The packing diagram of the tripeptide is shown in Fig. 2. The parameters of the hydrogen bonds that stabilize the structure are given in Table 3. As expected, the terminal amino N atom is involved in three N—H···O hydrogen bonds as a donor. None of the peptide N atoms is involved in a hydrogen bond. One of the peptide carbonyl O atoms is not involved in any hydrogen bond whereas the other accepts two. One of the terminal carboxylate O atoms accepts two hydrogen bonds whereas the other accepts one. Both water molecules in the structure accept one proton and donate two.

An interesting feature of the structure is an internal water bridge which connects the terminal amino group and the carbonyl group of the second residue. Such internal bridges involving one water molecule have been observed before in short peptides (*e.g.* Nair, Nagaraj, Ramaprasad, Balaram & Vijayan, 1981; Aubry, Vitoux, Boussard & Marraud, 1981; Toniolo *et al.*, 1987) but two-membered water bridges connecting adjacent residues, like that in the present structure, are less usual.

The original objective of the present investigation was to see if stereochemically constrained folded peptides like those containing Aib residues form head-to-tail sequences. The tripeptide in the present crystal structure does so even in the presence of disturbing influences such as those of water molecules. The structure contains a zigzag head-to-tail sequence centred around a 2_1 screw axis. This sequence is stabilized by the N1—H···O19 hydrogen bond and its symmetry equivalents. The sequence, which runs parallel to the *b* axis, and its translational equivalents are stacked together along the *a* and the *c* axes to form the crystal.

Financial support from SERC, Department of Science and Technology, is acknowledged.

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(1*R**,4*S**,10*S**)-2,2,10-Tribromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene

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(*Received* 30 *September* 1985; *accepted* 1 *April* 1987)

Abstract. $C_{12}H_{11}Br_3$, $M_r = 394{\cdot}9$, monoclinic, $P2_1/c$, $a = 7{\cdot}334\ (6)$, $b = 15{\cdot}305\ (26)$, $c = 11{\cdot}612\ (16)$ Å, $\beta = 73{\cdot}58\ (6)°$, $V = 1250{\cdot}25$ Å^3, $Z = 4$, $D_m = 2{\cdot}065$, $D_x = 2{\cdot}098$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 9{\cdot}45$ mm^{-1}, $F(000) = 752$, $T = 293$ K, $R = 0{\cdot}047$ for 816 unique reflections. The dibromocyclohexane frag-

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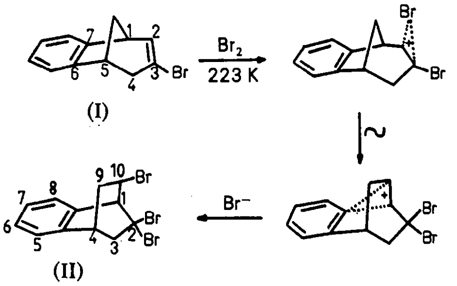
ment of the molecule has a boat conformation. The bridge gives slightly distorted boat conformations with the two parts of dibromocyclohexane. Br(2) and Br(3) are arranged *anti* with respect to the ring. The distortions of the boat conformations are due to the repulsive interaction of Br atoms.

Introduction. The addition of bromine to 3-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene (I) may lead to a multiplicity of products. Attack on the double bond may be *syn* or *anti* to the aromatic ring. In order to investigate the effect of the bromine substituent on the reaction we studied the addition of Br to (I) (see scheme).



The reaction was carried out at 223 K. ^{1}H NMR spectral studies revealed that a single product was formed, but it could not be identified with confidence. The reaction also raises interesting questions concerning the steric and electronic effects controlling the mode of addition of Br to (I) (Kitahonoki, Takono, Matsuura & Kotera, 1969). An X-ray structural determination was therefore carried out, which has established the formation of (II) as the product. The formation mechanism is depicted in the scheme.

An interesting feature of this reaction is the exclusive formation of the rearranged product (II). Therefore, Br must attack the double bond from the *exo* face. Attack from the *endo* face would not give the rearranged product (II).

Experimental. The sample slowly crystallized from *n*-hexane. Density measured by flotation in $ZnCl_2$ solution. Data collected by a Hilger & Watts Y290 four-circle automatic diffractometer, graphite-monochromated Mo $K\bar{\alpha}$, with a spherical single crystal (diameter *ca* 0·45 mm) mounted in a glass capillary.

