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PHOTOCYCLOADDITION OF 1,3-CYCLOHEXADIENE TO POLYNUCLEAR AROMATIC HYDROCARBONS†

NIEN-CHU C. YANG,* JOHN MASNOVI, WEI-LONG CHIANG, TOYUAN WANG,‡ HANSEN SHOU,§ and DING-DJUNG H. YANG
Department of Chemistry, University of Chicago, 5735 S. Ellis Avenue, Chicago, IL 60637, U.S.A.

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Abstract—Extending our investigations on the photochemical reactions between benzenoid aromatic hydrocarbons and conjugated polyunsaturated olefins to the higher arenes, we describe the pericyclic reactivity evidenced in the photochemical cycloaddition reactions of anthracene, tetracene, benz(a)anthracene, dibenz(a,c)anthracene, dibenz(a,h)anthracene, dibenz(a,j)anthracene and pentaphene with 1,3-cyclohexadiene. The divergent reactivities of these arenes is not explicable in terms of Woodward–Hoffmann or derivative theories. We attribute the proclivities of these systems to engage in pericyclic cycloaddition reactions, and in particular the failure of dibenz(a, h)anthracene and pentaphene to form "allowed" $4\pi_s + 4\pi_s$ meso cycloadducts, to a requirement for the preservation of "essential symmetry" about the reactive positions, wherein the local nodal structure of the reactants must correlate with that of the products for a pericyclic process to be energetically competitive with other modes of deactivation of the arene excited state. Applicability of this theory in thermal processes is also considered.

Since the eminent investigations by Woodward and Hoffmann,[1] the mechanisms of pericyclic reactions have proved increasingly tractable to theoretical analysis. Recently, however, studies have indicated that, in certain instances, pericyclic reactivity is not explicable in terms of Woodward–Hoffmann[2] or derivative theories.[3,4] In our investigations of the photochemical cycloaddition reactions of conjugated polyenes to arenes, we have discovered that the higher arenes provide a useful template for probing symmetry correlations in pericyclic reactions.[5] Our studies of the photochemical and thermal cycloaddition reactions of these systems, which we have now extended to include arenes containing five catacondensed benzenoid rings, have uncovered reactivity patterns which apparently can not be treated by application of the method of orbital correlations in the usual sense. The behavior evidenced in arene cycloaddition reactions has prompted us to derive an extension of the theory of pericyclic reactions wherein such reactivity can be described adequately by an analysis of reactant and product nodal patterns about the reactive centers in the frontier molecular orbitals (FMOs).

Although thermal reactions between benzenoid aromatic hydrocarbons (arenes) and olefins are well-known,[6] and the ability of certain arenes to form photodimers has long been recognized,[7] only recently have the cycloaddition reactions of arenes been subject to scrutiny in a mechanistic context. Historically, interest in the thermal reactivity has concerned the addition of olefins to arenes in the Diels–Alder reaction.[6,8] Study of the photochemical reactions between olefins and arenes principally focused on the additions of olefins to derivatives of benzene and naphthalene.[9] However, the modes of addition possible in such cases are limited, and the derived mechanistic insights are not always unambiguous. Frequently the origin of the observed adducts can be ascribed theoretically to more than a single pathway. For example, the $2\pi + 2\pi$ adducts isolated in the photochemical reaction between arenes and olefins (eqn 1) and the $4\pi + 2\pi$ adducts isolated in the Diels–Alder additions of olefins to arenes (eqn 2) can in principle result from concerted or stepwise mechanisms. In eqns (1) and (2), the intermediates indicated as diradicals in the stepwise pathway could, depending upon the situation, also be represented as dipolar entities (e.g. when substituents which stabilize charge separation are present). If bond rotation in the intermediates were to occur more slowly than the transformations of the intermediates into products (and back into reactants), the stereochemical integrity of the reactants and the intermediates would be maintained, and the reactions should be stereoselective. A product analysis would then not reveal which mechanism is operative.[9]

Following the initial discovery that conjugated olefins quench the fluorescence of aromatic hydrocarbons,[10] the photocycloaddition of these olefins to arenes has been studied extensively in our laboratory.[11-18] Such reactions provide a greater diversity of reactivity and accordingly disclose a larger amount of information than do reactions with simple olefins. In particular, reactions which occur by concerted mechanisms frequently afford a completely different set of products than are obtained from cycloadditions in which the mechanism of addition is nonconcerted. The thermodynamically more stable isomers generally are the major products isolated from reactions which occur in a non-concerted fashion, but the products derived from reactions with concerted mechanisms often represent more highly strained derivatives. Thus the photocycloaddition of s-*trans* dienes to arenes affords the highly strained *trans* $4\pi_s + 4\pi_s$ products in a concerted reaction,[11,13,15] but the thermodynamically favored $4\pi_s + 2\pi_s$ products result from a non-concerted

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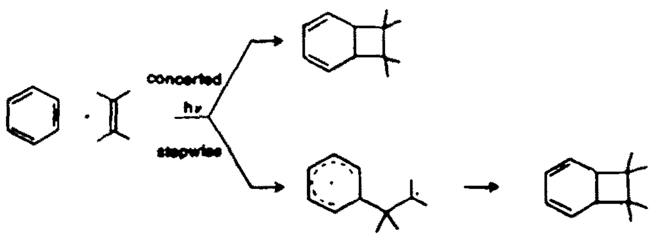
† A preliminary account of this work has been published, see footnote 5.

‡ Visiting Scholar, Institute of Photographic Chemistry, Academia Sinica, Beijing, 1979–1981.

§ Visiting Scholar, Institute of Photographic Chemistry, Academia Sinica, Beijing, 1979–1980.



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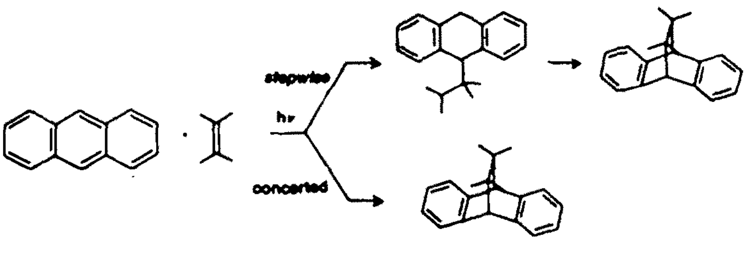

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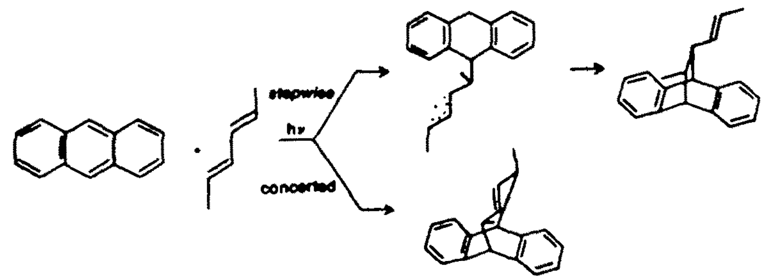

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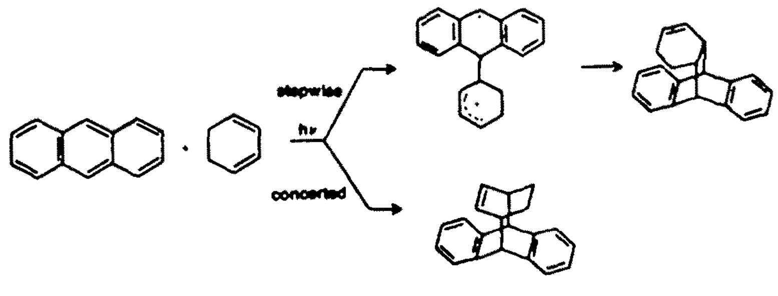


(4)

mechanism (eqn 3).[15,17,19] s-*cis*-Olefins behave similarly (eqn 4).[12,14,15]

The mode of addition then provides a way of distinguishing the type of mechanism which predominates, under any given set of conditions, in the photocycloaddition reactions between arenes and conjugated polyunsaturated olefins. Investigation of these reactions subsequently has provided significant implications concerning the generality of the application of correlational analysis and the Woodward-Hoffmann rule to photochemical processes.

EXPERIMENTAL

Instrumentation. Proton NMR spectra were obtained on a Bruker HX-270 (270 MHz) spectrometer in chloroform-d soln at ambient temp and using TMS as an internal standard. Data are reported in the following format: chemical shift in ppm upfield relative to TMS ($\delta^{TMS} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet and b = broadened), integration, and coupling constant (J, in hertz). The structural assignments of new compounds also is based in part, when possible, on NMR ^{1}H decoupling experiments. UV spectra were taken on a Varian Cary 219 spectrophotometer; absorption maxima (in units of nm.) are reported in the form of λ_{MAX} (ϵ_{MAX}). IR spectra were taken on a Perkin-Elmer model 283 IR spectrophotometer; strong absorption bands are reported in units of cm^{-1}. M.ps were taken in unsealed capillary tubes in a Hoover m.p. apparatus and are uncorrected. Microanalyses were performed at Micro-Tech Laboratories, Inc., Skokie, Illinois. High resolution mass spectra were determined on a AEI MS-9 spectrometer.[20]

Materials. Aldrich Gold Label benzene was used in the irradiations; Fischer reagent grade benzene and petroleum ether and MCB reagent grade CH_2Cl_2 were used in the chromatographies. 1,3-Cyclohexadiene (Chemical Samples Co.) was distilled and passed through a short column of alumina (Woelm, neutral, activity grade I from ICN) before use. Tetracene (Aldrich, lot No. 102087 PC, m.p. >300°) was chromatographed over activity I Woelm silica gel (ICN) using benzene-petroleum ether, and the material recovered from the column was recrystallized from this solvent system. Anthracene (Aldrich, Gold Label 99.9+%, lot No. 14,106–2, m.p. 216.2–216.4°) was used as received. Benz[a]anthracene (Eastman, lot No. A6B, m.p. 156–157°) was chromatographed over activity I Woelm silica gel (ICN) using benzene–petroleum ether and was recrystallized from ethanol. Dibenz[a,c]-anthracene (Aldrich, 97%, lot No. 073097 KD, m.p. 205–207°) was recrystallized from benzene–petroleum ether. Dibenz[a,h]anthracene (Aldrich 97%, lot No. 050667 BD, m.p. 266–267° and Eastman, lot No. A4T and A6X) was chromatographed over Woelm silica gel (ICN, activity I) using benzene–petroleum ether, and the recovered material was recrystallized from this same solvent system. All other materials were of standard reagent grade quality, purchased from Aldrich, Fisher, Mallinckrodt or MCB chemical companies.

