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An investigation of 2,4′-dihydroxy-3,3′-dimethoxy-5′-methylstilbene using X-ray crystallography and NMR spectroscopy

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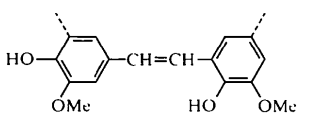
Abstract

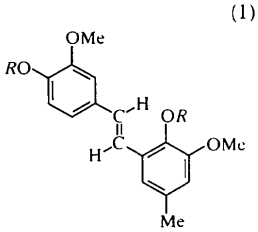
The *E* and *Z* forms of the title compound, $C_{17}H_{18}O_4$, were examined by ^{13}C NMR and ^1H NMR spectroscopy, and the crystal structure of the *E* form (m.p. 397–398 K) was determined by X-ray crystallography. Earlier reported spectral data for these two isomeric stilbenes are complemented or revised on the basis of these results.

Comment

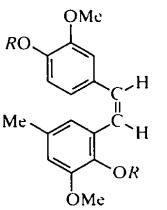
It is known from experiments with lignins and model compounds that stilbenes of type (1) are produced from lignin structures of the phenylcoumaran type by the action of various treatments such as alkaline pulping (Adler *et al.*, 1964; Yoon *et al.*, 1981), acidolysis (Li & Lundquist, 1999) and mechanical pulping (Lee *et al.*, 1990). Several stilbenes of type (1) have been reported to be present in spent liquors from alkaline pulping (Gierer & Lindeberg, 1980; Niemelä, 1990). One of these compounds is 2,4′-dihydroxy-3,3′-dimethoxy-5′-methylstilbene, (2). This stilbene has also been obtained through alkaline (Yoon *et al.*, 1981) and acid (Yasuda, 1988, and references therein) treatment of the phenylcoumaran model, *trans*-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzo[*b*]furan. In this study, a mixture of the stereoisomeric forms, (2*a*) and (2*b*), was prepared by a synthetic method involving a Wittig reaction; the method has been applied earlier to the synthesis of 8-(3,5-di-*tert*-butylstyryl)fluoranthene (Brink *et al.*, 1998). NMR examinations of the *E* form, (2*a*), and the *Z* form, (2*b*), and their acetate derivatives, (3*a*) and (3*b*), are reported in this paper. A crystal structure determination of (2*a*) provided evidence of the molecular structure of the compounds. The compounds were prone to photochemical isomerization on exposure to daylight in chloroform solution: after one week, about 10% of the *E* form, (2*a*), had been converted to the *Z* form, (2*b*). The acetate of the *E* form, (3*a*), also gave a mixture of the two possible stereoisomeric forms on exposure to daylight in chloroform solution; the *Z* form, (3*b*), dominated (*ca* 90%).



(1)



(2*a*) *R* = H
(3*a*) *R* = COMe



(2*b*) *R* = H
(3*b*) *R* = COMe

Gierer & Nilvebrandt (1991) reported the synthesis of (2) *via* a 1,1-diaryl-2-chloroethane intermediate. However, the ^1H NMR spectral data given in their paper for the acetylated product are not in accordance with the spectral data for (3*a*) or (3*b*) obtained in this study. It was noted in previous ^1H NMR spectral studies of stilbenes of type (1) (Stomberg *et al.*, 1998) that the signal from one of the methoxy groups in the *Z* forms is located at a comparatively high field (*ca* δ 3.5). The present study shows that this is also true for (2*b*) (δ 3.62) and (3*b*) (δ 3.54). Gierer & Lindeberg (1980) reported the isolation of the *Z* isomer, (2*b*), as the acetate derivative, (3*b*), from a Kraft pulping liquor. However, the NMR spectral data reported for the product isolated by Gierer & Lindeberg (1980) deviate considerably from those of (3*b*) [or (3*a*)]. Mörck & Kringstad (1985) report ^{13}C NMR spectral data for (3*a*) and (3*b*). Their data do not agree completely with the data obtained in this study.

