C2—N1—C2′	113 (2)	N1—C2′—C3′	112 (2)
N1—C2—C3	111 (2)	C2′—C3′—C5′	109 (2)
C2—C3—C5	108 (2)	C2′—C3′—O4′	109 (2)
C2—C3—O4	111 (2)	O4′—C3′—C5′	107 (2)
O4—C3—C5	111 (2)	C3′—C5′—C10′	114 (2)
C3—C5—C10	115 (2)	C3′—C5′—O6′	103 (2)
C3—C5—O6	104 (2)	O6′—C5′—C10′	106 (2)
O6—C5—C10	109 (2)	C5′—O6′—C7′	112 (2)
C5—O6—C7	116 (2)	O6′—C7′—C11′	109 (2)
O6—C7—C11	113 (2)	O6′—C7′—C8′	126 (2)
O6—C7—C8	127 (2)	C8′—C7′—C11′	125 (2)
C8—C7—C11	120 (2)	C7′—C8′—C14′	120 (2)
C7—C8—C14	119 (2)	C7′—C8′—C9′	120 (2)
C7—C8—C9	115 (2)	C9′—C8′—C14′	120 (2)
C9—C8—C14	125 (2)	C8′—C9′—C10′	111 (2)
C8—C9—C10	111 (2)	C5′—C10′—C9′	108 (2)
C5—C10—C9	109 (2)	C7′—C11′—C12′	117 (2)
C7—C11—C12	122 (2)	C11′—C12′—C13′	118 (2)
C11—C12—C13	115 (2)	C12′—C13′—F15′	121 (2)
C12—C13—F15	118 (3)	C12′—C13′—C14′	126 (2)
C12—C13—C14	124 (3)	C14′—C13′—F15′	113 (2)
C14—C13—F15	118 (3)	C8′—C14′—C13′	114 (2)
C8—C14—C13	120 (2)		

C2—N1—C2′—C3′	−176 (2)	O4—C3—C5—O6	65 (2)
C2′—N1—C2—C3	180 (2)	N1—C2′—C3′—C5′	−169 (2)
N1—C2—C3—C5	−179 (2)	O4′—C3′—C5′—O6′	169 (2)

The structure of (I) was solved by direct methods and that of (II) by a combination of Patterson functions and direct methods. Refinement was by full-matrix least-squares methods. H atoms were calculated, where possible, at geometrical positions. The hydroxyl H atoms in (I) were obtained from a difference Fourier synthesis and in (II) neither the hydroxyl nor the water H atoms could be located. Data collection: *DIF*4 (Stoe & Cie, 1985a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1985b). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980) for compound (1); *DIRDIF* (Beurskens *et al.*, 1992) for compound (II). Program(s) used to refine structure: *NRC-VAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983a).

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 71448 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1052]

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Structure and Absolute Configuration of (−)-(RS)-α-[(Benzylamino)methyl]-6-fluoro-3,4-dihydro-2H-1-benzopyran-2-methanol Hydrobromide†

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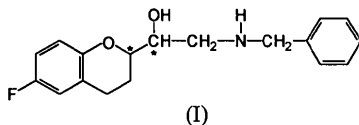
Abstract

The asymmetric unit of the title compound, $C_{18}H_{20}FNO_2^+ \cdot Br^-$, contains two molecules. The conformation of the bridging chain between the two rings is antiperiplanar/antiperiplanar/antiperiplanar in molecule *A* and antiperiplanar/synclinal/antiperiplanar in molecule *B*. The heterocyclic ring of the dihydrobenzopyran rings adopts a conformation halfway between a half-chair and an envelope with an apex at C10. The structure is stabilized by a network of hydrogen bonds between N, O and Br atoms. The absolute configuration is *R* for the asymmetric C atom in the dihydropyran ring and *S* for the hydroxyl-bearing C atom.

Comment

The title compound, (I).HBr, with two asymmetric C atoms, is a key intermediate in the synthesis of the ten possible isomers of α,α'-[iminobis(methylene)]bis(6-fluoro-3,4-dihydro-2H-1-benzopyran-2-methanol) (Van Lommen, De Bruyn & Schroven, 1990). The mixture containing equal amounts of $(-)$-$(RSSS)$ and $(+)$-$(SRRR)$ configurations of the latter compound is called nebivolol (Janssen, 1991).

