

Structure of Pentacyclo[8.6.3.0.0^{2,9}.3^{2,9}]docosane-17,20-dione

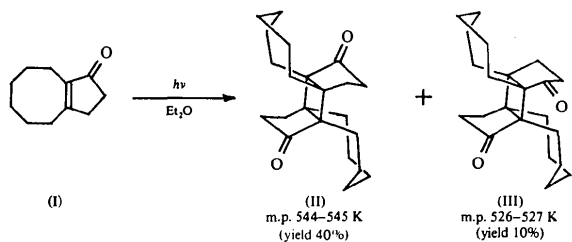
BY HIDEAKI MATSUURA, SHIGERU KOSHIBE, YASUSHI KAI, NORITAKE YASUOKA AND NOBUTAMI KASAI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

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Abstract. C₂₂H₃₂O₂, FW 328.5, monoclinic, space group $P2_1/c$, $a = 9.591(1)$, $b = 7.148(1)$, $c = 13.007(1)$ Å, $\beta = 97.08(1)^\circ$, $V = 883.1(1)$ Å³, $Z = 2$, $D_m = 1.229$, $D_x = 1.235$ Mg m⁻³, $R = 0.041$ for 1286 non-zero reflexions. The molecule is centrosymmetric and has an *anti-head-to-tail* configuration.

Introduction. The molecular structure of the high-melting-point isomer (II) of the photocyclodimers of bicyclo[6.3.0]undec-1(8)-en-9-one (Tobe, Kimura & Odaira, 1978) has been determined by means of X-ray diffraction.



For the data collection, a crystal $0.28 \times 0.25 \times 0.20$ mm was coated with collodion to prevent sublimation. A Rigaku automated four-circle diffractometer was used for the measurement of lattice parameters and intensities with Ni-filtered Cu $K\alpha$ radiation. Intensity data were collected by the θ - 2θ scan method at a 2θ rate of 2° min^{-1} . Backgrounds were counted for 10 s before and after the scan of each peak. 1317 independent data ($2\theta < 120^\circ$), 1286 of which were observed, were corrected for the Lp factor but not for absorption [$\mu(\text{Cu } K\alpha) = 0.6 \text{ mm}^{-1}$]. The crystal data showed that the dimeric molecule is located at the center of symmetry. The structure was solved by the direct method with *MULTAN 74* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Among trials with different sets of parameters to run the program, one set gave a fragment of plausible molecular structure. These atoms were then taken into account to recalculate E values with a spherically averaged molecular scattering factor. This feature of *MULTAN 74* seems to have played a decisive role in the phase-determining procedure (Lessinger, 1976). An E map with the highest figure of merit revealed the entire molecular structure, and H atoms were found by difference syntheses. The

refinement was carried out by block-diagonal least squares (*HBL5-V*; Ashida, 1973) with anisotropic temperature factors for heavy atoms and isotropic for H. The final R value was 0.041 for non-zero ($R = 0.042$ and $R_w = 0.035$ for all) reflexions. The weighting scheme used was $w = [\sigma(F_o)^2 + a|F_o| + b|F_o|^2]^{-1}$ and $w = c$ for observed and unobserved reflexions, respectively, where $a = -0.024$, $b = 0.045$ and $c = 7.587$. Atomic scattering factors for C and O atoms were taken from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson &

Table 1. Final atomic coordinates ($\times 10^4$, for H $\times 10^3$) and, for H, isotropic thermal parameters, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	
O	1222 (1)	3200 (1)	3543 (1)	
C(1)	974 (1)	-887 (1)	5168 (1)	
C(2)	1728 (1)	-1573 (1)	6222 (1)	
C(3)	3328 (1)	-1441 (1)	6496 (1)	
C(4)	3959 (1)	495 (1)	6727 (1)	
C(5)	3900 (1)	1812 (1)	5800 (1)	
C(6)	2797 (1)	3350 (1)	5757 (1)	
C(7)	1273 (1)	2730 (1)	5766 (1)	
C(8)	691 (1)	1254 (1)	4967 (1)	
C(9)	1153 (1)	1648 (1)	3914 (1)	
C(10)	1498 (1)	-150 (1)	3401 (1)	
C(11)	1690 (1)	-1623 (1)	4245 (1)	
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(2A)	133 (1)	-93 (2)	677 (1)	2.9 (3)
H(2B)	146 (1)	-294 (2)	628 (1)	3.3 (3)
H(3A)	381 (1)	-207 (2)	595 (1)	3.8 (3)
H(3B)	355 (1)	-216 (2)	714 (1)	4.9 (3)
H(4A)	350 (1)	112 (2)	732 (1)	5.3 (3)
H(4B)	493 (1)	32 (2)	700 (1)	5.5 (3)
H(5A)	481 (1)	239 (2)	582 (1)	4.3 (3)
H(5B)	374 (1)	107 (2)	515 (1)	4.5 (3)
H(6A)	308 (1)	417 (2)	637 (1)	4.3 (3)
H(6B)	285 (1)	412 (2)	513 (1)	3.9 (3)
H(7A)	67 (1)	389 (2)	564 (1)	3.3 (3)
H(7B)	114 (1)	224 (2)	646 (1)	2.5 (2)
H(10A)	233 (1)	7 (2)	310 (1)	4.0 (3)
H(10B)	66 (1)	-46 (2)	287 (1)	4.7 (3)
H(11A)	270 (1)	-182 (2)	450 (1)	3.8 (3)
H(11B)	137 (1)	-289 (2)	399 (1)	3.4 (3)

