$C_{22}H_{30}N_2O_5$

Chiral Hydroxylamines. II. (1R,2R)-N-Benzyl-N-[(3-tert-butoxycarbonyl-2,2-dimethyloxazol-4-yl)(furan-2-yl)methyl]-hydroxylamine†

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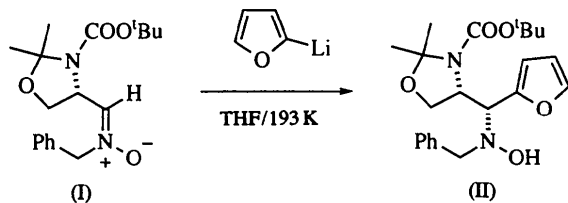
Abstract

The molecular structure of the title compound, $C_{22}H_{30}N_2O_5$, determined from the X-ray data, shows an intramolecular hydrogen bond of 2.735 (3) Å between the O atom of the hydroxylamine group and the O atom of the carbonylamino group. The packing in the crystal is entirely the result of van der Waals interactions.

Comment

Following our studies on the stereocontrolled synthesis of chiral heterocyclic hydroxylamines (Dondoni *et al.*, 1995 and references cited therein), we prepared the 2-furylalkylhydroxylamine, (II), by the addition of 2-furyllithium to the L-serine derived nitrone, (I), as described by Lanaspa, Merchan, Merino, Tejero & Dondoni (1995). The structure determination of the title compound, (II), was undertaken to establish the relative configuration of the newly formed chiral center at C(5). It was not necessary to determine the absolute configuration since the starting nitrone (I) was enantiomerically pure, having an *R* configuration at the only asymmetric center. Moreover, the conformation and the packing of (II) in the crystal was of interest for comparison with other chiral heterocyclic hydroxylamines (Merino, Merchan & Tejero, 1995) as well as for understanding the mechanism of the addition to the nitrone (I).

The molecular geometry and numbering scheme of the title compound are shown in Fig. 1. Bond distances and angles are within normal ranges. The oxazolidine

ring adopts a conformation which is intermediate between envelope and half-chair. The atoms C5 and C16 are coplanar with the furan and phenyl rings, respectively, C5—C1—O1—C4 and C16—C17—C18—C19 being −178.7 (3) and −177.8 (3), respectively. A similar kind of planarity is observed for the carbamate group at the oxazolidine ring [N2—C11—O2—C12 179.2 (2)]. The known *R* configuration at C6 and the torsion angles given in Table 2 show that the configuration at C5 is *R*, thus confirming the *syn*-addition to the nitrone (I). An intramolecular hydrogen bond of 2.735 (3) Å between atoms O5 and O3 is observed. The packing in the crystal is entirely due to van der Waals interactions. A view of the crystal packing is shown in Fig. 2.
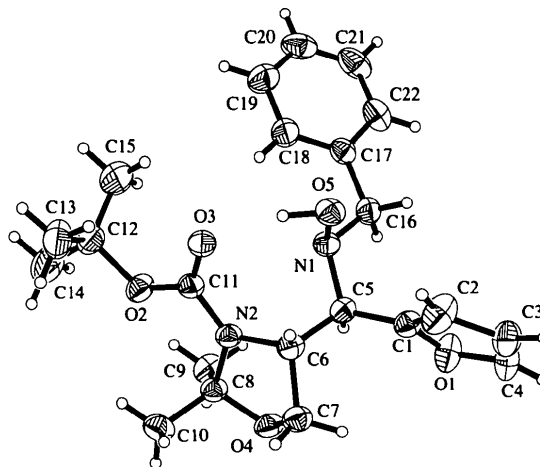

Fig. 1. Molecular geometry and the numbering scheme for the title compound. Displacement ellipsoids are plotted at the 30% probability level.
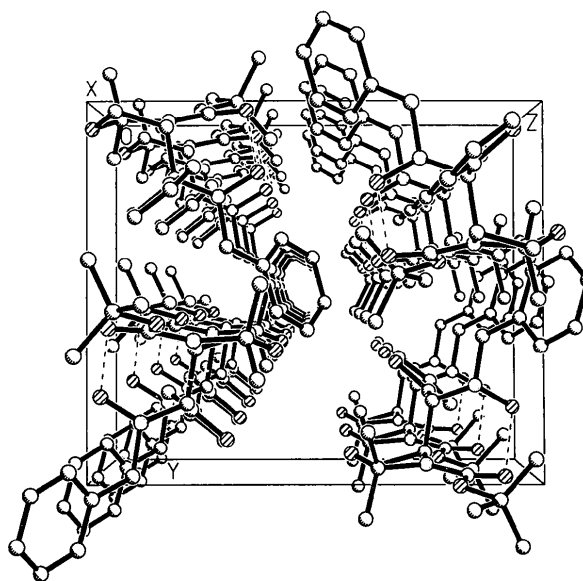

Fig. 2. Crystal packing of (II).

