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N,N'-Dimethylcryptand[2.2.2] Diiodide

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Abstract

The bisquaternary ammonium cation in 1,10-dimethyl-4,7,13,16,21,24-hexaoxa-1,10-diazoniabicyclo[8.8.8]-hexacosane diiodide displays an *exo-exo* conformation at the bridgehead N atoms and has a twofold crystallographic axis. The packing arrangement is closely related to that of the bisborohydride of cryptand[2.2.2].

Comment

The title compound was prepared and its structure determined in the course of an investigation of bisquaternary ammonium salts with wide separation of the two positive charges. *N,N'*-Dimethylcryptand[2.2.2] diiodide has already been reported by Pietraszkiewicz, Salanski & Jurczak (1985), who synthesized it *via* the high-pressure reaction of *N,N'*-dimethyldiaza-18-crown-6 with 1,2-bis(2-iodoethoxy)ethane. We chose to prepare the compound by methylating commercially available cryptand[2.2.2] with methyl iodide in methanol.

The bisquaternary ammonium cation has a crystallographic twofold axis and displays the expected *exo-exo* conformation (Fig. 1). A similar molecular structure has been determined for the bisborohydride of cryptand-[2.2.2], $(C_{18}H_{36}N_2O_6)(BH_3)_2$, by Metz, Moras & Weiss (1976). Given the different chemical nature of the bisborohydride compared with the bisquaternary diiodide, the parallels between the two crystal structures are rather

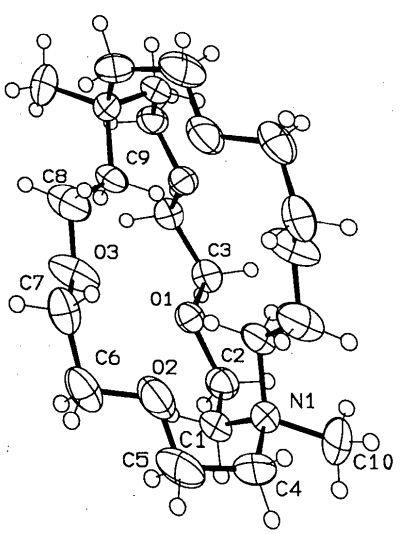

Fig. 1. View of $C_{20}H_{42}N_2O_6^{2+}$ showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.

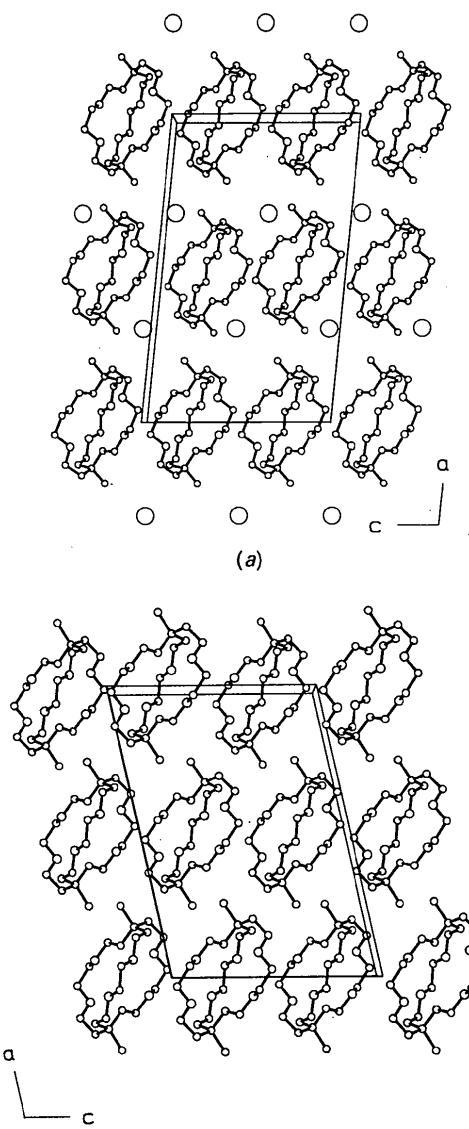

Fig. 2. Packing arrangement of (*a*) $C_{20}H_{42}N_2O_6^{2+}.2I^-$ and (*b*) $(C_{18}H_{36}N_2O_6)(BH_3)_2$.

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striking. They both crystallize in space group $C2/c$ with similar cell parameters [a = 18.849, b = 9.610, c = 13.291 Å, β = 102.25° for $(C_{18}H_{36}N_2O_6)(BH_3)_2$]. The macrobicyclic rings have the same conformation, and their packing arrangements are closely related. The addition of two bulky iodide anions per formula unit and the change from a crystal structure dominated by van der Waals interactions to an ionic structure produce only minor changes in the overall packing arrangement (Fig. 2). The monoclinic angle differs by 6° and the a axis is lengthened by 3.1 Å for the ionic compound relative to the bisborohydride, opening up interstices which are occupied by the iodide anion. It is rather surprising that a seemingly major change in the nature of the intermolecular forces affects the crystal structure to such a small extent, suggesting that ionic structures of this kind containing voluminous molecular species are dominated by packing optimization of these units rather than attractive or repulsive Coulombic interactions.

