Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2573 measured reflections
1603 independent reflections
1454 reflections with
$\quad I > 2\sigma(I)$
$R_{int} = 0.012$

$\theta_{max} = 23.05°$
$h = -9 \rightarrow 9$
$k = -6 \rightarrow 8$
$l = -14 \rightarrow 19$
3 standard reflections
$\quad$ frequency: 120 min
$\quad$ intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.045$
1601 reflections
168 parameters
H-atom parameters refined
$\quad$ only for H21
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.3151P]$
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.054$
$\Delta\rho_{max} = 0.11$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}
Extinction correction:
$\quad$ SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.039 (3)
Scattering factors from
$\quad$ *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

C13—N1—N2—C10	−20.3 (2)	C10—C11—C12—O2	171.38 (12)
C4—N2—C10—C11	−107.46 (14)	C10—C11—C12—C13	44.4 (2)
N1—N2—C10—C11	48.8 (2)	C11—C12—C13—C1	173.3 (2)
N2—C10—C11—C12	−61.0 (2)	C11—C12—C13—N1	−15.2 (2)
C9—C10—C11—C12	−172.55 (12)		

Data collection: *Enraf–Nonius SDP-Plus Structure Determination Package* (Frenz, 1985). Cell refinement: *SHELXL93* (Sheldrick, 1993). Data reduction: *REDU4* (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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1,3,3-Trimethyl-5-styryl-2-[(1,3,3-trimethyl-5-styryl-2-indolinylidene)methyl]-3*H*-indolium Picrate: an Extended Trichromophoric System

Hans-Hermann Johannes,[a] Walter Grahn,[a] Ina Dix[a] and Peter G. Jones[b]*

[a]*Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and* [b]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

Abstract

The trichromophoric system of the title compound, $C_{39}H_{39}N_2^+ \cdot C_6H_2N_3O_7^-$, adopts a di-*cis* conformation in which the indolenine end groups are mutually rotated; the interplanar angle is 47.1 (1)°. The *trans*-configurate styryl moieties are *anti* orientated relative to the cyanine unit. The length of the extended chromophore (H19···H19′) is 26.0 Å.

Comment

Organic non-linear materials possess promising properties for a wide range of applications. Cyanines and other polymethine dyes exhibit interesting third-order non-linear properties (Nalwa, 1993; Dirk *et al.*, 1995; Kawabe, Sakai, Ikeda, Hasegawa & Kawasaki, 1993; Werncke, Pfeiffer, Lau, Grahn & Johannes, 1997). In order to investigate structure–property relationships, we have developed new methods of functionalizing cyanines while conserving the chromophore (Grahn, Johannes, Rheinheimer, Knieriem & Würthwein, 1995; Johannes, Grahn, Reisner & Jones, 1995). Since polymethines that are halogenated in the chains and/or at the end groups are easily accessible (Tyutyulkov, Fabian, Mehlhorn, Dietz & Tadjer, 1991; Grahn *et al.*, 1995), we can introduce carbon substituents into the chain and/or the end groups by palladium-catalyzed cross-coupling reactions (Johannes & Grahn, 1997).

The title compound, (1*a*), was prepared by Heck reaction of the 5,5′-diiodoindocyanine (2) with an excess of styrene in DMF. The tetrafluoroborate counterion was replaced by picrate in order to fix the anion to the cyanine cation by π-stacking (In, Nagata, Doi, Ishida & Wakahara, 1997). We report here the crystal structure of (1*a*).

The cyanine adopts a di-*cis* conformation in the solid state as in solution (Johannes & Grahn, 1997); the

(2)

1. Pd(OAc)$_2$
2. C$_6$H$_2$N$_3$O$_7^-$Na$^+$

(1)

A^-: BF$_4$ (1b); C$_6$H$_2$N$_3$O$_7$ (1a)
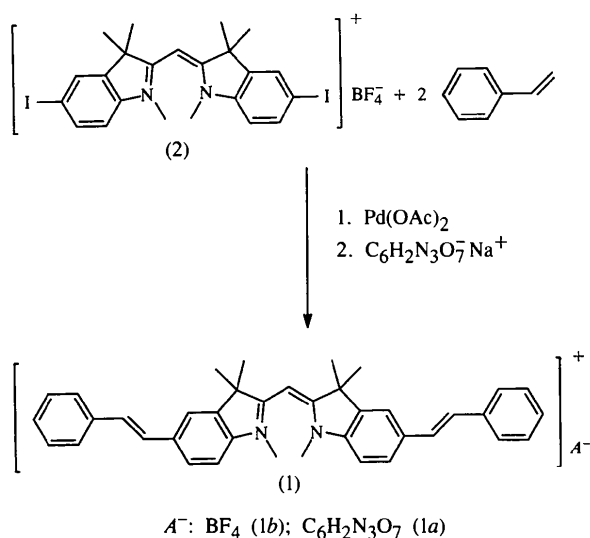
indolenine end groups are almost planar (mean deviations 0.03 Å) and are mutually rotated, the interplanar angle of 47.1 (1)° being larger than that in the parent cyanine-lacking styryl substituents (Allmann & Debaerdemaker, 1976; mean deviations 0.02 and 0.01 Å, interplanar angle 43°). The latter are almost planar (mean deviations 0.03 and 0.02 Å) and rotated with respect to the indolenine end groups, with interplanar angles 10.1 (2) and 8.3 (2)°.

