antiperiplanar to the C—O bond between C(1) and O(7), as the stereoelectronic principle (Deslong-champs, 1983) states in order to minimize the energy.

In order to investigate the rotational possibilities of the piperidine ring, conformational energy calculation of (1) using the MM2 program (Burkert & Allinger, 1982) was made. The electrostatic component was computed, using atomic partial charges calculated by the empirical method (Gasteiger & Marsili, 1980). The piperidine ring was rotated around the C(4)—C(2') axis and the total strain energy calculated for each 10° rotation. The torsional angle χ was defined by the atoms C(3), C(4), C(2'), and N(1') (0° corresponding to the eclipsed rotamer). Fig. 3(a) shows the results obtained from this procedure: the total strain energy is given as a function of the χ rotation. The global minimum was found for a χ value of 54° (rotamer A) which corresponds to the crystallographic conformation: $56 \cdot 1 (2)°$. Two local minima were also found for $\chi = 174°$ (rotamer B) and $\chi = -70°$ (rotamer C), 5·6 and 0·5 kcal mol^{-1} less stable than rotamer A respectively (1 kcal mol^{-1} = 4·2 kJ mol^{-1}). Fig. 3(b) presents the long range van der Waals interactions (1–5 and longer) and the electrostatic contribution to the total strain energy. It appears from this diagram that both components contribute to a destabilization of rotamer B. Therefore, the stabilization of rotamers A and C can be attributed to the effects of van der Waals (1–5 and

longer) interactions and electrostatic attractions induced by the I atom.

No abnormally short intermolecular contacts were noted in the crystal packing.

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Structure of 1,3-Xylyl-18-crown-5*

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Abstract. $C_{16}H_{24}O_5$, $M_r = 296·36$, triclinic, $P\bar{1}$, $a = 8·892$ (1), $b = 9·244$ (2), $c = 11·198$ (1) Å, $\alpha = 68·85$ (1), $\beta = 67·82$ (1), $\gamma = 86·83$ (1)°, $V = 791·4$ (2) Å^3, $Z = 2$, $D_x = 1·244$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·54184$ Å, $\mu = 7·1$ cm^{-1}, $F(000) = 320$, $T = 294$ K, $R = 0·0493$ for 2631 observed reflections with $I > 2·5\sigma(I)$. The ring conformation of the uncomplexed

1,3-xylyl-18-crown-5 ether differs in five of the eighteen endocyclic torsion angles from the ring conformation in complexes with diphenylmagnesium or with *tert*-butyl-ammonium perchlorate and dichloromethane.

Introduction. The crystal structure of 1,3-xylyl-18-crown-5 (I) was determined to compare the crown-ring conformation of the free molecule with the ring conformation in the recently studied rotaxane structure of 1,3-xylyl-18-crown-5 with diphenylmagnesium (Markies, Nomoto, Akkerman, Bickelhaupt, Smeets &

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* IUPAC name: 4*H*,18*H*-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzo[*ab*]cyclooctadecin.

