

# X-ray and neutron structure of 1,8-(3,6,9-trioxaundecane-1,11-diylldioxy)-9,10-dihydro-10,10-dimethylantracene-9-ol (P326); some pitfalls of automatic data collection

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The structure of the crown ether 1,8-(3,6,9-trioxaundecane-1,11-diylldioxy)-9,10-dihydro-10,10-dimethylantracene-9-ol,  $C_{24}H_{30}O_6 \cdot H_2O$  (1), code name P326, the parent compound for a series of derivatives, has been determined by both X-ray diffraction at room temperature and neutron diffraction at very low temperature. The unit cells are very similar at both temperatures and in both cases the crystals exhibit  $P2_1$  symmetry with  $Z = 4$  (two molecules, *A* and *B*, respectively, per asymmetric unit) and pseudosymmetry  $P2_1/c$ . The higher symmetry is broken mainly by the two independent water molecules in the unit cell, some reflections which would be absent in  $P2_1/c$  having strong intensities in both the X-ray and neutron data. In both molecules *A* and *B* hydrogen bonds involving the water molecule stabilize the macrocyclic ring structure, one involving the macrocyclic O(9) as a donor. Close contacts between the water and macrocyclic O atoms in each molecule also suggest the presence of two bifurcated hydrogen bonds, involving water HW2 to both O(16) and O(18), and water HW1 to both O(18) and O(20), respectively, with considerable variation in the geometry being present. Both molecules *A* and *B* exhibit very close pseudosymmetry across a plane perpendicular to the molecular plane and through atoms C(9) and O(18), and in addition are predominantly planar structures. The X-ray analysis failed to reveal one H atom per water molecule, each being subsequently included after location and refinement in the neutron analysis.

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*This paper is dedicated to the memory of Owen Mills who conceived this experiment and was taken ill whilst preparing the manuscript.*

## 1. Introduction

While crown ethers and related compounds are characterized by their ability to bind ions or neutral species by non-covalent interactions, carbocations form covalent bonds of widely varying lability to nucleophiles. Since nucleophilic substitutions can occur readily at a stable carbocationic centre, a single species incorporating such a centre within, or in close proximity to, a crown ether might serve as a precursor for a range of compounds in which exchangeable nucleophilic groups (for example, hydroxy, alkoxy, acyloxy, amine and amide) could interact with metal ions retained by the crown. The potential to turnover nucleophilic groups in this way offers a basis for catalysis of hydrolytic reactions to which we have already drawn attention (Cox *et al.*, 1995; Watt *et al.*, 1995).

Tricyclic arrays such as xanthene, acridine and anthracene offer an appropriate combination of functionalities, and we have prepared a number of crowns incorporating such arrays (Cox *et al.*, 1995; Cox *et al.*, 1999). The present paper describes the structure determination of the alcohol (1) (Fig. 1), which is the formal hydrolysis product of the carbocation (2) ( $pK_{R^+} = -2.28$ ) stabilized by delocalization of charge into the two

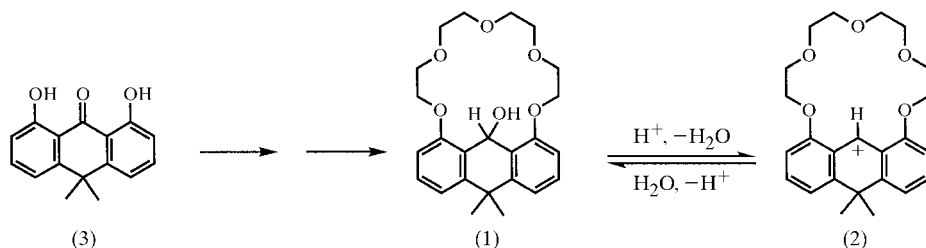
alkoxybenzene residues, which also serve to carry its 18-membered macrocyclic array. Related 18-membered crowns incorporating intra-crown ketone groups have been shown to include either water (Beddoes *et al.*, 1996) or hydronium ions (Young & Sykes, 1998; Young *et al.*, 1997) in their cavities by schemes involving the ketonic oxygen as a hydrogen-bond acceptor. The consequences of replacement of ketonic carbonyl by an alcoholic hydroxyl as in (1) to provide an additional hydrogen-bonding donor site were to be explored in this work. Structural determinations of simple crown ether alcohols are relatively rare, but in at least one case (Olsher *et al.*, 1989) a water complex has been found showing distinct hydrophilic channels within hydrophobic regions, possibly modelling the formation of pores in biological bilayers.

