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5-Chloro-2-hydroxycarbonylmethoxy-1,3-xylyl-18-crown-5 and 5-Chloro-2-ethoxycarbonylmethoxy-1,3-xylyl-18-crown-5

GEORGE FERGUSON AND BRANKO KAITNER

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

M. ANTHONY MCKERVEY

Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

MICHAEL OWENS

Department of Chemistry, University College, Cork, Eire

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Abstract

In the acid (1) {19-chloro-3,6,9,12,15-pentaoxabicyclo-[15.3.1]henicos-1(21),17,19-trien-21-yloxyacetic acid} there exists an intramolecular O—H...O hydrogen bond [O...O 2.658(3) Å], which is achieved with considerable distortion of the macrocycle ring. The macroring of the ethyl ester (2) has an essentially undistorted crown ether conformation, in which the side chain overhangs the macrocycle cavity with the carbonyl O atom directed *exo*.

Comment

As part of a programme of study of synergism in ion binding between strategically placed functional groups and macrocyclic receptors, we have studied crown ethers with pendant phenolic groups and have demonstrated cooperation in binding of ammonia and primary amines leading, *via* proton transfer, to the formation of ammonium phenoxide complexes (Browne, Ferguson, McKervey, Mulholland, O'Connor & Parvez, 1985; Ferguson, Kaitner, Browne & McKervey, 1988). The calixarene family of macrocycles, in which several phenolic functions are organized in metacyclophane arrays, also provides important examples of synergism in ion binding.

That carboxylic acid and ester functions can participate effectively in ion binding, particularly when attached to oxygenated macrocycles, is well known. We have extended our study of functionalized macrocycles to include carboxylic acids and esters attached to crown ethers and we describe here two such compounds, the chloro-acid (1) and its ethyl ester (2) in a metacyclophane environment. A search of the 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) shows that there is only one other report of a 1,3-xylyl-18-crown-5 moiety and that is for an aqua-nitrate samarium(III) complex of 2-methoxy-1,3-xylyl-18-crown-5 (Tomat, Valle, Cassol & di Bernardo, 1983).

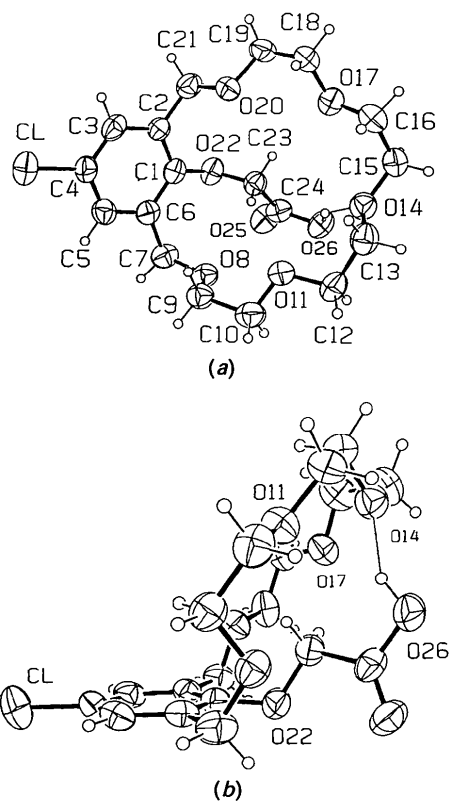
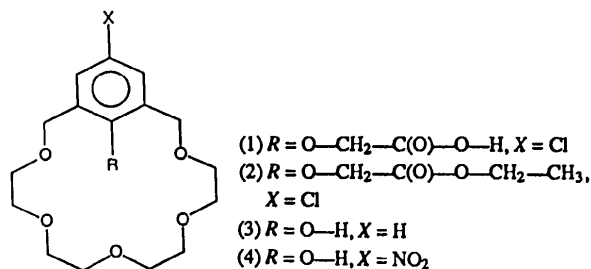


Fig. 1. Views of molecule (1): (a) plan view and (b) side-on view showing the general conformation and the intramolecular hydrogen bonding with the crystallographic numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size.

