2-[(3,3-Dimethylindolin-2-ylidene)methyl]-4-[(3,3-dimethyl-3H-indol-1-iium-2-yl)methylidene]-3-oxocyclobut-1-en-1-olate chloroform disolvate

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2-[(3,3-Dimethylindolin-2-ylidene)methyl]-4-[(3,3-dimethyl-3H-indol-1-ium-2-yl)methyldiene]-3-oxocyclobut-1-en-1-olate chloroform disolvate

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In the title squaraine dye solvate, C_{26}H_{24}N_{2}O_{2}.2CHCl{\textsubscript{3}}, the dye molecule is essentially planar, except for the methyl groups, having a maximum deviation over the 26-membered delocalized bond system of 0.060 (2) \text{	extdegree}. It possesses crystallographic twofold rotational symmetry with the indole ring systems adopting a \textit{syn} conformation. The molecular structure features intramolecular N—H···O hydrogen bonds enclosing conjoint \textit{S7} ring motifs about one of the dioxytetrocyclobutene O atoms, while the two chloroform solvent molecules are linked to the second O atom through C—H···O hydrogen bonds.

Related literature

For the first report of bis(indolenine)squaraine dyes with alkyl substituents on the N-atom of each of the indolenine rings, see: Sprenger Von & Ziegenbein (1967). For background to bis(indolenine)squaraine dyes as biomarkers, see: Patsenker et al. (2011); Sameiro & Gonçalves (2009). For the structures of bis(indolenine)squaraine dyes as biomarkers, see: Patsenker, L. D., Tatarets, A. L., Povrozin, Y. A. & Terpetschnig, E. A. (2011). For the first report of bis(indolenine)squaraine dyes with alkyl substituents on the N-atom of each of the indolenine rings, see: Sprenger Von & Ziegenbein (1967). For background to bis(indolenine)squaraine dyes as biomarkers, see: Patsenker, L. D., Tatarets, A. L., Povrozin, Y. A. & Terpetschnig, E. A. (2011).

Experimental

Crystal data

C_{26}H_{24}N_{2}O_{2}.2CHCl{\textsubscript{3}}

V = 2978.5 (3) \text{\AA}^{3}

Z = 4

Mo Ka radiation

\mu = 0.61 \text{mm}^{-1}

T = 200 K

0.40 \times 0.22 \times 0.20 \text{mm}

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2012)

\( R_{	ext{int}} = 0.027 \)

Refinement

\[ R[F^2 > 2\sigma(F^2)] = 0.044 \]

\[ wR(F^2) = 0.112 \]

\( S = 1.02 \)

2926 reflections

Table 1

Hydrogen-bond geometry (\text{\AA}, °).

Data collection: \textit{CrysAlis PRO} (Agilent, 2012); cell refinement: \textit{CrysAlis PRO}; data reduction: \textit{CrysAlis PRO}; program(s) used to solve structure: \textit{SHELXS97} (Sheldrick, 2008); program(s) used to refine structure: \textit{SHELXL97} (Sheldrick, 2008); molecular graphics: \textit{PLATON} (Spek, 2009); software used to prepare material for publication: \textit{PLATON}.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2588).

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supplementary materials

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2-[(3,3-Dimethylindolin-2-ylidene)methyl]-4-[(3,3-dimethyl-3H-indol-1-ium-2-yl)methyldiene]-3-oxocyclobut-1-en-1-olate chloroform disolvate

Graham Smith and Daniel E. Lynch

Comment

Bis(indolenine)squaraine dyes, in which there is an alkyl substituent on the N-atom of each of the indolenine rings, were first reported on by Sprenger Von & Ziegenbein (1967) and have been studied since then for a range of opto-electronic applications such as long-wavelength protein-sensitive bioprobes (Lynch et al., 2012; Patsenker et al., 2011; Sameiro & Gonçalves, 2009). However, the parent dye compound 2,4-[(3,3-dimethyl-2-indolylidene)methyl]cyclobutenediylio-1,3-diolate, which has no N-alkyl substituent (R) on the indolenine ring, has remained relatively untouched in the literature, including reporting of the crystal structure. The crystal structures of a number of analogues with such substituents have been reported; for e.g. R = methyl (Kobiyashi et al., 1986), ethyl (Natsukawa & Nakazumi, 1993), isopropyl (Tong & Peng, 1999), n-butyl (Matsui et al., 2012), n-hexyl (Lynch & Byriel, 1999) and n-octyl (Lynch, 2002). Evaporation of a solution of the dye in chloroform gave the title compound solvate as large green-black crystal prisms and its crystal structure is reported on herein. The dye molecule adopts the uncommon syn-conformation with respect to the indolenine rings, having crystallographic twofold rotational symmetry (Fig. 1). The structures of all other members of this series of N-alkyl-substituted squaraine dyes have the inversion-related anti-conformation.

