

compound (Borea, Hamor & Martin, 1988), thus excluding the possibility of any significant conjugation between the phenyl ring and the N(5)–C(6) double bond. Consistent with this the N(5)–C(6) length [1.287 (4) Å] corresponds, within the limits of experimental error, to a C=N double bond. The angle between the chlorophenyl ring and the fused benzo moiety is 67.1 (6)°. This is somewhat less than has been previously found in 5-(2-halophenyl)-1,4-benzodiazepines where the normal range for this angle is 73–86°.

The cation forms hydrogen bonds with two methanesulfonate anions, situated at equivalent positions ($\frac{1}{2} - x$, $-\frac{1}{2} - y$, $-z$) and (x , $-y$, $-\frac{1}{2} + z$). The pertinent distances and angles are N(5)⋯O(2) = 2.659 (5), H(5)⋯O(2) = 1.84 (5) Å, angle H(5)–N(5)⋯O(2) = 10 (3)° and N(2)⋯O(1) = 2.727 (4), H(2)⋯O(1) = 1.91 (5) Å, angle H(2)–N(2)⋯O(1) = 1 (3)°. The O atom of the methanol molecule may also be involved in a hydrogen bond with the anion, the distance O(4)⋯O(1) ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) being 2.91 (4) Å. Other intermolecular contact distances, apart from some short distances involving the partially occupied methanol sites, correspond to normal van der Waals interactions.

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Structure of a Photoresponsive Crown Ether, 21-(4'-Methoxyphenylazo)-1,4,7,14,23-pentaoxa[7.2.2]orthometathobenzophane

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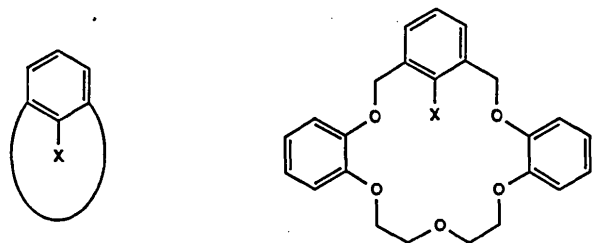
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Abstract. 3,10,13,16,23-Pentaoxatetracyclo-[23.3.1.0^{4,9}.0^{17,22}]nonacosia-1(29),4,6,8,17,19,21,25,27-nonaene-29-azo-(4'-methoxybenzene), C₃₁H₃₀N₂O₆, *M_r* = 526, monoclinic, *P*2₁/*n*, *a* = 14.564 (3), *b* = 19.177 (2), *c* = 10.025 (2) Å, β = 100.42 (1)°, *V* = 2754 (1) Å³, *Z* = 4, *D_x* = 1.269 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 0.95 cm⁻¹, *F*(000) = 1112, *T* = 293 K, final *R* = 0.050 for 2577 reflections with *I* > 3σ(*I*). The molecule resembles a butterfly with benzene rings for the wings and head. The *trans*-azobenzene moiety, which overlays one face of the crown oxygen ring, is in an orientation that creates a

partial steric block to cation⋯crown complex formation.

Introduction. Macrocyclic polyethers ('crown ethers') contain intramolecular cavities lined with molecular segments that are capable of binding cations. Crown ethers of type (I), which contain an intraannular substituent *X*, may bind metal cations in two ways. When *X* has no metal-coordination capability, *X* acts as a simple steric spacer and the crown-cation association constant decreases. In contrast, when *X* has a metal-coordination capability, it may act as a

ligand group and the association constant increases. Thus, potentially one can adjust the metal affinity and the metal selectivity of macrocyclic polyethers with such an intraannular substituent.



(I)

cis-(II) : X = cis-N=N-C₆H₄-4-OCH₃
 trans-(II) : X = trans-N=N-C₆H₄-4-OCH₃
 (III) : X = H

A crown ether (II) with an intraannular *trans*-azo substituent has been prepared by Shinkai, Miyazaki & Manabe (1987). The compound was designed to permit the cation-crown interaction to be altered by photoisomerization of the intraannular azo substituent from *trans* to *cis*. Two-phase solvent extraction experiments with alkali picrates established that Na⁺ was extracted by only the photoisomerized *cis*-(II) and not by *trans*-(II). In addition, both *cis*- and *trans*-(II) showed affinity for the larger cations K⁺, Rb⁺ and Cs⁺, although the association was always largest for the *cis* isomer.

