

**2,4-Bis[[6-(2,2-dimethylpropyl)-3-ethyl-1,3-benzothiazol-2(3*H*)-ylidene]methyl]cyclobutenediylum-1,3-diolate<sup>1,2</sup>**

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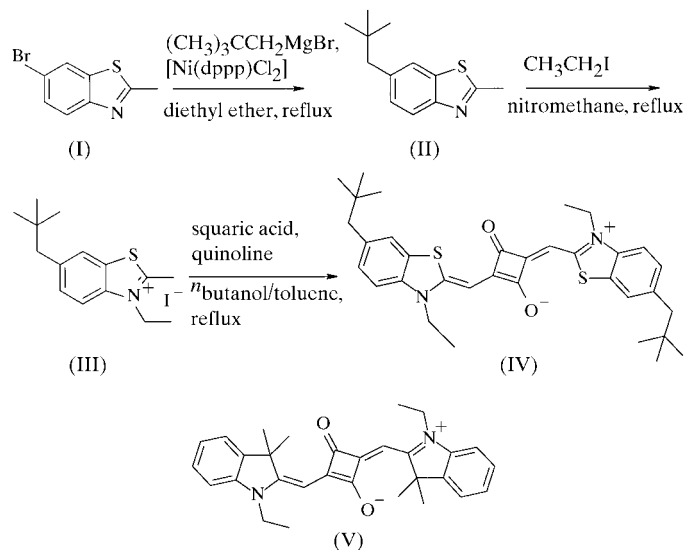
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The title compound, C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, adopts a *trans* conformation. The four conjugated Csp<sup>2</sup>–Csp<sup>2</sup> single and double bonds of the polymethinic moiety, which bridges both heterocyclic end groups and the central four-membered ring, display nearly equal bond lengths. The molecule is nearly planar, with interplanar angles between the benzothiazole end groups and the central four-membered ring of 6.9 (1) and 7.7 (1)°; the angle between the heterocyclic systems is 1.8 (1)°. The crystal packing involves π-stacking effects, with intermolecular C···C distances varying from 3.755 (3) to 3.991 (3) Å.

**Comment**

Squaraines (or squarylium dyes) such as the title compound, (IV), exhibit cyanine-like light absorption, with a sharp and intense absorption band in the long-wavelength range of the visible spectrum and in the near-IR region. They have gained importance as promising materials, e.g. as labels in fluorescence microscopy (Terpetschnig *et al.*, 1993) and as photoconductive materials (Law, 1993). More recently, their remarkably high third-order optical non-linearity was investigated intensively, with special respect to the contribution of two-photon states. A strong dependence of the optical properties on the molecular structure is expected (Andrews *et al.*, 1998). Although the crystal structure of a related dye, 2,4-bis(1,3,3-trimethyl-2-indolinylidene)methyl)cyclobutenediylum-1,3-diolate, (V) [Cambridge Crystallographic Database (CCD; Allen & Kennard, 1993) reference DONXEJ], was determined more than ten years ago (Kobayashi *et al.*, 1986), no structure of an analogous benzothiazole derivative has

been reported so far, probably because of the extremely low solubility of these dyes. We assume that merely lengthening the *N*-alkyl chain to increase the solubility would hamper crystallization. Therefore, we decided to introduce additional lipophilic substituents in the benzothiazole end groups. A comparison of the UV–visible spectrum of (IV) with that of an unsubstituted dye (Terpetschnig *et al.*, 1993) reveals that, as expected, the optical properties are essentially unaffected by this kind of substitution.



