Crystal Structure of 4-(1-Hydroxypropyl)-isochroman-1,3-dione

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The title compound ($C_{12}H_{10}O_4$) crystallizes in the triclinic space group $P\bar{1}$ with a = 7.367(3), b = 8.1188(3), c = 9.549(5) Å, α = 74.034(1)°, β = 84.374(2)°, γ = 64.581(3)°, Z = 2, and d_{calc} = 1.462 g cm^{-3}. It exhibits a strong intramolecular O–H$\cdots$O hydrogen bond and exists as the exocyclic enolic tautomer as it has been observed in solution. The structure is stabilized by C–H$\cdots\pi$, C–O$\cdots\pi$ and π-π stacking interactions between benzene and pyran rings.

Key words: 4-(1-Hydroxypropyl)-isochroman-1,3-dione, Exocyclic Enolic Tautomer, Hydrogen Bonds, π-π Stacking Interactions, Crystal Structure

Introduction

It has been previously shown by infrared analysis [1] that, in the solid state, the 4-benzoyl isochroman-1,3-dione has a dicarbonyl structure. In solution, this compound revealed the presence of an exocyclic enolic tautomer [2]. Structure determination of the 4-benzoyl substituted compounds and *para*-disubstituted isomers [3 – 5] has also shown an enolic form in the solid state. In addition, if the 4-aroyl-isochroman-1,3-dione exhibits fluorescence, the *para*-substituted derivatives do not present this property for examples with electron-withdrawing groups (NO_2 or CN). To better understand the tautomeric relation and its effects on physical and chemical properties (fluorescence, anti-oxydant, *etc.*) [6], the synthesis of the title compound, an alkanoyl substituted compound, has been carried out by the replacement of the 4-aroyl by a 4-alkanoyl substituent[2].

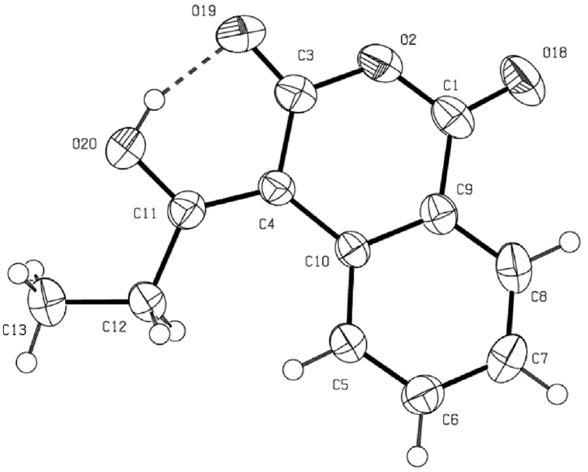

Fig. 1. The molecular structure of the title compound showing the atomic labeling scheme, with displacement ellipsoids drawn at the 50 % level. The dashed line indicates the hydrogen bond.

Results and Discussion

A view of the molecule with the numbering of the atoms is given in Fig. 1.

Assessment of tautomeric form

The title compound shows the exocyclic enolic tautomer as observed in solution. This tautomeric form is confirmed by the distances d(C3–O19) = 1.229(4) and d(C11–O20) = 1.308(3) Å which have intermediate values between a C(sp^3)–O (1.42 Å) group and the carbonyl form of an anhydride (1.16 Å) [7].

Geometry and conformation

The interatomic distances and bond angles, hydrogen bonds, C–O$\cdots\pi$ and π-π stacking interactions are reported in Tables 2 – 5, respectively. The analysis and interpretation of the geometrical characteristics relating to bond lengths compared to standard values [8] indicate that the carbon-oxygen bond C11–O20 (1.308(3) Å) is characteristic of a single bond C(sp^2)–O(sp^2) in enol tautomers with a standard value of 1.333 Å. The distances d(C1–O18) = 1.203(3) and d(C3–O19) = 1.229(4) Å are slightly shorter and longer, respectively, than the standard value (1.210 Å) indicating a double bond C=O. The bond length C4–C11 of 1.392(4) Å indicates an intermediate bond between C=C double bonds in enol tau-

Table 1. Crystal structure data.

Formula	$C_{12}H_{10}O_4$
M_r	218.21
Cryst. size, mm^3	$0.4 \times 0.2 \times 0.05$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	7.367(3)
b, Å	8.1188(3)
c, Å	9.549(5)
α, deg	74.034(1)
β, deg	84.374(2)
γ, deg	64.581(3)
V, Å^3	495.8(3)
D_{calc}, g cm^{-3}	1.462
μ(MoK_α), cm^{-1}	1.11
F(000), e	228
hkl range	$0 \le h \le +9$, $-9 \le k \le +10$, $-12 \le l \le +12$
2θ range, deg	4.4 – 57.4
Refl. measured / unique / R_{int}	5543 / 2428 / 0.065
Refl. ($I \ge 3\sigma I$)	1466
Param. refined	146
$R(F)\,/\,wR(F^2)$ ($I \ge 3\,\sigma(I)$)^a	0.0597 / 0.1383
$R(F)\,/\,wR(F^2)$ (all refl.)^a	0.0996 / 0.1668
Goodness of fit (F^2)	0.965
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.21 / −0.25

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.76P]$, $P = (\max(F_o{}^2, 0) + 2F_c{}^2)/3$.

