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)°. 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)°]. 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)° is much smaller, and C(7)—C(6)—C(22) of 121·8 (2)° and C(15)—C(6)—C(22) of 120·4 (2)° 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)°, $V = 578·20$ Å^3, $Z = 2$, $D_x = 1·34$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6·94$ cm^{-1}, $F(000) = 248$, 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 (1S,2R). Strong intermolecular hydrogen bonds exist between

$$C_{13}H_{15}NO_3$$

the H atom of a hydroxy group and the ketone O atoms of the neighbouring molecule.

Introduction. A general approach has been reported for the asymmetric synthesis of cyclopropane-containing amino acids bearing substituents on the 2-position, starting from a chiral synthon derived from (R)-phenylglycinol (Aitken, Royer & Husson, 1988). A working model was invoked to predict the absolute stereochemistry of these compounds, but experimental verification was not obtained. The title compound is obtained as a by-product of the synthetic scheme and contains both the target 2-hydroxymethylcyclopropane amino acid nucleus and the (R)-phenylglycinol-derived chiral template. The crystal structure of this compound was determined in order to establish the absolute stereochemistry at the cyclopropane amino acid chiral centres.

Experimental. Crystal of approximate dimensions $0.05 \times 0.3 \times 0.5$ mm cut from one of the slender needles formed by slow crystallization from ethyl acetate and hexane. Data collected on a Philips PW 1100 diffractometer using graphite monochromated Cu $K\alpha$ radiation and the θ–2θ scan technique up to $\theta = 68°$. Unit cell from setting angles of 24 accurately selected reflections $(6 \le \theta \le 43°)$. From the 2069 itensities measured $(-9 \le h \le 9, -7 \le k \le 7, l\ 0 \rightarrow 13)$, 1151 unique reflections $(R_{int} = 0.070)$ of which 1129 considered as observed having $I \ge 3\sigma(I)$, $\sigma(I)$ from counting statistics. Three standard reflections monitored every two hours showed no decay in intensity. Lorentz–polarization corrections, absorption ignored. The structure was solved by direct methods using the program DEVIN (Riche, 1982) and refined anisotropically by full-matrix least squares minimizing the function $\sum w(|F_o| - |F_c|)^2$. All the H atoms were located on successive difference Fourier maps and refined with an isotropic temperature factor equivalent to that of the bonded atom. Convergence was reached at $R = 0.0528$ and $wR = 0.0562$ where $w = 1/\sigma^2(F_o)$. $|\Delta/\sigma|_{max} = 0.7$. No residue higher than 0.15 e Å^{-3} in the final difference map. Calculations performed with the program SHELX76 (Sheldrick, 1976). Atomic scattering factors from International Tables for X-ray Crystallography (1974).

Discussion. Atomic coordinates are listed in Table 1.* Selected bond lengths, bond angles and torsion

* 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 52383 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates ($\times 10^4$ for non-H atoms, $\times 10^3$ for H atoms) and equivalent isotropic thermal factors U_{eq} ($\text{Å}^2 \times 10^3$) with standard deviations in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	7165 (4)	4640 (6)	6391 (3)	29 (2)
C(2)	8624 (4)	3233 (6)	6127 (3)	33 (2)
C(3)	9035 (4)	5046 (7)	6913 (3)	38 (2)
C(4)	8701 (5)	1020 (7)	6577 (3)	42 (3)
O(5)	10344 (4)	100 (6)	6646 (3)	66 (3)
N(6)	6007 (3)	3841 (6)	7163 (2)	35 (2)
C(7)	5044 (4)	5606 (6)	7568 (3)	33 (2)
C(8)	3950 (5)	6604 (7)	6563 (3)	44 (3)
O(9)	4947 (3)	7087 (6)	5618 (2)	44 (2)
C(10)	6442 (4)	6138 (6)	5496 (3)	33 (2)
O(11)	7122 (3)	6625	4661 (2)	44 (2)
C(12)	3903 (4)	4960 (7)	8461 (3)	35 (2)
C(13)	3141 (5)	3020 (7)	8453 (3)	45 (3)
C(14)	2079 (5)	2490 (8)	9282 (4)	53 (3)
C(15)	1782 (5)	3917 (9)	10114 (3)	56 (4)
C(16)	2541 (6)	5875 (9)	10125 (3)	58 (4)
C(17)	3596 (5)	6393 (7)	9301 (3)	48 (3)
H(2)	877 (4)	340 (6)	537 (3)	
H(3A)	923 (5)	482 (7)	770 (3)	
H(3B)	956 (5)	610 (7)	670 (3)	
H(4A)	850 (5)	65 (7)	747 (3)	
H(4B)	782 (5)	-3 (7)	620 (3)	
H(5)	1127 (6)	75 (9)	617 (4)	
H(6)	526 (5)	304 (7)	675 (3)	
H(7)	592 (4)	666 (7)	792 (3)	
H(8A)	350 (5)	793 (7)	675 (3)	
H(8B)	296 (5)	554 (7)	624 (3)	
H(13)	349 (5)	205 (7)	794 (3)	
H(14)	145 (5)	104 (8)	927 (3)	
H(15)	97 (5)	371 (8)	1073 (3)	
H(16)	232 (6)	700 (8)	1066 (4)	
H(17)	409 (5)	780 (7)	928 (3)	

angles are reported in Table 2. A perspective view of the molecule with atomic numbering is shown in Fig. 1.*

