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An X-ray Crystallographic and Computational Study of Intermolecular Edge-to-Face Aromatic Interaction in Crystal Structure of *exo* [4+2]π Cycloadduct of Phencyclone and *S*-Allyl *S*-Methyl Dithiocarbonate

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Abstract—Phencyclone reacted with *S*-allyl *S*-methyl dithiocarbonate derived from the [3,3]-sigmatropic rearrangement of *O*-allyl *S*-methyl dithiocarbonate to give an 1:1 mixture of *endo* and *exo* [4+2]π cycloadducts. The single crystal X-ray analysis of the *exo* [4+2]π cycloadduct was performed. The molecules are linked together with the intermolecular edge-to-face interaction between the phenyl hydrogen atom and the phenanthrene ring. The PM3 calculation reproduced the structural feature of the molecular packing. © 2000 Elsevier Science Ltd. All rights reserved.

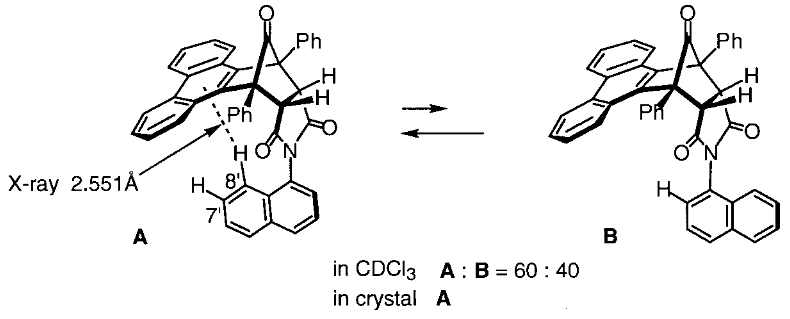
Edge-to-face interaction is one of the attractive interactions between aromatic rings, playing an important role in determination of molecular geometry such as protein folding and in molecular recognition in host–guest complexations.[1,2] In the course of the study of the inclusion behavior of non-hydroxylic hosts of a new type, which have a phenanthrene-condensed bicyclo[2.2.1]hepten-7-one framework, we found the conformational preference due to the intramolecular edge-to-face interaction in the *endo* [4+2]π cycloadduct (**A**) (Scheme 1) of phencyclone and *N*-(1-naphthyl)maleimide based on the X-ray crystallographic and ^{1}H NMR spectral data.[3]

On the other hand, we came across the intermolecular edge-to-face interaction in the crystal structure of the *exo* cycloadduct[4] of phencyclone and *S*-allyl *S*-methyl dithiocarbonate.[5] We now report the details of the crystal structure and molecular orbital calculation of the crystal structure of the *exo* [4+2]π cycloadduct.

Results

Cycloaddition reaction[6]

A mixture of phencyclone (**1**) (0.52 mmol) and *S*-allyl *S*-methyl dithiocarbonate (**2**) (2.3 mmol) in benzene (5 ml) was refluxed for 1 h. After evaporation of the solvent, the residue was chromatographed on silica gel using *n*-hexane–CHCl$_3$ solvent as an eluent to give the *exo* and *endo*



Scheme 1.

Keywords: *S*-allyl *S*-methyl dithiocarbonate; phencyclone; [4+2]π cycloadduct; molecular packing; edge-to-face interaction; PM3.

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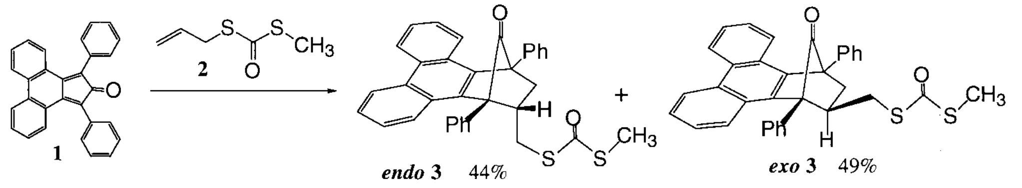


Scheme 2.

cycloadducts (**3**) in 49 and 44% yields, respectively (Scheme 2).

***exo* Cycloadduct (*exo* 3).** Colorless prisms; mp 257–259°C; IR (KBr) cm^{-1}; 1778 (bridge CO), 1630 and 880 (SCOS); ^{1}H NMR (400 MHz, $CDCl_3$): 2.31 (^{1}H, dd, J=12.2, 14.2 Hz, HC–H$_{endo}$), 2.41 (3H, m, SCH_3), 2.56–2.67 (2H, m, SCH_2), 3.20–3.11 (1H, m, CH$_{endo}$), 4.33 (1H, dd, J=2.6, 14.2 Hz, HC–H$_{exo}$), 7.02–7.55 (16H, aromatic H), 8.27 (1H, d, J=7.9 Hz, aromatic H), 8.68 (1H, d, J=8.6 Hz, aromatic H); Anal. Calcd for $C_{34}H_{26}O_2S_2$: C, 76.95; H, 4.94. Found: C, 76.60; H, 4.94.

