Acta Cryst. (1996). C**52**, 2775–2777

The Acetyl Derivative of a Novel Fries Rearrangement Product

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(*Received 18 April 1996; accepted 25 June 1996*)

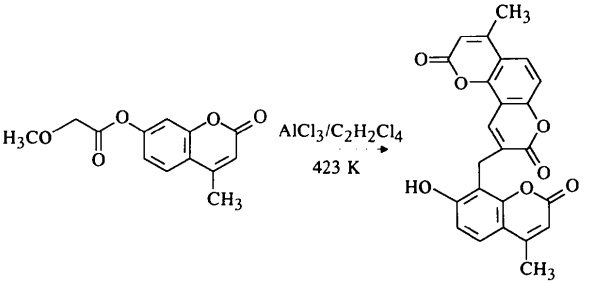
Abstract

The structure of the acetyl derivative of a novel Fries rearrangement product, 8,3′-methylene[7-acetoxy-4-methyl-2*H*-1-benzopyran-2-one][4″-methyl-2″*H*-1″-pyran-2″-one(5′,6′:6″,5″)-2′*H*-1′-benzopyran-2′-one] {IUPAC name 4-methyl-7-[(4-methyl-2,8-dioxo-2*H*,8*H*-pyrano[2,3-*h*]chromen-9-yl)methyl]-2-oxo-2*H*-chromen-6-yl acetate, $C_{26}H_{18}O_8$}, has been determined. The result confirms the somewhat surprising formation of a bis-coumarin derivative from a coumaryl ester. The planes of the two coumarin units are inclined at an angle of 74.7 (1)° with respect to one another and the exocyclic angles about the coumarin points of attachment to the methylene C atom show an interesting asymmetry.

Comment

Previous results from these laboratories (Jain *et al.*, 1996) have shown that when 7-*O*-methoxyacetyl-4-methyl-2*H*-1-benzopyran-2-one, (I), is subjected to a Fries (Martin, 1992) reaction under dry conditions using aluminium chloride as the Lewis acid, two new isomeric bis-coumarins, 8,8′-methylenebis(7-hydroxy-4-methyl-2*H*-1-benzopyran-2-one) and 6,8′-methylenebis(7-hydroxy-4-methyl-2*H*-1-benzopyran-2-one), are produced. This result was surprising because the simple rearrangement products, 7-hydroxy-8-methoxyacetyl-4-methyl-2*H*-1-benzopyran-2-one or 7-hydroxy-6-methoxyacetyl-4-methyl-2*H*-1-benzopyran-2-one, had been anticipated. Bis-coumarins are known to possess a wide range of activities such as antibacterial (Boguslaski, 1974), anti-asthmatic (Cairns *et al.*, 1972; Thaker & Dumir, 1977), antihelminthic (Sulko, 1971), anticancer (Frank, 1962), and insecticidal and pesticidal (McIntyre & Knight, 1970). We have thus repeated the reaction under different conditions with the objective of producing further bis-coumarins for biological testing.

When the reaction was repeated using acetylene tetrachloride as solvent, a new and unexpected product was obtained. This product differed in its physical and spectral properties from the earlier isomeric bis-coumarins and was not one of the simple rearrangement products. This novel Fries reaction product was characterized on the basis of detailed spectral studies as 8,3′-methylene-[7-hydroxy-4-methyl-2*H*-1-benzopyran-2-one][4″-methyl-2″*H*-1″-pyran-2″-one(5′,6′:6″,5″)-2′*H*-1′-benzopyran-2′-one], (II). However, as the proposed formulation was somewhat unexpected, an X-ray confirmation of the structure was desirable. All attempts to recrystallize (II) failed to give suitable single crystals and consequently the acetyl derivative was prepared and this gave crystals of the required quality.



