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

N1—C4	1.352 (4)	C2—C3	1.408 (4)
N1—C1	1.368 (3)	C3—C4	1.345 (5)
N1—H1	0.94 (3)	C5—C6	1.503 (4)
N2—C9	1.360 (4)	C5—C10	1.528 (3)
N2—C6	1.372 (3)	C6—C7	1.353 (4)
N2—H2	0.88 (3)	C7—C8	1.412 (4)
C1—C2	1.359 (4)	C8—C9	1.338 (4)
C1—C5	1.501 (3)		
C4—N1—C1	110.0 (3)	C1—C5—C10	112.8 (2)
C9—N2—C6	110.1 (2)	C6—C5—H5	108.4 (14)
C2—C1—N1	106.8 (2)	C1—C5—H5	105.3 (13)
C2—C1—C5	132.2 (2)	C10—C5—H5	108.1 (13)
N1—C1—C5	121.0 (2)	C7—C6—N2	106.8 (2)
C1—C2—C3	107.7 (3)	C7—C6—C5	131.5 (2)
C4—C3—C2	107.6 (3)	N2—C6—C5	121.7 (2)
C3—C4—N1	108.0 (3)	C6—C7—C8	107.5 (2)
C6—C5—C1	111.6 (2)	C9—C8—C7	108.2 (3)
C6—C5—C10	110.5 (2)	C8—C9—N2	107.4 (3)

Atoms C17, C18 and C19 were found to be disordered over two positions (C17/C17*A*, C18/C18*A* and C19/C19*A*). Their occupancies were initially refined and then later fixed at 0.6 (C17, C18 and C19) and 0.4 (C17*A*, C18*A* and C19*A*). The non-H atoms were refined anisotropically. The H atoms of the *meso*-C and N atoms were located on difference Fourier maps and were refined isotropically, while other H atoms were placed in idealized positions. The H atoms attached to C17, C18 and C19 have occupancies of 0.6 and those on C17*A*, C18*A* and C19*A* have occupancies of 0.4.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α,α-Diacetoxy-2,4-dichloro-5-nitrobenzaldehyde

Songping D. Huang,* Osvaldo Cox, Marisol Cordero and Sylvia Piñeiro

Department of Chemistry, University of Puerto Rico, PO Box 23346, San Juan, PR 00931, USA. E-mail: huang@zintl.chem.uprr.pr

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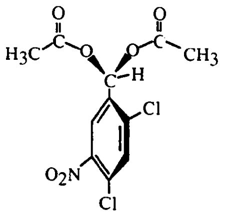
Abstract

The title compound, (2,4-dichloro-5-nitrophenyl)methylene diacetate, $C_{11}H_9Cl_2NO_6$, was obtained as an unexpected product from the reaction of 2,4-dichloro-5-nitrobenzaldehyde with 2-methylbenzothiazole in refluxing acetic anhydride. The single-crystal X-ray analysis showed the phenyl ring to be slightly disorientated with respect to the idealized C_s symmetry which the molecule would otherwise possess. Thus, the dihedral angle between C(1)—C(7)—H(3) and the phenyl ring is 29.8 (4)°.

Comment

As part of our continued interest in the synthesis of benzothiazolo[3,2-*a*]quinolinium salts (Cox *et al.*, 1982; Alegría, *et al.*, 1993) *via* the photochemically induced cyclization of 2-styrylbenzothiazoles, we investigated the reaction of 2,4-dichloro-5-nitrobenzaldehyde with 2-methylbenzothiazole in refluxing acetic anhydride. In addition to the expected 2-(2′,4′-dichloro-5′-nitrostyryl)-benzothiazole, an unknown product was also formed in the reaction. The ^{1}H and ^{13}C NMR studies showed that the latter is α,α-diacetoxy-2,4-dichloro-5-nitrobenzaldehyde, a product of the nucleophilic attack of 2,4-dichloro-5-nitrobenzaldehyde on the solvent. In order to



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confirm the identity of this compound, a single-crystal X-ray structure analysis was carried out. Fig. 1 shows the molecular structure of the title compound. The structure is consistent with all the spectroscopic data. All the bond distances and bond angles appear to be normal. The idealized symmetry for the molecule is C_s. However, the phenyl ring is rotated 29.8 (4)° away from its expected position. The reasons for such a deviation seem not to be steric, and may be the result of the crystal packing forces in the lattice.

