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DIELS-ALDER REACTIVITY OF POLYCYCLIC AROMATIC HYDROCARBONS-5

THEORETICAL CORRELATIONS

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Abstract—Second-order rate constants for the Diels-Alder reaction of 90 aromatic hydrocarbons with maleic anhydride, measured spectrophotometrically at 91.5° in 1,2,4-trichlorobenzene, are correlated with various reactivity indices, namely Herndon's structure count ratios, second-order perturbation energies, Brown's para-localization energies, Hess-Schaad resonance energy differences and Polansky indices. Apart from the latter theory, all methods yield satisfactory correlations, with the Hess-Schaad theory being marginally better. An explanation is given why the Hess-Schaad theory is superior to para-localization theory although both are based on Hückel π-electron energies. The observed regioselectivity is correctly accounted for by all except Polansky's theory which yields incorrect results for certain phenes and starphenes.

The reaction of 82 polycyclic benzenoid hydrocarbons with maleic anhydride has been reported previously[1-4] and discussed in connection with several theoretical models. Here we present the rates of Diels-Alder reaction for several additional compounds and examine these and the earlier data by new theoretical methods.

RESULTS

Rates of reaction for four new unsubstituted benzenoid hydrocarbons (**1**–**4**) are given in Table 1. Reaction sites are indicated by heavy dots on the drawings, which are representations of polybenzenoid structures, though not indicated as such.

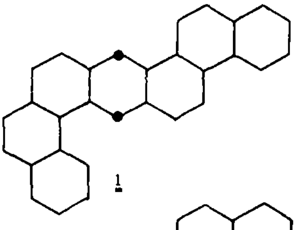
In addition the rates of reaction for four phenyl substituted compounds (**5**–**8**, R = Ph) are given in Table 2 along with the parent unsubstituted systems (**5**–**7**, R = H) which have previously been reported.

Discussion of theoretical treatments

In earlier papers it was noted that while the frontier orbital method did not give a useful correlation with Diels–Alder reaction rate data,[1] Herndon's structure count method,[5] para-localization energies,[6] and a second-order perturbation method were able to do so.[1] In Fig. 1–3 are presented results of these three successful methods plotted against the experimental log of the Diels–Alder rate constants for the 82 hydrocarbons previously reported and compounds **1**–**4**. In Table 3 are given the standard deviations obtained from a least squares treatment

Table 1. Second order rate constants $k_2(LM^{-1}s^{-1})$

compound	$10^6 k_2$
1	56.6
2	16.5
3	64
4	57700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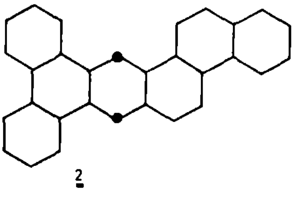
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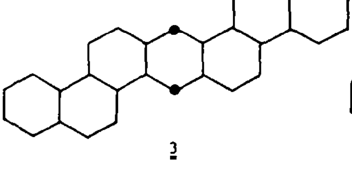
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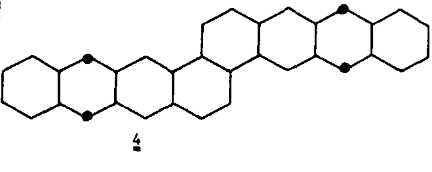
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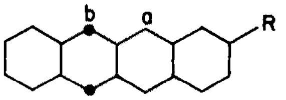

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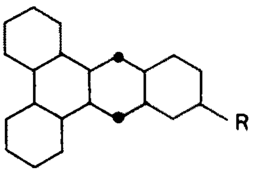

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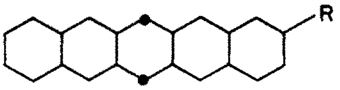

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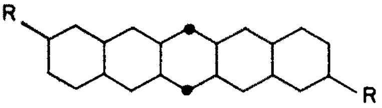

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Table 2. Second order rate constants $k_2(Lm^{-1}s^{-1})$ and ΔRE for phenyl substituted systems

compound	$10^6 k_2$	ΔRE
5(R=ϕ)	86400	a) 0.187
		b) 0.190
5(R=H)	94200	0.192
6(R=ϕ)	58.6	-0.001
6(R=H)	67.4	0.022
7(R=ϕ)	1300000	0.261
7(R=H)	1640000	0.275
8(R=ϕ)	893000	0.257

Table 3. Standard deviations of theoretical correlations

method	σ
Structure Count	0.309
Perturbation	0.320
Para-localization	0.320
Hess-Schaad	0.290
Polansky Indices	0.510

of these data. As can be seen from the plots all give reasonable correlations.

