of the approaching dienophile is to change the coulomb integral of these atoms then, Brown's notation (*J.*, 1951, 1950) being used :

$$\begin{aligned}\delta H_\pi = {} & (\partial H_\pi/\partial\alpha_a)\delta\alpha_a + (\partial H_\pi/\partial\alpha_b)\delta\alpha_b + \\ & \tfrac{1}{2}[(\partial^2 H_\pi/\partial\alpha_a^2)(\delta\alpha_a)^2 + 2(\partial^2 H_\pi/\partial\alpha_a\partial\alpha_b)\delta\alpha_a\delta\alpha_b + (\partial^2 H_\pi/\partial\alpha_a^2)(\delta\alpha_b)^2] + \cdot\ .\ .\ .\ \quad (1)\end{aligned}$$

It is reasonable to assume that the perturbations $\delta\alpha_a$ and $\delta\alpha_b$ to the coulomb integrals of the attacked atoms a and b are equal. For convenience we shall write them as $X\beta$, so that the energy change will be expressed in terms of the resonance integral, β, as is usual in the molecular-orbital method. Further, we can identify the differential coefficients with electron densities, q, and mutual polarizabilities, π (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39). With these substitutions (1) becomes

$$\begin{aligned}\delta H_\pi &= (q_a + q_b)X\beta + (\pi_{a,a} + 2\pi_{a,b} + \pi_{b,b})X^2\beta^2/2 + \ .\ .\ . \\ &= (2X + TX^2/2 + \ .\ .\ .\ )\beta \quad .\ .\ .\ .\ .\ .\ .\ .\ .\ . \quad (2)\end{aligned}$$

because for alternant hydrocarbons all the q are unity; for convenience T, which is a pure number, has been written for β times the second expression in parentheses (polarizabilities have the dimension of $1/\beta$).

If this perturbation to the coulomb integrals is the major effect of the dienophile, and if the higher terms of (2) can be neglected for the value of X corresponding to the transition state, then the pair of positions with the greatest value of T will correspond to the smallest activation energy and hence be most reactive. Some values of T are given in Table I. It is evident that T bears very little relationship to Diels–Alder reactivity. It is interesting that a similar state of affairs exists for bond reactivity (Brown, *J.*, 1951, 1950), so it appears that in both of these reactions *perturbations to the coulomb integrals are of minor importance.*

Table I.

Hydrocarbon	Position	$P(-\beta)$	T	Hydrocarbon	Position	$P(-\beta)$	T
Butadiene	1 : 4	2·47	0·716	Naphthalene	1 : 4	3·68	0·608
Hexatriene	1 : 4	2·99	0·713	Anthracene.........	1 : 4	3·63	0·607
	2 : 5	4·99	0·774		9 : 10	3·31	0·616
Benzene	—	4·00	0·593	Phenanthrene ...	1 : 4	3·77	0·627

A perturbation corresponding more closely to the localization process envisaged in the formation of the transition state would be brought about by reduction in magnitude of the resonance integrals of all bonds around a and b (I). In this case if all perturbations are taken

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* Part III, *J.*, 1951, 1612.

to be $X\beta$, and the differential coefficients are expressed in terms of mobile bond orders, p, and bond polarizabilities, the Taylor series becomes

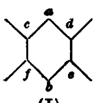
$$\delta H_{\pi} = (UX + VX^2 + \ldots)\beta \qquad (3)$$

where U and V represent

$$U = 2(p_{ca} + p_{ad} + p_{fb} + p_{be}) \qquad (4)$$

$$V = (\pi_{ca,ca} + \pi_{ad,ad} + \pi_{fb,fb} + \pi_{be,be} + 2\pi_{ca,ad} + 2\pi_{ca,fb} + 2\pi_{ca,be} + 2\pi_{ad,fb} + 2\pi_{ad,be} + 2\pi_{fb,be})\beta \qquad (5)$$

Suppose that, owing to X, V, or both, being sufficiently small, only the first term in (3) is significant for the value of X corresponding to the transition state. Then, since X must be negative, the smallest increase in the π-electron energy, *i.e.*, the smallest activation energy, will occur for the pair of positions for which the sum of bond orders, U, is *least*. Values of U for a number of hydrocarbons are listed in Table II.



(I)

There is seen to be quite a close correspondence between P and U, small values of P going with small values of U as required. However, there are some irregularities, the most important being the comparative figures for the 9 : 10-positions of anthracene and benzanthracene. The para-localization energies predict anthracene to be the more reactive, in accordance with experimental observation (*e.g.*, Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1938, **60**, 481). On the other hand the relative values of U would lead one to expect the opposite relative reactivites. This discrepancy must be due to the neglect of V and the higher coefficients in (3).*

TABLE II.