In view of the extensive interest in compounds with binding properties which may easily be switched in response to physical and chemical stimulation and the necessity for accurate H-atom positions for interpretation of these effects, neutron diffraction was considered to offer advantages over X-ray analysis to help to provide this information. Compound P326 crystallized as the water-bound adduct from slightly moist acetonitrile, was difficult to crystallize but did eventually form large crystals (*e.g.*  $2 \times 2 \times 0.25$  mm), which were marginally suitable for neutron diffraction and were accepted for data collection at ILL. The need for an X-ray structure prior to neutron data collection initially introduced an element of urgency not normally encountered in this type of work. As a consequence some corners were cut and the initial automatic assignment of a very convincing 'orthorhombic' X-ray unit cell caused some problems. The subsequent serendipitously ambiguous monoclinic transformations in the two analyses emphasize the need for caution in applying such procedures, particularly in view of the fact that different aspects of the work were being carried out almost simultaneously by two different groups in two different labs. As a consequence it was felt appropriate and timely to provide details here of how this situation was eventually resolved. These are presented below.

## 2. Experimental

### 2.1. Sample preparation

Details of the preparation, stability measurements and reactivity will be presented elsewhere, but we note here that (1) is available in three high-yielding steps from anthralin (3)



**Figure 1**  
Chemical structures of (1), (2) and (3).

by bis-methylation at the 10-position with methyl iodide, bis-O-alkylation with tetragol dibromide to give a ketone which is then reduced quantitatively by sodium amalgam to the alcohol (1). Slow evaporation of ethanolic solutions yielded crystals, m.p. 424–426 K, which were used in the crystallographic studies. No particular attempt was made to exclude water from the purified solvent used for crystallization, however, the presence of water in the crystalline material was not evident from its spectra.

### 2.2. X-ray study

**2.2.1. Orthorhombic data set.** A crystal was centred on a Nonius CAD4 diffractometer. The software package *CAD4 Express* (Enraf–Nonius, 1988) was used to define a unit cell and orientation matrix based on 25 reflections selected by the software, employing Cu  $K\alpha$  radiation. The diffractometer system, in automatic mode, favoured an orthorhombic C-centred cell which refined to  $a = 12.856$  (1),  $b = 24.397$  (4),  $c = 14.564$  (2) Å,  $\alpha = 89.98$  (1),  $\beta = 89.987$  (9),  $\gamma = 90.10$  (1)°. The assignment of the crystal system by the software was based solely on the close proximity of the cell angles to 90°. This software was designed to collect one asymmetric unit of intensity data for the initially assigned point group, there being no automatic Laue check facility at this stage. While it was possible to carry out a check for Laue symmetry after data collection, this was not an easy procedure to carry out with this version of the software. [We would like to point out, however, that the later version of the software (*CAD4 Express94*) does carry out, in automatic mode, a Laue check prior to the actual data collection.] Intensity data were thus routinely collected for one asymmetric unit of 'orthorhombic reciprocal space', for  $1 < \theta < 74^\circ$ . The space group was assigned, by inspection of systematic absences in the diffractometer intensity data, after processing, as  $C222_1$ . This cell was calculated to include eight molecules of  $C_{24}H_{30}O_6$  (two molecules per asymmetric unit). It was subsequently discovered during refinement of the structure that there were additionally two water molecules per asymmetric unit. It should be noted that the X-ray results were obtained under some pressure, being urgently required to coordinate with a scheduled neutron data collection at ILL, Grenoble. The X-ray analysis, therefore, proceeded at this stage without any hint that an extraordinary situation would soon arise as a result of a very unusual geometrical relationship between the unit-cell parameters. The cell parameters appeared to be quite reasonable for this stage of the analysis

(although with hindsight it might be argued that  $\gamma$  had a precision which precludes an orthorhombic cell). The crystal had moderate diffracting power and good single-crystal quality, as indicated from the diffractometer readings incorporated into the software.

