

Fig. 3. Packing of the molecules viewed down the *a* axis.

= 1.80 Å (Bondi, 1964)]. A similar observation has been made in the structure of 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile (Kamath & Venkatesan, 1984).

On the basis of the results reported on the directional preferences for the approach of electrophiles and nucleophiles to the divalent sulphur atom (Rosenfield, Parthasarathy & Dunitz, 1977) it appears that, in the present structure, O(6) acts as a nucleophile as it approaches the sulphur atom along the LUMO orbital of S. The oxygen atom is 34.8° out of the plane defined by atoms C(15), S(1) and C(3) and the C(15)–S(1)⋯O(6) angle is approximately linear [175.8 (3)°].

The packing of the molecule viewed down the *a* axis is displayed in Fig. 3. There are no intermolecular short contacts of special significance. The illustrations were made with ORTEP II (Johnson, 1976).

We thank the University Grants Commission of India for financial support.

Acta Cryst. (1984). **C40**, 1612–1614

Structure of *exo*-(8*bRS*,8*cSR*,12*aRS*,12*bSR*)-8*b*,8*c*,9,10,12*a*,12*b*-Hexahydrobenzo-cyclobuta[1,2-*e*]pyrene, C₂₂H₁₈

BY MASARU KIMURA, SETSUO KASHINO, SHIRO MOROSAWA AND MASAO HAISA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

(Received 29 March 1984; accepted 18 May 1984)

Abstract. $M_r = 282.38$, monoclinic, $P2_1/a$, $a = 21.698$ (2), $b = 13.240$ (1), $c = 5.1026$ (4) Å, $\beta = 93.802$ (7)°, $V = 1462.7$ (2) Å³, $Z = 4$, $D_m = 1.26$, $D_x = 1.282$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.51$ mm⁻¹, m.p. 404.5–405.5 K, $T = 300$ K, $F(000) = 600$, final $R = 0.050$ for 2044 reflexions above

1.0σ(*F*). The structure of one of the photocycloaddition products of pyrene and 1,3-cyclohexadiene has been determined. The configuration of the H atoms in the cyclobutane ring was confirmed to be *cis-anti*, leading to the conclusion that the title compound was formed by 2πs + 2πs photocycloaddition in solution.

0108-2701/84/091612-03\$01.50

© 1984 International Union of Crystallography

References

- ADHIKESAVALU, D., KAMATH, N. U. & VENKATESAN, K. (1983). *Proc. Indian Acad. Sci. Sect. A*, **92** (4 & 5), 449–456, and references cited therein.
- ALLEN, F. H., TROTTER, J. & ROGERS, D. (1970). *J. Chem. Soc. B*, pp. 166–171.
- ATEN, C. F., HEDBERG, L. & HEDBERG, K. (1968). *J. Am. Chem. Soc.* **90**, 2463–2467.
- AUGUSTIN, M., RICHTER, M. & SALAS, S. (1980). *J. Prakt. Chem.* **332**, 1, S. 55–68.
- BARTELL, L. S., ROTH, E. A., HOLLOWELL, C. D., KUCHITSU, K. & YOUNG, J. E. JR (1965). *J. Chem. Phys.* **42**, 2683–2686.
- BERNSTEIN, J., GREEN, B. S. & REJTÖ, M. (1980). *J. Am. Chem. Soc.* **102**, 323–328.
- BERTOLASI, V., GILLI, G. & VERONESE, A. C. (1982). *Acta Cryst.* **B38**, 502–511.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- BRAIBANTI, A., PELLINGHELLI, M. A., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1973). *Acta Cryst.* **B29**, 43–49.
- BRIANSÖ, J. L., MIRAVITLLES, C., PLANA, F. & FONT-ALTABA, M. (1973). *Cryst. Struct. Commun.* **2**, 551–553.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JANDAL, P., SEIP, H. M. & TORGRIMSEN, T. (1976). *J. Mol. Struct.* **32**, 369–377.
- JEFFREY, G. A., RUBLE, J. R. & POPLE, J. A. (1982). *Acta Cryst.* **B38**, 1975–1980.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KAMATH, N. U. & VENKATESAN, K. (1984). *Acta Cryst.* **C40**, 1211–1214.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- ROSENFELD, R. E. JR, PARTHASARATHY, R. & DUNITZ, J. D. (1977). *J. Am. Chem. Soc.* **99**, 4860–4862.
- SAARINEN, H., KORVENRANTA, J. & NÄSÄRKÄLÄ, E. (1977). *Cryst. Struct. Commun.* **6**, 557–559.
- SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
- TRÆTTEBERG, M. (1968). *Acta Chem. Scand.* **22**, 628–640.

