N1—C2—C3	122.7 (3)	C13—C8—N3	121.0 (3)
N1—C2—N2	118.7 (3)	C9—C8—N3	118.8 (3)
C3—C2—N2	118.6 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^{i}	0.89 (1)	2.54 (1)	3.414 (3)	168 (3)
C3—H3···S1^{i}	0.93 (1)	2.83 (1)	3.644 (4)	146.7 (3)
N3—H3*A*···N1	0.89 (1)	1.95 (3)	2.646 (4)	133 (3)

Symmetry code: (i) $-x, 1-y, 1-z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1068). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 813–815

7-Hydroxy-4-(4-methoxyphenyl)-3,4-dihydrocoumarin

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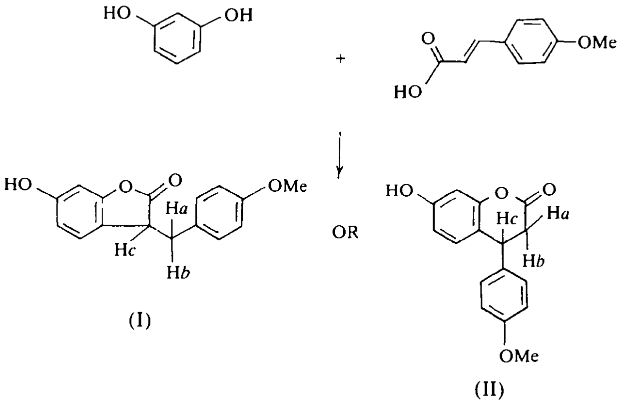
Abstract

The heterocyclic ring of the title compound, $C_{16}H_{14}O_4$, is in a half-chair conformation. The best planes through the two phenyl rings make an angle of 61.0 (1)°. The packing of the molecules is stabilized by intermolecular O—H···O and C—H···O hydrogen bonds.

Comment

Direct condensation between phenols and free cinnamic acids has been studied using concentrated hydrochloric acid (Simpson & Stephen, 1956), boron trifluoride (Main & Venkataraman, 1954), polyphosphoric acid (Reichel & Proksch, 1971; Talapatra *et al.*, 1986), trifluoroacetic acid (Chaturvedi & Mulchandani, 1990) and zinc chloride–oxotriphosphorus chloride (Suresh *et al.*, 1986) as the condensation reagent. Careful perusal of the reported results clearly indicates that the outcome of the reaction between the chalcone and 4-phenylcoumarin is highly dependent on the reagent, nature of the phenol and the acid (substitution). This report is primarily concerned with the reaction product obtained from the reaction between resorcinol and cinnamic acid in the presence of trifluoroacetic acid (TFA) as the condensation reagent. Two structures, (I) and (II), are possible for this product (see scheme). Its IR spectrum



shows a carbonyl absorption at 1740 cm^{-1}, but the ^{1}H NMR spectrum was not of sufficient quality to allow reliable assignment of proton signals. The X-ray studies established the dihydrocoumarin structure (II) for the reaction product. Likewise, all other examples reported by Chaturvedi & Mulchandani (1990) should be regarded as 3,4-dihydrocoumarins and not benzofuranones.

A perspective view of the molecule with atom numbering is shown in Fig. 1. Rings *A* and *B* are both planar within experimental observations. Ring *A* makes an angle of 61.0 (1)° with the best plane through *B* and an angle of 106.3 (2)° with the heterocyclic ring. The heterocyclic ring is in a half-chair conformation. The bonds C8—C7, C7—O2 and C5—O2 exhibit partial double-bond character. The methyl group (C16) lies almost in the plane of ring *A* as indicated by the value of 3.2 (3)° for the torsion angle C14—C13—O4—C16. The molecules are linked in the unit cell by one O—H···O and two C—H···O hydrogen bonds (Table 2).

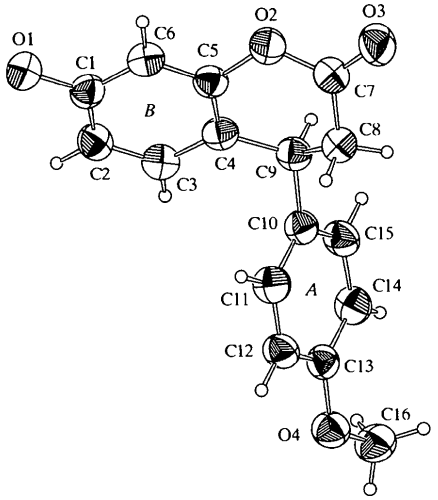


Fig. 1. A perspective view of the title compound showing the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

Experimental

The reaction between resorcinol and cinnamic acid gave 2′,4′-dihydroxychalcone in about 45% yield and the rest was a mixture of unchanged reactants. The TFA–resorcinol–cinnamic acid reaction proceeds slowly at room temperature but is nearly completed (no resorcinol, thin-layer chromatography) at reflux temperature in 2 h. The product of the reaction between resorcinol and 4-methoxycinnamic acid is a white crystalline solid (m.p. 451 K) formed in 80% yield as the only product (see Scheme). This compound is soluble in aqueous alkali and is regenerated on acidification. Single crystals were obtained by slow evaporation from a methanolic solution.