It has been shown[7] that Hess-Schaad resonance energies[8] correlate with the rates of a set of Diels-Alder reactions studied by Sondheimer[9] in which macrocyclic annulenes are formed as product. We shall now show that they also provide a somewhat better correlation for the benzenoid compounds here than do the theoretical models just mentioned. Resonance energy differences between product and reactant (ΔRE) were computed with eqn (1) for all 86 unsubstituted benzenoid hydrocarbons for which rate data are available.

$$RE_{\text{product}} - RE_{\text{reactant}} = \Delta RE \qquad (1)$$

Results plotted in Fig. 4 show an excellent correlation with log k_2. The standard deviation of 0.290 is the best of those listed in Table 3, though the difference between this and that of Herndon's structure count method cannot be considered significant.

At first sight it is surprising that ΔRE should give better results than para-localization energies. The π energies in both are calculated in exactly the same way using the Hückel method; yet the standard deviations (Table 3) are significantly different. The reason for this difference is best seen by examining in detail two examples. Consider the case of tetracene (the bonds indicated by the arrow will be needed later).

Para-localization energy is given by

$$\text{para-localization energy} = E^{\pi}_{\text{benzene}} + E^{\pi}_{\text{naphthalene}} - E^{\pi}_{\text{tetracene}} \qquad (2)$$

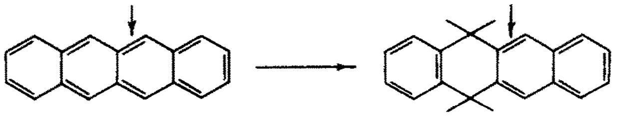
and ΔRE by

$$\Delta RE = RE_{\text{benzene}} + RE_{\text{naphthalene}} - RE_{\text{tetracene}} \qquad (3)$$

where

$$RE = E^{\pi} - E^{\text{ref}}. \qquad (4)$$

For each Kekulé structure of a given compound the "localized energy" is obtained by summing the bond energy terms of Table 1 of Ref. 8. The reference energy (E^{ref}) is then the average of these localized energies for all Kekulé forms. It is found [8,10] that localized energies vary little among the Kekulé structures of a compound so that E^{ref} can be approximated by the localized energy of any



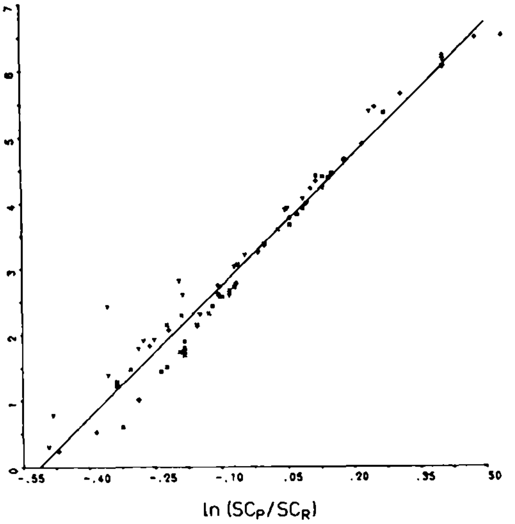


Fig. 1. Correlation of reaction rates and structure count. k_2 = rate of Diels–Alder reaction; SC_p = structure count of product; SC_R = structure count of reactant.

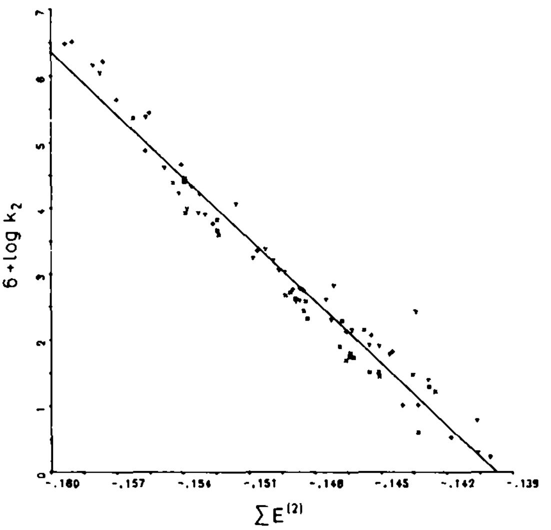


Fig. 2. Correlation of reaction rates and second-order stabilization energies, $\Sigma E^{(2)}$.

