Dyes and Pigments, Vol. 39, No. 4, pp. 259–266, 1998

Printed in Great Britain
PII: S0143-7208(98)00012-6 0143-7208/98 $—see front matter

Crystal Structure of a Photoconductive Dithiosquarylium Dye: 2,4-Bis(1,3,3-trimethyl-2-indolinylidenemethyl) Cyclobutenediylium-1,3-dithiolate

Sung Hoon Kim,[a]* Sun Kyung Han,[a] Jae Joon Kim,[a]
Woo Taik Lim,[b] Nam Ho Heo[b] & Kwang Nak Koh[c]

[a]Department of Dyeing and Finishing, Kyungpook National University, Taegu, 702-70 1, Korea
[b]Department of Industrial Chemistry, Kyungpook National University, Taegu, 702-70 1, Korea
[c]Sensor Technology Research Center, Kyungpook National University, Taegu, 702-70 1, Korea

(Received 15 January 1998; accepted 13 February 1998)

ABSTRACT

The crystal structure of a new dithiosquarylium dye (DTSQ), viz, 2,4-bis(1,3,3-trimethyl-2-indolinylidenemethyl) cyclobutenediylium-1,3-dithiolate, has been determined by X-ray crystallography. A crystal was grown from chloroform/ethylacetate (8:1/v:v) and found to exist in the monoclinic space group $P2_1/n$ (no. 14). The molecule is roughly planar and adopts the trans conformation. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: crystal structure, dithiosquarylium dye (DTSQ), organic photoreceptor, monoclinic.

INTRODUCTION

Squarylium dyes and derivatives are 1,3-disubstituted compounds synthesized from squaric acid and two equivalent of various types of electron donating carbocycles and heterocycles such as azulene [1], pyrroles [2], or heterocyclic methylene bases [3] in an azeotropic solvent.

Although squarylium dyes exhibit a sharp visible absorption in solvents, their absorption in the solid state is panchromatic and very intense [4].

This class of cyanine dyes have attracted much attention because of their potential application in xerographic organic photoreceptor [5,6], optical

---

*Corresponding author. Fax: 82 53 950 6617; e-mail: shokim@bh.kyungpook.ac.kr recording media [7] and organic solar cells [8] on account of their advantageous properties such as photoconductivity and their sharp and intense absorption in the visible or near infrared regions [9].

We have previously reported the synthesis [10], electrochromic properties [11] and electroluminescence properties [12] of squarylium dyes containing an indoline moiety. We have also reported that some novel dithiosquarylium dyes absorbed near-infrared light at 700–750 nm in the solid state, and had good electrophotographic properties as charge generation materials (CGM) [13].

In continuation of this work we now report the crystal structures of the DTSQ dye.

EXPERIMENTAL

The preparation of DTSQ dyes have been reported previously [13]. The single crystal was obtained by evaporating a chloroform/ethlyacetate (8:1/v:v) solution of the DTSQ dye. Preliminary experiments and data collection for the X-ray crystal structure determination were performed on an Enraf–Nonius CAD4/Turbo diffractometer using Mo K_α radiation ($\lambda = 0.71069$ Å). A small single crystal (0.5×0.5×0.5 mm) was cut from a larger one and glued to a glass fiber with an epoxy resin. Twenty-five reflections in diverse reciprocal space were centered by an automatic search program and used to obtain the cell parameters. After the preliminary cell was confirmed, high-angle data ($2\theta > 20°$) were collected and 25 of these reflections were centered and used to obtain more accurate cell parameters. Unit cell parameters and systematic absences indicated the monoclinic space group $P2_1/n$ (no. 14) [14] with $Z = 2$. Data were collected on this improved unit cell at ambient temperature up to $2\theta = 52.64°$. Data reduction, including the correlation for Lorentz-polarization, decay, and absorption, were performed. Crystal structure was solved and refined with full-matrix least-squares by using MolEN, the Enraf–Nouius structure determination package, resulting in final R_1 and R_w indices of 0.043 and 0.051, respectively. Other details of crystallographic data are summarized in Table 1. The final structural parameters are presented in Table 2. The selected bond distances and angles are tabulated in Table 4. The structure model was drawn using ORTEP, Oak Ridge Thermal Ellipsoid Plot Program [15].

