

## Structure of 1,9:4,10-Diethanotriptycene

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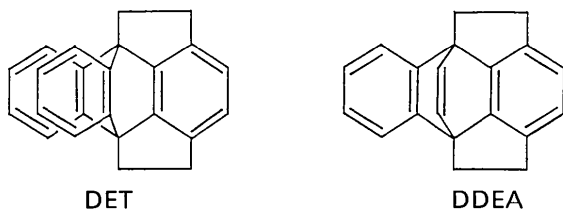
**Abstract.**  $C_{24}H_{18}$ ,  $M_r = 306.41$ , monoclinic,  $P2_1/n$ ,  $a = 14.460$  (1),  $b = 11.725$  (1),  $c = 9.334$  (2) Å,  $\beta = 98.97$  (2)°,  $V = 1563.2$  (4) Å<sup>3</sup> at 293 K,  $Z = 4$ ,  $D_m = 1.30$ ,  $D_x = 1.30$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.079$  mm<sup>-1</sup>,  $F(000) = 648$ , final  $R = 0.061$  for 3295 observed reflections. Two ethano bridges make the geometry of the triptycene skeleton unsymmetrical. All the bond lengths are quite normal, except for those of the two bridging ethano groups: C—C lengths are 1.581 (3) and 1.583 (3) Å. Unusual bond angles around the bridgehead suggest that there exists much strain in this molecule.

**Introduction.** In the course of our study on bridged anthracene derivatives, the title compound (DET) has been newly obtained by flash pyrolysis of 5-nitro-2,2,11,11-tetraoxo-2,11-dithia[2.2]paracyclo-(9,10)anthracenophane (procedure of the synthesis will be reported separately). This hydrocarbon molecule possesses a triptycene skeleton with two additional ethano bridges, and its stereochemical configuration has only ever been merely estimated with a molecular mechanical calculation (Fukazawa, Kikuchi, Kajita & Ito, 1984). In our previous report on an essentially similar bridge-type molecule, 9,10-dihydro-1,9:4,10-diethano-9,10-ethenoanthracene (DDEA), we found that the ethano bridges give

much strain in the ring system (Matsuzawa, Kozawa, Uchida, Tsuchiya & Mori, 1989). This paper concerns the X-ray structural analysis of DET to confirm its molecular structure, and to compare its geometry with that of DDEA.

**Experimental.** A colourless prism obtained from an *n*-hexane/benzene solution, 0.4 × 0.4 × 0.4 mm, mounted on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation. Lattice constants were determined by least-squares procedure with setting angles of 25 reflections with  $25.45 < 2\theta < 29.05^\circ$ . Intensities were measured by  $\theta$ - $2\theta$  scan method with scan width ( $\theta$ )  $(1.0 + 0.5 \tan \theta)^\circ$ , scan speed  $(\theta)$   $4^\circ \text{ min}^{-1}$ , back-grounds for 1.0 s at both ends of every scan. Three standard reflections (462,  $\bar{4}6\bar{2}$  and 553) monitored every 100 measurements, changed  $-1.2\%$ – $+1.2\%$  of  $F$ 's throughout the data collection. 4934 reflections measured up to  $2\theta < 60^\circ$ , index range  $0 \leq h \leq 20$ ,  $0 \leq k \leq 16$ ,  $-12 \leq l \leq 12$ ,  $R_{\text{int}} = 0.026$ . All reflections  $0k0$ ,  $k$  odd, and  $h0l$ ,  $h + l$  odd, were too weak to be observed as required by space group  $P2_1/n$ . Of the 4770 independent reflections, 3295 with  $|F_o| \geq 3\sigma(F)$  were used for further calculations. Lorentz and polarization factors were corrected as usual, but absorption correction was not applied. Density was determined by flotation method with aqueous  $K_2HgI_4$  solution.

