Synthesis and Solid-State Structure of the Unsymmetrical Squaraine Dye 2-[4-(Dibutylamino)-2-hydroxyphenyl]-4-[4-(dibutylamino)phenyl]cyclobutenebis(ylium)-1,3-diolate

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The synthesis of an unsymmetrical squaraine dye, 2-[4-(dibutylamino)-2-hydroxyphenyl]-4-[4-(dibutylamino)phenyl]cyclobutenebis(ylium)-1,3-diolate, has been achieved via a cross condensation reaction. In the solid state the compound is isomorphous with the known symmetrical dye bis[4-(dibutylamino)phenyl]squaraine. The single hydroxy group is found to be disordered equally over the centrosymmetrically *trans*-related *ortho* and *ortho'* phenyl ring sites.

Introduction

The zwitterionic compound (1)[†] belongs to a series of organic dyes commonly referred to as squaraines, so named because of their square central ring. Symmetrical squaraines are readily available from the condensation of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) with 2 mol. equiv. of an electron-rich aromatic compound, such as an aniline or phenol,¹ whilst unsymmetrical squaraines are generally synthesized by sequential cycloaddition and condensation procedures.² Both classes of dyes have been the subject of detailed studies because they exhibit a wide range of photophysical properties. These properties are the direct result of extensive delocalization within the squaraine chromophore. The resonances (Scheme 1) ensure that the atoms comprising the three constituent conjugated ring systems are all coplanar, a structural energy minimum also predicted by molecular modelling studies.³ The quinoidal resonance form is an interesting structural characteristic that is evident in the several known crystal structures of bis(aminophenyl) squaraines.[‡] Frequently bis(aminophenyl) squaraines have been observed to crystallize as a mixture of both dark-green monoclinic and purple triclinic crystals. Both polymorphs have been determined for ehsq $(P 2_1/a \text{ and } P \overline{1})$, whereas for the other bis(aminophenyl) squaraines only one form has been reported (mmsq, $P 2_1/n$ —solvated chloroform; bdsq, $P \bar{1}$; and bsq, $P 2_1/c$). A striking and recurrent feature of the solid-state packing of bis(aminophenyl) squaraines is that they form extended parallel stacks with the electron-rich amino groups aligned over the electron-deficient squarate rings. The only noticeable difference between the triclinic and monoclinic arrangements of a given dye is the perpendicular distance between the planes of the stacked molecules (3.4 Å for triclinic cf. 3.9 Å for monoclinic).⁵



Scheme 1

† 2-[4-(Dibutylamino)-2-hydroxyphenyl]-4-[4-(dibutylamino)phenyl]cyclobutenebis(ylium)-1,3-diolate. ‡ These compounds are 2,4-bis[4-(dimethylamino)-2-methylphenyl]cyclobutenebis(ylium)-1,3-diolate⁴ (mmsq), 2,4-bis[4-(diethylamino)-2-hydroxyphenyl]cyclobutenebis(ylium)-1,3-diolate⁵ (ehsq), 2,4-bis[4-(dibutylamino)-2,6-dihydroxyphenyl]cyclobutenebis-(ylium)-1,3-diolate⁶ (bdsq), and 2,4-bis[4-(dibutylamino)phenyl]cyclobutenebis(ylium)-1,3-diolate⁷ (bsq).

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Solution ¹H n.m.r. studies^{6,8} of bis(4-amino-2hydroxyphenyl) squaraines suggest that these dyes equilibrate (e.g. Scheme 2) between two isomeric *cis* and *trans* forms; in solution the ratio of *cis* to *trans* is c.1:3. Other classes of squaraine dyes exhibit structural isomerism, for example bis(indolinium) squaraines have available six isomeric forms.⁶ In solution the diethyl (ehsq) analogue of the pictured dye favours a similar isomeric ratio. However, in the solid state the hydroxy groups adopt a comparative percentage occupancy ratio of 10:90 in favour of the *trans* form.



Unsymmetrical squaraines have received much less attention than their symmetrical counterparts because of the more difficult procedures involved in their synthesis. In the present work a simple procedure has been employed for the synthesis of an unsymmetrical squaraine (1); this procedure may prove viable for the small-scale synthesis of other unsymmetrical aminophenyl squaraines. The single-crystal X-ray structure of the dye (1) is also reported and represents the first report of the crystal structure of an unsymmetrical squaraine dye.



