

sis of variance in terms of $\sin\theta$ and F_o . The refinement converged to $S = 1.96$, $R = 0.048$, $wR = 0.045$, $(\Delta/\sigma)_{\max} = 0.001$ (no extinction correction). The largest peaks in final $\Delta\rho$ map were ± 0.2 (1) $e \text{ \AA}^{-3}$. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were: *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987). The molecule and the numbering scheme are shown in Fig. 1. Positional parameters and the equivalent isotropic values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Bond lengths, bond angles, torsion angles, least-squares planes and dihedral angles are given in Table 2.

Related literature. 5H-Dibenz[*c,e*]azepines substituted with acceptor or donor groups at the α -posi-

* 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 53435 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tion of the heteroatom have been attracting increasing interest (Kreher & Morgenstern, 1983). Investigation of the conformational changes in the seven-membered heterocyclic system with a cyclic CN double bond (Röhrkasten, 1990) on the one hand and with an exocyclic CO double bond (Wahl, Wildonger & Bordner, 1973; 6-methyl-6,7-dihydro-5H-dibenz[*c,e*]azepin-5-one) on the other hand was the main purpose of the present investigation.

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Acta Cryst. (1991). **C47**, 666–668

Synthesis of a 2-Oxabrendane Derivative via Reaction of *endo*-5-Acetyl-7,7-dimethoxynorborn-2-ene with *N*-Bromosuccinimide

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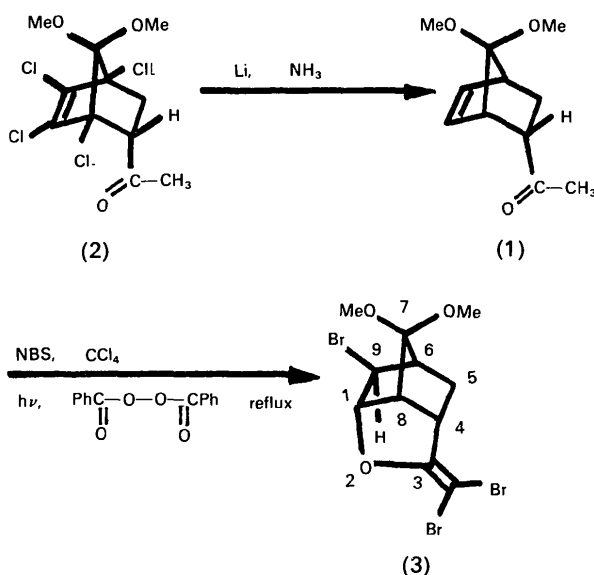
(Received 17 May 1990; accepted 17 July 1990)

Abstract. 9-Bromo-3-dibromomethylene-2-oxatricyclo[4.2.1.0^{4,8}]nonan-7-one dimethyl acetal (3), $C_{11}H_{13}Br_3O_3$, $M_r = 432.95$, triclinic, $P\bar{1}$, $a = 6.532$ (2), $b = 9.193$ (3), $c = 12.230$ (4) \AA , $\alpha = 78.02$ (3), $\beta = 79.08$ (2), $\gamma = 71.27$ (2) $^\circ$, $V = 674.3$ (4) \AA^3 , $Z = 2$, $D_x = 2.132$ g cm^{-3} , $\lambda(\text{Mo } K\alpha) = 0.71073$ \AA , $\mu = 88.80$ cm^{-1} , $F(000) = 416$, $T = 295$ K, $R = 0.0571$ for 2221 reflections. Compound (3) is composed of three fused five-membered rings in envelope conformations: a norbornane moiety with a five-membered ring fused along one side. The

fused five-membered ring results in a C(3)—C(7)—C(6) norbornane angle of 97.7 (4) $^\circ$ which is significantly smaller than the C(2)—C(1)—C(9) angle of 105.2 (5) $^\circ$. This leads to a decrease in the C(7)—C(8) distance of 1.501 (10) \AA relative to the C(1)—C(8) distance of 1.531 (7) \AA .

