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(1*R*,2*R*)-1,2-Diphenyl-1,2-ethanediamine Monohydrobromide

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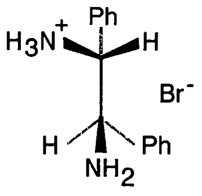
Abstract

The cation in (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediamine monohydrobromide has approximate twofold symmetry and is involved in a three-dimensional hydrogen-bond network with the bromide anion [H···Br 2.51(4)-2.82(3), N···Br 3.279(2)-3.560(3) Å]. Principal bond lengths include Csp^3—Csp^3 1.535(4), Csp^3—NH_3^+ 1.489(3), Csp^3—NH_2 1.469(4), and Csp^3—C_{ar} 1.517(3) and 1.528(3) Å. The main torsion angles defining the conformation are NH_3^+—Csp^3—Csp^3—NH_2 −44.3(2) and C_{ar}—Csp^3—Csp^3—C_{ar} 64.3(2)°. The absolute stereochemistry (known on chemical grounds) was confirmed by the analysis.

Comment

(1*R*,2*R*)-1,2-Diphenyl-1,2-ethanediamine monohydrobromide is a versatile chiral auxiliary (Corey, Imwinkelreid, Pikul & Xiang, 1989) that has also been investigated as a chiral solvating agent in NMR spectroscopy (Fullwood & Parker, 1992). It forms 2:1 complexes with a wide range of chiral carboxylic acids (e.g. α-arylpropionic, α-halo- and α-deuteriocarboxylic acids) in which sufficient ^1H NMR chemical shift non-equivalence is observed to allow the direct measurement of the enantiomeric purity of the acid.

The structure of the monohydrobromide salt (I) was undertaken to establish the geometry of the quaternary ammonium cation and investigate the three-dimensional hydrogen-bonding network in the lattice. Suitable crystals were grown by slow evaporation of an isopropyl alcohol-isopropyl ether solution.



(I)

The absolute configuration of the cation was established by the analysis (see *Experimental*) and is in agreement with that deduced chemically. The cation (see scheme above and Fig. 1) has approximate twofold symmetry through the midpoint of the C(1)—C(2) bond and the conformation about the central C—C bond has the C—H H atoms fully staggered, with torsion angles N(1)—C(1)—C(2)—N(2) -44.3(2), C(11)—C(1)—C(2)—C(21) 64.3(2) and H(1)—C(1)—C(2)—H(2) −173(2)°.

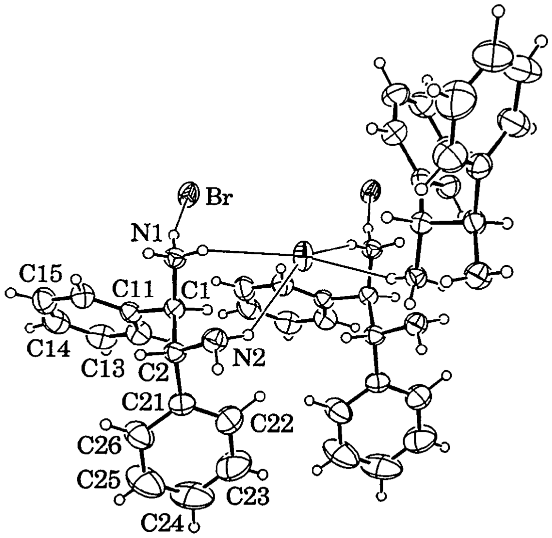


Fig. 1. A view of three formula units showing the general conformation, the intermolecular hydrogen bonding and the numbering scheme. The non-H atoms are shown with ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size.

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The bromide ion takes part in four N—H···Br hydrogen bonds (see Fig. 1) with three adjacent cations [H···Br 2.51(4)-2.82(3), N···Br 3.279(2)-3.560(3) Å]. The one N—H bond [N(2)—H(2*B*)] not involved in N—H···Br hydrogen bonding is oriented towards the π-cloud of a neighbouring phenyl ring C(11)—C(16) of an adjacent cation [H(2*B*)···C(13) 2.89(3) Å].

The present structural determination is the most precisely determined (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediamine derivative studied thus far. The principal bond lengths in the cation (Table 2) are essentially as anticipated with Csp^3—Csp^3 1.535(4), Csp^3—NH_3^+ 1.489(3), Csp^3—NH_2 1.469(4), Csp^3—C_{ar} 1.517(3) and 1.528(3), aromatic C—C 1.363(7)-1.395(4) [average 1.382(4)], N—H 0.78(4)-0.92(3) [average 0.85(4)] and C—H 0.86(4)-1.02(3) [average 0.96(3) Å], *i.e.* the typical ranges found by X-ray methods.