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Table 1. *Positional and (equivalent) isotropic thermal parameters for the* non-H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq} or $U(\text{Å}^2)$
O(1)	0·7545 (2)	0·1792 (2)	0·3434 (1)	0·0669 (5)
O(2)†	1·0978 (2)	0·2371 (2)	0·1566 (2)	0·0631 (7)
O(3)	1·3224 (2)	0·3830 (2)	0·2225 (2)	0·0644 (5)
O(4)	1·2219 (2)	0·3611 (2)	0·5083 (1)	0·0624 (5)
O(5)	0·9875 (2)	0·2239 (2)	0·7886 (1)	0·0646 (5)
C(1)	0·8142 (2)	0·1419 (2)	0·6513 (2)	0·0525 (6)
C(2)	0·7313 (2)	0·1533 (2)	0·7800 (2)	0·0540 (6)
C(3)	0·5628 (2)	0·1461 (2)	0·8306 (2)	0·0575 (6)
C(4)	0·4785 (2)	0·1261 (2)	0·7560 (2)	0·0582 (6)
C(5)	0·5619 (2)	0·1136 (2)	0·6285 (2)	0·0544 (6)
C(6)	0·7311 (2)	0·1212 (2)	0·5750 (2)	0·0476 (6)
C(7)	0·8266 (2)	0·1038 (2)	0·4393 (2)	0·0588 (7)
C(8)	0·8259 (2)	0·1523 (3)	0·2173 (2)	0·0673 (8)
C(9)†	0·9653 (4)	0·2655 (4)	0·1143 (3)	0·066 (1)
C(10)	1·2396 (3)	0·3463 (3)	0·0572 (2)	0·0710 (8)
C(11)	1·3613 (2)	0·3120 (2)	0·1230 (2)	0·0628 (7)
C(12)	1·4189 (2)	0·3373 (3)	0·3025 (2)	0·0653 (7)
C(13)	1·3780 (2)	0·4180 (2)	0·4032 (2)	0·0635 (7)
C(14)	1·1854 (3)	0·4288 (2)	0·6107 (2)	0·0664 (8)
C(15)	1·0118 (3)	0·3857 (3)	0·7059 (2)	0·0695 (8)
C(16)	0·8222 (3)	0·1699 (3)	0·8651 (2)	0·0755 (9)

Minor disorder positions [s.o.f. = 0·180 (5)]

	x	y	z	
O(2)′	1·0745 (9)	0·3544 (10)	0·1049 (8)	0·054 (3)
C(9)′	1·0138 (14)	0·1977 (16)	0·1313 (13)	0·056 (3)

† Major disorder positions [s.o.f. = 0·820 (5)].

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for the* non-H *atoms*

O(1)—C(7)	1·407 (2)	C(1)—C(6)	1·386 (3)
O(1)—C(8)	1·420 (3)	C(2)—C(3)	1·383 (3)
O(2)—C(9)	1·407 (4)	C(2)—C(16)	1·512 (3)
O(2)—C(10)	1·455 (3)	C(3)—C(4)	1·376 (3)
O(3)—C(11)	1·415 (3)	C(4)—C(5)	1·383 (3)
O(3)—C(12)	1·409 (2)	C(5)—C(6)	1·389 (3)
O(4)—C(13)	1·411 (2)	C(6)—C(7)	1·498 (3)
O(4)—C(14)	1·423 (2)	C(8)—C(9)	1·468 (4)
O(5)—C(15)	1·423 (3)	C(10)—C(11)	1·487 (3)
O(5)—C(16)	1·402 (3)	C(12)—C(13)	1·492 (3)
C(1)—C(2)	1·389 (3)	C(14)—C(15)	1·482 (3)

C(7)—O(1)—C(8)	113·4 (2)	C(1)—C(6)—C(7)	118·9 (2)
C(9)—O(2)—C(10)	111·5 (2)	C(5)—C(6)—C(7)	122·2 (2)
C(11)—O(3)—C(12)	112·1 (2)	O(1)—C(7)—C(6)	109·9 (2)
C(13)—O(4)—C(14)	111·5 (2)	O(1)—C(8)—C(9)	112·8 (2)
C(15)—O(5)—C(16)	112·8 (2)	O(2)—C(9)—C(8)	109·4 (2)
C(2)—C(1)—C(6)	121·2 (2)	O(2)—C(10)—C(11)	104·8 (2)
C(1)—C(2)—C(3)	118·7 (2)	O(3)—C(11)—C(10)	109·1 (2)
C(1)—C(2)—C(16)	121·0 (2)	O(3)—C(12)—C(13)	110·6 (2)
C(3)—C(2)—C(16)	120·3 (2)	O(4)—C(13)—C(12)	110·7 (2)
C(2)—C(3)—C(4)	120·8 (2)	O(4)—C(14)—C(15)	109·5 (2)
C(3)—C(4)—C(5)	120·2 (2)	O(5)—C(16)—C(2)	114·4 (2)
C(4)—C(5)—C(6)	120·2 (2)	O(5)—C(15)—C(14)	109·8 (2)
C(1)—C(6)—C(5)	118·9 (2)		