Experimental. The synthesis of compound (3) is indicated in the Scheme. Compound (1) was prepared via the lithium–ammonia promoted dechlorination of 1,2,3,4-tetrachloro-*endo*-5-acetyl-7,7-dimethoxynorborn-2-ene (2) (McBee, Dively & Burch, 1955). A refluxing carbon tetrachloride solu-

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tion of (1), excess NBS (*N*-bromosuccinimide), and benzoyl peroxide (catalytic amount) was irradiated with a 400 W medium-pressure Hanovia lamp (Pyrex filter) for 18 h. The reaction mixture was cooled and filtered to remove succinimide, and the filtrate was concentrated *in vacuo*. The residue was purified *via* column chromatography on silica gel yielding a bromine-containing material (3) in 41% yield. The structure could not be deduced unequivocally from analysis of the ^1H and ^{13}C NMR spectra. A single crystal of (3), m.p. 415–417 K, was obtained by recrystallization from hexane. A crystal of dimensions $0.55 \times 0.20 \times 0.10$ mm was mounted on a Nicolet R3M/ μ update of a $P2_1$ diffractometer; data

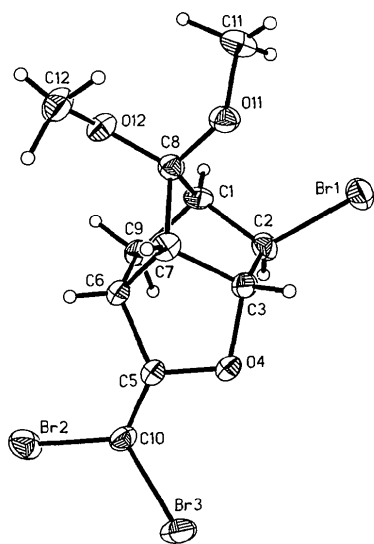


Fig. 1. Drawing of compound (3) with thermal ellipsoids at the 30% probability level. H atoms are represented by spheres of arbitrary size.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for compound (3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	-624 (10)	6247 (6)	2466 (5)	37 (2)
C(2)	1779 (10)	5707 (7)	2598 (5)	42 (2)
Br(1)	3741 (1)	4688 (1)	1387 (1)	60 (1)
C(3)	2252 (10)	7227 (7)	2692 (5)	39 (3)
O(4)	2573 (6)	7169 (5)	3843 (3)	47 (2)
C(5)	570 (9)	7752 (6)	4440 (5)	35 (2)
C(6)	-1170 (9)	8132 (6)	3696 (5)	36 (2)
C(7)	91 (9)	8481 (6)	2510 (5)	37 (2)
C(8)	-909 (9)	7868 (6)	1763 (5)	36 (2)
C(9)	-1822 (11)	6680 (7)	3615 (5)	39 (3)
C(10)	382 (9)	7890 (6)	5499 (5)	38 (2)
Br(2)	-2329 (1)	8690 (1)	6334 (1)	57 (1)
Br(3)	2800 (1)	7314 (1)	6283 (1)	58 (1)
O(11)	319 (6)	7945 (4)	685 (3)	43 (2)
C(11)	-351 (12)	7309 (8)	-121 (5)	64 (3)
O(12)	-3145 (6)	8591 (4)	1696 (3)	45 (2)
C(12)	-3666 (13)	10203 (8)	1256 (7)	58 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for compound (3)

C(1)—C(2)	1.516 (9)	C(1)—C(8)	1.531 (7)
C(1)—C(9)	1.536 (8)	C(2)—Br(1)	1.950 (5)
C(2)—C(3)	1.554 (10)	C(3)—O(4)	1.450 (8)
C(3)—C(7)	1.529 (7)	O(4)—C(5)	1.372 (6)
C(5)—C(6)	1.499 (9)	C(5)—C(10)	1.307 (9)
C(6)—C(7)	1.552 (7)	C(6)—C(9)	1.552 (10)
C(7)—C(8)	1.501 (10)	C(8)—O(11)	1.408 (6)
C(8)—O(12)	1.408 (7)	C(10)—Br(2)	1.873 (5)
C(10)—Br(3)	1.876 (6)	O(11)—C(11)	1.440 (10)
O(12)—C(12)	1.419 (8)		
C(2)—C(1)—C(8)	102.7 (5)	C(2)—C(1)—C(9)	105.2 (5)
C(8)—C(1)—C(9)	100.4 (4)	C(1)—C(2)—Br(1)	115.6 (4)
C(1)—C(2)—C(3)	103.3 (4)	Br(1)—C(2)—C(3)	111.5 (4)
C(2)—C(3)—O(4)	109.0 (4)	C(2)—C(3)—C(7)	103.4 (5)
O(4)—C(3)—C(7)	106.1 (4)	C(3)—O(4)—C(5)	107.9 (4)
O(4)—C(5)—C(6)	109.5 (5)	O(4)—C(5)—C(10)	121.1 (5)
C(6)—C(5)—C(10)	129.4 (5)	C(5)—C(6)—C(7)	101.8 (5)
C(5)—C(6)—C(9)	112.5 (4)	C(7)—C(6)—C(9)	102.8 (5)
C(3)—C(7)—C(6)	97.7 (4)	C(3)—C(7)—C(8)	104.3 (5)
C(6)—C(7)—C(8)	103.3 (5)	C(1)—C(8)—C(7)	96.4 (4)
C(1)—C(8)—O(11)	116.5 (4)	C(7)—C(8)—O(11)	107.8 (5)
C(1)—C(8)—O(12)	108.7 (5)	C(7)—C(8)—O(12)	116.0 (4)
O(11)—C(8)—O(12)	111.0 (4)	C(1)—C(9)—C(6)	103.4 (5)
C(5)—C(10)—Br(2)	122.0 (5)	C(5)—C(10)—Br(3)	122.4 (4)
Br(2)—C(10)—Br(3)	115.6 (3)	C(8)—O(11)—C(11)	114.9 (5)
C(8)—O(12)—C(12)	114.0 (5)		

