size that the relative P–O bond strengths are also strongly influenced by hydrogen bonding, which can stretch and weaken P–O acceptor bonds, and contract and strengthen P–OH donor bonds, by ~0·02 Å. This is a large effect, about a third of the ~0·06 Å change in P–O bond length that accompanies protonation or proton dissociation.

The geometries of N–H···O–C and of C–O–H···O–C hydrogen bonds have been reviewed recently by Taylor & Kennard (1984) and Jeffrey & Mitra (1983), respectively. By comparison, the present results show that N–H···O–P and P–O–H···O–P bonds are considerably stronger than N–H···O–C and C–O–H···O–C bonds, with normalized H···O distances (Table 3) shorter by ~0·2 Å, on average, in the phosphate hydrogen bonds. Indeed, hydrogen bonds involving phosphate groups are probably the strongest N–H···O and O–H···O bonds that form in biochemical systems. They should, therefore, be expected to play important roles in biomolecular structure, energetics and dynamics - especially so in the case of protein-nucleic acid interactions and in the many biochemical reaction mechanisms involving ATP hydrolysis or ADP phosphorylation. In particular, the strong effects of hydrogen bonding and proton transfer on P–O bond strengths are probably important factors for activating reactants and stabilizing intermediates in the reactions of the ATP-ADP biochemical energy cycle.

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Orientational Disorder in Cyclohepta[*de*]naphthalene. Structure Determination at 78, 100, 135, 200 and 295 K

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Abstract

Cyclohepta[*de*]naphthalene (pleiadiene), $C_{14}H_{10}$, $M_r = 178{\cdot}2$, monoclinic, $P2_1/c$, is disordered at room temperature, the molecules reorientating in their planes. The structure is ordered at 78 K with $a = 8{\cdot}210\,(4)$, $b = 10{\cdot}691\,(5)$, $c = 11{\cdot}034\,(5)$ Å, $\beta = 104{\cdot}75\,(3)°$, $V = 937\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}264\,(1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}0675\,(1)$ mm^{-1}, $F(000) = 376$. $R(F) = 0{\cdot}046$ for 976 reflexions $[I > 3\sigma(I)]$ and 63 variables. The disorder has been studied by energy calculations and by constrained least-squares refinements with data collected at five temperatures. Four possible orientations were

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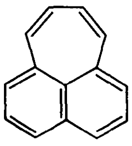
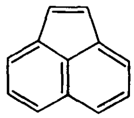
observed and their relative occupations determined as a function of temperature. The occupation factor for the most densely populated site varies from 100% at 78 K to 41·3% at room temperature. The fact that pleiadiene photodimerizes in the solid state at room temperature, but not at 78 K, is explained in terms of the disorder. The molecular geometry is compared with that of other strained perinaphthalenes and with calculated values.

Introduction

The bright-red aromatic hydrocarbon cyclohepta[*de*]naphthalene (I) (pleiadiene) (Boekelheide & Vick, 1956) is one of the simplest non-alternant hydrocarbons and as such has attracted the attention of experimental as well as theoretical chemists for some time (Michl, 1976, and references therein). Like acenaphthylene (II) (Cser, 1973, 1974; Welberry, 1973) the molecule is almost circular and was thus expected, like (II), to be disordered at room temperature. This was found to be so, but unlike acenaphthylene, which has a first-order phase transition, pleiadiene can be cooled to liquid-nitrogen temperature with no apparent change in space group. There are, however, marked changes in the relative intensities of some reflexions suggesting that the structure might become ordered at low temperatures.



(I)



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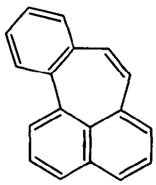


(III)