General irradiation procedure. A pyrex irradiation vessel equipped with N_2 inlet, a side-arm capped with a rubber septum, and a water-cooled reflux condenser with $CaCl_2$ drying tube was charged with a benzene soln of the arene and 1,3-cyclohexadiene (CHD, 1.0M). Deoxygenation was achieved by bubbling N_2 through the soln for 30 min prior to irradiation. The soln was stirred magnetically with a Teflon-coated magnetic stirbar and Corning magnetic stirrer. Irradiation was performed with stirring, under a N_2, using a Hanovia 450 W medium pressure mercury lamp housed in a water-cooled quartz immersion well. A cylindrical uranyl glass filter cut off light of wavelengths shorter than about 330 nm. The temp of the solns during irradiation was maintained at 22 ± 3°. Progress of the reactions was monitored by means of periodic extraction of alloquots through the rubber septum using a 50 μl syringe and UV analysis. When the arene was consumed ($\geq$90%), the solvent was stripped off under reduced pressure and the residue chromotographed over activated Woelm alumina (neutral, ICN, activity I or II). Products eluted with 2%–20% CH_2Cl_2–petroleum ether; fractions were analyzed by NMR, and those containing identical product were combined and recrystallized. Yields reported are isolated chemical yields. Duplicate runs were performed at low initial arene concentration and the crude reaction mixtures subject to careful NMR integration to ensure that the isolated chemical yields accurately reflected the relative yields of primary photochemical products formed.

Quantum yield determinations were made on a merry-go-round apparatus with a Corning glass 7–60 + 0–52 filter system to isolate the 365 nm emission of a 200 W Hanovia medium pressure lamp housed in a water-cooled quartz immersion well.[28] Irradiations were performed at 22 ± 2°. The quantum yields for the disappearance of arene were standardized using a benzophenone–benzhydrol actinometer ($\Phi = 0.69$).[28] All solutions were prepared in benzene containing 1,3-cyclohexadiene (1.0M); each sample (2.5 ml) was degassed in three freeze–thaw cycles at 10 microns pressure. Samples with dilute concentrations of arene were corrected for incomplete light absorption. Conversions of the arenes were monitored by UV spectroscopy and were terminated before 20% of the arenes had reacted.

Irradiation of anthracene, **1a**. Anthracene (0.867 g, 4.87 mmole) and 1,3-cyclohexadiene (CHD, 1.0M) in benzene (130 ml) was irradiated 2 hr. The crude soln was concentrated and filtered to give 0.27 g. (31%) of a white ppt identified as the dimer of anthracene. Chromatography of the filtrate afforded first 0.060 g of a colorless oil identified as a mixture of dimers of 1,3-cyclohexadiene. Continued elution with 2:98 CH_2Cl_2–petroleum ether gave 118 mg (9%) of a colorless solid which was the known $4\pi_s + 2\pi_s$ meso adduct **14a**.[21,22] Elution with 5:95 CH_2Cl_2–petroleum ether gave 446 mg (36%) of a colorless crystalline material which was the known $4\pi_s + 4\pi_s$ meso adduct **7a**.[15] Elution with 12:88 CH_2Cl_2–petroleum ether afforded 148 mg (12%) of a new product. Recrystallization from CH_2Cl_2–petroleum ether gave 100 mg (8%) of colorless crystals, m.p. 136–137°; UV (MeOH): 351 (696), 334 (773), 320 (438), 301 (23600), 289 (18500), 278.5 (14000), 269.5 (15500), 242 (84300); NMR ($\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$): 1.32 (m, 1H), 1.58–1.78 (m, 3H), 2.87 (m, 1H), 3.37 (b t, 1H, J = 9Hz), 3.61 (b t, 1H, J = 10 Hz), 4.10 (t, 1H, J = 9.5 Hz), 5.70 (b d, 1H, J = 11 Hz), 5.92 (m, 2H), 6.51 (d of d, 1H, J = 2 and 10 Hz), 7.35 (m, 4H), 7.69 (m, 2H). (Found: C, 93.03; H, 7.09. Calc. for $C_{20}H_{18}$: C, 92.98; H, 7.02%). This adduct was therefore identified as a $2\pi_s + 2\pi_s$ adduct of cyclohexadiene to an end ring of anthracene, **15a**. Continued elution with 15:86 CH_2Cl_2 petroleum ether gave a mixture of anthracene, anthracene dimer, and a new product. Careful rechromatography of this fraction afforded 12 mg (1%) of an unstable compound identified as a $4\pi_s + 4\pi_s$ adduct of cyclohexadiene to an end ring of anthracene, **13a**, on the basis of its spectral properties: m.p. 108–112° (solidifies and remelts 122–130°); UV (methanol): 318.5 (300), 310.5 (290), 301 (9040), 288 (13400), 277.5 (16500), 266.5 (18300), 234 (104000) nm.; NMR ($\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$): 1.35 (m, 4H), 3.02 (m, 2H), 3.82 (m, 2H), 6.04 (d of d, 2H, J = 5 and 5 Hz), 6.37 (d of d, 2H, J = 5 and 5 Hz), 7.38 (d of d, 2H, J = 6 and 6 Hz), 7.48 (s, 2H), 7.71 (d of d, 2H, J = 6 and 6 Hz). (Found: C, 92.78; H, 6.98. Calc. for $C_{20}H_{18}$: C, 92.98; H, 7.02%).

Upon refluxing in benzene for 30 min., this adduct (**13a**) underwent a Cope rearrangement to afford the $2\pi_s + 2\pi_s$ product **15a** quantitatively (**13a** → **15a**), analogous to the rearrangement observed for the naphthalene $4\pi_s + 4\pi_s$ adduct **10** (**10** → **12**).[12]

Irradiation of benz[a]anthracene, **16**. Benz[a]anthracene (0.860 g, 3.77 mole) and 1,3-cyclohexadiene (1.0 M) in benzene (120 ml) was irradiated 90 min. Chromatography afforded first 0.903 g of cyclohexadiene dimers. Elution with 2:98 CH_2Cl_2–petroleum ether afforded 0.805 g (69%) of a $4\pi_s + 4\pi_s$ adduct, **17**. Recrystallization from EtOH gave colorless needles, m.p. 152–153°; UV (MeOH): 320 (1010), 300 (1580), 291 (3980), 270 (8910) nm; NMR ($\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$): 1.42–1.66 (m, 4H), 3.21 (m, 1H), 3.32 (m, 1H), 4.38 (b d, 1H, J = 11 Hz), 5.08 (d, 1H, J = 11 Hz), 5.47 (t, 1H, J = 8 Hz), 5.56 (t, 1H, J = 8 Hz), 7.08 (m, 2H), 7.26 (m, 2H), 7.36 (d, 1H, J = 8 Hz), 7.42 (t, 1H, J = 8 Hz), 7.51 (t, 1H, J = 8 Hz), 7.66 (d, 1H, J = 7 Hz), 7.83 (d, 1H, J = 7 Hz), 8.16 (d, 1H, J = 8 Hz). (Found: C, 93.32; H, 6.50. Calc. for $C_{24}H_{20}$: C, 93.46; H, 6.54%).

Further elution with 10:90 CH_2Cl_2–petroleum ether gave 0.096 g (8%) of a $4\pi_s + 2\pi_s$ adduct, either **18a** or **b**. Recrystallization from ethanol gave colorless crystals, m.p. 141–143°; UV (MeOH): 329 (17400), 321 (1060), 290 (4270), 269 (9350) nm; NMR ($\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$): 0.81 (m, 1H), 1.56–1.88 (m, 3H), 2.20–2.50 (m, 2H), 4.29 (b s, 1H), 4.94 (b s, 1H). 5.67–5.78 (m, 2H), 7.07 (m, 2H), 7.27 (m, 2H), 7.38 (b t, 1H, J = 8 Hz), 7.49 (m, 2H), 7.62 (d of d, 1H, J = 2 and 8 Hz), 7.81 (d, 1H, J = 8 Hz), 8.25 (d, 1H, J = 8 Hz). (Found: C, 93.02; H, 6.62. Calc. for $C_{24}H_{20}$: C, 93.45; H, 6.54%).

The structure of the $4\pi_s + 4\pi_s$ adduct was verified in a single-crystal X-ray crystallographic study.[61]

Irradiation of dibenz[a,c]anthracene, **19**. Dibenz[a,c]anthracene (0.200 g, 0.719 mmole) and 1,3-cyclohexadiene (1.0 M) in benzene (100 ml) was irradiated 2 hr. Chromatography afforded first 6.0 g of cyclohexadiene dimers. Elution with 15:85 CH_2Cl_2–petroleum ether gave first an oily mixture of products (65 mg, 25%) which were identified by NMR to be a mixture of approximately equal proportions of two $4\pi_s + 2\pi_s$ 1:1 adducts of cyclohexadiene to the meso positions of the arene (**21a** and **21b**) and a $4\pi_s + 4\pi_s$ product, **20**. This mixture was not further purified. The pure $4\pi_s + 4\pi_s$ adduct **20** eluted next, and afforded 155 mg (60%) of colorless crystals after recrystallization from CH_2Cl_2–petroleum ether, m.p. 204–205°; UV (MeOH): 360 (501), 343 (430), 310.5 (4210), 299 (3980), 272 (11400), 258 (22100), 249 (21400), 227 (15900) nm; NMR ($\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$): 1.49 (m, 2H), 1.63 (m, 2H), .3.31 (m, 2H), 5.16 (d, 2H, J = 11 Hz), 5.49 (d of d, 2H, J = 4 and 5 Hz), 7.10 (d of d, 2H, J = 5 and 6 Hz), 7.31 (d of d, 2H, J = 5 and 6 Hz), 7.63 (m, 4H), 8.27 (b d, 2H, J = 9 Hz), 8.74 (b d, 2H, J = 9 Hz); IR (KBr): 604, 699, 721, 743, 751, 759, 770, 809, 1048, 1166, 1378, 1429, 1440, 1446, 1455, 1484, 1498, 1580, 2890, 2931, 3039 cm^{-1}. (Found: C, 93.53; H, 6.26. Calc. for $C_{28}H_{22}$: C, 93.81; H, 6.19%).

