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Tetraaza[3.3.3.3]- and Hexaaza[3.3.3.3.3.3]-paracyclophane Derivatives

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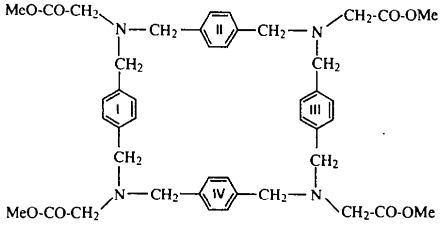
Abstract

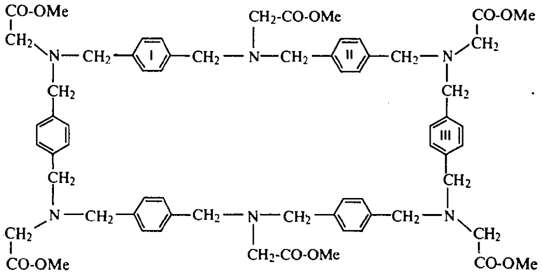
The macrocycle constituted by four [N*R*—CH_2—C_6H_4—CH_2] units, *N*,*N*′,*N*′′,*N*′′′-tetramethoxycarbonylmethylene-1,10,19,28-tetraaza[3.3.3.3]paracyclophane, [or tetramethyl 3,10,17,24-tetraazapentacyclo[24.2.2.2^{5,8}.2^{12,15}.2^{19,22}]hexatriconta-1(28),5,7,12,14,19,21,26,29,31,33,35-dodecaene-3,10,17,24-tetrayltetraacetate], $C_{44}H_{52}N_4O_8$, (1), has the shape of a rectangular dish. In all the four units, successive *gauche*,*anti* conformations can be observed for the endocyclic C—N bonds. The macrocycle with six [N*R*—CH_2—C_6H_4—CH_2] units, *N*,*N*′,*N*′′,*N*′′′,*N*′′′′,*N*′′′′′-hexamethoxycarbonylmethylene-1,10,19,28,37,46-hexaaza[3.3.3.3.3.3]paracyclophane, [or hexamethyl 3,10,17,24,31,38-hexaazaheptacyclo[38.2.2.2^{5,8}.2^{12,15}.2^{19,22}.2^{26,29}.2^{33,36}]tetrapentacosa-1(42),5,7,12,14,19,21,26,28,33,35,40,43,45,47,49,51,53-octadecaene-3,10,17,24,31,38-hexaylhexaacetate], $C_{66}H_{78}N_6O_{12}$, (2), is centrosymmetric; two of the three independent units have the same conformation as in (1), but in the third unit two adjacent C—N bonds are *anti*.

Comment

Cyclophanes are interesting compounds capable of forming inclusion complexes with organic guests. Some of them are soluble in aqueous solution where they form inclusion complexes with hydrophobic compounds (for a recent review, see Abbott, Barrett, Godfrey, Kalindjian, Simpson & Williams, 1982). The azaparacyclophanes possess these properties. The structure of a crystalline complex obtained from an aqueous solution of an acidified polyparacyclophane and durene has been determined by X-ray diffraction: the guest appears to be fully included. *N*,*N*′,*N*′′,*N*′′′-Tetramethyl-2,11,20,29-tetraaza[3.3.3.3]paracyclophane forms crystalline complexes from organic solvents with chloroform and dichloromethane (Odashima, Itai, Iitaka & Koga, 1980). The guest molecules have been shown to be exchangeable in the solid phase (Hirotsu, Kamitori, Higuchi, Tabushi, Yamamura & Nonoguchi, 1984). The title compounds, bearing glycine-derived side chains, afford crystals from concentrated acetonitrile solutions which display empty cavities. They have been prepared by condensation of *N*,*N*′-dimethoxycarbonylmethyl-*p*-xylene diamine with α,α'-dibromoparaxylene in boiling acetonitrile in the presence of potassium carbonate under high-dilution conditions, and purified by chromatography on a cation-exchange column (Pharmacia Sepharose fast flow S) in acid solutions.



