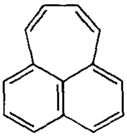
290. Photodimerization of Solid Pleiadiene; Isomerization and Cycloreversion of the Dimer

by **Alan C. Hazell**[1])
Kemisk Institut, Aarhus Universitet, Langelandsgade 140, DK-8000 Aarhus C, Denmark
and **Richard M. Pagni**
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916, U.S.A.
and **Gabriele Persy, Erika Rommel** and **Jakob Wirz**[1])
Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

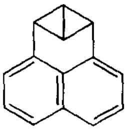
(7.X.81)

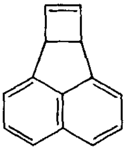
Summary

Irradiation ($\lambda > 400$ nm) of solid pleiadiene (**1**) yields a single, head-to-head $[_\pi 4_s + _\pi 4_s]$-photodimer (**2**) the structure of which was determined by X-ray analysis. The formation of **2** is entirely suppressed at 77 K, since properly oriented pairs of molecules arise only from thermal disorder in crystals of **1**. Upon pyrolysis (80°), the strained photodimer **2** rearranges to the $[_\pi 2_s + _\pi 4_s]$ dimer **3** by a 'forbidden' suprafacial [1,3]-C-atom migration. Both **2** and **3** are reconverted to **1** by UV. irradiation in solution, but the latter, 'forbidden' photoreaction is suppressed at 77 K. Discrepancies of the experimental observations with the predictive schemes of *Kaupp* or *Michl* are discussed.



1





The photochemical and thermal transpositions of pleiadiene[2a]) (**1**) and the valence isomers naphthobicyclobutane[2b]) and naphthocyclobutene[2c]) have been studied extensively [1] as well as the thermal reactions of the respective radical anions [2]. *Michl et al.* [3] have developed a theoretical framework for the analysis of these and related reactions. The predictive power of their scheme has provided an impressive example for the judicious application of *Woodward-Hoffmann*-type correlation diagrams to photoreactions.

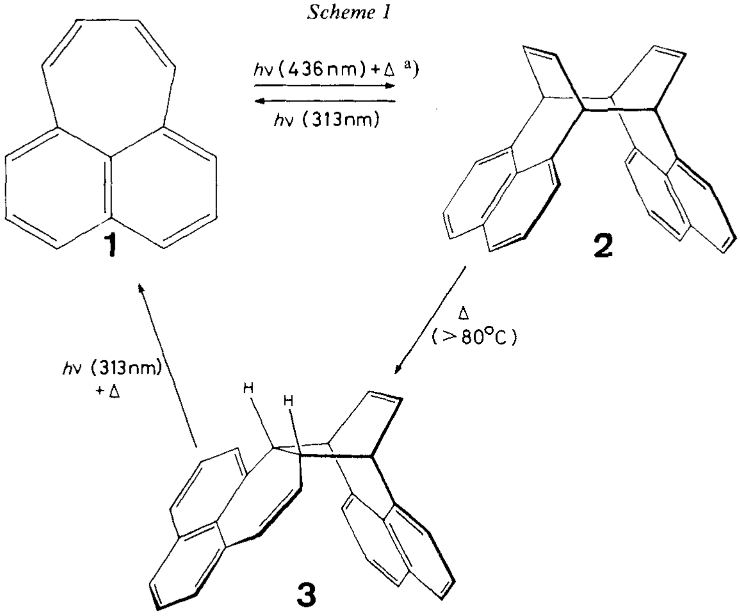
---

[1]) Correspondence authors (*A.C.H.* crystallography, *J.W.* chemistry).

[2]) IUPAC nomenclature: a) cyclohepta[*de*]naphthalene; b) 1,8-naphthotricyclo[4.1.0.0^{2,7}]hept-2-ene; c) 1,8-naphthobicyclo[3.2.0]hepta-2,6-diene.

0018-019X/81/8/2830-11$01.00/0

Scheme 1



a) The symbol $h\nu + \Delta$ designates photoreactions which are suppressed at low temperature.

In this paper we report the formation of a photodimer (**2**) by irradiation of solid pleiadiene (**1**), the identification of **2** by X-ray analysis, and the behaviour of **2** upon pyrolysis and photolysis *(Scheme 1)*. Surprisingly, the observed reactivity pattern does not agree with theoretical predictions.

Results. - *Photolysis of pleiadiene* (**1**). Solutions of **1** are fairly photostable and, upon prolonged irradiation, have yielded mainly polymeric material plus a small amount of naphthobicyclobutane [1d]. In contrast, crystalline **1** was rapidly converted to a single photodimer (**2**) by irradiation with light in the visible region. The photoreaction was suppressed when the vessel containing solid **1** was immersed in liquid nitrogen and irradiated under otherwise identical conditions; no trace of **2** was detected by TLC. analysis after an irradiation period sufficient to induce a 60% conversion of **1** at room temperature.

X-ray structure analysis of the photodimer **2**. The dimer (**2**) crystallized from chloroform as colourless plates, tabular on {100} and bounded by {011}. The crystals exhibited polysynthetic twinning on {100}. The crystallographic data are compared with those for pleiadiene (**1**) in *Table 1*.

