Acta Cryst. (1997). C**53**, 1102–1103

11-(2-Chloro-2-propenyl)-5,11-dihydroxy-2-methylanthra[1,2-*b*]furan-6(11*H*)-one

Richard C. Cambie, Jared B. J. Milbank,
Clifton E. F. Rickard and P. Stewart Rutledge

Department of Chemistry, University of Auckland,
Private Bag 92019, Auckland, New Zealand. E-mail:
c.rickard@auckland.ac.nz

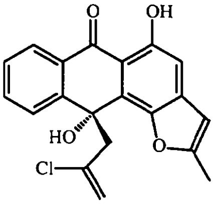
(*Received 23 December 1996; accepted 17 March 1997*)

Abstract

Reinvestigation of the reductive rearrangement of 1,4-bis(2-chloro-2-propenyl)-9,10-anthraquinone with high quality sodium dithionite has given new products. We report here the structure of one of these compounds, 11-(2-chloro-2-propenyl)-5,11-dihydroxy-2-methylanthra[1,2-*b*]furan-6(11*H*)-one, $C_{20}H_{15}ClO_4$.

Comment

During a reinvestigation of the reductive Claisen rearrangement of 1,4-bis(2-chloro-2-propenyl)-9,10-anthraquinone using sodium dithionite of high quality, a number of new compounds were isolated, including diastereomeric pairs of doubly rearranged leuco 1,4-dihydroxyanthraquinones in the keto form and products derived from attack on or rearrangement to a quinone carbonyl group (Harrington-Frost, Milbank & Rutledge, 1997). In order to confirm the structural assignment of one of the latter compounds, a single-crystal structural analysis was carried out on the rearranged furan 11-(2-chloro-2-propenyl)-5,11-dihydroxy-2-methylanthra[1,2-*b*]furan-6(11*H*)-one, (I).



(I)

The molecular structure of (I) is shown in Fig. 1, which also gives the labelling scheme. The ring system deviates somewhat from planarity. The molecule bends along the line joining C6 and C13, with the angle between the planes defined by C1–C6, C13, C14 and C6–C13 being 7.2 (1)°. These planes have r.m.s. deviations of 0.019 and 0.014 Å, respectively. The furan ring is coplanar with the fused aromatic ring. The 2-chloropropenyl group is twisted back over the top of the molecule and, from NMR evidence, seems to be locked in position. This appears to be due to a weak interaction between the Cl1 atom and the C7–C12 aromatic ring. The Cl atom makes close approaches of 3.563 (5) and 3.662 (5) Å to the C7 and C8 atoms, respectively.

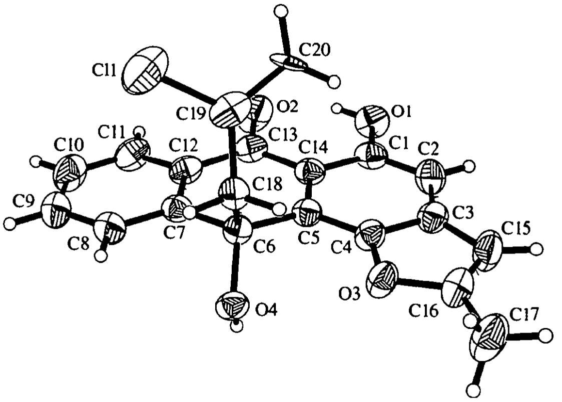


Fig. 1. Diagram of the title structure showing 50% probability displacement ellipsoids.

The ^1H chemical shifts of the olefinic methylene protons of the pendant group are shielded by *ca* 0.6 p.p.m. compared with the methylene protons of a freely rotating chloropropenyl group on an aromatic ring. The ^{13}C chemical shift for the terminal olefinic C atom of the pendant group also shows a deshielding effect of *ca* 2.4 p.p.m. relative to that of a freely rotating chloropropenyl group.

The hydroxyl proton on O1 hydrogen bonds to the ketonic O2 atom [O1···O2 2.489 (5) and H1—O2 1.77 Å]. There is an additional intermolecular hydrogen bond between the O4 hydroxyl group and the O1 hydroxyl group of an adjacent molecule [O4···O1($2-x$, $1-y$, $1-z$) 2.881 (5) Å].

