

# Diels–Alder Reactivity of Polycyclic Aromatic Hydrocarbons. 1. Acenes and Benzologs

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**Abstract:** As part of a continued study of the Diels–Alder reactivity of polycyclic aromatic hydrocarbons, the rates of reaction of 21 acene-type hydrocarbons with excess maleic anhydride have been measured at 91.5 °C in 1,2,4-trichlorobenzene. Except for benzene, naphthalene, phenanthrene, triphenylene, chrysene, 3,4-benzophenanthrene, and 1,2:7,8-dibenzochrysene, which show no noticeable Diels–Alder reactivity, all other compounds reacted cleanly under these conditions. The measured second-order rate constants  $k_2$  span a range of almost seven powers of ten, with hexacene being the most reactive, and tetrabenzanthracene the least reactive hydrocarbon. With the possible exceptions of tribenzotetracene and 1:2-benzohexacene, all reactions proved to be regioselective. To aid in the interpretation of the data, six theoretical models were tested: Clar's sextet theory, Brown's para-localization concept, Herndon's structure count method, the free-valence indices, Fukui's frontier-orbital theory, and complete second-order perturbation theory. While all six methods correctly account for the observed positional selectivity, they meet with different success regarding the rate constants, Herndon's treatment and second-order perturbation theory being the most successful ones, whereas frontier-orbital theory fails completely. In addition, empirical correlations between the rate constants and spectroscopic quantities ( $1P_1$  and  $1P_2$  from the photoelectron spectra; energies of the  $\alpha$ ,  $p$ , and  $\beta$  bands from the UV spectra; triplet lifetimes from the phosphorescence spectra) were found.

## Introduction

Although the addition of maleic anhydride and benzoquinone to aromatic hydrocarbons like anthracene was observed half a century ago by Clar<sup>1</sup> and shortly later by Diels and Alder,<sup>2</sup> no systematic kinetic study of this important reaction of aromatic hydrocarbons—the Diels–Alder reaction—has yet appeared.

In a series of now classical papers, Clar showed that the Diels–Alder reactivity of a given hydrocarbon is increased by linear annelation, while angular annelation has the opposite effect.<sup>3</sup> Using Robinson's aromatic sextet,<sup>4</sup> these observations led Clar<sup>5,6</sup> to develop a unified theory which treats reactivity and UV light absorption of this class of compounds on a common basis.

However, Clar's early observations were of a qualitative rather than quantitative nature. The desirability of having accurate rate data was emphasized 20 years later by Brown<sup>7</sup> in his theoretical treatment of the Diels–Alder reaction. Due to the work of Dewar<sup>8</sup> and Herndon,<sup>9</sup> such data became available only recently for the following hydrocarbons: anthracene, tetracene, the three isomeric dibenzanthracenes, tetracene, 1,2-benzotetracene, 1,2:3,4-dibenzotetracene, pentacene, and 1,2-benzopentacene. The rates of reaction of substituted anthracenes with various dienophiles were measured by Sauer.<sup>10</sup>

Unfortunately, the reaction conditions (solvent, temperature) in these studies were not standardized. Furthermore, some experiments were carried out at rather high temperatures where complications due to the retro-Diels–Alder reaction are to be expected.

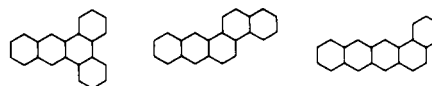
The object of this and subsequent papers is twofold: (a) to provide accurate second-order rate constants  $k_2$  measured under standardized conditions, the emphasis being on a wide coverage of compounds rather than on a detailed discussion of individual cases; (b) to test currently used reactivity theories in how far they reproduce the observed rates and regioselectivities, i.e., to establish structure/reactivity correlations.

Providing that this latter goal can be achieved, four practical applications of such correlations can be foreseen.

Firstly, the measured rate constant provides a stringent test whether the assumed constitution of the hydrocarbon is correct. This is an important consideration in the chemistry of aromatic hydrocarbons as many useful synthetic procedures (Lewis acid catalyzed cyclodehydrogenation, photocyclodehydrogenation,

Elbs pyrolysis) often result in unexpected skeletal isomerization and splitting or rearrangement of aryl rests. In the course of our kinetic and spectroscopic studies, some hitherto accepted structures of long-known hydrocarbons had to be revised, and the unknown structures of many hydrocarbons obtained by Clar as byproducts could be elucidated.<sup>11</sup>

Secondly, there is at present an urgent need of highly purified aromatic hydrocarbons for (photo)conduction<sup>12</sup> and luminescence<sup>13</sup> studies. If hydrocarbon mixtures, which cannot be separated by chromatography or fractional crystallization and sublimation, differ in their Diels–Alder reactivities, they can be separated by reacting them with maleic anhydride for an appropriate period of time. The adducts can then be extracted with alkali and the hydrocarbons recovered by decomposing them in vacuo. In this way, Clar was able to prepare pure samples of the following three hydrocarbons which were

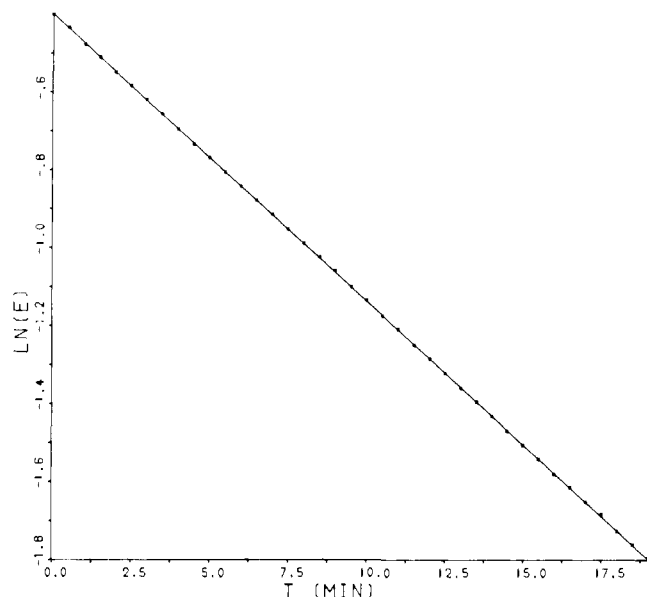


obtained as an inseparable mixture by an Elbs pyrolysis.<sup>14</sup> Conversely, the purity of a hydrocarbon which is able to add maleic anhydride can be assessed from the  $\ln E$  vs. time plot ( $E$  is the optical density at an appropriate absorption band). A curved plot or a nonzero optical density after completion of the reaction indicates contamination.

Thirdly, the available information in the literature<sup>15,16</sup> indicates that the ease of photooxidation of aromatic hydrocarbons parallels their Diels–Alder reactivity. Since certain hydrocarbons are useful phosphors, scintillators, and laser dyes, and since their performance is limited by photooxidation ("fatigue"), the availability of rate data would be of considerable value in selecting or designing improved materials for such applications.

Finally, the Diels–Alder reaction with maleic anhydride, *p*-benzoquinone, or 1,4-naphthoquinone has occasionally been used to build up higher annelated hydrocarbons ("benzogenic" diene synthesis<sup>5</sup>). For example, bisanthene, maleic anhydride, and chloranil as dehydrogenating agent give, after decarboxylation, 1,14-benzobisanthene and then ovalene:<sup>17</sup>





**Figure 1.** Kinetics of the Diels-Alder reaction of 1,2-benzotetracene with maleic anhydride, measured spectrophotometrically at 456 nm. Initial hydrocarbon concentration  $6.70 \times 10^{-5}$  mol/L, maleic anhydride concentration  $6.99 \times 10^{-2}$  mol/L.

For this reaction to take place, the diene sites (indicated in the structural formulas using Clar's notation<sup>6</sup>) must be sufficiently reactive. Unfortunately, the synthetic potential of this reaction type has hardly been explored because little is known about the relations between structure and diene reactivity.

### Experimental Section

**Aromatic Hydrocarbons.** All compounds except 1,2:9,10-dibenzotetracene, which was prepared according to Nichol et al.,<sup>18</sup> were taken from Professor Clar's collection of aromatic hydrocarbons; for their synthesis see ref 5. Since some of the samples were over 40 years old, their purity was checked by UV spectroscopy. Differences from the literature spectra<sup>5</sup> were found in the case of hexacene and 1,2-benzohexacene, indicating that partial oxidation to the quinones had taken place. Hexacene was therefore resublimed in vacuo. Lack of material prevented similar purification for 1,2-benzohexacene; however, as the quinone absorbs at considerably shorter wavelengths, it does not interfere with the kinetic measurements.

