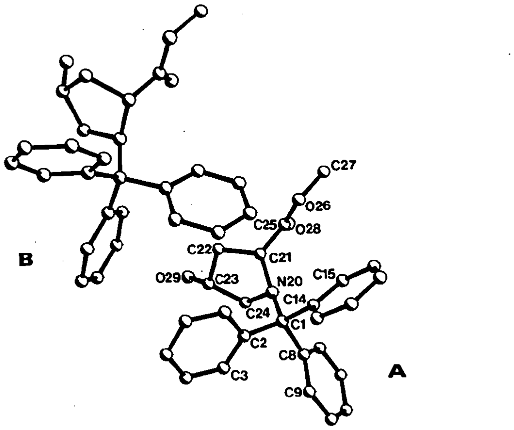

Fig. 1. Views of the two independent molecules, showing the atom-numbering scheme. The sequence of the phenyl ring C atoms is C(2)···C(7), C(8)···C(13) and C(14)···C(19).

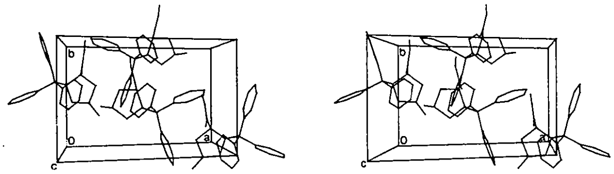

Fig. 2. Stereoscopic drawing of the packing of the title compound.

thereby avoiding steric congestion. By adopting this energetically favoured conformation the triphenylmethyl group alone does not hinder the carbonyl function from nucleophilic attack. Thus, the stability of (3) to ammonolysis must be related to the geometry of the ring portion of the molecule.

Both molecules show normal values of bond lengths and angles. Each *A* molecule forms an intermolecular O—H···O hydrogen bond with a neighbouring *B* molecule: O(29*A*)—H(29*A*)···O(29*B*^{i}) [(i): $1-x$, $-\frac{1}{2}+y$, $1-z$; O(29*A*)···O(29*B*) = 2·844 (6), H(29*A*)···O(29*B*) = 1·933 (61) Å and O(29*A*)—H(29*A*)···O(29B) = 160 (5)°]. There are no significant intramolecular contacts.

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11,28-Bis(chloroacetyl)-6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b*,*q*][1,4,7,10,16,19,22,25,13,28]octaoxadiazacyclotriacontine*

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Abstract. $C_{32}H_{44}Cl_2N_2O_{10}$, $M_r = 687·6$, monoclinic, $P2_1/c$, $a = 10·659$ (1), $b = 7·109$ (1), $c = 22·105$ (2) Å, $\beta = 90·80$ (1)°, $V = 1674·9$ (3) Å^3, $Z = 2$ (the molecule possesses a centre of symmetry), $D_x = 1·36$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1·54178$ Å, $\mu = 2·25$ mm^{-1}, $F(000) = 728$, $T = 293$ K, $R = 0·043$ for 2049 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The structure of (9) has an extended shape with the azapolyether chains, which contain an equal number of *gauche* and *anti* C—C bonds, filling the potential

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* 2,5,11,14,21,24,30,33-Octaoxa-8,27-diazatricyclo[32.4.0.0^{15,20}]-octatriaconta-15,17,19,34,36,38(1)-hexaene.

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macrocyclic cavity. There are major departures from coplanarity of the *ortho*-related methyleneoxy units with the benzo rings. In symmetry-related molecules, adjacent benzo rings interact in an edge-to-face manner with respect to each other.