To verify the stereochemistry of the $4\pi_s + 4\pi_s$ adduct, 50 mg of this isomer was hydrogenated over ~30 mg of 10% Pd/C. Hydrogenation was effected at atmospheric pressure and at 25° with stirring in EtOAc for ~20 hr. After filtration and evaporation of the solvent at reduced pressure, the residue was chromotographed on a short column of Woelm alumina (activity I) with CH_2Cl_2–petroleum ether. A single product was recovered; recrystallization from CH_2Cl_2–petroleum ether afforded 45 mg (90%) of colorless, flocculent plates of the dihydro derivative

20-H_2, m.p. 244–247° (dec), UV (MeOH): 358 (477), 341 (358), 308 (4890), 296 (4470), 283 (4500), 273 (1140), 258 (26100), 249 (21300), 266 (16400), 209 (18700) nm.; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 1.03 (b d, 2H, J = 9.5 Hz), 1.24 (b d, 2H, J = 9.5 Hz), 1.36 (b s, 4H), 2.98 (b d, 2H, J = 11 Hz), 5.20 (d, 2H, J = 11 Hz), 7.14 (d of d, 2H, J = 3.5 and 5.5 Hz), 7.33 (d of d, 2H, J = 3.5 and 5.5 Hz), 7.63 (m, 4H), 8.27 (b d, 2H, J = 8 Hz), 8.74 (b d, 2H, J = 8 Hz); IR (KBr): 569, 729, 750, 755, 1431, 1446, 1451, 1459, 1486, 1498, 2859, 2861, 2881, 2892, 2918, 2959 cm^{-1}. (Found: C, 93.02; H, 6.75. Calc. for $C_{28}H_{24}$: C, 93.29; H, 6.71%). Appearance of a new high-field NMR absorption (1.03 ppm) upon hydrogen of **20** indicates that this adduct has the olefin adding *syn* to the phenanthrene.

Irradiation of dibenz[a,j]anthracene, **22**. Dibenz[a,j]anthracene[23,24] (0.153 g, 0.55 mmole) and 1,3-cyclohexadiene (1.1M) in benzene (500 ml) was irradiated 4 hr. Chromatography afforded first 12 g of cyclohexadiene dimers. Elution with 5:95 CH_2Cl_2–petroleum ether afforded a mixture of $4\pi_s + 2\pi_s$ adducts; the major isomer **24** was obtained by recrystallization from CH_2Cl_2–petroleum ether to give 11 mg (9%) of colorless crystals, m.p. 160–162°; UV (cyclohexane); 325.5 (3290), 303 (4310), 282.5 (5860), 272 (6400), 260 (8020), 254 (9760), 243 (39200), 221 (66500) nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 0.68–1.91 (m, 4H), 2.43 (m, 1H), 2.55 (m, 1H), 4.51 (d, 1H, J = 2 Hz), 5.54 (m, 2H), 5.91 (d, 1H, J = 2 Hz), 7.69 (m, 8H), 7.81 (m, 2H), 8.38 (m, 2H), IR (KBr): 755, 810, 1170, 1260, 1380, 1455, 1510, 1585, 2920, 3050 cm^{-1}; mass spectrum (10 eV): (Found: *m/e* 358.1721. Calc for $C_{28}H_{22}$: *m/e* 358.1721 ($M^{+\cdot}$)).

Further elution with 15:85 CH_2Cl_2–petroleum ether afforded 0.100 g (84%) of a $4\pi_s + 4\pi_s$ adduct **23** as a colorless crystalline solid, m.p. 208–210°; UV (cyclohexane): 330 (3470), 315 (3370), 300 (5100), 289 (6110), 276.5 (5630), 249 (47900), 224 (69500) nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 1.38 (m, 4H), 3.17 (m, 1H), 3.38 (m, 1H), 4.50 (d, 1H, J = 11 Hz), 5.54 (m, 2H), 6.00 (d, 1H, J = 11 Hz), 7.14 (m, 8H), 7.81 (d, 2H, J = 8 Hz), 8.29 (m, 2H); IR (KBr): 705, 765, 820, 1020, 1165, 1380, 1455, 1510, 1585, 2945, 3030 cm^{-1}; mass spectrum (10 eV): (Found *m/e* 358.1721. Calc. for $C_{28}H_{22}$: *m/e* 358.1721 ($M^{+\cdot}$)).

Irradiation of dibenz[a,h]anthracene, **25**. Dibenz[a,h]anthracene (0.316 g, 1.13 mmole) and 1,3-cyclohexadiene (1.0 M) in benzene (120 ml) was irradiated 8.5 hr. Chromatography afforded first 6.01 g of cyclohexadiene dimers. Elution with 10:90 CH_2Cl_2–petroleum ether afforded 0.334 g (82%) of a $4\pi_s + 2\pi_s$ adduct (**26** or **27**). Recrystallization from EtOH gave colorless crystals, m.p. 162–164°; UV (MeOH): 325 (1710), 316 (1220), 308 (17900), 283 (6310) nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 0.87 (m, 1H), 1.50–1.76 (m, 2H), 1.91 (m, 1H), 2.38 (b q, 1H, J = 9 Hz), 2.63 (b d, 1H, J = 9 Hz), 5.13 (d, 1H, J = 2 Hz), 5.23 (d, 1H, J = 2 Hz), 5.56 (m, 1H), 5.76 (b d, 1H, J = 9 Hz), 7.41 (q, 2H, J = 7 Hz), 7.55–7.62 (m, 6H), 7.83 (t, 2H, J = 9 Hz), 8.32 (b t, 2H, J = 9 Hz). (Found: C, 93.75; H, 6.08. Calc. for $C_{28}H_{22}$: C, 93.81; H, 6.19%).

Further elution with 20:80 CH_2Cl_2–petroleum ether afforded 28 mg (7%) of a colorless oil. The structure of this product was assigned that of a $2\pi_s + 2\pi_s$ (**28**) adduct on the basis of its NMR spectrum and ^1H decoupling experiments: NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 1.60 (m, 1H), 1.89 (m, 1H), 2.22 (b d, 1H, J = 19 Hz), 2.44 (m, 1H), 2.84 (m, 2H), 3.58 (b d, 1H, J = 7 Hz), 3.77 (b t, 1H, J = 7 Hz), 5.96 (m, 1H), 6.10 (b d, 1H, J = 9 Hz), 7.25–7.36 (m, 3H), 7.44–7.89 (m, 5H), 8.11 (d, 1H, J = 9 Hz), 8.27 (s, 1H), 8.33 (s, 1H), 8.63 (d, 1H, J = 9 Hz).

Irradiation of tetracene, **29**. Tetracene (0.250 g, 1.10 mmole) and 1,3-cyclohexadiene (1.0 M) in benzene (140 ml) was irradiated 14 hr. The solvent was stripped off under reduced pressure and the residue was filtered from CCl_4. The pale yellow ppt was washed with $CHCl_3$ and dried to afford 128 mg (51%) of a 9:1 mixture of dimers of tetracene. The filtrate and washings were combined and chromatographed. First, 1.42 g of cyclohexadiene dimers were collected. Elution with 4:96 CH_2Cl_2–petroleum ether first afforded 25 mg (7%) of a $4\pi_s + 2\pi_s$ adduct **31** as colorless crystals after recrystallization from CH_2Cl_2–petroleum ether, m.p. 244–245° (dec); UV (MeOH): 318.5 (630), 287.5 (3380), 276.5 (6980), 270.5 (8140), 265.5 (8140), 258 (6560), 231 (94200) nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 0.75 (m, 1H), 1.66–1.79 (m, 3H), 2.35 (m, 1H), 2.49 (b d, 1H, J = 10 Hz), 4.25 (t, 2H, J = 2.5 Hz), 5.70 (b s, 2H), 7.12 (m, 2H), 7.32 (m, 2H), 7.37 (d of d, 2H, J = 6 and 6 Hz), 7.64 (s, 2H), 7.74 (d of d, 2H, J = 5 and 6 Hz). (Found: C, 93.22; H, 6.54. Calc. for $C_{24}H_{20}$:C, 93.46; H, 6.54%).

Continued elution with 4:96 CH_2Cl_2–petroleum ether next afforded an isomeric $4\pi_s + 2\pi_s$ adduct **32**, which was recrystallized from CH_2Cl_2–petroleum ether to give 25 mg (7%) colorless plates, m.p. 212–213° (dec); UV (MeOH): 318 (660), 304 (630), 287.5 (3950), 275.5 (7800), 270 (7470), 265.5 (8230), 257.5 (6400), 230.5 (95000) nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 0.79 (m, 1H), 1.75 (m, 3H), 2.37 (m, 1H), 2.52 (b d, 1H, J = 10 Hz), 4.26 (t, 2H, J = 3 Hz), 5.73 (b s, 2H), 7.09 (d of d, 2H, J = 5 and 5 Hz), 7.25 (d of d, 2H, J = 6 and 8 Hz), 7.39 (d of d, 2H, J = 6 and 6 Hz), 7.69 (s, 1H), 7.71 (s, 1H), 7.76 (d of d, 2H, J = 6 and 6 Hz). (Found: C, 93.29; H, 6.61. Calc. for $C_{24}H_{20}$: C, 93.46; H, 6.54%).