***endo* Cycloadduct (*endo* 3).** Colorless prisms; mp 253–255 °C; IR (KBr) cm^{-1}; 1784 (bridge CO), 1644 and 872 (SCOS); ^{1}H NMR (400 MHz, $CDCl_3$): 1.71 (1H, dd, J=11.9, 13.5 Hz, HC–H$_{endo}$), 1.83 (1H, dd, J=4.6, 12.2 Hz, HC–H$_{endo}$), 2.47 (3H, m, SCH_3), 3.84 (1H, m, CH$_{exo}$), 3.88 (1H, dd, J=3.3, 13.5 Hz, SCH–H), 3.16 (1H, dd, J=9.6, 12.2 Hz, HC–H$_{exo}$), 7.03–7.76 (16H, aromatic H), 8.72 (1H, d, J=8.3 Hz, aromatic H), 8.74 (1H, d, J=8.6 Hz, aromatic H).

Crystallographic study

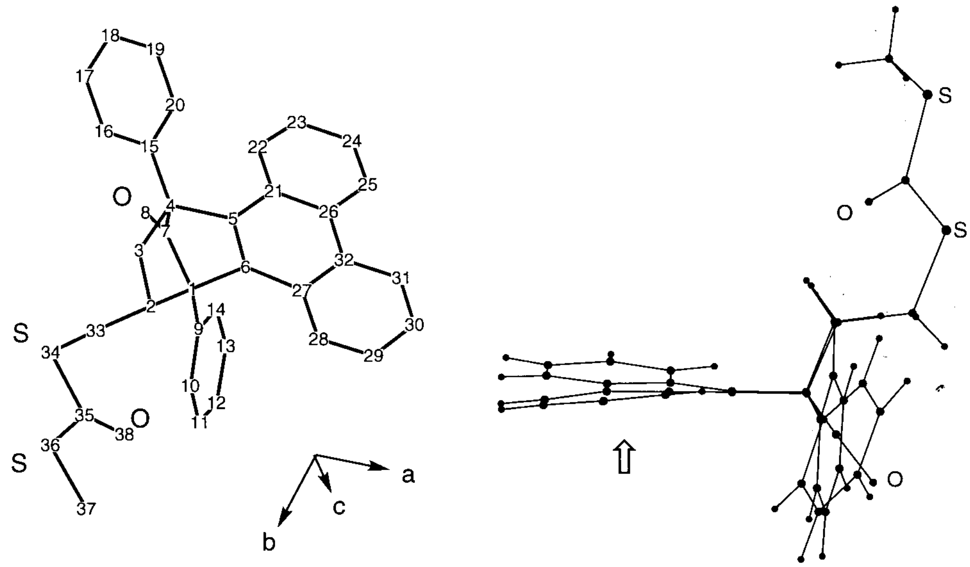
Crystal data for *exo* 3. M=531 ($C_{34}H_{26}O_2S_2$), triclinic, space group $P\bar{1}$ (No. 2), a=11.063(2), b=11.858(4), c=10.845(2) Å, α=102.13(2)°, β=99.59(1)°, γ=99.18(2)°, V=1343.3(5) Å^3, Z=2, D_c=1.312 g cm^{-3}, D_m=1.306 (aq. KI) g cm^{-3}.

The X-ray structure is shown in Fig. 1. All measurements were made on a Rigaku AFC7R four-circle autodiffractometer with a graphite monochromated MoKα radiation (λ=0.7107 Å) and a rotating anode generator. The reflection data were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°. Of the 6199 unique reflections, 2713 reflections (Io>2.00σI) were used. The structures were solved by the direct method.[7] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. The only three hydrogens on C(37) were located on the calculated positions and not refined. The final cycle of full-matrix least-square refinement was based on 2713 observed reflections and 435 variable parameters and converged with unweighted (R) and weighted agreement factors (R_w) of 0.060 and 0.043, respectively.

Neutral atom scattering factors were taken from International Tables for X-ray Crystallography.[8] All calculations were performed on a Silicon Graphics IRIS Indigo2 workstation with TEXSAN Crystal Structure Analysis Package.[9]

Molecular orbital calculation

The semi-empirical MO calculations of the four molecules (two unit cells) of *exo* **3** (Fig. 2) whose coordinates were



a) b)

Figure 1. (a) Molecular conformation and numbering sequence of *exo* **3**. (b) Distortion of the phenanthrene ring.

