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The crystal structure of a squarylium dye, 2,4-bis[(1-isopropyl-3,3-dimethyl-2-indolinyldene)-methyl]cyclobutenediylium-1,3-diolate

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Abstract

The crystal structure of 2,4-bis[(1-isopropyl-3,3-dimethyl-2-indolinyldene)methyl] cyclobutenediylium-1,3-diolate has been determined. It was found that the crystal system is orthorhombic and the space group is Pbca, with $a = 10.142(3)$, $b = 14.146(4)$, $c = 22.262(6)$ A, and $Z = 8$. The molecules have adopted the *trans*-conformation, and are held together by van de Waal's forces. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Squaraine; Squarylium indolenium dye; Squarylium cyanine dye; Single crystal structure; Molecule structure; XDS Determination

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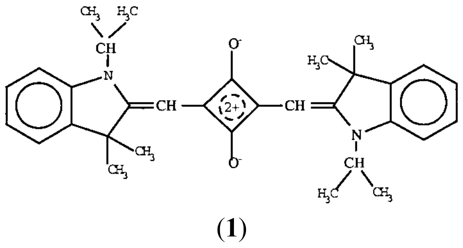
1. Introduction

In recent years squaraine dyes have been widely studied as substrates for photovoltaic devices [1], photoconductor photoreceptors [2], optical recording media [3] and nonlinear optics [4]. As a result of these potential applications, there has been an increasing interest in the solid-state properties, especially the crystal properties of squaraine dyes. In the case of indolenium squaraine (SQ) dyes, Kobayashi et al. have reported the single crystal structure of 2,4-bis[(1-methyl-3,3-dimethyl-2-indolinylidene)methyl]cyclobutenediylium-1,3-diolate (*N*-methyl SQ) [5]. As an extension of that work, we decided to study the single crystal properties of the *N*-isopropyl analog, 2,4-bis[(1-isopropyl-3,3-dimethyl-2-indolinylidene)methyl] cyclobutenediylium-1,3-diolate (*N*-isopropyl SQ), to determine whether the *N*-isopropyl group exerted a large effect on the crystal structure and solid state properties.

In this paper, we report the results from single crystal preparation and structure determination of *N*-isopropyl SQ (**1**) by the XDS method.



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2. Results and discussion

An ORTEP diagram displaying the molecular structure of dye **1** is shown in Fig. 1. It shows that the molecule possesses rotational symmetry of order 2. The final atomic coordinates of non-hydrogen atoms are listed in Table 1. A planar central four-membered ring can be found, and the indolenium rings are planar. The indolenium and cyclobuteneliylium-1,3-diolate moieties are slightly mutually twisted, forming a dihedral angle of 17.63°. In addition, the two indolenium planes are parallel to each other. Carbons C(5) and C(6) lie outside the indolenium ring plane forming an angle 112°. The *N*-isopropyl group is vertical to the indolenium ring, with C(15) and C(16) making an angle of 111.3°. The π-chromophoric system in the molecule is roughly planar and adopts a *trans*-orientation.

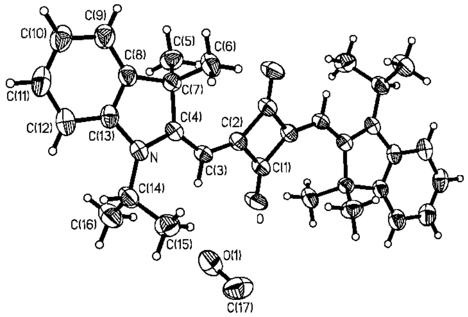

Fig. 1. ORTEP diagram of dye **1**. Displacement ellipsoids are shown at the 50% probability level.

Table 1
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) of title compound[a]

