Tamura, C., Sakurai, N. & Sato, S. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1473–1479.
Tamura, C., Sato, S. & Hata, T. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2388–2394.
Tamura, C., Yoshikawa, M., Sato, S. & Hata, T. (1973). *Chem. Lett.* pp. 1221–1224.
Tavale, S. S. & Sobell, H. M. (1970). *J. Mol. Biol.* **48**, 109–123.
Watenpaugh, K., Dow, J., Jensen, L. H. & Furberg, S. (1968). *Science*, **159**, 206.
Watson, D. G., Sutor, D. J. & Tollin, P. (1965). *Acta Cryst.* **19**, 111–124.

Acta Cryst. (1978). B**34**, 1263–1270

Structural Chemistry of Layered Cyclophanes.
III. Molecular Structures of [2.2](2,7)Pyrenophane-1,1′-diene and Pyrene (Redetermined) at −160°C

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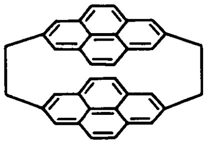
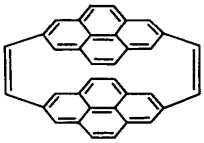
The molecular structure of [2.2](2,7)pyrenophane-1,1′-diene was determined from X-ray diffraction data collected on a four-circle diffractometer at −160°C. Crystals belong to the monoclinic space group $P2_1/c$ with two molecules per unit cell; a = 9·829 (2), b = 12·631 (2), c = 10·001 (2) Å and β = 113·82 (1)°. The structure was solved by the direct method and refined by block-diagonal least squares to an R of 0·064 for 2917 observed reflexions. The pyrene moieties have shallow-boat conformations connected by ethylenic bridges of length 1·344 (3) Å and with angles of 118·5 (2) and 119·3 (2)°. The molecular structure of pyrene was redetermined to compare its structure with that of [2.2](2,7)pyrenophane-1,1′-diene. The X-ray data were measured at −160°C to obtain standard data of high accuracy for the condensed aromatic compounds. The final R value was 0·063 for 2361 observed reflexions. Good agreement was observed between the chemically equivalent parts of the molecule.

Introduction

Studies of a wide variety of condensed aromatic [2.2]carbophanes have been extensively undertaken from the viewpoint of transannular interaction. Recently, Umemoto, Satani, Sakata & Misumi (1975) have synthesized a [2.2](2,7)pyrenophane (I) and its diene derivative (II), which are typical models for excimer fluorescence studies.


(I)


(II)

The molecular structure of [2.2](2,7)pyrenophane-1,1′-diene (II) has been determined from X-ray diffraction data collected on a four-circle diffractometer at −160°C. The molecular structure of (I) has been reported by Irngartinger, Kirrstetter, Krieger, Rodenwald & Staab (1977) in the course of our X-ray studies on (I). A comparison of the molecular structures of (I) and (II) is made in this paper.

The molecular structure of pyrene has been determined hitherto by the X-ray method by Robertson & White (1947), Camerman & Trotter (1965) and Allmann (1970), and by the neutron diffraction method by Hazell, Larsen & Lehmann (1972). Hazell *et al.* compared the molecular structures determined by neutron and X-ray methods. They stressed the marked differences between the bond distances obtained by the two methods and attributed them to the nonsphericities of the electron clouds. It is well known that rather short bond distances are observed because of the effect of thermal vibration in the molecular structure determined by the X-ray method. In fact, the results of Camerman & Trotter and of Allmann are significantly different. To make a strict comparison of the X-ray with the neutron structure we have carried out a redetermination of the molecular structure of pyrene at −160°C. The redetermination was also stimulated by the expectation of basic differences between the

Table 1. *Crystal data of* [2.2](2,7)*pyrenophane*-1,1′-*diene*

$C_{36}H_{20}$, FW 452·6
Monoclinic, $P2_1/c$
$F(000) = 472$, $\mu(\text{Mo } K\alpha) = 0{\cdot}80$ cm^{-1}

	−160°C	20°C
a	9·829 (2) Å	9·889 (2) Å
b	12·631 (2)	12·865 (3)
c	10·001 (2)	9·965 (2)
β	113·82 (1)°	113·96 (1)°
U	1135·9 (4) Å^3	1158·6 (4) Å^3
Z	2	2
D_x	1·323 g cm^{-3}	1·297 g cm^{-3}
D_m		1·298

molecular structures of the planar pyrene molecule and the supposed boat-shaped pyrene moieties in (I) and (II).

Experimental

[2.2](2,7)*Pyrenophane*-1,1′-*diene* (II)

Crystals of (II) are pale yellow, short prisms and are stable in air. The crystal data are listed in Table 1. The experimental conditions for the determination of the crystal data and for the measurement of diffraction intensities are the same as those of [2.2]metacyclophane described in the first paper of this series (Kai, Yasuoka & Kasai, 1977). The crystal used for the data collection was 0·3 × 0·3 × 0·3 mm. 3340 independent reflexions were measured within a sphere of $\sin\theta/\lambda = 0{\cdot}704$ Å^{-1} ($2\theta \le 60°$), among which 2917 were greater than $3\sigma(F)$. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

Pyrene

The crystal data are listed in Table 2. The experimental conditions are the same as those of (II). The crystal used was 0·25 × 0·3 × 0·3 mm. 2939 independent reflexions were collected ($\sin\theta/\lambda \le 0{\cdot}704$ Å^{-1}), among which 2361 were above background. No absorption correction was made.

