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Structures of Eleven Perylene-3,4:9,10-bis(dicarboximide) Pigments

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Abstract. (1): *N,N'*-Bis(2-ethoxyethyl)perylene-3,4:9,10-bis(dicarboximide), $C_{32}H_{26}N_2O_6$, M_r = 534·6, triclinic, $P\bar{1}$, a = 4·835 (2), b = 8·306 (3), c = 15·402 (6) Å, α = 86·46 (3), β = 85·45 (3), γ = 80·92 (3)°, V = 608·08 Å^3, Z = 1, D_m = 1·44, D_x = 1·46 g cm^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 0·60 cm^{-1}, $F(000)$ = 280, T = 295 K, R = 11·7% for 834 reflections, S = 1·90. (2): *N,N'*-Bis(3-methoxypropyl)-perylene-3,4:9,10-bis(dicarboximide), $C_{32}H_{26}N_2O_6$, M_r = 534·6, triclinic, $P\bar{1}$, a = 15·874 (26), b = 9·418 (13), c = 4·725 (7) Å, α = 108·12 (8), β = 82·59 (6), γ = 114·90 (9)°, V = 609·0 Å^3, Z = 1, D_m = 1·44, D_x = 1·46 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 7·35 cm^{-1}, $F(000)$ = 280, T = 295 K, R = 4·9% for 1282 reflections, S = 1·59. (3): *N,N'*-Di-*n*-pentylperylene-3,4:9,10-bis(dicarboximide), $C_{34}H_{30}N_2O_4$, M_r = 530·6, triclinic, $P\bar{1}$, a = 4·754 (2), b = 8·479 (4), c = 16·296 (13) Å, α = 86·88 (5), β = 83·50 (5), γ = 83·68 (4)°, V = 648·10 Å^3, Z = 1, D_m = 1·34, D_x = 1·36 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 6·29 cm^{-1}, $F(000)$ = 280, T = 295 K, R = 6·6% for 1253 reflections, S = 1·45. (4): *N,N'*-Bis(3-ethoxypropyl)perylene-3,4:9,10-bis(dicarboximide), $C_{34}H_{30}N_2O_6$, M_r = 562·6, triclinic, $P\bar{1}$, a = 16·665 (5), b = 8·657 (5), c = 4·747 (2) Å, α = 98·86 (4), β = 89·08 (2), γ = 97·49 (3)°, V = 670·9 Å^3, Z = 1, D_m = 1·39, D_x = 1·39 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 6·91 cm^{-1}, $F(000)$ = 296, T = 295 K, R = 3·9% for 1616 reflections, S = 1·62. (5): *N,N'*-Bis(2-phenylpropyl)perylene-3,4:9,10-bis(dicarboximide), $C_{42}H_{30}N_2O_4$, M_r = 626·7, triclinic, $P\bar{1}$, a = 16·826 (12), b = 9·141 (10), c = 4·982 (8) Å, α = 94·38 (7), β = 89·57 (8), γ = 99·82 (9)°, V = 752·82 Å^3, Z = 1, D_m = 1·37, D_x = 1·38 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 6·24 cm^{-1}, $F(000)$ = 328, T = 295 K, R = 12·9% for 838 reflections, S = 2·05. (6): *N,N'*-Bis(2-phenylethyl)perylene-3,4:9,10-bis(dicarboximide), $C_{40}H_{26}N_2O_4$, M_r = 598·7, monoclinic, $C2/c$, a = 20·131 (5), b = 4·741 (3), c = 29·953 (6) Å, β = 103·35 (9)°, V = 2781·49 Å^3, Z = 4, D_m = 1·43, D_x = 1·43 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 6·53 cm^{-1}, $F(000)$ = 1248, T = 295 K, R = 6·1% for 1309 reflections, S = 1·51. (7): *N,N'*-Bis(2-methylbutyl)perylene-3,4:9,10-bis(dicarboximide), $C_{34}H_{30}N_2O_4$, M_r = 530·6, monoclinic, $P2_1/c$, a = 8·157 (4), b = 25·358 (5), c = 8·789 (4) Å, β = 135·05 (10)°, V = 1284·4 Å^3, Z = 2, D_m = 1·35, D_x = 1·37 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 6·35 cm^{-1}, $F(000)$ = 560, T = 295 K, R = 6·4% for 1251 reflections, S = 2·21. (8): *N,N'*-Di-*n*-butylperylene-3,4:9,10-bis(dicarboximide), $C_{32}H_{26}N_2O_4$, M_r = 502·6, monoclinic, $P2_1/c$, a = 4·734 (1), b = 28·233 (4), c = 9·396 (1) Å, β = 110·86 (1)°, V = 1173·51 Å^3, Z = 2, D_m = 1·43, D_x = 1·42 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 7·18 cm^{-1}, $F(000)$ = 528, T = 295 K, R = 7·1% for 978 reflections. (9): *N,N'*-Dimethylperylene-3,4:9,10-bis(dicarboximide), $C_{26}H_{14}N_2O_4$, M_r = 418·4, monoclinic, $P2_1/c$, a = 3·874 (1), b = 15·580 (2), c = 14·597 (2) Å, β = 97·65 (2)°, V = 873·19 Å^3, Z = 2, D_m = 1·62, D_x = 1·59 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 7·90 cm^{-1}, $F(000)$ = 428, T = 295 K, R = 10·8% for 736 reflections, S = 3·11. (10): *N,N'*-Bis(4-methoxybenzyl)perylene-3,4:9,10-bis(dicarboximide), $C_{40}H_{26}N_2O_6$, M_r = 630·7, triclinic, $P\bar{1}$, a = 4·390 (1), b = 9·709 (2), c = 17·107 (5) Å, α = 98·82 (2), β = 91·07 (2), γ = 101·58 (2)°, V = 704·9 Å^3, Z = 1, D_x = 1·49 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 7·76 cm^{-1}, $F(000)$ = 328, T = 295 K, R = 4·8% for 1476 reflections, S = 1·41. (11): *N,N'*-Dibenzylperylene-3,4:9,10-bis(dicarboximide), $C_{38}H_{22}N_2O_4$, M_r = 570·6, monoclinic, $P2_1/c$, a = 16·783 (3), b = 4·746 (1), c = 34·927 (5) Å, β = 109·76 (1)°, V = 2618·19 Å^3, Z = 4, D_x = 1·50 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 7·84 cm^{-1}, $F(000)$ = 1184, T = 295 K, R = 14·1% for 1461 reflections, S = 1·99. All compounds were synthesized as part of a programme to develop new pigments. As the colours of the crystals show no correlation to the colours and the structures of the single molecules, the crystal packings were analysed. All the molecules have a flat perylenetetracarboxylic diimide portion with bent side chains. They pack in stacks. The mutual arrangement of neighbours in the stacks is dependent on the different substituents which determine the longitudinal and transverse shifting of the perylene π systems. The mutual exchange of the π electrons of neighbours in the stack is responsible for the different colours of the crystals.

