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The crystal structure of (4*Z*)-2-[(*E*)-(1-ethyl-3,3-dimethyl-1,3-dihydro-2*H*-indol-2-ylidene)methyl]-4-[(1-ethyl-3,3-dimethyl-3*H*-indolium-2-yl)methylidene]-3-oxocyclobut-1-en-1-olate, C₃₀H₃₂N₂O₂

Table 1: Data collection and handling.

Crystal:	Red prismatic
Size:	0.32 × 0.23 × 0.13 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	0.59 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ _{max} , completeness:	76.5°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	28307, 5211, 0.023
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4340
<i>N</i> (<i>param</i>) _{refined} :	321
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Abstract

C₃₀H₃₂N₂O₂, monoclinic, *P*₂/c (no. 14), *a* = 9.8611(2) Å, *b* = 15.8027(3) Å, *c* = 16.2473(3) Å, β = 100.150(2)°, *V* = 2492.23(8) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0542, *wR*_{ref}(*F*²) = 0.1677, *T* = 296(3) K.

CCDC no.: 1881665

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Equimolar amount of squaric acid and 2,3,3-trimethylindolenine were added to a round bottom flask

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.38808(13)	0.21079(8)	0.08798(7)	0.0593(3)
O2	0.18088(15)	0.03021(8)	−0.11097(8)	0.0643(4)
N1A ^a	0.4354(2)	−0.11640(16)	0.16244(15)	0.0479(5)
N2	0.10553(16)	0.35696(9)	−0.18202(8)	0.0528(4)
C1	0.17963(17)	0.31397(10)	−0.11580(9)	0.0468(4)
C2	0.1233(2)	0.44469(10)	−0.17267(11)	0.0548(4)
C3	0.0695(3)	0.50780(13)	−0.22790(13)	0.0755(6)
H3	0.013143	0.495695	−0.278699	0.091*
C4	0.1043(3)	0.58988(13)	−0.20335(16)	0.0917(8)
H4	0.072366	0.634167	−0.239284	0.110*
C5	0.1850(3)	0.60801(12)	−0.12698(16)	0.0838(7)
H5	0.205804	0.663965	−0.112118	0.101*
C6	0.2351(2)	0.54365(11)	−0.07252(13)	0.0643(5)
H6	0.287355	0.555929	−0.020470	0.077*
C7	0.20647(18)	0.46094(10)	−0.09646(10)	0.0510(4)
C8	0.24897(16)	0.37850(10)	−0.05228(9)	0.0460(4)
C9	0.40631(18)	0.36897(12)	−0.03608(13)	0.0622(5)
H9A	0.431343	0.316762	−0.007141	0.093*
H9B	0.447220	0.415439	−0.002534	0.093*
H9C	0.438780	0.368733	−0.088412	0.093*
C10	0.1902(2)	0.37246(13)	0.02901(11)	0.0618(5)
H10A	0.216428	0.319369	0.055891	0.093*
H10B	0.091560	0.376229	0.016342	0.093*
H10C	0.225902	0.417996	0.065610	0.093*
C11	0.0249(2)	0.31939(12)	−0.25722(11)	0.0588(4)
H11A	−0.047342	0.358317	−0.281291	0.071*
H11B	−0.018337	0.267792	−0.242399	0.071*
C12	0.1131(3)	0.2999(2)	−0.31999(15)	0.0974(8)
H12A	0.152958	0.351242	−0.336406	0.146*
H12B	0.058211	0.274021	−0.368095	0.146*
H12C	0.185127	0.261739	−0.296057	0.146*
C13	0.18389(18)	0.22682(10)	−0.11251(9)	0.0499(4)
H13	0.136232	0.200524	−0.160169	0.060*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C14	0.24657(16)	0.17051(10)	−0.05082(9)	0.0457(3)
C15	0.23683(17)	0.07805(10)	−0.05565(10)	0.0483(4)
C16	0.31739(16)	0.07047(10)	0.02944(10)	0.0478(4)
C17	0.32987(16)	0.16301(10)	0.03328(10)	0.0464(3)
C18	0.37367(19)	0.01451(11)	0.09213(11)	0.0595(5)
H18	0.435702	0.039208	0.135174	0.071*
C19	0.35424(19)	−0.07125(11)	0.10218(11)	0.0585(5)
C20	0.3714(2)	−0.19788(11)	0.17147(12)	0.0665(5)
C21	0.4087(3)	−0.25950(13)	0.23240(14)	0.0813(7)
H21	0.475742	−0.249589	0.279298	0.098*
C22	0.3409(3)	−0.33633(13)	0.21961(14)	0.0747(6)
H22	0.361706	−0.378803	0.259452	0.090*
C23	0.2430(2)	−0.35156(12)	0.14922(14)	0.0685(5)
H23	0.200635	−0.404249	0.141643	0.082*
C24	0.2075(2)	−0.28841(11)	0.08957(12)	0.0577(4)
H24	0.141319	−0.298389	0.042271	0.069*
C25	0.27176(17)	−0.21115(10)	0.10163(10)	0.0491(4)
C26	0.25535(16)	−0.13156(9)	0.04898(9)	0.0445(3)
C27	0.3007(2)	−0.14769(12)	−0.03531(12)	0.0616(5)
H27A	0.297568	−0.095606	−0.066003	0.092*
H27B	0.239860	−0.188097	−0.066827	0.092*
H27C	0.393036	−0.169450	−0.025821	0.092*
C28	0.10702(17)	−0.09921(11)	0.03629(11)	0.0545(4)
H28A	0.083609	−0.084940	0.089493	0.082*
H28B	0.045832	−0.142477	0.010161	0.082*
H28C	0.098487	−0.049893	0.001256	0.082*
C29A ^a	0.5472(3)	−0.0827(2)	0.22519(18)	0.0605(7)
H29A ^a	0.597763	−0.040594	0.199395	0.073*
H29B ^a	0.610406	−0.128103	0.245719	0.073*
C30A ^a	0.4948(4)	−0.0439(3)	0.2962(2)	0.0833(9)
H30A ^a	0.570732	−0.022582	0.336039	0.125*
H30B ^a	0.433540	0.001715	0.276270	0.125*
H30C ^a	0.446174	−0.085729	0.322559	0.125*
C29B ^b	0.4819(6)	−0.0757(4)	0.2561(4)	0.0605(7)
H29C ^b	0.455893	−0.017540	0.264582	0.073*
H29D ^b	0.472066	−0.107335	0.305894	0.073*
C30B ^b	0.6258(7)	−0.0775(5)	0.2466(4)	0.0833(9)
H30D ^b	0.681767	−0.053737	0.295443	0.125*
H30E ^b	0.653406	−0.134968	0.239678	0.125*
H30F ^b	0.637214	−0.045067	0.198317	0.125*
N1B ^b	0.3866(5)	−0.1107(3)	0.1847(3)	0.0479(5)

