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2-Aminoperimidinium Bromide Dihydrate

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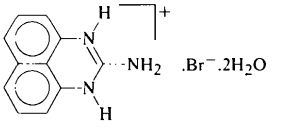
Abstract

The title compound, $C_{11}H_{10}N_3^+.Br^-.2H_2O$, is essentially planar along the aminoperimidine skeleton, with an r.m.s. deviation of 0.009 Å and a maximum deviation of 0.017 Å. Due to the presence of two water molecules, extensive hydrogen bonding exists in the crystal. Hydrogen bonds *via* the two water molecules join the Br^- ion to both the amine N atom and one of the ring N atoms. The other ring N atom and the amine N atom also form hydrogen bonds to the Br^- ion from the second molecule in the unit cell.

Comment

It is known that 2-aminoperimidylammonium chloride is an excellent reagent for the removal of sulfate ions (Stephen, 1970). However, the synthesis of this compound is inconvenient, and the purification procedure described by Stephen (1970) does not remove every trace of sulfur-containing impurities from the product (McClure, 1973). A synthetic method for the preparation of the bromide salt, free of sulfate impurities, is given by McClure (1973) and is suggested to be a simpler preparation of the sulfate-removing reagent. For experimental purposes, it was desired by one of the authors (CEM) to prepare a polymer of this compound to remove sulfate from water. It was also desired that the polymer be easy to handle and reusable. Such a polymer was prepared, but it retained sulfate too strongly to be regenerated efficiently. Subsequent work on the polymer has provided a way to regenerate the polymer and will be reported at a future date.

The crystal structure of the title compound, (I), was determined by three-dimensional X-ray diffraction analysis in order to study possible sulfate binding sites. An unsuccessful attempt was made to complex the title compound with sulfate using a gel-permeation technique in order to determine exactly how and where the compound binds to sulfate.



(I)

The plane defined by all the non-H atoms in the aminoperimidine skeleton displayed a maximum deviation of 0.017 Å for atom N1 and an r.m.s. deviation of

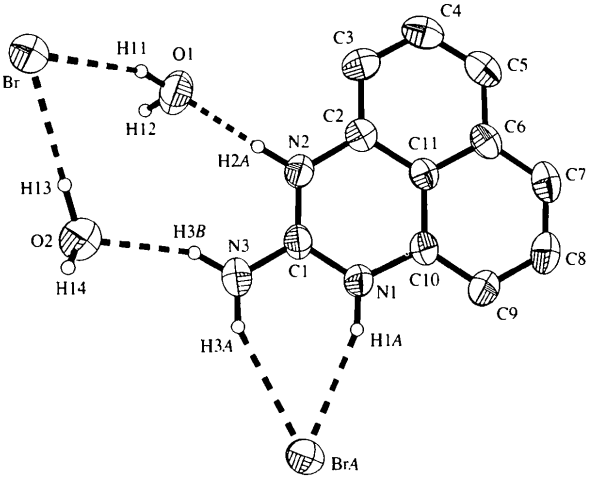


Fig. 1. View of the title compound. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small spheres of arbitrary radii.

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0.009 Å. Thus, the cation possesses near C_{2v} symmetry. Other deviations were Br at 1.939 (4), O1 at −0.124 (4) and O2 at 0.579 (4) Å.

Due to the presence of the two water molecules, several hydrogen bonds occur. As shown in Fig. 1, these hydrogen bonds join the Br^- ion to the N2 and N3 atoms *via* the two water molecules. The H atoms bound to the N1 and N3 atoms also bind to the Br^- ion translated one unit in the *y* direction.

Experimental

The title compound was obtained from the Aldrich Chemical Co. and crystals were grown by slow evaporation of an aqueous solution.