The stilbene chromophores are *trans*-configurate and *anti* oriented with respect to the central cyanine unit. The C=C—C angles at the ethylenic C atoms range from 126.1 (4) (C15'—C14'—C5') to 128.7 (4)° (C14'—C15'—C16') and are similar to the enlarged angle of 126.1° in non-substituted *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). The ethylenic C14=C15 and C14'=C15' bonds of the styryl units are significantly different in length, 1.279 (5) and 1.330 (5) Å (this bond in *trans*-stilbene itself is 1.338 Å) (Allinger, Li,

Yan & Tai, 1990; Hoekstra *et al.*, 1975); since the single bonds involving the ethylenic C atoms [1.457 (5) and 1.460 (5) Å *versus* 1.495 (5) and 1.491 (6) Å] are also significantly different, the electron delocalization over the indoline end group (N1' to C9') and the styryl substituent (C14' to C21') is more marked than in its counterpart (unprimed atoms), for reasons that are not apparent.

There are no indications of π-stacking between the cation and anion; the smallest relevant interplanar angle is between the phenyl ring of the picrate (*x*, *y* + 1, *z* + 1) and the stilbene moiety C14' to C21' of the cation [29.9 (1)°]. There are, however, C—H⋯O hydrogen bonds between the monomethinium and picrate ions; these are of the form C—H⋯O—Ar and C—H⋯⁻O₂N—Ar (Table 2), and correspond to the criteria of Desiraju (1996). The packing of (1a) involves strings of anions and cations parallel to 011.

An interesting feature of the cation is its maximum extension of 26.0 Å between H atoms H19 and H19'; this spatial parameter is important for packing in polymer films.

The picrate anion of (1a) is noticeably distorted from ideal geometry. The major distortions of the ring are found near C31. The bond lengths C31—C32 [1.458 (5) Å] and C31—C36 [1.461 (5) Å] show a large difference to C32—C33 [1.365 (5) Å] and C35—C36 [1.362 (5) Å]. A narrow angle of 110.8 (3)° can be found at C31, compensated by the adjacent angles at C32 and C36 of 124.3 (3) and 125.2 (4)°, respectively. The ring is planar (r.m.s. deviation 0.03 Å), but some direct nitrogen and oxygen substituents are significantly displaced from this plane [O1 0.240 (5), N2 −0.160 (6) and N4 −0.225 (6) Å]. The nitro groups are significantly rotated out of the ring plane, with interplanar angles 25.1 (5) at C32, 6.8 (4) at C34 and 35.5 (2)° at C36. The bond length C31—O1 [1.236 (4) Å] compares well with the mean value of 1.244 Å in 15 picrate structures (Guggis-
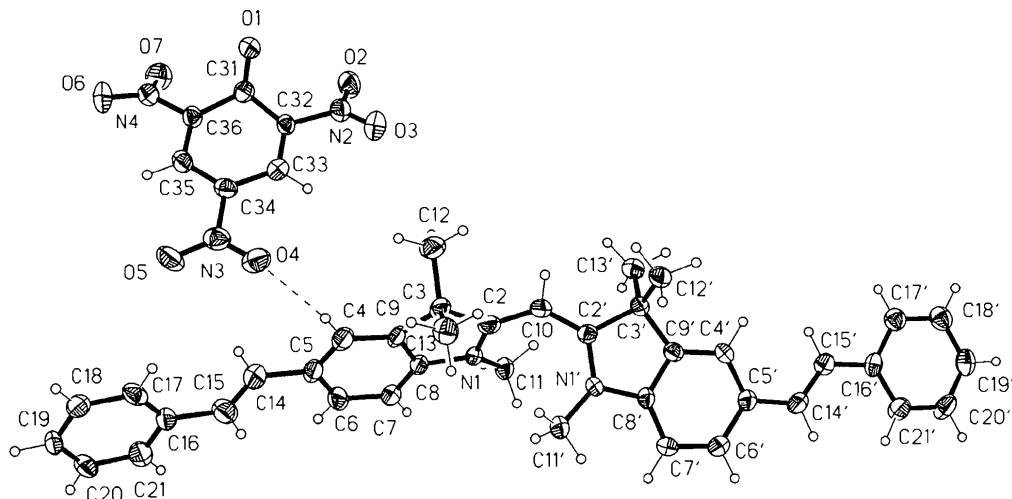

Fig. 1. The title compound (1a) in the crystal. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

berg, Prewo, Bieri & Hesse, 1982). The shortest contact between the anions is 3.01 (1) Å [O3$\cdots$O4($-x+1$, $-y$, $-z$)] and lies in the range of the van der Waals separation of 3.0 Å (Bondi, 1964).