Introduction. The structures of the compounds reported here have been determined as part of an investigation into a possible correlation between molecular packing

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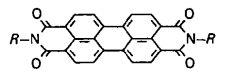
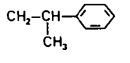
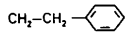
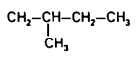
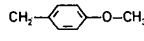
and colour of pigments (Graser & Hädicke, 1980, 1984).



	R	Colour of crystals
(1)	$CH_2-CH_2-O-CH_2-CH_3$	red
(2)	$CH_2-CH_2-CH_2-O-CH_3$	black
(3)	$CH_2-CH_2-CH_2-CH_2-CH_3$	red
(4)	$CH_2-CH_2-CH_2-O-CH_2-CH_3$	red
(5)		red
(6)		black
(7)		red
(8)	$CH_2-CH_2-CH_2-CH_3$	red-maroon
(9)	CH_3	red
(10)		black
(11)		red-violet

Experimental. Compounds (1) to (9) were recrystallized from nitrobenzene, (10) and (11) from *m*-cresol. Densities measured with a pycnometer. Crystal sizes: (1) 0·42 × 0·10 × 0·01 mm, (2) 0·55 × 0·20 × 0·06 mm, (3) 0·14 × 0·05 × 0·01 mm, (4) 0·37 × 0·27 × 0·06 mm, (5) 0·60 × 0·10 × 0·01 mm, (6) 0·48 × 0·08 × 0·02 mm, (7) 0·60 × 0·12 × 0·06 mm, (8) 0·35 × 0·04 × 0·02 mm, (9) 0·20 × 0·05 × 0·01 mm, (10) 1·70 × 0·05 × 0·03 mm and (11) 0·23 × 0·05 × 0·03 mm. Siemens AED diffractometer with Ni filter for (2), (4), (5), (6) and (7); $\theta/2\theta$ data collection; scan width 1·1–1·75°; five-value technique; scan rate 1–10° min^{-1} for (2), (4) and (7), 0·05–10° min^{-1} for (5) and (6). Syntex $P2_1$ diffractometer with graphite monochromator for other structures; $\theta/2\theta$ data collection; scan width 2·8° for (1), 1·8° (reflection) and 1·0° (background) for (3), 3·2° for (8), (9), (10) and (11). For structures (1), (8), (9), (10) and (11) the measurements with differential scans were analysed according to an algorithm of Lehmann & Larsen (1974) (see also Blessing, Coppens & Becker, 1974) by the program *LAUSANNE* (Schwarzenbach, 1977); scan rates for (1) 2–10° min^{-1}, for (3), (10) and (11) 1–30° min^{-1}, for (8) and (9) 0·5–30° min^{-1}. Lattice parameters were measured with 20 to 25 reflections up to 26° in θ for Mo and 46° for Cu radiation. $(\sin\theta/\lambda)_{max} = 0{\cdot}704$ $Å^{-1}$ for (1), 0·613 $Å^{-1}$ for (2), (4), (5), (6) and (7), 0·547 $Å^{-1}$ for (3), (8), (9), (10) and (11). Range of *hkl*: $+h \pm k \pm l$ for (1), (3) and (10); $\pm h \pm k + l$ for (2), (4) and (5); $\pm h + k + l$ for (6), (7) and (8); $+h + k \pm l$ for (9) and (11). Standard reflections: 1 standard reflection for each measurement [$12\bar{1}$ for (1), 112 for (3), $13\bar{2}$ for (8), 002 for (9), $01\bar{2}$ for (10) and 004 for (11)], monitored every 36 reflections for (1), every 20 reflections for (2), (4), (5), (6) and (7), every 50 reflections for (3) and every 26 reflections for (8), (9), (10) and (11) with intensity variations (1) 2·7, (2) 7·7, (3) 6·4, (4) 4·7, (5) 8·2, (6) 3·7, (7) 5·8, (8) 7·9, (9) 6·2, (10) 4 and (11) 8·4%. Corrections for Lorentz and polarization. Only (8) was corrected for absorption; 48 reflections give here (400 ω scans of equivalent reflections) $R_{merge} = 6{\cdot}0\%$ before correction and $R_{merge} = 4{\cdot}6\%$ after correction with $\mu r = 0{\cdot}14$ (ellipsoid estimated), max. transmission factor 0·826 and min. 0·519 (all measurements). For (1): 3674 reflections measured, 3563 unique ($R_{int} = 0{\cdot}004$), 2729 unobserved [criterion $4\sigma(F)$]; for (2): 1607 reflections measured and unique, 325 unobserved [criterion $4\sigma(F)$ and $\bar{7}30$, 18,$\bar{4}$,2, $\bar{1}0$,7,3, $\bar{9}$,10,1, 9,$\bar{1}1$,3]; for (3): 2480 reflections measured, 2124 unique ($R_{int} = 0{\cdot}01$), 871 unobserved [criterion $3\sigma(F)$ and $\bar{4}5\bar{7}$, 1,5,17, $\bar{4}5\bar{8}$, 1,4,18]; for (4): 1899 reflections measured and unique, 283 unobserved [criterion $4\sigma(F)$]; for (5): 2904 reflections measured and unique, 2066 unobserved [criterion $2\sigma(F)$ and $\bar{1}3,\bar{4},3$]; for (6): 2680 reflections measured and unique, 1371 unobserved [criterion $3\sigma(F)$ and $\bar{1}7,3,12$, $\bar{7},3,25$, $\bar{1}7,1,26$, $\bar{3}53$]; for (7): 1751 reflections measured and unique, 500 unobserved [criterion $4\sigma(F)$ and 110, 040]; for (8): 1739 reflections measured, 1531 unique ($R_{int} = 0{\cdot}016$), 553 unobserved [criterion $3\sigma(F)$]; for (9): 1306 reflections measured, 1117 unique ($R_{int} = 0{\cdot}015$), 381 unobserved [criterion $3\sigma(F)$]; for (10): 1743 reflections measured and unique, 267 unobserved [criterion $2\sigma(F)$]; for (11): 3522 reflections measured, 3407 unique ($R_{int} = 0{\cdot}031$), 1946 unobserved [criterion $3\sigma(F)$].