Awareness of the photochemical instability of (2) and (3) is of importance in connection with examination of these compounds. A partial explanation of the discrepancies between the NMR spectral data for (2) and (3) given in this paper and those given in the literature (see the papers referred to above) may be that the photochemical reactions have been overlooked in previous work.

The *E* stilbene, (2*a*), adopts a conformation that deviates only slightly from planarity [angle between the ring

planes 8.90 (9)°; torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 175.1 (2) and 175.4 (2)°, respectively]. It is noteworthy that a related 2-hydroxystilbene, (*E*)-2-hydroxy-3,3′,4′-trimethoxystilbene, also adopts a nearly planar conformation (Stomberg *et al.*, 1998). In (2*a*) there are intramolecular hydrogen bonds between the hydroxy groups and the adjacent methoxy-O atoms [O1···O2 2.598 (2) and O3···O4 2.716 (2) Å], as well as intermolecular hydrogen bonds [O1···O3($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) 2.760 (2) and O4···O1($\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) 2.838 (2) Å].

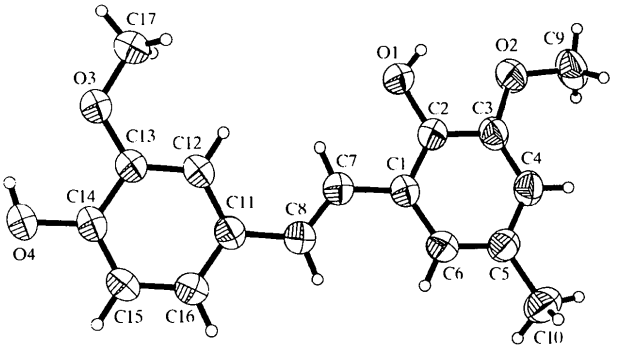


Fig. 1. A perspective drawing (*ORTEPII*; Johnson, 1976) of (2*a*), showing the atom-numbering scheme and with displacement ellipsoids at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

