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5-Iodo-2-[iodo(5-iodo-1,3,3-trimethyl-2-indolinylidene)methyl]-1,3,3-trimethyl-3H-indolium Perchlorate: a Highly Overcrowded Cyanine Dye

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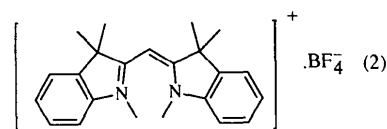
Abstract

The title compound, C₂₃H₂₄I₃N₂⁺·ClO₄⁻, adopts a *di-cis* conformation in which the indolenine end groups are mutually rotated; the interplanar angle is 50.2(1)°. There are secondary contacts (I···I and I···O) involving the terminal iodo substituents and the O atoms of the perchlorate.

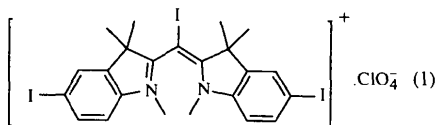
Comment

Cyanine dyes are promising components of non-linear optical materials (Nalwa, 1993). In order to design a specific cyanine dye we are interested in the effects of structural modifications on the conformational behaviour, the light absorption and other properties of the ground state.

In the cations of symmetrical monomethine cyanines, bulky terminal heterocyclic groups *E, E'* (see scheme below) and/or voluminous chain substituents *X* produce large steric interactions in the planar *di-trans* conformation (Tyutyulkov, Fabian, Mehlhorn, Dietz & Tadjer, 1991). These are relieved by conversion into twisted *di-cis* forms according to models (Grahn, 1979) and calculations (AM1) (Grahn, Johannes, Rheinheimer, Knieriem & Würthwein, 1995).



1. I₂, Ag₂SO₄
2. NaClO₄



The end groups of the cation of the cyanine dye 2-[(1,3,3-trimethyl-2-indolinylidene)methyl]-1,3,3-trimethyl-3H-indolium tetrafluoroborate, (2), are bulky. As expected, the calculated structure (Grahn *et al.*, 1995) exhibits planar indolenine end groups that are mutually rotated by an interplanar angle of 44.4°. In accordance with these results, the cation of (2) adopts a twisted *di-cis* conformation both in solution (Grahn *et al.*, 1995) and in the crystalline state (Allmann & Debaerdemaker, 1976). In the crystal, the indolenine end groups are almost planar (mean deviations 0.02 and 0.01 Å) and are mutually rotated by 43°.

According to AM1 calculations (Grahn *et al.*, 1995) the overcrowding in the cation of (2) should be enhanced by the introduction of large substituents such as bromine or iodine. We have prepared the 10-bromo and the 10-iodo derivative of cyanine (2), which also adopt the twisted *di-cis* conformation in solution (Grahn *et al.*, 1995), but could not obtain suitable single crystals. We did, however, succeed in obtaining single crystals of the title compound, the triiodo derivative (1), and report here its structure.

The indolenine end groups of (1) are indeed more mutually twisted than those of (2). The interplanar angle is increased to 50.2(1)° (calculated: 55.6°), whereas the central angle C2—C10—C2' is reduced from 130.3 in (2) to 124.5(4)° in (1). The methine bonds C10—C2 and C10—C2' of (2) [1.385(4) and 1.395(4) Å] are similar to those of (1) [1.392(6) and 1.398(6) Å].

Besides the primary I—C bonds involving the phenyl rings [2.097(4) and 2.101(5) Å], two types of secondary contact involving iodine are found: (i) each terminal I