(1)



(2)

As shown in Fig. 1, macrocycle (1) adopts a dish conformation; the shape of the molecule is rectangular with the phenyl rings nearly equally inclined over the plane of the N atoms. For rings I to IV, the dihedral angles between the mean plane of each aromatic ring and the mean plane through the four N atoms are 43, 29, 46 and 42°, respectively. The C—N and C—$C_{aromatic}$ torsion angles are similar in the four [N*R*—CH_2—C_6H_4—CH_2] independent units (Table 3). The conformation is characterized by the repetition (g^+,g^+,a,g^+) (or g^-,g^-,a,g^-) with all *gauche* bonds of the same sign in one unit, but with the sign alternating from one unit to another (Dale, 1980). The absolute values of the *gauche* bonds range from 45 to 76°. The conformation observed here is the same as that reported for uncomplexed *N*,*N*′,*N*′′,*N*′′′-tetramethyl-1,10,19,28-tetraaza[3.3.3.3]paracyclophane, but it is completely different from the square conformation of the inclusion complexes of that molecule with, for example, $CHCl_3$ or CH_2Cl_2 (Hirotsu *et al.*, 1984; Abbott *et al.*, 1982). The atoms of the ester group on C47 are highly agitated and their geometry has not been determined precisely.

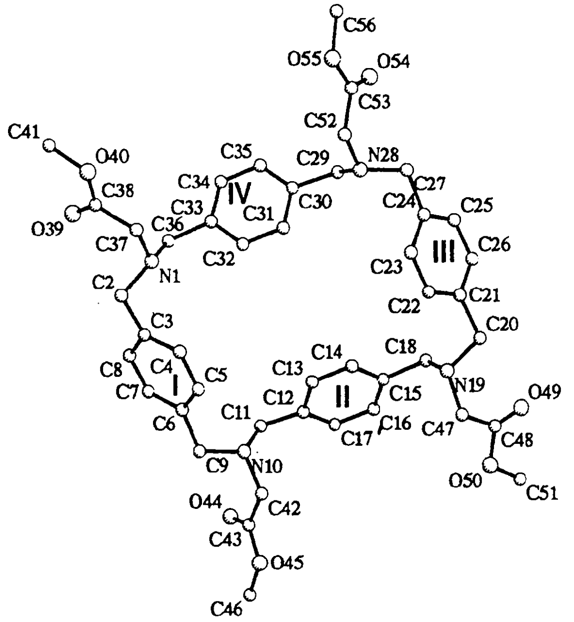


Fig. 1. View of molecule (1) with atom labelling.

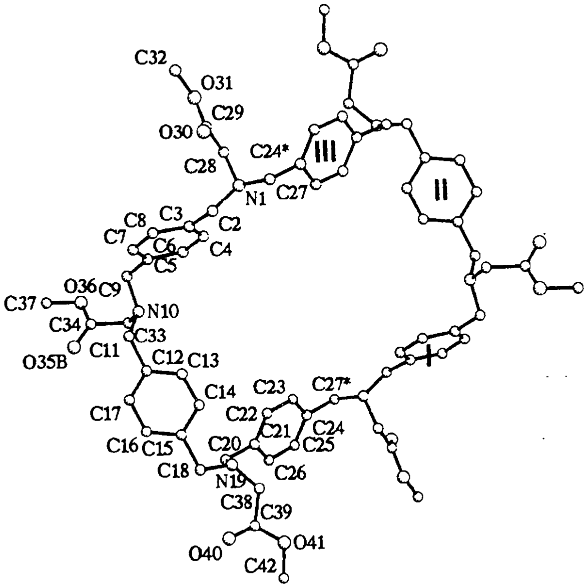


Fig. 2. View of molecule (2) with atom labelling.

The hexameric macrocycle (2) is centrosymmetric; the centre of symmetry coincides with an inversion centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) so that only one half molecule is the asymmetric part of the unit cell. The torsion angles around C—N and C—C$_{\rm aromatic}$ are similar to those observed for (1) in two of the three independent [N*R*—CH$_2$—C$_6$H$_4$—CH$_2$] units, *i.e.* (g^-,a,g^-,g^-) and (g^+,a,g^+,g^+). However, differences occur in the third unit where two adjacent C—N bonds adopt an *anti* conformation (g^+,a,a,g^-) (Dale, 1980). The phenyl rings I, II and III, make dihedral angles of 63, 20 and 68°, respectively, with the plane through the three independent N atoms.