This first X-ray data set, after processing and correction for Lorentz and polarization effects, gave 2572

**Table 1**  
Experimental details.

	X-ray	Neutron
Crystal data		
Chemical formula	C <sub>24</sub> H <sub>30</sub> O <sub>6</sub> ·H <sub>2</sub> O	C <sub>24</sub> H <sub>30</sub> O <sub>6</sub> ·H <sub>2</sub> O
Chemical formula weight	432.5	432.49
Cell setting, space group	Monoclinic, <i>P</i> 2 <sub>1</sub>	Monoclinic, <i>P</i> 2 <sub>1</sub>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.845 (5), 14.575 (3), 13.779 (2)	12.605 (5), 14.458 (3), 13.588 (2)
$\beta$ (°)	117.72 (2)	117.12 (2)
<i>V</i> (Å <sup>3</sup> )	2283.6 (11)	2204.1 (10)
<i>Z</i>	4	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.258	1.303
Radiation type	Cu <i>K</i> $\alpha$	Neutron
No. of reflections for cell parameters	25	25
$\theta$ range (°)	25–30	25–30
$\mu$ (mm <sup>-1</sup> )	0.754	0.000
Temperature (K)	293 (2)	15
Crystal form, colour	Plate, colourless	Plate, colourless
Crystal size (mm)	0.35 × 0.25 × 0.20	2.5 × 1.6 × 0.2
Data collection		
Diffractometer	Nonius CAD-4	D19 ILL
Data collection method	$\omega/2\theta$ scans	$\omega$ scans
No. of measured, independent and observed parameters	17 753, 9092, 4804	1931, 1931, 1881
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.0459	0.0000
$\theta$ <sub>max</sub> (°)	72.93	46.12
Range of <i>h</i> , <i>k</i> , <i>l</i>	–15 → <i>h</i> → 15 –18 → <i>k</i> → 18 –17 → <i>l</i> → 17	–10 → <i>h</i> → 11 0 → <i>k</i> → 13 –9 → <i>l</i> → 12
Refinement		
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.0619, 0.1506, 1.144	0.0462, 0.1184, 0.779
No. of reflections and parameters used in refinement	9092, 605	1881, 507
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0922P)^2 + 0.0000P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2 + 0.5955P]$ , where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.078	–0.123
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	0.232, –0.26	0.055, –0.058

unique intensities, 1395 with  $F > 4\sigma(F)$ . With few symmetry repeats *R*<sub>int</sub> was indeterminate. The direct methods program *SHELXS86* (Sheldrick, 1985) produced no solution when using space group *C*22<sub>1</sub>. Space group *C*2<sub>1</sub> (non-standard, *c*-unique monoclinic setting) was then tried and produced an outstanding solution with CFOM = 0.0573, which gave a promising E-map containing essential features of both molecules in the unit cell despite being based, because of the incorrect assumption regarding the crystal point group, on only part of the monoclinic data set. This structure failed to refine, due to the incomplete 'orthorhombic' intensity data. The best *R*-factor achieved with this model using isotropic thermal displacement parameters was 0.238, with a data/parameter ratio of 2572/238.

**2.2.2. Monoclinic data set.** A second set of intensity data was collected, with the unit cell constrained to be monoclinic, an option allowed by the software. The monoclinic cell showed the refined parameters given in Table 1 together with other data relating to the X-ray analysis. The space group was *P*2<sub>1</sub>,

with four molecules per unit cell (two per asymmetric unit). Lorentz and polarization corrections were initially applied, but no absorption corrections were made. Subsequent refinement of the X-ray structure (see below) confirmed this assignment of the unit cell and space group. As a check on the correct assignment of the space group the refined structure was input to the program *PLATON* (Spek, 1990, 2000). This indicated that with the exception of the water molecules the structure was close to *P*2<sub>1</sub>/*c*. The intensity data were then input to the space-group determining routine in *XSTEP* (Stoe & Cie, 1997), which indicated *P*2<sub>1</sub> or *P*2<sub>1</sub>/*m*, but not *P*2<sub>1</sub>/*c*. As a final check, manual inspection of the  $|F(hkl)|$  values easily revealed type hol reflections with  $l = 2n + 1$  (systematically absent in *P*2<sub>1</sub>/*c*) with values far greater than  $3\sigma|F(hkl)|$ . An example of such a reflection is 50 $\bar{5}$ , which in addition to having a strong intensity is well away from the centre of diffraction space where anomalies can occur due to streaking. Subsequent checks with the neutron data led to the same conclusion and the space group *P*2<sub>1</sub> was therefore retained.

