Crystal and Molecular Structures of 8,9-Dibromo-1,4,4,8-tetramethyltricyclo[5,4,0,$0^{2,5}$]undecane and 8,9-Dibromo-2,2,4,8-tetramethyltricyclo-[5,3,1,$0^{4,11}$]undecane, Derivatives of Rearrangement Products of Caryophyllene Dihydrochloride and Isocaryophyllene Respectively

By **A. Forbes Cameron,*** **Christine Hannaway,** and **J. Monteath Robertson,** Chemistry Department, University of Glasgow, Glasgow G12 8QQ

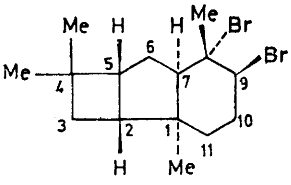
The structures of the title compounds (I) and (IV) have been determined by single-crystal X-ray analyses. Crystals of both are orthorhombic, space group $P2_12_12$ for (I), $P2_12_12_1$ for (IV), with $Z = 4$ in unit cells of dimensions: (I), $a = 15{\cdot}47(2)$, $b = 14{\cdot}02(1)$, $c = 7{\cdot}01(1)$ Å; (IV), $a = 6{\cdot}63(1)$, $b = 8{\cdot}96(1)$, $c = 26{\cdot}35(2)$ Å. Both structures were solved from photographic data by the heavy-atom method, and refined by least-squares calculations to R 0·106 for 1336 independent reflexions (I), and R 0·096 for 860 independent reflexions (IV). In each case the absolute stereochemistry was determined by consideration of anomalous dispersion effects. The analyses of the two dibromo-derivatives have allowed us to deduce the structures and stereochemistries of their parent hydrocarbons [(II) and (V)], and hence to postulate possible mechanisms by which these latter may be formed from caryophyllene dihydrochloride (III) and (−)-isocaryophyllene (VI) respectively.

DURING early investigations into the chemistry of caryophyllene, several workers used caryophyllene dihydrochloride as a suitably crystalline derivative. In an effort to elucidate the structure of caryophyllene, and unaware of the complexities inherent in the caryophyllene nucleus, these workers submitted this dihydrochloride to various mild and severe dehydrochlorination conditions.[1] Confusion then ensued as to the identity of the derived hydrocarbons because of the limited methods of comparison with other bicyclic and tricyclic hydrocarbons derived from caryophyllene and caryolan-1-ol.

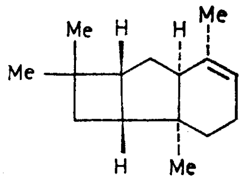
Gollnick and Schade [2] have recently repeated this dehydrochlorination using one of the earliest procedures,[1a] *viz*. heating caryophyllene dihydrochloride under reflux in acetic acid for 1 h, and found a complex mixture of hydrocarbons from which two main components could be isolated by fractional distillation and preparative g.l.c. techniques. Although one of the main components (34%) was identified as neoclovene,[3] spectrochemical evidence for the other hydrocarbon (46%) indicated only that it was tricyclic and contained a trisubstituted double-bond, no further structural information being readily available.

The acid-catalysed rearrangement of caryophyllene has also been shown [4] to produce three major products, caryolan-1-ol, clovene, and neoclovene.[3] Gollnick and Schade [5] repeated the same reaction for pure (−)-isocaryophyllene, and obtained a complex mixture of hydrocarbons from which two main components (35%) could be isolated. As with the caryophyllene dihydrochloride reaction, one of these hydrocarbons was identified as neoclovene, but little information could be obtained for the second product apart from its being a tricyclic hydrocarbon containing a trisubstituted double-bond.