Table 2. *Crystal data of pyrene*

$C_{16}H_{10}$, FW 202·3
Monoclinic, $P2_1/a$
$F(000) = 424$, $\mu(\text{Mo } K\alpha) = 0{\cdot}78$ cm^{-1}

	−160°C	20°C
a	13·532 (1) Å	13·667 (2) Å
b	9·159 (1)	9·267 (1)
c	8·387 (1)	8·479 (2)
β	100·25 (1)°	100·25 (2)°
U	1022·8 (1) Å^3	1056·8 (4) Å^3
Z	4	4
D_x	1·313 g cm^{-3}	1·271 g cm^{-3}
D_m		1·27*

* Camerman & Trotter (1965).

Structure determination and refinement

[2.2](2,7)*Pyrenophane*-1,1′-*diene* (II)

It is clear from Table 1 that the molecule is located at the centre of symmetry in the crystal. The structure was solved by the local version of *MULTAN* (Germain, Main & Woolfson, 1971) using 347 $|E|$ values greater than 1·5. From the E map calculated by a set of phases which gave the highest figure of merit, the eighteen crystallographically independent C atoms were easily

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *of the* C *atoms of* [2.2](2,7)*pyrenophane*-1,1′-*diene*

The estimated standard deviations, given in parentheses, refer to the last significant figure.

	x	y	z
C(1)	−105 (2)	5883 (1)	1924 (2)
C(2)	112 (2)	6558 (1)	3031 (2)
C(3)	1607 (2)	6612 (1)	4273 (2)
C(4)	1942 (2)	5977 (1)	5508 (2)
C(5)	3422 (2)	5765 (1)	6457 (2)
C(6)	3806 (2)	5015 (1)	7637 (2)
C(7)	5223 (2)	4678 (1)	8364 (2)
C(8)	6405 (2)	5049 (1)	7982 (2)
C(9)	7805 (2)	4550 (1)	8499 (2)
C(10)	8862 (2)	4845 (1)	7968 (2)
C(11)	8599 (2)	5734 (1)	7067 (2)
C(12)	7224 (2)	6248 (1)	6519 (2)
C(13)	6866 (2)	7060 (1)	5428 (2)
C(14)	5449 (2)	7400 (1)	4697 (2)
C(15)	4246 (2)	6956 (1)	4991 (2)
C(16)	2757 (2)	7147 (1)	4075 (2)
C(17)	4588 (2)	6221 (1)	6156 (2)
C(18)	6083 (2)	5867 (1)	6924 (2)

Table 4. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters* (Å^2) *of the hydrogen atoms of* [2.2](2,7)*pyrenophane*-1,1′-*diene*

The numbering follows that of the C atoms to which the H atoms are attached.

	x	y	z	B
H(1)	−108 (2)	583 (2)	107 (2)	2·9 (4)
H(2)	−73 (2)	704 (2)	296 (3)	3·8 (5)
H(4)	111 (2)	560 (2)	566 (2)	2·0 (4)
H(6)	302 (2)	471 (2)	789 (2)	3·1 (5)
H(7)	547 (2)	416 (2)	914 (2)	2·8 (4)
H(9)	808 (2)	386 (1)	927 (2)	1·7 (4)
H(11)	937 (2)	596 (2)	666 (2)	3·6 (5)
H(13)	765 (3)	740 (2)	516 (3)	4·3 (6)
H(14)	521 (2)	796 (2)	391 (2)	3·1 (5)
H(16)	249 (2)	766 (2)	320 (2)	1·9 (4)

located. Refinement of the molecular structure was carried out by the block-diagonal least-squares method using *HBLS* V (Ashida, 1973). The atomic scattering factors for C were taken from *International Tables for X-ray Crystallography* (1974) and those of H were from Stewart, Davidson & Simpson (1965). Three cycles of isotropic refinement gave a conventional R index of 0·129. After three cycles of anisotropic refinement a difference Fourier map revealed all the H atoms clearly. H atoms with isotropic temperature factors were then included in the refinement. The weighting scheme used was $w = Fwt$ for $|F_o| = 0{\cdot}0$ and $w = [\sigma(F_o)^2 + a|F_o| + b|F_o|^2]^{-1}$ for $|F_o| > 0{\cdot}0$, where Fwt, a and b were adjusted during the refinement. After five cycles the refinement converged; the final R was 0·064 for non-zero (0·078 for all) reflexions. The weighting parameters used in the final refinement were $Fwt = 0{\cdot}905$, $a = 0{\cdot}023$ and $b = 0{\cdot}001$, and the shifts for positional and thermal parameters for H atoms were less than $0{\cdot}05\sigma$ and $0{\cdot}3\sigma$ respectively. The weighted R index, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, was 0·087. The final atomic parameters for C and H atoms are given in Tables 3 and 4 respectively.*

Pyrene

The refinement of the molecular structure was started from the positional parameters of sixteen C atoms reported by Allmann (1970), each atom being assigned an isotropic temperature factor of 2·5 Å^2. The refinement was carried out by the same procedure as for (II). The final weighting parameters were $Fwt = 1{\cdot}294$, $a = 0{\cdot}006$ and $b = 0{\cdot}001$, and the shifts for positional and thermal parameters for H atoms were less than $0{\cdot}03\sigma$ and $0{\cdot}2\sigma$ respectively. The final R index was 0·063 for non-zero (0·086 for all) reflexions. The weighted R index was 0·084. The final atomic parameters for C and H are given in Tables 5 and 6 respectively.*