(I) (II)

The molecular structure of the acetyl derivative of (II) is illustrated in Fig. 1 and confirms the spectral conclusions. The only previously reported bis-coumarin structures linked *via* a single C atom are the 4-hydroxyl derivatives, dicoumarol (Bravic, Gaultier & Hauw, 1968), dibromodicoumarol (Alcock & Hough, 1972), phenyldicoumarol (Valente & Eggleston, 1989) and α-naphthyldicoumarol (Csöregh & Eckstein, 1979). In each of these structures, intramolecular hydrogen bonding between the OH and C=O groups is an

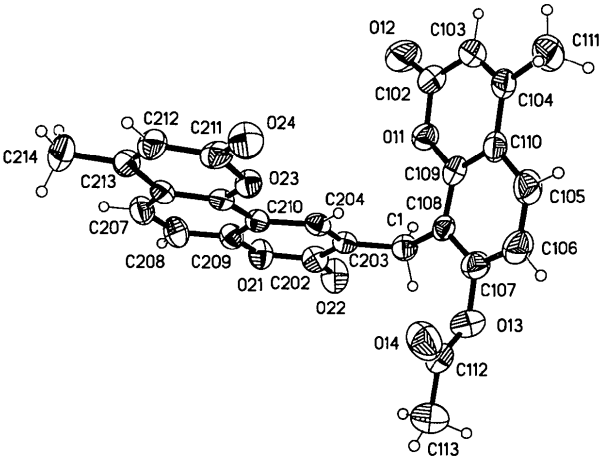


Fig. 1. View of the title molecule showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms C205 and C206 are not labelled.

important feature; the possibility of such an interaction in the title compound has been eliminated by the acetylation and thus the conformations of the title and parent compounds are likely to be significantly different.

The unit consisting of atoms O11 and C102–C110 is essentially planar [r.m.s. deviation 0.016 (3) Å] and is inclined at an angle of 74.7 (1)° with respect to the plane through atoms O21, O23 and C202–C213 [r.m.s. deviation 0.057 (3) Å]. The orientations of the coumarin rings with respect to the methylene bridge are given by the torsion angles C203—C1—C108—C107 of 107.0 (4) and C108—C1—C203—C202 of 177.0 (3)°.

Most of the bond lengths and angles are unexceptional, but the exocyclic angles about the coumarin points of attachment to the methylene carbon are of interest. The exocyclic angles at atom C203 [128.2 (3) and 111.4 (3)°] differ by 16.8°, but for those at C108 [122.5 (3) and 121.0 (3)°] the difference is only 1.5°; while this asymmetry has been previously noted for dicoumarols (*e.g.* Valente & Eggleston, 1989), the effect is largest in the title compound.

Experimental

Powdered anhydrous aluminium trichloride (1.9 g, 14.25 mmol) was added to a stirred mixture of (I) (1.0 g, 4.39 mmol) in 5 ml of acetylene tetrachloride. The reactants were maintained at a temperature of 423 K for ~2 h and then poured into an ice/HCl mixture. The solvent was removed under reduced pressure; cold water was then added and the water-soluble aluminium salts were filtered off to give a light-brown solid. The crude material was dissolved in $CHCl_3$–MeOH and compound (II) was isolated by column chromatography on silica gel using 5% MeOH in $CHCl_3$. A few drops of dry pyridine were added to a solution of (II) (0.02 g) in dry acetic anhydride (0.4 ml). The reaction mixture was warmed on a water bath and then maintained at room temperature for 24 h. The contents were poured into ice-cold water and the solid which separated was filtered and dried. The acetylated product was recrystallized from a chloroform–hexane mixture as a pale-yellow solid (m.p. 349 K).