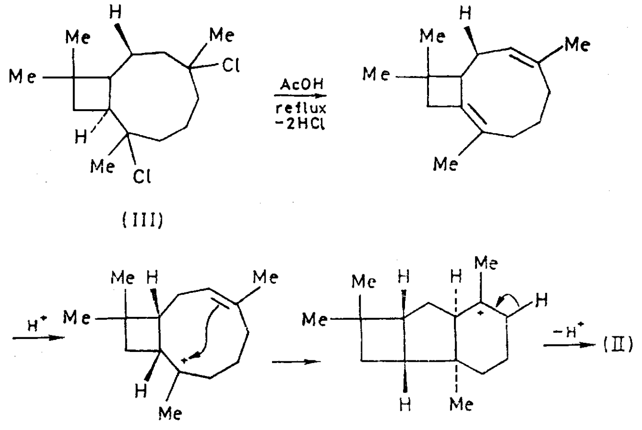
To resolve these problems, the dibromo-derivatives of the unidentified hydrocarbons from both reactions were prepared by adding bromine to ice-cold solutions of the compounds in carbon tetrachloride, and we undertook single-crystal analyses of both derivatives.[2,5] In the case of the dibromo-derivative resulting from the caryophyllene dihydrochloride reaction, we have shown conclusively that it possesses the structure and absolute stereochemistry (I), from which we deduce that the tricyclic hydrocarbon from which it is derived is 1,4,4,8-tetramethyltricyclo[5,4,0,$0^{2,5}$]undec-8-ene (II). This result has led us to speculate that (II) may be formed from caryophyllene dihydrochloride (III) by the mechanism shown.



(I)



(II)



(III)

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[1] (*a*) O. Schreiner and E. Kremers, *Pharm. Arch.*, 1901, **4**, 164; (*b*) F. W. Semmler and E. W. Hayes, *Ber.*, 1910, **43**, 3451; (*c*) G. G. Henderson, R. O. O. McCrone, and J. M. Robertson, *J. Chem. Soc.*, 1929, 1368.

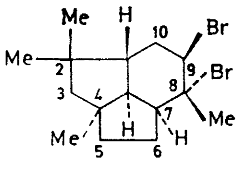
[2] K. Gollnick, G. Schade, A. F. Cameron, C. Hannaway, and J. M. Robertson, *Chem. Comm.*, 1971, 46.

[3] W. Parker, R. A. Raphael, and J. S. Roberts, *J. Chem. Soc.* (*C*), 1969, 2634.

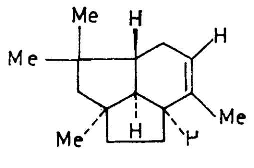
[4] A. Nickon, *Perfumery Essent. Oil Record*, 1954, **45**, 149; D. H. R. Barton and P. de Mayo, *Quart. Rev.*, 1957, **11**, 189; A. Nickon, F. Y. Edamura, T. Iwadare, K. Matsuo, F. J. McGuire, and J. S. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 4196.

[5] K. Gollnick, G. Schade, A. F. Cameron, C. Hannaway, J. S. Roberts, and J. M. Robertson, *Chem. Comm.*, 1970, 248.

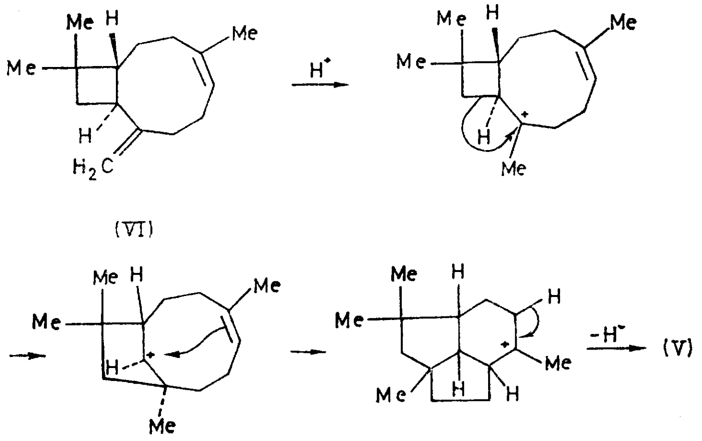
In the case of the (−)-isocaryophyllene rearrangement, we have similarly shown that the dibromo-derivative is (IV), the parent tricyclic hydrocarbon hence being, 2,2,4,8-tetramethyltricyclo[5,3,1,$0^{4,11}$]undec-8-ene (V), both with the absolute stereochemistries indicated. We can thus also suggest a mechanism by which (V) is formed from (−)-isocaryophyllene (VI).



(IV)



(V)



(VI)

EXPERIMENTAL

Crystal Data.—(I), $C_{15}H_{24}Br_2$, $M = 364{\cdot}2$. Orthorhombic, $a = 15{\cdot}47(2)$, $b = 14{\cdot}02(1)$, $c = 7{\cdot}01(1)$ Å, $U = 1520{\cdot}8$ Å^3, $D_m = 1{\cdot}60$ (by flotation in aqueous KI), $Z = 4$, $D_c = 1{\cdot}59$, $F(000) = 736$. Space group $P2_12_12$ (D_2^3). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\text{Cu-}K_\alpha) = 71$ cm^{-1}.

