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Electrocrystallization and Structures of Perylene Radical Salts: Hexaperylene Perchlorate, $(C_{20}H_{12})_6^+ClO_4^-$, Triperylene Perchlorate, $(C_{20}H_{12})_3^+ClO_4^-$, and Diperylene Hexafluorophosphate–Tetrahydrofuran (3/2), $(C_{20}H_{12})_2^+PF_6^-.\frac{2}{3}C_4H_8O$

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Abstract. Crystals grown by electrocrystallization, species obtained depending on perylene concentration. Room-temperature data collections, Mo $K\alpha$, $\lambda = 0.71069$ Å. 6:1 salt: $M_r = 1613.3$, triclinic, $P\bar{1}$, $a = 12.571$ (7), $b = 13.699$ (5), $c = 13.835$ (11) Å, $\alpha = 110.43$ (4), $\beta = 107.13$ (7), $\gamma = 107.09$ (4)°, $V = 1913$ Å^3, $Z = 1$, $D_x = 1.40$ g cm^{-3}, $\mu = 1.1$ cm^{-1}, $F(000) = 841$, final $R = 0.077$ for 3171 observed reflections. The structure contains three independent perylene π dimers arranged nearly perpendicularly to each other. The anions are severely disordered or freely rotating. 3:1 salt: $M_r = 856.4$, triclinic, $P\bar{1}$, $a = 13.009$ (8), $b = 13.821$ (10), $c = 13.850$ (15) Å, $\alpha = 66.05$ (7), $\beta = 83.36$ (8), $\gamma = 63.51$ (6)°, $V = 2030$ Å^3, $Z = 2$, $D_x = 1.40$ g cm^{-3}, $\mu = 1.5$ cm^{-1}, $F(000) = 890$, final $R = 0.138$ for 3523 observed reflections. Tetrameric perylene stacks are surrounded on four sides by single perylene species, having their planes nearly perpendicular to the molecular planes in the stacks. 2:1 salt: $M_r = 697.7$, monoclinic, $P2/m$, $a = 13.04$ (1), $b = 14.12$ (1), $c = 13.75$ (1) Å, $\beta = 110.80$ (2)°, $V = 2367$ Å^3, $Z = 3$, $D_x = 1.47$ g cm^{-3}, $\mu = 1.5$ cm^{-1}, $F(000) = 1079$, final $R = 0.121$ for 1737 observed reflections. Nearly regular perylene stacks are surrounded by single perylene species in a way similar to the 3:1 salt. The thf solvent and one of the perylene molecules are disordered over two orientations.

Introduction. Electrochemically prepared organic metals of simple hydrocarbons (radical cation salts) have aroused considerable interest, owing to their simple preparation and their electronic and magnetic properties (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980; Kröhnke, Enkelmann & Wegner, 1980; Eichele, Schwoerer, Kröhnke & Wegner, 1981; Koch, Schweitzer, Harms, Keller, Schäfer,

$(C_{20}H_{12})_6^+ClO_4^-$, $(C_{20}H_{12})_3^+ClO_4^-$ AND $(C_{20}H_{12})_2^+PF_6^-.\frac{2}{3}C_4H_8O$

Table 1. Experimental details

	6:1 salt	3:1 salt	2:1 salt
Crystal shape	Nearly cube	Irregular pyramid	Flat needle
Crystal size (mm³)	0·008	0·006	0·01
Diffractometer	Siemens AED	Siemens AED	CAD-4
Reflections for lattice constants	34	37	25
$2\theta_{max}$ ($\lambda = 0.71069$ Å)	50°	50°	50°
Intensity measurement method (θ–2θ)	'Five-value'	'Five-value'	Background–reflection–background
Range of hkl	$0,\overline{15},\overline{14}$ to $14,13,14$	$\overline{11},\overline{13},0$ to $16,13,16$	$\overline{16},0,0$ to $15,16,17$
Number of check reflections	2	2	3
Measured at intervals	5h	5h	100 reflections
Intensity variation (%)	±5·5	±3·8	±3·4
Reflections measured	6740	7152	5428
Observed unique reflections [$I > 2 \cdot 0\sigma(I)$]	3171	3523	1737
Merging R	No equivalent reflections	No equivalent reflections	0·013
Number of parameters	571	286	220
wR, R, S	0·063, 0·077, 3·5	0·116, 0·138, 6·5	0·093, 0·121, 7·1
$(\Delta/\sigma)_{max}$ in final LS cycle	0·70	0·42	0·03
$\Delta\rho$max (min) (e Å⁻³) in final difference map	0·44 (−0·42)	0·69 (−0·45)	0·71 (−0·51)

Helberg, Wilckens, Geserich & Ruppel, 1982; Wilckens, Geserich, Ruppel, Koch, Schweitzer & Keller, 1982; Höptner, Mehring, von Schütz, Wolf, Morra, Enkelmann & Wegner, 1982; Sigg, Prisner, Dinse, Brunner, Schweitzer & Hausser, 1983; Bender, Schweitzer & Keller, 1983). Radical cation salts of pyrene and perylene were first prepared by electrochemical methods by Chiang & Reddoch (1970) and by Chiang, Reddoch & Williams (1971), but at that time neither the metallic character of these salts nor their crystal structure was evaluated. This was probably because the conditions of the electrocrystallization process were not optimized for obtaining crystals of good quality. Important factors include: (a) the potential for the oxidation of the donor, (b) the current for which an optimum window for the rate of the electrochemical crystal growth exists, (c) the purity of the materials (dry and freshly distilled solvents, repeatedly recrystallized electrolyte salts, gradient-sublimed or zone-refined donor materials), (d) the type of electrochemical cell, (e) the temperature, which is critically related to the solubility of the donor.

