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16-(p-Butoxybenzylidene)androsta-1,4-diene-3,17-dione

KEIICHIRO OGAWA AND SHIN YOSHIMURA

Department of Chemistry, The College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

MAKOTO KAJI

Ibaraki Research Laboratory, Hitachi Chemical Co. Ltd, 4-13-1 Higashi-cho, Hitachi 317, Japan

HIROYUKI KAGAWA AND ATSUSHI KAKUTA

Hitachi Research Laboratory, Hitachi Ltd, 4026 Kuji-cho, Hitachi, Ibaraki 319-12, Japan

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Abstract

The cyclohexa-1,4-dien-3-one ring in the androsta-1,4-dien-3-one skeleton adopts a nearly planar conformation. The conformation of the styryl ketone fragment slightly deviates from planarity. The crystals show significant second-order-harmonic generation and short cut-off wavelength for absorption.

Comment

One of the obstacles to the realization of organic materials for an effective second-order-harmonic generation (SHG) device of a diode laser is an undesirable tendency for molecules with a large SHG hyperpolarizability to have a longer cut-off wavelength for light absorption (Itoh, Oono, Isogai & Kakuta, 1989; Prasad & Williams, 1991). In the course of our attempt to overcome this obstacle by molecular design (Oono, Itoh, Hamada, Isogai & Kakuta, 1990; Ogawa, Yoshimura, Takeuchi, Katritzky & Murugan, 1992), it was found that the title compound shows an appreciable deviation from this tendency. The basic idea for the design of the new molecule is that the styryl ketone fragment as a polarizable unit is incorporated into the steroidal skeleton as a chiral backbone unit.
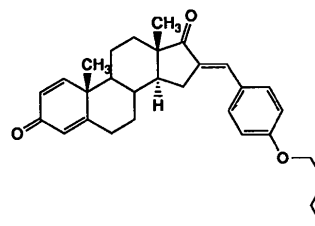
The compound was readily obtained as noncentrosymmetric crystals from the condensation reaction of androsta-1,4-diene-3,17-dione with 4-butoxybenzaldehyde. It showed a powder SHG efficiency 6.7 times that of urea for a fundamental wavelength of 1.064 μm of an Nd^{3+}:YAG laser using the technique of Kurtz & Perry (1968) and showed no absorption at λ longer than 420 nm.

A search of the January 1992 Version of the Cambridge Structural Database (1992) revealed that this paper is the first report on the crystal structure of the compound with an androsta-1,4-diene fragment attached to the styryl unit. The bond lengths and angles of the androstadiene skeleton are essentially as expected. The cyclohexa-1,4-dien-3-one ring adopts a nearly planar conformation.

The dihedral angle between the benzene ring and the plane of the ethylene unit C16=C20 deviates slightly from 0° and the ethylene bond angle C16=C20–C21 is significantly larger than 120°. These features of the styryl ketone fragment geometry of the title compound are essentially the same as those of chalcones (Rabinovich & Shakked, 1974; Rabinovich, Schmidt & Shakked, 1973) and 2-benzyl-5-benzylidenecyclopentanones (Theocharis, Nakanishi & Jones, 1981).
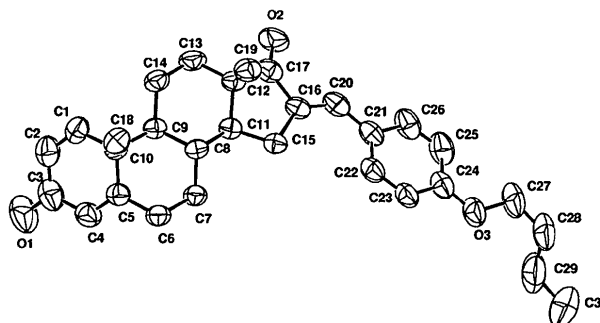

Fig. 1. Perspective view of the title compound.

Diagrams and most calculations were performed with the *Xtal*3.0 package (Hall & Stewart, 1990), as was the generation of the Crystallographic Information File used for the submission of this paper.

Experimental

Androsta-1,4-diene-3,17-dione and 4-butoxybenzaldehyde were purchased from the Tokyo Kasei Co., Ltd and used without further purification. Reagent-grade methanol was used for the reaction without further purification. To the solution of 0.940 g (5.28 mmol) of 4-butoxybenzaldehyde and 1.5 g (5.28 mmol) of androsta-1,4-diene-3,17-dione in methanol (5 ml) was added 0.5 ml of an aqueous 35% NaOH solution. The solution was re-fluxed for 1 h and then cooled to room temperature. The solid precipitate was collected by filtration, washed with methanol and dried *in vacuo*: colourless crystals, yield 1.900 g (81%). The single crystals for the X-ray measurements were obtained from slow evaporation of an acetone solution at room temperature.