Maleic anhydride was sublimed in vacuo; 1,2,4-trichlorobenzene was fractionated over KOH.

**Kinetic Measurements.** The Diels-Alder reactions were followed directly in the 1-cm quartz cell of a Zeiss PMQ II spectrophotometer, using a suitable, usually the longest wavelength, absorption band of the starting hydrocarbon.<sup>19</sup> Provided that the hydrocarbon contains at least an anthracene chromophore, there is no overlap with the absorption bands of maleic anhydride and the Diels-Alder adduct. All measurements were carried out in trichlorobenzene at  $91.5 \pm 0.2$  °C. Besides the necessary correction for the thermal expansion of the solvent, the volume expansion due to the added maleic anhydride was taken into account. To ensure pseudo-first-order rate behavior, maleic anhydride was added in large (between 50- and 1000-fold) molar excess, depending on the rate of the reaction; the second-order rate constant  $k_2$  is then obtained by dividing the pseudo-first-order constant  $k_1'$  by the maleic anhydride concentration.

All reactions took place cleanly, giving satisfactory linear  $\ln E$  vs. time plots over several half-reaction times (see Figure 1 for an example). Each rate constant was measured twice, the values usually agreeing within  $\pm 3\%$ . Owing to poor solubility and consequent low initial optical density, hexacene and 1,2-benzohexacene showed larger errors of  $\pm 9\%$ . Because of the very extended reaction time, a similar error holds for tetrabenzanthracene.

Attempts to observe the Diels-Alder reaction of naphthalene, phenanthrene, chrysene, triphenylene, 3,4-benzophenanthrene, and 1,2:7,8-dibenzochrysene failed. For example, UV spectra of a naphthalene/maleic anhydride mixture taken at intervals of 1 week showed no significant change over 4.5 months, indicating that the reaction

**Table I.**

solvent	$\alpha$ bands, $\text{cm}^{-1}$	$\rho$ and $\beta$ bands, $\text{cm}^{-1}$
alkanes, cycloalkanes, $\text{CHCl}_3$ , EtOH, MeOH, THF	+250	+900
dioxane	+350	+900
benzene, xylene	+350	+1200
trichlorobenzene	+350	+1400
1-methylnaphthalene	+400	+1500

is either extremely slow or that the equilibrium is strongly on the side of the reactants. This accords with earlier findings<sup>3,20-22</sup> that only hydrocarbons with at least an anthracene chromophore add maleic anhydride.

**Spectroscopic Measurements.** The energies of the vibrational 0-0 components of the three main UV transitions were estimated<sup>23</sup> from the solution spectra and extrapolated to the gas phase using the corrections<sup>5</sup> indicated in Table I. For example, if the solution spectrum was taken in trichlorobenzene, we have to add  $350 \text{ cm}^{-1}$  to the wavenumber of the 0-0 transition of the  $\alpha$  band in order to obtain the energy of the  $\alpha$  state in the gas phase.

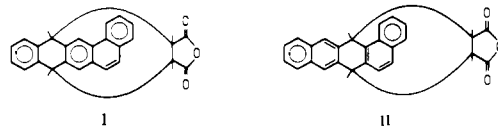
Photoelectron spectra were recorded in the gas phase using the procedure outlined in ref 23. The first few  $\pi$  bands are usually very sharp, with dominant 0-0 transitions, so that the IPs can be measured within  $\pm 0.01$  eV.

### Experimental Results

The  $k_2$  data, multiplied by  $10^6$  for convenience, and the  $6 + \log k_2$  values for 21 hydrocarbons are collected in Table II. Note that the  $k_2$  values of tetracene, 1,2:7,8- and 1,2:9,10-dibenzotetracene, tetrabenzotetracene, and hexacene must be divided by a statistical factor of 2 because the attacking dienophile finds two equivalent reaction sites. Also contained in the table are the energies  $E_\alpha$ ,  $E_\rho$ , and  $E_\beta$  of the pertinent UV absorption bands, plus the IPs of those photoelectron bands which correspond to the occupied orbitals of highest angular quantum number (see ref 23 and Discussion). These IPs are usually the first and second ones, except in pentacene, 1,2-benzopentacene, hexacene, and 1,2-benzohexacene, where they are the first and third ones. For simplicity, these IPs have been termed  $\text{IP}_1$  and  $\text{IP}_2$ .

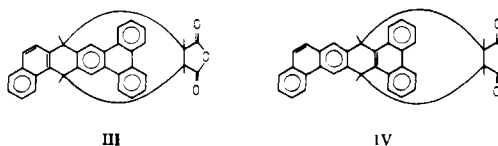
With the possible exceptions of tribenzotetracene and 1,2-benzohexacene, all hydrocarbons reacted regioselectively, i.e., among several reactive "meso" sites only one is attacked by maleic anhydride, namely, that indicated by dots in the structural formulas (Table II).

In 1,2-benzotetracene, for example, the Diels-Alder adduct has structure I because the UV spectrum, after completion of



the reaction, reveals a phenanthrene chromophore. If the adduct had structure II, two naphthalene chromophores would be generated, absorbing at considerably shorter wavelengths<sup>24</sup> (the  $\alpha$  bands of phenanthrene and naphthalene differ by 30 nm).

However, as phenanthrene and triphenylene have almost identical  $\alpha$ -band positions, we cannot decide, on the basis of the UV spectrum, whether the adduct of tribenzotetracene has structure III or IV. A similar ambiguity exists for 1,2-benzo-

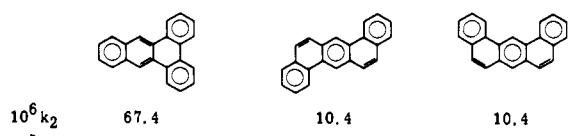


hexacene, whose adduct spectrum could not be obtained owing to overlap with the spectrum of the quinone. The structures suggested in Table II for these two adducts should therefore be regarded as tentative as they are entirely based on theoretical predictions (see Discussion).

### Discussion

In accord with Clar's findings,<sup>3,5</sup> the rate constant increases rapidly on linear annelation so that, for example, hexacene reacts 1450 times faster than anthracene. The increment between successive members of the acene series alternates slightly (it is larger in going from an even to an odd acene) and diminishes gradually. As a result of this,  $k_2$  appears to converge to a limiting value, just as does the first IP and the long-wavelength absorption band.

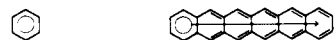
Angular annelation has the opposite effect,  $k_2$  decreasing with an increasing number of angular benzo rings. On passing from anthracene to tetrabenzanthracene,  $k_2$  is lowered by a factor of 1300. In the tetracenes, the factor is 400, and in the pentacenes 75. Among the hydrocarbons with two angular benzo rests, e.g., the three isomeric dibenzanthracenes, the first one is always the most reactive, while the syn and anti isomers show no significant difference within experimental error.



Thus, the rate behavior of the present hydrocarbons follows a simple and transparent pattern, indicating that steric factors play a minor, if any, role. In particular, the angular annelation effect within the anthracene series cannot be ascribed to steric repulsion ("back strain") of the angular benzo rings in the transition state because a similar decline of  $k_2$  holds also in the pentacene series, where this steric factor cannot be operative. The assertion of negligible steric contributions is further substantiated by the success of most theoretical models in rationalizing the rate data and by the observations made in other series of hydrocarbons, e.g., the naphthologs of the acenes, the perylenes, coronenes, pyrenes, and fluoranthenes.<sup>25</sup> For example, in accord with all theories, 1,2:5,6- and 1,2:7,8-dibenzanthracene have identical  $k_2$  values, although the back strain, if operative, would lead us to expect a lower  $k_2$  value for the syn isomer.

In the following various theories will be tested with regard to the rate data and regioselectivities.

**Clar's Sextet Concept.** The rapidly increasing reactivity in the acene series benzene through hexacene is according to Clar<sup>5,6</sup> due to a gradual loss of benzenoid character. While all six  $\pi$  electrons of benzene can be accommodated in an aromatic sextet (indicated by a circle), this is not so in hexacene,



which has only one sextet shared among six rings. Clar symbolizes this migration of the sextet by an arrow.