Experimental

The title compound was obtained by reduction of 1,4-bis(2-chloro-2-propenyl)-9,10-anthraquinone with sodium dithionite followed by chromatography on silica. Crystallization from chloroform/pentane yielded yellow prisms (m.p. 460–461 K).

Crystal data

$C_{20}H_{15}ClO_4$
$M_r = 354.77$
Monoclinic
$P2_1/c$
$a = 11.120\ (2)$ Å
$b = 18.280\ (2)$ Å
$c = 7.917\ (2)$ Å
$\beta = 98.23\ (2)°$
$V = 1592.8\ (5)$ Å^3
$Z = 4$
$D_x = 1.479$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–$10°$
$\mu = 0.263$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.32 × 0.22 × 0.20 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2939 measured reflections
2771 independent reflections
1676 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0372$

$\theta_{\max} = 25°$
$h = -13 \rightarrow 0$
$k = -23 \rightarrow 0$
$l = -9 \rightarrow 9$
3 standard reflections every 100 reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0678$
$wR(F^2) = 0.2370$
$S = 1.017$
2726 reflections
229 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1112P)^2 + 2.3877P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.008$
$\Delta\rho_{\max} = 0.552$ e Å^{-3}
$\Delta\rho_{\min} = -0.600$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cl1—C19	1.688 (5)	O4—C6	1.425 (5)
O1—C1	1.352 (5)	C3—C15	1.395 (7)
O2—C13	1.225 (5)	C15—C16	1.333 (7)
O3—C16	1.355 (6)	C18—C19	1.477 (6)
O3—C4	1.363 (5)	C19—C20	1.416 (7)
C18—C19—Cl1	115.2 (4)	C5—C6—O4	110.6 (3)
C20—C19—Cl1	118.2 (4)	C7—C6—O4	108.0 (3)
C14—C13—O2	120.3 (4)	C4—O3—C16	104.1 (4)
C12—C13—O2	121.1 (4)	C2—C1—O1	116.8 (4)
C14—C1—O1	121.8 (4)		
C5—C6—C18—C19	68.0 (5)	C6—C18—C19—Cl1	106.8 (4)

The diffraction pattern was rather weak, falling off rapidly with θ. The low intensity of the data, particularly for high θ reflections, contributes to the rather high residual. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for the methyl group), and with $U_{\rm iso}$ constrained to be $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local programs. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1287). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Harrington-Frost, N. M., Milbank, J. M. J. & Rutledge, P. S. (1997). *Aust. J. Chem.* In the press.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *SHELXTL.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 1103–1105

2,2′-Diaminodiphenyl Disulfide Hemihydrate

Branko Kaitner and Gordana Pavlović

Chemistry Department, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia. E-mail: kaitner@olimp.irb.hr

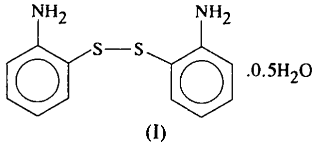
(*Received 1 February 1996; accepted 20 March 1997*)

Abstract

The stereochemistry of 2,2′-diaminodiphenyl disulfide hemihydrate, $C_{12}H_{12}N_2S_2.0.5H_2O$, differs significantly from that of the corresponding anhydrous compound. The conformational difference is a consequence of the O—H···N and N—H···O intermolecular hydrogen bonding between the $C_{12}H_{12}N_2S_2$ and water molecules. The molecule is characterized by a skewed central moiety with a C—S—S—C torsion angle of 75.2 (1)°.

Comment

Two products were obtained in an attempt to prepare the tridentate Schiff base *N*-(2-mercaptophenyl)-2-hydroxy-1-naphthaldimine from 2-hydroxy-1-naphthaldehyde and 2-aminothiophenol in a template condensation reaction, namely, *N*,*N*′-[dithiobis(*o*-phenylene)]bis(2-hydroxy-1-naphthaldimine), as a yellow precipitate in lower yield, and 2,2′-diaminodiphenyl disulfide in higher yield. The latter crystallized as a hemihydrate, (I), in the form of regular transparent ochre prisms from a red–brown solution in methanol at low temperature.



(I)

The stereochemistry of diphenyl disulfide is known (Lee & Bryant, 1969; Sacerdoti, Gilli & Domiano, 1975), together with many substituted diaryl disulfides (Lee & Bryant, 1970; Spirlet, Van den Bossche, Dideberg & Dupont, 1979; Ricci & Bernal, 1969, 1970; Mak,