Experimental

Preparation

Squaric acid and N,N-dibutylaniline were purchased from the Aldrich Chemical Company (U.K.); tributyl orthoformate was obtained from Lancaster Synthesis (U.K.). 3-(Dibutylamino)phenol was prepared from the reaction of 3aminophenol with tributyl phosphate, and passed down a column of silica gel immediately prior to use in the squaraine-formation reaction. $^{\rm 8}$

A mixture of squaric acid (50 mg, 0.44 mmol), N,Ndibutylaniline (90 mg, 0.44 mmol) and 3-(dibutylamino)phenol (97 mg, 0.44 mmol) was refluxed in a mixture of propan-2-ol (35 ml) and tributyl orthoformate (0.70 ml, 610 mg, 2.63 mmol) for 6 h in a nitrogen atmosphere. On cooling, a green semicrystalline deposit formed which was collected by filtration, dried and then subjected to flash column chromatography (SiO₂; CHCl₃/n-hexane, 1:1). Three deep blue fractions were obtained; thin-layer chromatographic analysis identified the first and last fractions as the symmetrical dihydroxy⁸ (14 mg, 12%) and non-hydroxy⁹ (17 mg, 16%) substituted dyes respectively. The middle fraction was evaporated to afford a blue-green powder (42 mg, 19%; assuming a quantitative, statistical distribution of products the maximum possible yield would be 50%), m.p. 185–187°C (Found: C, 76.0; H, 8.8; N, 5.4. $\rm C_{32}H_{44}N_2O_3$ requires C, 76.2; H, 8.8; N, 5.6%). F.a.b. mass spectrum (3-nitrobenzyl alcohol) m/z 504 (M, 100%). Visible (CHCl₃) 643 nm (log ϵ 5.30). I.r. (cm⁻¹) 1611s (C=O). $\delta_{\rm H}$ (CDCl₃, 250 MHz) 0.98, 12H, t, J 7 Hz, CH₃; 1.38, 8H, sextet, J 7 Hz, CH₂CH₃; 1.60, 8H, quintet, J 7 Hz, NCH₂CH₂; 3.40, 8H, t, J 7 Hz, NCH₂; 6.09, 1H, d, J 2 Hz, H_c; 6.34, 1H, dd, J 9, 2 Hz, Hb; 6.69, 2H, d, J 9 Hz, He; 8.07, 1H, d, J 9 Hz, Ha; 8.17, 2H, d, J 9 Hz, Hd; 13.05, 1H, s, OH (see Fig. 1 for proton identification).



Fig. 1. Key for n.m.r. assignments.

Slow evaporation of a solution of a small portion of the dye in dichloromethane/hexane (1:1) afforded a single crystal suitable for the X-ray structural determination.

Spectroscopy

The infrared spectrum was recorded as a pressed KBr disk on a Nicolet 205 Fourier-transform infrared spectrophotometer. Ultraviolet-visible measurements were made on a Shimadzu UV-2100 spectrophotometer. The ¹H n.m.r. spectrum was recorded on a Bruker AC250 spectrometer. The f.a.b. mass spectrum was recorded in positive-ion mode on a VG analytical double-focusing mass spectrometer.

Crystallography

Crystal Data

 $\rm C_{32}H_{43}N_2O_3,~mol.~wt~503\cdot7,~monoclinic,~space~group <math display="inline">P\,2_1/a,~a~9\cdot129(2),~b~19\cdot804(4),~c~9\cdot160(2)$ Å, $\beta~116\cdot89(1)^\circ,~V~1477\cdot0(5)$ Å³, F(000) 546, $D_c(Z=2)~1\cdot132~g~cm^{-3},~\mu(Mo~K\alpha)~0\cdot72~cm^{-1},~temperature~298(2)~K.$

Data Collection, Structure Solution and Refinement

Intensity data were collected by means of a Rigaku AFC7R four-circle diffractometer with a 12 kW rotating-anode Mo K α source (graphite crystal monochromatized), from an uncut specimen measuring 0.50 by 0.50 by 0.25 mm. Of 2858 unique reflections collected up to $2\theta_{\rm max}$ 50°, 2685 were unique ($R_{\rm int} = 0.058$) while 1383 with $I > 3.0\sigma(I)$ were used in refinement. Corrections were made for absorption (transmission factors 0.96 and 1.00) and extinction. A loss in intensity of c. 1.4% in the standards indicated some crystal deterioration

which was allowed for by using a linear correction. The structure was solved by direct methods and refined (on F) with the TeXsan structure determination package,¹⁰ giving residuals† R, Rw and S of 0.071, 0.059 and 4.7 respectively, with anisotropic thermal parameters for all non-hydrogens. Hydrogen atoms, with the exception of the hydroxy proton, which was located by difference methods, were included at calculated positions as riding models. The site occupancy factor of the hydroxy oxygen was determined by refinement to be 50% and was subsequently fixed at that value. This indicates that the hydroxy group is disordered equally over the centrosymmetrically related ortho and ortho' sites of the phenyl rings.