Crystal data

$C_{16}H_{14}O_4$
$M_r = 270.27$
Orthorhombic
Pbca
$a = 7.669\,(5)$ Å
$b = 12.402\,(8)$ Å
$c = 27.204\,(7)$ Å
$V = 2587.4\,(25)$ Å^3
$Z = 8$
$D_x = 1.388$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 9–30°$
$\mu = 0.824$ mm^{-1}
$T = 293\,(2)$ K
Rectangular prism
0.4 × 0.4 × 0.3 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2450 measured reflections
2450 independent reflections
2240 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 70.04°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 33$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.192$
$S = 1.114$
2441 reflections
237 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1273P)^2 + 0.9638P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.365 (3)	O4—C13	1.368 (3)
O2—C7	1.352 (3)	O4—C16	1.422 (3)
O3—C7	1.200 (3)	C9—C10	1.522 (3)
O1—C1—C2—C3	−177.3 (2)	C4—C9—C10—C15	134.9 (2)
C3—C4—C5—C6	1.5 (3)	C8—C9—C10—C15	−103.0 (2)
C9—C4—C5—C6	−179.2 (2)	C4—C9—C10—C11	−48.6 (3)
C3—C4—C5—O2	−176.9 (2)	C16—O4—C13—C14	3.2 (3)
C9—C4—C5—O2	2.4 (3)	C16—O4—C13—C12	−177.2 (2)
O1—C1—C6—C5	177.4 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—HO1···O3^{i}	0.87 (2)	1.94 (2)	2.806 (3)	174 (3)
C8—H82···O1^{ii}	0.97 (2)	2.53 (2)	3.457 (3)	160 (2)
C15—H15···O4^{iii}	0.97 (2)	2.46 (2)	3.314 (3)	146 (2)

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SDP* (Frenz, 1978). Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1983).

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A chain of fused $R_2^2(10)$ and $R_6^4(12)$ rings in the hydrogen-bonded structure of 1,4,8,11-tetraazacyclotetradecane–2,2′-biphenol (1/2)

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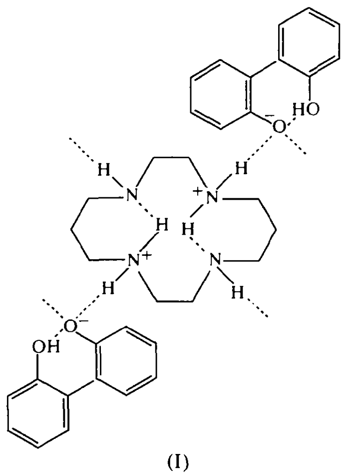
Abstract

The title compound is a salt, *i.e.* 4,11-diaza-1,8-diazoniacyclotetradecane bis[2-(2-hydroxyphenyl)phenolate], $C_{10}H_{26}N_4^{2+}\cdot 2HOC_6H_4C_6H_4O^-$. The centrosymmetric cation contains two intramolecular N—H···N hydrogen bonds, with an N···N distance of 2.865 (2) Å, and the anion contains an intramolecular O—H···O hydrogen bond, with an O···O distance of 2.486 (2) Å. The ions are linked into continuous chains by means of two types of N—H···O hydrogen bond having N···O distances of 2.682 (2) and 3.273 (2) Å.

Comment

The macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane (cyclam, $C_{10}H_{24}N_4$) forms adducts with both 4,4′-thiodiphenol and 4,4′-sulfonyldiphenol of 1:2 stoichiometry which are salts $[cyclamH_2]^{2+}\cdot 2[HOC_6H_4X\text{-}C_6H_4O]^-$, where X = S or SO_2 (Ferguson *et al.*, 1998). In each of these adducts, the bis-phenol molecules have each transferred one proton to the cyclam, and the resulting phenolate anions are linked by means of O—H···O hydrogen bonds. Pairs of antiparallel chains are then linked by centrosymmetric $[cyclamH_2]^{2+}$ cations to form molecular ladders.

While the disposition of the hydroxy groups in 4,4′-disubstituted bis-phenols is ideal for the formation of extended chains, this is by no means obviously the case for 2,2′-biphenol, where the formation of an intramolecular O—H···O hydrogen bond is a plausible alternative. We report here the formation and structure of the 1:2 adduct (I), formed between cyclam and 2,2′-biphenol. The resulting structure is a one-dimensional hydrogen-bonded polymer, but this takes the form of a chain-of-rings (Bernstein *et al.*, 1995), rather than that of a molecular ladder (Ferguson *et al.*, 1998).



(I)

The constitution of the 1:2 adduct (I) is that of a salt, $[C_{10}H_{26}N_4]^{2+}\cdot 2[HOC_6H_4C_6H_4O]^-$, in which the asymmetric unit consists of one phenolate anion and one half of a $[cyclamH_2]^{2+}$ cation lying across a centre of inversion (Fig. 1). As observed previously

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