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Imipraminium picrate

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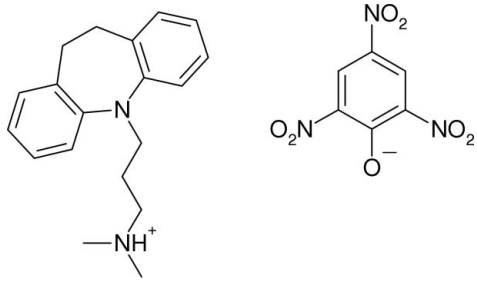
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.127; data-to-parameter ratio = 13.8.

The title compound, $C_{19}H_{25}N_2^+\cdot C_6H_2N_3O_7^-$, is a molecular salt arising from the reaction of imipramine and picric acid. The tertiary N atom of the side chain of the cation is protonated and forms a bifurcated N—H···(O,O) hydrogen bond to the anion. One of the acceptor O atoms is the deprotonated phenol O atom and the other is part of a nitro group. The dihedral angle between the mean planes of the benzene rings in the cation is 56.13 (6)° and the two bridging methylene groups in the central seven-membered ring are probably disordered. In the crystal structure, π–π stacking occurs [ring centroid separations = 3.6805 (12) and 3.7726 (14) Å], resulting in centrosymmetric associations of two cations and two anions.

Related literature

For the crystal structure of impramine hydrochloride, see: Post *et al.* (1975). For recent background on the neurochemistry of imapramine, see: Zanoveli *et al.* (2007).



Experimental

Crystal data

$C_{19}H_{25}N_2^+\cdot C_6H_2N_3O_7^-$
M_r = 509.52
Triclinic, $P\overline{1}$
a = 10.5204 (10) Å
b = 10.6661 (10) Å
c = 11.7603 (11) Å
α = 77.292 (1)°
β = 73.862 (1)°
γ = 84.590 (1)°
V = 1235.8 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 (2) K
0.40 × 0.30 × 0.30 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: none
7898 measured reflections
4674 independent reflections
2818 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.127
S = 0.95
4674 reflections
339 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1···O1	0.90 (2)	1.88 (2)	2.686 (2)	148.2 (17)
N2—H1···O6	0.90 (2)	2.53 (2)	3.189 (2)	130.0 (16)

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2401).

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Zanoveli, J. M., Nogueira, R. L. & Zangrossi, H. (2007). *Neuropharmacology*, **52**, 1188–1195.

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supplementary materials

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Imipraminium picrate

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Comment

Imipramine, $C_{19}H_{20}N_2$, a tricyclic molecule containing two tertiary amine moieties, inhibits the re-uptake of serotonin more effectively than most secondary amine tricyclics, meaning that it blocks the re-uptake of the neurotransmitters serotonin and noradrenaline almost equally. It has been widely used to treat depression and neurosis for the past 50 years and is still under intensive study (Zanoveli *et al.*, 2007).

Here we describe the title compound, (I), (Fig. 1), $C_{19}H_{25}N_2{\cdot}C_6H_2N_3O_7$, a molecular salt of imipramine and picric acid.

Compound (I) formally arises *via* proton transfer from the phenol group of the picric acid to the tertiary N atom of the imipramine side chain. The resulting cation and anion interact *via* a bifurcated N—H···(O,*O*) hydrogen bond (Table 1). One of the acceptor oxygen atoms is the deprotonated phenolic O atom, and the other is part of a nitro group.

The dihedral angle between the aromatic rings in the cation is 56.13 (6)°. The conformation of the seven-membered ring in (I) is uncertain because of probable disorder of the bridging methylene C6 and C7 species. The bond angle sum at N1 of 351.0° is ambiguous with respect to the hybridization of this nitrogen atom (nominal values for sp^2 and sp^3 hybridization = 360 and 328°, respectively). The N1—C15—C16—C17 and C15—C16—C17—N2 conformations in the side chain in (I) are both *gauche* [torsion angles = 53.8 (2) and 57.8 (2)°, respectively].

