

Fig. 2. Molécule du (diphényl-2,6 dioxo-1,3 aza-6 phospho-2 cyclooctyl-2)trihydroboron.

Dans le cas de la structure décrite dans le présent article, l'interaction stérique entre les trois cycles phényle liés à l'atome de phosphore et la chaîne aliphatique porteuse de la fonction amine est importante: l'angle C(3)–C(2)–P(1) s'est ouvert [115,1 (2)°] et traduit bien cette interaction stérique. Cette dernière, pour des raisons énergétiques évidentes, est à l'origine

de l'empêchement de la 'cyclisation' intramoléculaire par interaction électrostatique entre P(1) et N(5).

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Structure of 4,7,13,16-Tetraoxa-1,10,26-triazatricyclo[8.8.7.1^{20,24}]-hexacos-20,22,24(26)-triene

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Abstract. $C_{19}H_{31}N_3O_4$, $M_r = 365.47$, monoclinic, $C2/c$, $a = 19.319$ (4), $b = 9.098$ (1), $c = 15.014$ (4) Å, $\beta = 131.52$ (1)°, $V = 1975.8$ (7) Å³, $Z = 4$, $D_x = 1.228$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.5$ cm⁻¹, $F(000) = 792$, $T = 298$ K, final $R = 0.041$ for 1643 observed reflections. The title compound is a bicyclic cryptand with an internal cavity defined by a near-planar array of the four O atoms in the 18-membered subunit perpendicular to a plane containing the three N atoms. The introduction of the rigid pyridine moiety into the shorter bridging strand results in a cryptand conformation with the bridgehead N atoms separated by only 4.561 (2) Å.

Introduction. The kinetic parameters of the reactions of macrobicyclic polyethers (cryptands) with metal ions and the complexation selectivity patterns exhibited by these ligands are strongly influenced by structural factors such as cavity size, type of donor atoms and the

introduction of rigid spacer groups into the ligand structure (Lehn, 1973; Cox, van Truong & Schneider, 1984; Bemtgen, Springer, Loyola, Wilkins & Taylor, 1984).

Replacement of the $-\text{CH}_2-\text{O}-\text{CH}_2-$ segment of the monoxy bridge of cryptand 2.2.1 with a 2,6-disubstituted pyridine moiety results in the title compound, cryptand 2.2.1py. The latter compound exhibits the same complexation selectivity pattern for alkali- and alkaline-earth cations as the diaza-polyether analog, cryptand 2.2.1 (Wehner & Vögtle, 1976; Lehn, 1973). However, the formation and dissociation kinetics with Na^+ and K^+ (Tümmeler, Maass, Weber, Wehner & Vögtle, 1977) and the acid-catalyzed dissociation of the alkaline-earth complexes (Taylor, Heeg, Fields & Vu, 1984) show distinct differences from the behavior of cryptand 2.2.1 (Cox & Schneider, 1977; Loyola, Pizer & Wilkins, 1977).

As part of our studies on the relationship between ligand structure and complexation behavior we have determined the crystal structure of cryptand 2.2.1py.

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Experimental. Prepared according to literature method (Tümmler *et al.*, 1977) and recrystallized twice from diethyl ether. Colorless crystalline parallelepipeds, $0.5 \times 0.5 \times 0.5$ mm, D_m not determined. Nonius CAD-4 diffractometer, monochromated $\text{Mo K}\alpha$, $\theta/2\theta$ scans, $2.5 \leq 2\theta \leq 52^\circ$, data collected on the triclinic cell $a = 9.086$ (2), $b = 10.665$ (2), $c = 12.112$ (3) Å, $\alpha = 79.46$ (2), $\beta = 68.04$ (2), $\gamma = 64.76$ (2)°, 0 to 11 h , -13 to 13 k , -14 to 14 l , three intensity monitors varied 2%, 3951 total reflections. Prior to structure solution, the axes were transformed according to the

matrix $\begin{pmatrix} 1 & -2 & 0 \\ 1 & 0 & 0 \\ -1 & 1 & 1 \end{pmatrix}$ yielding the monoclinic C -

centered cell. An ancillary dataset confirmed the centering. Cell parameters refined by measuring 50 high-angle reflections at $\pm 2\theta$, 1928 unique reflections. $R_{\text{int}} = 0.026$. Calculation of I : $I = S - rB$ where $S = \text{scan counts}$, $r = \text{scan time/background ratio}$, $B = \text{sum background counts}$; calculation of $\sigma(I)$: $\sigma_I^2 = S + r^2B + (pI)^2$ where $p = 0.04$. Direct methods, H atoms placed in observed positions and refined positionally. All $U(H)$ parameters tied to a single variable. No absorption correction made. A systematic empirical correction for secondary extinction was applied. The corrected F_c values were of the form: $F_c(\text{corr}) = F_c(1 - 0.001xF_c^2/\sin\theta)$ which is the usual *SHELX* correction. The final value of x in the equation was 4.3×10^{-3} . Three reflections most seriously affected by secondary extinction were removed: 310, 020, $\bar{3}13$.