All structures were solved by direct methods using the program *MULTAN*74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) on a Honeywell Bull 6060 computer [structures (2), (3), (4) and (7)] or the program *SHELXTL* (Sheldrick, 1978) on a Data General Eclipse S/200 minicomputer (remaining structures). In the asymmetric units of structures (1)–(10) there is half a molecule with an inversion centre at the middle of the compound. In (11) the single molecule has no symmetry element. With the program *SHELXTL* the refinement was carried out with a block-cascade algorithm. H atoms initially placed at calculated positions were constrained to give C—H 0·96 Å, H—C—H 109·5°, rigid CH_3 groups, riding CH_2 and CH groups with equal C—C—H angles. For C, N, and O atoms anisotropic thermal parameters were refined and for the H atoms the refinement of isotropic thermal parameters was carried out in correlated groups. In all cases the function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights w are calculated based on counting statistics with a term g included for random error:

$w = [\sigma^2(F) + gF^2]^{-1}$ [g for: (1) 0·00015, (2) 0·0009, (3) 0·0005, (4) 0·0007, (5) 0·002, (6) 0·00025, (7) 0·00055, (8) 0·0007, (9) 0·0005, (10) 0·00072 and (11) 0·00075]. For structures (9), (10) and (11) the extinctions were corrected with an empirical isotropic extinction parameter x, where the calculated structure factor becomes $F_c' = F_c/(1 + xF^2/\sin 2\theta)^{1/4}$ [x for: (9) 20 (8) $\times 10^{-6}$, (10) 20 (4) $\times 10^{-6}$ and (11) 11 (6) $\times 10^{-7}$]. Convergences were achieved and a weighting scheme was applied to obtain a flat variance in terms of $\sin\theta$ and the magnitude of F_o. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). (1) $R = 11{\cdot}7\%$, $wR = 7{\cdot}4\%$ for 834 reflections, (2) $R = 4{\cdot}9\%$, $wR = 5{\cdot}2\%$ for 1282 reflections, (3) $R = 6{\cdot}6\%$, $wR = 6{\cdot}3\%$ for 1253 reflections, (4) $R = 3{\cdot}9\%$, $wR = 4{\cdot}2\%$ for 1616 reflections, (5) $R = 12{\cdot}9\%$, $wR = 13{\cdot}3\%$ for 838 reflections, (6) $R = 6{\cdot}1\%$, $wR = 5{\cdot}3\%$ for 1309 reflections (7) $R = 6{\cdot}4\%$, $wR = 7{\cdot}0\%$ for 1251 reflections, (8) $R = 7{\cdot}1\%$, $wR = 6{\cdot}1\%$ for 978 reflections, (9) $R = 10{\cdot}8\%$, $wR = 9{\cdot}8\%$ for 736 reflections, (10) $R = 4{\cdot}8\%$, $wR = 5{\cdot}3\%$ for 1476 reflections and (11) $R = 14{\cdot}1\%$, $wR = 12{\cdot}5\%$ for 1461 reflections. $(\Delta/\sigma)_{max}$ in final refinement cycle: (1) 0·02, (2) 0·13, (3) 0·24, (4) 0·02, (5) 0·07, (6) 0·02, (7) 0·21, (8) 0·05, (9) 0·05, (10) 0·03 and (11) 0·01. Max. height in final difference Fourier synthesis: (1) 0·60, (2) 0·14, (3) 0·20, (4) 0·14, (5) 0·38, (6) 0·21, (7) 0·32, (8) 0·30, (9) 0·47, (10) 0·15 and (11) 0·51 e Å^{-3}.

The growing of crystals was very difficult and as a result crystals of compounds (1), (5), (9) and (11) were of an unsatisfactory quality. With the measured data of these compounds we could only achieve a rather poor fit.

Discussion. Tables 1–22 list final refined coordinates, U_{eq} values for the non-hydrogen atoms and the bond lengths in molecules (1)–(11).* The atomic numbering schemes for all compounds are similar. H atoms are given the number of the C atoms to which they are attached. By way of example, Fig. 1 shows the molecular structure of (1).

The flat portions of neighbouring molecules are 3·345–3·476 Å (with e.s.d.'s of 0·003–0·029 Å) apart and pack in stacks. This packing is illustrated in Figs. 2 and 3 for structures (1) and (7).

The molecules show a flat perylenetetracarboxylic diimide part with bent side chains. The phenyl rings of the side chains of compounds (5), (6) and (10) are turned 13·5 (25), 19·0 (7) and 70·7 (6)° out of the plane of the perylene-imide ring systems.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles for the eleven compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42364 (254 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Structure* (1): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

For structures (1)–(10): $U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
O(1)	5903 (12)	−1068 (7)	3377 (4)	50 (4)
O(2)	9962 (13)	−4635 (7)	1371 (4)	52 (4)
O(3)	7932 (15)	−6101 (9)	3329 (4)	74 (5)
N(1)	7894 (14)	−2911 (8)	2396 (4)	36 (4)
C(1)	−87 (19)	653 (10)	861 (5)	30 (5)
C(2)	1927 (17)	−716 (10)	591 (6)	28 (5)
C(3)	2134 (16)	−1397 (10)	−255 (5)	23 (5)
C(4)	4251 (15)	−2624 (9)	−466 (5)	30 (5)
C(5)	6182 (15)	−3300 (9)	136 (5)	32 (5)
C(6)	6008 (16)	−2716 (10)	953 (5)	32 (5)
C(7)	3905 (16)	−1399 (9)	1175 (6)	34 (5)
C(8)	3918 (17)	−821 (11)	2012 (6)	40 (6)
C(9)	2014 (18)	486 (10)	2249 (5)	41 (6)
C(10)	56 (17)	1218 (9)	1671 (5)	35 (5)
C(11)	5959 (17)	−1572 (10)	2651 (6)	37 (6)
C(12)	8125 (17)	−3510 (11)	1556 (6)	37 (6)
C(13)	9817 (18)	−3665 (11)	3039 (5)	49 (5)
C(14)	8438 (22)	−4738 (12)	3719 (6)	66 (7)
C(15)	6334 (27)	−7124 (15)	3909 (8)	101 (10)
C(16)	7973 (29)	−8043 (15)	4581 (8)	119 (10)

Table 2. *Structure* (1): *bond lengths* (Å)

O(1)–C(11)	1·215 (11)	O(2)–C(12)	1·215 (10)
O(3)–C(14)	1·377 (13)	O(3)–C(15)	1·456 (14)
N(1)–C(11)	1·391 (10)	N(1)–C(12)	1·405 (11)
N(1)–C(13)	1·457 (10)	C(1)–C(2)	1·435 (13)
C(1)–C(3')	1·454 (11)	C(1)–C(10)	1·371 (11)
C(2)–C(3)	1·442 (12)	C(2)–C(7)	1·396 (12)
C(3)–C(4)	1·361 (10)	C(4)–C(5)	1·398 (11)
C(5)–C(6)	1·368 (11)	C(6)–C(7)	1·410 (10)
C(6)–C(12)	1·486 (11)	C(7)–C(8)	1·403 (13)
C(8)–C(9)	1·356 (11)	C(8)–C(11)	1·488 (12)
C(9)–C(10)	1·393 (11)	C(13)–C(14)	1·515 (13)
C(15)–C(16)	1·458 (17)		