Structure was solved by *MULTAN84* (Main, Germain & Woolfson, 1984). All the non-H atoms were found on the Fourier map, and after several cycles of the block-diagonal least-squares refinements, the H atoms were located on a difference Fourier map. Final refinement with anisotropic thermal factors for non-H atoms and fixed isotropic thermal factors for H atoms,  $B_{\text{iso}} = 4.0$  Å<sup>2</sup>. Final  $R = 0.061$  and  $wR = 0.037$ ,  $S = 0.79$ , function minimized  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma^2(F)$ ,  $(\Delta/\sigma)_{\text{max}} = 0.56$ , max. and min. heights in final difference Fourier syntheses 0.15,



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Table 1. Fractional atomic coordinates and equivalent isotropic thermal factors with e.s.d.'s for non-H atoms

$$B_{eq} = (4/3) \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )
C(1)	1.0200 (1)	-0.0009 (2)	0.2289 (2)	3.46 (5)
C(2)	0.9673 (1)	-0.0743 (2)	0.3048 (2)	4.19 (6)
C(3)	0.8940 (1)	-0.0318 (2)	0.3735 (2)	4.08 (6)
C(4)	0.8714 (1)	0.0846 (2)	0.3680 (2)	3.46 (5)
C(5)	0.9225 (1)	0.1504 (1)	0.2885 (2)	3.06 (5)
C(6)	0.9177 (1)	0.2768 (1)	0.3030 (2)	2.98 (5)
C(7)	0.9183 (1)	0.3249 (1)	0.1497 (2)	2.98 (5)
C(8)	0.8560 (1)	0.4032 (2)	0.0798 (2)	3.57 (6)
C(9)	0.8653 (1)	0.4412 (2)	-0.0591 (2)	4.37 (6)
C(10)	0.9371 (1)	0.3996 (2)	-0.1260 (2)	4.59 (7)
C(11)	1.0004 (1)	0.3202 (2)	-0.0572 (2)	3.85 (6)
C(12)	0.9918 (1)	0.2816 (1)	0.0807 (2)	3.07 (5)
C(13)	1.0565 (1)	0.1971 (1)	0.1738 (2)	3.07 (5)
C(14)	0.9931 (1)	0.1100 (1)	0.2234 (2)	3.13 (5)
C(15)	1.0163 (1)	0.3066 (1)	0.3832 (2)	2.98 (5)
C(16)	1.0366 (1)	0.3657 (2)	0.5116 (2)	3.81 (6)
C(17)	1.1295 (1)	0.3855 (2)	0.5724 (2)	4.70 (7)
C(18)	1.2015 (1)	0.3472 (2)	0.5040 (2)	4.63 (7)
C(19)	1.1820 (1)	0.2871 (2)	0.3738 (2)	3.73 (6)
C(20)	1.0906 (1)	0.2655 (1)	0.3140 (2)	2.98 (5)
C(21)	0.8131 (1)	0.1662 (2)	0.4448 (2)	4.32 (6)
C(22)	0.8304 (1)	0.2883 (2)	0.3815 (2)	4.12 (6)
C(23)	1.1262 (1)	0.1175 (2)	0.1083 (2)	4.11 (6)
C(24)	1.1101 (1)	-0.0075 (2)	0.1631 (2)	4.51 (7)

$-0.22 \text{ e } \text{Å}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). The calculations were performed by a PANAFACOM U-1200 II computer with the Rigaku RASA-5P program package and on the HITAC M-680H at the Computer Centre of the University of Tokyo with the *UNICS* (1967) program system.

**Discussion.** The final atomic parameters with their e.s.d.'s are listed in Table 1, and the bond lengths and angles are given in Table 2. Fig. 1 shows an *ORTEP* drawing (Johnson, 1976) with the atom numbering.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52393 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)–C(2)	1.411 (3)	C(2)–C(3)	1.412 (3)
C(3)–C(4)	1.402 (3)	C(4)–C(5)	1.365 (3)
C(5)–C(6)	1.491 (2)	C(6)–C(7)	1.539 (2)
C(7)–C(8)	1.377 (2)	C(8)–C(9)	1.397 (3)
C(9)–C(10)	1.381 (3)	C(10)–C(11)	1.391 (3)
C(11)–C(12)	1.388 (3)	C(12)–C(13)	1.536 (2)
C(13)–C(14)	1.493 (2)	C(14)–C(1)	1.356 (2)
C(5)–C(14)	1.352 (2)	C(7)–C(12)	1.420 (2)
C(6)–C(15)	1.544 (2)	C(15)–C(16)	1.376 (3)
C(16)–C(17)	1.394 (3)	C(17)–C(18)	1.379 (3)
C(18)–C(19)	1.395 (3)	C(19)–C(20)	1.376 (3)
C(20)–C(13)	1.548 (2)	C(15)–C(20)	1.421 (2)
C(4)–C(21)	1.526 (3)	C(21)–C(22)	1.583 (3)
C(6)–C(22)	1.561 (3)	C(13)–C(23)	1.566 (3)
C(23)–C(24)	1.581 (3)	C(1)–C(24)	1.526 (3)