**2.2.3. X-ray structure determination and refinement.** Using the monoclinic X-ray data set, the direct methods routine in *SHELXS86* (Sheldrick, 1985) produced an outstanding solution to the structure

in space group *P*2<sub>1</sub> with figure of merit CFOM = 0.0520. The corresponding E-map revealed the positions of all non-H atoms in both molecules (designated *A* and *B*, respectively). Difference electron density maps, calculated with *SHELXL93* (Sheldrick, 1993), indicated the presence of water bound to each molecule. The same program was used to complete and refine the structure. Refinement was undertaken by full-matrix least-squares on *F*<sup>2</sup>, with anisotropic displacement parameters for non-H atoms, and isotropic for H atoms which were geometrically fixed and in riding mode. CH<sub>3</sub> H atoms were located using the circular Fourier facility in *SHELXL93*; only one H atom was found on each water molecule in difference electron density maps. The structure was refined to convergence using *SHELX97* (Sheldrick, 1997), with some soft constraints (SADI) being applied in order to equilibrate bond distances between molecules *A* and *B*. Details of the refinement are given in Table 1. Least-squares refinement converged with a mean  $\Delta/\sigma$  of 0.020 (max. 0.0708). The conformation and hydrogen bonding in molecule *A* is shown

**Table 2**  
Selected torsion angles ( $^{\circ}$ ) of the X-ray structure.

	Molecule A	Molecule B
C(8)–O(8)–C(15)–C(16)	–172.3 (2)	–162.3 (3)
O(8)–C(15)–C(16)–O(16)	–71.6 (3)	–71.0 (3)
C(15)–C(16)–O(16)–C(17)	–168.1 (3)	–162.0 (3)
C(16)–O(16)–C(17)–C(18)	–74.3 (4)	–77.2 (4)
O(16)–C(17)–C(18)–O(18)	–64.0 (4)	–62.7 (4)
C(17)–C(18)–O(18)–C(19)	–179.6 (3)	–178.1 (3)
C(1)–C(13)–C(9)–C(12)	164.9 (3)	165.2 (3)
O(1)–C(1)–C(13)–C(9)	–7.4 (4)	–7.7 (4)
C(22)–O(1)–C(1)–C(13)	–165.1 (3)	178.2 (3)
Mirror		
C(12)–C(8)–O(8)–C(15)	178.3 (3)	165.5 (3)
C(9)–C(12)–C(8)–O(8)	11.0 (4)	5.4 (4)
C(13)–C(9)–C(12)–C(8)	–167.2 (3)	–164.2 (3)
C(18)–O(18)–C(19)–C(20)	177.5 (3)	–179.9 (3)
O(18)–C(19)–C(20)–O(20)	64.7 (5)	65.9 (4)
C(19)–C(20)–O(20)–C(21)	73.0 (4)	76.2 (4)
C(20)–O(20)–C(21)–C(22)	166.5 (3)	168.2 (3)
O(20)–C(21)–C(22)–O(1)	71.2 (3)	69.9 (4)
C(21)–C(22)–O(1)–C(1)	163.4 (3)	171.7 (3)
C(24)–C(10)–C(14)–C(13)	131.7 (3)	131.6 (3)
C(23)–C(10)–C(14)–C(13)	–106.7 (3)	–107.2 (3)
C(11)–C(10)–C(14)–C(13)	11.0 (4)	11.4 (4)
C(24)–C(10)–C(14)–C(4)	–53.2 (4)	–52.1 (4)
C(23)–C(10)–C(14)–C(4)	68.4 (3)	69.0 (4)
C(11)–C(10)–C(14)–C(4)	–173.9 (3)	–172.4 (3)
C(14)–C(13)–C(9)–O(9)	99.8 (3)	100.6 (3)
C(1)–C(13)–C(9)–O(9)	–76.7 (3)	–74.9 (3)
C(14)–C(13)–C(9)–C(12)	–18.6 (4)	–19.4 (4)
O(9)–C(9)–C(12)–C(11)	–98.2 (3)	–99.0 (3)
C(13)–C(9)–C(12)–C(11)	20.9 (4)	20.3 (4)
O(9)–C(9)–C(12)–C(8)	73.7 (3)	76.5 (3)
C(24)–C(10)–C(11)–C(12)	–131.2 (3)	–132.8 (3)
C(23)–C(10)–C(11)–C(12)	111.7 (3)	111.7 (3)
C(24)–C(10)–C(11)–C(5)	49.5 (4)	46.6 (4)
C(23)–C(10)–C(11)–C(5)	–67.6 (4)	–68.9 (3)

in Fig. 2 (*SNOOPI*; Karaulov, 1992), which also indicates the atom numbering used. The corresponding view of molecule B is very similar. Table 1 provides crystal data, both X-ray and neutron; X-ray atom coordinates and  $U_{\text{iso}}$  values have been deposited.<sup>1</sup> Table 2 gives, for the X-ray structure, selected torsion angles, discussed below.