Table 3. *Structure* (2): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	3479 (1)	1596 (2)	6714 (4)	61 (1)
O(2)	1408 (1)	−3587 (2)	5670 (4)	66 (1)
O(3)	3803 (1)	−3705 (2)	7817 (5)	75 (1)
N(1)	2417 (1)	−964 (2)	6353 (4)	42 (1)
C(1)	887 (1)	1305 (2)	1097 (4)	36 (1)
C(2)	613 (1)	−238 (2)	1586 (4)	35 (1)
C(3)	−259 (1)	−1553 (2)	558 (4)	36 (1)
C(4)	−488 (1)	−3009 (2)	1173 (5)	43 (1)
C(5)	112 (1)	−3235 (3)	2722 (5)	45 (1)
C(6)	957 (1)	−1999 (2)	3700 (5)	38 (1)
C(7)	1216 (1)	−477 (2)	3184 (4)	34 (1)
C(8)	2082 (1)	809 (2)	4238 (5)	40 (1)
C(9)	2326 (1)	2286 (3)	3748 (5)	47 (1)
C(10)	1739 (1)	2535 (3)	2207 (5)	46 (1)
C(11)	2713 (1)	547 (3)	5857 (5)	43 (1)
C(12)	1584 (1)	−2281 (3)	5302 (5)	44 (1)
C(13)	3058 (1)	−1254 (3)	7887 (5)	49 (1)
C(14)	3724 (2)	−1801 (3)	5718 (6)	58 (1)
C(15)	4330 (2)	−2245 (3)	7163 (6)	61 (1)
C(16)	4354 (2)	−4258 (4)	8962 (7)	90 (2)

Table 4. *Structure* (2): *bond lengths* (Å)

O(1)–C(11)	1·218 (2)	O(2)–C(12)	1·205 (3)
O(3)–C(15)	1·384 (3)	O(3)–C(16)	1·416 (5)
N(1)–C(11)	1·385 (3)	N(1)–C(12)	1·392 (2)
N(1)–C(13)	1·477 (4)	C(1)–C(2)	1·416 (3)
C(1)–C(3')	1·473 (3)	C(1)–C(10)	1·390 (2)
C(2)–C(3)	1·429 (2)	C(2)–C(7)	1·418 (3)
C(3)–C(4)	1·377 (3)	C(4)–C(5)	1·392 (4)
C(5)–C(6)	1·370 (2)	C(6)–C(7)	1·407 (3)
C(6)–C(12)	1·475 (4)	C(7)–C(8)	1·416 (2)
C(8)–C(9)	1·365 (4)	C(8)–C(11)	1·474 (4)
C(9)–C(10)	1·385 (4)	C(13)–C(14)	1·512 (4)
C(14)–C(15)	1·501 (5)		

Table 5. *Structure* (3): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	−10349 (6)	4494 (3)	1268 (2)	63 (2)
O(2)	−7814 (6)	766 (3)	3218 (2)	72 (2)
N(1)	−9101 (6)	2631 (3)	2241 (2)	50 (2)
C(1)	−1908 (7)	1341 (3)	−253 (2)	40 (2)
C(2)	−2293 (7)	656 (4)	564 (2)	40 (2)
C(3)	−477 (7)	−680 (4)	825 (2)	40 (2)
C(4)	−1021 (8)	−1308 (4)	1621 (2)	50 (2)
C(5)	−3275 (8)	−664 (4)	2163 (2)	51 (2)
C(6)	−5034 (7)	625 (4)	1927 (2)	45 (2)
C(7)	−4600 (7)	1296 (3)	1120 (2)	39 (2)
C(8)	−6452 (7)	2607 (3)	867 (2)	41 (2)
C(9)	−6061 (8)	3233 (4)	74 (2)	44 (2)
C(10)	−3812 (7)	2620 (4)	−479 (2)	44 (2)
C(11)	−8774 (8)	3325 (4)	1450 (2)	49 (2)
C(12)	−7379 (8)	1309 (4)	2518 (2)	53 (2)
C(13)	−11258 (8)	3421 (4)	2849 (2)	57 (2)
C(14)	−9999 (8)	4702 (4)	3266 (2)	60 (2)
C(15)	−12194 (8)	5731 (4)	3802 (2)	61 (2)
C(16)	−10893 (10)	7005 (5)	4207 (3)	76 (3)
C(17)	−13043 (12)	8105 (5)	4719 (3)	104 (3)

Table 6. *Structure* (3): *bond lengths* (Å)

O(1)–C(11)	1·219 (4)	O(2)–C(12)	1·212 (4)
N(1)–C(11)	1·386 (5)	N(1)–C(12)	1·399 (5)
N(1)–C(13)	1·474 (4)	C(1)–C(2)	1·423 (4)
C(1)–C(3′)	1·465 (4)	C(1)–C(10)	1·396 (4)
C(2)–C(3)	1·424 (4)	C(2)–C(7)	1·420 (4)
C(3)–C(4)	1·382 (5)	C(4)–C(5)	1·391 (5)
C(5)–C(6)	1·367 (4)	C(6)–C(7)	1·405 (4)
C(6)–C(12)	1·477 (5)	C(7)–C(8)	1·414 (4)
C(8)–C(9)	1·370 (5)	C(8)–C(11)	1·473 (5)
C(9)–C(10)	1·391 (4)	C(13)–C(14)	1·522 (6)
C(14)–C(15)	1·514 (5)	C(15)–C(16)	1·517 (6)
C(16)–C(17)	1·514 (6)		

Table 7. *Structure* (4): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	3171 (1)	−327 (2)	−6570 (3)	61 (1)
O(2)	1232 (1)	−4251 (1)	−10178 (3)	56 (1)
O(3)	3926 (1)	−6297 (1)	−10817 (3)	54 (1)
N(1)	2189 (1)	−2247 (2)	−8449 (3)	40 (1)
C(1)	814 (1)	802 (2)	−119 (3)	33 (1)
C(2)	553 (1)	−563 (2)	−2124 (3)	31 (1)
C(3)	−248 (1)	−1388 (2)	−2070 (3)	32 (1)
C(4)	−461 (1)	−2705 (2)	−4091 (3)	38 (1)
C(5)	78 (1)	−3239 (2)	−6159 (3)	38 (1)
C(6)	851 (1)	−2468 (2)	−6248 (3)	35 (1)
C(7)	1099 (1)	−1121 (2)	−4238 (3)	33 (1)
C(8)	1894 (1)	−334 (2)	−4322 (3)	37 (1)
C(9)	2136 (1)	980 (2)	−2359 (4)	42 (1)
C(10)	1600 (1)	1539 (2)	−296 (3)	41 (1)
C(11)	2476 (1)	−928 (2)	−6478 (3)	41 (1)
C(12)	1413 (1)	−3072 (2)	−8443 (3)	39 (1)
C(13)	2759 (1)	−2900 (2)	−10573 (4)	45 (1)
C(14)	3144 (1)	−4205 (2)	−9561 (4)	48 (1)
C(15)	3631 (1)	−5044 (2)	−11855 (4)	53 (1)
C(16)	4463 (1)	−7052 (2)	−12748 (5)	63 (1)
C(17)	4711 (1)	−8418 (3)	−11545 (6)	80 (1)