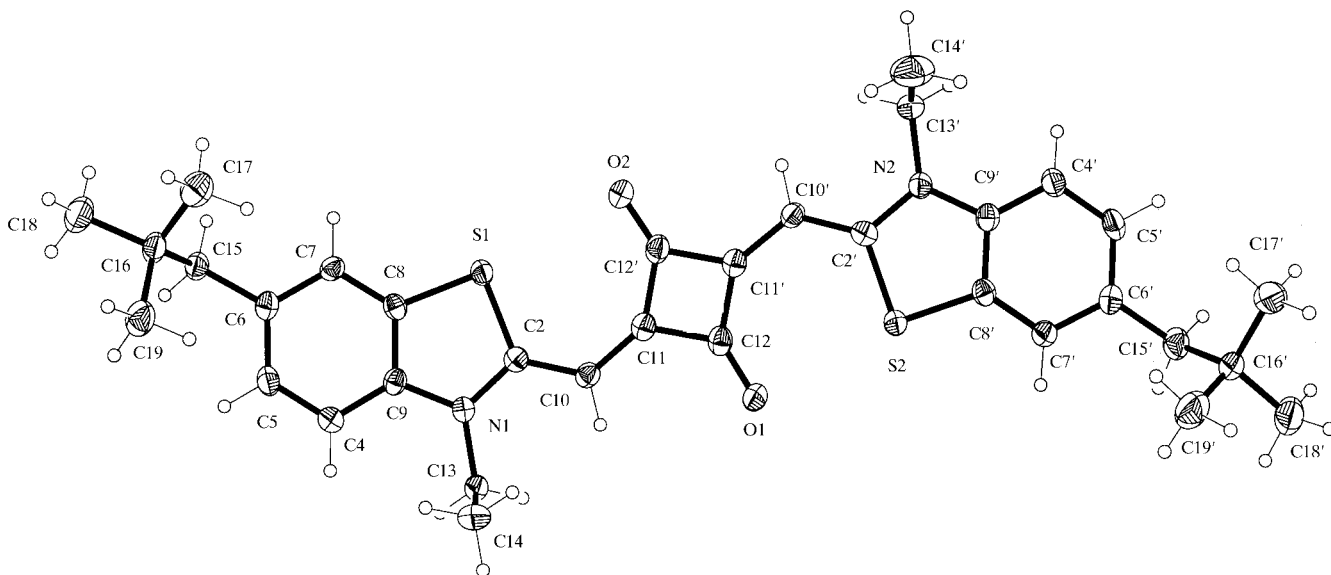
The structure of (IV) is shown in Fig. 1. The benzothiazole ring systems S1/C2/N1/C9/C4/C5/C6/C7/C8 and S2/C2'/N2'/C9'/C4'/C5'/C6'/C7'/C8' are planar, with mean deviations from planarity of 0.021 and 0.023 Å, respectively. The central four-membered ring C11/C12/C11'/C12' is also planar, with a mean deviation of 0.019 Å, and is a nearly perfect square, with bond lengths ranging from 1.461 (3) to 1.468 (3) Å and bond angles from 89.72 (16) to 90.13 (16)° (Table 1). This geometry is slightly more regular than that of the related compound (V) [1.450 to 1.485 Å and 89.8 to 90.5°, respectively].

The two O atoms are displaced from the square plane by 0.132 (4) (O1) and 0.091 (4) Å (O2) in the same direction, whereas the bridging atoms C10 and C10' lie 0.011 (4) and 0.056 (4) Å, respectively, on the other side of the plane. The deviation of these C atoms from the plane of the respective heterocyclic end group is distinctly larger, at 0.132 (3) Å for C10 and 0.110 (2) Å for C10'.

The entire molecule of (IV) is nearly planar, with interplanar angles between the benzothiazole ring systems and the central four-membered ring of 6.9 (1) (S1–C8) and 7.7 (1)° (S2–C8'). The interplanar angle between the two heterocyclic end groups is 1.8 (1)°. These small but non-zero interplanar angles lead to a highly flattened 'S'-form of the molecule when viewed sideways on. Compound (V) shows markedly larger corresponding interplanar angles of 24.6, 20.4 and 7.8°. Additionally, a considerable decrease in bond length alternation within the conjugated polymethinic chain of (IV) can be recognized. This is a typical feature of cyanine-like molecules. The bond lengths of C2–C10, C10–C11, C2'–C10'

<sup>1</sup>This name conforms with systematic nomenclature but does not represent the most important resonance structure.

<sup>2</sup>Dedicated to Professor Henning Hopf on the occasion of his 60th birthday.



