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2-(4-Bromophenyl)-1-(methylsulfanyl)-naphtho[2,1-*b*]furan

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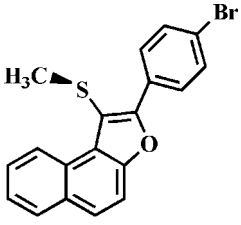
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.026; wR factor = 0.071; data-to-parameter ratio = 14.5.

The title compound, $C_{19}H_{13}BrOS$, was synthesized by the Lewis acid-catalyzed reaction of 2-naphthol with 4′-bromo-2-chloro-2-(methylsulfanyl)acetophenone. The methyl group lies above the naphthofuran ring system and the benzene ring is rotated out of the naphthofuran plane with a dihedral angle of 42.29 (8)°. The crystal structure is stabilized by aromatic π–π stacking between the furan and benzene rings, C—H···O and C—H···Br hydrogen bonds, and a Br···Br interaction.

Related literature

For the crystal structures of isomers of the title compound, see: Choi, Seo, Kang *et al.* (2006) and Choi, Seo, Son & Lee (2006). For details of the biological and pharmacological activity of naphthofuran compounds, see: Goel & Dixit (2004); Hagiwara *et al.* (1999); Piloto *et al.* (2005).



(I)

Experimental

Crystal data

$C_{19}H_{13}BrOS$
M_r = 369.26
Triclinic, $P\overline{1}$
a = 9.359 (1) Å
b = 9.487 (1) Å
c = 9.860 (1) Å
α = 94.352 (2)°
β = 115.271 (2)°
γ = 105.312 (2)°
V = 745.50 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.90 mm^{-1}
T = 173 (2) K
0.53 × 0.42 × 0.35 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan *SADABS* (Sheldrick, 1999)
T_{min} = 0.239, T_{max} = 0.371
5896 measured reflections
2878 independent reflections
2644 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.071
S = 1.04
2878 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O^{i}	0.95	2.70	3.635 (3)	170
C19—H19A···Br^{i}	0.98	3.01	3.885 (3)	149

Symmetry code: (i) $x+1, y, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2304).

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supplementary materials

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2-(4-Bromophenyl)-1-(methylsulfanyl)naphtho[2,1-*b*]furan

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Comment

Naphthofuran compounds have attracted widespread interest in view of their biological and pharmacological activities (Goel & Dixit, 2004; Hagiwara *et al.*, 1999; Piloto *et al.*, 2005). As part of our ongoing work on the synthesis and structures of naphthofuran derivatives, the crystal structures of 1-methylsulfinyl-2-phenylnaphtho[2,1-b]furan (Choi, Seo, Kang *et al.*, 2006) and 7-bromo-1-methylsulfanyl-2-phenylnaphtho[2,1-b]furan (Choi, Seo, Son & Lee, 2006) have been described to the literature. Herein we report the molecular and crystal structure of the title compound (I) (Fig. 1).

The naphthofuran unit is essentially planar, with a mean deviation of 0.049 Å from the least-squares plane defined by the thirteen constituent atoms. The dihedral angle in (I) formed by the plane of the naphthofuran ring and the plane of phenyl ring is 42.29 (8)°. The molecular packing (Fig. 2) is stabilized by aromatic π–π stacking interactions between adjacent naphthofuran units. The Cg1···Cg2 ^{i} distance is 3.649 (3) Å (Cg1 and Cg2 are the centroids of the C1/C2/O/C3/C12 and C6—C11 rings; symmetry code as in Fig. 2). Further stability comes from weak C—H···O and C—H···Br hydrogen bonds in Table 1, and a Br···Br interaction at 3.6890 (6) Å.

Experimental

Zinc chloride (273 mg, 2.0 mmol) was added at room temperature to a stirred solution of 2-naphthol (288 mg, 2.0 mmol) and 4'-bromo-2-chloro-2-(methylsulfanyl)acetophenone (559 mg, 2.0 mmol) in CH_2Cl_2 (30 ml), and stirred for 40 min. The mixture was quenched with water and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated in vacuum. The residue was purified by column chromatography (CCl_4) to afford the title compound as white needles (450 mg, 61%). M.p. 411-412 K). Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a dilute solution of title compound (I) in benzene at room temperature.