Elution with 15:85 CH_2Cl_2–petroleum ether afforded a $4\pi_s + 4\pi_s$ adduct **30**, which was recrystallized from CH_2Cl_2–petroleum ether to give 51 mg (15%) of colorless needles, m.p. 207–208° (dec); UV (MeOH): 322.5 (938), 310 (750), 290.5 (2730), 279 (5000), 275.5 (6410), 269 (6990), 261 (5500), 241.5 (38250), 235 (40000) nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$); 1.35 (b d, 2H, J = 11 Hz), 1.54 (b d, 2H, J = 9 Hz), 3.19 (m, 2H), 4.39 (d, 2H, J = 11 Hz), 5.70 (d of d, 2H, J = 6 and 6 Hz), 7.14 (m, 4H), 7.39 (d of d, 2H, J = 6 and 6 Hz), 7.61 (s, 2H), 7.73 (d of d, 2H, J = 6 and 6 Hz). (Found: C, 93.31; H, 6.59. Calc. for $C_{24}H_{20}$: C, 93.46: H, 6.54%).

The stereochemistry of these adducts (**30**–**32**) could not be assigned with certainty and should be considered as tentative, based upon the spectroscopic evidence.

Irradiation of pentaphene, (**37**). Pentaphene[25–27] (0.245 g, 0.880 mmole) and 1,3-cyclohexadiene (1.0 M) in benzene (200 ml) was irradiated for 4 hr using a 250 W medium pressure mercury lamp through a Corning glass filter number 3–74 to cut off light of wavelength shorter than 400 nm. Chromatography afforded first 10 g of cyclohexadiene dimers. Elution with 20:80 CH_2Cl_2–petroleum ether afforded 0.028 g (9%) of a yellow crystalline adduct identified as a single $4\pi_2 + 2\pi_s$ isomer (**38** or **39**) on the basis of its spectral properties; m.p. 174–5°; UV (cyclohexane): 356 (3180), 313 (12800), 282 (35300), 270 (37600), 258 (29500) nm with a long tailing absorption extending to 400 nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 0.84 (m, 1H), 1.83 (m, 1H), 2.16 (m, 1H), 2.38 (m, 1H), 2.70 (m, 1H), 2.79 (m, 1H), 3.70 (m, 2H), 5.93 (m, 1H), 6.07 (m, 1H), 7.36 (m, 4H), 7.52 (s, 1H), 7.69 (m, 3H), 7.85 (m, 2H), 8.50 (s, 1H), 8.53 (s, 1H); mass spectrum (10 eV). (Found *m/e* 358.1721. Calc. for $C_{28}H_{22}$: *m/e* 358.1721 ($M^{+\cdot}$)). No other 1:1 adduct was detected.

When pentaphene is irradiated with a uranyl glass filter (admitting light of wavelength longer than about 300 nm), secondary photoproducts are isolated. These adducts arise from the photocycloaddition of a second molecule of diene to the meso positions of the anthracene chromophore of the primary photoproduct. An inseparable mixture of isomeric 2:1 adducts, 90 mg (30%), can be isolated under these conditions. The second molecule of diene appears to add to the anthracene chromophore to afford both $4\pi_s + 2\pi_s$ and $4\pi_s + 4\pi_s$ secondary 2:1 adducts. The structure of these compounds was assigned on the basis of their spectral data: UV (cyclohexane): 264 (977), 240 (1820), 230 (4680), 220 (8910), 210 (11500), nm; NMR ($\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$): 0.72 (m, 1H), 1.20–1.89 (m, 4H), 2.18 (m, 1H), 2.28 (m, 1H), 3.07 (m, 1H), 3.21 (m, 1H), 4.10 (b s, 3H), 4.19 (d of d, 1H, J = 11 and 11 Hz). 4.44–4.88 (m, 3H), 5.44–5.73 (m, 4H), 7.95–8.00 (m, 2H), 8.11–8.39 (m, 8H); mass spectrum (10 eV). (Found *m/e* 438. Calc. for $C_{34}H_{30}$: *m/e* 438.

Thermal reactions with tetracyanoethylene. Solns of arene (0.0333 M) and of tetracyanoethylene (TCNE, 0.0333 M) in air-saturated CH_2Cl_2 (Aldrich, Gold Label) were prepared separately at room temperature (22° ± 3°). Equal volumes of each soln were then mixed thoroughly in a volumetric flask. The UV absorption spectra of the resulting intensely colored solns were taken immediately, and then the solns were stored stoppered in the dark. The decrease in absorbances of the maxima due to charge-transfer complexes was monitored periodically by UV spectroscopy. In this way, the times required for the absorbances of these maxima to decrease to 50% of their initial intensities ($\tau_{1/2}$) were determined for dibenz[a,c]anthracene, dibenz[a,j]anthracene, and pentaphene. The insolubility of the charge transfer complex formed between TCNE and dibenz[a,h]anthracene prepared in this manner required the initial concentration of this arene to be reduced from 0.0333 to 0.0267 M before mixing with

Table 1. Product distribution in the photocycloaddition of 1,3-cyclohexadiene[a] to arenes in benzene[b]

Arene	Products, %[c]				Φ_{-ArH}[d]
	$4\pi_s + 4\pi_s$	$4\pi_s + 2\pi_s$	$2\pi_s + 2\pi_s$	arene dimer	
9[e]	70[f]	0	—[g]	0	0.23
1a	38[f]	9	8	31	0.28[e]
1b[h]	59	10	0	11	—[g]
1c[e]	75	3	tr[i]	—[g]	—[g]
1d[e]	87	0	tr[i]	—[g]	0.52
1e[e]	87	0	0	—[g]	0.65
29	15	14	0	51	(0.05)[j]
16	69	8	0	—[g]	0.16
19	73	13	0	—[g]	0.27
25	0	82	7	0	0.0016
22	84	9	—[g]	0	0.0015
37	0	9	—[g]	0	0.004

[a] 1.0M [b] 22 ± 3° C. [c] isolated chemical yields. [d] quantum yields for disappearance of arene at low initial arene concentration. [e] reference 15. [f] combined yields of meso and end-ring $4\pi_s + 4\pi_s$ adducts. [g] not determined. [h] reference 29. [i] trace amount formed as indicated by NMR spectroscopy; not isolated. [j] estimated.

Table 2. Reactions of TCNE[a] with arenes[a] in dichloromethane[b]

Arene	λ_{MAX}(nm)[c]	$\tau_{1/2}$(min)[d]
1a[e]	"green"	>5[f]
1b[e]	"yellow"	0[f]
1d[g]	—[g]	—[g]
16[e]	"light violet"	60[f]
19	550, 660[h]	240
25[i]	594, 690[j]	5900
22	626	6800
37	673	135

[a] 0.0166M unless otherwise noted. [b] 22 ± 3° C. [c] absorption maximum of charge transfer complexes. [d] time required for absorption maximum to decrease to 50% of its initial intensity. [e] reference 79. [f] reaction rate (see reference 79). [g] reference 80. A reaction occurred, although these parameters were not specified. [h] double maxima observed. [i] the insolubility of the charge-transfer complex forced us to use an arene concentration of 0.0133M in this case. [j] a shoulder appears at 690 nm.

TCNE. Furthermore, double maxima were observed in the absorption spectra of the charge transfer complexes formed between TCNE and dibenz[a,h]anthracene and dibenz[a,c]anthracene. This data is summarized in Table 4.

RESULTS

The product distributions found for the cycloaddition reactions between arenes and 1,3-cyclohexadiene are summarized in Table 1. The Woodward-Hoffman "allowed" $4\pi_s + 4\pi_s$ adducts are the predominant or exclusive products formed in all cases except for tetracene, dibenz[a,h]anthracene, and pentaphene. With tetracene, another "allowed" photoproduct (the photodimers of tetracene) is the major product, and the $4\pi_s + 4\pi_s$ adduct of cyclohexadiene remains the principal 1:1 product isolated, although in lower relative yield than is obtained with the other arenes which afford a

Table 3. Physical properties of arenes

Arene	IP(eV)[a]	EA(eV)[b]	RSE(eV)[c]	E_{S_1} (10^2cm^{-1})[d]	E_{T_1} (10^2cm^{-1})[e]	PLE(β)[f]
4	9.24	-1.07	0.869	384(^1L_b)	295	-4.000
9	8.15	-0.06	1.323	322(^1L_a)	213	-3.683
1a	7.41	0.49	1.600	267(^1L_a)	147	-3.314
29	6.97	0.84	1.822	212(^1L_b)	103	-3.248
16	7.41	0.42	2.291	260(^1L_b)	165	-3.418
19	7.39	0.34	3.058	267(^1L_b)	178	-3.494
25	7.38	0.37	2.948	253(^1L_b)	183	-3.514
22	7.40	0.33	2.948	254(^1L_b)	183	-3.513
37	7.27	0.44		236(^1L_b)	170	-3.449

[a] Ionization potentials, reference 46. [b] Electron affinities, reference 64. [c] Resonance energies, references 62 and 63. [d] Energy and Platt notation of the first excited singlet state, reference 54. [e] Energy of the first triplet state, reference 54. [f] Para localization energy, reference 46.

Table 4. Lifetimes[a] of arene first excited singlet states at room temperature

Arene	Solvent		
	Benzene	Methanol	Cyclohexane
4			29[b]
9	110[c]		96[b]
1a	4.5[c]	5.0[d]	4.9[b,e]
1b		5.2[d]	4.6[b,e]
1c			1.1[b]
1d			1.9
1e			13.8
29	5.3[c]		6.4[b]
16	47[c]	40.1[d]	49.4[b,e]
19	45[c]		53.5[e]
25		22.5[d]	37.5[e]
22			160[b]

[a] nsec. [b] reference 54. [c] reference 66. [d] reference 67. [e] reference 68.

similar adduct. Dibenz[a,h]anthracene affords a $4\pi_s+2\pi_s$ adduct in high chemical yield. Pentaphene also affords a $4\pi_s+2\pi_s$ primary product, although secondary photochemical reactions of the primary product lower the yield of material which can be isolated.