RESULTS AND DISCUSSION

We have found, for the first time, that thio analogues of the squarylium (SQ) dye (DTSQ dye) can be synthesized by the reaction of the SQ dye with

TABLE 1
Crystallographic Data and Intensity Collection

Empirical formular	$S_2N_2C_{28}H_{28}$
Formula weight	456.40
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
Z	2
a (Å)	7.654 (2)
b (Å)	11.438 (2)
c (Å)	13.598 (2)
β (°)	90.33 (2)
V (Å^3)	1190.03 (4)
$D_{\text{calc.}}$ (g cm^{-3})	1.252
μ_{cal} (cm^{-1})	2.3
Transmission factors (%)	96.55–99.95
Scan mode	$\omega - 2\ \theta$
Scan width (ω) (deg)	$1.10 + 0.52 \tan(\theta)$
2 θ_{max} (deg)	52.64
No. of reflections measured	2736
No. of reflections observed (I > 3 σ (I))	1621
No. of variables	201
$R_1{}^a$	0.043
$R_w{}^b$	0.051
Goodness of fit^c	1.57
Maximum shift in final cycles	Less than 0.01

$^aR = \Sigma|F_o - |F_c|/\Sigma F_o|$.
$^bR_w = [(\Sigma_w(F_o -_c|)^2/\Sigma_w(F_o^2)]^{1/2}$, where $w = [\sigma(F^2)]^{-1}$.
^{c}Estimated standard deviation of an observation of unit weight; $[\Sigma_w(F_o - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

Lawnesson's reagent or P_4S_{10} [13] (Scheme 1). Introduction of the thio group as electron donor into the SQ dye produced a bathochromic shift of 27 nm compared to the SQ dye. Electrophotographic characteristics of negatively charged dual layered photoreceptors with DTSQ for charge generation materials (CGM) and 1-phenyl-1,2,3,4-tetrahydroquinoline-6-carboxyaldehyde-1′,1′-diphenyl hydrazone as a charge transport material (CTM) have already been investigated. The photoreceptor that used DTSQ exhibited high photosensitivity to white light. The maximum absorption wavelength was 660 nm, and the maximum emission wavelength 691 nm in chloroform. The fluorescence lifetime seems to be very short. We used an LS-100PTI with time correlated single photon counting, and measured a biexponential fluorescence decay. Component one is 36.6% with 0.38 ns, and component two is 63.7% with 0.13 ns. The fit has a chi square of 1.25. The bond lengths of DTSQ are virtually identical with those observed in the 2,4-bis(1,3,3-trimethyl-2-indolynylidene methyl) cyclobutenediylium-1,3-diolxate reported by Kobayashi *et al.* [16].

TABLE 2
Final Atomic Coordinates and Thermal Parameter[a]

Atom	X	Y	Z	B^b (Å^2)
S (1)	8669 (1)	1679 (7)	61467 (5)	4.37 (1)
N (1)	4816 (3)	562 (2)	3071 (2)	3.06 (4)
C (1)	4134 (3)	97 (2)	2187 (2)	3.18 (5)
C (2)	2675 (3)	433 (3)	1663 (2)	4.14 (6)
C (3)	2330 (4)	−160 (3)	800 (2)	4.98 (7)
C (4)	3377 (4)	−1038 (3)	477 (2)	5.29 (7)
C (5)	4851 (4)	−1373 (3)	1010 (2)	4.35 (6)
C (6)	5227 (3)	−791 (2)	1869 (2)	3.23 (5)
C (7)	6755 (3)	−892 (2)	2569 (2)	2.96 (5)
C (8)	6337 (3)	45 (2)	3327 (2)	2.81 (5)
C (9)	8433 (3)	−590 (2)	2018 (2)	3.68 (6)
C (10)	6811 (4)	−2103 (2)	3045 (2)	4.25 (6)
C (11)	3936 (3)	1488 (3)	3603 (2)	4.21 (6)
C (12)	7278 (3)	3902 (2)	4150 (2)	3.09 (5)
C (13)	8875 (3)	88 (2)	4575 (2)	2.76 (5)
C (14)	9553 (3)	643 (2)	5469 (2)	2.96 (5)
H (1)	203 (3)	101 (2)	189 (2)	3.9 (6)*
H (2)	141 (3)	7 (2)	41 (2)	5.4 (7)*
H (3)	323 (3)	−148 (3)	−13 (2)	6.0 (7)*
H (4)	410 (4)	221 (3)	330 (2)	10 (1)*
H (5)	940 (3)	−59 (2)	247 (2)	4.0 (6)*
H (6)	696 (3)	−268 (2)	254 (2)	5.5 (7)*
H (7)	676 (2)	98 (2)	452 (2)	2.9 (5)*
H (8)	563 (3)	−197 (2)	80 (2)	4.7 (6)*
H (9)	283 (4)	138 (3)	356 (2)	8.5 (9)*
H (10)	418 (5)	147 (4)	426 (3)	12 (1)*
H (11)	561 (4)	−231 (3)	339 (3)	8.9 (9)*
H (12)	834 (3)	18 (2)	173 (2)	4.0 (6)*
H (13)	771 (3)	−213 (2)	345 (2)	4.3 (6)*
H (14)	860 (3)	115 (2)	150 (2)	4.8 (6)*

