

## 4-[(1,3-Dioxoisochroman-4-ylidene)-hydroxymethyl]benzonitrile

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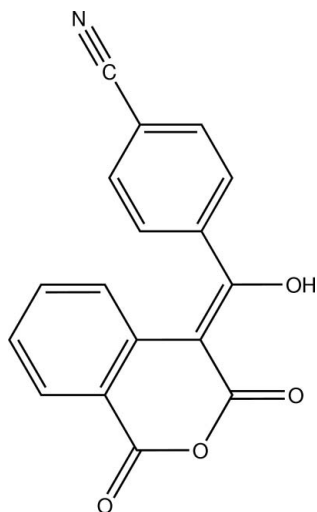
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Key indicators: single-crystal X-ray study;  $T = 294$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.050;  $wR$  factor = 0.125; data-to-parameter ratio = 11.8.

The crystal structure of the title compound,  $\text{C}_{17}\text{H}_9\text{NO}_4$ , shows that the exocyclic enolic tautomer exists as it has been observed in solution. The structure is stabilized by intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding.

## Related literature

For related literature, see: Saba *et al.* (1996); Saba (1996); Schenckenburger (1965). For related structures, see: Kakou-Yao *et al.* (1999*a,b*); Kakou-Yao, Saba, Ebby, Pierrot & Aycard (1999).



## Experimental

## Crystal data

$\text{C}_{17}\text{H}_9\text{NO}_4$	$V = 1326.77$ (7) Å <sup>3</sup>
$M_r = 291.26$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.9944$ (3) Å	$\mu = 0.11$ mm <sup>-1</sup>
$b = 9.3091$ (3) Å	$T = 294$ K
$c = 14.3752$ (5) Å	$0.40 \times 0.40 \times 0.40$ mm
$\beta = 97.245$ (1)°	

## Data collection

Nonius KappaCCD diffractometer	3886 independent reflections
Absorption correction: none	2342 reflections with $I > 3\sigma(I)$
4113 measured reflections	$R_{\text{int}} = 0.041$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	199 parameters
$wR(F^2) = 0.125$	H-atom parameters not refined
$S = 0.91$	$\Delta\rho_{\text{max}} = 0.27$ e Å <sup>-3</sup>
2342 reflections	$\Delta\rho_{\text{min}} = -0.25$ e Å <sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}20-\text{H}20\cdots\text{O}19$	0.87	1.74	2.523 (2)	149

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

We thank Laboratoire de Spectropôle, Université Paul Cézanne, Marseille, France.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN3062).

## References

- Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Kakou-Yao, R., Saba, A., Ebby, N. & Aycard, J. P. (1999*a*). *Z. Kristallogr. New Cryst. Struct.* **214**, 483–484.
- Kakou-Yao, R., Saba, A., Ebby, N. & Aycard, J. P. (1999*b*). *Z. Kristallogr. New Cryst. Struct.* **214**, 485–486.
- Kakou-Yao, R., Saba, A., Ebby, N., Pierrot, M. & Aycard, J. P. (1999). *Acta Cryst.* **C55**, 1591–1593.
- Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Saba, A. (1996). Thèse d'état ès Sciences Physiques, Ouagadougou, Burkina Faso.
- Saba, A., Sib, F. S., Faure, R. & Aycard, J. P. (1996). *Spectrosc. Lett.* **29**, 1649–1657.
- Schenckenburger, J. (1965). *Arch. Pharm.* **298**, 411–423.

**supplementary materials**

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## 4-[(1,3-Dioxoisochroman-4-ylidene)hydroxymethyl]benzotrile

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### Comment

It has been previously shown by infrared analysis (Schenckenburger, 1965) that, in solid state, the isochroman-1,3-dione has a dicarbonyl structure. In solution this compound, revealed the presence of an exocyclic enolic tautomer (Saba *et al.*, 1996). Structural determination of the same compound by (Kakou-Yao *et al.*, 1999a,b; Kakou-Yao, Saba, Ebby, Pierrot & Aycard, 1999) has shown also an enolic form in the solid. In addition, if the 4-aryl isochroman-1,3-diones exhibits fluorescence property, the *para* substituted derivatives does not present this property when the group in *para* position is a high electron withdrawing group (NO<sub>2</sub> or CN). To understand the tautomeric problem and its effects on fluorescence properties, the synthesis of the title compound has been carried out by making *para* substitution on the benzyl cycle of the isochroman-1,3-dione molecule.