Each time an angular benzo rest is added to an acene (beginning with naphthalene), a new sextet is generated, resulting in increased benzenoid character and decreasing reactivity. Thus, the sextet concept accounts well for the linear and angular annelation effects on the rate constants.

In hydrocarbons with several reactive meso sites, e.g., 1,2-benzotetracene, the adduct with the largest possible number of sextets is predicted to be preferentially formed. Adduct I has three sextets and is therefore favored over II with two sextets, as is experimentally observed. In the case of tribenzotetracene, the adducts III and IV have both four sextets so that they may be formed at the same time. As already mentioned, experimental information is lacking because the

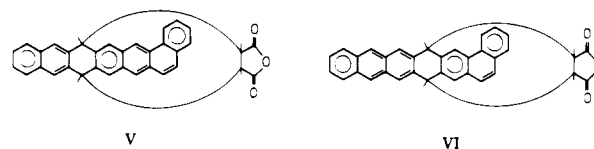
spectra of both adducts would be very similar. Thus, at the present state of our experimental knowledge, the orientation effects are correctly described, provided that the sextet concept makes a clear-cut prediction.

Considering the fact that no cumbersome and capricious calculations are involved, Clar's theory correctly describes the observed trends and qualitative aspects. We may anticipate that this is true also for the peri-condensed and nonalternant hydrocarbons.<sup>25</sup> A serious flaw with Clar's theory is that it makes no distinction between sextet isomers, i.e., between compounds with the same number of sextets per number of rings (cf. the three dibenzanthracenes above).

**Brown's Para-Localization Concept.** In this theory,<sup>7</sup> the activation energy is taken as the difference in  $\pi$ -electron energies of the adduct and the starting hydrocarbon. Since the adduct contains two  $\pi$  electrons less, its  $\pi$ -electron energy is smaller than that of the hydrocarbon, making the localization energy  $P$  (in  $\beta$  units) negative.

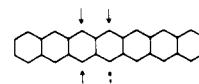
The  $P$  values calculated by the Hückel method are collected in Table III and are plotted against the  $6 + \log k_2$  data in Figure 5 of part 2 of this series.<sup>47</sup> Only the smallest  $P$  values corresponding to the most reactive meso positions are quoted in the table. The plot for the acenes and their benzologs alone has a standard deviation of 0.387, which seems satisfactory in view of the simplicity of the Hückel method. Linear and angular annelation effects are correctly described, as are the differences between sextet isomers. The convergence of the  $k_2$  values with ever increasing length of the acene and the alternating differences come out nicely, and the observation that an angular benzo rest quenches the reactivity of anthracene more than that of hexacene is also reproduced. We may add that Brown's theory correctly predicts the rate-diminishing effect of  $\beta$ -phenyl substitution in the acenes, but fails for the rate-enhancing effect of  $\alpha$ -phenyl groups.<sup>25</sup>

Orientation phenomena are equally well handled. Adduct I of 1,2-benzotetracene is favored over II by  $0.082\beta$  and is therefore exclusively formed, within the limits of our analytical capabilities. In the case of tribenzotetracene, adduct III is predicted to be more stable than IV by  $0.062\beta$ . The adduct of 1,2-benzohexacene has structure V, but the energetic prefer-



ence ( $0.022\beta$ ) is so subtle that VI may be formed to some extent.

These predictions can be grossly paraphrased by saying that among two otherwise equivalent meso sites of a tetracene or hexacene chromophore those are more reactive which are farther away from the more strongly benzoannulated end of the acene chromophore. However, as the above numbers show, the "polarizing" effect of angular benzo rings fades with increasing length of the acene. The same is predicted to happen in the acenes themselves. Thus, while anthracene reacts exclusively in the "middle" of the molecule, this may not necessarily be the case in the hypothetical heptacene, the  $P$  values



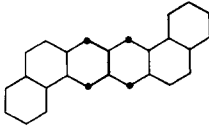
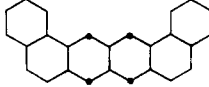
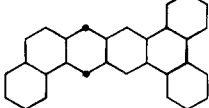
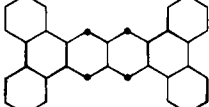
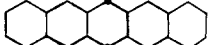
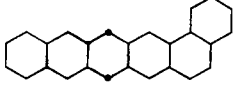
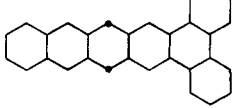
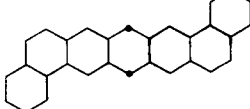
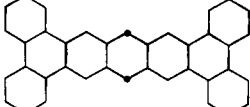
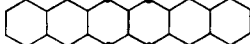
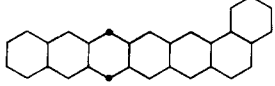
of which differ by only  $0.014\beta$  for the sites marked above with arrows. In other words, regioselectivity may be partly lost in the higher acenes and their benzologs.

**Herndon's Structure Count Method.** More elaborate schemes for calculating resonance energies than that due to Brown<sup>7</sup> have recently been advanced by Dewar,<sup>26</sup> Hess and Schaad,<sup>27</sup> Herndon,<sup>28</sup> and Aihara.<sup>29</sup> As these theories are partly inter-

**Table II.** Second-Order Rate Constants  $k_2$  ( $L M^{-1} s^{-1}$ ) and Their Logarithms,  $1P_1$  and  $1P_2$  (See Text) (eV), and Energies of the  $\alpha$ ,  $p$ , and  $\beta$  Absorption Bands in the Gas Phase (eV)<sup>a</sup>

hydrocarbon	$10^6 k_2$	$6 + \log k_2$	$1P_1$	$1P_2$	$E_\alpha$	$E_p$	$E_\beta$
benzene			9.24	9.24	4.73	5.96	6.64
naphthalene			8.15	8.88	4.03	4.38	5.62
phenanthrene			7.86	8.15	3.63	4.23	4.93
triphenylene			7.87	7.87	3.55	4.36	4.74
chrysene			7.59	8.10	3.46	3.87	4.65
3,4-benzophenanthrene			7.61	8.03	3.38	3.84	4.48
1,2:7,8-dibenzochrysene			7.20	7.82	3.15	3.43	4.18
anthracene	2270	3.36	7.41	8.54	3.57	3.38	4.86
tetraphene	136	2.13	7.41	8.04	3.26	3.53	4.36
1,2:3,4-dibenzanthracene	67.4	1.83	7.39	7.91	3.34	3.56	4.39
1,2:5,6-dibenzanthracene	10.4	1.02	7.38	7.80	3.18	3.57	4.29
1,2:7,8-dibenzanthracene	10.4	1.02	7.40	7.79	3.19	3.60	4.20
1,2:3,4:5,6-tribenzanthracene	3.4	0.53	7.40	7.56	3.24	3.68	4.15
tetrabenzanthracene	1.8	0.24	7.42	7.42	3.14	3.71	4.09
tetracene	94 200	4.97	6.97	8.41	3.32	2.71	4.52
1,2-benzotetracene	17 000	4.23	6.96	7.92		2.83	3.96
1,2:3,4-dibenzotetracene	5910	3.77	6.97	7.83		2.92	3.94

Table II (Continued)

hydrocarbon	$10^6 k_2$	$6 + \log k_2$	IP <sub>1</sub>	IP <sub>2</sub>	$E_\alpha$	$E_p$	$E_\beta$
1,2:7,8-dibenzotetracene		1230	3.09	6.96	7.74	2.95	3.92
1,2:9,10-dibenzotetracene		1200	3.08	6.97 <sup>b</sup>	7.72 <sup>b</sup>	2.95	3.88
1,2:3,4:7,8-tribenzotetracene		575	2.76	6.99	7.63	3.03	3.85
tetrabenzotetracene		238	2.38	7.00	7.53	2.89	3.08
pentacene		1 640 000	6.22	6.61	8.32	3.05	4.14
1,2-benzopentacene		447 000	5.65	6.61	7.90	2.37	3.71
1,2:3,4-dibenzopentacene		284 000	5.45	6.62	7.77	2.42	3.69
1,2:8,9-dibenzopentacene		76 500	4.88	6.64	7.68	2.47	3.62
tetrabenzopentacene		22 000	4.34	6.65	7.52	2.57	3.56
hexacene		6 570 000	6.82	6.36	8.14	2.80	1.90
1,2-benzohexacene		3 050 000	6.48	6.36 <sup>b</sup>	7.80 <sup>b</sup>	2.00	

<sup>a</sup> The dots in the structural formulas indicate the most reactive meso positions. The rate constants are not corrected for statistical factor.  
<sup>b</sup> IPs of 1,2:9,10-dibenzotetracene and 1,2-benzohexacene extrapolated.

related, a detailed discussion seems unwarranted here. We note in passing that the Hess and Schaad method represents a significant improvement over Brown's theory, the standard deviation dropping to 0.211 for the present hydrocarbons.<sup>30</sup> Dewar's PMO treatment<sup>31</sup> is also successful, the standard deviation being 0.249.