The absolute configuration is deduced from the known (R) stereochemistry of the chiral centre C(7), which originated from (R)-phenylglycinol (Aitken, Royer & Husson, 1988). This study thus establishes unambiguously the absolute stereochemistry of the cyclopropane amino acid moiety as (1S,2R).

The six-membered ring adopts a half-chair conformation in which atoms C(7) and N(6) are displaced from the plane defined by the other four atoms by -0.43 and 0.31 Å respectively. The N(6)—C(7)—C(12)—C(13) torsion angle of $-32.1°$ indicates that the pseudo-equatorial aromatic ring is conveniently orientated in a conformation which avoids eclipsing of C(7) and C(12) substituents. The bond angles at C(10) add up to 360°, testifying to the planarity of the carbonyl function.

The unusual width of the N(6)—C(1)—C(10) bond angle of 117.5° has been observed in other cyclopropane amino acid derivatives (Elrod, Holt, Mapelli & Stammer, 1988; Pirrung, 1987; Varughese, Srinivasan

* Note that the numbering system adopted in the discussion and for presentation of crystallographic results emphasizes that the compound is a cyclopropane amino acid derivative, rather than following the IUPAC system which is used only to name the compound in the title.

Table 2. *Bond lengths* (Å), *selected bond angles* (°) *and torsion angles* (°) *with standard deviations in parentheses*

C(1)—C(2)	1·510 (5)	C(15)—C(16)	1·381 (8)
C(1)—C(3)	1·527 (5)	C(16)—C(17)	1·387 (6)
C(1)—N(6)	1·451 (4)	C(2)—H(2)	0·92 (4)
C(1)—C(10)	1·478 (5)	C(3)—H(3A)	0·93 (4)
C(2)—C(3)	1·489 (6)	C(3)—H(3B)	0·84 (4)
C(2)—C(4)	1·506 (6)	C(4)—H(4A)	1·10 (4)
C(4)—O(5)	1·400 (5)	C(4)—H(4B)	1·01 (4)
N(6)—C(7)	1·465 (5)	O(5)—H(5)	1·05 (5)
C(7)—C(8)	1·505 (5)	N(6)—H(6)	0·87 (4)
C(7)—C(12)	1·515 (4)	C(7)—H(7)	1·01 (4)
C(8)—O(9)	1·467 (4)	C(8)—H(8A)	0·96 (4)
O(9)—C(10)	1·336 (4)	C(8)—H(8B)	1·06 (4)
C(10)—O(11)	1·212 (4)	C(13)—H(13)	0·93 (4)
C(12)—C(13)	1·372 (6)	C(14)—H(14)	1·04 (5)
C(12)—C(17)	1·388 (5)	C(15)—H(15)	1·03 (4)
C(13)—C(14)	1·397 (5)	C(16)—H(16)	0·98 (5)
C(14)—C(15)	1·376 (6)	C(17)—H(17)	0·98 (5)

C(2)—C(1)—C(3)	58·7 (2)	C(1)—C(10)—O(9)	118·3 (3)
C(2)—C(1)—N(6)	117·6 (3)	C(1)—C(10)—O(11)	125·1 (3)
C(2)—C(1)—C(10)	117·8 (3)	O(9)—C(10)—O(11)	116·6 (3)
C(3)—C(1)—N(6)	116·4 (3)	C(7)—C(12)—C(13)	122·1 (3)
C(3)—C(1)—C(10)	115·6 (3)	C(7)—C(12)—C(17)	118·8 (3)
N(6)—C(1)—C(10)	117·5 (3)	C(13)—C(12)—C(17)	119·0 (3)
C(1)—C(2)—C(3)	61·2 (2)	C(12)—C(13)—C(14)	120·5 (4)
C(1)—C(2)—C(4)	118·8 (3)	C(13)—C(14)—C(15)	120·2 (4)
C(1)—C(3)—C(2)	60·1 (2)	C(14)—C(15)—C(16)	119·7 (4)
C(2)—C(4)—O(5)	114·1 (3)	C(15)—C(16)—C(17)	119·9 (4)
C(3)—C(2)—C(4)	121·0 (3)	C(12)—C(17)—C(16)	120·7 (4)
C(1)—N(6)—C(7)	108·5 (3)	C(4)—O(5)—H(5)	119 (3)
N(6)—C(7)—C(8)	109·4 (3)	C(1)—N(6)—H(6)	107 (3)
N(6)—C(7)—C(12)	112·7 (3)	C(7)—N(6)—H(6)	108 (3)
C(8)—C(7)—C(12)	109·5 (3)		
C(7)—C(8)—O(9)	112·4 (3)		
C(8)—O(9)—C(10)	122·6 (3)		