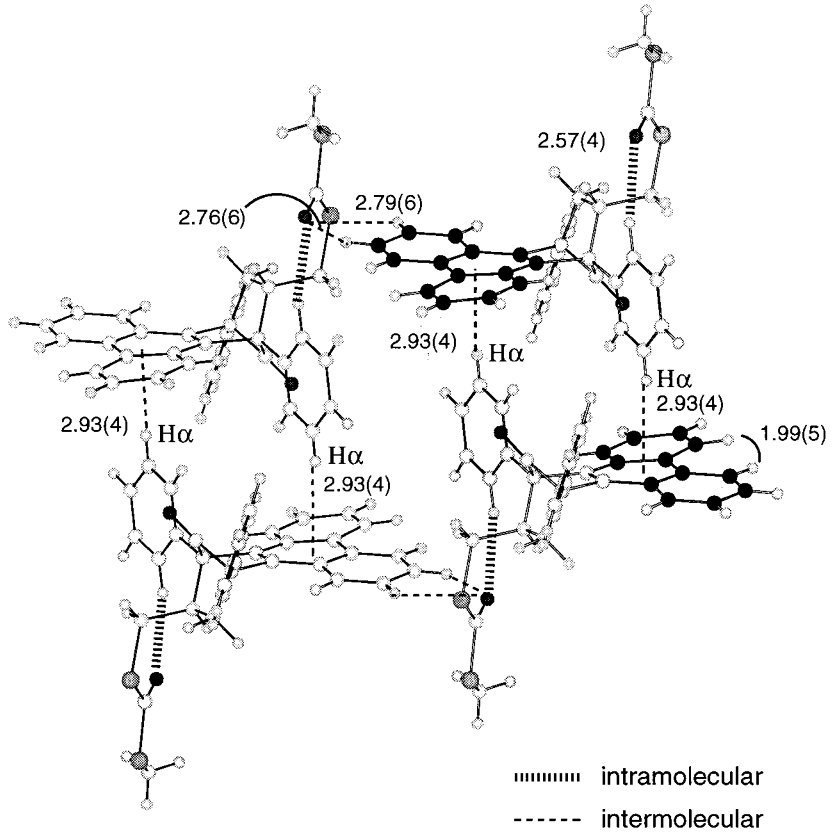


Figure 2. Computer-generated drawing of crystal structure of the *exo* [4+2]π cycloadduct.

extracted from the molecular packing coordinates were carried out using a locally modified version of the MOPAC package[10a] on a Scientists' Paradise Dragon AXP433 computer or MOPAC 2000 (Fujitsu Limited) on a Hewlett-Packard (HP) Exemplar Technical Server V2250KS in the Kumamoto University Information Processing Center. In the light of the large number of doubly occupied levels (372 for $C_{136}H_{104}O_8S_8$, $M_W=2123$), to save the CPU time, the geometry optimization termination criteria (GNORM) in both gradient minimization and energy minimization was set to 1.0. After 725 cycles (cpu time=1 day 12 h 6 min 53 s), the optimization converged (gradient norm=0.669, heat of formation=299.284 kcal mol^{-1}).

The single molecule calculations and graphical analysis of the molecular geometries were run through the ANCHOR II[11] interface using MOPAC 6.0[10a] on a Fujitsu S4/2 WS or through the CS Chem3D Pro interface using MOPAC97 (Fujitsu Limited) on a Power Macintosh G3 computer.

Discussion

The computer-generated drawing of the molecular structure of the cycloadduct is depicted in Fig. 1 with the numbering sequence used in this paper. The molecular structure is firmly established to be *exo* [4+2]π cycloadduct. So far as we know, this is the first example of crystallographic analysis of the *exo* [4+2]π cycloadduct of phencyclone.

The bicyclo[2.2.1]heptenone moiety is strained considerably in which the angle of the bridged carbonyl [C(1)–C(7)–C(4)] is 99.1(4)°. The bond length of the carbonyl [C(7)–O(8)] is 1.194(5) Å, almost the same as that of the dithiocarbonyl group [C(35)–O(38), 1.198(5) Å]. The bond elongations were found in C(1)–C(2) [1.576(6) Å] and C(2)–C(3) [1.561(6) Å], presumably due to the steric repulsion between the substituents and the bond strain of the bicyclo[2.2.1]heptenone skeleton.

The dihedral angle [C(25)–C(26)–C(32)–C(31)] of the biphenyl moiety of the phenanthrene ring is 7.9(7)°, indicating that the phenanthrene ring plane is considerably twisted. The angle between the two phenyl rings based on the least-squares plane calculations is 9.0(2)°.[12] This may be due to the close contact (<1.99(5) Å)[13] of the two hydrogen atoms on C(25) and C(31) of the phenanthrene ring (Tables 1–3).

