

considers the standard deviations of the bond lengths. We have therefore recalculated the bond lengths, angles and e.s.d.'s for the room-temperature structure.) The advantage in determining the structure at 120 K is reflected by significantly smaller standard deviations in the bond lengths. A similar observation has been made for *p*-chloranil where the low-temperature crystal structure (van Weperen & Visser, 1972) agrees better with the electron diffraction results than it does with the room-temperature structure (Chu *et al.*, 1962). In particular, the C=C bonds of the electron diffraction solution of *p*-fluoranil are now confirmed and reproduced by this work. It has previously been pointed out that the chloro derivatives of *p*-benzoquinone have a tendency to non-planarity, the chlorine and oxygen atoms bonded to neighbouring carbon atoms alternating 0.05 Å above and below the best plane through the carbon atoms (van Weperen & Visser, 1972). This feature, although not so dominant, is also exhibited by fluoranil. Thus, the perpendicular distances (Å) of the O and F atoms of the asymmetric unit from the best plane through the six carbon atoms are O4 = -0.036 (2), F5 = -0.006 (2), F6 = +0.019 (2). The corresponding values for the room-temperature solution, calculated here to be O4 = +0.033 (7), F5 = -0.001 (7), F6 = +0.011 (7), are indistinguishable within the experimental errors.

It is well known that aggregation often results in different degrees of deviations from the free-molecule geometries. Nevertheless, the non-planarity of the substituents observed in the solid state for the chloro derivative has been ascribed (van Weperen & Visser, 1972) to intramolecular interactions between the substituents and hence must also extend to the free

molecule. Whereas the non-bonded halogen-oxygen and halogen-halogen distances in chloranil are significantly shorter than the sum of the van der Waals radii the same is only true to a lesser extent for *p*-fluoranil. Therefore, it is not unexpected that the observed deviations from planarity are more pronounced in *p*-chloranil. Furthermore, the planar model used in the electron diffraction study gives bond lengths and angles which accord with the present X-ray diffraction results.

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Acta Cryst. (1987). C43, 1961-1964

endo,endo-5,9-Dibromo-cis-transoid-cis-13,oxatricyclo[8.2.1.0^{2,6}]tridecane

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Abstract. C₁₂H₁₈Br₂O, *M_r* = 338.09, monoclinic, *P*2₁/*c*, *a* = 6.352 (1), *b* = 12.002 (1), *c* = 16.378 (3) Å, β = 97.17 (1)°, *V* = 1238.8 Å³, *Z* = 4, *D_x* = 1.81 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 6.45 mm⁻¹, *F*(000) = 336, *T* = 296 K, final *R* = 0.033 for 1690 unique observed reflections. A surprising tricyclic

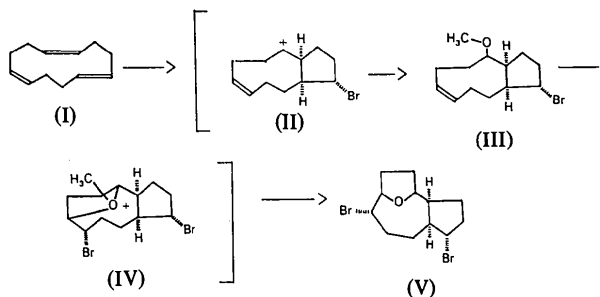
tetrahydrofuran derivative was obtained, *via* trans-annular π-cyclization and O-heterocyclization, by methoxybromination reaction of (*E,Z,Z*)-cyclododeca-1,5,9-triene. The compound has two five-membered rings with an envelope conformation and one eight-membered ring with a distorted crown conformation.

Introduction. Studies in recent years have established that transannular reactions, which are characteristic for electrophilic addition reactions to unsaturated medium-sized cyclic hydrocarbons (Sutherland, 1974; Haufe & Mühlstädt, 1979), are not restricted to eight- to eleven-membered compounds, but can also occur in larger rings. Transannular O-heterocyclization occurs when the methoxybromination procedure is applied to twelve- and thirteen-membered 1,5-dienes or 1,5,9-trienes (Haufe & Mühlstädt, 1984; Trauer, 1985; Haufe, 1987), whereas transannular π -cyclizations are the main processes for nine- to eleven-membered 1,5-dienes under similar conditions (Haufe & Mühlstädt, 1979).

