

Table 2. Bond lengths (Å) and valency and torsion angles (°)

N(1)—N(11)	1.387 (2)	N(1)—C(1)	1.457 (3)
N(1)—C(2)	1.361 (3)	N(11)—C(12)	1.331 (2)
C(2)—O(2)	1.212 (3)	C(12)—O(12)	1.220 (3)
C(2)—C(3)	1.492 (3)	C(12)—C(13)	1.483 (3)
C(3)—C(4)	1.307 (3)	C(13)—C(14)	1.313 (4)
C(4)—C(5)	1.491 (4)	C(14)—C(15)	1.473 (4)
C(5)—O(5)	1.193 (3)	C(15)—O(15)	1.203 (3)
C(5)—O(6)	1.314 (3)	C(15)—O(16)	1.320 (3)
O(6)—C(7)	1.453 (3)	O(16)—C(17)	1.438 (4)
C(1)—N(1)—C(2)	120.5 (2)	C(1)—N(1)—N(11)	116.2 (2)
N(11)—N(1)—C(2)	120.3 (2)	N(1)—N(11)—C(12)	120.7 (2)
N(1)—C(2)—O(2)	120.1 (2)	N(11)—C(12)—O(12)	121.9 (2)
N(1)—C(2)—C(3)	117.4 (2)	N(11)—C(12)—C(13)	115.3 (2)
O(2)—C(2)—C(3)	122.5 (2)	O(12)—C(12)—C(13)	122.8 (2)
C(2)—C(3)—C(4)	120.7 (2)	C(12)—C(13)—C(14)	122.1 (2)
C(3)—C(4)—C(5)	121.1 (2)	C(13)—C(14)—C(15)	121.4 (2)
C(4)—C(5)—O(5)	124.3 (2)	C(14)—C(15)—O(15)	124.9 (2)
C(4)—C(5)—O(6)	111.6 (2)	C(14)—C(15)—O(16)	111.8 (2)
O(5)—C(5)—O(6)	124.1 (2)	O(15)—C(15)—O(16)	123.3 (2)
C(5)—O(6)—C(7)	116.1 (2)	C(15)—O(16)—C(17)	116.7 (2)
C(1)—N(1)—C(2)—O(2)	4.7 (3)	C(1)—N(1)—N(11)—C(12)	77.3 (2)
C(1)—N(1)—C(2)—C(3)	-178.3 (2)	C(2)—N(1)—N(11)—C(12)	-83.3 (2)
N(11)—N(1)—C(2)—O(2)	164.6 (2)	N(1)—N(11)—C(12)—O(12)	9.5 (3)
N(11)—N(1)—C(2)—C(3)	-18.5 (3)	N(1)—N(11)—C(12)—C(13)	-173.2 (2)
N(1)—C(2)—C(3)—C(4)	174.0 (2)	N(11)—C(12)—C(13)—C(14)	-160.1 (2)
O(2)—C(2)—C(3)—C(4)	-9.1 (4)	O(12)—C(12)—C(13)—C(14)	17.1 (3)
C(2)—C(3)—C(4)—C(5)	176.4 (2)	C(12)—C(13)—C(14)—C(15)	178.1 (2)
C(3)—C(4)—C(5)—O(5)	3.3 (4)	C(13)—C(14)—C(15)—O(15)	16.0 (4)
C(3)—C(4)—C(5)—O(6)	-175.2 (2)	C(13)—C(14)—C(15)—O(16)	-161.4 (2)
C(4)—C(5)—O(6)—C(7)	-180.0 (2)	C(14)—C(15)—O(16)—C(17)	179.6 (2)
O(5)—C(5)—O(6)—C(7)	1.6 (4)	O(15)—C(15)—O(16)—C(17)	2.2 (4)

the whole molecule is bent at the central N—N bond [C(2)—N(1)—N(11)—C(12) = -83.3 (2)°]. The configurations at the C(3)=C(4) and C(13)=C(14) bonds are *trans* and all four carbonyl groups are *syn* in relation to the double C=C bonds. Similar geometries have been observed in the crystal structures of funaltrexamines (Griffin, Larson & Porthoghese, 1986) and in dimethyl 4,4'-(2,5-dioxo-1,4-piperazinediyl)bis(4-oxo-2-butenoate) (Głowska &

Iwanicka, 1990). The bond lengths and angles in the two equivalent 4-oxo-2-butenoate moieties agree to within 3σ except for N(1)—C(2), N(1)—C(2)—O(2), N(1)—C(2)—C(3) and C(2)—C(3)—C(4) (Table 2) which differ by about 10σ. These differences result from methyl substitution at N(1), from different crystallographic environments of the moieties and from N(11)—H...O(12) (x - 1, y, z) hydrogen bonds which join molecules of (1) into infinite chains running in the [100] direction. N...O, H...O distances and the N—H...O angle are 2.796 (2), 2.07 (3) Å and 147 (3)°, respectively.