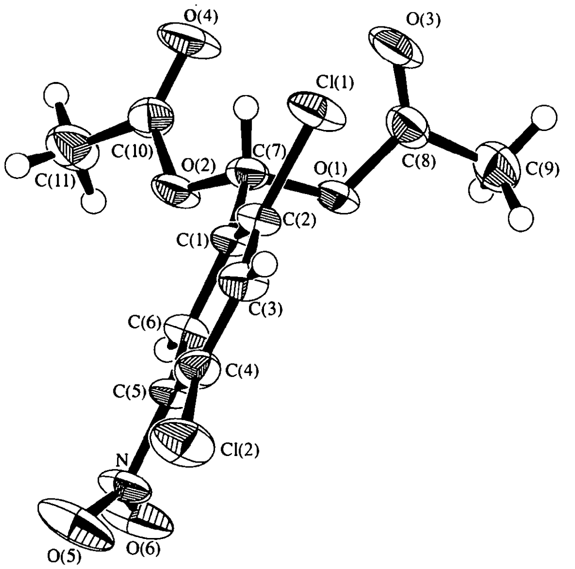

Fig. 1. *ORTEP*II (Johnson, 1976) representation of the title compound showing 50% probability displacement ellipsoids.

In summary, the structure determination of the title compound by single-crystal X-ray crystallography confirmed that a different compound can also be formed under the synthetic conditions. The formation of such a product is probably induced by water molecules generated from the condensation reaction.

Experimental

When 2,4-dichloro-5-nitrobenzaldehyde and 2-methylbenzothiazole were refluxed in acetic anhydride, the title compound, along with a condensation product 2-(2′,4′-dichloro-5′-nitrostyryl)benzothiazole, was obtained. After chromatographic separation, the compound (m.p. 401–403 K) was recrystallized from acetonitrile by slow evaporation of the solvent.

Crystal data

$C_{11}H_9Cl_2NO_6$
$M_r = 322.10$
Monoclinic
$P2_1/c$
$a = 12.661\ (3)$ Å
$b = 7.216\ (1)$ Å
$c = 14.796\ (2)$ Å
$\beta = 105.44\ (2)$°
$V = 1303.0\ (4)$ Å^3
$Z = 4$
$D_x = 1.642$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 15 reflections
$\theta = 15.0$–20.0°
$\mu = 0.522$ mm^{-1}
$T = 296.2$ K
Cuboid
0.24 × 0.21 × 0.21 mm
Yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2115 measured reflections
2049 independent reflections
1471 observed reflections $[I > 2.5\sigma(I)]$

$R_{\rm int} = 0.0427$
$\theta_{\rm max} = 25$°
$h = -14 \rightarrow 0$
$k = 0 \rightarrow 7$
$l = -15 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0571$
$wR = 0.0665$
$S = 2.630$
1471 reflections
182 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0009F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.0299$

$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.40$ e Å^{-3}
Extinction correction: Zachariasen type 2 Gaussian isotropic
Extinction coefficient: 0.57957
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
Cl(1)	0.35683 (9)	−0.1543 (2)	0.05874 (9)	0.0519 (4)
Cl(2)	−0.0268 (1)	−0.3676 (2)	0.1001 (1)	0.0613 (5)
O(1)	0.2840 (2)	0.3278 (4)	0.0336 (2)	0.0374 (9)
O(2)	0.2970 (2)	0.3647 (4)	0.1888 (2)	0.0396 (9)
O(3)	0.4499 (3)	0.2664 (6)	0.0129 (2)	0.068 (1)
O(4)	0.4723 (2)	0.4531 (5)	0.2149 (2)	0.059 (1)
O(5)	−0.1020 (3)	−0.0662 (6)	0.1901 (3)	0.084 (2)
O(6)	−0.0810 (3)	0.2075 (6)	0.1433 (3)	0.070 (1)
N	−0.0536 (3)	0.0490 (7)	0.1565 (3)	0.047 (1)
C(1)	0.2245 (3)	0.0858 (6)	0.1166 (3)	0.031 (1)
C(2)	0.2386 (3)	−0.0927 (6)	0.0897 (3)	0.035 (1)
C(3)	0.1617 (3)	−0.2285 (6)	0.0852 (3)	0.040 (1)
C(4)	0.0654 (3)	−0.1898 (6)	0.1089 (3)	0.037 (1)
C(5)	0.0480 (3)	−0.0099 (7)	0.1335 (3)	0.035 (1)
C(6)	0.1254 (3)	0.1258 (6)	0.1380 (3)	0.034 (1)
C(7)	0.3086 (3)	0.2357 (6)	0.1217 (3)	0.033 (1)
C(8)	0.3626 (4)	0.3343 (7)	−0.0155 (3)	0.040 (1)
C(9)	0.3201 (4)	0.4344 (7)	−0.1044 (4)	0.055 (2)
C(10)	0.3864 (3)	0.4678 (6)	0.2331 (3)	0.038 (1)
C(11)	0.3608 (4)	0.5919 (7)	0.3034 (4)	0.055 (2)

