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An Unexpected Product of an Indium-Mediated Carbon–Carbon Coupling: 2-(1-Phenyl-1,3-butadien-2-yl)benzoic Acid

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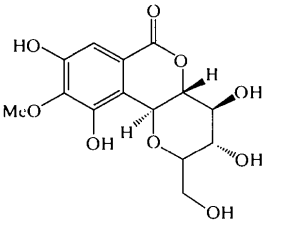
Abstract

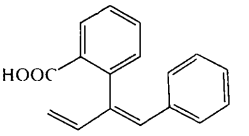
The title compound, 2-(1-phenyl-1,3-butadien-2-yl)-benzoic acid, $C_6H_5CH{=}C(C_6H_4COOH)CH{=}CH_2$ (or $C_{17}H_{14}O_2$), has been obtained as the major product from an indium-mediated coupling of benzaldehyde with methyl *o*-(3-bromo-1-propynyl)benzoate. The compound crystallizes as centrosymmetric hydrogen-bonded dimers. The diene portion is in the *s-trans* conformation, with the aromatic groups *cis* to one another.

Comment

Recent developments in Barbier–Grignard-type C—C bond-formation reactions in aqueous media (Li, 1993; Li & Chan, 1997; Lubineau *et al.*, 1994) present opportunities for the synthesis of heavily oxygenated compounds of biological significance. The success of a synthesis of (+)-goniofufurone *via* a highly regio- and diastereoselective indium-mediated allenylation of carbonyl compounds in an aqueous medium (Yi *et al.*, 1998) led us to consider similar chemistry in a synthesis of bergenin (*A*). To model the initial step of the proposed synthesis, which was expected to generate a δ-lactone, the indium-mediated coupling of aldehydes with methyl *o*-(3-bromo-1-propynyl)benzoate in aqueous DMF was studied (Hua *et al.*, 1998). Under these conditions, several linear aldehydes, for example hexaldehyde, gave the desired δ-lactone but, in the case of benzaldehyde, it was evident from spectroscopic data that the major product obtained (55% yield) was not the expected δ-lactone, although these data did not enable an unequivocal determination of its structure to be made. Because this last reaction took a course different from that expected, it was of interest to determine the structure of the product, although, even with this in hand, the mechanism by which it is formed is still unclear.



(*A*)



(1)

2-(1-Phenyl-1,3-butadien-2-yl)benzoic acid, (1), exists in the solid as hydrogen-bonded dimers disposed about centers of symmetry [*e.g.* $(1,1,\frac{1}{2})$]. There is disorder in the carboxyl group, as evidenced both by a difference map, which showed somewhat elongated regions of electron density close to both O atoms, and also by the

C—O distances. As is evident from Fig. 1, (1) is in the *s-trans* conformation and the two phenyl substituents are *cis* to one another. A small number of 1,2-diarylbuta-1,3-dienes are known (Häussinger & Kresze, 1978; Takahashi *et al.*, 1995, 1997), with both *cis* and *trans* dispositions of the aryl substituents, but (1) appears to be the first example containing an *o*-substituted aryl group. The dihedral angles between the mean plane through C2/C3/C4/C11 and the planes of the phenyl groups attached to C3 and C4 are, respectively, 66.08 (6) and 39.01 (5)°. The C4—C5 distance is significantly shorter than the C3—C11 distance, suggesting a degree of π interaction between the diene unit and the phenyl group attached to C4.

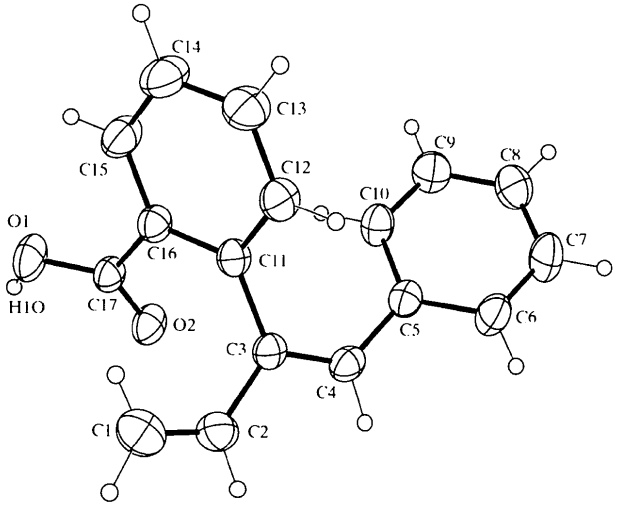


Fig. 1. Perspective view of (1). Displacement ellipsoids are drawn at the 30% probability level, and H atoms are represented by circles of an arbitrary radius. Only the major orientation of the carboxyl group is shown.

Experimental

Compound (1) was prepared by stirring a suspension of methyl *o*-(3-bromo-1-propynyl)benzoate (0.10 g, 0.40 mmol), benzaldehyde (0.084 g, 0.79 mmol) and indium (0.14 g, 1.2 mmol) in an H_2O/DMF mixture (6 ml, 2:3 *v*/*v*) for 15 h. The mixture was washed with water and extracted with 50 ml of dichloromethane. Further extraction of the aqueous layer was followed by combination of the dichloromethane extracts and drying over magnesium sulfate. Removal of the solvent afforded the crude product, which was purified by chromatography on silica gel [16.7% ethyl acetate in hexanes; yield: 0.54 g (55%)]. The sample for X-ray analysis was recrystallized from ethyl acetate. ^{1}H NMR ($CDCl_3$, p.p.m.): δ 8.12 (*d*, 1H, J = 8 Hz), 7.54 (*t*, 1H, J = 7 Hz), 7.45 (*t*, 1H, J = 7.5 Hz), 6.82–7.20 (*m*, 6H), 6.76 (*dd*, 1H, J = 17.2, 10.6 Hz), 6.64 (*s*, 1H), 5.07 (*d*, 1H, J = 10.3 Hz), 4.58 (*d*, 1H, J = 17.2 Hz); ^{13}C NMR ($CDCl_3$, p.p.m.): δ 171.77, 141.65, 141.15, 140.02, 136.56, 133.61, 131.50, 131.47, 130.89, 129.87, 129.18, 128.06, 127.71, 126.89, 115.18.