The authors wish to thank the Polish Ministry of National Education (research project RP.II.10) for financial support.

References

- GŁOWKA, M. L. & IWANICKA, I. (1990). *Acta Cryst.* **C46**, 1262–1264.
- GRACZYK, J., PAKULSKA, W., GROSZKOWSKI, S. & NAJMAN, L. (1980). *Acta Pol. Pharm.* **37**, 249–254.
- GRIFFIN, J. F., LARSON, D. L. & PORTHOGHESE, P. S. (1986). *J. Med. Chem.* **29**, 778–783.
- GROSZKOWSKI, S. & NAJMAN, L. (1979). *Pol. J. Pharmacol. Pharm.* **31**, 157–159.
- GROSZKOWSKI, S. & NAJMAN, L. (1983). *Pol. J. Pharmacol. Pharm.* **35**, 517–521.
- GROSZKOWSKI, S. & NAJMAN, L. (1986). *Acta Pol. Pharm.* **43**, 327–330.
- GROSZKOWSKI, S., NAJMAN, L. & SIENKIEWICZ, J. (1972). *Rocz. Chem.* **46**, 269–273.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1991). **C47**, 620–623

Structure of 8-Chloro-6-(2-chlorophenyl)-2*H*,4*H*-[1,2,3]triazolo[5,4-*d*][2]-benzazepinium Methanesulfonate Methanol Solvate*

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(Received 8 January 1990; accepted 2 July 1990)

Abstract. [C₁₆H₁₁Cl₂N₄]⁺. [CH₃O₃S]⁻. 0.25CH₄O, *M*_r = 433.3, monoclinic, *C*2/*c*, *a* = 23.234 (5), *b* =

10.624 (2), *c* = 16.552 (6) Å, β = 100.95 (4)°, *V* = 4011 Å³, *Z* = 8, *D*_x = 1.435 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 4.42 cm⁻¹, *F*(000) = 1780, *T* = 293 K, *R* = 0.041 for 2340 observed reflections. The benzazepine N atom is protonated, causing a signifi-

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham, England.

cant increase in the endocyclic C—N—C bond angle [observed value 126.1 (3)°]. The angle between the mean planes of the chlorophenyl ring and the fused benzo moiety is 67.1 (6)°. The seven-membered heterocyclic ring adopts a cycloheptatriene-like boat conformation with bow and stern angles of 45.6 (6) and 27.2 (6)°. The triazolo ring and the two benzene rings are each planar to within 0.015 Å. Bond lengths and angles are normal.

Introduction. The title compound (Trybulski, Benjamin, Vitone, Walser & Fryer, 1983) has a similar pharmacological profile to the benzodiazepines and has a strong affinity for the benzodiazepine receptor *in vitro*. It is related to the classical psychoactive 5-phenyl-1,4-benzodiazepin-2-ones such as diazepam, but differs from these in having the N atom at the 1-position of the seven-membered ring replaced by a C atom. Further, a triazolo ring is fused across the C(1)—C(3) bond (corresponding to the N(1)—C(2) bond of the 1,4-benzodiazepine parent system). In the *in vitro* binding assays (Mohler & Okada, 1977; Squires & Braestrup, 1977) the title compound was found to be about seven times more potent than diazepam, but *in vivo*, using the antipentylentetrazole test, its efficacy was slightly smaller than that of diazepam (Trybulski *et al.*, 1983).

Experimental. Crystals were grown from methanol (Trybulski *et al.*, 1983). A crystal of size 0.3 × 0.2 × 0.15 mm was mounted on an Enraf-Nonius CAD-4 diffractometer and cell dimensions determined from the setting angles of 25 reflections in the range 10 < θ < 14°. Intensity data were measured with graphite-monochromated Mo Kα radiation. 6672 reflections were scanned by ω/2θ scans up to θ = 25° of which 3386 were unique (R_{int} 0.028). 2340 [I > 2.5σ(I)] reflections were considered observed and used in the analysis, index range h -27 to 26, k 0 to 12, l 0 to 19. Two standard reflections measured every 2 h showed no significant variation in intensity. No absorption corrections were applied.