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

Cl(1)—C(2)	1.735 (4)	O(3)—C(8)	1.180 (5)
Cl(2)—C(4)	1.716 (4)	O(4)—C(10)	1.192 (5)
O(1)—C(7)	1.422 (5)	O(5)—N	1.214 (5)
O(1)—C(8)	1.380 (5)	O(6)—N	1.196 (5)
O(2)—C(7)	1.397 (5)	N—C(5)	1.479 (5)
O(2)—C(10)	1.368 (5)		
C(7)—O(1)—C(8)	119.1 (3)	O(1)—C(7)—C(1)	108.1 (3)
C(7)—O(2)—C(10)	118.2 (3)	O(2)—C(7)—C(1)	107.9 (3)
O(5)—N—O(6)	124.4 (4)	O(1)—C(8)—O(3)	122.4 (4)
Cl(1)—C(2)—C(1)	120.3 (3)	O(1)—C(8)—C(9)	110.2 (4)
Cl(1)—C(2)—C(3)	117.1 (3)	O(3)—C(8)—C(9)	127.4 (4)
N—C(5)—C(4)	122.7 (4)	O(2)—C(10)—O(4)	122.2 (4)
N—C(5)—C(6)	115.9 (4)	O(2)—C(10)—C(11)	111.0 (3)
O(1)—C(7)—O(2)	107.5 (3)	O(4)—C(10)—C(11)	126.8 (4)

Data collection: *CAD-4/PC* (Enraf–Nonius, 1994). Cell refinement: *CAD-4/PC*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Z)-2-Acetoxy-3,3′,4′-trimethoxystilbene

Shiming Li,[a] Knut Lundquist[a] and Rolf Stomberg[b]

[a]*Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden, and* [b]*Department of Inorganic Chemistry, University of Gothenburg, S-412 96 Gothenburg, Sweden. E-mail: rolf@inoc.chalmers.se*

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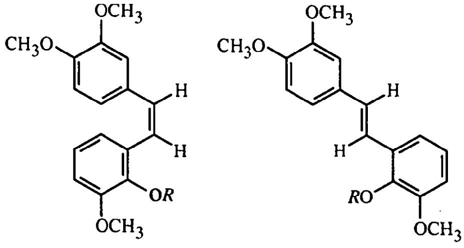
Abstract

The crystal structure determination demonstrates unambiguously that the title compound, 2-[(*Z*)-3,4-dimethoxyphenylethenyl]-6-methoxypheenyl acetate, $C_{19}H_{20}O_5$, has the *Z* configuration. The title compound was prepared by decarboxylation of (*E*)-3-(2-acetoxy-3-methoxyphenyl)-2-(3,4-dimethoxyphenyl)propenoic acid; this compound was in turn obtained by condensation of 2-acetoxy-3-methoxybenzaldehyde with (3,4-dimethoxyphenyl)acetic acid. ^{1}H NMR data for the title compound and the isomeric (*E*)-2-acetoxy-3,3′,4′-trimethoxystilbene are reported.

Comment

Structural elements in lignins of the phenylcoumaran type are converted into stilbene structures during alkaline pulping (Adler, Marton & Falkehag, 1964; Gierer, Lenic, Norén & Szabo-Lin, 1974; Gierer, Pettersson & Szabo-Lin, 1974) or mechanical pulping (Lee, Matsuoka & Sumimoto, 1990). Stilbenes (1*a*) and (2*a*) are model compounds representative of such stilbene structures. Acid-catalysed reactions of phenylcoumaran structures also give rise to stilbenes. Stilbene (2*a*) (m.p. 439 K, from ethyl acetate) is obtained on acid treatment of a model compound of the phenylcoumaran type [*trans*-2-(3,4-dimethoxyphenyl)-2,3-dihydro-3-hydroxymethyl-7-methoxybenzofuran] (Li, Lundquist & Stomberg, 1996). To ensure the steric assignments of stilbenes (1) and (2), we have examined the acetate derivative of (1*a*) [*i.e.* compound (1*b*)] by X-ray crystallography.



(1*a*) R=H (2*a*) R=H
(1*b*) R=$COCH_3$ (2*b*) R=$COCH_3$

Stilbene (1*b*) was obtained by decarboxylation of (5) (see reaction scheme). The decarboxylation reaction also leads to the formation of the isomeric stilbene (2*b*). The formation of this latter stilbene is unexpected, since the decarboxylation of acids of type (5) are reported to occur with retention of the configuration (*cf.* Battersby & Greenock, 1961). The starting material (5) was prepared by condensation of (3) with (4) in a reaction of the Perkin type (see reaction scheme). Substantial amounts of lactone (6) were obtained as a by-product.

The crystal structure determination demonstrates unambiguously that (1*b*) has the *Z* configuration. Fig. 1 gives a perspective view of (1*b*) with the atomic numbering. The angle between the aromatic ring planes is 55.1 (1)°. The torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 are 36.7 (5) and 55.2 (5)°, respectively. Similar conformations are adopted by other (*Z*)-stilbene derivatives examined by X-ray crystallography, *e.g.* (*Z*)-2-nitrostilbene (Todres, Gridunova, Dyusengaliev & Struchkov, 1987), (*Z*)-5-methoxymethyl-3-[4-(phenylethenyl)phenyl]-2-oxazolidinone (Durant, Lefevre, Norberg & Evrard, 1982),