The solubility of the neutral donor and of the electrochemically generated radical salt in the solvent is one of the most important parameters in the electrocrystallization process. So, for example, from a dichloromethane solution saturated with perylene (pe) and anions like $X = PF_6^-$ or AsF_6^- only crystals of type $(pe)_2X_{1.1}.0.8CH_2Cl_2$ are obtained (Keller et al., 1980). Using tetrahydrofuran (thf), in which about ten times as much perylene can be dissolved, yields a larger number of different compounds, depending on the concentration of the donor during the electrocrystallization process, viz (pe)$_6X$ (I), (pe)$_3X$ (II), (pe)$_2X.\frac{2}{3}$thf (III), (pe)$_2X_{1.5}.$$\frac{1}{2}$thf (IV), (pe)$X$ (V), all with different crystal structures.

Crystals of III and IV are quasi-one-dimensional organic metals (Keller et al., 1980; Koch et al., 1982; Bender et al., 1983). The lattice constants of IV lead to the conclusion that it is isostructural with (pe)$_2$-

$(PF_6)_{1.1}.0.8CH_2Cl_2$ (Keller et al., 1980). The room-temperature conductivity of crystals of III is of the order of 200 $(\Omega\,cm)^{-1}$, while that of IV is up to 800 $(\Omega\,cm)^{-1}$. Crystals of I [$\sim10^{-2}$ $(\Omega\,cm)^{-1}$] and II [0·5–2$(\Omega\,cm)^{-1}$] are organic semiconductors. Crystals of V are insulators and are green, in contrast to the black crystals of I–IV (Sato, Kinoshita, Sano & Akamatu, 1969).

In this paper we describe the structures of crystals I, II and III.

Experimental. 800 mg perylene dissolved in 100 ml thf. Electrolyte salts [2g (Bu$_4$N)PF$_6$ or 2g (Bu$_4$N)ClO$_4$] added. Solutions saturated with dry N$_2$ in a three-compartment electrochemical cell. Potential 2·8 V, current 20–30 μA for several days, yielding crystals of I–V with decreasing concentration of perylene.

Black crystals mounted on a glass capillary. Details of data collections in Table 1. No absorption correction. Refinement based on F, $w = 1/\sigma^2(F)$, cascade-matrix least squares on a Nova 3 computer, plots on a Tektronix plotter. SHELXTL program system (Sheldrick, 1981), scattering factors from International Tables for X-ray Crystallography (1974), anomalous dispersion included. All structures solved by direct methods. H positions of ordered perylene species calculated and included riding on corresponding C atoms. In the 2:1 salt H atoms of disordered perylene and thf ignored. Anisotropic temperature factors used for atoms of PF$_6^-$ and ClO$_4^-$ anions in 2:1 and 3:1 salts; other atoms refined isotropically. High R values due to moderate crystal quality, typical for this class of compounds. In 6:1 salt disordered ClO$_4^-$ anion, occupying crystallographic inversion centre, refined using model involving six O positions; their isotropic temperature factors fixed at $U = 0.1$ Å², site occupation factors refined; Cl and C atoms refined anisotropically. Further details in Table 1.

Discussion. Atomic coordinates of the 6:1, 3:1 and 2:1 salts are listed in Tables 2, 3 and 4, respectively.* The

* Lists of structure amplitudes, anisotropic thermal parameters, bond angles, and Figs. 2, 5, 7, 13, 14 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39946 (64 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. $(pe)_6ClO_4$ *atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