Views of acid (1) are shown in Fig. 1, and corresponding views of ester (2) are presented in Fig. 2. Molecular dimensions for both (1) and (2) are normal; principal bond lengths are summarized in Table 3. Both crystal structures contain discrete molecules separated by normal van der Waals distances. Significant differences exist between the conformations of the two molecules *vis-à-vis* the presence of the intraannular substituents. In ester (2), the conformation of the macroring is that of an essentially undistorted crown ether with all ring C—O—C—C torsion angles close to 180° and all O—C—C—O torsion angles close to *gauche*. The angle which the aromatic ring plane makes with the plane of the macrocycle O atoms is 44.0(1)°, which compares with 28° for crown ether phenol (3) and 47° for the *p*-nitro crown ether phenol (4). The ester side chain in (2) overhangs the cavity and the —CH₂—C—O—CH₂—CH₃ moiety is maximally extended, with its carbonyl O atom pointing away from the central cavity of the macrocycle; in achieving this conformation the phenoxy O atom O(22) is displaced 0.19(1) Å from the aromatic ring plane away from the macrocycle ring centre. Distances between the side chain and the macrocycle ring correspond to normal van der Waals interactions.

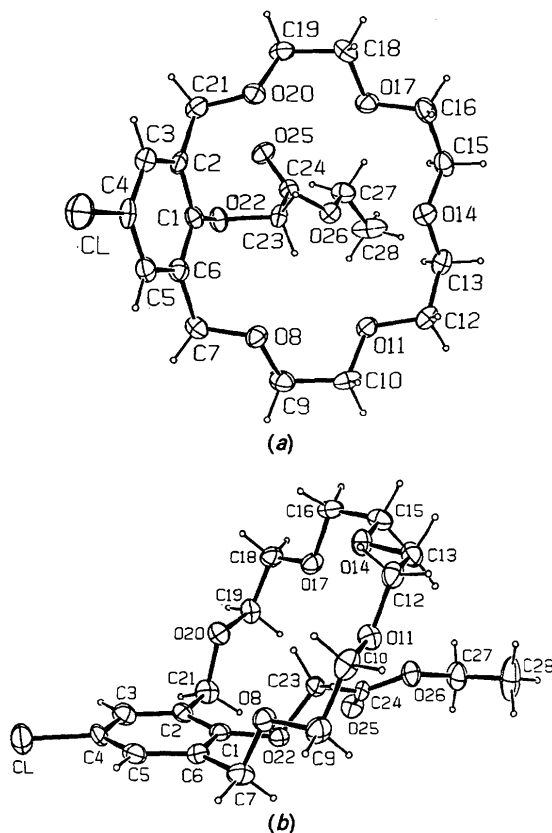


Fig. 2. Views of molecule (2): (a) plan view and (b) side-on view showing the general conformation with the crystallographic numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 20% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size.

The presence of the free hydroxyl group has a significant influence in determining the macrocycle conformation in the free acid (1). In particular, there is a well defined intramolecular transannular O—H...O hydrogen bond between the hydroxyl O atom O(26) (Fig. 1a) and the distal O atom O(14) [O...O 2.658(3), O(26)—H 0.85(3), H...O(14) 1.83(3) Å, O(26)—H...O(14) 164(3)°]. This is achieved by major distortion of the macrocycle conformation away from that exhibited by ester (2). In particular, the C(6)—C(7)—O(8)—C(9) and C(13)—O(14)—C(15)—C(16) torsion angles [which were -169(1) and 180(1)° in ester (2)] are now 67.2(2) and -78.7(2)° respectively; other ring torsion angles lie close to the *gauche* (O—C—C—O) or fully staggered (C—O—C—C) values found in (2). As in the ester, the phenoxy O atom O(22) of (1) is displaced 0.111(3) Å from the aromatic ring plane away from the macrocycle ring centre.

Experimental

Compound (1)

Crystal data

C₁₈H₂₅ClO₈
M_r = 404.84
 Orthorhombic
Pbca
a = 13.8560 (20) Å
b = 18.783 (4) Å
c = 15.2090 (20) Å
V = 3958.3 (11) Å³
Z = 8
D_x = 1.359 Mg m⁻³
 Mo *K*α radiation

λ = 0.70930 Å
 Cell parameters from 25 reflections
 θ = 10.00–15.00°
 μ = 0.23 mm⁻¹
T = 293 K
 Needle
 0.15 × 0.15 × 0.35 mm
 Colourless
 Crystal source: synthesized by the authors

Data collection

Enraf-Nonius CAD-4 diffractometer
 θ/2θ scans [θ-scan width (0.6 + 0.35tanθ)°, θ-scan rate 3.3° min⁻¹, background counts for 15 s on each side of every scan]
 Absorption correction: none
 4301 measured reflections