Experimental

Compound (1)

Crystal data

$C_{44}H_{52}N_4O_8$
M_r = 764.90
Triclinic
$P\overline{1}$
a = 14.663 (1) Å
b = 10.109 (1) Å
c = 14.837 (1) Å
α = 80.76 (1)°
β = 81.71 (1)°
γ = 80.71 (1)°
V = 2126.4 (3) Å^3
Z = 2
D_x = 1.195 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54180 Å
Cell parameters from 20 reflections
θ = 3–12°
μ = 0.669 mm^{-1}
T = 293 (2) K
Parallelepiped
0.33 × 0.18 × 0.13 mm
Colourless

Data collection

Huber four circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7656 measured reflections
7656 independent reflections
4260 observed reflections [$I > 2\sigma(I)$]

$\theta_{\rm max}$ = 67.49°
h = −17 → 17
k = −11 → 12
l = 0 → 17
1 standard reflection monitored every 50 reflections
intensity variation: 4% (corrected)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0691
$wR(F^2)$ = 0.2002
S = 1.255
7656 reflections
636 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1306P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.420
$\Delta\rho_{\rm max}$ = 0.368 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.244 e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0038 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.4076 (2)	0.3950 (2)	0.7848 (2)	0.0668 (6)
C2	0.3106 (2)	0.4055 (4)	0.7666 (2)	0.0744 (8)
C3	0.2909 (2)	0.5072 (3)	0.6825 (2)	0.0653 (7)
C4	0.3510 (2)	0.5039 (3)	0.6013 (2)	0.0693 (8)
C5	0.3296 (2)	0.5914 (3)	0.5227 (2)	0.0715 (8)
C6	0.2486 (2)	0.6826 (3)	0.5235 (2)	0.0666 (7)
C7	0.1904 (2)	0.6875 (3)	0.6056 (2)	0.0753 (8)
C8	0.2113 (2)	0.6000 (3)	0.6839 (2)	0.0719 (8)
C9	0.2214 (2)	0.7692 (4)	0.4360 (3)	0.0838 (10)
N10	0.3003 (2)	0.8261 (2)	0.3801 (2)	0.0715 (7)
C11	0.3269 (2)	0.9374 (4)	0.4181 (2)	0.0757 (8)
C12	0.4258 (2)	0.9592 (3)	0.3866 (2)	0.0670 (7)