The course of O-heterocyclizations is strongly directed by the conformational arrangement of substituents in the transition state leading to transannular O-bridging. The structure of this transition state is dependent on the conformation and configuration of the starting diene or triene. Thus two bicyclic tetrahydrofuran derivatives were obtained as transannular O-heterocyclization products in the reaction of (*E,E,Z*)-cyclododeca-1,5,9-triene with *N*-bromo-succinimide in methanol (Haufe & Mühlstädt, 1984). And one bicyclic and two tricyclic tetrahydropyran derivatives were formed from (*E,E,E*)-cyclododeca-1,5,9-triene by transannular π -cyclization and subsequent transannular O-heterocyclization (Haufe, 1987; Haufe, Faure & Loiseleur, 1987). A similar reaction pathway has apparently been described earlier only in the oxymercuration of the natural eleven-membered triene, humulene (Misumi, Ohfuné, Furusaki, Shirahama & Matsumoto, 1976; Misumi, Ohtsuda, Hashimoto, Ohfuné, Shirahama & Matsumoto, 1979; Misumi, Ohtsuda, Ohfuné, Sugita, Shirahama & Matsumoto, 1979).

In the present paper we report the structure of a surprising tricyclic tetrahydrofuran derivative recently isolated from the methoxybromination reaction of (*E,Z,Z*)-cyclododeca-1,5,9-triene. The tricyclic tetrahydrofuran derivative can be presumed to form by the following mechanism (scheme). The starting compound, (*E,Z,Z*)-cyclododeca-1,5,9-triene (I), has a favourable conformation for the electrophilic bromonium ion to attack the more reactive *E* double bond of the starting triene. Then, by participation of one of the *Z* double bonds, a cross-transannular π -cyclization occurs and a bicyclo[7.3.0]dodec-2-yl carbonium ion (II), containing one Br atom in the five-membered ring, is formed. The carbonium ion is trapped by methanol acting as a nucleophile and this is followed by deprotonation (III) of the oxonium ion. The second bromonium ion attacks the remaining *Z* double bond, which is now located in a nine-membered ring. Transannular participation of the methoxy group (transannular O-heterocyclization) and subsequent demethylation of the formed tetrahydrofuranium ion

(IV) complete the formation of this surprising product (V).



Experimental. Colourless crystals synthesized by known method (Haufe, 1987), 0.20 × 0.20 × 0.20 mm, mounted on a glass fibre; Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo *K* α , ω -2 θ method; lattice parameters from 25 reflections with $8 < \theta < 12^\circ$; two standard reflections measured every hour, no loss of intensity; 3591 reflections (*h*: 0→8, *k*: 0→16, *l*: -23→23) with $\theta < 30^\circ$, 3591 independent, 1690 with $I > 3\sigma(I)$; Lp correction; empirical absorption correction (Walker & Stuart, 1983), correction factors: max. = 1.580 and min. = 0.468; direct methods; refinement by full-matrix least-squares method using unit weights and F^2 's, all non-H atoms anisotropic, H atoms (from difference map) isotropic with fixed temperature factor ($B = 5.0 \text{ \AA}^2$); 208 parameters; max. shift/ $\sigma = 0.03$ on final cycle; $R = 0.033$, $wR = 0.033$, $S = 1.34$; final difference map with no features greater than $0.52(8) e \text{ \AA}^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs: *MULTAN11/82* (Main *et al.*, 1982), *SDP* (Frenz, 1978) and *ORTEPII* (Johnson, 1976).*

Discussion. The atomic coordinates are listed in Table 1 and bond distances and selected torsion angles are given in Table 2. A view of the molecule and the numbering scheme are shown in Fig. 1. The stereoscopic packing scheme is presented in Fig. 2.