C(8)—O(1)—C(7)—C(6)	−172·8 (2)	C(16)—O(5)—C(15)—C(14)	−170·4 (2)
C(7)—O(1)—C(8)—C(9)	−88·2 (2)	C(15)—O(5)—C(16)—C(2)	74·0 (3)
C(10)—O(2)—C(9)—C(8)	179·8 (2)	C(1)—C(2)—C(16)—O(5)	20·3 (3)
C(9)—O(2)—C(10)—C(11)	174·3 (2)	C(1)—C(6)—C(7)—O(1)	−142·9 (2)
C(12)—O(3)—C(11)—C(10)	171·7 (2)	O(1)—C(8)—C(9)—O(2)	71·1 (3)
C(11)—O(3)—C(12)—C(13)	178·3 (2)	O(2)—C(10)—C(11)—O(3)	−79·5 (2)
C(14)—O(4)—C(13)—C(12)	175·9 (2)	O(3)—C(12)—C(13)—O(4)	70·2 (2)
C(13)—O(4)—C(14)—C(15)	170·9 (2)	O(4)—C(14)—C(15)—O(5)	69·5 (2)

Spek, 1988). In particular, it was of interest to observe the degree of conformational changes in this ligand upon complexation and to determine the size of the cavity inside the crown ether in connection with the mechanism of insertion of an organometallic molecule through this ligand cavity. Related molecular mechanics studies for this type of compound have been published by Grootenhuis, van Eerden, Sudhölter, Reinhoudt, Roos, Harkema & Feil (1987). An X-ray study of a ternary complex of 1,3-xylyl-18-crown-5 with *tert*-butylammonium perchlorate and dichloromethane was published by van Eerden, Harkema & Sudhölter (1986).

Experimental. Crystals of (I) (prepared following Newcomb, Moore & Cram, 1977) suitable for X-ray diffraction were obtained by slow crystallization from diethyl ether at 253 K. A block-shaped, transparent, colourless crystal 1·13 × 0·70 × 0·43 mm, was glued on top of a glass fiber and transferred to an Enraf–Nonius CAD-4F diffractometer (Ni-filtered Cu $K\alpha$ radiation). Unit-cell parameters and their e.s.d.'s were derived from a least-squares treatment of the angular settings of 25 reflections with $19·6 < \theta < 32·0°$. Intensity data for 6011 reflections were collected ($-10 \le h \le 10; -11 \le k \le 11; -13 \le l \le 13; 4·6 < \theta < 70·0°$) in $\omega/2\theta$ scan mode with $\Delta\omega = (0·60 + 0·15\tan\theta)°$. Two reference reflections [$1\bar{2}3$ (r.m.s.d. = 0·77%) and $12\bar{4}$ (r.m.s.d. = 1·26%)], measured every hour showed

a small linear decay of 0·6% during the 36 hours of X-ray exposure time. The intensity data were corrected for this small decay and for Lp but not for absorption. Standard deviations in the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0·0139I)^2$ (McCandlish, Stout & Andrews, 1975). Reflections were merged ($R_{int} = 0·048$) to 2631 unique observed reflections with $I > 2·5\sigma(I)$. Space group $P\bar{1}$ was discriminated from $P1$ during the structure determination process. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1986), the solution with the best figure of merit revealed all non-H atoms. H atoms were introduced on calculated positions (C—H = 0·98 Å) and included in weighted full-matrix least-squares refinement (on F) riding on their carrier atom. Two atoms [C(9) and O(2)] were found to be disordered over two positions with site occupation factors 0·820 (5) and 0·180 (5), respectively. H atoms were refined with one common isotropic thermal parameter [$U = 0·079$ (1) Å²], the minor disorder atoms with individual isotropic thermal parameters, the remaining atoms with anisotropic thermal parameters. The too strong 120 reflection was excluded from the final refinement cycles. Convergence with 201 parameters was reached at $R = 0·0493$ [$wR = 0·0596$, $w = 1/\sigma^2(F)$, $S = 0·33$, $(\Delta/\sigma)_{max} = 0·003$]. The final

difference Fourier synthesis shows no residual densities outside the range 0·22 to −0·20 e Å⁻³. The crystal exhibited some extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter X [=1·11(3)×10⁻⁵]: $F_c' = F_c[1 − (XF_c^2/\sin\theta)]$. Scattering factors were taken from Cromer & Mann (1968). Calculations performed with *SHELX*76 (Sheldrick, 1976) and the *EUCLID* package (geometry calculations and illustrations) (Spek, 1982) on a MicroVAX-II.

