Acta Cryst. (1996). C52, 2318-2320

4-(4-Chlorophenyl)-2,6-diphenyl-(4*H*)-pyran-3,5-dicarbaldehyde

R. Murugesan,[a] S. Selladurai,[a] K. Subramaniam,[a] D. Velmurugan,[b] John R. Hamilton,[c] Yu-Sheng Chen,[c] Philip J. Schapiro[c]† and S. Narasinga Rao[c]

[a]*Department of Physics, Anna University, Madras, India,* [b]*Department of Biophysics and Crystallography, University of Madras, Madras 25, India,* [c]*Department of Physics, University of Central Oklahoma, Edmond, Oklahoma 73034, USA*

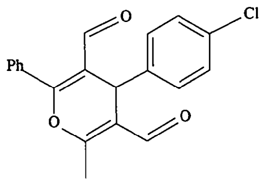
(*Received 3 January 1995; accepted 5 March 1996*)

Abstract

This study is part of a series undertaken to examine the conformation of 2,4,6-substituted phenylpyran derivatives. These derivatives of pyran have been reported to be antimicrobial and cocidiostatic, antischistosmal and intermediates in the synthesis of sugars. We report here the structure of the title compound, $C_{25}H_{17}ClO_3$.

Comment

Derivatives of pyran have been reported to be antimicrobial and cocidiostatic (Georgiadis, 1976) and antischistosmal as well as being intermediates in the synthesis of sugars (Achmatowicz, Grynkilewicz & Szechner, 1976). These biological metabolites play an important role in the interpretation and correlation of a structure with biological activity (Bergmann & Pullman, 1974). We present here the structure analysis of 4-(4-chlorophenyl)-2,6-diphenyl-(4*H*)-pyran-3,5-dicarbaldehyde, (I).



(I)

The conformation of the pyran ring is intermediate between half-chair and sofa (Duax & Norton, 1975). In this structure, the C2—C3 and C5—C6 bonds are Csp^2—Csp^2 with bond lengths of 1.321 (9) and 1.345 (9) Å, respectively, compared to the normal distance of 1.330 Å. The atoms O1—C2═C3—C13═O14 and O1—C6═C5—C21═O22 form a conjugated system of alternating single and double bonds. The average endocyclic angle is 118.0°, close to those reported in similar structures (Thailambal & Vasantha Pattabhi, 1985). The Csp^2—Csp^3 bonds (C3—C4, C5—C4 and C4—C15) are 1.530 (8), 1.488 (8) and 1.531 (9) Å, respectively, and are comparable with those in other known structures (Semmingsen, 1974).

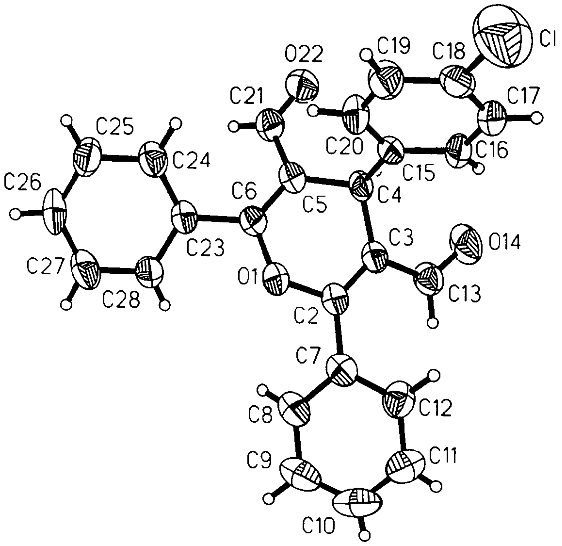


Fig. 1. ORTEPII plot (Johnson, 1976) of 4-(4-chlorophenyl)-2,6-diphenyl-(4*H*)-pyran-3,5-dicarbaldehyde. Displacement ellipsoids are plotted at the 50% probability level.

