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# Structure of 1,2,2,3,3,4,4,5-Octamethyl-6,7,8-trioxabicyclo[3.2.1]octane

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## Abstract

Crystals of the unusually stable secondary symmetric ozonide of the title compound (m.p. 374–376 K) contain two crystallographically independent but very similar molecules. The five-membered trioxolane rings have envelope conformations and the pyran rings have chair conformations in both molecules, with ether O-atom apices. The seven-membered dioxepine rings have boat conformations with the peroxide O atoms and the opposite C atom out of the plane of the other ring atoms.

## Comment

The structure determination of the title compound was undertaken in order to establish the mechanism of the 1,3-dipolar cycloadditions. Details of the synthetic work will be published elsewhere (Mayr, 1991). Fig. 1 illustrates one of the two crystallographically independent molecules *A* and *B*, with the non-H atoms of the two molecules fitted, and the atomic numbering system. Final atomic parameters are given in Table 1 and selected interatomic distances and bond angles in Table 2. The two molecules have the same geometry (within the limits of 3 e.s.d.). An important structural aspect of this study is the conformation of the ozonide rings; for their description,

the method of Cremer & Pople (1975) was employed, in which the geometry of the puckered plane is represented in terms of amplitudes and phase coordinates. A list of puckering parameters has been deposited (see footnote). The trioxolane rings have envelope conformations with ether O atom O3 above the plane of C9, C13, O1 and O2. The pyran rings have chair conformations deformed towards envelope conformations with ether O atom O3 under the plane of C9, C10, C12 and C13. The conformation of the dioxepine ring may be described as a boat with peroxide O atoms O1 and O2, and the opposite C atom C11 above the plane of C9, C10, C12 and C13. As a consequence of the conformation, short intramolecular C4—H43···O1 and C4—H43···O2 contacts are observed (Table 2). Similar close contacts between C—H groups and O atoms have also been found in other organic compounds (Ilczyszyn, Lis, Baran & Ratajczak, 1992, and references therein). The C3 and C6 methyl groups are in axial positions. As a result, the C11—C12 and C10—C11 bonds are longer than the standard $Csp^3$—$Csp^3$ bond distance. The observed O—O and C—O bond lengths are in reasonable agreement with the values reported for the ozonides (Miura *et al.*, 1983; Miljković *et al.*, 1984; Karban *et al.*, 1978; Mullica *et al.*, 1979; Oliver *et al.*, 1979). The crystal packing scheme is shown in Fig. 2. The whole structure is held together by van der Waals interactions.
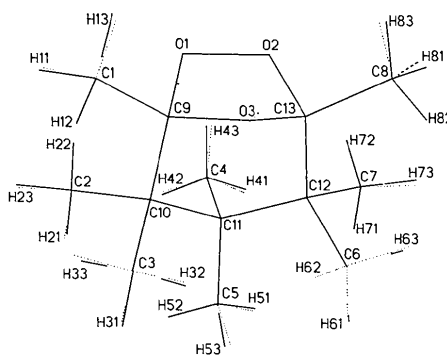


Fig. 1. A view of one of the two crystallographically independent molecules *A* and *B*, with the non-H atoms of the two molecules fitted.
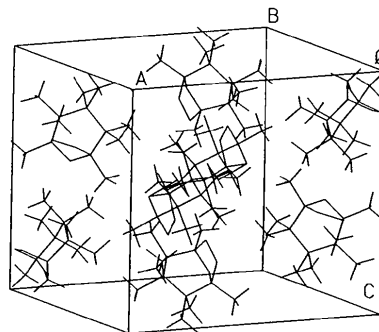


Fig. 2. Molecular packing in the crystal of 1,2,2,3,3,4,4,5-octamethyl-6,7,8-trioxabicyclo[3.2.1]octane.