The molecular structure of the title compound, 4-( $\alpha$ -hydroxy-*p*-cyanobenzyl)isochroman-1,3-dione, shows the same enolic tautomer as the nitro and fluoro compounds already reported (Kakou-Yao *et al.*, 1999a,b; Kakou-Yao, Saba, Ebby, Pierrot & Aycard, 1999). This tautomeric form is confirmed by the distances C3—O19 = 1.216 (2) Å and C11—O20 = 1.323 (2) Å which are intermediate values between Csp<sub>3</sub>—O (1.42 Å) group and anhydride of carbonylform (1.16 Å). There is a strong intramolecular O—H···O bond which stabilizes the conformation (Table 1).

The two fused six membered rings are nearly planar with the largest deviation being 0.148 at C3. They make a dihedral angle of 54.07 (4)° with the cyanobenzyl plane. The pseudo six-membered ring formed by the intramolecular O—H···O bond is roughly planar and is twisted by 17.61 (4)° with the two fused rings plane.

In conclusion, the results of our investigation show that the nitro, fluoro and cyano *para* substituted compounds have the same enolic tautomer forms. This form may be induced by the formation of the strong intramolecular O—H···O hydrogen bond.

### Experimental

The compound is obtained from a previously described procedure (Saba, 1996) by reaction of 200 ml of THF with 40 mmol of chlorure of benzoyl, 0.12 mol of triethylamine and HCl diluted solution. The organic phase is washed, neutralized, dried and evaporated. The compound was crystallized in CH<sub>2</sub>Cl<sub>2</sub>.

### Refinement

H atoms attached to carbon are treated as riding on their parent C atoms. H20 is obtained by Fourier difference but treated as riding on the parent O atom.

## Figures

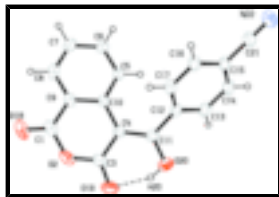


Fig. 1. Molecular view showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii. Hydrogen bond is shown as dashed line.

## 4-[(1,3-Dioxoisochroman-4-ylidene)hydroxymethyl]benzonitrile

### Crystal data

$C_{17}H_9N_1O_4$

$M_r = 291.26$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.9944$  (3) Å

$b = 9.3091$  (3) Å

$c = 14.3752$  (5) Å

$\beta = 97.2450$  (10)°

$V = 1326.77$  (7) Å<sup>3</sup>

$Z = 4$

$F_{000} = 600$

$D_x = 1.458$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 21043 reflections

$\theta = 2.1$ – $30.2$ °

$\mu = 0.11$  mm<sup>-1</sup>

$T = 294$  K

Cubic, yellow

$0.40 \times 0.40 \times 0.40$  mm

### Data collection

Nonius KappaCCD  
diffractometer

Monochromator: graphite

$T = 294$  K

$\varphi$  scans

Absorption correction: none

4113 measured reflections

3886 independent reflections

2342 reflections with  $I > 3\sigma(I)$

$R_{int} = 0.041$

$\theta_{max} = 30.2$ °

$\theta_{min} = 2.1$ °

$h = 0 \rightarrow 14$

$k = 0 \rightarrow 13$

$l = -20 \rightarrow 20$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters not refined

Chebyshev polynomial [Watkin, D. (1994). *Acta Cryst.* A50, 411–437. Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science* Springer-Verlag, New York.] [weight] =  $1.0/[A_0 * T_0(x) + A_1 * T_1(x) \dots + A_{n-1} * T_{n-1}(x)]$

where  $A_i$  are the Chebyshev coefficients listed below and  $x = F/F_{max}$  Method = Robust Weighting

(Prince, 1982)  $W = [\text{weight}] * [1 - (\Delta F / 6 * \sigma_{\text{ma}F})^2]^2$   $A_i$  are: 333. 498. 301. 108.  
 $(\Delta/\sigma)_{\text{max}} = 0.0004$   
 $\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.25 \text{ e } \text{Å}^{-3}$   
 Extinction correction: None

$wR(F^2) = 0.125$   
 $S = 0.91$   
 2342 reflections  
 199 parameters  
 Primary atom site location: structure-invariant direct methods

