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Acta Cryst. (1996). **C52**, 368–369

4a-Phenylperhydro-1,4-dioxacyclopropa[cd]pentalene

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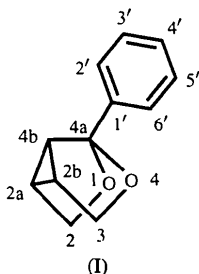
(Received 19 May 1995; accepted 7 August 1995)

Abstract

The title compound, C₁₂H₁₂O₂, represents the first example of a molecule containing the perhydro-1,4-dioxacyclopropa[cd]pentalene ring system which has been subjected to single-crystal X-ray analysis.

Comment

We have been developing methods for the synthesis of molecular clefts based on cyclopropylidene dimers derived from ring-fused *gem*-dibromocyclopropanes (Banwell, Gable, Greenwood, Lambert, Mackay & Walter, 1995). As part of this work, we had occasion to attempt the dimerization of the dibromocarbene adducts of 4,7-dihydro-2-phenyl-1,3-dioxepin (Bulman-Page, Rayner & Sutherland, 1990) using methyl lithium. However, the major isolable product of the reaction was not the hoped-for dimer, but rather, a monomeric species. Given the propensity of certain cyclopropylidenes to undergo intramolecular C—H insertion (Banwell & Reum, 1991), it seemed plausible that this product was the title compound, (I), but the spectroscopic data obtained were inconclusive. Consequently, a single-crystal X-ray structure determination was undertaken, the results of which are reported here.



The 1,4-dioxacyclopropa[cd]pentalene framework associated with compound (I) closely resembles that of the all-carbon analogue (cyclopropa[cd]pentalene) and several molecules embodying this latter ring system have been the subject of X-ray crystallographic studies (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990; Pokkuluri, Scheffer & Trotter, 1993*a,b*; Pokkuluri, Scheffer, Trotter & Yap, 1994; Pokkuluri & Trotter, 1994).

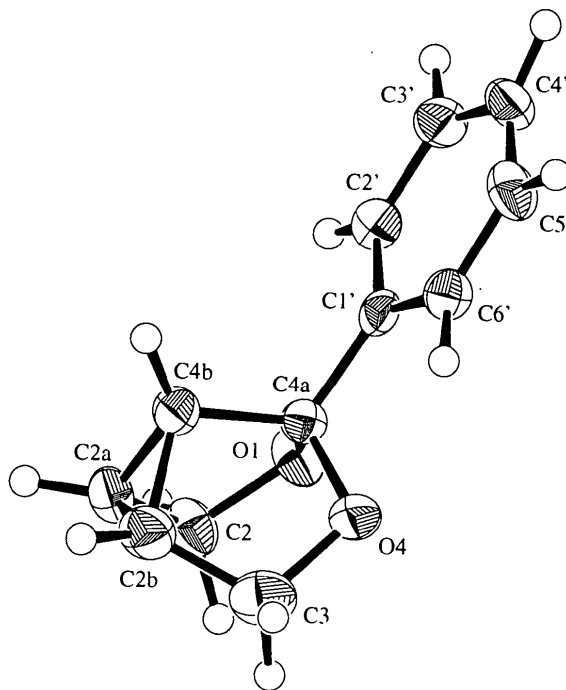


Fig. 1. View of 4a-phenylperhydro-1,4-dioxacyclopropa[cd]pentalene, (I), showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

Experimental

The title compound, (I), was prepared by treating the dibromocarbene adducts of 4,7-dihydro-2-phenyl-1,3-dioxepin with 2.2 equivalents of methyl lithium in diethyl ether at 193 K for 4 h. The reaction mixture was then allowed to warm to room temperature over a period of 4 h and quenched with water. The crude product obtained after extractive work-up was subjected to high-performance liquid chromatography (1:9 ethyl acetate/hexane elution, semi-preparative μ -Porasil column, flow rate 2 ml min⁻¹) and the appropriate fractions (*t_R* = 21 min) concentrated under reduced pressure to give the title compound (m.p. 380–381 K).