Experimental

Crystals were kindly provided by Josef Michl of the University of Utah and by Richard Pagni of the University of Tennessee. Precession photographs were taken at temperatures down to 78 K, the crystal being cooled with a CRYO-TIP refrigerator. A preliminary data set was collected on a Supper diffractometer using a large crystal. The low-temperature data and another set of room-temperature data were collected on a Picker FACS-I diffractometer with a crystal $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}4$ mm. The crystal was cooled by liquid nitrogen with a local modification of the cryostat described by Coppens *et al.* (1974). Standard reflexions $13\bar{5}$ and 302 were monitored every 60 reflexions. The intensity of 302 was temperature-sensitive and was used to check the temperature stability. If the intensity of 302 deviated by more than 2% from the value corresponding to the desired temperature, the data were discarded and if possible remeasured. The temperature variation was generally ±2%. The crystal was mounted in a Lindemann-glass capillary mounted on a copper block; the temperatures quoted are those of the copper block. The weakness of reflexions at the higher temperatures made the accurate determination of cell dimensions difficult. For the 200 K data the dimensions were obtained from the three strong reflexions which were used to determine the orientation matrix. The cell dimensions at room temperature were obtained from films. Crystal data and details of data collection are given in Table 1.

Structural determination

Approximate orientations of the molecular planes and the positions of the centres of the molecules were obtained from room-temperature data by direct methods. Attempts at refining with an ordered structure failed as did models which allowed free rotation or symmetrical hindered rotation in the molecular plane. The structure was solved from the 21 lowest-order reflexions from a data set measured at 100 K. Constrained least-squares refinements (Pawley, 1971) assuming an idealized geometry and knowing approximate values for the coordinates of the centre of the molecule and for two Euler angles and with various starting positions for the third (in-plane) Euler angle yielded an unambiguous solution. The structure was refined on F to $R(F) = 0{\cdot}06$ with the full 100 K data set, but a difference map (Fig. 1*a*) showed that there was disorder, some 5% of the molecules being rotated *ca* 180° in the molecular plane. Energy calculations (Fig. 2) in which the potential energy was calculated for various orientations of one molecule, the remaining molecules being kept fixed, showed a minimum, *A*, corresponding to the site with 95% occupation in the refinement of the 100 K data, and a shallower one, *C*, corresponding to that with 5% occupation. There was, however, a third minimum, *B*, *ca* 90° from *A*. With data collected at 200 K the structure could not be refined even in terms of disorder between orientations *A* and *C*. A difference map (Fig. 1*b*) based on structure factors for *A* alone showed the third site, *B*, to be more highly populated than *C*. Further data sets were collected at 78 K, at which temperature no significant disorder was observed, at 135 K and at room temperature. Refinements were carried out with molecules in up to four orientations, the fourth, *D*, being approximately 180° from *B*. The fourth site does not quite correspond to the fourth-deepest local minimum in the potential-energy calculation (Fig. 2); however, the calculation assumes the reorienting molecule to be in an otherwise ordered structure, which is far from true at 200 K. At the higher temperatures the disorder is complex, but insufficient data were observable to warrant the inclusion of more than four orientations. In the final refinements only orientations

Table 1. *Crystal data, collection and reduction of intensity data and least-squares-refinement details*