The planarity of the delocalized 26-membered linked ring system in the overall molecule is indicated by maximum deviations of 0.059 (2) (C6 and C6’) and 0.060 (2) (C4 and C4’) from the least-squares plane [symmetry code (i): -x, y, -z + 3/2]. This planarity is further stabilized by the intramolecular N—H···O hydrogen bonds to O2 of the dioxocyclobutene ring (Table 1), closing conjoint S7 ring motifs.

Inter-species C—H···O hydrogen-bonding interactions link the two chloroform molecules to the second O-atom (O1). Although chloroform is a common solvent for the crystallization of squaraine dyes, chloroform solvates are uncommon with only three such structures reported on previously (Natsukawa & Nakazumi, 1993; Lynch & Byriel, 1999; Arunkumar et al., 2007).

Experimental

Squaric acid (200 mg, 1.75 mmol) was added to 2.0 molar equivalents of 2,3,3-trimethylindolenine (0.56 g, 3.5 mmol) and quinoline (0.45 g, 3.5 mmol) in a 1:1 v/v mix of 1-butanol:toluene (30 ml) and the mixture was then refluxed for 16 h using a Dean and Stark apparatus. Upon cooling, metallic green crystals were collected in vacuo, washed with petroleum ether (60/40), and were used without further purification [Yield: 0.31 g (45%)]. Spectroscopic data are available in the archived CIF. For the X-ray diffraction analysis large green-black lustrous crystal prisms of the title compound were obtained from the room temperature evaporation of a solution of the dye in chloroform. A cleaved crystal specimen was used for the actual analysis.
Refinement

The H atom of the N—H group was located in a difference Fourier but was subsequently refined as a riding atom: N-H = 0.88 Å with $U_{iso}(H) = 1.2U_{eq}(N)$. C-bound H atoms were included in calculated positions and refined as riding atoms: C—H = 0.93 Å (aromatic or ethylenic), 0.96 Å (methyl) or 0.98 Å (methine) with $U_{iso}(H) = 1.5U_{eq}(C$-methyl) and = 1.2$U_{eq}(C)$ for other H atoms.

Computing details

Data collection: CrysAlis PRO (Agilent, 2012); cell refinement: CrysAlis PRO (Agilent, 2012); data reduction: CrysAlis PRO (Agilent, 2012); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON (Spek, 2009).

Figure 1

The molecular conformation and atom-numbering scheme for the title compound (symmetry code: (i) -x, y, -z + 3/2). The displacement ellipsoids are drawn at the 40% probability level. The intra- and inter-species N-H···O and C-H···O hydrogen bonds are shown as dashed lines.
2-[(3,3-Dimethylindolin-2-ylidene)methyl]-4-[(3,3-dimethyl-3H-indol-1-ium-2-yl)methylidene]-3-oxocyclobut-1-en-1-olate chloroform disolvate

Crystal data

C₃₀H₂₄N₂O₂·2CHCl₃
Mr = 635.21
Monoclinic, C2/c
Hall symbol: -C 2yc
a = 20.4270 (11) Å
b = 13.5433 (5) Å
c = 11.4259 (5) Å
β = 109.561 (5)°
V = 2978.5 (3) Å³
Z = 4

F(000) = 1304
D_x = 1.416 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
θ = 3.3–28.8°
µ = 0.61 mm⁻¹
T = 200 K
Prism, green
0.40 × 0.22 × 0.20 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlis PRO; Agilent, 2012)

10054 measured reflections
2926 independent reflections
2415 reflections with I > 2σ(I)

R(int) = 0.027
θ(max) = 26.0°, θ(min) = 3.5°
h = −22→25
k = −16→16
l = −13→14

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.044
wR(F²) = 0.112
S = 1.02
2926 reflections
176 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
w = 1/[σ²(Fo)² + (0.047P)² + 4.0361P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max < 0.001
Δρ(max) = 0.54 e Å⁻³
Δρ(min) = −0.50 e Å⁻³

Special details

Experimental. Spectroscopic details of the as synthesized metallic green crystals of the title dye: UV/Vis (CHCl₃), recorded on a Nicolet 205 F T—IR spectrometer: λmax (log ε): 665(5.54). IR (KBr, cm⁻¹) recorded on a Unicam UV-4 spectrometer: λmax: 1623 (C—O). Electrospray mass spectra recorded in the the positive (ES+) ion mode: 397.1 [M+H]+, 460.1 [M+Na+MeCN]+, 815.3 [2M+Na]+, 1211.6 [3M+Na]+.