Table 8. *Structure* (4): *bond lengths* (Å)

O(1)–C(11)	1·210 (2)	O(2)–C(12)	1·217 (2)
O(3)–C(15)	1·405 (2)	O(3)–C(16)	1·418 (2)
N(1)–C(11)	1·397 (2)	N(1)–C(12)	1·393 (2)
N(1)–C(13)	1·474 (2)	C(1)–C(2)	1·423 (2)
C(1)–C(3′)	1·469 (2)	C(1)–C(10)	1·386 (2)
C(2)–C(3)	1·432 (2)	C(2)–C(7)	1·416 (2)
C(3)–C(4)	1·383 (2)	C(4)–C(5)	1·387 (2)
C(5)–C(6)	1·375 (2)	C(6)–C(7)	1·409 (2)
C(6)–C(12)	1·471 (2)	C(7)–C(8)	1·411 (2)
C(8)–C(9)	1·375 (2)	C(8)–C(11)	1·479 (2)
C(9)–C(10)	1·389 (2)	C(13)–C(14)	1·512 (3)
C(14)–C(15)	1·500 (2)	C(16)–C(17)	1·496 (3)

Table 9. *Structure* (5): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	−1492 (5)	5674 (9)	1361 (21)	87 (5)
O(2)	−2626 (5)	2589 (9)	−5587 (19)	89 (6)
N(1)	−2060 (6)	4155 (10)	−2110 (20)	67 (6)
C(1)	49 (7)	1392 (13)	1578 (30)	68 (7)
C(2)	−535 (7)	1024 (12)	−473 (27)	56 (7)
C(3)	−625 (7)	−378 (13)	−2103 (25)	57 (7)
C(4)	−1206 (7)	−685 (14)	−4094 (29)	75 (9)
C(5)	−1705 (8)	328 (15)	−4534 (30)	84 (9)
C(6)	−1650 (7)	1673 (15)	−3001 (30)	70 (9)
C(7)	−1066 (7)	2030 (12)	−1043 (28)	59 (7)
C(8)	−988 (8)	3432 (13)	507 (33)	72 (9)
C(9)	−426 (9)	3739 (15)	2491 (37)	105 (10)
C(10)	111 (8)	2781 (13)	3054 (29)	79 (9)
C(11)	−1548 (7)	4426 (12)	118 (22)	52 (7)
C(12)	−2160 (8)	2796 (14)	−3643 (32)	86 (9)
C(13)	−2531 (8)	5315 (14)	−2894 (34)	85 (9)
C(14)	−3242 (8)	5387 (14)	−942 (35)	87 (9)
C(15)	−3864 (9)	4024 (17)	−900 (43)	149 (15)
C(16)	−3597 (7)	6798 (13)	−1478 (31)	73 (8)
C(17)	−3290 (10)	8069 (17)	83 (36)	110 (11)
C(18)	−3593 (12)	9387 (19)	−364 (47)	144 (15)
C(19)	−4141 (10)	9434 (19)	−2261 (44)	115 (12)
C(20)	−4405 (11)	8194 (19)	−3859 (44)	138 (15)
C(21)	−4136 (10)	6841 (17)	−3371 (41)	130 (12)

Table 10. *Structure* (5): *bond lengths* (Å)

O(1)–C(11)	1·245 (14)	O(2)–C(12)	1·233 (17)
N(1)–C(11)	1·391 (15)	N(1)–C(12)	1·393 (16)
N(1)–C(13)	1·504 (18)	C(1)–C(2)	1·404 (18)
C(1)–C(3′)	1·488 (18)	C(1)–C(10)	1·406 (17)
C(2)–C(3)	1·450 (16)	C(2)–C(7)	1·431 (17)
C(3)–C(4)	1·378 (18)	C(4)–C(5)	1·382 (20)
C(5)–C(6)	1·387 (19)	C(6)–C(7)	1·372 (18)
C(6)–C(12)	1·499 (20)	C(7)–C(8)	1·432 (17)
C(8)–C(9)	1·353 (22)	C(8)–C(11)	1·440 (19)
C(9)–C(10)	1·405 (21)	C(13)–C(14)	1·542 (21)
C(14)–C(15)	1·486 (18)	C(14)–C(16)	1·552 (19)
C(16)–C(17)	1·373 (19)	C(16)–C(21)	1·320 (23)
C(17)–C(18)	1·419 (26)	C(18)–C(19)	1·333 (30)
C(19)–C(20)	1·346 (25)	C(20)–C(21)	1·425 (25)

Table 11. *Structure* (6): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	3552 (1)	11051 (7)	1529 (1)	70 (2)
O(2)	5028 (1)	9967 (7)	601 (1)	69 (2)
N(1)	4275 (1)	10601 (7)	1052 (1)	47 (2)
C(1)	2331 (2)	3764 (8)	400 (1)	38 (2)
C(2)	2946 (2)	4537 (8)	266 (1)	38 (2)
C(3)	3126 (2)	3322 (8)	−126 (1)	40 (2)
C(4)	3729 (2)	4163 (9)	−237 (1)	48 (2)
C(5)	4156 (2)	6168 (9)	22 (1)	51 (2)
C(6)	3999 (2)	7331 (9)	401 (1)	45 (2)
C(7)	3392 (2)	6554 (8)	529 (1)	39 (2)
C(8)	3229 (2)	7778 (8)	919 (1)	43 (2)
C(9)	2634 (2)	6993 (9)	1045 (1)	52 (2)
C(10)	2194 (2)	5041 (9)	783 (1)	49 (2)
C(11)	3676 (2)	9922 (9)	1194 (1)	52 (2)
C(12)	4477 (2)	9345 (9)	680 (1)	50 (2)
C(13)	4743 (2)	12679 (9)	1326 (1)	56 (2)
C(14)	5311 (2)	11275 (9)	1680 (1)	58 (2)
C(15)	5841 (2)	13368 (9)	1907 (1)	47 (2)
C(16)	5896 (2)	14240 (11)	2349 (2)	71 (3)
C(17)	6366 (2)	16214 (13)	2550 (2)	92 (3)
C(18)	6797 (2)	17353 (11)	2309 (2)	85 (3)
C(19)	6768 (2)	16500 (11)	1871 (2)	76 (3)
C(20)	6287 (2)	14549 (10)	1668 (2)	60 (2)

Table 12. *Structure* (6): *bond lengths* (Å)