Crystal data

C₁₂H₁₂O₂
M_r = 188.23

Cu K α radiation
 λ = 1.5418 Å

Monoclinic	Cell parameters from 24 reflections
$P2_1/n$	$\theta = 41.7\text{--}49.8^\circ$
$a = 6.178 (2) \text{ \AA}$	$\mu = 0.729 \text{ mm}^{-1}$
$b = 12.083 (1) \text{ \AA}$	$T = 213.2 \text{ K}$
$c = 12.492 (2) \text{ \AA}$	Plate
$\beta = 91.73 (2)^\circ$	$0.14 \times 0.12 \times 0.03 \text{ mm}$
$V = 932.1 (2) \text{ \AA}^3$	Colourless
$Z = 4$	
$D_x = 1.341 \text{ Mg m}^{-3}$	
Data collection	
Rigaku AFC-6R diffractometer	783 observed reflections
$\omega/2\theta$ scans	$[I > 3\sigma(I)]$
Absorption correction: empirical using azimuthal (ψ) scans (North, Phillips & Mathews, 1968)	$R_{\text{int}} = 0.047$
$T_{\text{min}} = 0.898$, $T_{\text{max}} = 0.992$	$\theta_{\text{max}} = 60.01^\circ$
1533 measured reflections	$h = -6 \rightarrow 6$
1463 independent reflections	$k = 0 \rightarrow 13$
	$l = 0 \rightarrow 14$
	3 standard reflections monitored every 150 reflections
	intensity decay: 4.4%
Refinement	
Refinement on F^2	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
$R = 0.038$	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
$wR = 0.035$	Extinction correction: Zachariasen (1968) type
$S = 1.62$	2 Gaussian isotropic
783 reflections	Extinction coefficient: $7 (3) \times 10^{-7}$
176 parameters	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
All H-atom parameters refined	
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.010F_o^2)^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.033$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	0.5875 (4)	0.0874 (2)	0.7111 (2)	0.0381 (8)
O(4)	0.9227 (4)	0.0679 (2)	0.7981 (2)	0.0400 (8)
C(1')	0.6337 (5)	0.1555 (3)	0.8911 (3)	0.028 (1)
C(2a)	0.5927 (6)	-0.1053 (3)	0.7354 (3)	0.039 (1)
C(2b)	0.8116 (7)	-0.1194 (4)	0.7944 (3)	0.043 (1)
C(2)	0.5706 (7)	-0.0153 (3)	0.6531 (3)	0.039 (1)
C(2')	0.4252 (6)	0.1996 (3)	0.8898 (3)	0.032 (1)
C(3)	0.9923 (7)	-0.0412 (4)	0.7687 (4)	0.047 (1)
C(3')	0.3698 (6)	0.2757 (3)	0.9660 (3)	0.040 (1)
C(4b)	0.6368 (6)	-0.0520 (3)	0.8419 (3)	0.032 (1)
C(4a)	0.6943 (5)	0.0667 (3)	0.8124 (3)	0.029 (1)
C(4')	0.5176 (7)	0.3103 (3)	1.0443 (3)	0.040 (1)
C(5')	0.7234 (7)	0.2663 (4)	1.0459 (3)	0.041 (1)
C(6')	0.7828 (6)	0.1895 (3)	0.9704 (3)	0.033 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O(1)—C(2)	1.440 (4)	C(2a)—C(4b)	1.495 (5)
O(1)—C(4a)	1.431 (4)	C(2b)—C(3)	1.505 (6)
O(4)—C(3)	1.438 (5)	C(2b)—C(4b)	1.490 (5)
O(4)—C(4a)	1.428 (4)	C(2')—C(3')	1.374 (5)
C(1')—C(2')	1.393 (4)	C(3')—C(4')	1.382 (5)
C(1')—C(4a)	1.511 (5)	C(4b)—C(4a)	1.525 (5)
C(1')—C(6')	1.394 (4)	C(4')—C(5')	1.378 (5)

C(2a)—C(2b)	1.530 (5)	C(5')—C(6')	1.380 (5)
C(2a)—C(2)	1.500 (5)		
C(2)—O(1)—C(4a)	108.6 (3)	C(2')—C(3')—C(4')	121.3 (4)
C(3)—O(4)—C(4a)	109.1 (3)	C(2a)—C(4b)—C(2b)	61.7 (3)
C(2')—C(1')—C(4a)	120.7 (3)	C(2a)—C(4b)—C(4a)	103.1 (3)
C(2')—C(1')—C(6')	119.1 (3)	C(2b)—C(4b)—C(4a)	103.9 (3)
C(4a)—C(1')—C(6')	120.1 (3)	O(1)—C(4a)—O(4)	108.6 (3)
C(2b)—C(2a)—C(2)	118.2 (4)	O(1)—C(4a)—C(1')	109.6 (3)
C(2b)—C(2a)—C(4b)	59.0 (2)	O(1)—C(4a)—C(4b)	105.9 (3)
C(2)—C(2a)—C(4b)	108.0 (3)	O(4)—C(4a)—C(1')	109.9 (3)
C(2a)—C(2b)—C(3)	118.5 (4)	O(4)—C(4a)—C(4b)	106.1 (3)
C(2a)—C(2b)—C(4b)	59.3 (2)	C(1')—C(4a)—C(4b)	116.5 (3)
C(3)—C(2b)—C(4b)	107.0 (4)	C(3')—C(4')—C(5')	118.9 (4)
O(1)—C(2)—C(2a)	106.0 (3)	C(4')—C(5')—C(6')	120.9 (4)
C(1')—C(2')—C(3')	119.8 (4)	C(1')—C(6')—C(5')	120.0 (3)
O(4)—C(3)—C(2b)	106.9 (3)		

The θ -scan width used was $(1.30 + 0.3 \tan\theta)^\circ$ at a speed of $8.0^\circ \text{ min}^{-1}$ (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement. The structure was solved by direct methods (*SAP91*; Fan, 1991) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). H atoms were refined isotropically. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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