Synthesis and Characterization of Bismuth Bromide–Arene π Complexes. *X*-Ray Structure of Bismuth(III) Bromide–Fluoranthene–*p*-Xylene (4/2/1)†

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A structural and spectroscopic investigation of a charge-transfer complex of bismuth(III) bromide with fluoranthene is reported. Charge-transfer spectra of some complexes formed by $BiBr_3$ with a series of polycyclic benzenoid and non-benzenoid hydrocarbons were recorded. The charge-transfer band energies, $E_{c.t.}$, and the ionization potentials of the electron donors are linearly correlated with a slope of one. A linear correlation is also observed for $E_{c.t.}$ and the first π–π^* singlet transition energies of the benzenoid hydrocarbons. The crystal and molecular structure of bismuth(III) bromide–fluoranthene–*p*-xylene (4/2/1) was determined: crystals are triclinic, space group $P\bar{1}$, with a = 9.812(6), b = 11.199(7), c = 12.861(8) Å, α = 71.59(6), β = 80.28(6), γ = 74.38(7)°, Z = 2, and R = 0.0848. The structure is formed by tetrameric Bi_4Br_{12} centrosymmetric units in which three bromine atoms bridge adjacent bismuths, which show distorted octahedral co-ordination having five sites occupied by bromines and the sixth by a benzene ring of the fluoranthene at longer distances.

Aromatic hydrocarbons as π donors are of considerable practical and theoretical interest. The most important basic information concerning their properties as photoconductors, photoreceptors, sensitizers, and their high mutagenic and tumoral activity has been obtained from detailed studies of their π complexes. To correlate with previous work on the crystal structures of antimony(III) bromide[1] and bismuth(III) chloride[2] with pyrene, a benzenoid non-carcinogenic alternant polycyclic aromatic hydrocarbon (aromatic hydrocarbons containing a five-membered conjugated ring are non-alternant benzenoid hydrocarbons), the present paper describes a study on the bismuth(III) bromide complex with fluoranthene, a non-benzenoid non-alternant aromatic hydrocarbon, which has been demonstrated to be carcinogenic and identified as a widespread environmental contaminant.[3]

Table 1. Wavelengths of the maximum charge–transfer absorption band, $\lambda_{max.}$(nm), charge-transfer transition energies $E_{c.t.}$ (eV), π–π^* singlet transition energies E_a (eV), and ionization potentials, I_p (eV) of the donor molecules

Adduct of $2BrBr_3$ with	Colour of crystals	$\lambda_{max.}$	$E_{c.t.}$	I_p[a]	E_a[b]
Perylene	Dark green	685	1.74	7.00	2.85
Pyrene	Dark red	510	2.42	7.41	3.71
Acenaphthene	Orange	490	2.52	7.82	
Phenanthrene	Yellow-orange	468	2.65	7.91	4.23
Fluorene	Light yellow	460	2.69	7.93	4.74
Fluoranthene–*p*-xylene (1/0.5)	Red-purple	455	2.70	7.95	3.45

[a] R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, 1974, **60**, 4406.
[b] From ref. 13.

Experimental

All the reagents were of the best commercial grade: $BiBr_3$ was recrystallized from ethylbenzene and dried on P_4O_{10}; hydrocarbons were purified by chromatography on neutral alumina and dried. All solvents were dehydrated and kept on metallic sodium. All manipulations were performed in a dry-box.