## Experimental

### Crystal data

$C_{13}H_{24}O_3$
$M_r = 228.33$
Monoclinic
$P2_1/c$
$a = 14.91$ (2) Å
$b = 13.48$ (2) Å
$c = 13.01$ (1) Å
$\beta = 90.47$ (7)°
$V = 2615$ (6) Å$^3$
$Z = 8$
$D_x = 1.160$ (3) Mg m$^{-3}$
$D_m = 1.18$ Mg m$^{-3}$

Density measured by flota-
tion in H$_2$O/glycerol
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25
reflections
$\theta = 8-15°$
$\mu = 0.61$ mm$^{-1}$
$T = 293$ (1) K
Plate
$0.3 \times 0.3 \times 0.2$ mm
Colourless

### Data collection

Kuma KM4 computer-
controlled four-cicle $\kappa$-
axis diffractometer
$\omega/2\theta$ scans
5537 measured reflections
5479 independent reflections
3523 observed reflections
$[F > 6\sigma(F)]$
$R_{int} = 0.0090$ for 58 reflec-
tions

$\theta_{max} = 75°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 16$
$l = -16 \rightarrow 16$
3 standard reflections
monitored every 50
reflections
intensity variation: $-11\%$

### Refinement

Final $R = 0.037$
$wR = 0.035$
3348 reflections
481 parameters
All H-atom parameters re-
fined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.03$

$\Delta\rho_{max} = 0.16$ e Å$^{-3}$
$\Delta\rho_{min} = -0.17$ e Å$^{-3}$
Atomic scattering factors
from *International Tables
for X-ray Crystallogra-
phy* (1974, Vol. IV, Table
2.2B)

Data collection: Kuma KM4 software (Kuma Diffraction, 1989).
Program(s) used to solve structure: *SHELXS*86 (Sheldrick,
1990). Program(s) used to refine structure: *XTL/E-XTL* (Syn-
tex, 1976) (block-diagonal least squares).

Table 1. *Fractional atomic coordinates and equivalent
isotropic thermal parameters* (Å$^2$)

$$B_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| O1A | −0.03319 (9) | 0.10320 (10) | 0.18787 (10) | 3.77 (6) |
| O2A | 0.03274 (9) | 0.02573 (10) | 0.16350 (11) | 4.27 (7) |
| O3A | 0.07097 (8) | 0.16596 (10) | 0.08248 (9) | 3.43 (6) |
| C1A | −0.06356 (14) | 0.25761 (17) | 0.11008 (16) | 4.46 (10) |
| C2A | −0.00867 (15) | 0.27092 (17) | 0.33347 (16) | 4.46 (11) |
| C3A | 0.10439 (15) | 0.33787 (16) | 0.21527 (19) | 5.05 (12) |
| C4A | 0.08571 (16) | 0.09188 (18) | 0.37398 (16) | 5.13 (12) |
| C5A | 0.20299 (16) | 0.21705 (20) | 0.36181 (19) | 5.91 (14) |
| C6A | 0.25657 (14) | 0.15880 (18) | 0.15697 (18) | 4.95 (12) |
| C7A | 0.21823 (16) | 0.00327 (18) | 0.24713 (19) | 5.29 (12) |
| C8A | 0.14069 (17) | 0.01451 (19) | 0.03185 (18) | 5.65 (13) |
| C9A | 0.00983 (12) | 0.19544 (14) | 0.15964 (13) | 3.10 (8) |
| C10A | 0.06097 (12) | 0.24041 (14) | 0.25189 (14) | 3.21 (8) |
| C11A | 0.13172 (13) | 0.16261 (15) | 0.29626 (14) | 3.53 (9) |
| C12A | 0.17880 (12) | 0.10151 (14) | 0.20697 (15) | 3.50 (9) |
| C13A | 0.10928 (13) | 0.07760 (14) | 0.12152 (14) | 3.48 (8) |
| O1B | 0.46641 (10) | 0.75607 (10) | 0.71159 (10) | 4.26 (7) |
| O2B | 0.45803 (10) | 0.83539 (10) | 0.78815 (10) | 4.42 (7) |
| O3B | 0.50479 (9) | 0.90081 (9) | 0.63907 (11) | 3.80 (6) |
| C1B | 0.53907 (16) | 0.75031 (17) | 0.55070 (18) | 5.17 (12) |
| C2B | 0.33967 (16) | 0.71189 (17) | 0.53900 (19) | 5.46 (13) |
| C3B | 0.38469 (16) | 0.87083 (18) | 0.46107 (17) | 5.16 (12) |
| C4B | 0.26884 (15) | 0.79921 (18) | 0.72077 (19) | 5.25 (12) |
| C5B | 0.22827 (15) | 0.91651 (20) | 0.58487 (20) | 5.87 (13) |
| C6B | 0.36811 (15) | 1.05656 (16) | 0.63947 (19) | 4.95 (12) |
| C7B | 0.31349 (16) | 0.98796 (18) | 0.80310 (18) | 5.43 (13) |
| C8B | 0.51597 (16) | 0.99884 (18) | 0.79165 (20) | 5.94 (14) |
| C9B | 0.46946 (13) | 0.80666 (14) | 0.61320 (15) | 3.54 (9) |
| C10B | 0.37491 (13) | 0.81682 (14) | 0.56530 (15) | 3.64 (9) |
| C11B | 0.31023 (13) | 0.87347 (15) | 0.64344 (15) | 3.73 (9) |
| C12B | 0.36160 (13) | 0.95979 (14) | 0.70297 (15) | 3.65 (9) |
| C13B | 0.45792 (13) | 0.92670 (14) | 0.72924 (15) | 3.79 (9) |