In the crystal of (I), π-π stacking is evident. The C20—C25 aromatic ring (centroid = *Cg*1) of the anion interacts with a symmetry related partner [$Cg1\cdots Cg1^{i}$ = 3.6805 (12) Å, i = 1 − *x*, 1 − *y*, 1 − *z*) and also with the C1—C6 ring (centroid = *Cg*2) of the cation [$Cg1\cdots Cg2$ = 3.7726 (14) Å].

The structure of imipramine hydrochloride, (II), was determined by Post *et al.* (1975). They also found unresolvable disorder for the bridging methylene groups in the seven-membered rings of the two unique cations. The dihedral angles between the aromatic rings in the cations in (II) were calculated to be 49.7° and 57° (standard uncertainties not stated). One cation in (II) has a *gauche-gauche* conformation in its side chain, the other a *gauche-trans* conformation.

Experimental

Two solutions were made up: imipramine hydrochloride (0.95 g, 0.03 mol) in 50 ml of water and picric acid (1.1 g, 0.03 mol) in 50 ml of water. The solutions were mixed and stirred for few minutes. The resulting salt was filtered off and dried over P_2O_5. Red-orange chunks of (I) were recrystallized from methylethylketone (m.p.: 415 K).

Refinement

The displacement ellipsoids for C7 and C8 are elongated, suggesting disorder, but no convincing models could be developed to describe this. A very similar situation was seen in imipramine hydrochloride (Post *et al.*, 1975).

The N-bound hydrogen atom was located in a difference map and its position was freely refined with $U_{iso}(H) = 1.2U_{eq}(N)$. The C-bound hydrogen atoms were geometrically placed (C—H = 0.93–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}$(carrier). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density.

Figures

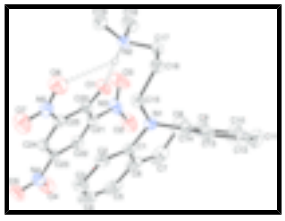

Fig. 1. View of the molecular structure of (I) showing 30% displacement ellipsoids (arbitrary spheres for the H atom). The hydrogen bonds are shown as double-dashed lines. All C-bound H atoms omitted for clarity.

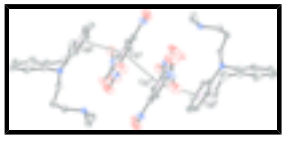

Fig. 2. π-π Stacking interactions in (I) shown as open lines between the centroids of C20—C25 (*Cg*1) and C1—C6 (*Cg*2). Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*. All H atoms omitted for clarity.

Imipraminium picrate

Crystal data

$C_{19}H_{25}N_2^+ \cdot C_6H_2N_3O_7^-$	$Z = 2$
$M_r = 509.52$	$F_{000} = 536$
Triclinic, $P\overline{1}$	$D_x = 1.369$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 10.5204$ (10) Å	Cell parameters from 2120 reflections
$b = 10.6661$ (10) Å	θ = 4.4–25.7º
$c = 11.7603$ (11) Å	μ = 0.10 mm^{-1}
α = 77.292 (1)º	$T = 295$ (2) K
β = 73.862 (1)º	Chunk, red-orange
γ = 84.590 (1)º	0.40 × 0.30 × 0.30 mm
$V = 1235.8$ (2) Å^3	