The structure was determined by direct methods and refined by least squares using anisotropic thermal parameters for the heavier atoms. H atoms were located from a difference map and refined isotropically, except for those of the methanesulfonate methyl group. This was treated as a rigid CH₃ group and allowed to rotate. A difference map calculated at this stage contained two peaks of significant electron density, about 1.4 Å apart. These were considered to correspond to one quarter of a molecule of methanol. The atoms of the methanol molecule were refined isotropically; the H atoms were not included. Total number of parameters refined = 302. Weights, w = 1/[σ²(F) + 0.005F²], which resulted in a satisfactory weighting analysis were used in the least-squares

Table 1. Fractional atomic coordinates (× 10⁴) with e.s.d.'s in parentheses and equivalent isotropic temperature factors (Å² × 10³)

$U_{eq} = 1/3$ (trace of the orthogonalized U_{ij} tensor).				
	x	y	z	U_{eq}
S*	1364 (1)	1303 (1)	321 (1)	35
Cl(8)	183 (1)	-4031 (1)	1637 (1)	74
Cl(2')	2047 (1)	-2214 (1)	901 (1)	60
N(1)	850 (1)	-2559 (3)	-2064 (2)	43
N(2)	1088 (1)	-2892 (3)	-2692 (2)	44
N(3)	1404 (1)	-3930 (3)	-2611 (2)	42
N(5)	1964 (1)	-5228 (2)	-655 (2)	32
C(1)	1024 (1)	-3482 (3)	-1522 (2)	35
C(3)	1361 (1)	-4324 (3)	-1864 (2)	34
C(4)	1610 (2)	-5508 (3)	-1470 (2)	39
C(6)	1774 (1)	-4748 (3)	-41 (2)	28
C(7)	966 (1)	-4387 (4)	662 (2)	38
C(8)	440 (1)	-3857 (4)	727 (2)	44
C(9)	110 (2)	-3178 (4)	90 (3)	50
C(10)	317 (2)	-3043 (4)	-621 (3)	45
C(11)	843 (1)	-3601 (4)	-725 (2)	34
C(12)	1176 (1)	-4265 (3)	-68 (2)	31
C(1')	2199 (1)	-4750 (3)	748 (2)	31
C(2')	2328 (1)	-3675 (3)	1238 (2)	38
C(3')	2708 (2)	-3740 (4)	1993 (3)	47
C(4')	2966 (2)	-4858 (4)	2255 (3)	52
C(5')	2854 (2)	-5922 (4)	1775 (3)	50
C(6')	2473 (2)	-5864 (3)	1035 (2)	39
O(1)*	988 (1)	1472 (3)	916 (2)	54
O(2)*	1937 (1)	851 (3)	720 (2)	56
O(3)*	1390 (1)	2380 (3)	-189 (2)	68
C(13)*	1041 (2)	91 (5)	-319 (3)	70
O(4)†	4564 (14)	4258 (38)	3526 (20)	186 (19)
C(14)†	4727 (14)	4611 (30)	2654 (25)	125 (14)

* Atom of methanesulfonate anion.

† Atom of methanol molecule, site occupation 0.25. Refined isotropically.

refinement. The refinement was carried out on F values and converged to $R = 0.041$, $wR = 0.064$ with maximum shift/e.s.d. ratio < 0.1. The residual electron density in a final difference map was within $\pm 0.5 e \text{ \AA}^{-3}$. No correction for secondary extinction was applied.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computations were carried out on the University of Birmingham Honeywell DPS 8/70 computer and on the CDC 7600 at the University of Manchester Regional Computer Centre with the *SHELX76* (Sheldrick, 1976) and *PLUTO* (Motherwell & Clegg, 1978) programs.

Discussion. Final atomic parameters are listed in Table 1* and bond lengths, bond angles and selected torsion angles are in Table 2. The atomic numbering scheme is shown in Fig. 1.

* 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 53367 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and angles are generally in close agreement with values found previously in 9-chloro-7-(2-fluorophenyl)-5*H*-pyrimido[5,4-*d*][2]benzazepine (Kemmish & Hamor, 1990) and in 1,4-benzodiazepin-2-one structures (Hamor & Martin, 1983; Borea, Hamor & Martin, 1988). The major difference is that the protonation of N(5) has caused

Table 2. Molecular geometry; values given in parentheses are e.s.d.'s

(a) Bond lengths (Å)

