Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dimethyl{3-[1-methyl-4-(1-methyl-4-nitropyrrole-2-carboxamido)pyrrole-2-carboxamido]propyl}ammonium chloride methanol solvate

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.005 Å
R factor = 0.068
wR factor = 0.097
Data-to-parameter ratio = 12.7

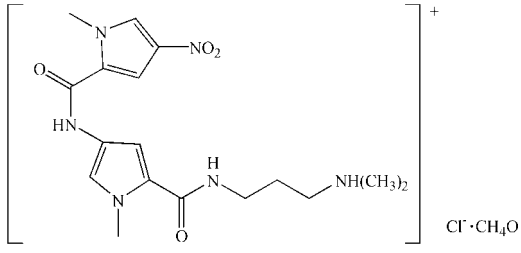
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 18 February 2003
Accepted 27 February 2003
Online 7 March 2003

In the title compound, $C_{17}H_{25}N_6O_4^+\cdot Cl^-\cdot CH_4O$, the cation adopts a bowed conformation with π-conjugation *via* two pyrrole rings and and two peptide groups.

Comment

All living organisms (excluding certain viruses) store their genetic information in the form of double-helical DNA. Biochemical access to this information is based on specific protein–DNA interactions. Despite recent progress using biological selection methods (phage display), predictive chemical principles for protein–DNA recognition are still considered complex (Greisman & Pabo, 1997; Choo & Klug, 1997). Thus, this problem has prompted chemists to synthesize small molecules relevant to the problem of DNA recognition. Inspired by the natural products netropsin and ditamycin, which bind to the AATT and AAATT sequences, respectively, in the minor groove of DNA, chemists have recently developed polyamides containing *N*-methylpyrrole and *N*-methylimidazole amino acids which can recognize and bind in the minor groove of predetermined DNA sequences with high affinity and specificity comparable to naturally occurring DNA-binding proteins (Trauger *et al.*, 1996; Swalley *et al.*, 1997; Turner *et al.*, 1997; Trauger *et al.*, 1998; Dervan & Buril, 1999). The co-crystal structures of netropsin, ditamycin and some polyamides showed that the polyamides exerted an influence on DNA structures, and DNA also influenced the structure of the polyamides (Berman *et al.*, 1979; Kopka *et al.*, 1985; Collect et al., 1987; Balendiran *et al.*, 1995; Kielkopf, Baird *et al.*, 1998; Kielkopf, White *et al.*, 1998; Shi *et al.*, 2002). To understand the principle of the interaction, which is significant for the design of new DNA-binding compounds, more structural information is needed on polyamide–DNA and polyamides themselves. In this paper, we discuss the structure of the title polyamide, which contains two *N*-methylpyrrole rings.



(I)

The overall appearance of the cation in the title compound, (I), is a bowed molecule (Fig. 1). The bond lengths and angles

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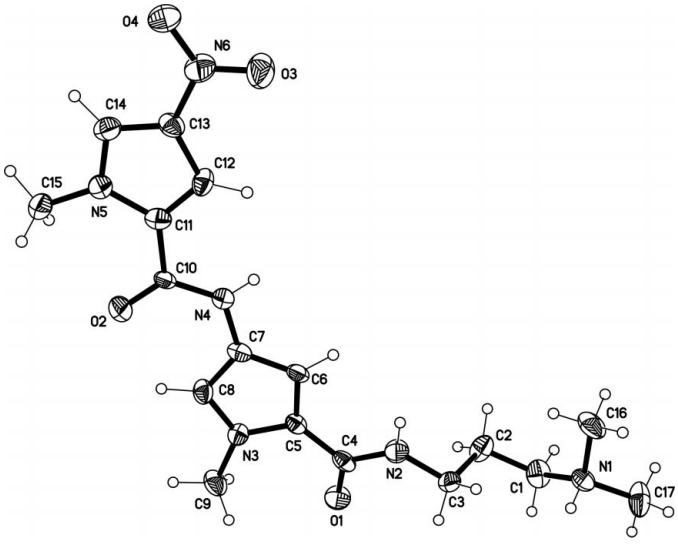

Figure 1
The structure of the cation in the title compound, (I), with displacement ellipsoids drawn at the 50% probability level for non-H atoms.

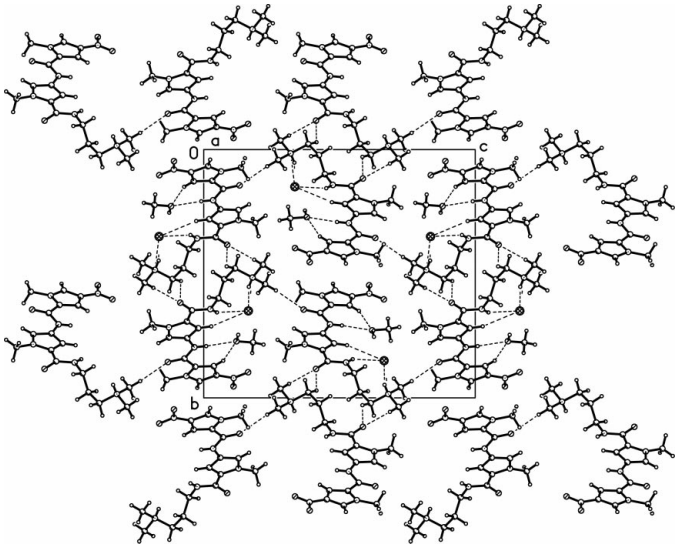

Figure 2
The packing diagram of (I), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

