ω scans
Absorption correction:
none
2061 measured reflections
1519 independent reflections
925 observed reflections
$[F > 4\sigma(F)]$

$h = -10 \rightarrow 10$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 8$
3 standard reflections
monitored every 97
reflections
intensity decay: 2.0%

Refinement

Refinement on F
$R = 0.0536$
$wR = 0.0603$
$S = 1.51$
925 reflections
127 parameters
H atoms were refined as a riding model with fixed isotropic U

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
O(1)	0.4549 (3)	0.2094 (2)	0.1065 (4)	0.077 (1)
O(2)	0.2602 (3)	0.2718 (2)	−0.0838 (4)	0.077 (1)
O(3)	0.7418 (3)	0.4752 (2)	−0.1287 (4)	0.070 (1)
O(4)	0.9021 (3)	0.3648 (2)	−0.1442 (4)	0.068 (1)
O(5)	0.8259 (3)	0.4024 (2)	0.3067 (4)	0.074 (1)
N(1)	0.6253 (3)	0.3650 (2)	0.0926 (4)	0.052 (1)
C(1)	0.4676 (4)	0.3647 (3)	0.0059 (5)	0.051 (2)
C(2)	0.3963 (4)	0.2733 (3)	0.0190 (6)	0.049 (2)
C(3)	0.1762 (5)	0.1878 (3)	−0.0882 (8)	0.098 (3)
C(4)	0.7216 (4)	0.3255 (3)	−0.0066 (6)	0.059 (2)
C(5)	0.7871 (4)	0.3984 (3)	−0.0987 (5)	0.050 (2)
C(6)	0.9768 (4)	0.4271 (4)	−0.2367 (6)	0.078 (2)
C(7)	0.6906 (4)	0.4020 (3)	0.2524 (5)	0.050 (2)
C(8)	0.5968 (4)	0.4405 (3)	0.3607 (6)	0.066 (2)

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

O(1)—C(2)	1.193 (5)	O(2)—C(2)	1.313 (4)
O(2)—C(3)	1.444 (6)	O(3)—C(5)	1.190 (6)
O(4)—C(5)	1.322 (5)	O(4)—C(6)	1.453 (6)
O(5)—C(7)	1.227 (4)	N(1)—C(1)	1.453 (4)
N(1)—C(4)	1.463 (6)	N(1)—C(7)	1.347 (5)
C(1)—C(2)	1.499 (6)	C(4)—C(5)	1.502 (7)
C(7)—C(8)	1.492 (7)		
C(2)—O(2)—C(3)	117.6 (3)	C(5)—O(4)—C(6)	116.9 (3)
C(1)—N(1)—C(4)	116.9 (3)	C(1)—N(1)—C(7)	125.7 (4)
C(4)—N(1)—C(7)	117.4 (3)	N(1)—C(1)—C(2)	112.9 (3)
O(1)—C(2)—O(2)	124.1 (4)	O(1)—C(2)—C(1)	125.3 (3)
O(2)—C(2)—C(1)	110.6 (3)	N(1)—C(4)—C(5)	112.3 (3)
O(3)—C(5)—O(4)	124.4 (4)	O(3)—C(5)—C(4)	125.3 (4)
O(4)—C(5)—C(4)	110.3 (4)	O(5)—C(7)—N(1)	119.3 (4)
O(5)—C(7)—C(8)	121.3 (4)	N(1)—C(7)—C(8)	119.4 (3)

The crystal was mounted on the tip of a glass fiber with epoxy. Data collection was carried out on an upgraded Nicolet/Siemens *R*3*m*/*V* four-circle diffractometer using *XSCANS* (Siemens, 1994). The structure was solved by direct methods, and refinement and molecular graphics were obtained using standard *SHELXTL-Plus* programs (Sheldrick, 1991).