**Figure 1**

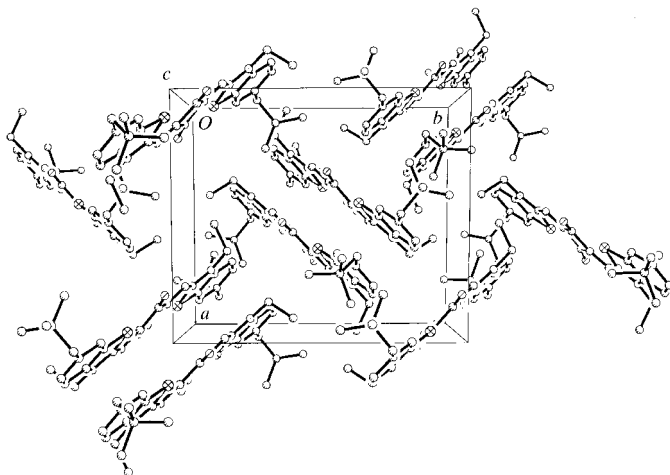
The molecular structure of (IV) with displacement ellipsoids at the 50% probability levels. H atoms are shown as small spheres of arbitrary radii.

and  $C10'-C11'$  vary from 1.381 (3) to 1.398 (3) Å. In contrast, the bond length alternation in compound (V) is more distinct, with bond lengths varying from 1.372 (12) to 1.404 (12) Å, although the s.u.'s in (V) are much larger. The angles in the polymethinic chains,  $C2-C10-C11$  and  $C2'-C10'-C11'$ , are 127.24 (19) and 126.60 (19)°, respectively. The analogous trimethylindoline derivative, (V), shows a significantly larger value of 133.1 (8)°. The enlargement of these angles was stated (Kobayashi *et al.*, 1986) to be caused by interactions of the geminal methyl groups and the O atoms.

The molecules of (IV) pack as antiparallel pairs that are oriented nearly perpendicular to each other (Fig. 2). The angle between two orthogonal planes (defined as the whole molecule, but excluding the alkyl substituents) is 89.4 (2)°. The intermolecular  $C\cdots C$  distances vary from 3.755 (3) Å for  $C7\cdots C7^i$  to 3.991 (3) Å for  $C12\cdots C12^i$  [symmetry code: (i)

$1-x, 1-y, 1-z$ ]. These  $C\cdots C$  distances are similar to those observed in bisanilinosquaraines (*ca* 3.5 Å). In contrast, the  $O\cdots O$  distance is larger, at 4.147 (2) Å for  $O1\cdots O2^i$ .

Various types of intermolecular donor–acceptor (*D–A*) interactions have been described for squaraines. Firstly, for several dyes an intermolecular charge transfer between a donor anilino moiety of one dye molecule and an acceptor  $C_4O_2$  unit of another has been proposed (Wingard, 1982; Tristani-Kendra & Eckhardt, 1984; Bernstein & Goldstein, 1988, CCD reference VAYSET). A similar *D–A* arrangement was observed for a benzothiazole-substituted ethoxycyclobutene-1,2-dione, which is a squaraine precursor (Jones *et al.*, 1997, CCD reference RUHFIJ). Dipole–dipole interactions represent a second possibility. A staircase-like arrangement of the compound with CCD reference MXPBUQ [Law (1988), a redetermination of the structure first reported by Farnum *et al.* (1974)] results from the interaction of polarized  $C–O$  units of neighbouring molecules. Similar effects have also been observed for several squaraines in Langmuir–Blodgett films (Law & Chen, 1989). Finally, in contrast to the previous two types of interaction,  $\pi$ -stacking can be recognized in the crystal packing of (IV); the mean distance between two aligned molecules is 3.86 Å. The molecules in an antiparallel aligned pair do not lie exactly above one another. However, the plane defined by the whole molecule (excluding the alkyl substituents; mean deviation from planarity 0.111 Å) subtends an angle of 76° with a line connecting  $C11$  and  $C11^i$ , indicating a reasonable degree of overlap.



**Figure 2**

The packing diagram for (IV) viewed parallel to the  $z$  axis. H atoms have been omitted for clarity.

## Experimental

3-Ethyl-6-(2,2-dimethylpropyl)-2-methylbenzothiazolium iodide, (III), was obtained from 6-bromo-2-methylbenzothiazole, (I), *via* Kumada coupling with 2,2-dimethylpropylmagnesium bromide and subsequent *N*-alkylation with ethyl iodide according to known methods (Tamao *et al.*, 1976; Goerdeler, 1958) in an overall yield of