Crystals from benzene were light-sensitive and decomposed in the *X*-ray beam.

(IV), $C_{15}H_{24}Br_2$, $M = 364{\cdot}2$. Orthorhombic, $a = 6{\cdot}63(1)$, $b = 8{\cdot}96(1)$, $c = 26{\cdot}35(2)$ Å, $U = 1565{\cdot}2$ Å^3, D_m (by flotation in aqueous KI) = 1·51, $Z = 4$, $D_c = 1{\cdot}53$, $F(000) = 736$. Space group $P2_12_12_1$ (D_2^4). $\mu(\text{Cu-}K_\alpha) = 71$ cm^{-1}.

Crystals from ethyl acetate were light-sensitive needles which decomposed in the *X*-ray beam.

Crystallographic Measurements.—Unit-cell parameters for both crystals were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α radiation. The space groups were determined from systematic absences. Small crystals were exposed to Cu-K_α radiation, and for (I), 1336 independent reflexions from the reciprocal-lattice nets *hk*0—6 were recorded on Weissenberg photographs by the multiple-film technique. For (IV), 860 independent reflexions from the reciprocal-lattice nets 0—5*kl* were similarly recorded.* All intensity measurements were made by visual comparison with a calibrated strip, and were corrected for the appropriate Lorentz and polarisation factors. For each compound the intensities were subsequently placed on an approximate absolute scale by making $k\Sigma|F_o| = \Sigma|F_c|$ for each layer. Absorption effects, although appreciable, were not considered.

Structure Determinations.—The positions of all the bromine atoms for both compounds were determined by inspections of the three-dimensional Patterson functions, both analyses thereafter proceeding on the basis of the phase-determining heavy-atom method, the complete structures being revealed in the course of several cycles of structure-factor and electron-density calculations in each case.

The absolute stereochemistries of both (I) and (IV) were determined [6] by comparing the differences observed in the intensities of Bijvoet pairs of reflexions [28 for (I), 17 for (IV)] with differences calculated for the same pairs of reflexions on the basis of anomalous scatter by the bromine atoms.

Structure Refinements.—For (I), the refinement of positional, vibrational, and scale parameters by full-matrix least-squares calculations converged after nine cycles, when R was 0·107, and R' $(= \Sigma w\Delta^2|\Sigma w|F_o|^2)$ was 0·019. After cycle 5, the data were converted to an overall absolute scale by use of the refined values of the layer-scale factors, and the bromine atoms were also allowed to refine anisotropically.

Six cycles of full-matrix least-squares calculations were required for the complete refinement of (IV), the final R and R' values being 0·096 and 0·014 respectively. Anisotropic thermal parameters for the bromine atoms were also refined after the fourth cycle.

In both refinements a weighting scheme of the form

$$\sqrt{w} = \{[1\text{-}\exp(-p_1(\sin\theta/\lambda)^2)]/[1 + p_2|F_o| + p_3|F_o|^2]\}^{1/2}$$

was applied in all cycles. Initially the p parameters were chosen to give unit weights to all reflexions, but were varied at later stages of the refinements as indicated by the ($|F_o|$ and $\sin\theta/\lambda$) analyses of $w\Delta^2$. For (I) final values

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* Crystals of both compounds were not only volatile, but also decomposed rapidly in the *X*-ray beam. These characteristics precluded the use of diffractometer techniques of data collection, and necessitated the use of several crystals during data collection. The diffraction data are therefore of limited accuracy.

[6] J. M. Bijvoet, *Proc. Acad. Sci.* (*Amsterdam*), 1949, **52**, 313; see also S. Ramaseshan in 'Advanced Methods of Crystallography,' Academic Press, London, 1964, pp. 67—95.

were: p_1 100, p_2 0·1, p_3 0; and for (IV): p_1 100, p_2 0·001, and p_3 0·0001.

At the conclusion of both refinements, structu refactors were calculated, and electron-density distributions and difference syntheses were evaluated. In neither case were any errors revealed in the structures, and although there were occasional peaks in positions stereochemically acceptable for hydrogen atoms, it was impossible to determine their co-ordinates with any accuracy. Both refinements were therefore considered complete at this stage.