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > σ(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x      | y       | z       | Uiso*/Ueq |
|----|--------|---------|---------|-----------|
| O1 | 0.00000| 0.35895 | 0.75000 | 0.0420 (8) |
| O2 | 0.00000| 0.02418 | 0.75000 | 0.0330 (7) |
| N1 | 0.08460| 0.01681 | 0.60326 | 0.0292 (5) |
| C1 | 0.00000| 0.2681 (2)| 0.75000 | 0.0308 (9) |
| C2 | 0.03058| 0.19196 | 0.69306 | 0.0283 (6) |
| C3 | 0.00000| 0.1172 (2)| 0.75000 | 0.0273 (8) |
| C4 | 0.07197| 0.19354 | 0.61835 | 0.0300 (6) |
| C5 | 0.09788| 0.11037 | 0.57941 | 0.0272 (6) |
| C6 | 0.14808| 0.10979 | 0.50618 | 0.0298 (6) |
| C7 | 0.19200| −0.05112| 0.4256 (2)| 0.0364 (7) |
| C8 | 0.18945| −0.15368| 0.4251 (2)| 0.0400 (8) |
| C9 | 0.15195| −0.20386| 0.4872 (2)| 0.0390 (7) |
| C10| 0.11502| −0.15347| 0.55071 (19)| 0.0333 (7) |
| C11| 0.11792| −0.05144| 0.54957 (18)| 0.0278 (6) |
| C12| 0.15568| 0.00001 (15)| 0.48861 (18)| 0.0293 (6) |
| C13| 0.21729| 0.15545 | 0.5872 (2)| 0.0397 (7) |
| C14| 0.11833| 0.16552 | 0.3829 (2)| 0.0400 (8) |
| C15| 0.10014| 0.46856 | 0.50703 (7)| 0.0756 (3) |
| C16| 0.09545| 0.60290 | 0.70002 (8)| 0.0724 (3) |
| C17| 0.17949| 0.42725 | 0.76203 (7)| 0.0650 (3) |
| C18| 0.10219| 0.47904 (18)| 0.6610 (2)| 0.0444 (8) |
| H1 | 0.05820| 0.00030 | 0.64720 | 0.0350* |
| H4 | 0.08300| 0.25470 | 0.59290 | 0.0360* |
| H7 | 0.21760| −0.01770| 0.38450 | 0.0440* |
| H8 | 0.21330| −0.18910| 0.38230 | 0.0480* |
| H9 | 0.15150| −0.27250| 0.48640 | 0.0470* |
| H10| 0.08950| −0.18680| 0.59210 | 0.0400* |
| H131| 0.23420| 0.12070 | 0.66480 | 0.0600* |
| H132| 0.21030| 0.22370 | 0.60240 | 0.0600* |
| H133| 0.25060| 0.15050 | 0.54490 | 0.0600* |
| H141| 0.15020| 0.16100 | 0.33750 | 0.0600* |
| H142| 0.11160| 0.23360 | 0.39920 | 0.0600* |
| H143| 0.07460| 0.13680 | 0.33480 | 0.0600* |
| H15| 0.06270| 0.44250 | 0.66990 | 0.0530* |

Atomic displacement parameters (Å²)

