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Dyes and Pigments 65 (2005) 281–283
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Short communication

Crystal structure of anthraquinone-1,5-dithiol

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Received 23 February 2004; received in revised form 17 May 2004; accepted 30 July 2004
Available online 18 October 2004

Abstract

The X-ray crystal structure of anthraquinone-1,5-dithiol has been determined. The compound $C_{14}H_8O_2S_2$ is monoclinic in Pc with $a = 3.8625(8)$ Å, $b = 10.395(2)$ Å, $c = 13.734(3)$ Å, $\beta = 93.609(4)°$, $V = 550.31(19)$ Å^3, $D_{calc} = 1.643$ g/cm^3 and $Z = 2$. The crystal packing scheme indicates a π–π interaction. An intermolecular hydrogen bond of sp^2C–H···S has been found between the H4 atom and the S2 atom.

Keywords: Anthraquinone-1,5-dithiol; X-ray; Crystal structure; π–π Interaction; Hydrogen bond

1. Introduction

Anthraquinone and its derivatives are important compounds used in the field of dyes and pigments [1,2]. The dyeing and photochemical properties of them are often affected by the intermolecular interactions. With effective hydrogen donors and acceptors in their structures, hydrogen bond might be the dominant type of intermolecular interaction [3]. Besides hydrogen bond, the anthraquinone derivatives typically have large p-conjugated planar structures, which would lead to other types of intermolecular interactions, such as interlayer π–π interactions [4] and C–H interactions [5]. On the other hand, alkanethiols are often used as molecular anchors to lead the functional molecules arraying on some basal planes by absorption [6]. These intermolecular interactions are helpful to the effective three dimensional molecular stacking of anthraquinone dyes, which made them valuable candidates for organic functional materials [7].

Our continued investigation is to focus on preparation and characterization of functional organic dyes. In this paper, a novel anthraquinone dye with two symmetric thiol substituents is synthesized, and then, its crystal structure is determined by X-ray diffraction and the molecular stacking behavior is demonstrated.

2. Experimental

Anthraquinone-1,5-dithiol was prepared by refluxing a mixture of 1,5-dichloroanthraquinone, $Na_2S{\cdot}9H_2O$, NaOH, zinc powder and ethylene glycol for 2 h. Single crystals suitable for investigation were grown from ethanol by slow evaporation. ^{1}H NMR was recorded in $CDCl_3$ solution on a Varian Mercury Plus 400 Spectrometer using $(CH_3)_4Si$ as an internal standard. ^{1}H NMR spectrum (δ, ppm (J, Hz)): 8.28 (2H, q, $J = 1.2$, 7.6); 7.79 (2H, q, $J = 1.2$, 8.0); 7.70 (2H, m, $J = 7.8$); 3.52 (2H, br s, SH).

X-ray diffraction data were collected at 293(2) K on a Bruker SMART diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal structure was solved and refined with standard

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doi:10.1016/j.dyepig.2004.07.022

Table 1
Crystal data and experimental details

Compound	$C_{14}H_8O_2S_2$
Crystal dimensions, mm	$0.458 \times 0.103 \times 0.096$
Crystal system	Monoclinic
Space group	Pc
Unit cell dimensions	$a = 3.8625(8)$ Å
	$b = 10.395(2)$ Å
	$c = 13.734(3)$ Å
	$\beta = 93.609(4)^\circ$
Volume, Å^3	550.31(19)
Z	2
Density (calculated), g/cm^3	1.643
Temperature, K	293
Wavelength, Å	0.71073
θ Range for data collection	$1.96-28.27^\circ$
Reflections collected	Total: 3259
	Unique: 1669 ($R_{int} = 0.0871$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1669/6/184
Goodness-of-fit on F^2	0.887
Final R indices ($I>2\sigma(I)$)	$R1 = 0.0485$, $wR2 = 0.1030$
R indices	$R1 = 0.0605$, $wR2 = 0.1069$
Absolute structure parameter	0.20(13)
Extinction coefficient	0.005(3)
Largest diff. peak and hole	0.226 and -0.254 e$^-$/Å^3

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters

	x/a	y/b	z/c	B_{eq}
S1	0.4563(4)	1.03403(12)	0.16579(11)	0.0576(4)
S2	1.2022(3)	0.35445(11)	0.39812(10)	0.0504(4)
O1	1.2785(11)	0.6250(3)	0.4312(3)	0.0603(11)
O2	0.6176(14)	0.7828(4)	0.1035(3)	0.0907(16)
C1	1.0799(12)	0.6536(4)	0.3634(3)	0.0378(11)
C2	0.9441(11)	0.7882(4)	0.3546(3)	0.0384(10)
C3	0.9978(14)	0.8659(5)	0.4361(4)	0.0483(13)
C4	0.8829(15)	0.9910(5)	0.4332(4)	0.0562(14)
C5	0.7107(15)	1.0388(5)	0.3491(5)	0.0548(14)
C6	0.6640(12)	0.9623(4)	0.2678(4)	0.0432(11)
C7	0.7758(12)	0.8342(4)	0.2680(3)	0.0377(10)
C8	0.7272(13)	0.7449(5)	0.1826(3)	0.0450(11)
C9	0.8109(11)	0.6081(4)	0.1982(3)	0.0358(10)
C10	0.7191(14)	0.5245(5)	0.1217(4)	0.0457(12)
C11	0.7826(14)	0.3950(5)	0.1308(4)	0.0500(13)
C12	0.9347(14)	0.3476(4)	0.2155(4)	0.0471(12)
C13	1.0256(11)	0.4272(4)	0.2936(3)	0.0396(10)
C14	0.9689(11)	0.5602(4)	0.2850(3)	0.0351(10)
S1	0.4563(4)	1.03403(12)	0.16579(11)	0.0576(4)
S2	1.2022(3)	0.35445(11)	0.39812(10)	0.0504(4)
O1	1.2785(11)	0.6250(3)	0.4312(3)	0.0603(11)
H2	0.9205	1.0437	0.4876	0.067
H3	0.6268	1.1227	0.3478	0.066
H5	0.7219	0.3398	0.0792	0.060
H1	1.120(11)	0.834(5)	0.491(3)	0.064(18)
H4	0.611(11)	0.558(4)	0.065(4)	0.041(13)
H6	0.997(12)	0.260(2)	0.226(4)	0.057(14)
H8	1.438(8)	0.334(7)	0.418(5)	0.13(3)
H7	0.276(14)	0.972(6)	0.143(6)	0.12(3)

