Instrumental Achievements

Crystal Structure of 2,6-Dicarbomethoxy-5-pivaloyloxymethyl-1,3-benzenediol

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Although the synthetic approaches to highly substituted phenols are limited¹⁻⁶, the construction of these aromatic systems is of great synthetical utility. We developed a route to highly substituted aromatic rings starting from aliphatic compounds;⁷ using our method, we could obtain 2,6-dicarbomethoxy-5-pivaloyloxymethyl-1,3-benzenediol, **1** (Fig. 1). The molecular structure was confirmed by X-ray diffraction. Data were collected on a Siemens P4 diffractometer. Crystallographic data, details of an X-ray data collection and a structure refinement as well are summarized in Table 1. The intensities were collected using nickel-filtered Cu K α radiation ($\lambda=1.54178$ Å) at room temperature, and were corrected for Lorentz and polarization effects.⁸ The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic temperature factors for the non-hydrogen atoms.⁹ The hydrogen atoms were placed at their idealized positions and included in a structure-factor calculation with fixed isotropic thermal parameters ($U=0.06$ Å²). The hydroxyl H-atoms were located on a difference Fourier map, and their positional parameters were refined.

A diagram of the structure of compound **1** is shown in Fig. 2. The bond lengths and angles (Tables 2 and 3) agree with the expected values. Two intramolecular hydrogen bonds [H4...O5, 1.67(5)Å; O4...O5, 2.490(4)Å; O4...H4...O5, 157(3)°; H1...O2, 1.65(3)Å; O1...O2, 2.551(4)Å; O1...H1...O2, 148(2)°] keep the carbonyl

Fig. 1 Structure of 2,6-dicarbomethoxy-5-pivaloyloxymethyl-1,3-benzenediol.

Table 1 Crystallographic data for 2,6-dicarbomethoxy-5-pivaloyloxymethyl-1,3-benzenediol

Formula: C ₁₆ H ₂₀ O ₈
Formula weight=340
Crystal system: triclinic
Space group: <i>P</i> ₁
<i>Z</i> =2
Crystal dimensions=0.4×0.18×0.14 mm
<i>a</i> =7.087(1) Å
<i>b</i> =10.702(1) Å
<i>c</i> =11.810(1) Å
α =94.144(8)°
β =95.473(8)°
γ =108.15(1)°
<i>V</i> =842.37(12) Å ³
<i>D</i> _x =1.342 g/cm ³
2 θ range=3–110°
Scan type= $\theta/2\theta$
Scan speed=variable, 4–100.00° min ⁻¹ in θ
<i>h k l</i> range=0< <i>h</i> <7, –11< <i>k</i> <10 and –12< <i>l</i> <12
<i>F</i> (0 0 0)=360
μ =0.922 mm ⁻¹
<i>R</i> =0.063
<i>R</i> _w =0.0958
Goodness-of-fit=1.64
Independent reflections=2116(<i>R</i> _{int} =0.0226)
Observed reflections=1751 (<i>F</i> >4 σ <i>F</i>)
$\Delta\rho_{\max}(\text{e}\cdot\text{\AA}^{-3})/\Delta\rho_{\min}(\text{e}\cdot\text{\AA}^{-3})=0.24/-0.26$

and hydroxy groups coplanar, and at the same time account for the low frequency observed for the stretching carbonyl absorption in the IR spectrum (1660 cm⁻¹).

Contribution No. 1629 of the Instituto de Química, UNAM. This research was supported by a Grant-in-Aid for Scientific Research (No. 40361-5-3352E) from CONACYT, México.