The Herndon method, which requires no computer operations, is particularly simple and elegant and has therefore been explicitly tested. His reactivity index is defined as  $\ln(SC_P/SC_R)$ , where  $SC_P$  and  $SC_R$  are the numbers of classical Kekulé structures for products and reactants. As simple pencil and paper procedures for counting these structures are now available,<sup>32</sup> the method can be applied to hydrocarbons of any size. The  $SC_P/SC_R$  ratios are given in Table III, and a plot of the  $6 + \log k_2$  data (including a wider range of compounds) against the  $\ln(SC_P/SC_R)$  values is shown in Figure 6 of part 2. The standard deviation for the acenes and benzologs is 0.236, i.e., comparable to that with the Hess and Schaad method, and the

predictions regarding the most reactive meso atoms in a given hydrocarbon (or most stable adducts) are in complete harmony with those of all previously discussed theories. In particular, adduct III of tribenzotetracene with 27 Kekulé structures is predicted to be more stable than IV with only 25. In the case of 1,2-benzohexacene, adduct V with 21 Kekulé structures is only slightly favored over VI with 20 structures. Using the regression of Figure 6 of part 2, adducts V and VI are predicted to be formed in the ratio 69:31; i.e., regioselectivity is lost, and a fractional statistical factor would be opportune.

A particularly attractive aspect of the structure count method stems from the fact that closed formulas can be derived for the  $SC_P/SC_R$  ratios within many homologous series, e.g., the acenes, benzacenes, dibenzacenes, tetrabenzacenes, phenes, starphenes, zigzag and helically annelated compounds, linear and angular pyrenes, etc.<sup>33</sup> This allows a systematic interrelation of molecules belonging to different annelation series.

**Free Valence Index.** Providing that the energy levels of the

**Table III.** Para-Localization Energies  $P$ , Structure Count Ratios  $SC_P/SC_R$ , Sum of Free Valences  $\Sigma F_\mu$ , Frontier Orbital Stabilization Energies  $E^{(2)}$ , and Total Stabilization Energies  $\Sigma E^{(2)}$  for the Most Reactive Meso Positions

hydrocarbon	$P[\beta]$	$SC_P/SC_R$	$\Sigma F_\mu$	$E^{(2)}[\beta^2]$	$\Sigma E^{(2)}[\beta^2]$
benzene	-4.0000	1/2	0.7974	-0.0769	-0.1314
naphthalene	-3.6832	2/3	0.9056	-0.0477	-0.1394
phenanthrene	-3.7651	3/5	0.8907	-0.0225	-0.1386
triphenylene	-3.8262	5/9	0.8781	-0.0284	-0.1371
chrysene	-3.7439	5/8	0.8933	-0.0205	-0.1392
3,4-benzophenanthrene	-3.7392	5/8	0.8953	-0.0279	-0.1398
1,2:7,8-dibenzochrysene	-3.7963	14/24	0.8835	-0.0319	-0.1388
anthracene	-3.3137	4/4	1.0397	-0.0565	-0.1506
tetraphene	-3.4180	6/7	1.0167	-0.0514	-0.1466
1,2:3,4-dibenzanthracene	-3.4935	10/13	0.9987	-0.0524	-0.1445
1,2:5,6-dibenzanthracene	-3.5141	9/12	0.9958	-0.0399	-0.1440
1,2:7,8-dibenzanthracene	-3.5131	9/12	0.9963	-0.0483	-0.1433
1,2:3,4:5,6-tribenzanthracene	-3.5834	15/22	0.9797	-0.0395	-0.1418
tetrabenzanthracene	-3.6495	25/40	0.9644	-0.0445	-0.1400
tetracene	-3.2476	6/5	1.0590	-0.0460	-0.1541
1,2-benzotetracene	-3.2773	10/9	1.0524	-0.0480	-0.1533
1,2:3,4-dibenzotetracene	-3.2959	18/17	1.0481	-0.0515	-0.1527
1,2:7,8-dibenzotetracene	-3.3857	15/16	1.0276	-0.0424	-0.1487
1,2:9,10-dibenzotetracene	-3.3854	15/16	1.0277	-0.0433	-0.1490
1,2:3,4:7,8-tribenzotetracene	-3.4021	27/30	1.0240	-0.0464	-0.1485
tetrabenzotetracene	-3.4786	45/56	1.0054	-0.0440	-0.1455
pentacene	-3.1776	9/6	1.0802	-0.0468	-0.1576
1,2-benzopentacene	-3.2098	15/11	1.0726	-0.0469	-0.1570
1,2:3,4-dibenzopentacene	-3.2298	27/21	1.0676	-0.0475	-0.1555
1,2:8,9-dibenzopentacene	-3.2408	25/20	1.0654	-0.0471	-0.1557
tetrabenzopentacene	-3.2787	81/72	1.0563	-0.0503	-0.1536
hexacene	-3.1590	12/7	1.0854	-0.0410	-0.1590
1,2-benzohexacene	-3.1698	21/13	1.0828	-0.0414	-0.1594

aromatic hydrocarbon are only slightly perturbed by the attacking dienophile ("early" transition state), the sum of the free valencies,  $\Sigma F_\mu$ , of the meso carbon atoms should provide a useful measure of reactivity. As has been noted by other authors,<sup>34</sup> the  $\Sigma F_\mu$  values of alternant hydrocarbons parallel the para-localization energies  $P$  to an amazing degree so that the discussion given above carries over. In particular, the meso positions of highest  $\Sigma F_\mu$  (for numerical values see Table III) are without exception those of highest  $P$  value.

**Fukui's Frontier Orbital Theory.** In the context of this model,<sup>35</sup> which likewise presumes an early transition state, the Diels-Alder reaction of aromatic hydrocarbons with maleic anhydride has to be classified as mainly HOMO (aromatic hydrocarbon)-LUMO (maleic anhydride) controlled; this follows from the fact that the center of gravity of the occupied ( $IP = 11.02$  eV<sup>36</sup>) and unoccupied ( $EA = +0.57$  eV<sup>37</sup>)  $\pi$  orbitals of maleic anhydride is at lower energies than in the case of the aromatic hydrocarbons (cf. Table II for the  $\pi$  IPs and ref 38 for the EAs of some hydrocarbons). Assuming the above orbital interaction to be the predominant one, the  $\log k_2$  data should correlate with second-order stabilization energies  $E^{(2)}$  defined as

$$E^{(2)} = \frac{(c_1 c_3 + c_2 c_4)^2}{\Delta E} \beta^2 \quad (1)$$

Here  $c_1$  and  $c_2$  are the meso AO coefficients of the highest occupied orbitals of the aromatic hydrocarbon;  $c_3$  and  $c_4$  are the AO coefficients of the  $\pi^*$  orbital of maleic anhydride;  $\beta$  is the resonance integral of the newly formed  $\sigma$  bonds, as the transition state is approached;  $\Delta E$  is the difference in energies of the highest occupied hydrocarbon and lowest unoccupied maleic anhydride orbitals, as determined by photoelectron and electron transmission spectroscopy. Since, for symmetry reasons,  $c_3 = -c_4$  and since  $\beta$  is a constant for homologous series of compounds, the above equation simplifies to

$$E^{(2)} = 0.5 \frac{(c_1 - c_2)^2}{-IP_1 + 0.57} \beta^2 \quad (2)$$

where  $c_3 = -c_4$  have been set  $1/\sqrt{2}$ .

Using Hückel AO coefficients for the highest occupied hydrocarbon orbitals and  $IP_1$  values from Table II, the following results (for numerical values see Table III) are obtained.