This twisted ring conformation could not be reproduced by the semiempirical MO calculations,[10] showing the phenanthrene ring to be planar and the distance between C(25)–H···Hα–C(31) is 1.86 Å for AM1 and 1.76 Å for PM3.

The *S*-alkyl groups of the dithiolcarbonate moiety (R-SCOS-Me) take the *syn–syn* conformation with regard to the carbonyl group. The dithiocarbonyl oxygen atom makes intramolecular C–H···O= type hydrogen bond [C(10)–H···O(38) 2.57(4) Å, C(10)–H 1.02(4) Å, C(10)···H–O(38) 166°, C(35)=O(38)···H 131°] with the 2-hydrogen atom of the phenyl substituent. The AM1 and PM3 calculated distances are 2.46 and 2.93 Å, respectively.

Table 1. Atomic coordinates of *exo* **3** with their standard deviations in parentheses

Atom	*x*	*y*	*z*	*B*(eq)	Atom	*x*	*y*	*z*	*B*(eq)
S(34)	0.0320(1)	0.2496(1)	0.8524(1)	5.33(3)	C(17)	−0.1615(5)	−0.3191(5)	0.5564(5)	5.8(1)
S(36)	0.0813(1)	0.4042(2)	1.1063(1)	10.01(5)	C(18)	−0.1335(5)	−0.4017(4)	0.4635(5)	6.1(1)
O(8)	0.1533(2)	−0.0286(2)	0.4704(3)	5.08(8)	C(19)	−0.0160(5)	−0.3872(4)	0.4360(5)	5.6(1)
O(38)	0.2556(2)	0.3715(2)	0.9754(3)	5.06(8)	C(20)	0.0741(4)	−0.2887(4)	0.5057(5)	4.8(1)
C(1)	0.2910(3)	0.0764(3)	0.6841(3)	3.53(9)	C(21)	0.3106(3)	−0.2015(3)	0.7919(3)	3.7(1)
C(2)	0.2032(3)	0.1145(3)	0.7788(4)	3.6(1)	C(22)	0.2220(4)	−0.2953(4)	0.8035(4)	4.6(1)
C(3)	0.1117(4)	−0.0024(3)	0.7719(4)	4.0(1)	C(23)	0.2584(4)	−0.3798(4)	0.8619(5)	5.4(1)
C(4)	0.1472(3)	−0.0974(3)	0.6712(4)	3.6(1)	C(24)	0.3844(5)	−0.3740(4)	0.9088(5)	5.5(1)
C(5)	0.2770(3)	−0.1096(3)	0.7342(3)	3.6(1)	C(25)	0.4723(4)	−0.2829(4)	0.9012(4)	4.8(1)
C(6)	0.3608(3)	−0.0098(3)	0.7413(3)	3.5(1)	C(26)	0.4391(4)	−0.1927(3)	0.8438(3)	3.8(1)
C(7)	0.1905(3)	−0.0193(3)	0.5826(4)	3.9(1)	C(27)	0.4925(3)	0.0043(3)	0.7967(3)	3.7(1)
C(9)	0.3656(3)	0.1713(3)	0.6377(4)	3.7(1)	C(28)	0.5841(4)	0.1030(4)	0.8037(4)	5.0(1)
C(10)	0.4002(4)	0.2868(4)	0.7095(4)	4.2(1)	C(29)	0.7085(4)	0.1063(5)	0.8456(5)	5.9(1)
C(11)	0.4725(4)	0.3719(4)	0.6676(5)	5.2(1)	C(30)	0.7461(4)	0.0099(5)	0.8812(5)	6.1(2)
C(12)	0.5134(5)	0.3422(5)	0.5556(5)	5.8(1)	C(31)	0.6601(4)	−0.0861(5)	0.8803(4)	5.1(1)
C(13)	0.4814(5)	0.2273(5)	0.4844(5)	5.9(1)	C(32)	0.5307(3)	−0.0918(4)	0.8404(3)	3.9(1)
C(14)	0.4067(4)	0.1421(4)	0.5241(4)	4.9(1)	C(33)	0.1279(4)	0.2033(4)	0.7393(4)	4.3(1)
C(15)	0.0484(4)	−0.2042(3)	0.6023(4)	4.0(1)	C(35)	0.1470(4)	0.3467(3)	0.9783(4)	4.4(1)
C(16)	−0.0709(4)	−0.2209(4)	0.6263(5)	4.8(1)	C(37)	0.2104(5)	0.5095(5)	1.2062(5)	10.5(2)
H(1)	0.252(3)	0.150(2)	0.864(3)	2.3(7)	H(14)	0.130(3)	−0.300(3)	0.775(3)	4.3(9)
H(2)	0.113(3)	−0.022(3)	0.861(3)	4.7(9)	H(15)	0.196(3)	−0.445(3)	0.868(3)	5.2(9)
H(3)	0.028(3)	0.007(2)	0.743(3)	3.5(7)	H(16)	0.410(3)	−0.431(3)	0.950(4)	5(1)
H(4)	0.374(3)	0.311(3)	0.795(3)	3.3(8)	H(17)	0.561(3)	−0.279(3)	0.936(3)	5(1)
H(5)	0.491(3)	0.449(3)	0.722(3)	4(1)	H(18)	0.564(4)	0.168(3)	0.785(4)	4(1)
H(6)	0.565(3)	0.400(3)	0.522(4)	6(1)	H(19)	0.771(3)	0.179(3)	0.850(4)	5(1)
H(7)	0.509(4)	0.206(3)	0.413(4)	5(1)	H(20)	0.827(3)	0.010(3)	0.908(4)	6(1)
H(8)	0.383(3)	0.068(3)	0.471(3)	4(1)	H(21)	0.689(3)	−0.154(3)	0.906(3)	4(1)
H(9)	−0.092(3)	−0.163(3)	0.693(3)	3.3(10)	H(22)	0.066(3)	0.166(3)	0.657(3)	3.9(8)
H(10)	−0.243(4)	−0.325(4)	0.582(4)	6(1)	H(23)	0.185(3)	0.275(3)	0.736(3)	4.4(9)
H(11)	−0.193(3)	−0.469(3)	0.411(3)	6(1)	H(24)	0.1894	0.5687	1.2635	10.0
H(12)	0.011(4)	−0.447(4)	0.364(4)	7(1)	H(25)	0.2620	0.5460	1.1531	10.0
H(13)	0.157(3)	−0.277(3)	0.488(3)	3.4(9)	H(26)	0.2679	0.4710	1.2544	10.0