Crystal data

$C_{17}H_{14}O_2$
M_r = 250.28
Triclinic
$P\bar{1}$
a = 8.7367 (5) Å
b = 10.2118 (5) Å
c = 8.3386 (8) Å
α = 111.508 (6)°
β = 95.216 (6)°
γ = 87.374 (4)°
V = 689.22 (8) Å^3
Z = 2
D_x = 1.206 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 17.8–25.1°
μ = 0.078 mm^{-1}
T = 293 (2) K
Block
0.53 × 0.53 × 0.46 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2887 measured reflections
2700 independent reflections
1858 reflections with $I > 2\sigma(I)$

R_{int} = 0.017
θ_{max} = 25.98°
h = 0 → 10
k = −12 → 12
l = −10 → 10
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.098
S = 1.098
2698 reflections
181 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.1049P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.006

$\Delta\rho_{max}$ = 0.171 e Å^{-3}
$\Delta\rho_{min}$ = −0.128 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.126 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C17	1.276 (2)	C3—C11	1.490 (2)
O2—C17	1.246 (2)	C4—C5	1.465 (2)
C1—C2—C3	126.7 (2)	O2—C17—O1	122.94 (14)
C3—C4—C5	129.32 (14)	O2—C17—C16	120.50 (13)
C6—C5—C10	117.4 (2)	O1—C17—C16	116.52 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2^i	0.82	1.82	2.630 (2)	169 (1)
O2—H2O···O1^i	0.82	1.83	2.630 (2)	164 (1)

Symmetry code: (i) $2-x, 2-y, 1-z$.

H atoms attached to C were placed in calculated positions (C—H = 0.96 Å) and allowed to ride, with isotropic displacement parameters 20% larger than the corresponding C atom. The disordered carboxyl-H atoms could be seen in a difference map and the two sites were refined as riding OH groups based on O1 (H1O) and O2 (H2O), using the *SHELXL AFIX*147 instruction, with isotropic displacement parameters 20% larger than those of the corresponding O atoms and subject to the restraint that the sum of the site occupancy factors = 1.0 [final occupancies 0.64 (3) and 0.36 (3)].

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Operations Manual*. Data re-

duction: *XCAD*4 (Harms & Wocadlo, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1488). Services for accessing these data are described at the back of the journal.

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Classical Packing and Stacking in 6-Phenyl-5-azauracil

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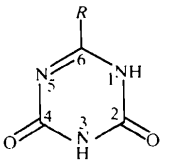
Abstract

Although probably not incorporated directly into nucleic acids, the title compound, 6-phenyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione ($C_9H_7N_3O_2$), resembles the pyrimidine bases in such nucleic acids. In the solid state, molecules base pair about a centre of symmetry into a dimer arrangement along the *a* axis and are linked firmly in the *c* direction by an N1—H1···O4 interaction related by the glide plane. The remaining intermolecular forces are achieved by the alternate stacking of phenyl and triazine rings in columns along the *b* axis.

Comment

Although the title compound, (1) (trivial name 6-phenyl-5-azauracil), has shown little biological activity, some azauracils have shown considerable promise in cancer chemotherapy. The parent compound, 5-azauracil, (2), is an antimetabolite (Suhadolnik, 1970) which inhibits the biosynthesis of pyrimidine bases and thus the production of nucleic acids (Adams & Davidson, 1981), whilst 6-azauracil has also revealed antineoplastic activity in animal tumours (Swindler & Welch, 1957). Since the extensive possibilities for hydrogen bonding in the triazinedione ring system in such compounds are likely to be important in such biological activity, the structure of (1) has been determined.



(1) *R* = Ph
(2) *R* = H

The two carbonyl bonds, C2=O2 and C4=O4, are almost equal in length [1.215 (1) and 1.218 (1) Å, respectively], thus confirming the diketo tautomeric form of the molecule in the solid state. Location of the H atoms at N1 and N3 by difference Fourier synthesis, together with the N5=C6 bond distance of 1.297 (2) Å confirms the correct assignment of protonation at these sites rather than at N5. In agreement with Chatar Singh's rule (Singh, 1965), an empirical form of the valence-shell electron-pair repulsion (VSEPR) theory (Gillespie, 1963), the ring bond angles at protonated N1 and N3 of 121.8 (1) and 124.6 (1)°, respectively, are much greater than the angle of 118.7 (1)° at the unprotonated N5 atom.

The angle of 7.2 (1)° between the least-squares planes of the triazine and phenyl rings could allow extensive conjugation, yet the degree to which electrons are attracted by the triazine ring from the phenyl ring seems very limited. The C6—C1′ bond length of 1.482 (2) Å is slightly longer than the average of 1.476 (14) Å for C_{sp^2}—C_{ar} bonds in conjugated C_{ar}—C=N—C systems (Allen *et al.*, 1987). The packing arrangement of the molecules is shown in Fig. 2. Stacking produces infinite columns of molecules in the *b* direction with alternating