Full-matrix refinement with all non-H atoms described anisotropically yielded $R = 0.041$, $wR = 0.051$, $S = 2.4$, $w = (\sigma_F)^{-2}$ for 1643 observed reflections. For all 1925 reflections, $R = 0.051$ and $wR = 0.052$. $(\Delta/\sigma)_{\text{max}}$ in final least-squares cycle ≤ 0.1 , final ΔF map showed 0.18 and -0.14 e \AA^{-3} as max. and min. peaks. Neutral-atom scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974), calculations performed with local modifications of *SHELX76* (Sheldrick, 1976) crystallographic programs.

Discussion. The atom-labeling scheme for non-H atoms, bond distances and bond angles are shown in Fig. 1. The atomic coordinates are listed in Table 1* and selected torsion angles are listed in Table 2. A stereoview of the molecule is shown in Fig. 2.

* Lists of complete bond lengths, anisotropic thermal parameters, H atomic parameters, structure factors and least-squares planes and deviations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42493 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

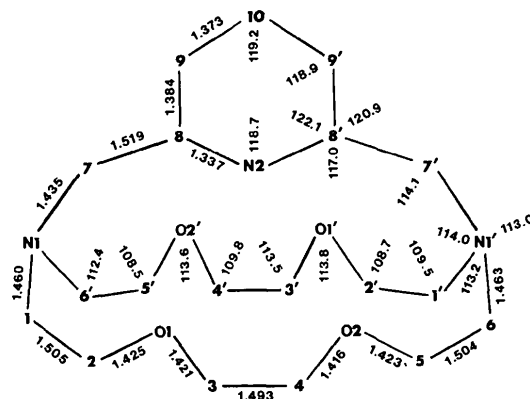


Fig. 1. Atom numbering, bond distances (Å) and bond angles (°) in cryptand 2.2.1py. The standard deviations for the bond lengths and angles involving C, N and O atoms range from 0.001 to 0.002 Å and 0.1 to 0.2°, respectively.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N(1)	0.05474 (8)	0.2434 (1)	0.6542 (1)	0.0426 (8)
N(2)	0.00000	0.4101 (2)	0.75000	0.042 (1)
C(1)	-0.0426 (1)	0.2168 (2)	0.5509 (1)	0.046 (1)
C(2)	-0.0786 (1)	0.0950 (2)	0.5785 (1)	0.048 (1)
O(1)	-0.17139 (7)	0.0630 (1)	0.47401 (9)	0.0521 (7)
C(3)	-0.2135 (1)	-0.0492 (2)	0.4900 (2)	0.055 (1)
C(4)	-0.2521 (1)	0.0049 (2)	0.5432 (2)	0.061 (1)
O(2)	-0.17998 (7)	0.0228 (1)	0.6675 (1)	0.0567 (8)
C(5)	-0.2043 (1)	0.1137 (2)	0.7202 (2)	0.059 (1)
C(6)	-0.1177 (1)	0.1519 (2)	0.8443 (1)	0.055 (1)
C(7)	0.0801 (1)	0.3959 (2)	0.6758 (2)	0.050 (1)
C(8)	0.03603 (9)	0.4850 (1)	0.7125 (1)	0.0409 (9)
C(9)	0.0362 (1)	0.6371 (2)	0.7100 (1)	0.054 (1)
C(10)	0.00000	0.7135 (2)	0.75000	0.0600 (2)

Table 2. Selected torsion angles (°) with the *e.s.d.*'s for the last digit in parentheses

N(1)-C(1)-C(2)-O(1)	-175.6 (1)	C(2)-C(1)-N(1)-C(6')	88.5 (1)
N(1)-C(7)-C(8)-N(2)	16.8 (2)	C(2)-C(1)-N(1)-C(7)	-140.5 (1)
N(1)-C(7)-C(8)-C(9)	-165.1 (1)	C(2)-C(1)-C(3)-C(4)	82.7 (2)
N(1')-C(6)-C(5)-O(2)	65.7 (2)	O(1)-C(3)-C(4)-O(2)	-78.8 (2)
C(1)-N(1)-C(7)-C(8)	66.8 (1)	C(3)-C(4)-O(2)-C(5)	162.1 (1)
C(1)-C(2)-O(1)-C(3)	-178.9 (1)	C(4)-O(2)-C(5)-C(6)	-167.4 (1)
C(1')-N(1')-C(6)-C(5)	-147.9 (1)	C(6')-N(1)-C(7)-C(8)	-162.2 (1)