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

	x	y	z	U_{eq}	
C(1)	−1746 (5)	286 (5)	1605 (5)	62 (4)	
C(2)	−2127 (5)	−459 (5)	477 (5)	61 (4)	
C(3)	−2969 (5)	−417 (4)	−401 (5)	53 (3)	
C(4)	−3438 (4)	392 (4)	−171 (5)	43 (3)	
C(5)	−3058 (4)	1182 (4)	996 (4)	44 (3)	
C(6)	−2183 (4)	1131 (4)	1888 (4)	50 (3)	
C(7)	−1805 (5)	1909 (5)	3037 (5)	68 (4)	
C(8)	−2258 (5)	2708 (5)	3312 (5)	67 (4)	
C(9)	−3093 (5)	2769 (5)	2454 (5)	56 (4)	
C(10)	−3510 (4)	2020 (4)	1294 (5)	45 (3)	
C(11)	−4321 (4)	435 (4)	−1098 (4)	43 (3)	
C(12)	−4739 (5)	−314 (4)	−2253 (4)	56 (4)	
C(13)	−5606 (5)	−272 (5)	−3119 (5)	67 (4)	
C(14)	−6073 (5)	511 (5)	−2846 (5)	66 (4)	
C(15)	−5677 (5)	1293 (5)	−1703 (4)	52 (4)	
C(16)	−4800 (4)	1265 (4	−801 (5)	42 (3)	
C(17)	−4403 (5)	2061 (5)	364 (5)	46 (3)	
C(18)	−4893 (5)	2860 (5)	595 (5)	56 (4)	
C(19)	−5760 (5)	2884 (5)	−277 (6)	66 (4)	
C(20)	−6153 (6)	2121 (6)	−1406 (6)	72 (5)	
C(21)	3300 (6)	1397 (5)	4324 (5)	67 (4)	
C(22)	4493 (6)	1879 (5)	5114 (5)	73 (5)	
C(23)	5401 (5)	2837 (5)	5210 (4)	57 (4)	
C(24)	5137 (4)	3314 (4)	4499 (4)	46 (3)	
C(25)	3872 (4)	2797 (4)	3632 (4)	46 (3)	
C(26)	2956 (5)	1811 (4)	3537 (5)	53 (4)	
C(27)	1715 (6)	1306 (5)	2686 (6)	69 (4)	
C(28)	1408 (6)	1732 (5)	1950 (5)	70 (4)	
C(29)	2302 (5)	2687 (5)	2036 (5)	57 (4)	
C(30)	3523 (5)	3233 (4)	2852 (4)	46 (3)	
C(31)	6063 (5)	4327 (4)	4595 (4)	43 (3)	
C(32)	7270 (5)	4883 (4)	5418 (4)	54 (4)	
C(33)	8162 (5)	5851 (4)	5515 (4)	60 (4)	
C(34)	7833 (5)	6279 (5)	4779 (5)	61 (4)	
C(35)	6618 (5)	5757 (5)	3922 (5)	52 (4)	
C(36)	5698 (4)	4770 (4)	3824 (4)	43 (3)	
C(37)	4450 (4)	4246 (4)	2956 (4)	45 (3)	
C(38)	4169 (5)	4736 (4)	2254 (4)	55 (3)	
C(39)	5074 (6)	5695 (5)	2349 (5)	67 (4)	
C(40)	6262 (6)	6186 (5)	3160 (5)	65 (4)	
C(41)	9896 (5)	7886 (5)	11130 (5)	60 (4)	
C(42)	10605 (5)	8165 (5)	10600 (5)	66 (4)	
C(43)	10512 (5)	7302 (5)	9637 (4)	60 (4)	
C(44)	9729 (4)	6145 (5)	9180 (4)	47 (3)	
C(45)	8991 (4)	5839 (4)	9726 (4)	41 (3)	
C(46)	9079 (4)	6724 (4)	10710 (4)	49 (3)	
C(47)	8365 (5)	6421 (5)	11270 (5)	62 (4)	
C(48)	7586 (5)	5290 (5)	10856 (5)	62 (4)	
C(49)	7485 (5)	4414 (5)	9876 (5)	58 (4)	
C(50)	8166 (4)	4655 (4)	9309 (4)	43 (3)	
C(51)	9644 (5)	5229 (5)	8171 (4)	45 (3)	
C(52)	10354 (5)	5479 (5)	7618 (5)	61 (4)	
C(53)	10300 (5)	4602 (5)	6677 (5)	73 (4)	
C(54)	9557 (5)	3475 (5)	6290 (5)	70 (4)	
C(55)	8785 (5)	3166 (5)	6798 (4)	52 (3)	
C(56)	8836 (5)	4048 (5)	7758 (4)	46 (3)	
C(57)	8076 (5)	3749 (5)	8300 (4)	51 (3)	
C(58)	7287 (5)	2584 (5)	7826 (5)	63 (4)	
C(59)	7228 (5)	1715 (5)	6893 (5)	73 (4)	
C(60)	7982 (5)	1994 (5)	6405 (5)	67 (4)	
Cl	10000	0	5000	90 (2)	
O(1)	9874 (12)	766 (11)	4547 (11)	100	0·348 (6)*
O(2)	9178 (14)	449 (14)	4987 (12)	100	0·335 (8)*
O(3)	8676 (18)	−652 (17)	4326 (17)	100	0·277 (8)*
O(4)	9863 (11)	−515 (11)	3802 (11)	100	0·359 (6)*
O(5)	9221 (14)	−1253 (13)	4219 (13)	100	0·298 (7)*
O(6)	10868 (18)	301 (17)	4597 (19)	100	0·244 (8)*

* Refined site occupation factor.

asymmetric unit of the 6:1 salt comprises three perylene species at general positions, and a severely disordered ClO_4^- anion on a crystallographic inversion centre. A reasonable superposition of ClO_4^- tetrahedra cannot be recognized, and a nearly free rotation of the anion is a possibility. Cl—O bond distances range from 1·35 (2) to 1·49 (1) Å; bond angles are meaningless. The numbering scheme and bond distances in the three perylene species are shown in Fig. 1. Each of these molecules