Data collection

Bruker SMART 1000 CCD diffractometer	2818 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.021$
Monochromator: graphite	$\theta_{max} = 26.0$º
$T = 295(2)$ K	$\theta_{min} = 4.3$º
ω scans	$h = -12 \rightarrow 12$
Absorption correction: none	$k = -13 \rightarrow 13$
7898 measured reflections	$l = -14 \rightarrow 13$
4674 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap (N-H) and geom (C-H)
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.127$	$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} < 0.001$
4674 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
339 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.19775 (18)	0.83478 (18)	0.27495 (19)	0.0455 (5)
C2	0.1915 (2)	0.9091 (2)	0.1636 (2)	0.0557 (6)
H2	0.2345	0.9867	0.1359	0.067*
C3	0.1235 (2)	0.8713 (3)	0.0929 (2)	0.0760 (8)
H3	0.1214	0.9228	0.0185	0.091*
C4	0.0589 (2)	0.7578 (3)	0.1327 (3)	0.0913 (10)
H4	0.0126	0.7314	0.0858	0.110*
C5	0.0636 (2)	0.6838 (3)	0.2424 (3)	0.0819 (9)
H5	0.0189	0.6072	0.2689	0.098*
C6	0.1323 (2)	0.7176 (2)	0.3168 (2)	0.0613 (6)
C7	0.1284 (3)	0.6248 (2)	0.4349 (3)	0.0854 (9)
H7A	0.1469	0.5390	0.4178	0.102*
H7B	0.0385	0.6265	0.4859	0.102*
C8	0.2204 (3)	0.6445 (2)	0.5079 (2)	0.0761 (8)
H8A	0.2139	0.5735	0.5766	0.091*
H8B	0.3111	0.6461	0.4582	0.091*
C9	0.1852 (2)	0.7681 (2)	0.5516 (2)	0.0595 (6)