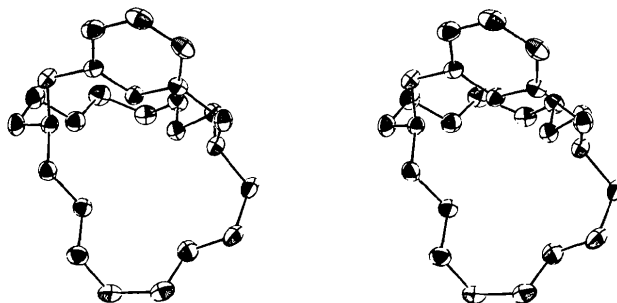


Fig. 2. Stereoview (ORTEP, Johnson, 1965) of cryptand 2.2.1py. Thermal ellipsoids are drawn at the 30% probability level.

The structure consists of discrete molecules, one half per asymmetric unit in the cell. The molecule possesses a crystallographic twofold axis passing through the N atom of the substituted pyridine moiety. As shown in Fig. 2 the bridgehead atoms N(1) and N(1') adopt the *endo-endo* conformation (Simmons & Park, 1968; Lehn, 1973) in the crystalline state. The atoms N(1), N(1'), N(2), O(2) and O(2') are directed toward the center of the ligand cavity while O(1) and O(1') point away from the center of the ligand cavity. The four O atoms form a near-planar array (average deviation 0.18 Å) that is essentially perpendicular [89.5 (1)°] to a plane defined by the pyridine ring and the methylene substituents [N(2), C(7), C(8), C(9), C(10)] (average deviation 0.02 Å). The N(1)⋯N(1') nonbonding distance is 4.561 (2) Å which is toward the lower end of the range of values [4.20–5.143 (4) Å] found for several complexes of the unsubstituted cryptand, 2.2.1 (Mathieu & Weiss, 1973; Mathieu, Metz, Moras & Weiss, 1978). The conformation of the 18-membered macrocyclic subunit (N₂O₄) is less symmetric than that found for the free macrocycle (2.2) and its K⁺ and Pb²⁺ complexes. The sequence of torsion angles, starting at N(1) of the macrocyclic subunit, is (*gaa*, *gga*, *aga*)₂ for 2.2.2py (*a*: *anti*, |θ| ≥ 150°; *g*: *gauche*, |θ| ≤ 75°). For the macrocycle 2.2, K(2.2)⁺ and Pb(2.2)²⁺ the analogous torsion-angle sequence is (*aga*)₆ (Herceg & Weiss, 1972; Moras, Metz, Herceg & Weiss, 1972; Metz & Weiss, 1973). For the K⁺ and Na⁺ complexes of the macrobicyclic analog, cryptand 2.2.1, an even less symmetric sequence is found (Mathieu *et al.*, 1978).

The C(sp³)–C(sp³) bond lengths in the O–C–C–O and N–C–C–O segments in the 18-membered macrocyclic subunit of 2.2.1py are 1.493 (2) and 1.505 (3) Å respectively. The corresponding values for a series of related macrocycles are: 2.2, 1.477 (9) and 1.513 (10) Å (Herceg & Weiss, 1972); 2.2.2, 1.482 (10) and 1.508 (6) Å (Metz, Moras & Weiss, 1976) and 2_B.2_B.2, 1.494 (3) and 1.514 (3) Å (Ott, Barnes, Taylor & van der Helm, 1982). These values are all shorter than the expected paraffinic value of 1.537 (5) Å (Sutton, 1965). The apparent bond-length shortening has been ascribed in part to inadequate treatment of curvilinear vibrational motion (Maverick, Seiler, Schweizer & Dunitz, 1980) and to specific interactions between the C and O (or N) atoms (Goldberg, 1975, 1978) and the effect is larger in the O–C–C–O segments than in the N–C–C–O segments (Ott *et al.*, 1982). The average C(sp³)–O bond length of 2.2.1py is 1.421 (4) Å which is close to the expected value of 1.426 (5) Å (Sutton, 1965) and those found in 2.2, 1.433 (26) Å; 2.2.2, 1.408 (19) Å and 2_B.2_B.2, 1.430 (10) Å. The average C(sp³)–N(sp³) bond length of the N₂O₄ macrocyclic subunit of 2.2.1py

is 1.462 (3) Å which is close to the expected value of 1.472 (5) Å (Sutton, 1965) and similar to those found in 2.2, 1.456 (6) Å; 2.2.2, 1.460 (12) Å and 2_B.2_B.2, 1.466 (5) Å.

The aromatic C–C bond lengths are 1.373 (2) to 1.384 (2) Å with an average value of 1.379 Å which is close to the expected value of 1.394 (1) Å and the C–N bond length is 1.337 (1) Å which is close to the expected value of 1.340 (1) Å (Sutton, 1965).

In the crystal, no strong interaction is observed between the molecules.

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