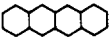
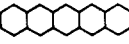
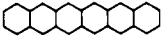



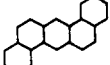
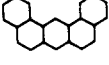
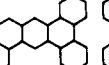
The most reactive meso positions are the same as those calculated by the two previous models; in that respect Fukui's theory proves successful. However, the linear annelation effect on the  $k_2$  data is not correctly reproduced, benzene being predicted to be more reactive than hexacene! This absurd result can be traced to the fact that the meso coefficients decrease rapidly with increasing molecular size because of the normalization constraint. Since the AO coefficients appear as squares in the numerator of eq 2, their decrease more than outweighs the lowering of  $IP_1$  in the denominator. For this very reason the angular annelation effect on  $k_2$  is in most cases correctly described: adding further benzo rings does not affect  $IP_1$  but lowers the AO coefficients as a result of the increasing molecular size.

Thus, we have to conclude that the frontier orbital model is unsuitable to describe and correlate the rate behavior of aromatic hydrocarbons, although this model proved very successful in other areas of organic chemistry.<sup>39</sup> The reason for this failure becomes immediately obvious from the discussion in the next section.

**Complete Second-Order Perturbation Treatment.** In a hydrocarbon with  $N$  carbon atoms there are  $N/2$   $\pi$  MO (aromatic hydrocarbon)-LUMO (maleic anhydride) and the same number of HOMO (maleic anhydride)- $\pi^*$  MO (aromatic hydrocarbon) interactions. On grounds of the generally high meso coefficients in the highest occupied orbitals and the relatively small energy gaps, the frontier orbital term of eq 2 is usually the largest one of all the  $N$  interaction terms, but its importance diminishes with increasing molecular size. Thus, the frontier orbital terms need not necessarily correlate with the total interaction energies  $\Sigma E^{(2)}$ , obtained by summing over all orbital interactions.

In order to calculate the interaction terms, we need to know

Chart I

						
IP <sub>1</sub>	9.24	8.15	7.41	6.97	6.61	6.36
IP <sub>2</sub>	9.24	8.88	8.54	8.41	8.32	8.14
ΔIP	0.0	0.73	1.13	1.44	1.71	1.78
10 <sup>6</sup> k <sub>2</sub>	-	-	2270	94200	1640000	6570000
						
IP <sub>1</sub>	7.41	7.41	7.39	7.38	7.40	7.40
IP <sub>2</sub>	8.54	8.04	7.91	7.80	7.79	7.56
ΔIP	1.13	0.63	0.52	0.42	0.39	0.16
10 <sup>6</sup> k <sub>2</sub>	2270	136	67.4	10.4	10.4	3.4

IP<sub>1</sub>, IP<sub>2</sub>, . . . , IP<sub>N/2</sub> and EA<sub>1</sub>, EA<sub>2</sub>, . . . , EA<sub>N/2</sub>. Only two-thirds of the required IPs are accessible from the photoelectron spectra,<sup>40</sup> and in the larger hydrocarbons identification of the individual IPs is sometimes hampered by band overlap, especially in the region above 9 eV. However, as the π IPs of aromatic hydrocarbons can be calculated within ±0.10 eV by a modified Hückel theory,<sup>41</sup> an alternative approach would be to base the perturbation treatment entirely on calculated IPs. Analogously, the mostly unknown EAs can be obtained by assuming a linear relation between IP<sub>i</sub> (experimental or calculated) and EA<sub>i</sub>. By fitting the 12 known EAs of benzene, naphthalene, and anthracene measured by electron transmission spectroscopy<sup>38</sup> to the corresponding experimental IPs (Table IV), the following regression with standard deviation of 0.300 eV is obtained:

$$EA_i = 8.898 - 1.100IP_i \quad (3)$$

Equation 3 of course holds only for alternant hydrocarbons. As expected on the basis of the pairing theorem, the slope of this regression is approximately -1, but the mean of corresponding IP<sub>i</sub> and EA<sub>i</sub> value varies considerably (cf. Table IV), suggesting that the role of double-bond localization or other factors is different for positive and negative ion states. This matter should be examined with care when more EA data become available.

The above procedure of using calculated IPs and EAs for the perturbation treatment has the added advantage of being applicable to as yet unknown hydrocarbons, thus providing us with a useful means for purposes of structure elucidation.

The ΣE<sup>(2)</sup> values for the present series of hydrocarbons are given in Table III, last entry, and plotted vs. the 6 + log k<sub>2</sub> data in Figure 7 of part 2, where further data are included. The overall quality of the regression (standard deviation 0.234 for the acenes and benzologs) is practically the same as that with the structure count and Hess-Schaad theories. Not surprisingly, the predictions regarding the most reactive meso positions are in harmony with all previously discussed theories.

As has been suspected above, the contribution of the frontier orbital term to ΣE<sup>(2)</sup> decreases with increasing molecular size, e.g., from 59% in benzene to 26% in hexacene. There is hardly any correlation between these two reactivity indexes. Owing to the smaller energy gaps, the interaction between the occupied orbitals of the hydrocarbons and the π\* orbital of maleic anhydride exceeds the converse interaction (relative contributions about 60:40%, independent of size and topology of the hydrocarbons). Thus, in alternant hydrocarbons, the first-mentioned interactions describe the rate behavior equally well as the sum of both.

The overall agreement improves slightly (standard deviation 0.220) if experimental rather than calculated IPs are used when available. This may be related to the fact that certain

Table IV. Electron Affinities,<sup>a</sup> EA<sub>i</sub>, Ionization Potentials,<sup>b</sup> IP<sub>i</sub>, and Their Mean (eV) to Check the Validity of the Pairing Theorem

hydrocarbon	EA <sub>i</sub>	IP <sub>i</sub>	(EA <sub>i</sub> + IP <sub>i</sub> )/2
benzene	-1.15	9.24	4.05
	-1.15	9.24	4.05
	-4.85	12.25	3.70
naphthalene	-0.19	8.15	3.98
	-0.90	8.88	3.99
	-1.67	9.98	4.16
	-3.37	10.84	3.74
anthracene	-4.72		
	0.5	7.41	3.96
	-0.63	8.54	3.96
	-1.15	9.19	4.02
	-1.69	10.18	4.25
	-2.61	10.28	3.84
	-4.44		
	-6.02		

<sup>a</sup> EA data of benzene and naphthalene from ref 38, of anthracene from K. D. Jordan, personal communication, May 1979. <sup>b</sup> IP data from ref 23.

trends in the experimental IPs, e.g., the insensitivity upon angular annelation of IP<sub>1</sub>, are badly reproduced by Hückel theory.

As with all previous models, the effect of phenyl substitution on the rate constants is not in all cases satisfactorily described.

**Empirical Correlations with the Photoelectron Data.** The availability of accurate IPs for the present hydrocarbons and the approximate validity of the pairing theorem (the sum of IP<sub>i</sub> and EA<sub>i</sub> is approximately constant; see eq 3) offer a unique opportunity to test some assertions proposed in the literature. For example, it is an article of faith among organic chemists that molecules possessing high-lying occupied and low-lying unoccupied orbitals (that is, low first IPs and high first EAs) are highly reactive.<sup>42</sup>

The rapidly increasing reactivity in going from benzene to hexacene, which is accompanied by a fall of IP<sub>1</sub> from 9.24 to 6.36 eV, provides a classical example which appears to support this claim; see upper half of Chart I. However, adding angular benzo rings to an acene like anthracene quenches the reactivity without concomitantly changing IP<sub>1</sub>; see lower half of Chart I. Thus, the above idea must be refuted; i.e., the reactivity is not related to IP<sub>1</sub>.

