

**(E)-1-(2-Bromo-4,5-dimethoxyphenyl)-2-(2-hydroxy-3,4-dimethoxyphenyl)ethylene,\***  
**C<sub>18</sub>H<sub>19</sub>BrO<sub>5</sub>**

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**Abstract.**  $M_r = 395.26$ , monoclinic,  $P2_1/c$ ,  $a = 12.971$  (6),  $b = 8.069$  (5),  $c = 16.158$  (6) Å,  $\beta = 95.04$  (3)°,  $V = 1684$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.56$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 2.61$  mm<sup>-1</sup>,  $F(000) = 808$ , room temperature,  $R = 0.043$  for 1713 observed reflections. The molecule is in the *trans* form. Although both benzene rings are planar, they show a slight distortion. The planarity of the molecule is only disturbed by the 3-methoxy group of the phenol ring which is oriented out of the plane of the ring.

**Introduction.** In a continuation of our studies on the classical Bischler–Napieralski cyclization (Domínguez & Lete, 1983), we have undertaken the preparation of the 1,2-diarylethylamine derivatives (1), in order to synthesize the corresponding isoindoles. Thus, the *A* ring has been deactivated by a bromine atom, while the *B* ring has been activated by electron-donating substituents, to direct the cyclization to the *B* ring. Trimethoxybenzene was acylated by treatment with 2-bromo-4,5-dimethoxyphenylacetyl chloride, yielding a ketonic compound, which differed from the expected ketone (2) only in possessing one hydroxyl group in place of one methoxy group. Since, in its NMR spectrum the phenolic proton appeared as a singlet at  $\delta = 12$  p.p.m., a fact which was indicative of the presence of a carbonyl group in the *ortho* position, the structure 2'-bromo-2-hydroxy-3,4,4',5'-tetramethoxydeoxybenzoin (3) was assigned to this compound. Subsequent reductive amination (Lukasiewicz, 1963) of the ketone (3) afforded, however, an unusual product: the (*E*)-1-(2-bromo-4,5-dimethoxyphenyl)-2-(2-hydroxy-3,4-dimethoxyphenyl)ethylene (4), instead of the desired amine. In the present paper, the crystal-structure determination of this asymmetrical stilbene is described.

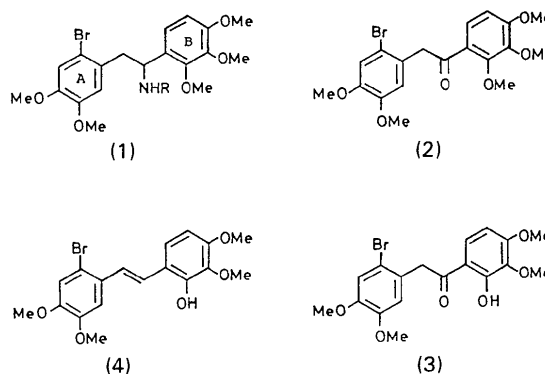


Table 1. Fractional atomic coordinates ( $\times 10^5$  for Br,  $\times 10^4$  for C and O) and equivalent isotropic temperature factors, calculated according to Willis & Pryor (1975)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
Br(1)	12604 (5)	16540 (10)	67724 (5)	4.14
C(2)	397 (4)	2233 (6)	5789 (3)	2.52
C(3)	-512 (4)	3070 (6)	5926 (3)	2.62
C(4)	-1165 (4)	3580 (6)	5256 (3)	2.34
C(5)	-907 (4)	3234 (6)	4446 (3)	2.49
C(6)	0 (4)	2393 (6)	4342 (3)	2.44
C(7)	690 (4)	1879 (6)	5010 (3)	2.40
C(8)	1654 (4)	1030 (7)	4879 (3)	2.68
C(9)	2128 (4)	993 (6)	4176 (3)	2.50
C(10)	3123 (4)	154 (6)	4086 (3)	2.31
C(11)	3498 (4)	-1121 (6)	4597 (3)	2.82
C(12)	4425 (4)	-1944 (6)	4496 (3)	2.75
C(13)	5006 (4)	-1426 (6)	3852 (3)	2.52
C(14)	4666 (4)	-115 (6)	3349 (3)	2.38
C(15)	3740 (4)	670 (7)	3453 (3)	2.59
O(16)	3406 (3)	1963 (5)	2958 (2)	3.48
O(17)	5209 (3)	404 (5)	2693 (2)	3.39
O(18)	5913 (3)	-2168 (5)	3668 (2)	3.18
O(19)	-1620 (3)	3754 (5)	3827 (2)	3.46
O(20)	-2061 (3)	4435 (4)	5318 (2)	2.79
C(21)	-2355 (4)	4724 (8)	6134 (3)	3.64
C(22)	-1368 (5)	3545 (8)	2993 (3)	3.95
C(23)	6121 (5)	1343 (8)	2960 (4)	4.79
C(24)	6273 (5)	-3580 (7)	4145 (4)	3.95

\* 2-(2-Bromo-4,5-dimethoxystyryl)-5,6-dimethoxyphenol.