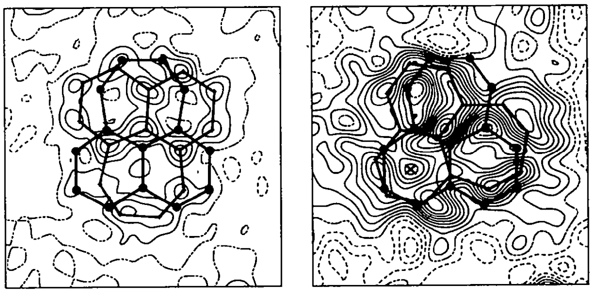
T (K)	78	100	135	200	295
a (Å)	8·210 (4)	8·220 (5)	8·245 (8)	8·14 (1)	8·144 (6)
b (Å)	10·691 (5)	10·687 (6)	10·754 (7)	10·89 (2)	10·940 (10)
c (Å)	11·034 (5)	11·067 (7)	11·174 (7)	11·33 (1)	11·481 (6)
β (°)	104·75 (3)	104·92 (4)	105·18 (5)	106·5 (1)	106·93 (10)
V (Å^3)	937 (1)	939 (1)	956 (1)	963 (2)	979 (1)
D_x (Mg m^{-3})	1·264 (1)	1·260 (1)	1·238 (2)	1·229 (3)	1·210 (2)
Cell determined from:					
No. reflexions	10, 12, 10	9	11	3	*
θ range (°)	9·5–17·8	8·0–20·4	8·0–17·8	7·9–17·4	
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
Monochromator	Graphite	Graphite	Graphite	Graphite	Ni filter
μ (mm^{-1})	0·0675 (1)	0·0673 (1)	0·0661 (1)	0·0657 (2)	0·4815 (7)
Data collection (ω–2θ scan):					
Step (°)	0·04	0·04	0·04	0·04	0·04
Width (°)	3·92	3·92	3·92	3·92	3·00
+ 0·692° tan θ for all					
Time/step (s)	2	2	2	2	4
θ_{max} (°)	25·0	25·0	25·0	22·5	45·0
Min. hkl	−9 0 0	0 −10 −14	−9 0 −13	−6 0 −12	−7 0 −10
Max. hkl	9 11 13	8 12 13	9 11 11	6 8 12	6 10 10
Reflexions	1855	1974	2960	1953	3480
Independent reflexions	1491	1366	1563	1004	801
R_{int} (reflexions)	0·083 (325)	0·050 (480)	0·098 (1115)	0·060 (699)	0·050 (801)
Refinements:					
$R(F)$	0·046	0·047	0·046	0·083	0·087
$wR(F)$	0·057	0·055	0·054	0·104	0·129
S	1·919	1·908	1·711	3·403	4·799
N_v	63	70	84	48	48
N_o [$I > 3\sigma(I)$]	976	857	646	387	384
$(\Delta/\sigma)_{max}$	0·06	0·03	0·27	0·68	0·14
$\Delta\rho_{max}$ (e Å^{-3})	0·26	0·22	0·11	0·16	0·15
$\Delta\rho_{min}$ (e Å^{-3})	−0·20	−0·21	−0·10	−0·14	−0·16

* From film.

with an occupation factor of more than 2% were included, *i.e.* one at 78 K, two at 100 K, and four for higher temperatures.

Refinement

Constrained refinements were carried out assuming molecules on all sites to be identical and generated from A by a rotation in the plane. Thermal parameters were determined by **T**, **L** and **S** in the third-cumulant approximation (Sygusch, 1976) so that the refined coordinates are corrected for libration. The tensors for the molecules in different orientations were assumed to be identical. Thermal motion was sufficiently large that neglect of internal modes, even at 78 K, was justified. The mean corrections to the C—C bond distances were 0·002 Å at 78 K, 0.005 Å at 100 K, and 0.006 Å at 135 K. H-atom positions were calculated for each cycle assuming C—H = 0·95 Å. Occupation factors p_i were constrained so that their sum was unity; they were always found to be positive although not constrained to be so, and to vary monotonically with temperature (Fig. 4). Refinements were first carried out varying all the Euler angles and centres, which necessitates that six coordinates be kept fixed. In the final cycles the Euler angles and centre for the primary molecule were fixed, so that standard deviations for all the coordinates could be obtained. For the 200 K and the 295 K data an idealized geometry of the molecule with symmetry



(*a*) (*b*)

Fig. 1. Difference maps in the plane of the molecule after refining with an ordered structure (full circles). Contours are drawn at intervals of 0·05 e Å^{-3}. (*a*) 100 K, (*b*) 200 K, × marks a local minimum.

Fig. 2. Energy in kJ mol^{-1} as a function of the in-plane Euler angle (°).

Table 2. *Occupation factors, p_i, Euler angles (°), and origins of the molecular axial systems (Å) referred to orthogonal axes with $X \| a$, $Z \| c^*$ and Y perpendicular to X and Z*

The Euler angles are defined as in Goldstein (1969). E.s.d.'s for angles and centres for site *A* at 78, 100 and 135 K are from refinements with some coordinates fixed.