C(2)–C(1)–C(14)	115.5 (2)	C(2)–C(1)–C(24)	137.1 (2)
C(14)–C(1)–C(24)	106.9 (2)	C(1)–C(2)–C(3)	121.0 (2)
C(2)–C(3)–C(4)	120.9 (2)	C(3)–C(4)–C(5)	115.3 (2)
C(3)–C(4)–C(21)	137.4 (2)	C(5)–C(4)–C(21)	106.7 (2)
C(4)–C(5)–C(6)	118.4 (2)	C(4)–C(5)–C(14)	123.8 (2)
C(6)–C(5)–C(14)	116.0 (2)	C(5)–C(6)–C(7)	105.8 (1)
C(5)–C(6)–C(15)	102.5 (1)	C(5)–C(6)–C(22)	100.4 (1)
C(7)–C(6)–C(15)	103.3 (1)	C(7)–C(6)–C(22)	121.8 (2)
C(15)–C(6)–C(22)	120.4 (2)	C(6)–C(7)–C(8)	125.9 (2)
C(6)–C(7)–C(12)	113.8 (1)	C(8)–C(7)–C(12)	120.3 (2)
C(7)–C(8)–C(9)	120.1 (2)	C(8)–C(9)–C(10)	119.7 (2)
C(9)–C(10)–C(11)	121.0 (2)	C(10)–C(11)–C(12)	119.9 (2)
C(7)–C(12)–C(11)	119.1 (2)	C(7)–C(12)–C(13)	114.0 (1)
C(11)–C(12)–C(13)	126.9 (2)	C(12)–C(13)–C(14)	105.5 (1)
C(14)–C(13)–C(20)	102.8 (1)	C(12)–C(13)–C(20)	103.3 (1)
C(14)–C(13)–C(23)	122.4 (2)	C(14)–C(13)–C(23)	100.2 (1)
C(20)–C(13)–C(23)	119.9 (2)	C(1)–C(14)–C(5)	123.4 (2)
C(1)–C(14)–C(13)	118.8 (2)	C(5)–C(14)–C(13)	116.3 (2)
C(6)–C(15)–C(16)	126.3 (2)	C(6)–C(15)–C(20)	114.2 (1)
C(16)–C(15)–C(20)	119.5 (2)	C(15)–C(16)–C(17)	120.0 (2)
C(16)–C(17)–C(18)	120.4 (2)	C(17)–C(18)–C(19)	120.2 (2)
C(18)–C(19)–C(20)	119.8 (2)	C(13)–C(20)–C(15)	113.3 (1)
C(13)–C(20)–C(19)	126.7 (2)	C(15)–C(20)–C(19)	120.0 (2)
C(4)–C(21)–C(22)	105.1 (2)	C(21)–C(22)–C(6)	106.5 (2)
C(13)–C(23)–C(24)	106.9 (2)	C(1)–C(24)–C(23)	105.1 (2)

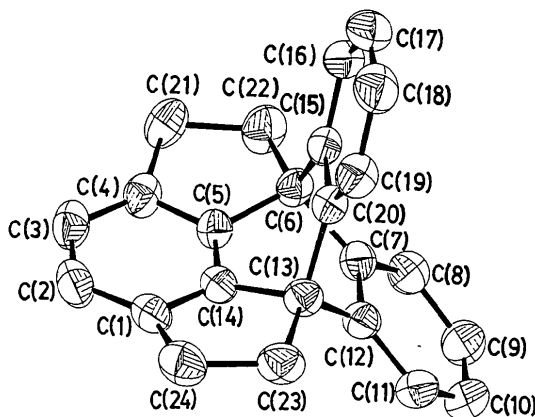
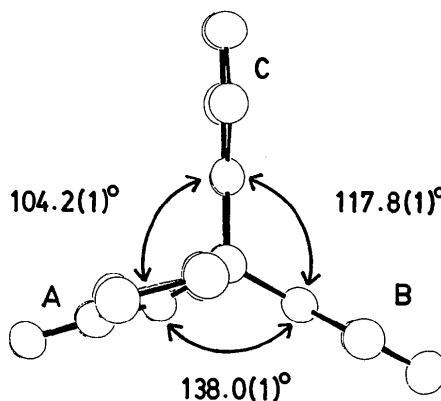
Fig. 1. *ORTEP* view of the molecule with the atom numbering. H atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Fig. 2. Side view of the molecule projected along the C(6)–C(13) direction. The ethano-bridged benzene is named plane A, and the others are plane B and plane C, respectively.