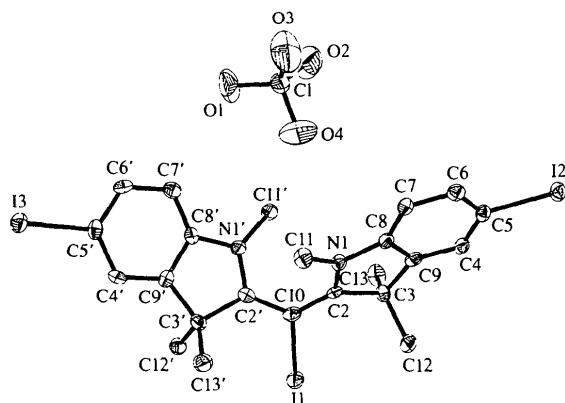


Fig. 1. The title compound (1) in the crystal. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

atom is connected to one O atom from a perchlorate counteranion; the $I \cdots O$ contacts of 3.119 (5) [$I3 \cdots O2(x, \frac{1}{2} - y, -\frac{1}{2} + z)$] and 3.346 (5) Å [$I2 \cdots O3(-x + 2, -y, -z + 1)$] are shorter than the sum of the van der Waals radii (3.5 Å) (Bondi, 1964); (ii) intermolecular $I \cdots I$ contacts of 4.142 (1) [$I1 \cdots I2(-x + 2, -y + 1, -z + 1)$] and 3.659 (1) Å [$I1 \cdots I3(x, \frac{3}{2} - y, \frac{1}{2} + z)$] are observed, the latter appreciably shorter than the van der Waals separation of about 4.0 Å (Bondi, 1964) and similar to those found in, *e.g.*, hexaiodobenzene (3.76 Å; Steer, Watkins & Woodward, 1970). The angles $I3 \cdots I1 \cdots I2$ of 65.88 (1) and $I \cdots I \cdots O$ of 62.31 (3) ($O3 \cdots I2 \cdots I1$) and 51.35 (2)° ($I1 \cdots I3 \cdots O2$) also indicate secondary bonding about iodine (Liu, Knobler, Trueblood & Helgeson, 1985). The secondary interactions link the molecules in layers parallel to xy (Fig. 2).

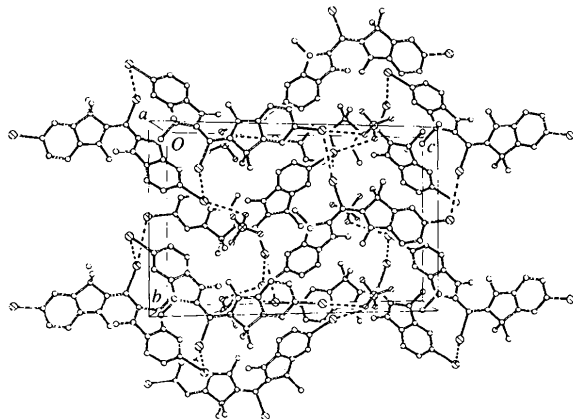


Fig. 2. Packing diagram of the title compound viewed down the x axis. $I \cdots I$ and $O \cdots I$ contacts (see text) are indicated by dashed lines. H atoms are omitted.

Experimental

A mixture of bis(1,3,3-trimethylindolin-2-yl)monomethinium tetrafluoroborate (2) (5 mmol), I_2 (15 mmol) and silver sulfate (15 mmol) in ethanol (125 ml) was stirred for 24 h at 293–

298 K. The precipitate was filtered off and washed first with ethanol (75 ml) and then with CH_2Cl_2 (75 ml). Work-up of the filtrate as described previously by us gave the 5,5'-diiodo derivative of the parent dye (2) (Grahn *et al.*, 1995). Subsequently, the still reddish residue containing cyanine (1) and silver iodide was washed again with CH_2Cl_2 (300 ml) as long as the filtrate was pale red–violet. Then this filtrate was shaken with 15% aqueous sodium perchlorate solution (100 ml). The organic phase was dried with Na_2SO_4 and concentrated to about 50 ml at 308 K. Diethyl ether was allowed to diffuse into the solution; after crystals formed they were redissolved and this procedure repeated to give 205 mg (6%) of the title compound as green crystals with metallic lustre; m.p. 528–530 K (dec.). The I atom at C10 is very mobile and can be easily removed giving the 5,5'-diiodo derivative of (2). Therefore, Heck-type coupling reactions (De Meijere & Meyer, 1994) with 10-iodo derivatives of (2) are not possible (Johannes, Grahn, Reisner & Jones, 1995). In contrast, 5,5'-diiodo derivatives of cyanine (2), such as (1), are convenient halogenated building blocks for the synthesis of cyanine oligomers (Johannes & Grahn, 1997) by palladium-mediated coupling reactions (Stille, 1986; Takahashi, Kuroyama, Sonogashira & Hagihara, 1980).