Introduction. Dibenzo-30-crown-10 (1) has been shown (Colquhoun, Goodings, Maud, Stoddart, Wolstenholme & Williams, 1985; Stoddart, 1988) to form 1:1 complexes in both the solution and solid states with the bipyridinium dication, Diquat. On the other hand, the chemically related dication, Paraquat, is bound only very weakly by (1). This observation has been used electrochemically (Moody, Owusu & Thomas, 1987) to develop a selective molecular sensor device for Diquat. This selectivity is retained (Anelli, Spencer & Stoddart, 1988; Anelli, Slawin, Stoddart & Williams, 1988*a*) in the diazadibenzo-30-crown-10 derivatives (2)–(6). By contrast, bis-*p*-phenylene-34-crown-10 (11) is well known (Allwood, Spencer, Shahriari-Zavareh, Stoddart & Williams, 1987*a*,*b*; Ashton, Slawin, Spencer, Stoddart & Williams, 1987) to form 1:1 complexes equally well with both Diquat and Paraquat in the solid and solution states. Obviously, the presence of two NH groups in (2) replacing O atoms in the middle of the polyether chains of (1) affords the opportunity to introduce a bridging unit into the macrocycle parallel to the two benzo rings. Thus, macrobicyclic derivatives such as (10) have already been synthesized (Anelli *et al.*, 1988). Experiments have failed to reveal any complexing affinity of the intermediate compounds (7)–(9) towards Diquat or Paraquat (Anelli *et al.*, 1988; Anelli, Slawin, Stoddart & Williams, 1988*b*).

On account of their redox properties (Summers, 1980), Paraquat (methyl viologen) and analogous bipyridinium dications have been the subject of much interest and research activity. It occurred to us that the redox properties of these dications might be influenced and manipulable by incorporating them covalently into the π-electron-rich receptor sites provided by the two catechol residues. Inspection of CPK space-filling molecular models suggests that it should be possible to prepare macrobicyclic dications such as those illustrated in Fig. 1.

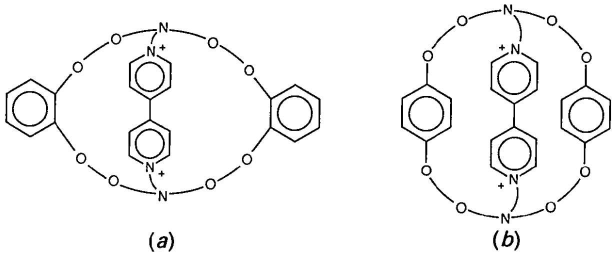
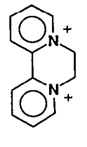
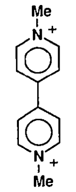
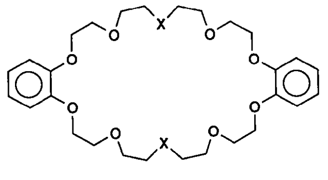

(*a*) (*b*)

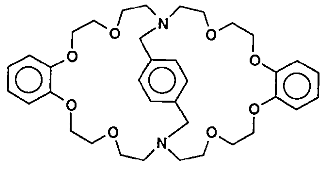
Fig. 1. Diagrammatic representations of macrobicyclic bipyridinium dications based on (*a*) diazadibenzo-30-crown-10 and (*b*) diazabis-*p*-phenylene-34-crown-10 constitutions. The lines joining O atoms, and O and N atoms correspond to —CH_2CH_2— units. The lines joining N atoms correspond to chains containing up to three C atoms.

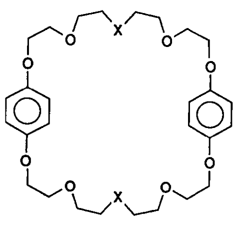
Here we describe the X-ray crystal structure of an intermediate (9) which is a potential precursor of macrobicyclic dications of the type shown in Fig. 1(*a*). The conformational properties of (9) are compared with those reported previously for dibenzo-30-crown-10 (1) (Bush & Truter, 1972) and the diazadibenzo-30-crown-10 disulfonamide (7) (Anelli *et al.*, 1988*b*).