Experimental

The title compound was prepared from 2-acetoxy-3-methoxy-5-methylbenzaldehyde (5 mmol) and 4-acetoxy-3-methoxybenzyltriphenylphosphonium bromide (5 mmol). 2-Acetoxy-3-methoxy-5-methylbenzaldehyde was obtained by acetylation of 2-hydroxy-3-methoxy-5-methylbenzaldehyde, which had been prepared according to the procedure of Byck & Dawson (1968). 4-Acetoxy-3-methoxybenzyltriphenylphosphonium bromide was obtained from 4-acetoxy-3-methoxybenzyl bromide (*cf.* Brink *et al.*, 1998), which had been prepared by treatment of 4-acetoxy-3-methoxybenzyl alcohol [obtained by reduction of the acetate of vanillin by $BH_3{\cdot}S(CH_3)_2$] with PBr_3. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) of 2-acetoxy-3-methoxy-5-methylbenzaldehyde: δ 2.39 (3H, *s*, CH_3CO), 2.40 (3H, *br. s*, Ar-CH_3), 3.86 (3H, *s*, OCH_3), 7.03 (1H, *d*, *J* = 2.0 Hz, H-Ar), 7.26 (1H, *dd*, *J* = 0.8 and 2.0 Hz, H-Ar), 10.09 (1H, *s*, CHO); ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) of 4-acetoxy-3-methoxybenzyltriphenylphosphonium bromide: δ 2.28 (3H, *s*, CH_3CO), 3.49 (3H, *s*, OCH_3), 5.43 (2H, *d*, *J* = 14.0 Hz, CH_2), 6.61 (1H, *td*, *J* = 2.4 and 8.4 Hz, H-Ar), 6.76 (1H, *d*, *J* = 8.4 Hz, H-Ar), 7.14 (1H, ~*t*, *J* = 2 Hz, H-Ar), 7.5–7.8 (15H, *m*, H-Ar). The synthesis of (2) was accomplished by a method used by Brink *et al.* (1998) for the preparation of 8-(3,5-di-*tert*-butylstyryl)fluoranthene. Column chromatography (30 g SiO_2; eluent: dichloromethane–ethyl acetate 20:1) of the crude product (1.9 g) gave a fraction (120 mg) consisting of a mixture of the stereoisomeric forms [(2*a*) and (2*b*)] of (2). Crystallization of the acetylated product from ethanol gave crystals of (3*a*) (85 mg; m.p. 439–440 K). Column chromatography (50 g SiO_2; eluent: dichloromethane–ethyl acetate 30:1) of the materials in the mother liquor (75 mg) gave essentially pure (3*b*) (45 mg, oil). Reduction of (3*a*) and (3*b*) with $LiAlH_4$ afforded (2*a*) and (2*b*) [contaminated with (2*a*)], respectively. Crystallization of (2*a*) from chloroform–hexane gave a product melting at 397–398 K [Yoon *et al.* (1981) report m.p. 399–401 K]. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) of (2*a*): δ 2.31 (3H, *br. s*, Ar-CH_3), 3.89 (3H, *s*, OCH_3), 3.95 (3H, *s*, OCH_3), 5.64 (1H, *s*, OH), 5.78 (1H, *s*, OH), 6.59 (1H, *d*, *J* = 1.7 Hz, H-Ar), 6.89 (1H, *d*, *J* = 8.3 Hz, H-Ar), 6.98 (1H, *br. s*, H-Ar), 7.03 (1H, *dd*, *J* = 1.8 and 8.3 Hz, H-Ar), 7.08 (1H, *d*, *J* = 1.8 Hz, H-Ar), 7.09 (1H, *d*, *J* = 16.4 Hz, vinyl-H), 7.24 (1H, *d*, *J* = 16.4 Hz, vinyl-H); ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) of (3*a*): δ 2.33 (3H, *s*, CH_3CO), 2.36 (3H, *s*, CH_3CO), 2.37 (3H, *br. s*, Ar-CH_3), 3.82 (3H, *s*, OCH_3), 3.88 (3H, *s*, OCH_3), 6.71 (1H, *d*, *J* = 1.5 Hz, H-Ar), 7.00 (1H, *d*, *J* = 16.2 Hz, vinyl-H), 7.02 (1H, *d*, *J* = 8.1 Hz, H-Ar), 7.04–7.06 (2H, *m*, H-Ar), 7.05 (1H, *d*, *J* = 16.2 Hz, vinyl-H), 7.08 (1H, *dd*, *J* = 1.8 and 8.1 Hz, H-Ar); ^{13}C NMR (100.6 MHz, $CDCl_3$, 293 K, TMS) of (3*a*): δ 20.5, 20.7, 21.6 (3C, Ar-CH_3 and CH_3CO), 55.8 (OCH_3), 55.9 (OCH_3), 110–152 (110.5, 112.2, 118.3, 119.2, 122.5, 122.9, 130.49, 130.54, 135.5, 136.2, 136.4, 139.5, 151.1, 151.2) (14C, aromatic and vinyl-C), 168.95 (CO), 168.98 (CO); ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) of (2*b*): δ 2.18 (3H, *br. s*, Ar-CH_3), 3.62 (3H, *s*, OCH_3), 3.87 (3H, *s*, OCH_3), 5.58 (1H, *s*, OH), 5.59 (1H, *s*, OH), 6.54 (2H, *AB* spectrum, δ_A = 6.53 and δ_B = 6.55, *J* = 12.2 Hz, vinyl-H), 6.57 (1H, *d*, *J* = 1.2 Hz, H-Ar), 6.69 (1H, *br. s*, H-Ar), 6.77 (1H, *d*, *J* = 8.1 Hz, H-Ar), 6.81 (1H, *dd*, *J* = 1.8 and 8.1 Hz, H-Ar), 6.84 (1H, *d*, *J* = 1.8 Hz, H-Ar); ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) of (3*b*): δ 2.20 (3H, *br. s*, Ar-CH_3), 2.27 (3H, *s*, CH_3CO), 2.28 (3H, *s*, CH_3CO), 3.54 (3H, *s*, OCH_3), 3.81 (3H, *s*, OCH_3), 6.44 (1H, *d*, *J* = 12.2 Hz, vinyl-H), 6.58 (1H, *d*, *J* = 12.2 Hz, vinyl-H), 6.60 (1H, *m*, H-Ar), 6.66 (1H, *d*, *J* = 1.6 Hz, H-Ar), 6.80 (1H, *dd*, *J* = 1.8 and 8.0 Hz, H-Ar), 6.85 (1H, *d*, *J* = 1.8 Hz, H-Ar), 6.88 (1H, *d*, *J* = 8.0 Hz, H-Ar); ^{13}C NMR (100.6 MHz, $CDCl_3$, 293 K, TMS) of (3*b*): δ 20.5, 20.7, 21.4 (3C, Ar-CH_3 and CH_3CO), 55.5 (OCH_3), 55.9 (OCH_3), 111–152 (111.9, 113.1, 121.75 122.0, 122.2, 124.9, 131.5, 131.6, 135.3, 135.6, 136.1, 138.8, 150.3, 151.1) (14C, aromatic and vinyl-C), 169.0 (2C, CO).