S—O(1)	1.446 (3)	C(6)—C(12)	1.474 (4)
S—O(2)	1.452 (3)	C(7)—C(8)	1.368 (5)
S—O(3)	1.429 (3)	C(7)—C(12)	1.393 (5)
S—C(13)	1.744 (4)	C(8)—C(9)	1.383 (5)
Cl(8)—C(8)	1.733 (4)	C(9)—C(10)	1.361 (5)
Cl(2')—C(2')	1.733 (3)	C(10)—C(11)	1.399 (5)
N(1)—N(2)	1.316 (4)	C(11)—C(12)	1.400 (5)
N(1)—C(1)	1.339 (4)	C(1')—C(2')	1.401 (5)
N(2)—N(3)	1.317 (4)	C(1')—C(6')	1.384 (5)
N(3)—C(3)	1.327 (4)	C(2')—C(3')	1.388 (5)
N(5)—C(4)	1.470 (5)	C(3')—C(4')	1.364 (6)
N(5)—C(6)	1.287 (4)	C(4')—C(5')	1.378 (6)
C(1)—C(3)	1.380 (5)	C(5')—C(6')	1.369 (6)
C(1)—C(11)	1.463 (5)	C(6)—C(1')	1.480 (5)
C(3)—C(4)	1.482 (5)	C(14)—O(4)	1.604 (42)

(b) Bond angles (°)

O(1)—S—O(2)	110.6 (2)	Cl(8)—C(8)—C(7)	119.0 (3)
O(1)—S—O(3)	113.7 (2)	Cl(8)—C(8)—C(9)	119.0 (3)
O(2)—S—O(3)	113.3 (2)	C(7)—C(8)—C(9)	121.9 (3)
O(1)—S—C(13)	105.0 (2)	C(8)—C(9)—C(10)	118.7 (3)
O(2)—S—C(13)	106.5 (2)	C(9)—C(10)—C(11)	121.4 (4)
O(3)—S—C(13)	107.1 (2)	C(1)—C(11)—C(10)	118.8 (3)
N(2)—N(1)—C(1)	102.4 (3)	C(1)—C(11)—C(12)	122.2 (3)
N(1)—N(2)—N(3)	117.0 (3)	C(10)—C(11)—C(12)	119.0 (3)
N(2)—N(3)—C(3)	102.7 (3)	C(6)—C(12)—C(7)	115.2 (3)
C(4)—N(5)—C(6)	126.1 (3)	C(6)—C(12)—C(11)	125.3 (3)
N(1)—C(1)—C(3)	108.8 (3)	C(7)—C(12)—C(11)	119.2 (3)
N(1)—C(1)—C(11)	124.4 (3)	C(6)—C(1')—C(2')	122.9 (3)
C(3)—C(1)—C(11)	126.6 (3)	C(6)—C(1')—C(6')	119.4 (3)
N(3)—C(3)—C(1)	109.1 (3)	C(2')—C(1')—C(6')	117.7 (3)
N(3)—C(3)—C(4)	125.8 (3)	Cl(2')—C(2')—C(1')	121.2 (3)
C(1)—C(3)—C(4)	125.1 (3)	Cl(2')—C(2')—C(3')	118.1 (3)
N(5)—C(4)—C(3)	109.6 (3)	C(1')—C(2')—C(3')	120.6 (3)
N(5)—C(6)—C(12)	125.2 (3)	C(2')—C(3')—C(4')	119.8 (4)
N(5)—C(6)—C(1')	115.2 (3)	C(3')—C(4')—C(5')	120.5 (4)
C(12)—C(6)—C(1')	119.6 (3)	C(4')—C(5')—C(6')	119.9 (4)
C(8)—C(7)—C(12)	119.7 (3)	C(1')—C(6')—C(5')	121.5 (4)

(c) Selected torsion angles (°); e.s.d.'s are ca 0.6°

C(1)—C(3)—C(4)—N(5)	-55.4	C(12)—C(11)—C(1)—C(3)	28.2
C(3)—C(4)—N(5)—C(6)	62.6	C(11)—C(1)—C(3)—C(4)	-1.0
C(4)—N(5)—C(6)—C(12)	-6.8	C(12)—C(6)—C(1')—C(2')	-53.1
N(5)—C(6)—C(12)—C(11)	-38.1	N(5)—C(6)—C(1')—C(2')	129.4
C(6)—C(12)—C(11)—C(1)	9.8		

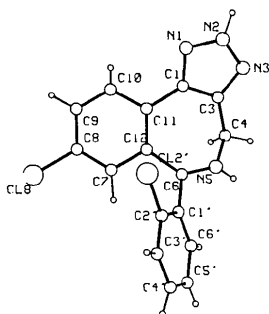
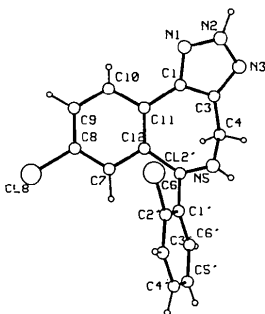