† Alternative name: *tert*-butyl 4-[(*N*-benzyl-*N*-hydroxyamino)(2-furyl)methyl]-2,2-dimethyloxazole-3-carboxylate.

Experimental

Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of (II) in 1:6 diethyl ether–hexane solution, m.p. 385 K, $[\alpha]_D$ = +32.57° (*c* 5.2 g l^{-1}, chloroform).

Crystal data

$C_{22}H_{30}N_2O_5$	Mo $K\alpha$ radiation
M_r = 402.48	λ = 0.71073 Å
Orthorhombic	Cell parameters from 40
$P2_12_12_1$	reflections
a = 12.3140 (10) Å	θ = 10–25°
b = 12.4250 (10) Å	μ = 0.083 mm^{-1}
c = 14.855 (5) Å	T = 293 (2) K
V = 2272.8 (8) Å^3	Transparent block
Z = 4	0.52 × 0.50 × 0.30 mm
D_x = 1.176 Mg m^{-3}	Colourless
D_m not measured	

Data collection

Siemens *P4* diffractometer	θ_{max} = 22.49°
Profile data from $2\theta/\omega$ scans	h = -1 → 13
Absorption correction:	k = -1 → 13
none	l = -1 → 15
2256 measured reflections	3 standard reflections
2092 independent reflections	monitored every 97
2007 observed reflections	reflections
[$I > 2\sigma(I)$]	intensity decay: 3.09%
R_{int} = 0.0791	

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.133 e Å^{-3}
$R[F^2 > 2\sigma(F^2)]$ = 0.0375	$\Delta\rho_{min}$ = -0.127 e Å^{-3}
$wR(F^2)$ = 0.1049	Extinction correction:
S = 1.045	*SHELXL93* (Sheldrick,
2092 reflections	1993)
268 parameters	Extinction coefficient:
H atoms riding [except	0.0474 (37)
H(O)]	Atomic scattering factors
$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2$	from *International Tables*
$+ 0.2834P]$	*for Crystallography* (1992,
where $P = (F_o^2 + 2F_c^2)/3$	Vol. C, Tables 4.2.6.8 and
$(\Delta/\sigma)_{max}$ = -0.003	6.1.1.4)

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

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

	x	y	z	U_{eq}
O1	0.5478 (2)	0.1710 (2)	0.8350 (2)	0.0817 (7)
C1	0.5119 (2)	0.2392 (2)	0.7693 (2)	0.0558 (7)
C2	0.5968 (3)	0.2740 (4)	0.7225 (2)	0.0924 (12)
C3	0.6913 (3)	0.2213 (4)	0.7601 (2)	0.0841 (10)
C4	0.6577 (3)	0.1625 (3)	0.8261 (3)	0.0850 (10)
C16	0.3495 (2)	0.1039 (2)	0.6689 (2)	0.0613 (7)
C17	0.2701 (2)	0.0612 (2)	0.6007 (2)	0.0552 (7)
C18	0.1887 (2)	0.1237 (2)	0.5656 (2)	0.0669 (8)
C19	0.1141 (3)	0.0811 (3)	0.5050 (2)	0.0815 (9)
C20	0.1209 (3)	-0.0252 (3)	0.4806 (2)	0.0905 (11)
C21	0.2012 (3)	-0.0886 (3)	0.5152 (3)	0.0918 (11)
C22	0.2756 (3)	-0.0466 (2)	0.5749 (2)	0.0734 (9)
O4	0.30016 (15)	0.3757 (2)	0.92914 (11)	0.0639 (5)
C7	0.3921 (2)	0.4101 (3)	0.8787 (2)	0.0640 (7)
C6	0.3634 (2)	0.3769 (2)	0.7830 (2)	0.0527 (6)
N2	0.2461 (2)	0.3970 (2)	0.78406 (13)	0.0511 (5)
C8	0.2049 (2)	0.4033 (2)	0.8790 (2)	0.0561 (7)
C9	0.1213 (2)	0.3179 (3)	0.8993 (2)	0.0715 (8)
C10	0.1682 (3)	0.5158 (3)	0.9039 (2)	0.0763 (9)
C11	0.1896 (2)	0.4182 (2)	0.7082 (2)	0.0514 (6)
O3	0.2289 (2)	0.4235 (2)	0.63310 (11)	0.0577 (5)
O2	0.08402 (14)	0.4342 (2)	0.72687 (12)	0.0659 (5)
C12	0.0040 (2)	0.4602 (3)	0.6563 (2)	0.0699 (8)
C13	0.0355 (3)	0.5660 (3)	0.6125 (2)	0.0954 (12)
C14	-0.0994 (3)	0.4740 (4)	0.7101 (3)	0.1051 (14)
C15	-0.0045 (3)	0.3703 (4)	0.5898 (3)	0.118 (2)
O5	0.3875 (2)	0.2722 (2)	0.60851 (11)	0.0607 (5)
N1	0.3369 (2)	0.2192 (2)	0.68500 (13)	0.0516 (5)
C5	0.3912 (2)	0.2576 (2)	0.7663 (2)	0.0507 (6)