4301 independent reflections
 1930 observed reflections [I_{net} > 3.0σ(I_{net})]
 θ_{max} = 26.92°
h = 0 → 17
k = 0 → 23
l = 0 → 19
 3 standard reflections
 frequency: 120 min
 intensity variation: < 1.0%

Refinement

Refinement on *F*
 Final *R* = 0.036
wR = 0.048
S = 1.24
 1930 reflections
 249 parameters
w = 1/[σ²(*F*) + 0.0008*F*²]
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.20 e Å⁻³
 Δρ_{min} = -0.21 e Å⁻³

Extinction correction: Larson (1970)
 Extinction coefficient: 4730 (20)
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (2)*Crystal data*C₂₀H₂₉ClO₈*M_r* = 432.89

Orthorhombic

*Pca*2₁*a* = 17.884 (3) Å*b* = 8.792 (3) Å*c* = 13.918 (3) Å*V* = 2188.4 (10) Å³*Z* = 4*D_x* = 1.314 Mg m⁻³Mo *K*α radiation

λ = 0.70930 Å

Cell parameters from 25 reflections

θ = 10.00–18.00°

μ = 0.21 mm⁻¹*T* = 293 K

Plate

0.43 × 0.20 × 0.08 mm

Colourless

Crystal source: synthesized by authors

Data collection

Nonius CAD-4 diffractometer

θ/2θ scans [θ-scan width (0.6 + 0.35tanθ)°, θ-scan rate 3.3° min⁻¹, background counts for 15 s on each side of every scan]

Absorption correction: none

2482 measured reflections

2482 independent reflections

816 observed reflections

[*I*_{net} > 3.0σ(*I*_{net})]θ_{max} = 26.90°*h* = 0 → 22*k* = 0 → 11*l* = 0 → 17

3 standard reflections

frequency: 120 min

intensity variation: < 1.0%

*Refinement*Refinement on *F*²Final *R* = 0.033*wR* = 0.040*S* = 1.07

816 reflections

262 parameters

w = 1/[σ²(*F*) + 0.0008*F*²](Δ/σ)_{max} = 0.000Δρ_{max} = 0.15 e Å⁻³Δρ_{min} = -0.13 e Å⁻³

For both compounds: Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER* (Gabe *et al.*, 1989). Program(s) used to refine structure: *NRCVAX LSTSQ* (Gabe *et al.*, 1989). Molecular graphics: *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *NRCVAX TABLES* (Gabe *et al.*, 1989).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for (1)

	$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl	0.50333 (7)	0.89173 (4)	0.60044 (6)	0.0797 (5)
C(1)	0.35520 (19)	1.06334 (14)	0.75566 (17)	0.0449 (14)
C(2)	0.33193 (19)	0.99214 (14)	0.77150 (17)	0.0440 (14)
C(3)	0.37679 (21)	0.94001 (14)	0.72211 (17)	0.0496 (16)
C(4)	0.44394 (22)	0.95809 (15)	0.65933 (17)	0.0507 (16)
C(5)	0.46675 (21)	1.02842 (15)	0.64367 (18)	0.0521 (16)
C(6)	0.42213 (20)	1.08182 (14)	0.69149 (18)	0.0465 (15)
C(7)	0.44606 (22)	1.15886 (16)	0.67325 (19)	0.0582 (17)
O(8)	0.49328 (14)	1.19327 (9)	0.74421 (14)	0.0517 (11)
C(9)	0.58755 (21)	1.16658 (15)	0.76058 (19)	0.0539 (17)
C(10)	0.62738 (22)	1.20324 (15)	0.83945 (20)	0.0574 (18)
O(11)	0.57928 (13)	1.17780 (9)	0.91546 (12)	0.0526 (11)

