

***N,N'*-Diacetyl-1,13-diaza-24-crown-8**

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Key indicators

Single-crystal X-ray study

$T = 101\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.032

w R factor = 0.087

Data-to-parameter ratio = 19.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Half of the title compound (*N,N'*-diacetyl-1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane), $\text{C}_{20}\text{H}_{38}\text{N}_2\text{O}_8$, makes up the asymmetric unit. The crown ring is relatively flat, and though collapsed in on itself, would require little change to adopt a binding conformation. $\text{C}-\text{H}\cdots\text{O}$ bonding is also observed.

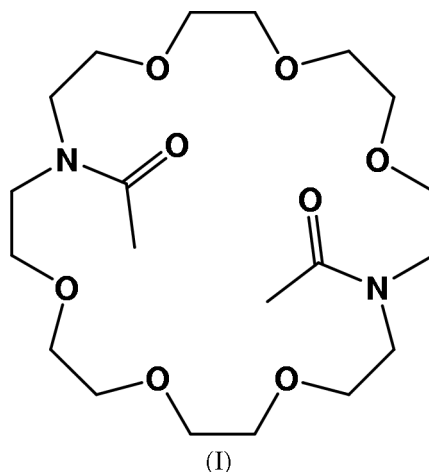
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Comment

As part of a continuing research program that involves the synthesis of cage-annulated crown ethers, cryptands, and molecular boxes (Macias *et al.*, 2000; Watson *et al.*, 2000; Marchand *et al.*, 1998), we prepared *N,N'*-diacetyl-1,13-diaza-24-crown-8, (I), as a precursor to *N,N'*-ethyl-1,13-diaza-24-crown-8.



Half of the molecule makes up the asymmetric unit, the other half is generated through the crystallographic inversion center. The crown ring lies in a rough plane with the acetyl groups roughly orthogonal to that plane, but placed on opposite sides. The crown ether is collapsed in on itself, as is commonly observed in the structures of large, uncomplexed crown ethers (Bryan *et al.*, 2000). Its conformation can be described in terms of the torsion angles around the ring (Dale, 1980) where *g* and *a* represent *gauche* and *anti*, respectively, and a superscript following the *g* indicates the sign. Starting with $\text{N}-\text{C}1-\text{C}2-\text{O}1$, the conformation is $g^-aa\ g^-aa\ g(a)(a)\ g^-gg$, which is then repeated, although inverted, for the other half of the molecule. The "*a*" values refer to $\text{C}7-\text{O}3-\text{C}6-\text{C}5^i$ [symmetry code: (i) $1-x, 2-y, 1-z$] and $\text{C}6-\text{O}3-\text{C}7-\text{C}8$ which are $143.41(9)$ and $-148.26(9)^\circ$, respectively. They are marked in parenthesis because of their proximity to

the intermediate torsion value of 120°. To bind a cation, the pattern $g^{\pm}aa$ should repeat around the ring. This structure only needs to change two torsion angles to meet this criterion.

This is the first X-ray structure of a 24-crown-8 ether without sterically constraining groups on the crown backbone (such as benzo or cyclohexano). As such, it may represent a relatively low energy conformation for 24-crown-8.

The collapse of an uncomplexed crown ring typically leads to favorable intramolecular C—H···O bonding (Bryan *et al.*, 1999; Steiner, 1996), which may influence the observed conformation. Only one such bond is observed here (C1—H1B···O3), but an intramolecular H bond is also observed between one of the acetyl methyl H atoms and O1 (Table 2). The orientation of the acetyl group may also be affected by a short contact between O4 and H8B (2.42 Å, see Table 2).

Experimental

To a solution of 1,13-diaza-24-crown-8 (Dietrich *et al.*, 1973; Johnson *et al.*, 1985) (820 mg, 2.34 mmol), 4-dimethylaminopyridine (DMAP, 57 mg, 0.468 mmol) and Et₃N (824 mg, 8.1 mmol) in dry CH₂Cl₂ (40 ml) was added freshly distilled Ac₂O (529 mg, 5.2 mmol), and the resulting mixture was refluxed for 2 d. The reaction mixture was allowed to cool gradually to ambient temperature and then was washed with water (3 × 50 ml). The organic layer was dried (MgSO₄) and filtered, and the filtrate concentrated *in vacuo*. The residue was purified *via* column chromatography on silica gel by eluting with 5% MeOH—CHCl₃. Workup of the eluate afforded the title compound (280 mg, 27%) as a colorless waxy solid. Single crystals, m.p. 85.5–86.5 °C, were obtained *via* fractional recrystallization from CH₂Cl₂–hexane. IR (KBr) 2880 (*m*), 2865 (*m*), 1638 (*s*), 1100 cm⁻¹ (*s*); ¹H NMR (CDCl₃) δ 2.09 (*s*, 6H), 3.48–3.65 (*m*, 32H); ¹³C NMR (CDCl₃) δ 21.6 (*q*, 2C), 46.6 (*t*), 46.8 (*t*), 49.9 (*t*, 2C), 69.4 (*t*), 69.6 (*t*), 69.7 (*t*), 70.0 (*t*), 70.3 (*t*), 70.4 (*t*), 70.5 (*t*), 70.56 (*t*, 2C), 70.62 (*t*), 70.8 (*t*), 71.0 (*t*), 171.0 (*t*, 2C). Analysis calculated for C₂₀H₃₈N₂O₈: C 55.26, H 8.82%; found: C 55.35, H 8.76%. Elemental microanalyses were performed by M. H. W. Laboratories, Phoenix, AZ.