T (K)	Site	p_i	φ	θ	ψ	X	Y	Z
78	*A*	1·000	53·3 (0·2)	39·5 (0·1)	209·0 (0·2)	1·250 (2)	6·828 (2)	9·508 (2)
100	*A*	0·935 (2)	52·8 (0·2)	39·5 (0·1)	209·2 (0·2)	1·252 (2)	6·825 (3)	9·540 (2)
100	*C*	0·065 (2)	236·1 (0·5)	45·0 (0·5)	210·2 (0·6)	0·639 (11)	6·937 (15)	9·323 (11)
135	*A*	0·802 (4)	52·3 (0·2)	39·6 (0·1)	209·3 (0·3)	1·213 (3)	6·868 (4)	9·623 (3)
135	*B*	0·075 (4)	150·3 (0·9)	44·2 (0·8)	214·3 (1·1)	1·016 (19)	6·580 (24)	9·352 (21)
135	*C*	0·087 (3)	238·5 (0·6)	41·9 (0·5)	209·4 (0·7)	0·641 (11)	6·934 (18)	9·342 (13)
135	*D*	0·037 (3)	347·7 (1·7)	40·0 (1·5)	199·3 (2·0)	0·649 (33)	7·187 (41)	9·725 (36)
200	*A*	0·569 (6)	52·0 (0·4)	40·1 (0·3)	210·3 (0·5)	0·913 (6)	6·929 (9)	9·731 (8)
200	*B*	0·248 (6)	150·7 (0·9)	40·8 (0·7)	212·3 (1·2)	0·725 (16)	6·641 (23)	9·374 (22)
200	*C*	0·114 (6)	239·5 (1·2)	43·9 (1·0)	208·1 (1·4)	0·382 (23)	7·047 (38)	9·531 (25)
200	*D*	0·069 (6)	334·9 (2·6)	32·1 (1·4)	207·9 (2·9)	0·656 (39)	7·066 (51)	9·735 (40)
295	*A*	0·413 (7)	52·5 (0·7)	39·9 (0·5)	210·1 (0·9)	0·856 (11)	6·944 (14)	9·859 (15)
295	*B*	0·311 (7)	152·1 (1·0)	41·4 (0·8)	210·5 (1·2)	0·609 (16)	6·694 (20)	9·491 (22)
295	*C*	0·152 (6)	237·6 (1·4)	44·0 (1·0)	209·6 (1·6)	0·277 (25)	6·960 (30)	9·549 (28)
295	*D*	0·124 (6)	339·9 (1·8)	36·9 (1·3)	203·6 (2·1)	0·691 (31)	7·266 (33)	10·081 (36)

*mm*2 was assumed and was not refined; the geometry was a weighted mean of the results from the lower temperatures. The weighting scheme used was $w = \{[\sigma_{CS}(F^2) + 1{\cdot}03F^2]^{1/2} - |F|\}^{-2}$, where $\sigma_{CS}(F^2)$ is the standard deviation from counting statistics. It was not necessary to refine an extinction parameter. The results of the refinements* are summarized in Tables 2 and 3.

The energy calculations which gave Fig. 2 were based on coordinates from the 100 K data, refining sites *A* and *C* with planar molecules. The axis of rotation was taken to be perpendicular to the plane of *A* and to intersect it at its centre of gravity. A completely ordered structure was assumed and then the energies calculated as one molecule was rotated in steps of 5°. The positions of the other molecules were assumed to be unchanged. The non-binding interaction between the molecule and its neighbours was calculated as $E = \sum (A\,e^{-Br_{ij}} - Cr_{ij}^{-6})$. Interactions of more than 5 Å were not included. The constants used were those of Mirsky & Cohen (1976). Calculations were carried out on a VAX 11/780 computer with the following programs: *DATAP* and *DSORT* (State University of New York, Buffalo), data processing; *KONSLS*, constrained least-squares refinement; *ORTEP* (Johnson, 1965), drawings; *MMP*2 (Burkert & Allinger, 1982), molecular-mechanics calculations. Atomic scattering factors were those of Cromer & Mann (1968) for C and of Stewart, Davidson & Simpson (1965) for H.