Space-filling molecular models of *trans*-(II) suggested that the intraannular azo substituent could interfere with the approach of the metal cation to the crown moiety, and that this azo block was effectively removed by photoisomerization to the *cis*-azo geometry. The question remained, however, why *trans*-(II) showed an affinity only with cations larger than sodium. The crystal structure of *trans*-(II) was undertaken in order to understand these data more fully.

Experimental. Red-brown crystals from CF₃CH₂OH; 0.3 × 0.3 × 0.4 mm crystal for X-ray experiments; Enraf-Nonius CAD-4 diffractometer; Mo K α radiation with incident-beam graphite monochromator; cell parameters from 25 reflections centered in the range 9.4 < θ < 17.8°; 2 θ - θ scan at variable θ scan speed of 4.12–0.87° min⁻¹, θ scan range of 1.5(1.0 + 0.35tan θ)°, scan recorded as 96 steps with two outermost 16 step blocks for background determination; six standard reflections measured every two hours of X-ray exposure; 5473 data (includes standards) measured for $\theta = 2$ –25°; index range for *h*, *k*, *l* of -17–17, 0–22, 0–11; 4994 unique data, 2577 reflections with $I > 3\sigma(I)$; average change in standard intensities of 0.9% with range of -1.2–+2.1%; $R_{\text{int}} = 0.017$ for 299 data; absorption ignored. All crystallographic calculations performed with the

Table 1. Fractional coordinates and equivalent isotropic temperature factors with *e.s.d.*'s in parentheses for *trans*-(II)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B _{eq} (Å ²)
O	0.6802 (2)	0.0569 (1)	-0.2300 (3)	5.7 (2)
O(1)	0.9127 (2)	0.3846 (1)	-0.3013 (3)	4.9 (1)
O(4)	0.7206 (2)	0.3925 (2)	-0.4396 (3)	5.7 (2)
O(7)	0.5617 (2)	0.4117 (2)	-0.3060 (3)	6.0 (2)
O(14)	0.5816 (2)	0.4339 (1)	-0.0489 (2)	4.1 (1)
O(23)	0.9563 (2)	0.4003 (1)	-0.0399 (2)	4.1 (1)
N(1)	0.7914 (2)	0.3203 (2)	-0.0356 (3)	4.7 (2)
N(2)	0.7467 (2)	0.3473 (2)	0.0437 (3)	3.6 (2)
C(2)	0.8812 (4)	0.3728 (3)	-0.4420 (5)	5.8 (3)
C(3)	0.7991 (4)	0.4187 (3)	-0.4875 (6)	5.9 (3)
C(5)	0.6373 (4)	0.4317 (4)	-0.4899 (6)	7.2 (4)
C(6)	0.5565 (4)	0.3966 (4)	-0.4463 (6)	6.9 (3)
C(8)	0.4993 (3)	0.3786 (2)	-0.2409 (5)	4.8 (2)
C(9)	0.4278 (4)	0.3350 (3)	-0.3017 (6)	6.7 (3)
C(10)	0.3672 (4)	0.3050 (3)	-0.2279 (7)	6.9 (3)
C(11)	0.3770 (4)	0.3183 (3)	-0.0948 (7)	6.2 (3)
C(12)	0.4475 (3)	0.3613 (2)	-0.0290 (5)	4.8 (2)
C(13)	0.5099 (3)	0.3909 (2)	-0.1016 (4)	3.9 (2)
C(15)	0.6089 (3)	0.4342 (2)	0.0961 (4)	3.8 (2)
C(16)	0.7086 (3)	0.4566 (2)	0.1304 (3)	3.3 (2)
C(17)	0.7318 (3)	0.5198 (2)	0.1919 (4)	4.2 (2)
C(18)	0.8239 (3)	0.5397 (2)	0.2255 (4)	4.7 (2)
C(19)	0.8926 (3)	0.4973 (2)	0.1957 (4)	4.2 (2)
C(20)	0.8724 (3)	0.4341 (2)	0.1317 (3)	3.3 (2)
C(21)	0.7790 (2)	0.4134 (2)	0.0994 (3)	2.9 (2)
C(22)	0.9515 (3)	0.3913 (3)	0.1002 (4)	4.0 (2)
C(24)	1.0067 (3)	0.3518 (2)	-0.0940 (4)	3.8 (2)
C(25)	1.0768 (3)	0.3126 (2)	-0.0231 (5)	4.5 (2)
C(26)	1.1251 (3)	0.2650 (3)	-0.0888 (6)	5.7 (3)
C(27)	1.1033 (3)	0.2569 (3)	-0.2247 (6)	5.7 (3)
C(28)	1.0319 (3)	0.2956 (3)	-0.2986 (6)	5.1 (3)
C(29)	0.9482 (3)	0.3432 (2)	-0.2366 (4)	4.0 (2)
C(1')	0.7583 (3)	0.2528 (2)	-0.0868 (4)	4.0 (2)
C(2')	0.8113 (3)	0.2181 (3)	-0.1671 (5)	6.2 (3)
C(3')	0.7883 (3)	0.1524 (2)	-0.2177 (5)	5.1 (2)
C(4')	0.7105 (3)	0.1215 (2)	-0.1870 (4)	4.0 (2)
C(5')	0.6563 (3)	0.1560 (3)	-0.1124 (5)	6.0 (3)
C(6')	0.6793 (3)	0.2216 (3)	-0.0630 (5)	5.8 (3)
C(7')	0.7275 (5)	0.0194 (3)	-0.3217 (6)	6.3 (3)