Unit-cell dimensions obtained from Weissenberg photographs, refined by least-squares fit to 12 reflections ($5 < \theta < 20°$). Systematic absences $h0l$: l odd and $0k0$: k odd. Intensities measured for $-8 \leq h \leq 8$, $0 \leq k \leq 10$, $0 \leq l \leq 10$ ($2{\cdot}5 < \theta < 25°$) using ω–2θ scan technique. One standard reflection monitored every 20 reflections showed 9·6% decrease during data collection: data rescaled to correct for this. Total of 1721 reflections measured, 869 of them rejected under $I < 3\sigma(I)$ level, 852 unique reflections corrected for Lorentz, polarization and absorption effects, the last with a program written by Richards (1984). Heavy atoms were located by Patterson synthesis and light atoms then found on successive Fourier syntheses. Anisotropic temperature factors for all non-H atoms. H atoms given fixed isotropic temperature factors, $U = 0{\cdot}05$ Å^2. H atoms were not found in the difference map, and their positions were calculated assuming bond lengths to be 1·08 Å and not refined. Structure refined by full-matrix least squares using F's. The largest positive and negative peaks on a final difference Fourier synthesis were of height 2·02 and −2·64 e Å^{-3}, with all the large residuals close to Br atoms. wR minimized with unit weights, since analysis showed statistical weights not to be satisfactory. 36 poorly agreeing reflections were omitted. Final $R = 0{\cdot}047$. Maximum shift/e.s.d. in final cycle 0·303. The standard deviations of the molecular parameters are rather large, probably because of the limited amount of data.

All crystallographic calculations were performed with *SHELX76* (Sheldrick, 1976), running on an ICL2980 computer. Atomic scattering factors taken from Cromer & Mann (1968). The numbering system and the conformation of the molecule as shown in Fig. 1. Fractional atomic coordinates with standard deviations and the equivalent isotropic temperature factors of non-H atoms are given in Table 1.*

Discussion. Bond lengths and angles with their standard deviations are given in Table 2. The bicyclo[2.2.2]-octane group is fused to the phenyl ring at atoms C(1) and C(6). By inspection of the torsion angles from Table 3 it may be concluded that the dibromo-cyclohexane fragment of the bicyclic group has a boat conformation. A bridge is constructed by linking C(8)

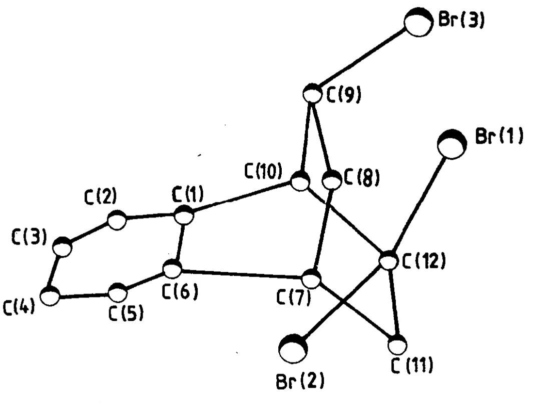


Fig. 1. View of the molecule, showing atom numbering.

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* 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 43934 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* ($\times 10^2$ Å^2)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}
Br(1)	2565 (3)	−0042 (1)	3031 (2)	9·6
Br(2)	3290 (3)	1362 (1)	1024 (2)	9·3
Br(3)	6790 (3)	−1001 (1)	3145 (2)	8·5
C(1)	7551 (18)	1308 (9)	1091 (13)	4·1
C(2)	8562 (21)	1412 (12)	−0070 (14)	6·5
C(3)	9635 (22)	2134 (15)	−0418 (13)	7·8
C(4)	9652 (21)	2775 (12)	0420 (16)	6·9
C(5)	8649 (22)	2676 (12)	1581 (14)	6·5
C(6)	7586 (18)	1908 (10)	1959 (14)	5·0
C(7)	6433 (18)	1718 (10)	3209 (12)	5·2
C(8)	7112 (20)	0835 (11)	3581 (12)	6·2
C(9)	7358 (19)	0187 (10)	2579 (12)	5·7
C(10)	6377 (19)	0537 (10)	1660 (12)	5·3
C(11)	4417 (18)	1603 (11)	3184 (13)	6·7
C(12)	4360 (17)	0875 (11)	2255 (13)	6·2

Table 2. *Interatomic distances* (Å) *and angles* (°) *of non-hydrogen atoms*

C(1)—C(2)	1·35 (2)	C(8)—C(9)	1·50 (2)
C(2)—C(3)	1·35 (2)	C(9)—C(10)	1·54 (2)
C(3)—C(4)	1·39 (2)	C(10)—C(1)	1·50 (2)
C(4)—C(5)	1·35 (2)	C(10)—C(12)	1·54 (2)
C(5)—C(6)	1·41 (2)	C(12)—C(11)	1·56 (2)
C(6)—C(1)	1·37 (2)	C(12)—Br(1)	1·96 (1)
C(6)—C(7)	1·49 (2)	C(12)—Br(2)	1·96 (1)
C(7)—C(8)	1·54 (2)	C(9)—Br(3)	1·94 (2)
C(7)—C(11)	1·50 (2)		