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

O1—C4	1.365 (4)	C7—C6	1.521 (4)
O1—C1	1.366 (3)	C6—N2	1.466 (3)
C1—C2	1.327 (4)	C6—C5	1.541 (4)
C1—C5	1.504 (4)	N2—C11	1.351 (3)
C2—C3	1.447 (5)	N2—C8	1.501 (3)
C3—C4	1.291 (5)	C8—C9	1.509 (4)
C16—N1	1.461 (4)	C8—C10	1.515 (4)
C16—C17	1.504 (4)	C11—O3	1.218 (3)
C17—C18	1.372 (4)	C11—O2	1.344 (3)
C17—C22	1.395 (4)	O2—C12	1.475 (3)
C18—C19	1.391 (4)	C12—C15	1.494 (5)
C19—C20	1.372 (6)	C12—C14	1.513 (5)
C20—C21	1.364 (5)	C12—C13	1.518 (5)
C21—C22	1.378 (5)	O5—N1	1.453 (3)
O4—C7	1.423 (3)	N1—C5	1.461 (3)
O4—C8	1.431 (3)		
C4—O1—C1	107.4 (3)	C6—N2—C8	110.6 (2)
C2—C1—O1	108.8 (3)	O4—C8—N2	101.5 (2)
C2—C1—C5	135.5 (3)	O4—C8—C9	106.7 (2)
O1—C1—C5	115.8 (2)	N2—C8—C9	112.5 (2)
C1—C2—C3	106.5 (3)	O4—C8—C10	109.8 (2)
C4—C3—C2	107.0 (3)	N2—C8—C10	112.2 (2)
C3—C4—O1	110.3 (3)	C9—C8—C10	113.4 (2)
N1—C16—C17	112.8 (2)	O3—C11—O2	124.5 (2)
C18—C17—C22	118.3 (3)	O3—C11—N2	124.7 (2)
C18—C17—C16	122.1 (2)	O2—C11—N2	110.8 (2)
C22—C17—C16	119.5 (3)	C11—O2—C12	122.1 (2)
C17—C18—C19	120.9 (3)	O2—C12—C15	110.7 (3)
C20—C19—C18	119.8 (4)	O2—C12—C14	102.2 (2)
C21—C20—C19	120.0 (3)	C15—C12—C14	112.1 (3)
C20—C21—C22	120.4 (3)	O2—C12—C13	108.9 (3)
C21—C22—C17	120.6 (3)	C15—C12—C13	112.4 (3)
C7—O4—C8	107.8 (2)	C14—C12—C13	110.1 (3)
O4—C7—C6	103.1 (2)	O5—N1—C5	107.6 (2)
N2—C6—C7	99.9 (2)	O5—N1—C16	105.7 (2)
N2—C6—C5	112.6 (2)	C5—N1—C16	114.0 (2)
C7—C6—C5	111.1 (2)	N1—C5—C1	115.3 (2)
C11—N2—C6	122.2 (2)	N1—C5—C6	110.2 (2)
C11—N2—C8	126.9 (2)	C1—C5—C6	111.2 (2)
N2—C6—C5—N1	53.1 (3)	N2—C11—O2—C12	179.2 (2)
N2—C6—C5—C1	-177.8 (2)	O4—C8—N2—C6	-5.4 (3)
C16—C17—C18—C19	-177.8 (3)	C6—C7—O4—C8	-42.8 (3)
C17—C18—C19—C20	0.9 (5)		

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXTL93*.