Results and discussion

Pyrene

A perspective view of the molecule with the atom numbering is shown in Fig. 1 (*ORTEP* II, Johnson, 1976). The analysis of the molecular thermal vibrations in the crystal was undertaken by the method of Schomaker & Trueblood (1968) with the *MV*-60 program of the *UNICS* II system (Sakurai, Iwasaki,

Table 5. *Fractional atomic coordinates* ($\times 10^4$) *of the C atoms of pyrene*

The estimated standard deviations, given in parentheses, refer to the last significant figure.

	x	y	z
C(1)	2822 (1)	−354 (2)	4173 (2)
C(2)	2945 (1)	302 (2)	2734 (2)
C(3)	2299 (1)	−38 (2)	1280 (2)
C(4)	2409 (1)	591 (2)	−245 (2)
C(5)	1779 (1)	247 (2)	−1632 (2)
C(6)	967 (1)	−762 (2)	−1637 (2)
C(7)	304 (1)	−1145 (2)	−3054 (2)
C(8)	−469 (1)	−2126 (2)	−3020 (2)
C(9)	−601 (1)	−2763 (2)	−1577 (2)
C(10)	44 (1)	−2422 (2)	−120 (2)
C(11)	−61 (1)	−3063 (2)	1406 (1)
C(12)	575 (1)	−2733 (2)	2792 (2)
C(13)	1388 (1)	−1720 (2)	2803 (2)
C(14)	2063 (1)	−1364 (2)	4214 (2)
C(15)	1504 (1)	−1052 (1)	1318 (2)
C(16)	833 (1)	−1407 (1)	−145 (2)

Table 6. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters* (Å^2) *of the hydrogen atoms of pyrene*

The numbering follows that of the C atoms to which the H atoms are attached.

	x	y	z	B
H(1)	326 (1)	−10 (2)	519 (2)	3·8 (4)
H(2)	349 (1)	101 (2)	269 (2)	3·1 (4)
H(4)	296 (1)	127 (2)	−26 (2)	2·6 (4)
H(5)	187 (1)	68 (2)	−265 (2)	2·9 (4)
H(7)	41 (1)	−70 (2)	−405 (2)	3·3 (4)
H(8)	−93 (1)	−239 (2)	−404 (2)	3·5 (4)
H(9)	−117 (1)	−342 (2)	−150 (2)	3·4 (4)
H(11)	−62 (1)	−374 (2)	144 (2)	3·4 (4)
H(12)	49 (1)	−320 (2)	385 (2)	2·8 (4)
H(14)	198 (1)	−187 (2)	525 (2)	2·8 (4)

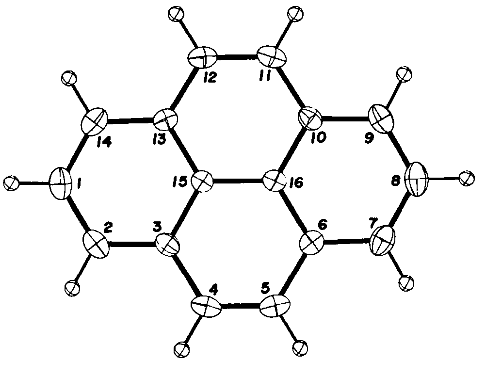


Fig. 1. The molecular structure and atomic numbering scheme of pyrene. The thermal ellipsoids include 50% probability and H atoms are drawn as spheres of radius 0·1 Å.

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33162 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Watanabe, Kobayashi, Bando & Nakamichi, 1974). The results are given in Table 7. The interatomic bond distances and bond angles are listed in Table 8 together with the bond distances corrected for thermal vibration. Differences between the corrected and uncorrected bond distances are in the range 0·001–0·003 Å, *i.e.* ≤1·0σ of the observed C–C distances. Discussion will be based, therefore, on the structure uncorrected for thermal vibration. Selected bond distances and bond angles are shown in Fig. 2. On the assumption of molecular symmetry *mmm*, mean bond distances ($\bar{x}$) are calculated and listed in Table 9 together with the standard deviation of the mean, $\sigma(\bar{x})$, to estimate the correlation between the chemically equivalent parts of the molecule. X-ray molecular structures determined by Camerman & Trotter (1965) and Allmann (1970), and the neutron structure determined by Hazell *et al.* (1972) are compared in Table 9 with that of the present work. The smallest $\sigma(\bar{x})$ values are obtained in the present work. This indicates that the reliability of the

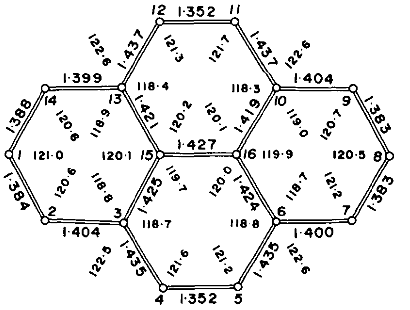


Fig. 2. Selected bond distances (Å) and bond angles (°) of pyrene projected on the least-squares plane of the C atoms.