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{Å}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.50626 (15)	-0.04093 (16)	0.61652 (10)	0.0649
O20	0.84144 (19)	-0.11007 (16)	0.80705 (11)	0.0770
C17	0.76804 (17)	0.2051 (2)	0.91579 (12)	0.0500
C15	0.95922 (17)	0.28840 (19)	1.01898 (11)	0.0479
O18	0.33737 (15)	0.0948 (2)	0.55713 (13)	0.0874
C5	0.72805 (16)	0.32456 (17)	0.71405 (11)	0.0431
C10	0.65110 (15)	0.20037 (17)	0.69253 (10)	0.0393
C14	1.04403 (18)	0.2052 (2)	0.97158 (14)	0.0572
C4	0.69481 (17)	0.05562 (17)	0.72106 (11)	0.0453
C6	0.68116 (18)	0.45734 (18)	0.68391 (13)	0.0499
C11	0.79395 (19)	0.02193 (19)	0.79341 (13)	0.0509
N22	1.0467 (2)	0.4419 (2)	1.16293 (14)	0.0748
C7	0.55762 (19)	0.4727 (2)	0.62919 (15)	0.0593
C12	0.85219 (17)	0.11981 (19)	0.86907 (11)	0.0470
C8	0.48183 (18)	0.3526 (2)	0.60371 (14)	0.0587
C13	0.99018 (19)	0.1196 (2)	0.89771 (13)	0.0564
C21	1.0108 (2)	0.3743 (2)	1.09855 (13)	0.0557
C16	0.82107 (17)	0.2886 (2)	0.99060 (12)	0.0502
C9	0.52799 (16)	0.2176 (2)	0.63462 (12)	0.0469
C1	0.44722 (19)	0.0937 (2)	0.60105 (13)	0.0583
O19	0.6651 (2)	-0.18811 (16)	0.67563 (13)	0.0859
C3	0.6269 (2)	-0.0640 (2)	0.67100 (13)	0.0580
H17	0.6742	0.2041	0.8961	0.0585*
H5	0.8133	0.3177	0.7492	0.0513*
H14	1.1405	0.2077	0.9902	0.0668*
H6	0.7339	0.5410	0.6999	0.0591*
H7	0.5251	0.5689	0.6082	0.0712*
H8	0.3977	0.3597	0.5659	0.0690*
H13	1.0472	0.0619	0.8657	0.0672*