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Comment

We decided to combine a hydrogen-bond donor molecule (pyromellitic acid, PMA) and a hydrogen-bond acceptor molecule having two basic N atoms (2,2'-bipyridine, BPY), (I), in order to explore the influence of weak forces such as hydrogen bonds and electrostatic interactions on the potential self-organization of molecules (Reetz, Höger & Harms, 1994). Also, in the course of a systematic investigation of compounds with short intramolecular hydrogen bonds (Jeffrey, 1995), acid salts of pyromellitic acid were of special interest.

(I)

Hydrogen Bonding in the 2,2'-Bipyridinium Salt of 1,2,4,5-Benzenetetracarboxylic Acid (Pyromellitic Acid)

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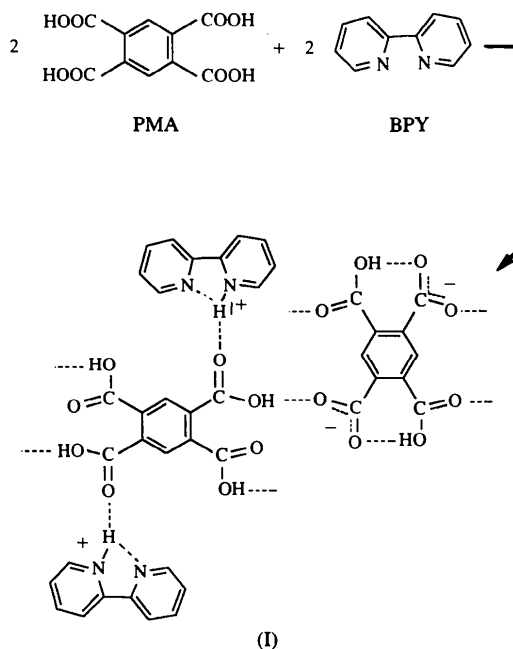
Abstract

The 2,2'-bipyridinium salt of pyromellitic acid (PMA, 1,2,4,5-benzenetetracarboxylic acid), 2,2'-bipyridinium hemi[1,2,4,5-benzenetetracarboxylate(2−)] hemi(1,2,-4,5-benzenetetracarboxylic acid), C$_{10}$H$_8$N$_2$H$^+$.$\frac{1}{2}$[C$_6$H$_2$(COO)$_4$H$_2$]$^{2-}$.$\frac{1}{2}$[C$_6$H$_2$(COO)$_4$H$_4$], has been prepared and studied by X-ray diffraction and IR spectroscopy. 2,2'-Bipyridine acts as a proton sponge by accepting a proton from pyromellitic acid. The transfer of protons results in strong asymmetric intramolecular hydrogen bonds; H(N)···N 2.603 (2) Å in the bipyridinium cation, which has a *syn* conformation, and H(O)···O 2.396 (2) Å in the pyromellitate anion. The N—H···N hydrogen bond is part of a three-centre hydrogen bond with a carbonyl group of the neutral pyromellitic acid; N—H···N/O with an N···O distance of 2.805 (2) Å. Each neutral PMA molecule is connected by hydrogen bonds to two cations and four anions forming a two-dimensional network with plane indices (112). The IR spectrum also suggests the presence of strong hydrogen bonds.

One of the two crystallographically independent molecules of pyromellitic acid in (I) is deprotonated, with the two protons transferred to the N atoms of two bipyridine groups. The pyromellitate anion, PMA^{2-}, and the neutral PMA molecule lie on crystallographic centres of symmetry (0,$\frac{1}{2}$,0) and (0,$\frac{1}{2}$,$\frac{1}{2}$), respectively. They are connected by H(O3)···O5 2.569 (2) (Fig. 1) and H(O1)···O7^i 2.636 (2) Å hydrogen bonds [symmetry code: (i) 1 − x, 2 − y, −z]. The bond distances in the neutral PMA molecule and the PMA^{2-} anion are consistent with those usually found (Jessen, Küppers & Luehrs, 1992). The structure of the pyromellitate anion differs from that of the neutral acid. The ring of the neutral PMA molecule is planar, with the carboxyl groups rotated out of plane by 11.96 (8) and 75.6 (1)°, values which are similar to those found in PMA dihydrate (18 and 75°; Takusagawa, Hirotsu & Shimada, 1971). The carboxyl groups of the PMA^{2-} anion are twisted by 18.0 (1) and 6.9 (1)° with respect to the benzene ring, and the two neighbouring carboxylic acid groups are connected by a very short intramolecular hydrogen bond [O6···O8 2.396 (2) Å] which is clearly asymmet-