A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) yielded only five structures which contain the 1,2-diphenyl-1,2-ethanediamine [$(PhCNH_2)_2$] fragment; all were metal complexes and none involved a monoammonium salt. Four of the complexes were racemic [aquabis(*meso*-1,2-diphenylethane-1,2-diamine-*N*,*N*′)nitronickel(II) and bis(*meso*-1,2-diphenyl-1,2-ethanediamine-*N*,*N*′)(nitrito-*O*,*O*′)nickel(II) chloride (Finney, Hitchman, Raston, Rowbottom & White, 1981); bis(*meso*-1,2-diphenyl-1,2-ethanediamine-*N*,*N*′)-nickel(II) dichloride dihydrate (García-Granda & Gómez-Beltrán, 1984); bis(acetato-*O*)(*meso*-1,2-diphenyl-1,2-ethanediamine-*N*,*N*′)nickel(II) trihydrate (García-Granda, Díaz & Gómez-Beltrán, 1991)]. The fifth complex [(+)-tris[(−)-1,2-diphenylethylenediamine]-cobalt(III) nitrate monohydrate (Kuroda & Mason, 1977)] is chiral and the ligand has the *S*,*S* configuration. The N—C—C—N torsion angles in the complexes are in the range 35(1)-58(1)°.

Experimental

Crystal data

$C_{14}H_{17}N_2^+.Br^-$
M_r = 293.20
Monoclinic
$P2_1$
a = 6.1749 (4) Å
b = 8.0494 (4) Å
c = 14.0057 (5) Å
β = 96.078 (4)°
V = 692.23 (6) Å^3
Z = 2
D_x = 1.407 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.70930 Å
Cell parameters from 25 reflections
θ = 15.00-20.00°
μ = 2.92 mm^{-1}
T = 293 K
Plate
0.12 × 0.25 × 0.55 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.3107, T_{max} = 0.5302
2997 measured reflections
2866 independent reflections

2578 observed reflections [$I_{net} > 3.0\sigma(I_{net})$]
R_{int} = 0.008
θ_{max} = 26.91°
$h = 0 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity variation: 2.5%

Refinement

Refinement on F
Final R = 0.021
wR = 0.026
S = 1.09
2578 reflections
222 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F)+0.0004F^2]$
$(\Delta/\sigma)_{max}$ = 0.003

$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 3075(389)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	U_{eq}
Br	0.37639 (3)	0.00000	0.994824 (15)	0.04367 (12)
N(1)	0.1306 (3)	0.3485 (3)	0.03900 (13)	0.0333 (8)
N(2)	0.1801 (5)	0.6511 (3)	0.12321 (18)	0.0409 (13)
C(1)	0.1918 (4)	0.3495 (3)	0.14472 (18)	0.0320 (10)
C(11)	0.0964 (3)	0.20056 (24)	0.19176 (16)	0.0333 (9)
C(12)	0.2225 (4)	0.1178 (3)	0.26511 (17)	0.0445 (11)
C(13)	0.1358 (5)	−0.0166 (5)	0.31114 (17)	0.0522 (14)
C(14)	−0.0736 (5)	−0.0690 (4)	0.28361 (19)	0.0526 (13)
C(15)	−0.1995 (4)	0.0112 (6)	0.21076 (17)	0.0501 (13)
C(16)	−0.1146 (4)	0.1471 (3)	0.16541 (18)	0.0419 (11)
C(2)	0.1209 (3)	0.5154 (4)	0.18564 (13)	0.0342 (9)
C(21)	0.2086 (4)	0.53170 (25)	0.29143 (15)	0.0382 (11)
C(22)	0.4186 (5)	0.5824 (4)	0.31980 (21)	0.0566 (15)
C(23)	0.4930 (7)	0.6004 (5)	0.4159 (3)	0.0771 (20)
C(24)	0.3557 (7)	0.5679 (7)	0.48433 (22)	0.091 (3)
C(25)	0.1472 (6)	0.5179 (9)	0.45749 (20)	0.088 (3)
C(26)	0.0730 (4)	0.4976 (7)	0.36117 (16)	0.0602 (14)