(I)

To confirm the absolute configuration of $(+)$-$(SRRR)$-nebivolol hydrobromide dihydrate (Peeters, Blaton & De Ranter, 1993), the structure and absolute configuration of the title compound were determined. The asymmetric unit contains two molecules and the corresponding bond lengths do not deviate significantly from each other or from those in other closely related structures (Peeters, Verlinde, Blaton & De Ranter, 1989; Peeters et al., 1993). The differences in equivalent bond angles can be discussed in the same way as in the nebivolol paper (Peeters et al., 1993). The conformation of the chain between the two rings is antiperiplanar/antiperiplanar/antiperiplanar in molecule A and antiperiplanar/synclinal/antiperiplanar in molecule B. The molecules in the unit cell are stabilized by a hydrogen-bonding network involving N, O and Br atoms. Chains are formed in the a and b directions. The absolute configuration was determined by calculating the Bijvoet coefficient according to a selection procedure of Beurskens, Noordik & Beurskens (1980). For the configuration with C5 = R and C3 = S the Bijvoet coefficient was exactly 1 for the 213 most significant Friedel pairs. This confirms that $(-)$-nebivolol has the $(RSSS)$ configuration.
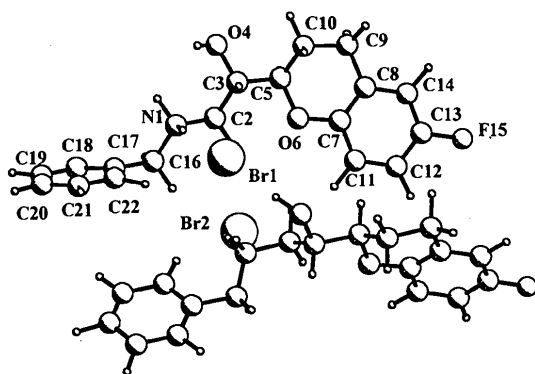
Experimental

Crystal data

$C_{18}H_{20}FNO_2^+.Br^-$
$M_r = 382.27$
Monoclinic
$P2_1$
$a = 7.672$ (4) Å
$b = 15.37$ (2) Å
$c = 15.053$ (9) Å
$\beta = 90.54$ (5)°
$V = 1774$ (2) Å^3
$Z = 4$
$D_x = 1.431$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10$-12.5°
$\mu = 2.309$ mm^{-1}
$T = 293$ K
Thin plate
$0.84 \times 0.40 \times 0.08$ mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω scans (0.8-2.4° min^{-1})
Absorption correction: empirical (EMPIR, Stoe & Cie, 1988b)
$T_{min} = 0.293$, $T_{max} = 0.589$
13 012 measured reflections
5960 independent reflections

4688 observed reflections
[$I > 2.0\sigma(I)$]
$R_{int} = 0.0440$
$\theta_{max} = 24.95°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = -17 \rightarrow 17$
4 standard reflections
frequency: 60 min
intensity variation: 4.6%

Refinement

Refinement on F
$R = 0.0538$
$wR = 0.0424$
$S = 1.55$
4688 reflections
414 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.00020F^2]$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction: none

Atomic scattering factors from International Tables for X-ray Crystallography [1974, Vol. IV, Tables 2.2B, 2.3.1 (Br, N, C, O, F), 2.2B (H)]
Absolute configuration: the Bijvoet coefficient was between 0.9665(3) and exactly 1 for 917 and 213 selected Bijvoet pairs, respectively.

Fig. 1. PLUTO diagram (Motherwell & Clegg, 1978) of both molecules with atom-numbering scheme for molecule A only.

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

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

	x	y	z	U_{eq}
Br1	0.50952 (7)	0.24340	0.48384 (5)	0.0590 (3)
Br2	0.00194 (8)	0.41421 (5)	0.52239 (5)	0.0657 (3)
N1	0.5482 (5)	0.4515 (3)	0.5583 (3)	0.041 (2)
C2	0.4724 (8)	0.4868 (4)	0.4741 (4)	0.047 (2)
C3	0.5966 (7)	0.4750 (4)	0.3977 (4)	0.045 (2)
O4	0.7439 (5)	0.5313 (3)	0.4078 (3)	0.059 (1)
C5	0.5140 (9)	0.4945 (6)	0.3074 (4)	0.057 (3)
O6	0.3564 (5)	0.4424 (3)	0.3058 (3)	0.056 (2)
C7	0.2825 (7)	0.4251 (4)	0.2240 (4)	0.046 (2)
C8	0.3603 (8)	0.4432 (5)	0.1446 (4)	0.058 (3)
C9	0.538 (1)	0.4851 (6)	0.1438 (5)	0.083 (3)
C10	0.6307 (8)	0.4721 (5)	0.2323 (4)	0.069 (3)
C11	0.1201 (7)	0.3841 (4)	0.2279 (4)	0.052 (2)
C12	0.0348 (8)	0.3623 (4)	0.1494 (5)	0.059 (2)
C13	0.1127 (9)	0.3839 (5)	0.0715 (5)	0.068 (3)
C14	0.2736 (8)	0.4230 (5)	0.0662 (4)	0.066 (2)
F15	0.0288 (5)	0.3639 (3)	-0.0064 (3)	0.103 (2)
C16	0.4299 (8)	0.4585 (5)	0.6346 (5)	0.061 (3)

