

Akira Mori,* Kanji Kubo,
Bing Zhu Yin and Hitoshi
TakeshitaInstitute of Advanced Material Study, 86,
Kyushu University, Kasuga-koen, Kasuga,
Fukuoka 816-8580, JapanCorrespondence e-mail:
kubo-k@cm.kyushu-u.ac.jp

Key indicators

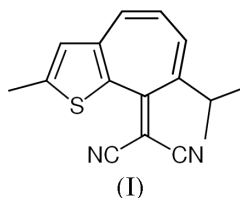
Single-crystal X-ray study
 $T = 296\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.052
 wR factor = 0.143
Data-to-parameter ratio = 16.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2-(7-Isopropyl-2-methylcyclohepta[*b*]thiophen-8-yl-
idene)propanedinitrile

The exocyclic double-bond length of the title compound, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}$, is 1.366 (4) Å. The planarity of the seven-membered ring is decreased by the isopropyl group and the thiophene ring. The dicyanomethylene group intersects the seven-membered ring at an angle of 45.9 (2)°.

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Comment

8,8-Dicyanoheptafulvene (DCH), a non-benzenoid aromatic compound, has a brilliant red color and a large dipole moment (7.49 D; Shimanouchi *et al.*, 1966). The introduction of substituent groups to the seven-membered ring causes the color to change. For example, the crystal colors of 1,6-dimethyl-8,8-dicyanoheptafulvene (DMDCH; Shimanouchi *et al.*, 1974*a*) and 1-isopropyl-8,8-dicyanoheptafulvene (IPDCH; Shimanouchi *et al.*, 1974*b*) are yellow. It is observed by the X-ray crystallographic analyses of DMDCH and IPDCH that the conjugation between the exocyclic double bond and the seven-membered ring is largely hindered by the substituent at the neighboring position. We now report the structure of the title compound, (I), which has a yellow color, with the aim of contributing to a deeper understanding of the relationships between the 8,8-dicyanoheptafulvene moiety and neighboring substituents.



The seven-membered ring in (I) has a twisted conformation; the intersection angles between the least-squares planes *A* (defined by C1/C2/C7) and *B* (defined by C2/C3/C6/C7), and between the least-squares planes *B* and *C* (defined by C3–C6) are 45.2 (3) and 22.2 (2)°, respectively. The deviations of each atom from the seven-membered ring are -0.39 \AA for C1, 0.12 \AA for C2, 0.22 \AA for C3, 0.18 \AA for C4, -0.24 \AA for C5, -0.18 \AA for C6 and 0.22 \AA for C7, resulting from the intramolecular steric hindrance between the isopropyl and the cyano groups. The dicyanomethylene group is inclined to the seven-membered ring (defined by C1–C7) at an angle of 45.9 (2)°, which is distinct from that (4.8°) of DCH (Shimanouchi *et al.*, 1966), similar to that (47.5°) of DMDCH (Shimanouchi *et al.*, 1974*a*), and larger than that (39.2°) of IPDCH (Shimanouchi *et al.*, 1974*b*). These observations result from the intramolecular steric hindrance between the thiophene ring and the cyano groups in addition to the steric

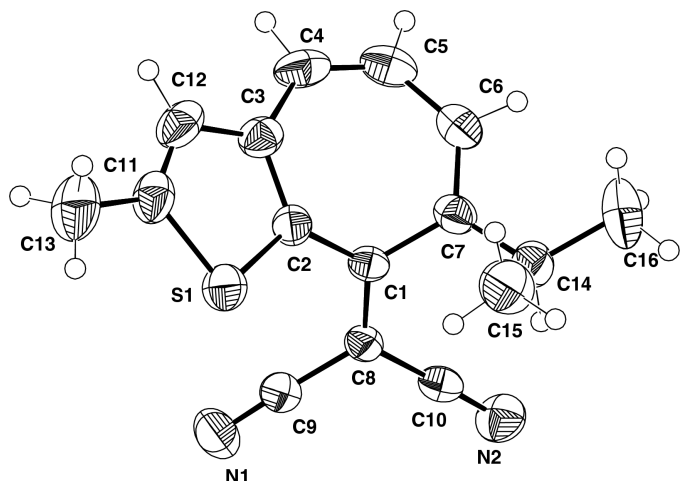


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

hindrance between the isopropyl and the cyano groups. The dihedral angle between the thiophene ring and the least-squares plane *B* is 22.2 (1)°. The deviations of each atom from the thiophene ring plane are within 0.02 Å. It is interesting that the exocyclic C1=C8 bond length [1.366 (4) Å] of (I) is shorter than that (1.422 Å) of DCH, and similar to those (1.361 and 1.367 Å) of DMDCH and IPDCH (Shimanouchi *et al.*, 1974*a,b*).

Experimental

Compound (I) was prepared from 7-isopropyl-2-methylcyclohepta-*b*thiophen-8-one (Ikeda *et al.*, 1994) and malononitrile by reflux in acetic anhydride. Single crystals of (I) were obtained by recrystallization from chloroform.

Crystal data

C₁₆H₁₄N₂S
M_r = 266.35
 Monoclinic, *P*2₁/*a*
a = 17.174 (5) Å
b = 7.380 (5) Å
c = 11.393 (5) Å
 β = 100.647 (5)°
V = 1419.1 (12) Å³
Z = 4

D_x = 1.247 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 20 reflections
 θ = 10.1–18.0°
 μ = 0.22 mm⁻¹
T = 296 (2) K
 Prism, red
 0.27 × 0.27 × 0.23 mm

Data collection

Enraf–Nonius FR590 diffractometer
 ω –2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.959, *T_{max}* = 1.000
 3016 measured reflections
 2871 independent reflections
 1396 reflections with *I* > 2 σ (*I*)

R_{int} = 0.039
 θ_{\max} = 26.3°
h = –21 → 21
k = –9 → 0
l = –14 → 0
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.5%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.052
wR(*F*²) = 0.143
S = 0.99
 2871 reflections
 172 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.0071P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.275 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.287 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1–C11	1.719 (4)	C3–C12	1.422 (5)
S1–C2	1.725 (3)	C3–C4	1.442 (5)
N1–C9	1.137 (4)	C4–C5	1.334 (5)
N2–C10	1.133 (4)	C5–C6	1.436 (5)
C1–C8	1.366 (4)	C6–C7	1.350 (4)
C1–C2	1.441 (4)	C8–C10	1.441 (4)
C1–C7	1.480 (4)	C8–C9	1.441 (5)
C2–C3	1.386 (4)	C11–C12	1.346 (5)
C1–C7–C14–C15	–63.0 (4)	C1–C7–C14–C16	172.9 (3)

All H atoms were located at ideal positions and constrained with *U_{iso}* held fixed to 1.2 or 1.5 (H₂O) times *U_{eq}* of the parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL97*.

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