C13	0.4983 (2)	0.8636 (3)	0.4159 (2)	0.0785 (9)
C14	0.5896 (2)	0.8848 (3)	0.3926 (2)	0.0783 (9)
C15	0.6125 (2)	1.0031 (3)	0.3393 (2)	0.0691 (7)
C16	0.5405 (3)	1.0971 (3)	0.3101 (3)	0.0927 (11)
C17	0.4486 (3)	1.0754 (4)	0.3336 (3)	0.0969 (12)
C18	0.7124 (2)	1.0271 (4)	0.3186 (3)	0.0793 (9)
N19	0.7675 (2)	0.9330 (3)	0.2597 (2)	0.0738 (7)
C20	0.8675 (3)	0.9116 (4)	0.2708 (3)	0.0865 (10)
C21	0.8849 (2)	0.8355 (3)	0.3648 (2)	0.0752 (8)
C22	0.8530 (3)	0.7130 (4)	0.3967 (3)	0.0843 (10)
C23	0.8712 (3)	0.6427 (4)	0.4810 (3)	0.0852 (10)
C24	0.9217 (2)	0.6911 (3)	0.5371 (2)	0.0780 (9)
C25	0.9513 (2)	0.8153 (4)	0.5049 (3)	0.0926 (11)
C26	0.9343 (2)	0.8851 (4)	0.4206 (3)	0.0916 (11)
C27	0.9484 (2)	0.6102 (5)	0.6264 (3)	0.0894 (10)
N28	0.8717 (2)	0.5458 (3)	0.6804 (2)	0.0749 (7)
C29	0.8039 (2)	0.6418 (4)	0.7266 (3)	0.0795 (9)
C30	0.7093 (2)	0.5951 (3)	0.7538 (2)	0.0676 (7)
C31	0.6618 (2)	0.5628 (4)	0.6885 (2)	0.0823 (9)
C32	0.5718 (2)	0.5327 (4)	0.7110 (2)	0.0826 (9)
C33	0.5270 (2)	0.5341 (3)	0.7995 (2)	0.0649 (7)
C34	0.5766 (3)	0.5611 (4)	0.8640 (2)	0.0916 (11)
C35	0.6664 (2)	0.5902 (4)	0.8413 (2)	0.0900 (11)
C36	0.4261 (2)	0.5124 (3)	0.8215 (2)	0.0733 (8)
C37	0.4422 (3)	0.2688 (4)	0.8356 (2)	0.0788 (9)
C38	0.3921 (3)	0.2337 (4)	0.9312 (3)	0.0932 (10)
O39	0.3203 (2)	0.2871 (3)	0.9623 (2)	0.1184 (10)
O40	0.4373 (3)	0.1315 (4)	0.9770 (3)	0.215 (2)
C41	0.3980 (6)	0.0808 (7)	1.0680 (4)	0.262 (5)
C42	0.2909 (3)	0.8531 (4)	0.2836 (2)	0.0798 (9)
C43	0.2053 (3)	0.9481 (4)	0.2555 (3)	0.0893 (10)
O44	0.1509 (2)	1.0162 (3)	0.3052 (2)	0.1202 (10)
O45	0.1949 (2)	0.9458 (4)	0.1710 (2)	0.1388 (12)
C46	0.1161 (4)	1.0342 (7)	0.1344 (4)	0.178 (3)
C47	0.7485 (3)	0.9633 (4)	0.1654 (2)	0.0918 (10)
C48	0.7738 (5)	1.0978 (7)	0.1132 (3)	0.146 (2)
O49	0.8362 (6)	1.1413 (8)	0.1144 (4)	0.346 (6)
O50	0.7158 (3)	1.1490 (4)	0.0547 (3)	0.182 (2)
C51	0.7362 (6)	1.2742 (6)	−0.0017 (5)	0.262 (5)
C52	0.9012 (3)	0.4237 (4)	0.7402 (3)	0.0886 (10)
C53	0.9546 (3)	0.4363 (5)	0.8164 (3)	0.1043 (12)
O54	0.9796 (3)	0.5374 (4)	0.8317 (2)	0.1484 (14)
O55	0.9709 (3)	0.3183 (3)	0.8688 (2)	0.1500 (13)
C56	1.0237 (8)	0.3137 (8)	0.9471 (6)	0.201 (4)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