The authors wish to thank the University of Massachusetts Dartmouth for financial support and the Chemistry Department of Brown University for the use of their X-ray facilities.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Molecular, Crystal Structure and Fluorescence Emission Properties of Diprotonated 7,10,19,22-Tetraoxa-4,13-diaza[16.8^{4,13}](9,10)anthracenophane (A_{33}.2H$^+$)

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(*Received 1 February 1995; accepted 16 June 1995*)

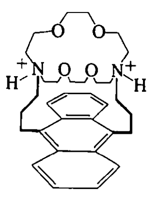
Abstract

7,10,19,22-Tetraoxa-4,13-diaza[16.8^{4,13}](9,10)anthracenophane.2HClO$_4$.C$_6$H$_5$CH$_3$, $C_{32}H_{44}N_2O_4.2HClO_4.C_7H_8$, is a diprotonated form of a molecular receptor described previously and the homologue of A_{22}.2H$^+$ is also described. The present A_{33}.2H$^+$ compound crystallizes with one molecule of solvent (toluene) and the N$^+$—H bonds are oriented outside the empty cavity towards

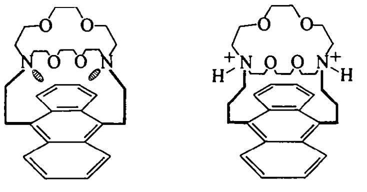
the ClO_4^- anions. The single-crystal fluorescence spectra of the free base (A_{33}) and of the title compound are reported.

Comment

Two (9,10)monoanthracenocryptands (A_{22} and A_{33}) exhibit remarkable cation-modulated fluorescence properties (Fages *et al.*, 1989). $A_{33}.2H^+$ (1) is a protonated for of the A_{33} free ligand. The crystal structure and fluorescence emission spectra of the free ligands have already been reported (Guinand *et al.*, 1986; Marsau *et al.*, 1988). In the lattice, the nitrogen lone pairs of A_{33} are oriented outside ('out-out') the molecular cavity in contrast to A_{22} where the lone pairs are directed inside ('in-in') towards the aromatic central ring (see Scheme below). The fluorescence properties of the crystal could be explained in relation to these conformations: A_{22} displays a non-structured redshifted exciplex-type spectrum originating in the overlap between the nitrogen lone pairs and the anthracene ring in the excited state, and A_{33} a lesser redshifted emission as these intramolecular interactions are significantly minimized (Marsau *et al.*, 1988). It was shown that protonation of A_{22} ($A_{22}.2H^+$) maintains the stereochemistry of the N atoms ('in-in' orientation) since a molecule of water imprisoned inside the small cavity is associated with the protons linked to the N atoms (Lahrahar, Marsau, Bouas-Laurent, Desvergne & Fages, 1995). The fluorescence of the crystal ($A_{22}.2H^+$) is that of a non-perturbed anthracene spectrum, as the N atoms cannot further interact with the aromatic ring. Similarly to A_{22}, A_{33} can be diprotonated in solution with acids. However, kinetic studies reveal distinct behaviours of the two ligands *versus* protonation which could be connected with structural differences of the reaction products (Fages *et al.*, 1989; Al-Joubbeh, 1990). Thus, it was of importance to elucidate the molecular structure of protonated A_{33}.



$A_{33}.2H^+$



A_{22}: 'in-in' A_{33} and $A_{33}.2H^+$: 'out-out'

The resolution of the crystal structure shows that (Fig. 1) compared with the non-protonated form the molecular conformation undergoes a few modifications. The N atoms keep an 'out-out' configuration (Fig. 2). The attraction of the ClO_4^- anions, however, induces a lengthening of the cavity along the axis passing through the N atoms; the N—N distance increases from 6.17 Å (A_{33}) to 6.69 (1) Å and, correspondingly, the distances between the O atoms that are facing each other in the half crowns, decrease from 5.8 (A_{33}) to 4.6 (1) Å. These modifications confirm the well known adaptability of the complexing part of that molecule. It is appropriate to recall that in the two conformers of the complex $A_{33}.Ag^+$, the N—N distances were found to be 4.72 and 4.46 Å, respectively (Andrianatoandro *et al.*, 1995). Thus, the distance between the N atoms undergoes a variation of *ca* 2.2 Å among the known configurations of this ligand. The cell contains one

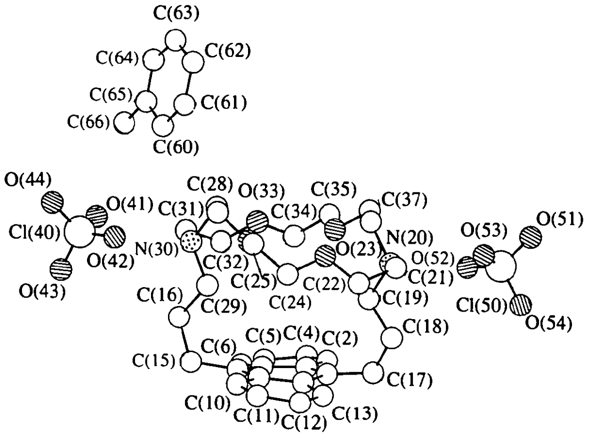


Fig. 1. Partial labelling of the non-H atoms of $A_{33}.2H^+$.

