

Hendrik G. Kruger, Melanie Rademeyer* and Reshika Ramdhani

School of Chemistry, Howard College Campus,
University of KwaZulu–Natal, Durban 4041,
South AfricaCorrespondence e-mail:
rademeyerm@ukzn.ac.za

Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(C-C) = 0.002$ Å
Disorder in main residue
 R factor = 0.042
 wR factor = 0.132
Data-to-parameter ratio = 17.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

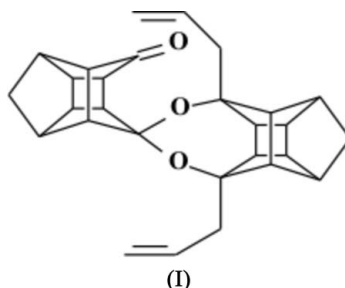
A pentacycloundecane dimer

The title compound, 6,6-(3,6-diprop-2-enylpentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane-3,6-diylldioxy)pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecan-3-one, $C_{28}H_{30}O_3$, is a pentacycloundecane dimer. The molecule is chiral and contains two polycyclic pentacycloundecane cage units. Both enantiomers are present in the crystal structure. In the molecule, certain C–C bond lengths deviate from the normal value, with both short and long bonds present.

Received 8 November 2005
Accepted 2 February 2006

Comment

The structure of the pentacycloundecane (PCU) dimer, (I), was determined as part of an ongoing study of the chemical reactivity and solid-state structures of substituted polycyclic PCU cage compounds.



The Grignard reaction with pentacycloundecane dione was first reported by Marchand *et al.* (2001). Nucleophilic attack on the PCU dione occurs almost exclusively from the *exo* face, producing an *endo-endo* diol as the main product. The cage dimer, (I), is formed when the cage dione is reacted with an equimolar amount of allyl magnesium bromide (1:1 instead of 4:1), but the mechanism for the formation of the cage dimer is not obvious.

A number of studies have focused on the molecular geometries of PCU cage derivatives, and it has been reported that these compounds exhibit C–C single bonds for which the bond lengths deviate from the expected value of 1.54 Å (Flippen-Anderson *et al.*, 1991; Linden *et al.*, 2005; Kruger *et al.*, 2005). These reports indicated that in a typical simple PCU cage derivative, the C9–C10 bond may be longer than normal, whereas some bonds involving atoms C4, C8 and C11 may be shorter than expected.

The asymmetric unit of (I) comprises one molecule (Fig. 1), and both enantiomers are present in the unit cell. Two PCU cage units are connected *via* a double ether bridge. The mouth of the first cage (C8 and C11) is connected through two ether linkages to the same C atom (C28) on the second cage (defined by atoms C18–C28). The second cage contains a ketone substituent at atom C25.

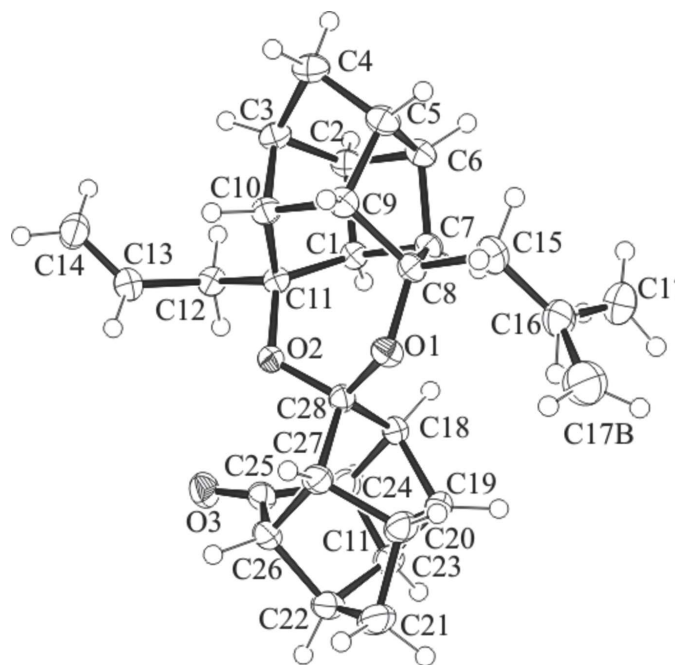


Figure 1

Molecular structure of (I) showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level for non-H atoms (ORTEP-3; Farrugia, 1997).

