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Recently, we have resorted to the related ability to staple the proton, and indirectly the bromide ion, in (–)-sparteinium bromide, (I), to resolve 1,2-dibromohexafluoropropane into single enantiomers (Farina *et al.*, 1999). This procedure relies on the self-assembly of the sparteinium bromide unit with one of the enantiomers of the perhalocarbon into a chiral cocrystal. Since the procedure is general, the crystal structure of (I) is reported herein to show how the interactions of additional species with the Br<sup>–</sup> ion influence the relation of the halide to the sparteinium ion.

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### (–)-Sparteinium bromide

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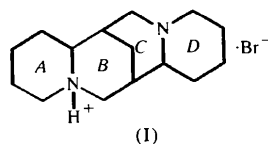
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#### Abstract

The title compound, (7*S*)-(7 $\alpha$ ,7 $\alpha$ ,14 $\alpha$ ,14 $\alpha$ )-1,3,4,7,7a,8,9,10,11,13,14,14a-dodecahydro-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1',2'-*e*][1,5]diazocin-5-ium bromide (C<sub>15</sub>H<sub>27</sub>N<sub>2</sub><sup>+</sup>·Br<sup>–</sup>), is an effective reagent for the resolution of chiral perhalocarbons. All four rings in the sparteinium ion adopt a chair conformation, allowing an intramolecular N—H···N hydrogen bond. Weak hydrogen-bond-like interactions between the cation and anion are apparent.

#### Comment

(–)-Sparteine is one of the best known members of the lupin alkaloids (Merck, 1989). It has been isolated from various *Lupinus* and *Cytisus* species and is widely distributed in the *Papilionaceae* (Hesse, 1981). From the pharmacological point of view, this alkaloid is endowed with oxytoxic activity, while from the chemical point of view it has been used effectively as a chiral catalyst and as a reagent in asymmetric synthesis (Hashihayata *et al.*, 1997; Nishimura *et al.*, 1997; Hoppe *et al.*, 1990). (–)-Sparteine has a semi-rigid structure; in the free base, ring *C* adopts a boat conformation but, upon chelation of a cation, inversion of configuration occurs on N16 and ring *C* adopts a chair conformation. In the resulting nest-like structure, the nitrogen lone pairs converge towards the centre of the molecular concavity, allowing an effective bidentate interaction with metal ions (Lopez *et al.*, 1998; Hoppe *et al.*, 1995; Motevalli *et al.*, 1993).



Consistent with the results and the literature data discussed by Kubicki *et al.* (1996), all four rings in the sparteinium ion of (I) adopt chair conformations, with the N16 configuration inverted with respect to that of the free base. In this conformation, the distance between N1 and N16 is 2.714 (8) Å, allowing an intramolecular hydrogen-bond interaction between N16 and the proton on N1 (Table 2). The structural and conformational features of the sparteinium ion in (I) are very similar to those found in the sparteinium hydrobromide–perhalocarbon cocrystal (Farina *et al.*, 1999). A significant difference is that the protonated nitrogen is N1 in the pure hydrobromide and N16 in the cocrystal. Shorter Br···N distances reasonably involve the protonated nitrogen, and accordingly the Br···N1 and the Br···N16 distances change from 3.552 (6) and 3.672 (6) in (I) to 3.622 (6) and 3.548 (6) Å in the cocrystal. Related minor differences involve the short quasi-hydrogen-bond interactions between cation H atoms and the bromide ion. Relevant parameters of these interactions for (I) are given in Table 2.

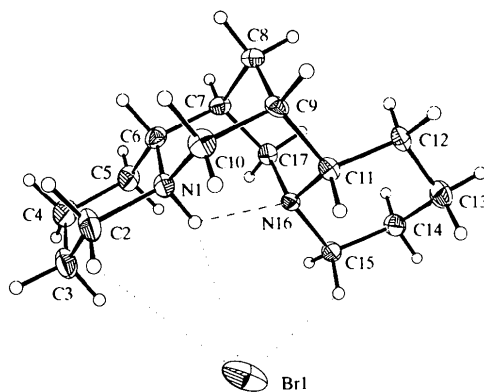


Fig. 1. A view of (I) showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 40% probability level, while H atoms are of an arbitrary size. Geometric parameters of the bromide ion interactions and of the hydrogen bond involving N16 are given in Table 2.