Synthesis of the Complexes.—A *p*-xylene saturated solution of $BiBr_3$ was added dropwise to a stirred hydrocarbon solution with metal to ligand molar ratios ranging from 1:2 to 2:1, the mixture was heated at 80 °C, and then n-hexane was added to the cloud point. After several days well shaped crystals separated suitable for *X*-ray study: bismuth(III) bromide–fluoranthene–*p*-xylene (4/2/1) (Found: C, 20.75; H, 1.30; Bi, 36.10; Calc. for $C_{20}H_{15}Bi_2Br_6$: C, 20.80; H, 1.30; Bi, 36.25%); bismuth(III) bromide–perylene (2/1) (Found: C, 20.85; H, 1.00; Bi, 36.10. Calc. for $C_{20}H_{12}Bi_2Br_6$: C, 20.85; H, 1.05; Bi, 36.35%); bismuth(III) bromide–pyrene (2/1) (Found: C, 17.20; H, 1.10; Bi, 37.50. Calc. for $C_{16}H_{10}Bi_2Br_6$: C, 17.45; H, 0.90; Bi, 38.00%); bismuth(III) bromide–acenaphthene (2/1) (Found: C, 13.70; H, 0.95; Bi, 39.30. Calc. for $C_{12}H_{10}Bi_2Br_6$: C, 13.55; H, 0.95; Bi, 39.75%); bismuth(III) bromide–phenanthrene (2/1) (Found: C, 15.40; H, 0.95; Bi, 38.50. Calc. for $C_{14}H_{10}Bi_2Br_6$: C, 15.60; H, 0.95; Bi, 38.85%); bismuth(III) bromide–fluorene (2/1) (Found: C, 14.75; H, 0.90; Bi, 39.10. Calc. for $C_{13}H_{10}Bi_2Br_6$: C, 14.65; H, 0.95; Bi, 39.30%).

Physical Measurements.—I.r. spectra in Polythene pellets (60—600 cm^{-1}) were recorded on a Bruker TTIR 113V spectrophotometer, electronic spectra of solid samples in Nujol mull with Polythene as support on a Shimadzu MPS50L spectrophotometer (Table 1). The thermogravimetric analysis was performed with a heating rate of 10 °C min^{-1} on a Netsch STA 409 thermobalance.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

Crystallography.—The more relevant details of the data collection and refinements are summarized in Table 2. The crystal was sealed in a glass capillary under dry nitrogen and mounted in a random orientation on a Enraf-Nonius CAD4 single-crystal diffractometer: the resulting cell dimensions were determined using 25 accurately centred reflections. During the intensity measurements one standard reflection was monitored every hour: no significant changes were observed. The intensity data were collected using the five-points technique and variable speed; after the usual data reduction [$I > 3\sigma(I)$] the structure amplitudes were corrected for absorption and put on an absolute scale by least squares. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic thermal parameters only for Bi and Br atoms; the final R index was 0.0848. The final atomic parameters are quoted in Table 3; all the calculations were performed using a Gould 32/77 computer using SHELX 76,[4] ORTEP,[5] and PARST[6] programs; the atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Table 2. Experimental data for the crystallographic analysis

Formula	$C_{20}H_{15}Bi_2Br_6$
M	1 152.7
Space group	$P\bar{1}$
a/Å	9.812(6)
b/Å	11.199(7)
c/Å	12.861(8)
α/°	71.59(6)
β/°	80.28(6)
γ/°	74.38(7)
U/Å^3	1 286(1)
Z	2
D_c/g cm^{-3}	2.977
No. of reflections for lattice parameters	25 (θ 10—16°)
λ(Mo-K_α)/Å	0.7107
F(000)	1 022
T/K	293
Crystal size/mm^3	0.20 × 0.39 × 0.88
μ/cm^{-1}	228.7
Absorption correction (min, max)	0.98, 1.13
Scan speed/° min^{-1}	1.27—4.12
Scan width/°	1.2 + 0.35 tanθ
θ range/°	2.5—20.0
h range	−9 to 9
k range	−10 to 10
l range	0 to 12
Standard reflection	1 − 5 1
Scan mode	ω—2θ
No. of measured reflections	2 399
No. of reflections used in the refinement	1 637 [$I > 3\sigma(I)$]
Min., max. heights in final difference maps eÅ^{-3}	−1.08, 1.32
No. of refined parameters	153
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0848
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}$	0.0915
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$ *	5.5
k,g in $w = k[\sigma^2(F_o) + gF_o^{\,2}]^{-1}$	4.5, 8.7 × 10^{-4}

* N = no. of observations, P = no. of parameters.