Simpson (1965). The final atomic parameters are listed in Table 1.*

Discussion. An *ORTEP* (Johnson, 1976) drawing of the molecular structure is given in Fig. 1. Bond lengths and angles are shown in Fig. 2. The most remarkable feature of the structure is that the molecule is centrosymmetric and has a planar cyclobutane ring. The cyclobutane bonds joining the halves [C(1)–C(8')] are 1.604 (2) Å, and the other two cyclobutane bonds [C(1)–C(8)] are 1.570 (2) Å. Two independent cyclobutane angles are equal [C(8)–C(1)–C(8') = 89.7 (1) and C(1)–C(8)–C(1') = 90.3 (1)°]. Similarly, the 9,10-benzotricyclo[3.3.2.0^{3,7}]deca-3(7),9(10)-diene dimer (Greenhouse, Borden, Hirotzu & Clardy, 1977) is also a centrosymmetric molecule and has a planar cyclobutane ring, in which the bonds formed by the dimerization [1.589 (3) Å] are shorter than the corresponding bonds in (II). Photoaddition products of bicyclo[4.3.0]non-1(6)-en-7-one with cyclohexane [(IV), Harada, Kai, Yasuoka & Kasai, 1976] and cyclooctadiene [(V), Koshibe, Kai, Yasuoka & Kasai, 1977] have puckered cyclobutane rings, in which the bonds joining the two added ring systems [(IV), 1.571 (2) and 1.552 (2) Å; (V), 1.581 (3) and 1.550 (3) Å] are also shorter than the cyclobutane bonds joining the halves in the present complex. Short non-bonded intermolecular atomic contacts are found

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34152 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

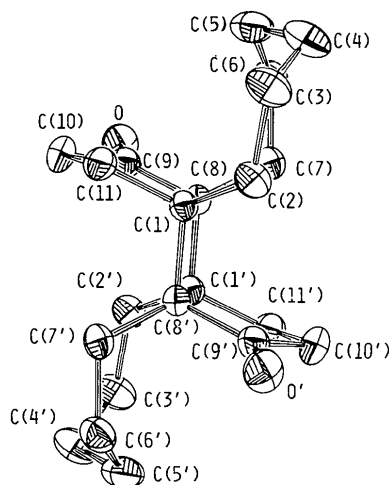


Fig. 1. An *ORTEP* drawing of the molecule.

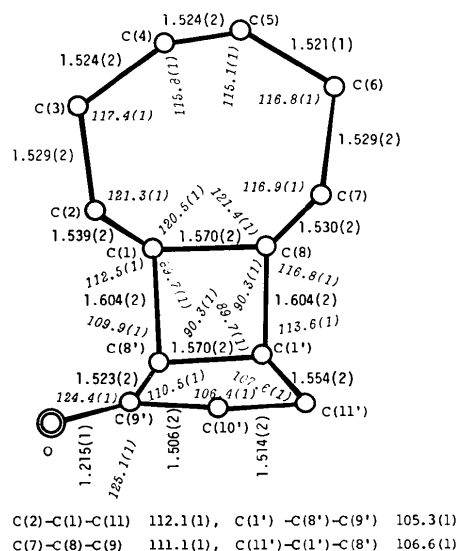


Fig. 2. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

between asymmetric units: C(2)···C(9') = 2.744 (2), C(7)···C(11') = 2.947 (2), H(2A)···H(10B') = 2.27 (2) and H(7A)···H(11B') = 2.20 (2) Å.

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