Table 3. $(pe)_3ClO_4$ *atomic coordinates* $(\times 10^4)$ *and temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U
C(1)	2817 (9)	3451 (9)	4092 (7)	75 (3)
C(2)	3505 (8)	3148 (9)	4952 (7)	74 (3)
C(3)	4563 (8)	2244 (8)	5196 (7)	64 (3)
C(4)	5049 (7)	1545 (7)	4596 (7)	49 (3)
C(5)	4346 (7)	1842 (7)	3708 (7)	46 (2)
C(6)	3250 (8)	2779 (8)	3453 (7)	60 (3)
C(7)	2526 (8)	3073 (8)	2569 (7)	67 (3)
C(8)	2970 (8)	2430 (8)	1960 (8)	69 (3)
C(9)	4047 (8)	1536 (8)	2173 (7)	59 (3)
C(10)	4786 (7)	1186 (7)	3057 (7)	49 (3)
C(11)	6184 (7)	586 (7)	4852 (6)	46 (2)
C(12)	6907 (7)	218 (8)	5751 (7)	60 (3)
C(13)	7969 (8)	−679 (8)	5962 (7)	66 (3)
C(14)	8428 (9)	−1309 (9)	5343 (7)	70 (3)
C(15)	7725 (8)	−990 (8)	4430 (7)	57 (3)
C(16)	6619 (7)	−57 (7)	4198 (6)	45 (2)
C(17)	5922 (7)	232 (7)	3297 (6)	47 (2)
C(18)	6436 (7)	−425 (8)	2667 (7)	60 (3)
C(19)	7509 (8)	−1313 (8)	2901 (7)	69 (3)
C(20)	8181 (9)	−1641 (8)	3777 (7)	70 (3)
C(21)	9434 (8)	514 (8)	3159 (7)	64 (3)
C(22)	8960 (8)	1151 (8)	3763 (7)	63 (3)
C(23)	7873 (8)	2037 (8)	3527 (7)	59 (3)
C(24)	7152 (7)	2367 (7)	2648 (6)	46 (2)
C(25)	7644 (7)	1686 (7)	2010 (7)	58 (3)
C(26)	8745 (7)	776 (8)	2261 (7)	58 (3)
C(27)	9229 (8)	97 (8)	1637 (7)	72 (3)
C(28)	8585 (8)	373 (8)	768 (7)	71 (3)
C(29)	7496 (8)	1265 (8)	518 (7)	60 (3)
C(30)	6954 (7)	1962 (7)	1097 (7)	50 (3)
C(31)	6006 (7)	3321 (7)	2381 (7)	51 (3)
C(32)	5501 (8)	4034 (8)	2955 (7)	65 (3)
C(33)	4408 (8)	4923 (8)	2699 (7)	71 (3)
C(34)	3752 (9)	5169 (8)	1848 (7)	72 (3)
C(35)	4206 (8)	4488 (8)	1229 (7)	60 (3)
C(36)	5318 (7)	3574 (8)	1489 (7)	53 (3)
C(37)	5791 (7)	2888 (7)	855 (6)	47 (2)
C(38)	5072 (7)	3153 (8)	13 (7)	57 (3)
C(39)	3967 (8)	4067 (8)	−221 (7)	64 (3)
C(40)	3519 (9)	4721 (8)	357 (7)	72 (3)
C(41)	−684 (10)	5092 (10)	2681 (9)	105 (4)
C(42)	−958 (10)	4265 (11)	2716 (10)	115 (5)
C(43)	−828 (10)	3930 (10)	1903 (9)	105 (4)
C(44)	−414 (9)	4439 (10)	946 (8)	71 (3)
C(45)	−135 (8)	5367 (10)	864 (7)	63 (3)
C(46)	−257 (9)	5703 (10)	1751 (9)	89 (4)
C(47)	50 (10)	6577 (10)	1665 (10)	110 (4)
C(48)	446 (9)	7084 (10)	765 (9)	96 (4)
C(49)	557 (9)	6831 (10)	−129 (9)	94 (4)
C(50)	276 (8)	5932 (9)	−102 (8)	64 (3)
C(51)	4757 (8)	7579 (8)	2409 (8)	68 (3)
C(52)	5869 (8)	7080 (9)	2258 (8)	69 (3)
C(53)	6376 (9)	7644 (8)	1433 (7)	68 (3)
C(54)	5710 (7)	8805 (7)	717 (7)	52 (3)
C(55)	4520 (7)	9358 (7)	877 (7)	51 (3)
C(56)	4016 (8)	8765 (8)	1715 (7)	61 (3)
C(57)	2830 (8)	9341 (8)	1840 (7)	66 (3)
C(58)	2174 (9)	10443 (8)	1190 (7)	75 (3)
C(59)	2641 (8)	11028 (9)	358 (7)	68 (3)
C(60)	3775 (8)	10560 (8)	153 (7)	56 (3)
Cl	1823 (3)	6762 (3)	4191 (3)	85 (2)*
O(1)	1838 (10)	7088 (9)	3101 (7)	167 (10)*
O(2)	1124 (8)	7702 (7)	4458 (7)	148 (7)*
O(3)	1192 (11)	6076 (10)	4485 (9)	199 (12)*
O(4)	2890 (7)	6091 (10)	4697 (8)	194 (9)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. $(pe)_2PF_6 \cdot \frac{2}{3}(thf)$ *atomic coordinates* $(\times 10^4)$ *and temperature factors* $(Å^2 \times 10^3)$

	x	y	z	U
C(1)	4481 (7)	519 (6)	6148 (7)	30 (3)
C(2)	3531 (8)	1052 (7)	5962 (7)	46 (3)
C(3)	3563 (10)	2049 (9)	5984 (7)	61 (4)
C(4)	4513 (8)	2516 (8)	6167 (7)	58 (4)
C(5)	5472 (8)	2025 (8)	6347 (7)	41 (3)
C(6)	6460 (9)	2505 (8)	6537 (7)	60 (4)
C(7)	7418 (10)	2048 (9)	6711 (7)	64 (4)
C(8)	7456 (9)	1053 (8)	6709 (7)	51 (3)
C(9)	6483 (7)	512 (6)	6520 (7)	38 (3)
C(10)	5485 (7)	1006 (7)	6350 (6)	29 (3)
C(11)	6081 (8)	492 (6)	8932 (7)	44 (3)
C(12)	7046 (9)	1050 (8)	9109 (7)	52 (3)
C(13)	6988 (10)	2023 (9)	9125 (8)	60 (3)
C(14)	6051 (9)	2516 (9)	8977 (8)	69 (4)
C(15)	5070 (9)	2000 (9)	8766 (8)	48 (3)
C(16)	4096 (9)	2519 (8)	8604 (7)	58 (4)
C(17)	3158 (9)	1996 (9)	8424 (7)	56 (4)
C(18)	3141 (9)	1043 (8)	8395 (7)	56 (4)
C(19)	4090 (8)	491 (6)	8556 (7)	39 (3)
C(20)	5082 (8)	1008 (8)	8749 (7)	41 (3)
C(21)	4740 (12)	5000	2229 (12)	66 (5)
C(22)	4217 (14)	5000	7343 (12)	74 (6)
C(23)	3707 (13)	5000	6267 (11)	58 (5)
C(24)	4334 (11)	5000	5640 (11)	42 (4)
C(25)	3852 (10)	5000	4516 (10)	35 (4)
C(26)	2736 (12)	5000	4016 (11)	62 (5)
C(27)	2236 (15)	5000	2940 (13)	81 (6)
C(28)	2872 (14)	5000	2361 (14)	82 (6)
C(29)	4021 (13)	5000	2775 (12)	58 (5)
C(30)	4519 (10)	5000	3901 (10)	36 (4)
P(1)	1956 (5)	5000	8960 (4)	63 (3)*
F(1)	3264 (9)	5000	9459 (8)	133 (7)*
F(2)	691 (8)	5000	8484 (10)	162 (8)*
F(3)	1969 (6)	4218 (5)	9781 (6)	127 (5)*
F(4)	1996 (7)	4215 (6)	8176 (6)	152 (6)*
P(2)	0	0	5000	79 (4)*
F(5)	916 (9)	0	5991 (8)	289 (14)*
F(6)	609 (8)	687 (7)	4592 (9)	235 (8)*
C(31)†	122 (20)	763 (18)	9167 (19)	38 (8)
C(32)†	202 (15)	1522 (18)	8581 (16)	35 (6)
C(33)†	161 (19)	2488 (17)	8911 (20)	39 (8)
C(34)	0	2705 (12)	10000	82 (6)
C(35)†	−67 (16)	1976 (17)	10519 (14)	43 (7)
C(36)†	−235 (20)	2265 (22)	11521 (20)	52 (9)
C(37)†	−312 (16)	1500 (18)	12148 (16)	52 (7)
C(38)†	−297 (14)	583 (13)	11876 (15)	36 (6)
C(39)†	−133 (16)	235 (22)	10919 (14)	43 (9)
C(40)†	−48 (16)	966 (12)	10284 (13)	10 (5)
O(1)†	1031 (15)	3712 (14)	5000 (14)	104 (6)
C(51)†	172 (24)	3629 (22)	4100 (22)	93 (10)
C(52)†	518 (26)	3145 (22)	4498 (25)	97 (11)
C(53)	747 (11)	3399 (10)	5767 (10)	120 (5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Site occupation factor = 0·5.
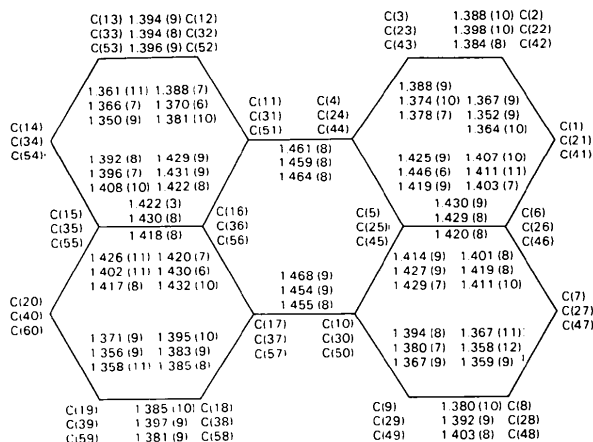