Refinement

All H atoms were geometrically located in ideal positions and refined using a riding model, with C—H = 0.95 Å for aromatic H atoms and C—H=0.98 Å for methyl H atoms, and with Uiso(H) = 1.2Ueq(C) for aromatic H atoms, and Uiso(H) = 1.5Ueq(C) for methyl H atoms. The highest peak in the difference map is 0.97 Å from Br and the largest hole is 1.00 Å from Br.

Figures

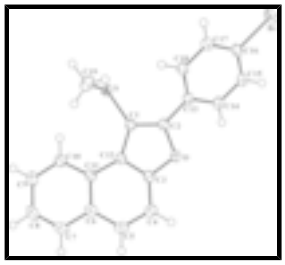


Fig. 1. The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level.

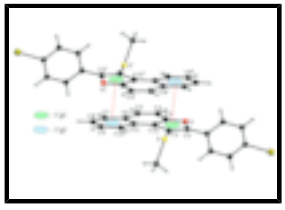


Fig. 2. π—π interactions in (I). Cg denotes ring centroids. [Symmetry code: (i) 2-x, 1-y, 1-z.]

2-(4-Bromophenyl)-1-(methylsulfanyl)naphtho[2,1-b]furan

Crystal data

$C_{19}H_{13}BrOS$	$Z = 2$
$M_r = 369.26$	$F_{000} = 372$
Triclinic, $P\overline{1}$	$D_x = 1.645$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 411-412 K
$a = 9.359$ (1) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 9.487$ (1) Å	Cell parameters from 4258 reflections
$c = 9.860$ (1) Å	$\theta = 2.3$–28.2º
$\alpha = 94.352$ (2)º	$\mu = 2.90$ mm^{-1}
$\beta = 115.271$ (2)º	$T = 173$ (2) K
$\gamma = 105.312$ (2)º	Block, colorless
$V = 745.50$ (14) Å^3	0.53 × 0.42 × 0.35 mm

Data collection

Bruker SMART CCD diffractometer	2878 independent reflections
Radiation source: fine-focus sealed tube	2644 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.021$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 26.0$º
$T = 173(2)$ K	$\theta_{min} = 2.3$º
φ and ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan SADABS (Sheldrick, 1999)	$k = -11 \rightarrow 11$
$T_{min} = 0.239$, $T_{max} = 0.371$	$l = -12 \rightarrow 12$
5896 measured reflections	

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.071$

$S = 1.04$

2878 reflections

199 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.3452P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = <0.001$

$\Delta\rho_{max} = 0.72$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.20442 (3)	0.97204 (2)	0.56099 (3)	0.03172 (10)
S	0.91609 (6)	0.70175 (5)	0.72850 (6)	0.02278 (13)
O	0.56320 (17)	0.44038 (16)	0.80420 (16)	0.0229 (3)
C1	0.7820 (2)	0.5608 (2)	0.7661 (2)	0.0201 (4)
C2	0.6367 (2)	0.5661 (2)	0.7640 (2)	0.0214 (4)
C3	0.6644 (2)	0.3531 (2)	0.8272 (2)	0.0216 (4)
C4	0.6264 (3)	0.2104 (2)	0.8593 (2)	0.0246 (4)
H4	0.5305	0.1687	0.8728	0.030*
C5	0.7350 (3)	0.1345 (2)	0.8700 (2)	0.0263 (5)
H5	0.7122	0.0363	0.8886	0.032*
C6	0.8815 (3)	0.1983 (2)	0.8540 (2)	0.0234 (4)
C7	0.9922 (3)	0.1173 (2)	0.8657 (2)	0.0282 (5)
H7	0.9652	0.0174	0.8796	0.034*
C8	1.1365 (3)	0.1793 (3)	0.8574 (2)	0.0304 (5)
H8	1.2099	0.1235	0.8676	0.037*
C9	1.1769 (3)	0.3259 (3)	0.8338 (2)	0.0278 (5)