C10	0.1256 (3)	0.7721 (3)	0.6715 (2)	0.0825 (8)
H10	0.1110	0.6958	0.7287	0.099*
C11	0.0875 (3)	0.8877 (3)	0.7073 (2)	0.0803 (8)
H11	0.0475	0.8890	0.7883	0.096*
C12	0.1085 (2)	0.9995 (2)	0.6245 (2)	0.0612 (6)
H12	0.0831	1.0774	0.6489	0.073*
C13	0.16742 (19)	0.99837 (19)	0.50393 (19)	0.0475 (5)
H13	0.1811	1.0754	0.4475	0.057*
C14	0.20606 (18)	0.88278 (18)	0.46723 (18)	0.0426 (5)
C15	0.36804 (18)	0.97595 (17)	0.27865 (17)	0.0409 (5)
H15A	0.3221	1.0591	0.2668	0.049*
H15B	0.4122	0.9577	0.1996	0.049*
C16	0.47105 (18)	0.98213 (17)	0.34556 (18)	0.0444 (5)
H16A	0.5360	1.0440	0.2952	0.053*
H16B	0.4278	1.0140	0.4185	0.053*
C17	0.54306 (19)	0.85605 (19)	0.38034 (17)	0.0471 (5)
H17A	0.6065	0.8710	0.4216	0.056*
H17B	0.4793	0.7969	0.4373	0.056*
C18	0.6879 (2)	0.6759 (2)	0.3248 (2)	0.0674 (7)
H18A	0.6273	0.6209	0.3884	0.101*
H18B	0.7551	0.7003	0.3559	0.101*
H18C	0.7284	0.6309	0.2608	0.101*
C19	0.7051 (2)	0.8795 (2)	0.17754 (19)	0.0585 (6)
H19A	0.6545	0.9491	0.1421	0.088*
H19B	0.7523	0.8320	0.1172	0.088*
H19C	0.7670	0.9132	0.2086	0.088*
N1	0.27124 (15)	0.87742 (13)	0.34391 (14)	0.0404 (4)
N2	0.61469 (17)	0.79317 (14)	0.27744 (15)	0.0444 (4)
H1	0.555 (2)	0.7628 (18)	0.2485 (18)	0.053*
C20	0.41881 (19)	0.57369 (17)	0.17240 (18)	0.0422 (5)
C21	0.3622 (2)	0.44759 (17)	0.21547 (17)	0.0447 (5)
C22	0.2846 (2)	0.39896 (18)	0.16199 (18)	0.0471 (5)
H22	0.2469	0.3195	0.1971	0.057*
C23	0.26218 (19)	0.46791 (18)	0.05557 (18)	0.0447 (5)
C24	0.31935 (19)	0.58543 (18)	0.00231 (17)	0.0443 (5)
H24	0.3059	0.6306	−0.0709	0.053*
C25	0.39595 (18)	0.63523 (16)	0.05766 (17)	0.0406 (4)
N3	0.3867 (2)	0.36765 (17)	0.32566 (18)	0.0648 (5)
N4	0.18039 (18)	0.4167 (2)	−0.00232 (19)	0.0618 (5)
N5	0.45440 (18)	0.75804 (16)	−0.00482 (17)	0.0538 (5)
O1	0.47543 (16)	0.62008 (13)	0.23215 (14)	0.0649 (4)
O2	0.2998 (2)	0.29774 (18)	0.39253 (17)	0.0990 (7)
O3	0.4926 (2)	0.3707 (2)	0.3451 (2)	0.1137 (8)
O4	0.13910 (18)	0.30810 (18)	0.04328 (17)	0.0885 (6)
O5	0.15606 (18)	0.48256 (19)	−0.09388 (17)	0.0863 (6)
O6	0.52913 (19)	0.80446 (16)	0.03556 (17)	0.0852 (6)
O7	0.4274 (2)	0.81032 (16)	−0.09792 (17)	0.0897 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0343 (11)	0.0464 (11)	0.0570 (14)	−0.0002 (9)	−0.0054 (10)	−0.0225 (10)
C2	0.0436 (12)	0.0712 (14)	0.0598 (15)	0.0016 (10)	−0.0185 (11)	−0.0241 (12)
C3	0.0506 (15)	0.117 (2)	0.0771 (18)	0.0103 (15)	−0.0275 (14)	−0.0464 (16)
C4	0.0429 (15)	0.138 (3)	0.122 (3)	0.0032 (16)	−0.0239 (17)	−0.087 (2)
C5	0.0435 (14)	0.0834 (18)	0.128 (3)	−0.0160 (13)	0.0009 (16)	−0.0647 (19)