However, by focusing on ΔIP = IP<sub>2</sub> - IP<sub>1</sub> rather than on IP<sub>1</sub>, the effect of linear and angular annelation on the rate constants is correctly reproduced, at least qualitatively: the higher ΔIP, the more reactive is the hydrocarbon. Note that the spectral differences between the three isomeric dibenz-

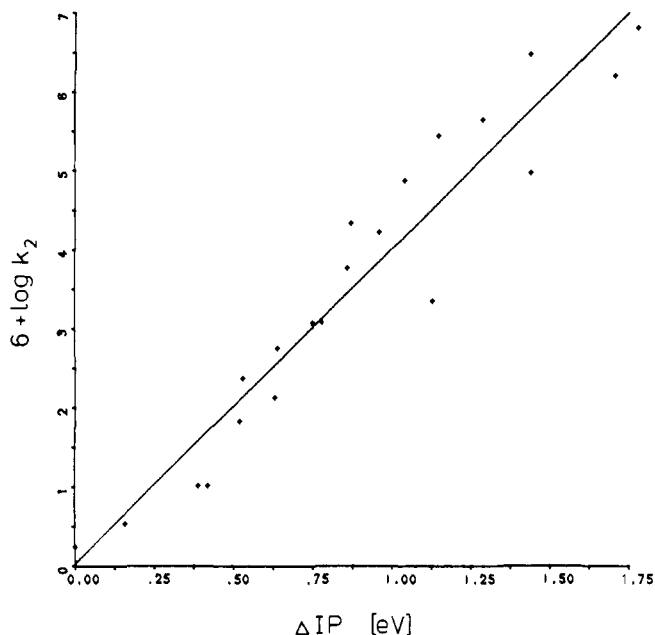


Figure 2. Plot of rate data on  $\Delta IP = IP_2 - IP_1$ . Least-squares regression:  $6 + \log k_2 = 0.029 + 3.983\Delta IP$ .

anthracenes are adequately reflected in the  $k_2$  values. The linear regression of the  $6 + \log k_2$  data, uncorrected for multiple reaction sites, on the  $\Delta IP$  values is shown in Figure 2.

The standard deviation of the above plot (0.589) is lowered to 0.265 if  $IP_2$  and  $IP_1$  are allowed to enter the regression with different weight, namely, in the ratio 35:65. Figure 3 is a plot of the uncorrected  $6 + \log k_2$  values against the function  $0.347IP_2 - 0.653IP_1$ .

As  $IP_1$  and  $IP_2$  can be estimated with sufficient accuracy by either Hückel theory or by an extension of Clar's annelation rules,<sup>43</sup> the above function is useful in rationalizing, correlating, and predicting the reactivities of a wide range of hydrocarbons, known or unknown. The only drawback is that the position of attack of maleic anhydride cannot be predicted, i.e., only "global" reactivities are obtained.

How can we understand that the reactivity is related to  $\Delta IP$  or, more precisely, to the above function rather than to  $IP_1$  as commonly assumed? In what follows, we try to provide a qualitative answer in terms of second-order perturbation theory and the regularities observed in the photoelectron spectra.<sup>23</sup>

In Figure 4 are correlated the occupied Hückel orbitals of two isomeric  $C_{22}H_{14}$  hydrocarbons, namely, 1,2:7,8-dibenzanthracene and pentacene, with those of the pertinent  $(4n + 2)$  annulene, where  $n = 5$ . As is well known, the orbitals of the annulene can be classified by their angular orbital quantum number  $\lambda$ , running from 0 for the lowest (nondegenerate) to 5 for the highest (degenerate) occupied orbitals. On introducing the cross bonds into the annulene skeleton, the following observations are made: (a) The  $\lambda = 0$  orbital is markedly stabilized for both hydrocarbons. (b) The  $\lambda = 1-5$  orbitals split only slightly in going to dibenzanthracene, but sizably in going to pentacene. Thus, the  $\Delta IP$  value defined above is dependent on the topology of the resulting hydrocarbon. (c) Orbitals with a given  $\lambda$  have roughly the same mean energies in both hydrocarbons, namely, about  $0.5\beta$  for the  $\lambda = 5$  orbitals, about  $0.9\beta$  for the  $\lambda = 4$  orbitals, etc. As a result of this,  $\overline{IP} = (IP_1 + IP_2)/2$  is approximately constant for the two isomers. (d) Orbitals belonging to the same  $\lambda$  (e.g.,  $\lambda = n$ ) can be recognized in the photoelectron spectrum in that the upper component gives rise to a sharp, fine-structured band, whereas the lower one is associated with a diffuse, structureless band (see ref 23 for the spectra and discussion). (e) For orbitals with a given  $\lambda$ , sizable meso coefficients appear only in the upper

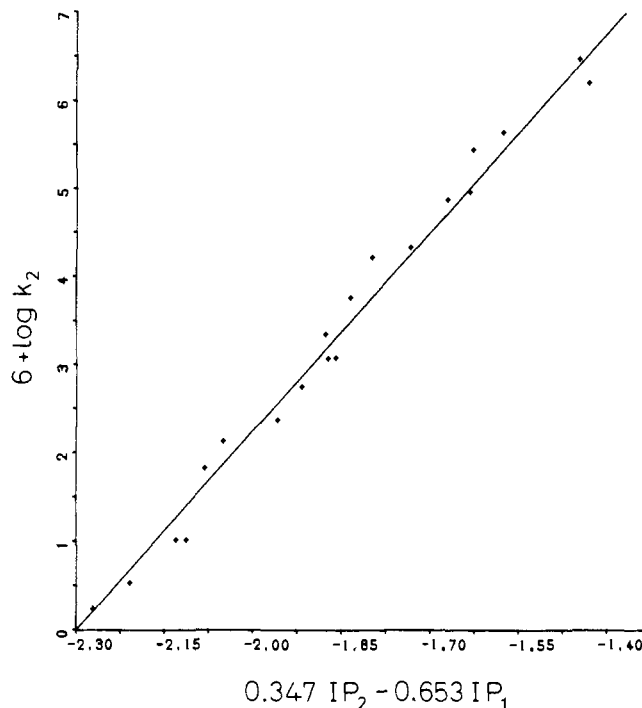


Figure 3. Plot of rate data on the function  $0.347IP_2 - 0.653IP_1$ . Least-squares regression:  $6 + \log k_2 = 17.28 + 7.52(0.347IP_2 - 0.653IP_1)$ .

component, whereas they vanish in the lower one for symmetry reasons. That is, only the orbitals which relate to "sharp" photoelectron bands contribute to the second-order stabilization energy.

Generalizing these observations we find that  $\overline{IP}$  depends in the first place on the size of the hydrocarbon (it is lowered with increasing size of the reference annulene),  $\Delta IP$  on its topology (linear vs. angular annelation or benzenoidity, in Clar's language). In hydrocarbons with low benzenoidity,  $\Delta IP$  can be so large that orbitals of different  $\lambda$  cross over, a process for which we propose the term "inversion". For example, in pentacene, 1,2-benzopentacene, hexacene, and 1,2-benzohexacene, the  $\lambda = n$  orbitals are not the highest and second highest, but the highest and third highest occupied orbitals; in these hydrocarbons  $\overline{IP}$  and  $\Delta IP$  refer therefore to  $IP_1$  and  $IP_3$ , that is, to the first "sharp" and first "diffuse" photoelectron bands.

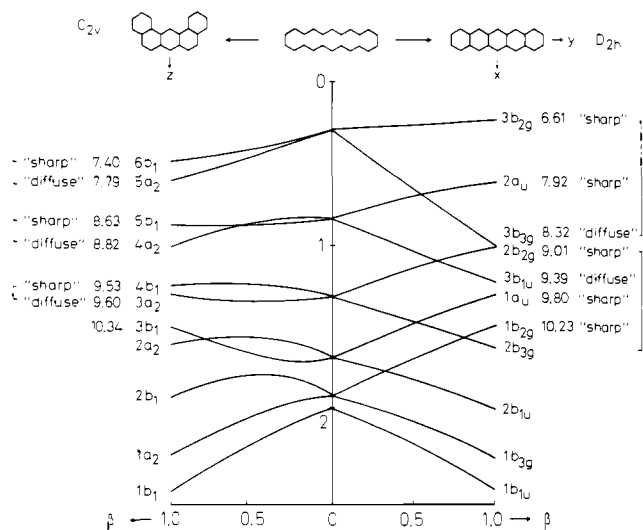
Returning to the reactivity problem, these consequences follow.