H9	1.2783	0.3693	0.8295	0.033*
C10	1.0704 (3)	0.4066 (2)	0.8168 (2)	0.0241 (4)
H10	1.0981	0.5047	0.7988	0.029*
C11	0.9206 (2)	0.3460 (2)	0.8258 (2)	0.0202 (4)
C12	0.8019 (2)	0.4214 (2)	0.8082 (2)	0.0197 (4)
C13	0.5404 (2)	0.6688 (2)	0.7216 (2)	0.0218 (4)
C14	0.4509 (3)	0.6956 (2)	0.7985 (2)	0.0240 (4)
H14	0.4585	0.6515	0.8836	0.029*
C15	0.3515 (3)	0.7858 (2)	0.7518 (2)	0.0253 (4)
H15	0.2918	0.8042	0.8048	0.030*
C16	0.3406 (2)	0.8483 (2)	0.6275 (2)	0.0236 (4)
C17	0.4267 (3)	0.8236 (2)	0.5482 (2)	0.0239 (4)
H17	0.4173	0.8673	0.4625	0.029*
C18	0.5266 (3)	0.7343 (2)	0.5961 (2)	0.0239 (4)
H18	0.5866	0.7172	0.5430	0.029*
C19	0.8666 (3)	0.6152 (3)	0.5368 (3)	0.0325 (5)
H19A	0.9338	0.6829	0.4998	0.049*
H19B	0.7475	0.5947	0.4679	0.049*
H19C	0.8916	0.5211	0.5390	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.02759 (14)	0.03285 (15)	0.03671 (15)	0.01813 (10)	0.01196 (10)	0.00744 (10)
S	0.0213 (3)	0.0187 (3)	0.0288 (3)	0.0045 (2)	0.0135 (2)	0.0039 (2)
O	0.0213 (7)	0.0222 (7)	0.0292 (8)	0.0080 (6)	0.0147 (6)	0.0064 (6)
C1	0.0203 (10)	0.0186 (10)	0.0220 (10)	0.0057 (8)	0.0110 (8)	0.0027 (8)
C2	0.0223 (10)	0.0193 (10)	0.0228 (10)	0.0057 (8)	0.0116 (8)	0.0029 (8)
C3	0.0219 (10)	0.0214 (10)	0.0211 (10)	0.0078 (8)	0.0095 (8)	0.0027 (8)
C4	0.0240 (10)	0.0236 (11)	0.0233 (10)	0.0032 (8)	0.0112 (9)	0.0039 (8)
C5	0.0317 (11)	0.0193 (10)	0.0240 (11)	0.0055 (9)	0.0111 (9)	0.0053 (8)
C6	0.0267 (10)	0.0227 (10)	0.0182 (9)	0.0092 (8)	0.0078 (8)	0.0026 (8)
C7	0.0394 (12)	0.0236 (11)	0.0227 (10)	0.0162 (10)	0.0116 (9)	0.0061 (9)
C8	0.0356 (12)	0.0365 (13)	0.0268 (11)	0.0238 (10)	0.0140 (10)	0.0079 (10)
C9	0.0251 (11)	0.0377 (13)	0.0259 (11)	0.0154 (9)	0.0135 (9)	0.0071 (9)
C10	0.0256 (10)	0.0247 (11)	0.0241 (10)	0.0107 (9)	0.0118 (9)	0.0060 (8)
C11	0.0219 (10)	0.0196 (10)	0.0182 (9)	0.0079 (8)	0.0083 (8)	0.0012 (8)
C12	0.0227 (10)	0.0173 (10)	0.0184 (9)	0.0057 (8)	0.0098 (8)	0.0014 (7)
C13	0.0188 (9)	0.0201 (10)	0.0257 (10)	0.0065 (8)	0.0101 (8)	0.0020 (8)
C14	0.0229 (10)	0.0258 (11)	0.0256 (10)	0.0082 (8)	0.0133 (9)	0.0048 (8)
C15	0.0211 (10)	0.0287 (11)	0.0285 (11)	0.0092 (9)	0.0134 (9)	0.0028 (9)
C16	0.0180 (10)	0.0203 (10)	0.0283 (11)	0.0062 (8)	0.0079 (8)	0.0004 (8)
C17	0.0229 (10)	0.0229 (10)	0.0241 (10)	0.0071 (8)	0.0100 (9)	0.0034 (8)
C18	0.0233 (10)	0.0243 (11)	0.0264 (10)	0.0084 (8)	0.0135 (9)	0.0028 (8)
C19	0.0343 (12)	0.0369 (13)	0.0283 (12)	0.0069 (10)	0.0196 (10)	0.0039 (10)