The non-bonding distance between the two N atoms across the macrobicyclic rings is 6.668 (4) Å, compared to 6.759 Å in $(C_{18}H_{36}N_2O_6)(BH_3)_2$, the change upon the introduction of positive charges at these atoms thus being small. The bond angles at the C1, C4 and C9 atoms are larger than expected for ideal tetrahedral geometry, indicating the presence of strain in the rings caused by the sp^3 hybridization of the bridgehead N atoms in combination with the *exo-exo* conformation. This confirms the recent findings of Suwińska (1992) for the closely related *N,N,N′,N′*-tetramethyldiazonia-18-crown-6 diiodide.

Experimental

Crystal data

$C_{20}H_{42}N_2O_6^{2+}.2I^-$
M_r = 660.36
Monoclinic
$C2/c$
a = 21.953 (5) Å
b = 8.961 (3) Å
c = 13.588 (3) Å
β = 96.07 (3)°
V = 2658.1 (12) Å^3
Z = 4
D_x = 1.650 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12-20°
μ = 2.400 mm^{-1}
T = 295.0 (5) K
Prism
0.76 × 0.38 × 0.18 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
Variable-speed $\omega/2\theta$ scans
Absorption correction: Gaussian
T_{min} = 0.9114, T_{max} = 0.3973
4798 measured reflections
2348 independent reflections
2178 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.0311
θ_{max} = 25.04°
$h = -25 \rightarrow 26$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 0$
2 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
Final R = 0.0298
wR = 0.0772
S = 1.165
2348 reflections
139 parameters
Calculated weights $w = 1/\{\sigma^2[F_o^2 + (0.0415P)^2] + 2.0246P\}$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.002
$\Delta\rho_{max}$ = 0.753 e Å^{-3}
$\Delta\rho_{min}$ = −0.873 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Refinement on F^2 for all reflections except those flagged for possible systematic errors; the observed threshold $F > 4\sigma(F)$ is used only for calculating R(obs.) *etc.*, given here for comparison with refinements on F. H atoms were treated as riding on their C atoms with a common isotropic displacement parameter for both CH_2 and CH_3 groups.

Data collection: CAD-4 software (Enraf-Nonius, 1989). Cell refinement: *CELDIM* (CAD-4 software). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *ORTEP* (Johnson, 1971). Software used to prepare material for publication: *SHELXL*92 (Sheldrick, 1992).

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

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
I1	0.692045 (9)	0.52585 (3)	0.442933 (15)	0.0521 (2)
N1	0.84859 (11)	0.5274 (3)	0.2598 (2)	0.0422 (12)
O1	0.94579 (8)	0.7916 (2)	0.30043 (14)	0.0424 (10)
O2	0.91981 (11)	0.2897 (3)	0.3783 (2)	0.0644 (15)
O3	1.04238 (13)	0.3807 (3)	0.4065 (2)	0.068 (2)
C3	0.96571 (13)	0.9144 (3)	0.2474 (2)	0.042 (2)
C2	0.88140 (13)	0.7954 (4)	0.3058 (2)	0.0456 (15)
C1	0.86009 (13)	0.6460 (4)	0.3394 (2)	0.0457 (15)
C9	1.09355 (14)	0.5021 (4)	0.2891 (2)	0.043 (2)
C4	0.82518 (14)	0.3853 (4)	0.3048 (3)	0.056 (2)
C8	1.0965 (2)	0.3715 (5)	0.3602 (3)	0.067 (2)
C5	0.8612 (2)	0.3279 (5)	0.3975 (3)	0.067 (2)
C6	0.9592 (2)	0.2574 (5)	0.4664 (2)	0.062 (2)
C7	1.0222 (2)	0.2409 (4)	0.4372 (2)	0.056 (2)
C10	0.7975 (2)	0.5779 (5)	0.1839 (3)	0.066 (2)

Table 2. *Geometric parameters* (Å, °)