C6	0.0419 (12)	0.0521 (13)	0.0879 (18)	−0.0065 (10)	0.0039 (12)	−0.0348 (13)
C7	0.0818 (19)	0.0418 (13)	0.110 (2)	−0.0195 (12)	0.0233 (17)	−0.0223 (14)
C8	0.0834 (18)	0.0413 (13)	0.0789 (18)	0.0003 (12)	0.0023 (16)	0.0076 (12)
C9	0.0602 (14)	0.0513 (13)	0.0524 (15)	0.0020 (10)	−0.0015 (12)	0.0012 (10)
C10	0.090 (2)	0.0821 (19)	0.0527 (17)	−0.0011 (15)	−0.0016 (15)	0.0109 (14)
C11	0.0763 (18)	0.105 (2)	0.0515 (16)	0.0011 (16)	−0.0019 (14)	−0.0205 (16)
C12	0.0508 (13)	0.0760 (16)	0.0637 (17)	0.0054 (12)	−0.0131 (12)	−0.0346 (13)
C13	0.0428 (12)	0.0480 (11)	0.0548 (14)	0.0029 (9)	−0.0160 (11)	−0.0148 (10)
C14	0.0387 (11)	0.0449 (11)	0.0413 (12)	0.0015 (8)	−0.0086 (9)	−0.0066 (9)
C15	0.0438 (11)	0.0377 (10)	0.0406 (11)	−0.0035 (8)	−0.0121 (9)	−0.0047 (8)
C16	0.0472 (12)	0.0440 (11)	0.0439 (12)	−0.0050 (9)	−0.0115 (10)	−0.0122 (9)
C17	0.0488 (12)	0.0575 (12)	0.0373 (12)	−0.0015 (10)	−0.0148 (10)	−0.0104 (9)
C18	0.0751 (16)	0.0605 (14)	0.0795 (18)	0.0191 (12)	−0.0425 (15)	−0.0218 (12)
C19	0.0501 (13)	0.0732 (15)	0.0520 (14)	−0.0097 (11)	−0.0062 (11)	−0.0185 (11)
N1	0.0435 (9)	0.0365 (8)	0.0400 (10)	−0.0080 (7)	−0.0083 (8)	−0.0065 (7)
N2	0.0483 (10)	0.0426 (9)	0.0504 (11)	0.0004 (8)	−0.0235 (9)	−0.0136 (8)
C20	0.0453 (11)	0.0380 (10)	0.0457 (12)	−0.0003 (8)	−0.0128 (10)	−0.0133 (9)
C21	0.0580 (13)	0.0396 (10)	0.0365 (11)	−0.0012 (9)	−0.0129 (10)	−0.0073 (8)
C22	0.0574 (13)	0.0390 (10)	0.0447 (13)	−0.0085 (9)	−0.0090 (10)	−0.0110 (9)
C23	0.0468 (12)	0.0507 (11)	0.0404 (12)	−0.0071 (9)	−0.0102 (10)	−0.0168 (9)
C24	0.0477 (12)	0.0493 (11)	0.0344 (11)	0.0047 (9)	−0.0098 (10)	−0.0092 (9)
C25	0.0441 (11)	0.0334 (10)	0.0418 (12)	−0.0023 (8)	−0.0072 (9)	−0.0069 (8)
N3	0.0959 (16)	0.0504 (11)	0.0547 (13)	−0.0132 (11)	−0.0340 (12)	−0.0017 (9)
N4	0.0588 (12)	0.0745 (13)	0.0596 (13)	−0.0115 (10)	−0.0158 (11)	−0.0253 (11)
N5	0.0604 (12)	0.0436 (10)	0.0505 (12)	−0.0037 (8)	−0.0067 (10)	−0.0047 (9)
O1	0.0853 (11)	0.0562 (9)	0.0676 (10)	−0.0135 (8)	−0.0376 (9)	−0.0155 (7)
O2	0.1468 (18)	0.0813 (12)	0.0686 (12)	−0.0507 (13)	−0.0436 (13)	0.0244 (10)
O3	0.1231 (17)	0.1125 (16)	0.1131 (17)	−0.0232 (13)	−0.0787 (15)	0.0300 (13)
O4	0.1012 (14)	0.0870 (13)	0.0932 (14)	−0.0402 (11)	−0.0334 (12)	−0.0256 (10)
O5	0.0975 (14)	0.1118 (14)	0.0655 (12)	−0.0157 (11)	−0.0453 (11)	−0.0157 (10)
O6	0.1030 (14)	0.0667 (11)	0.0918 (14)	−0.0421 (10)	−0.0330 (12)	−0.0026 (9)
O7	0.1236 (16)	0.0688 (11)	0.0703 (13)	−0.0279 (10)	−0.0366 (12)	0.0238 (9)

