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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in main residue
 R factor = 0.059
 wR factor = 0.149
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4'-Acetylbenzo-15-crown-5 2-naphthyl-
oxyacetylhydrazone

The title compound, $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_7$, which was obtained by condensation of 4'-acetylbenzo-15-crown-5 and 2-naphthyl-oxyacetic acid hydrazide, adopts a *syn-anti* conformation, which enables $\text{N}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds to be formed between centrosymmetrically related molecules. The resulting eight-membered rings join these molecules together as characteristic dimers. The naphthalene ring system is almost perpendicular to the crown ether ring.

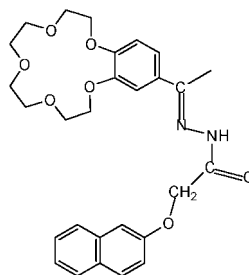
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Comment

Aryloxyacetic acids and their derivatives often possess many important biological activities. Some of these compounds are used as herbicides and plant-growth regulators. In continuation of our previous work on synthesis and biological activities (Chen & Wei, 1993; Wei *et al.*, 1995, 1996), we decided to design a series of compounds containing the aryloxyacetyl group and crown ether in order to study the variation of bioactivities and the effect of the substituents on the ability of the crown ether to bind metal ions (Zhang, Lu, Song & Zhang, 1992; Zhang, Lu, Zhang & Zhao, 1992). Recently, we determined related crystal structures (Zhang, Wei *et al.* 2003; Zhang, Xian, Wei & Cai, 2003; Zhang, Xian & Wei, 2003), in order to study both bioactivities and coordination behaviour. In view of these encouraging results, the structure of the title compound, (I), was obtained and is reported here.



(I)

The title compound contains a naphthalene ring system, a crown ether ring and a fused benzene ring. The least-squares planes of the naphthalene (C19–C28) and the benzene (C1–C6) rings have mean deviations of 0.0085 and 0.0024 Å, respectively. The naphthalene ring system is inclined at 69.8° to the benzene ring.

There is a distinct bend in the crown ether ring, imposed by the benzene ring (Wei *et al.*, 1988), where O1 and O2 are approximately coplanar with the benzene ring. Their positions deviate by 0.0279 and 0.0252 Å, respectively, from C1–C6. There is disorder in the crown ether ring, namely O3/O4/C8/C9/C10/C11/C12 and O3'/O4'/C8'/C9'/C10'/C11'/C12'. These two conformations are present in the ratio 0.612 (8):0.388 (8).

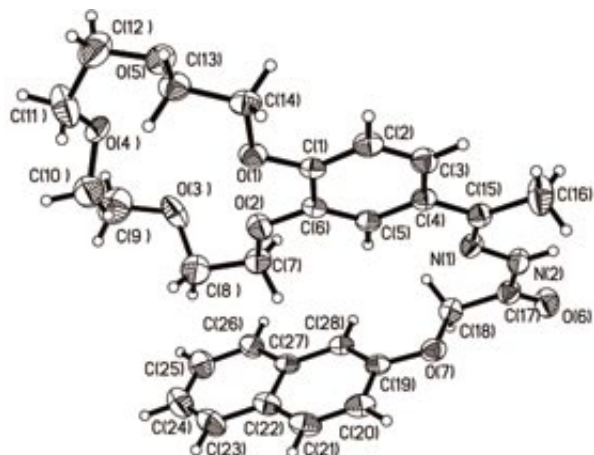


Figure 1
The molecular configuration and atom-numbering scheme for the title compound, showing displacement ellipsoids at the 50% probability level.

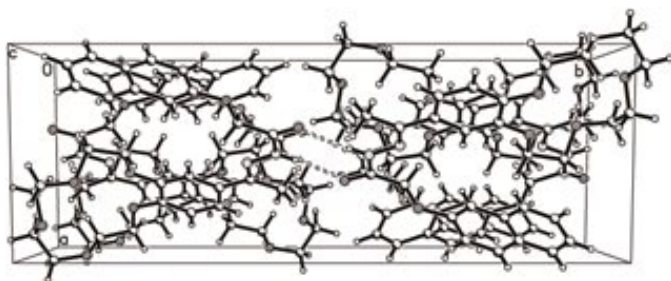


Figure 2
Packing diagram of the title compound.