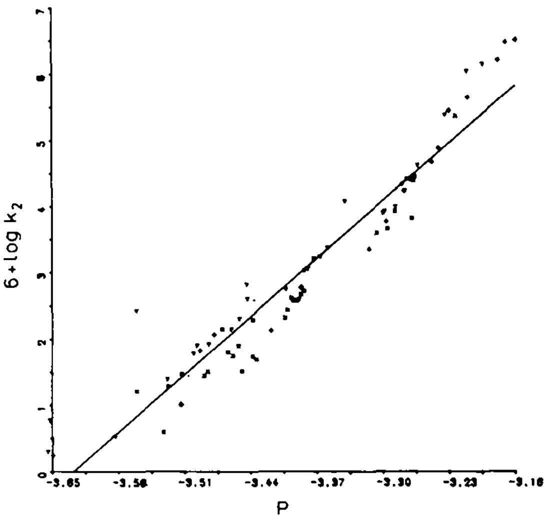


Fig. 3. Correlation of reaction rates and para localization energies, P.

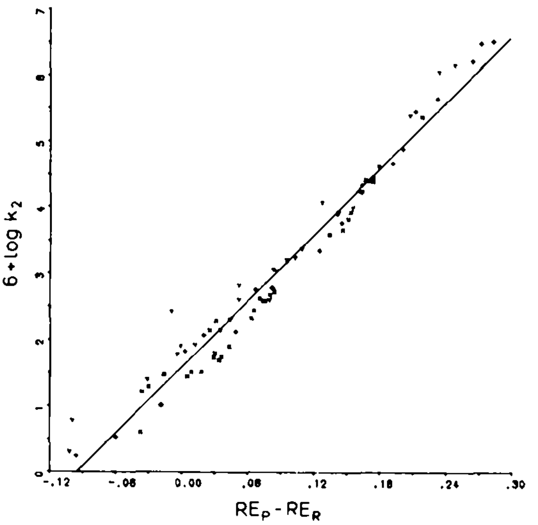


Fig. 4. Correlation of reaction rates and Hess–Schaad $\Delta RE = RE_p - RE_R$.

one Kekulé form. For the Kekulé structures shown above

$$E^{ref}_{tetracene} = 3E_{22} + 6E_{21} + 3E_{12} + 6E_{11} + 3E_{10} = 24.1551\beta \quad (5)$$

$$E^{ref}_{benzene} = 3E_{22} + 3E_{12} = 7.6077\beta \quad (6)$$

$$E^{ref}_{naphthalene} = 3E_{22} + 2E_{21} + 3E_{12} + 2E_{11} + E_{10} = 13.1280\beta \quad (7)$$

and

$$\Delta RE = E^{\pi}_{benzene} - E^{ref}_{benzene} + E^{\pi}_{naphthalene} - E^{ref}_{naphthalene} - (E^{\pi}_{tetracene} - E^{ref}_{tetracene}). \quad (8)$$

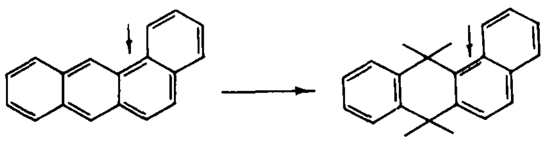
Substituting eqns (5)–(7) for the reference energies gives

$$\Delta RE = E^{\pi}_{benzene} + E^{\pi}_{naphthalene} - E^{\pi}_{tetracene} + 4E_{21} + 4E_{11} + 2E_{10} - 3E_{22} - 3E_{12}. \quad (9)$$

This differs from the para-localization energy by

$$4E_{21} + 4E_{11} + 2E_{10} - 3E_{22} - 3E_{12} = 3.4239\beta. \quad (10)$$

However, in the series anthracene, tetracene, pentacene.... the difference of 3.4239β remains constant, and hence for this series correlations with para-localization energy and ΔRE would in fact yield the same fit. Consider now the following example.