Geometric parameters (Å, °)

C1—C2	1.389 (3)	C16—C17	1.512 (3)
C1—C6	1.408 (3)	C16—H16A	0.9700
C1—N1	1.428 (2)	C16—H16B	0.9700
C2—C3	1.377 (3)	C17—N2	1.496 (2)
C2—H2	0.9300	C17—H17A	0.9700

C3—C4	1.370 (4)	C17—H17B	0.9700
C3—H3	0.9300	C18—N2	1.489 (2)
C4—C5	1.367 (4)	C18—H18A	0.9600
C4—H4	0.9300	C18—H18B	0.9600
C5—C6	1.398 (3)	C18—H18C	0.9600
C5—H5	0.9300	C19—N2	1.483 (3)
C6—C7	1.511 (4)	C19—H19A	0.9600
C7—C8	1.516 (4)	C19—H19B	0.9600
C7—H7A	0.9700	C19—H19C	0.9600
C7—H7B	0.9700	N2—H1	0.90 (2)
C8—C9	1.496 (3)	C20—O1	1.239 (2)
C8—H8A	0.9700	C20—C25	1.439 (3)
C8—H8B	0.9700	C20—C21	1.451 (2)
C9—C10	1.383 (3)	C21—C22	1.356 (2)
C9—C14	1.388 (3)	C21—N3	1.460 (2)
C10—C11	1.378 (4)	C22—C23	1.375 (3)
C10—H10	0.9300	C22—H22	0.9300
C11—C12	1.356 (3)	C23—C24	1.383 (3)
C11—H11	0.9300	C23—N4	1.442 (2)
C12—C13	1.383 (3)	C24—C25	1.371 (2)
C12—H12	0.9300	C24—H24	0.9300
C13—C14	1.383 (3)	C25—N5	1.453 (2)
C13—H13	0.9300	N3—O3	1.203 (2)
C14—N1	1.433 (2)	N3—O2	1.217 (2)
C15—N1	1.464 (2)	N4—O5	1.227 (2)
C15—C16	1.519 (2)	N4—O4	1.229 (2)
C15—H15A	0.9700	N5—O7	1.210 (2)
C15—H15B	0.9700	N5—O6	1.214 (2)
C2—C1—C6	118.95 (19)	C17—C16—H16B	108.4
C2—C1—N1	119.71 (17)	C15—C16—H16B	108.4
C6—C1—N1	121.34 (19)	H16A—C16—H16B	107.5
C3—C2—C1	121.9 (2)	N2—C17—C16	115.19 (15)
C3—C2—H2	119.0	N2—C17—H17A	108.5
C1—C2—H2	119.0	C16—C17—H17A	108.5
C4—C3—C2	119.8 (3)	N2—C17—H17B	108.5
C4—C3—H3	120.1	C16—C17—H17B	108.5
C2—C3—H3	120.1	H17A—C17—H17B	107.5
C5—C4—C3	119.0 (2)	N2—C18—H18A	109.5
C5—C4—H4	120.5	N2—C18—H18B	109.5
C3—C4—H4	120.5	H18A—C18—H18B	109.5
C4—C5—C6	123.3 (2)	N2—C18—H18C	109.5
C4—C5—H5	118.3	H18A—C18—H18C	109.5
C6—C5—H5	118.3	H18B—C18—H18C	109.5
C5—C6—C1	117.1 (2)	N2—C19—H19A	109.5
C5—C6—C7	116.7 (2)	N2—C19—H19B	109.5
C1—C6—C7	126.2 (2)	H19A—C19—H19B	109.5
C6—C7—C8	118.57 (19)	N2—C19—H19C	109.5
C6—C7—H7A	107.7	H19A—C19—H19C	109.5
C8—C7—H7A	107.7	H19B—C19—H19C	109.5