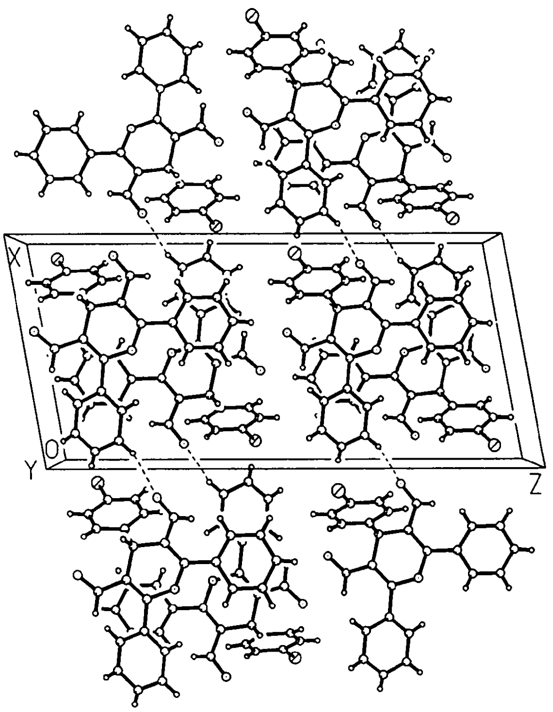


Fig. 2. Packing diagram of 4-(4-chlorophenyl)-2,6-diphenyl-(4*H*)-pyran-3,5-dicarbaldehyde.

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† Department of Mathematics, Langston University, Langston, Oklahoma, USA.

The phenyl ring at the 2-position and the phenyl ring at the 6-position are planar. The dihedral angles between the pyran ring and phenyl rings are 35.29 (17) and 29.81 (13)°, respectively, indicating that the pyran ring and the 2,6-substituted phenyl rings are not all coplanar.

The chlorine-substituted phenyl ring C15–C20 is planar. The bond lengths and bond angles in this ring are normal and agree well with the reported values for phenyl rings in many structures. The dihedral angle between the pyran ring and chlorophenyl ring is 77.07 (17)°.

The structure is stabilized by van der Waals interactions and hydrogen bonds.

Experimental

Crystals of chloropyran were obtained by the slow evaporation of an aqueous solution of methanol.

Crystal data

$C_{25}H_{17}ClO_3$
$M_r = 400.87$
Monoclinic
$P2_1/c$
$a = 10.917\ (4)$ Å
$b = 7.933\ (5)$ Å
$c = 23.137\ (2)$ Å
$\beta = 99.93\ (1)°$
$V = 1973.63\ (4)$ Å^3
$Z = 4$
$D_x = 1.35$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.191$ mm^{-1}
$T = 293$ K
Needle
$0.53 \times 0.23 \times 0.10$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
4822 measured reflections
4053 independent reflections
2405 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.053$
$\theta_{\rm max} = 34°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 28$
3 standard reflections monitored every 100 reflections intensity decay: <5%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.065$
$S = 1.265$
2405 reflections
313 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.1022P)^2 + 2.76P]$
where $P = [\max(F_o^2+2F_c^2)]/3$
$(\Delta/\sigma)_{\rm max} = 0.161$