The molecular packing structure is interesting, which is shown in Fig. 2. The molecules are arranged in a herring bone pattern along the axis *c*, in which the 3-hydrogen [C(13)–Hα] of the phenyl ring of an adjacent molecule of *exo* **3** is located at close-contact perpendicular distance of 2.93(4) Å above the face of the central benzene ring of the phenancerene moiety.[12] The closest aromatic carbon from the hydrogen atom is C(32) [C(13)–H···C(32) 2.72(5) Å, C(13)···C(32) 3.522(7)] (see Table 4). As the X-ray bond distance of C(13)–Hα is 0.88(4) Å, which is significantly shorter than the ideal value, the edge-to-face interaction distance is ca. 0.2 Å shorter than the experimental value.

As reported in the previous paper, in the crystal structure of the [4+2]π cycloadduct (**A**) of phencyclone and *N*-(1-naphthyl)maleimide (see Scheme 1), the plane of the naphthalene ring is almost perpendicular to the maleimide ring and is covered with the phenanthrene ring in an 'edge-to-face' manner (T-shaped conformation). The H8′ proton on the 1-naphthyl ring is located at close-contact perpendicular distance of 2.551 Å above the face of the phenanthrene ring. This special geometrical feature is also observed in solutions. The PM3-calculated edge-to-face distance of **A** is 2.56 Å.[10b]

Boyd et al.[2] reported the NMR spectroscopic and X-ray crystallographic evidences that edge-to-face interactions have an important role in determination of the preferred

Table 2. Bond distances (Å) of *exo* **3** with their standard deviations in parentheses

Atom	Atom	Distance	Atom	Atom	Distance	Atom	Atom	Distance
C(1)	C(2)	1.576(6)	C(1)	C(6)	1.545(5)	C(1)	C(7)	1.549(6)
C(1)	C(9)	1.509(5)	C(2)	C(3)	1.561(6)	C(2)	C(33)	1.528(6)
C(3)	C(4)	1.544(6)	C(4)	C(5)	1.527(5)	C(4)	C(7)	1.548(6)
C(4)	C(15)	1.499(5)	C(5)	C(6)	1.362(5)	C(5)	C(21)	1.434(5)
C(6)	C(27)	1.449(5)	C(9)	C(10)	1.384(6)	C(9)	C(14)	1.380(6)
C(10)	C(11)	1.386(6)	C(11)	C(12)	1.364(7)	C(12)	C(13)	1.376(7)
C(13)	C(14)	1.387(7)	C(15)	C(16)	1.379(6)	C(15)	C(20)	1.390(6)
C(16)	C(17)	1.392(7)	C(17)	C(18)	1.362(8)	C(18)	C(19)	1.374(8)
C(19)	C(20)	1.392(7)	C(21)	C(22)	1.402(6)	C(21)	C(26)	1.418(5)
C(22)	C(23)	1.370(6)	C(23)	C(24)	1.388(7)	C(24)	C(25)	1.360(7)
C(25)	C(26)	1.412(6)	C(26)	C(32)	1.450(6)	C(27)	C(28)	1.399(6)
C(27)	C(32)	1.421(6)	C(28)	C(29)	1.367(7)	C(29)	C(30)	1.383(8)
C(30)	C(31)	1.360(7)	C(31)	C(32)	1.411(6)	O(8)	C(7)	1.194(5)
O(38)	C(35)	1.198(5)	S(34)	C(33)	1.808(5)	S(34)	C(35)	1.760(5)
S(36)	C(35)	1.738(5)	S(36)	C(37)	1.766(6)			