The quantum yields of arene consumption listed in Table 1 are also revealing. The quantum yields for the consumption of naphthalene and the derivatives of anthracene are relatively large. Values for anthracene, benz[a]anthracene, and dibenz[a,c]anthracene are substantial, falling in the range of 0.15–0.3. The quantum yield for the consumption of tetracene, while not explicitly determined, was estimated to be of the order of 0.05 (the low solubility of tetracene in benzene makes accurate estimation difficult since, at low concentration, only a small fraction of the incident light is absorbed). It thus appears that the amount of $4\pi_s+4\pi_s$ adduct formed in the photolysis of arenes with 1,3-cyclohexadiene correlates in a qualitative manner with the quantum yield for arene consumption: the reactions which occur with a high quantum yield in general afford a higher chemical yield of $4\pi_s+4\pi_s$ product.

Data for the reactions of tetracyanoethylene with arenes is summarized in Table 2. The reactions seem to be complex, with the formation of charge transfer complexes which have very broad absorption spectra and, in some cases, exhibit more than a single maximum. The relative rates of reaction can be correlated rather crudely with the wavelength of maximum absorption for the charge transfer complexes: the longer the wavelength of this maximum, the faster the reaction. With dibenz[a,h]anthracene, this correlation holds for the maximum appearing at 594 nm; a shoulder is evident at about 690 nm, however, and the relative intensities of these two maxima are not constant during the reaction (the shoulder at 690 nm decreases in intensity less rapidly than does the 594 nm maximum). Dibenz[a,c]anthracene also exhibits a double maximum in the absorption spectrum of its tetracyanoethylene complex; in this case both maxima are approximately equal in intensity and show no change in their relative intensities as the reaction progresses.

DISCUSSION

The mechanism of pericyclic reactions has intrigued chemists for many years. The theory of Woodward and Hoffmann[2] provided a major contribution toward the interpretation of the mechanistic significance of these reactions. The determination of reactant and product orbital correlations can afford a qualitative description of the potential energy surfaces for pericyclic reactions. However, orbital correlations strictly are obtained only for the choice of a reaction coordinate along which some element of symmetry common to reactants and products is preserved.

Since the Woodward–Hoffmann approach is intended to provide merely the qualitative features of the potential energy surface along an appropriately chosen reaction coordinate, minor perturbations from a symmetrical case can be treated by largely ignoring the source of the asymmetry. Indeed, the interpretive power of the Woodward–Hoffmann rules derives from their applicability to asymmetrical reactants and reaction pathways as well as to reactions in which symmetry is believed to be strictly maintained.

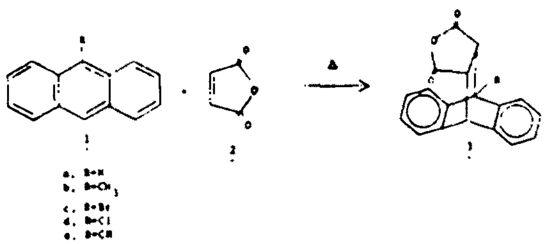
Following the proposal of the Woodward–Hoffmann rules, considerable attention was devoted to the study of reactions devoid of any recognizable symmetry element which nonetheless seem to be amenable to a Woodward–Hoffmann correlation analysis. Subsequently, various alternative expressions were developed and applied to define pericyclic reactivity.[30–40] In these extended or simplified theoretical treatments, consideration of the symmetry involved in the overall reaction effectively is bypassed or is held to be derivative, and, in general, the direct local interactions between reacting fragments are believed preeminant. In assessing the "allowedness" of pericyclic processes, most such theories recognize the importance of orbital phase properties near the reacting positions. However, in the application of the aforementioned formalisms, the consideration of symmetry is not explicitly entertained. Symmetry, when it is fortuitiously maintained in a pericyclic reaction, can be treated as a special case of the more general circumstance in which symmetry is not necessarily conserved. Woodward–Hoffmann correlations merely are considered to represent a shorthand method which pertain only to the appropriate specific instance in which symmetry is present.

For Woodward–Hoffmann "allowed" reactions, theoretical investigations have indicated that, since pericyclic bonding exists in the transition state, nascent bond formation must be essentially synchronous at the appropriate interacting positions.[2,30–41] It is reasonable to assume that a similar situation would obtain for modestly asymmetric substrates, as long as the electronic properties of the reactants are not meaningfully altered from those of the symmetrical substrates. Bond formation may become more non-synchronous, but the essential features of concerted behavior should persist provided that the perturbation caused by the asymmetry only exerts minor effects on the reacting centers themselves. Then the local nodal structure about the reacting positions should be essentially retained, and, despite the strict absence of overall symmetry, this local "essential symmetry" can be used as an approximation in the construction of orbital correlations. In this sense, photochemical and thermal pericyclic reactions should conform to description by a modified correlation analysis whenever symmetry or local symmetry exists along a reaction coordinate. (This is the basis for a number of simplified approaches derived from the Woodward–Hoffmann theory of orbital correlations which explicitly ignore the role of symmetry in pericyclic processes.)[30–40]

Recently, a number of theoretical studies have indicated that a more complete description of the potential energy surface is required to determine adequately the energy barrier for concerted reactions when the reactant asymmetry[3] or polarity[4] is extreme. However, the sophistication in calculation necessary for a reliable estimate of the potential energy surfaces involved is difficult to effect. Simplifying, though qualitative, analyses then continue to be convenient and valuable in the prediction of sizable potential energy barriers along a given reaction coordinate. Theories based upon the Woodward–Hoffmann rules, as previously presented,[30–40] largely ignore the situation in which marked deviations from the symmetric case are observed in reactants and products and where, as a consequence, significant asymmetry is intrinsic to the reaction.

Although the understanding of thermal pericyclic reactivity is relatively advanced, the mechanisms of most photochemical processes are less well established. This derives, in part, from the large energy content of excited states which is available for manifestation in chemical reactivity, the closeness in energy and potential mixing of excited states along a reaction coordinate, and the requisite non-adiabatic transitions observed in the deactivation of excited states.[41] It is experimentally difficult to prove singularity in reaction mechanism and, for example, to rule out the possibility of short-lived biradical intermediates in photochemical reactions which are, allegedly, concerted.

Since many states and intermediates are energetically accessible in photochemical reactions, it becomes important to determine conditions which influence the choice of reaction path. Toward this end, much recent attention has focused on the study of the pericyclic reactivity of the cata-condensed benzenoid aromatic hydrocarbons.[5,9–19,42–43] These compounds and their derivatives are known to engage in pericyclic reactions which are typical of s-*cis*-1,3-dienes;[6,8,44] the meso positions tend to be most susceptible toward reaction due to the high electron density and the large coefficients in the frontier molecular orbitals at these centers,[45] and geometrical constraints and energetic considerations usually require arenes to function as $4\pi_s$ components in their general patterns of reactivity. For example, a large diversity of arenes evidence reactivity toward thermal cycloaddition to olefins. Thus, maleic anhydride (MA, 2) and its derivatives will undergo Diels–Alder addition with a variety of aromatic hydrocarbons (eqn 5).[6,46] These reactions are analogous to the Diels–Alder reactions of MA and s-*cis*-1,3-dienes (eqn 6).[8] The olefins add in a $4\pi_s + 2\pi_s$ fashion at the meso positions of the arenes, as anticipated. When such addition is not feasible



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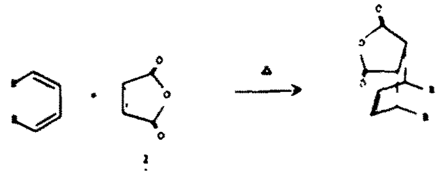

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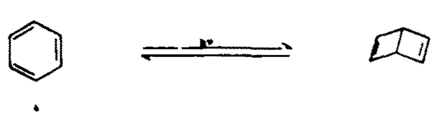

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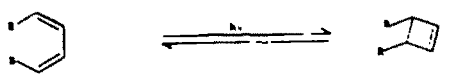

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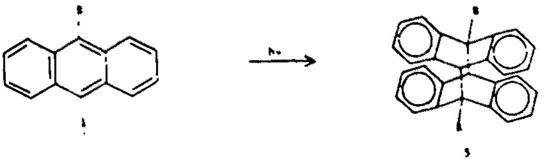

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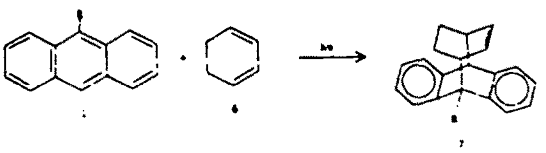


(11)

thermodynamically (e.g., benzene is inert to most dienophiles), the respective retro–Diels–Alder reactions are exceptionally facile.[47]

The photochemical reactivity of arenes also parallels that of their non-aromatic s-*cis*-1,3-diene counterparts. The disrotatory electrocyclic interconversion of arenes and their Dewar isomers[48–53] (eqns 7 and 8) mimics the classical butadiene–cyclobutene valence isomerization problem treated by Woodward and Hoffmann.[1,2] In photocycloaddition reactions, the arenes again are obliged to participate as $4\pi_s$ components, and addition would be "allowed" between an arene functioning in this sense and a partner which formally donates 4n electrons suprafacially. Therefore, in the presence of appropriate quenchers such as conjugated olefins, arenes react in their first singly excited singlet states to afford the respective "allowed" $4\pi_s + 4\pi_s$ meso adducts.[11–18] As a special instance of such reactivity, upon singlet excitation most arenes will yield a photodimer; excimers are known to be intermediates in these cycloadditions.[54–56] Arenes which heretofore have failed to form stable photodimers are usually prevented from doing so because of the steric (e.g. 9-phenylanthracene and 9,10-dimethylanthracene) or the thermodynamic (e.g. benzene) inaccessibility of the adducts.[54–56] When arenes are irradiated with conjugated olefins, analogous $4\pi_s + 4\pi_s$ addition usually will predominate in the formation of products; exciplexes are believed to be intermediates in these cycloadditions.[57]

The thermal addition of MA and the photochemical addition of 1,3-cyclohexadiene (CHD, **6**) to anthracene (An, **1a**) can be considered as prototypical cases. An reacts thermally with MA to afford the expected "allowed" meso $4\pi_s + 2\pi_s$ cycloadduct (eqn 6, R = H). This reaction has been well characterized.[6,46] An in its first singlet excited state, $^1An^*$, can form a photodimer[7,54-56] (eqn 10, R = H) or, in dilute solution and in the presence of CHD, will add to CHD to form predominantly the "allowed" meso $4\pi_s + 4\pi_s$ cycloadduct[15,17] (eqn 11, R = H). In these reactions, a plane of symmetry is retained along the reaction coordinate; thus they conform to analysis by Woodward–Hoffmann theory.