Fig. 1. Numbering scheme and bond distances (Å) in the perylene species of the 6:1 salt. Upper numbers refer to molecule I, centred at −0·39, 0·12, 0·01, middle to molecule II, centred at 0·48, 0·38, 0·37, lower to molecule III at 0·89, 0·49, 0·88.
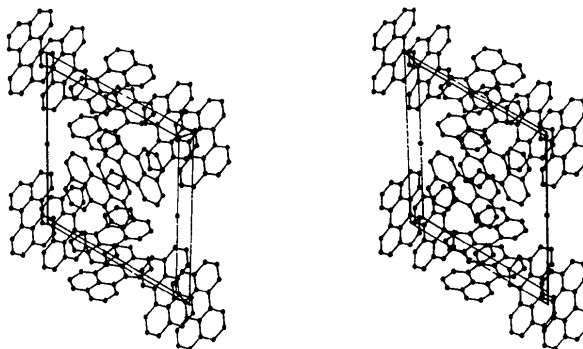

Fig. 3. Stereoview, along **a**, of the 6:1 salt. The disordered ClO_4^- O atoms are omitted.

forms a π dimer with its counterpart generated by the nearest inversion centre. Interplanar distances are 3·38 (2), 3·44 (2) and 3·46 (3) Å for the dimers of molecules I, II and III, respectively. The three overlap patterns are very similar to each other. As an example, the overlap in dimer I is shown in Fig. 2 (deposited). The dimers form isolated units in the crystal, which are strongly tilted with respect to each other (see Fig. 3). Dihedral angles are: I–II 102 (2), I–III 84 (2), II–III 103 (2)°. The structure gives no information concerning the distribution of the positive charge.

The asymmetric unit of the 3:1 salt comprises two perylene species at general positions, two half molecules, the second halves of which are generated by inversion centres, and an ordered ClO_4^- anion at a general position. The numbering scheme is shown in
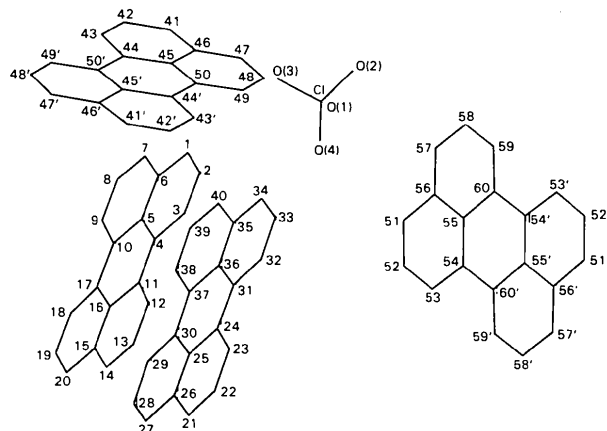

Fig. 4. Relative orientation and numbering scheme of the molecules in the 3:1 salt. Numbers without atom designation refer to C atoms; code for symmetry-equivalent atoms is defined in Table 5.

