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# The Structure of 2-Ammonio-$\gamma$-butyrolactone Bromide*

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**Abstract.** $C_4H_8NO_2^+.Br^-$, $M_r$ = 182·02, orthorhombic, *Pbca*, $a$ = 11·786 (3), $b$ = 9·499 (2), $c$ = 11·594 (3) Å, $Z$ = 8, $D_c$ = 1·85 Mg m$^{-3}$, $V$ = 1298·01 Å$^3$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu$ = 8·058 mm$^{-1}$. The structure was solved by direct methods and refined by full-matrix least squares to a final $R$ of 0·065 for 1024 observed reflections. The ring shows a typical envelope conformation while the lactone moiety is planar. The ammonio group, which in the solid state is bound to the bromine through hydrogen bonds, occupies a pseudo-axial position.

**Introduction.** The present study is part of a series of X-ray and NMR investigations on six- and five-membered rings carried out in our laboratories to compare the results obtained by these two different types of analysis and to have more data to check the Lambert theory (Lambert, 1967; Lambert & Sun, 1977).

A pale-yellow crystal of about 0·71 × 0·45 × 0·23 mm was selected, after recrystallization from a cyclohexane–diethyl ether mixture, to be used in the data collection.

Approximate cell dimensions were deduced from rotation and Weissenberg photographs. The cell constants were refined by a least-squares fit to the $(\theta,\chi,\varphi)_{hkl}$ values of 23 reflections carefully measured on the diffractometer.

During the data collection a check reflection was monitored periodically for crystal and instrument stability and did not show a significant variation. Using Cu $K\alpha$ radiation ($\lambda$ = 1·5418 Å) a total of 2403 ($\pm h,k,l$) intensities with $\theta \leq 70°$ were measured on a Siemens AED single-crystal diffractometer. These were merged on 1235 unique reflections and 191 of them were considered unobserved on the basis that the intensities were less than $3\sigma(I)$.

The structure was solved by direct methods using *SHELX* (Sheldrick, 1975). Refinement of all heavy atoms began with a residual $R$ of 0·22. A few cycles of isotropic full-matrix least squares reduced $R$ to 0·99 and further cycles of anisotropic full-matrix refinement gave an $R$ of 0·071. All the H atoms were located in the difference Fourier map computed at this stage. The final refinement including the H atoms with isotropic temperature factors reduced $R$ and $R_w$ to final values of 0·065 and 0·077 respectively. The weighting scheme used was $w = \sigma^2(F_o) + c|F_o|^2$, where $c$ = 0·005. 20 reflections affected by large errors were removed from the final calculations.

Positional parameters are listed in Table 1.† All the calculations were performed on the Cyber 76 com-

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* Stereochemistry of Rings. IV. $\gamma$-Lactone Derivatives. 2. Part III.1: Bocelli & Grenier-Loustalot (1981). Part IV.1: Bocelli & Grenier-Loustalot (1980). Alternative name for title compound: 2-oxo-3-tetrahydrofurylammonium bromide.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36104 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$ *for* Br, O, N *and* C, $\times 10^3$ *for* H *atoms) and equivalent isotropic thermal parameters*

$B_{eq}$ is defined according to Hamilton (1959).

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Br | −6276 (1) | 2031 (1) | 569 (1) | 3·32 (4) |
| O(1) | −4136 (5) | 2404 (6) | 3277 (5) | 3·85 (5) |
| O(2) | −3457 (5) | 3715 (5) | 1833 (6) | 4·03 (5) |
| N | −3478 (6) | 1196 (7) | 497 (6) | 3·10 (4) |
| C(1) | −3626 (5) | 2589 (8) | 2274 (7) | 3·85 (4) |
| C(2) | −3326 (6) | 1160 (7) | 1774 (6) | 4·03 (5) |
| C(3) | −4104 (9) | 180 (10) | 2408 (9) | 3·10 (5) |
| C(4) | −4278 (9) | 895 (9) | 3548 (8) | 2·81 (5) |
| H(1) | −251 (6) | 102 (6) | 195 (5) | |
| H(2) | −374 (9) | −48 (8) | 255 (9) | |
| H(3) | −485 (9) | 6 (10) | 201 (7) | |
| H(4) | −511 (12) | 67 (13) | 386 (11) | |
| H(5) | −363 (10) | 53 (11) | 416 (11) | |
| H(6) | −340 (9) | 24 (11) | 25 (9) | |
| H(7) | −298 (9) | 183 (12) | −7 (9) | |
| H(8) | −437 (5) | 157 (6) | 38 (5) | |