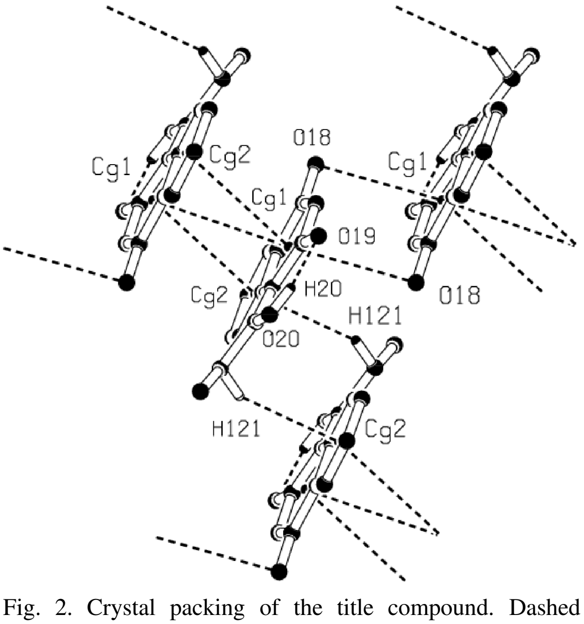

Fig. 2. Crystal packing of the title compound. Dashed lines indicate hydrogen bonds O–H···O and π-π, C–H··· π, C–O··· π stacking interactions. H atoms not involved in hydrogen bonds or π-ring interactions have been omitted for clarity.

tomers and C(sp^2)–C(sp^2) single bonds with standard values of 1.362 and 1.460 Å, respectively. All

Table 2. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses.

O18–C1	1.203(3)	O19–C3	1.229(4)
O20–C11	1.308(4)	C1–O2	1.372(4)
O2–C3	1.363(3)	C4–C11	1.392(4)
O20–H20	0.853		
O19–C3–C4	125.8(3)	C3–C4–C11	115.2(2)
C4–C11–O20	120.9(3)	O20–C11–C12	112.1(2)

Table 3. Hydrogen bond parameters (Å, deg) [9]^a.

D–H···A	D–H	H···A	D···A	D–H···A
O20–H20···O19	0.853	1.63	2.438(4)	156
C12–H121···Cg2^i	0.96	2.84	3.668(5)	145

[a] Symmetry code: ^{i} x, $-1-y$, $1-z$.

Table 4. π Ring Y–X···Cg interactions geometry (Å, deg) [9]^a.

Y–X···A	Y–X	X···Cg	Y···Cg	Y–X···Cg
C1–O18···Cg1^i	1.203(3)	3.376(4)	3.556 (4)	88.6(2)

[a] Symmetry code: ^{i} $1-x$, $-y$, $1-z$.

Table 5. Short ring interactions (π-π stacking interactions) geometry (Å) [9].

Cg(I)···Cg(J)	Symmetry code Cg(J)	Distance Cg(I)···Cg(J)	Cg(I)_Perp
Cg1···Cg1	$-x$, $-y$, $1-z$	3.810(3)	3.3805(13)
Cg1···Cg2	$-x$, $-y$, $1-z$	3.635(3)	3.4233(13)
Cg2···Cg1	$-x$, $-y$, $1-z$	3.635(3)	3.5038(14)

these values are in good agreement with our earlier reports [7].

In the crystal structure, the two fused six-membered rings are essentially planar with the maximum deviation from planarity being 0.076(4) Å for atom C3. The six-membered ring formed by the strong intramolecular O–H···O hydrogen bond is roughly planar and makes a dihedral angle of 8.39(13)° with the two fused ring planes. Furthermore, the face-to-face separation of 3.504(1) Å between parallel molecules of the title compound, the C–H···Cg2 angle of 145° and H···Cg2 separation of 2.84 Å, the C–O···Cg1 angle of 88.6(2)° and O···Cg1 separation of 3.376(4) Å (where Cg2 and Cg1 are the centroids of the benzene and pyran rings, respectively) suggest the existence of π-π, C–H···π and C–O···π stacking interactions (Tables 3 – 5) [9]. The molecules interconnected by these interactions are shown in Fig. 2.

Conclusion

The results of our investigation show that the alkanoyl substituted compound, the 4-benzoyl substituted compounds and its *para*-disubstituted isomers have the same enolic tautomer forms. This form may be induced by the formation of the strong intramolecular O–H···O hydrogen bond.

Experimental Section

Synthesis of 4-(1-hydroxypropyl)-isochroman-1,3-dione

The compound was obtained by a previously described procedure [2] by adding successively 28 mL of anhydrous pyridine and 0.07 mol of propionic anhydride to 150 mL of diethyl ether. To this mixture, 0.065 mol of commercial homophthalic anhydride was added in small portions during about 30 min. At the end of the addition, the reaction mixture was left under agitation for 3 h at room temperature. The resulting precipitate was filtered off with suction, washed with hexane and dissolved in a minimum of chloroform by heating under agitation. To this hot mixture, pentane was added until the formation of a new precipitate started which dissolved in the resulting mixture upon heating. Upon cooling white crystals of the title compound precipitated in a yield of 90 %; m. p. 116 – 118 °C.

X-Ray structure determination

Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from chloroform/pentane. Lattice parameters and X-ray intensity data were measured with a Nonius KappaCCD diffractometer using a graphite monochromator and MoK_α radiation (Table 1). The structure was solved by Direct Methods using SIR2004 [10] and refined with the program CRYSTALS [11]. Non-hydrogen atoms parameters were refined anisotropically. Hydrogen atoms were placed at calculated positions with C–H = 0.93 Å (aromatic) or 0.96 Å (methylene and methyl) except for the H atom bonded to the oxygen atom which was found in the difference Fourier map. Their positions were refined using a riding model.

CCDC 707004 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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