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2,4-Bis(3,3-dimethyl-1-octylindolin-2-ylidenemethyl)cyclobutenediylio-1,3-diolate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.070
wR factor = 0.208
Data-to-parameter ratio = 19.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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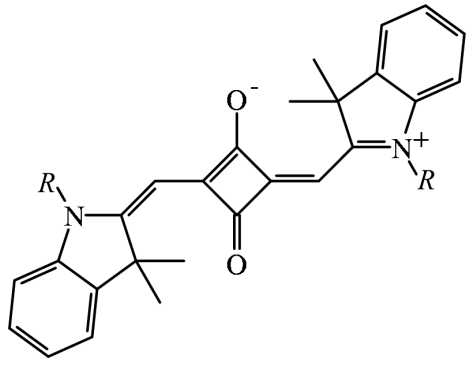
The structure of the title compound, $C_{42}H_{56}N_2O_2$, comprises a centrosymmetric molecule, with only half of the molecule in the asymmetric unit and with an inversion centre in the middle of the squarate ring. The squaraine moiety is planar and extensively delocalized, with the dihedral angle between the squarate and indoline planes being 3.9 (2)°.

Comment

The 1-alkyl derivatives of 2,4-bis(3,3-dimethylindolin-2-ylidenemethyl)cyclobutenediylio-1,3-diolate (InSq) have been studied for a variety of photophysical effects (for example, Kuramoto *et al.*, 1989; Dirk & Kuzyk, 1990; Terpetschnig *et al.*, 1993; Zhang *et al.*, 1997). In several other studies of squaraine dyes, the only known crystal structure of an InSq derivative, InSq1 (Kobayashi *et al.*, 1986), was cited and a discussion of molecular behaviour based on the non-planar conformation of this structure given. In the structure of InSq1, one indolinyl ring is twisted by *ca* 25° away from the plane of the central ring, while the other ring is twisted by *ca* 8°. Certainly, before the structures of InSq2 (Natsukawa & Nakazumi, 1993), InSq3 (Tong & Bi-Xian, 1999), InSq4 and InSq5 (Lynch & Byriel, 1999) were published, the structure of InSq1 was the only guide as to the conformation of any InSq derivative. The significance of these latter InSq structures is that they are all planar across the bis(indolinylidene)squarate moiety, a characteristic of all other known squaraine structures (Lynch & Byriel, 1999).



InSq1: R = CH_3
InSq2: R = CH_2CH_3 (methanol solvate)
InSq3: R = $CH(CH_3)_2$ (methanol solvate)
InSq4: R = CH_2CH_2OH
InSq5: R = C_6H_{13}
InSq6: R = C_8H_{17}

As part of a series of studies on the structural aspects of squaraine dyes, the 1-octyl derivative of InSq, InSq6, was

prepared and the structure determined (Fig. 1). Similar to InSq2–InSq5, InSq6 is planar, with the dihedral angle between the squarate and indoline planes being 3.9 (2)°. However, unlike InSq2 and InSq3, InSq6 is solvent-free and displays a similar packing mode to InSq4 and InSq5, with only half of the molecule in the asymmetric unit. The paper reporting the structures of InSq4 and InSq5 also reviewed the role of C—H···O close contacts in the packing of all known squaraine structures at that time. The results suggested that most solvent-free structures had the planar molecules stacked in rows of columns, with the individual molecules forming C—H···O close contacts with another molecule in either an adjacent column of a different row (of opposing direction) or the next column in the same row. InSq6 displays the same ribbon network arrangement as InSq5, through C—H···O close contacts, but InSq6 is not stacked. This rearrangement in the structure may be necessary to compensate for the extended alkyl chain, although no other *N*-octyl (or longer) squaraine analogue has been studied for comparison, so the obvious bulkiness of the alkyl chain may only be part of the reason for the difference in packing.

In conclusion, five of the six known structures of InSq derivatives are planar across the central ring system, suggesting that this is a more representative conformation than that of InSq1. This has a bearing on the discussion of the structure–property relationships of this squaraine analogue.

Experimental

The title compound was prepared according to the literature procedures described by Lynch & Byriel (1999), and crystals were grown from a chloroform solution.

