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Crystal structure of 10-chloro-3,3,3′,3′-tetramethyl-1,1′-diethylindodicarbocyanine

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Abstract

The single crystal X-ray structure of indodicarbocyanine dye has been determined at room temperature and its chemical structure confirmed. A unit cell consists of four organic cations, four iodide anions and four H_2O molecules; H_2O molecules are involved into the unit cell during the crystallization. Hydrogen bond interaction probably exists between the iodide anion and a H_2O molecule. The N-atoms are in a *cis*-type arrangement with respect to the methine chain, and the distributions of bond lengths indicate extended delocation of π-electrons. The molecules are stacked face-to-face to form a column along the *b* axis direction, and some dimerization is observed. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Indodicarbocyanines; Cyanines; Spectral sensitizer; Crystal structure; Single crystal; X-ray structure

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1. Introduction

In the past three decades, a large amount of scientific work has been done on cyanine dyes. This is because they have been widely used as spectral sensitizers of photographic emulsions [1,2], in optical recording materials [3,4], in laser technologies [5], as photoinitiators in photopolymerization [6], as probes for the physical state and membrane potential of liposomes and synthetic bilayers [7,8], as well as potential sensitizer for photodynamic therapy [9].

Dicarbocyanine dyes with long polymethine chains are attractive mainly due to their ability to absorb light strongly in the red and near-IR region [10]. They shift the threshold of spectral sensitivity of silver halide and non-conventional recording media to longer wavelength. An increase in the stability may be achieved by the introduction of a chloro atom on their meso carbon atom. As compared with other cyanine dyes, indocarbocyanine dyes have high solubility in solvents and offer good thermal and photostability [11–13], and as a result, they are extensively applied in above fields.

Some cyanine dyes have been studied using X-ray crystallography [14–17]. These studies have provided detailed reformation about the ground states of single dye molecules, as well as the intermolecular arrangements. Smith [11–13] reviewed the crystal-structure analyses of cyanine dyes. Most typical sensitizers were nearly planar, with angles of less than 15° between planes defined by heterocyclic rings. The bond lengths agreed with

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those observed for simpler molecules and theoretical bond orders. X-ray crystal analysis also provided intermolecular data. Smith [14,17] concluded that the intermolecular geometry for most planar dyes was a layered arrangement, with a plane to plane stacking of the cations on edge and with a lateral displacement of adjacent chromophores that was highly influenced by substituents. However, no X-ray structure analysis of meso chloro-substituted indodicarbocyanine dye has been reported. We present here the crystal structure of 10-chloro-3,3,3′,3′-tetramethyl-1,1′-diethylindocarbocyanine and the results should be useful in the interpretation of NMR spectra, the photophysical process, as well as in rationalization of sensitometric data from the sensitizing performance of the dye in actual photographic emulsions.

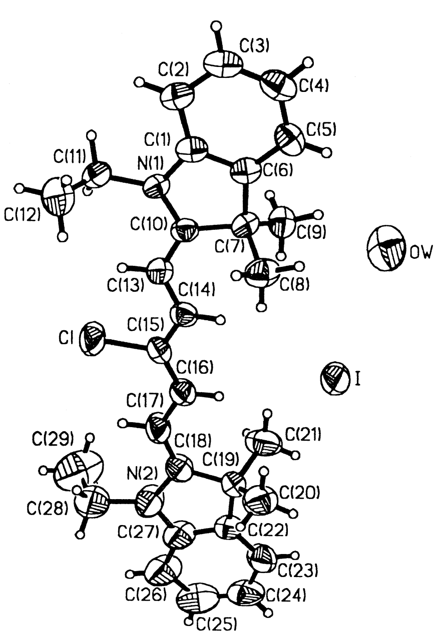

Fig. 1. ORTEP diagram with labelling scheme of the dye.