C17	0.5060 (7)	0.4215 (5)	0.7186 (4)	0.052 (2)
C18	0.5331 (9)	0.4728 (4)	0.7933 (5)	0.063 (3)
C19	0.600 (1)	0.4379 (7)	0.8704 (4)	0.081 (3)
C20	0.642 (1)	0.3519 (8)	0.8753 (5)	0.107 (5)
C21	0.611 (2)	0.3003 (7)	0.8039 (7)	0.132 (5)
C22	0.547 (1)	0.3343 (6)	0.7255 (5)	0.098 (4)
N31	0.0919 (6)	0.2068 (3)	0.5272 (3)	0.046 (2)
C32	0.0494 (8)	0.2139 (4)	0.4292 (4)	0.048 (2)
C33	0.0737 (7)	0.1287 (4)	0.3803 (4)	0.044 (2)
O34	0.2536 (5)	0.1017 (2)	0.3813 (2)	0.055 (1)
C35	0.0170 (7)	0.1407 (4)	0.2829 (4)	0.048 (2)
O36	−0.1590 (5)	0.1721 (3)	0.2880 (3)	0.061 (2)
C37	−0.2541 (8)	0.1739 (4)	0.2096 (4)	0.051 (2)
C38	−0.2001 (8)	0.1317 (4)	0.1339 (4)	0.058 (2)
C39	−0.0313 (9)	0.0814 (6)	0.1318 (4)	0.082 (3)
C40	0.0252 (8)	0.0599 (4)	0.2282 (4)	0.064 (2)
C41	−0.4124 (8)	0.2165 (4)	0.2153 (4)	0.056 (2)
C42	−0.5212 (8)	0.2185 (5)	0.1395 (5)	0.073 (3)
C43	−0.463 (1)	0.1787 (5)	0.0648 (5)	0.072 (3)
C44	−0.3082 (9)	0.1384 (5)	0.0588 (4)	0.068 (3)
F45	−0.5695 (7)	0.1824 (4)	−0.0089 (3)	0.116 (2)
C46	−0.0516 (8)	0.1762 (5)	0.5828 (5)	0.052 (3)
C47	−0.0091 (9)	0.1801 (5)	0.6801 (4)	0.050 (3)
C48	−0.0480 (9)	0.1125 (5)	0.7346 (5)	0.069 (3)
C49	−0.014 (1)	0.1166 (5)	0.8256 (5)	0.077 (3)
C50	0.067 (1)	0.1851 (7)	0.8603 (5)	0.086 (4)
C51	0.103 (2)	0.2545 (8)	0.8090 (6)	0.148 (6)
C52	0.069 (1)	0.2536 (6)	0.7189 (6)	0.128 (5)

C8—C14—C13	118.2 (6)	C38—C44—C43	119.9 (6)
N1—C16—C17	113.0 (5)	N31—C46—C47	112.8 (6)
C16—C17—C22	121.2 (6)	C46—C47—C52	121.9 (7)
C16—C17—C18	121.4 (6)	C46—C47—C48	120.8 (7)
C18—C17—C22	117.3 (6)	C48—C47—C52	117.3 (7)
C17—C18—C19	121.0 (7)	C47—C48—C49	121.3 (7)
C18—C19—C20	120.7 (7)	C48—C49—C50	120.4 (8)
C19—C20—C21	119.1 (9)	C49—C50—C51	120.1 (8)
C20—C21—C22	121 (1)	C50—C51—C52	121 (1)
C17—C22—C21	120.8 (8)	C47—C52—C51	119.7 (9)
C2—N1—C16—C17	179.0 (5)	C32—N31—C46—C47	−173.4 (6)
C16—N1—C2—C3	−178.0 (5)	C46—N31—C32—C33	−85.4 (6)
N1—C2—C3—C5	169.4 (5)	N31—C32—C33—C35	176.6 (5)
O4—C3—C5—O6	−174.0 (5)	O34—C33—C35—O36	−176.9 (5)

