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Structure of a 2,6-Pyridinophane

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Abstract. 2,5,11,14-Tetraoxa-19,20-diazatricyclo-[13.3.1.1^{6,10}]icosa-1(19),6,8,10(20),15,17-hexaene, $C_{14}H_{14}N_2O_4$, $M_r = 274 \cdot 3$, monoclinic, $P2_1/c$, $a = 9 \cdot 354$ (2), $b = 9 \cdot 011$ (3), $c = 7 \cdot 954$ (2) Å, $\beta = 101 \cdot 75$ (2)°, $V = 656 \cdot 4$ (6) Å^3, $Z = 2$, $D_x = 1 \cdot 388$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0 \cdot 97$ cm^{-1}, $F(000) = 288$, $T = 299$ K, $R = 0 \cdot 035$ for 834 observations with $I > 3\sigma(I)$. The molecule lies on an inversion center and is in the *anti* or stepped conformation. The ethylene glycol chains are fully extended, and the two N—C—O—C torsion angles about the ring-O bonds are near zero, 1·6 (2) and $-2 \cdot 3$ (2)°.

Introduction. From crystallographic and NMR studies, [2.2]metacyclophanes possess a 'stepped' (*anti*) conformation (Majestic & Newkome, 1982; Newkome, Nayak, McClure, Danish-Koshboo & Broussard-Simpson, 1977). With 3-substituted 2,6-pyridinophanes, the observed NMR data could not be accommodated with this model, thus an '*anti*, transverse' isomerization was proposed (Newkome & Kawato, 1979) to rationalize the variable-temperature solution studies. This investigation confirms the *anti* conformation in the crystalline state (Fronczek, 1982).

Experimental. The title metacyclophane was obtained (16%) from the reaction of 2,6-dibromopyridine and sodioethyleneglycolate (Newkome *et al.*, 1977) in the form of analytically pure colorless crystals: m.p. 488–489 K, ^{1}H NMR (CDCl$_3$, 311 K) δ 4·66 (*bs*, CH$_2$O, 8H), 6·30 (*d*, 3,5-pyrH, $J = 8$ Hz, 4H), 7·50 (*t*, 4-pyrH, $J = 8$ Hz, 2H). Crystals were grown from cyclohexane/ethyl acetate. A single crystal of dimensions 0·18 × 0·33 × 0·60 mm was used for intensity-data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. The space group was determined from systematic absences $h0l$ with l odd and $0k0$ with k odd. Cell dimensions were determined from the setting angles of 25 reflections having $13 < \theta < 15°$. Data were collected by ω–2θ scans designed for $I = 25\sigma(I)$, subject to a maximum scan time of 120 s.

Scan rates varied $0 \cdot 49$–$20 \cdot 0°$ min^{-1}. Reflections having $-11 \le h \le 11$, $0 \le k \le 10$, $0 \le l \le 9$ and $2 < \theta < 25°$ were measured and corrected for background, Lorentz and polarization. Standard reflections 700, 040 and 004 exhibited only random fluctuations, and no decay corrections were made. A total of 1320 data were measured. Redundant $0kl$ and $0k\bar{l}$ data were averaged ($R_{int} = 0 \cdot 021$) yielding 1151 unique data, of which 834 had $I > 3\sigma(I)$ and were used in the refinement. The structure was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least squares based on F with weights $w = 4F_o^2[\sigma^2(I) + (0 \cdot 02F_o^2)^2]^{-1}$, using the Enraf-Nonius *SDP* (Frenz, 1980), and scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Fractional coordinates and aniso-tropic thermal parameters were refined for non-H atoms, while H-atom positions were located from ΔF maps and were refined with isotropic thermal parameters. Final $R = 0 \cdot 035$, $wR = 0 \cdot 045$, $S = 2 \cdot 011$ for 120 variables. Maximum shift/e.s.d. $= 0 \cdot 01$ in the final cycle; max. residual density $0 \cdot 13$, min. $-0 \cdot 10$ e Å^{-3}; extinction coefficient $g = 8 \cdot 9$ (3) $\times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c. Coordinates are given in Table 1,* and bond distances, angles and torsion angles are given in Table 2.