Diquat


Paraquat


(1) X = O
(2) X = NH
(3) X = NMe
(4) X = NCH_2CO_2Et
(5) X = NCH_2Ph
(6) X = NCH_2-*p*-C_6H_4OMe
(7) X = NTs
(8) X = NCO_2Et
(9) X = $NCOCH_2Cl$


(10)


(11) X = O
(12) X = NH

Experimental. Compound (2) was acylated with chloroacetyl chloride in benzene in the presence of triethylamine at room temperature for 16 hours to afford the title compound (9) in 43% yield after column chromatography on silica gel using ethyl acetate as eluant. Single crystals (m.p. 407–408 K) of (9) were obtained by vapour diffusion of light petroleum (b.p. 40–60°C) into a chloroform solution. Crystal size 0·07 × 0·47 × 0·57 mm. Refined unit-cell parameters obtained from setting angles of 18 reflections with $8 \le \theta \le 32°$. Nicolet *R*3*m* diffractometer. 2255 independent reflections ($\theta \le 58°$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. 2049 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range *h* −11/11, *k* 0/7, *l* 0/24; two check reflections measured every 50 reflections, *ca* 2% decay over data collection; Lorentz and polarization corrections, numerical absorption correction, min. and max. transmission factors 0·64, 0·85. Structure solved by direct methods; non-H atoms refined anisotropically; positions of H atoms calculated (C—H = 0·96 Å); H atoms assigned isotropic thermal parameters, $U(\mathrm{H}) = 1{\cdot}2U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on parent C atoms. An empirical extinction correction was applied [$g = 0{\cdot}0048\,(9)$]. Refinement using *F* magnitudes by block-cascade full-matrix least squares; $R = 0{\cdot}043$, $wR = 0{\cdot}052$ [$w^{-1} = \sigma^2(F) + 0{\cdot}00050F^2$]. $(\Delta/\sigma)_{\max}$ 0·008; 209 refined parameters, $S = 1{\cdot}87$, residual electron density in difference map within −0·34 and 0·36 e Å^{-3}, atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. The structure of (9) with atomic numbering is shown in Fig. 2(*a*). Table 1* lists the fractional atomic coordinates of the non-H atoms and Table 2 the bond lengths, bond angles and selected torsion angles.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}(Å^2)
O(1)	0·7650 (2)	0·1584 (2)	−0·2288 (1)	0·048 (1)
C(2)	0·7764 (2)	0·2487 (3)	−0·1704 (1)	0·049 (1)
C(3)	0·6926 (2)	0·1462 (4)	−0·1285 (1)	0·053 (1)
O(4)	0·7137 (2)	0·2205 (2)	−0·0698 (1)	0·050 (1)
C(5)	0·6455 (2)	0·1212 (3)	−0·0254 (1)	0·048 (1)
C(6)	0·6848 (2)	0·1885 (3)	0·0367 (1)	0·048 (1)
N(7)	0·6339 (2)	0·3720 (2)	0·0538 (1)	0·043 (1)
C(8)	0·5105 (2)	0·3702 (3)	0·0828 (1)	0·044 (1)
C(9)	0·5247 (2)	0·3131 (4)	0·1482 (1)	0·050 (1)
O(10)	0·4065 (1)	0·3162 (2)	0·1759 (1)	0·047 (1)
C(11)	0·4137 (2)	0·2455 (3)	0·2360 (1)	0·046 (1)
C(12)	0·2982 (2)	0·2983 (3)	0·2694 (1)	0·046 (1)
O(13)	0·2957 (1)	0·4983 (2)	0·2725 (1)	0·048 (1)
C(14)	0·1918 (2)	0·5827 (3)	0·2959 (1)	0·040 (1)
C(15)	0·1195 (2)	0·5074 (4)	0·3413 (1)	0·048 (1)
C(16)	0·0207 (2)	0·6092 (4)	0·3645 (1)	0·057 (1)
C(17)	−0·0060 (2)	0·7861 (4)	0·3429 (1)	0·058 (1)
C(18)	0·0652 (2)	0·8624 (4)	0·2971 (1)	0·052 (1)
C(19)	0·1631 (2)	0·7618 (3)	0·2733 (1)	0·042 (1)
C(20)	0·6960 (2)	0·5370 (3)	0·0505 (1)	0·044 (1)
O(20)	0·6531 (2)	0·6852 (2)	0·0692 (1)	0·059 (1)
C(21)	0·8257 (2)	0·5262 (4)	0·0221 (1)	0·060 (1)
Cl	0·8951 (1)	0·7487 (1)	0·0151 (1)	0·082 (1)

