

Crystal Structure and Synthesis of a Quadricyclane Derivative

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The first direct X-ray crystal structure determination of a simple substituted quadricyclane, dimethyl 2,3,3,4,6,7-hexachlorotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylate, is reported.

The potential energy storage capability of quadricyclane (**1**) has renewed interest in this class of compounds.¹ Measurements of strain energy have been reported² and the geometry of (**1**) has been calculated by different methods.³ However only two reports have as yet appeared on the experimental structure determination of (**1**) or its derivatives. Mizuno *et al.*⁴ determined in 1972 the geometry of (**1**) by gas-phase electron diffraction measurements. Recently, Szeimies *et al.*⁵ reported the crystal structure determination of a highly strained [4.2.1]propellane derivative containing the quadricyclane moiety.

In this paper we report the preparation and X-ray structure determination of a relatively simple quadricyclane derivative, *i.e.* dimethyl 2,3,3,4,6,7-hexachlorotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylate (**2**).

Compound (**2**) was prepared from the related dimethyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate⁶ by irradiation of its solution in dry diethyl ether with a high pressure mercury lamp for 25 h. After the removal of solvent, colourless crystals of (**2**) (m.p. 95–96 °C) were

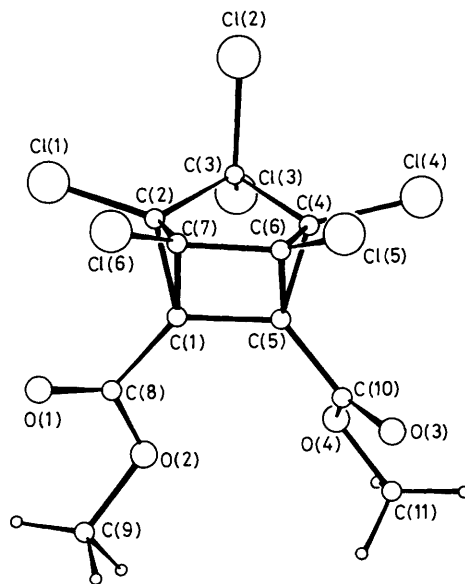
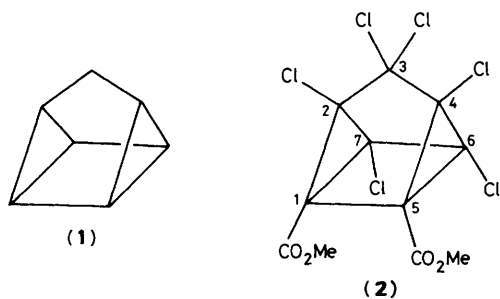


Figure 1. The perspective drawing and numbering scheme of (**2**). Selected bond distances: C(1)–C(2) 1.530(9); C(1)–C(5) 1.553(9); C(1)–C(7) 1.579(9); C(2)–C(3) 1.524(9); C(2)–C(7) 1.479(9); C(3)–C(4) 1.512(10); C(4)–C(5) 1.502(10); C(4)–C(6) 1.480(9); C(5)–C(6) 1.533(8); C(6)–C(7) 1.552(9) Å. Bond angles: C(2)–C(1)–C(5) 104.0(5); C(2)–C(1)–C(7) 56.8(4); C(5)–C(1)–C(7) 89.6(5); C(1)–C(2)–C(3) 108.9(5); C(1)–C(2)–C(7) 63.3(5); C(3)–C(2)–C(7) 110.8(6); C(2)–C(3)–C(4) 97.8(6); C(3)–C(4)–C(5) 110.7(6); C(3)–C(4)–C(6) 112.1(5); C(5)–C(4)–C(6) 61.9(4); C(4)–C(5)–C(1) 104.1(5); C(4)–C(5)–C(6) 58.4(4); C(1)–C(5)–C(6) 90.3(5); C(4)–C(6)–C(7) 103.9(6); C(4)–C(6)–C(5) 59.8(4); C(5)–C(6)–C(7) 91.3(5); C(1)–C(7)–C(2) 59.9(4); C(1)–C(7)–C(6) 88.7(4); C(2)–C(7)–C(6) 104.9(5)°.

obtained.† Single crystals for X-ray analysis were prepared by crystallization from light petroleum.

Crystal data: C₁₁H₆Cl₅O₄, monoclinic, space group *P*2₁/*a*, *a* = 11.732(3), *b* = 12.594(4), *c* = 10.558(3) Å, β = 96.33(2)°, *D*_c = 1.78 g cm⁻³ for *Z* = 4, *F*(000) = 824, μ(Cu-Kα) = 104.9 cm⁻¹. Intensities of 2240 reflections with *I* > 3σ(*I*) were collected on a Siemens AED diffractometer using Cu-Kα radiation in the θ range 3–70°. The structure was solved using 2093 unique absorption corrected reflections and refined to *R* = 0.0798 and *R*_w = 0.0881 with SHELX-76.‡ The methyl groups were treated as idealised rigid groups (*d*_{C-H} 1.080 Å).

The molecular structure established by X-ray study is illustrated in Figure 1.

The most important feature in this highly strained molecule is the difference in lengths of two identical bonds which are common to the four- and three-membered rings, *i.e.* C(1)–C(7) 1.579(9) and C(5)–C(6) 1.533(8) Å. Thus the base of the molecule is an irregular square. We suspect that this could be caused by repulsive non-bonded interactions between the two large electronegative atoms, *i.e.* O(1) and Cl(6). However in

the cyclopropane rings the distances between adjacent carbon atoms substituted with chlorine atoms are shorter than bond distances in cyclopropane (1.479 vs. 1.512 Å). The bond angle at the bridgehead atom is 97.8(6)° in agreement with the electron diffraction data⁴ for the parent compound [98.5(2)°].

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† Compound (2): i.r. 2995 (CH₃ str.), 1750 cm⁻¹ (C=O str.); ¹H n.m.r. (CDCl₃) δ 3.85 (s, 6H); ¹³C n.m.r. (CDCl₃) δ 44.58 (s), 53.31 (q), 58.72 (s), 65.83 (s), 90.64 (s), 160.42 (s).

‡ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.