Table 1. *Crystal data for pleiadiene* (**1**) [16] *and for its photodimer* (**2**)

	1	**2**
a	8.220 (5)	16.468 (3)
b	10.687 (6)	10.479 (2)
c	11.067 (7)	10.586 (2)
β	104.92 (4)	98.72 (2)
Space group	$P2_1/c$	$P2_1/n$
Z	4	4

A crystal, 0.60×0.44×0.23 mm, was mounted on a *Picker* diffractometer and reflections measured with Ni-filtered Cu$K\alpha$ radiation out to $2\theta = 110°$ using an ω-2θ step scanning technique. 1898 reflections were measured of which 1616 were regarded as observed ($I > 3\sigma_I$). Twinning led to complete overlap of h00 reflections and approximate overlap for several other reflections. All reflections for which the scan contained two maxima, or for which the maximum was not at the centre of the scan, were rejected, leaving 1486 reflections.

The structure was solved by direct methods (MULTAN [4]) and refined by least-squares. C-Atoms were refined anisotropically, H-atoms (the positions of which were obtained from a difference *Fourier* synthesis) were refined isotropically. An isotropic extinction correction gave a minimum value of I/I_{corr} of 0.47. The final R-value was 0.035 for 334 parameters. Computer programs used were: LINUS [5] for least-squares refinement, ORFFE [6] geometry, ORTEP [7] for drawings, TLS [8] thermal vibration correction. Atomic scattering factors used were those of *Cromer & Mann* [9] for C and *Stewart et al.* [10] for H.

Atomic coordinates and thermal parameters are given in *Table 2;* bond distances and angles in *Tables 3* and *4*. A perspective view of the molecule is shown in *Figure 1.*

Pyrolysis of the photodimer (**2**). On vacuum sublimation at 150° the dimer **2** was quantitatively transformed to the $[_\pi 2_s + {}_\pi 4_s]$-isomer **3**. The progress of the rearrangement **2**→**3** in solution was monitored by UV. spectroscopy ($k \cong 1 \cdot 10^{-4}\,s^{-1}$

Table 2. *Fractional atomic coordinates, and thermal parameters in Å²*

	X	Y	Z	U11	U22	U33	U12	U13	U23
C(1)	.1973(1)	.2182(2)	-.1336(2)	.034(1)	.032(2)	.032(1)	-.002(1)	.012(1)	.004(1)
C(2)	.2275(1)	.1175(2)	-.2073(2)	.035(1)	.034(2)	.035(1)	-.001(1)	.011(1)	.006(1)
C(3)	.1778(2)	.0729(3)	-.3133(2)	.047(2)	.039(2)	.040(2)	.004(1)	.008(1)	-.003(1)
C(4)	.0983(2)	.1176(3)	-.3515(3)	.045(2)	.054(2)	.040(2)	-.003(1)	.001(1)	.003(1)
C(5)	.0675(2)	.2093(3)	-.2824(2)	.033(2)	.053(2)	.047(2)	.001(1)	.007(1)	.012(1)
C(6)	.1152(1)	.2603(2)	-.1720(2)	.035(1)	.037(2)	.038(2)	.003(1)	.012(1)	.008(1)
C(7)	.0803(2)	.3543(3)	-.1011(3)	.047(2)	.055(2)	.052(2)	.014(1)	.014(1)	.006(2)
C(8)	.1246(2)	.4069(3)	.0035(3)	.065(2)	.052(2)	.057(2)	.019(2)	.024(2)	-.005(2)
C(9)	.2061(2)	.3691(3)	.0399(3)	.058(2)	.042(2)	.043(2)	.004(1)	.008(2)	-.004(2)
C(10)	.2438(2)	.2775(2)	-.0234(2)	.041(1)	.031(2)	.039(2)	-.002(1)	.011(1)	.007(1)
C(11)	.2083(1)	.0074(2)	.1015(2)	.043(2)	.032(2)	.033(2)	.004(1)	.008(1)	.007(1)
C(12)	.2291(1)	-.0625(2)	-.0072(2)	.040(2)	.033(2)	.033(1)	.002(1)	.005(1)	.003(1)
C(13)	.1725(2)	-.1462(3)	-.0676(3)	.048(2)	.048(2)	.041(2)	-.006(1)	.007(1)	-.004(1)
C(14)	.0952(2)	-.1652(3)	-.0319(3)	.050(2)	.062(2)	.057(2)	-.018(2)	.004(2)	-.001(2)
C(15)	.0745(2)	-.1009(3)	.0694(3)	.038(2)	.063(2)	.063(2)	-.004(1)	.017(1)	.014(2)
C(16)	.1296(2)	-.0146(2)	.1380(2)	.048(2)	.039(2)	.047(2)	.003(1)	.016(1)	.011(1)
C(17)	.1054(2)	.0514(3)	.2437(3)	.071(2)	.057(2)	.065(2)	.011(2)	.039(2)	.012(2)
C(18)	.1566(2)	.1349(3)	.3113(3)	.097(3)	.047(2)	.056(2)	.010(2)	.037(2)	-.001(2)
C(19)	.2341(2)	.1576(3)	.2772(3)	.083(2)	.040(2)	.045(2)	-.002(2)	.018(2)	.001(2)
C(20)	.2612(2)	.0989(2)	.1749(2)	.052(2)	.034(2)	.033(2)	.003(1)	.007(1)	.003(1)
C(21)	.3327(2)	.2500(3)	.0319(2)	.041(2)	.033(2)	.047(2)	-.007(1)	-.000(1)	.001(1)
C(22)	.3896(2)	.2319(3)	-.0651(3)	.031(2)	.048(2)	.060(2)	-.006(1)	.005(1)	.013(2)
C(23)	.3799(2)	.1444(3)	-.1539(3)	.035(2)	.052(2)	.050(2)	.006(1)	.016(1)	.014(2)
C(24)	.3096(1)	.0528(2)	-.1734(2)	.041(2)	.041(2)	.037(2)	.008(1)	.012(1)	.001(1)
C(25)	.3090(1)	-.0540(2)	-.0625(2)	.039(2)	.033(2)	.040(2)	.005(1)	.009(1)	-.002(1)
C(26)	.3849(2)	-.0512(3)	.0328(3)	.039(2)	.038(2)	.053(2)	.006(1)	.007(1)	.008(1)
C(27)	.3998(2)	.0347(3)	.1229(3)	.039(2)	.044(2)	.050(2)	.001(1)	-.005(1)	.009(2)
C(28)	.3431(2)	.1419(2)	.1433(2)	.050(2)	.039(2)	.035(2)	-.006(1)	-.002(1)	-.003(1)