TABLE 1

(*a*) Fractional co-ordinates and thermal parameters ($Å^2 \times 10^3$) for (I)

	x/a	y/b	z/c	U_{iso}
Br(1)	545·2(2)	371·1(2)	744·3(4)	*
Br(2)	550·6(1)	131·6(2)	294·2(3)	*
C(1)	279(1)	190(1)	654(3)	55(4)
C(2)	353(1)	258(1)	606(3)	47(4)
C(3)	369(1)	257(1)	386(3)	54(4)
C(4)	454(1)	308(1)	334(3)	63(5)
C(5)	530(1)	255(1)	432(3)	55(4)
C(6)	520(1)	238(1)	650(3)	55(4)
C(7)	428(1)	211(1)	714(2)	43(3)
C(8)	414(1)	102(1)	694(3)	46(4)
C(9)	318(1)	86(1)	677(3)	51(4)
C(10)	263(1)	78(1)	865(3)	54(4)
C(11)	245(1)	187(1)	855(3)	53(4)
C(12)	331(1)	361(1)	665(3)	61(4)
C(13)	592(1)	176(1)	727(3)	59(4)
C(14)	179(2)	20(2)	818(4)	75(6)
C(15)	308(2)	40(2)	1047(4)	72(6)

* Anisotropic thermal parameters † U_{ij} ($Å^2 \times 10^3$) for bromine atoms

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(1)	84(1)	75(2)	85(2)	−28(2)	−10(2)	−43(2)
Br(2)	77(1)	85(2)	71(2)	−21(2)	49(2)	7(2)

(*b*) Fractional co-ordinates and thermal parameters ($Å^2 \times 10^3$) for (IV)

	x/a	y/b	z/c	U_{iso}
Br(1)	138·2(6)	442·9(4)	262·6(1)	*
Br(2)	−400·0(6)	222·8(4)	346·9(2)	*
C(1)	−972(5)	718(3)	403(1)	67(7)
C(2)	−338(7)	757(4)	382(1)	123(13)
C(3)	−369(5)	630(3)	341(1)	79(8)
C(4)	−150(5)	588(3)	322(1)	77(8)
C(5)	−138(4)	440(3)	297(1)	72(7)
C(6)	−115(5)	296(3)	329(1)	76(8)
C(7)	4(5)	315(3)	375(1)	77(9)
C(8)	−84(4)	454(3)	403(1)	61(7)
C(9)	12(5)	502(4)	458(1)	71(9)
C(10)	−89(6)	665(4)	459(1)	80(10)
C(11)	−32(4)	590(3)	370(1)	55(7)
C(12)	39(5)	862(3)	398(1)	90(9)
C(13)	−281(5)	420(4)	249(1)	83(9)
C(14)	242(7)	498(5)	457(2)	106(13)
C(15)	−82(6)	398(4)	499(1)	97(11)

* Anisotropic thermal parameters † U_{ij} ($Å^2 \times 10^3$) for bromine atoms

	U_{11}	U_{22}	U_{33}	$2U_{24}$	$2U_{23}$	$2U_{12}$
Br(1)	94(2)	89(2)	91(2)	−38(4)	17(4)	−7(4)
Br(2)	99(3)	86(2)	140(3)	−13(4)	9(5)	−45(4)

† Anisotropic thermal parameters have the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

In all the previous structure-factor calculations, atomic scattering factors were taken from ref. 7. Observed and calculated structure amplitudes for both compounds are listed in Supplementary Publication No. SUP 20772 (4 pp.).* Fractional co-ordinates and thermal parameters for both (I) and (IV) are given in Table 1, while Table 2 contains all bonded distances, valence angles, and certain intra- and inter-molecular non-bonded distances. The σ values recorded in Tables 1 and 2 are derived from the inverse of the least-squares normal-equation matrices, and are best regarded as minimum values. A number of planes have been calculated for portions of the molecular frameworks (Table 3).