Results and Discussion

Thermal gravimetric analysis data show that the fluoranthene complex is stable up to its melting point (145 °C). The i.r. spectrum of the fluoranthene in the range 100—500 cm^{-1} presents bands at 484m, 427s, 178vs, 128ms, and 116ms cm^{-1}; the out-of-plane bands of the free ligand at 484, 128, and 116 cm^{-1} do not appear in the spectrum of the complex. In the range 100—220 cm^{-1} a multiplet of well resolved bands is present for the complex; the band at 178vs cm^{-1} corresponds to a ligand vibration, while the bands at 211s, 194s, 184s, and 163s cm^{-1} can be tentatively assigned to the metal–bromine stretching vibrations arising from the 'multiplicity' of Bi–Br bond distances. The room-temperature solid-state electronic spectra of the fluoranthene complex showed a band centred at 455 nm which is absent for the original components, due to a charge transfer from the π system of a benzene ring to the vacant sp^3d orbital of bismuth. In order to evaluate the applicability of the π-complex theory[8–12] to these compounds we isolated a series of $BiBr_3$ derivatives with donors such as the non-alternant non-benzenoid hydrocarbons fluorene and acenaphthene, and the alternant benzenoid hydrocarbons phenanthrene, pyrene, and perylene. The dependences of the charge-transfer transition energies $E_{c.t.}$ on the π–π* singlet transition E_a and the ionization potential I_p of the donor molecules are reported in Figures 1 and 2, showing a behaviour very similar (see Figure 1) to that reported in the case of 2,4,7-trinitrofluorenone[13] (it is worthy of note that in this case the acceptor is an organic molecule) with the same deviation from the line by the non-alternant hydrocarbons fluoranthene and fluorene. The deviation from linearity of the pyrene derivatives (Figure 2) could be associated with the polymeric nature of the inorganic framework which acts to lower the bismuth–hydrocarbon interactions.*

The structure is depicted in Figure 3: the asymmetric unit contains two independent bismuth atoms each bonded to three bromines, Bi(1) with Br(1), Br(2), and Br(3), Bi(2) with Br(4),

Table 3. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Bi(1)	4 199(2)	6 337(2)	1 256(2)	C(7)	1 750(57)	8 946(47)	44(40)
Bi(2)	5 259(2)	8 026(2)	−2 593(2)	C(8)	2 070(54)	9 140(46)	1 038(39)
Br(1)	5 665(6)	8 031(5)	−72(4)	C(9)	1 391(61)	8 406(54)	2 092(43)
Br(2)	4 952(8)	6 395(7)	3 056(5)	C(10)	687(69)	7 454(60)	2 072(50)
Br(3)	6 389(6)	4 331(5)	1 086(4)	C(11)	332(49)	7 261(42)	1 194(35)
Br(4)	4 961(6)	7 755(6)	−4 487(4)	C(12)	−446(51)	6 517(45)	1 212(37)
Br(5)	7 408(6)	5 939(5)	−2 182(4)	C(13)	−629(66)	6 336(56)	239(48)
Br(6)	7 059(7)	9 503(6)	−3 315(5)	C(14)	−20(67)	7 168(58)	−794(48)
C(1)	1 318(67)	3 991(56)	−1 633(47)	C(15)	599(45)	8 063(39)	−763(34)
C(2)	1 501(54)	9 423(47)	−2 838(40)	C(16)	872(54)	7 979(45)	165(39)
C(3)	2 198(58)	10 185(49)	−3 341(40)	C(1A)	1 295(99)	6 494(89)	5 702(72)
C(4)	2 927(49)	10 777(42)	−2 819(36)	C(2A)	692(60)	5 834(52)	5 334(43)
C(5)	2 759(48)	10 553(40)	−1 694(34)	C(3A)	−979(67)	6 226(56)	5 082(47)
C(6)	1 965(51)	9 487(44)	−1 070(37)	C(4A)	1 441(82)	4 731(73)	5 268(56)