Bond distances and angles are normal. Some contacts between H and Br atoms, Br1-H15(inter), Br2-H3(inter), Br2-H8(inter) and Br2-H12(intra), 3.11 (5), 3.11 (5), 3.06 (5) and 3.05 (5) Å, respectively, are slightly shorter than the sum of the van der Waals radii of H and Br atoms (3.15 Å). Owing to the conformation, there are also some short intramolecular H-H contacts, H11-H18, H6-H10 and H7-H9,

* Lists of structure factors, anisotropic thermal parameters, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44058 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2.27 (8), 2.31 (8) and 2.32 (8) Å, respectively, compared with the sum of the van der Waals radii of H atoms (2.40 Å).

Table 1. Fractional coordinates and equivalent isotropic thermal parameters for the tricyclic ether with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Br1	0.3915 (1)	-0.48785 (5)	0.11187 (4)	4.34 (1)
Br2	0.3725 (1)	0.19382 (5)	0.15482 (4)	4.59 (1)
O1	-0.0307 (5)	-0.0737 (3)	0.1030 (2)	3.03 (7)
C1	-0.0097 (7)	-0.1667 (5)	0.1590 (3)	3.3 (1)
C2	0.1016 (7)	-0.2625 (4)	0.1232 (3)	2.9 (1)
C3	-0.0134 (8)	-0.3060 (5)	0.0412 (4)	3.9 (1)
C4	0.1579 (9)	-0.3483 (5)	-0.0085 (3)	3.8 (1)
C5	0.3604 (7)	-0.3462 (4)	0.0508 (3)	3.0 (1)
C6	0.3375 (7)	-0.2483 (4)	0.1082 (3)	2.6 (1)
C7	0.3943 (7)	-0.1402 (4)	0.0652 (3)	3.1 (1)
C8	0.4403 (7)	-0.0360 (4)	0.1195 (3)	3.0 (1)
C9	0.2610 (8)	0.0500 (4)	0.1079 (3)	3.0 (1)
C10	0.0575 (7)	0.0247 (5)	0.1433 (3)	3.3 (1)
C11	0.0734 (8)	0.0020 (5)	0.2350 (3)	4.2 (1)
C12	0.0984 (9)	-0.1222 (6)	0.2411 (3)	4.3 (1)
H1	-0.167 (8)	-0.193 (5)	0.163 (3)	5.0
H2	0.119 (8)	-0.319 (5)	0.162 (3)	5.0
H3	-0.089 (8)	-0.242 (5)	0.010 (3)	5.0
H4	-0.102 (8)	-0.368 (5)	0.046 (3)	5.0
H5	0.127 (8)	-0.425 (5)	-0.028 (3)	5.0
H6	0.173 (8)	-0.292 (5)	-0.047 (3)	5.0
H7	0.473 (9)	-0.348 (5)	0.032 (3)	5.0
H8	0.462 (8)	-0.270 (5)	0.164 (3)	5.0
H9	0.527 (9)	-0.157 (5)	0.040 (3)	5.0
H10	0.270 (8)	-0.122 (5)	0.013 (3)	5.0
H11	0.497 (8)	-0.049 (5)	0.184 (3)	5.0
H12	0.576 (8)	0.001 (5)	0.107 (3)	5.0
H13	0.213 (8)	0.071 (5)	0.047 (3)	5.0
H14	-0.039 (8)	0.088 (5)	0.127 (3)	5.0
H15	0.197 (8)	0.041 (5)	0.266 (3)	5.0
H16	-0.070 (8)	0.027 (5)	0.255 (3)	5.0
H17	0.046 (8)	-0.153 (5)	0.272 (3)	5.0
H18	0.266 (8)	-0.145 (5)	0.253 (3)	5.0

Table 2. Bond distances (Å) and selected torsion angles (°) in the tricyclic ether with *e.s.d.*'s in parentheses