Geometric parameters (Å, °)

Br—C16	1.904 (2)	C8—H8	0.9500

S—C1	1.757 (2)	C9—C10	1.374 (3)
S—C19	1.810 (2)	C9—H9	0.9500
O—C3	1.376 (2)	C10—C11	1.412 (3)
O—C2	1.387 (2)	C10—H10	0.9500
C1—C2	1.365 (3)	C11—C12	1.431 (3)
C1—C12	1.449 (3)	C13—C18	1.399 (3)
C2—C13	1.463 (3)	C13—C14	1.402 (3)
C3—C12	1.377 (3)	C14—C15	1.387 (3)
C3—C4	1.402 (3)	C14—H14	0.9500
C4—C5	1.367 (3)	C15—C16	1.378 (3)
C4—H4	0.9500	C15—H15	0.9500
C5—C6	1.425 (3)	C16—C17	1.388 (3)
C5—H5	0.9500	C17—C18	1.385 (3)
C6—C7	1.419 (3)	C17—H17	0.9500
C6—C11	1.432 (3)	C18—H18	0.9500
C7—C8	1.363 (3)	C19—H19A	0.9800
C7—H7	0.9500	C19—H19B	0.9800
C8—C9	1.406 (3)	C19—H19C	0.9800
C1—S—C19	100.23 (10)	C11—C10—H10	119.5
C3—O—C2	105.97 (15)	C10—C11—C12	124.79 (19)
C2—C1—C12	106.68 (17)	C10—C11—C6	118.69 (19)
C2—C1—S	124.75 (16)	C12—C11—C6	116.51 (18)
C12—C1—S	128.55 (15)	C3—C12—C11	119.16 (18)
C1—C2—O	110.67 (17)	C3—C12—C1	105.39 (17)
C1—C2—C13	134.46 (19)	C11—C12—C1	135.40 (18)
O—C2—C13	114.78 (17)	C18—C13—C14	118.57 (19)
O—C3—C12	111.26 (18)	C18—C13—C2	120.25 (18)
O—C3—C4	123.56 (18)	C14—C13—C2	121.04 (19)
C12—C3—C4	125.13 (19)	C15—C14—C13	120.83 (19)
C5—C4—C3	116.29 (19)	C15—C14—H14	119.6
C5—C4—H4	121.9	C13—C14—H14	119.6
C3—C4—H4	121.9	C16—C15—C14	119.06 (19)
C4—C5—C6	122.0 (2)	C16—C15—H15	120.5
C4—C5—H5	119.0	C14—C15—H15	120.5
C6—C5—H5	119.0	C15—C16—C17	121.69 (19)
C7—C6—C5	120.9 (2)	C15—C16—Br	119.84 (16)
C7—C6—C11	118.3 (2)	C17—C16—Br	118.46 (16)
C5—C6—C11	120.81 (19)	C18—C17—C16	118.9 (2)
C8—C7—C6	121.5 (2)	C18—C17—H17	120.5
C8—C7—H7	119.2	C16—C17—H17	120.5
C6—C7—H7	119.2	C17—C18—C13	120.94 (19)
C7—C8—C9	120.0 (2)	C17—C18—H18	119.5
C7—C8—H8	120.0	C13—C18—H18	119.5
C9—C8—H8	120.0	S—C19—H19A	109.5
C10—C9—C8	120.3 (2)	S—C19—H19B	109.5
C10—C9—H9	119.8	H19A—C19—H19B	109.5
C8—C9—H9	119.8	S—C19—H19C	109.5
C9—C10—C11	121.0 (2)	H19A—C19—H19C	109.5
C9—C10—H10	119.5	H19B—C19—H19C	109.5