C(12)	0.60844 (22)	1.21292 (16)	0.99360 (20)	0.0588 (17)
C(13)	0.56436 (22)	1.17673 (15)	1.07095 (19)	0.0593 (18)
O(14)	0.46227 (14)	1.18589 (9)	1.06965 (12)	0.0534 (11)
C(15)	0.41449 (24)	1.15934 (17)	1.14635 (19)	0.0653 (19)
C(16)	0.4016 (3)	1.08075 (17)	1.14657 (20)	0.0696 (20)
O(17)	0.33303 (15)	1.06211 (10)	1.08145 (12)	0.0619 (12)
C(18)	0.31863 (24)	0.98798 (15)	1.07711 (20)	0.0623 (19)
C(19)	0.25789 (24)	0.97177 (16)	1.00013 (19)	0.0618 (18)
O(20)	0.31356 (13)	0.98347 (9)	0.92366 (12)	0.0516 (10)
C(21)	0.26298 (21)	0.97313 (15)	0.84338 (19)	0.0545 (17)
O(22)	0.30339 (13)	1.11582 (9)	0.79835 (13)	0.0552 (11)
C(23)	0.34527 (19)	1.14527 (14)	0.87641 (18)	0.0476 (15)
C(24)	0.32590 (20)	1.22368 (15)	0.87846 (21)	0.0488 (16)
O(25)	0.28043 (15)	1.25648 (10)	0.82499 (15)	0.0694 (13)
O(26)	0.36141 (15)	1.25680 (11)	0.94949 (16)	0.0598 (13)

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for (2)

	$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl	0.32614 (16)	0.0732 (3)	0.0	0.0970 (20)
C(1)	0.4416 (5)	-0.1099 (9)	0.2619 (8)	0.050 (6)
C(2)	0.3638 (5)	-0.0940 (9)	0.2628 (8)	0.052 (6)
C(3)	0.3291 (4)	-0.0387 (9)	0.1817 (9)	0.064 (6)
C(4)	0.3705 (6)	0.0004 (9)	0.1011 (8)	0.062 (6)
C(5)	0.4469 (6)	-0.0186 (9)	0.1002 (8)	0.063 (7)
C(6)	0.4838 (4)	-0.0714 (9)	0.1821 (8)	0.056 (6)
C(7)	0.5665 (5)	-0.0938 (10)	0.1809 (8)	0.071 (6)
O(8)	0.5804 (3)	-0.2510 (6)	0.1660 (5)	0.058 (4)
C(9)	0.6557 (5)	-0.2950 (11)	0.1815 (7)	0.068 (7)
C(10)	0.6602 (4)	-0.4654 (12)	0.1788 (8)	0.068 (7)
O(11)	0.6209 (3)	-0.5234 (6)	0.2592 (5)	0.059 (4)
C(12)	0.6149 (4)	-0.6844 (11)	0.2611 (8)	0.062 (6)
C(13)	0.5715 (5)	-0.7340 (10)	0.3462 (7)	0.065 (6)
O(14)	0.4939 (3)	-0.7035 (6)	0.3343 (5)	0.062 (4)
C(15)	0.4519 (6)	-0.7625 (10)	0.4113 (7)	0.069 (6)
C(16)	0.3704 (6)	-0.7273 (11)	0.3969 (7)	0.072 (7)
O(17)	0.3591 (3)	-0.5727 (7)	0.4196 (5)	0.064 (4)
C(18)	0.2835 (5)	-0.5325 (10)	0.4165 (8)	0.070 (6)
C(19)	0.2776 (4)	-0.3644 (10)	0.4261 (7)	0.063 (6)
O(20)	0.3066 (3)	-0.2953 (7)	0.3418 (5)	0.063 (4)
C(21)	0.3193 (5)	-0.1362 (10)	0.3492 (8)	0.068 (6)
O(22)	0.4779 (3)	-0.1481 (6)	0.3461 (5)	0.059 (4)
C(23)	0.4895 (4)	-0.3067 (9)	0.3662 (7)	0.054 (6)
C(24)	0.4893 (5)	-0.3212 (10)	0.4752 (7)	0.048 (5)
O(25)	0.4486 (3)	-0.2531 (7)	0.5267 (5)	0.064 (4)
O(26)	0.5403 (3)	-0.4222 (6)	0.5019 (4)	0.057 (4)
C(27)	0.5472 (5)	-0.4479 (11)	0.6047 (8)	0.073 (7)
C(28)	0.6181 (6)	-0.5116 (16)	0.6270 (8)	0.116 (9)

Table 3. Summary of principal bond lengths (Å) for (1) and (2)

	(1)	(2)
C—Cl	1.742(3)	1.737(10)
C(ar)—C(ar)	1.385(4)	1.387(15)
C(ar)—C(sp ²)	1.503(4)	1.490(14)
C(sp ²)—C(sp ³)	1.485(5)	1.494(14)
C(sp ³)—O(ether)	1.419(3)	1.414(12)
C(ar)—O(phenoxide)	1.381(3)	1.381(13)
C(sp ²)—O(phenoxide)	1.433(3)	1.437(10)
C(sp ³)—C(sp ²)	1.497(4)	1.522(14)
C(sp ²)=O	1.199(4)	1.184(12)
C(sp ²)—O(H or Et)	1.340(4)	1.327(11)