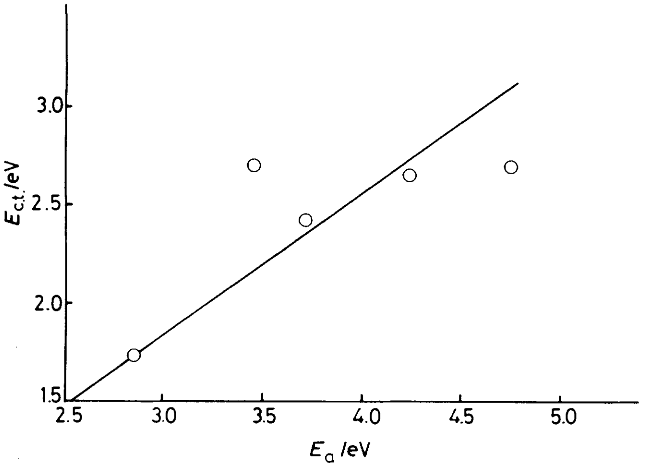

Figure 1. The dependence of charge-transfer transition energies $E_{c.t.}$ on the π–π^* singlet transition energy E_a

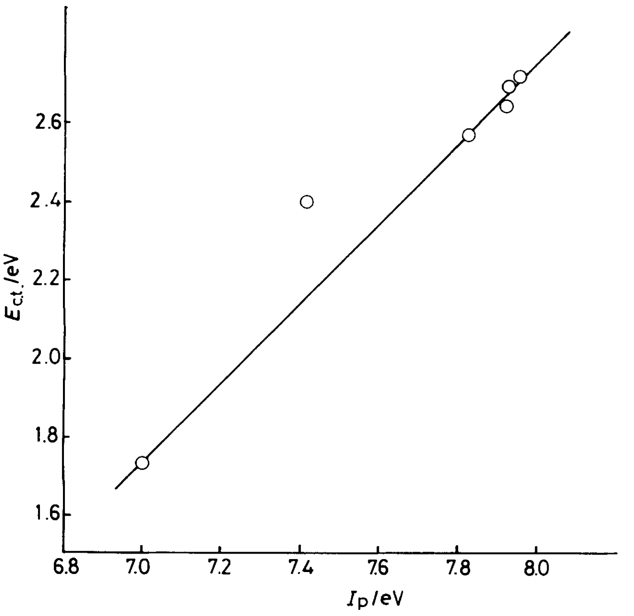

Figure 2. The dependence of charge-transfer transition energies $E_{c.t.}$ on the ionization potential I_p