Table 5. *Bond distances* (Å) *in the* 3:1 *salt*

C(1)–C(2)	1·379 (16)	C(1)–C(6)	1·431 (17)
C(2)–C(3)	1·342 (11)	C(3)–C(4)	1·418 (15)
C(4)–C(5)	1·426 (14)	C(4)–C(11)	1·433 (10)
C(5)–C(6)	1·391 (11)	C(5)–C(10)	1·430 (15)
C(6)–C(7)	1·440 (16)	C(7)–C(8)	1·368 (17)
C(8)–C(9)	1·354 (11)	C(9)–C(10)	1·426 (14)
C(10)–C(17)	1·433 (10)	C(11)–C(12)	1·422 (14)
C(11)–C(16)	1·420 (14)	C(12)–C(13)	1·342 (11)
C(13)–C(14)	1·369 (17)	C(14)–C(15)	1·443 (16)
C(15)–C(16)	1·397 (10)	C(15)–C(20)	1·428 (16)
C(16)–C(17)	1·439 (14)	C(17)–C(18)	1·414 (15)
C(18)–C(19)	1·347 (11)	C(19)–C(20)	1·374 (16)
C(21)–C(22)	1·360 (16)	C(21)–C(26)	1·443 (16)
C(22)–C(23)	1·357 (11)	C(23)–C(24)	1·415 (14)
C(24)–C(25)	1·444 (15)	C(24)–C(31)	1·441 (10)
C(25)–C(26)	1·381 (10)	C(25)–C(30)	1·454 (14)
C(26)–C(27)	1·425 (16)	C(27)–C(28)	1·368 (16)
C(28)–C(29)	1·362 (11)	C(29)–C(30)	1·400 (15)
C(30)–C(37)	1·443 (10)	C(31)–C(32)	1·404 (15)
C(31)–C(36)	1·440 (15)	C(32)–C(33)	1·365 (11)
C(33)–C(34)	1·372 (16)	C(34)–C(35)	1·419 (16)
C(35)–C(36)	1·392 (11)	C(35)–C(40)	1·428 (16)
C(36)–C(37)	1·443 (15)	C(37)–C(38)	1·403 (14)
C(38)–C(39)	1·387 (11)	C(39)–C(40)	1·343 (16)
C(41)–C(42)	1·323 (24)	C(41)–C(46)	1·433 (16)
C(42)–C(43)	1·350 (22)	C(43)–C(44)	1·399 (15)
C(44)–C(45)	1·441 (19)	C(44)–C(50′)	1·422 (19)
C(45)–C(46)	1·450 (19)	C(45)–C(50)	1·430 (14)
C(46)–C(47)	1·390 (23)	C(47)–C(48)	1·331 (17)
C(48)–C(49)	1·394 (20)	C(49)–C(50)	1·427 (21)
C(51)–C(56)	1·437 (11)	C(51)–C(52)	1·330 (13)
C(53)–C(54)	1·406 (10)	C(52)–C(53)	1·382 (15)
C(55)–C(60)	1·463 (10)	C(54)–C(55)	1·425 (12)
C(57)–C(58)	1·328 (11)	C(55)–C(56)	1·407 (13)
C(59)–C(60)	1·369 (13)	C(56)–C(57)	1·414 (13)
Cl–O(1)	1·390 (11)	C(58)–C(59)	1·368 (14)
Cl–O(3)	1·429 (17)	C(60)–C(54″)	1·466 (13)
		Cl–O(2)	1·381 (10)
		Cl–O(4)	1·352 (9)

Symmetry code: (′) $-x$, $1-y$, $-z$; (″) $1-x$, $2-y$, $-z$.

Fig. 6. Stereoview, along **c**, of the 3:1 salt, showing two perylene species of adjacent tetramers.

Fig. 8. Relative orientation and numbering scheme in the 2:1 salt, analogous to Fig. 4. Only one orientation is shown for the disordered molecules. Symmetry code is defined in Table 6.

Fig. 4. Bond distances are listed in Table 5. The perylene molecules at general positions, molecule I [C(1)–C(20)] with its centroid at (0·55, 0·09, 0·39) and molecule II [C(21)–C(40)], centroid (0·65, 0·26, 0·18), form a tetrameric unit together with their counterparts generated by the inversion centre ($\frac{1}{2}$,0,$\frac{1}{2}$); the alternation of the molecules is II, I, I′, II′.

The molecular planes of II and I are parallel within the standard deviation [dihedral angle 1 (2)°], I and I′ are parallel by symmetry. The two independent inter-planar distances, II–I 3·39 (8), I–I′ 3·36 (5) Å, do not differ significantly. This is also true for the two overlap patterns, shown in Fig. 5 (deposited). These tetramers are aligned along [011] (see Fig. 6). There is only a weak link between molecules II and II″ of adjacent tetrameric units related by the inversion centre ($\frac{1}{2}$,$\frac{1}{2}$,0). The overlap between these two molecules is indicated in Fig. 7 (deposited). The interplanar distance, 3·36 (5) Å, corresponds to the distances within a tetramer.

The two remaining perylene species, molecule III [C(41)–C(50)], centred at (0,$\frac{1}{2}$,0), and molecule IV [C(51)–C(60)] at ($\frac{1}{2}$,1,0) flank the tetramers on four sides (Fig. 6); interplanar angles are: I–III 88 (2), I–IV 73 (2), III–IV 78 (2)°. One is tempted to ascribe the positive charge to the tetrameric units, but there is no structural proof for this.
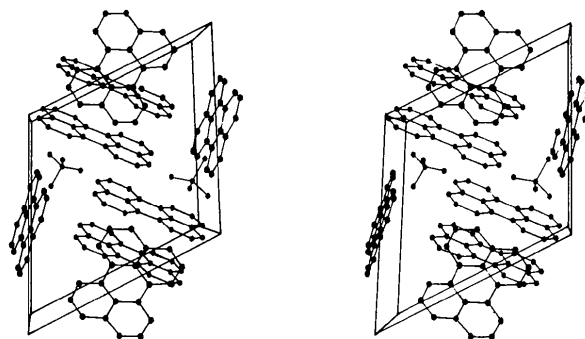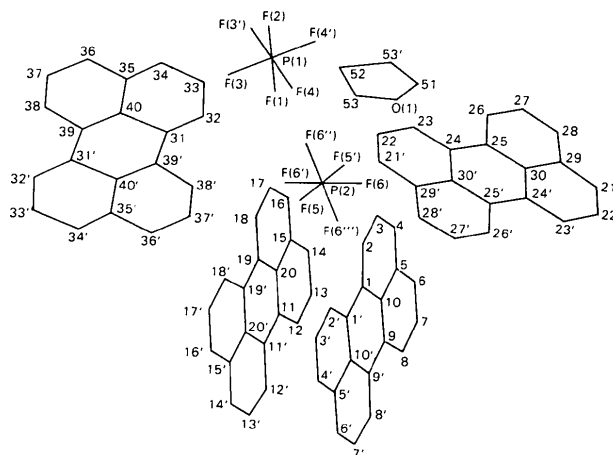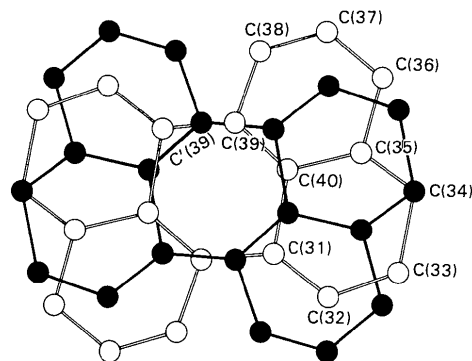