Table 3. Bond angles (°) of *exo* **3** with their standard deviations in parentheses

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(2)	C(1)	C(6)	105.7(3)	C(2)	C(1)	C(7)	97.0(3)	C(2)	C(1)	C(9)	117.9(4)
C(6)	C(1)	C(7)	96.1(3)	C(6)	C(1)	C(9)	118.3(4)	C(7)	C(1)	C(9)	117.9(4)
C(1)	C(2)	C(3)	104.3(4)	C(1)	C(2)	C(33)	113.3(4)	C(3)	C(2)	C(33)	109.3(4)
C(2)	C(3)	C(4)	105.3(4)	C(3)	C(4)	C(5)	104.6(4)	C(3)	C(4)	C(7)	98.6(4)
C(3)	C(4)	C(15)	117.8(4)	C(5)	C(4)	C(7)	97.1(3)	C(5)	C(4)	C(15)	120.7(4)
C(7)	C(4)	C(15)	114.0(4)	C(4)	C(5)	C(6)	108.8(4)	C(4)	C(5)	C(21)	128.4(4)
C(6)	C(5)	C(21)	122.4(4)	C(1)	C(6)	C(5)	109.0(4)	C(1)	C(6)	C(27)	129.5(4)
C(5)	C(6)	C(27)	121.5(4)	O(8)	C(7)	C(1)	130.9(4)	O(8)	C(7)	C(4)	129.9(4)
C(1)	C(7)	C(4)	99.1(4)	C(1)	C(9)	C(10)	121.8(4)	C(1)	C(9)	C(14)	119.7(4)
C(10)	C(9)	C(14)	118.4(5)	C(9)	C(10)	C(11)	121.1(5)	C(10)	C(11)	C(12)	120.2(5)
C(11)	C(12)	C(13)	119.3(6)	C(12)	C(13)	C(14)	120.9(6)	C(9)	C(14)	C(13)	120.2(5)
C(4)	C(15)	C(16)	122.7(5)	C(4)	C(15)	C(20)	119.7(5)	C(16)	C(15)	C(20)	117.4(5)
C(15)	C(16)	C(17)	121.0(6)	C(16)	C(17)	C(18)	120.5(6)	C(17)	C(18)	C(19)	120.1(6)
C(18)	C(19)	C(20)	119.2(6)	C(15)	C(20)	C(19)	121.7(6)	C(5)	C(21)	C(22)	122.9(4)
C(5)	C(21)	C(26)	117.5(4)	C(22)	C(21)	C(26)	119.5(4)	C(21)	C(22)	C(23)	120.8(5)
C(22)	C(23)	C(24)	119.9(5)	C(23)	C(24)	C(25)	120.6(6)	C(24)	C(25)	C(26)	121.5(5)
C(21)	C(26)	C(25)	117.6(5)	C(21)	C(26)	C(32)	120.1(4)	C(25)	C(26)	C(32)	122.3(4)
C(6)	C(27)	C(28)	124.5(5)	C(6)	C(27)	C(32)	116.9(4)	C(28)	C(27)	C(32)	118.5(5)
C(27)	C(28)	C(29)	121.7(6)	C(28)	C(29)	C(30)	119.7(6)	C(29)	C(30)	C(31)	120.6(6)
C(30)	C(31)	C(32)	121.4(6)	C(26)	C(32)	C(27)	120.8(4)	C(26)	C(32)	C(31)	121.2(5)
C(27)	C(32)	C(31)	118.0(5)	C(33)	S(34)	C(35)	100.3(2)	C(35)	S(36)	C(37)	101.1(3)
S(34)	C(33)	C(2)	112.6(4)	S(34)	C(35)	S(36)	110.9(3)	S(34)	C(35)	O(38)	124.7(4)
S(36)	C(35)	O(38)	124.4(4)								

conformations of some alkenes, nitrones and imines both in solution and in the crystalline state, in which the close-contact distances are found to be 2.63–2.68 Å.