TEXSAN (Molecular Structure Corporation, 1987) program system on a DEC MicroVAX II computer; structure resolved with MITHRIL (Gilmore, 1983) direct-methods link; refinement by full-matrix least squares with anisotropic temperature factors for C, N and O; $\sum w(F_o - F_c)^2$ minimized, $w = 1/\sigma^2(F_o)$; H atoms were positioned from the C-atom framework and refined with isotropic terms; secondary-extinction parameter [method of Zachariasen (1968)] refined, 0.218 (7) × 10⁻⁵; final *S*, *R* and *wR* values of 2.6, 0.050, 0.032; maximum Δ/σ of 0.59; minimum and maximum values in the final difference map of -0.22 and 0.20 e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* The drawings shown in Figs. 1 and 2 were labelled with the PLOTMD program (Luo, Ammon & Gilliland, 1989).

* Lists of structure factors, anisotropic temperature factors and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53328 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. An ORTEP drawing (Johnson, 1965) is shown in Fig. 1 and bond lengths and angles are listed in Tables 2 and 3. These parameters have normal values.

The molecule has a butterfly-like shape with benzene rings C(8)–C(13) and C(24)–C(29) forming the wings and C(16)–C(21) as the head; O(4) is at the tail. The body of the butterfly is formed by the crown-ether ring plus the C(16)–C(21) fragment of the head. If one excludes the 4-methoxyphenylazo moiety, the molecule has approximate mirror symmetry through O(4)–C(21)–C(18). The five central O atoms of the crown are reasonably coplanar with a 0.05 Å r.m.s. deviation from their least-squares plane. The wings are inclined by 42.3 and 37.5° from the five-O-atom crown body, and the plane of the head ring is inclined by 56.1°. The benzene-ring head is tipped so that the phenyl azo group is over the crown body. Steric interactions prevent the two benzene rings of the azobenzene moiety from being strictly coplanar; the dihedral angle between the C(1')–C(6') and C(16)–C(21) rings is 28.2°. This angle arises primarily from the overall twist in the azo linkage with torsions of 32.2° in N(2)–C(21) [N(1)=N(2)–C(21)–C(16) = 150.0 (3), N(1)=N(2)–C(21)–C(20) = –34.6 (5)°], 2.6° in N(1)=N(2) [C(1')–N(1)=N(2)–C(21) = 178.4 (3)°] and 5.6° in C(1')–N(1) [C(2')–C(1')–N(1)=N(2) = –174.6 (4), C(6')–C(1')–N(1)=N(2) = 5.9 (6)°].