Discussion. Refined atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1.* Bond lengths, bond angles and relevant endocyclic torsion angles are listed in Table 2. The molecular structure and the adopted atom numbering are presented in Fig. 1.

The triclinic unit cell contains two discrete molecules without unusual intermolecular short contacts. The title crown ether molecule (I) was previously studied as part of a ternary complex with *tert*-butylammonium perchlorate and dichloromethane (II) (van Eerden *et al.*, 1986) and in a complex with diphenylmagnesium (III) (Markies *et al.*, 1988). The present free crown-ether conformation is different from that observed in the two aforementioned complexes. This can be seen from the

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and geometrical data concerning H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51437 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
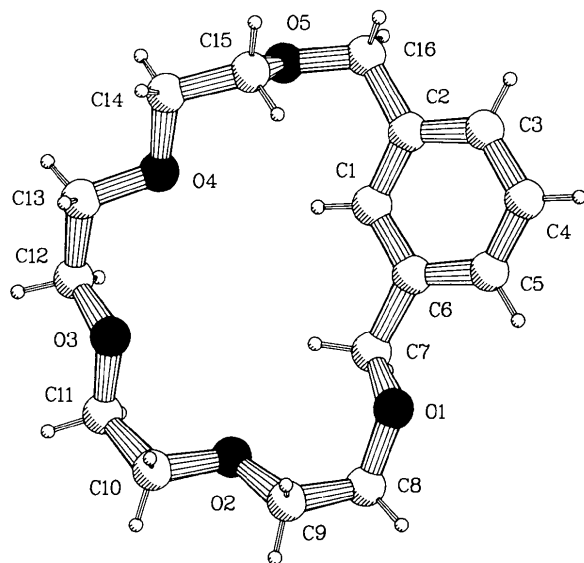
torsion codes (ap = antiperiplanar; ac = anticlinal; sp = synperiplanar; sc = synclinal) of the relevant endocyclic torsion angles which are represented by the following sequence:

($A,ap,B,+sc,ap,ap,−sc,ap,ap,+sc,ap,ap,C,ap,D,E$) in which A,B,C,D,E are $−ac,−sc,+sc,+sc,+sp$ for (I); $−sc,ap,−sc,ap,+sc$ for (II) and $−sc,ap,+sc,+sc,+sc$ for (III). Thus, for these three compounds 11 of the 16 relevant endocyclic torsion angles within the crown moieties have equal torsion descriptors. The conformational differences are therefore caused chiefly by the changes of five torsion angles situated near the xylyl ring.

Bond distances and angles are within normal ranges for crown ethers; $C(sp^3)–C(sp^3)$ distances range from 1·468 (4) to 1·492 (3) Å, C—O distances are in the range 1·402 (3) to 1·455 (3) Å. C—O—C angles lie between 111·5 (2) and 113·4 (2)° in the present compound, between 110·9 (3) and 113·5 (3)° in the complex with *tert*-butylammonium perchlorate and between 111·4 (4) and 113·8 (4)° for the diphenylMg complex.

The conformations of the title compound in its free form and in the reference compounds [(II) and (III)] were minimized by molecular mechanics [MMP2(85); Allinger, 1985]; see also Grootenhuis *et al.* (1987). The differences between the observed and minimized conformations are rather small (0–17° with an average of 4·8°, for the endocyclic torsion angles). The final steric energies of the three conformations after minimization are equal within 2·5 kJ mol⁻¹. The present study shows that the 1,3-xylyl-18-crown-5 system has a conformational flexibility similar to that observed in other crown ethers such as 18-crown-6 upon complexation (Trueblood, 1984).