Crystal data

$C_{23}H_{24}I_3N_2^+.ClO_4^-$

$M_r = 808.59$

Monoclinic

$P2_1/c$

$a = 11.448$ (2) Å

$b = 12.098$ (2) Å

$c = 19.305$ (3) Å

$\beta = 106.30$ (2)°

$V = 2566.4$ (7) Å³

$Z = 4$

$D_x = 2.093$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 52 reflections

$\theta = 10$ – 11.5 °

$\mu = 3.790$ mm⁻¹

$T = 143$ (2) K

Tablet

$0.42 \times 0.24 \times 0.12$ mm

Dark red in transmitted light,
metallic green in reflected light

Data collection

Stoe Stadi-4 diffractometer

ω/θ scans

Absorption correction:

ψ scans (XEMP; Siemens, 1994a)

$T_{min} = 0.728$, $T_{max} = 0.895$

4672 measured reflections

4519 independent reflections

3933 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.020$

$\theta_{max} = 25.02$ °

$h = -13 \rightarrow 13$

$k = -14 \rightarrow 1$

$l = 0 \rightarrow 22$

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.060$

$S = 1.076$

4519 reflections

304 parameters

H-atom parameters

constrained

$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 5.0588P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.586$ e Å⁻³

$\Delta\rho_{min} = -0.554$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

I1—C10	2.116 (4)	N1'—C2'	1.351 (6)
I2—C5	2.097 (4)	N1'—C11'	1.457 (6)
I3—C5'	2.101 (5)	C2—C10	1.392 (6)
N1—C2	1.360 (6)	C2'—C10	1.398 (6)
N1—C11	1.452 (5)		
C2—N1—C11	126.6 (4)	C2—C10—C2'	124.5 (4)
C2'—N1'—C11'	126.3 (4)	C2—C10—I1	118.6 (3)
N1—C2—C10	121.9 (4)	C2'—C10—I1	116.8 (3)
N1'—C2'—C10	121.5 (4)		

Methyl groups were refined as rigid groups allowed to rotate but not tip from the starting position. Other H atoms were included with a riding model.

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1330). Services for accessing these data are described at the back of the journal.

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1-Acetamidoadamantane†

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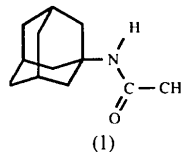
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Abstract

In the title compound, C₁₂H₁₉NO, the bond lengths and angles are closely similar to those of two cage-substituted 1-acetamidoadamantanes. The molecules are linked into polymeric chains through a weak N—H···O hydrogen bond [H···O 2.04 (2), N···O 2.928 (2) Å and N—H···O 168 (1)°].

Comment

The title compound, (1), was originally synthesized via typical Ritter reactions from 1-hydroxy- or 1-bromo-adamantane and acetonitrile in the presence of concentrated sulfuric acid (Stetter, Schwarz & Hirschhorn, 1959; Stetter, Mayer, Schwarz & Wulff, 1960). In a more direct approach, the 1-adamantyl carbocation was generated by oxidation of adamantane with nitric acid and then reacted with acetonitrile or acetamide (Bakke & Storm, 1989; Klimochkin, Bagrii, Dolgoplova & Moiseev, 1988). We have now obtained (1) by another method based on the well known process of silver(I)-promoted halide abstraction from 1-halogeno-adamantanes (e.g. Kevill & Weitl, 1970) and determined its structure as part of the identification procedure.



The molecular structure of (1) is shown in Fig. 1. The bond lengths and angles are closely similar to the cor-

† Alternative name: 1-acetamidotricyclo[3.3.1.1^{3,7}]decane.