Table 7. *Analysis of molecular thermal vibrations of pyrene*

Translational, **T** (Å^2), rotational, **L** (deg^2), and their correlation, **S** (Å deg), tensors

$$\mathbf{T}\ (\sigma\mathbf{T}) = \begin{pmatrix} 0{\cdot}0237\ (3) & 0{\cdot}0012\ (2) & -0{\cdot}0008\ (3) \\ & 0{\cdot}0182\ (3) & -0{\cdot}0005\ (3) \\ & & 0{\cdot}0130\ (5) \end{pmatrix}$$

$$\mathbf{L}\ (\sigma\mathbf{L}) = \begin{pmatrix} 6{\cdot}9\ (4) & 0{\cdot}5\ (2) & 0{\cdot}5\ (3) \\ & 3{\cdot}2\ (2) & -0{\cdot}2\ (2) \\ & & 7{\cdot}8\ (2) \end{pmatrix}$$

$$\mathbf{S}\ (\sigma\mathbf{S}) = \begin{pmatrix} * & -0{\cdot}005\ (9) & 0{\cdot}013\ (5) \\ -0{\cdot}036\ (7) & * & 0{\cdot}004\ (3) \\ 0{\cdot}009\ (4) & -0{\cdot}021\ (3) & * \end{pmatrix}$$

R.m.s. displacements along, and directions of, the principal vibrational axes

		R.m.s. displacements	Direction cosines of principal vibrational axes **p** along inertial axes **l**†		
			l_1	l_2	l_3
	p_1	0·114 (Å)	0·0668	0·0769	0·9948
T	p_2	0·134	0·2112	−0·9755	0·0613
	p_3	0·155	0·9752	0·2060	−0·0814
	p_1	1·77 (°)	−0·1250	0·9904	0·0596
L	p_2	2·61	−0·9107	−0·1383	0·3893
	p_3	2·83	0·3938	−0·0056	0·9192

* $S_{11} - S_{33} = -0{\cdot}016\ (9)$, $S_{33} - S_{22} = -0{\cdot}011\ (6)$.

† The inertial axes **l** are defined by **l** = **ma**, where the elements of **m** are

$$\mathbf{m} = \begin{pmatrix} 0{\cdot}0469 & 0{\cdot}0252 & 0{\cdot}1025 \\ -0{\cdot}0373 & -0{\cdot}0677 & 0{\cdot}0617 \\ 0{\cdot}0452 & -0{\cdot}0819 & -0{\cdot}0195 \end{pmatrix}$$

and **a** is the column vector composed of the dimensions of three crystal axes *a*, *b* and *c*.

Table 8. *Interatomic bond distances* (Å) *and bond angles* (°) *in pyrene*

Standard deviations in parentheses refer to the last figure. The columns of bond distances headed by asterisks show the values corrected for thermal vibration.

C(1)–C(2)	1·384 (2)	1·386*	C(8)–C(9)	1·383 (2)	1·385*
C(1)–C(14)	1·388 (2)	1·389	C(9)–C(10)	1·404 (2)	1·406
C(2)–C(3)	1·404 (2)	1·404	C(10)–C(11)	1·437 (2)	1·440
C(3)–C(4)	1·435 (2)	1·436	C(10)–C(16)	1·419 (2)	1·421
C(3)–C(15)	1·425 (2)	1·428	C(11)–C(12)	1·352 (2)	1·353
C(4)–C(5)	1·352 (2)	1·353	C(12)–C(13)	1·437 (2)	1·440
C(5)–C(6)	1·435 (2)	1·437	C(13)–C(14)	1·399 (2)	1·400
C(6)–C(7)	1·400 (2)	1·401	C(13)–C(15)	1·421 (2)	1·423
C(6)–C(16)	1·424 (2)	1·427	C(15)–C(16)	1·427 (2)	1·430
C(7)–C(8)	1·383 (2)	1·385			

C(1)–H(1)	0·98 (2)	C(8)–H(8)	0·99 (2)
C(2)–H(2)	0·99 (2)	C(9)–H(9)	0·99 (2)
C(4)–H(4)	0·98 (2)	C(11)–H(11)	0·98 (2)
C(5)–H(5)	0·97 (2)	C(12)–H(12)	1·01 (2)
C(7)–H(7)	0·96 (2)	C(14)–H(14)	1·00 (2)

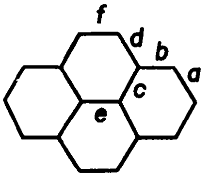
C(2)–C(1)–C(14)	121·0 (2)	C(8)–C(9)–C(10)	120·7 (2)
C(2)–C(1)–H(1)	120 (1)	C(8)–C(9)–H(9)	123 (1)
C(14)–C(1)–H(1)	119 (1)	C(10)–C(9)–H(9)	116 (1)
C(1)–C(2)–C(3)	120·6 (1)	C(9)–C(10)–C(11)	122·6 (1)
C(1)–C(2)–H(2)	121 (1)	C(9)–C(10)–C(16)	119·0 (1)
C(3)–C(2)–H(2)	118 (1)	C(11)–C(10)–C(16)	118·3 (1)
C(2)–C(3)–C(4)	122·5 (1)	C(10)–C(11)–C(12)	121·7 (2)
C(2)–C(3)–C(15)	118·8 (1)	C(10)–C(11)–H(11)	119 (1)
C(4)–C(3)–C(15)	118·7 (1)	C(12)–C(11)–H(11)	119 (1)
C(3)–C(4)–C(5)	121·6 (1)	C(11)–C(12)–C(13)	121·3 (1)
C(3)–C(4)–H(4)	118 (1)	C(11)–C(12)–H(12)	121 (1)
C(5)–C(4)–H(4)	120 (1)	C(13)–C(12)–H(12)	118 (1)
C(4)–C(5)–C(6)	121·2 (1)	C(12)–C(13)–C(14)	122·6 (1)
C(4)–C(5)–H(5)	120 (1)	C(12)–C(13)–C(15)	118·4 (1)
C(6)–C(5)–H(5)	118 (1)	C(14)–C(13)–C(15)	118·9 (1)
C(5)–C(6)–C(7)	122·6 (1)	C(1)–C(14)–C(13)	120·6 (1)
C(5)–C(6)–C(16)	118·8 (1)	C(1)–C(14)–H(14)	121 (1)
C(7)–C(6)–C(16)	118·7 (1)	C(13)–C(14)–H(14)	118 (1)
C(6)–C(7)–C(8)	121·2 (2)	C(3)–C(15)–C(13)	120·1 (1)
C(6)–C(7)–H(7)	117 (1)	C(3)–C(15)–C(16)	119·7 (1)
C(8)–C(7)–H(7)	122 (1)	C(13)–C(15)–C(16)	120·2 (1)
C(7)–C(8)–C(9)	120·5 (2)	C(6)–C(16)–C(10)	119·9 (1)
C(7)–C(8)–H(8)	120 (1)	C(6)–C(16)–C(15)	120·0 (1)
C(9)–C(8)–H(8)	119 (1)	C(10)–C(16)–C(15)	120·1 (1)