2. Experimental

The dye was synthesized from our laboratory according to the method given by Zhifei Dai et al. [2]. Crystals suitable for X-ray analysis were obtained by slow evaporation of an alcohol/water solution. A purple tabular crystal was used for single-crystal X-ray diffraction measurement at room temperature. The diffraction data were recorded on a Siemens P4 four-cycle diffractometer with graphite-monochromated Mo K α radiation. Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement with 30 automatically centered reflections in the range $10° < 2\theta < 30°$. Three standard reflections were remeasured after every 97 reflections with no indication of crystal decay, and intensifies were corrected for Lorentz, polarization and absorption effects. The atomic

Table 1
Crystal data and structure refinement

Empirical formula	$C_{29}H_{36}ClIN_2O$	Crystal size	0.4×0.3×0.1 mm
Formula weight	590.95	Data collection range	$1.29° \leqslant \theta \leqslant 24.99°$
Temperature	293(2) K		$1 \leqslant h \leqslant 19, 1 \leqslant k \leqslant 11$
Wavelength	0.71073 Å		$-23 \leqslant l \leqslant 22$
Crystal system	MONOCLINIC	Reflections collected	6449
Space group	$P2_1/c$	Independent reflections	5120
a	16.235(5) Å	R (int)	0.0418
b	9.545(4) Å	Data/restraints/parameters	5120/0/342
c	19.351(6) Å	Goodness-of-fit on F^2	0.952
β	104.03°	Final R indices ($I > 2\sigma(I)$)	$R = 0.0527$,
Volume, Z	2909(2) Å^3, 4	wR(F^2)	0.1279
Density (calculated)	1.349 Mg/m^3	Weighting scheme	$w = 1/[\sigma^3(F_0^2) + (0.0739P)^2]$
Absorption coefficient	1.215 mm^{-1}		where $P = (F_0^2 + 2F_c^2)/3$
Absorption correction	psi scans	(Δ/σ)max	0.002
Transmission faction	0.518–0.916	Extinction coefficient	0.0002(3)
F(000)	1208	Largest diff. peak	0.875e/Å^3
		Largest diff. hole	−0.813e/Å^3

coordinates of non-hydrogen atoms were determined using direct methods in the SHELXS-86 program [18] and calculated positions were used for H atoms in the dye molecules. The thermal parameters of hydrogen atoms were refined isotropically, but not for the hydrogen positions in water molecules. The structure was refined in the SHELXL-93 system [19] by the full-matrix least-squares methods to $R = 0.0527$ for 342 variable parameters and 5120 structure factors. Atomic scattering factors and anomalous dispersion corrections were taken from International tables for X-ray crystallography [20]. Crystallographic data and some results are summarized in Table 1.

3. Results and discussion

A unit cell consists of four organic cations, four iodide anions and four H_2O molecules. H_2O molecules are involved into the unit cell during the crystallization. A general view of the molecule with the labelling of the atoms is shown in Fig. 1. Atomic coordinates and equivalent isotropic