The introduction of a minor perturbation of the molecular symmetry in these reactions, as would be observed in the case of unsymmetrically substituted anthracenes, has little effect on the course of the cycloadditions as long as steric factors are not severe. 9-Methylanthracene (**1b**), for example, engages in thermal reactions with MA[6,58] (eqn 5, R = Me) and in photochemical reactions (eqns 11, 14, R = Me) which do not differ appreciably with respect to their product distributions from the reaction of An itself.[29] Other meso substituted anthracenes, such as the 9-bromo-, 9-chloro- and 9-cyano-derivatives (**1c–e**), were found to behave in a similar manner. These compounds afford Diels–Alder adducts with MA[6] (eqn 5, R = Br, Cl) and react photochemically to form dimers[54] and with CHD to afford predominantly or exclusively the $4\pi_s + 4\pi_s$ products (eqn 11, R = CN and eqn 14, R = Br, Cl).[15] Symmetry is not necessarily conserved in these transformations, but, despite the strict absence of overall symmetry, the local "essential symmetry" (i.e. the local nodal environment near the reacting centers) does not change in the course of the reactions. Non-linear benzannelation of the An nucleus causes a more significant perturbation of the wavefunction about the reactive meso positions of the arene[45] (Fig. 1); nevertheless, even with this more extreme induction of asymmetry, the pericyclic reactivity of benz(a)anthracene (BA, **16**) is entirely analogous to that observed in the symmetrical case, with An. BA reacts thermally with MA to give the meso Diels–Alder adduct[6,58] and photochemically with CHD to give the meso $4\pi_s + 4\pi_s$ adduct (in the absence of diene, BA forms a photodimer).[59,60] The photocycloaddition reaction is illustrated in eqn 15, where the regiochemistry of $4\pi_s + 4\pi_s$ adduct **17** is that anticipated from consideration of the effects of maximum secondary overlap and of bond orders.[61]

The reactivity of the dibenzanthracenes represents an interesting comparison since dibenz(a,c)anthracene (a,c-DBA **19**), dibenz(a,h)anthracene (a,h-DBA **25**) and dibenz(a,j)-anthracene (a,j-DBA **22**) possess similar physical properties. The singlet and triplet excitation energies, ionization potentials and electron affinities, and aromatic stabilization energies and para localization energies (Table 3)[46,54,62-24] are nearly identical for these compounds. However, their reactivities are quite dissimilar. Thermal addition of MA to a,h-DBA has a lower rate constant than has the addition of MA to a,c-DBA.[6a,b,46] More significantly, the photocycloaddition of CHD to a,h-DBA follows a different course. Irradiation of a,c-DBA in the presence of CHD readily yields the expected "allowed" meso $4\pi_s + 4\pi_s$ adduct (eqn 16). (This product also has the regiochemistry expected from consideration of the effects of maximum secondary overlap and of bond orders.) Additionally, photoaddition of a,j-DBA with CHD affords the $4\pi_s + 4\pi_s$ adduct at

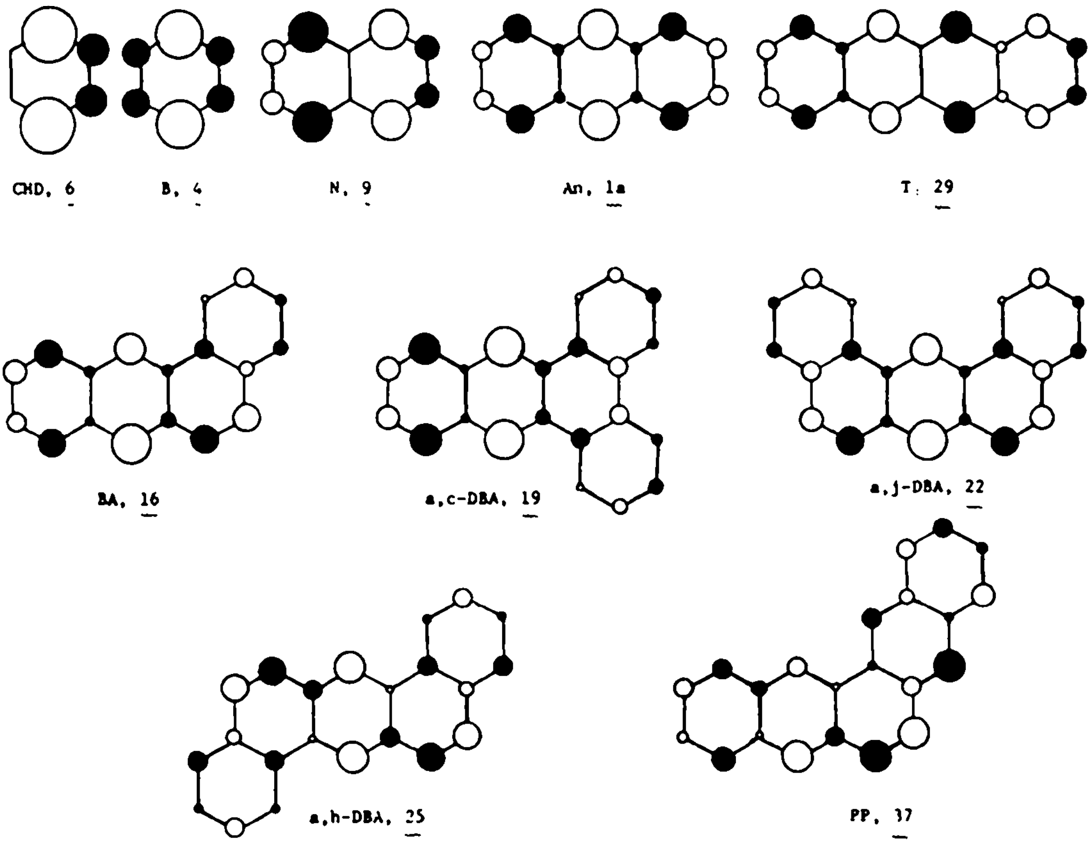
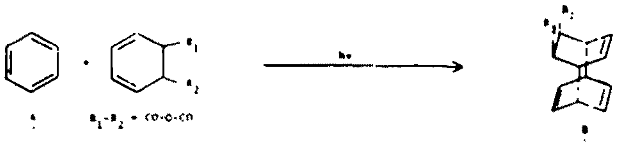


Fig. 1. LUMOs of 1,3-cyclohexadiene and aromatic hydrocarbons.[45]



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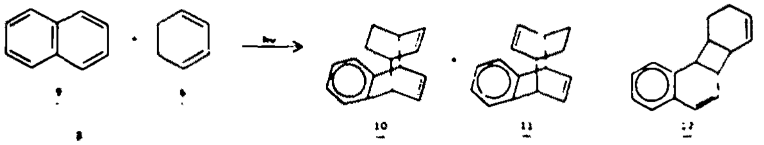

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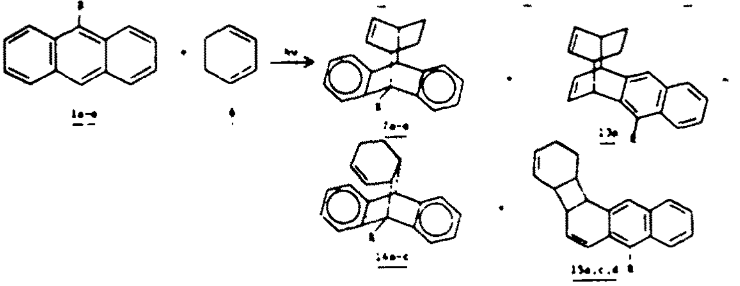

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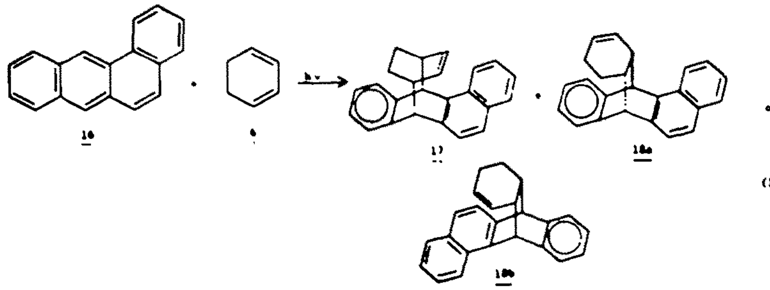

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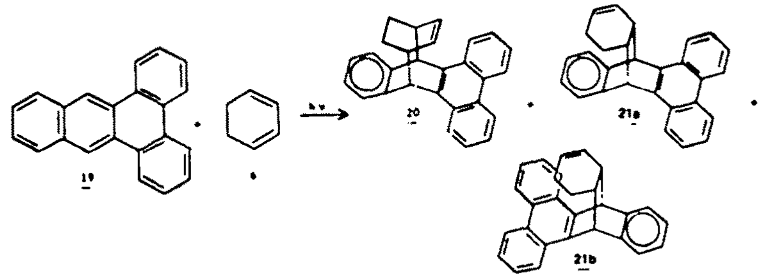

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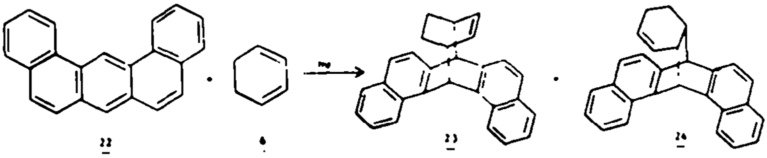
low initial concentration of a,j-DBA (eqn 17), albeit with some reluctance; the quantum yield for the reaction is relatively low, and the product distribution is concentration dependent. Photocycloaddition of CHD to a,h-DBA also occurs with a very small quantum yield, and, even at low initial concentration of a,h-DBA, the principal adduct isolated is the meso "disallowed" $4\pi_s+2\pi_s$ compound (eqn 18). A small amount of a $2\pi_s+2\pi_s$ adduct is obtained as well. Further evidence of the uncharacteristically low reactivity of a,h-DBA toward concerted photocycloadditions can be found in the arene photodimerization propensities. Although BA[39,40] and a,c-DBA[45] form photodimers, a,h-DBA has not been reported to photodimerize.