techniques (SHELXS-90 [8]; SHELXL-97 [9]). All U values of H-atoms refine to realistic values. Relevant numerical data are given in Table 1; final fractional atomic coordinates are listed in Table 2.

3. Results and discussion

A general view of one molecule is shown in Fig. 1. Anthraquinone-1,5-dithiol is a planar molecule and the distortion from the planarity is small. Results of calculations of least-squares planes are given in Table 3.

Crystal packing scheme is shown in Fig. 2. In the direction of a-axis, molecules stand face to face in a straight line and look like a stack of pennies, which indicate a typical behavior of $\pi-\pi$ electron interaction. The stacking distance between planes of the neighboring molecules is 3.4262 Å and the normal to the molecular plane is inclined 27.5° to the stack axis.

A special intermolecular hydrogen bond of $sp^2C-H\cdots S$ has been found between the H4 atom at aromatic hydrogen carbon and the S2 atom at the other molecule (Fig. 2). The distance between the H4 atom and the S2 atom is 2.848 Å. The formation of this hydrogen bond is probably due to the acidity of H4

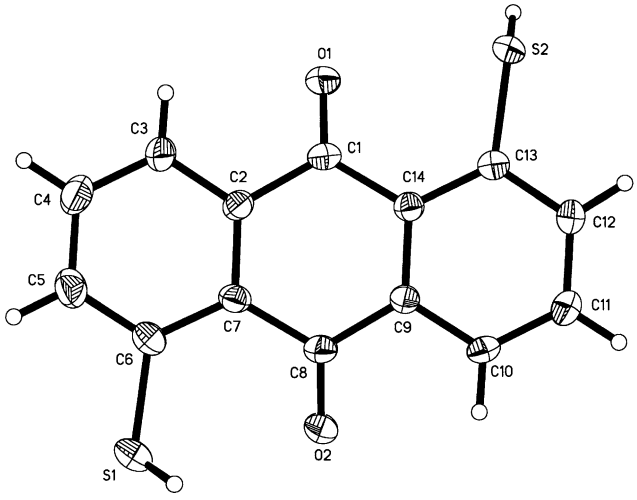

Fig. 1. Molecular structure and atomic numbering of anthraquinone-1,5-dithiol.

Table 3
Dihedral angles between planes (x, y, z in crystal coordinates)

Plane	Equation	Angle to previous plane
1	$3.4748x + 3.0961y - 5.1541z = 3.8978$	
2	$3.5176x + 2.1999y - 5.6490z = 3.0920$	5.38°
3	$3.5775x + 1.3009y - 5.6752z = 2.5687$	5.04°

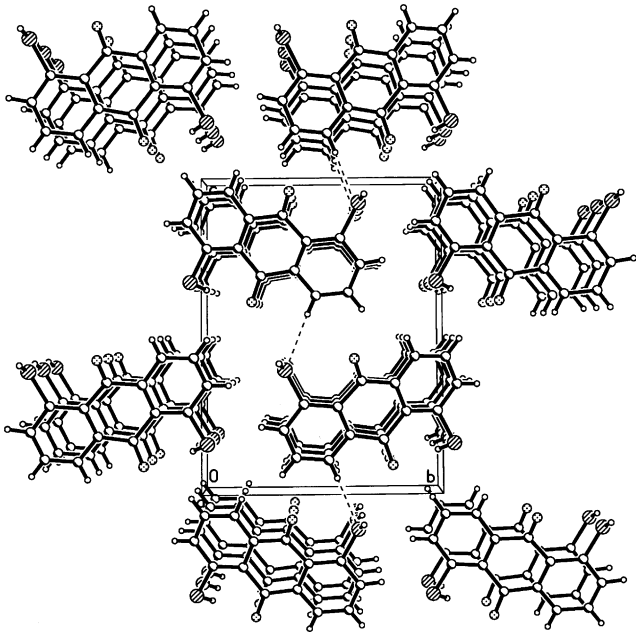

Fig. 2. Crystal packing scheme of anthraquinone-1,5-dithiol.

enhanced by conjugated carbonyl groups in the middle ring of anthraquinone structure. Both the intermolecular hydrogen bond and π–π interplanar interaction contribute to the orientation of molecular aggregation in the crystal.

Acknowledgements

The authors are very grateful to Dr. Mouhai Shu for the experimental assistance and helpful discussion.

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