Table 3. *Bond angles* (°) *involving the non*-H *atoms with e.s.d.'s in parentheses*

C(2)—C(1)—C(8)	106·0 (10)	C(2)—C(1)—C(7)	110·1 (10)
C(8)—C(1)—C(7)	100·3 (9)	Br(1)—C(2)—C(1)	112·2 (8)
Br(1)—C(2)—C(3)	109·6 (8)	C(1)—C(2)—C(3)	113·4 (9)
C(2)—C(3)—C(4)	115·9 (9)	C(2)—C(3)—O(1)	123·4 (10)
C(4)—C(3)—O(1)	120·7 (10)	Br(2)—C(4)—C(3)	105·8 (7)
Br(2)—C(4)—C(5)	111·8 (8)	C(3)—C(4)—C(5)	113·3 (9)
C(4)—C(5)—C(8)	110·4 (11)	C(4)—C(5)—C(6)	106·9 (10)
C(8)—C(5)—C(6)	102·7 (10)	C(1)—C(8)—C(5)	101·0 (9)
C(1)—C(7)—C(6)	110·5 (10)	C(1)—C(7)—C(12)	129·2 (10)
C(6)—C(7)—C(12)	120·3 (11)	C(5)—C(6)—C(7)	107·5 (10)
C(5)—C(6)—C(9)	131·7 (11)	C(7)—C(6)—C(9)	120·8 (11)
C(6)—C(9)—C(10)	119·1 (11)	C(9)—C(10)—C(11)	122·7 (12)
C(10)—C(11)—C(12)	118·6 (13)	C(7)—C(12)—C(11)	118·5 (11)

value of 1·384 (18) Å, a little shorter than 1·395 Å, the characteristic bond length in an aromatic molecule. All of the other C—C single-bond lengths of the molecule range from 1·493 (18) to 1·536 (18) Å. C—Br bond lengths, 1·944 (13) and 1·975 (14) Å, agree with those observed in $C_{12}H_{11}Br_3$ (Ergin, Harmandar & Balcı, 1987; Büyükgüngör, Harmandar & Balcı, 1989). The length of the C=O double bond is 1·194 (14) Å, a little shorter than 1·23 Å, the characteristic double-bond length in cyclohexanone (*CRC Handbook of Chemistry and Physics*, 1979–1980). The three atoms attached to the C(3) atom lie in a plane with bond angles of 115·9 (9), 123·4 (10) and 120·7 (10)° (total 360·0°).

The molecule mainly consists of two non-planar carbon rings fused to the benzene ring at the C(6) and C(7) atoms and also sharing the two atoms C(1) and C(5). The C(1)—C(2)···C(5) plane makes angles of 101·5 and 99·9° with the C(1)—C(5)—C(6)—C(7) and benzene ring planes, respectively. This indicates that C(1) and C(5) lie nearly in the plane of the benzene ring.

In the refinement, the coordinates of the two H atoms of C(8) could not be found from the difference Fourier maps. This is probably due to the close proximity of the two Br atoms. For this reason, the positions of these H atoms were calculated geometrically and held fixed.

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Structure of 9,10,10-Tribromotricyclo[6.3.1.0^{2,7}]dodeca-2(7),3,5-triene

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Abstract. $C_{12}H_{11}Br_3$, $M_r = 394·97$, monoclinic, $C1c1$, $a = 10·086\ (3)$, $b = 12·302\ (4)$, $c = 10·165\ (2)$ Å, $\beta = 102·36\ (2)°$, $V = 1232\ (1)$ Å^3, $Z = 4$, $D_x = 2·13$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 96·96$ cm^{-1}, $F(000) = 752$, $T = 295$ K, $R = 0·032$ for 1117 observed reflections. The compound studied has a benzene ring fused to a bicyclo[3.2.1]octane ring. The three Br atoms, one being in an *exo* position, are bonded to the seven-membered ring at two C atoms.

Introduction. In connection with our studies on bicyclic allenes and alkynes (Balcı & Harmandar, 1984) we were interested in the synthesis of (1). Therefore, we studied the bromination of 10-bromotricyclo[6.3.1.0^{2,7}]dodeca-2(7),3,5,9-tetraene (2). The bromination reaction was carried out at 273 and 223 K. Surprisingly, we obtained a completely different product distribution. From the reaction at 223 K we isolated as the sole product the rearranged tribromide

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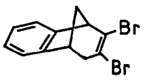
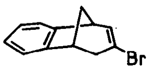
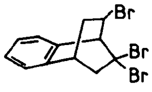
(3) (Balcı, Çakmak & Harmandar, 1985). However, the reaction mixture at 273 K was very complex (Harmandar & Balcı, 1985). The compound (4) was formed in a yield of 23% besides other products. The crystal structure of this title compound was determined as part of these investigations.