	x	y	z	U(eq)
O	1604(3)	5717(2)	4471(1)	101(1)
O(1)	3022(4)	5029(3)	3556(2)	126(2)
N	−356(4)	2554(2)	3511(1)	70(1)
C(1)	738(5)	5328(3)	4767(2)	72(1)
C(2)	−37(4)	4472(3)	4663(2)	65(1)
C(3)	91(4)	3859(3)	4184(2)	62(1)
C(4)	−659(4)	3104(3)	4000(2)	64(1)
C(5)	−2968(4)	3533(4)	4307(2)	96(2)
C(6)	−1703(5)	2266(3)	4875(2)	92(2)
C(7)	−1950(4)	2756(3)	4260(2)	68(1)
C(8)	−2360(5)	2016(3)	3809(2)	74(1)
C(9)	−3474(6)	1476(4)	3782(2)	98(2)
C(10)	−3621(6)	834(4)	3318(3)	105(2)
C(11)	−2658(7)	741(4)	2887(3)	103(2)
C(12)	−1522(6)	1280(4)	2910(2)	90(2)
C(13)	−1406(5)	1922(3)	3387(2)	73(1)
C(14)	827(5)	2572(4)	3138(2)	86(1)
C(15)	2107(5)	2520(4)	3486(2)	101(2)
C(16)	852(4)	3334(3)	2702(2)	123(2)
C(17)	4161(4)	4820(3)	3808(2)	146(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The bond lengths and bond angles determined for dye **1** are listed in Table 2. It was found that the squarylium ring has bond angles of 92.0° and 88.0°. Also, the C–C bond lengths in the squarylium ring are 1.461 and 1.481 Å, which are longer than the normal C=C double bond. The lower bond angles and longer bond lengths imply that the ring has high strain. A bond angle of 131.8° was observed for C(2)–C(3)–C(4). Such an angle is much larger than that of the ideal sp^2 C-atom bond angle, and may arise from steric crowding of the indolenium and the squarylium rings.

Fig. 2 shows that the benzene rings exhibit little bond alternation, and the bond alternation is low for C(13)–N–C(4)–C(3)–C(2)–C(1)–O. Judging by the C–O bond length (from [6] the C–O bond length is 1.413 Å for methanol and 1.198 Å for the cyclobutanone), the C(1)–O is also conjugated, and hence is a part of the cyanine chromophore.

The atomic coordinates for non-hydrogen atoms are also listed in Table 1. No H-bond exists between methanol and the O-atom of squarylium ring, as the distance between them is too large.

The crystal packing structure is provided in Fig. 3. The dye molecules are held together mainly by

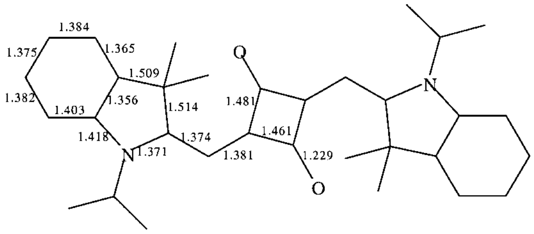

Fig. 2. The molecular structure and π-atoms bond lengths of compound **1**.

Table 2
Bond lengths [Å] and angles (°) for dye **1**

Bond lengths			
O–C(1)	1.229(4)	C(5)–C(7)	1.512(6)
O(1)–C(17)	1.318(5)	C(6)–C(7)	1.554(5)
N–C(4)	1.372(4)	C(7)–C(8)	1.509(6)
N–C(13)	1.418(5)	C(8)–C(13)	1.356(5)
N–C(14)	1.459(5)	C(8)–C(9)	1.365(6)
C(1)–C(2)	1.461(6)	C(9)–C(10)	1.384(7)
C(1)–C(2)#1[a]	1.481(5)	C(10)–C(11)	1.375(6)
C(2)–C(3)	1.381(5)	C(11)–C(12)	1.382(6)
C(2)–C(1)#1	1.481(5)	C(12)–C(13)	1.403(6)
C(3)–C(4)	1.374(5)	C(14)–C(16)	1.449(6)
C(4)–C(7)	1.514(5)	C(14)–C(15)	1.514(6)
Bond angles			
C(4)–N–C(13)	110.1(4)	C(8)–C(7)–C(6)	108.7(3)
C(4)–N–C(14)	128.7(4)	C(5)–C(7)–C(6)	112.0(4)
C(13)–N–C(14)	121.2(4)	C(4)–C(7)–C(6)	110.0(3)
O–C(1)–C(2)	132.1(4)	C(13)–C(8)–C(9)	120.3(5)
O–C(1)–C(2)#1	135.8(4)	C(13)–C(8)–C(7)	109.4(4)
C(2)–C(1)–C(2)#1	92.0(4)	C(9)–C(8)–C(7)	130.3(5)
C(3)–C(2)–C(1)	126.2(4)	C(8)–C(9)–C(10)	119.4(5)
C(3)–C(2)–C(1)#1	145.8(4)	C(11)–C(10)–C(9)	120.4(5)
C(1)–C(2)–C(1)#1	88.0(4)	C(10)–C(11)–C(12)	120.9(5)
C(4)–C(3)–C(2)	131.8(4)	C(11)–C(12)–C(13)	117.1(5)
N–C(4)–C(3)	123.6(4)	C(8)–C(13)–C(12)	121.9(5)
N–C(4)–C(7)	108.3(4)	C(8)–C(13)–N	109.8(4)
C(3)–C(4)–C(7)	128.1(4)	C(12)–C(13)–N	128.2(5)
C(8)–C(7)–C(5)	111.2(4)	C(16)–C(14)–N	114.1(4)
C(8)–C(7)–C(4)	102.1(3)	C(16)–C(14)–C(15)	111.3(4)
C(5)–C(7)–C(4)	112.4(4)	N–C(14)–C(15)	114.4(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z+1$.