The cage skeleton has two faces, a ‘front side’ and a ‘back side’. The front side is where the C–O–C ether bridge can form and the back side is where the cyclobutane is positioned. In principle, two sets of diastereomers can form when the cage dimerizes, the starting material being a *meso* compound. One set can potentially dimerize at atom C1 with (a) the cyclobutane rings of the two cages in a *cis* position and (b) the cyclobutane rings in a *trans* position. The second set of diastereomeric dimers can potentially dimerize at atom C8 with the same *cis* and *trans* configurations. The mechanism of the dimerization reaction is not obvious and it is not clear why the two diastereomeric dimers do not form. In (I), the two cyclobutane rings on each cage skeleton are in a *cis* position.

As observed for other PCU cage derivatives, the cage dimer exhibits C–C single bond lengths (Table 1) that deviate from the expected value. The longest bonds observed in both cages are opposite to the cyclobutane ring [C9–C10 = 1.5866 (17) Å and C26–C27 = 1.5805 (19) Å]. In both cages, the four bonds forming the cyclobutane rings are longer than expected (Table 1). The bonds involving the bridgehead atoms C4 and C21 are short [range 1.521 (2)–1.531 (2) Å].

The unsymmetrical substitution at the mouth of cage two appears to affect the bond lengths in this cage; the bonds involving atom C25, at the ketone substituent, are shorter than normal [C24–C25 = 1.5185 (18) Å and C25–C26 = 1.514 (2) Å]. In the related dione cage (Linden *et al.*, 2005), the corresponding bond lengths are also short, and range from 1.503 (4) to 1.517 (4) Å. The corresponding bonds on the opposite side of the second cage are not affected as severely, with C18–C28 falling within the expected range, and C27–C28 slightly shorter than normal. In the same way, C22–C23

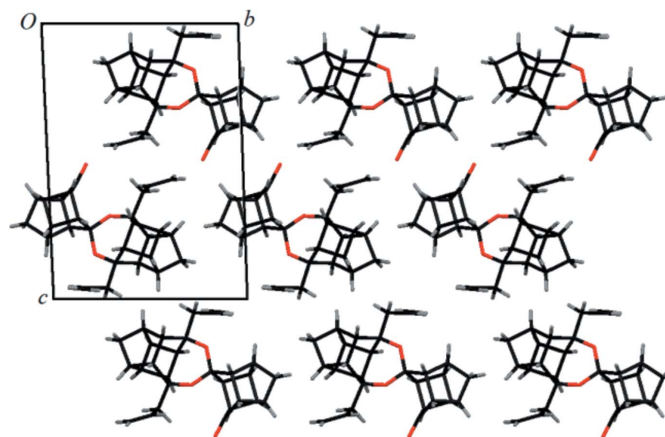


Figure 2

Packing diagram of (I) (Bruno *et al.*, 2002).

and C22–C26 on the ketone-substituted side of the second cage are long, 1.563 (2) and 1.5585 (19) Å (also observed for the dione), but the C19–C20 and C20–C27 bonds on the other side of the cage do not deviate significantly from the expected value.

The five-membered rings defined by atoms C2–C6 and C3–C5/C9/C10 adopt envelope conformations, with C4 in the flap positions, and the rings C1–C3/C10/C11 and C5–C9 are twisted about C10–C11 and C8–C9, respectively. The five-membered rings defined by C19–C23 and C20–C22/C26/C27 in the second cage exhibit envelope conformations, with C21 in the flap positions, and the rings defined by C18–C20/C27/C28 and C22–C26 are twisted about C27–C28 and C25–C26, respectively.

The molecular packing is illustrated in Fig. 2. Molecules pack in layers parallel to the crystallographic *bc* plane.

Experimental

The synthesis of the *endo-endo* cage diol is described by Marchand *et al.* (2001) and Govender *et al.* (2003). When the ratio of Grignard reagent to dione is limited to 1:1, the dimer (I) is formed and may be recrystallized from an ethyl acetate–*n*-hexane (3:2) mixture.