Crystal data

$C_{17}H_{18}O_4$
M_r = 286.31
Monoclinic
$P2_1/n$
a = 8.4341 (1) Å
b = 15.5112 (3) Å
c = 11.4293 (1) Å
β = 90.397 (1)°
V = 1495.18 (4) Å^3
Z = 4
D_x = 1.272 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7340 reflections
θ = 2.21–26.39°
μ = 0.090 mm^{-1}
T = 293 (2) K
Prism
0.50 × 0.27 × 0.27 mm
Colourless

Data collection

Siemens SMART CCD diffractometer

2411 reflections with $I > 2\sigma(I)$

ω oscillation 0.30°; 30 s/frame	R_{int} = 0.036
Absorption correction: none	θ_{max} = 26.39°
15 404 measured reflections	$h = -10 \rightarrow 10$
3064 independent reflections	$k = -19 \rightarrow 19$
	$l = -14 \rightarrow 14$
	Intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
$wR(F^2)$ = 0.127	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
S = 1.053	Extinction coefficient: 0.0103 (16)
3064 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
196 parameters	
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.3262P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} < 0.001$	

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

C1—C7	1.463 (2)	C8—C11	1.468 (2)
C7—C8	1.324 (2)		
O2—C3—C4	126.9 (1)	C7—C8—C11	125.6 (2)
C8—C7—C1	128.7 (2)	O3—C13—C12	124.9 (1)
C6—C1—C7—C8	−5.1 (3)	C7—C8—C11—C12	−3.4 (3)
C1—C7—C8—C11	−178.3 (2)		

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1994*a*). Data reduction: *SAINT* and *XPREP* (Siemens, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1301). Services for accessing these data are described at the back of the journal.

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5-Methyl-1*H*-tetrazole

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Abstract

We have determined the molecular structure of the title compound, $C_2H_4N_4$, using X-ray crystallography. The tetrazole ring is expected to be an aromatic system. The ring structure is not very different from that of 1-methyltetrazole. The C—C bond length is shorter than expected and this indicates that the electron of the tetrazole ring expands to the methyl group.

Comment

As part of a study of the aromaticity of tetrazole rings, we are interested in the effects of substituents on the ring structure. Some crystal structures of tetrazole derivatives have been reported previously. The parent compound, 1*H*-tetrazole (1HT), was reported by Goddard *et al.* (1997). The compound substituted with a methyl group at the 1-position, 1-methyltetrazole (1MT), was reported by Palmer & Parsons (1996). However, the structure of 5-methyl-1*H*-tetrazole (5MT), which is substituted at the 5-position by a methyl group, has not been previously reported. We therefore determined the crystal structure of the title compound using X-ray crystallography, and compared it with the earlier compounds. It has also been reported that 1HT and 1MT have almost the same