The unusual behavior of a,h-DBA compared with the other arenes studied is not due to the supervention of an extraordinarily rapid photophysical deactivation of the excited singlet state of a,h-DBA. The lifetimes of the lowest excited singlet states of the three isomeric DBAs are similar (Table 4).[66-69] The similarities in the photophysical properties of the various dibenzanthracenes evinces the unlikelihood of these being the cause of the disparity in the reactivities of these compounds (Table 3). Application of perturbation molecular orbital (PMO) theory indicates that the relatively small size of the meso coefficients in the FMOs may be the cause of the anamalous behavior of a,h-DBA. However, this difference in reactivity cannot be due entirely to the relative magnitudes of the FMO coefficients at the reacting positions[70] because tetracene (T 29), which has meso coefficients in the FMOs of a similarly small magnitude as does a,h-DBA (Fig. 1),[45] nevertheless does photodimerize.[40,71-3] Furthermore, we have found that CHD adds to T to afford a $4\pi_s+4\pi_s$ adduct as the major product (eqn 19). In addition, because the formation of $4\pi_s+2\pi_s$ products depends preponderantly on one-cen-



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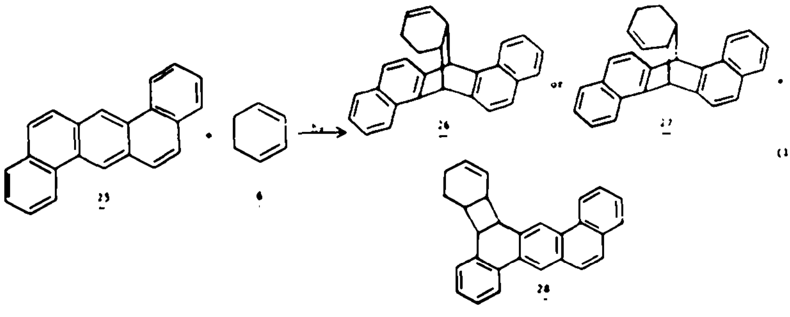

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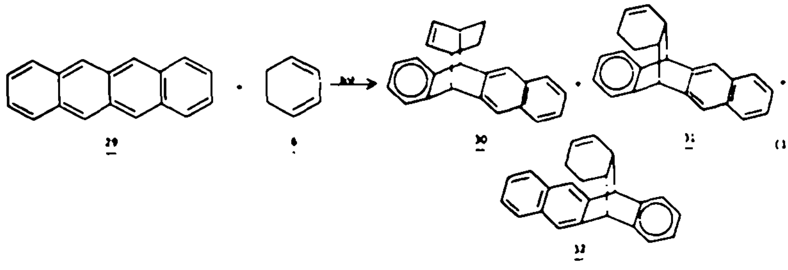

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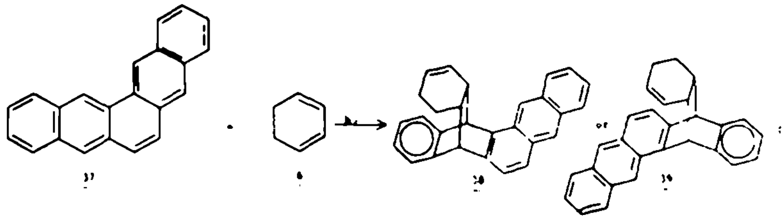

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ter overlap, $4\pi_s + 2\pi_s$ reactivity might be expected to become increasingly favored as the meso coefficients increasingly differ in magnitude. When the meso coefficients have similar magnitudes, $4\pi_s + 4\pi_s$ addition of CHD to photoexcited arene is expected. Clearly, arene reactivity does not in fact correlate with this argument, since, as a result, increased proportions of $4\pi_s + 2\pi_s$ adducts would have been predicted to have formed in the photolysis of BA and a,j-DBA as compared to An, a,c-DBA and a,h-DBA. Consequently, the differences in the behavior of the dibenzanthracenes must have some other origin.

Consideration of the overall symmetry preserved in the transformations itself does not supply an explanation for the contrasting behavior of the dibenzanthracenes. An and a,c-DBA retain a plane of symmetry throughout the transformations and react to form predominantly the "allowed" $4\pi_s + 4\pi_s$ adducts. BA and a,j-DBA, lacking any symmetry element retained throughout the transformations, again afford the "allowed" $4\pi_s + 4\pi_s$ products. But a,h-DBA, which also is devoid of any persisting symmetry in the reactions, affords the $4\pi_s + 2\pi_s$ product in low quantum yield. Application of Woodward–Hoffmann[2] or derivative theories[30–40] does not result in an anticipation of this difference in behavior. However, examination of the local symmetry about the reaction meso positions provides insight toward an explanation of this disparate reactivity.

For those substrates which react in a typically "allowed" fashion, the local nodal structure persists throughout the reactions; in these cases, reactant orbitals evolve smoothly into occupied product orbitals with minimal change in nodal properties. This is demonstrated schematically for the thermal reactions of arenes in Fig. 2. A similar situation can be shown to obtain for the corresponding photochemical reactions between CHD and arenes; the thermal reactions are illustrated for convenience. The essential features of the orbitals of the reactants and products are shown in Fig. 2; i.e. the local butadiene-like orbitals of the arenes which participate in the transformations. The lowest π orbital (π_1) of each arene evolves into the symmetric σ orbital (σ_s) of the products without a change in its nodal properties. For An, the highest occupied molecular orbital (HOMO), π_7,

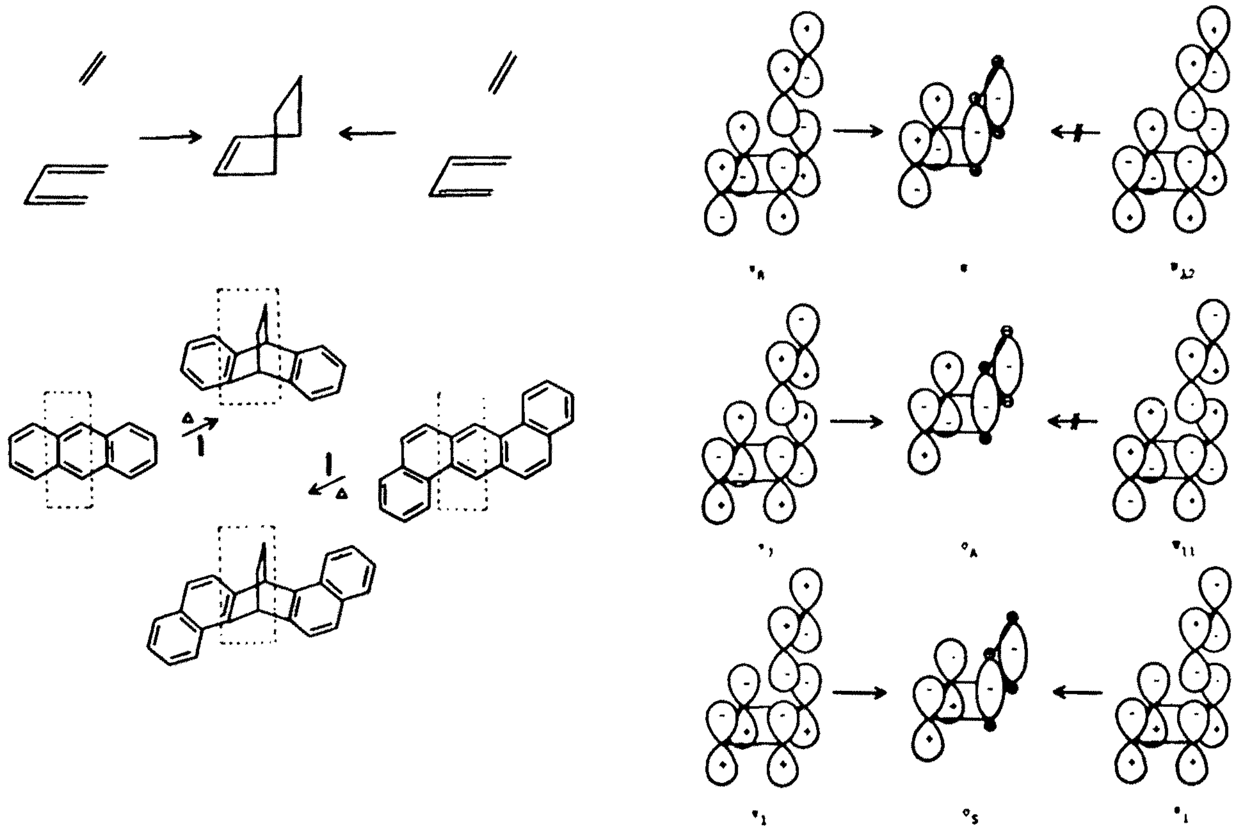
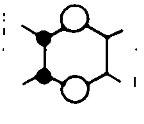


Fig. 2. Schematic representation of the butadiene-like π orbitals of anthracene (above, left) and dibenz[a,h]anthracene (above, right) involved in the thermal addition to ethylene. The lowest (π_1), highest occupied (HOMOs, π_7 and π_{11}), and lowest unoccupied (LUMOs, π_8 and π_{12}) π orbitals of the arenes, their interactions with the appropriate π orbitals of ethylene, and the resulting product orbitals are indicated (far right). Orbitals π_{11} and π_{12} of dibenz[a,h]anthracene do not correlate directly with product orbitals; a change in nodal properties during the reaction is necessary in these orbitals.