The intermolecular close contact described here is considered to belong to the category of 'edge-to-face' interaction. The intermolecular distance in the crystal structure is found to be close to the reported intramolecular edge-to-face distances. The present result together with the previous paper[3] suggests that the phenanthrene ring which has a high-lying π-HOMO and a low-lying π-LUMO[14] plays an important role as a hydrogen acceptor in edge-to-face Ar-H···π interactions between aromatic rings.

Table 4. Intermolecular distances involving the non-hydrogen atoms (symmetry operations: (1) *x*, *y*, *z*; (2) −*x*, −*y*, −*z*)

Atom	Atom	Distance	ADC
O(8)	C(16)	3.541(6)	55602
O(8)	C(33)	3.570(6)	55602
O(38)	C(24)	3.398(7)	56501
O(38)	C(23)	3.424(6)	56501
O(38)	C(25)	3.495(6)	65702
C(11)	C(37)	3.489(8)	66702
C(12)	C(37)	3.584(9)	66702
C(13)	C(32)	3.522(7)	65602
C(18)	C(19)	3.473(8)	54602
C(18)	C(33)	3.543(8)	55602
C(19)	C(19)	3.30(1)	54602
C(19)	C(33)	3.423(7)	55602
C(20)	C(33)	3.599(7)	55602

Inspection of the PM3 two-center energy terms between the hydrogen atom (Hα) and the carbon atoms [C(5), C(6), C(21), C(26), C(27) and C(32)] of the phenanthrene moiety using the molecular packing coordinates suggests that the resonance energy[15] plays a leading role in the intermolecular edge-to-face interaction (Table 5).

It is interesting to know whether the MO calculations can evaluate the intermolecular weak interactions observed in crystals. For this purpose, ab initio or DFT calculations are desirable. However, the ab initio calculations of the molecular packing are still beyond the capacity of the present computer system. We tried to perform the AM1 and PM3 structure optimization of the neighboring four molecules using the coordinates of the molecular packing in the crystal.

The PM3-calculated structure is depicted in Fig. 3. The essential conformational feature of *exo* **3** observed in the crystal is reproduced by the PM3 calculation.[16]

Table 5. Total of electronic and nuclear energies (extracted from the two center terms of the total energy partitioning calculated by PM3 using the ENPART keyword) (E_{total}) for the atom pairs between the hydrogen (Hα) and the aromatic carbon atoms participated in the edge-to-face interaction calculated by PM3 (the 1SCF MO calculation was performed on the two molecules of *exo* **3a** extracted from the crystal coordinates)

Atom	Resonance energy	Exchange energy	Coulombic interaction	E_{total}	
				In eV	In kcal mol^{-1}
C(6)	−0.0067	−0.0003	−0.0222	−0.0291	−0.671
C(5)	−0.0069	−0.0003	−0.0198	−0.0270	−0.623
C(21)	−0.0175	−0.0008	0.0065	−0.0118	−0.272
C(26)	−0.0556	−0.0038	0.0049	−0.0545	−1.257
C(32)	−0.0280	−0.0016	0.0004	−0.0292	−0.673
C(27)	−0.0081	−0.0003	0.0005	−0.0080	−0.185