molecular structure achieved in the present work is high. By comparison of the neutron structure with the present X-ray work some remarkable features are revealed: (1) the bond distances *b* through *e* are identical in both works, (2) the bond distances *a* and *f* of the X-ray structure are significantly shorter than those of the neutron one, (3) the bond distance *f* of the X-ray structure is much shorter than that of the neutron one. Hazell *et al.* (1972) pointed out that the centres of the charge clouds will be displaced in the direction of the bond of the highest bond order. From this point of view it is understandable that greater shrinkage is observed in bonds *f* and *a* in the X-ray structure, *i.e.* the bond order of *f* is the largest and that of *a* is the second largest.

Deviations of atoms from the least-squares plane through the C atoms are listed in Table 10 together with those of Hazell *et al.* (neutron) and Allmann (X-ray). The pyrene molecule deviates significantly from the planar structure. As mentioned by Allmann and Hazell *et al.* the pyrene molecule is slightly folded about a line passing through C(3) and C(10). The dihedral angle between the best planes of these two naphthalene moieties is 0·9°.

Table 9. *Comparison of the structures of pyrene*

In each row two values are given: The upper number shows the mean bond distance, $\bar{x} = \Sigma x_i/n$, where x_i is the individual bond distance observed, and n is the number of chemically equivalent bond distances; the lower number shows the estimated standard deviation of the mean, $\sigma(\bar{x}) = (s^2/n)^{1/2}$, where s is the variance, $s^2 = \Sigma(x_i - \bar{x})^2/(n-1)$ (in Å).



		X-ray			Neutron	MO	$\Delta(N-X)$*
Bond	*n*	(i)	(ii)	(iii)	(iv)	(v)	
a	4	1·3758	1·3730	1·3865	1·3948	1·396	0·0083
		122	19	8	13		
b	4	1·4163	1·4008	1·4020	1·4055	1·407	0·0035
		29	34	15	47		
c	4	1·4113	1·4170	1·4220	1·4253	1·419	0·0033
		119	30	15	16		
d	4	1·4365	1·4278	1·4363	1·4378	1·437	0·0015
		123	30	6	24		
e	1	1·411	1·422	1·427	1·430	1·427	0·0030
		—	—	—	—		
f	2	1·3150	1·3365	1·3530	1·3670	1·369	0·0140
		0	15	0	20		
σ†		0·014	0·004	0·002	0·002		
		~23	~6	~3	~4		

References: (i) Cammerman & Trotter (1965). (ii) Allmann (1970). (iii) Present work. (iv) Hazell *et al.* (1972). (v) Warren & Yandle (1968).

* Difference between neutron and X-ray (present work) bond distances.

† Estimated standard deviation of individual bond distance observed.

Table 10. *Atomic deviations* (Å ×10³) *from the least-squares plane of pyrene*

	Plane 1			Plane 2	Plane 3
	(i)	(ii)	(iii)		
C(1)	−1	−1	2		6
C(2)	12	14	10		9
C(3)	8	9	3	−1	−4
C(4)	−7	−3	−2	−2	
C(5)	−3	−9	−4	−2	
C(6)	0	1	−4	4	
C(7)	−9	−11	−6	−1	
C(8)	−6	−6	−4	0	
C(9)	3	0	3	−3	
C(10)	7	8	2	−3	−5
C(11)	4	8	4		8
C(12)	−3	−1	1		6
C(13)	−4	−7	−4		−4
C(14)	−20	−26	−20		−15
C(15)	9	11	8	−2	2
C(16)	10	15	10	9	−2
H(1)		25			37
H(2)		21			13
H(4)		−23		−20	
H(5)		−27		−13	
H(7)		−29		−12	
H(8)		−16		−5	
H(9)		60		54	
H(11)		35		38	
H(12)		−5		12	
H(14)		−64		−44	

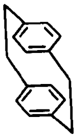
Plane 1: best plane through all C atoms: (i) Allmann (1970). (ii) Present work. (iii) Hazell *et al.* (1972).

Plane 2: best plane through C(3) to C(10), C(15) and C(16).

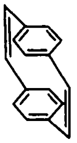
Plane 3: best plane through C(1) to C(3), and C(10) to C(16).