The DET molecule consists of a triptycene skeleton and two additional ethano bridges, each of which links a triptycene bridgehead atom, C(6) or C(13), and a common benzene ring forming a five-membered ring. Consequently, the central bicyclo[2.2.2]octatriene system deviates from  $D_{3h}$  symmetry. Fig. 2 illustrates clearly the unsymmetrical geometry of the molecule. The ethano-bridged benzene ring (plane *A*) is tilted to plane *C* [C(15), C(16), C(17), C(18), C(19), C(20)] with a dihedral angle of  $104.2(1)^\circ$ . Both C(22) and C(23) atoms shift to plane *A*, resulting in the two five-membered rings having envelope forms [torsion angles: C(1)—C(24)—C(23)—C(13)  $11.7(2)$ , C(4)—C(21)—C(22)—C(6)  $14.9(2)^\circ$ ]. The ethano bridges affect the bond lengths of the related moiety of the molecule. Namely, distances C(4)—C(5), C(5)—C(6), C(1)—C(14), and C(13)—C(14) [1.365 (2), 1.491 (2), 1.356 (2) and 1.493 (2) Å, respectively] are significantly shorter than the corresponding bond lengths of the other moieties in the same molecule. The bond lengths of the ethano group itself [C(21)—C(22) and C(23)—C(24), 1.583 (3) and 1.581 (3) Å, respectively] are slightly longer than the normal C—C single bond. Similar geometries are found in 9-methoxy-1,10:6,7-diethanotriptycene (Fukazawa, Kikuchi, Kajita & Ito, 1984) and DDEA (Matsuzawa, Kozawa, Uchida, Tsuchiya & Mori, 1989), but not in 1,4,9,10-tetramethyltriptycene that has no 'ethano bridge' (Imashiro, Hirayama, Takegoshi, Terao, Saika & Taira, 1988). The 'ethano-bridge effect' is more distinct around the bridgehead bond angles. Of the six bond angles around C(6), C(5)—C(6)—C(22) of  $100.4(1)^\circ$  is much smaller, and C(7)—C(6)—C(22) of  $121.8(2)^\circ$  and C(15)—C(6)—C(22) of  $120.4(2)^\circ$  are

much larger than those of non-'ethano-bridged' triptycene, while the values of the other three angles are almost the same as those of triptycene within e.s.d.'s (Anzenhofer & Bore, 1970). The same geometry is also found around C(13). The length of C(7)—C(12), 1.420 (2) Å or C(15)—C(20), 1.421 (2) Å of DET has a slightly higher value than that of the ethano-bridged DDEA [1.302 (7) Å] because the former is part of a benzene ring and the latter is a non-conjugated double bond. So, the strain of the bicyclo[2.2.2]octatriene system is slightly relaxed in DET compared with DDEA. All the bond lengths and angles related to the benzene moieties are within the range of normal values, and they are planar within e.s.d.'s.

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## Structure of a 2-Substituted Cyclopropane Amino Acid Derivative: 1-Hydroxymethyl-5-phenyl-7-oxa-4-azaspiro[2.5]octan-8-one

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**Abstract.**  $C_{13}H_{15}NO_3$ ,  $M_r = 233.27$ , monoclinic,  $P2_1$ ,  $a = 7.783(4)$ ,  $b = 6.379(4)$ ,  $c = 11.743(5)$  Å,  $\beta = 97.37(2)^\circ$ ,  $V = 578.20$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.34$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 6.94$  cm<sup>-1</sup>,  $F(000) = 248$ , final  $R = 0.0528$  for 1129 observed reflections. The

title compound's six-membered ring adopts a half-chair conformation in which the amino H atom occupies an axial configuration. The stereochemistry of the cyclopropane moiety is deduced as (1*S*,2*R*). Strong intermolecular hydrogen bonds exist between