

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Zn	0.00872 (4)	0.20622 (3)	0.33385 (2)	0.03926 (7)
Cl	0.0569 (1)	0.25974 (8)	0.18980 (5)	0.0543 (2)
Cl'	0.09802 (9)	0.00353 (7)	0.37414 (5)	0.0501 (2)
S(1)	-0.5236 (1)	0.2592 (1)	0.33853 (7)	0.0743 (3)
S(1')	0.2658 (1)	0.52918 (9)	0.49490 (6)	0.0694 (3)
N	-0.2988 (3)	0.3660 (3)	0.2384 (2)	0.0762 (9)
N'	0.1711 (4)	0.5127 (3)	0.3216 (2)	0.0686 (8)
N(3)	-0.2281 (3)	0.2081 (2)	0.3495 (1)	0.0412 (6)
N(3')	0.1130 (3)	0.3371 (2)	0.4198 (1)	0.0404 (6)
C(2)	-0.3325 (3)	0.2793 (3)	0.3036 (2)	0.0470 (7)
C(2')	0.1754 (3)	0.4542 (3)	0.4019 (2)	0.0458 (7)
C(4)	-0.2990 (4)	0.1342 (3)	0.4150 (2)	0.0609 (9)
C(4')	0.1348 (4)	0.3062 (3)	0.5103 (2)	0.0583 (9)
C(5)	-0.4549 (4)	0.1503 (4)	0.4189 (3)	0.084 (1)
C(5')	0.2123 (5)	0.3962 (4)	0.5597 (2)	0.071 (1)

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), and hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

Zn—Cl	2.2548 (8)	N—C(2)	1.337 (4)			
Zn—Cl'	2.2386 (8)	N'—C(2')	1.328 (4)			
Zn—N(3)	2.024 (2)	N(3)—C(2)	1.307 (4)			
Zn—N(3')	2.011 (2)	N(3)—C(4)	1.376 (4)			
S(1)—C(2)	1.726 (3)	N(3')—C(2')	1.316 (4)			
S(1)—C(5)	1.703 (4)	N(3')—C(4')	1.384 (4)			
S(1')—C(2')	1.726 (3)	C(4)—C(5)	1.332 (5)			
S(1')—C(5')	1.712 (4)	C(4')—C(5')	1.321 (5)			
Cl—Zn—Cl'	113.47 (3)	Zn—N(3')—C(4')	120.7 (2)			
Cl—Zn—N(3)	108.54 (7)	C(2')—N(3')—C(4')	110.7 (2)			
Cl—Zn—N(3')	110.94 (7)	S(1)—C(2)—N	121.2 (2)			
Cl'—Zn—N(3)	107.69 (7)	S(1)—C(2)—N(3)	113.7 (2)			
Cl'—Zn—N(3')	106.50 (7)	N—C(2)—N(3)	125.0 (3)			
N(3)—Zn—N(3')	109.61 (9)	S(1')—C(2')—N'	121.6 (2)			
C(2)—S(1)—C(5)	89.1 (2)	S(1')—C(2')—N(3')	113.3 (2)			
C(2')—S(1')—C(5')	89.6 (2)	N'—C(2')—N(3')	125.1 (3)			
Zn—N(3)—C(2)	126.8 (2)	N(3)—C(4)—C(5)	114.9 (3)			
Zn—N(3)—C(4)	122.2 (2)	N(3')—C(4')—C(5')	115.7 (3)			
C(2)—N(3)—C(4)	111.0 (2)	S(1)—C(5)—C(4)	111.2 (3)			
Zn—N(3')—C(2')	128.5 (2)	S(1')—C(5')—C(4')	110.7 (3)			
D	H	A	D—H	H...A	D...A	D—H...A
N	H(N1)	Cl	0.87 (3)	2.50 (3)	3.294 (3)	152 (3)
N'	H(N1')	Cl	0.82 (3)	2.59 (3)	3.323 (3)	150 (3)
N	H(N2)	Cl'	0.84 (3)	2.46 (3)	3.287 (3)	174 (3)
N'	H(N2')	Cl	0.83 (3)	2.56 (3)	3.385 (3)	171 (3)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55683 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1019]

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## Structure of 4-(9-Phenanthryl)-*N,N*-dimethylaniline

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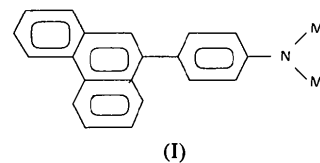
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### Abstract

The molecular shape of this intramolecular donor–acceptor complex in the crystalline state is characterized by a dihedral angle of  $65.0(1)^\circ$  between the phenanthrene plane and the almost planar dimethylanilino group.