|    | U¹¹ | U¹² | U¹³ | U¹²¹ | U¹²² | U¹²³ |
|----|-----|-----|-----|------|------|------|
| O1 | 0.0502 (14)| 0.0225 (10)| 0.0651 (15)| 0.0000 | 0.0351 (12)| 0.0000 |
| O2 | 0.0396 (12)| 0.0231 (10)| 0.0439 (12)| 0.0000 | 0.0240 (10)| 0.0000 |
| N1 | 0.0351 (9)| 0.0247 (9)| 0.0344 (9)| 0.0005 (7)| 0.0203 (8)| 0.0024 (7) |
| C1 | 0.0302 (15)| 0.0265 (15)| 0.0392 (16)| 0.0000 | 0.0161 (13)| 0.0000 |
| C2 | 0.0261 (10)| 0.0252 (10)| 0.0342 (11)| −0.0004 (8)| 0.0111 (9)| 0.0009 (8) |
| C3 | 0.0260 (14)| 0.0265 (15)| 0.0304 (14)| 0.0000 | 0.0108 (12)| 0.0000 |
| C4 | 0.0336 (11)| 0.0229 (10)| 0.0377 (11)| −0.0023 (8)| 0.0176 (9)| 0.0028 (8) |
| C5 | 0.0268 (10)| 0.0281 (10)| 0.0272 (10)| −0.0018 (8)| 0.0099 (8)| 0.0017 (8) |
| C6 | 0.0315 (11)| 0.0308 (11)| 0.0310 (10)| −0.0012 (9)| 0.0156 (9)| 0.0018 (8) |
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|    | Value (sig. digits) |
|----|---------------------|
| C7 | 0.0336 (12)         |
| C8 | 0.0399 (13)         |
| C9 | 0.0432 (13)         |
| C10| 0.0392 (12)         |
| C11| 0.0291 (10)         |
| C12| 0.0272 (10)         |
| C13| 0.0350 (12)         |
| C14| 0.0524 (15)         |
|    |                     |
| Cl1| 0.0984 (7)          |
| Cl2| 0.0981 (6)          |
| Cl3| 0.0658 (5)          |
| Cl4| 0.0548 (15)         |

Geometric parameters (Å, °)

| Distances | Cl1—C15 | C7—C8 | C11—C15 |
|-----------|---------|-------|---------|
|           | 1.751 (2) | 1.390 (3) | 1.389 (3) |
| Cl2—C17  | 1.753 (3) | 1.384 (3) |         |
| Cl3—C15  | 1.760 (3) |       | 1.383 (3) |
| O1—C1    | 1.230 (3) |       | 1.387 (3) |
| O2—C3    | 1.260 (3) |       |         |
| N1—C5    | 1.343 (3) |       |         |
| N1—C11   | 1.405 (3) |       |         |
| C1—C2    | 0.8800   |       | 0.9300  |
| C2—C4    | 1.466 (3) |       | 1.380 (3) |

Supplementary materials

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C5—C6—C12 101.26 (16)  
C12—C6—C13 111.12 (18)  
C12—C6—C14 112.84 (17)  
C13—C6—C14 110.92 (18)  
C5—C6—C13 108.62 (17)  
C5—C6—C14 111.66 (19)  
C8—C7—C12 118.5 (2)  
C7—C8—C9 121.0 (2)  
C8—C9—C10 121.2 (2)  
C9—C10—C11 117.0 (2)  
N1—C11—C12 108.72 (17)  
C10—C11—C12 122.6 (2)  
N1—C11—C10 128.7 (2)  
C7—C12—C11 119.8 (2)  
C11—N1—C5—C4 179.2 (2)  
C11—N1—C5—C6 −2.7 (2)  
C5—N1—C11—C10 −177.9 (2)  
C5—N1—C11—C12 0.8 (2)  
O1—C1—C2—C3 180.00 (2)  
C2—C1—C2—C3 0.02 (16)  
C4—C2—C3—O2 −0.9 (3)  
C4—C2—C3—C2′ 0.00 (11)  
C4—C2—C3—O2′ −179.1 (2)  
C4—C2—C3—C2 179.1 (3)  
C1—C2—C3—O2 180.00 (1)  
C1—C2—C3—C2′ 0.00 (11)  
C1—C2—C3—O2′ 179.1 (2)  
C1—C2—C3—C2 179.1 (3)  
C1—C2—C4—C5 176.79 (19)  
C3—C2—C4—C5 −1.9 (4)  
C2—C4—C5—N1 3.0 (3)  
C2—C4—C5—C6 −174.8 (2)  
N1—C5—C6—C12 3.3 (2)  
N1—C5—C6—C13 −113.77 (19)  
N1—C5—C6—C14 123.59 (19)  
Symmetry code: (i) −x, y, −z+3/2.

Hydrogen-bond geometry (Å, º)

| D—H···A | D—H  | H···A | D···A  | D—H···A |
|---------|------|------|--------|---------|
| N1—H1···O2  | 0.88 | 1.96 | 2.7835 (18) | 156 |
| C15—H15···O1 | 0.98 | 2.13 | 3.075 (3) | 161 |