Table 2. *Selected interatomic distances* (Å) *and bond
angles* (°)

| | Molecule A | Molecule B |
|---|---|---|
| O1—O2 | 1.471(2) | 1.467(2) |
| O1—C9 | 1.448(2) | 1.451(2) |
| O2—C13 | 1.449(2) | 1.450(2) |
| O3—C9 | 1.418(2) | 1.414(2) |
| O3—C13 | 1.414(2) | 1.414(2) |
| C1—C9 | 1.518(3) | 1.526(3) |
| C2—C10 | 1.547(3) | 1.546(3) |
| C3—C10 | 1.542(3) | 1.547(3) |
| C4—C11 | 1.554(3) | 1.551(3) |
| C5—C11 | 1.543(3) | 1.548(3) |
| C6—C12 | 1.542(3) | 1.548(3) |
| C7—C12 | 1.539(3) | 1.540(3) |
| C8—C13 | 1.521(3) | 1.531(3) |
| C9—C10 | 1.541(3) | 1.543(3) |
| C10—C11 | 1.592(3) | 1.601(3) |
| C11—C12 | 1.592(3) | 1.591(3) |
| C12—C13 | 1.548(3) | 1.539(3) |
| C4···O1 | 2.993(3) | 3.006(3) |
| C4···O2 | 2.980(3) | 2.987(3) |
| C4—H43 | 0.95(2) | 0.99(2) |
| O1···H43 | 2.38(2) | 2.40(2) |
| O2···H43 | 2.38(2) | 2.34(2) |
| C3···C6 | 3.403(3) | 3.424(3) |
| O1—O2—C13 | 105.6(2) | 105.0(2) |
| O2—O1—C9 | 104.9(2) | 105.0(2) |
| C9—O3—C13 | 104.0(2) | 103.5(2) |
| C1—C9—O1 | 105.2(2) | 105.2(2) |
| C1—C9—O3 | 108.6(2) | 108.7(2) |
| C1—C9—C10 | 117.6(2) | 116.9(2) |
| O1—C9—O3 | 103.2(2) | 103.1(2) |
| C10—C9—O3 | 110.2(2) | 110.7(2) |
| C10—C9—O1 | 111.0(2) | 111.3(2) |
| C9—C10—C2 | 108.0(2) | 108.4(2) |
| C2—C10—C3 | 105.7(2) | 105.7(2) |
| C9—C10—C11 | 110.2(2) | 109.8(2) |
| C3—C10—C11 | 113.2(2) | 113.2(2) |
| C2—C10—C11 | 111.9(2) | 111.8(2) |
| C3—C10—C9 | 107.5(2) | 107.7(2) |
| C10—C11—C4 | 110.2(2) | 110.4(2) |
| C4—C11—C5 | 103.8(2) | 104.2(2) |
| C5—C11—C12 | 110.1(2) | 109.9(2) |
| C10—C11—C12 | 111.8(2) | 111.6(2) |
| C4—C11—C12 | 110.9(2) | 110.4(2) |
| C5—C11—C10 | 109.8(2) | 110.1(2) |
| C11—C12—C6 | 112.7(2) | 112.9(2) |
| C11—C12—C13 | 109.6(2) | 109.9(2) |
| C7—C12—C13 | 108.4(2) | 108.9(2) |
| C6—C12—C7 | 106.7(2) | 106.0(2) |
| C6—C12—C13 | 107.6(2) | 107.5(2) |
| C7—C12—C11 | 111.5(2) | 111.5(2) |
| C12—C13—C8 | 117.3(2) | 117.1(2) |
| O2—C13—C12 | 110.8(2) | 111.1(2) |
| C12—C13—O3 | 110.4(2) | 110.7(2) |
| C8—C13—O3 | 108.8(2) | 108.4(2) |
| C8—C13—O2 | 105.5(2) | 105.1(2) |
| O2—C13—O3 | 103.0(2) | 103.3(2) |
| C4—H43···O1 | 121.7(16) | 119.2(15) |
| C4—H43···O2 | 120.9(16) | 122.7(15) |