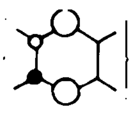
and the lowest unoccupied molecular orbital (HOMO), π_8, similarly transform into occupied product orbitals without any change in nodal properties of the reacting centers. In contrast, with a,h-DBA, a nodal displacement must occur in the evolution of the HOMO (π_{11}) and the LUMO (π_{12}) such that a change in nodal properties must occur in these reactant orbitals to afford the corresponding σ_A and π product orbitals. Such a process, which would introduce a new node in the MO wavefunctions of products, is assumed to require a substantial energy barrier.[74]

Examination of the local "essential symmetry" as indicated in Fig. 2 then provides a criterion which reflects the requirements for the extensive reorganization of the MO nodal properties in the wave functions of the reactants. Increasing discord in the correspondence of the nodal properties between occupied reactant and product MOs should represent a gradual erosion of the energetic advantage for a process which is "allowed" in the symmetrical case: the greater the perturbation demonstrated in the local wavefunctions about the reactive positions, the more extensive must be the requisite orbital nodal reorganization in achieving the proper nodal structure of the product orbitals. This would induce an increasing barrier to reaction, which must arise from the disjunction in the evolution of the occupied orbital nodal patterns as the reaction progresses. The mismatch of the local "essential symmetry" of the reactants and products, indicated in Fig. 2, is identifiable by the comparison of the local nodal structure about the reacting positions.

Although the change in nodal properties should be monitored for the entirety of all occupied orbitals[75] and such a more rigorous approach would be implicitly quantitative, the reactivity of arenes in concerted processes depends upon a number of factors in addition to the effects of nodal structure and symmetry correlations. The magnitudes and the relative signs of the meso coefficients in the FMOs, the formation, stability, and geometry of intermediate complexes, and the lifetimes, energies, and character (singlet or triplet, π,π^* or n,π^*, etc.) of the reacting states all must influence pericyclic reactivity to some extent. Consequently, by itself, the consideration of the local nodal structure about the reacting centers in the FMOs can provide only a qualitative distinction between the pericyclic reactivities observed in our systems. We propose that the requisite changes in this nodal structure in proceeding from reactants to products finally becomes sufficiently extreme to result in a difference in reactivity when the induction of substantial local perturbation in the MOs near the reacting positions is evidenced (this prospect is revealed most extensively in the FMOs: see Figs. 1 and 2). Thus, pericyclic reactivity will correlate qualitatively with the presence or absence of a butadiene-like nodal pattern in the FMOs about the reacting positions of the diene, i.e.



A correlation exists;
the pericyclic process
is energetically
"accessible".



No correlation exists;
the pericyclic process
is energetically
"inaccessible".

In this sense, the relative signs of the FMO coefficients about the reacting positions can be used as an approximation to estimate the "allowedness" (i.e. the energetic "accessibility") of a transformation which is "allowed" in the Woodward–Hoffmann sense.

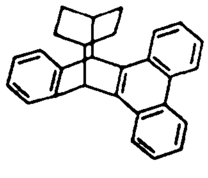
It is then reasoned that, for An and a,c-DBA, but less so for BA and a,j-DBA, product orbitals will be mapped into reactant orbitals such that no large electronic energy barrier will be imposed in the transformations, and the "allowed" $4\pi_s + 4\pi_s$ adducts will form. In these cases, each occupied reactant orbital transforms directly into a unique occupied product orbital without change in nodal structure, so that minimal energy expenditure should be required for electronic and nuclear reorganization along the reaction coordinate for the concerted reactions. In the case of a,h-DBA, the required nodal reorganization is sufficiently extreme (as reflected in the lack of correlation found between reactant and product orbitals near the reacting positions) that a substantial energy barrier is imposed upon the pericyclic transformations of this molecule. Since a low energy concerted reaction path is unavailable, a,h-DBA reacts slowly, in a non-concerted manner, to afford the cycloadducts of CHD.

A stepwise mechanism would be expected to yield the thermodynamically most stable products through a biradical intermediate. Since the $4\pi_s + 4\pi_s$ products are less stable thermodynamically than the corresponding $4\pi_s + 2\pi_s$ adducts,[76] the latter should be formed predominantly when a reaction occurs via non-concerted mechanism; the $4\pi_s + 4\pi_s$ adducts, on the other hand, would be produced preferentially via a concerted mechanism. Whereas for the other arenes, the "allowed" products are the major adducts isolated, and presumably are formed by a concerted mechanism in the case of a,h-DBA the formation of a $4\pi_s + 2\pi_s$ adduct as the preferred isomer is inconsistent with a concerted mechanism. The thermal reaction between a,h-DBA and MA might then also occur by stepwise mechanism; however, as both concerted and stepwise mechanisms ostensibly would afford the identical $4\pi_s + 2\pi_s$ adduct, isolation of this product is not diagnostic of the mechanism by which it is formed.

The requirement of local nodal correspondence in the pericyclic transformations can be extended to the other higher arenes. Thus, T (29) has been observed to react photochemically with CHD to form a $4\pi_s + 4\pi_s$ adduct as the major product (eqn 19) and reacts readily thermally with MA to form the Diels–Alder adduct. Pentacene (33) should exhibit behavior similar to that of An and T and has been reported to react readily with MA;[46] pentacene also forms a photodimer.[71] Dibenzo(b,g)phenanthrene (34), benzo(a)tetracene (35) and benzo(b)chrysene (BC, 36), which possess nodal structure about the meso positions which is appropriate for the smooth transformation of reactant orbitals into product orbitals, also would be predicted to readily react with MA (this has been observed for BC),[46] and should react photochemically with CHD to form the $4\pi_s + 4\pi_s$ adducts under appropriate conditions. Pentaphene (PP, 37), however, lacks the requisite nodal structure for "allowed" behavior (Fig. 1), and should react poorly with MA; the photochemical reaction with CHD would be expected to afford the $4\pi_s + 2\pi_s$ adduct in a non-concerted manner. Thermal addition of MA to PP was reported to occur under forcing conditions[77] (see however, the more recent result from a kinetic study).[46] The photochemical addition of CHD to PP results in the exclusive formation of a $4\pi_s + 2\pi_s$ adduct was a primary product, in very low quantum yield (eqn 20). (When the irradiation is effected with light of wavelength shorter than 400 nm, secondary 1:2 and 2:2 adducts arise from the photochemical reaction of the An chromophore of the primary products to give secondary "allowed" $4\pi_s + 4\pi_s$ products).

Additionally, it is anticipated that the non-linearly benzannelated arenes (e.g. phenanthrene **40**, pyrene **41**, chrysene **42**, benzo(c)phenanthrene **43** and triphenylene **44**) should show an extremely low reactivity toward concerted cycloadditions. This results from the unsuitability of the internal rings of these arenes to engage in reaction as 4π components, due to the thermodynamic unfavorability of the formation of adducts which are responsible for the disruption of the aromaticity of these molecules. Addition in a $4\pi_s$ manner to an end ring is possible (except for pyrene); however, the relatively small size of the coefficients in the FMO,[45] and the relatively high resonance energies present in these compounds,[63,78] mitigates against addition to the end rings. Then the only feasible mode of reactivity for these arenes would be their participation as $2\pi_s$ components. Thermal concerted additions should be highly unfavorable (MA does not add thermally to these arenes)[46] and photochemical cycloadditions with CHD, if they occur at all, should result in the formation of $2\pi_s + 2\pi_s$ adducts with low quantum yield. The formation of $2\pi_s + 2\pi_s$ adducts might be concerted, although a stepwise mechanism can not be ruled out unequivocally since both mechanisms could afford this type of adduct. The photoreactivity of these arenes will then be less informative in a mechanistic sense if $2\pi_s + 2\pi_s$ adducts are produced.[9]

The thermal reactivity of the higher arenes with tetracyanoethylene (TCNE) was determined in an attempt to estimate the abilities of the arenes to engage in pericyclic reactions in the ground state. In these reactions, some element of symmetry is conserved for the acenes and for the dibenzanthracenes, but none exists for bimolecular reaction with BA and PP. Cycloadditions occurring with TCNE generally were found to proceed more rapidly for those arenes possessing the proper local nodal structure to allow a correlation of reactant and product orbitals, but proceeded more slowly with a,h-DBA[79] and with PP. However, the reactivity seemed to be better correlated with the energy of the lowest transition of the charge transfer complexes formed between TCNE and the arenes (Table 1). These cycloadditions therefore may proceed *via* a multitude of pathways, involving mitigating effects due to the high polarity involved.[4,80-83] Similar considerations may apply to the thermal additions of MA. The theory for concerted cycloadditions may have



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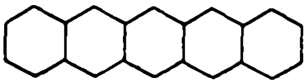

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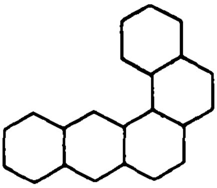

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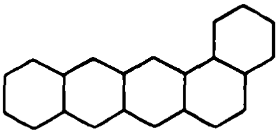

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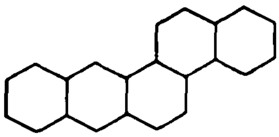

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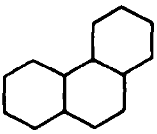

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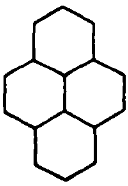

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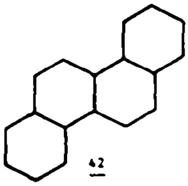

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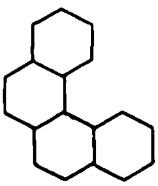

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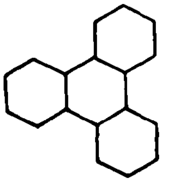

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only limited application for ground state reactions of arenes with electron-deficient olefins which take place under forcing conditions.

CONCLUSIONS

The pericyclic reactivity of the higher arenes is not explicable by the usual application of Woodward–Hoffmann or derivative theories. Adoption of a modified theoretical procedure, in which the local nodal structure about the reactive positions in the frontier MOs is considered, can provide a partial description of the concerted photochemical and thermal behavior in these systems. It is proposed that this principle represents an important factor which determines general pericyclic reactivity.

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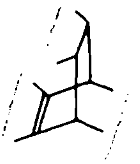

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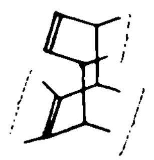

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