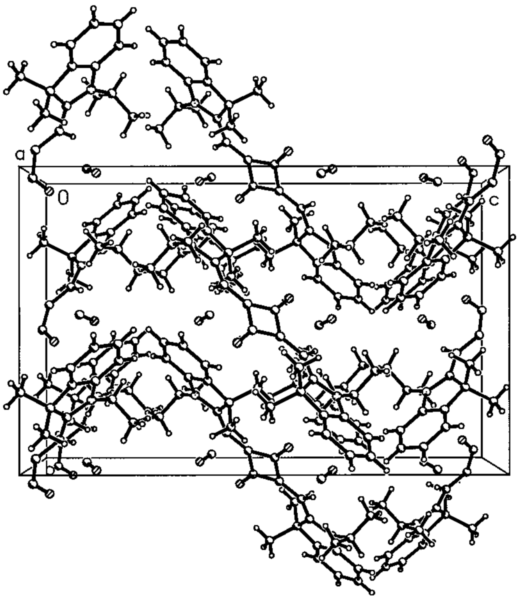

Fig. 3. Crystal packing structure of compound **1**.

Table 3
The single crystal data and condition used[a]

Crystal data	
Molecular formula	$[C_{17}H_{22}O_2NO]_2$
Molecular weight	$M_r = 272.36$
Crystal system	Orthorhombic
Space group	Pbca
Unit cell	$a = 10.142(3)$ Å $b = 14.146(4)$ Å $c = 22.262(6)$ Å
Crystal volume	3194(2) Å^3
Z	8
Density (calculated)	1.133 Mg m^{-3}
Absorption coefficient	0.07 mm^{-1}
F(000)	1176
Crystal size	0.8×0.7×0.7 mm
Crystal color	Green
Crystal Description	Prism
Data collection and refinement	
Determination instrument	Siemens P4 four-circle diffratometer
Ambient temperature	$T = 293(2)$ K
Radiation wavelength	$\lambda = 0.71073$ Å
Radiation type	Mo Kα
Scan method	θ–2θ
Final R indices [$F^2 > 2s(F^2)$]	$R1 = 0.0696$, w$R2 = 0.1864$
R indies (all data)	$R1 = 0.1797$, w$R2 = 0.2317$
Largest difference in peak and hill	0.441 and −0.295 eÅ^{-3}
Extinction correction	SHELXL93
Extinction coefficient	0.008(2)
H-atoms	Only H-atom Us refined

[a] Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to refine structure: SHELXL93 (Shelrich, 1993). Molecular graphics: XP (Siemens, 1991). Software used to prepare material for publication: *SHELXL93*.

van der Waal's forces. Rotation of the indolenium ring away from squarylium ring probably arises from molecular packing.

The single crystal structure of the *N*-methyl SQ dye is much different. In this case the published crystal system is monoclinic and the space group is P2$_1$/c, but the *N*-isopropyl analog is orthorhombic and the space group is Pbca. While we found little differences in the bond lengths of these two dyes, the bond angles are significantly different. The differences suggest that the *N*-substituent exerts a large effect not only on the molecular space arrangements but also on molecular conformation.

3. Experimental

Dye **1** was synthesized by condensing 1-isopropyl-2,3,3-trimethylindolenium iodinate and squaric acid (1,2-dihydroxylcycolbutene-3,4-dione) in *n*-butanol/pyridine, the details of which are described elsewhere [7]. The single crystal was prepared by slow evaporation of a methanol solution. The single crystal data and methods employed are listed in Table 3.

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