We conclude by noticing that the location of the bromide ion would be compatible with the transformation to a phase-centred orthorhombic lattice. Space group  $C222_1$  would be applicable, in principle, if the twofold rotor through C8, relating ring *B* of the sparteinium ion to ring *C*, applied also to rings *A* and *B*.

C17—N16—C11	114.7 (7)	C10—C9—C11	111.3 (7)
C17—N16—C15	111.3 (7)	C10—N1—C2	110.9 (7)
C11—N16—C15	110.8 (7)	C10—N1—C6	112.4 (6)
C12—C11—C9	113.6 (7)	C2—N1—C6	112.2 (6)
C6—C7—C17	114.0 (6)	C7—C6—C5	113.2 (7)
C7—C8—C9	107.0 (6)		
C15—N16—C11—C12	55.0 (10)	C2—N1—C6—C5	-56.2 (9)
N16—C11—C9—C10	67.4 (9)	C8—C7—C6—N1	-57.1 (8)
N16—C11—C9—C8	-54.6 (9)	C17—C7—C6—N1	65.0 (9)

## Experimental

The title compound was obtained by dissolving (–)-sparteine (Aldrich) and HBr in  $\text{CHCl}_3$  in a 1:1 ratio and subsequently removing the solvent under reduced pressure. The residue was recrystallized from  $\text{CHCl}_3$ /diisopropyl ether.

### Crystal data

$\text{C}_{15}\text{H}_{27}\text{N}_2^+\cdot\text{Br}^-$   
 $M_r = 315.30$   
 Monoclinic  
 $P2_1$   
 $a = 8.3779 (5) \text{ \AA}$   
 $b = 10.7496 (8) \text{ \AA}$   
 $c = 8.3805 (5) \text{ \AA}$   
 $\beta = 101.099 (6)^\circ$   
 $V = 740.62 (7) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.414 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Cu  $K\alpha$  radiation  
 $\lambda = 1.54178 \text{ \AA}$   
 Cell parameters from 30 reflections  
 $\theta = 11.1\text{--}16.6^\circ$   
 $\mu = 3.649 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Plate  
 $0.25 \times 0.20 \times 0.03 \text{ mm}$   
 Colourless

### Data collection

Siemens P4 diffractometer  
 $\theta/2\theta$  scan  
 Absorption correction:  
 by integration (XPREP;  
 Siemens, 1996)  
 $T_{\min} = 0.524$ ,  $T_{\max} = 0.894$   
 2649 measured reflections  
 1428 independent reflections  
 (plus 910 Friedel-related reflections)

1889 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$   
 $\theta_{\max} = 68^\circ$   
 $h = -10 \rightarrow 9$   
 $k = -10 \rightarrow 12$   
 $l = 0 \rightarrow 10$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: <0.5%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.079$   
 $wR(F^2) = 0.228$   
 $S = 1.099$   
 2338 reflections  
 164 parameters  
 H atoms riding  
 $w = 1/[\sigma^2(F_o^2) + (0.1515P)^2 + 0.5774P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.45 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.69 \text{ e \AA}^{-3}$

Extinction correction:  
 SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient:  
 $0.0027 (15)$   
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)  
 Absolute structure:  
 Flack (1983)  
 Flack parameter =  $-0.02 (6)$

Table 2. Bromide ion contact and hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D\cdots H\cdots A$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ Br1	2.92	3.552 (6)	128
C2—H2B $\cdots$ Br1	3.05	3.674 (7)	121
C15—H15B $\cdots$ Br1	3.06	3.778 (7)	132
N1—H1 $\cdots$ N16	2.10	2.714 (8)	124

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SIR97 (Altomare *et al.*, 1994). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTL/PC (Sheldrick, 1994). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1317). Services for accessing these data are described at the back of the journal.

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Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

N16—C17	1.481 (10)	C10—N1	1.480 (11)
N16—C11	1.486 (11)	N1—C2	1.488 (9)
N16—C15	1.494 (10)	N1—C6	1.502 (10)