Br(5), and Br(6). The atoms Br(1) and Br(3^I) (I $1 - x$, $1 - y$, $-z$) connect the two independent bismuth atoms [Bi $\cdots$ Bi 4.751(4) Å]; in addition Br(3^I) and Br(5) bridge Bi(2) with Bi(1^I) of one adjacent molecule [Bi $\cdots$ Bi 5.428(4) Å]; the result is a tetrameric centrosymmetric Bi_4Br_{12} unit interlayered by fluoranthene molecules. The environment of the metal atoms can be described as a very distorted octahedron, the sites being occupied from three closely bonded bromides, two bridging Br atoms with longer distances, and a benzene ring of the fluoranthene molecule [C(1)—C(6) for Bi(2) and C(7)—C(16) for Bi(1)]. The main plane including atoms Br(1), Br(2), Br(3^I), Br(4), Br(5^I), and Br(6) [maximum displacements from the plane $-0.153(8)$ and 0.163(7) Å] is parallel to the plane of the fluoranthene molecule, the dihedral angle formed being only 1.3(5)°; Bi(1) and Bi(2) are out from this plane by 0.217(4) and 0.194(4) Å respectively towards the fluoranthene. The range of the Bi–Br bond distances (Table 4) is large [2.570(8)—2.769(4) Å]. The shorter ones involve the unshared Br(2), Br(4), and Br(6) and are similar to the values of 2.63(2) and 2.65(3) Å found in 2-methylpyridinium tetrabromobismuthate.[14] All these bonds are shorter than the values found in octahedral bromobismuthates, *e.g.* 2.822(9)—2.852(8) Å in $[NMe_2H_2]_3[BiBr_6]$,[15] 2.704(5)—2.766(5) Å in $[PPh_4]_3[Bi_2Br_9]$,[16] and 2.713(2) Å in $Cs_3[Bi_2Br_9]$.[17] This fact is not surprising, an analogous situation was also recognized in bismuth(III) chloride–pyrene (2/1)[2] and in $[C_6H_3Me_3\text{-}2,4,6]BiCl_3$.[18] The values of the Bi–Br bridging distances ranging from 3.165(7) to 3.494(7) Å are similar to the 3.169 8(3) Å found in BiOBr[19] and to 3.08(2) and 3.27(2) Å found in the above quoted 2-methylpyridinium tetrabromobismuthate; the longest, 3.494(7) Å, just involves the triply bridging Br(3) atom. The interbond angles [range 90.1(3)—97.6(2)°] are less than the tetrahedral angle as usually found and this fact was explained by means of lone pair–bond pair electron repulsions.[20] In each co-ordination polyhedron the longest Bi–Br bonds are opposite to the bismuth–fluoranthene interaction as in 2:1 $SbCl_3$ adducts of naphthalene,[21] *p*-xylene,[22] and phenanthrene,[23] and can be justified in terms of the π donation from the hydrocarbon to the metal. As found in several of these compounds the bismuth–arene distances fall in a wide range: 3.23(4)—3.66(5) Å for Bi(1) and 3.27(4)—3.82(5) Å for Bi(2) showing the presence of a differentiated interaction with values very similar to those of bismuth(III) chloride–pyrene (2/1).

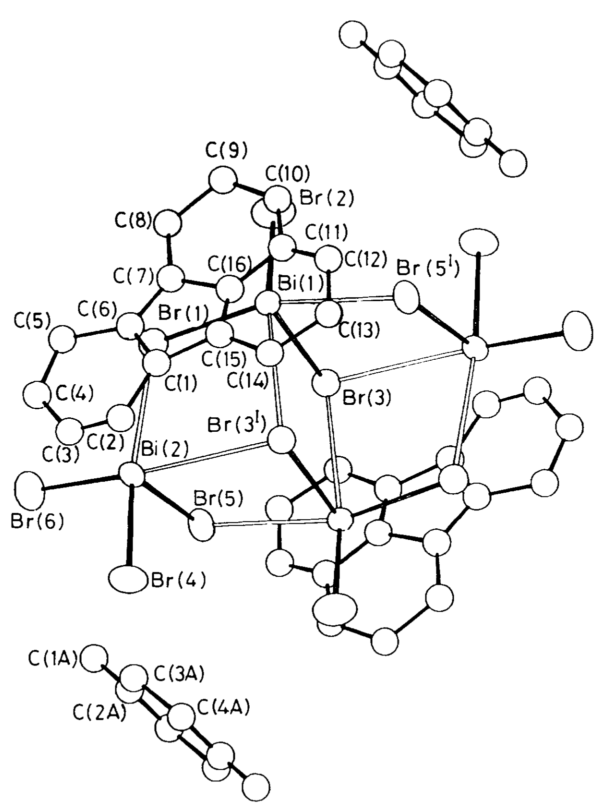

Figure 3. Perspective view of the Bi_4Br_{12}·2fluoranthene units

Bond distances and angles of the fluoranthene (Table 4) are affected by large errors due to the presence of the heavy bismuth and bromine atoms so that some relevant differences are not significant; the molecule is planar within the experimental

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* The crystals of bismuth(III) bromide–pyrene (2/1) were preliminarily investigated by *X*-ray diffraction using Mo-K_α radiation. Crystal data : $a = 10.589(4)$, $b = 13.208(20)$, $c = 7.533(6)$ Å, $\beta = 91.60(4)°$, $Z = 4$, space group $P2_1/c$. These results are strictly similar to those previously found for the corresponding chloride: $a = 10.564(3)$, $b = 12.564(3)$, $c = 7.220(1)$ Å, $\beta = 90.33(7)°$, $Z = 4$, space group $P2_1/c$. The compounds can be considered isostructural.

