Crystal structure of tetramethyl (1 α ,2 β ,3 α ,5 α ,6 β ,7 α ,8 β ,9 α ,11 α ,12 β)-4,10-dioxahexacyclo[5.5.1.0^{2,6}.0^{3,5}.0^{8,12}.0^{9,11}]tridecane-3,5,9,11-tetracarboxylate, C₁₉H₂₀O₁₀

I. B. Mahadevan^I, R. A. Russell^I, R. N. Warrener^{II} and E. R. T. Tiekink^{*,III,I}^I Deakin University, Centre for Chiral and Molecular Technologies, Geelong, Victoria 3217, Australia^{II} Central Queensland University, Centre for Molecular Architecture, Rockhampton, Queensland 4702, Australia^{III} The University of Adelaide, Department of Chemistry, Australia 5005

Received January 19, 2002, accepted and available on-line March 22, 2002; CCDC-No. 1267/787

Abstract

C₁₉H₂₀O₁₀, monoclinic, *P*12₁/*c*1 (No. 14), *a* = 7.309(2) Å, *b* = 12.471(3) Å, *c* = 20.930(7) Å, β = 95.96(2)°, *V* = 1897.5 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.076, *wR*_{ref}(*F*²) = 0.226, *T* = 293 K.

Source of material

The compound was prepared as described in the literature [1]. Colourless crystals were obtained from the slow evaporation of a dichloromethane/hexane solution of the compound; mp 469 K – 471 K.

Experimental details

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation. The crystal chosen for the analysis was weakly diffracting and the structure determination is less than optimal. Nevertheless, the molecular connectivity has been established unambiguously.

Discussion

The molecular structure of the title compound was determined as part of a synthetic program designed to generate functionalised cavity structures [1–3]. The X-ray analysis shows an absence of crystallographically imposed symmetry. However, approximate mirror symmetry is found (the C1, C7 and C13 atoms define a pseudo mirror plane) with the major deviation been found in the

orientation of the C14 and C20 ester groups. The four carbonyl groups lie to one side of the molecule and the two epoxides to the other.

Table 1. Data collection and handling.

Crystal:	colourless needle, size 0.05 × 0.16 × 0.39 mm
Wavelength:	Mo <i>K</i> α radiation (0.7107 Å)
μ :	1.17 cm ^{−1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
2 θ _{max} :	55.2°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	4943, 4388
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1536
<i>N</i> (<i>param</i>) _{refined} :	263
Programs:	SIR92 [4], teXsan [5], SHELXL-97 [6], DIBABS [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.3881	0.7865	−0.2271	0.091(4)
H(2)	4e	0.7318	0.7391	−0.2370	0.091
H(6)	4e	0.7614	0.5465	−0.2410	0.091
H(7)	4e	0.4427	0.4610	−0.2376	0.091
H(8)	4e	0.5603	0.5477	−0.3390	0.091
H(12)	4e	0.5198	0.7404	−0.3330	0.091
H(13a)	4e	0.2156	0.6122	−0.2332	0.091
H(13b)	4e	0.3511	0.6140	−0.1686	0.091
H(15a)	4e	0.7229	0.8000	0.0555	0.109(5)
H(15b)	4e	0.5273	0.8129	0.0179	0.109
H(15c)	4e	0.6858	0.8922	0.0049	0.109
H(17a)	4e	0.8690	0.4037	0.0342	0.109
H(17b)	4e	0.7657	0.3323	−0.0196	0.109
H(17c)	4e	0.6552	0.4135	0.0187	0.109
H(19a)	4e	−0.1668	0.3912	−0.4641	0.109
H(19b)	4e	−0.2010	0.4107	−0.3923	0.109
H(19c)	4e	−0.0622	0.3220	−0.4094	0.109
H(21a)	4e	−0.0622	0.9791	−0.3453	0.109
H(21b)	4e	−0.1540	0.8854	−0.3102	0.109
H(21c)	4e	−0.1667	0.8876	−0.3855	0.109

* Correspondence author (e-mail: chmtert@nus.edu.sg)

^I Current address: National University of Singapore,
Department of Chemistry, Singapore 117543