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (A^2). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
1	0.1815(1)	0.5117(1)	0.0547(1)	0.086(1)	C(13)	0.2017(3)	0.595(6)	0.2068(3)	0.048(1)
Cl	0.3798(1)	0.7096(3)	−0.1716(1)	0.101(1)	C(14)	0.2434(3)	0.6030(6)	−0.1364(3)	0.046(1)
OW	−0.0106(3)	0.7381(7)	0.0024(2)	0.113(2)	C(15)	0.3257(3)	0.6512(6)	−0.1092(3)	0.051(2)
N(1)	0.0823(3)	0.5612(5)	−0.3060(2)	0.043(1)	C(16)	0.3670(3)	0.6582(6)	−0.0388(3)	0.051(2)
N(2)	0.5802(3)	0.7325(7)	0.0759(2)	0.085(2)	C(17)	0.4502(4)	0.6969(8)	−0.0119(3)	0.067(2)
C(1)	−0.0030(3)	0.5175(5)	−0.3212(3)	0.044(1)	C(18)	0.4949(3)	0.7070(7)	0.0579(3)	0.058(2)
C(2)	−0.0597(4)	0.5083(6)	−0.3876(3)	0.054(2)	C(19)	0.4660(3)	0.6893(6)	0.1255(3)	0.053(2)
C(3)	−0.1421(4)	0.4686(6)	−0.3873(3)	0.059(2)	C(20)	0.4325(5)	0.5431(8)	0.1351(4)	0.082(2)
C(4)	−0.1650(4)	0.4407(6)	−0.3244(3)	0.061(2)	C(21)	0.3984(5)	0.8009(0)	0.1303(4)	0.093(3)
C(5)	−0.1074(4)	0.4519(6)	−0.2589(3)	0.054(2)	C(22)	0.5459(4)	0.7165(6)	0.1818(3)	0.053(2)
C(6)	−0.0253(3)	0.4875(6)	−0.2583(3)	0.044(1)	C(23)	0.5642(4)	0.7158(8)	0.2552(3)	0.082(2)
C(7)	0.0509(3)	0.5097(6)	−0.1972(2)	0.044(1)	C(24)	0.6446(5)	0.7491(9)	0.2933(3)	0.091(3)
C(8)	0.0779(4)	0.3700(7)	−0.1582(3)	0.062(2)	C(25)	0.7082(5)	0.7802(8)	0.2601(4)	0.093(2)
C(9)	0.0317(4)	0.6222(6)	0.1462(3)	0.054(2)	C(26)	0.6931(5)	0.7771(8)	0.1880(4)	0.088(2)
C(10)	0.1172(3)	0.5565(6)	−0.2359(3)	0.042(1)	C(27)	0.6118(4)	0.7463(7)	0.1512(3)	0.068(2)
C(11)	0.1242(4)	0.6073(7)	−0.3619(3)	0.060(2)	C(28)	0.6375(5)	0.7470(10)	0.0251(4)	0.095(3)
C(12)	0.1662(6)	0.4883(10)	−0.3894(5)	0.100(3)	C(29)	0.6368(8)	0.8905(13)	0.0042(7)	0.148(4)
H(2)	−0.0436(4)	0.5275(6)	0.4295(3)	0.089(23)	H(16)	0.3359(3)	0.6345(6)	−0.0060(3)	0.062(17)
H(3)	−0.1825(4)	0.4606(6)	−0.4303(3)	0.078(20)	H(17)	0.4803(4)	0.7194(8)	−0.0456(3)	0.057(16)
H(4)	−0.2205(4)	0.4138(6)	−0.3261(3)	0.054(16)	H(20A)	0.3814(5)	0.5264(8)	0.0989(4)	0.117(29)
H(5)	−0.1238(4)	0.4358(6)	−0.2168(3)	0.0440(5)	H(20B)	0.4206(5)	0.5362(8)	0.1912(4)	0.147(38)
H(8A)	0.1265(4)	0.3853(7)	−0.1194(3)	0.055(16)	H(2OC)	0.4745(5)	0.4746(8)	0.1312(4)	0.096(27)
H(8B)	0.0919(4)	0.3037(7)	−0.1909(3)	0.145(36)	H(21A)	0.3474(5)	0.7832(10)	0.0943(4)	0.066(18)
H(8C)	0.0319(4)	0.3341(7)	−0.1402(3)	0.094(23)	H(21B)	0.4196(5)	0.9924(10)	0.1233(4)	0.124(37)
H(8C)	0.0807(4)	0.6355(6)	−0.1075(3)	0.039(14)	H(21C)	0.3962(5)	0.7964(10)	0.1764(4)	0.136(32)
H(9B)	−0.0153(4)	0.5924(6)	−0.1278(3)	0.066(1.7)	H(23)	0.5223(4)	0.6930(8)	0.2786(3)	0.057(17)
H(9C)	0.0177(4)	0.7088(6)	−0.1715(3)	0.054(17)	H(24)	0.6564(5)	0.7506(9)	0.3428(3)	0.102(23)
H(11A)	0.1663(4)	0.6783(7)	−0.3426(3)	0.075(20)	H(25)	0.7619(5)	0.8036(8)	0.2872(4)	0.100(24)
H(11B)	0.0823(4)	0.06491(7)	−0.4009(3)	0.049(15)	H(26)	0.7358(5)	0.7949(8)	0.1648(4)	0.123(31)
H(12A)	0.1928(6)	0.5215(10)	−0.4255(5)	0.129(32)	H(28A)	0.6948(5)	0.7182(10)	0.0484(4)	0.041(14)
H(12B)	0.1245(6)	0.4186(10)	−0.4093(5)	0.207(60)	H(28B)	0.6171(5)	0.6881(10)	−0.0164(4)	0.064(19)
H(12C)	0.2094(6)	0.4479(10)	−0.3511(5)	0.083(24)	H(29A)	0.6729(9)	0.9024(13)	−0.0281(7)	0.205(57)
H(13)	0.2332(3)	0.6193(6)	−0.2393(3)	0.044(14)	H(29B)	0.6573(9)	0.9479(13)	0.0456(7)	0.171(52)
H(14)	0.2139(3)	0.5729(6)	−0.1035(3)	0.036(13)	H(W29C)	0.5799(8)	0.9179(13)	−0.0189(7)	0.243(68)

