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2,4,6-Triphenyl-4*H*-pyran-3,5-dicarboxaldehyde

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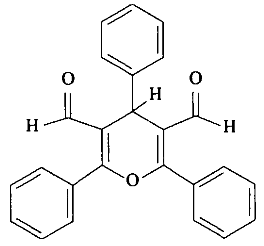
Abstract

The structure of 2,4,6-triphenyl-4*H*-pyran-3,5-dicarboxaldehyde, $C_{25}H_{18}O_3$, a potential fungicide, has a pyran ring in a flattened boat conformation, with the C4 and O3 atoms displaced from the basal plane by 0.299 and 0.159 Å, respectively. The aldehyde groups display an *ap* orientation with respect to the double bonds of that plane.

Comment

Pyran derivatives have shown biological activity as fungicides and insecticides. In particular, pyran derivatives have shown activity against the growth of *Pyricularia Oryzae cav.*, a virulent systemic fungus observed in rice plants and responsible for significant yield losses in temperate climates. In an effort to maximize the activity of the antifungicide, studies of the activity of substituted pyran molecules have been undertaken. In these studies, chloropyran derivatives have shown greater activity than the parent compound, pyran, or its methoxy- or benzo-substituted modifications.

We have determined the solid-state structure of the 2,4,6-triphenyl-3,5-dicarboxaldehyde derivative of pyran, (I), as part of a study linking the structure and activity of the compounds of this family, in an effort to understand the geometry of the receptor site.



(I)

Pyran rings normally adopt a flattened boat conformation, but there is considerable variation in the flatness of such a hetero-ring. Measures of flatness are (i) the distance of the O and C4 atoms from the plane of the base of the boat (atoms C2, C3, C5 and C6) and (ii) the sum of the absolute values of the intra-ring torsion angles which should be zero for a totally planar ring and 360° for an idealized boat conformation.

In the title compound, (I), the pyran ring exists with the C2═C3 and C5═C6 double bonds coplanar (deviation 0.013 Å) and the O3 and C4 atoms displaced from this plane by 0.159 and 0.299 Å, respectively (Fig. 1). The sum of the intra-ring torsion angles is 88.7°. These values may be compared with the similar degree of nonplanarity observed in 2-amino-3-cyano-4-isopropyl-5-cyano-6-methyl-4*H*-pyran [deviations of the O1 and C4 atoms from the basal plane are −0.154 (1) and −0.301 Å, respectively; the sum of the intra-ring torsion angles is 89.0°] (Bellanato, Florencio, García-Blanco, Martin & Seoane, 1987), and the greater planarity of the pyran rings in both 2-amino-6-chloromethyl-3-cyano-5-ethoxycarbonyl-4-(2-furyl)-4*H*-pyran [O1 and C4 are −0.125 (2) and −0.265 (2) Å, respectively, from the basal plane and the torsion angle sum is 77.9°] (Lokaj, Kettmann, Pavelčík, Ilavský & Marchalín, 1990) and 2-amino-3-ethoxycarbonyl-4-phenyl-5-cyano-6-phenyl-4*H*-pyran [O1 and O4 are −0.095 (7) and −0.198 (7) Å, respectively, from the basal plane and the torsion angle sum is 67.5°] (Bellanato, Florencio, Martin & Seoane, 1988). 2,6-Dimethyl-4-phenyl-4*H*-pyran-3,5-dicarbonitrile, in comparison, crystallizes with a more planar pyran ring (O1 and C4 are −0.0334 and −0.0762 Å, respectively, from the basal plane and the torsion angle sum is 22.3°) (Florencio & García-

Blanco, 1987). In all of these compounds, the substituent at C4 projects upwards in a pseudo-axial conformation and not outwards from the 'prow' of the boat. There appears to be a correlation between increased nonplanarity of the pyran ring and increasing bulk of the substituents at the C3 and C5 positions in the sequence 3,5-dicarboxaldehyde > 3-cyano-5-ethoxycarbonyl > 3,5-dicyano. The structure of 2,6-diphenyl-4-*p*-chlorophenyl-4*H*-pyran-3,5-dicarboxaldehyde, however, which differs from the title compound only in the presence of a *para*-chloro substituent on the phenyl ring at C4 and which shows O1 and C4 displacements of 0.211 and 0.403 Å, respectively, from the C2, C3, C5, C6 plane, and an intra-planar angle sum of 119° for the pyran ring, argues for the influence of solid-state packing on the observed conformation of this ring (Murugesan, Selladurai, Subramanian, Velmurugan, Hamilton, Chen, Schapiro & Narasinga Rao, 1996).