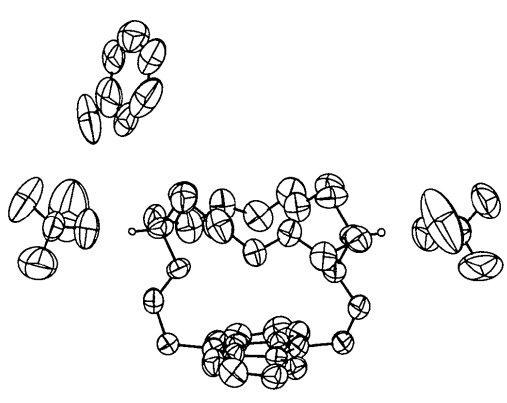


Fig. 2. Molecular conformation of $A_{33}.2HClO_4.C_6H_5CH_3$ viewed along a direction near the long axis of the anthracene. Displacement ellipsoids are at the 50% probability level.

molecule of solvent [toluene, C atoms C(60)–C(66)]. Contrary to the homologue $A_{22}.2H^+$ the ionic pairs are maintained. An attempt to determine the positions of the H atoms fixed on the N atoms [H(120), H(130)] on a Fourier difference map failed. The conformation of the N atoms [N(20), N(30)] is not perfectly tetrahedral. H atoms have been calculated in mean positions [H(120) x, y, z = 0.693, 1.014, 1.220 and H(130) x, y, z = 0.413, 0.467, 0.502 were not introduced in the table of parameters] in order to demonstrate (Fig. 2) the incontestable 'out-out' orientation of the protons. Large thermal motion is observed for the O atoms of the ClO_4^- groups, whereas the positions of the Cl atoms are clearly defined. Consequently, the abnormally short Cl—O bonds are probably not significant (Table 2).

As recorded from fluid solutions and for $A_{22}.2H^+$, the fluorescence emission spectrum of the monocrystal of $A_{33}.2H^+$ is that of a non-perturbed anthracene where no significant exciplex contribution is detectable (Fig. 3). The two nitrogen lone pairs are both involved in the protonation preventing any overlap with the anthracene π cloud. It is interesting to point out that the stereochemistry of the N atoms of the protonated species is similar to that of the free ligand. The $-(CH_2)_2-$ spacer in A_{22} induces some strain forcing the nitrogen lone pairs or N—H bonds to turn inside the cavity, the N—H orientation being assisted by the inclusion of a water molecule, whereas the $-(CH_2)_3-$ spacer in A_{33} imposes a preference for the 'out-out' conformation (lone pairs) or configuration (N—H). These structural results allow a deeper insight into the understanding of the discrepancy in the kinetics of protonation observed in fluid solution for A_{22} and A_{33}.

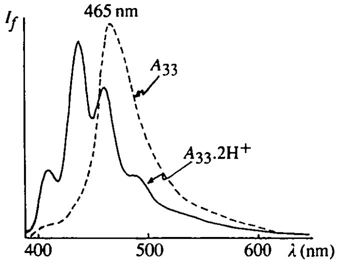


Fig. 3. Single-crystal corrected fluorescence spectra of the free ligand A_{33} (dotted line) and of $A_{33}.2HClO_4.C_6H_5CH_3$ (full line) at room temperature.

Experimental

The title compound was crystallized from methanol and $HClO_4$ solution; recrystallization of the residue from chloroform/toluene solution.

Crystal data

$C_{32}H_{44}N_2O_4.2HClO_4.C_7H_8$
M_r = 813.8
Triclinic
$P1$
a = 8.818 (2) Å
b = 10.875 (1) Å
c = 12.023 (2) Å
α = 110.45 (1)°
β = 92.53 (2)°
γ = 107.30 (1)°
V = 1017.1 (4) Å^3
Z = 1
D_x = 1.328 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 6.5–21°
μ = 1.971 mm^{-1}
T = 293 K
Prism
0.37 × 0.20 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical, ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.935, T_{max} = 1.000
3460 measured reflections
2710 independent reflections
2315 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.0231
θ_{max} = 65°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
1 standard reflection monitored every 150 reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
R = 0.060
wR = 0.048
S = 1.47
2315 reflections
704 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max}$ = 0.27