Table 3. Hydrogen-bonding geometry (Å, °)

D	H	A	D—H	H⋯A	D⋯A	D—H⋯A
N1	H1A	Br1	1.077	2.426	3.400 (6)	149.8
N31	H31A	Br2	1.111	2.402	3.262 (6)	132.9
O34	H34	Br1	1.068	2.239	3.305 (4)	175.3
N1	H1B	O34^i	1.079	1.980	2.905 (6)	141.6
O4	H4	Br2^{ii}	0.947	2.234	3.173 (4)	171.4
N31	H31B	O4^{iii}	1.074	2.284	3.129 (7)	134.2

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

Structure solution was by combined Patterson and direct methods. H atoms were calculated at geometrical positions except those of the OH groups which were obtained from difference Fourier syntheses. Refinement was by full-matrix least-squares. Data collection: *DIF*4 (Stoe & Cie, 1988a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988c). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Table 2. Geometric parameters (Å, °)

N1—C2	1.492 (7)	N31—C32	1.512 (6)
N1—C16	1.475 (7)	N31—C46	1.467 (7)
C2—C3	1.511 (8)	C32—C33	1.514 (8)
C3—O4	1.430 (7)	C33—O34	1.442 (6)
C3—C5	1.523 (9)	C33—C35	1.536 (7)
C5—O6	1.451 (8)	C35—O36	1.437 (7)
C5—C10	1.490 (9)	C35—C40	1.490 (9)
O6—C7	1.376 (6)	O36—C37	1.382 (7)
C7—C8	1.369 (8)	C37—C38	1.379 (8)
C7—C11	1.398 (7)	C37—C41	1.383 (8)
C8—C9	1.508 (9)	C38—C39	1.508 (9)
C8—C14	1.385 (8)	C38—C44	1.399 (9)
C9—C10	1.517 (9)	C39—C40	1.547 (9)
C11—C12	1.386 (8)	C41—C42	1.408 (9)
C12—C13	1.363 (9)	C42—C43	1.36 (1)
C13—C14	1.376 (9)	C43—C44	1.35 (1)
C13—F15	1.367 (7)	C43—F45	1.370 (8)
C16—C17	1.499 (8)	C46—C47	1.498 (9)
C17—C18	1.388 (9)	C47—C48	1.36 (1)
C17—C22	1.38 (1)	C47—C52	1.40 (1)
C18—C19	1.37 (1)	C48—C49	1.39 (1)
C19—C20	1.36 (1)	C49—C50	1.33 (1)
C20—C21	1.35 (1)	C50—C51	1.35 (1)
C21—C22	1.38 (1)	C51—C52	1.38 (1)
C2—N1—C16	113.4 (5)	C32—N31—C46	115.1 (5)
N1—C2—C3	111.1 (5)	N31—C32—C33	112.7 (5)
C2—C3—C5	113.3 (6)	C32—C33—C35	109.0 (5)
C2—C3—O4	110.4 (5)	C32—C33—O34	111.5 (5)
O4—C3—C5	107.3 (5)	O34—C33—C35	107.9 (5)
C3—C5—C10	112.6 (6)	C33—C35—C40	114.5 (5)
C3—C5—O6	104.2 (5)	C33—C35—O36	104.3 (5)
O6—C5—C10	111.5 (6)	O36—C35—C40	110.7 (5)
C5—O6—C7	117.2 (5)	C35—O36—C37	116.7 (5)
O6—C7—C11	114.1 (5)	O36—C37—C41	114.4 (6)
O6—C7—C8	124.2 (6)	O36—C37—C38	122.5 (6)
C8—C7—C11	121.6 (6)	C38—C37—C41	123.0 (6)
C7—C8—C14	119.2 (6)	C37—C38—C44	116.9 (6)
C7—C8—C9	119.7 (6)	C37—C38—C39	121.5 (6)
C9—C8—C14	121.1 (6)	C39—C38—C44	121.5 (6)
C8—C9—C10	110.7 (6)	C38—C39—C40	108.8 (6)
C5—C10—C9	110.8 (6)	C35—C40—C39	109.2 (6)
C7—C11—C12	119.2 (6)	C37—C41—C42	118.3 (6)
C11—C12—C13	117.8 (6)	C41—C42—C43	117.8 (7)
C12—C13—F15	118.5 (6)	C42—C43—F45	117.0 (7)
C12—C13—C14	123.9 (7)	C42—C43—C44	123.9 (7)
C14—C13—F15	117.6 (6)	C44—C43—F45	119.0 (7)

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lation as $C_5H_5NCH_2CH_2C{\equiv}CH^+.CH_3C_6H_4SO_3^-$ (1), Fig. 1. A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) shows that the cation $pyCH_2CH_2C{\equiv}CH^+$ in (1) has not been reported previously. This cation is disordered such that a major (85%) and a minor (15%) orientation occupy the same volume element in the lattice. The methyl H atoms and sulfonate O atoms of the p-toluenesulfonate anion are also disordered over two orientations.