A treatment similar to that for tetracene gives

$$\Delta RE = E^{\pi}_{benzene} + E^{\pi}_{naphthalene} - E^{\pi}_{tetraphene} + 2E_{21} + E_{20} + 4E_{11} + 2E_{10} - 2E_{22} - 3E_{12} \quad (11)$$

or

$$\Delta RE = \text{para-localization energy} + 3.4578\beta. \quad (12)$$

Note that the value 3.4578β is different from that of the linear polyacene series. This difference in the bond energy terms of eqns (9) and (11) is

$$2E_{21} - E_{20} - E_{22} \quad (13)$$

Suppose that the Diels–Alder transition state resembles the product in that the conjugation is broken by the dienophile, but suppose this transition state occurs early so that the bond lengths in the conjugated system are more like those of reactant than product. The activation energy of the reaction will be the para-localization energy corrected for these bond length changes. Consider the bond indicated by the arrow in tetracene above. In the reference structures this bond has energy E_{21} in the reactant and E_{22} in the product so this particular bond leads to a difference between para-localization energy and ΔRE as given in eqn (14).

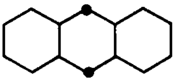
$$\Delta RE = \text{para-localization energy} + (E_{21} - E_{22}). \quad (14)$$

We have previously shown that in acyclic hydrocarbons, which have only one Kekulé structure for which the actual and reference structures are therefore identical, there is a correlation between the bond energy terms and bond lengths.[11] If it is assumed that the correction to para-localization energy due to bond-length differences between product and transition state is the same as in the corresponding reference structures, then this is exactly the difference between ΔRE and para-localization energy. With these assumptions ΔRE is expected to correlate better than para-localization energy with the Diels–Alder reaction rates.

As a test of this hypothesis both ΔRE's (open circles) and para-localization energies (open triangles) are plotted in Fig. 5 for a set of compounds [**5**(R = H), **7**(R = H), **9–14**] of the tetracene type vs the log of their rate constants.

The lines drawn are those based on these eight compounds. As expected the fit to the two straight lines is identical because of the constant difference of eqn (10). If results for compounds of the tetraphene type [**6** (R = H), **15–20**] are included on the same figure, ΔRE points (closed circles) fall nearly on the ΔRE line for the tetracene series, but para-localization energy points (closed triangles) are considerably farther from their line.

This provides some weak support for our explanation of why ΔRE should correlate better than para-localization energy with the rate of Diels–Alder reaction. There is no reason to suppose that in the transition state all parts of the system have advanced the same fraction of the way from reactant to product. We suggest that those



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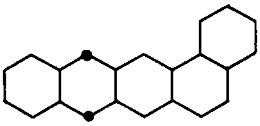

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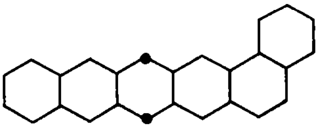

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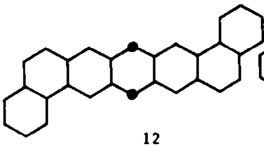

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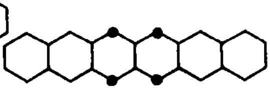

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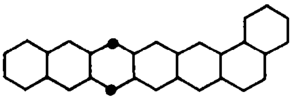

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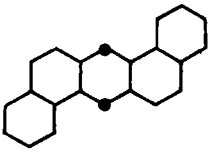

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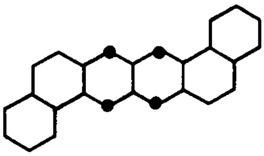

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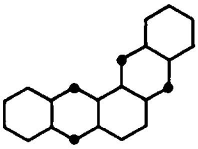

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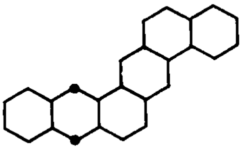

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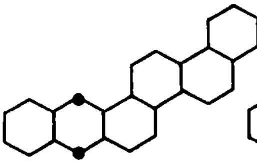

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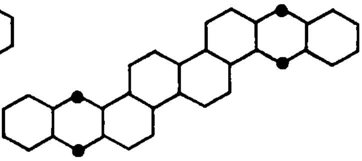

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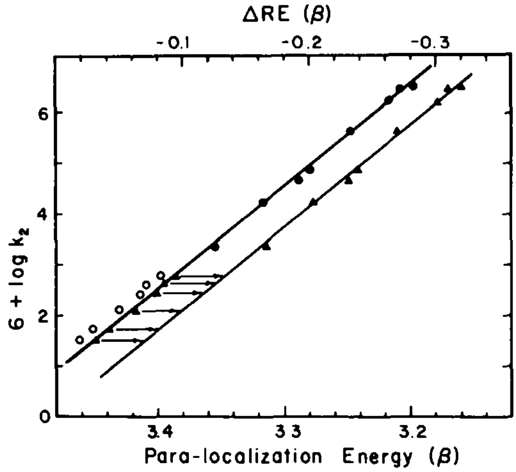

