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Crystal and molecular structure of 6-phenyl-13*H*-pyrimido [4,3-b:6,1-b] bis-benzothiazolium-12 triiodide

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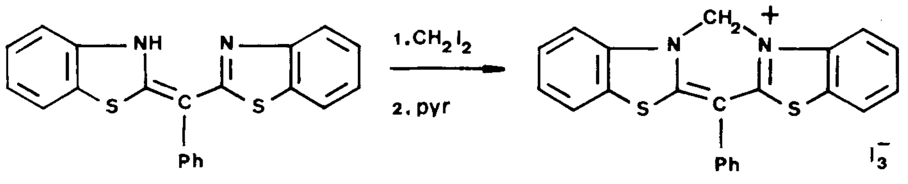
Crystals of the synthesized title compound ($C_{22}H_{15}I_3N_2S_2$) are monoclinic. Space group $P2_1/a$, $a = 15.072(2)$, $b = 10.936(1)$, $c = 15.363(2)$ Å, $\beta = 108.49(1)°$. The structure was solved by direct methods and refined by block-matrix least-squares procedure to give $R = 0.059$ and $Rw = 0.043$ for 3658 reflections above $2\sigma(I)$. The central hexaatomic ring is in a very flattened envelope conformation being the methylene group very little deviated from the plane defined by the other five atoms. The phenyl group is rotated 63.40° from that plane.

Introduction

It has been reported that reactions of difunctional alkylating reagents with diquinolylmethanes (Scheibe and Fischer, 1926) and bis(N-alkyl-benzimidazolyl)methanes (Klapproth and Dimroth, 1975; Brooker and Eastman Kodak Co., 1949) give N,N′-alkylenecyanine derivatives in poor yields. As regards di-2-benzothiazolylmethane derivatives, only the corresponding dimethylene bridge cyanine has been reported (Boyer, 1974; Ewen *et al.*, 1977; Klanderman and Hoesterey, 1969). Since these rigid structures show a physicochemical behavior very different from that usually described for other cyanines, we synthesized 6-phenyl-13*H*-pyrimido[4,3-b;6,1-b]bis-benzothiazolium-12 triiodide by heating di-2-benzothiazolylphenylmethane **1** (Ramos *et al.*, 1989a) with diiodomethane under nitrogen atmosphere in the absence of light to prevent photo-oxidation reactions (Ramos *et al.*, 1989b) (Scheme 1).

Experimental

Melting point is uncorrected; the IR spectrum was recorded on a Perkin–Elmer 577 spectrophotometer; the ^{1}HNMR spectrum was recorded on a Brucker AM-200 (200 MHz), using TMS as internal standard; UV-visible spectra were recorded on a Bausch & Lomb Spectronic 2000 Spectrophotometer. Fluorescence spectra were obtained with a Perkin–Elmer MPF-44A spectrofluorimeter and corrections were made with a 5% solution on rhodamine in ethylene glycol.



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The cyanine 2 synthesis

A mixture of 0.895 g (2.5 mmol) of **1** and 2 g (7.5 mmol) of diiodomethane was slowly heated up to 160°C and let to stand at this temperature for 2.5 h under a nitrogen atmosphere. Then, 8 ml of pyridine were added and refluxed for 5 min. After cooling, pyridinium salts were filtered off and the filtrate was concentrated to dryness. The residue was treated with ethanol and chloroform, affording **2** after filtration and recrystallization in acetonitrile. Yield: 6%, mp 253–55°C. Anal. Calcd. for $C_{22}H_{15}I_3N_2S_2$: C, 35.13; H, 2.01; N, 3.72. Found: C, 35.54; H, 2.35; N, 3.33%. IR(KBr): 1555 (w), 1490(s), 1400(s), 1365(s) cm^{-1}. ^1H NMR δ (DMSO-d_6): 8.05 (H1, H4, H8 and H11, m), 7.75 (H2 and H10, m) 7.65 (Ph, m), 7.53 (H3 and H9, m) and 6.78 (CH_2, s) ppm. UV (acetonitrile) λ (log ϵ): 469(4.61), 360(4.32), 288(4.73), and 239(4.34) nm. UV (methanol) λ(log ϵ): 470(4.60), 355(3.83), 287(4.41), and 219(4.72) nm. UV (THF) λ(log ϵ): 474(4.58), 366(4.41), and 291(4.78) nm.

X-ray structure

Crystal data: $C_{22}H_{15}I_3N_2S_2$; M = 752.207; monoclinic; a = 15.072(2), b = 10.936(1), c = 15.363(2) Å; β = 108.49(1)°; V = 2401.5(5) Å^3; z = 4; Dc = 2.080 g cm^{-3}; λ (Mo Kα) = 0.7107 Å; μ = 40.421 cm^{-1}; F(000) = 1408; T = 293K; space group $P2_1/a$.