[2.2](2,7)*Pyrenophane*-1,1′-*diene* (II)

A perspective view of the molecule with the atom numbering is shown in Fig. 3 (*ORTEP* II). The analysis of the molecular thermal vibrations in the crystal was undertaken by the method of Cruickshank (1956) with the *RSMV* 4 program of *UNICS* (Ito & Sakurai, 1967). The results are shown in Table 11. The interatomic bond distances and bond angles are listed in Table 12 together with the bond distances corrected for thermal vibration. Differences between the corrected and uncorrected bond distances are within 0·002 Å, which is less than 1·0σ of the observed bond distances. Discussion hereafter will be based on the structure uncorrected for thermal vibration. Selected bond distances and bond angles are shown in Fig. 4. On the assumption of molecular symmetry *mm*2 for the framework of the pyrene moiety in (II), the mean structure is calculated and listed in Table 13 together with the corresponding data for pyrene. Noticeable differences are: (1) bond distance *a* in (II) is significantly (0·010 Å) longer than that in pyrene, (2) bond distances *b* through *f* are exactly the same in both structures, and (3) the standard deviation of the mean, $\sigma(\bar{x})$, of *b* in (II) is relatively large. The elongation of *a* in (II) is attributed to the change of hybrid state of C(3) and C(10) caused by the molecular distortion. The out-of-plane deformations of the C(2)–C(3) and C(10)–C(1′) bonds from the planes defined by C(3), C(4) and C(16), and C(10), C(11) and C(9) are described with the aid of the angle *p* (Fig. 5*b*) (10·5 and 11·1° respectively). The deformation angles are the same as the corresponding angle in [2.2]paracyclophane (III) (11·2°) but are slightly smaller than that in [2.2]paracyclophane-1,9-diene (IV) (15·2°).



(III)



(IV)

The dihedral angles *q* (Fig. 5*b*) [between the planes defined by C(3), C(4) and C(16), and C(4), C(5), C(15) and C(16) and between the planes defined by C(10), C(11) and C(9), and C(8), C(9), C(11) and C(12)] are 6·8 and 7·5°, which are much smaller than the corresponding angles in (III) (12·6°) and its diene derivative (IV) (13·7°). This may be due to the long shallow-boat

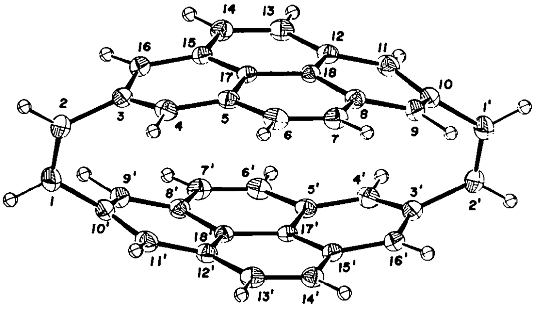


Fig. 3. The molecular structure and atomic numbering scheme of (II). The thermal ellipsoids include 50% probability and H atoms are drawn as spheres of radius 0·1 Å.

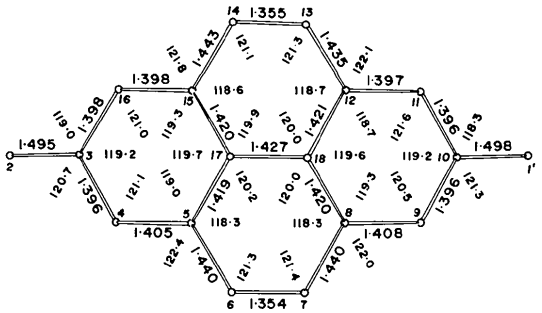


Fig. 4. Selected bond distances (Å) and bond angles (°) of (II) projected on the least-squares plane of C(5), C(8), C(12) and C(15).

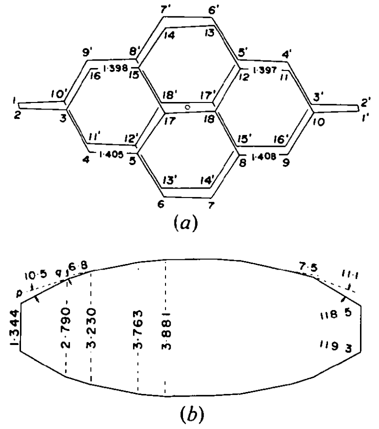


Fig. 5. The molecular projections of (II) (*a*) on the least-squares plane of C(5), C(8), C(12) and C(15) and (*b*) along the vector connecting C(5) and C(15). Selected bond distances (Å), angles (°), non-bonded atomic contacts (Å) and out-of-plane deformations (°) are given.

Table 11. *Analysis of molecular thermal vibration of* [2.2](2,7)*pyrenophane*-1,1′-*diene*

Translational, **T** (Å^2), and rotational, **ω** (deg^2), tensors

$$\mathbf{T}\ (\sigma\mathbf{T}) = \begin{pmatrix} 0{\cdot}018\ (1) & 0{\cdot}000\ (1) & -0{\cdot}001\ (1) \\ & 0{\cdot}016\ (1) & 0{\cdot}000\ (1) \\ & & 0{\cdot}017\ (1) \end{pmatrix}$$

$$\boldsymbol{\omega}\ (\sigma\boldsymbol{\omega}) = \begin{pmatrix} 1{\cdot}5\ (6) & 0{\cdot}3\ (3) & -0{\cdot}3\ (4) \\ & 3{\cdot}6\ (3) & -1{\cdot}2\ (2) \\ & & 2{\cdot}0\ (3) \end{pmatrix}$$

R.m.s. displacements along, and directions of, the principal vibrational axes

		R.m.s. displacements	Direction cosines of principal vibrational axes **p** along inertial axes **l*** l_1	l_2	l_3
T	p_1	0·125 (Å)	0·2036	0·9219	0·3295
	p_2	0·129	−0·5977	0·3836	−0·7040
	p_3	0·137	0·7755	0·0536	−0·6291
ω	p_1	1·10 (°)	0·6051	0·3094	0·7336
	p_2	1·24	−0·7847	0·3876	0·4837
	p_3	2·07	0·1347	0·8683	−0·4774

* The inertial axes **l** are defined by **l** = **ma**, where the elements of **m** are:

$$\mathbf{m} = \begin{pmatrix} 0{\cdot}1047 & -0{\cdot}0248 & 0{\cdot}0541 \\ -0{\cdot}0092 & -0{\cdot}0454 & -0{\cdot}0851 \\ 0{\cdot}0364 & 0{\cdot}0599 & -0{\cdot}0422 \end{pmatrix}$$

and **a** is the column vector composed of the dimensions of three crystal axes *a*, *b* and *c*.