$\Delta\rho_{max}$ = 0.1 e Å^{-3}
$\Delta\rho_{min}$ = −0.1 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	0.1506 (8)	0.7959 (7)	1.0104 (6)	4.5 (3)
C(2)	0.1012 (8)	0.6485 (7)	0.9689 (6)	4.5 (3)
C(3)	0.1041 (9)	0.5761 (8)	1.0465 (6)	5.5 (3)
C(4)	0.0500 (1)	0.4360 (9)	1.0056 (8)	7.2 (4)
C(5)	−0.0184 (9)	0.3564 (8)	0.8865 (7)	6.2 (4)
C(6)	−0.0199 (9)	0.4175 (7)	0.8063 (6)	5.4 (3)
C(7)	0.0458 (8)	0.5659 (7)	0.8439 (6)	4.4 (3)
C(8)	0.0516 (8)	0.6288 (7)	0.7571 (6)	4.5 (3)
C(9)	0.0951 (8)	0.7752 (7)	0.7990 (6)	4.5 (3)
C(10)	0.0927 (9)	0.8462 (8)	0.7201 (6)	5.8 (3)
C(11)	0.1213 (10)	0.9867 (8)	0.7616 (7)	6.4 (4)
C(12)	0.1499 (9)	1.0629 (8)	0.8851 (7)	5.8 (3)
C(13)	0.1616 (9)	1.0040 (7)	0.9661 (6)	5.1 (3)
C(14)	0.1353 (8)	0.8566 (7)	0.9259 (6)	4.4 (3)
C(15)	0.0186 (8)	0.5390 (8)	0.6235 (6)	4.8 (3)
C(16)	0.1422 (9)	0.4623 (8)	0.5834 (6)	5.4 (3)
C(17)	0.2161 (9)	0.8833 (8)	1.1404 (6)	5.4 (3)
C(18)	0.3916 (10)	0.9754 (10)	1.1697 (7)	8.0 (4)
C(19)	0.4955 (9)	0.9116 (9)	1.0941 (6)	6.2 (3)
N(20)	0.6701 (6)	0.9975 (6)	1.1335 (5)	5.3 (3)
C(21)	0.7193 (9)	1.1396 (8)	1.1250 (7)	6.0 (3)
C(22)	0.6474 (10)	1.1440 (8)	1.0129 (7)	6.7 (4)
O(23)	0.6926 (6)	1.0622 (5)	0.9101 (4)	5.9 (2)
C(24)	0.5992 (10)	1.0392 (8)	0.8013 (6)	6.0 (3)

C(25)	0.6489 (11)	0.9417 (9)	0.6991 (7)	7.8 (4)
O(26)	0.6003 (6)	0.8105 (5)	0.7096 (4)	6.3 (2)
C(27)	0.6454 (10)	0.7135 (8)	0.6187 (7)	7.2 (4)
C(28)	0.6029 (9)	0.5745 (8)	0.6402 (7)	6.8 (4)
C(29)	0.3108 (8)	0.5541 (7)	0.6434 (6)	5.1 (3)
N(30)	0.4293 (7)	0.4833 (6)	0.5892 (5)	5.0 (2)
C(31)	0.4040 (10)	0.3412 (8)	0.5954 (6)	6.7 (4)
C(32)	0.3775 (12)	0.3311 (9)	0.7121 (8)	8.0 (4)
O(33)	0.5050 (7)	0.4229 (5)	0.8012 (5)	7.4 (3)
C(34)	0.4769 (11)	0.4352 (8)	0.9190 (8)	7.3 (4)
C(35)	0.6167 (11)	0.5430 (9)	1.0056 (8)	7.6 (4)
O(36)	0.6248 (7)	0.6763 (5)	1.0043 (5)	6.5 (2)
C(37)	0.7582 (10)	0.7889 (8)	1.0872 (7)	6.9 (4)
C(38)	0.7771 (9)	0.9213 (8)	1.0699 (8)	6.7 (4)
Cl(40)*	0.3530 (3)	0.3552 (3)	0.2559 (2)	7.9 (1)
O(41)	0.3812 (18)	0.2767 (12)	0.3182 (8)	22.9 (8)
O(42)	0.4064 (9)	0.4824 (7)	0.3439 (6)	12.9 (4)
O(43)	0.1905 (10)	0.3128 (9)	0.2187 (8)	16.0 (5)
O(44)	0.4329 (10)	0.3281 (7)	0.1645 (6)	12.8 (4)
Cl(50)	0.7664 (3)	1.1183 (2)	1.4633 (2)	6.6 (1)
O(51)	0.8906 (8)	1.1304 (7)	1.5445 (6)	10.6 (3)
O(52)	0.6848 (8)	0.9768 (6)	1.3828 (6)	11.1 (3)
O(53)	0.8266 (14)	1.1856 (12)	1.3926 (9)	22.8 (7)
O(54)	0.6591 (10)	1.1690 (9)	1.5313 (9)	18.6 (5)
C(60)	0.9674 (12)	0.7990 (9)	0.3978 (7)	8.2 (5)
C(61)	1.1049 (16)	0.9170 (13)	0.4371 (9)	11.9 (6)
C(62)	1.2605 (13)	0.9167 (10)	0.4497 (8)	9.2 (5)
C(63)	1.2732 (12)	0.7849 (11)	0.4104 (8)	9.8 (5)
C(64)	1.1383 (11)	0.6614 (9)	0.3710 (7)	7.3 (4)
C(65)	0.9894 (13)	0.6692 (12)	0.3611 (7)	11.3 (6)
C(66)	0.8504 (14)	0.5495 (12)	0.3202 (8)	13.3 (6)