are not unusual (Table 1). There is conjugation involving the two pyrrole rings and the two peptide groups. Their atoms are essentially coplanar, forming a plane consisting of 22 atoms (N2—N6, O1—O4 and C3—C15). The maximum deviations from the plane are 0.250 (2) and −0.247 (2) Å for O1 and O2, and the minimum deviations only 0.001 (3) and −0.003 (3) Å for C13 and N5, respectively. The dihedral angle between the two pyrrole rings is 3.7 (2)°. An obvious difference from a similar compound, such as netropsin, is a smaller rotation [8.7 (5)°] about the C10—C11 bond than that of netropsin (26° rotation about the C6—C9 bond); this causes the two pyrrole groups of netropsin to be skewed with respect to one another (Berman *et al.*, 1979). The dihedral angle between the two peptide units is 16.9 (2)°. This is larger than that between the two pyrrole rings, and may be due to one peptide bond being linked to an unconjugated dimethylaminopropyl group.

Hydrogen-bond parameters are listed in Table 2 and a packing diagram is shown in Fig. 2. In the crystal packing, the molecules are held together by a number of intermolecular hydrogen bonds involving atoms N1, N2 and N4 of the cation, as well as the O atom of the solvent methanol molecule and the chloride anion.

Experimental

The literature procedure, slightly modified, for the preparation of 3-[1-methyl-4-(1-methyl-4-nitropyrrole-2-carboxamido)pyrrole-2-carboxamido]dimethylaminopropane was followed (Nishiwaki *et al.*, 1988). The resulting compound was dissolved in methanol (100%) with a few drops of 1 *N* HCl. The solution was left at 277 K and crystals of (I) appeared after several months.

Crystal data

$C_{17}H_{25}N_6O_4^+\cdot Cl^-\cdot CH_4O$
$M_r = 444.92$
Monoclinic, $P2_1/c$
$a = 6.2129$ (13) Å
$b = 17.801$ (4) Å
$c = 19.442$ (4) Å
$\beta = 90.765$ (4)°
$V = 2150.1$ (8) Å^3
$Z = 4$
$D_x = 1.374$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1027 reflections
$\theta = 2.4$–19.6°
$\mu = 0.22$ mm^{-1}
$T = 183$ (2) K
Block, yellow
0.20 × 0.20 × 0.20 mm

Data collection

SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: none
8201 measured reflections
3529 independent reflections
2335 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 24.8°$
$h = -7 \rightarrow 6$
$k = -20 \rightarrow 19$
$l = -22 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.097$
$S = 0.98$
3529 reflections
278 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0108P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.499 (4)	C10—O2	1.227 (4)
C1—C2	1.514 (5)	C10—N4	1.337 (4)
C2—C3	1.499 (4)	C10—C11	1.490 (4)
C3—N2	1.448 (4)	C11—C12	1.359 (5)
C4—O1	1.225 (4)	C11—N5	1.387 (4)
C4—N2	1.351 (4)	C12—C13	1.390 (4)
C4—C5	1.470 (5)	C13—C14	1.372 (5)
C5—C6	1.368 (4)	C13—N6	1.430 (4)
C5—N3	1.381 (4)	C14—N5	1.355 (4)
C6—C7	1.389 (5)	C15—N5	1.463 (4)
C7—C8	1.387 (5)	C16—N1	1.489 (4)
C7—N4	1.411 (4)	C17—N1	1.488 (4)
C8—N3	1.368 (4)	N6—O4	1.225 (3)
C9—N3	1.460 (4)	N6—O3	1.247 (4)
N2—C4—C5—C6	12.2 (5)	C5—C4—N2—C3	−178.6 (3)
N4—C10—C11—C12	−8.7 (5)	O2—C10—N4—C7	−0.7 (5)
O1—C4—N2—C3	2.0 (5)	C11—C10—N4—C7	179.2 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···Cl1^{i}	0.84	2.34	3.152 (3)	162
N1—H1···Cl1^{ii}	0.85	2.28	3.099 (3)	161
N4—H4···O5^{iii}	0.86	2.22	3.060 (4)	164
N2—H2···Cl1^{iv}	0.77	2.72	3.430 (3)	154

Symmetry codes: (i) $1+x, y, z$; (ii) $-x, 1-y, 1-z$; (iii) $2-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$.

H atoms attached to C and O atoms were placed in geometrically idealized positions, with Csp^2—H = 0.95 Å, Csp^3—H = 0.98 Å, Csp^3—H = 0.98 Å, and Osp^3—H = 0.84 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H) = 1.5U_{eq}(O). H atoms on N atoms were located in a difference Fourier map and refined with a common U_{iso} value. The N—H distances are in the range 0.77–0.86 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

The work was supported financially by the National Natural Science Foundation of China (No. 20171031 to PY), the Provincial Natural Foundation of Shanxi for Youth (No. 20011007 to LPL), and the Overseas Returned Scholar Foundation of Shanxi Province in 2002 for MLZ. We also thank Miss Huang Suping in the Analysis and Measurement Center of Shanxi University for the X-ray data collection.

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