	X	Y	Z	UISO		X	Y	Z	UISO
H(3)	.197(1)	.005(2)	-.362(2)	.042(7)	H(18)	.145(2)	.180(2)	.384(2)	.069(9)
H(4)	.063(1)	.086(2)	-.429(2)	.051(8)	H(19)	.271(2)	.221(2)	.324(2)	.061(9)
H(5)	.010(1)	.240(2)	-.307(2)	.046(6)	H(22)	.438(1)	.289(2)	-.054(2)	.048(7)
H(7)	.022(1)	.380(2)	-.128(2)	.061(8)	H(23)	.422(1)	.133(2)	-.210(2)	.042(6)
H(8)	.103(2)	.467(2)	.053(2)	.068(8)	H(26)	.426(1)	-.113(2)	.026(2)	.043(6)
H(9)	.237(1)	.409(2)	.113(2)	.055(8)	H(27)	.452(1)	.034(2)	.181(2)	.053(7)
H(13)	.187(1)	-.194(2)	-.140(2)	.052(7)	H(21)	.348(1)	.328(2)	.079(2)	.049(8)
H(14)	.058(2)	-.224(3)	-.078(2)	.076(9)	H(24)	.316(1)	.005(2)	-.250(2)	.041(8)
H(15)	.020(2)	-.107(2)	.092(2)	.057(6)	H(25)	.311(1)	-.133(2)	-.109(2)	.025(6)
H(17)	.052(2)	.036(2)	.262(2)	.070(8)	H(28)	.369(1)	.189(2)	.220(2)	.043(8)

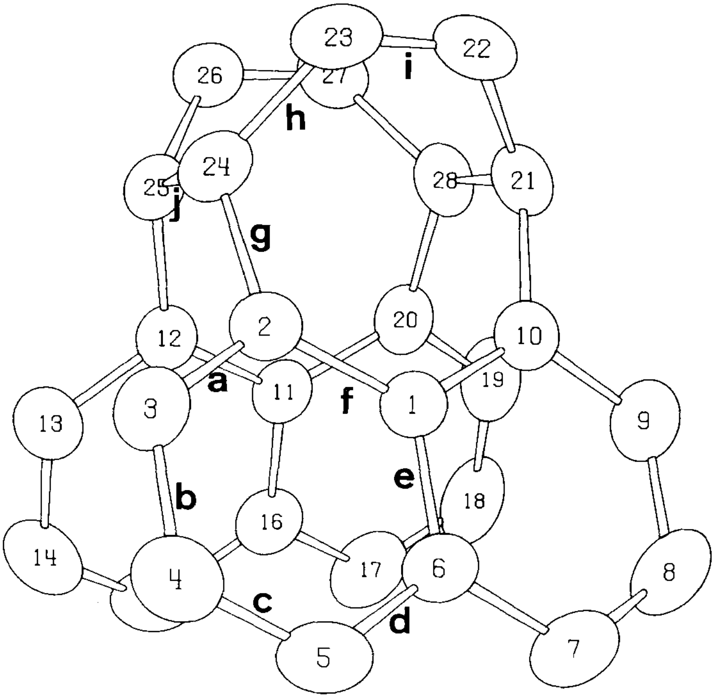


Fig. 1. *A perspective view of the dimer* **2** *showing the numbering of the C-atoms and the labelling of the bonds.* C(15) is hidden behind C(4). In *Tables 3* and *4* the quarter of the molecule containing C(2)–C(6) is referred to as A, C(6)–C(10) as B, C(12)–C(16) as C, C(16)–C(20) as D.

at 80°). The molecular constitution of **3** was revealed unambiguously by a 360-MHz-H-NMR. spectrum[3]). Except for the local symmetry in the 1,4-substituted pleiadiene-moiety, all protons and coupling constants could be rigorously assigned with the aid of double resonance experiments. Of the four possible diastereomeric structures (the 1,4-substituted cycloheptene ring must be *cis*-fused due to geometrical restrictions) only the $[_{\pi}2_s+{}_{\pi}4_s]$-*endo*-isomer shown in *Scheme 1* reasonably accounts for the strong diamagnetic shielding of protons H(1) δ 5.39, H(19) 6.56, and H(20) 5.78 ppm (proton numbering refers to the structure shown in the *Exper. Part*). Two diastereoisomers are also eliminated by adopting the unavoidable assumption that the *erythro*-configuration around the C(9),C(11)-bond is retained from **2** during the intramolecular [1,3]-C-atom shift.

In the absence of light, no pleiadiene (**1**) was formed during the isomerization **2**→**3**. It was ascertained that **1** is stable under the mild pyrolytic conditions used. The 'allowed' *retro-Diels-Alder* reaction **3**→**1** was observed only at temperatures above 200° and was accompanied by further decomposition.

Photolysis of the dimers **2** *and* **3**. Both dimers were rapidly converted to pleiadiene (**1**) when irradiated by 313 nm light in solution. Several isosbestic points were

---

[3]) We are most grateful to Prof. *Hans Fritz, Ciba-Geigy SA*, Basel, for the permission to use his facilities and for valuable assistance during the analysis of the spectrum.