Table 12. *Interatomic bond distances* (Å) *and bond angles* (°) *in* [2.2](2,7)*pyrenophane*-1,1′-*diene*

Standard deviations in parentheses refer to the last significant figures. The columns of bond distances headed by asterisks show the values corrected for thermal vibration.

C(1)–C(2)	1·344 (3)	1·344*	C(9)–C(10)	1·396 (2)	1·397*
C(2)–C(3)	1·495 (3)	1·495	C(10)–C(11)	1·396 (2)	1·397
C(3)–C(4)	1·396 (2)	1·397	C(10)–C(1′)	1·498 (3)	1·498
C(3)–C(16)	1·398 (2)	1·399	C(11)–C(12)	1·397 (2)	1·397
C(4)–C(5)	1·405 (2)	1·405	C(12)–C(13)	1·435 (2)	1·435
C(5)–C(6)	1·440 (2)	1·441	C(12)–C(18)	1·421 (2)	1·422
C(5)–C(17)	1·419 (2)	1·421	C(13)–C(14)	1·355 (2)	1·356
C(6)–C(7)	1·354 (2)	1·355	C(14)–C(15)	1·443 (2)	1·444
C(7)–C(8)	1·440 (2)	1·440	C(15)–C(16)	1·398 (2)	1·399
C(8)–C(9)	1·408 (2)	1·409	C(15)–C(17)	1·420 (2)	1·421
C(8)–C(18)	1·420 (2)	1·421	C(17)–C(18)	1·427 (2)	1·428

C(1)–H(1)	0·99 (2)	C(9)–H(9)	1·12 (2)
C(2)–H(2)	1·00 (3)	C(11)–H(11)	1·03 (3)
C(4)–H(4)	1·01 (2)	C(13)–H(13)	1·01 (3)
C(6)–H(6)	0·98 (2)	C(14)–H(14)	1·01 (2)
C(7)–H(7)	0·97 (2)	C(16)–H(16)	1·04 (2)

C(2)–C(1)–C(10′)	118·5 (2)	C(9)–C(10)–C(11)	119·2 (2)
C(2)–C(1)–H(1)	122 (1)	C(9)–C(10)–C(1′)	121·3 (2)
H(1)–C(1)–C(10′)	120 (1)	C(11)–C(10)–C(1′)	118·3 (2)
C(1)–C(2)–C(3)	119·3 (2)	C(10)–C(11)–C(12)	121·6 (2)
C(1)–C(2)–H(2)	118 (1)	C(10)–C(11)–H(11)	120 (1)
C(3)–C(2)–H(2)	123 (1)	C(12)–C(11)–H(11)	118 (1)
C(2)–C(3)–C(4)	120·7 (2)	C(11)–C(12)–C(13)	122·1 (2)
C(2)–C(3)–C(16)	119·0 (2)	C(11)–C(12)–C(18)	118·7 (2)
C(4)–C(3)–C(16)	119·2 (2)	C(13)–C(12)–C(18)	118·7 (2)
C(3)–C(4)–C(5)	121·1 (2)	C(12)–C(13)–C(14)	121·3 (2)
C(3)–C(4)–H(4)	119 (1)	C(12)–C(13)–H(13)	122 (2)
C(5)–C(4)–H(4)	119 (1)	C(14)–C(13)–H(13)	117 (2)
C(4)–C(5)–C(6)	122·4 (2)	C(13)–C(14)–C(15)	121·1 (2)
C(4)–C(5)–C(17)	119·0 (2)	C(13)–C(14)–H(14)	121 (1)
C(6)–C(5)–C(17)	118·3 (1)	C(15)–C(14)–H(14)	118 (1)
C(5)–C(6)–C(7)	121·3 (2)	C(14)–C(15)–C(16)	121·8 (2)
C(5)–C(6)–H(6)	119 (1)	C(14)–C(15)–C(17)	118·6 (1)
C(7)–C(6)–H(6)	119 (1)	C(16)–C(15)–C(17)	119·3 (1)
C(6)–C(7)–C(8)	121·4 (2)	C(3)–C(16)–C(15)	121·0 (2)
C(6)–C(7)–H(7)	121 (1)	C(3)–C(16)–H(16)	118 (1)
C(8)–C(7)–H(7)	118 (1)	C(15)–C(16)–H(16)	120 (1)
C(7)–C(8)–C(9)	122·0 (2)	C(5)–C(17)–C(15)	119·7 (1)
C(7)–C(8)–C(18)	118·3 (1)	C(5)–C(17)–C(18)	120·2 (1)
C(9)–C(8)–C(18)	119·3 (1)	C(15)–C(17)–C(18)	119·9 (1)
C(8)–C(9)–C(10)	120·5 (2)	C(8)–C(18)–C(12)	119·6 (1)
C(8)–C(9)–H(9)	122 (1)	C(8)–C(18)–C(17)	120·0 (1)
C(10)–C(9)–H(9)	117 (1)	C(12)–C(18)–C(17)	120·0 (1)

Table 13. *Mean molecular structures of pyrene,* (II) *and* (I)

The mean bond distance, $\bar{x}$, and its estimated standard deviation, $\sigma(\bar{x})$, are given in each row (in Å). See Table 9 for the bond-labelling system.