Table 1. Final atomic parameters (positional $\times 10^4$) with e.s.d.'s in parentheses

C(1)	$B_{eq} = \frac{4}{3} \sum \beta_{ii} / a_i^{*2}$			$B_{eq}(\text{\AA}^2)$
	x	y	z	
C(1)	7471.8 (9)	2484 (2)	3383 (4)	4.05 (8)
C(2)	8102 (1)	2623 (2)	4064 (5)	4.54 (9)
C(3)	8286.4 (9)	3276 (2)	6041 (5)	4.40 (8)
C(4)	8040 (1)	4512 (2)	9467 (4)	4.58 (11)
C(5)	7625 (1)	5068 (2)	10674 (4)	4.81 (10)
C(6)	6554 (1)	5661 (2)	11016 (5)	5.14 (10)
C(7)	5944 (1)	5646 (2)	10145 (5)	5.45 (11)
C(8)	5738 (1)	4976 (2)	8184 (5)	4.64 (10)
C(9)	4963 (1)	2394 (2)	4310 (5)	5.22 (13)
C(10)	4956 (1)	1592 (2)	2763 (5)	5.61 (13)
C(11)	5487 (1)	893 (2)	2604 (5)	5.06 (12)
C(12)	5944 (1)	947 (2)	4964 (4)	4.14 (9)
C(13)	7854.0 (9)	3830 (2)	7367 (4)	3.78 (8)
C(14)	6980 (1)	5022 (1)	9871 (4)	4.04 (9)
C(15)	6772.4 (9)	4338 (1)	7882 (4)	3.27 (8)
C(16)	7217.0 (8)	3717 (1)	6624 (4)	3.25 (7)
C(17)	6136.6 (9)	4316 (1)	7050 (4)	3.53 (8)
C(18)	5886.3 (8)	3593 (1)	4976 (4)	3.48 (7)
C(19)	5499.1 (9)	2709 (2)	6102 (4)	3.92 (8)
C(20)	6066.3 (8)	2015 (1)	5926 (4)	3.29 (7)
C(21)	6357.0 (8)	2803 (1)	4096 (4)	3.25 (7)
C(22)	7031.2 (8)	3011 (1)	4659 (4)	3.26 (7)

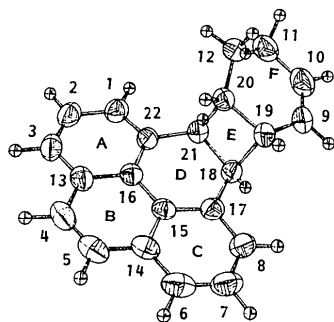
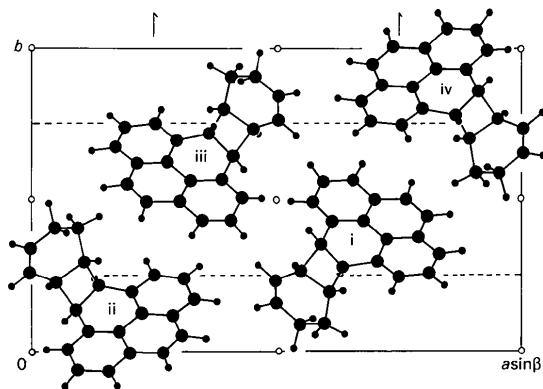
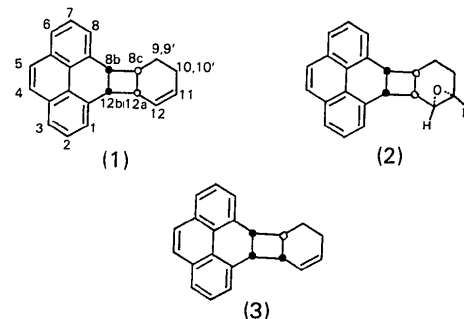