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**Experimental.** Colourless plate-like crystals grown from ethanol; data collected from crystal approximately 0.4 × 0.2 × 0.03 mm; cell parameters determined by least squares from the setting angles of 15 reflections; 2379 independent reflections measured, Syntex P2<sub>1</sub> diffractometer, graphite-monochromated Mo K $\alpha$  radiation,  $\omega$  scans up to  $2\theta = 47^\circ$ ; 1 standard reflection measured every 50 reflections showed only random deviations from mean intensity; Lorentz and polarization but not absorption corrections; 1713 reflections [ $I \geq 2.5\sigma(I)$ ] considered observed and included in refinement; index range  $h \pm 12$ ,  $k$  0–9,  $l$  0–18; structure solved by direct methods with LSAM (Main, Woolfson & Germain, 1964); refinement by least squares with SHELX76 (Sheldrick, 1976),  $\sum w(AF)^2$  minimized, completed with anisotropic thermal parameters for the non-H atoms; H atoms included in calculations with an overall isotropic temperature factor in idealized positions, their coordinates, apart from H(8) and H(9), not refined; hydroxylic H atom not included at all; final  $R$  and  $R_w$  0.043 and 0.047  $\{w = K/[\sigma^2(F) + 0.00369F^2]\}$ ; scattering factors from *International Tables for X-ray Crystallography* (1974), max. and min. electron densities in final difference map 0.40 and  $-0.76 \text{ e } \text{\AA}^{-3}$ , max.  $A/\sigma$  (for non-H atoms) = 0.17.\*

**Discussion.** Final atomic parameters are given in Table 1. Fig. 1 shows a stereoscopic view of the molecule and the atom numbering (Motherwell & Clegg, 1978). Bond lengths and angles are given in Fig 2. Both benzene rings are slightly distorted, the angle C(2)–C(7)–C(6) being only  $115.8(4)^\circ$ ; however, the angle values do not differ significantly from those found in similar compounds (Arrieta, Lete, Dominguez, Germain, Declercq & Amigó, 1982). The two benzene rings are linked by an ethylenic double bond whose length C(9)–C(8) [1.338 (7) Å] is longer than the longest values found in stilbene molecules, 1.318 Å (Finder, Newton & Allinger, 1974) and 1.313 Å (Bernstein, 1975; Arrieta *et al.*, 1982). One exocyclic single-bond length, C(8)–C(7) [1.458 (7) Å], is shorter than the distance reported in symmetrical *trans*-stilbenes, 1.471 Å (Bernstein, 1975), while the other one C(9)–C(10) [1.476 (7) Å] is basically the same. Both benzene rings are planar, the displacements of the atoms from the mean planes being less than 0.007 (1) Å in the bromobenzene ring and 0.013 (1) Å in the other ring. The planarity of the molecule is disturbed by the rotation of the methoxy group attached to C(14), probably due to steric interactions. This methoxy group is orientated out of

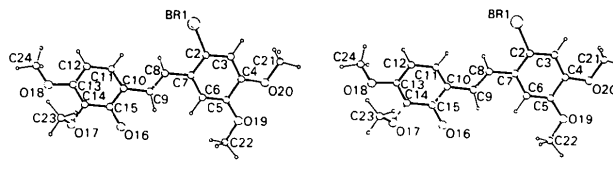


Fig. 1. Stereoscopic view of the molecule with the atom numbering.

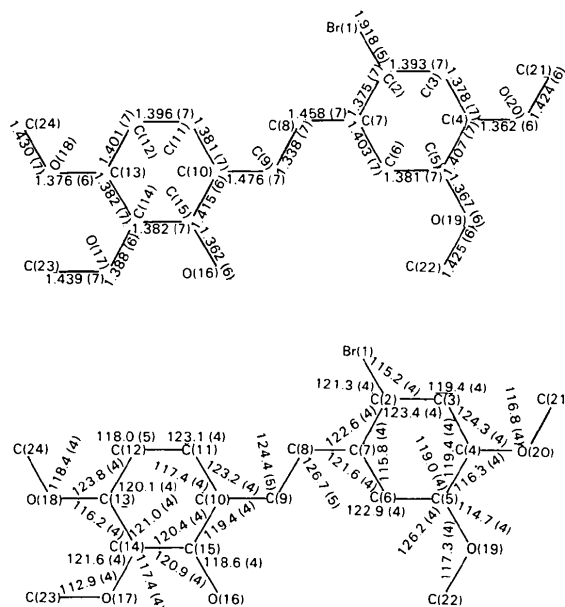


Fig. 2. Bond lengths (Å) and bond angles ( $^\circ$ ).

the plane of the benzene ring, as can be seen from the torsion angles C(13)–C(14)–O(17)–C(23)  $-76(2)^\circ$  and C(15)–C(14)–O(17)–C(23)  $107(2)^\circ$ . The ethylenic C atoms also show deviations from planarity, torsion angles C(2)–C(7)–C(8)–C(9)  $-162(2)$ , C(6)–C(7)–C(8)–C(9)  $18(2)$ , C(8)–C(9)–C(10)–C(11)  $23(2)$  and C(8)–C(9)–C(10)–C(15)  $-157(2)^\circ$ .\*

Intermolecular distances O(17)···O(16) and O(18)···O(16) are 2.72 (1) and 2.93 (1) Å, indicating hydrogen bonds, the latter being only a weak bond.

