Haiqing Huang* and Li Xu

Crystal structure of (*E*)-2-(5,5-dimethyl-3-(4-((7-nitrobenzo[*c*][1,2,5]oxadiazol-4-yl)oxy)styryl)cyclohex-2-en-1-ylidene)malononitrile, C₂₅H₁₉N₅O₄

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Abstract

C₂₅H₁₉N₅O₄, triclinic, $P\bar{1}$ (no. 2), $a = 7.5952(11)$ Å, $b = 9.4729(13)$ Å, $c = 16.260(2)$ Å, $\alpha = 76.559(2)^\circ$, $\beta = 87.394(2)^\circ$, $\gamma = 73.886(2)^\circ$, $V = 1092.9(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0433$, $wR_{\text{ref}}(F^2) = 0.1293$, $T = 296(2)$ K.

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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

The title compound was synthesized by condensation reaction of a (*E*)-2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile [5] and 4-chloro-7-nitrobenzo[*c*][1,2,5]oxadiazole in 90% yield. M.p.: 528 K–529 K. The title compound crystallized from hexane-dichloromethane cosolvent at room temperature and produced the suitable yellow crystals for X-ray analysis.

*Corresponding author: Haiqing Huang, School of Chemistry, Biology and Material Science, East China University of Technology, NanChang, Jiangxi 344000, China, e-mail: mouse2020_up@126.com. <https://orcid.org/0000-0001-5984-955X>

Li Xu: School of Chemistry, Biology and Material Science, East China University of Technology, NanChang, Jiangxi 344000, China

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.26 × 0.24 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.10 mm ^{−1}
Diffractometer, scan mode:	APEX2/D8, φ and ω
θ_{max} , completeness:	26.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6064, 4252, 0.016
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3017
$N(\text{param})_{\text{refined}}$:	307
Programs:	Bruker [1], SHELX [2–4]

Experimental details

The hydrogen atoms were located by geometrical calculations, and their positions and thermal parameters were fixed during the structure refinement.

Comment

It is well known that chemosensors with high sensitivity and selectivity for important biologically relevant components for their vital roles *in vivo*, such as, ions and biothiols, have attracted considerable interest for their extensive applications [5–11]. Among these chemosensors, the fluorescent probe exhibits certain uniqueness and indispensability for the evaluation of physiological processes of biologic compared with some conventional methods, such as HPLC, UV/vis absorption spectroscopy, and mass spectrometry [12–14]. The fluorescent probe responds to the specific target ions or molecules with different response mechanisms, such as self-assembly, chemical reaction [15–17]. In recent years, chemical reactional fluorescent probes have been extensively used in chemosensors due to their significant difference in fluorescent intensity with specific target [18]. Although many chemical reactional fluorescent probe compounds have been reported so far, very few of them having chemical reaction unit have been shown in the crystalline phase.

To date, crystal structures of fluorescent probes have been reported [19, 20]. However, few of them investigate the molecular structural conformation behaviors in the crystalline phase because the crystal structure can effectively help us to design and synthesize new fluorescent probes [21, 22].