Crystals were obtained from methanol solution by slow evaporation. A parallelepiped crystal fragment was cut from a larger crystal and mounted in a Lindemann capillary to prevent its sublimation. During the data collection intensities of the standard reflections ($\bar{2}\bar{2}1$, 004 and 400) dropped by up to 89% of their initial values. Data were corrected for crystal decay.

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## Structure of 1,3-Xylyl-(18-crown-5)–Ammonium Catecholborate (1/1)

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### Abstract

In the title compound, 3,6,9,12,15-pentaoxabicyclo-[15.3.1]henicosa-1(21),17,19-triene–ammonium bis(1,2-

benzenediolato)borate (1/1), the ammonium cation is hydrogen bonded by three of its H atoms to the crown ether, and by the remaining H atom to the O atom of the catecholborate anion. Thus the crown ether competes favourably with the catechol ligands for hydrogen bonding with the ammonium cation.

### Comment

The title compound (1) was obtained as a by-product of the reaction of ammonia with the crown ether borate 1,3-xylyl-(18-crown-5)-2-catecholborate (2) (Reetz, Niemeyer, Hermes & Goddard, 1992). Dry ammonia was passed through a dry solution of 0.6 mmol of the crown ether borate dissolved in 10 ml of dichloromethane for 30 s at 273 K. The solution immediately became cloudy. The solution was then diluted fivefold and filtered to remove any insoluble deposits. Careful layering with diethyl ether resulted in the formation of crystals of the title compound together with those of the $NH_3$ adduct of the crown ether borate (Reetz, Niemeyer, Hermes & Goddard, 1992). We report here the structure of the title compound.
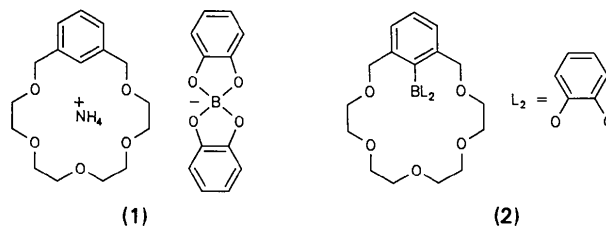


The results of the structure analysis are summarized in Fig. 1 which shows an ion-pair complex comprising ammonium catecholborate attached to a macrocyclic crown ether. The ammonium cation is bonded on one side by three hydrogen bonds to a 1,3-xylyl-(18-crown-5) polyether and on the other through a single hydrogen bond to a catecholborate anion. Interestingly, the ammonium cation forms hydrogen bonds preferentially with the O atoms of the crown ether in spite of the fact that the catecholborate anion is negatively charged and carries four O atoms that are eminently suited to form hydrogen bonds. By way of comparison, ammonium tetrafluoroborate crystallizes as a three-dimensional structure with each H atom of the ammonium cation hydrogen bonded, albeit weakly (Pendred & Richards, 1955), to an F atom of a neighbouring tetrafluoroborate anion (Clark & Lynton, 1969; Van Rensburg & Boeyens, 1972; Stromme, 1974). The crown ether thus competes effectively with the borate for hydrogen bonding. This is reflected in the similar N···O hydrogen-bonded distances to the crown ether and the borate anion [N···O1 2.978(4), N···O3 2.827(4), N···O5 2.999(4), N···O8 2.827(4) Å]. The H···O distances are also comparable [H1···O1 1.98(4), H3···O3 2.00(3), H2···O5 2.13(3), H4···O8 1.98(4) Å] although