### 2.3. Neutron study

**2.3.1. Neutron diffraction measurements.** Prior to the start of neutron diffraction data collection, the reflection indices and cell parameters of the octant of X-ray diffraction data, which had been collected in the monoclinic C-face-centred  $c$ -axis unique setting, were transformed into a primitive, monoclinic setting with the  $b$  axis unique and space group  $P2_1$ . A crystal with approximate dimensions  $2.5 \times 1.6 \times 0.2$  mm was mounted on a vanadium support on the D19 four-circle diffractometer at ILL with the longest dimension of the plate along the  $\Phi$  axis. The neutron wavelength was 1.538 Å. An

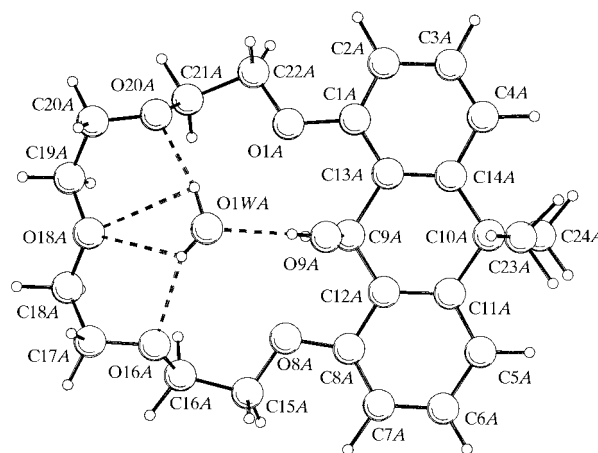
initial scan of reciprocal space located six reflections which could be indexed and a preliminary orientation matrix calculated. Additional reflections, which were expected to be of significant intensity on the basis of the X-ray data, were then located and an improved orientation matrix established.

The  $4 \times 64^{\circ}$  area detector of D19 enabled the three-dimensional peak shapes of the Bragg reflections to be monitored and neither splitting nor streaking was observed. The crystal was cooled to 15 K whilst a strong reflection was continuously monitored and a new orientation matrix established. The peak shapes of a number of reflections were checked. Data collection for  $\pm h, -k, -l$  commenced in shells of  $2\theta$  up to  $2\theta = 92^{\circ}$  using  $\omega$ -scans in equatorial geometry. The area detector allowed additional reflections to be measured and so checks were made of mirror-related reflections and repeated measurements of the same or Friedel-related reflections as well as the usual three reference reflections repeated regularly during data collection. The wavelength was then changed to 1.312 Å in order to measure higher-angle data, a new orientation matrix calculated and data collection continued using the normal beam geometry.

Owing to a slow He leak, a significant reduction in detector efficiency occurred. Nevertheless, the efficiency was effectively constant on the time scale of the experiment, but this situation, and the rather small crystal volume ( $0.8 \text{ mm}^3$ ), contributed to the fact that half the intensity data were weak although significantly above background.

The procedure of Wilkinson *et al.* (1988) was used (program *RETREAT*) to integrate the Bragg peaks in three dimensions. No absorption correction was applied, although the crystal shape would have caused certain reflections to have suffered significant absorption effects. The data were merged and sorted to provide 1931 unique reflections.

**2.3.2. Unit-cell relationships.** At the start of the refinement, the coordinates from the X-ray refinement were used together with the  $F_{\text{obs}}$  from the neutron data collection. Unexpectedly there was no agreement, although the unit-cell parameters from the two sets of measurements were in close agreement



**Figure 2**  
Atom numbering used for molecule A in the X-ray analysis and later neutron analysis. Hydrogen bonds are indicated (see Table 3).

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0566). Services for accessing these data are described at the back of the journal.