A crystal of about 0.2 × 0.2 × 0.3 mm was mounted along the long axis. The cell dimensions were refined from 42 general reflections with the Bragg angle θ_{max} 20° on a CAD-4 diffractometer. Independent reflections (6427) were measured in the range $2 < \theta < 30°$ of which 3658 were considered as observed with the $I > 2\,\sigma(I)$ criterion. Two standard reflections were monitored every 100 min and no decomposition was detected during processing. Corrections were made for Lorentz and polarization effects.

The structure was solved by direct and Fourier methods. These showed the complete cation and other three peaks corresponding to the anion I_3^-. Refinement was performed by full-matrix least-squares procedures, minimizing $\Sigma(\Delta F)^2$ with isotropic temperature factors. An absorption correction following the DIFABS procedure (Walker and Stuart; 1983) was applied to the isotropically refined data, the maximum and minimum absorption factors being 1.070 and 0.780, respectively. Refinement was continued by full-matrix least-squares methods with anisotropic temperature factors. Hydrogen atoms were located from difference synthesis and included with isotropic temperature factors. Final refinement led to R = 0.059 and Rw = 0.043, with w from an empirical weighing scheme that fits so as to give no trends in $\langle w\Delta^2 F \rangle$ vs. F_0 and sin θ/λ (Martínez-Ripoll and Cano; 1975). $(\Delta/\delta)_{max}$ = 0.005 and residual electronic density in final difference map 0.30 eÅ^{-3}, S = 0.936.

The atomic scattering factors were taken from *International Tables for X-Ray Crystallography* (Vol. IV, 1974). The computation was made on a Vax 11/750 with MULTAN80 (Main *et al.*, 1980), DIRDIF (Beurskens *et al.*, 1981), XRAY (Stewart *et al.*, 1976) and PARST (Nardelli, 1983).

Results and discussion

The excitation and emission fluorescence spectra of compound **2** were recorded in methanol, tetrahydrofurane and acetonitrile. Excitation maxima in all these solvents were found at 220, 295 and 475 nm, and fluorescent emission occurred at 540 nm (λ_{exc} = 475 nm). Values of relative fluorescence indicated that fluorescence of **2** in methanol is enhanced relative to the other solvents (Tables 1 and 2)

X-ray structure analysis of compound 2

Figure la, b shows a view of molecule **2** and the numbering for the crystallographic study. Bond lengths and bond angles can be found in Tables 3, 4.

Table 1. Experimental conditions for the recording of the fluorescence spectra

		Sensitivity		Slits (nm)	
Solvent	Spectrum	Coarse	Fine	Exc.	Em.
MeOH	excitation	30	4	12	2
	emission	0.3	max.	2	0.5
THF	excitation	30	0	18	4
	emission	0.1	max.	11	0.5
CH_3CN	excitation	100	4	12	2
	emission	3	0	4	0.5

Table 2. Relative fluorescence of 2

Solvent	Conc. (mol/l)	Exc.	Em.	F_{rel} (%)
MeOH	$5.84 \cdot 10^{-7}$	475	540	100
THF	$3.98 \cdot 10^{-7}$	475	540	18.7
CH_3CN	$3.32 \cdot 10^{-8}$	475	540	1.9