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Fig. 2 Molecular structure of compound 1, showing the numbering scheme for the atoms.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U(eq)
O(1)	779(5)	7186(2)	10969(2)	70(1)
O(2)	264(8)	5759(3)	9068(3)	110(2)
O(3)	1043(5)	6595(3)	7487(2)	69(1)
O(4)	2320(5)	9095(3)	7519(2)	71(1)
O(5)	3605(6)	11550(3)	7594(2)	89(2)
O(6)	4237(4)	12815(2)	9238(2)	61(1)
O(7)	3189(4)	11612(2)	12374(2)	52(1)
O(8)	4156(7)	13741(3)	12968(2)	95(2)
C(1)	2894(5)	10505(3)	9280(3)	41(1)
C(2)	2248(5)	9234(3)	8644(3)	45(1)
C(3)	1558(5)	8074(3)	9176(3)	45(1)
C(4)	1467(5)	8210(3)	10360(3)	47(1)
C(5)	2084(5)	9453(3)	10983(3)	45(1)
C(6)	2776(4)	10586(3)	10471(3)	40(1)
C(7)	904(6)	6714(3)	8583(3)	54(1)
C(8)	3590(6)	11647(3)	8632(3)	50(1)
C(9)	3445(5)	11905(3)	11217(3)	42(1)
C(10)	3656(6)	12629(3)	13180(3)	52(1)
C(11)	397(8)	5270(4)	6916(4)	78(2)
C(12)	4920(9)	13957(4)	8610(4)	82(2)
C(13)	3525(6)	12206(3)	14380(3)	55(1)
C(14)	2670(10)	10703(4)	14366(4)	86(2)
C(15)	5614(9)	12674(6)	15004(4)	95(2)
C(16)	2180(10)	12837(6)	14959(4)	96(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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Table 3 Geometric parameters

Bond lengths ($\text{\AA}$).			
O(1)-C(4)	1.343 (4)	O(2)-C(7)	1.193 (5)
O(3)-C(7)	1.308 (5)	O(3)-C(11)	1.440 (5)
O(4)-C(2)	1.333 (4)	O(5)-C(8)	1.224 (4)
O(6)-C(8)	1.317 (4)	O(6)-C(12)	1.452 (5)
O(7)-C(9)	1.440 (4)	O(7)-C(10)	1.328 (4)
O(8)-C(10)	1.184 (4)	C(1)-C(2)	1.423 (4)
C(1)-C(6)	1.415 (4)	C(1)-C(8)	1.467 (5)
C(2)-C(3)	1.403 (5)	C(3)-C(4)	1.406 (5)
C(3)-C(7)	1.481 (5)	C(4)-C(5)	1.392 (4)
C(5)-C(6)	1.368 (4)	C(6)-C(9)	1.522 (4)
C(10)-C(13)	1.521 (5)	C(13)-C(14)	1.530 (5)
C(13)-C(15)	1.504 (7)	C(13)-C(16)	1.514 (9)

Bond Angles ($^\circ$)			
C(7)-O(3)-C(11)	116.6 (3)	C(8)-O(6)-C(12)	116.7 (3)
C(9)-O(7)-C(10)	117.4 (2)	C(2)-C(1)-C(6)	118.5 (3)
C(2)-C(1)-C(8)	116.7 (3)	C(6)-C(1)-C(8)	124.8 (3)
O(4)-C(2)-C(1)	121.2 (3)	O(4)-C(2)-C(3)	117.2 (3)
C(1)-C(2)-C(3)	121.5 (3)	C(2)-C(3)-C(4)	117.7 (3)
C(2)-C(3)-C(7)	125.0 (3)	C(4)-C(3)-C(7)	117.4 (3)
O(1)-C(4)-C(3)	123.8 (3)	O(1)-C(4)-C(5)	115.2 (3)
C(3)-C(4)-C(5)	121.0 (3)	C(4)-C(5)-C(6)	121.6 (3)
C(1)-C(6)-C(5)	119.7 (3)	C(1)-C(6)-C(9)	122.0 (3)
C(5)-C(6)-C(9)	118.3 (3)	O(2)-C(7)-O(3)	120.6 (3)
O(2)-C(7)-C(3)	122.4 (3)	O(3)-C(7)-C(3)	117.0 (3)
O(5)-C(8)-O(6)	120.7 (3)	O(5)-C(8)-C(1)	123.4 (3)
O(6)-C(8)-C(1)	115.9 (3)	O(7)-C(9)-C(6)	106.9 (2)
O(7)-C(10)-O(8)	122.5 (3)	O(7)-C(10)-C(13)	112.9 (3)
O(8)-C(10)-C(13)	124.6 (3)	C(10)-C(13)-C(14)	112.1 (3)
C(10)-C(13)-C(15)	107.4 (3)	C(14)-C(13)-C(15)	109.0 (4)
C(10)-C(13)-C(16)	108.3 (4)	C(14)-C(13)-C(16)	108.9 (4)
C(15)-C(13)-C(16)	111.2 (4)		

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(Received November 18, 1997)

(Accepted February 16, 1998)