[a] Positional parameters × 10^4 are given. Numbers in parameters are the estimated standard deviations in unit of the least significant figure given for the corresponding parameters. Starred atoms were refined isotropically.

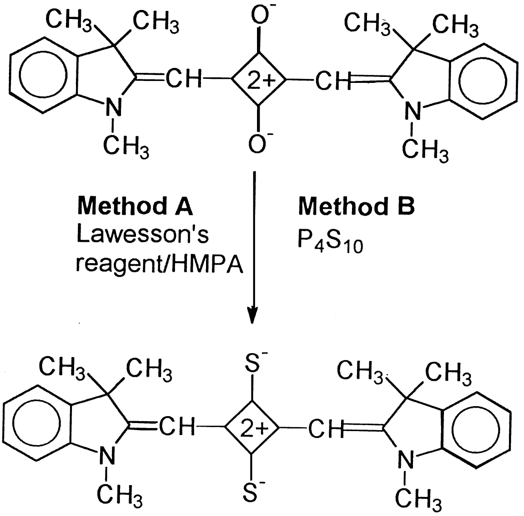
[b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) *(a2* B (1,1) + b2* B (2,2) + c2*B (3,3) + ab (cos gamma)*B (1,2) + ac (cos beta)*B (1,3) + bc (cos alpha)*B (2,3)).

The molecules of DTSQ arrange themselves in a monoclinic unit cell of dimensions $a = 7.654$, $b = 11.438$, $c = 13.598$ Å with $\beta = 90.330°$. The space group is $P2_1/n$ (no. 14), the most common space group for organic materials.

From the ORTEP diagram, we can conclude that the molecule is roughly planar and adopts the trans conformation Fig. 1. The bond lengths of C8–C12 and C12–C13 fall in the range of those of conjugated C–C bonds. The bond lengths of N1–C8, compared with the corresponding bond in N-thioacetyl indoline [17] and 3-hydroxy-2,3-diphenyl indoline [18], are indicative of a conjugated polymethine framework in the DTSQ dye. For C13–C14, these

TABLE 3
Bond Lengths (Å) With e.s.d. Values Given in Parentheses

S (1) – C (14)	1.649 (3)	C (7) – C (9)	1.539 (4)
N (1) – C (1)	1.411 (3)	C (7) – C (9)	1.503 (4)
N (1) – C (8)	1.350 (3)	C (8) – C (12)	1.386 (3)
N (1) – C (11)	1.450 (3)	C (9) – H (5)	0.96 (2)
C (1) – C (2)	1.376 (4)	C (9) – H (12)	0.97 (2)
C (1) – C (6)	1.386 (3)	C (9) – H (14)	0.96 (3)
C (2) – C (3)	1.379 (4)	C (10) – H (6)	0.96 (3)
C (2) – H (1)	0.88 (2)	C (10) – H (11)	1.06 (3)
C (3) – C (4)	1.359 (4)	C (10) – H (13)	0.89 (2)
C (3)– H (2)	0.93 (3)	C (11) – H (4)	0.93 (4)
C (4) – C (5)	1.390 (4)	C (11) – H (9)	0.86 (3)
C (4) – H (3)	0.97 (3)	C (11) – H (10)	0.91 (4)
C (5) – C (6)	1.374(4)	C (12) – C (13)	1.392 (3)
C (5) – H (8)	0.95 (2)	C (12) – H (7)	0.93 (2)
C (6) – C (7)	1.508 (3)	C (13) – C (14)	1.464 (3)
C (7) – C (8)	1.522 (3)		



Scheme 1

are clearly shorter than the value of 1.544 Å obtained in the planar 2,2,4,4-tetramethyl cyclobutene-trans-1,3-diol [19] and indicated the presence of significant double bond character in the squarylium ring. As the solvent polarity increased, a hypsochromic shift was observed (i.e. negative solvatochromism). From the solvatochromism, it was concluded that the structure of the DTSQ has a more polar dithiolate structure.