O(1)–C(11)	1·212 (5)	O(2)–C(12)	1·223 (5)
N(1)–C(11)	1·405 (5)	N(1)–C(12)	1·405 (5)
N(1)–C(13)	1·473 (5)	C(1)–C(2)	1·434 (5)
C(1)–C(3′)	1·465 (5)	C(1)–C(10)	1·380 (5)
C(2)–C(3)	1·428 (5)	C(2)–C(7)	1·420 (5)
C(3)–C(4)	1·390 (5)	C(4)–C(5)	1·393 (5)
C(5)–C(6)	1·364 (6)	C(6)–C(7)	1·410 (5)
C(6)–C(12)	1·471 (5)	C(7)–C(8)	1·409 (5)
C(8)–C(9)	1·386 (5)	C(8)–C(11)	1·477 (5)
C(9)–C(10)	1·391 (5)	C(13)–C(14)	1·523 (5)
C(14)–C(15)	1·499 (5)	C(15)–C(16)	1·367 (6)
C(15)–C(20)	1·387 (6)	C(16)–C(17)	1·367 (7)
C(17)–C(18)	1·361 (8)	C(18)–C(19)	1·361 (7)
C(19)–C(20)	1·376 (6)		

Table 13. *Structure* (7): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	6085 (5)	1614 (1)	7252 (5)	92 (2)
O(2)	10129 (4)	686 (1)	6398 (5)	85 (2)
N(1)	8093 (5)	1167 (1)	6772 (5)	64 (2)
C(1)	−86 (5)	410 (1)	1086 (5)	54 (2)
C(2)	2051 (5)	293 (1)	1718 (5)	53 (2)
C(3)	2162 (5)	−115 (1)	661 (5)	54 (2)
C(4)	4285 (6)	−212 (1)	1380 (6)	61 (2)
C(5)	6260 (6)	76 (1)	3036 (6)	65 (2)
C(6)	6165 (6)	472 (1)	4034 (6)	59 (2)
C(7)	4054 (6)	588 (1)	3403 (5)	54 (2)
C(8)	3970 (6)	982 (1)	4447 (5)	60 (2)
C(9)	1931 (6)	1087 (1)	3847 (6)	68 (2)
C(10)	−59 (6)	804 (1)	2195 (6)	66 (2)
C(11)	6065 (6)	1280 (1)	6230 (6)	65 (2)
C(12)	8267 (6)	772 (1)	5789 (6)	65 (2)
C(13)	10243 (7)	1449 (2)	8600 (6)	74 (2)
C(14)	10849 (9)	1901 (2)	7867 (9)	110 (3)
C(15)	9201 (12)	2347 (3)	6793 (12)	165 (5)
C(16)	13376 (11)	2084 (2)	9943 (11)	151 (5)
C(17)	15218 (11)	1680 (3)	10697 (12)	164 (5)

Table 14. *Structure* (7): *bond lengths* (Å)

O(1)–C(11)	1·225 (7)	O(2)–C(12)	1·220 (6)
N(1)–C(11)	1·390 (7)	N(1)–C(12)	1·394 (6)
N(1)–C(13)	1·476 (4)	C(1)–C(2)	1·437 (7)
C(1)–C(3′)	1·452 (4)	C(1)–C(10)	1·384 (7)
C(2)–C(3)	1·435 (6)	C(2)–C(7)	1·413 (4)
C(3)–C(4)	1·382 (7)	C(4)–C(5)	1·389 (4)
C(5)–C(6)	1·372 (7)	C(6)–C(7)	1·416 (7)
C(6)–C(12)	1·468 (4)	C(7)–C(8)	1·391 (7)
C(8)–C(9)	1·369 (7)	C(8)–C(11)	1·469 (4)
C(9)–C(10)	1·386 (4)	C(13)–C(14)	1·557 (9)
C(14)–C(15)	1·478 (8)	C(14)–C(16)	1·572 (7)
C(16)–C(17)	1·528 (12)		

Table 15. *Structure* (8): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	−6326 (7)	1815 (1)	762 (3)	55 (2)
O(2)	−5840 (7)	736 (1)	4420 (3)	55 (2)
N(1)	−6032 (8)	1281 (1)	2612 (4)	40 (2)
C(1)	−920 (9)	460 (1)	−672 (4)	36 (2)
C(2)	−1538 (9)	322 (1)	640 (4)	34 (2)
C(3)	−639 (8)	−132 (1)	1340 (4)	34 (2)
C(4)	−1333 (9)	−246 (1)	2621 (4)	38 (2)
C(5)	−2819 (9)	66 (1)	3241 (4)	37 (2)
C(6)	−3702 (9)	505 (1)	2606 (4)	34 (2)
C(7)	−3055 (9)	640 (1)	1296 (4)	31 (2)
C(8)	−3954 (9)	1088 (1)	648 (4)	36 (2)
C(9)	−3320 (10)	1217 (1)	−629 (5)	44 (2)
C(10)	−1863 (10)	906 (1)	−1279 (4)	43 (2)
C(11)	−5504 (9)	1423 (1)	1293 (4)	39 (2)
C(12)	−5263 (9)	837 (1)	3282 (5)	40 (2)
C(13)	−7549 (10)	1626 (1)	3282 (5)	48 (3)
C(14)	−5349 (12)	1993 (2)	4283 (5)	61 (3)
C(15)	−3144 (12)	1797 (2)	5710 (5)	68 (3)
C(16)	−1041 (13)	2176 (2)	6704 (6)	83 (4)

Table 16. *Structure* (8): *bond lengths* (Å)

O(1)–C(11)	1·220 (5)	O(2)–C(12)	1·227 (6)
N(1)–C(11)	1·407 (6)	N(1)–C(12)	1·391 (5)
N(1)–C(13)	1·477 (6)	C(1)–C(2)	1·419 (6)
C(1)–C(3′)	1·459 (6)	C(1)–C(10)	1·390 (5)
C(2)–C(3)	1·434 (5)	C(2)–C(7)	1·421 (6)
C(3)–C(4)	1·394 (6)	C(4)–C(5)	1·380 (6)
C(5)–C(6)	1·374 (5)	C(6)–C(7)	1·422 (6)
C(6)–C(12)	1·471 (6)	C(7)–C(8)	1·402 (5)
C(8)–C(9)	1·385 (7)	C(8)–C(11)	1·456 (6)
C(9)–C(10)	1·385 (7)	C(13)–C(14)	1·531 (6)
C(14)–C(15)	1·482 (6)	C(15)–C(16)	1·530 (7)

Table 17. *Structure* (9): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	−5107 (16)	3015 (3)	2129 (4)	55 (4)
O(2)	−1281 (17)	3882 (4)	−517 (4)	65 (4)
N(1)	−2954 (18)	3453 (4)	844 (4)	45 (4)
C(1)	−1276 (19)	208 (4)	844 (5)	33 (5)
C(2)	−743 (19)	867 (5)	210 (5)	32 (5)
C(3)	586 (20)	686 (4)	−638 (5)	30 (5)
C(4)	993 (21)	1352 (4)	−1222 (5)	40 (5)
C(5)	317 (21)	2207 (5)	−1016 (5)	40 (5)
C(6)	−931 (22)	2389 (5)	−206 (5)	42 (6)
C(7)	−1496 (22)	1721 (4)	431 (5)	38 (5)
C(8)	−2811 (21)	1937 (4)	1258 (5)	35 (5)
C(9)	−3351 (20)	1298 (5)	1863 (5)	38 (5)
C(10)	−2528 (25)	454 (5)	1662 (5)	55 (6)
C(11)	−3714 (23)	2826 (5)	1458 (6)	46 (5)
C(12)	−1704 (23)	3286 (5)	−1 (6)	47 (5)
C(13)	−3678 (26)	4373 (5)	1080 (6)	60 (6)