Results

Final atomic coordinates for (1) are given in Table 1. Torsion angles are given in Table 2. Lists of bond distances and angles, anisotropic thermal parameters, observed and calculated structure factors, and hydrogen

 Table 1. Atomic coordinates and equivalent isotropic thermal parameters for (1)

$B_{\rm eq} = \frac{8}{3}\pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2$
$+2U_{12} aa^* bb^* \cos \gamma + 2U_{13} aa^* cc^* \cos \beta$
$+2U_{23} bb^* cc^* \cos \alpha$

Atom	x	\boldsymbol{y}	z	$B_{\rm eq}$ (Å ²)
O(1)	-0.0531(3)	0.57513(9)	$1 \cdot 1570(2)$	5.37(6)
$O(4)^A$	-0.1441(6)	0.6676(2)	0.9299(5)	$7 \cdot 0(1)$
N(1)	-0.2162(3)	0.7290(1)	0.4088(2)	$4 \cdot 19(5)$
C(1)	-0.0240(3)	0.5344(1)	1.0719(3)	4.02(7)
C(2)	-0.0311(3)	0.5360(1)	0.9077(3)	3.54(6)
C(3)	-0.0739(3)	0.5844(1)	0.7836(3)	$3 \cdot 46(6)$
C(4)	-0.1262(3)	0.6501(1)	0.8023(3)	$3 \cdot 81(6)$
C(5)	-0.1699(3)	0.6973(1)	0.6811(3)	3.90(7)
C(6)	-0.1675(3)	0.6826(1)	0.5310(3)	3.62(6)
C(7)	-0.1138(3)	0.6160(1)	0.5138(3)	3.79(7)
C(8)	-0.0673(3)	0.5688(1)	0.6351(3)	3.78(6)
C(9)	-0.2613(3)	0.7980(1)	0.4321(3)	4.50(7)
C(10)	-0.1118(4)	0.8426(1)	0.5322(3)	4.91(7)
C(11)	-0.1601(4)	0.9138(2)	0.5539(4)	6.87(9)
C(12)	-0.0141(4)	0.9561(2)	0.6687(5)	$8 \cdot 8(1)$
C(13)	-0.2233(4)	0.7156(1)	0.2484(3)	4.95(7)
C(14)	-0.3946(4)	0.6997(2)	0.1152(4)	6.53(9)
C(15)	-0.4623(4)	0.6354(2)	0.1358(4)	$7 \cdot 47(10)$
C(16)	-0.6401(5)	0.6226(2)	0.0008(5)	10.9(1)

^A Site occupancy factor 0.5.



Fig. 2. Molecular conformation and atom numbering scheme for (1). Unless otherwise indicated, atoms are carbon.

Table 2. Comparative torsion angles (degrees) for the alkyl chains in (1) and bsq⁷

Atoms	(1)	bsq
C(7)-C(6)-N(1)-C(13)	$1 \cdot 8(9)$	0.1(3)
C(6) - N(1) - C(13) - C(14)	$99 \cdot 9(7)$	$101 \cdot 2(3)$
N(1) - C(13) - C(14) - C(15)	-67.9(8)	-67.0(3)
C(13) - C(14) - C(15) - C(16)	$177 \cdot 7(6)$	$176 \cdot 1(3)$
C(5)-C(6)-N(1)-C(13)	$4 \cdot 7(9)$	$4 \cdot 0(3)$
C(6)-N(1)-C(9)-C(10)	$77 \cdot 1(7)$	$77 \cdot 1(3)$
N(1)-C(9)-C(10)-C(11)	$179 \cdot 5(5)$	$-179 \cdot 8(3)$
C(9)-C(10)-C(11)-C(12)	$173 \cdot 6(6)$	$172 \cdot 3(3)$
C(14)-C(13)-N(1)-C(9)	$-81 \cdot 9(7)$	$-81 \cdot 9(3)$
C(13)-N(1)-C(9)-C(10)	$-101 \cdot 2(6)$	$-99 \cdot 9(3)$