TABLE 4
Bond Angles (degree) for DTSQ

C (1) – N (1) – C (8)	111.6 (2)	C (6) – C (7) – C (9)	108.9 (2)
C (1) – N (1) – C (11)	122.0 (2)	C (6) – C (7) – C (10)	110.9 (2)
C (8) – N (1) – C (11)	126.4 (2)	C (8) – C (7) – C (9)	110.7 (2)
N (1) – C (1) – C (2)	129.1 (2)	C (8) – C (7) – C (10)	110.9 (2)
N (1) – C (1) – C (6)	108.7 (2)	C (9) – C (7) – C (10)	113.0 (2)
C (2) – C (1) – C (6)	122.2 (2)	N (1) – C (8) – C (7)	108.6 (2)
C (1) – C (2) – C (3)	117.0 (3)	N (1) – C (8) – C (12)	121.8 (2)
C (1) – C (2) – H (1)	119.0 (1)	C (7) – C (8) – C (12)	129.6 (2)
C (3) – C (2) – H (1)	124.0 (1)	C (7) – C (9) – H (5)	109.0 (1)
C (2) – C (3) – C (4)	121.9 (3)	C (7) – C (9) – H (12)	110.0 (1)
C (2) – C (3) – H (2)	120.0 (2)	C (7) – C (9) – H (14)	109.0 (1)
C (4) – C (3) – H (2)	118.0 (2)	H (5) – C (9) – H (12)	108.0 (2)
C (3) – C (4) – C (5)	120.9 (2)	H (5) – C (9) – H (14)	112.0 (2)
C (3) – C (4) – H (3)	126.0 (2)	H (12) – C (9) – H (14)	109.0 (2)
C (5) – C (4) – H (3)	113.0 (2)	C (7) – C (10) – H (6)	109.0 (2)
C (4) – C (5) – C (6)	118.3 (3)	C (7) – C (9) – H (11)	111.0 (2)
C (4) – C (5) – H (8)	123.0 (1)	C (7) – C (10) – H (13)	108.0 (2)
C (6) – C (5) – H (8)	118.0 (1)	H (6) – C (10) – H (11)	106.0 (2)
C (1) – C (6) – C (5)	119.8 (2)	H (6) – C (10) – H (13)	109.0 (2)
C (1) – C (6) – C (7)	109.0 (2)	H (11) – C (10) – H (13)	113.0 (2)
C (5) – C (6) – C (7)	131.1 (2)	N (1) – C (11) – H (4)	112.0 (2)
C (6) – H (7) – C (8)	102.0 (2)	N (1) – C (11) – H (9)	109.0 (2)
N (1) – C (11) – H (10)	112.0 (3)	C (8) – C (12) – H (7)	114.0 (1)
H (4) – C (11) – H (9)	103.0 (3)	C (13) – C (12) – H (7)	110.0 (1)
H (4) – C (11) – H (10)	115.0 (3)	C (12) – C (13) – C (14)	122.9 (2)
H (9) – C (11) - H (10)	105.0 (3)	S (1) – C (14) – C (13)	129.1 (21)
C (8) – C (12) – C (13)	135.7 (2)		

Number in parentheses are estimated standard deviations in the least significant digits.

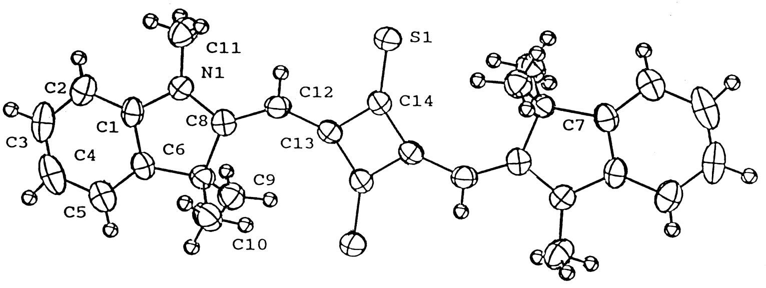


Fig. 1. ORTEP view of molecular structure of DTSQ dye with thermal ellipsoids drawn at 50% probability level.