C6—C7—H7B	107.7	C1—N1—C14	117.96 (15)
C8—C7—H7B	107.7	C1—N1—C15	116.68 (15)
H7A—C7—H7B	107.1	C14—N1—C15	116.36 (14)
C9—C8—C7	110.5 (2)	C19—N2—C18	110.88 (17)
C9—C8—H8A	109.5	C19—N2—C17	113.60 (15)
C7—C8—H8A	109.5	C18—N2—C17	108.74 (16)
C9—C8—H8B	109.5	C19—N2—H1	109.5 (13)
C7—C8—H8B	109.5	C18—N2—H1	104.2 (12)
H8A—C8—H8B	108.1	C17—N2—H1	109.5 (13)
C10—C9—C14	118.9 (2)	O1—C20—C25	126.36 (17)
C10—C9—C8	122.5 (2)	O1—C20—C21	122.04 (18)
C14—C9—C8	118.5 (2)	C25—C20—C21	111.57 (16)
C11—C10—C9	120.9 (2)	C22—C21—C20	124.55 (18)
C11—C10—H10	119.5	C22—C21—N3	117.02 (17)
C9—C10—H10	119.5	C20—C21—N3	118.42 (17)
C12—C11—C10	119.9 (2)	C21—C22—C23	119.55 (18)
C12—C11—H11	120.0	C21—C22—H22	120.2
C10—C11—H11	120.0	C23—C22—H22	120.2
C11—C12—C13	120.4 (2)	C22—C23—C24	120.44 (17)
C11—C12—H12	119.8	C22—C23—N4	119.96 (18)
C13—C12—H12	119.8	C24—C23—N4	119.59 (18)
C12—C13—C14	120.0 (2)	C25—C24—C23	119.82 (18)
C12—C13—H13	120.0	C25—C24—H24	120.1
C14—C13—H13	120.0	C23—C24—H24	120.1
C13—C14—C9	119.83 (19)	C24—C25—C20	123.72 (17)
C13—C14—N1	121.85 (17)	C24—C25—N5	116.59 (17)
C9—C14—N1	118.30 (17)	C20—C25—N5	119.68 (16)
N1—C15—C16	112.33 (15)	O3—N3—O2	122.7 (2)
N1—C15—H15A	109.1	O3—N3—C21	119.0 (2)
C16—C15—H15A	109.1	O2—N3—C21	118.3 (2)
N1—C15—H15B	109.1	O5—N4—O4	123.49 (19)
C16—C15—H15B	109.1	O5—N4—C23	118.9 (2)
H15A—C15—H15B	107.9	O4—N4—C23	117.6 (2)
C17—C16—C15	115.34 (15)	O7—N5—O6	121.92 (18)
C17—C16—H16A	108.4	O7—N5—C25	117.90 (18)
C15—C16—H16A	108.4	O6—N5—C25	120.17 (18)
C6—C1—C2—C3	−0.1 (3)	C13—C14—N1—C15	38.7 (2)
N1—C1—C2—C3	179.10 (18)	C9—C14—N1—C15	−139.54 (18)
C1—C2—C3—C4	0.4 (3)	C16—C15—N1—C1	−160.55 (15)
C2—C3—C4—C5	−0.1 (4)	C16—C15—N1—C14	52.9 (2)
C3—C4—C5—C6	−0.5 (4)	C16—C17—N2—C19	52.0 (2)
C4—C5—C6—C1	0.7 (3)	C16—C17—N2—C18	176.04 (17)
C4—C5—C6—C7	−179.6 (2)	O1—C20—C21—C22	171.0 (2)
C2—C1—C6—C5	−0.4 (3)	C25—C20—C21—C22	−6.9 (3)
N1—C1—C6—C5	−179.61 (18)	O1—C20—C21—N3	−7.3 (3)
C2—C1—C6—C7	180.0 (2)	C25—C20—C21—N3	174.70 (18)
N1—C1—C6—C7	0.7 (3)	C20—C21—C22—C23	4.0 (3)
C5—C6—C7—C8	169.2 (2)	N3—C21—C22—C23	−177.59 (18)
C1—C6—C7—C8	−11.1 (3)	C21—C22—C23—C24	0.8 (3)

C6—C7—C8—C9	65.1 (3)	C21—C22—C23—N4	179.67 (18)
C7—C8—C9—C10	108.0 (3)	C22—C23—C24—C25	−1.8 (3)
C7—C8—C9—C14	−68.1 (3)	N4—C23—C24—C25	179.26 (17)
C14—C9—C10—C11	−0.1 (4)	C23—C24—C25—C20	−1.8 (3)
C8—C9—C10—C11	−176.2 (3)	C23—C24—C25—N5	179.00 (17)
C9—C10—C11—C12	0.0 (4)	O1—C20—C25—C24	−172.09 (19)
C10—C11—C12—C13	0.3 (4)	C21—C20—C25—C24	5.8 (3)
C11—C12—C13—C14	−0.4 (3)	O1—C20—C25—N5	7.1 (3)
C12—C13—C14—C9	0.2 (3)	C21—C20—C25—N5	−175.09 (16)
C12—C13—C14—N1	−177.97 (17)	C22—C21—N3—O3	145.3 (2)
C10—C9—C14—C13	0.0 (3)	C20—C21—N3—O3	−36.2 (3)
C8—C9—C14—C13	176.3 (2)	C22—C21—N3—O2	−32.7 (3)
C10—C9—C14—N1	178.3 (2)	C20—C21—N3—O2	145.8 (2)
C8—C9—C14—N1	−5.5 (3)	C22—C23—N4—O5	176.3 (2)
N1—C15—C16—C17	53.8 (2)	C24—C23—N4—O5	−4.8 (3)
C15—C16—C17—N2	57.8 (2)	C22—C23—N4—O4	−4.0 (3)
C2—C1—N1—C14	127.93 (19)	C24—C23—N4—O4	174.97 (19)
C6—C1—N1—C14	−52.8 (2)	C24—C25—N5—O7	3.0 (3)
C2—C1—N1—C15	−18.1 (2)	C20—C25—N5—O7	−176.15 (19)
C6—C1—N1—C15	161.15 (17)	C24—C25—N5—O6	−175.99 (19)
C13—C14—N1—C1	−107.4 (2)	C20—C25—N5—O6	4.8 (3)
C9—C14—N1—C1	74.3 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···O1	0.90 (2)	1.88 (2)	2.686 (2)	148.2 (17)
N2—H1···O6	0.90 (2)	2.53 (2)	3.189 (2)	130.0 (16)