Discussion

The structure of (1) is isomorphous with the monoclinic squaraine bsq.[§] with the asymmetric unit comprising half of the molecule (Fig. 2). Consequently, the hydroxy group is disordered equally in a trans configuration. The unambiguous chemical characterization of (1) eliminates the possibility that the observed structure corresponds to a cocrystal of alternating bsq and trans-dihydroxy bsg (i.e. a mixture of the symmetrical reaction products), which would give rise to identical disorder. The observed disorder indicates that the inclusion of one hydroxy group does not alter the mode of crystallization for bis[(dibutylamino)phenyl] squaraines, although an increase in volume of $c. 34 \text{ Å}^3$ in the unit cell is noted. In contrast, when four o-hydroxy groups are present (bdsq) the triclinic phase dominates.

The two main features of the packing of (1) are the parallel stacks presented along the a axis and the lateral three-centred hydrogen-bonding interactions (Figs 3 and 4) involving a proton on the α -carbon of one of the butyl side chains [C(13)] and both a squarate oxygen $[O(1) \cdots C(13), 3 \cdot 469(10) \text{ Å}]$ and hydroxy oxygen $[O(4) \cdots C(13), 3 \cdot 433(10) \text{ Å}]$ of an adjacent molecule. In addition, the hydroxy group of (1) is involved in an intermolecular interaction with the β -carbon in the same butyl side chain $[O(4) \cdots C(14),$ $3 \cdot 39(1)$ Å], and forms an intramolecular hydrogen bond with the squarate oxygen $[O(4) \cdots O(1), 2 \cdot 609(9) \text{ Å}].$ These packing interactions differ (Fig. 4) from those of bsq where three-centred interactions involving a meta ring hydrogen, a proton on the α -carbon and the squarate oxygen are observed. Mass spectrometry studies have recently shown that interactions of this kind influence the way that bis(aminophenyl) squaraines

 $\dagger R = \Sigma ||F_{\rm o}| - |F_{\rm c}|| / \Sigma |F_{\rm o}|, \ Rw = [\Sigma w (|F_{\rm o}| - |F_{\rm c}|)^2 / \Sigma w (F_{\rm o})^2]^{1/2}, \ w = [\sigma^2 (F_{\rm o})^2]^{-1}.$

[‡] Copies are available, until 31 December 2001, from the Australian Journal of Chemistry. P.O. Box 1139, Collingwood, Vic. 3066. [§] Comparative cell parameters for the isomorphous P_{21}/c bsq: a 9.055(1), b 19.615(2), c 9.046(1) Å, $\beta 116.07(5)^{\circ}$. associate in solution.¹¹ Notably, with both (1) and bsq the alkyl chain involved in these interactions folds away from the neighbouring squaraine $[N(1)-C(13)-C(14)-C(15), -67\cdot9(8)^{\circ}]$, whereas the second chain

is conformationally unhindered [comparative torsion angle is $179 \cdot 5(5)^{\circ}$].

In a recent research report on the second-order nonlinear optical properties of centrosymmetric bis(amino-



Fig. 3. Packing of (1) viewed down the approximate c cell direction showing the hydrogen-bonding interactions as broken lines.



Fig. 4. Comparative hydrogen-bonding interactions in (1) and bsq: schematic representation.

phenyl) squaraines, Ashwell¹² has used a selected view of the packing of bsq to propose an explanation of the observed optical behaviour. It is suggested that the chromophores arrange in a 'T-shaped' configuration¹³ which may pack in the films to give rise to a noncentrosymmetric arrangement. This particular diagram (taken from the unit cell packing of bsq viewed down $a)^7$ suggests an intermolecular interaction between the dialkylamino group of one molecule and the -C₄O₂centroid ring of another. However, no such interaction was evident in the computational analyses¹⁴ for both bsg and (1) indicating that the actual distance between these two groups is >3.8 Å, i.e. the intermolecular contact is too long to have any significant impact on the way in which these molecules pack in the solid state. As previously mentioned, the closest intermolecular interactions in both structures are lateral three-centred hydrogen bonds, as shown in Figs 3 and 4.

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