Discussion

In cyclohepta[*de*]naphthalene at 78 K the molecules pack in pairs around a centre of symmetry (Fig. 3*a*); the packing is similar to that of pyrene (Robertson & White, 1947). A difference synthesis in the plane of the molecule showed no evidence of disorder. At 100 K some of the molecules reorientate by an in-plane rotation of 180°. At higher temperatures the site at 90° becomes more densely populated but the 180° site is still occupied (Fig. 4). From the X-ray data alone it is difficult to distinguish the situation where one molecule of a pair is disordered from that where both molecules rotate together. Evidence that the pair of molecules does not rotate together is afforded by a photochemical study of the crystals (Hazell, Pagni, Persy, Rommel & Wirz, 1981). Irradiation of the crystals with light causes the crystals to turn white due to the formation of the *syn* photodimer. The molecules in a pair are already at a suitable distance, 3·6 Å, for dimerization but are in the ordered structure in the wrong orientation. Rotation of one of the molecules by 180° puts the pair in the correct orientation for dimerization (Figs. 3*b* and 3*c*). This mechanism successfully predicted that photodimerization does not occur at liquid-nitrogen temperature, where the molecules are always in the wrong orientation for *syn* dimerization. Molecular reorientation in aromatic hydrocarbons is not uncommon, although it is not always observable by X-ray diffraction. NMR studies of solid pyrene (Fyfe, Gilson & Thompson, 1970) show line-width narrowing characteristic of reorientation. As the molecule has approximate *mm*2 symmetry it is not possible from diffraction studies to observe a 180° reorientation. Pleiadiene, acepleiadylene and perylene all pack like pyrene. Acepleiadylene (Hanson, 1960) is completely disordered at room temperature, but perylene shows no signs of disorder from the X-ray structure (Camerman & Trotter, 1964) or from solid-state NMR measure-

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* Lists of structure factors, fractional atomic coordinates derived from those in the molecular system and anisotropic thermal parameters, H parameters, T, L and S, and references to the perinaphthalenes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43172 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Coordinates* (Å) *relative to molecular axes,* U_{eq} ($Å^2 \times 10^{-3}$) *and distances* (Å) *from the best plane through the* C *atoms*

$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$

	x	y	z	U_{eq}	d
78 K					
C (1)	−0·001 (3)	−0·002 (2)	−0·003 (2)	23 (1)	−0·017 (2)
C (2)	−1·305 (3)	0·633 (2)	0·009 (2)	23 (1)	−0·011 (2)
C (3)	−2·452 (3)	−0·146 (2)	0·058 (2)	26 (1)	0·020 (2)
C (4)	−2·418 (3)	−1·551 (2)	0·095 (2)	29 (1)	0·043 (2)
C (5)	−1·212 (3)	−2·186 (2)	0·064 (2)	29 (1)	0·017 (2)
C (6)	0·000 (3)	−1·462 (2)	0·004 (2)	26 (1)	−0·025 (2)
C (7)	1·236 (3)	−2·177 (2)	−0·014 (3)	30 (1)	−0·039 (3)
C (8)	2·431 (3)	−1·532 (2)	−0·002 (3)	32 (1)	−0·009 (3)
C (9)	2·450 (3)	−0·118 (2)	0·011 (2)	31 (1)	0·019 (2)
C (10)	1·289 (3)	0·646 (2)	0·005 (2)	26 (1)	0·010 (2)
C (11)	1·540 (3)	2·101 (2)	0·022 (2)	31 (1)	0·045 (2)
C (12)	0·708 (3)	3·146 (2)	−0·007 (3)	33 (1)	0·019 (3)
C (13)	−0.746 (3)	3·134 (2)	−0·042 (3)	30 (1)	−0·030 (3)
C (14)	−1·566 (3)	2·085 (2)	−0·034 (3)	26 (1)	−0·041 (3)
100 K					
C (1)	0·001 (3)	−0·001 (2)	0·000 (2)	37 (1)	−0·013 (2)
C (2)	−1·293 (3)	0·654 (3)	0·010 (2)	42 (1)	−0·008 (2)
C (3)	−2·426 (3)	−0·125 (3)	0·047 (3)	49 (1)	0·016 (3)
C (4)	−2·408 (3)	−1·518 (3)	0·074 (3)	52 (1)	0·036 (3)
C (5)	−1·224 (3)	−2·159 (3)	0·041 (3)	48 (1)	0·008 (3)
C (6)	−0·002 (3)	−1·440 (2)	0·000 (2)	40 (1)	−0·020 (2)
C (7)	1·221 (3)	−2·162 (3)	−0·020 (3)	50 (1)	−0·036 (3)
C (8)	2·414 (3)	−1·524 (3)	−0·001 (3)	54 (1)	−0·004 (3)
C (9)	2·441 (3)	−0·131 (3)	0·016 (3)	48 (1)	0·021 (3)
C (10)	1·297 (3)	0·648 (2)	0·009 (2)	41 (1)	0·009 (2)
C (11)	1·547 (3)	2·078 (3)	0·026 (3)	50 (1)	0·037 (3)
C (12)	0·728 (4)	3·131 (3)	−0·008 (3)	59 (1)	0·002 (3)
C (13)	−0.719 (4)	3·132 (3)	−0·018 (3)	62 (1)	−0·019 (3)
C (14)	−1·535 (3)	2·095 (3)	−0·018 (3)	54 (1)	−0·030 (3)
135 K					
C (1)	0·012 (5)	0·000 (3)	−0·001 (4)	48 (1)	−0·017 (4)
C (2)	−1·279 (5)	0·674 (4)	0·022 (5)	56 (1)	−0·002 (5)
C (3)	−2·439 (6)	−0·091 (5)	0·063 (6)	66 (2)	0·027 (6)
C (4)	−2·430 (6)	−1·501 (4)	0·069 (6)	69 (2)	0·028 (6)
C (5)	−1·242 (6)	−2·152 (4)	0·037 (5)	64 (2)	0·002 (5)
C (6)	−0·007 (5)	−1·442 (4)	0·001 (5)	54 (1)	−0·021 (5)
C (7)	1·211 (6)	−2·195 (4)	−0·014 (6)	67 (2)	−0·029 (6)
C (8)	2·407 (5)	−1·555 (5)	−0·005 (6)	73 (2)	−0·008 (6)
C (9)	2·440 (5)	−0·162 (4)	0·020 (4)	64 (2)	0·023 (4)
C (10)	1·300 (5)	0·642 (4)	0·017 (4)	53 (1)	0·014 (4)
C (11)	1·554 (5)	2·091 (4)	0·034 (4)	65 (2)	0·040 (4)
C (12)	0·748 (6)	3·150 (4)	−0·008 (5)	77 (2)	−0·004 (5)
C (13)	−0·686 (6)	3·152 (4)	−0·018 (6)	82 (2)	−0·026 (6)
C (14)	−1·517 (6)	2·107 (4)	−0·006 (5)	72 (2)	−0·025 (5)