collected in the ω -scan mode ($3.0 \leq 2\theta \leq 55^\circ$), variable scan rate ($4\text{--}29.3^\circ \text{min}^{-1}$), graphite-monochromated $\text{Mo } K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($23.63 \leq 2\theta \leq 29.17^\circ$), intensity statistics were consistent with space group $P\bar{1}$; monitored reflections ($\bar{1}50$ and $\bar{2}13$) showed variations of intensities of less than 2%; 4420 reflections measured ($-8 \leq h \leq 8$, $-11 \leq k \leq 11$, $-2 \leq l \leq 15$), 3095 unique ($R_{int} = 0.0099$), $2221 \geq 3\sigma(I)$; Lorentz-polarization corrections, ψ -scan-based empirical absorption correction (transmission factors 0.262 to 0.132) applied; structure solved by direct-methods techniques, block-

cascade least-squares refinement, H atoms located in difference maps and refined with isotropic thermal parameters; $R = 0.0571$, $wR = 0.0386$ for 206 parameters and 2221 reflections ($R = 0.0846$ and $wR = 0.0404$ for all 3095 unique reflections), $S = 1.801$, $(\Delta/\sigma)_{\max} = 0.004$; largest peaks in the final difference map of -0.70 and $0.90 \text{ e } \text{\AA}^{-3}$ (adjacent to Br atoms); $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.00002F_o^2]^{-1}$; isotropic extinction correction applied, $F = F_c/[1.0 + 2.6(4) \times 10^{-6}F_c^2/\sin(2\theta)]^{0.25}$. All computer programs supplied by Nicolet Instrument Corporation (1986) for Desktop 30 Microeclipse and Nova 4/C configuration; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Fig. 1 is a drawing of compound (3), Table 1 lists atomic positional parameters while Table 2 gives interatomic distances and bond angles.*

Related literature. The synthesis and reactions of brendanes (Arbuzov, Gevorkyan, Pekhk, Bobyleva & Belikova, 1984; Adam, Carballeira, Peters, Peters & Von Schnering, 1983; Hamlin & Toyne, 1981; Casanova, Waegell, Koukoua & Toure, 1979; Nickon, Kwasnik, Mathew, Swartz, Williams & DiGiorgio, 1978) and oxabrendanes (Inokuma, Sugie, Moriguchi, Shimomura & Katsube, 1982; Ranganathan, Ranganathan & Mehrotra, 1976;

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53410 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fritz, Weis & Winkler, 1975) have been reported. The ring strain and heats of formation have been discussed (Gasteiger & Dammer, 1978; Carballeira, Casado & Rios, 1977); however, no structural work has been reported.

We thank the Robert A. Welch Foundation (P-074 to WHW and B-963 to APM), the Air Force Office of Scientific Research (AFOSR-88-0132 to APM) and the Texas Christian University and University of North Texas Faculty Research Committees for financial support.

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Acta Cryst. (1991). **C47**, 668–670

Structure of Ethyl 4-Oxo-1,2,3,4-tetrahydrocinnoline-2-acetate

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(Received 22 May 1990; accepted 7 August 1990)

Abstract. C₁₂H₁₄N₂O₃, $M_r = 234.3$, monoclinic, $P2_1/c$, $a = 8.760(1)$, $b = 13.550(3)$, $c = 10.456(2)$ Å, $\beta = 104.62(1)^\circ$, $V = 1200.9(4)$ Å³, $Z = 4$, $D_x = 1.296 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, Ni filter, $\mu =$

0.74 mm^{-1} , $F(000) = 496$, $T = 293 \text{ K}$. Final $R = 0.062$ for 2182 observed reflections. 4-Oxo-1,2,3,4-tetrahydrocinnoline is in its standard N(2) sofa conformation. The orientation of the ethyl acetate group