Br1 C5	1.969 (5)	C6 C7	1.540 (7)	
Br2 C9	1.984 (5)	C6 H8	1.16 (5)	
O1 C1	1.441 (6)	C7 C8	1.542 (7)	
O1 C10	1.432 (6)	C7 H9	1.00 (6)	
C1 C2	1.506 (7)	C7 H10	1.11 (5)	
C1 C12	1.529 (7)	C8 C9	1.531 (7)	
C1 H1	1.05 (5)	C8 H11	1.09 (5)	
C2 C3	1.538 (7)	C8 H12	1.02 (6)	
C2 C6	1.557 (6)	C9 C10	1.512 (7)	
C2 H2	0.93 (5)	C9 H13	1.04 (5)	
C3 C4	1.525 (8)	C10 C11	1.518 (8)	
C3 H3	1.01 (5)	C10 H14	0.99 (5)	
C3 H4	0.94 (6)	C11 C12	1.501 (9)	
C4 C5	1.513 (7)	C11 H15	1.00 (5)	
C4 H5	0.98 (6)	C11 H16	1.05 (6)	
C4 H6	0.93 (6)	C12 H17	0.73 (6)	
C5 C6	1.522 (7)	C12 H18	1.09 (5)	
C5 H7	0.82 (6)			
C10 O1	C1 C2	-125.5	C10 O1 C1 C12	0.6
C4 C5	C6 C2	41.7	C4 C5 C6 C7	-81.3
C1 O1	C10 C9	108.4	C1 O1 C10 C11	-18.0
O1 C1	C2 C3	-59.7	O1 C1 C2 C6	65.2
C2 C6	C7 C8	83.4	C12 C1 C2 C3	179.2
C12 C1	C2 C6	-55.9	C5 C6 C7 C8	-164.0
O1 C1	C12 C11	17.0	C6 C7 C8 C9	-106.5
C2 C1	C12 C11	140.4	C1 C2 C3 C4	148.5
C7 C8	C9 C10	73.1	C6 C2 C3 C4	16.5
C1 C2	C6 C5	-164.1	C1 C2 C6 C7	-46.9
C3 C2	C6 C5	-35.1	C3 C2 C6 C7	82.1
C8 C9	C10 O1	-62.0	C8 C9 C10 C11	57.4
C2 C3	C4 C5	9.2	O1 C10 C11 C12	28.0
C9 C10	C11 C12	-91.8	C3 C4 C5 C6	-32.4
C10 C11	C12 C1	-27.0		

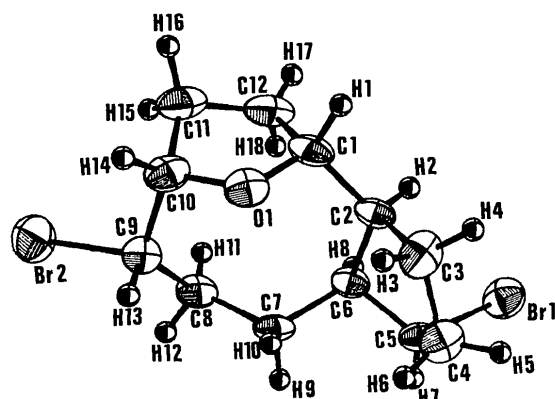


Fig. 1. ORTEP plot (Johnson, 1976) and numbering scheme for 5,9-dibromo-13-oxatricyclo[8.2.1.0^{2,6}]tridecane. The thermal ellipsoids are shown at the 50% probability level.

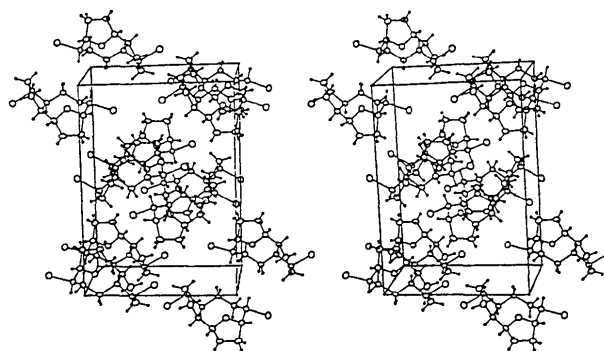


Fig. 2. Stereoscopic packing scheme for 5,9-dibromo-13-oxatricyclo[8.2.1.0^{2,6}]tridecane. The *b* axis is horizontal and *c* axis vertical.