Crystal data

$C_{42}H_{56}N_2O_2$
M_r = 620.89
Monoclinic, $P2_1/n$
a = 9.2547 (4) Å
b = 16.2169 (8) Å
c = 12.2437 (7) Å
β = 103.569 (2)°
V = 1786.28 (16) Å^3
Z = 2
D_x = 1.154 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7704 reflections
θ = 2.9–27.5°
μ = 0.07 mm^{-1}
T = 150 (2) K
Plate, blue
0.20 × 0.07 × 0.02 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.986, T_{max} = 0.999
16116 measured reflections
4051 independent reflections
1951 reflections with $I > 2\sigma(I)$
R_{int} = 0.125
θ_{max} = 27.5°
$h = -11 \rightarrow 11$
$k = -17 \rightarrow 21$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.208
S = 0.98
4051 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1015P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

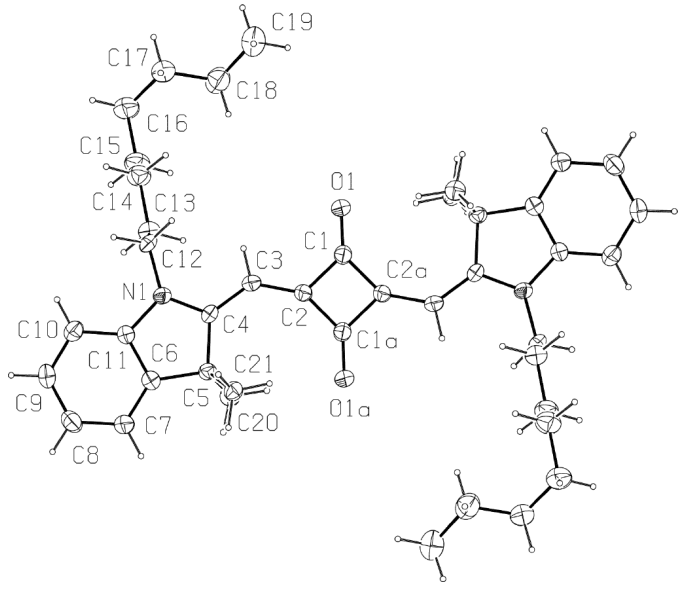


Figure 1
The molecular configuration and atom-numbering scheme for the title compound, showing 50% probability ellipsoids. [Symmetry code: (*a*) $1 - x, -y, 1 - z$.]

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C20—H201···O1^{i}	0.98	2.59	3.561 (3)	172
C20—H202···O1^{ii}	0.98	2.37	3.263 (3)	151
C21—H212···O1^{ii}	0.98	2.42	3.287 (3)	147

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, -y, 1 - z$.

All H atoms were included in the refinement at calculated positions as riding models, with C—H set to 0.95 (Ar–H), 0.99 (CH_2) and 0.98 Å (CH_3). The high R_{int} value of 0.125 is the result of weak high-angle data.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Dirk, C. W. & Kuzyk, M. G. (1990). *Chem. Mater.* **2**, 4–6.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Kobayashi, Y., Goto, M. & Kurahashi, M. (1986). *Bull. Chem. Soc. Jpn*, **59**, 311–312.
Kuramoto, N., Natsukawa, K. & Asao, K. (1989). *Dyes Pigm.* **11**, 21–35.
Lynch, D. E. & Byriel, K. A. (1999). *Cryst. Eng.* **2**, 225–239.
Natsukawa, K. & Nakazumi, H. (1993). *Sangyo Gij. Sogo Kenk. Hokuku*, **6**, 16–21.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1997). *PLATON*97. Version of May 1997. University of Utrecht, The Netherlands.
Terpetschnig, E., Szmacinski, H. & Lakowicz, J. R. (1993). *Anal. Chim. Acta*, **282**, 633–641.
Tong, L. & Bi-Xian, P. (1999). *Dyes Pigm.* **43**, 73–76.
Zhang, B., Zhao, W., Cao, Y., Wang, X., Zhang, Z., Jiang, X. & Xu, S. (1997). *Synth. Met.* **91**, 237–241.