Crystal data

$C_{11}H_{10}N_3^+.Br^-.2H_2O$
M_r = 300.16
Triclinic
$P\bar{1}$
a = 7.1560 (10) Å
b = 8.599 (4) Å
c = 11.060 (4) Å
α = 100.02 (3)°
β = 104.81 (2)°
γ = 96.20 (3)°
V = 639.6 (4) Å^3
Z = 2
D_x = 1.559 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 5.6–12.2°
μ = 3.208 mm^{-1}
T = 288 (2) K
Prism
0.58 × 0.28 × 0.19 mm
Colorless

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: six ψ scans, 10° steps (Siemens, 1991*a*)
T_{min} = 0.16, T_{max} = 0.54
4501 measured reflections
2266 independent reflections
1720 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0307
θ_{max} = 25.05°
h = −8 → 8
k = −10 → 10
l = −13 → 13
3 standard reflections monitored every 50 reflections
intensity decay: average 2.5% in $\sigma(I)$

Refinement

Refinement on F^2
$R(F)$ = 0.0364
$wR(F^2)$ = 0.0777
S = 1.036
2257 reflections
166 parameters
H atoms riding (included in least-squares refinement with C—H 0.96, O—H 1.00 and N—H 0.90 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.1304P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.289 e Å^{-3}
$\Delta\rho_{min}$ = −0.280 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Br	0.3419 (1)	−0.2366 (1)	0.5796 (1)	0.060 (1)
O1	0.1042 (4)	0.0100 (3)	0.7289 (3)	0.061 (1)
O2	0.2427 (4)	0.0931 (3)	0.4680 (3)	0.062 (1)
N1	0.2870 (4)	0.5927 (3)	0.8210 (2)	0.039 (1)
N2	0.2092 (4)	0.3313 (3)	0.8368 (2)	0.040 (1)
N3	0.2334 (4)	0.3913 (3)	0.6455 (3)	0.053 (1)
C1	0.2424 (5)	0.4364 (4)	0.7675 (3)	0.038 (1)
C2	0.2161 (4)	0.3754 (4)	0.9664 (3)	0.037 (1)
C3	0.1798 (5)	0.2649 (4)	1.0363 (3)	0.046 (1)
C4	0.1894 (5)	0.3180 (5)	1.1651 (4)	0.053 (1)
C5	0.2329 (5)	0.4767 (5)	1.2231 (3)	0.051 (1)
C6	0.2704 (4)	0.5932 (4)	1.1530 (3)	0.040 (1)
C7	0.3151 (5)	0.7597 (4)	1.2050 (3)	0.050 (1)
C8	0.3466 (5)	0.8655 (4)	1.1311 (3)	0.052 (1)
C9	0.3371 (5)	0.8135 (4)	1.0015 (3)	0.045 (1)
C10	0.2970 (4)	0.6533 (4)	0.9499 (3)	0.037 (1)
C11	0.2623 (4)	0.5405 (3)	1.0231 (3)	0.033 (1)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.339 (4)	N1—C10	1.411 (4)
N2—C1	1.323 (4)	N2—C2	1.404 (4)
N3—C1	1.320 (4)	C2—C3	1.369 (4)
C2—C11	1.414 (4)	C3—C4	1.399 (5)
C4—C5	1.368 (5)	C5—C6	1.413 (5)
C6—C11	1.414 (4)	C6—C7	1.415 (5)
C7—C8	1.362 (5)	C8—C9	1.407 (5)
C9—C10	1.365 (4)	C10—C11	1.408 (4)
N3—C1—N2	121.6 (3)	C5—C6—C11	118.1 (3)
N2—C1—N1	120.0 (3)	C11—C6—C7	118.0 (3)
C3—C2—C11	120.7 (3)	C7—C8—C9	121.4 (3)
C2—C3—C4	118.8 (3)	C9—C10—C11	121.4 (3)
C4—C5—C6	120.1 (3)	C11—C10—N1	116.8 (3)
C5—C6—C7	123.9 (3)	C10—C11—C6	119.7 (3)
C8—C7—C6	120.7 (3)	C1—N1—C10	122.9 (3)
C10—C9—C8	118.8 (3)	C1—N1—H1*A*	118.6 (2)
C9—C10—N1	121.9 (3)	C10—N1—H1*A*	118.6 (2)
C10—C11—C2	120.2 (3)	C1—N2—C2	123.0 (3)
C2—C11—C6	120.1 (3)	C1—N2—H2*A*	118.6 (2)
N3—C1—N1	118.5 (3)	C2—N2—H2*A*	118.5 (2)
C3—C2—N2	122.1 (3)	C1—N3—H3*A*	118.9 (2)
N2—C2—C11	117.2 (3)	C1—N3—H3*B*	121.1 (2)
C5—C4—C3	122.2 (3)	H3*A*—N3—H3*B*	120.0