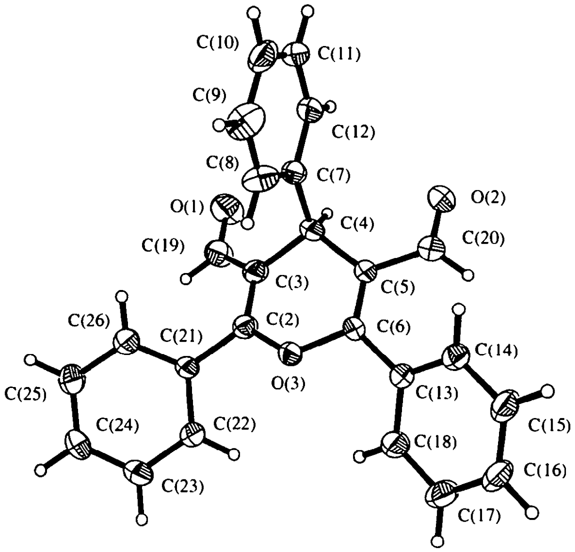


Fig. 1. A projection view of 2,4,6-triphenyl-4*H*-pyran-3,5-dicarboxaldehyde with ellipsoids shown at the 50% probability level.

In the title compound, the carbonyl groups substituted at the C3 and C5 positions display an *ap* (*anti*) orientation with respect to the double bonds of the basal plane of the pyran ring.

The phenyl rings substituted at C2 and C6 subtend angles of 38.7 (3) and 39.3 (3)°, respectively, with the C2, C3, C5, C6 plane. The phenyl group substituted at the C4 position is approximately perpendicular to this basal plane [91.7 (3)°].

Experimental

The title compound was synthesized using literature procedures and crystallized from aqueous methanol.

Crystal data

$C_{25}H_{18}O_3$
$M_r = 366.4$
Monoclinic
$P2_1$
$a = 10.566\ (1)$ Å
$b = 7.880\ (1)$ Å
$c = 11.572\ (1)$ Å
$\beta = 99.18\ (1)°$
$V = 951.3\ (2)$ Å^3
$Z = 2$
$D_x = 1.279$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 66 reflections
$\theta = 3.748–12.442°$
$\mu = 0.083$ mm^{-1}
$T = 298$ K
Needle
0.3 × 0.2 × 0.2 mm
Colorless

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1393 measured reflections
1152 independent reflections
1048 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.0223$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 7$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 97 min
intensity decay: 0.0001%

Refinement

Refinement on F
$R = 0.0377$
$wR = 0.0446$
$S = 1.10$
1152 reflections
253 parameters
H atoms were allowed to ride on their attached atoms at fixed distances of 0.97 Å and isotropic displacement parameters were held constant