^{1}H NMR (CDCl$_3$): δ=7.483 (*d*, 8.85 Hz, 2H, ArH), 7.411 (*s*, 1H), 7.072 (*d*, 10.37 Hz, 1H), 6.931 (*d*, 8.85 Hz, 2H, ArH), 6.253 (*dd*, 1.83 Hz, 10.07 Hz, 1H, ArH), 6.102 (*s*, 1H), 4.019 (*t*, 2.44 Hz, 2H), 1.297 (*s*, 3H), 1.027 (*s*, 3H), 0.982 (*t*, 7.33 Hz, 3H). λ_{max} (CH$_2$Cl$_2$)=322.5 nm (ε = 3.09 x 10^4). MS (EI, 70 eV) m/e 444.2649 (444.2666 for C$_{30}$H$_{36}$O$_3$).

Crystal data

C$_{30}$H$_{36}$O$_3$	V = 2509 (2) Å^3
M_r = 444.61	Z = 4
Orthorhombic	D_x = 1.177 Mg m^{-3}
$P2_12_12_1$	D_m = 1.124 Mg m^{-3}
a = 10.928 (4) Å	λ = 1.54184 Å
b = 37.398 (4) Å	μ = 0.55 mm^{-1}
c = 6.139 (4) Å	T = 297 K
Cell parameters from 25	Rectangular
reflections	0.45 × 0.4 × 0.4 mm
θ = 49.7–72.5°	Colourless

Data collection

Rigaku AFC6A diffractome-	R_{int} = 0.004
ter	θ_{max} = 60°
$\theta/2\theta$ scans	h = 0 → 12
Absorption correction:	k = 0 → 42
none	l = 0 → 6
2246 measured reflections	3 standard reflections
2189 independent reflections	monitored every 150
1922 observed reflections	reflections
[I_{net} > 2.000$\sigma(I_{net})$]	intensity variation: 0%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.507
Final R = 0.05	$\Delta\rho_{max}$ = 0.176 e Å^{-3}
wR = 0.058	$\Delta\rho_{min}$ = −0.267 e Å^{-3}
S = 2.58	Extinction correction: none
1922 reflections	Atomic scattering factors
442 parameters	from *International Tables*
Bond lengths and angles	*for X-ray Crystallogra-*
restrained	*phy* (1974, Vol. IV, Table
Calculated weights	2.2B)
w=1/[$\sigma^2(F)$+0.0002F^2]	

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

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.3082 (5)	0.0886 (1)	0.5591 (8)	0.070 (3)
C2	0.4073 (5)	0.0694 (1)	0.5104 (9)	0.081 (3)
C3	0.5195 (5)	0.0728 (1)	0.631 (1)	0.086 (3)
C4	0.5190 (4)	0.0984 (1)	0.808 (1)	0.075 (3)
C5	0.4218 (3)	0.1182 (1)	0.8585 (7)	0.057 (2)
C6	0.4265 (4)	0.1462 (1)	1.0369 (8)	0.061 (2)
C7	0.4018 (4)	0.1831 (1)	0.9354 (7)	0.056 (2)
C8	0.2818 (3)	0.18395 (9)	0.8097 (6)	0.046 (2)
C9	0.2751 (3)	0.15351 (9)	0.6393 (6)	0.048 (2)
C10	0.3020 (3)	0.11556 (9)	0.7392 (6)	0.053 (2)
C11	0.2641 (3)	0.21898 (9)	0.6887 (6)	0.047 (2)
C12	0.1417 (3)	0.2212 (1)	0.5666 (6)	0.053 (2)
C13	0.1341 (4)	0.1914 (1)	0.3998 (7)	0.067 (3)
C14	0.1559 (4)	0.1551 (1)	0.5079 (7)	0.063 (2)
C15	0.2746 (4)	0.25553 (9)	0.8033 (7)	0.052 (2)
C16	0.2185 (3)	0.2808 (1)	0.6394 (6)	0.056 (2)
C17	0.1501 (4)	0.2587 (1)	0.4749 (7)	0.064 (2)
C18	0.2000 (4)	0.1035 (1)	0.8960 (8)	0.068 (3)
C19	0.0305 (4)	0.2210 (1)	0.7212 (8)	0.066 (3)
C20	0.2175 (4)	0.3164 (1)	0.6229 (7)	0.063 (2)
C21	0.2676 (3)	0.3436 (1)	0.7646 (7)	0.059 (2)
C22	0.3098 (4)	0.3371 (1)	0.9767 (8)	0.063 (2)
C23	0.3520 (4)	0.3642 (1)	1.1071 (9)	0.067 (3)
C24	0.3505 (4)	0.3996 (1)	1.0351 (9)	0.068 (3)
C25	0.3077 (5)	0.4066 (1)	0.8261 (9)	0.084 (3)
C26	0.2676 (6)	0.3795 (1)	0.7008 (9)	0.080 (3)
C27	0.3741 (6)	0.4616 (1)	1.132 (1)	0.098 (4)
C28	0.4114 (7)	0.4826 (1)	1.326 (1)	0.110 (5)
C29	0.5406 (9)	0.4773 (2)	1.383 (3)	0.170 (8)
C30	0.593 (1)	0.4992 (3)	1.564 (2)	0.182 (9)
O1	0.6100 (3)	0.05480 (9)	0.5861 (9)	0.122 (3)
O2	0.1126 (3)	0.26883 (8)	0.2979 (5)	0.086 (2)
O3	0.3904 (3)	0.42417 (7)	1.1827 (6)	0.081 (2)