In the benzocrown ether moiety, the substituent gives rise to some structural differences in comparison with benzo-15-crown-5, namely an increase in the C3–C4 bond length [1.386 (4) Å] and a decrease in the C3–C4–C5 angle [117.6 (2)°]. However, the most important feature is that the plane of symmetry through O4 and the mid-points of C1–C6 and C3–C4 has disappeared (Hanson, 1978). We also found that the magnitudes of the crown ring torsion angles O2–C7–C8–O3, O3–C9–C10–O4, O4–C11–C12–O5 and O5–C13–C14–O1 and those in similar positions in benzo-15-crown-5 are all greater than those found in the coordinated species (Mallinson & Truter, 1972; Bush & Truter, 1972; Owen, 1978). The main reason for this result is that the O atoms in the complexes are located in suitable positions for coordination with metal ions.

The acylhydrazone group has two tautomers, namely the keto form and enol form. Most uncomplexed acylhydrazone compounds exist in the keto form, because the enol form is not stable in the free ligand. The title compound apparently takes the keto form, which can be seen from the molecular structure (Fig. 1). The keto form enables the formation of an N–H...O hydrogen bond. Moreover, the two substituents of the acylhydrazone group (the 2-naphthylxymethylene group and the benzo-15-crown-5 group) adopt a *syn-anti* conformation with respect to the acylhydrazone moiety, shown by the torsion angles N1–N2–C7–C18 [–3.5 (4)°] and N2–N1–C15–C4 [–179.9 (2)°]. The *syn-anti* conformation enables the forma-

tion of the intermolecular N2–H...O6(–x + 1, –y + 2, –z + 1) hydrogen bond (Table 2), resulting in an eight-membered ring (Fig. 2) composed of two molecules related by a centre of inversion.

The formation of the hydrogen bond, therefore, will help prevent the keto rearranging to the enol form, thereby potentially influencing the coordination properties of this ligand.

Experimental

The title compound was obtained by condensing a mixture of 4'-acetylbenzo-15-crown-5 with 2-naphthylxyacetic acid hydrazide in ethanol and recrystallizing from dimethylformamide (DMF) and ethyl acetate. The product was dissolved in a mixture of DMF and ethyl acetate and crystals suitable for X-ray determination were obtained after one month. Analysis calculated for C₂₈H₃₂N₂O₇ (508.56): C 66.13, H 6.34, N 5.51%; found: C 65.99, H 6.39, N 5.44%.

Crystal data

C₂₈H₃₂N₂O₇
M_r = 508.56
Monoclinic, P2₁/c
a = 8.808 (3) Å
b = 24.579 (7) Å
c = 11.984 (4) Å
β = 97.248 (6)°
V = 2573.6 (13) Å³
Z = 4

D_x = 1.313 Mg m⁻³
Mo Kα radiation
Cell parameters from 920 reflections
θ = 2.4–25.4°
μ = 0.10 mm⁻¹
T = 293 (2) K
Block, colourless
0.38 × 0.22 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
14670 measured reflections
5263 independent reflections
2575 reflections with I > 2σ(I)

R_{int} = 0.051
θ_{max} = 26.4°
h = –11 → 9
k = –30 → 30
l = –14 → 14

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.059
wR(F²) = 0.149
S = 1.01
5263 reflections
368 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0576P)² + 0.3872P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.19 e Å⁻³
Δρ_{min} = –0.17 e Å⁻³

Table 1

Selected torsion angles (°).

O1–C1–C6–O2	–2.0 (3)	O5–C13–C14–O1	–69.8 (3)
O2–C7–C8–O3	74.0 (5)	N2–N1–C15–C4	–179.9 (2)
O3–C9–C10–O4	151.1 (11)	N1–N2–C17–C18	–3.5 (4)
O4–C11–C12–O5	–77.4 (11)		

Table 2

Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N2–H2...O6 ⁱ	0.86	2.15	2.963 (3)	157

Symmetry code: (i) 1 – x, 2 – y, 1 – z.

All H atoms were positioned geometrically, with C–H distances in the range 0.93–0.97 Å and an N–H distance of 0.86 Å [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$], and were refined as riding.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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