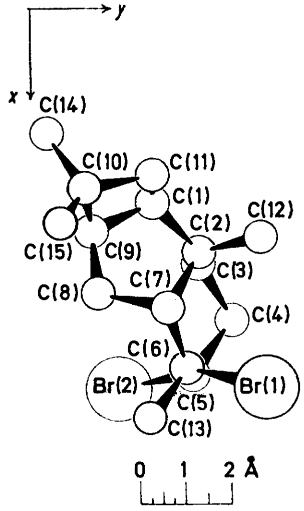

FIGURE 1 A view of the molecule of (I) showing the atomic numbering system used in the analysis

The atomic numbering system used in the crystallo-

TABLE 2

Bond lengths, interbond angles, and relevant intra- and inter-molecular non-bonded distances for (I) and (IV)

(*a*) Dimensions of (I)

(i) Bond lengths (Å)

Br(1)–C(6)	2·01(2)	C(5)–C(6)	1·55(3)
Br(2)–C(5)	2·00(2)	C(6)–C(7)	1·54(3)
C(1)–C(2)	1·52(3)	C(6)–C(13)	1·51(3)
C(1)–C(9)	1·59(3)	C(7)–C(8)	1·55(3)
C(1)–C(11)	1·51(4)	C(8)–C(9)	1·50(3)
C(2)–C(3)	1·56(3)	C(9)–C(10)	1·58(3)
C(2)–C(7)	1·54(3)	C(10)–C(11)	1·56(3)
C(2)–C(12)	1·55(3)	C(10)–C(14)	1·56(3)
C(3)–C(4)	1·54(3)	C(10)–C(15)	1·55(3)
C(4)–C(5)	1·55(3)		

(ii) Valence angles (°)

C(2)–C(1)–C(9)	108(1)	C(7)–C(6)–Br(1)	116(2)
C(2)–C(1)–C(11)	119(2)	C(13)–C(6)–Br(1)	106(1)
C(9)–C(1)–C(11)	91(2)	C(6)–C(7)–C(2)	117(2)
C(1)–C(2)–C(7)	102(1)	C(2)–C(7)–C(8)	105(2)
C(1)–C(2)–C(12)	111(2)	C(6)–C(7)–C(8)	110(1)
C(3)–C(2)–C(7)	111(2)	C(7)–C(8)–C(9)	107(1)
C(3)–C(2)–C(12)	108(1)	C(1)–C(9)–C(8)	104(1)
C(2)–C(3)–C(4)	112(2)	C(1)–C(9)–C(10)	87(1)
C(3)–C(4)–C(5)	109(1)	C(8)–C(9)–C(10)	119(2)
C(4)–C(5)–C(6)	116(2)	C(9)–C(10)–C(11)	89(1)
C(4)–C(5)–Br(2)	109(1)	C(9)–C(10)–C(14)	108(2)
C(6)–C(5)–Br(2)	111(1)	C(11)–C(10)–C(15)	117(2)
C(5)–C(6)–C(7)	114(2)	C(14)–C(10)–C(15)	112(2)
C(5)–C(6)–C(13)	100(2)		

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2 (*Continued*)

(iii) Some intramolecular non-bonded distances (Å)

Br(1) ··· C(2)	3·52	C(3) ··· C(9)	3·24
Br(1) ··· C(4)	3·33	C(4) ··· C(7)	3·02
Br(2) ··· C(3)	3·38	C(4) ··· C(12)	3·10
Br(2) ··· C(8)	3·54	C(5) ··· C(8)	3·34
Br(2) ··· C(13)	3·16	C(6) ··· C(12)	3·41
C(1) ··· C(14)	3·06	C(7) ··· C(10)	3·35
C(1) ··· C(15)	3·50	C(7) ··· C(11)	3·02
C(2) ··· C(5)	3·00	C(8) ··· C(11)	3·09
C(2) ··· C(10)	3·41	C(8) ··· C(15)	3·09
C(3) ··· C(6)	3·00	C(11) ··· C(12)	3·08
C(3) ··· C(8)	3·14		

(iv) Some intermolecular distances (Å) $<4{\cdot}0$ Å

Br(1) ··· Br(1$^{\mathrm{I}}$)*	3·88	C(8) ··· C(8$^{\mathrm{VI}}$)	3·91
C(1) ··· C(5$^{\mathrm{II}}$)	3·98	C(8) ··· C(13$^{\mathrm{VI}}$)	3·91
C(3) ··· C(15$^{\mathrm{III}}$)	3·97	C(9) ··· C(13$^{\mathrm{VI}}$)	3·94
C(4) ··· C(14$^{\mathrm{IV}}$)	3·77	C(12) ··· C(15$^{\mathrm{VII}}$)	3·94
C(5) ··· C(11$^{\mathrm{V}}$)	3·97	C(15) ··· Br(2$^{\mathrm{VIII}}$)	3·68