Fig. 1. *PLUTO* (*EUCLID* version) drawing of the title compound with the adopted atom numbering.

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Structure of 6-Amino-1-hydroxyhexylidenebis(phosphonic acid)

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Abstract. $C_6H_{17}NO_7P_2$, $M_r = 277.1$, monoclinic, $P2_1/c$, $a = 6.960$ (2), $b = 13.127$ (5), $c = 12.056$ (3) Å, $\beta = 95.89$ (2)°, $V = 1095.6$ (6) Å^3, $Z = 4$, $D_x = 1.68$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 4.24$ cm^{-1}, $F(000) = 584$, $T = 293$ K, final $R = 0.043$ ($wR = 0.065$) for 2798 observed reflections. The title compound exists as a zwitterion and the alkylamino side chain adopts a *trans–trans–trans–gauche$^-$–gauche$^-$* backbone conformation. The phosphonate O atoms form a nearly planar W configuration. There are seven independent hydrogen bonds in the structure, three bifurcated of type N—H···O and four of type O—H···O.

Introduction. Diphosphonate compounds, owing to their ability to inhibit either dissolution or formation of crystals of hydroxyapatite (King, Francis & Michael, 1971), find therapeutic use in diseases related to the metabolism of calcium and phosphates (Francis & Centner, 1978). Among them, *gem*-diphosphonates, in which the linkage P—C(R')R—P' simulates the linkage P—O—P present in pyrophosphates, are particularly important, due to an increased resistance to the hydrolysis. Different substitution patterns of groups R and R' might modify their chemical and biological properties. The structure determination of the title compound was undertaken to characterize a new series of compounds, exhibiting calcium binding properties, in which $R = OH$ and $R' =$ an alkyl chain with a terminal amino group.

Experimental. Colourless prismatic-shaped crystals of the title compound were grown from water. Preliminary oscillation and Weissenberg photographs indicated crystals to be monoclinic, $P2_1/c$. A crystal *ca* $0.2 \times 0.3 \times 0.5$ mm was selected for the data collection and set on a Nicolet $R3$ diffractometer equipped with Mo $K\alpha$ radiation and graphite monochromator.

Intensity data were collected at room temperature, the experimental conditions being: $2\theta_{max} \le 73°$, hkl ranges $h -11\rightarrow11$, $k\,0\rightarrow20$, $l\,0\rightarrow21$, θ–2θ scan mode, scan range $1.2°$, scan rate 2.0–$29.3°$ min^{-1} (depending on the reflection intensity), background-count time equal to the scan time. Accurate unit-cell parameters were determined by least-squares fit of the setting angles of 15 selected reflections with $10 \le 2\theta \le 42°$.

Four control reflections monitored every hundred indicated a smooth variation (crystal decay of *ca* 1%) of intensity during data collection. The data were processed and corrected for the average change in the intensity of the reference reflections. Lorentz and polarization corrections were applied but no absorption or extinction corrections were made.

Merging equivalents gave 5423 unique reflections ($R_{int} = 0.027$), of which 2798 with $I \ge 3\sigma(I)$ were used for the structure refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures minimizing the function $\sum w|\Delta F|^2$ with $w = (a + |F_o| + b|F_o|^2)^{-1}$. The parameters a and b were given values of $2 \times F_{omin}$ and $2/F_{omax}$ in order to obtain $\langle w|\Delta F|^2 \rangle$ nearly constant in ranges of F_o and $\sin\theta/\lambda$.

The H atoms were located by difference Fourier syntheses. Non-H atoms were refined anisotropically and H atoms refined with isotropic temperature factors. The final R value is 0.043 ($wR = 0.065$). At convergence, the maximum shift-to-e.s.d. ratio was 2.60, which corresponds to B_{iso} of H(41), meanwhile the other parameters have shift-to-e.s.d. ratios less than 0.2; $S = 0.31$. Maximum and minimum $\Delta\rho$ in the final difference Fourier synthesis were 0.3 and -0.5 e Å^{-3}. All calculations were performed on a Data General