Table 18. *Structure* (9): *bond lengths* (Å)

O(1)–C(11)	1·216 (11)	O(2)–C(12)	1·220 (10)
N(1)–C(11)	1·384 (10)	N(1)–C(12)	1·408 (11)
N(1)–C(13)	1·509 (10)	C(1)–C(2)	1·417 (10)
C(1)–C(3′)	1·457 (10)	C(1)–C(10)	1·401 (11)
C(2)–C(3)	1·430 (10)	C(2)–C(7)	1·408 (10)
C(3)–C(4)	1·365 (10)	C(4)–C(5)	1·399 (10)
C(5)–C(6)	1·365 (11)	C(6)–C(7)	1·433 (11)
C(6)–C(12)	1·468 (11)	C(7)–C(8)	1·411 (11)
C(8)–C(9)	1·365 (10)	C(8)–C(11)	1·468 (10)
C(9)–C(10)	1·394 (11)		

Table 19. *Structure* (10): *atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
O(1)	8490 (4)	1906 (2)	2998 (1)	69 (1)
O(2)	10516 (4)	5051 (2)	1269 (1)	68 (1)
O(3)	7094 (5)	8648 (2)	4642 (1)	74 (1)
N(1)	9545 (4)	3470 (2)	2129 (1)	50 (1)
C(1)	657 (5)	−407 (2)	751 (1)	42 (1)
C(2)	2409 (5)	870 (2)	536 (1)	41 (1)
C(3)	1830 (5)	1302 (2)	−204 (1)	43 (1)
C(4)	3634 (5)	2553 (2)	−379 (1)	50 (1)
C(5)	5977 (6)	3388 (3)	145 (1)	51 (1)
C(6)	6555 (5)	3008 (2)	865 (1)	45 (1)
C(7)	4795 (5)	1742 (2)	1068 (1)	43 (1)
C(8)	5428 (5)	1334 (2)	1802 (1)	45 (1)
C(9)	3713 (6)	96 (3)	1995 (1)	54 (1)
C(10)	1365 (5)	−757 (3)	1479 (1)	53 (1)
C(11)	7898 (6)	2225 (3)	2360 (2)	52 (1)
C(12)	9009 (5)	3925 (3)	1415 (1)	50 (1)
C(13)	11944 (6)	4422 (3)	2702 (2)	59 (1)
C(14)	10608 (5)	5523 (3)	3228 (1)	50 (1)
C(15)	9211 (6)	5233 (3)	3910 (1)	56 (1)
C(16)	8009 (6)	6238 (3)	4399 (2)	58 (1)
C(17)	8179 (5)	7578 (3)	4202 (1)	56 (1)
C(18)	9564 (7)	7881 (3)	3509 (2)	66 (1)
C(19)	10777 (6)	6874 (3)	3037 (2)	63 (1)
C(20)	5928 (7)	8438 (3)	5394 (2)	81 (1)

Table 20. *Structure* (10): *bond lengths* (Å)

O(1) C(11)	1·216 (4)	O(2)–C(12)	1·222 (4)
O(3) C(17)	1·358 (4)	O(3)–C(20)	1·422 (4)
N(1) C(11)	1·395 (4)	N(1)–C(12)	1·393 (4)
N(1) C(13)	1·489 (4)	C(1)–C(2)	1·425 (4)
C(1) C(3')	1·468 (4)	C(1)–C(10)	1·386 (4)
C(2) C(3)	1·427 (4)	C(2)–C(7)	1·420 (4)
C(3) C(4)	1·387 (4)	C(4) C(5)	1·387 (4)
C(5) C(6)	1·372 (4)	C(6)–C(7)	1·409 (4)
C(6) C(12)	1·470 (4)	C(7)–C(8)	1·413 (4)
C(8) C(9)	1·374 (4)	C(8)–C(11)	1·473 (4)
C(9) C(10)	1·388 (4)	C(13)–C(14)	1·509 (5)
C(14) C(15)	1·368 (4)	C(14)–C(19)	1·387 (5)
C(15) C(16)	1·380 (5)	C(16)–C(17)	1·381 (5)
C(17) C(18)	1·387 (5)	C(18)–C(19)	1·369 (5)

Table 21. *Structure* (11): *atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times 10^3$)

	x	*y*	*z*	*U*
O(1)	1732 (6)	−10166 (22)	880 (3)	62 (3)
O(2)	3647 (6)	−12282 (22)	2109 (3)	65 (3)
O(21)	8317 (6)	3038 (21)	1539 (3)	63 (3)
O(23)	6341 (5)	5477 (21)	338 (3)	62 (3)
N(1)	2683 (6)	−11149 (24)	1504 (3)	47 (3)
N(21)	7317 (7)	4293 (24)	941 (3)	45 (3)
C(1)	4174 (8)	−3830 (29)	930 (4)	39 (4)
C(2)	4433 (8)	−5358 (30)	1295 (4)	46 (4)
C(3)	5249 (8)	−5049 (30)	1599 (4)	38 (4)
C(4)	5421 (8)	−6657 (30)	1952 (4)	48 (4)
C(5)	4854 (8)	−8541 (30)	2018 (4)	47 (4)
C(6)	4074 (8)	−8905 (28)	1718 (4)	39 (4)
C(7)	3836 (8)	−7329 (31)	1356 (4)	40 (4)
C(8)	3038 (8)	−7706 (31)	1059 (4)	45 (4)
C(9)	2816 (9)	−6172 (31)	704 (4)	50 (4)
C(10)	3382 (8)	−4274 (30)	644 (4)	47 (4)
C(11)	2442 (9)	−9784 (31)	1137 (4)	50 (4)
C(12)	3489 (9)	−10877 (32)	1805 (4)	50 (4)
C(13)	2064 (8)	−13090 (31)	1587 (4)	53 (4)
C(14)	1575 (5)	−11609 (20)	1816 (2)	33 (4)
C(15)	913 (5)	−9799 (20)	1611 (2)	60 (5)
C(16)	450 (5)	−8455 (20)	1822 (2)	73 (5)
C(17)	648 (5)	−8922 (20)	2238 (2)	64 (5)
C(18)	1309 (5)	−10732 (20)	2443 (2)	66 (5)
C(19)	1772 (5)	−12076 (20)	2232 (2)	57 (5)
C(21)	5830 (8)	−3044 (31)	1518 (4)	42 (4)
C(22)	5587 (7)	−1463 (28)	1153 (4)	38 (4)
C(23)	4761 (8)	−1818 (31)	860 (4)	44 (4)
C(24)	4572 (9)	−165 (31)	509 (4)	53 (4)
C(25)	5140 (8)	1779 (31)	444 (4)	49 (4)
C(26)	5928 (8)	2051 (31)	731 (4)	48 (4)
C(27)	6179 (8)	482 (29)	1087 (4)	40 (4)
C(28)	6994 (8)	725 (29)	1379 (4)	43 (4)
C(29)	7209 (8)	832 (29)	1725 (4)	49 (4)
C(30)	6635 (8)	−2705 (31)	1801 (4)	52 (4)
C(31)	7603 (9)	2800 (34)	1296 (4)	58 (5)
C(32)	6527 (8)	4150 (32)	649 (4)	52 (4)
C(33)	7940 (8)	6251 (31)	879 (4)	52 (4)
C(34)	8533 (6)	4951 (17)	690 (2)	47 (4)
C(35)	9369 (6)	5891 (17)	819 (2)	67 (5)
C(36)	9932 (6)	4844 (17)	638 (2)	80 (6)
C(37)	9657 (6)	2857 (17)	326 (2)	76 (6)
C(38)	8821 (6)	1918 (17)	197 (2)	72 (5)
C(39)	8258 (6)	2965 (17)	378 (2)	65 (5)