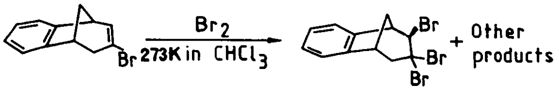
(1)



(2)



(3)



(2) (4)

Experimental. Pale-yellow bipyramidal crystals, 0·5 × 0·3 × 0·3 mm, Syntex *R*3 diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from setting angles of 18 reflections, $9 < 2\theta < 19°$, intensity data measured by ω-scan technique, variable scan speed: max. 12, min. 2° $\min^{-1}$, scan range from 0·9° below $K\alpha_1$ to 0·9° above $K\alpha_2$, background/scan ratio 0·5; 3628 reflections measured, $4·5 \leq 2\theta \leq 58°$, *hkl* range 0, 0, −13 to 14, 16, 13, 1117 reflections considered observed, $I \geq 3\sigma(I)$; two check reflections at intervals of 100, variation ±2·8%; intensities corrected for Lp and for absorption effects by empirical method of *SHELXTL* (Sheldrick, 1983) using 385 ψ-scan data for 11 reflections (merging *R* value before correction $R_{\rm int} = 0·063$, after correction $R_{\rm int} = 0·024$, max. transmission 0·071, min. transmission 0·039). Structure solved by Patterson methods. Positions of Br atoms from Patterson map, other non-H atoms from Fourier map, all H atoms except the four H atoms of the two CH_2 groups from difference Fourier map. Refinement based on $|F|$ values carried out with block-cascade algorithm, non-H atoms anisotropically, H atoms isotropically refined. The positions of the four H atoms of the two CH_2 groups were calculated geometrically and their interatomic distances were constrained to be 1·018 Å with a max. standard deviation of 0·07 Å. Final $R = 0·032$, $wR = 0·032$ with weighting scheme $w^{-1} = \sigma^2(F) + 0·0005F^2$, $S = 1·18$, normal-probability-slope value 1·036, max. final shift-to-e.s.d. ratio 0·35, mean 0·009; max. and min. heights in final difference Fourier map 0·56 and −0·47 e Å^{-3}, all calculations performed with *SHELXTL* (Sheldrick, 1983) on a Nova 3 computer, scattering factors taken from *International Tables for X-ray Crystallography* (1974).

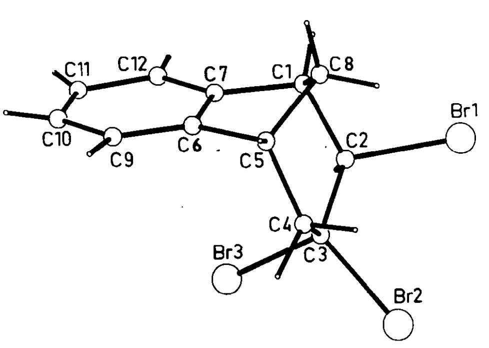


Fig. 1. Perspective view of the molecule with the labelling of the atoms.

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2×10^3) *of the non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm eq}$*
Br(1)	12709 (2)	12211 (1)	8872 (2)	65 (1)
Br(2)	12873 (1)	10352 (1)	11252 (1)	69 (1)
Br(3)	10000	9505 (1)	10000	54 (1)
C(1)	9825 (9)	12101 (7)	8420 (9)	47 (3)
C(2)	11047 (9)	11358 (7)	8914 (8)	43 (3)
C(3)	11058 (8)	10873 (7)	10294 (8)	42 (3)
C(4)	10521 (10)	11619 (8)	11274 (9)	50 (3)
C(5)	9346 (10)	12361 (7)	10554 (8)	47 (3)
C(6)	8199 (9)	11734 (7)	9719 (8)	46 (3)
C(7)	8493 (8)	11551 (6)	8440 (8)	42 (3)
C(8)	9819 (9)	13015 (7)	9455 (9)	46 (3)
C(9)	6984 (10)	11354 (8)	9979 (11)	57 (4)
C(10)	6147 (11)	10764 (9)	9015 (11)	62 (4)
C(11)	6433 (11)	10547 (8)	7791 (10)	63 (4)
C(12)	7621 (10)	10954 (8)	7494 (9)	50 (3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *involving the non*-H *atoms with e.s.d.'s in parentheses*

Br(1)—C(2)	1·986 (9)	Br(2)—Br(3)	3·086 (2)
Br(2)—C(3)	1·987 (8)	Br(3)—C(3)	1·981 (8)
C(1)—C(2)	1·530 (12)	C(1)—C(8)	1·541 (13)
C(1)—C(7)	1·508 (13)	C(2)—C(3)	1·522 (12)
C(3)—C(4)	1·536 (13)	C(4)—C(5)	1·550 (12)
C(5)—C(8)	1·533 (13)	C(5)—C(6)	1·494 (12)
C(7)—C(6)	1·412 (13)	C(7)—C(12)	1·369 (11)
C(6)—C(9)	1·389 (14)	C(9)—C(10)	1·359 (14)
C(10)—C(11)	1·362 (16)	C(11)—C(12)	1·390 (15)