## supplementary materials

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H16	0.7651	0.3500	1.0216	0.0599*
H20	0.8026	-0.1604	0.7606	0.1115*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O2	0.0704 (8)	0.0638 (9)	0.0580 (8)	-0.0242 (7)	-0.0012 (7)	-0.0132 (6)
O20	0.1147 (13)	0.0427 (7)	0.0672 (9)	0.0149 (8)	-0.0142 (8)	0.0028 (6)
C17	0.0426 (8)	0.0604 (10)	0.0456 (8)	0.0014 (7)	0.0007 (6)	0.0007 (7)
C15	0.0523 (9)	0.0505 (9)	0.0386 (8)	-0.0006 (7)	-0.0028 (6)	0.0058 (7)
O18	0.0541 (8)	0.1130 (14)	0.0896 (12)	-0.0251 (9)	-0.0129 (8)	-0.0120 (11)
C5	0.0415 (7)	0.0436 (8)	0.0425 (8)	-0.0016 (6)	-0.0019 (6)	0.0015 (6)
C10	0.0391 (7)	0.0419 (8)	0.0367 (7)	-0.0017 (6)	0.0037 (6)	-0.0020 (6)
C14	0.0450 (9)	0.0691 (12)	0.0543 (10)	0.0069 (8)	-0.0063 (7)	0.0020 (9)
C4	0.0545 (9)	0.0387 (8)	0.0417 (8)	-0.0043 (6)	0.0015 (6)	-0.0025 (6)
C6	0.0536 (9)	0.0412 (8)	0.0541 (9)	-0.0015 (7)	0.0037 (7)	0.0007 (7)
C11	0.0651 (10)	0.0390 (8)	0.0477 (8)	0.0037 (7)	0.0032 (7)	0.0027 (7)
N22	0.0824 (13)	0.0750 (12)	0.0628 (11)	-0.0076 (10)	-0.0067 (9)	-0.0104 (9)
C7	0.0558 (10)	0.0549 (10)	0.0658 (12)	0.0124 (8)	0.0017 (9)	0.0105 (8)
C12	0.0539 (9)	0.0456 (8)	0.0396 (8)	0.0037 (7)	-0.0011 (7)	0.0044 (7)
C8	0.0425 (8)	0.0733 (13)	0.0571 (10)	0.0064 (8)	-0.0056 (7)	0.0069 (9)
C13	0.0512 (9)	0.0640 (12)	0.0522 (9)	0.0148 (8)	0.0002 (7)	-0.0020 (8)
C21	0.0598 (10)	0.0564 (11)	0.0481 (9)	-0.0038 (8)	-0.0038 (8)	0.0020 (8)
C16	0.0490 (9)	0.0585 (10)	0.0429 (8)	0.0048 (7)	0.0055 (7)	-0.0003 (7)
C9	0.0384 (7)	0.0589 (10)	0.0429 (8)	-0.0076 (7)	0.0032 (6)	-0.0036 (7)
C1	0.0498 (9)	0.0716 (12)	0.0526 (10)	-0.0162 (9)	0.0035 (8)	-0.0068 (9)
O19	0.1348 (16)	0.0405 (8)	0.0770 (11)	-0.0089 (8)	-0.0074 (10)	-0.0063 (7)
C3	0.0797 (13)	0.0445 (9)	0.0488 (9)	-0.0144 (8)	0.0042 (9)	-0.0048 (7)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O2—C1	1.392 (3)	C14—H14	0.968
O2—C3	1.369 (3)	C4—C11	1.379 (2)
O20—C11	1.323 (2)	C4—C3	1.448 (2)
O20—H20	0.867	C6—C7	1.385 (3)
C17—C12	1.390 (2)	C6—H6	0.952
C17—C16	1.378 (3)	C11—C12	1.481 (2)
C17—H17	0.945	N22—C21	1.139 (3)
C15—C14	1.389 (3)	C7—C8	1.374 (3)
C15—C21	1.437 (3)	C7—H7	0.987
C15—C16	1.389 (2)	C12—C13	1.389 (2)
O18—C1	1.195 (2)	C8—C9	1.392 (3)
C5—C10	1.401 (2)	C8—H8	0.945
C5—C6	1.373 (2)	C13—H13	0.945
C5—H5	0.937	C16—H16	0.949
C10—C4	1.459 (2)	C9—C1	1.455 (2)
C10—C9	1.405 (2)	O19—C3	1.216 (2)
C14—C13	1.381 (3)		

C1—O2—C3	123.92 (14)	C6—C7—C8	119.31 (17)
C11—O20—H20	105.7	C6—C7—H7	120.2
C12—C17—C16	120.19 (16)	C8—C7—H7	120.5
C12—C17—H17	119.2	C11—C12—C17	120.05 (15)
C16—C17—H17	120.6	C11—C12—C13	120.05 (16)
C14—C15—C21	121.41 (16)	C17—C12—C13	119.76 (16)
C14—C15—C16	120.14 (16)	C7—C8—C9	120.00 (16)
C21—C15—C16	118.44 (17)	C7—C8—H8	121.1
C10—C5—C6	121.14 (14)	C9—C8—H8	118.9
C10—C5—H5	120.0	C12—C13—C14	120.23 (17)
C6—C5—H5	118.9	C12—C13—H13	119.6
C5—C10—C4	124.28 (14)	C14—C13—H13	120.2
C5—C10—C9	116.86 (15)	C15—C21—N22	177.2 (2)
C4—C10—C9	118.73 (14)	C15—C16—C17	119.90 (16)
C15—C14—C13	119.74 (15)	C15—C16—H16	119.1
C15—C14—H14	119.9	C17—C16—H16	120.9
C13—C14—H14	120.3	C10—C9—C8	121.50 (16)
C10—C4—C11	125.67 (14)	C10—C9—C1	120.92 (17)
C10—C4—C3	117.75 (15)	C8—C9—C1	117.51 (16)
C11—C4—C3	116.56 (16)	C9—C1—O2	117.05 (16)
C5—C6—C7	121.10 (16)	C9—C1—O18	127.1 (2)
C5—C6—H6	120.3	O2—C1—O18	115.75 (19)
C7—C6—H6	118.6	C4—C3—O2	119.16 (17)
C4—C11—O20	122.23 (16)	C4—C3—O19	125.4 (2)
C4—C11—C12	126.33 (16)	O2—C3—O19	115.37 (17)
O20—C11—C12	111.24 (15)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O20—H20...O19	0.87	1.74	2.523 (2)	149

Fig. 1