Table 4. *Bond distances* (Å) *and angles* (°) *together with the weighted mean and the sample standard deviation, S*

The labelling of the bonds is as shown on Fig. 5.

Bond	78 K		100 K		135 K		Mean	S
a	1·387 (4)	1·389 (4)	1·375 (4)	1·384 (4)	1·390 (7)	1·395 (6)	1·385 (2)	7
b	1·407 (4)	1·414 (4)	1·394 (4)	1·393 (4)	1·410 (8)	1·394 (7)	1·402 (2)	9
c	1·363 (4)	1·357 (4)	1·348 (4)	1·352 (4)	1·355 (7)	1·357 (7)	1·355 (2)	5
d	1·413 (4)	1·429 (4)	1·418 (4)	1·420 (4)	1·425 (7)	1·431 (7)	1·421 (2)	7
e	1·460 (4)		1·439 (4)		1·442 (6)		1·448 (3)	11
f	1·451 (4)	1·444 (4)	1·451 (4)	1·449 (4)	1·457 (6)	1·440 (6)	1·449 (2)	6
g	1·476 (4)	1·477 (4)	1·461 (4)	1·452 (4)	1·453 (7)	1·471 (6)	1·466 (2)	11
h	1·331 (4)	1·336 (4)	1·320 (5)	1·334 (4)	1·335 (7)	1·331 (7)	1·332 (2)	6
i	1·455 (4)		1·447 (5)		1·434 (7)		1·449 (3)	11
Angle								
ab	122·8 (3)	122·6 (3)	123·8 (3)	123·2 (3)	123·1 (5)	123·9 (5)	123·2 (1)	5
bc	119·1 (3)	119·1 (3)	119·1 (3)	119·2 (3)	119·0 (5)	119·5 (5)	119·1 (1)	2
cd	121·4 (3)	121·6 (3)	121·1 (3)	121·3 (3)	121·4 (5)	120·1 (5)	121·3 (1)	6
de	120·8 (2)	120·1 (2)	120·6 (3)	120·4 (3)	120·6 (4)	121·0 (4)	120·5 (1)	3
dd	119·1 (2)		119·0 (3)		118·4 (5)		119·0 (2)	4
ef	116·0 (2)	116·6 (2)	116·7 (2)	116·7 (2)	116·8 (4)	117·2 (4)	116·6 (1)	4
ff	127·4 (2)		126·6 (3)		125·9 (4)		127·0 (2)	9
af	119·9 (3)	120·0 (2)	118·6 (3)	119·1 (3)	119·0 (4)	118·3 (4)	119·4 (1)	7
ag	114·1 (2)	113·6 (2)	115·0 (3)	114·3 (3)	114·0 (5)	115·3 (4)	114·2 (1)	7
fg	126·1 (3)	126·5 (2)	126·4 (3)	126·5 (3)	127·0 (4)	126·4 (4)	126·5 (1)	3
gh	131·8 (3)	131·6 (3)	132·2 (3)	132·1 (3)	132·1 (5)	132·7 (5)	132·0 (1)	4
hi	128·5 (3)	128·1 (3)	128·2 (3)	127·9 (3)	128·4 (6)	127·4 (5)	128·1 (1)	4