Fig. 9. The disordered perylene molecule IV in the 2:1 salt. Its centroid is at (0,0,1), site symmetry 2/m. Atoms C(34) and C′(34) lie on the twofold axis, the mirror plane bisects the line C(39)–C′(39).

Table 6. *Bond distances* (Å) *in the* 2:1 *salt*

C(1)–C(2)	1·393 (14)	C(1)–C(10)	1·416 (12)
C(1)–C(1')	1·466 (16)	C(2)–C(3)	1·409 (16)
C(3)–C(4)	1·346 (16)	C(4)–C(5)	1·372 (15)
C(5)–C(6)	1·397 (15)	C(5)–C(10)	1·439 (14)
C(6)–C(7)	1·349 (17)	C(7)–C(8)	1·406 (17)
C(8)–C(9)	1·423 (14)	C(9)–C(10)	1·420 (13)
C(9)–C(9')	1·447 (17)	C(11)–C(12)	1·430 (15)
C(11)–C(20)	1·434 (15)	C(11)–C(11')	1·391 (18)
C(12)–C(13)	1·377 (17)	C(13)–C(14)	1·357 (18)
C(14)–C(15)	1·410 (17)	C(15)–C(16)	1·414 (17)
C(15)–C(20)	1·402 (17)	C(16)–C(17)	1·375 (17)
C(17)–C(18)	1·346 (17)	C(18)–C(19)	1·412 (15)
C(19)–C(20)	1·426 (15)	C(19)–C(19'')	1·387 (17)
C(21)–C(29)	1·394 (27)	C(21)–C(22'')	1·276 (22)
C(22)–C(23)	1·390 (20)	C(24)–C(25)	1·446 (18)
C(23)–C(24)	1·384 (25)	C(25)–C(26)	1·371 (18)
C(24)–C(30'')	1·401 (10)	C(26)–C(27)	1·388 (22)
C(25)–C(30)	1·412 (22)	C(28)–C(29)	1·401 (23)
C(27)–C(28)	1·337 (31)	P(1)–F(2)	1·543 (11)
C(29)–C(30)	1·452 (20)	P(1)–F(4)	1·559 (10)
P(1)–F(1)	1·597 (12)	P(2)–F(6)	1·485 (12)
P(1)–F(3)	1·575 (9)	C(31)–C(40)	1·652 (35)
P(2)–F(5)	1·458 (9)	C(32)–C(33)	1·445 (35)
C(31)–C(32)	1·367 (37)	C(34)–C(35)	1·272 (27)
C(31)–C(39''')	1·415 (40)	C(35)–C(40)	1·465 (29)
C(33)–C(34)	1·613 (29)	C(36)–C(37)	1·409 (39)
C(35)–C(36)	1·525 (37)	C(39)–C(40)	1·382 (33)
C(37)–C(38)	1·349 (32)	O(1)–C(51)	1·348 (29)
C(38)–C(39)	1·490 (31)	O(1)–C(53)	1·312 (26)
C(52)–C(53)	1·701 (37)	C(51)–C(53'''')	1·316 (37)
		C(53'''')–C(52)	1·599 (36)

Symmetry code: (') x, $-y$, z; ('') $1-x$, $1-y$, $1-z$; (''') $-x$, $-y$, $2-z$; ('''') $-x, y$, $1-z$.

The structure of the 2:1 salt (Fig. 8) is complicated by the presence of disordered solvent (thf) and by disorder of one of the perylene molecules. The centroids of all the molecules lie on special positions; perylene I [C(1)–C(10)], centred at (0·54,0,0·63), and perylene II [C(11)–C(20)], centred at (0·51,0,0·87), lie perpendicular to the mirror plane $y = 0$. Perylene III [C(21)–C(30)] has all its atoms in the mirror plane $y = \frac{1}{2}$, and its centroid at the inversion centre $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The fourth independent perylene species, IV [C(31)–C(40)], centred at (0,0,1), is disordered over two symmetry-related positions, as indicated in Fig. 9.

There are two independent PF_6^- anions in the structure; P(1), F(1) and F(2) lie on the mirror plane $y = \frac{1}{2}$, and the octahedron is completed by F(3) and F(4) in general positions. The second anion occupies a site of symmetry $2/m$, $(0,0,\frac{1}{2})$, with F(5) on the mirror plane and F(6) in a general position. The thf molecule [O(1)–C(53)] is disordered having its centroid on a twofold axis at $(0,0·35,\frac{1}{2})$. Bond distances are listed in Table 6.

Perylene molecules I and II, together with their symmetry-related counterparts, form nearly regularly spaced infinite stacks along **c**. A section of a stack with surrounding PF_6^- anions is shown in Fig. 10. The same molecules projected along the stacking direction (**c**) are plotted in Fig. 11 to demonstrate that the perylene stacks are surrounded by anions. The perylene molecules of the stack are slightly displaced with respect to each other along their short molecular axis. This slip results in an arrangement with a step after four molecules.