In common with the dibenzo-30-crown-10 (1) (Bush & Truter, 1972) and the diazadibenzo-30-crown-10 sulfonamide (7) (Anelli *et al.*, 1988*b*), the title compound adopts a centrosymmetric extended conformation with no free pathway through the centre of the macrocyclic ring (Fig. 2*b*). However, there is a marked difference in the orientations of the chloroacetyl ($COCH_2Cl$) groups in (9) compared with the *p*-toluenesulfonyl (Ts) groups in (7). In (7), the Ts groups are directed away from the centre of the macrocycle whilst in (9) the $COCH_2Cl$ groups are oriented inwards (Fig. 2*a*). Furthermore, there is an absence of coplanarity (Makriyannis & Fesik, 1982; Kruse & Cha, 1982; Mersh, Saunders & Matlin, 1983; Colquhoun *et al.*, 1985; Allwood, Shahriari-Zavareh, Stoddart & Williams, 1987; Allwood *et al.*, 1987*a*) of both the *ortho*-related oxymethylene units with their associated benzo rings. In one instance, the O(1)—C(2) bond is rotated 69° out of plane whereas, in the other instance, the C(12)—O(13) bond is rotated 30° out of plane. Whereas in (1) and (7), the torsional angles associated with the CH_2CH_2 units are all *gauche*, in (9), half of them are *anti*. There is a small pyramidalization at the N atoms, each lying 0·05 (1) Å from the planes of their substituents. In addition to the expected, essentially coplanar,

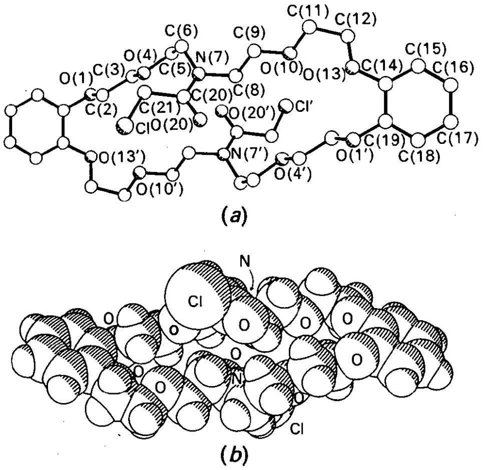


Fig. 2. (*a*) Ball-and-stick representation of the structure of (9) showing the atomic numbering scheme. (*b*) A space-filling representation of (9) showing the self-filling of the potential macrocyclic cavity in the solid state.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52749 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

O(1)—C(2)	1·444 (3)	O(1)—C(19′)	1·378 (3)
C(2)—C(3)	1·486 (3)	C(3)—O(4)	1·417 (3)
O(4)—C(5)	1·417 (3)	C(5)—C(6)	1·508 (3)
C(6)—N(7)	1·465 (3)	N(7)—C(8)	1·471 (3)
N(7)—C(20)	1·350 (3)	C(8)—C(9)	1·506 (3)
C(9)—O(10)	1·409 (3)	O(10)—C(11)	1·423 (3)
C(11)—C(12)	1·493 (3)	C(12)—O(13)	1·423 (3)
O(13)—C(14)	1·368 (3)	C(14)—C(15)	1·381 (3)
C(14)—C(19)	1·400 (3)	C(15)—C(16)	1·382 (3)
C(16)—C(17)	1·373 (4)	C(17)—C(18)	1·385 (4)
C(18)—C(19)	1·376 (3)	C(19)—O(1′)	1·378 (3)
C(20)—O(20)	1·223 (3)	C(20)—C(21)	1·527 (3)
C(21)—Cl	1·754 (3)		