$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.8506 (4)	0.0367 (8)	0.2273 (3)	0.089 (2)
O(2)	0.5285 (3)	0.1332 (8)	0.4922 (3)	0.077 (2)
O(3)	0.4798 (3)	0.3670	0.1128 (2)	0.048 (1)
C(2)	0.5934 (4)	0.2948 (8)	0.0938 (4)	0.047 (2)
C(3)	0.6741 (4)	0.2192 (8)	0.1794 (4)	0.049 (2)
C(4)	0.6527 (4)	0.2297 (8)	0.3050 (3)	0.047 (2)
C(5)	0.5109 (4)	0.2615 (8)	0.3063 (4)	0.045 (2)
C(6)	0.4344 (4)	0.3291 (8)	0.2158 (4)	0.043 (2)
C(7)	0.7360 (4)	0.3653 (10)	0.3733 (4)	0.050 (2)
C(8)	0.7384 (5)	0.5290 (10)	0.3341 (5)	0.069 (3)
C(9)	0.8104 (6)	0.6508 (10)	0.4000 (6)	0.082 (3)
C(10)	0.8862 (5)	0.6102 (12)	0.5048 (6)	0.076 (3)
C(11)	0.8848 (5)	0.4494 (13)	0.5426 (5)	0.078 (3)
C(12)	0.8129 (5)	0.3237 (10)	0.4784 (4)	0.066 (2)
C(13)	0.2975 (4)	0.3731 (8)	0.2047 (3)	0.047 (2)
C(14)	0.2463 (4)	0.4547 (9)	0.2926 (4)	0.056 (2)
C(15)	0.1167 (5)	0.4876 (10)	0.2803 (4)	0.071 (2)
C(16)	0.0386 (4)	0.4455 (11)	0.1791 (4)	0.077 (3)
C(17)	0.0869 (5)	0.3684 (11)	0.0899 (4)	0.080 (3)
C(18)	0.2165 (5)	0.3317 (9)	0.1015 (4)	0.063 (2)
C(19)	0.7779 (5)	0.1124 (9)	0.1547 (5)	0.064 (2)

C(20)	0.4609 (5)	0.1995 (9)	0.4091 (4)	0.061 (2)
C(21)	0.6112 (4)	0.3210 (8)	−0.0298 (3)	0.045 (2)
C(22)	0.5101 (4)	0.2963 (9)	−0.1206 (4)	0.055 (2)
C(23)	0.5286 (5)	0.3163 (10)	−0.2356 (4)	0.067 (2)
C(24)	0.6467 (5)	0.3628 (10)	−0.2603 (4)	0.064 (2)
C(25)	0.7453 (5)	0.3912 (10)	−0.1722 (4)	0.071 (2)
C(26)	0.7278 (5)	0.3707 (10)	−0.0571 (4)	0.064 (2)