Table 3. *Bond distances* (l) *and values* (l′) *of the dimer* **2** (corrected for thermal vibration)[a]). Subscripts refer to the ring with which the bonds are associated, bond labelling and ring labelling are shown in *Fig. 1*. C–H distances range from 0.92 (2) to 1.01 (2) Å.

	l_A	l_B	l_C	l_D	l'_A	l'_B	l'_C	l'_D
a	1.372 (3)	1.370 (3)	1.370 (3)	1.374 (3)	1.375	1.373	1.373	1.378
b	1.394 (3)	1.398 (4)	1.393 (4)	1.395 (4)	1.397	1.401	1.396	1.399
c	1.351 (3)	1.353 (4)	1.352 (4)	1.347 (4)	1.354	1.356	1.355	1.350
d	1.415 (3)	1.410 (3)	1.407 (4)	1.421 (4)	1.418	1.413	1.411	1.424
e	1.426 (3)		1.423 (3)		1.429		1.427	
f	1.441 (3)	1.442 (3)	1.447 (3)	1.445 (3)	1.445	1.445	1.450	1.448
g	1.509 (3)	1.524 (3)	1.517 (3)	1.505 (3)	1.512	1.527	1.521	1.508
h	1.496 (3)	1.498 (3)	1.491 (3)	1.496 (3)	1.499	1.502	1.494	1.499
i	1.306 (3)		1.308 (3)		1.309		1.311	
j	1.623 (3)		1.626 (3)		1.624		1.628	

[a]) Standard deviations in bond lengths are *ca.* 0.003 Å.

observed throughout the reaction in both cases and ED. plots [11] were linear. Thus there was no spectroscopically detectable intermediate in the photoreactions and, specifically, the photocleavage of **2** did not proceed by the pathway $\mathbf{2} \xrightarrow{h\nu} \mathbf{3} \xrightarrow{h\nu} 2\,\mathbf{1}$.

The photodimer **2** was found to be non-fluorescent within our limits of detection and the reaction $\mathbf{2} \xrightarrow{h\nu} 2\,\mathbf{1}$ proceeded with about the same rate at room temperature and at 77 K in an EPA glass (five parts ether, five parts isopentane, two parts alcohol). In contrast, the [2+4]-dimer **3** exhibited moderately intense fluorescence emission upon 313 nm excitation in hexane solution (λ_{max} 380 nm, lifetime estimated to 3 ns by oxygen quenching experiments) and was photostable in EPA at 77 K.

Triplet sensitization of **2** by 365 nm irradiation of degassed carbon tetrachloride or acetonitrile solutions containing benzophenone also promoted the cleavage to **1**, whereas only polymeric material was formed in the case of **3**. However, the main course of the reaction after direct irradiation of **2** does not involve the triplet. This

Table 4. *Angles (θ) of the dimer* **2** (for bond labelling and ring labelling see *Fig. 1*)

	θ_A	θ_B	θ_C	θ_C	$<\theta>$
ab	123.2 (2)	123.2 (2)	123.6 (3)	122.7 (3)	123.2 (1)
af	118.7 (2)	118.2 (2)	118.2 (2)	118.8 (2)	118.5 (1)
ag	116.7 (2)	115.0 (2)	115.3 (2)	116.4 (2)	115.9 (1)
bc	119.5 (2)	119.5 (2)	119.2 (3)	119.9 (3)	119.5 (1)
cd	120.6 (2)	120.5 (2)	120.8 (2)	120.6 (3)	120.6 (1)
dd	118.9 (2)		119.1 (2)		119.0 (1)
de	120.6 (2)	120.5 (2)	120.6 (2)	120.3 (2)	120.5 (1)
ef	117.3 (2)	118.0 (2)	117.6 (2)	117.6 (2)	117.6 (1)
ff	124.7 (2)		124.8 (2)		124.8 (1)
fg	124.5 (2)	126.8 (2)	126.5 (2)	124.7 (2)	125.6 (1)
gh	113.2 (2)	114.9 (2)	115.4 (2)	113.9 (2)	114.4 (1)
gj	112.5 (2)	113.9 (2)	114.6 (2)	111.4 (2)	113.1 (1)
hi	124.1 (2)	124.0 (2)	123.9 (2)	124.5 (2)	124.1 (1)
hj	115.3 (2)	113.4 (2)	112.6 (2)	114.9 (2)	114.1 (1)