C19—S—C1—C2	−104.63 (19)	O—C3—C12—C11	−179.22 (16)
C19—S—C1—C12	77.0 (2)	C4—C3—C12—C11	−1.8 (3)
C12—C1—C2—O	0.9 (2)	O—C3—C12—C1	−1.5 (2)
S—C1—C2—O	−177.72 (14)	C4—C3—C12—C1	175.89 (19)
C12—C1—C2—C13	−175.2 (2)	C10—C11—C12—C3	−176.75 (19)
S—C1—C2—C13	6.1 (3)	C6—C11—C12—C3	3.4 (3)
C3—O—C2—C1	−1.8 (2)	C10—C11—C12—C1	6.5 (4)
C3—O—C2—C13	175.11 (16)	C6—C11—C12—C1	−173.4 (2)
C2—O—C3—C12	2.1 (2)	C2—C1—C12—C3	0.4 (2)
C2—O—C3—C4	−175.38 (19)	S—C1—C12—C3	178.95 (15)
O—C3—C4—C5	176.22 (18)	C2—C1—C12—C11	177.5 (2)
C12—C3—C4—C5	−0.9 (3)	S—C1—C12—C11	−3.9 (3)
C3—C4—C5—C6	1.8 (3)	C1—C2—C13—C18	37.9 (3)
C4—C5—C6—C7	180.0 (2)	O—C2—C13—C18	−138.13 (19)
C4—C5—C6—C11	0.0 (3)	C1—C2—C13—C14	−146.5 (2)
C5—C6—C7—C8	−177.0 (2)	O—C2—C13—C14	37.4 (3)
C11—C6—C7—C8	2.9 (3)	C18—C13—C14—C15	−0.3 (3)
C6—C7—C8—C9	−1.3 (3)	C2—C13—C14—C15	−175.99 (19)
C7—C8—C9—C10	−0.9 (3)	C13—C14—C15—C16	0.5 (3)
C8—C9—C10—C11	1.3 (3)	C14—C15—C16—C17	−0.1 (3)
C9—C10—C11—C12	−179.43 (19)	C14—C15—C16—Br	179.83 (15)
C9—C10—C11—C6	0.4 (3)	C15—C16—C17—C18	−0.3 (3)
C7—C6—C11—C10	−2.4 (3)	Br—C16—C17—C18	179.75 (15)
C5—C6—C11—C10	177.53 (19)	C16—C17—C18—C13	0.4 (3)
C7—C6—C11—C12	177.40 (18)	C14—C13—C18—C17	−0.1 (3)
C5—C6—C11—C12	−2.6 (3)	C2—C13—C18—C17	175.60 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O^{i}	0.95	2.70	3.635 (3)	170
C19—H19A···Br^{i}	0.98	3.01	3.885 (3)	149

Symmetry codes: (i) *x*+1, *y*, *z*.