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsional angles* (°)

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·321 (10) | C(2)–H(1) | 0·99 (7) |
| O(1)–C(4) | 1·477 (10) | C(3)–H(2) | 0·78 (9) |
| O(2)–C(1) | 1·202 (9) | C(3)–H(3) | 1·00 (10) |
| N–C(2) | 1·492 (10) | C(4)–H(4) | 1·07 (11) |
| C(1)–C(2) | 1·518 (10) | C(4)–H(5) | 1·10 (12) |
| C(2)–C(3) | 1·499 (12) | N–H(6) | 0·96 (10) |
| C(3)–C(4) | 1·500 (13) | N–H(7) | 1·07 (11) |
| | | N–H(8) | 1·12 (6) |
| | | | |
| C(1)–O(1)–C(4) | 111·6 (6) | C(1)–C(2)–C(3) | 103·0 (6) |
| O(1)–C(1)–O(2) | 124·6 (7) | N–C(2)–C(3) | 115·3 (7) |
| O(2)–C(1)–C(2) | 126·5 (7) | C(2)–C(3)–C(4) | 103·6 (7) |
| O(1)–C(1)–C(2) | 108·9 (6) | O(1)–C(4)–C(3) | 103·7 (7) |
| N–C(2)–C(1) | 109·3 (6) | | |
| | | | |
| C(1)–O(1)–C(4)–C(3) | −16·9 (9) | O(1)–C(1)–C(2)–C(3) | −158·4 (8) |
| C(4)–O(1)–C(1)–C(2) | 176·5 (8) | O(1)–C(1)–C(2)–C(3) | 20·1 (8) |
| C(4)–O(1)–C(1)–C(2) | −2·1 (8) | C(1)–C(2)–C(3)–C(4) | −29·3 (8) |
| O(1)–C(1)–C(2)–N | 143·2 (6) | N–C(2)–C(3)–C(4) | −148·3 (7) |
| O(2)–C(1)–C(2)–N | −35·3 (10) | C(2)–C(3)–C(4)–O(1) | 28·3 (9) |

Table 3. *Deviations* (Å) *from mean planes*

| | Plane 1 | Plane 2 |
|---|---|---|
| O(1) | −0·003 (6)* | −0·008 (6)* |
| C(1) | 0·056 (7)* | 0·009 (7)* |
| C(2) | −0·105 (7)* | −0·006 (7)* |
| C(3) | 0·245 (11)* | 0·469 (11) |
| C(4) | −0·148 (11)* | 0·014 (10)* |
| N | 0·770 (6) | 0·851 (7) |
| O(2) | 0·236 (7) | 0·059 (6) |

* Atoms defining the planes.

Table 4. *Contacts* <3·5 Å (<2·7 Å *if involving* H *atoms*)

| | | | |
|---|---|---|---|
| $N\cdots O(1^{i})$ | 3·00 (1) | $C(3)\cdots O(2^{iii})$ | 3·31 (1) |
| $H(7)\cdots O(1^{i})$ | 2·46 (11) | $C(4)\cdots O(2^{iii})$ | 3·41 (1) |
| $H(8)\cdots O(1^{i})$ | 2·64 (6) | $H(4)\cdots O(2^{iii})$ | 2·64 (12) |
| $C(2)\cdots O(2^{ii})$ | 3·13 (1) | $N\cdots Br^{iv}$ | 3·32 (1) |
| $C(3)\cdots O(2^{ii})$ | 3·39 (1) | $H(6)\cdots Br^{iv}$ | 2·39 (10) |
| $H(1)\cdots O(2^{ii})$ | 2·47 (6) | $Br\cdots N^{v}$ | 3·33 (1) |
| $C(3)\cdots O(1^{iii})$ | 3·45 (1) | $Br\cdots H(7^{v})$ | 2·35 (11) |

Symmetry code: (i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $-\frac{1}{2}-x, -\frac{1}{2}+y, z$; (iii) $-1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-1-x, -y, -z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$.

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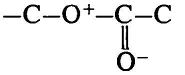
**Discussion.** Fig. 1 shows a projection of the molecule. Bond distances, bond angles and torsion angles are listed in Table 2.