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	−0.0847(2)	0.19063(19)	−0.03072(11)	0.0418(4)
C2	−0.0846(3)	0.2297(2)	0.04443(12)	0.0483(5)
H2A	−0.1791	0.2186	0.0816	0.058*
C3	0.0549(3)	0.2871(2)	0.06839(12)	0.0509(5)
H3A	0.0490	0.3134	0.1203	0.061*
C4	0.1963(3)	0.3039(2)	0.01654(11)	0.0438(4)
C5	0.1988(2)	0.2655(2)	−0.06337(11)	0.0406(4)
C6	0.0601(2)	0.20720(19)	−0.08750(11)	0.0401(4)
C7	0.4073(3)	0.3279(2)	0.11397(11)	0.0430(4)
C8	0.4391(3)	0.1874(2)	0.16747(12)	0.0485(5)
H8A	0.4069	0.1098	0.1513	0.058*
C9	0.5199(3)	0.1634(2)	0.24570(11)	0.0444(4)
H9A	0.5417	0.0685	0.2821	0.053*
C10	0.5697(2)	0.27760(19)	0.27181(10)	0.0361(4)
C11	0.5410(3)	0.4169(2)	0.21405(11)	0.0435(4)
H11A	0.5766	0.4942	0.2288	0.052*
C12	0.4612(3)	0.4419(2)	0.13573(12)	0.0450(5)
H12A	0.4438	0.5350	0.0979	0.054*
C13	0.6440(2)	0.24891(19)	0.35725(10)	0.0359(4)
H13A	0.6661	0.1509	0.3899	0.043*
C14	0.6830(2)	0.35092(19)	0.39267(11)	0.0365(4)
H14A	0.6670	0.4473	0.3585	0.044*
C15	0.7475(2)	0.32757(18)	0.47837(10)	0.0345(4)
C16	0.7981(3)	0.17242(18)	0.53595(11)	0.0397(4)
H16A	0.9187	0.1175	0.5212	0.048*
H16B	0.7119	0.1191	0.5260	0.048*
C17	0.7999(2)	0.17128(18)	0.63008(11)	0.0382(4)
C18	0.9042(3)	0.28234(19)	0.64350(11)	0.0429(4)
H18A	0.8950	0.2893	0.7022	0.051*
H18B	1.0329	0.2432	0.6321	0.051*
C19	0.8329(2)	0.43698(19)	0.58811(11)	0.0367(4)
C20	0.7649(2)	0.44832(19)	0.50569(11)	0.0374(4)
H20A	0.7308	0.5430	0.4689	0.045*
C21	0.8390(2)	0.5631(2)	0.61409(11)	0.0399(4)
C22	0.9128(3)	0.5555(2)	0.69531(13)	0.0467(5)
C23	0.7775(3)	0.7102(2)	0.55965(13)	0.0456(5)
C24	0.6040(3)	0.2184(2)	0.66108(13)	0.0533(5)
H24A	0.5430	0.3181	0.6297	0.080*
H24B	0.5392	0.1488	0.6529	0.080*
H24C	0.6069	0.2179	0.7201	0.080*
C25	0.8976(3)	0.0122(2)	0.68010(12)	0.0543(5)
H25A	1.0206	−0.0174	0.6606	0.081*
H25B	0.9005	0.0116	0.7391	0.081*
H25C	0.8328	−0.0575	0.6719	0.081*
N1	−0.2278(2)	0.12845(18)	−0.05175(12)	0.0512(4)
N2	0.1002(2)	0.1736(2)	−0.16136(10)	0.0544(4)
N3	0.3229(2)	0.2681(2)	−0.12230(10)	0.0543(4)
N4	0.7283(3)	0.8263(2)	0.51463(13)	0.0660(5)
N5	0.9738(3)	0.5502(2)	0.75903(12)	0.0685(5)
O1	−0.2297(2)	0.1071(2)	−0.12275(11)	0.0763(5)
O2	−0.3361(2)	0.09799(19)	0.00277(11)	0.0724(5)
O3	0.2623(2)	0.21216(18)	−0.18275(8)	0.0629(4)
O4	0.3365(2)	0.35869(16)	0.03166(8)	0.0559(4)

The molecular structure of the title compound is shown in the figure. The main frame of (*E*)-2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile is in the same plane, except C17 atom and two methyl groups. It is interesting that the molecule is packed with two molecules in the cell related by inversion symmetry. In the cyclohexene unit, the ring of C16, C17, C18 and the ring of C15, C16, C18, C19, C20 form an envelope structure with a dihedral angle of 44.1°. From the crystal data, two double bonds can be seen, the C13=C14 1.337(2) Å and C15=C20 1.360(2) Å which is shorter than the formal single bond (such as C5–C16, 1.505(2) Å and C13–C10, 1.460(2) Å). The molecular moieties (*E*)-2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile [23] and 4-chloro-7-nitrobenzo[c][1,2,5]oxadiazole are connected by an oxygen atom and the mean planes of these moieties show a dihedral angle 114.9°.

The fluorescent probe characteristics of the title compound was tested in ethanol. Upon addition of Hcy/Cys other thiols, and aminoacids, only the Hcy/Cys can exhibit the selective fluorescence signals, when excited with 400 nm light and 543 nm high-brightness fluorescence signal, which can be rationally explained by the nucleophilic aromatic substitution reaction promoted by the sulfhydryl group of thiols.

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