### Comment

The structure determination of the title compound (I) was undertaken in order to establish the mutual orientation of the two ring systems and thereby explain its donor–acceptor properties.



The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. A labelled view of the molecular structure is shown in Fig. 1, and bond distances and bond angles are given in Table 2.

As a result of steric overcrowding on the C(4)–C(7) side of the phenanthrene, the ring is slightly bent. The angle between the best planes through the C(1), C(2), C(3), C(4), C(5), C(14) and C(6), C(7),

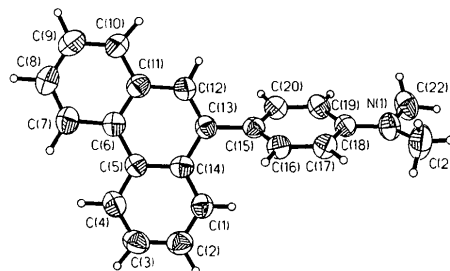


Fig. 1. *SHLXTL/PC* view of the molecule showing labelling scheme. Thermal ellipsoids are drawn at 50% probability levels with H atoms shown as small circles of arbitrary radii.

C(8), C(9), C(10), C(11) rings is  $3.0(1)^\circ$ . The H(4)···H(7) distance of  $1.92(5) \text{ \AA}$ , well below the van der Waals distance ( $2.4 \text{ \AA}$ ), clearly shows the overcrowding. The amino N atom N(1) adopts an  $sp^2$  configuration, being only  $0.084(3) \text{ \AA}$  from the plane through its three substituents C(18), C(21) and C(22) (*cf.*  $0.49 \text{ \AA}$  for 100%  $sp^3$  hybridization). The best plane through the phenanthrene ring [mean deviation  $0.024(4) \text{ \AA}$ ] makes an angle of  $65.0(1)^\circ$  (*gauche* conformation) with the best plane through the dimethyl-anilino group [mean deviation  $0.030(4) \text{ \AA}$ ].

The crystal packing is dominated by interactions between the planar aromatic rings. The distance between the best planes through two stacked phenanthrene rings is  $3.574(8) \text{ \AA}$  and between two aniline rings  $3.565(8) \text{ \AA}$ .

A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for phenanthrene compounds with aromatic substituents at the 9-position revealed five 9,9'-biphenanthryl-10,10'-diol clathrates (Lee, Wang, Tanaka & Toda, 1988; Toda, Tanaka, Nassimbeni & Niven, 1988; Toda, Tanaka, Yagi, Stein & Goldberg, 1990). The dihedral angle between the two phenanthrene rings in these compounds varies from  $68$  to  $102^\circ$ .

## Experimental

### Crystal data

C<sub>22</sub>H<sub>19</sub>N

$M_r = 297.4$

Triclinic

$P\bar{1}$

$a = 8.583(2) \text{ \AA}$

$b = 10.076(2) \text{ \AA}$

$c = 10.149(2) \text{ \AA}$

$\alpha = 67.50(2)^\circ$

$\beta = 79.84(2)^\circ$

$\gamma = 86.26(2)^\circ$

$V = 798.2(3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.237 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation

$\lambda = 1.54178 \text{ \AA}$

Cell parameters from 29 reflections

$\theta = 5-15^\circ$

$\mu = 0.509 \text{ mm}^{-1}$

$T = 289 \text{ K}$

Parallelepiped

$0.4 \times 0.3 \times 0.1 \text{ mm}$

Transparent

Crystal source: crystallized by evaporation from hexane/ether

### Data collection

Siemens P4/PC diffractometer

$\theta-2\theta$  scans

Absorption correction: none

1822 measured reflections

1678 independent reflections

1367 observed reflections

$[F > 4\sigma(F)]$

$R_{\text{int}} = 0.0096$

$\theta_{\text{max}} = 50.45^\circ$

$h = 0 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -9 \rightarrow 10$

2 standard reflections

monitored every 50

reflections

intensity variation: 1.5%

### Refinement

Refinement on  $F$

Final  $R = 4.0\%$

$wR = 3.5\%$

Unit weights applied

$(\Delta/\sigma)_{\text{max}} = 0.064$

$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$

$S = 0.46$

1367 reflections

266 parameters

All H-atom parameters refined except methyl H atoms

$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
C(1)	0.6097 (4)	0.0792 (3)	1.0969 (4)	0.056 (2)
C(2)	0.7312 (4)	-0.0148 (4)	1.0860 (4)	0.064 (2)
C(3)	0.8314 (4)	-0.0584 (4)	1.1869 (4)	0.066 (2)
C(4)	0.8109 (4)	-0.0097 (3)	1.2982 (4)	0.062 (2)
C(5)	0.6887 (3)	0.0855 (3)	1.3131 (3)	0.047 (1)
C(6)	0.6612 (3)	0.1375 (3)	1.4292 (3)	0.051 (1)
C(7)	0.7629 (4)	0.1016 (4)	1.5347 (3)	0.064 (2)
C(8)	0.7335 (5)	0.1514 (4)	1.6446 (4)	0.073 (2)
C(9)	0.6045 (5)	0.2402 (4)	1.6550 (4)	0.074 (2)
C(10)	0.5051 (4)	0.2769 (4)	1.5555 (3)	0.061 (2)
C(11)	0.5324 (3)	0.2269 (3)	1.4414 (3)	0.054 (1)
C(12)	0.4302 (4)	0.2679 (3)	1.3348 (3)	0.055 (1)
C(13)	0.4546 (3)	0.2265 (3)	1.2204 (3)	0.049 (1)
C(14)	0.5850 (3)	0.1316 (3)	1.2072 (3)	0.050 (1)
C(15)	0.3447 (3)	0.2778 (3)	1.1111 (3)	0.047 (1)
C(16)	0.3956 (4)	0.3642 (3)	0.9689 (3)	0.052 (2)
C(17)	0.2942 (4)	0.4156 (3)	0.8685 (3)	0.054 (2)
C(18)	0.1326 (3)	0.3791 (3)	0.9084 (3)	0.049 (1)
C(19)	0.0805 (4)	0.2946 (3)	1.0520 (3)	0.053 (2)
C(20)	0.1840 (4)	0.2455 (3)	1.1504 (4)	0.053 (1)
N(1)	0.0318 (3)	0.4249 (3)	0.8072 (3)	0.062 (1)
C(21)	0.0814 (5)	0.5286 (5)	0.6659 (4)	0.091 (2)
C(22)	-0.1350 (4)	0.3883 (4)	0.8532 (4)	0.071 (2)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C(1)—C(2)	1.381 (5)	C(1)—C(14)	1.390 (5)
C(2)—C(3)	1.378 (6)	C(3)—C(4)	1.375 (6)
C(4)—C(5)	1.402 (4)	C(5)—C(6)	1.442 (5)
C(5)—C(14)	1.437 (4)	C(6)—C(7)	1.425 (5)
C(6)—C(11)	1.399 (4)	C(7)—C(8)	1.368 (6)
C(8)—C(9)	1.393 (6)	C(9)—C(10)	1.365 (6)
C(10)—C(11)	1.409 (5)	C(11)—C(12)	1.434 (5)
C(12)—C(13)	1.356 (5)	C(13)—C(14)	1.446 (4)
C(13)—C(15)	1.501 (4)	C(15)—C(16)	1.377 (4)
C(15)—C(20)	1.391 (4)	C(16)—C(17)	1.383 (5)
C(17)—C(18)	1.406 (4)	C(18)—C(19)	1.385 (4)
C(18)—N(1)	1.384 (4)	C(19)—C(20)	1.381 (5)
N(1)—C(21)	1.424 (4)	N(1)—C(22)	1.451 (4)
C(2)—C(1)—C(14)	121.9 (3)	C(1)—C(2)—C(3)	119.5 (4)
C(2)—C(3)—C(4)	120.6 (3)	C(3)—C(4)—C(5)	121.6 (3)
C(4)—C(5)—C(6)	123.5 (3)	C(4)—C(5)—C(14)	117.7 (3)
C(6)—C(5)—C(14)	118.8 (3)	C(5)—C(6)—C(7)	122.1 (3)
C(5)—C(6)—C(11)	120.5 (3)	C(7)—C(6)—C(11)	117.5 (3)
C(6)—C(7)—C(8)	121.0 (3)	C(7)—C(8)—C(9)	120.7 (4)
C(8)—C(9)—C(10)	119.8 (4)	C(9)—C(10)—C(11)	120.6 (3)
C(6)—C(11)—C(10)	120.4 (3)	C(6)—C(11)—C(12)	118.8 (3)
C(10)—C(11)—C(12)	120.8 (3)	C(11)—C(12)—C(13)	122.9 (3)
C(12)—C(13)—C(14)	119.3 (3)	C(12)—C(13)—C(15)	119.6 (3)
C(14)—C(13)—C(15)	121.1 (3)	C(1)—C(14)—C(5)	118.7 (3)
C(1)—C(14)—C(13)	121.5 (3)	C(5)—C(14)—C(13)	119.7 (3)
C(13)—C(15)—C(16)	122.1 (3)	C(13)—C(15)—C(20)	121.3 (2)
C(16)—C(15)—C(20)	116.5 (3)	C(15)—C(16)—C(17)	122.5 (3)
C(16)—C(17)—C(18)	120.5 (3)	C(17)—C(18)—C(19)	117.1 (3)
C(17)—C(18)—N(1)	120.9 (2)	C(19)—C(18)—N(1)	122.0 (3)
C(18)—C(19)—C(20)	121.2 (3)	C(15)—C(20)—C(19)	122.1 (3)
C(18)—N(1)—C(21)	121.1 (3)	C(18)—N(1)—C(22)	119.3 (2)
C(21)—N(1)—C(22)	118.5 (3)		