Structure of 1-(3-Butynyl)pyridinium p-Toluenesulfonate

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Abstract

The 1-(3-butynyl)pyridinium p-toluenesulfonate salt, $C_9H_{10}N^+.C_7H_7O_3S^-$, contains a C—H$\cdots$O hydrogen bond between the acetylenic H atom of the cation and a sulfonate O atom of the anion in the solid state [C$\cdots$O 3.32 (1), H$\cdots$O 2.49 Å, C—H$\cdots$O 159°]. The X-ray analysis was complicated by disorder in both the cation and anion. A major (85%) and a minor (15%) component of the 1-(3-butynyl)pyridinium cation are present, both occuping the same volume element in the lattice. The methyl H atoms and sulfonate O atoms of the p-toluenesulfonate anion are disordered over two orientations.

Comment

The pyridinium salt, 1-(3-butynyl)pyridinium p-toluenesulfonate, (1), was synthesized from the reaction of 3-butynol and p-toluenesulfonyl chloride in pyridine. The present structural determination establishes the formu-

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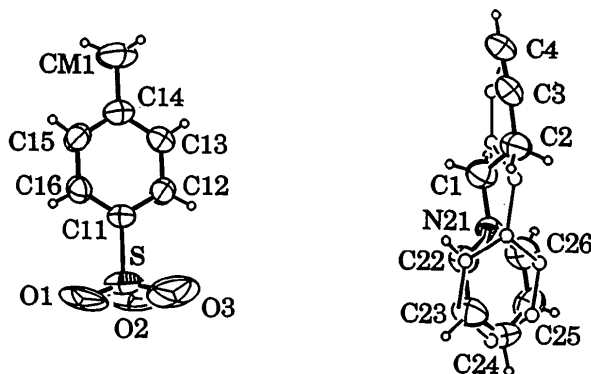
Fig. 1. An *ORTEP* view of the major and minor sites of the alkynyl pyridinium cation with the hydrogen-bonded p-toluenesulfonate anion. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity, only one of the two possible locations of the methyl H and sulfonate O atoms is shown; the H atoms and the non-H atoms of the minor site are drawn as small spheres of arbitrary size.

Despite the disorder, dimensions of the anion and of the major component of the 1-(3-butynyl)pyridinium cation are as expected, with acetylenic HC(4)≡C(3) 1.167 (6) Å and C(4)≡C(3)—C(2) 173.8 (5)°. The acetylenic H atom H(4) was positioned at the coordinates obtained from a difference map (C—H 0.87 Å, C≡C—H 176°). This acetylenic C≡C—H group is involved in hydrogen bonding with an O atom of the disordered sulfonate group of a neighbouring anion: C(4)$\cdots$O(1) 3.32 (1), H(4)$\cdots$O(1) 2.49 Å, C(4)—H(4)$\cdots$O(1) 159°. Such acetylenic C≡C—H$\cdots$O hydrogen bonding is well established, e.g. in o-bromobenzoylacetylene with C$\cdots$O 3.260 (15) Å (Ferguson & Tyrrell, 1965) and in o-chlorobenzoylacetylene with C$\cdots$O 3.212 (9) Å (Ferguson & Islam, 1966). Coordinates for the minor cation component were obtained from difference maps and idealized. The dihedral angle between the major and minor aromatic ring planes is 23°.

The single bond C(1)—C(2) is 1.506 (7) Å, while C(2)—C(3) is 1.458 (6) Å. The N—C bonds in the pyridinium ring are similar, 1.328 (5) and 1.339 (5) Å; the four C—C bond lengths are in the range 1.337 (7)–1.374 (7) Å, with a mean value of 1.360 (7) Å. The C_{ar}—C_{ar} bond lengths in the p-toluenesulfonate anion are normal and in the range 1.360 (5)–1.392 (5) Å with a mean value of 1.378 (5) Å.