thermal parameters are listed in Table 2. Selected bond distances and bond angles are given in Table 3. In the title compound, the N atoms are in a *cis*-type arrangement with respect to the methine chain. This is the conformation usually found in cyanine dyes, and a similar situation has also been observed in the literature [9]. In the framework molecule, 24 atoms (C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(10), N(1), C(13), C(14), C(15), Cl, C(16), C(17) C(18), C(19), N(2), C(22), C(23), C(24), C(25), C(26), C(27)) have good coplanarity. The average atomic root-mean square (nw) deviation from the least-squares plane is 0.076 Å. OW and iodide anion are displaced from this L.S. plane by 0.316(4) Å and 2.570(8) Å, respectively. The two indo-rings (one consisting of C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(10) and N(1); the other consisting of C(18), C(19), C(22), C(23), C(24), C(25) C(26), C(27) and N(2)) are coplanar to a good approximation. Their atomic root-mean-square deviations from the least-square planes are 0.019 Å and 0.023 Å, respectively. These two indo-rings are slightly rotated with respect to each other by 3.96(12)°. As seen in Table 3, the observed C–C bond lengths in the framework molecule vary from 1.356(9) to 1.519(7) Å, which lies between the length of a C–C single bond (1.54 Å) and that of a C=C double bond (1.34 Å)

Table 3
Bond lengths (Å) and angles (°)

Cl–C(15)	1.746(5)	C(10)–N(1)–C(1)	110.9(4)	C(17)–C(18)–C(19)	130.3(5)
N(1)–C(10)	1.339(6)	C(10)–N(1)–C(11)	126.5(5)	C(22)–C(19)–C(18)	102.4(4)
N(1)–C(1)	1.406(7)	C(1)–N(1)–C(11)	122.6(4)	C(22)–C(19)–C(20)	109.9(5)
N(1)–C(11)	1.480(6)	C(1)–N(2)–C(27)	111.5(5)	C(18)–C(19)–C(20)	113.8(6)
N(2)–C(18)	1.365(7)	C(18)–N(2)–C(28)	126.5(5)	C(22)–C(19)–C(21)	109.7(5)
N(2)–C(27)	1.429(7)	C(27)–N(2)–C(28)	121.9(5)	C(19)–C(19)–C(21)	110.6(5)
N(2)–C(28)	1.514(8)	C(6)–C(1)–C(2)	123.0(5)	C(20)–C(19)–C(21)	110.1(6)
C(1)–C(6)	1.382(7)	C(6)–C(1)–N(1)	109.3(4)	C(27)–C(22)–C(23)	116.9(6)
C(1)–C(2)	1.389(7)	C(2)–C(1)–N(1)	127.6(5)	C(27)–C(22)–C(19)	110.5(4)
C(2)–C(3)	1.391(8)	C(1)–C(2)–C(3)	115.8(5)	C(23)–C(22)–C(19)	132.8(6)
C(3)–C(4)	1.381(8)	C(4)–C(3)–C(2)	121.4(6)	C(24)–C(23)–C(22)	119.5(7)
C(4)–C(5)	1.385(8)	C(3)–C(4)–C(5)	121.7(6)	C(23)–C(24)–C(25)	121.5(6)
C(5)–C(6)	1.373(9)	C(6)–C(5)–C(4)	117.8(6)	C(26)–C(25)–C(24)	120.5(7)
C(6)–C(7)	1.505(7)	C(5)–C(6)–C(1)	120.3(5)	C(25)–C(26)–C(27)	116.7(7)
C(7)–(10)	1.519(7)	C(5)–C(6)–C(7)	130.8(5)	C(22)–C(27)–C(26)	125.0(6)
C(7)–C(9)	1.541(7)	C(1)–C(6)–C(7)	108.8(5)	C(22)–C(27)–N(2)	107.3(5)
C(7)–C(8)	1.542(7)	C(6)–C(7)–C(10)	101.5(4)	C(26)–C(27)–N(2)	127.7(6)
C(10)–C(13)	1.401(7)	C(6)–C(7)–C(9)	110.2(5)	C(29)–C(28)–N(2)	107.9(9)
C(11)–C(12)	1.488(9)	C(10)–C(7)–C(9)	112.9(5)		
C(13)–C(14)	1.369(7)	C(6)–C(7)–C(8)	110.1(5)		
C(14)–C(15)	1.390(7)	C(10)–C(7)–C(8)	110.2(5)		
C(15)–C(16)	1.367(7)	C(9)–C(7)–C(8)	111.5(4)		
C(16)–C(17)	1.376(7)	N(1)–C(10)–C(13)	122.1(5)		
C(17)–C(18)	1.373(7)	N(1)–C(10)–C(7)	109.4(4)		
C(18)–C(19)	1.502(7)	C(13)–C(10)–C(7)	128.4(4)		
C(19)–C(22)	1.501(7)	N(1)–C(11)–C(12)	111.5(6)		
C(19)–C(20)	1.526(18)	C(14)–C(13)–C(10)	127.9(5)		
C(19)–C(21)	1.549(8)	C(13)–C(14)–C(15)	126.3(5)		
C(22)–C(27)	1.372(7)	C(16)–C(15)–C(14)	125.90(5)		
C(22)–C(23)	1.378(7)	C(16)–C(15)–Cl	117.8(4)		
C(23)–C(24)	1.373(9)	C(14)–C(15)–Cl	116.3(4)		
C(24)–C(25)	1.374(9)	C(15)–C(16)–C(17)	126.1(5)		
C(25)–C(26)	1.356(9)	C(18)–C(17)–C(16)	128.8(5)		
C(26)–C(27)	1.372(8)	N(2)–C(18)–C(17)	121.6(5)		
C928)–C(29)	1.428(10)	N(2)–C(18)–C(19)	108.0(5)		