Discussion. The metacyclophane, illustrated in Fig. 1, has crystallographic $\bar{1}$ symmetry and possesses a stepped (*anti*) conformation. The pyridine ring is nearly planar [maximum deviation $0 \cdot 0079$ (11) Å for N]. The O atoms lie $0 \cdot 0292$ (11) (O1) and $0 \cdot 0348$ (11) Å (O2) out of the plane. The ethylene glycol chains are in the extended conformation. Torsional angles C7—O1—C1—N $-2 \cdot 3$ (2), C6—O2—C5—N $1 \cdot 6$ (2), C7—O1—C1—C2 $177 \cdot 94$ (14) and C6—O2—C5—C4 $-178 \cdot 95$ (14)° confirm the calculated (*MINDO*3; Gandour, 1978) and observed (Newkome, Majestic, Fronczek & Atwood, 1979; Newkome & Kawato, 1979) torsion angle of 0–10° for the imidate moiety (—N= C—O—CH$_2$—). The nearly orthogonal torsional angles C1—O1—C7—C6′ $-89 \cdot 7$ (2) and C5—O2—C6—C7′ $87 \cdot 7$ (2)° confirm the favored trans-verse orientation in the solid state. Bond distances and angles (Table 2) further support the predominance of the imidate substructure by diminished bond lengths [N—C1 $1 \cdot 323$ (2), N—C2 $1 \cdot 327$ (2) Å] and bond angles larger than 120° [N—C1—C2

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* Tables of H-atom parameters, distances and angles involving H atoms, least-squares planes, anisotropic thermal parameters, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53135 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
O1	0·2036 (1)	0·6045 (1)	1·0034 (1)	4·89 (3)
O2	0·4726 (1)	0·3776 (1)	0·6507 (1)	5·09 (3)
N	0·3396 (1)	0·4880 (1)	0·8310 (1)	3·43 (2)
C1	0·2102 (2)	0·5139 (2)	0·8680 (2)	3·67 (3)
C2	0·0807 (2)	0·4555 (2)	0·7778 (2)	4·84 (4)
C3	0·0885 (2)	0·3663 (2)	0·6406 (2)	5·21 (4)
C4	0·2198 (2)	0·3382 (2)	0·5962 (2)	4·93 (4)
C5	0·3428 (2)	0·4027 (2)	0·6958 (2)	3·80 (3)
C6	0·6015 (2)	0·4419 (2)	0·7550 (2)	4·50 (3)
C7	0·3388 (2)	0·6622 (2)	1·1023 (2)	4·50 (4)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

O1—C1	1·363 (2)	C1—C2	1·380 (2)
O1—C7	1·443 (2)	C2—C3	1·369 (3)
O2—C5	1·353 (2)	C3—C4	1·369 (3)
O2—C6	1·439 (2)	C4—C5	1·385 (2)
N—C1	1·323 (2)	C6—C7′	1·490 (2)
N—C5	1·327 (2)		

C1—O1—C7	118·1 (1)	C2—C3—C4	120·7 (2)
C5—O2—C6	118·1 (1)	C3—C4—C5	117·3 (2)
C1—N—C5	117·1 (1)	O2—C5—N	118·8 (1)
O1—C1—N	118·2 (1)	O2—C5—C4	117·6 (1)
O1—C1—C2	117·6 (1)	N—C5—C4	123·6 (2)
N—C1—C2	124·2 (1)	O2—C6—C7′	109·0 (1)
C1—C2—C3	117·0 (2)	O1—C7—C6′	109·8 (1)

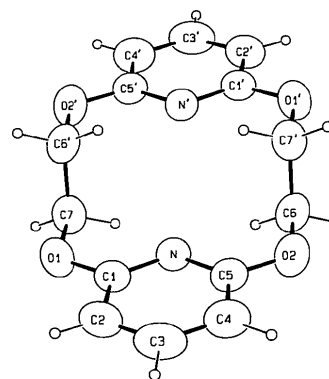| C7—O1—C1—N	$-2 \cdot 3$ (2)	C6—O2—C5—C4	$-178 \cdot 95$ (14)
C7—O1—C1—C2	177·94 (14)	C5—O2—C6—C7′	86·7 (2)
C1—O1—C7—C6′	$-89 \cdot 7$ (2)	O2—C6—C7′—O1′	175·93 (12)
C6—O2—C5—N	1·6 (2)		