The crystal structure of (II) and data from a model of the *cis* isomer were studied to assist our analysis of the solution complexation experiments of *cis*- and *trans*-(II) with various alkali picrates (Shinkai *et al.*, 1987). A search of the current Cambridge Structural Database (1990) for Na⁺...15-crown-5 complexes revealed Na⁺...O distances of 2.40–2.66 Å (AMPICCO2, DECVAI, GEWKIC, SAMRIH*) and Na⁺...N(*sp*²) complexes revealed Na⁺...N distances of 2.47–2.73 Å (Na⁺...pyridine and

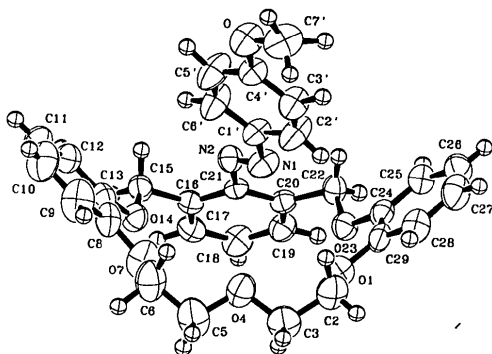


Fig. 1. ORTEP drawing of *trans*-(II). The C, N and O atoms are shown as 50% ellipsoids and the H atoms as spheres with $B = 1.5 \text{ \AA}^2$.

Table 2. Bond distances (Å) with *e.s.d.*'s in parentheses for *trans*-(II)

O–C(4')	1.358 (4)	C(12)–C(13)	1.385 (5)
O–C(7')	1.438 (6)	C(15)–C(16)	1.493 (5)
O(1)–C(2)	1.420 (5)	C(16)–C(17)	1.374 (5)
O(1)–C(29)	1.376 (4)	C(16)–C(21)	1.397 (4)
O(4)–C(3)	1.410 (6)	C(17)–C(18)	1.375 (5)
O(4)–C(5)	1.439 (6)	C(18)–C(19)	1.364 (5)
O(7)–C(6)	1.425 (5)	C(19)–C(20)	1.379 (5)
O(7)–C(8)	1.368 (4)	C(20)–C(21)	1.398 (4)
O(14)–C(13)	1.360 (4)	C(20)–C(22)	1.494 (5)
O(14)–C(15)	1.437 (4)	C(24)–C(25)	1.360 (5)
O(23)–C(22)	1.429 (4)	C(24)–C(29)	1.418 (5)
O(23)–C(24)	1.357 (4)	C(25)–C(26)	1.389 (6)
N(1)–N(2)	1.230 (3)	C(26)–C(27)	1.351 (6)
N(1)–C(1')	1.442 (4)	C(27)–C(28)	1.379 (6)
N(2)–C(21)	1.430 (4)	C(28)–C(29)	1.363 (5)
C(2)–C(3)	1.488 (7)	C(1')–C(2')	1.383 (5)
C(5)–C(6)	1.489 (7)	C(1')–C(6')	1.356 (5)
C(8)–C(9)	1.387 (6)	C(2')–C(3')	1.376 (6)
C(8)–C(13)	1.398 (5)	C(3')–C(4')	1.363 (5)
C(9)–C(10)	1.376 (7)	C(4')–C(5')	1.353 (5)
C(10)–C(11)	1.340 (7)	C(5')–C(6')	1.371 (5)
C(11)–C(12)	1.387 (6)		

Table 3. Bond angles (°) with *e.s.d.*'s in parentheses for *trans*-(II)