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

N(1)—C(1)	1.489 (3)	C(15)—C(16)	1.395 (4)
N(2)—C(2)	1.469 (4)	C(2)—C(21)	1.528 (3)
C(1)—C(11)	1.517 (3)	C(21)—C(22)	1.377 (4)
C(1)—C(2)	1.535 (4)	C(21)—C(26)	1.380 (3)
C(11)—C(12)	1.391 (3)	C(22)—C(23)	1.383 (4)
C(11)—C(16)	1.384 (3)	C(23)—C(24)	1.370 (6)
C(12)—C(13)	1.395 (4)	C(24)—C(25)	1.363 (7)
C(13)—C(14)	1.376 (4)	C(25)—C(26)	1.388 (4)
C(14)—C(15)	1.376 (4)		
N(1)—C(1)—C(11)	110.97 (21)	N(2)—C(2)—C(1)	109.00 (19)
N(1)—C(1)—C(2)	108.89 (20)	N(2)—C(2)—C(21)	115.35 (23)
C(11)—C(1)—C(2)	112.71 (20)	C(2)—C(21)—C(22)	122.10 (21)
C(1)—C(11)—C(12)	119.11 (21)	C(2)—C(21)—C(26)	119.32 (21)
C(1)—C(11)—C(16)	121.84 (21)	C(1)—C(2)—C(21)	110.54 (21)
C2—C1—C11—C12	−98.0 (2)	C1—C2—C21—C22	81.4 (2)
C2—C1—C11—C16	80.3 (2)	C1—C2—C21—C26	−99.7 (3)
N1—C1—C2—N2	−44.3 (2)	H1—C1—C2—H2	−173 (2)
C11—C1—C2—C21	64.3 (2)		

Br—N(1)^{i}	3.346 (2)	Br—N(1)^{iii}	3.359 (2)
Br—N(1)^{ii}	3.279 (2)	Br—N(2)^{iii}	3.560 (3)

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

Data collection and cell refinement: Enraf-Nonius CAD-4 software. Data reduction program used to solve and refine structure, software used to prepare material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The *ORTEP* diagram was prepared using *ORTEPII* (Johnson, 1976).

The θ-scan width was $(0.8+0.35\tan\theta)^\circ$ with a θ-scan rate of 5.79° min^{-1} and background counts for 5 s on each side of every scan.

The absolute configuration was determined unequivocally by refinement of the chirality value η to a value of +1.02(2) (Rogers, 1981). Least-squares refinement (with η fixed at 1.00) and subsequent analysis of the reflections for which the Bijvoet differences were most significant readily demonstrated that this is the correct model. Of the top 144 pairs of Bijvoet reflections, none was in disagreement with the model. The absorption correction (ψ scans) using nine strong low-angle (χ values close to 90°) reflections, on the full dataset using the *NRCVAX* programs, lowered the R factor from 0.060 to 0.021. All H atoms were refined isotropically and gave reasonable U values and dimensions.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55474 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1027]

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Structure of 3,6-Bis(dimethylamino)-2,5-diisopropylthieno[3,2-*b*]thiophene

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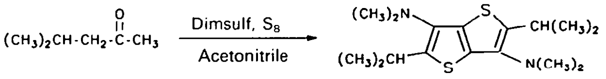
Abstract

The bicyclic thieno[3,2-*b*]thiophene skeleton of the title compound has an inversion centre and is exactly planar. The two C—S bond lengths differ by a small but significant amount (0.032 Å) and are somewhat longer than the standard C—S value. All other bond distances and bond angles are in the expected ranges.

Comment

Substituted acetophenones react with the 1:1 addition compound of dimethylamine and sulfur dioxide (dimsulf) to yield dark red betaines (Matschiner, Maschmeier & Hansen, 1992). We have determined the structure of 2-(*N*,*N*-dimethyliminio)-2-phenyldithioacetate (Heinemann, Hartung, Hansen, Maschmeier & Matschiner, 1992) formed by this reaction. In contrast to the previous results, under the same reaction conditions isobutyl methyl ketone (1) gave the white 3,6-bis(dimethylamino)-2,5-diisopropylthieno[3,2-*b*]thiophene (2) rather than a betaine.



(1) (2)

Fig. 1. shows the molecular structure of (2). As the molecule has an inversion centre in the middle of the C1—C1′ bond and the thiophene ring is planar to within experimental error, the whole thienothiophene skeleton is also planar. In addition, the attached atoms N1 and C6 deviate only very slightly [0.024 (1) and 0.027 (2) Å respectively] from the ring plane. Both C—S bonds [C1—S1 = 1.728 (2), C5—S1 = 1.750 (2) Å] are somewhat longer than the standard value [1.712 (13) Å] derived from the structures of 60 thiophene derivatives (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). All other dimensions of the ring system agree well with those expected and are in complete agreement with corre-

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