Fig. 1. The numbering scheme and thermal ellipsoids drawn at the 50% probability level. Primes indicate inversion through $\frac{1}{2}$, $\frac{1}{2}$, 1.
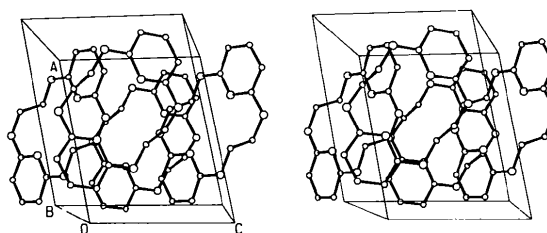

Fig. 2. Stereoview of the unit cell.

124·2 (1), N—C5—C4 123·6 (2)°]. The molecular packing is illustrated in Fig. 2; no intermolecular contacts less than 3·3 Å involving non-H atoms exist.

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Structure du (Méthoxy-4 phényl)-2 Méthyl-3 Phényl-4 Oxazole-1,3 Ylio-5 Oxyde–Acétonitrile (1/0,5)

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Abstract. $C_{17}H_{15}NO_3.\frac{1}{2}CH_3CN$, $M_r = 301\cdot8$, orthorhombic, *Pbcn*, $a = 13\cdot086$ (9), $b = 11\cdot805$ (9), $c = 19\cdot580$ (7) Å, $V = 3025$ (2) Å^3, $Z = 8$, $D_x = 1\cdot32$ Mg m^{-3}, $\mu = 0\cdot082$ mm^{-1}, $T = 293$ K, $F(000) = 1232$, $wR = 0\cdot064$ for 1058 observations. The mesoionic character of the molecule is unambiguously established.

Introduction. Les oxydes-5 de Δ^2-oxazolium, ou 'munchnones' (2) sont de véritables ylures d'azométhine dont la cycloaddition aux alcènes et alcynes conduit respectivement, après départ de CO_2, à des pyrrolines (Gotthardt & Huisgen, 1970) et à des pyrroles (Dalla Croce & La Rosa, 1988).
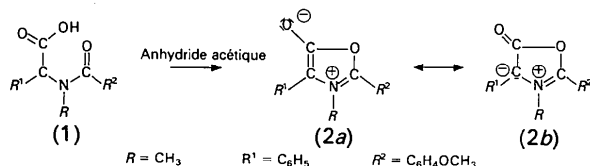
Lors de l'étude de la régiosélectivité de la cycloaddition de ces munchnones, à l'aide de la méthode de variation–perturbation (Sustmann & Vahrenholt, 1973) il nous a paru indispensable de déterminer à l'aide des rayons X la structure d'une munchnone isolable, afin de pouvoir disposer de données fiables (longueurs des liaisons, angles de torsion, *etc.*) pour nos calculs (Texier, Mazari, Yebdri, Tonnard & Carrié, 1990).

Nous avons choisi le composé du titre ($R = CH_3$, $R^1 = C_6H_5$, $R^2 = C_6H_4OCH_3$) qui a été préparé par lactonisation du dérivé acylé correspondant (1), dans l'anhydride acétique (Bayer, Huisgen, Knorr & Schaefer, 1970).

Partie expérimentale. Cristaux préparés par évaporation lente, sous atmosphère sèche, d'une solution du produit dans l'acétonitrile additionné de 1% d'anhydride acétique; échantillon (aiguille 0,12 × 0,12 × 0,30 mm) étudié à l'aide d'un diffractomètre auto-

(1)   (2a)   (2b)

$R = CH_3$ $R^1 = C_6H_5$ $R^2 = C_6H_4OCH_3$