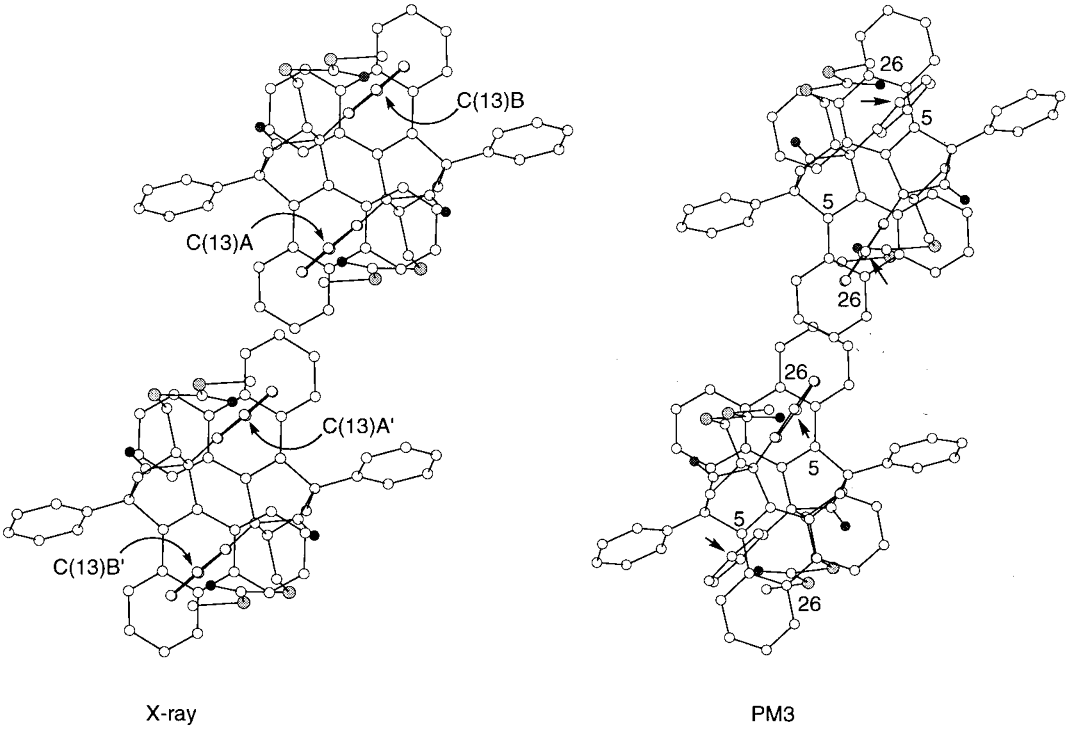


Figure 3. Comparison of the X-ray and PM3-calculated structures for the molecular packing of *exo* **3** viewed down the axis C(10)···C(13). Arrows (A, A′, B and B′) show the carbon atom positions having the interacting hydrogen.

The intramolecular $-C_6H_4-H\cdots O{=}C(SMe)-S-$ hydrogen bond (2.937 Å) is longer than those of the X-ray and AM1 structures. The twist of the phenanthrene ring is not observed in the calculated structures showing a planar one (dihedral angle [C(25)–C(26)–C(32)–C31)]=0.5°). The PM3 structure optimization (gradient norm=0.669) approximately reproduced the edge-to-face interaction distance in which the average of the distances of the four adjacent interactions [C(13)A–H···C(5), C(13)A′–H···C(5), C(13)B–H···C(5) and C(13)B′–H···C(5)] is 2.68 Å. In the B and B′ interactions, the nearest point on the phenanthrene face from the interacting hydrogen atom [C(13)–**H**] moved toward the C(5) atom. This may be due to the use of the minimum coordinate data of the endless molecular arrangement in the crystal. The stabilization energy for the interaction among four molecules is 8.5 kcal mol^{-1}, in which all of the intermolecular interaction forces are included (Table 6).

In contrast, the AM1 calculation could not reproduce the features of the intermolecular edge-to-face interaction. The optimized intermolecular distance along the axis *c* (gradient norm=0.854) is far longer than the observed value, in which the distance of C(13)–H···C(32) is beyond 3.6 Å.

Table 6. PM3 Calculated heats of formation of the molecular and crystal structures of *exo* **3**

Optimized structure	ΔH_f (kcal mol^{-1})	Stabilization energy
Exo **3**	76.93	
Exo **3** (4 molecules)	307.72	0.0
Exo **3** (4 molecules) interacted in crystal structure[a]	299.28	−8.5

[a] The neighboring four molecules are extracted from the crystal packing coordinates.

It is noteworthy that the PM3 level of theory provides molecular packing structure in reasonable agreement with that from X-ray analysis at a much lower computational cost.

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10. (a) The AM1 and PM3 calculations were performed using MOPAC; Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10: Revised as Ver. 6.02 by the present authors for a Scientists' Paradise Dragon AXP433 computer. (b) The semiempirical calculation at PM3 level could not reproduce the relative stability between **A** and **B** in which **B** is 0.15 kcal mol^{-1} more stable than **A**.

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12. The least-squares plane calculations were performed using the following planes; Plane1 (5-6-21-22-23-24-25-26-27-28-29-30-31-2), Plane2 (5-6-21-26-32-27), Plane3 (21-22-23-24-25-26) and Plane4 (27-28-29-30-31-32). Angles (θ) between the PlaneA and PlaneB are 2.6(1)° for Plane1/Plane2, 3.4(1)° for Plane1/Plane3, 6.2(1)° for Plane1/Plane4, 5.8(1)0 for Plane2/Plane3, 5.8(2)° for Plane2/Plane 4 and 9.0(2)° for Plane3/Plane4. The intermolecular edge-to-face interaction distance was calculated on the basis of the least-squares plane of Plane2.

13. The C(25)–H and C(31)–H bond lengths are 0.98(4) and 0.99(4) Å, respectively. The ideal C(25)–H···H–C(31) distance is shorter than the observed value.

14. Benzene HOMO −9.65, LUMO 0.56: naphthalene HOMO −8.71, LUMO −0.27: phenanthrene HOMO, −8.62, LUMO −0.41.

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16. The coordinates of the X-ray and calculated structures are available on our web site (http://yakko.pharm.kumamoto-u.ac.jp).