* *x* and *z* coordinates of this atom were fixed to define origin and relaxed at the final cycle of refinement without any significant change.

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

C(1)—C(2)	1.42 (1)	C(25)—O(26)	1.42 (1)
C(1)—C(14)	1.41 (1)	O(26)—C(27)	1.39 (1)
C(1)—C(17)	1.50 (1)	C(27)—C(28)	1.56 (1)
C(2)—C(3)	1.42 (1)	C(28)—N(30)	1.51 (1)
C(2)—C(7)	1.43 (1)	C(29)—N(30)	1.52 (1)
C(3)—C(4)	1.35 (1)	N(30)—C(31)	1.52 (1)
C(4)—C(5)	1.38 (2)	C(31)—C(32)	1.47 (2)
C(5)—C(6)	1.35 (1)	C(32)—O(33)	1.37 (1)
C(6)—C(7)	1.43 (1)	O(33)—C(34)	1.42 (1)
C(7)—C(8)	1.43 (1)	C(34)—C(35)	1.47 (2)
C(8)—C(9)	1.41 (1)	C(35)—O(36)	1.44 (1)
C(8)—C(15)	1.52 (1)	O(36)—C(37)	1.44 (1)
C(9)—C(10)	1.42 (1)	C(37)—C(38)	1.49 (2)
C(9)—C(14)	1.43 (1)	Cl(40)—O(41)	1.38 (2)
C(10)—C(11)	1.37 (1)	Cl(40)—O(42)	1.34 (1)
C(11)—C(12)	1.39 (1)	Cl(40)—O(43)	1.36 (1)
C(12)—C(13)	1.35 (1)	Cl(40)—O(44)	1.33 (1)
C(13)—C(14)	1.44 (1)	Cl(50)—O(51)	1.378 (9)
C(15)—C(16)	1.56 (1)	Cl(50)—O(52)	1.436 (9)
C(16)—C(29)	1.50 (1)	Cl(50)—O(53)	1.34 (1)
C(17)—C(18)	1.52 (1)	Cl(50)—O(54)	1.39 (1)
C(18)—C(19)	1.46 (2)	C(60)—C(61)	1.40 (2)
C(19)—N(20)	1.50 (1)	C(60)—C(65)	1.40 (2)
N(20)—C(21)	1.52 (1)	C(61)—C(62)	1.38 (2)
N(20)—C(38)	1.50 (1)	C(62)—C(63)	1.38 (2)
C(21)—C(22)	1.49 (1)	C(63)—C(64)	1.41 (2)
C(22)—O(23)	1.40 (1)	C(64)—C(65)	1.34 (2)
O(23)—C(24)	1.42 (1)	C(65)—C(66)	1.41 (2)
C(24)—C(25)	1.50 (2)		