Table 4. Interatomic contacts (Å) and angles (°)

Bi(1)–Br(1)	2.769(4)	Bi(2)–Br(5)	2.670(6)	Br(1)–Bi(1)–Br(2)	95.5(3)	Br(4)–Bi(2)–Br(5)	92.7(2)
Bi(1)–Br(2)	2.570(8)	Bi(2)–Br(6)	2.601(8)	Br(1)–Bi(1)–Br(3)	91.3(2)	Br(4)–Bi(2)–Br(6)	97.6(2)
Bi(1)–Br(3)	2.695(6)	Bi(1) ··· Br(3$^{\mathrm{I}}$)	3.494(7)	Br(2)–Bi(1)–Br(3)	92.6(3)	Br(5)–Bi(2)–Br(6)	90.1(3)
Bi(1) ··· Br(5$^{\mathrm{I}}$)	3.165(7)	Bi(2) ··· Br(3)	3.369(6)	Br(1)–Bi(1)–Br(3$^{\mathrm{I}}$)	87.9(2)	Br(1)–Bi(2)–Br(3$^{\mathrm{I}}$)	80.3(2)
Bi(2)–Br(4)	2.620(7)	Bi(2) ··· Br(1)	3.335(7)	Br(1)–Bi(1)–Br(5$^{\mathrm{I}}$)	162.8(2)	Br(1)–Bi(2)–Br(4)	173.9(2)
Bi(1) ··· C(7)	3.37(4)	Bi(2) ··· C(1)	3.82(5)	Br(2)–Bi(1)–Br(5$^{\mathrm{I}}$)	100.0(2)	Br(1)–Bi(2)–Br(5)	83.0(2)
Bi(1) ··· C(8)	3.23(4)	Bi(2) ··· C(2)	3.62(5)	Br(3)–Bi(1)–Br(5$^{\mathrm{I}}$)	80.7(2)	Br(1)–Bi(2)–Br(6)	86.8(2)
Bi(1) ··· C(9)	3.35(5)	Bi(2) ··· C(3)	3.37(5)	Br(2)–Bi(1)–Br(3$^{\mathrm{I}}$)	169.0(2)	Br(3$^{\mathrm{I}}$)–Bi(2)–Br(4)	94.5(2)
Bi(1) ··· C(10)	3.44(6)	Bi(2) ··· C(4)	3.27(4)	Br(3$^{\mathrm{I}}$)–Bi(1)–Br(3)	76.9(2)	Br(3$^{\mathrm{I}}$)–Bi(2)–Br(5)	77.3(2)
Bi(1) ··· C(11)	3.66(5)	Bi(2) ··· C(5)	3.57(4)	Br(3$^{\mathrm{I}}$)–Bi(1)–Br(5$^{\mathrm{I}}$)	75.5(1)	Br(3$^{\mathrm{I}}$)–Bi(2)–Br(6)	163.0(2)
Bi(1) ··· C(16)	3.56(5)	Bi(2) ··· C(6)	3.74(4)				
C(1)–C(2)	1.47(7)	C(7)–C(16)	1.51(8)	C(2)–C(1)–C(6)	118(5)	C(9)–C(10)–C(11)	127(6)
C(1)–C(6)	1.35(9)	C(8)–C(9)	1.50(7)	C(2)–C(1)–C(15)	137(5)	C(10)–C(11)–C(16)	115(5)
C(1)–C(15)	1.49(7)	C(9)–C(10)	1.43(10)	C(6)–C(1)–C(15)	104(5)	C(10)–C(11)–C(12)	126(5)
C(2)–C(3)	1.20(8)	C(10)–C(11)	1.33(9)	C(1)–C(2)–C(3)	123(5)	C(12)–C(11)–C(16)	119(4)
C(3)–C(4)	1.45(9)	C(11)–C(12)	1.27(8)	C(2)–C(3)–C(4)	123(5)	C(11)–C(12)–C(13)	119(5)
C(4)–C(5)	1.38(6)	C(11)–C(16)	1.41(6)	C(3)–C(4)–C(5)	120(4)	C(12)–C(13)–C(14)	116(5)
C(5)–C(6)	1.54(7)	C(12)–C(13)	1.38(9)	C(4)–C(5)–C(6)	114(4)	C(13)–C(14)–C(15)	121(5)
C(6)–C(7)	1.37(6)	C(13)–C(14)	1.50(8)	C(1)–C(6)–C(5)	120(4)	C(1)–C(15)–C(14)	133(5)
C(7)–C(8)	1.46(8)	C(14)–C(15)	1.32(9)	C(5)–C(6)–C(7)	129(4)	C(14)–C(15)–C(16)	114(5)
C(1A)–C(2A)	1.29(14)	C(15)–C(16)	1.24(7)	C(1)–C(6)–C(7)	111(5)	C(1)–C(15)–C(16)	111(5)
C(2A)–C(3A)	1.64(9)	C(3A)–C(4A$^{\mathrm{II}}$)	1.48(12)	C(6)–C(7)–C(16)	105(4)	C(11)–C(16)–C(15)	128(5)
C(2A)–C(4A)	1.28(9)			C(6)–C(7)–C(8)	137(5)	C(7)–C(16)–C(15)	108(4)
				C(8)–C(7)–C(16)	118(4)	C(7)–C(16)–C(11)	123(4)
				C(7)–C(8)–C(9)	115(5)	C(1A)–C(2A)–C(4A)	116(7)
				C(8)–C(9)–C(10)	119(5)	C(1A)–C(2A)–C(3A)	125(6)
				C(3A)–C(2A)–C(4A)	118(6)	C(2A)–C(3A)–C(4A$^{\mathrm{II}}$)	115(5)