* The superscripts refer to the following equivalent positions:

I $1-x, 1-y, z$
II $-1/2+x, 1/2-y, 1-z$
III $x, y, z-1$
IV $1/2-x, 1/2+y, 1-z$
V $1/2+x, 1/2-y, 1-z$
VI $1-x, -y, z$
VII $1/2-x, 1/2+y, 2-z$
VIII $1-x, -y, 1+z$

(*b*) Dimensions of (IV)

(i) Bond lengths (Å)

Br(1)–C(5)	2·04(3)	C(5)–C(13)	1·57(4)
Br(2)–C(6)	2·06(3)	C(6)–C(7)	1·45(5)
C(1)–C(2)	1·63(5)	C(7)–C(8)	1·57(5)
C(1)–C(10)	1·55(5)	C(8)–C(9)	1·64(5)
C(1)–C(12)	1·58(5)	C(8)–C(11)	1·55(5)
C(2)–C(3)	1·58(5)	C(9)–C(10)	1·61(4)
C(3)–C(4)	1·58(5)	C(9)–C(14)	1·53(4)
C(4)–C(5)	1·49(4)	C(9)–C(15)	1·55(5)
C(5)–C(6)	1·56(5)		

(ii) Valence angles (°)

C(2)–C(1)–C(11)	103(2)	C(5)–C(6)–Br(2)	107(2)
C(2)–C(1)–C(12)	109(3)	C(7)–C(6)–Br(2)	110(2)
C(10)–C(1)–C(11)	108(2)	C(6)–C(7)–C(8)	107(2)
C(10)–C(1)–C(12)	108(2)	C(7)–C(8)–C(9)	120(3)
C(1)–C(2)–C(3)	101(2)	C(7)–C(8)–C(11)	106(2)
C(2)–C(3)–C(4)	106(2)	C(9)–C(8)–C(11)	102(3)
C(3)–C(4)–C(5)	114(3)	C(8)–C(9)–C(10)	95(3)
C(3)–C(4)–C(11)	102(2)	C(8)–C(9)–C(14)	111(2)
C(5)–C(4)–C(11)	112(2)	C(10)–C(9)–C(15)	112(2)
C(4)–C(5)–C(6)	120(3)	C(14)–C(9)–C(15)	114(3)
C(4)–C(5)–Br(1)	104(1)	C(9)–C(10)–C(1)	107(2)
C(6)–C(5)–C(13)	114(2)	C(1)–C(11)–C(4)	111(2)
C(13)–C(5)–Br(1)	101(2)	C(1)–C(11)–C(8)	102(3)
C(5)–C(6)–C(7)	115(2)	C(4)–C(11)–C(8)	111(3)

(iii) Some intramolecular non-bonded distances (Å)

Br(1) ··· C(7)	3·29	C(3) ··· C(13)	3·12
Br(1) ··· C(11)	3·32	C(4) ··· C(7)	2·99
Br(2) ··· C(8)	3·30	C(4) ··· C(12)	3·40
Br(2) ··· C(13)	3·22	C(5) ··· C(8)	2·84
C(1) ··· C(14)	3·30	C(6) ··· C(11)	2·90
C(2) ··· C(8)	3·25	C(7) ··· C(14)	3·14
C(3) ··· C(6)	3·45	C(7) ··· C(15)	3·41
C(3) ··· C(8)	2·96	C(11) ··· C(14)	3·04

(iv) Some intermolecular distances (Å) $<4{\cdot}0$ Å

C(4) ··· Br(1$^{\mathrm{I}}$)†	3·89	C(13) ··· Br(1$^{\mathrm{IV}}$)	3·89
C(6) ··· Br(1$^{\mathrm{II}}$)	3·98	C(14) ··· C(15$^{\mathrm{V}}$)	3·92
C(10) ··· C(14$^{\mathrm{III}}$)	3·91		

† The superscripts refer to the following equivalent positions:

I $-x, 1/2+y, 1/2-z$
II $-x, -1/2+y, 1/2-z$
III $-1/2+x, 3/2-y, 1-z$
IV $x-1, y, z$
V $1/2+x, 1/2-y, 1-z$

graphic analysis and molecular packing of (I) are shown in Figures 1 and 2, while Figures 3 and 4 contain the corresponding information for (IV) [systematic numbering for (I) and (IV) is shown in the formulae].