C(2)—C(1)—C(14)	118.2 (8)	O(23)—C(24)—C(25)	108.4 (8)
C(2)—C(1)—C(17)	120.3 (8)	C(24)—C(25)—O(26)	107.2 (8)
C(14)—C(1)—C(17)	121.4 (8)	C(25)—O(26)—C(27)	111.1 (8)
C(1)—C(2)—C(3)	123.1 (8)	O(26)—C(27)—C(28)	109.4 (8)
C(1)—C(2)—C(7)	120.1 (8)	C(27)—C(28)—N(30)	112.0 (8)
C(3)—C(2)—C(7)	116.8 (8)	C(16)—C(29)—N(30)	110.0 (7)
C(2)—C(3)—C(4)	121.9 (9)	C(28)—N(30)—C(29)	112.7 (7)
C(3)—C(4)—C(5)	121 (1)	C(28)—N(30)—C(31)	109.1 (7)
C(4)—C(5)—C(6)	120 (1)	C(29)—N(30)—C(31)	115.5 (7)
C(5)—C(6)—C(7)	120.6 (9)	N(30)—C(31)—C(32)	116.2 (9)
C(2)—C(7)—C(6)	118.8 (8)	C(31)—C(32)—O(33)	111.4 (9)
C(2)—C(7)—C(8)	121.1 (8)	C(32)—O(33)—C(34)	114.4 (8)
C(6)—C(7)—C(8)	120.0 (8)	O(33)—C(34)—C(35)	108.8 (9)
C(7)—C(8)—C(9)	118.3 (8)	C(34)—C(35)—O(36)	109.1 (9)
C(7)—C(8)—C(15)	120.0 (8)	C(35)—O(36)—C(37)	113.1 (8)
C(9)—C(8)—C(15)	121.7 (8)	O(36)—C(37)—C(38)	111.4 (9)
C(8)—C(9)—C(10)	122.4 (8)	N(20)—C(38)—C(37)	113.8 (9)
C(8)—C(9)—C(14)	119.8 (8)	O(41)—Cl(40)—O(42)	100.1 (8)
C(10)—C(9)—C(14)	117.8 (8)	O(41)—Cl(40)—O(43)	108.1 (8)
C(9)—C(10)—C(11)	122.2 (9)	O(41)—Cl(40)—O(44)	104.6 (8)
C(10)—C(11)—C(12)	119.3 (9)	O(42)—Cl(40)—O(43)	111.4 (6)
C(11)—C(12)—C(13)	121.9 (9)	O(42)—Cl(40)—O(44)	118.8 (6)
C(12)—C(13)—C(14)	120.3 (8)	O(43)—Cl(40)—O(44)	112.3 (7)
C(1)—C(14)—C(9)	121.5 (8)	O(51)—Cl(50)—O(52)	112.6 (5)
C(1)—C(14)—C(13)	120.2 (8)	O(51)—Cl(50)—O(53)	109.0 (7)
C(9)—C(14)—C(13)	118.3 (8)	O(51)—Cl(50)—O(54)	106.2 (7)
C(8)—C(15)—C(16)	113.8 (7)	O(52)—Cl(50)—O(53)	105.2 (7)
C(15)—C(16)—C(29)	111.6 (8)	O(52)—Cl(50)—O(54)	109.4 (6)
C(1)—C(17)—C(18)	116.3 (8)	O(53)—Cl(50)—O(54)	114.6 (8)
C(17)—C(18)—C(19)	114.0 (9)	C(61)—C(60)—C(65)	117 (1)
C(18)—C(19)—N(20)	112.7 (8)	C(60)—C(61)—C(62)	125 (1)
C(19)—N(20)—C(21)	116.4 (7)	C(61)—C(62)—C(63)	114 (1)
C(19)—N(20)—C(38)	112.3 (7)	C(62)—C(63)—C(64)	123 (1)
C(21)—N(20)—C(38)	108.4 (7)	C(63)—C(64)—C(65)	120 (1)
N(20)—C(21)—C(22)	115.6 (8)	C(60)—C(65)—C(64)	120 (1)
C(21)—C(22)—O(23)	112.0 (8)	C(60)—C(65)—C(66)	117 (1)
C(22)—O(23)—C(24)	113.2 (7)	C(64)—C(65)—C(66)	122 (1)

The structure was solved by direct methods and subsequent difference syntheses. Towards the end of the refinement all H atoms were positioned geometrically except for those linked to N(20) and N(30) (see above). The positional parameters of all atoms and anisotropic (H atoms isotropic) displacement parameters were refined by block-diagonal least squares on *F*, using local programs.

Data collection: *Structure Determination Package* (Enraf–Nonius, 1985). Cell refinement: *Structure Determination Package*. Data reduction: local programs. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: local programs. Molecular graphics: local program. Software used to prepare material for publication: local program.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and complete geometry have been deposited with the IUCr (Reference: PA1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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