Hydrocarbon	Position	$P(-\beta)$	U	Hydrocarbon	Position	$P(-\beta)$	U
Benzene	—	4·00	5·33	Picene	1 : 4	3·75	5·15
Naphthalene	1 : 4	3·68	5·12	1 : 2-Benzanthracene	1′ : 4′	3·78	5·15
					9 : 10	3·41	4·83
Anthracene	1 : 4	3·63	5·09		5 : 8	3·64	5·10
	9 : 10	3·31	4·85				
				1 : 2-3 : 4-Dibenzanthracene	1′ : 4′	3·83	5·17
Naphthacene	1 : 4	3·62	5·08		9 : 10	3·49	4·93
	5 : 12	3·25	4·81		5 : 8	3·70	5·10
Pentacene	1 : 4	3·61	5·08	1 : 2-5 : 6-Dibenzanthracene	1′ : 4′	3·79	5·15
	5 : 14	3·23	4·80		9 : 10	3·51	4·94
	6 : 13	3·18	4·77				
				1 : 2-7 : 8-Dibenzanthracene	1′ : 4′	3·79	5·15
Phenanthrene	1 : 4	3·77	5·14		9 : 10	3·51	4·94
	4 : 5	4·37	5·17				
				Pentaphene	1 : 4	3·67	5·10
Chrysene	3 : 6	3·74	5·14		5 : 14	3·45	4·90
3 : 4-Benzophenanthrene	1′ : 4′	3·74	5·14				

To illustrate the order of magnitude of V some values are listed in Table III. Although small compared with U, V is seen to be by no means negligible, and although the data in Table III are too meagre to lead to a definite conclusion, it would appear that V increases with decreasing P or U. Obviously the good correlation between P and U must be attributable in part to further monotonic relationships between V and P, and perhaps to higher coefficients also.

TABLE III.

Hydrocarbon	Position	V	$P(-\beta)$	U
Benzene	1 : 4	0·296	4·00	5·33
Naphthalene	1 : 4	0·374	3·68	5·12
Styrene	2 : 5	0·322	3·95	5·25

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* *Added in Proof.*—Dr. H. H. Greenwood has kindly informed me that this discrepancy is due to an error in the published bond-order data for benzanthracene (*Compt. rend.*, 1948, **226**, 1906). The corrected value for the 9 : 10-positions is $U = 490$.

The preceding discussion of U as a criterion of Diels–Alder reactivity leads directly to free valence in the following way. The free valence of an atom a is defined by the relation

$$F_a = N_{\text{max.}} - \Sigma_i p_{ai} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the summation is over all atoms, i, adjacent to a, and $N_{\text{max.}}$ is some arbitrary constant which has been given various values in the literature, the two most popular being 1·680 and $\sqrt{3}$. From (4) and (6) it is obvious that

$$U = 4N_{\text{max.}} - 2(F_a + F_b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Consequently if U is a criterion of Diels–Alder reactivity then ΣF is also. Moreover a high value of ΣF will correspond to a high reactivity. Since ΣF and U are related by (7) there is no point in listing values of the former in Table II, and of course the same discrepancy between the reactivities of anthracene and benzanthracene will still be present. A disadvantage in using free-valence data from the literature is that one has to be careful that all values correspond to the same value of $N_{\text{max.}}$. It is partly for this reason that we have chosen to discuss mainly U in the above treatment rather than the more familiar ΣF.

Evans (*Trans. Faraday Soc.*, 1946, **42**, 113) and Diatkina and Syrkin (*Acta Physicochim.*, 1946, **21**, 921) have found approximate linear correlations between quantities equivalent to para-localization energies and oxidation–reduction potentials of the corresponding *p*-quinones. This of course means that there will be a correlation between the latter and the Diels–Alder reactivity, similar to the correlation of oxidation–reduction potentials of *o*-quinones with bond reactivity (Brown, *J.*, 1951, 1950). However this does not mean that the transition state is quinonoid in structure; rather it implies that the quinone oxidation–reduction potentials can be related to the π-electron energies of *essentially non-quinonoid conjugated systems.* The correlation of the experimental oxidation–reduction potential with para-localization energy is not particularly good so we cannot expect this experimental quantity to be of very great value as an index of Diels–Alder reactivity.

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