Hydrogen-bonding geometry

Br···H11	2.348 (7)	Br···H3A^i	2.627 (3)
Br···H13	2.358 (3)	O1···H2*A*	1.854 (3)
Br···H1A^i	2.491 (3)	O2···H3*B*	2.153 (4)
H11···Br···H13	64 (1)	O1···H2*A*—N2	174.7 (1)
H1A^i···Br···H3A^i	51.32 (8)	N3—H3A···Br^{ii}	153.31 (6)
Br···O1···H2*A*	128.0 (2)	O2···H3*B*—N3	149.5 (1)
H3*B*···O2—H13	113 (2)	Br···H11—O1	168 (2)
N1—H1A···Br^{ii}	159.38 (5)	Br···H13—O2	178 (3)

Symmetry codes: (i) $x, y-1, z$; (ii) $x, 1+y, z$.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991*a*). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC* and *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(4-Nitrophenyl)-4-piperidinol

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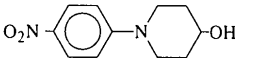
Abstract

The title compound, $C_{11}H_{14}N_2O_3$, is a non-linear optical chromophore. The piperidinol ring is in a chair conformation. The C—N—C fragment of the piperidinol moiety is nearly coplanar with the nitrophenyl ring system. The molecular stacking allows hydrogen bonding between the piperidinol hydroxy group and the nitro group.

Comment

The present study is part of a program designed to investigate the structure–property relationships among non-linear optical (NLO) materials. Organic NLO materials have potential for use in optical limiting devices for applications in sensor protection, optical storage devices and waveguides (Prasad & Williams, 1991). Owing to their versatility of chemical synthesis, organic materials are increasingly being investigated for their NLO properties (Prasad & Williams, 1991; Hann & Bloor, 1991; Chemla & Zyss, 1987; Miyata, 1992). Organic structures are versatile because they may be grown as single crystals, as Langmuir–Blodgett films or incorporated as chromophoric mesogens in polymer systems (Prasad & Williams, 1991).

Second-order NLO effects are highly dependent on the geometrical arrangement of the molecules in the crystal phase. For a crystalline material to exhibit second-order optical non-linearity, the crystal must be non-centrosymmetric (Prasad & Williams, 1991; Hann & Bloor, 1989). The present crystals, (I), are centrosymmetric and therefore do not exhibit NLO behavior. The production of a non-centrosymmetric material by using the compound as a chromophoric mesogen on a polymer backbone is being investigated. Molecular substitution on the piperidinol moiety is also being investigated, but the substituent must not interfere with the molecular features responsible for the optical non-linearity (Zyss & Oudar, 1982).



(I)

Bond lengths and angles in the nitrophenyl group are consistent with those of both nitrobenzene itself (Trotter, 1959) and the nitrophenyl moiety found in related compounds (Fkyerat *et al.*, 1995; Ishihara *et al.*, 1992; Hall *et al.*, 1986; Twieg & Dirk, 1986). Bond lengths and angles in the piperidinol ring are consistent with those of piperidine (Suwinska, Palenik & Gerdil, 1986). The piperidinol moiety adopts a chair conformation

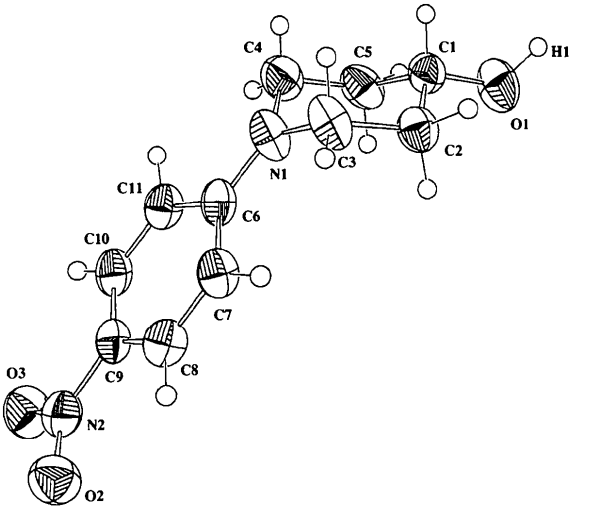


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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