15%. Condensation of (III) (500 mg, 1.33 mmol) with squaric acid (76 mg, 0.66 mmol) was carried out in the presence of quinoline (0.16 ml, 1.35 mmol) in refluxing toluene/*n*-butanol (1:1, 20 ml) for 20 h using a Dean–Stark trap (Sprenger & Ziegenbein, 1967). After removal of solvent and column chromatography (SiO<sub>2</sub>; chloroform/ethanol, 20:1), the product was extracted with boiling methanol and the resulting deep-blue solution was concentrated to ca 5 ml. Compound (IV) was obtained in 16% yield as metallic green square plates (60 mg, m.p. 557 K). Analytical data for compound (IV): <sup>1</sup>H NMR (δ, p.p.m.): 7.28 (broad s, 2H, H7, H7'), 7.11 (dd, <sup>3</sup>J<sub>5,4</sub> = <sup>3</sup>J<sub>5',4'</sub> = 8.4 Hz, <sup>4</sup>J<sub>5,7</sub> = <sup>4</sup>J<sub>5',7'</sub> = 1.5 Hz, 2H, H5, H5'), 7.03 (d, <sup>3</sup>J<sub>4,5</sub> = <sup>3</sup>J<sub>4',5'</sub> = 8.4 Hz, 2H, H4, H4'), 5.84 (s, 2H, H10, H10'), 4.13 (q, <sup>3</sup>J<sub>13,14</sub> = <sup>3</sup>J<sub>13',14'</sub> = 7.2 Hz, 4H, H13, H13'), 2.52 (s, 4H, H15, H15'), 1.41 (t, <sup>3</sup>J<sub>14,13</sub> = <sup>3</sup>J<sub>14',13'</sub> = 7.2 Hz, 6H, H14, H14'), 0.90 (s, 18H, H17, H17', H18, H18', H19, H19'); <sup>13</sup>C NMR (δ, p.p.m.): 158.8 (s, C2, C2'), 139.0 (s, C9, C9'), 136.0 (s, C8, C8'), 129.3 (d, C5, C5'), 128.3 (s, C6, C6'), 123.5 (d, C7, C7'), 110.1 (d, C4, C4'), 84.7 (d, C10, C10'), 49.7 (t, C15, C15'), 40.9 (t, C13, C13'), 31.9 (s, C16, C16'), 29.2 (q, C17, C17', C18, C18', C19, C19'), 12.4 (q, C14, C14'); signals for C11, C11', C12 and C12' were not observed; MS (*m/z*, %): 572 (100) (*M*<sup>+</sup>); UV–visible [CHCl<sub>3</sub>, λ<sub>max</sub> (log ε)]: 672 nm (5.41); analysis calculated for C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 71.29, H 7.04, N 4.89, S 11.20%; found: C 70.93, H 7.10, N 4.76, S 11.24%.

Crystal data

C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 572.80  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 12.4285 (14) Å  
*b* = 14.4182 (14) Å  
*c* = 17.8511 (18) Å  
 β = 100.129 (3)°  
*V* = 3149.0 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.208 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 6569 reflections  
 θ = 2–28°  
 μ = 0.201 mm<sup>-1</sup>  
*T* = 143 (2) K  
 Tablet, metallic green  
 0.42 × 0.31 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer  
 ω scans  
 42 373 measured reflections  
 6437 independent reflections  
 3919 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.119  
 θ<sub>max</sub> = 26.37°  
*h* = -15 → 15  
*k* = -18 → 18  
*l* = -22 → 22

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR* (*F*<sup>2</sup>) = 0.092  
*S* = 0.90  
 6437 reflections  
 369 parameters

H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0396*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.31 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.21 e Å<sup>-3</sup>

The methyl groups were obtained from difference syntheses and were treated as rigid groups allowed to rotate but not tip from the starting positions. The remaining H atoms were included with a riding model (C–H range 0.95–0.99 Å) starting from calculated positions.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP*

Table 1

Selected geometric parameters (Å, °).

C2–C10	1.383 (3)	C11–C12	1.466 (3)
C2'–C10'	1.381 (3)	C11–C12'	1.468 (3)
C10–C11	1.387 (3)	C11'–C12	1.461 (3)
C10'–C11'	1.398 (3)	C11'–C12'	1.465 (3)
C2–C10–C11	127.24 (19)	C12–C11'–C12'	90.07 (16)
C2'–C10'–C11'	126.60 (19)	C11'–C12–C11	90.13 (16)
C12–C11–C12'	89.72 (16)	C11'–C12'–C11	89.92 (16)
C9–N1–C13–C14	-86.0 (2)	C7–C6–C15–C16	-89.0 (2)
C9'–N2–C13'–C14'	-92.0 (2)	C7'–C6'–C15'–C16'	-95.5 (2)

(Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1026). Services for accessing these data are described at the back of the journal.

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