**Table 3**  
Hydrogen bonds and other short contacts for the neutron structure.

Molecule	$D-H$ (Å)	$D\cdots A$ (Å)	$H\cdots A$ (Å)	$D-H\cdots A$ (°)
(1) <i>A</i>	O(9A)—H(9A1) 0.73 (4)	O(9A) $\cdots$ O(A) 2.57 (2)	H(9A1) $\cdots$ O(A) 1.84 (3)	O(9A)—H(9A1) $\cdots$ O(A) 177 (2)
<i>B</i>	O(9B)—H(91B) 1.07 (2)	O(9B) $\cdots$ O(B) 2.81 (2)	H(91B) $\cdots$ O(B) 1.75 (2)	O(9B)—H(91B) $\cdots$ O(B) 173 (1)
(2) <i>A</i>	OWA—HWA2 0.90 (3)	OWA $\cdots$ O(16A) 2.99 (2)	HWA2 $\cdots$ O(16A) 2.15 (1)	OWA—HWA2 $\cdots$ O(16A) 156.8 (8)
<i>B</i>	OWB—HWB2 0.91 (3)	OWB $\cdots$ O(16B) 2.87 (2)	HWB2 $\cdots$ O(16B) 1.97 (3)	OWB—HWB2 $\cdots$ O(16B) 169 (2)
(3) <i>A</i>	OWA—HWA2 0.90 (3)	OWA $\cdots$ O(18A) 2.95 (2)	HWA2 $\cdots$ O(18A) 2.34 (1)	OWA—HWA2 $\cdots$ O(18A) 125.4 (8)
<i>B</i>	OWB—HWB2 0.91 (3)	OWB $\cdots$ O(18B) 2.93 (2)	HWB2 $\cdots$ O(18B) 2.49 (2)	OWB—HWB2 $\cdots$ O(18B) 111 (1)
(4) <i>A</i>	OWA—HWA1 1.03 (3)	OWA $\cdots$ O(18A) 2.95 (2)	HWA1 $\cdots$ O(18A) 2.68 (2)	OWA—HWA1 $\cdots$ O(18A) 95 (1)
<i>B</i>	OWB—HWB1 1.02 (3)	OWB $\cdots$ O(18B) 2.93 (2)	HWB1 $\cdots$ O(18B) 2.54 (2)	OWB—HWB1 $\cdots$ O(18B) 103 (2)
(5) <i>A</i>	OWA—HWA1 1.03 (3)	OWA $\cdots$ O(20A) 3.04 (2)	HWA1 $\cdots$ O(20A) 2.03 (1)	OWA—HWA1 $\cdots$ O(20A) 170 (2)
<i>B</i>	OWB—HWB1 1.02 (3)	OWB $\cdots$ O(20B) 3.15 (2)	HWB1 $\cdots$ O(20B) 2.14 (2)	OWB—HWB1 $\cdots$ O(20B) 174 (2)
(6) <i>A</i>	O(9A)—H(9A1) 0.73 (4)	O(9A) $\cdots$ O(8A) 2.93 (1)	H(9A1) $\cdots$ O(8A) 2.89 (2)	O(9A)—H(9A1) $\cdots$ O(8A) 86 (2)
<i>B</i>	O(9B)—H(91B) 1.07 (2)	O(9B) $\cdots$ O(8B) 3.05 (2)	H(91B) $\cdots$ O(8B) 2.81 (2)	O(9B)—H(91B) $\cdots$ O(8B) 93 (1)
(7) <i>A</i>	OWA—HWA1 1.03 (3)	OWA $\cdots$ O(1A) 3.46 (2)	HWA1 $\cdots$ O(1A) 2.86 (3)	OWA—HWA1 $\cdots$ O(1A) 117 (1)
<i>B</i>	OWB—HWB1 1.02 (3)	OWB $\cdots$ O(1B) 3.76 (2)	HWB1 $\cdots$ O(1B) 3.17 (2)	OWB—HWB1 $\cdots$ O(1B) 116 (1)

Symmetry code:  $x - 1, y, z$

and any difference could be ascribed to the temperature difference between the two sets of measurements. This situation, which gave considerable cause for concern, was eventually traced to the idiosyncrasies of the unit-cell shape. Thus, when the transformation from the original X-ray, apparently rectangular, centred cell (see above) to the symmetry-correct, primitive monoclinic cell was made, two alternative but extremely similar unit cells could be chosen, as shown in Fig. 3. If the  $\beta$  angle of the centred cell had appeared to be precisely  $90^\circ$ , the transformed parameters for both these cells would be identical and would differ only slightly if  $\beta$  differed from  $90^\circ$  by a small amount, although both primitive cells would still have the same volume. It transpired that one cell had been chosen for the X-ray data collection and the other for the neutron data. Since the primitive triplets which described the reciprocal lattice differed, so did the indices. We chose to modify the indices and cell parameters of the neutron data rather than the coordinates from the X-ray analysis.