Fig. 5. Comparison of effect of benzannelation on para-localization energy (triangles) and ΔRE (circles). Solid points are for the tetracene series and open points for the tetraphene series.

parts more distant from the reactant site still resemble the reactant while those parts near the reaction site are more product-like. An STO 3G study of the reaction surface for butadiene + ethylene[12] suggests that the Diels–Alder reaction proceeds by a concerted rather than a two-step process and that product double bond formation is nearly complete in the transition state. This relatively small system already presents a formidable problem for *ab initio* calculation and no molecules large enough to examine the behavior of their distant parts have been treated.

Using the Hückel method, Polansky and Derflinger[13] in 1967 published a quantification of Clar's idea of benzenoid character. We have used this to compute the "dienoid character" of our 86 Diels–Alder reactions, and results are shown in Fig. 6. There is some correlation between ρ_{dienoid} and the logarithm of the reaction rate, but the fit is the worst of the five models considered. In addition, while all other models correctly account for the observed positional selectivity of the maleic anhydride attack, the Polansky index fails for hexaphene, heptaphene, 7,8-benzoheptaphene, 2,3-benzonaphthopicene and dianthracenopyrene. Presumably the poor results are due to an inopportune definition of ρ_{dienoid}.

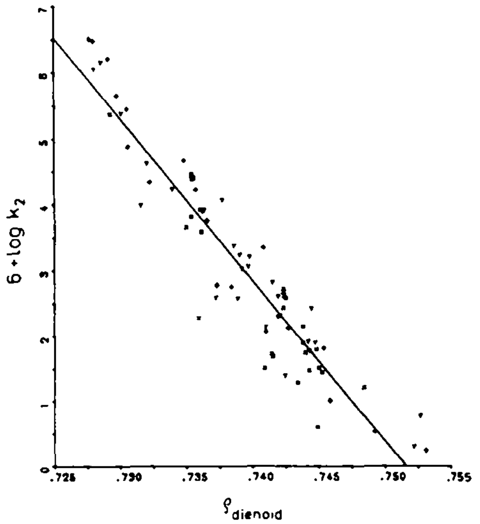

Fig. 6. Correlation of reaction rates and the Polansky index ρ_{dienoid}.

We consider finally the effect of phenyl substitution. An examination of the results in Table 2 indicates that ΔRE for all four phenyl substituted systems predicts a decrease in rate of these compounds when compared to the unsubstituted parent systems. This prediction is in qualitative agreement with our finding that β-phenyl substitution does indeed bring about a rate retardation. In the Herndon method, each added phenyl ring doubles the number of resonance structures of both reactant and product and hence makes no contribution to the difference in computed resonance energies. Thus this method does not predict the small observed rate changes due to phenyl substitution, although in general it is as good a predictor of the Diels–Alder reaction rates as ΔRE.

EXPERIMENTAL

Kinetic measurements were made spectrophotometrically at 91.5° in 1,2,4-trichlorobenzene, using a Zeiss PMQII instrument or a Perkin-Elmer model 555 kinetics system. The decay of the hydrocarbon concentration was monitored directly in the 1 cm quartz cell, using a suitable, usually the longest-wavelength absorption band. Since maleic anhydride was present in large molar excess (between 50- and 1000-fold, depending on the reactivity of the hydrocarbon), the second-order rate constant k_2 is obtained by dividing the pseudo first-order rate constant k_1' by the maleic anhydride concentration. Due to the elevated temperature and the low hydrocarbon concentration (between 10^{-3} and 10^{-6} mol/L, depending on the ε value of the absorption band), no charge-transfer complexation was observed. Each rate constant was measured twice, using different hydrocarbon and maleic anhydride concentrations; the resulting k_2 values usually agreed within ± 3%.

For the hydrocarbons not previously studied, the position of attack of maleic anhydride was deduced, as in Clar's work[14], from the UV spectra of the Diels–Alder adducts. The syntheses of **1–4** will be reported in due course.[15] The syntheses of **5**, **7** and **8** (R = H) have been described by Clar and McAndrew.[16] 6-Phenyldibenzanthracene (**6**, R = ϕ) was a gift from Prof. H. J. Bestmann, Universität Erlangen.

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