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

O(3)—C(6)	1.386 (5)	C(22)—C(21)	1.388 (6)
O(3)—C(2)	1.378 (6)	C(22)—C(23)	1.384 (7)
C(5)—C(4)	1.522 (6)	C(14)—C(13)	1.383 (7)
C(5)—C(6)	1.328 (6)	C(14)—C(15)	1.379 (7)
C(5)—C(20)	1.461 (7)	C(18)—C(13)	1.392 (6)
C(3)—C(4)	1.509 (6)	C(18)—C(17)	1.384 (7)
C(3)—C(2)	1.339 (7)	O(1)—C(19)	1.203 (7)
C(3)—C(19)	1.447 (8)	C(17)—C(16)	1.365 (9)
C(7)—C(4)	1.523 (8)	C(8)—C(9)	1.377 (10)
C(7)—C(8)	1.369 (11)	C(10)—C(11)	1.341 (14)
C(7)—C(12)	1.390 (6)	C(10)—C(9)	1.380 (9)
C(6)—C(13)	1.473 (6)	C(25)—C(24)	1.356 (7)
C(2)—C(21)	1.486 (6)	C(11)—C(12)	1.389 (11)
O(2)—C(20)	1.220 (7)	C(24)—C(23)	1.374 (8)
C(26)—C(21)	1.376 (7)	C(16)—C(15)	1.362 (7)
C(26)—C(25)	1.384 (7)		
C(6)—O(3)—C(2)	118.6 (3)	C(21)—C(22)—C(23)	120.2 (5)
C(4)—C(5)—C(6)	122.4 (4)	C(2)—C(21)—C(26)	121.0 (4)
C(4)—C(5)—C(20)	115.9 (4)	C(2)—C(21)—C(22)	120.6 (4)
C(6)—C(5)—C(20)	121.5 (4)	C(26)—C(21)—C(22)	118.4 (4)
C(4)—C(3)—C(2)	120.9 (5)	C(13)—C(14)—C(15)	120.6 (4)
C(4)—C(3)—C(19)	117.2 (4)	C(13)—C(18)—C(17)	119.8 (5)
C(2)—C(3)—C(19)	121.7 (4)	C(6)—C(13)—C(14)	122.6 (4)
C(4)—C(7)—C(8)	121.9 (4)	C(6)—C(13)—C(18)	118.7 (4)
C(4)—C(7)—C(12)	119.8 (6)	C(14)—C(13)—C(18)	118.7 (4)
C(8)—C(7)—C(12)	118.2 (6)	C(18)—C(17)—C(16)	120.2 (5)
C(5)—C(4)—C(3)	108.5 (3)	C(7)—C(8)—C(9)	120.8 (5)
C(5)—C(4)—C(7)	111.6 (5)	C(11)—C(10)—C(9)	118.1 (7)
C(3)—C(4)—C(7)	112.0 (4)	C(26)—C(25)—C(24)	120.0 (5)
O(3)—C(6)—C(5)	120.9 (4)	C(10)—C(11)—C(12)	122.2 (6)
O(3)—C(6)—C(13)	110.1 (3)	C(25)—C(24)—C(23)	120.1 (5)
C(5)—C(6)—C(13)	128.9 (4)	C(22)—C(23)—C(24)	120.2 (4)
O(3)—C(2)—C(3)	122.3 (4)	C(17)—C(16)—C(15)	120.7 (5)
O(3)—C(2)—C(21)	110.1 (4)	C(3)—C(19)—O(1)	124.7 (5)
C(3)—C(2)—C(21)	127.6 (5)	C(7)—C(12)—C(11)	119.6 (7)
C(5)—C(20)—O(2)	122.9 (5)	C(14)—C(15)—C(16)	119.9 (5)
C(21)—C(26)—C(25)	121.1 (4)	C(8)—C(9)—C(10)	121.1 (7)

Data were collected with a variable scan rate and a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *XP* (Siemens, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Four Diterpene Isonitriles from the Sponge *Cymbastela hooperi*

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Abstract

The low-temperature X-ray structures of four isomeric diterpene isonitriles, $C_{21}H_{31}N$, obtained from the sponge *Cymbastela hooperi*, are reported. These are the tetracyclic compounds, (1*S**,3*S**,4*R**,7*S**,8*S**,12*S**,13*S**)-7-isocyanocycloamphilect-11(20)-ene (alternative name: 1,4,7,7-tetramethyl-1,2,3,3a,4,5,5a,6,7,9,10,10a,10b,10c-tetradecahydropyrenyl 1-isocyanide) and (1*S**,3*S**,4*R**,7*S**,8*S**,11*R**,12*R**,13*S**,20*S**)-7-isocyanoisocycloamphilect-14-ene (alternative name: 1,4,7,8-tetramethyl-1,2,3,3a,4,5,5a,8,8a,9,10,10a,10b,10c-tetradecahydropyrenyl 1-isocyanide), and the tricyclic compounds, (1*S**,3*S**,4*R**,7*S**,8*S**,12*S**,13*S**)-7-isocyanoamphilecta-11(20),15-diene [alternative name: 1,4-dimethyl-7-methylene-6-(2-methyl-2-propenyl)perhydro-1*H*-phenalenyl 1-isocyanide] and (1*R**,3*S**,4*R**,7*S**,8*S**,13*R**)-7-isocyanoamphilecta-11,14-diene [alternative name: 1,4,7-trimethyl-6-(2-methyl-1-propenyl)-2,3,3a,4,5,6,8,9,9a,9b-decahydro-1*H*-phenalenyl 1-isocyanide]. All of the structures exhibit *trans*-fused ring systems.

Comment

Naturally occurring isonitriles are relatively rare, although diterpene isonitriles are often found in sponges (Baker, Wells, Oberhänsli & Hawes, 1976; Wratten, Faulkner, Hirotsu & Clardy, 1978; Kazlauskas, Murphy,

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