N1—C9^i	1.511 (4)	O3—C8	1.404 (4)
N1—C10	1.512 (4)	O3—C7	1.407 (4)
N1—C1	1.519 (4)	C3—C3^i	1.500 (6)
N1—C4	1.525 (4)	C2—C1	1.505 (5)
O1—C3	1.410 (4)	C9—C8	1.515 (5)
O1—C2	1.424 (3)	C4—C5	1.505 (5)
O2—C5	1.382 (4)	C6—C7	1.486 (5)
O2—C6	1.430 (4)		
C9^i—N1—C10	110.1 (3)	O1—C3—C3^i	109.9 (2)
C9^i—N1—C1	109.5 (2)	O1—C2—C1	109.7 (2)
C10—N1—C1	109.4 (3)	C2—C1—N1	116.1 (2)
C9^i—N1—C4	112.7 (2)	N1^i—C9—C8	114.5 (3)
C10—N1—C4	105.5 (3)	C5—C4—N1	116.8 (3)
C1—N1—C4	109.6 (2)	O3—C8—C9	105.1 (3)
C3—O1—C2	111.8 (2)	O2—C5—C4	110.1 (3)
C5—O2—C6	112.6 (3)	O2—C6—C7	107.0 (3)
C8—O3—C7	112.9 (3)	O3—C7—C6	108.8 (3)
C10—N1—C1—C2	−62.8 (3)	C4—C5—O2—C6	170.5 (3)
N1—C1—C2—O1	−82.5 (3)	C5—O2—C6—C7	−171.6 (3)
C1—C2—O1—C3	165.8 (2)	O2—C6—C7—O3	67.9 (4)

C2—O1—C3—C3^{i}	174.2 (3)	C6—C7—O3—C8	−168.8 (3)
C10—N1—C4—C5	−167.6 (3)	C7—O3—C8—C9	151.6 (3)
N1—C4—C5—O2	−62.7 (4)	O3—C8—C9—N1^{i}	172.2 (3)

Symmetry code: (i) $2-x, y, \frac{1}{2}-z$.

Synthesis: 0.00797 mol (3 g) cryptand[2.2.2] were allowed to react with 0.017 mol (1.06 ml) methyl iodide in 30 ml methanol for 6 h. The solvent was evaporated *in vacuo* and the white product recrystallized from methanol and washed with dry diethyl ether, yielding 4.37 g (83%) of the title compound as colourless crystals.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55958 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1028]

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(*R*)-2-Bromo-1,4-butanedioic Acid

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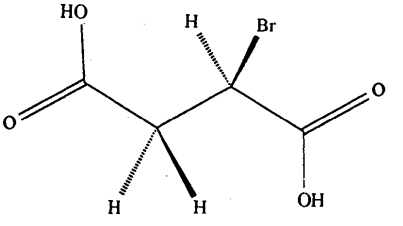
Abstract

The absolute configuration of (+)-bromosuccinic acid has been determined to be (*R*). Bond lengths and angles are normal.

Comment

Thiol and phosphine thiol complexes of gold(I) are used in the treatment of rheumatoid arthritis (Skosey, 1985). D-Penicillamine has similar efficacy and toxicity (Howard-Lock, Lock, Mewa & Kean, 1986). We have shown that this drug and other thiols inhibit activation of the protein kinase *C* pathway, the pathway of action in all inflammatory cells, in a similar fashion to the gold drug, disodium aurothiomalate (McKague, Lock, McCrae, Smith, Buchanan, Kean & Reglinski, 1993). These facts raise the question as to whether gold is a necessary constituent of the gold drugs or whether it is acting as an expensive carrier for the thiol ligand. Thus, we have been examining the biochemistry and structure of various thiol ligands, particularly the separate enantiomers of chiral molecules, since these can have dramatically different biological effects (Kean, Lock & Howard-Lock, 1991).



We attempted to synthesize the (*S*) enantiomer of thiomalic acid, from (−)-(*R*)-aspartic acid, by diazotization and bromination to give (*R*)-bromosuccinic acid, followed by reaction with *O*-ethyl dithiocarbonic acid in cold aqueous Na_2CO_3, to give (*S*)-2-(*O*-ethyl dithiocarbonato)succinic acid. Hydrolysis of the protected thiol group should give the desired compound. Structural studies showed that the protected compound was a racemate (Duarte, Frampton, Howard-Lock, Lock & Wu, 1989).

Diazotization reactions can proceed both by mechanisms where configuration is retained or where configuration is inverted; the configuration of the brominated product is very dependent on the reaction conditions (Brewster, Hughes, Ingold & Rao, 1950; Ingold, 1953). The reaction undertaken here had the important requirement for retention of configuration, namely an α-carboxyl group, and we conducted the preparation under conditions which should retain the configuration. We also wished to confirm that racemization had not taken place in this step of the reaction and to this end we determined the absolute configuration of the bromosuccinic acid.

All the crystals examined were twinned and a number were studied by X-ray diffraction before a suitable one was obtained. Even then, refinement showed that many of the reflections in the $k = 6$ layer had F_o much smaller than F_c, and the peak profiles showed a large and skewed background, suggesting overlap with the twinned reflections. Thus, all reflections from the $k = 6$ layer were omitted from the refinement.

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