N1—C37	1.430 (4)	C29—C30	1.515 (4)
N1—C36	1.461 (4)	C33—C36	1.511 (4)
N1—C2	1.469 (4)	C37—C38	1.517 (5)
C2—C3	1.514 (4)	C38—O39	1.169 (4)
C6—C9	1.512 (4)	C38—O40	1.285 (5)
C9—N10	1.464 (4)	O40—C41	1.437 (5)
N10—C42	1.437 (4)	C42—C43	1.518 (5)
N10—C11	1.464 (4)	C43—O44	1.213 (4)
C11—C12	1.498 (4)	C43—O45	1.289 (4)
C15—C18	1.504 (4)	O45—C46	1.456 (5)
C18—N19	1.462 (4)	C47—C48	1.525 (7)
N19—C47	1.441 (4)	C48—O49	1.080 (6)
N19—C20	1.477 (4)	C48—O50	1.293 (6)
C20—C21	1.514 (5)	O50—C51	1.449 (6)
C24—C27	1.508 (5)	C52—C53	1.496 (6)
C27—N28	1.462 (4)	C53—O54	1.204 (5)
N28—C52	1.444 (4)	C53—O55	1.323 (5)
N28—C29	1.451 (4)	O55—C56	1.478 (8)
C37—N1—C36	113.2 (3)	C52—N28—C27	114.1 (3)
C37—N1—C2	114.4 (2)	C29—N28—C27	111.9 (3)
C36—N1—C2	113.0 (3)	N28—C29—C30	113.4 (3)
N1—C2—C3	111.5 (2)	C35—C30—C29	121.7 (3)
C8—C3—C2	120.7 (3)	C31—C30—C29	120.6 (3)
C4—C3—C2	120.3 (3)	C34—C33—C36	122.3 (3)
C5—C6—C9	120.8 (3)	C32—C33—C36	120.5 (3)
C7—C6—C9	120.7 (3)	N1—C36—C33	112.3 (3)
N10—C9—C6	112.3 (3)	N1—C37—C38	116.3 (3)
C42—N10—C9	113.3 (3)	O39—C38—O40	121.5 (4)
C42—N10—C11	114.9 (3)	O39—C38—C37	126.9 (3)
C9—N10—C11	112.8 (3)	O40—C38—C37	111.6 (4)
N10—C11—C12	112.9 (3)	C38—O40—C41	119.1 (4)
C17—C12—C11	122.4 (3)	N10—C42—C43	116.8 (3)
C13—C12—C11	120.2 (3)	O44—C43—O45	122.8 (4)
C16—C15—C18	122.5 (3)	O44—C43—C42	125.6 (3)
C14—C15—C18	120.3 (3)	O45—C43—C42	111.5 (4)
N19—C18—C15	111.9 (3)	C43—O45—C46	117.3 (4)
C47—N19—C18	113.3 (3)	N19—C47—C48	116.1 (4)
C47—N19—C20	114.1 (3)	O49—C48—O50	121.3 (6)
C18—N19—C20	112.6 (3)	O49—C48—C47	127.3 (7)
N19—C20—C21	111.3 (3)	O50—C48—C47	110.8 (5)
C26—C21—C20	121.0 (3)	C48—O50—C51	115.2 (6)
C22—C21—C20	121.3 (3)	N28—C52—C53	117.6 (3)
C23—C24—C27	122.2 (3)	O54—C53—O55	122.4 (4)
C25—C24—C27	121.2 (3)	O54—C53—C52	127.1 (4)
N28—C27—C24	112.7 (3)	O55—C53—C52	110.5 (4)
C52—N28—C29	113.5 (3)	C53—O55—C56	117.1 (5)
C36—N1—C2—C3	73.1 (4)	C18—N19—C20—C21	68.3 (4)
N1—C2—C3—C4	48.1 (4)	N19—C20—C21—C22	53.7 (5)
C5—C6—C9—N10	−43.7 (5)	C23—C24—C27—N28	−43.9 (5)
C6—C9—N10—C11	−74.5 (4)	C24—C27—N28—C29	−76.7 (4)
C9—N10—C11—C12	157.0 (3)	C27—N28—C29—C30	159.1 (3)
N10—C11—C12—C13	−68.5 (4)	N28—C29—C30—C31	−56.9 (4)
C14—C15—C18—N19	67.0 (4)	C2—N1—C36—C33	−153.5 (3)
C15—C18—N19—C20	−154.8 (3)	C32—C33—C36—N1	48.3 (4)

Compound (2)

Crystal data

$C_{66}H_{78}N_6O_{12}$
$M_r = 1147.34$
Monoclinic
$P2_1/c$
$a = 18.075\ (3)$ Å
$b = 17.946\ (2)$ Å
$c = 9.658\ (2)$ Å
$\beta = 90.04\ (1)°$
$V = 3132.8\ (9)$ Å^3
$Z = 2$
$D_x = 1.216$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 18 reflections
$\theta = 5–13°$
$\mu = 0.681$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
$0.48 \times 0.17 \times 0.04$ mm
Colourless

Data collection

Huber four circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5668 measured reflections
5668 independent reflections
3546 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 67.50°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 11$
1 standard reflection monitored every 50 reflections
intensity variation: 8% (corrected)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0564$
$wR(F^2) = 0.1512$
$S = 1.245$
5668 reflections
482 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0952P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.498$
$\Delta\rho_{\max} = 0.213$ e Å^{-3}
$\Delta\rho_{\min} = -0.222$ e Å^{-3}

Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0012 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (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	$U_{\rm eq}$
N1	0.73910 (10)	0.64184 (10)	0.1396 (2)	0.0561 (5)
C2	0.7821 (2)	0.57360 (14)	0.1349 (3)	0.0637 (7)
C3	0.80668 (14)	0.54745 (12)	0.2756 (2)	0.0554 (6)
C4	0.7597 (2)	0.55048 (14)	0.3888 (3)	0.0626 (7)
C5	0.7805 (2)	0.52158 (14)	0.5156 (3)	0.0646 (7)
C6	0.84883 (14)	0.48851 (12)	0.5333 (3)	0.0576 (6)
C7	0.8956 (2)	0.48605 (14)	0.4213 (3)	0.0634 (7)
C8	0.87535 (15)	0.51574 (14)	0.2941 (3)	0.0623 (6)
C9	0.8709 (2)	0.4570 (2)	0.6724 (3)	0.0682 (7)
N10	0.82533 (11)	0.39284 (10)	0.7108 (2)	0.0559 (5)
C11	0.8425 (2)	0.32696 (14)	0.6251 (3)	0.0579 (6)
C12	0.78607 (13)	0.26627 (12)	0.6404 (2)	0.0494 (5)
C13	0.71672 (14)	0.27377 (14)	0.5810 (3)	0.0586 (6)
C14	0.66437 (14)	0.21875 (14)	0.5917 (3)	0.0597 (6)
C15	0.67889 (13)	0.15333 (12)	0.6625 (2)	0.0536 (6)
C16	0.74819 (14)	0.14569 (13)	0.7223 (3)	0.0564 (6)
C17	0.80085 (14)	0.20115 (13)	0.7108 (2)	0.0558 (6)
C18	0.62137 (14)	0.09257 (14)	0.6722 (3)	0.0610 (7)
N19	0.54980 (10)	0.12304 (10)	0.7127 (2)	0.0529 (5)
C20	0.54605 (15)	0.1405 (2)	0.8609 (3)	0.0583 (6)
C21	0.48330 (12)	0.19203 (13)	0.8939 (2)	0.0510 (6)
C22	0.47893 (15)	0.26065 (14)	0.8293 (3)	0.0624 (7)
C23	0.42264 (15)	0.30921 (15)	0.8589 (3)	0.0622 (7)
C24	0.36824 (13)	0.29148 (13)	0.9529 (2)	0.0535 (6)
C25	0.3726 (2)	0.2231 (2)	1.0170 (3)	0.0688 (7)
C26	0.42962 (15)	0.1739 (2)	0.9878 (3)	0.0670 (7)
C27	0.69323 (15)	0.6544 (2)	0.0170 (3)	0.0628 (7)
C28	0.7808 (2)	0.70681 (15)	0.1798 (3)	0.0618 (7)
C29	0.8397 (2)	0.7329 (2)	0.0812 (3)	0.0734 (8)
O30	0.85469 (13)	0.70438 (15)	−0.0281 (3)	0.1069 (8)
O31	0.87238 (14)	0.79273 (12)	0.1240 (3)	0.1108 (8)
C32	0.9314 (2)	0.8214 (2)	0.0391 (5)	0.131 (2)
C33	0.8267 (2)	0.3783 (2)	0.8587 (3)	0.0669 (7)
C34	0.9013 (2)	0.3600 (2)	0.9170 (3)	0.0767 (8)
O35*A*†	0.9639 (14)	0.3362 (22)	0.8509 (14)	0.167 (13)
O35*B*†	0.9268 (4)	0.2993 (2)	0.9036 (9)	0.084 (3)
O36	0.92589 (11)	0.40933 (13)	1.0023 (3)	0.1010 (7)
C37	0.9966 (2)	0.3941 (3)	1.0674 (5)	0.142 (2)
C38	0.48551 (15)	0.08500 (14)	0.6621 (3)	0.0576 (6)
C39	0.46934 (15)	0.00932 (14)	0.7222 (3)	0.0598 (6)
O40	0.51120 (11)	−0.02780 (10)	0.7877 (2)	0.0908 (7)
O41	0.40068 (10)	−0.01186 (10)	0.6923 (2)	0.0817 (6)
C42	0.3772 (2)	−0.0827 (2)	0.7450 (4)	0.0957 (10)

† Occupancy factors: $A = 0.34$ (2), $B = 0.66$ (2).