As shown in Fig. 2, the molecules are disposed on top and bottom, right and left, respectively, of each other, in a parallel fashion and each of the two groups is in nearly a perpendicular environment.

From the results of the intermolecular distance S1···C2 = 3.463 Å, the molecules are concluded to be held together by Van der Waal forces.

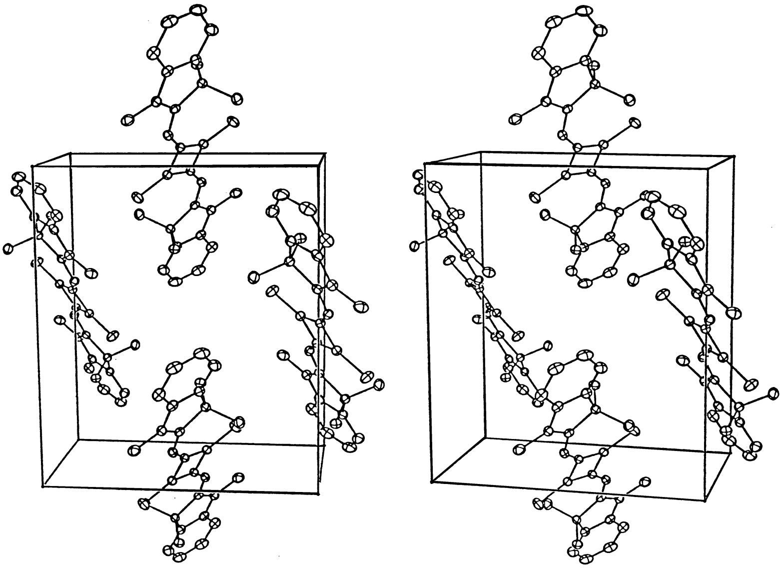


Fig. 2. Stereoview of crystal structure of DTSQ dye.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Korea Research foundation made in the Program Year 1997. The authors thank Dr J. Wolfrum and Dr M. Deimel (Universität Heidelberg) for the fluorescent measurements.

REFERENCES

1. Ziegenbein, W. and Sprenger, H. E., *Angew. Chem.*, 1966, **78**, 937.
2. Treibs, A. and Jacob, K., *Angew. Chem.*, 1965, **77**, 680.
3. Sprenger, H. E. and Ziegenbein, W., *Angew. Chem.*, 1967, **79**, 581–582.
4. Loutfy, R. O., Hsiao, C. K. and Kazmaier, P. M., *Photogr. Sci. Eng.*, 1983, **27**, 5–9.
5. Tam, A. C., *Appl. Phys. Lett.*, 1980, **37**, 978–981.
6. Law, K. Y. and Bailey, F. C., *J. Imaging Sci.*, 1987, **31**, 172–177.
7. Gravesteijin, D. J., Steenbergen, C. and Vander Veen, J., *Proc. SPIE Int. Soc. for Opt, Eng.*, 1988, **420**, 327.
8. Merritt, V. Y. and Hovel, H. J., *Appl. Phys. Lett.*, 1976, **29**, 414.
9. Fabian, J., Nakazumi, H. and Matsuoka, M., *Chem. Rev.*, 1992, **92**, 1197–1225.
10. Kim, S. H. and Hwang, S. H., *Dyes and Pigments*, 1997, **35**, 111–121.
11. Kim, S. H. and Hwang, S. H., *Dyes and Pigments*, 1998, **36**, 139–148.
12. Kim, S. H., Han, S. K., Park, S. H. and Park, L. S., *Dyes and Pigments*, 1998, **38**, 4956.

13. Kim, S. H., Han, S. K., Kim, J. J., Hwang, S. H., Yoon, C. M. and Keum, S. R., *Dyes and Pigments*, submitted for publication.
14. Henry, N. F. M., Lonsdale, K., Ed., *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1952.
15. Johnson, C. K., ORTED (II). Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
16. Kobayashi, Y., Goto, M. and Kurahashi, M., *Bull. Chem. Chem. Jpn.*, 1986, **59**, 311–312.
17. Schmalle, H. W, and Jarchow, O., *Acta Crystallogr. Sect. B.*, 1978, **34**, 1371–1374.
18. Berti, C., Greci, L., Poloni, M., Andreetti, G. D., Boceill, G. and Sgarabotto, D., *Chem. Soc., Perkin Trans. II.*, 1980, 339–346.
19. Margulis, T. N., *J Chem. Soc., Chem. Commum.*, 1969, 215.