C(10)—C(1)—N(6)—C(7)	−46·7 (3)	N(6)—C(1)—C(2)—C(3)	−105·7 (3)
C(1)—N(6)—C(7)—C(8)	62·7 (3)	N(6)—C(1)—C(2)—C(4)	6·0 (3)
N(6)—C(7)—C(8)—O(9)	−50·6 (3)	C(10)—C(1)—C(2)—C(4)	−143·8 (4)
C(7)—C(8)—O(9)—C(10)	21·2 (3)	C(10)—C(1)—C(3)—C(2)	−108·3 (4)
C(8)—O(9)—C(10)—C(1)	−3·9 (3)	C(8)—C(7)—C(12)—C(13)	−90·0 (4)
O(9)—C(10)—C(1)—N(6)	17·1 (3)	N(6)—C(7)—C(12)—C(13)	−32·1 (3)
C(10)—C(1)—C(2)—C(3)	104·6 (4)	C(8)—C(7)—C(12)—C(17)	−89·0 (3)
C(1)—C(2)—C(4)—O(5)	−86·9 (4)		

Fig. 1. Perspective view of the molecule with the atomic numbering.
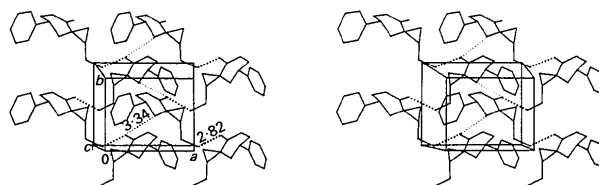
Fig. 2. Stereo-packing of the molecules viewed down the *c* axis.

& Stammer, 1985) and is related to the narrowing of the C(3)—C(1)—C(2) bond angle to 58·7°. The amino acid moiety's χ_1 torsion angle C(4)—C(2)—C(1)—N(6) is twisted by 6·0° from the theoretical value (0°) for a Z-disubstituted cyclopropane.

Unexpectedly, the sp^3 hybridized N atom N(6) bears hydrogen H(6) in an axial position [N(6)—H(6) = 0·87 (4) Å], with the latter directed towards atom O(11) of the second molecule of the cell. However, the interatomic distances N(6)···O(11) and H(6)···O(11) of 3·344 (5) and 2·50 (5) Å respectively and the angle N(6)—H(6)···O(11) of 165° suggest only a weak hydrogen bond. The axial configuration of H(6) is more easily explained by intramolecular steric interactions. Two MNDO calculations (Stewart, 1983) were performed starting from the crystal coordinates. The equatorial configuration is preferred by 5·4 kJ mol⁻¹ if all the atoms are allowed to move, while the axial configuration is more stable by 2·1 kJ mol⁻¹ when only the H atoms are varied.

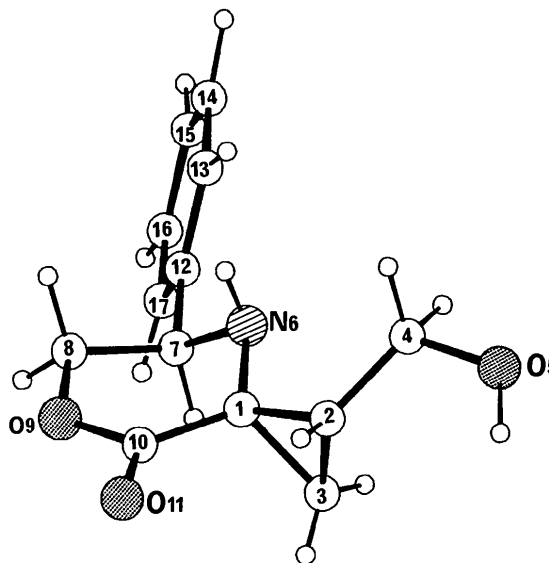The molecules are linked together in the crystal as shown in Fig. 2, by virtue of a strong hydrogen bond

between the hydroxyl group atom H(5) of one molecule and atom O(11) of the nearest molecule in the next cell [distances O(5)—H(5) = 1·05 (5), O(5)···O(11) = 2·823 (5), H(5)···O(11) = 1·77 (5) Å, bond angle O(5)—H(5)···O(11) = 175°].

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