Fig. 1

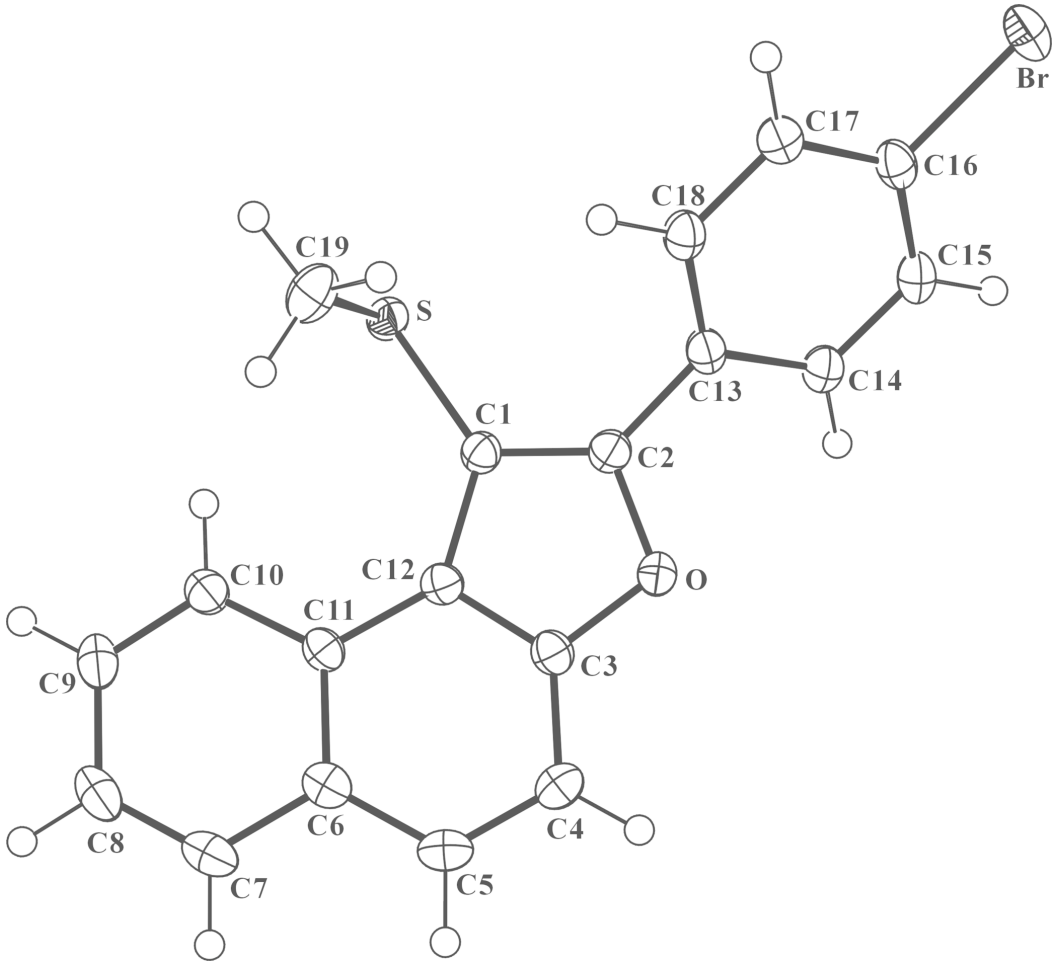
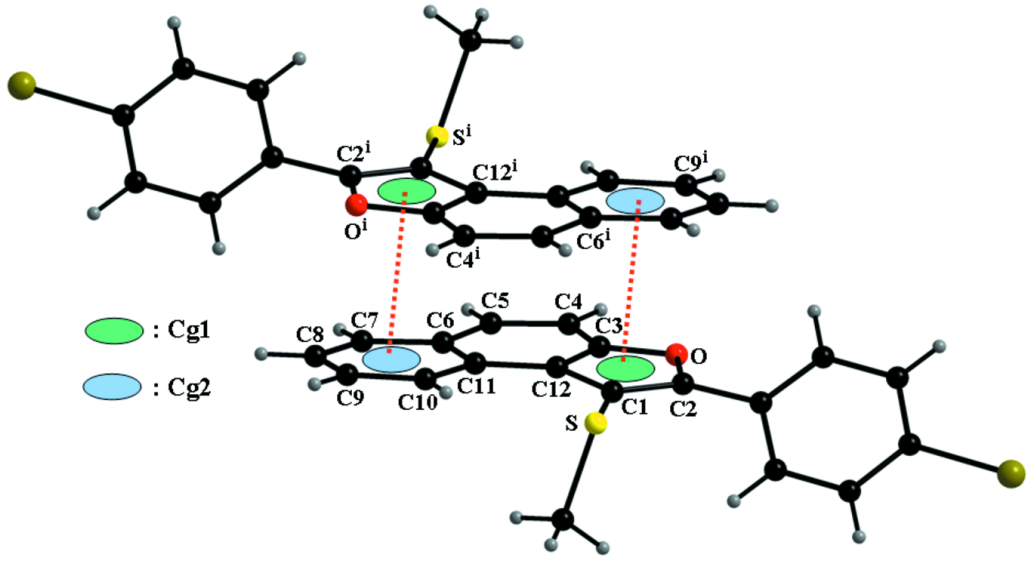

Br
C17
C16
C18
C15
C19
S
C13
C14
C1
C2
C10
C12
O
C11
C3
C9
C6
C4
C8
C7
C5

Fig. 2


: Cg1
: Cg2
C2i
Si
C12i
C9i
Oi
C4i
C6i
C5
C4
C7
C6
C8
C3
O
C9
C10
C11
C12
C1
C2
S