Symmetric equivalents: I $1 - x, 1 - y, \bar{z}$; II $\bar{x}, 1 - y, 1 - z$.

Table 5. Intermolecular contacts less than 3.60 Å

Br(3) ··· C(14$^{\mathrm{I}}$)	3.52(6)	C(2) ··· C(9$^{\mathrm{III}}$)	3.42(7)
Br(3) ··· C(15$^{\mathrm{I}}$)	3.48(4)	C(5) ··· C(10$^{\mathrm{III}}$)	3.53(7)
Br(5) ··· C(12$^{\mathrm{I}}$)	3.56(4)	C(5) ··· C(11$^{\mathrm{III}}$)	3.45(6)
Br(5) ··· C(3A$^{\mathrm{II}}$)	3.56(6)	C(7) ··· C(7$^{\mathrm{III}}$)	3.60(7)
C(1) ··· C(8$^{\mathrm{III}}$)	3.52(7)	C(8) ··· C(15$^{\mathrm{III}}$)	3.46(6)
C(1) ··· C(9$^{\mathrm{III}}$)	3.34(7)	C(13) ··· C(13$^{\mathrm{IV}}$)	3.13(9)

I $1 - x, 1 - y, -z$; II $1 + x, y, z - 1$; III $-x, 2 - y, -z$; IV $-x, 1 - y, -z$.

errors. Packing is due to fluoranthene–fluoranthene and bromine–fluoranthene contacts; the *p*-xylene centrosymmetric molecule is little involved in the packing interactions showing only the weak contact Br(5) ··· C(3A$^{\mathrm{II}}$) II $1 + x, y, z - 1$ 3.56(6) Å (Table 5).

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