Fig. 1. Stereoscopic view of the cation in a direction perpendicular to the mean plane through atoms C(7)—C(12).

the angle C(4)—N(5)—C(6) to increase from 116.5 (2)° in the free-base benzazepine (Kemmish & Hamor, 1990) to 126.1 (3)°. Similarly, an increase in this angle of 7° occurs on protonating 7-chloro-2,3-dihydro-1-methyl-5-phenyl-1*H*-1,4-benzodiazepine (medazepam) (Gilli, Bertolosi, Sacerdoti & Borea, 1978; Chananont, Hamor & Martin, 1980).

As in the 1,4-benzodiazepin-2-ones and in the free-base benzazepine, cited above, the seven-membered ring of the title compound adopts a cycloheptatriene-like boat conformation, defined by a bow plane [atoms C(3), C(4), N(5)], stern plane [C(1), C(11), C(12), C(6)] and central plane [C(1), C(3), N(5), C(6)]. The three double bonds are the C(11)—C(12) aromatic bond, the N(5)—C(6) double bond and C(1)—C(3), which has the geometry of an aromatic bond, length 1.380 (5) Å and near-planar disposition of valencies, presumably due to electron delocalization over the N(1)=C(1)—C(3)=N(3) system. The 'boat' is, however, relatively flat, with bow and stern angles of 45.6 (6) and 27.2 (6)°, whereas the usual ranges for these angles are 58–64 and 32–40°, respectively. This appears to be a consequence of the large angle at N(5) caused by protonation, although some flattening occurs in most benzodiazepines having, as in the title compound, an additional five-membered ring fused across the 'a face' of the seven-membered ring (Kemmish & Hamor, 1989). The deviation parameter (Hamor & Martin, 1983), which quantifies the deviation of the seven-membered ring from mirror symmetry and zero torsion angles about the three double bonds of the ideal cycloheptatriene boat conformation, is 7.7°. This value is near the upper end of the range of values, 1–9°, found for this parameter in this class of compounds. Both the triazolo ring and the 6-chlorophenyl ring are planar to within 0.01 Å and the fused benzene ring is planar to within 0.015 (7) Å. The disposition of valencies at N(2) is essentially planar (sum of bond angles 359.9°) and electron delocalization appears to extend over the entire triazolo ring.

The C(6)—C(1') bond length of 1.480 (5) Å corresponds to a single bond between *sp*²-hybridized C atoms, as is commonly found in this type of

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.

We thank Dr R. I. Fryer, Hoffman-LaRoche, for materials and biological data, Dr I. L. Martin for affinity measurements and the SERC for financial support to HJK.

References

- BOREA, P. A., HAMOR, T. A. & MARTIN, I. L. (1988). *Neuromethods*, Vol. 10, edited by A. A. BOULTON, G. B. BAKER & R. T. COUTTS, pp. 473–531. New York: Humana Press.
- CHANANONT, P., HAMOR, T. A. & MARTIN, I. L. (1980). *Acta Cryst.* B36, 898–902.
- GILLI, G., BERTOLASI, V., SACERDOTI, M. & BOREA, P. A. (1978). *Acta Cryst.* B34, 3793–3795.
- HAMOR, T. A. & MARTIN, I. L. (1983). *Progress in Medicinal Chemistry*, Vol. 20, edited by G. P. ELLIS & G. B. WEST, pp. 157–223. Amsterdam: Elsevier.
- KEMMISH, H. J. & HAMOR, T. A. (1989). *Acta Cryst.* C45, 475–478.
- KEMMISH, H. J. & HAMOR, T. A. (1990). *Acta Cryst.* C46, 246–248.
- MOHLER, H. & OKADA, T. (1977). *Science*, 198, 849–851.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SQUIRES, R. F. & BRAESTRUP, C. (1977). *Nature (London)*, 266, 732–734.
- TRYBULSKI, E. J., BENJAMIN, L., VITONE, S., WALSER, A. & FRYER, R. I. (1983). *J. Med. Chem.* 26, 367–372.

Acta Cryst. (1991). C47, 623–626

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

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(Received 6 March 1990; accepted 25 June 1990)

Abstract. 3,10,13,16,23-Pentaoxatetracyclo-[23.3.1.0^{4,9}.0^{17,22}]nonacosal(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