ments (Fyfe, Dunell & Ripmeester, 1971). The latter authors suggest that in perylene the out-of-plane distortion increases the barrier to rotation.

Bond distances and angles from the 78, 100 and 135 K studies are given in Table 4, the labelling of atoms and bonds is shown in Fig. 5. The values obtained at the three temperatures are very similar, the biggest discrepancy being for bonds *e*, *g* and *i*. The molecule is almost planar (Table 3), the maximum deviation of a C atom from the best plane being *ca* 0·04 Å. For the 100 K and the 135 K data the deviations from planarity are the weighted means of the contributions from molecules in different orientations, which need not necessarily be identical.

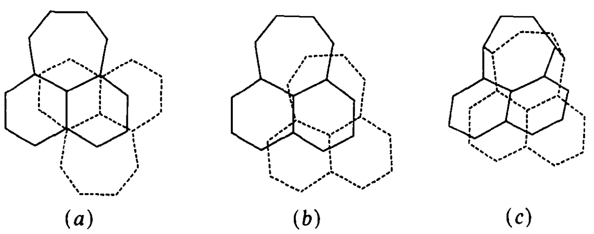

Fig. 3. A pair of molecules (*a*) in the ordered structure, (*b*) head-to-tail disordered, (*c*) the *syn* dimer.

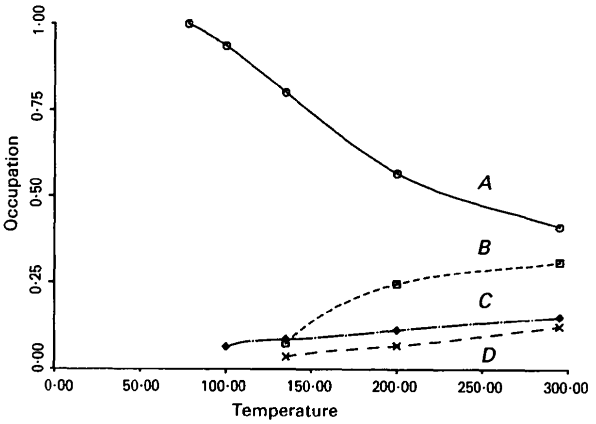

Fig. 4. Occupation factors as a function of temperature (K).

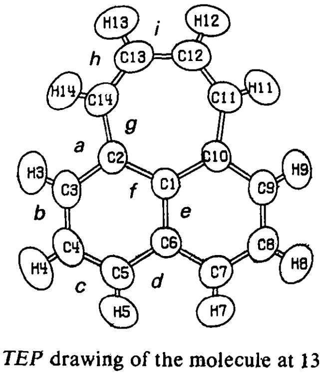

Fig. 5. An *ORTEP* drawing of the molecule at 135 K showing the numbering of the atoms and the labelling of the bonds.