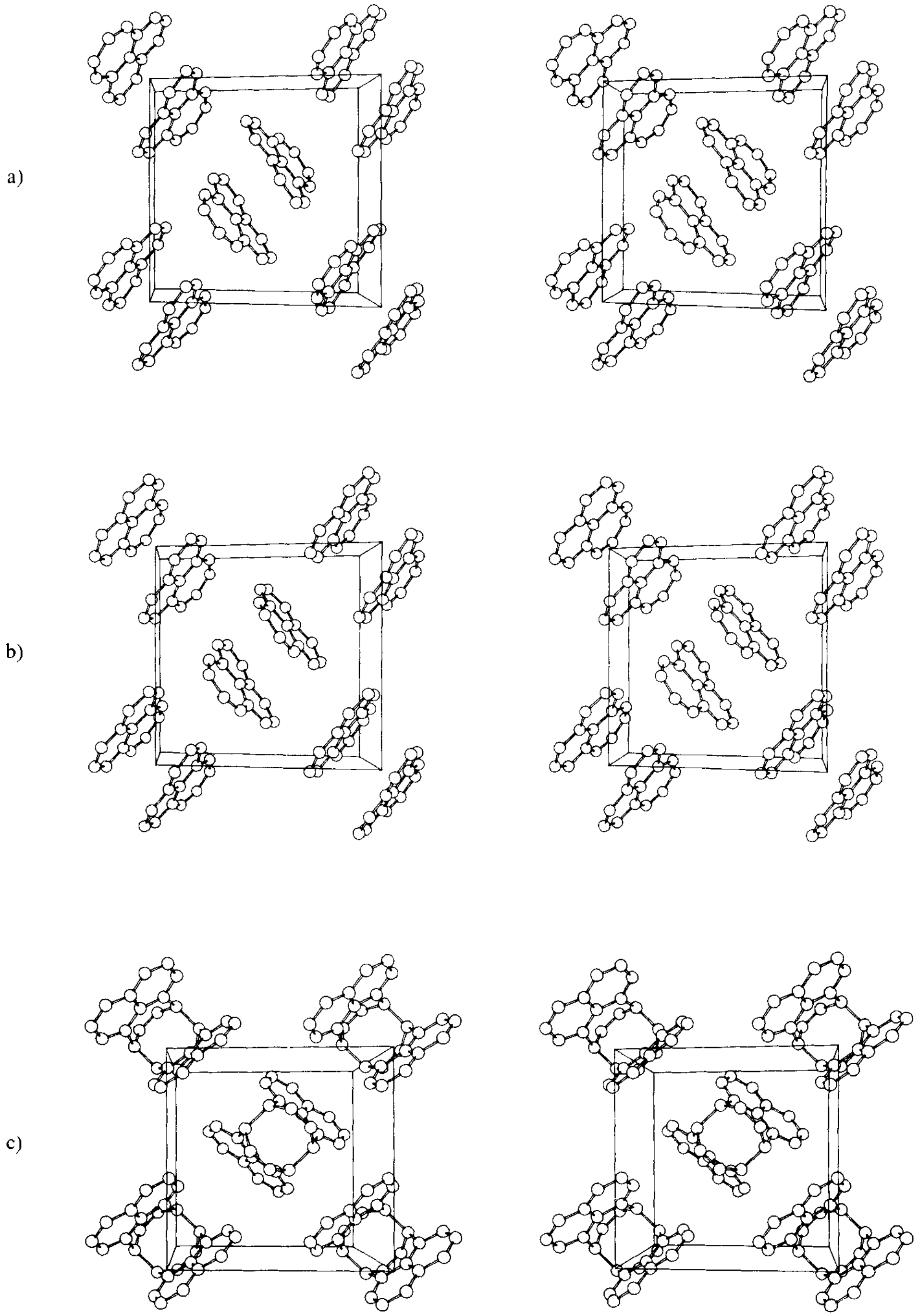


Fig. 2. *Stereo drawings of* a) *ordered pleiadiene,* b) *pleiadiene with half of the molecules disordered,* c) *the dimer* **2**. The x-axis is out of the page, *y* up the page and z across the page.

is shown by the following results of *kinetic flash photolysis*. Frequency-tripled (353 nm) or quadrupled (265 nm) light pulses of *ca.* 20 ns duration from a Nd-glass laser were used for sensitized and direct excitation, respectively. *a*) The near diffusion-controlled quenching of triplet benzophenone (λ_{max} 530 nm) by **2** was accompanied by the formation of a strong transient absorption at shorter wavelengths (λ_{max} 415 nm; grow-in matching the decay kinetics at 530 nm) which was attributed to the absorption of **2** in its lowest triplet state. T_1 (**2**) decayed with a first-order rate of $8 \cdot 10^5 s^{-1}$ and was quenched by piperylene and oxygen. Yet, the conversion of **2** to **1** upon direct irradiation was not appreciably retarded in air-saturated solution or by the addition of up to 0.1 M piperylene. *b*) The formation of **1** occurred within less than 30 ns after 265 nm excitation of **2** as monitored by the increase in absorption in the range of 360 to 380 nm.

Discussion. - The photodimer **2**, which has the *endo*-configuration, is distorted slightly from *mm2* (C_{2v}) symmetry. The naphthalene moieties are slightly nonplanar, being twisted about their long axes, so that the *peri*-methine substituents are bent to opposite sides of the naphthalene mean plane. The strain from the in-plane splaying of the bonds in the *peri*-positions leads, as expected [12], to a deformation of the angles and to only small changes in bond distances. The bridging bonds are very long: C(21)–C(28) = 1.624 (2) Å and C(24)–C(25) = 1.628 (2) Å *(Fig. 1)*, as observed in other molecules with a similar arrangement of π- and σ-bonds [13-15].

The cell dimensions of pleiadiene (**1**) and its dimer **2** are closely related *(Table 1)*, the a-axis of **2** being twice that of **1**. In **1** at 78 K [16] the molecules are stacked in pairs in a head-to-tail arrangement *(Fig. 2a)*. At higher temperatures the structure becomes disordered so that some of the pairs of molecules are in a head-to-head arrangement. Thus they are in the correct orientation and at the right distance for the solid state reaction giving the dimer to take place. *Figure 2b* shows the situation in which half of the molecules are disordered, which is very similar to the structure of **2** *(Fig. 2c)*. As expected from these considerations, the photodimerization of **1** is entirely suppressed at 77 K[4]).