(a) Among isomeric hydrocarbons (where  $\overline{IP} \approx \text{constant}$ ), that with the lower  $IP_1$  value (or, equivalently, the higher  $\Delta IP$  value) will be more reactive because the orbitals with the meso coefficients (which are roughly the same for isomers) are at higher energies and interact more efficiently with the  $\pi^*$  orbital of maleic anhydride. Thus,  $IP_1$  or, equivalently,  $\Delta IP$  closely parallel  $\Sigma E^{(2)}$ , and plots with the  $6 + \log k_2$  data show excellent linearity, in accord with expectations based on simple theory.<sup>42</sup>

(b) In hydrocarbons with the same  $\Delta IP$  but derived from different  $(4n + 2)$  annulenes,  $\overline{IP}$  decreases with increasing  $n$ , thereby enhancing the interaction with the  $\pi^*$  orbital of maleic anhydride. As a result of the increasing molecular size, the meso coefficients decrease also, but this effect is almost perfectly compensated by the larger number of interaction terms. This hitherto unrecognized size effect on  $\Sigma E^{(2)}$  can thus be approximately described by  $\overline{IP}$ . It follows that large hydrocarbons are generally more reactive than small ones, even if  $\Delta IP$  is the same.

(c) If the reactivities of hydrocarbons with different  $\Delta IP$  and different  $\overline{IP}$  values are compared, both factors have to be taken into account. Factor (a) would demand a correlation of  $6 + \log$





**Figure 4.** Correlation diagram, showing the effect of "cross" bonds on the occupied Hückel orbitals of (22)annulene: left, 1,2:7,8-dibenzanthracene; right, pentacene.  $\beta$  is the resonance integral of the intraannular cross bonds. Orbitals correlating with annulene orbitals of the same angular quantum number  $\lambda$  are connected by brackets.

$k_2$  with  $\Delta IP = IP_2 - IP_1$ , factor (b) a correlation with  $-\overline{IP} = -0.51IP_2 - 0.51IP_1$ . If both terms are combined, a correlation with the function  $aIP_2 - bIP_1$  is expected, where  $a < b$ . As the regression depicted in Figure 3 shows, this is the case indeed.

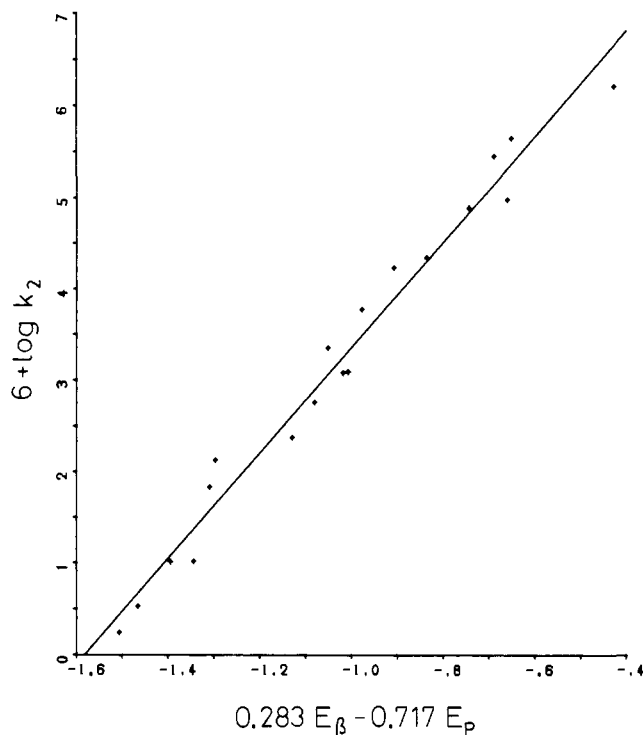
Thus, the empirical correlation with the photoelectron data is in harmony with second-order perturbation theory, and  $\Sigma E^{(2)}$  can be replaced by just two terms in which the AO coefficients do not appear. This latter fact may be the reason why the correlation with the  $6 + \log k_2$  data is better when the statistical correction for multiple reaction sites is neglected.

Although the standard deviation of this empirical correlation is not significantly lower than that with the purely theoretical models, it is the only one which correctly predicts the effect of  $\alpha$ - and  $\beta$ -phenyl substitution on the rate constants.

**Empirical Correlations with the UV Data.** In an earlier paper,<sup>23</sup> we have shown that the energies of the  $\alpha$ , p,  $\beta$ , and  $\beta'$  bands in the UV spectra of alternant hydrocarbons (for which the pairing theorem holds) can be predicted from the IPs of the first "sharp" and first "diffuse" photoelectron bands. In the acenes and their benzologs, these are the first and second bands, except in the four hydrocarbons mentioned above, where they are the first and third ones. As discussed above, the first sharp and first diffuse photoelectron bands originate from orbitals of the same  $\lambda$ , namely,  $\lambda = n$ . In other words, the two IPs relevant to the UV spectra are precisely those used in the preceding paragraph to correlate the rate behavior. It is only natural, therefore, to seek for correlations between the UV data and the rate constants. Such correlations would be of great practical interest in that they would allow us to substitute the gas-phase IPs (which are notoriously difficult to measure) by easily accessible solution data.

Clar was the first to notice a striking parallel<sup>1,3,5,6,44</sup> between Diels-Alder reactivity (or "para" reactivity, as he termed it) and the position of the p band (hence the name) in many homologous series, e.g., the acenes or the pyrenes. However, he also amply demonstrated that angular annelation lowers the reactivity without significantly shifting the p band. That is, the reactivity bears no simple relation to the p-band position (just as it was not related to  $IP_1$ , see above), despite claims of the opposite.<sup>42</sup>

Since the sequence of the  $\alpha$  and p bands is directly related<sup>23</sup> to  $\Delta IP$ , and since the  $E_\beta/E_\alpha$  ratio is constant at about 1.3 (cf. Table II), we would expect the reactivity to correlate in a first



**Figure 5.** Plot of the rate data on the function  $0.283E_\beta - 0.717E_p$ . Least-squares regression:  $6 + \log k_2 = 9.107 + 5.76(0.283E_\beta - 0.717E_p)$ .

**Table V.** Triplet Lifetimes  $\tau_{1/2}$  (s), Rate Constants  $10^6k_2$ , and Their Products for Some Hydrocarbons

hydrocarbon	$\tau_{1/2}$	$10^6k_2$	$10^6k_2\tau_{1/2}$
anthracene	0.034 <sup>a</sup>	2270	77
tetraphene	0.25 <sup>a</sup>	136	34
1,2:3,4-dibenzanthracene	0.56 <sup>a</sup>	67.4	38
1,2:5,6-dibenzanthracene	1.0 <sup>b</sup>	10.4	10
tetrabenzanthracene	6.7 <sup>b</sup>	1.8	12
tetracene	0.0019 <sup>a</sup>	47 100 <sup>c</sup>	89

<sup>a</sup> Reference 45. <sup>b</sup> Reference 44. <sup>c</sup> Corrected for statistical factor of 2.

approximation with the  $E_p - E_\alpha$  or  $E_\beta - E_p$  separations. This proved to be the case. If  $E_\beta$  and  $E_p$  are allowed to enter the regression with different weight, the correlation depicted in Figure 5 is obtained. As expected, the standard deviation (0.287) is comparable to that using the  $IP_1$  and  $IP_2$  values. A similar correlation, not shown here, is obtained if the  $E_\alpha$  and  $E_p$  values are employed. However, this correlation is of little practical value because the  $\alpha$  bands are often buried underneath the more intense p bands. This is never the case with the  $\beta$  bands, which are the most intense in these spectra.

The correlation shown in Figure 5 can qualitatively be paraphrased by saying that the reactivity increases with increasing  $E_\beta - E_p$  gap (the  $\beta$  band is always the third one in these spectra; the sequence of the  $\alpha$  and p bands is variable). Large  $E_\beta - E_p$  separations are found in the higher acenes, and very small ones in molecules like tetrabenzanthracene, triphenylene, or benzene. This is equivalent to saying that hydrocarbons with the p band as the first band in the UV spectrum readily undergo the Diels-Alder reaction, and those with the  $\alpha$  band only with difficulties.

**Empirical Correlations with Triplet Lifetimes.** Finally, we found a rough correlation (cf. Table V) between the triplet half-lifetimes  $\tau_{1/2}$  from the phosphorescence spectra and the rate constants  $k_2$ : the larger  $\tau_{1/2}$ , the smaller is  $k_2$ . Within the

limited accuracy of the lifetime data (which are difficult to measure for short-lived phosphorescences and which depend on the temperature, the solvent, and impurities), the product of both quantities appears to be roughly constant. For example, the increasing reactivity within the acenes benzene through tetracene is accompanied by a decline of the lifetimes: 11.1, 1.7, 0.03, and 0.002 s. On going from anthracene to tetrabenzanthracene,  $\tau_{1/2}$  increases from 0.03 to 6.7 s.