C(2)—O(1)—C(19′)	114·5 (2)	O(1)—C(2)—C(3)	107·2 (2)
C(2)—C(3)—O(4)	107·4 (2)	C(3)—O(4)—C(5)	111·8 (2)
O(4)—C(5)—C(6)	109·4 (2)	C(5)—C(6)—N(7)	114·8 (2)
C(6)—N(7)—C(8)	116·2 (2)	C(6)—N(7)—C(20)	125·1 (2)
C(8)—N(7)—C(20)	118·3 (2)	N(7)—C(8)—C(9)	110·0 (2)
C(8)—C(9)—O(10)	109·5 (2)	C(9)—O(10)—C(11)	111·3 (2)
O(10)—C(11)—C(12)	109·8 (2)	C(11)—C(12)—O(13)	106·9 (2)
C(12)—O(13)—C(14)	118·2 (2)	O(13)—C(14)—C(15)	124·6 (2)
O(13)—C(14)—C(19)	116·0 (2)	C(15)—C(14)—C(19)	119·4 (2)
C(14)—C(15)—C(16)	120·1 (2)	C(15)—C(16)—C(17)	120·4 (2)
C(16)—C(17)—C(18)	119·9 (2)	C(17)—C(18)—C(19)	120·2 (2)
C(14)—C(19)—C(18)	120·0 (2)	C(14)—C(19)—O(1′)	120·5 (2)
C(18)—C(19)—O(1′)	119·4 (2)	N(7)—C(20)—O(20)	123·0 (2)
N(7)—C(20)—C(21)	115·3 (2)	O(20)—C(20)—C(21)	121·8 (2)
C(20)—C(21)—Cl	112·1 (2)		

C(19′)—O(1)—C(2)—C(3)	179·6 (2)	C(8)—N(7)—C(20)—O(20)	− 1·7 (3)
C(2)—O(1)—C(19′)—C(14′)	− 69·0 (2)	C(8)—N(7)—C(20)—C(21)	177·6 (2)
C(2)—O(1)—C(19′)—C(18′)	113·4 (2)	N(7)—C(8)—C(9)—O(10)	178·6 (2)
O(1)—C(2)—C(3)—O(4)	173·7 (2)	C(8)—C(9)—O(10)—C(11)	174·3 (2)
C(2)—C(3)—O(4)—C(5)	− 175·2 (2)	C(9)—O(10)—C(11)—C(12)	164·6 (2)
C(3)—O(4)—C(5)—C(6)	172·3 (2)	O(10)—C(11)—C(12)—O(13)	− 63·1 (2)
O(4)—C(5)—C(6)—N(7)	75·9 (2)	C(11)—C(12)—O(13)—C(14)	173·7 (2)
C(5)—C(6)—N(7)—C(8)	87·9 (2)	C(12)—O(13)—C(14)—C(15)	33·0 (3)
C(5)—C(6)—N(7)—C(20)	− 98·9 (2)	C(12)—O(13)—C(14)—C(19)	− 150·3 (2)
C(6)—N(7)—C(8)—C(9)	78·0 (2)	O(13)—C(14)—C(19)—O(1′)	1·9 (3)
C(20)—N(7)—C(8)—C(9)	− 95·7 (2)	N(7)—C(20)—C(21)—Cl	176·1 (2)
C(6)—N(7)—C(20)—O(20)	− 174·8 (2)	O(20)—C(20)—C(21)—Cl	− 4·6 (3)
C(6)—N(7)—C(20)—C(21)	4·5 (3)		

arrangement of the atoms comprising each amide group, the associated chlorine atoms also lie approximately in these planes.

The packing of the molecules involves edge-to-face interactions (Gould, Gray, Taylor & Walkinshaw, 1985) between the benzo rings. The ring centroid to ring centroid distance is 5·07 (1) Å with the centroid–centroid vector inclined by 67° to one of the ring planes. The C(18)—H(18) bond in one molecule is directed towards the centre of the C(14) to C(19) benzo ring in another at a distance of 3·02 Å. This electrostatic interaction, which corresponds to a global potential-energy minimum (Burley & Petsko, 1985, 1986) for an interaction between aromatic rings, appears to be a remarkably common feature occurring in both intramolecular (Slawin, Spencer, Stoddart & Williams, 1987; Ashton, Chrystal, Mathias, Parry, Slawin, Spencer, Stoddart & Williams, 1987) and intermolecular (Alston, Slawin, Stoddart, Williams & Zarzycki, 1987; Moody, Owusu, Slawin, Spencer, Stoddart, Thomas & Williams, 1987; Anelli *et al.*, 1988*b*) situations.

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