 Fig. 1. View of the molecule with numbering of C atoms and nomenclature of the rings. Ellipsoids of 50% probability are used for the C atoms; the H atoms are represented as spheres equivalent to $B = 1.0 \text{\AA}^2$.

 Fig. 2. Projection of the crystal structure along c (●:C, ○:H). Symmetry code: (i) x, y, z ; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (iii) $1 - x, 1 - y, 2 - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, 2 - z$.

 Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

C(1)–C(2)	1.401 (3)	C(11)–C(12)	1.510 (3)
C(1)–C(22)	1.381 (3)	C(12)–C(20)	1.514 (3)
C(2)–C(3)	1.367 (3)	C(13)–C(16)	1.417 (3)
C(3)–C(13)	1.401 (3)	C(14)–C(15)	1.412 (3)
C(4)–C(5)	1.344 (3)	C(15)–C(16)	1.449 (3)
C(4)–C(13)	1.438 (3)	C(15)–C(17)	1.417 (3)
C(5)–C(14)	1.433 (3)	C(16)–C(22)	1.410 (3)
C(6)–C(7)	1.368 (4)	C(17)–C(18)	1.502 (3)
C(6)–C(14)	1.408 (4)	C(18)–C(19)	1.572 (3)
C(7)–C(8)	1.389 (4)	C(18)–C(21)	1.549 (3)
C(8)–C(17)	1.383 (3)	C(19)–C(20)	1.543 (3)
C(9)–C(10)	1.323 (4)	C(20)–C(21)	1.561 (3)
C(9)–C(19)	1.491 (4)	C(21)–C(22)	1.498 (3)
C(10)–C(11)	1.484 (4)		
C(2)–C(1)–C(22)	120.8 (2)	C(13)–C(16)–C(15)	119.2 (2)
C(1)–C(2)–C(3)	119.9 (2)	C(13)–C(16)–C(22)	119.2 (2)
C(2)–C(3)–C(13)	121.0 (2)	C(15)–C(16)–C(22)	121.6 (2)
C(5)–C(4)–C(13)	121.5 (2)	C(8)–C(17)–C(15)	119.0 (2)
C(4)–C(5)–C(14)	121.1 (2)	C(8)–C(17)–C(18)	119.4 (2)
C(7)–C(6)–C(14)	120.3 (3)	C(15)–C(17)–C(18)	121.6 (2)
C(6)–C(7)–C(8)	120.1 (3)	C(17)–C(18)–C(19)	113.2 (2)
C(7)–C(8)–C(17)	121.7 (2)	C(17)–C(18)–C(21)	114.8 (2)
C(10)–C(9)–C(19)	124.6 (3)	C(19)–C(18)–C(21)	89.0 (2)
C(9)–C(10)–C(11)	123.7 (3)	C(9)–C(19)–C(18)	113.5 (2)
C(10)–C(11)–C(12)	113.5 (2)	C(9)–C(19)–C(20)	113.0 (2)
C(11)–C(12)–C(20)	113.2 (2)	C(18)–C(19)–C(20)	88.5 (2)
C(3)–C(13)–C(4)	121.7 (2)	C(12)–C(20)–C(19)	116.8 (2)
C(3)–C(13)–C(16)	119.2 (2)	C(12)–C(20)–C(21)	120.0 (2)
C(4)–C(13)–C(16)	119.1 (2)	C(19)–C(20)–C(21)	89.6 (2)
C(5)–C(14)–C(6)	120.7 (2)	C(18)–C(21)–C(20)	88.7 (2)
C(5)–C(14)–C(15)	119.5 (2)	C(18)–C(21)–C(22)	118.3 (2)
C(6)–C(14)–C(15)	119.8 (2)	C(20)–C(21)–C(22)	115.9 (2)
C(14)–C(15)–C(16)	119.5 (2)	C(1)–C(22)–C(16)	119.7 (2)
C(14)–C(15)–C(17)	119.1 (2)	C(1)–C(22)–C(21)	121.0 (2)
C(16)–C(15)–C(17)	121.3 (2)	C(16)–C(22)–C(21)	119.2 (2)