TABLE 3

Least-squares planes calculated for various portions of the molecular frameworks. The equations are in the form $kX' + lY' + mZ' = n$, where X', Y', and Z' are coordinates in Å

(*a*) Calculations for molecule (I)

Plane (1): $0{\cdot}845X' + 0{\cdot}287Y' + 0{\cdot}451Z' = -6{\cdot}5666$
Plane (2): $0{\cdot}150X' - 0{\cdot}010Y' + 0{\cdot}989Z' = -3{\cdot}890$
Plane (3): $0{\cdot}219X' + 0{\cdot}857Y' + 0{\cdot}467Z' = -6{\cdot}293$

Distances (Å) of atoms from planes:

Plane (1): C(1)* − 0·088, C(9)*, 0·084, C(10)* − 0·086, C(11)* 0·090, C(14) − 1·562, C(15) 0·931

Plane (2): C(1)* − 0·033, C(9)* 0·052, C(8)* − 0·053, C(7)* 0·034, C(2) − 0·528

Plane (3): C(2)* − 0·029, C(7)* 0·028, C(5)* − 0·028, C(4)* 0·028, C(3) 0·698, C(6) − 0·453

(*b*) Calculations for molecule (IV)

Plane (1): $0{\cdot}925X' + 0{\cdot}379Y' + 0{\cdot}034Z' = -2{\cdot}160$
Plane (2): $-0{\cdot}351X' - 0{\cdot}627Y' + 0{\cdot}695Z' = -3{\cdot}551$
Plane (3): $0{\cdot}981X' - 0{\cdot}155Y' - 0{\cdot}120Z' = -2{\cdot}323$

Distances (Å) of atoms from planes:

Plane (1): C(1)* 0·039, C(9)* 0·023 (C(10)* − 0·038 C(11)* − 0·025, C(8) − 0·776

Plane (2): C(1)* 0·025, C(2)* − 0·024, C(3)* 0·018, C(11)* − 0·019, C(4) − 0·599

Plane (3): C(5)* − 0·125, C(6)* 0·127, C(8)* − 0·127, C(11)* 0·125 (C(7) 0·726, C(4) − 0·490

* Atoms defining planes.

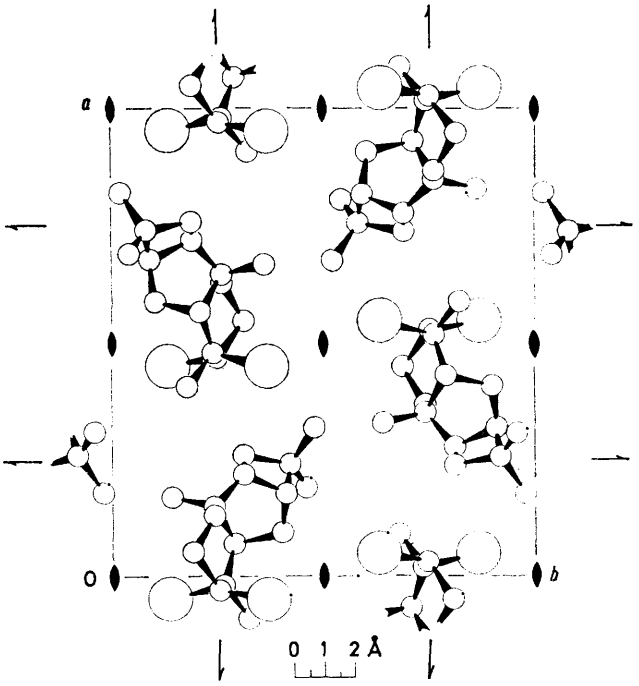

FIGURE 2 The molecular packing of (I) viewed down *c*

DISCUSSION

The presence of two bromine atoms in each of two relatively small molecules, in addition to the radiation damage to the crystals and the neglect of absorption effects, has resulted in analyses of limited accuracy.

For this reason we confine our discussion of the molecular geometries to the salient features of the conformations.