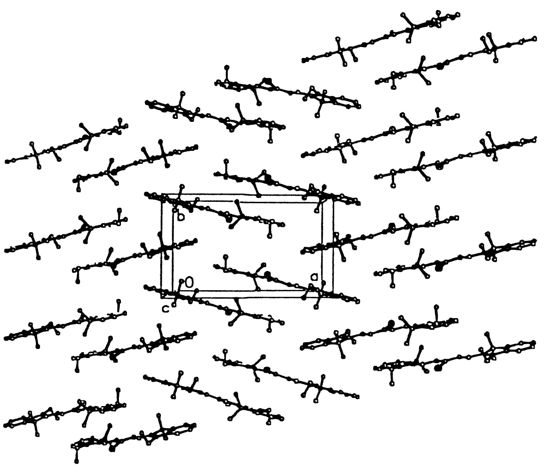

Fig. 2. Packing diagram of the unit cell viewed down the c axis.

[21]; similarly, the C–N distances of the framework molecule in the range of 1.338(6)–1.429(7) Å are also intermediate between those for a C–N single bond (1.48 Å) and a C=N double bond (1.28 Å). These data taken together suggest an extended π electron delocalization over the system. The other atomic bond lengths are what one would expect for such a molecule. In addition, done probably exists hydrogen bond interaction between the iodide anion and the H_2O molecules and this is reflected by the relatively short intermolecular nonbonded distances in the structure, i.e. I... OW^i, 3.62(5) Å; symmetry code (i): $-x, -y+1, -z$.

A packing diagram of the unit cell of the dye viewed down the *c*-axis (Fig. 2) shows that the molecules form a layer structure in the *ac* plane. The molecules are face-to-face stacked to form a column along the *b*-axis direction and some dimerization is observed. Within each dimer the separation between two neighbouring molecules is 4.020(7) Å and intermolecular distance between two adjacent dimers is 5.027(7) Å. There are two types of the column in the structure which have a dihedral angle of 37.2(1)°.

As far as the relationship between the crystal structure of the title compound and its sensitometric property is concerned, these details will be reported elsewhere [22].

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