With reference to Fig. 3, it can be seen that only the values of  $c$  and  $\beta$  will be changed when making this modification. The experimental and derived values (primed) were  $c = 13.688$ ,  $c' = 13.588$  Å,  $\beta = 117.93$  and  $\beta' = 117.12^\circ$ . The relationship between the indices consequential to the choice was

$$h' = h, \quad k' = -k, \quad l' = -(l + h).$$

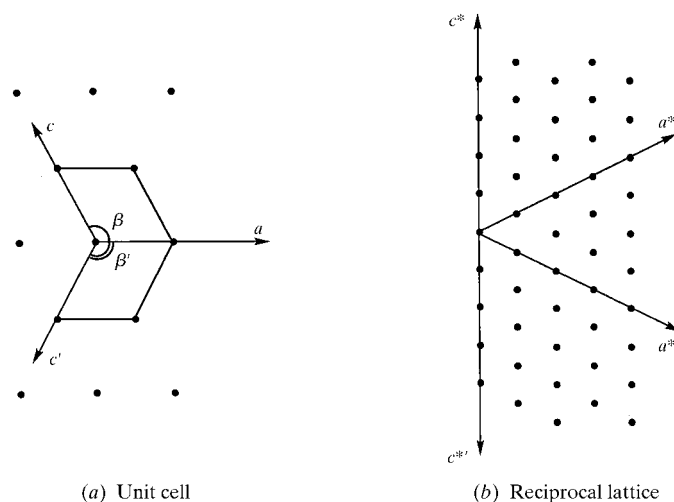
The unit-cell dimensions for the rectangular cell suggested by the version of the software for the CAD4 then available to us were  $a = 12.856$  (1),  $b = 24.396$  (4),  $c = 14.564$  (2) Å,  $\alpha = 89.98$  (1),  $\beta = 89.987$  (9),  $\gamma = 90.10$  (1)°. Although with the

benefit of hindsight it might be argued that  $\gamma$  had a precision which precludes an orthorhombic cell, it should be remembered, for the reasons presented recently by Marsh (1995), that the accuracy of the angle determinations would be lower and would be considered by most crystallographers as such as not to preclude the cell.

**Indeed even if the angles are all indistinguishable from  $90^\circ$ , the crystal system is not necessarily orthorhombic.** The potential for designing automated diffractometer systems with adequate symmetry checks, the dangers of misuse of some automated diffractometer systems, the importance of the role of photographic methods, which are still in use in many laboratories and teaching schools, and/or an early Laue check in the determination of the correct Laue group and hence crystal system cannot be overemphasized. We believe that many important structures may be passed over or

discarded through the failure to use these procedures or simply a lack of awareness of them. The other crystallographic situation illustrated by this structure is the possibility of different unit-cell choices appearing identical, with the consequential difficulties in the comparison of structural data.

**2.3.3. Structure refinement and neutron structure.** The atomic coordinates from the X-ray refinement (at  $R = 0.10$ ) were used as the starting set for the neutron structure. Isotropic refinement rapidly led to an  $R$  factor of 0.06.



**Figure 3**  
Relationship between alternative unit-cell transformations: (a) unit cell; (b) reciprocal lattices.

Although the X-ray structure had revealed most of the H atoms, one hydrogen from each water molecule had been undetected. A difference neutron synthesis revealed the missing atoms. Refinement was undertaken by full-matrix least-squares on  $F^2$ , with isotropic displacement parameters for all atoms. The structure was refined to convergence using *SHELX97* (Sheldrick, 1997). Data relating to the analysis are given in Table 1. Least-squares refinement converged with a mean  $\Delta/\sigma$  of 0.006 (max.  $-0.123$ ). Hydrogen bonds and other short contacts derived from the neutron data are in Table 3 and are discussed below. Neutron scattering lengths were taken from Volume III of the *International Tables for X-ray Crystallography* (1952).

### 3. Discussion

#### 3.1. Hydrogen bonding (neutron structure)

The patterns of possible hydrogen bonds and other short contacts exhibited by molecules *A* and *B* (Table 3) are similar, but with some noticeably different geometry values, due mainly to the local variation in the water molecule positions which, as noted previously, are responsible for breaking the approximate  $P2_1/c$  pseudosymmetry of the structure. In both molecules *A* and *B* the crown ether oxygen O(9) (donor) forms a strong hydrogen bond with the water O atoms OW [entry (1), Table 3]. In both molecules the water molecule forms through HW2 bifurcated hydrogen bonds to O(16) [entry (2)] and O(18) [entry (3)], the latter being the weaker of the two in view of the greater bending of its O—H...OW angle. There are similar interactions in both molecules through the water HW1 H atoms to atoms O(18) [entry (4)] and O(20) [entry (5)], but these are relatively weak in view of either greater bending or longer OW...O distances. While O(9) forms a short contact with O(8) in both molecules [entry (6)] it fails to donate its hydrogen, which is already occupied with hydrogen bonding to OW. OW also fails to form a strong interaction with O(8) [entry (7)]. The hydrogen bonding is illustrated in Figs. 3(*a*) and (*b*). There is no hydrogen bond between the two molecules *A* and *B*.