$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.55$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer (1974) and Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl	0.0856 (3)	0.9340 (5)	0.4234 (2)	11.0 (1)
O1	0.4937 (4)	1.4925 (6)	0.2848 (2)	3.3 (1)
O14	0.4160 (5)	1.7071 (7)	0.4647 (2)	5.1 (1)
O22	0.1021 (4)	1.7444 (7)	0.2810 (2)	4.9 (1)
C2	0.5308 (6)	1.5355 (8)	0.3439 (3)	2.9 (1)
C3	0.4472 (5)	1.5850 (8)	0.3754 (3)	3.0 (1)
C4	0.3084 (5)	1.5788 (8)	0.3496 (2)	2.9 (1)
C5	0.2943 (5)	1.6070 (8)	0.2852 (3)	3.1 (1)
C6	0.3822 (6)	1.5524 (8)	0.2555 (3)	3.0 (1)
C7	0.6667 (6)	1.5175 (9)	0.3615 (3)	3.5 (2)
C8	0.7454 (6)	1.5747 (9)	0.3243 (3)	3.9 (2)
C9	0.8729 (7)	1.567 (1)	0.3413 (4)	5.0 (2)
C10	0.9213 (7)	1.497 (1)	0.3962 (4)	5.8 (2)
C11	0.8443 (7)	1.437 (1)	0.4319 (3)	5.2 (2)
C12	0.7186 (6)	1.4458 (9)	0.4152 (3)	4.0 (2)
C13	0.4874 (6)	1.6622 (9)	0.4326 (3)	3.9 (2)
C15	0.2503 (5)	1.4139 (8)	0.3661 (2)	2.7 (1)
C16	0.2515 (6)	1.3759 (9)	0.4258 (3)	3.8 (2)
C17	0.2017 (6)	1.231 (1)	0.4431 (3)	4.0 (2)
C18	0.1477 (6)	1.1145 (9)	0.4012 (3)	3.8 (2)
C19	0.1422 (7)	1.148 (1)	0.3420 (3)	4.3 (2)
C20	0.1951 (6)	1.2987 (9)	0.3257 (3)	3.9 (2)
C21	0.1860 (6)	1.7015 (9)	0.2563 (3)	3.6 (2)
C23	0.3786 (6)	1.5469 (8)	0.1913 (2)	3.1 (1)
C24	0.2711 (6)	1.4997 (9)	0.1532 (2)	3.7 (2)
C25	0.2691 (7)	1.496 (1)	0.0932 (3)	4.2 (2)
C26	0.3734 (7)	1.535 (1)	0.0711 (3)	4.5 (2)
C27	0.4814 (7)	1.577 (1)	0.1080 (3)	4.6 (2)
C28	0.4867 (6)	1.5808 (9)	0.1677 (3)	3.7 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cl—C18	1.701 (8)	C8—C9	1.381 (9)
O1—C2	1.399 (7)	C9—C10	1.40 (1)
O1—C6	1.372 (7)	C10—C11	1.36 (1)
O14—C13	1.219 (9)	C11—C12	1.36 (1)
O22—C21	1.209 (9)	C15—C16	1.411 (8)
C2—C3	1.321 (9)	C15—C20	1.370 (9)
C2—C7	1.476 (9)	C16—C17	1.36 (1)
C3—C4	1.530 (8)	C17—C18	1.393 (9)
C3—C13	1.457 (9)	C18—C19	1.39 (1)
C4—C5	1.488 (8)	C19—C20	1.41 (1)
C4—C15	1.531 (9)	C23—C24	1.391 (8)
C5—C6	1.345 (9)	C23—C28	1.41 (1)
C5—C21	1.461 (9)	C24—C25	1.385 (9)
C6—C23	1.481 (8)	C25—C26	1.36 (1)
C7—C8	1.39 (1)	C26—C27	1.37 (1)
C7—C12	1.396 (9)	C27—C28	1.37 (1)
C2—O1—C6	118.7 (5)	C10—C11—C12	120.6 (7)
O1—C2—C3	120.0 (5)	C7—C12—C11	120.5 (7)
O1—C2—C7	110.7 (5)	O14—C13—C3	123.6 (6)
C3—C2—C7	129.4 (5)	C4—C15—C16	119.5 (5)
C2—C3—C4	120.5 (5)	C4—C15—C20	123.5 (5)
C2—C3—C13	119.9 (5)	C16—C15—C20	117.0 (6)
C4—C3—C13	119.3 (5)	C15—C16—C17	122.0 (6)
C3—C4—C5	108.1 (5)	C16—C17—C18	119.8 (6)
C3—C4—C15	110.8 (5)	Cl—C18—C17	119.3 (5)
C5—C4—C15	113.7 (5)	Cl—C18—C19	120.6 (5)
C4—C5—C6	120.2 (5)	C17—C18—C19	120.1 (7)
C4—C5—C21	118.1 (6)	C18—C19—C20	118.6 (6)
C6—C5—C21	121.6 (5)	C15—C20—C19	122.5 (6)
O1—C6—C5	120.7 (5)	O22—C21—C5	123.2 (6)
O1—C6—C23	110.7 (5)	C6—C23—C24	121.1 (6)
C5—C6—C23	128.6 (5)	C6—C23—C28	120.3 (5)
C2—C7—C8	119.8 (6)	C24—C23—C28	118.5 (6)
C2—C7—C12	121.3 (6)	C23—C24—C25	120.4 (7)
C8—C7—C12	119.0 (6)	C24—C25—C26	120.1 (6)
C7—C8—C9	120.5 (6)	C25—C26—C27	120.4 (6 (
C8—C9—C10	118.7 (7)	C26—C27—C28	120.9 (7)
C9—C10—C11	120.7 (7)	C23—C28—C27	119.6 (6)