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(4)	4e	0.8679(4)	0.6405(2)	−0.1307(2)	0.044(2)	0.051(2)	0.061(2)	−0.004(2)	0.003(2)	−0.002(2)
O(10)	4e	0.2727(4)	0.6347(3)	−0.4087(2)	0.071(2)	0.068(2)	0.041(2)	−0.001(2)	0.011(2)	0.001(2)
O(14)	4e	0.5241(6)	0.8370(4)	−0.1057(2)	0.104(3)	0.120(4)	0.073(3)	0.061(3)	−0.003(2)	−0.022(3)
O(15)	4e	0.7106(5)	0.7486(3)	−0.0349(2)	0.104(3)	0.099(3)	0.051(2)	0.036(3)	−0.007(2)	−0.010(2)
O(16)	4e	0.5299(5)	0.4354(3)	−0.1030(2)	0.057(2)	0.071(2)	0.076(3)	−0.016(2)	−0.005(2)	0.019(2)
O(17)	4e	0.7947(4)	0.4842(3)	−0.0467(2)	0.072(2)	0.062(2)	0.052(2)	−0.006(2)	−0.005(2)	0.006(2)
O(18)	4e	0.1016(5)	0.4244(3)	−0.3115(2)	0.095(3)	0.077(3)	0.086(3)	−0.032(2)	−0.012(2)	0.022(3)
O(19)	4e	0.0368(5)	0.4696(3)	−0.4142(2)	0.070(2)	0.072(3)	0.067(2)	−0.018(2)	−0.008(2)	−0.011(2)
O(20)	4e	−0.0814(5)	0.6927(3)	−0.3449(2)	0.064(3)	0.074(3)	0.127(4)	−0.009(2)	0.012(2)	−0.001(3)
O(21)	4e	0.0799(4)	0.8425(3)	−0.3445(2)	0.053(2)	0.052(2)	0.109(3)	0.002(2)	0.027(2)	0.005(2)
C(1)	4e	0.4395(6)	0.7177(4)	−0.2390(2)	0.049(3)	0.040(3)	0.046(3)	0.002(2)	0.008(2)	−0.003(2)
C(2)	4e	0.6435(6)	0.6996(4)	−0.2138(2)	0.044(2)	0.047(3)	0.044(3)	−0.001(2)	0.009(2)	0.000(2)
C(3)	4e	0.6926(6)	0.6936(4)	−0.1417(2)	0.038(3)	0.046(3)	0.049(3)	0.000(2)	0.004(2)	−0.003(2)
C(5)	4e	0.7080(6)	0.5733(4)	−0.1440(2)	0.039(3)	0.047(3)	0.051(3)	0.001(2)	0.002(2)	−0.002(3)
C(6)	4e	0.6615(6)	0.5720(4)	−0.2171(2)	0.046(3)	0.047(3)	0.053(3)	0.001(2)	0.008(2)	−0.002(2)
C(7)	4e	0.4711(6)	0.5366(4)	−0.2447(2)	0.045(3)	0.041(3)	0.051(3)	0.002(2)	0.007(2)	−0.002(2)
C(8)	4e	0.4579(6)	0.5711(4)	−0.3156(2)	0.048(3)	0.051(3)	0.049(3)	−0.004(2)	0.010(2)	−0.006(3)
C(9)	4e	0.2679(7)	0.5654(4)	−0.3538(2)	0.058(3)	0.052(3)	0.037(3)	−0.001(3)	0.009(2)	−0.003(2)
C(11)	4e	0.2433(6)	0.6827(4)	−0.3481(2)	0.056(3)	0.046(3)	0.040(3)	0.001(2)	0.005(2)	0.003(2)
C(12)	4e	0.4329(6)	0.6978(4)	−0.3109(2)	0.046(3)	0.045(3)	0.045(3)	−0.002(2)	0.005(2)	0.000(2)
C(13)	4e	0.3429(6)	0.6181(3)	−0.2151(2)	0.044(2)	0.044(3)	0.051(3)	−0.003(2)	0.007(2)	0.004(2)
C(14)	4e	0.6316(7)	0.7669(4)	−0.0921(3)	0.045(3)	0.062(3)	0.053(3)	0.003(3)	0.008(2)	−0.002(3)
C(15)	4e	0.657(1)	0.8194(5)	0.0151(3)	0.143(6)	0.133(6)	0.062(4)	0.034(5)	0.002(4)	−0.032(4)
C(16)	4e	0.6643(6)	0.4907(4)	−0.0959(2)	0.045(3)	0.050(3)	0.054(3)	0.006(2)	0.004(2)	0.005(3)
C(17)	4e	0.7690(9)	0.4013(4)	0.0007(3)	0.101(5)	0.079(4)	0.060(3)	−0.009(4)	0.000(3)	0.021(3)
C(18)	4e	0.1268(7)	0.4791(4)	−0.3566(3)	0.054(3)	0.046(3)	0.060(4)	0.004(3)	0.000(3)	−0.005(3)
C(19)	4e	−0.1107(8)	0.3918(5)	−0.4205(3)	0.073(4)	0.085(5)	0.113(5)	−0.018(4)	−0.011(4)	−0.015(4)
C(20)	4e	0.0628(7)	0.7392(4)	−0.3460(2)	0.055(3)	0.048(3)	0.056(3)	−0.006(3)	−0.003(2)	0.004(3)
C(21)	4e	−0.0903(7)	0.9039(4)	−0.3466(3)	0.062(4)	0.067(4)	0.127(6)	0.015(3)	0.040(4)	0.007(4)

Acknowledgment. The Australian Research Council is thanked for support.

References

- Warrener, R. N.; Margetic, D.; Amarasekara, A. S.; Russell, R. A.: Synthesis of functionalized cavity structures via 1,3-dipolar cycloaddition of angle-shaped alkenes to curved norbornene-framed dipoles. *Org. Lett.* **1** (1999) 203–206.
- Warrener, R. N.; Schultz, A. C.; Butler, D. N.; Wang, S.; Mahadevan, I. B.; Russell, R. A.: A new building BLOCK technique based on cycloaddition chemistry for the regiospecific linking of alicyclic sub-units as a route to large, custom-functionalized structures. *J. Chem. Soc., Chem. Commun.* (1997) 1023–1024.
- Liu, L.; Warrener, R. N.; Russell, R. A.; Tiekink, E. R. T.: Crystal structure of dimethyl 4,5-dimethylene-15-oxahexa-cyclo-[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]-heptane heptan-1,8-dicarboxylate, C₂₂H₂₆O₅. *Z. Kristallogr. NCS* **216** (2001) 533–534. The title of the compound reported in this paper should be corrected to dimethyl 4,5-dimethylene-15-oxahexacyclo [6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]heptadecan-1,8-dicarboxylate.
- Altomare, G.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M.: SIR92 - a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **27** (1994) 435.
- teXsan: Single Crystal Structure Analysis Software. Version 1.04. Molecular Structure Corporation. The Woodlands, TX, USA 1997.
- Sheldrick, G. M.: SHELXL-97. Program for crystal structure refinement. University of Göttingen, Germany 1997.
- Walker, N.; Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr. A* **39** (1983) 159–166.