Discussion. The final atomic coordinates with the equivalent isotropic temperature factors $U_{\rm eq}$ of the non-H atoms are listed in Table 1 according to the labelling of the atoms in Fig. 1. The bond lengths and angles of the non-H atoms are given in Table 2 and Table 3 respectively.* Three bonds of the benzene ring, C(7)—C(12), C(9)—C(10) and C(10)—C(11), are found to be equal to 1·36 Å, but they are not significantly

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51297 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°) *involving the non-*H *atoms with e.s.d.'s in parentheses*

Br(3)—Br(2)—C(3)	38·9 (2)	Br(2)—Br(3)—C(3)	39·0 (2)
C(2)—C(1)—C(8)	109·4 (7)	C(2)—C(1)—C(7)	112·6 (7)
C(8)—C(1)—C(7)	100·7 (8)	Br(1)—C(2)—C(1)	107·5 (6)
Br(1)—C(2)—C(3)	112·8 (5)	C(1)—C(2)—C(3)	112·5 (8)
Br(2)—C(3)—Br(3)	102·1 (4)	Br(2)—C(3)—C(2)	113·7 (6)
Br(3)—C(3)—C(2)	107·2 (5)	Br(2)—C(3)—C(4)	106·9 (5)
Br(3)—C(3)—C(4)	110·6 (6)	C(2)—C(3)—C(4)	115·5 (7)
C(3)—C(4)—C(5)	112·6 (7)	C(4)—C(5)—C(8)	109·1 (8)
C(4)—C(5)—C(6)	112·6 (7)	C(8)—C(5)—C(6)	100·5 (7)
C(1)—C(8)—C(5)	99·3 (7)	C(1)—C(7)—C(6)	107·7 (7)
C(1)—C(7)—C(12)	132·1 (9)	C(6)—C(7)—C(12)	120·2 (8)
C(5)—C(6)—C(7)	108·4 (8)	C(5)—C(6)—C(9)	132·3 (9)
C(7)—C(6)—C(9)	119·2 (8)	C(6)—C(9)—C(10)	118·7 (11)
C(9)—C(10)—C(11)	122·9 (11)	C(10)—C(11)—C(12)	119·3 (9)
C(7)—C(12)—C(11)	119·6 (9)		

shorter than 1·39 Å, the characteristic bond length of a C—C bond in an aromatic molecule. The other bonds of the benzene ring are nearly 1·39 Å. All of the other C—C single-bond lengths of the molecule range from 1·49 to 1·55 Å with a mean value of 1·53 Å. The three C—Br bonds are very nearly equal (1·98 Å) and agree with those observed in dibromocyclopertilide (Nagumo, Kawai & Iitaka, 1982). In the refinement, we could not find the coordinates of the two H atoms of both C(4) and C(8) from the difference Fourier maps. This is probably due to the motion of these H atoms. So, applying an interatomic distance constraint of 1·01782 Å with an e.s.d. of 0·07 Å to the C—H bond, the positions and isotropic temperature factors of these H atoms were refined.

The addition of bromine to unsaturated bicyclic systems can lead to a multiplicity of products. This kind of system can easily undergo Wagner–Meerwein rearrangement to give rearranged and unrearranged products (Provolotskaya, Limasova, Berus, Exner & Barkash, 1969). X-ray structural determination of (2) has confirmed that one part of this bromination at 273 K proceeds without rearrangement. Furthermore, it was found that the bromine of C(2) is in the *exo* position. From the *exo* configuration of this bromine, we are not able to predict whether the initial attack of bromine on the double bond in (2) is *endo* or *exo*.

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Structure of a 2:1 Addition Compound of Methyl Deoxycholate with Methanol

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Abstract. Methyl 3α,12α-dihydroxy-5β-cholan-24-oate–methanol (2/1), $C_{25}H_{42}O_4.\frac{1}{2}CH_4O$, $M_r = 422{\cdot}63$, monoclinic, $P2_1$, $a = 16{\cdot}543$ (3), $b = 12{\cdot}109$ (3), $c = 12{\cdot}477$ (1) Å, $\beta = 102{\cdot}12$ (1)°, $U = 2443{\cdot}6$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}149$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6{\cdot}13$ cm^{-1}, $F(000) = 932$, $T = 295$ K, $R = 0{\cdot}062$ for 3135 observed reflections. The molar ratio between methyl deoxycholate (MDC) and methanol is 2:1. The

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