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

N1—C28	1.441 (3)	C24—C27$^{\rm i}$	1.504 (3)
N1—C2	1.451 (3)	C28—C29	1.504 (4)
N1—C27	1.463 (3)	C29—O30	1.203 (3)
C2—C3	1.504 (3)	C29—O31	1.293 (3)
C6—C9	1.511 (4)	O31—C32	1.441 (4)
C9—N10	1.464 (3)	C33—C34	1.498 (4)
N10—C33	1.453 (3)	C34—O35B	1.190 (5)
N10—C11	1.477 (3)	C34—O36	1.288 (3)
C11—C12	1.500 (3)	O36—C37	1.450 (4)
C15—C18	1.510 (3)	C38—C39	1.506 (4)
C18—N19	1.458 (3)	C39—O40	1.189 (3)
N19—C38	1.433 (3)	C39—O41	1.330 (3)
N19—C20	1.467 (3)	O41—C42	1.434 (3)
C20—C21	1.498 (3)		
C28—N1—C2	114.3 (2)	N19—C20—C21	112.1 (2)
C28—N1—C27	112.9 (2)	C26—C21—C20	122.2 (2)
C2—N1—C27	114.1 (2)	C22—C21—C20	119.7 (2)
N1—C2—C3	113.1 (2)	C25—C24—C27$^{\rm i}$	122.0 (2)
C8—C3—C2	120.8 (2)	C23—C24—C27$^{\rm i}$	120.5 (2)
C4—C3—C2	121.3 (2)	N1—C27—C24$^{\rm i}$	111.2 (2)
C7—C6—C9	121.7 (2)	N1—C28—C29	116.8 (2)
C5—C6—C9	120.4 (3)	O30—C29—O31	122.0 (3)
N10—C9—C6	111.8 (2)	O30—C29—C28	125.7 (3)
C33—N10—C9	112.4 (2)	O31—C29—C28	112.3 (3)
C33—N10—C11	113.8 (2)	C29—O31—C32	116.9 (3)
C9—N10—C11	111.7 (2)	N10—C33—C34	115.1 (2)
N10—C11—C12	112.5 (2)	O35B—C34—O36	124.5 (3)
C17—C12—C11	122.2 (2)	O35B—C34—C33	120.5 (3)
C13—C12—C11	120.3 (2)	O36—C34—C33	113.6 (3)
C14—C15—C18	120.9 (2)	C34—O36—C37	116.8 (3)
C16—C15—C18	121.7 (2)	N19—C38—C39	117.1 (2)
N19—C18—C15	110.9 (2)	O40—C39—O41	123.3 (2)
C38—N19—C18	116.7 (2)	O40—C39—C38	125.9 (2)
C38—N19—C20	113.4 (2)	O41—C39—C38	110.8 (2)
C18—N19—C20	112.6 (2)	C39—O41—C42	116.9 (2)
C27—N1—C2—C3	−159.4 (2)	C14—C15—C18—N19	−48.0 (3)
N1—C2—C3—C4	41.3 (3)	C15—C18—N19—C20	−76.7 (3)
C5—C6—C9—N10	66.3 (3)	C18—N19—C20—C21	162.6 (2)
C6—C9—N10—C11	71.0 (3)	N19—C20—C21—C22	−57.4 (3)
C9—N10—C11—C12	−167.4 (2)	C2—N1—C27—C24$^{\rm i}$	159.8 (2)
N10—C11—C12—C13	73.3 (3)	N1$^{\rm i}$—C27—C24—C23$^{\rm i}$	−65

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

In compound (2), the crystals are monoclinic metrically pseudo-orthorhombic, β being very near 90°. The accuracy of the choice of space group is based on the fact that the $F_o(hkl)$'s differ from the $F_o(-hkl)$'s. For both compounds, only H-atom U's were refined with a common $U_{\rm iso}$: U(H) = 0.114 in (1) and U(H) = 0.0859 Å^2 in (2).

Data collection, cell refinement and data reduction were performed using a local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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