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Key indicators

Single-crystal X-ray study T = 93 K Mean σ (C–C) = 0.003 Å R factor = 0.022 wR factor = 0.045 Data-to-parameter ratio = 19.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e. The title compound, $C_{18}H_{14}Br_2Cl_2O$, is an ether-bridged pair of identical homocubanes. It is an unexpected product obtained in an attempt to chlorinate a bromo–keto–homocubane. No homocubyl or cubyl ethers are currently found in the crystal structure literature.

Bis(1-bromo-9-chlorohomocub-9-yl) ether

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Comment

The title compound, (3), is one of several new compounds discovered in a study by Tang (2002) of the reactions of halogenated polycyclic compounds, especially homocubanes. In an attempt to add chloro substituents to 1-bromo-9-keto-homocubane, (2), an unexpected product was formed.



Its ¹H and ¹³C NMR spectra showed seven different H atoms and nine different C atoms, thus suggesting a dichloro compound with no symmetry, if the molecule was a still a homocubane. However, the X-ray diffraction analysis reported herein showed that the product is instead a dihomocubyl ether, with a molecular twofold axis of symmetry, shown in Fig. 1.

A search of the Cambridge Structural Database (CSD; Version 5.22 of October 2001, using Conquest 1.3; Allen & Kennard, 1993) for ether-bridged cubanes or homocubanes, allowing any or no substituents, revealed no hits. The bond distances within the title compound are not unusual, compared to those seen in cubanes and homocubanes. The C-C distances herein range from 1.520(3) to 1.576(3) Å. The exocyclic bonds to substituent atoms are all slightly (0.03-0.04 Å) shortened, compared to similar substituent bond lengths to tertiary C atoms in the CSD. The two C-Br distances are 1.928 (2) and 1.929 (2) Å, compared to an average of 1.97 (3) Å for 100 C_{tert}-Br distances tabulated by Allen et al. (1987). The two C-Cl bonds are 1.818 (2) and 1.824 (2) Å, compared to the CSD average of 1.849 (11) Å, and the two C–O bonds are 1.408(2) and 1.405(2)Å, compared to the CSD average of 1.452 (11) Å. This exocyclic shortening has been seen and discussed before, and is attributed to a carbon rehybridization to accommodate the severe bond-angle strain of cage closure (Gilardi et al., 1988; Ermer & Lex, 1987).

© 2002 International Union of Crystallography Printed in Great Britain – all rights reserved Fig. 2 illustrates the packing of (3), an example of simple close packing, marked by no particularly close interactions.



Figure 1

A view of the title compound, with 50% probability ellipsoids, down an approximate molecular twofold symmetry axis. This does not coincide with any crystallographic symmetry axis.

There are a few intermolecular $H \cdots H$ contacts, barely less than van der Waals distances, in the 2.3-2.4 Å range, and one intermolecular $H \cdots Cl$ contact of 2.80 Å that is 0.15 Å less than the $H \cdot \cdot \cdot Cl$ van der Waals distance (Rowland & Taylor, 1996).

Experimental

A mixture of a ketal [(1), 0.31 g] and aqueous hydrochloric acid (1 M, 5 ml) was stirred and heated at 368 K. After 3 h, the reaction mixture was cooled to room temperature and then extracted with ether. The extract was washed (water and brine) and dried over MgSO4. Removal of solvent by rotary evaporation afforded a white waxy solid, (2), which was mixed with phosphorus pentachloride (0.34 g) under nitrogen. The mixture was stirred and heated at 393 K for 3 h, and then it was cooled to room temperature. Ice water was slowly added to the residue. The crude reaction product was extracted with ether. The extract was washed (water and brine) and dried over



Figure 2

A view, down the b axis, of the lower half of the unit cell. The unshown upper half is related by a screw axis along b at x = 0.5, z = 0.25. No intermolecular contacts are more than 0.2 Å below normal van der Waals distances

MgSO₄. Removal of solvent followed by column chromatography (pentane) afforded the title compound [(3), 122 mg, 43%] as a white solid. ¹H NMR (CDCl₃): δ 3.89 (t, 1H), 3.75 (m, 1H), 3.66 (m, 1H), 3.60 (m, 1H), 3.51 (m, 1H), 3.45 (m, 1H), 3.28 p.p.m. (m, 1H); ¹³C NMR (acetone- d_6): δ 117.3, 71.1, 51.6, 49.54, 49.47, 44.9, 44.1, 40.3, 38.3 p.p.m.

Crystal data C18H14Br2Cl2O

Mo Ka radiation Cell parameters from 5103 $M_{\rm w} = 477.01$ Orthorhombic, Pbca reflections a = 13.763 (4) Å $\theta = 2.5 - 28.2^{\circ}$ $\mu=5.18~\mathrm{mm}^{-1}$ b = 11.909 (4) Åc = 20.357 (6) Å T = 93 (2) K $V = 3336 (3) \text{ A}^{-1}$ Irregular chunk, colorless Z = 8 $0.31 \times 0.26 \times 0.22 \text{ mm}$ $D_r = 1.899 \text{ Mg m}^{-3}$ Data collection Bruker CCD area-detector 4074 independent reflections diffractometer 2956 reflections with $I > 2\sigma(I)$ φ and ω scans $R_{\rm int} = 0.042$ $\theta_{\rm max} = 28.3^{\circ}$ Absorption correction: by integration (Wuensch & Prewitt, $h=-17\rightarrow 18$ $k = -15 \rightarrow 15$ 1965)

Refinement

 $T_{\min} = 0.255, \ T_{\max} = 0.389$

20768 measured reflections

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.022$ $wR(F^2) = 0.045$ S = 0.86 4074 reflections 209 parameters	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0202P)^{2}]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$ $(\Delta/\sigma)_{max} = 0.001$ $\Delta\rho_{max} = 0.48 \text{ e} \text{ Å}^{-3}$ $\Delta\rho_{min} = -0.64 \text{ e} \text{ Å}^{-3}$ Extinction correction: SHELXL97
209 parameters	Extinction correction: <i>SHELXL</i> 97
n-atom parameters constrained	Extiliction coefficient. $0.0057(1)$

 $l = -26 \rightarrow 24$

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXTL (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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