C(1)—C(2)—C(3)	120·2 (15)	C(10)—C(9)—Br(3)	117·6 (11)
C(2)—C(3)—C(4)	119·3 (14)	C(9)—C(10)—C(12)	112·6 (11)
C(3)—C(4)—C(5)	120·9 (17)	C(9)—C(10)—C(1)	104·8 (11)
C(4)—C(5)—C(6)	120·1 (16)	C(12)—C(10)—C(1)	107·0 (11)
C(5)—C(6)—C(1)	117·0 (14)	C(10)—C(12)—C(11)	110·0 (10)
C(5)—C(6)—C(7)	125·3 (15)	C(10)—C(12)—Br(1)	113·7 (11)
C(1)—C(6)—C(7)	117·6 (13)	C(10)—C(12)—Br(2)	109·5 (9)
C(6)—C(1)—C(2)	122·4 (14)	C(11)—C(12)—Br(1)	109·9 (9)
C(6)—C(7)—C(8)	107·7 (11)	C(11)—C(12)—Br(2)	109·1 (11)
C(6)—C(7)—C(11)	107·2 (11)	Br(1)—C(12)—Br(2)	104·6 (6)
C(8)—C(7)—C(11)	107·5 (12)	C(10)—C(1)—C(2)	128·0 (14)
C(7)—C(8)—C(9)	109·8 (11)	C(10)—C(1)—C(6)	109·3 (13)
C(8)—C(9)—C(10)	109·3 (12)	C(12)—C(11)—C(7)	108·5 (11)
C(8)—C(9)—Br(3)	112·9 (10)		

Table 3. *Torsion angles* (°)

Dibromocyclohexane		Distorted boat rings	
C(6)—C(1)—C(10)—C(12)	60·9	C(1)—C(10)—C(9)—C(8)	68·5
C(1)—C(10)—C(12)—C(11)	−57·6	C(10)—C(9)—C(8)—C(7)	−14·4
C(10)—C(12)—C(11)—C(7)	1·3	C(9)—C(8)—C(7)—C(6)	−44·3
C(12)—C(11)—C(7)—C(6)	55·4	C(8)—C(7)—C(6)—C(1)	58·0
C(11)—C(7)—C(6)—C(1)	−55·2	C(6)—C(1)—C(10)—C(9)	−58·9
C(7)—C(6)—C(1)—C(10)	3·4	C(11)—C(12)—C(10)—C(9)	57·2
		C(12)—C(10)—C(9)—C(8)	−47·6
Br atoms		C(9)—C(8)—C(7)—C(11)	−71·0
C(7)—C(11)—C(12)—Br(1)	124·6	C(8)—C(7)—C(11)—C(12)	59·9
C(7)—C(11)—C(12)—Br(2)	−121·3		
C(7)—C(8)—C(9)—Br(3)	147·3		

and C(9) to C(7) and C(10) respectively.The bridge forms two six-membered rings with the C(1), C(6) and C(11), C(12) atoms, which have a slightly distorted boat conformation (torsion angles in Table 3). The distortion is due to the interaction between the two Br atoms mentioned below. The angles about the bridgehead atom C(7) are equal, but those at the other bridgehead, C(10), have C(9)—C(10)—C(12) larger than the other angles because of the repulsion between Br(1) and Br(3).

From the Br(1)—Br(3) (3·47 Å) and Br(2)—Br(3) (5·41 Å) distances, and the torsional angles involving the Br atoms, it appears that Br(2) and Br(3) are arranged *anti* with respect to the ring plane. The C—Br distances are equal within the margin of experimental error. The C(12) atom has an approximate tetrahedral environment, but the Br(1)—C(12)—Br(2) angle is less than tetrahedral in spite of the bulk of the Br atoms. This distortion can be attributed to a higher *p*-orbital contribution to the two orbitals directed towards the Br atoms. A similiar phenomenon is observed in 2,2-dibromo-3,4-dihydro-1(2*H*)-naphthalenone (Haddad, 1986). On the other hand, the Br(1)—C(12)—C(10) angle is larger than the tetrahedral angle. This appears to be a result of a repulsion interaction between Br(1) and Br(3). The C(10)—C(9)—Br(3) angle is also larger than the other angles about C(9), probably owing to the same interaction.

C—C bond lengths are in the expected range. The sum of the angles about C(1) is 359·7°, the sum of the angles about C(6) is 359·9° and the C(7)—C(6)—C(1)—C(10) torsion angle is 3·4°. This indicates that the C(10) and C(7) atoms are in the plane of the phenyl ring. The H—Br distance, C(5)—H(4)···Br(1) ($-x$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$), is 2·94 Å, indicating a hydrogen bond.

The authors thank the Scientific and Technical Research Council of Turkey and the British Council for financial support, Dr J. Richards for measuring the intensities and M. Anderson for assistance in computing.

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