C(4')–O–C(7')	119.6 (4)	C(16)–C(17)–C(18)	120.2 (4)
C(2)–O(1)–C(29)	117.2 (4)	C(17)–C(18)–C(19)	120.2 (4)
C(3)–O(4)–C(5)	112.3 (4)	C(18)–C(19)–C(20)	121.5 (4)
C(6)–O(7)–C(8)	117.0 (4)	C(19)–C(20)–C(21)	118.3 (4)
C(13)–O(14)–C(15)	116.6 (3)	C(19)–C(20)–C(22)	118.3 (4)
C(22)–O(23)–C(24)	115.9 (3)	C(21)–C(20)–C(22)	123.4 (4)
N(2)–N(1)–C(1')	115.2 (3)	N(2)–C(21)–C(16)	114.2 (3)
N(1)–N(2)–C(21)	116.8 (3)	N(2)–C(21)–C(20)	125.4 (3)
O(1)–C(2)–C(3)	107.8 (5)	C(16)–C(21)–C(20)	120.3 (3)
O(4)–C(3)–C(2)	109.9 (5)	O(23)–C(22)–C(20)	108.5 (3)
O(4)–C(5)–C(6)	108.8 (6)	O(23)–C(24)–C(25)	125.4 (4)
O(7)–C(6)–C(5)	107.1 (5)	O(23)–C(24)–C(29)	116.1 (4)
O(7)–C(8)–C(9)	125.5 (5)	C(25)–C(24)–C(29)	118.5 (4)
O(7)–C(8)–C(13)	115.8 (4)	C(24)–C(25)–C(26)	120.8 (5)
C(9)–C(8)–C(13)	118.7 (5)	C(25)–C(26)–C(27)	120.5 (5)
C(8)–C(9)–C(10)	121.2 (5)	C(26)–C(27)–C(28)	119.8 (5)
C(9)–C(10)–C(11)	119.6 (5)	C(27)–C(28)–C(29)	120.9 (5)
C(10)–C(11)–C(12)	121.5 (5)	O(1)–C(29)–C(24)	115.2 (4)
C(11)–C(12)–C(13)	119.5 (5)	O(1)–C(29)–C(28)	125.2 (4)
O(14)–C(13)–C(8)	115.4 (4)	C(24)–C(29)–C(28)	119.6 (4)
O(14)–C(13)–C(12)	125.1 (4)	N(1)–C(1')–C(2')	117.0 (4)
C(8)–C(13)–C(12)	119.4 (4)	N(1)–C(1')–C(6')	125.0 (4)
O(14)–C(15)–C(16)	108.3 (3)	C(2')–C(1')–C(6')	118.1 (4)
C(15)–C(16)–C(17)	120.5 (4)	C(1')–C(2')–C(3')	122.1 (5)
C(15)–C(16)–C(21)	120.0 (4)	C(2')–C(3')–C(4')	118.1 (4)
C(17)–C(16)–C(21)	119.5 (4)	O–C(4')–C(3')	124.1 (4)
O–C(4')–C(5')	115.6 (4)		
C(3')–C(4')–C(5')	120.3 (4)		
C(4')–C(5')–C(6')	121.3 (5)		
C(1')–C(6')–C(5')	120.1 (5)		

phenanthroline: DETPIB, CESRAT, SAJJES*). There were, unfortunately, no examples of Na⁺...azo complexes. In the case of the 15-crown-5 complexes, the cation is usually positioned slightly above the O atoms which form the points of the crown. For the *trans*-(II) structure, a hypothetical cation has been positioned close to the circle of the five O atoms both to minimize the M⁺...O distances and to make the distances as similar as possible. The M⁺...O contacts of 2.94–3.07 Å provide a somewhat loose fit for Na⁺ in this 'structure'. Although both the N(1) and N(2) distances to the putative cation site (2.62, 2.50 Å) in this model are within the observed range for Na⁺...N

* Cambridge Structural Database reference codes.

contacts, the N(2)⋯N distance is impossibly short because the electron pair on the *sp*²-hybridized N(2) atom is pointing away from, not towards, the cation binding site. If the cation is dropped below the crown ring to increase the Na⁺⋯N(2) contact to 2.70 Å [Na⁺⋯N(1) = 2.79 Å], the O-atom fit becomes even looser with M⁺⋯O distances of 2.99–3.11 Å.