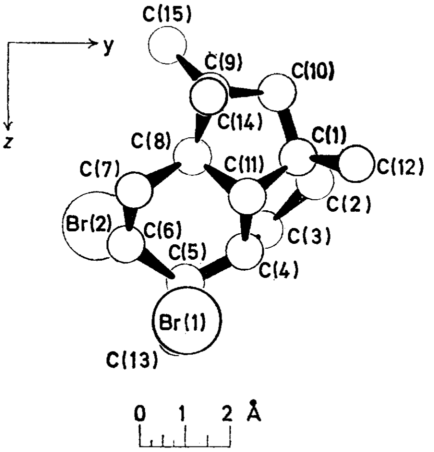

FIGURE 3 A view of the molecule of (IV) showing the atomic numbering system used in the analysis

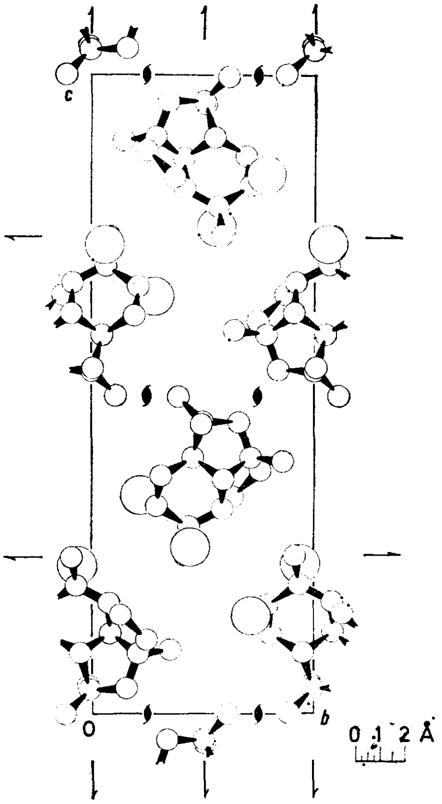

FIGURE 4 The molecular packing of (IV) viewed down *a*

The tricyclic ring system of (I) consists of a cyclobutane and a cyclohexane ring, both *cis*-fused to a central cyclopentane ring, but extending on opposite sides of the central ring. The molecule thus has an overall chair-like conformation. The cyclobutane ring is itself non-planar, the dihedral angle between the planes defined by atoms C(9), C(10), C(11) and C(1), C(10), C(11) being 162°. Buckling to this extent has been observed in other similar molecules although there are also well-known cases of planar cyclobutane rings. The mean valence angle within the four-membered ring is 89·3°, which compares well with values observed elsewhere.

The central cyclopentane ring adopts a flattened envelope conformation in which C(2) is unique, but is displaced by only 0·55 Å from the best plane through the other four atoms. This flattening may presumably be attributed, at least in part, to the steric strain implicit in the fusion to the cyclobutane ring. The cyclohexane ring, which is in the chair form, is similarly flattened, atoms C(3) and C(6) being displaced below and above the best-plane of atoms C(2), C(4), C(5), and C(7) by 0·70 and 0·45 Å respectively. In this conformation the two bromine atoms are in axial positions, while the methyl group bonded to C(6) is equatorial. An examination of a molecular model reveals that alternative conformations tend to result in this methyl group lying in positions where severe steric interaction is likely with other substituents.

The substituted tricyclo[5,3,1,$0^{4,11}$]undecane system of (IV) contains two five-membered rings which are *cis*-fused to each other, and a six-membered ring which is *cis*-fused to one of the cyclopentane rings, but *trans*-fused to the other. Both cyclopentane rings adopt envelope conformations in which C(4) and C(8) are respectively unique (Table 3). As a result of the stereochemical restrictions of its environment, the cyclohexane ring possesses a flattened and distorted chair conformation, in which atoms C(5), C(6), C(8), and C(11) lie alternately above and below the mean plane calculated through their positions, and with C(7) lying above this plane by 0·73 Å, although C(4) is displaced below it by only 0·49 Å. As with the previous molecule, the bromine atoms occupy axial sites, and the C(5) methyl group is equatorial. It would again appear that alternative conformations would result in this methyl group becoming involved in severe steric interactions.

Neither crystal structure displays any abnormally short intermolecular contacts, indicating that the packing in both crystals is dominated by van der Waals' forces.

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