The presence of considerable strain in the photodimer (**2**) is evident from the structural data discussed above. This explains the ease by which the 'forbidden' suprafacial [1,3]-C-atom migration to form **3** takes place. A rough estimate of the strain energy of **2** may be obtained by comparing the activation enthalpy $\Delta H^{\neq}$ of the reaction $\mathbf{2} \rightarrow \mathbf{3}$ with the value predicted for the bond dissociation enthalpy (BDE) of **2**, ignoring the presence of ring strain. Using, *e.g.*, the data of *Rüchardt* [18] and *Herndon* [19] we obtain a prediction of 182 kJ/mol for the BDE of **2**. Assuming a 'normal' A-factor of $10^{14} s^{-1}$ (see, *e.g.*, [20a]) we obtain $\Delta H^{\neq} \cong 117$ kJ/mol from the observed rate $k(\mathbf{2} \rightarrow \mathbf{3}) \cong 1 \cdot 10^{-4} s^{-1}$ at 80°. Thus the ring strain energy present in **2** is estimated to *ca.* 65 kJ/mol, a value which appears to be reasonable.

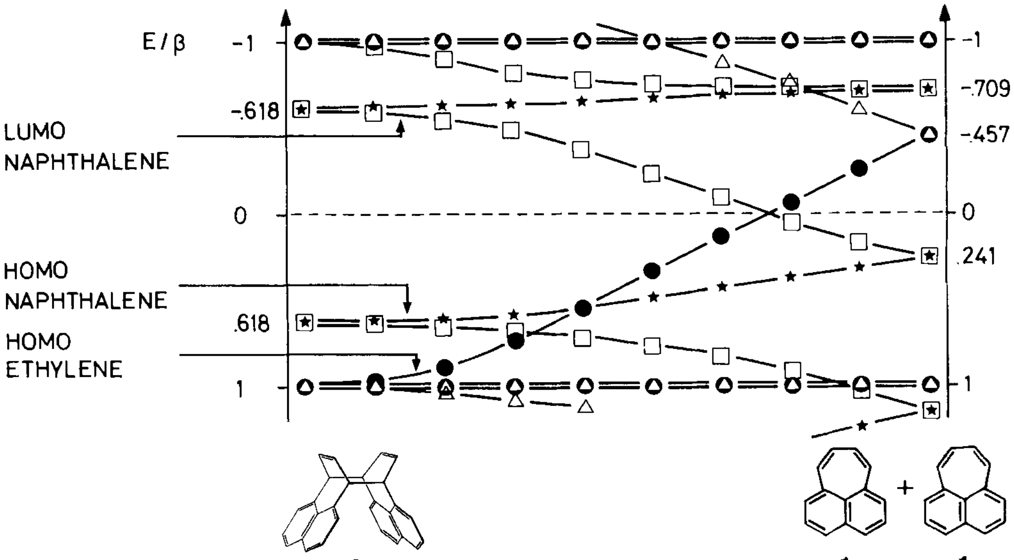
More surprising is the behaviour of the photodimer **2** upon photolysis. The cycloreversion of **2** can be induced by sensitization, but upon direct irradiation the reaction does not proceed by the triplet pathway as shown by the results of flash

---

[4]) For reviews on crystal lattice control of solid state photoreactions see [17].

photolysis. The cleavage of singlet-excited **2** proceeds with a high quantum yield even at 77 K and appears to be too fast to allow for efficient fluorescence or intersystem crossing. At first sight these observations seem to agree with the predictions of the *Woodward-Hoffmann* rules, since the reaction **2**$\xrightarrow{h\nu}$2 **1** is classified as 'excited-state-allowed'. Indeed, the 'excited-state-forbidden' reaction **3**$\xrightarrow{h\nu}$1 **1** is hindered by a thermal barrier (**3** exhibits fluorescence) and is suppressed at low temperature. However, a closer inspection of the correlation diagram for the cleavage of **2** leads to the conclusion that the reaction should be inhibited by a large 'symmetry-imposed' barrier not only in the ground state but also in the lowest excited singlet or triplet states. In fact, the diagram for the reaction **2**→2 **1** *(Fig. 3)* is essentially identical with the diagram constructed for the disrotatory ring opening naphthocyclobutene→**1** [3c, d] which was used by *Michl* to explain why the latter reaction proceeds only upon (biphotonic or short wavelength) excitation to high energy upper excited states. The arguments need not be reproduced here. Suffice it to say that the upper excited electronic configuration (HOMO(ethylene)→LUMO-(naphthalene)), which would make the cleavage of **2** 'allowed', represents a highly energetic charge transfer state.

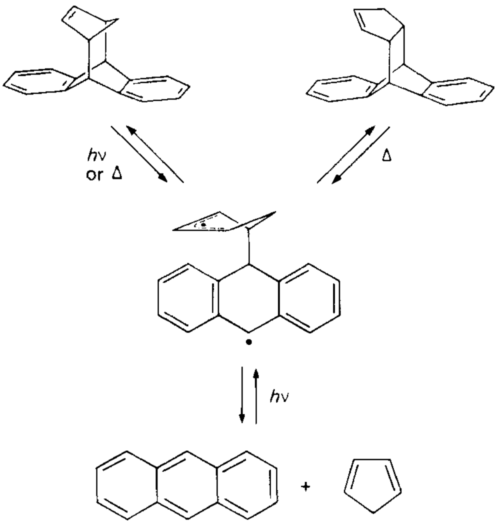
It is unlikely that exciton interactions between the adjacent chromophores in **2** are responsible for the totally different behaviour of naphthocyclobutene. However, it may be argued that the concerted, symmetry-conserving reaction path is irrelevant for the cleavage of **2** which might proceed *via* a biradical intermediate (**4**). Two-step reaction mechanisms have repeatedly been advocated by *Kaupp et al.* [20], *e.g.* in the photocycloaddition and cycloreversion of cyclopentadiene + anthracene [20a].