As observed in other analogous compounds (Jeffrey, Rosenstein & Vlasse, 1967; Berman, Rosenstein & Southwick, 1971; Harlow & Simonsen, 1976; Bocelli & Grenier-Loustalot, 1980), the lactone moiety is nearly planar while the ring shows a typical furan-envelope conformation with C(3) out of the mean plane by 0·245 Å (see Table 3).

The C=O bond [C(1)–O(2) = 1·202 (9) Å] agrees well with the accepted value [1·215 (5) Å; Sutton, 1965], while the two C–O bonds are significantly different [1·321 (10), 1·477 (10) Å]. This difference is often observed in lactone derivatives and may be interpreted as due to a valence-bond resonance form  $-C-O^{+}-\underset{\underset{O^{-}}{\|}}{C}-C$ (Hvoslef, 1968; Jeffrey *et al.*, 1967; Mo & Sivertsen, 1971). The largest internal angles of the lactone ring are at the carbonyl carbon [108·9 (6)°] and at the oxygen [111·6 (6)°]. The ammonio group is in a pseudo-axial position, the angle formed by the N–C line and the normal to the mean ring plane being 54·1°.

In the solid state the molecule is bound to the bromide anion by hydrogen bonds: Br···H(7) = 2·35 (11), Br···N = 3·33 (1) Å, Br···H(7)–N =

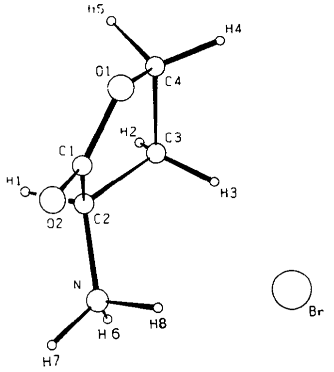


Fig. 1. Projection of the molecule.

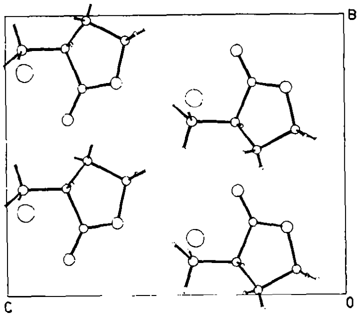


Fig. 2. Projection of the structure on (100).

151·7 (2)°; N···Br = 3·32 (1), H(6)···Br = 2·39 (10) Å, N—H(6)···Br = 164·0 (1)°. Other significant contacts are listed in Table 4 and the packing of the molecules is represented in Fig. 2.

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# A 2:1 Complex of 2,4-Dinitroaniline and 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)

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**Abstract.** $2C_6H_5N_3O_4.C_{12}H_{24}O_6$, $M_r$ = 630·57, monoclinic, $C2/c$, $a$ = 14·609 (6), $b$ = 10·843 (4), $c$ = 18·951 (8) Å, $\beta$ = 99·34 (9)°, $Z$ = 4, $d_c$ = 1·414 Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 0·110 mm$^{-1}$, $R$ = 0·074, $R_w$ = 0·057 for 1360 independent data. The two 2,4-dinitroaniline molecules, related by a centre of inversion, are arranged perpendicularly 'above' and 'below' the plane formed by the six O atoms of the crown ether. They are linked to the latter by a system of bifurcated N—H···O bridges in which each O atom of the crown and additionally one O atom of each *o*-nitro group receives one hydrogen bond from the $NH_2$ groups. The conformation of the macrocyclic ligand differs from the approximate $D_{3d}$ symmetry normally found.

**Introduction.** In addition to their well-known ability for ligating alkali- and alkaline-earth-metal ions, annular and linear oligoethers reveal some tendency towards forming crystalline host–guest complexes with hydrogen-bond donors such as malononitrile (Kaufmann, Knöchel, Kopf, Oehler & Rudolph, 1977), dimethyl acetylenedicarboxylate (Goldberg, 1975), thiourea (Suh & Saenger, 1978; Weber & Saenger, 1980), water (Goldberg, 1978; Bombieri, de Paoli & Immirzi, 1978; Weber & Sheldrick, 1980), benzenesulphonamide (Knöchel, Kopf, Oehler & Rudolph, 1978*a*) and (2,4-dinitrophenyl)hydrazine (Hilgenfeld & Saenger, 1981). A comparison of the last structure with the present one seemed interesting.

Yellow irregular blocks of the adduct were crystallized from ethyl acetate. Systematic absences indicated the space group $Cc$ or $C2/c$; the latter was confirmed

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