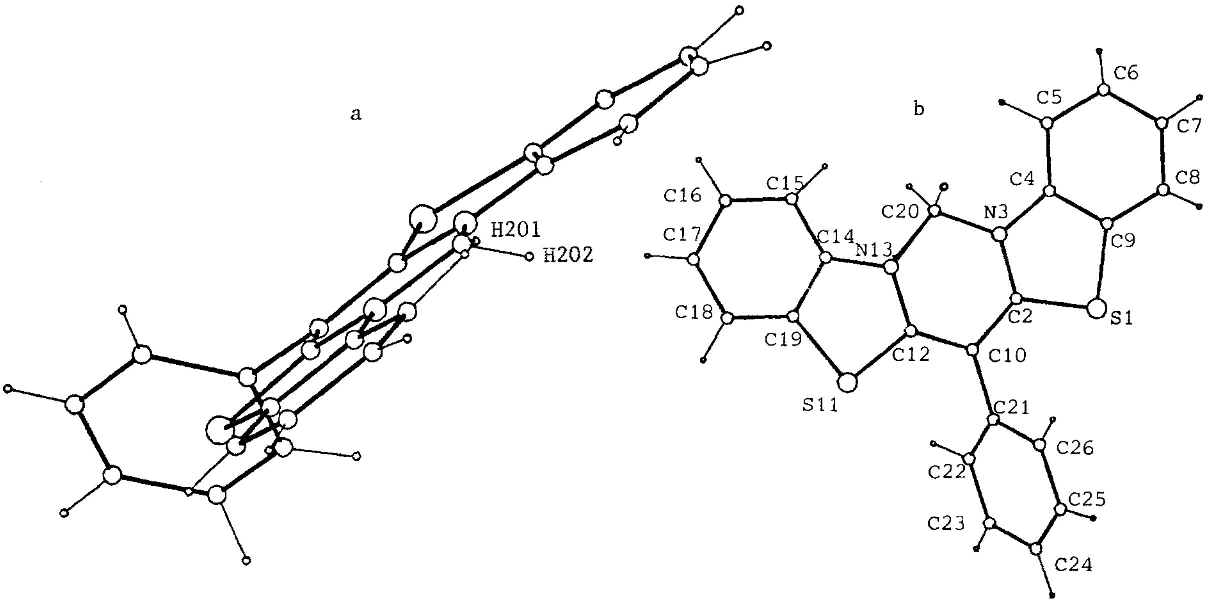

Fig. 1. (a) Projection of a molecule of compound **2**. (b) Atom numbering.

Table 3. Bond lengths (Å) of **2**

S1—C2	1.722(9)	S1—C9	1.749(9)
C2—N3	1.356(9)	C2—C10	1.395(13)
N3—C4	1.386(12)	N3—C20	1.451(12)
C4—C5	1.392(12)	C4—C9	1.396(12)
C5—C6	1.382(15)	C6—C7	1.406(15)
C7—C8	1.363(14)	C8—C9	1.381(15)
C10—C12	1.367(13)	C10—C21	1.495(11)
S11—C12	1.728(10)	S11—C19	1.760(8)
C12—N13	1.357(11)	N13—C14	1.382(12)
N13—C20	1.487(14)	C14—C15	1.389(12)
C14—C19	1.390(13)	C15—C16	1.396(15)
C16—C17	1.391(17)	C17—C18	1.382(14)
C18—C19	1.377(14)	C21—C22	1.395(13)
C21—C26	1.370(12)	C22—C23	1.398(15)
C23—C24	1.379(16)	C24—C25	1.372(18)
C25—C26	1.385(15)		

Table 4. Bond angles (°)

C2—S1—C9	91.1(4)	S1—C2—C10	125.2(6)
S1—C2—N3	111.3(6)	N3—C2—C10	123.4(8)
C2—N3—C20	124.4(7)	C2—N3—C4	115.3(7)
C4—N3—C20	120.3(7)	N3—C4—C9	111.5(7)
N3—C4—C5	127.9(8)	C5—C4—C9	120.6(8)
C4—C5—C6	117.5(9)	C5—C6—C7	121.4(9)
C6—C7—C8	120.6(10)	C7—C8—C9	118.6(9)
C4—C9—C8	121.2(8)	S1—C9—C8	127.9(7)
S1—C9—C4	110.8(6)	C2—C10—C21	120.8(8)
C2—C10—C12	115.3(8)	C12—C10—C21	123.9(8)
C12—S11—C19	91.5(4)	C10—C12—S11	125.6(7)
S11—C12—N13	110.5(6)	C10—C12—N13	123.9(8)
C12—N13—C20	123.6(8)	C12—N13—C14	115.5(7)
C14—N13—C20	120.8(7)	N13—C14—C19	112.4(7)
N13—C14—C15	127.0(8)	C15—C14—C19	120.6(8)
C14—C15—C16	117.4(9)	C15—C16—C17	121.4(10)
C16—C17—C18	120.6(10)	C17—C18—C19	118.1(9)
C14—C19—C18	121.9(8)	S11—C19—C18	128.1(7)
S11—C19—C14	109.9(6)	N3—C20—N13	109.3(7)
C10—C21—C26	120.4(8)	C10—C21—C22	120.4(8)
C22—C21—C26	119.2(9)	C21—C22—C23	119.6(10)
C22—C23—C24	120.6(11)	C23—C24—C25	119.0(11)
C24—C25—C26	121.0(11)	C21—C26—C25	120.6(10)

The central hexaatomic ring is in a very flattened envelope conformation, the C20 carbon atom deviating only 0.027(10) Å from the plane defined by the other atoms. Bond lengths at this moiety and those of S1—C2 and S11—C12 bonds show evidence of positive charge delocalization along the N3—C2(—S1)—C10—C12(—S11)—N13 atoms.

The geometry of the I_3^- ion is as follows: $I_1—I_2$ = 2.955(1) Å, $I_1—I_3$ = 2.882(1) Å and $I_2—I_1—I_3$ = 175.1°.

The phenyl group attached to the C10 atom is rotated 63.40° from the plane defined by the above mentioned central hexagonal ring. C21 and C24 atoms deviate 0.061(9) and 0.222(13) Å, respectively, from this plane, in the same sense as the C20 carbon atom. The benzothiazolyl groups show deviations from planarity less than 0.05 Å and the dihedral angle between them is 174.3(1)°.

Acknowledgments

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Structure factor, atomic coordinate and thermal parameter data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 63136 (30 pages).