Corrections for Lorentz and polarization effects were applied, but not for absorption or decay. The structure was solved by Patterson synthesis and Fourier methods, and refined by full-matrix least-squares techniques on F using modified weights.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: modified *SDP* (Frenz, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2320–2323

Biphenyl-3-carboxylic Acid at 296 and 203 K

Anthony C. Blackburn, Allison J. Dobson and Roger E. Gerkin*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

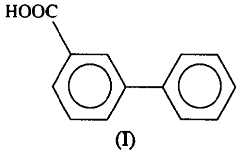
(*Received 4 December 1995; accepted 11 March 1996*)

Abstract

In biphenyl-3-carboxylic acid, $C_{13}H_{10}O_2$, hydrogen bonding is of the cyclic-dimer type about a center of symmetry. The carboxyl H atom is ordered. The dihedral angle between the planar phenyl rings is 31.78 (8)° at 296 K and 31.27 (6)° at 203 K. The data show that the larger-than-average magnitudes of the displacement parameters of the carboxylic O atoms are due to thermal motion rather than static disorder.

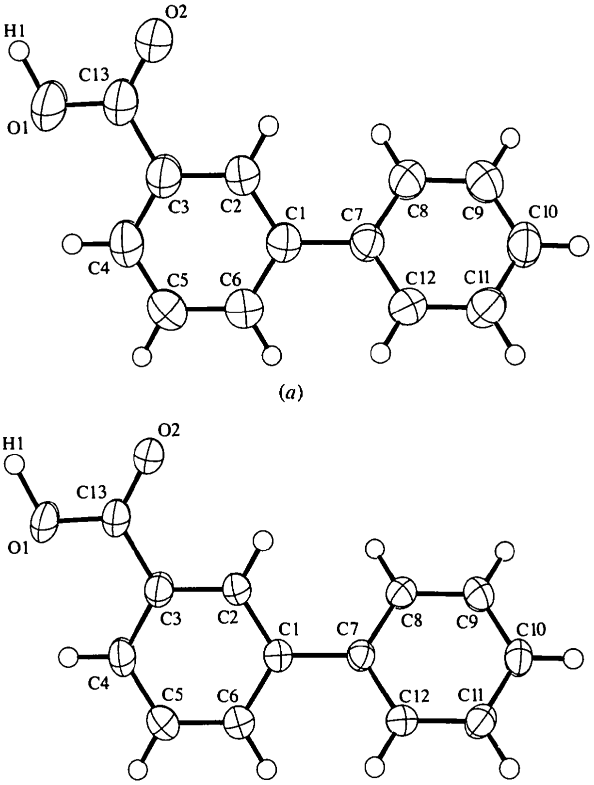
Comment

The present study of biphenyl-3-carboxylic acid, (I), is part of a series of studies on hydrogen bonding in carboxylic acids. In this case, the value of the dihedral angle between the phenyl rings is also a matter of interest.



(I)

The hydrogen bonding is of the cyclic-dimer type about a center of symmetry (Fig. 1 and Table 5). The C—O and O—H distances found in the carboxyl group (Table 2) are entirely consistent with an ordered carboxylic H atom.



(*a*)

(*b*)

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the biphenyl-3-carboxylic acid molecule (*a*) at 296 and (*b*) at 203 K, showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms for which they have been set artificially small.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996