A model for the *cis*-(II) was built with the MacroModel (1989) system, starting with the basic *trans*-(II) crystal structure and a *cis*-azo moiety, followed by molecular-mechanics energy minimization (Fig. 2). The azobenzene fragment is oriented away from the crown ring and steric interactions have resulted in an azo linkage with twist angles for the C(21)—N(2)=N(1)—C(1') unit of 71, 5 and 52°. As with *trans*-(II), a hypothetical cation was positioned in the crown circle to optimize the M⁺⋯O contacts. In this 'structure', the M⁺⋯O distances ranged from 2.77 to 2.85 Å and M⁺⋯N(2) was 2.70 Å. N(1) is now remote from the complexation area because of the *cis*-azo geometry. The relative complexation capabilities of *cis*- and *trans*-(II) with the sodium cation, which is capable of fitting inside the crown circle, can be attributed to the azo steric block present in *trans*-(II), to the absence of this block in *cis*-(II) and to the presence of a favorable Na⁺⋯N contact in the latter. The O-atom crown ring provides a somewhat loose fit for the sodium cation and the extra Na⁺⋯N interaction in *cis*-(II) is probably the key factor in the complexation of this cation. We speculate that a phenylazo-less analog [(III); previously synthesized by Weber & Vogtle (1976)] would complex sodium more weakly than *cis*-(II) because of the loss of one heteroatom ligand. It should be noted that problems associated with the electron pair on N(2) in *trans*-(II) pointing in the wrong direction for interaction with a central Na⁺ could be corrected by an approximately 180° rotation about C(21)—N(2) from the observed

conformation; the inability of *trans*-(II) to form a complex with Na⁺ is evidence against this conformation. Additionally, we note that the *trans*-(II) crystal structure was subjected to molecular-mechanics minimization with the MacroModel (1989) system in an attempt to obtain a model that could be used to judge the validity of the *cis*-(II) model. The resulting *trans* model contained a severely distorted crown ring and an azo link with a C—N=N—C twist of only 12°, smaller than the 32° found in the crystal structure; the crown asymmetry presumably arises from the phenylazo⋯crown non-bonded interactions.

In the case of the potassium cation, a search of the Cambridge Structural Database (1990) gave K⁺⋯O and K⁺⋯N distances in 18-crown-6 and cryptand structures (Cambridge Structural Database reference codes FESZIM, FETJOD, GAVFIS, FUHVOT, GANSIX) with ranges 2.74–2.91 and 2.96–3.03 Å, respectively. As with Na⁺ complexation, K⁺ should bind more tightly to the *cis* isomer but the larger cation presumably cannot fit as deeply into the crown ring as Na⁺ and thereby the *trans*-azo steric block should be less important. That is, larger cations can be imagined to perch on the lower lip of the crown somewhat in the way a hat (crown) sits on the top of a head that is too big (cation). Although binding of K⁺ and larger cations must occur primarily *via* the oxygen crown ring, photoisomerization of *trans* to *cis* would always be expected to result in an increase in cation-binding efficiency because of conversion of the *trans*-azo steric block in *trans*-(II) to the ligand-binding *cis*-azo geometry in *cis*-(II).

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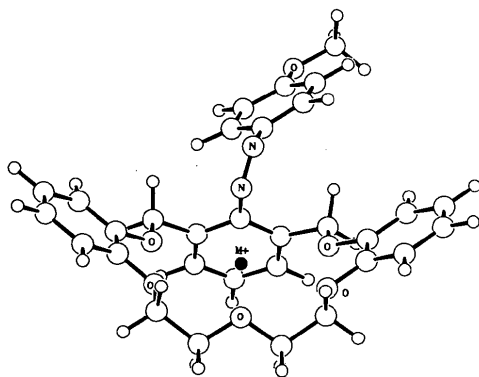


Fig. 2. Model for *cis*-(II) created with the MacroModel system. The solid circle labeled M⁺ is a hypothetical cation positioned to minimize the five M⁺⋯O contacts.