2 **1** **1**

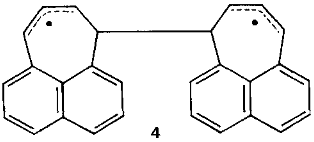
Fig. 3. Hückel *orbital correlation diagram for the* $[_{\pi}4_s + _{\pi}4_s]$ *head-to-head dimerization of pleiadiene* (**1**). Orbital symmetry representations under C_{2v}: ● = a_1, □ = a_2, △ = b_1, * = b_2. For clarity, only the frontier orbitals are shown. *Hückel* β-parameters as in [3c, d].

Scheme 2



Kinetic and thermodynamic data were combined with product ratios to show that all the photochemical and thermal reactions proceed *via* the same biradical intermediate *(Scheme 2)*.

Yet, in the present case it is clear that the thermal and photochemical reactions of **2** do not proceed *via* one and the same biradical intermediate **4** since the reactions lead to different products (**3** and **1**, respectively) at similar temperatures (80° and 25°, respectively). If anything, one would expect the yield of **1** from **4** to increase with increasing temperature. In conclusion, we cannot offer a convincing explanation for the photochemical reactivity of the pleiadiene dimer **2**, unless we resort to *ad hoc* arguments such as a 'memory effect' in the presumed biradical intermediate **4**.



4

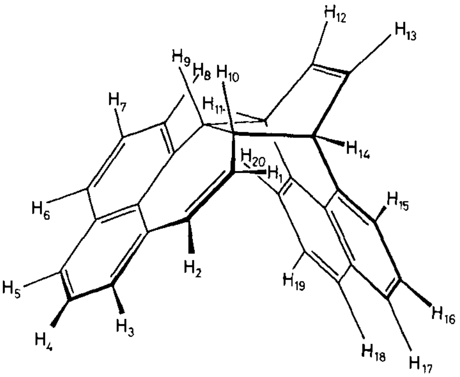
Financial support by *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*, by *Ciba-Geigy SA*, *F. Hoffmann-La Roche & Cie. SA*, and *Sandoz SA* is gratefully acknowledged. We wish to thank Profs. *G. Kaupp*, Freiburg i.Br., and *J. Michl*, Salt Lake City, for reading the manuscript and providing helpful comments.

Experimental Part

UV./VIS. absorption maxima (or shoulders (*S*)) are given in nm (logε), NMR. spectra are quoted in δ(ppm) relative to internal TMS (splitting pattern designated as doublet (*d*), doublet of doublets (*d*×*d*), ... multiplet (*m*), coupling constants in Hz). The molecular ion (M^+) and dominant fragment ion peaks in the mass spectrum are given in units of *m/z* (percent relative intensity).

Photodimerization of pleiadiene (**1**) *to the dimer* **2**. Pulverized **1** (100 mg) was irradiated for 3 h with visible light (cut-off filter $\lambda < 400$ nm) from a high-pressure mercury arc (*Osram* HBO 200 W). During the irradiation, the powder was mixed several times to ensure uniform exposure. Unreacted **1** (40 mg) was recovered by extraction of the solid with hexane (prolonged irradiation of **1** yields increasing amounts of intractable side products). The residue was dissolved in toluene (< 60°), filtered and cooled yielding chromatographically pure, colourless crystals of the dimer **2** (44 mg), 180° (dec.). Crystals for X-ray analysis were obtained by recrystallization from chloroform. - UV. (acetonitrile): 218 (4.92), 288 (4.15), 296 (4.16), 308 *S* (4.04), 312 *S* (3.99), 322 *S* (3.55). - ^{1}H-NMR. ($CDCl_3$): 4.4-4.7 (symm. *m*. 4 H); 6.2-6.5 (symm. *m*, 4 H); 6.8-7.3 (*m*, 12 H). - MS. (field ionization): 356 (100).

Thermal isomerization of the photodimer **2** *to the isomer* **3**. Sublimation of **2** at 150° in an evacuated (10^{-3} Torr) glass tube yielded the single isomer **3**. For analytical purposes a sample was crystallized from hexane and resublimed yielding colourless crystals of **3**, m.p. 153°. - UV. (hexane): 296 (4.03), 308 (4.03), 318 (4.02), 338 (3.91). - ^{1}H-NMR. ($CDCl_3$, 360 MHz): 3.18 (*d*×*d*×*d*, $^3J(11,12)=7$, $^3J(9,11)=3.5$, $^4J(11,13)=1.3$, H_{11}); 3.66 (*d*×*d*×*d*×*d*, $^3J(9,10)=10.7$, $^3J(1,10)=5$, $^3J(10,14)=5$, $^4J(2,10)=1.7$, H_{10}); 3.89 (*d*×*d*×*d*, $^3J(13,14)=7.5$, $^3J(10,14)=5$, $^4J(12,14)=1.5$, H_{14}); 4.28 (br. *d*×*d*, $^3J(9,10)=10.7$, $^3J(9,11)=3.5$, H_9); 5.39 (*d*×*d*, $^3J(1,2)=12.4$, $^3J(1,10)=5$, H_1); 5.75 (br. *d*×*d*, $^3J(1,2)=12.4$, $^4J(2,10)=1.7$, H_2); 5.78 (*d*×*d*, $^3J(19,20)=7.1$, $^4J(18,20)=1.2$, H_{20}); 6.45 (br. *d*, $^3J(3,4)=7.1$, H_3); 6.50-6.60 (symm. *m*, H_{12} and H_{13}); 6.56 (*d*×*d*, $^3J(18,19)=8.2$, $^3J(19,20)=7.1$, H_{19}); 6.99 (*d*×*d*, $^3J(4,5)=8.1$, $^3J(3,4)=7.1$, H_4); 7.10 (*d*×*d*, $^3J(15,16)=6.9$, $^4J(15,17)=1.2$, H_{15}); 7.25 (*d*×*d*, $^3J(16,17)=8.2$, $^3J(15,16)=6.9$, H_{16}); 7.29 (*d*×*d*, $^3J(18,19)=8.2$, $^4J(18,20)=1.2$, H_{18}); 7.42 (*d*×*d*, $^3J(6,7)=7.9$, $^3J(7,8)=7.2$, H_7); 7.43 (br. *d*, $^3J(4,5)=8.1$, H_5); 7.49 (*d*×*d*, $^3J(16,17)=8.2$, $^4J(15,17)=1.2$, H_{17}); 7.57 (br. *d*, $^3J(7,8)=7.2$, H_8); 7.63 (*d*×*d*, $^3J(6,7)=7.9$, $^4J(6,8)=1.3$, H_6). - MS.: 356 (3), 178 (100), 152 (50).