Introduction. As part of a study of novel photocycloaddition between pyrene and cyclohexadiene (Kimura, Nukada, Satake, Morosawa & Tamagake, 1984), the X-ray structure analysis of the title compound (1) has been undertaken; the ^1H NMR spectrum of (1) was too complicated to be analyzed and ^1H NMR coupling constants for the corresponding epoxidized compound (2) could not differentiate the $2\pi s + 2\pi s$ structure (1) from the $2\pi s + 2\pi a$ structure (3).



Experimental. Compound (1) prepared by the irradiation of pyrene and 1,3-cyclohexadiene in benzene with a 450 W high-pressure Hg lamp at room temperature (Kimura *et al.*, 1984). Colorless prisms (slow evaporation from ethanol) elongated along c . D_m by flotation in aqueous KI. Crystal $0.15 \times 0.15 \times$

Table 3. Torsion angles (°) around the bonds in the cyclobutane ring

C(17)–C(18)–C(19)–C(9)	144.3 (2)	C(19)–C(18)–C(21)–C(22)	–134.3 (2)	C(19)–C(20)–C(21)–C(18)	15.6 (1)
C(17)–C(18)–C(19)–C(20)	–101.2 (2)	C(9)–C(19)–C(20)–C(12)	–24.2 (3)	C(19)–C(20)–C(21)–C(22)	136.8 (2)
C(21)–C(18)–C(19)–C(9)	–99.0 (2)	C(9)–C(19)–C(20)–C(21)	99.6 (2)	H(18)–C(18)–C(21)–H(21)	–21 (2)
C(21)–C(18)–C(19)–C(20)	15.5 (1)	C(18)–C(19)–C(20)–C(12)	–139.2 (2)	H(18)–C(18)–C(19)–H(19)	–106 (2)
C(17)–C(18)–C(21)–C(20)	99.9 (2)	C(18)–C(19)–C(20)–C(21)	–15.4 (1)	H(21)–C(21)–C(20)–H(20)	149 (2)
C(17)–C(18)–C(21)–C(22)	–19.1 (3)	C(12)–C(20)–C(21)–C(18)	136.7 (2)	H(19)–C(19)–C(20)–H(20)	–23 (2)
C(19)–C(18)–C(21)–C(20)	–15.3 (1)	C(12)–C(20)–C(21)–C(22)	–102.1 (2)		

0.40 mm. Rigaku AFC-5 four-circle diffractometer. Lattice parameters determined from 20 reflexions by least-squares method. Intensities measured up to $2\theta = 120^\circ$, ω - 2θ scan method [scan speed 4° min^{-1} in 2θ ; scan range (2θ): $1.2^\circ + 0.15^\circ \tan\theta$], Ni-filtered Cu K α , 40 kV, 200 mA, background measured for 4 s on either side of the peak. Three reference reflexions showed no intensity deterioration. Lorentz and polarization corrections; no absorption correction. 2179 unique data, 2044 (ranging over $h = -24$ to 24, $k = 0$ to 14, $l = 0$ to 5) with $|F_o| > 1.0\sigma(F)$ used in refinement. Structure solved by *MULTAN78*, and refined (C atoms anisotropic) by block-diagonal least squares; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1.0$ for $0 < |F_o| \leq 15.0$ and $(15.0/|F_o|)^2$ for $|F_o| > 15.0$. H-atom positions determined from a difference Fourier map, and refined (isotropically) by least squares. $R = 0.050$, $R_w = 0.061$, $S = 0.529$, $(\Delta/\sigma)_{\text{max}}$ in final refinement cycle for C and H atoms 0.3 and 1.2 respectively, max. and min. $\Delta\rho$ in final difference Fourier map $\pm 0.17 \text{ e } \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center. Programs *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *HBLVS* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1965).