The five-membered rings have an envelope conformation with C10 and C6 as out-of-plane atoms in the heterocyclic and pentane ring, respectively. The eight-membered ring has a distorted crown conformation. Never before has this kind of tricyclic tetrahydrofuran derivative been obtained from methoxybromination applied to twelve- or thirteen-membered trienes. Bicyclic tetrahydrofuran or tetrahydropyran derivatives are obtained in similar reactions from isomeric or homologous trienes (Haufe & Mühlstädt, 1984; Trauer, 1985; Haufe, 1987).

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Structure of Racemic Isoptychanolide

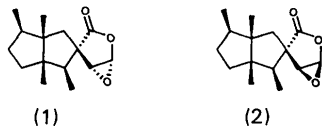
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Abstract. C₁₅H₂₂O₃, $M_r = 250.34$, triclinic, $P\bar{1}$, $a = 6.890(1)$, $b = 6.971(1)$, $c = 15.829(2)$ Å, $\alpha = 87.15(2)$, $\beta = 80.33(2)$, $\gamma = 61.97(1)^\circ$, $V = 661.2(2)$ Å³, $Z = 2$, $D_x = 1.26$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.80$ cm⁻¹, $F(000) = 272$, $T \approx 130$ K, $R = 0.057$ for 6933 reflections. The configurations of all asymmetric carbon atoms except those in the oxirane ring are equal to those in ptychanolide.

Introduction. Ptychanolide (1) is a natural product whose crystal structure has been published previously (Takeda, Naoki, Iwashita, Mizukawa, Hirose, Isida & Inoue, 1983). The diastereoisomer isoptychanolide (2) has been synthesized in racemic form (Huguet, Karpf & Dreiding, 1983; Šolaja, Huguet, Karpf & Dreiding, 1987). To establish the configuration at the spiro centre and at the oxirane moiety, we have determined its crystal structure.



Experimental. A colourless parallelepiped, $ca\ 0.6 \times 0.35 \times 0.3$ mm, crystallized from pentane at room temperature, was mounted on a Nicolet R3 four-circle diffractometer with LT-1 low-temperature device and graphite monochromator. Unit-cell parameters were obtained from least-squares refinement (Stewart,

Kruger, Ammon, Dickinson & Hall, 1972) of both 'positive' and 'negative' 2θ values of 72 automatically centered reflection positions, $45 < |2\theta| < 54^\circ$. 6934 unique reflections, $0 \leq h \leq 11$, $-10 \leq k \leq 11$, $-26 \leq l \leq 27$, were measured in the ω -scan technique within $(\sin\theta)/\lambda = 0.857$ Å⁻¹. Owing to beam-stop impairment 001 was omitted. Three standard reflections, repeated after each 100 reflections, varied at most by 3.5% from their initial intensities. The intensities were corrected for standard intensity variation and Lp effects but not for absorption. Reflections with $I < 0.5\sigma(I)$ were set to $I = 0.25\sigma(I)$. The structure was solved by direct methods and the 251 parameters (isotropic temperature factors for the H atoms after their location in a difference density map, anisotropic temperature factors for the other atoms, positional parameters for all atoms) were refined by a blocked-cascade least-squares refinement algorithm with $ca\ 100$ variables per block using all 6933 unique structure factors, $R = 0.057$, $wR = 0.054$, $w = [\sigma^2(F) + 0.0004F^2]^{-1}$, $S = 2.1$, $(\Delta/\sigma)_{\max} = 0.04$, $(\Delta\rho)_{\max} = 0.47$ (on a bond), $(\Delta\rho)_{\min} = -0.25$ e Å⁻³, 0.35 Å apart from C(10). Scattering and dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Unless otherwise stated the program system *SHELXTL* (Sheldrick, 1981) was used for all computerized calculations.

Discussion. Fractional atomic coordinates are given in Table 1, § bond lengths and bond angles in

§ 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 44061 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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