Experimental

A mixture of bis(5-iodo-1,3,3-trimethylindoline-2-yl)-monomethinium tetrafluoroborate, (2) (1.5 mmol), styrene (5.3 mmol), anhydrous triethylamine (8.4 mmol), palladium acetate (0.07 mmol) and triphenylphosphine (0.15 mmol) in anhydrous DMF (15 ml) was stirred for 24 h at 353–363 K under nitrogen. After addition of water (90 ml), an oily solid precipitated which was washed with water (70 ml) and then with diethyl ether (70 ml). The crude product was purified by column chromatography over 70 g of silica gel (CH$_2$Cl$_2$/ethanol 50:1) and by twofold extraction with boiling 3-pentanone (60 ml). After drying in high vacuum at 353 K, 385 mg (41%) of (1*b*) were obtained as a deep orange powder; m.p. 586–588 K (dec.). Replacement of the tetrafluoroborate counterion was effected by the following procedure: a solution of (1*b*) (60 mg, 0.096 mmol) in CH$_2$Cl$_2$ (150 ml) was shaken twice with 50 ml of a 2% aqueous sodium picrate solution and then with 50 ml of distilled water. After evaporation of the CH$_2$Cl$_2$ and drying *in vacuo* the product was dissolved in nitromethane (15 ml). Slow evaporation yielded 50 mg (68%) of the title compound, (1*a*), as orange crystals; m.p. 393 K (dec.).

Crystal data

C$_{39}$H$_{39}$N$_2^+$.C$_6$H$_2$N$_3$O$_7^-$
M_r = 763.83
Triclinic
$P\bar{1}$
a = 11.697 (6) Å
b = 12.788 (7) Å
c = 14.138 (7) Å
α = 99.72 (4)°
β = 100.14 (4)°
γ = 109.04 (3)°
V = 1908.9 (17) Å^3
Z = 2
D_x = 1.329 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 48 reflections
θ = 10.0–11.5°
μ = 0.091 mm^{-1}
T = 143 (2) K
Tablet
0.42 × 0.30 × 0.15 mm
Orange

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
8626 measured reflections
6676 independent reflections
3515 reflections with
$\quad I > 2\sigma(I)$
R_{int} = 0.050

θ_{max} = 25.03°
h = $-5 \rightarrow 13$
k = $-15 \rightarrow 14$
l = $-16 \rightarrow 16$
3 standard reflections
$\quad$ frequency: 60 min
$\quad$ intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.145
S = 1.041

w = $1/[\sigma^2(F_o^2) + (0.0272P)^2 + 1.2459P]$
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

6676 reflections
520 parameters
H atoms: methyls rigid, others riding

$\Delta\rho_{max}$ = 0.382 e Å^{-3}
$\Delta\rho_{min}$ = -0.249 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C31	1.236 (4)	N1'—C8'	1.424 (4)
C31—C32	1.458 (5)	N1'—C11'	1.466 (4)
C31—C36	1.461 (5)	C2—C10	1.391 (5)
C32—C33	1.365 (5)	C2'—C10	1.384 (5)
C33—C34	1.392 (5)	C5—C14	1.495 (5)
C34—C35	1.387 (5)	C5'—C14'	1.457 (5)
C35—C36	1.362 (5)	C14—C15	1.279 (5)
N1—C2	1.343 (5)	C14'—C15'	1.330 (5)
N1—C8	1.425 (5)	C15—C16	1.491 (6)
N1—C11	1.466 (5)	C15'—C16'	1.460 (5)
N1'—C2'	1.346 (4)		
C32—C31—C36	110.8 (3)	C2'—N1'—C8'	110.9 (3)
C33—C32—C31	124.3 (3)	C2'—N1'—C11'	125.4 (3)
C32—C33—C34	119.3 (4)	C8'—N1'—C11'	122.1 (3)
C35—C34—C33	121.3 (4)	N1—C2—C10	125.9 (4)
C36—C35—C34	118.6 (4)	N1'—C2'—C10	126.0 (3)
C35—C36—C31	125.2 (4)	C15—C14—C5	126.6 (4)
C2—N1—C8	110.5 (3)	C15'—C14'—C5'	126.1 (4)
C2—N1—C11	125.9 (3)	C14—C15—C16	127.3 (5)
C8—N1—C11	122.0 (3)	C14'—C15'—C16'	128.7 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots$A	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A
C4—H4$\cdots$O4	0.95	2.305	3.171 (5)	151
C11—H11B$\cdots$O1^i	0.95	2.465	3.134 (5)	125

Symmetry code: (i) $-x, -y, -z$.

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. Because the crystal diffracted weakly, an extensive system of restraints to components of displacement parameters was employed; for the same reason the final $R(F)$ value is high.

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

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