	Pyrene	(II)	(I)
a	1·3865	1·3965	1·390
	8	4	
b	1·4020	1·4020	1·395
	15	27	
c	1·4220	1·4200	1·419
	15	3	
d	1·4363	1·4395	1·434
	6	16	
e	1·427	1·427	1·419
	—	—	
f	1·3530	1·3545	1·344
	0	10	

conformation of pyrene moieties connected by ethylenic bridges, which show little deformation of distance [1·344 (3) Å] and angles [118·5 (2), 119·3 (2)°] from the standard values of 1·337 Å and 120°. The shortest inter-ring distance C(3)···C(10′) is 2·790 (2) Å (Fig. 5*b*), which is equal to those of (I) (2·79 Å), (III) (2·78 Å) and (IV) (2·80 Å). The inter-ring separation between the centres of pyrene moieties [3·903 (2) Å, C(17)···C(18′)] is slightly longer than that in (I) (3·76 Å). These separations are much greater than the corresponding values of (III) (3·09 Å) and (IV) (3·14 Å). The relatively large $\sigma(\bar{x})$ of bond *b* in (II) may be attributed to the essentially different feature of four crystallographically independent but chemically equivalent *b* bonds. They are divided into two types: relatively longer [C(4)–C(5) 1·405 (2) Å and C(8)–C(9) 1·408 (2) Å] and shorter [C(11)–C(12) 1·397 (2) Å and C(15)–C(16) 1·398 (2) Å]. As seen in Fig. 5(*a*), which is the projection of (II) onto the plane defined by C(5), C(8), C(12) and C(15), two pyrene moieties shift each other away from the exactly overlapping position. The torsional angle around the C(1)–C(2) bond is 4·2°. Two shorter *b* bonds correspond to those on

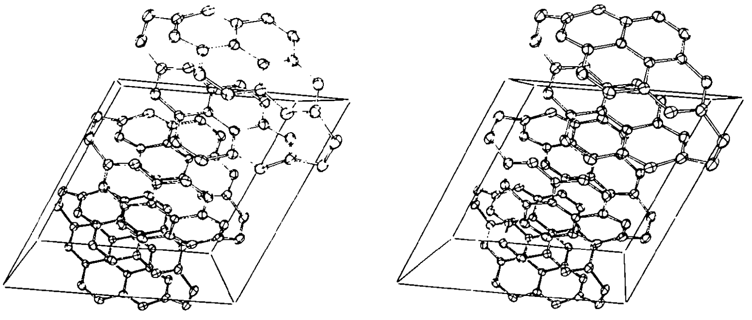


Fig. 6. The crystal structure of (II). The direction of view is close to **b**, **a** is nearly horizontal, **c** is nearly vertical. The parallelepiped outlined has dimensions *a*, *b* and *c*.

which the other pyrene moiety overlaps and two longer ones lie out of the range of its overlapping. The mean structure of (I) (Irngartinger *et al.*, 1977) is also listed in Table 13. A remarkable feature is that in contrast to the present work a short *f* bond is observed.

Crystal structure

The crystal structure of (II) is shown in Fig. 6. No intermolecular atomic contact shorter than the van der Waals distance is found in the crystal.

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References

ALLMANN, R. (1970). *Z. Kristallogr.* **132**, 129–151.

ASHIDA, T. (1973). *The Universal Crystallographic Computing System – Osaka*, pp. 55–61. The Computation Center, Osaka Univ.

CAMERMAN, A. & TROTTER, J. (1965). *Acta Cryst.* **18**, 636-643.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Act Cryst.* A**27**, 368–376.

HAZELL, A. C., LARSEN, F. K. & LEHMANN, M. S. (1972) *Acta Cryst.* B**28**, 2977–2984.

International Tables for X-ray Crystallography (1974). Vol IV. Birmingham: Kynoch Press.

IRNGARTINGER, H., KIRRSTETTER, R. G. H., KRIEGER, C. RODENWALD, H. & STAAB, H. A. (1977). *Tetrahedro Lett.* pp. 1425–1428.

ITO, T. & SAKURAI, T. (1967). *The Universal Crystallographic Computing System* (I), edited by T. SAKURAI Tokyo: The Crystallographic Society of Japan.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138 Oak Ridge National Laboratory, Tennessee.

KAI, Y., YASUOKA, N. & KASAI, N. (1977). *Acta Cryst.* B**33** 754–762.

ROBERTSON, J. M. & WHITE, J. G. (1947). *J. Chem. Soc.* pp 358–368.

SAKURAI, T., IWASAKI, H., WATANABE, Y., KOBAYASHI, K. BANDO, Y. & NAKAMICHI, Y. (1974). *Rep. Inst. Chem Res.* **50**, 75.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst* B**24**, 63–76.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965) *J. Chem. Phys.* **42**, 3175–3187.

UMEMOTO, T., SATANI, S., SAKATA, Y. & MISUMI, S. (1975) *Tetrahedron Lett.* pp. 3159–3162.

WARREN, K. D. & YANDLE, J. R. (1968). *Theor. Chim Acta*, **12**, 279–292.