P3/PC software (Siemens, 1989) was used for data collection, data reduction and absorption correction. All calculations were performed and the figures drawn with *SHELXTL/PC* (Siemens, 1990). Refinement was by full-matrix least-squares methods.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55602 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1026]

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## Structures of Two (1:1) Adducts of $[\alpha, \alpha$ -Bis(3,3,3-trifluoropropynyl)]benzyl Benzoate and Furan

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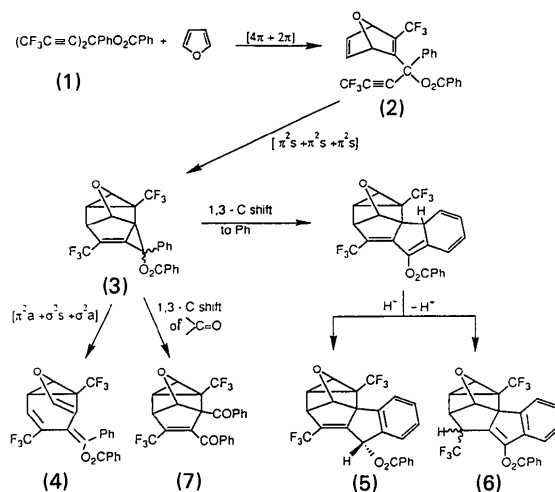
### Abstract

[(*Z*)-5-(Benzoyloxybenzylidene)]-1,4-bis(trifluoromethyl)-8-oxatricyclo[4.3.0.0<sup>2,9</sup>]nona-3,6-diene (4) and 11,12-benzo-10-benzoyloxy-2,8-bis(trifluoromethyl)-5-oxapentacyclo[7.3.0.0<sup>1,6</sup>.0<sup>2,4</sup>.0<sup>3,7</sup>]dodeca-8-ene (5) are two of four main (1:1) adducts of the title reactants. The crystallographical characterization of (4) and (5) assists in establishing the mechanistic pathways of the reaction. The ring strain in isomer (4) is particularly marked at double-bonded C6 where the three angles sum to 344.4 (7)°; in the three-membered ring,

C2—C9 [1.542 (7) Å] is significantly longer than C1—C2 and C1—C9 [1.479 (6) and 1.470 (6) Å respectively] and the angles C2—C1—C9, C1—C2—C9 and C1—C9—C2 [63.1 (3), 58.2 (3) and 58.8 (3)° respectively] are all significantly different from 60°. The strain in isomer (5), which has two molecules of the same chirality in the asymmetric unit, does not distort the three-membered ring but gives rise to a long bond [C1—C6 = 1.59 (2) and 1.62 (2) Å in molecules 1 and 2, respectively], angles around C1 considerably distorted from tetrahedral, and a large angle at double-bonded C9 [C8—C9—C10 = 142 (1), 138 (1)°].

### Comment

When [ $\alpha, \alpha$ -bis(3,3,3-trifluoropropynyl)]benzyl benzoate (1) undergoes Diels–Alder reaction with furan, four major (1:1) adducts C<sub>24</sub>H<sub>14</sub>F<sub>6</sub>O<sub>3</sub> (4)–(7) can be isolated (besides minor components) from a solid product; crystallographic identification of (4) and (5) confirms the participation of the unstable intermediate adduct (3) formed by intramolecular ( $\pi^2s + \pi^2s + \pi^2s$ ) cycloaddition from the initial alkyne Diels–Alder adduct (2) (Barlow, Tajammal & Tipping, 1989). Adducts (6) and (7) were identified by <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR; details of the preparation of all the materials have been given by Tajammal (1991). After chromatographic separation of (4)–(7) from the initial solid, (4) was recrystallized slowly from a mixture of petroleum ether (b.p. 313–333 K) and dichloromethane (3:5:1 v/v), and (5) from pentane.



A crystal structure determination of a saturated 7-oxa lactone derivative of the tricyclic ring system in (4) has been reported (Dulcere & Crandall, 1990). No other crystal structure with the ring system of (5) appears to have been reported.