\* A list of selected torsion angles has been deposited. See previous footnote.

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\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39146 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 1,2,2a,4a,5,6,7,8-Octahydro-5,8-methanocyclobut[*c*]indene-1,1,2,2-tetracarbonitrile, C<sub>16</sub>H<sub>12</sub>N<sub>4</sub>

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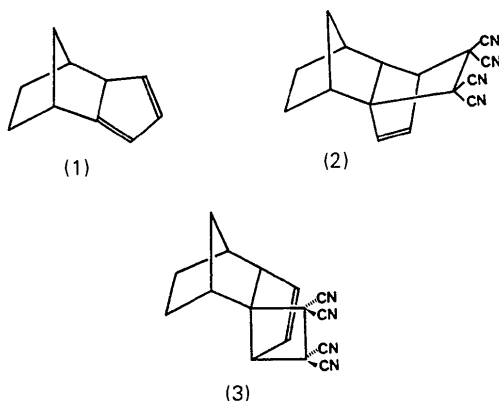
(Received 26 September 1983; accepted 20 December 1983)

**Abstract.**  $M_r = 260.30$ , monoclinic,  $P2_1/n$ ,  $a = 11.415$  (2),  $b = 15.401$  (3),  $c = 7.751$  (1) Å,  $\beta = 96.90$  (1)°,  $V = 1352.8$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.278$  g cm<sup>-3</sup>,  $\text{Cu } K\alpha$ ,  $\lambda = 1.54178$  Å,  $\mu = 6.43$  cm<sup>-1</sup>,  $F(000) = 544$ , room temperature,  $R = 0.040$  for 1508 unique reflections with  $I > 3\sigma(I)$ . The tetracyanoethylene adduct contains a four-membered ring with three long C–C distances of 1.581 (3), 1.582 (3) and 1.596 (3) Å. Both N–C–C–N moieties are planar and almost perpendicular to the four-membered ring and to each other. Although there is little steric hindrance within the molecule, there is considerable angle strain as evidenced by the fourteen C(sp<sup>3</sup>) valence angles of less than 104°.

**Introduction.** The least reactive isomer (1) of isodicyclopentadiene (Bartlett & Wu, 1984*a*) reacts with tetracyanoethylene (TCNE) at 273 K in acetonitrile to form adduct (2). In the presence of polar solvents (2) rearranges to form the title compound (3) (Bartlett &

Wu, 1984*b*). Both steps in this reaction are solvent dependent.

**Experimental.** Bipyramidal-shaped crystal, 0.6 × 0.3 × 0.3 mm, Syntex  $P2_1$  diffractometer,  $\theta:2\theta$  scan, variable scan rate,  $2\theta_{\text{max}} = 120^\circ$ , graphite-monochromated  $\text{Cu } K\alpha$  radiation; lattice parameters from least squares of 15 medium-angle reflections with angles measured by centering routine associated with the diffractometer system (systematic absences  $h + l = 2n + 1$  for  $h0l$ ); monitored reflections showed no change in intensity greater than  $3\sigma(I)$ ; 1842 independent reflections ( $0 \leq h \leq 12$ ,  $0 \leq k \leq 16$ ,  $-8 \leq l \leq 8$ ), 1508 with intensities  $> 3\sigma(I)$ ; Lorentz and polarization but no absorption corrections; direct methods (*MULTAN78*: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms; H atoms located in difference synthesis but not refined, full-matrix least-squares anisotropic refinement;  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = 1/\sigma^2(F_o)$ ; 181 parameters refined, final  $R = 0.040$ ,  $R_w = 0.059$ ,  $S = 2.79$ ,  $(\Delta/\sigma)_{\text{av}} = 0.014$ ,  $(\Delta/\sigma)_{\text{max}} = 0.12$ , highest peak in difference Fourier map  $0.17 \text{ e } \text{Å}^{-3}$ ; locally written programs used for data reduction and initial block-diagonal least-squares refinement, *MULTAN78* for direct-methods calculations and *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all other computations; atomic scattering factors for C, O and N from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Table 1 lists atomic positional parameters and  $U_{\text{eq}}$  values while Table 2 gives bond lengths and valence angles.†



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† Lists of structure factors, H-atom parameters, torsion angles and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39149 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.