Discussion. The final atomic parameters are listed in Table 1.* The thermal ellipsoids with atomic numbering are shown in Fig. 1. Bond lengths and angles are given in Table 2. The torsion angles around the bonds in the cyclobutane ring are given in Table 3. A projection of the crystal structure viewed along *c* is shown in Fig. 2.

The molecule has the *transoid* configuration (Fig. 1, Table 3). This leads to the conclusion that (1) is formed by $2\pi s + 2\pi s$ photocycloaddition. The cyclobutane ring takes a skewed conformation with C–C–C–C torsion angles of $15.3(1)$ – $15.6(1)^\circ$ in the ring. The C–C bond lengths [$1.572(3)$ and $1.561(3) \text{ Å}$] at the ring junction are comparable to those found in some

* Lists of structure factors, anisotropic thermal parameters, coordinates of the H atoms and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39499 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

photodimers containing the cyclobutane ring (Karle, 1982*a,b*).

The phenanthrene ring in the molecule is planar within $0.109(2) \text{ Å}$, the largest deviations being found at C(22) [$-0.109(2) \text{ Å}$] and at C(3) [$0.104(2) \text{ Å}$]. Inspection of the bond lengths and angles shows that the ring has a pseudo mirror plane bisecting the C(4)–C(5) and C(15)–C(16) bonds perpendicular to the ring plane. The shortest bond in the ring is C(4)–C(5), $1.344(3) \text{ Å}$, which is shorter than the 1.372 Å of the corresponding bond in phenanthrene (Trotter, 1963), but longer than the 1.320 Å in pyrene (Camerman & Trotter, 1965).

The six-membered rings *D* and *F* take the half-chair conformation: C(15), C(16), C(17), C(18) and C(22) in ring *D*, and C(9), C(10), C(11), C(19) and C(20) in ring *F* form planes within $0.023(3)$ and $0.014(3) \text{ Å}$, respectively. C(21) and C(12) are displaced by $0.126(3)$ and $0.507(3) \text{ Å}$ respectively from each plane.

The molecules are hexagonally packed *via* van der Waals interactions to form a sheet parallel to (001). The sheets are stacked along *c* to complete the structure. A short contact of $2.62(2) \text{ Å}$ is observed between H(6) and C(2^{iv}).

The authors thank the staff of the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the facility.

References

- ASHIDA, T. (1973). *HBLVS. The Universal Crystallographic Computing System—Osaka*. The Computation Center, Osaka Univ., Japan.
- CAMERMAN, A. & TROTTER, J. (1965). *Acta Cryst.* **18**, 636–643.
- FUJII, S. (1979). *MOLCON. The Universal Crystallographic Computing System—Osaka*. The Computation Center, Osaka Univ., Japan.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KARLE, I. L. (1982*a*). *Acta Cryst.* **B38**, 1016–1018.
- KARLE, I. L. (1982*b*). *Acta Cryst.* **B38**, 1019–1022.
- KIMURA, M., NUKADA, K., SATAKE, K., MOROSAWA, S. & TAMAGAKE, K. (1984). *J. Chem. Soc. Perkin Trans.* 1. In the press.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- TROTTER, J. (1963). *Acta Cryst.* **16**, 605–608.