This inverse correlation between  $\tau_{1/2}$  and  $k_2$  (which also holds in the peri-condensed series) is of considerable value in ascertaining whether the observed phosphorescence is authentic or due to an impurity.

**Concluding Remarks.** We have shown that the Diels–Alder rate constants can be successfully correlated with theoretical and spectroscopic quantities.

First of all, this attests that the activation entropies are either constant for the present compounds or depend linearly on the  $k_2$  values. Variable-temperature studies aimed at discerning between these alternatives are now underway. Furthermore, it is safe to conclude that steric factors play a minor role, except perhaps for hydrocarbons bearing phenyl groups at the reactive meso positions.

On the experimental side, it will be interesting to see whether more powerful dienophiles like tetracyanoethylene are able to react with less reactive hydrocarbons such as naphthalene or phenanthrene.

Because of internal topological symmetries genuine to alternant hydrocarbons, many of the theories and concepts examined in this paper are interrelated so that the present rate data provide no answer to vexing questions<sup>46</sup> such as concertedness of the Diels–Alder reaction or “earliness” of the transition state (Brown’s theory assumes a late transition state, perturbation theory an early one—both are successful!). Hopefully, the latter question can be answered with the rate data of the nonalternant hydrocarbons.

It is important to emphasize that  $IP_1$  and the position of the p band have no bearing on the Diels–Alder reactivity. Deeply colored hydrocarbons with low first  $IP$  need not necessarily be highly reactive. Only for compounds derived from the same  $(4n + 2)$  annulene can useful conclusions be drawn from the  $IP_1$  or  $E_p$  values. This is because  $\overline{IP}$  is constant for isomers so that the  $\alpha$  and  $\beta$  bands are each found at the same wavelengths; in this case  $-IP_1$  and  $\Delta IP$  (or equivalently,  $-E_p$  and  $E_\beta - E_p$ ) parallel each other.

The results reported in this paper suggest that alternant hydrocarbons may be roughly classified according to their  $\Delta IP$  value.

(a) On the one side are compounds with small  $\Delta IP$  values, i.e., near degeneracy of orbitals of the same  $\lambda$ . These are distinguished by low Diels–Alder reactivity and high phosphorescence quantum yield and lifetime and have the  $\alpha$  band as the first band in the UV spectrum. Because of the similarity of their orbital energy spectrum with that of the  $(4n + 2)$  annulenes it is tempting to call these hydrocarbons “annulenoid”. Extreme examples are provided by benzene, triphenylene, and tetrabenzanthracene.

(b) On the other side are compounds with high  $\Delta IP$  values, i.e., large gaps between orbitals of the same  $\lambda$ . They show high Diels–Alder reactivities and low phosphorescence quantum yields and lifetimes, and the p band is the first UV band. Their orbital energy spectrum resembles that of the polyenes so that they may be termed “polyenoid”. Extreme examples are pentacene and hexacene.

This classification bears a superficial relationship to that proposed long ago by Clar on the basis of his sextet theory. Indeed, low  $\Delta IP$  values are generally associated with high benzenoidities (that is, high ratio of number of sextets per number of rings) and vice versa, although some exceptions do exist in the peri-condensed series. Later work will show whether

useful insights into the interplay between structure and physicochemical properties can be gained along these lines.

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## Diels–Alder Reactivity of Polycyclic Aromatic Hydrocarbons. 2. Phenenes and Starphenes

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**Abstract:** In continuation of earlier work on the acenes and their benzologs, the second-order rate constants of 25 cata-condensed hydrocarbons of the phene and starphene type with maleic anhydride at 91.5 °C in 1,2,4-trichlorobenzene have been measured. Parallel UV measurements provided information on the structure of the Diels–Alder adducts. Two- and even three-fold addition was observed with certain hydrocarbons. The rate data could be successfully correlated with theoretical (localization energies, second-order stabilization energies) and spectroscopic (photoelectron and UV spectra) quantities. Qualitatively, the data provide support to ideas propounded long ago by Clar in the context of his sextet theory of aromaticity. The potential of these structure/reactivity relationships in checking the assumed constitution of a hydrocarbon and for detecting minute impurities is demonstrated with several examples.

### Introduction

Although the stabilities of aromatic hydrocarbons have repeatedly been calculated by a variety of models ( $\pi$  resonance theories, localization methods), few experimental rate data were until recently available to check these theories. In the preceding paper of this series,<sup>1</sup> the second-order rate constants for the Diels–Alder reaction with maleic anhydride of all acenes and benzologs known to date were reported. These measurements, which were carried out in 1,2,4-trichlorobenzene at 91.5 °C, have now been extended to all other cata-condensed hydrocarbons not belonging to the above series, i.e., to the phenes, starphenes, zigzag-annelated hydrocarbons, and helicenes. So far no experimental rate data were available for these compounds.

Unlike the acenes and their benzologs, some of these hydrocarbons react twice and even thrice with maleic anhydride, thus making the evaluation of the rate constant more difficult. There is the added complication that for some hydrocarbons the structure was uncertain; it is deduced here on the basis of the photoelectron, UV spectral, and kinetic data in conjunction with theoretical calculations described in part 1. From the linearity of the  $\ln E$  vs. time plot ( $E$  being the optical density at an appropriate UV absorption band of the starting hydrocarbon), minute impurities can be detected; this is particularly important for those compounds synthesized by the Elbs pyrolysis, a method known to often result in partial or complete skeletal isomerization.<sup>2</sup> Very recently, it has been recognized that this complication must also be considered for hydrocarbons prepared by photocyclodehydrogenation<sup>3</sup> and Lewis acid catalyzed cyclodehydrogenation<sup>4–6</sup> methods.

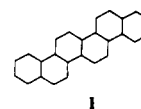
### Experimental Section

**Aromatic Hydrocarbons.** The phenes, starphenes, and zigzag-annelated compounds were taken from Professor Clar's collection of aromatic hydrocarbons; their synthesis is mostly described in his monograph.<sup>2</sup> The synthesis of tetrapheno(6',5':5,6)tetraphene, naphtho(2',1':1,2)tetracene, and 1,2-benzophenanthreno(9'',10'':3,4)tetracene is described in ref 7, that of tetrabenzohaptaphene in ref 8, and that of naphtho(2',3':1,2)pentacene in ref 9. The helicenes up to [14]helicene were kindly provided by Professors Martin and

Jutz, but not investigated in detail as it was quickly realized that they do not react with maleic anhydride under standard conditions.

Some hydrocarbons deserve special mention in that their constitution has now been firmly established on the basis of new spectroscopic and kinetic results.

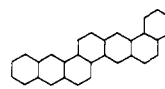
Fulminene I, not mentioned in Clar's book, was isolated in 1944



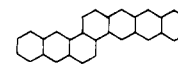
I

from the highest boiling fraction of coal tar; its constitution, tentatively deduced at that time on the basis of its chemical behavior, melting point, and IR spectrum,<sup>10</sup> could now be confirmed by the photoelectron spectrum.<sup>11</sup>

The sample of anthraceno(2',1':8,9)tetraphene (II), obtained in 1931 by an Elbs pyrolysis,<sup>12</sup> proved to contain an isomer, namely, anthraceno(2',1':1,2)tetracene (III), as shown by comparing the UV



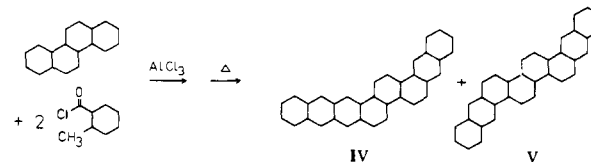
II



III

spectrum and rate behavior with those of pure III obtained by Clar<sup>13</sup> in a different way. Owing to lack of material, the photoelectron spectrum of III could not yet be recorded.

Similarly, the sample believed to be 2,3-benzonaphtho(2',3':8,9)picene (IV) was mainly tetrapheno(4',3':3,4)tetraphene (V) containing only a few percent of the expected isomer IV. They were obtained by condensing chrysene with 2 mol of *o*-toluoyl chloride and subjecting the resulting diketone to an Elbs pyrolysis:<sup>14</sup>



IV

V

We shall briefly outline how this structural problem could be solved.

The specimen provided by Clar had a very diffuse UV spectrum (Figure 1) which defied simple interpretation. Repeated recrystallization from trichlorobenzene and sublimation did not change the