Crystal data

C ₂₀ H ₃₈ N ₂ O ₈	Z = 1
M _r = 434.5	D _x = 1.311 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
a = 7.4145 (12) Å	Cell parameters from 25 reflections
b = 8.145 (2) Å	θ = 10.2–15.8°
c = 10.299 (3) Å	μ = 0.10 mm ⁻¹
α = 98.95 (2)°	T = 100 K
β = 105.103 (18)°	Prism, colorless
γ = 108.424 (17)°	0.52 × 0.43 × 0.30 mm
V = 550.2 (3) Å ³	

Data collection

Nonius CAD-4 diffractometer	h = -9 → 9
ω scans	k = -10 → 10
5289 measured reflections	l = -13 → 13
2644 independent reflections	3 standard reflections
2357 reflections with I > 2 σ (I)	frequency: 120 min
R _{int} = 0.015	intensity decay: 4%
θ_{\max} = 28.0°	

Refinement

Refinement on F ²	w = 1/[$\sigma^2(F_o^2) + (0.0475P)^2 + 0.1429P$]
R(F) = 0.032	where P = (F _o ² + 2F _c ²)/3
wR(F ²) = 0.087	(Δ/σ) _{max} < 0.001
S = 1.03	$\Delta\rho_{\max}$ = 0.34 e Å ⁻³
2644 reflections	$\Delta\rho_{\min}$ = -0.23 e Å ⁻³
137 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

O1—C2	1.4297 (13)	O3—C7	1.4202 (12)
O1—C3	1.4218 (11)	O4—C9	1.2342 (12)
O2—C4	1.4209 (13)	N—C1	1.4666 (13)
O2—C5	1.4292 (14)	N—C8	1.4642 (14)
O3—C6	1.4268 (12)	N—C9	1.3511 (14)
C2—O1—C3	112.18 (8)	O2—C4—C3	109.46 (8)
C4—O2—C5	111.43 (7)	O2—C5—C6 ⁱ	108.89 (8)
C6—O3—C7	115.90 (7)	O3—C6—C5 ⁱ	109.48 (7)
C1—N—C8	116.92 (8)	O3—C7—C8	108.01 (8)
C1—N—C9	125.10 (9)	N—C8—C7	110.81 (8)
C8—N—C9	117.65 (8)	O4—C9—N	121.24 (10)
N—C1—C2	112.95 (8)	O4—C9—C10	120.40 (10)
O1—C2—C1	108.27 (8)	N—C9—C10	118.36 (9)
O1—C3—C4	109.16 (8)		
C3—O1—C2—C1	175.08 (8)	C7—O3—C6—C5 ⁱ	143.41 (9)
C2—O1—C3—C4	174.85 (8)	C6—O3—C7—C8	-148.26 (9)
C5—O2—C4—C3	-178.31 (7)	C1—N—C8—C7	-93.00 (9)
C4—O2—C5—C6 ⁱ	173.89 (7)	C8—N—C1—C2	-87.04 (10)

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

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O3	0.99	2.49	3.1181 (15)	121
C2—H2A···O4 ⁱ	0.99	2.52	3.4804 (16)	163
C6—H6A···O2 ⁱⁱ	0.99	2.58	3.5592 (16)	169
C8—H8A···O4	0.99	2.42	2.6822 (15)	94
C10—H10B···O1	0.98	2.42	3.2613 (16)	144

Symmetry codes: (i) -x, 1 - y, 1 - z; (ii) x, y, 1 + z.

A 1.1 mm collimator was used. All C-bound H atoms were placed in calculated positions, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 (CH₂) or 1.5 (CH₃) times the equivalent isotropic displacement parameter of the atom to which they were attached. The C—H distances used depend on the type of C atom: C_{methylene}—H = 0.99 and C_{methyl}—H = 0.98 Å. Methyl H atoms were allowed to rotate about the adjacent C—C bond.

Data collection: CAD-4/PC (Nonius, 1996); cell refinement: CAD-4/PC; data reduction: XCAD4 (Harms, 1993); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: PLATON (Spek, 2000).

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