For (1), the systematic absences (*0kl* absent if *k* = 2*n* + 1, *h0l* absent if *l* = 2*n* + 1, *hk0* absent if *h* = 2*n* + 1) uniquely determined the centrosymmetric space group *Pbca*. All H atoms were visible in difference maps. All C-bonded H atoms were considered as riding atoms (C—H = 0.95 Å); the carboxyl H atom [H(O26)] was refined isotropically. For (2), the systematic absences (*0kl* absent if *l* = 2*n* + 1, *h0l* absent if *h* = 2*n* + 1) allow the space group to be either *Pca*2₁ (No. 29) or *Pcam* (No. 57). The latter

choice would have demanded mirror, twofold or inversion symmetry for the molecule. The polar space group $Pca2_1$ was assumed and confirmed by the analysis. Refinement of the model and its enantiomorph yielded no significant differences in R , wR , goodness of fit or molecular dimensions. All H atoms were visible in difference maps and were included as riding atoms (C—H 0.95 Å) during the refinement.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55594 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1013]

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Structure of 1,1,2,2,3,3-Hexamethyl-4-(2-ethynylphenyl)-1,2,3-trigermacyclopent-4-ene

HANS PREUT, MARKUS P. WEISBECK AND
WILHELM PAUL NEUMANN

*Fachbereich Chemie, Universität Dortmund, Postfach
500500, D-4600 Dortmund 50, Germany*

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Abstract

This is the first crystal structure determination of a member of the new germacyclic system of 1,2,3-trigermacyclopent-4-enes. The five-membered heterocycle is nearly planar with a maximum deviation of 0.139(10) Å from the least-squares plane through these

atoms. The Ge—Ge, Ge—C and C—C distances in the ring are 2.411(3), 2.406(2), 1.979(9), 1.954(8) and 1.30(1) Å and the bond angles in the ring are Ge—Ge—Ge 92.8(1), Ge—Ge—C 99.4(3), 99.3(3) and Ge—C—C 125.3(7), 122.4(7)°. The remaining exocyclic bond angles at the three Ge atoms are in the range 108.2(5)–116.0(4)°. The tetrahedral coordination around the Ge atoms is mainly distorted because of the conditions imposed by the ring geometry. The exocyclic Ge—C bond distances are in the range 1.92(1)–1.95(1) Å [mean value 1.94(1) Å]. The dihedral angle between the heterocycle and the phenyl ring is 99.5(3)°.

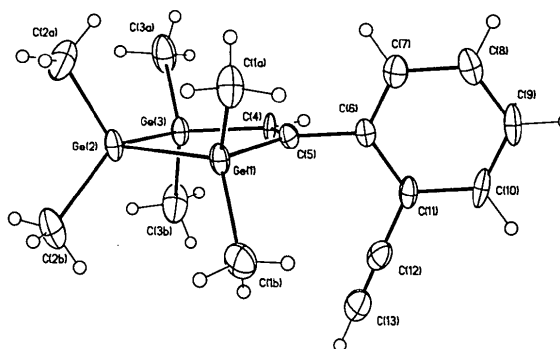


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

Comment

The title compound is the first crystalline member of the fascinating germacyclic system of 1,2,3-trigermacyclopent-4-enes. The reaction and the recrystallization was carried out under dry argon because the crystals are air sensitive. The exact mechanism is unknown. A cyclotrigermane (Me_2Ge)₃ is proposed as a reaction intermediate (Neumann, 1991). *Ab initio* quantum-mechanical determinations of the strain enthalpy of a hexamethylcyclotrigermane show a strong instability (Horner, Grev & Schäfer, 1992). This reactive intermediate reacts with 1,2-diethynylbenzene to give a trigermacyclopentene. The second ethynyl group does not react with another dimethylgermylene or cyclotrigermane. Presumably additional steric hindrance prevents access to the triple bond and prevents the reaction. Surprisingly the remarkable five-membered germaheterocycle is nearly planar. Evidence of this has also been provided by NMR spectroscopy (¹H NMR: only three GeMe resonance signals).