Crystal data

$C_{26}H_{18}O_8$
M_r = 458.40
Monoclinic
$P2_1/n$
a = 13.630 (5) Å
b = 10.897 (4) Å
c = 14.546 (4) Å
β = 90.08 (3)°
V = 2160.5 (13) Å^3
Z = 4
D_x = 1.409 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 18 reflections
θ = 7–13°
μ = 0.106 mm^{-1}
T = 220 (2) K
Block
0.23 × 0.19 × 0.12 mm
Yellow

Data collection

Siemens $P3R3$ diffractometer
ω–2θ scans
R_{int} = 0.0425
θ_{max} = 27.52°
Absorption correction: analytical
T_{min} = 0.98, T_{max} = 0.99
3827 measured reflections
2594 independent reflections
1621 observed reflections [$I > 2\sigma(I)$]
$h = -17 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -14 \rightarrow 18$
3 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0475
$wR(F^2)$ = 0.1172
S = 1.021
2592 reflections
311 parameters
H atoms riding (see text)
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.4311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.006$
$\Delta\rho_{max}$ = 0.168 e Å^{-3}
$\Delta\rho_{min}$ = −0.189 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0060 (8)
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)*

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

	x	y	z	U_{eq}
O11	0.2692 (2)	−0.0913 (2)	0.4165 (2)	0.0449 (7)
O12	0.3713 (2)	0.0633 (3)	0.4310 (2)	0.0791 (11)
O13	0.0661 (2)	−0.4345 (2)	0.3701 (2)	0.0571 (8)
O14	−0.0705 (2)	−0.3541 (3)	0.3084 (2)	0.0737 (10)
O21	0.2973 (2)	−0.2109 (2)	0.0747 (2)	0.0449 (7)
O22	0.3498 (2)	−0.3552 (2)	0.1688 (2)	0.0558 (8)
O23	0.0363 (2)	0.0570 (2)	0.1502 (2)	0.0368 (7)
O24	−0.0810 (2)	0.1836 (2)	0.1928 (2)	0.0546 (8)
C1	0.2309 (3)	−0.2975 (3)	0.3132 (2)	0.0410 (10)
C102	0.3010 (3)	0.0122 (4)	0.4623 (3)	0.0553 (12)
C103	0.2440 (3)	0.0503 (4)	0.5404 (3)	0.0579 (12)
C104	0.1634 (3)	−0.0082 (3)	0.5674 (3)	0.0515 (12)
C105	0.0507 (3)	−0.1890 (4)	0.5408 (3)	0.0572 (12)
C106	0.0279 (3)	−0.2920 (4)	0.4918 (3)	0.0577 (12)
C107	0.0848 (3)	−0.3246 (3)	0.4177 (3)	0.0472 (11)
C108	0.1648 (3)	−0.2572 (3)	0.3903 (2)	0.0347 (9)
C109	0.1867 (3)	−0.1550 (3)	0.4425 (2)	0.0386 (10)
C110	0.1320 (3)	−0.1162 (3)	0.5179 (2)	0.0440 (10)
C111	0.1031 (4)	0.0379 (4)	0.6467 (3)	0.079 (2)
C112	−0.0132 (4)	−0.4369 (4)	0.3133 (3)	0.0556 (12)
C113	−0.0166 (4)	−0.5549 (4)	0.2611 (3)	0.084 (2)
C202	0.2936 (3)	−0.2711 (4)	0.1577 (3)	0.0427 (10)
C203	0.2227 (2)	−0.2280 (3)	0.2251 (2)	0.0319 (9)
C204	0.1618 (2)	−0.1368 (3)	0.2046 (2)	0.0330 (9)
C205	0.1065 (3)	0.0208 (3)	0.0890 (2)	0.0323 (9)
C206	0.1190 (3)	0.0819 (3)	0.0061 (2)	0.0368 (9)
C207	0.1909 (3)	0.0362 (4)	−0.0538 (3)	0.0468 (11)
C208	0.2477 (3)	−0.0624 (4)	−0.0311 (2)	0.0465 (11)
C209	0.2349 (3)	−0.1170 (3)	0.0535 (2)	0.0366 (10)
C210	0.1656 (2)	−0.0779 (3)	0.1166 (2)	0.0331 (9)
C211	−0.0219 (3)	0.1595 (3)	0.1348 (3)	0.0434 (10)
C212	−0.0052 (3)	0.2250 (3)	0.0508 (3)	0.0459 (11)
C213	0.0609 (3)	0.1891 (3)	−0.0121 (3)	0.0441 (10)
C214	0.0746 (3)	0.2588 (4)	−0.1002 (3)	0.0618 (13)