Crystal data

C₂₈H₃₀O₃
M_r = 414.52
 Triclinic, *P* $\bar{1}$
a = 6.1843 (17) Å
b = 10.963 (3) Å
c = 15.572 (4) Å
 α = 86.327 (5)°
 β = 83.046 (5)°
 γ = 80.221 (5)°
V = 1031.7 (5) Å³

Z = 2
D_x = 1.334 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 990 reflections
 θ = 3.4–28.3°
 μ = 0.09 mm^{−1}
T = 173 (2) K
 Irregular fragment, colourless
 0.51 × 0.44 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 10401 measured reflections
 4949 independent reflections

3894 reflections with *I* > 2σ(*I*)
R_{int} = 0.016
 θ_{max} = 28.0°
h = −8 → 7
k = −14 → 14
l = −20 → 20

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.132$
 $S = 1.05$
 4949 reflections
 284 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0843P)^2 + 0.1152P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected bond lengths (Å).

C1—C2	1.5688 (17)	C15—C16	1.504 (2)
C1—C7	1.5575 (17)	C16—C17	1.324 (2)
C2—C6	1.5645 (18)	C16—C17B	1.324 (3)
C3—C2	1.5539 (18)	C18—C19	1.5583 (18)
C4—C3	1.5292 (18)	C20—C19	1.550 (2)
C5—C4	1.528 (2)	C20—C21	1.531 (2)
C5—C6	1.5562 (18)	C21—C22	1.521 (2)
C7—C6	1.5657 (17)	C22—C23	1.563 (2)
C8—O1	1.4408 (15)	C23—C19	1.566 (2)
C8—C7	1.5333 (17)	C24—C18	1.5718 (18)
C8—C9	1.5498 (17)	C24—C23	1.570 (2)
C8—C15	1.5422 (18)	C25—O3	1.2150 (17)
C9—C5	1.5502 (18)	C25—C24	1.5185 (18)
C9—C10	1.5866 (17)	C26—C22	1.5585 (19)
C10—C3	1.5505 (18)	C26—C25	1.514 (2)
C10—C11	1.5371 (16)	C27—C20	1.5504 (18)
C11—C1	1.5354 (17)	C27—C26	1.5805 (19)
C11—O2	1.4458 (14)	C28—O1	1.4139 (15)
C11—C12	1.5389 (17)	C28—O2	1.4049 (14)
C12—C13	1.4962 (18)	C28—C18	1.5416 (17)
C13—C14	1.321 (2)	C28—C27	1.5292 (17)

Atom C17, belonging to an allyl group, was found to be disordered and was refined over two positions, C17 and C17B, with C16—C17 and C16—C17A bond lengths restrained to be equal with an s.u. of 0.02 Å. Site occupancy factors were refined with their sum constrained to 1, and converged to 0.872 (4) for C17 and 0.128 (4) for C17B. Atom C17B, having a small contribution to the structure factors, was refined with an isotropic displacement parameter. All H

atoms were placed in calculated positions and refined using a riding model (C—H = 1.00 Å for methine CH, 0.99 Å for methylene CH₂ and 0.95 Å for allyl CH). For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: SMART-NT (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Bruker, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: MERCURY (Bruno *et al.*, 2002) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON (Spek, 2003).

The authors thank the Jan Boeyens Structural Chemistry Laboratory of the University of the Witwatersrand, South Africa, for the structure analysis.

References

Bruker (1998). SMART-NT. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (1999). SAINT-Plus (Version 6.02) and SHELXTL (Version 5.1). Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Flippin-Anderson, J. L., George, C., Gilardi, R., Zajac, W. W., Walters, T. R., Marchand, A., Dave, P. R. & Arney, B. E. Jr (1991). *Acta Cryst.* **C47**, 813–817.
 Govender, T., Hariprakash, H. K., Kruger, H. G. & Marchand, A. P. (2003). *Tetrahedron Asymmetry*, **14**, 1553–1557.
 Kruger, H. G., Rademeyer, M. & Ramdhani, R. (2005). *Acta Cryst.* **E61**, o3968–o3970.
 Linden, A., Romanski, J., Mloston, G. & Heimgartner, H. (2005). *Acta Cryst.* **C61**, o221–o226.
 Marchand, A. P., Huang, Z., Chen, Z., Hariprakash, H. K., Namboothiri, I. N. N., Brodbelt, J. S. & Reyzer, M. L. J. (2001). *J. Heterocycl. Chem.* **38**, 1361–1368.
 Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.