^aOccupancy: 0.65, ^bOccupancy: 0.35.

containing toluene (20 mL) and connected with Dean-Stark apparatus. The mixture was refluxed for 20 h. The progress was monitored using thin layer chromatographic (TLC) technique. Upon reaction completion, the mixture was cooled to room temperature, which provided dark red crystalline material. The product was washed with petroleum ether and dried.

Experimental details

Data collection was accomplished using CrysAlis^{PRO} software [1] at 296 K using Cu *K*α radiation. Structure solution was performed using SHELXS-2016/6 [2] and refined by full-matrix least-squares methods on *F*² using SHELXL-2016/6 [3], in-built within WinGX [4]. All non-hydrogen atoms were

refined anisotropically. The figure was generated through ORTEP [4]. All the aromatic C-H hydrogen atoms were positioned geometrically with C-H = 0.93 Å and treated as riding atoms with *U*_{iso}(H) = 1.2 *U*_{eq}(C). Methyl and methylene hydrogen atoms were also positioned geometrically with C-H = 0.96 Å for methyl and C-H = 0.97 Å for methylene and treated as riding atoms where *U*_{iso}(H) was set to 1.5 *U*_{eq}(C) for methyl and 1.2 *U*_{eq}(C) for methylene hydrogen atoms.

Comment

Since the first report appeared by Von Sprenger and Ziegenbein [5], bis(indolenine)squaraine based molecules have been studied for their remarkable fluorescence activities [6, 7]. There are many reports favouring these materials for sensing protein molecules [8, 9]. Smith and Lynch reported the parent dye 2,4-[(3,3-dimethyl-2-indolylidene)methyl]cyclobutenediyl-1,3-diolate with two chloroform solvent molecules [10]. Natsukawa and Nakazumi reported the crystal structure of the methanol solvate of the title compound [11]. In the crystal structure of the title compound (cf. the figure), two indole ring systems (C1-C8/N1) & (C19-C26/N2) are attached to the oxo-cyclobutene moiety. The ambient-temperature data indicates the presence of disorder, over two positions, in both N-ethyl functional groups, which was successfully modelled for one of the two groups. The N-ethyl group (N2/C29/C30), was refined using the restraints and constraints with the occupancy ratio fixed to 0.65:0.35 for (N2A/C29A/C30A) and (N2B/C29B/C30B) parts, respectively. The disorder involving N2 produced two different planes containing the atoms (C19-C26/N2A) and (C19-C26/N2B). In the literature, the structures reported by Smith and Lynch [10] and by Natsukawa and Nakazumi [11] both have a plane of symmetry passing through the cyclobutene ring, while there is no plane symmetry in the structure of title compound. The root mean square deviation values for the planes produced from the fitted atoms belonging to the indole rings are 0.0184(2) Å, 0.0624(2) Å and 0.1129(2) Å for the (C1-C8/N2), (C19-C26/N2A) and (C19-C26/N2B), respectively. The central cyclobutene ring is oriented at dihedral angles of 2.651(3)°, 19.647(6)° and 14.657(3)° with respect to the (C1-C8/N2), (C19-C26/N2A) and (C19-C26/N2B) rings. These values indicate that this dye molecule is nonplanar. We have observed two non-classical hydrogen-bonding interactions which connect molecules to generate a two-dimensional network along the diagonal of the *ac*-plane.

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