#### 3.2. Molecular pseudosymmetry and conformation

Both molecules *A* and *B* exhibit very close pseudosymmetry across a plane perpendicular to the molecular plane and through atoms C(9) and O(18), as suggested in the chemical and structure drawings. The effect may be quantified from the asymmetry parameter (Duax & Norton, 1975) for  $\Delta C_s(9-18)$ , the r.m.s. value of  $|\varphi - \varphi'|^2$ , where  $\varphi$  and  $\varphi'$  are the corresponding torsion angles across the '*m* plane', which has the relatively small values of 5.83 and 6.73° for molecules *A* and *B*, respectively. Breakdown of this pseudosymmetry occurs for both molecules mainly towards the dihydroanthracene ring, with deviations in the absolute value of the torsion angle of up to 13.9 and 15.4° in molecules *A* and *B*, respectively. The same region shows the greatest lack of correspondence in conformation between the two molecules. Although the average difference in torsion angle is only 4.4°, the maximum deviation

is 15.6°. Consequently, the molecules have appreciable flexibility, which, it may be argued, at least in part explains why the crystal asymmetric unit contains two non-exact copies of the molecule.

It is of interest to note that within the polyethylene glycol portions of the macrocycle the preferred sequence of *gauche-anti-anti* conformations for C—C—O—C arrays is interrupted only at the O atoms O(16) and O(20), both involved in strong hydrogen bonding to the water. The conformations about O(16)—C(17) and C(20)—O(20) are both *gauche* rather than *anti*.

#### 3.3. Planarity

The fitting of least-squares planes reveals that atoms C(1)—C(9) in the dihydroanthracene ring are planar within 0.061 Å in molecule *A* and 0.078 Å in molecule *B* [atoms C(9) and C(10) are out of the plane by 0.332 (3) and 0.171 (4) Å, respectively, in molecule *A* and by 0.356 (4) and 0.205 (4) Å in molecule *B*]. The approximate plane of the rest of the macrocycle to these planar regions makes angles of 2.62 (9) and 3.40 (9)°, respectively, in molecules *A* and *B*. Consequently, as may have been expected, both molecules are predominantly planar in structure. Interestingly, there is a further essentially planar feature in both molecules involving atoms C(23), C(24), C(10), C(9), O(9), OW and O(18) with r.m.s. deviations of 0.062 and 0.066 Å in molecules *A* and *B*, respectively. These planes make angles close to 90° with the rest of the molecule in both cases.

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### References

- Beddoes, R. S., Cox, B. G., Mills, O. S., Mooney, N. J., Watt, C. I. F., Kirkland, D. & Martin, D. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 2091–2098.
- Cox, B. G., Hurwood, T. V., Prodi, L., Montalti, M., Bolletta, F. & Watt, C. I. F. (1999). *J. Chem. Soc. Perkin Trans. 2*, pp. 289–296.
- Cox, B. G., Mills, O. S., Mooney, N. J., Robinson, P. M. & Watt, C. I. F. (1995). *J. Chem. Soc. Perkin Trans. 2*, pp. 697–706.
- Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. 1. New York: IFI/Plenum Data Company.
- Enraf–Nonius (1988). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
- Karaulov, S. (1992). *SNOOPI*. University of Wales, Cardiff.
- Marsh, R. E. (1995). *Acta Cryst.* **B51**, 897–907.
- Olsher, U., Frolow, F., Bartsch, R. A., Pugia, M. J. & Shoham, G. (1989). *J. Am. Chem. Soc.* **111**, 9217–9222.
- Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.

- Stoe & Cie (1997). *X-STEP*. Stoe and Cie, GmbH (richter@stoe.com).
- Watt, C. I. F., Cox, B. G., Mills, O. S., Mooney, N. J. & Robinson, P. M. (1995). *Crown ethers with embedded 1,8-dioxy-9-xanthyli cations*. ESOR-V, Santiago de Compostela, July 1995.
- Wilkinson, C., Khamis, H. W., Stansfield, R. F. D. & McIntyre, G. J. (1988). *J. Appl. Cryst.* **21**, 471–478.
- Young, V. G., Quiring, H. L. & Sykes, A. G. (1997). *J. Am. Chem. Soc.* **119**, 12477–12480.
- Young, V. G. & Sykes, A. G. (1998). *Inorg. Chem.* **37**, 376–378.