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

O11—C109	1.376 (4)	O21—C202	1.375 (4)
O11—C102	1.379 (5)	O22—C202	1.205 (4)
O12—C102	1.199 (4)	O23—C205	1.366 (4)
O13—C112	1.361 (5)	O23—C211	1.387 (4)
O13—C107	1.406 (4)	O24—C211	1.197 (4)
O14—C112	1.195 (5)	C1—C203	1.491 (4)
O21—C209	1.365 (4)	C1—C108	1.506 (4)

C109—O11—C102	122.4 (3)	O14—C112—O13	122.7 (4)
C112—O13—C107	117.3 (3)	O22—C202—O21	117.2 (3)
C203—C1—C108	116.6 (3)	O21—C202—C203	117.5 (3)
O12—C102—O11	116.6 (4)	C204—C203—C1	128.2 (3)
C107—C108—C1	122.5 (3)	C202—C203—C1	111.4 (3)
C109—C108—C1	121.0 (3)	O23—C205—C210	115.9 (3)
O11—C109—C108	115.6 (3)		

O12—C102—C103—C104	176.1 (4)
C112—O13—C107—C108	−108.8 (4)
O13—C107—C108—C1	−0.2 (5)
C203—C1—C108—C107	107.0 (4)
C203—C1—C108—C109	−78.5 (4)
C103—C104—C110—C105	177.7 (4)
O22—C202—C203—C204	−177.8 (4)
C108—C1—C203—C204	−2.3 (5)
C108—C1—C203—C202	177.0 (3)
O24—C211—C212—C213	−177.7 (4)

The temperature of the crystal was controlled using an Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model including free rotation of methyl groups about C—C bonds. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: Siemens *P3R3* system. Cell refinement: Siemens *P3R3* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

The authors wish to acknowledge the use of the Cambridge Structural Database (Allen *et al.*, 1991) through the EPSRC's Chemical Database Service at Daresbury. We also wish to thank the Council of Scientific and Industrial Research (CSIR, New Delhi, India) and the University Grants Commission (UGC, New Delhi, India) for the award of research fellowships.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1115). 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**, 2777–2779

2-{1-[(2-Amino-4,5-dimethylphenyl)imino]-ethyl}phenol

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(Received 7 March 1996; accepted 30 May 1996)

Abstract

In the title compound, $C_{16}H_{18}N_2O$, the imine N···O separation is 2.521 (2) Å, indicative of intramolecular hydrogen bonding within the salicylideneimine unit. The two aromatic rings are inclined at an angle of 50.04 (6)° with respect to one another, which results in a conformation unsuitable for meridional tridentate ligand complexation to a metal.

Comment

The X-ray structures of various metal complexes with tridentate Schiff base ligands have been reported (Elias, Hilms & Paulus, 1982; Roper, Paulus & Elias, 1989). Both square-planar and octahedral geometries are known, and in the latter case, the two ligands occupy meridional positions (Sim, Sinn, Petty, Merrill & Wilson, 1981). However, no X-ray structures of uncoordinated tridentate ligands of this type have yet been reported. We have therefore determined the crystal structure of the new NNO-donor tridentate ligand, (I), in order to assess the structural changes which occur upon coordination to a metal species and to compare these changes with those of the related ONNO-donor tetradentate ligands (Corden, Errington, Moore & Wallbridge, 1996; Cannadine, Corden, Errington, Moore & Wallbridge, 1996).