Fig. 1

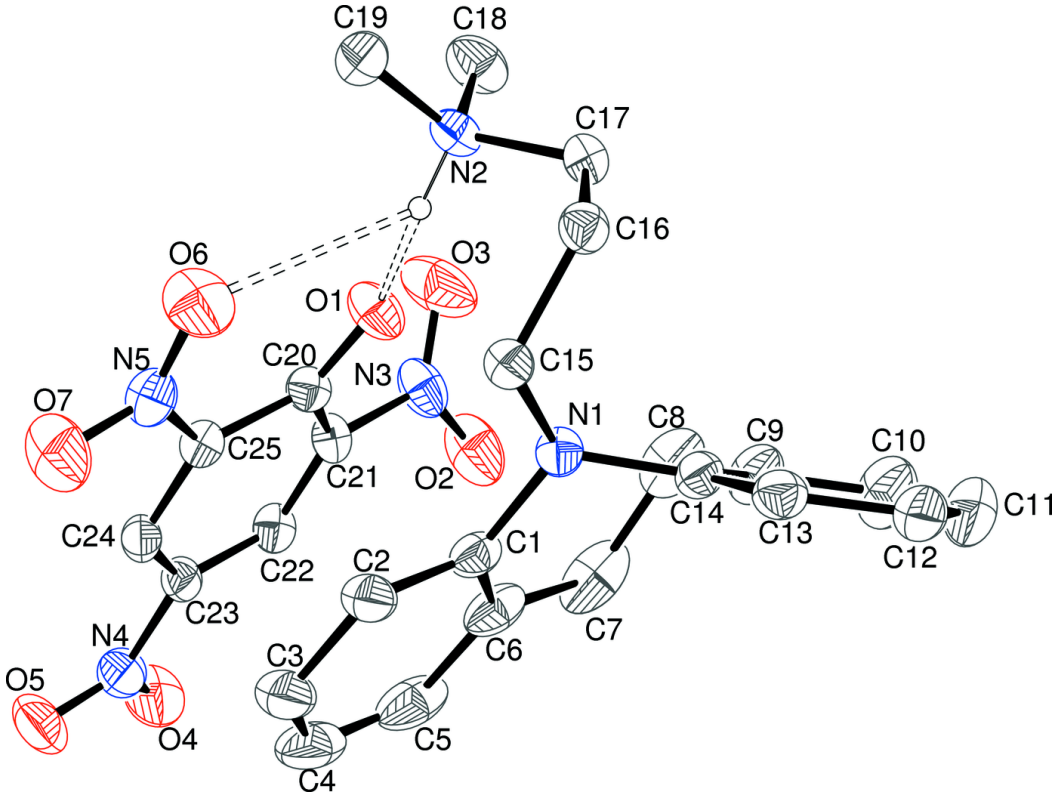
C19
C18
C17
N2
C16
O6
O3
O1
N5
C20
N3
C15
O7
N1
C8
C9
C10
C25
C21
O2
C14
C13
C11
C24
C22
C1
C12
C2
C23
C7
N4
C6
C3
O5
O4
C5
C4

Fig. 2