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

C1—C2	1.334 (7)	C4—C5	1.330 (6)
C1—C10	1.498 (6)	C5—C10	1.504 (5)
C2—C3	1.438 (7)	C16—C20	1.338 (6)
C3—C4	1.450 (8)	C20—C21	1.446 (6)
C3—O1	1.227 (6)		
C16—C20—C21	130.7 (4)		
C10—C1—C2—C3	0.5 (7)	C3—C4—C5—C10	0.9 (7)
C2—C1—C10—C5	−0.1 (6)	C4—C5—C10—C1	−0.6 (6)
C1—C2—C3—C4	−0.3 (7)	C16—C20—C21—C22	−12.6 (7)
C2—C3—C4—C5	−0.4 (7)		

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Redetermination of the Structure of Zinc Disilver(I) Tetrathiocyanate (at 178 K)

Peter G. Jones and Eberhard Bembenek

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany

Abstract

The structure of $ZnAg_2(SCN)_4$, previously reported in *Cc*, should be described in the centrosymmetric space group *C2/c*. The Zn atom occupies a special position on the twofold axis $\frac{1}{2}$, y, $\frac{1}{4}$. Both metal atoms are tetrahedrally coordinated (zinc by thiocyanate N, silver by S), although the coordination at silver is appreciably distorted.

Comment

In the course of our structural investigations of silver complexes with sulfur-containing ligands (Roesky, Schimkowiak, Meyer-Bäse & Jones, 1986, and references therein), our attention was drawn (Herbst-Irmer, 1990) to the structure of $ZnAg_2(SCN)_4$ (Fig. 1) (Shaofang, Meiyun & Jinling, 1982). The published space group was *Cc*, but an inspection of the coordinates suggested that the true space group might be *C2/c*. We therefore redetermined the struc-

ture, growing crystals as described in the original paper.

The structure can indeed be successfully refined in *C2/c*, whereby the Zn atom occupies a special position on a twofold axis. The Zn—N bonds are almost equal at 1.963, 1.965 (2) Å, in contrast to the spread of 1.87–2.06 Å in the previous determination; it is well known that apparent inequalities in bond lengths arise when a centrosymmetric structure is refined in a non-centrosymmetric space group (*e.g.* Ermer & Dunitz, 1970). The Ag—S bond lengths, 2.552–2.663 (2) Å, are far from equal in *C2/c*, but again the spread is less than in *Cc* (2.53–2.71 Å). Coordination at Ag^I is often irregular, as can also be seen from the bond angles 99.2–135.7 (1)°.

In other respects the structure is qualitatively as described by Lu *et al.* (1982). As expected, the softer metal Ag^I is coordinated by the softer donor S atoms. Each S atom coordinates two Ag atoms, but the angles at S(1), 100.7–113.0 (1)°, are much larger than those at S(2), 92.6–103.1 (1)°. A greater p character in the bonding at S(2) would account for the bond-length differences noted above. The C—N—Zn angles show appreciable deviations from linearity.

The thiocyanate groups bridge Zn and Ag centres to form a three-dimensional polymer, in which the
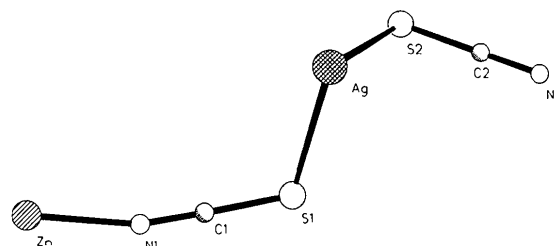

Fig. 1. The asymmetric unit of the title compound, showing the atom-numbering scheme.
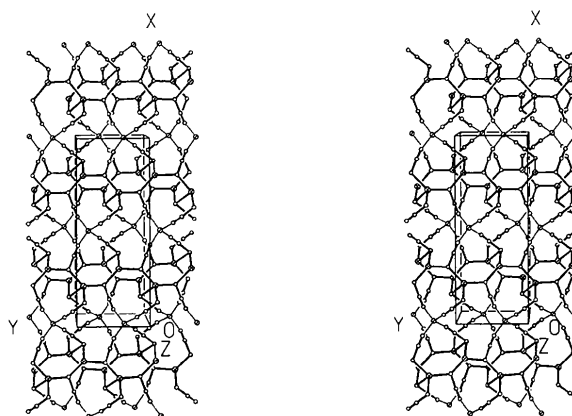

Fig. 2. Stereographic packing diagram of the title compound, viewed along the *z* axis.