The environment of the stacks is completed by thf and by perylene species III and IV, which have their molecular planes perpendicular (I–III 90° by symmetry) or nearly perpendicular [I–IV 73 (2)°] to the molecules of the stack. The planes of III and IV are perpendicular by symmetry. An impression of this is given in Fig. 12, the same view as in Fig. 11, but with the perylene species III and IV and thf molecules instead of the anions. The rather complicated structure can then be visualized as a superposition of Figs. 11 and 12.

Within a stack the molecules are parallel [dihedral angle I–II 0·3 (20)°] and the crystallographically independent interplanar distances are identical within their standard deviations: I–I' 3·40 (2), II–II' 3·39 (2),
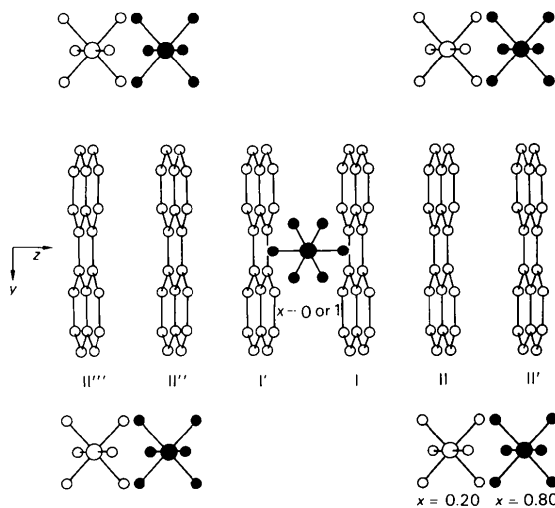

Fig. 10. Section of a stack in the 2:1 salt with surrounding PF_6^- anions, viewed along **a**. The centroids of perylene molecules I and II are close to $x = 0·50$, the shaded PF_6^- groups are above this ($x = 1$ or 0·80), the open ones below ($x = 0·20$).
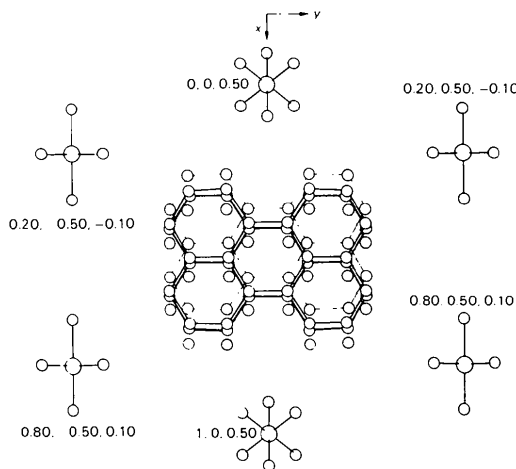

Fig. 11. The same molecules as in Fig. 10, viewed along **c**. The positions of the PF_6^- anions are given in the figure.
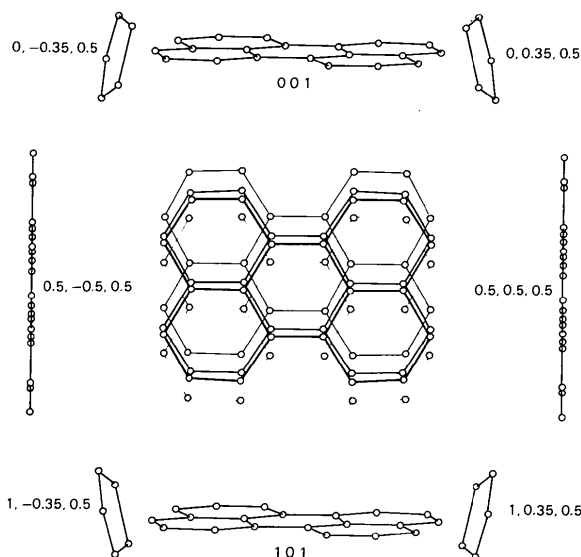
Fig. 12. The same view as in Fig. 11, with perylene species III and IV and thf molecules shown instead of the PF$_6^-$ anions. The centroids of some molecules are indicated.

I–II 3·38 (2) Å. The crystallographically independent overlap patterns within a stack are almost indistinguishable and differ only in the direction of the slips. The two extreme examples, overlaps I–II and I–I', are shown in Fig. 13 (deposited). As in the 6:1 and 3:1 salts there is no structural evidence concerning the localization of the positive charges. Intuition would suggest that the charges are distributed in the stacks, but there are some physical arguments against this idea.

Obviously the structure of the 6:1 salt is quite different from those of the 3:1 and 2:1 salts. The latter two have some features in common: stacks of perylene molecules flanked by other perylene species and by the anions. In the 3:1 salt the stacks are clearly tetrameric, with only a weak overlap between the tetramers. The stacks of the 2:1 salt bear some similarity to the tetrameric nature of the stacks of the 3:1 compound. However, as all the interplanar distances in the stacks are identical and the relative displacements of adjacent

molecules are very similar, the stacks are much more regular than in the 3:1 salt. These three compounds differ markedly from the previously reported (perylene)$_2$(PF$_6$)$_{1.1}$.0·8CH$_2$Cl$_2$ (Keller et al., 1980). In this salt regular perylene stacks occur with the molecules inclined to the stacking axis, resulting in a herring-bone arrangement (Fig. 14, deposited), and there are no additional perylene species flanking the stacks.

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Structure Determination of p-Chloroaniline Hydrochloride, C$_6$H$_7$ClN$^+$.Cl$^-$, and Redetermination of p-Chloroaniline, C$_6$H$_6$ClN

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Abstract. p-Chloroaniline hydrochloride, $M_r = 164·1$, monoclinic, $P2_1/c$, $a = 8·728$ (1), $b = 9·649$ (1), $c = 9·823$ (1) Å, $\beta = 108·6$ (1)°, $V = 784·0$ (3) Å^3, $Z = 4$, $D_m = 1·390$ (1), $D_x = 1·389$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·74$ mm^{-1}, $F(000) = 336$, $T = 295$ K. $R = 0·04$ for 1959 unique observed reflexions. The