REFERENCES

[1] a) *J. Meinwald, G.E. Samuelson & M. Ikeda,* J. Am. Chem. Soc. *92*, 7604 (1970); b) *R.M. Pagni & C.R. Watson,* Tetrahedron Lett. *1973*, 59; c) *I. Murata & K. Nakasuji, ibid. 1973*, 47; d) *N.J. Turro, V. Ramamurthy, R.M. Pagni & J.A. Butcher, jr.*, J. Org. Chem. *42*, 92 (1977).

[2] a) *S.F. Nelsen & J.P. Gillespie,* J. Org. Chem. *38*, 3592 (1973); *J.R. Dodd, R.F. Winton, R.M. Pagni, C.R. Watson, jr. & J. Bloor,* J. Am. Chem. Soc. *96*, 7846 (1974).

[3] a) *J. Michl & J. Kolc,* J. Am. Chem. Soc. *92*, 4147 (1970); *A. Castellan, J. Kolc & J. Michl, ibid. 100*, 6687 (1978); b) *J. Michl, ibid. 93*, 523 (1971); c) *J. Michl,* Mol. Photochem. *4*, 287 (1972); d) *J. Michl,* in 'Chemical Reactivity and Chemical Paths', Chapter 8, G. Klopman ed., Wiley, New York (1974); e) *J. Kolc & J. Michl,* J. Am. Chem. Soc. *95*, 7391 (1973); *J.M. Labrum, J. Kolc & J. Michl, ibid. 96*, 2636 (1974).

[4] *G. Germain, P. Main & M.M. Woolfson,* Acta Crystallogr. Sect. A *27*, 368 (1971).

[5] *P. Coppens & W.C. Hamilton,* Acta Crystallogr. Sect. A *26*, 71 (1970).

[6] *W.R. Busing, K.O. Martin & H.A. Levy,* ORFFE. Report ORNL-TM 306. Oak Ridge National Laboratory, Tennessee (1964).

[7] *C.K. Johnson,* ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee (1965).

[8] *V. Schomaker & K.N. Trueblood,* Acta Crystallogr. Sect. B *24,* 63 (1968).

[9] *D.T. Cromer & J.B. Mann,* Acta Crystallogr. Sect. A *24,* 321 (1968).

[10] *R.F. Stewart, E.R. Davidson & W.T. Simpson,* J. Chem. Phys. *42,* 3175 (1965).

[11] *H. Mauser,* Z. Naturforsch. *23b,* 1025 (1968); see also *G. Quinkert,* Angew. Chem. *84,* 1157 (1972); Angew. Chem. Int. Ed. *11,* 1072 (1972).

[12] *A.C. Hazell,* Acta Crystallogr. Sect. A *34,* S97 (1978).

[13] *D.A. Dougherty, W.D. Hounshell, H.B. Schlegel, R.A. Bell & K. Mislow,* Tetrahedron Lett. *1976,* 3479 (1976).

[14] *W.D. Hounshell, D.A. Dougherty, J.P. Hummel & K. Mislow,* J. Am. Chem. Soc. *99,* 1916 (1979).

[15] *K. Harano, T. Ban, M. Yasuda, E. Osawa & K. Kanematsu, ibid. 103,* 2310 (1981).

[16] *A.C. Hazell, R.G. Hazell & F.K. Larsen,* 5th European Crystallographic Meeting. Copenhagen, Denmark 70 (1979).

[17] *G.M.J. Schmidt,* Pure Applied Chem. *27,* 647 (1971); *M.D. Cohen,* Angew. Chem. *87,* 439 (1975); Angew. Chem. Int. Ed. *14,* 386 (1975); *J.R. Scheffer,* Accounts Chem. Research *13,* 283 (1980).

[18] *C. Rüchardt & H.-D. Beckhaus,* Angew. Chemie *92,* 417 (1980); Angew. Chem. Int. Ed. *19,* 429 (1980).

[19] *W.C. Herndon,* J. Org. Chem. *46,* 2119 (1981).

[20] a) *G. Kaupp & R. Dyllick-Brenzinger,* Angew. Chem. *86,* 523 (1974); Angew. Chem. Int. Ed. *13,* 478 (1974); b) *G. Kaupp & H.-W. Grüter,* Angew. Chem. *92,* 735 (1980); Angew. Chem. Int. Ed. *19,* 714 (1980); Chem. Ber. *114,* 2844 (1981), and references therein.