Table 5. *Bond distances* (Å) *and angles* (°) *for pleiadiene* (I) *and the benzo derivative* (III), *together with values for pleiadiene from MMP*2 *calculations, MO calculations, and empirical values for fg* = 126.5°

Bond	(I)	(III)	*MMP*2	MO	Empir.
a	1·385 (2)	1·393 (3)	1·392	1·39	1·383
b	1·402 (2)	1·399 (3)	1·412	1·41	1·396
c	1·355 (2)	1·354 (4)	1·371	1·38	1·353
d	1·421 (2)	1·422 (3)	1·426	1·42	1·414
e	1·448 (3)	1·434 (4)	1·420	1·41	1·438
f	1·449 (2)	1·442 (3)	1·439	1·43	1·439
g	1·466 (2)	1·477*	1·465	1·46	
h	1·332 (2)	1·330 (4)	1·351	1·36	
i	1·449 (3)	1·467 (4)	1·444	1·45	

Angle	(I)	(III)	*MMP*2	Empir.
ab	123·2 (1)	122·6 (2)	122·9	122·7
bc	119·1 (1)	119·5 (3)	118·0	119·3
cd	121·3 (1)	120·9 (3)	120·0	121·0
de	120·5 (1)	120·3 (2)	122·0	120·8
dd	119·0 (2)	119·4 (3)	115·9	118·3
ef	116·6 (1)	117·2 (2)	116·9	116·9
ff	127·0 (2)	125·7 (3)	126·2	126·7
af	119·4 (1)	118·6 (2)	119·3	119·3
ag	114·2 (1)	115·6*	112·9	114·2
fg	126·5 (1)	125·3*	127·9	126·5†
gh	132·0 (1)	131·2 (3)		
hi	128·1 (1)	129·7 (3)		

* Mean of two bonds or angles which are not chemically equivalent.

† Assumed.

The geometry is very similar to that of benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene (III) (Hazell, 1978*a*). The strain induced by the seven-membered ring is spread throughout the molecule distorting both angles and bond lengths. Hazell (1978*b*) showed that for 1,8-disubstituted naphthalenes there is a linear correlation, $r_i = r_i^{120} + k_f(fg - 120)$, between the geometrical parameters r_i and the angle fg, where r_i is a bond length or angle, r_i^{120} its value at 120° and k_i a constant. The observed geometry of the naphthalene is in good agreement with that predicted from the observed value of $fg = 126{\cdot}5°$ and the values of k_i (Table 6) obtained from 23 structure determinations in which fg ranged from 105·5 to 125·6°. The biggest discrepancy is for bond *e*, one of the bonds for which there is a large discrepancy between the three low-temperature determinations of pleiadiene. A characteristic feature of the compounds in which the substituents are splayed apart is the very short value for *c* as compared with that for *a*. Although it is to be expected that for aromatic hydrocarbons a structure determination with X-rays will give the short bonds too short and the long bonds too long (Hazell, Larsen & Lehmann, 1973), this effect seems unimportant here since *a* and *c* have similar bond orders. Molecular-mechanics calculations taking electron delocalization into account were carried out using the *MMP*2 program (Burkert & Allinger, 1982). The calculated minimum-energy structure (Table 5) has symmetry *mm*2 and models the deformations reasonably well. Bond-length deformations are underestimated, but not as badly as by conventional SCF LCAO π-electron calculations (*e.g.* DasGupta & DasGupta, 1977).

Table 6. *Parameters for the empirical relationship* $r_i = r_i^{120} + k_i(fg - 120)$ *between the geometrical parameters* r_i *and the angle fg*

Bond	r^{120}	k	Angle	r^{120}	k
a	1·379 (2) Å	0·0006 (2)	*ab*	121·3 (2)°	0·21 (2)
b	1·405 (2)	−0·0013 (2)	*bc*	120·4 (1)	−0·17 (1)
c	1·360 (2)	−0·0011 (2)	*cd*	120·7 (1)	0·04 (2)
d	1·416 (2)	−0·0004 (2)	*de*	119·2 (1)	0·25 (1)
e	1·426 (2)	0·0018 (2)	*ef*	119·3 (2)	−0·37 (2)
f	1·431 (2)	0·0013 (2)	*af*	119·1 (2)	0·03 (2)
			ag	120·9 (2)	−1·03 (2)
			dd	121·6 (1)	−0·50 (1)
			ff	121·8 (3)	0·76 (4)

The combination of constrained least-squares refinement and potential-energy calculations provided a means of studying crystal structures with complicated rotational disorder. Studies at different temperatures gave information about the temperature variation of the disorder, which provided insight into the mechanism of the solid-state dimerization reaction.

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