In structures (1), (2), (3), (4), (5) and (10) there is one molecule in the cell (space group $P\bar{1}$). In structure (6) (space group $C2/c$) all four stacks in the cell are arranged in parallel. The other packings [structures (7), (8) and (9), space group $P2_1/c$] have two identical stacks which form angles of 84·0 (8), 44·7 (7) and 13·1 (13)°. The perylene-imide ring systems of neighbours in the stacks overlap to an extent of 9·2 to 55·6% and are shifted against each other longitudinally (8·3–48·1%) and transversely (8·1–70·5%). The different arrangement of neighbours in the stacks determines the colour of the crystals. These correlations are discussed elsewhere in detail (Graser & Hädicke, 1980, 1984).

Table 22. *Structure* (11): *bond lengths* (Å)

O(1)–C(11)	1·239 (15)	O(2)–C(12)	1·204 (19)
O(21)–C(31)	1·217 (16)	O(23)–C(32)	1·202 (18)
N(1) C(11)	1·372 (18)	N(1)–C(12)	1·411 (16)
N(1)–C(13)	1·489 (20)	N(21)–C(31)	1·367 (19)
N(21)–C(32)	1·374 (16)	N(21)–C(33)	1·469 (20)
C(1)–C(2)	1·402 (19)	C(1)–C(10)	1·381 (16)
C(1)–C(23)	1·452 (21)	C(2)–C(3)	1·429 (16)
C(2)–C(7)	1·439 (22)	C(3)–C(4)	1·396 (20)
C(3) C(21)	1·456 (22)	C(4)–C(5)	1·380 (22)
C(5)–C(6)	1·384 (16)	C(6)–C(7)	1·406 (19)
C(6)–C(12)	1·461 (22)	C(7)–C(8)	1·401 (17)
C(8)–C(9)	1·375 (20)	C(8)–C(11)	1·492 (23)
C(9)–C(10)	1·377 (22)	C(13)–C(14)	1·500 (19)
C(21) C(22)	1·417 (19)	C(21)–C(30)	1·387 (17)
C(22)–C(23)	1·427 (16)	C(22)–C(27)	1·430 (20)
C(23)–C(24)	1·397 (20)	C(24)–C(25)	1·399 (22)
C(25)–C(26)	1·369 (17)	C(26)–C(27)	1·389 (19)
C(26)–C(32)	1·508 (24)	C(27)–C(28)	1·406 (16)
C(28)–C(29)	1·359 (19)	C(28)–C(31)	1·515 (24)
C(29) C(30)	1·400 (22)	C(33)–C(34)	1·501 (20)

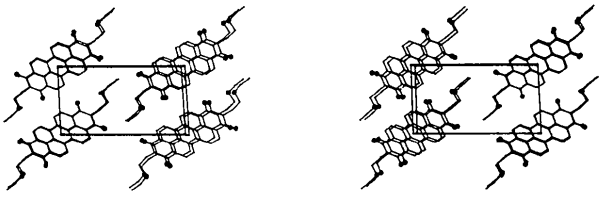


Fig. 2. A stereo packing plot projected down **a** for (1). The *c* axis is horizontal, left to right; the *b* axis is vertical, top to bottom.

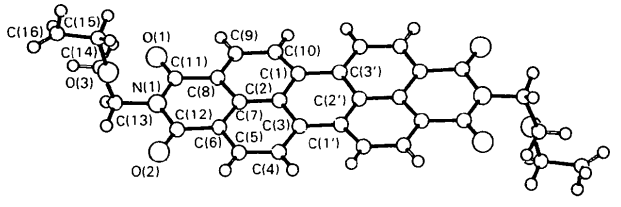


Fig. 1. The molecular structure of (1).

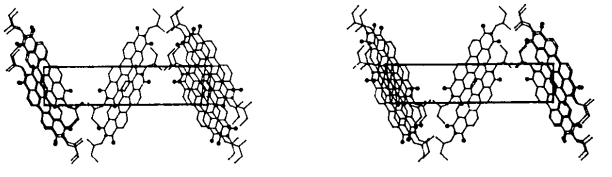


Fig. 3. A stereo packing plot projected down **c** for (7). The *b* axis is horizontal, left to right; the *a* axis is vertical, top to bottom.

In contrast to the other perylenetetracarboxylic diimide pigments investigated, the single molecules of pigment (11) (Kalle AG, 1972) have no symmetry element at the centre. The flat parts of neighbouring molecules are 3·412 (38) Å apart, pack in stacks, overlap to an extent of 48·2% and are shifted against each other 27·4% longitudinally and 23·8% transversely. The two identical stacks form an angle of 87·8 (25)°. The plane of the phenyl rings is turned 71·8 (25) and 104·5 (25)° out of the plane of the perylene-imide ring system.

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Structures of Three Perylene-3,4:9,10-bis(dicarboximide) Pigments

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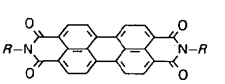
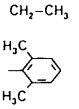
Abstract. (1): *N,N'*-Dipropylperylene-3,4:9,10-bis(dicarboximide), $C_{30}H_{22}N_2O_4$, $M_r = 474{\cdot}5$, triclinic, $P\bar{1}$, $a = 18{\cdot}077$ (4), $b = 14{\cdot}258$ (3), $c = 4{\cdot}689$ (3) Å, $\alpha = 89{\cdot}93$ (8), $\beta = 111{\cdot}30$ (9), $\gamma = 104{\cdot}24$ (9)°, $V = 1086{\cdot}2$ Å^3, $Z = 4$, $D_m = 1{\cdot}50$, $D_x = 1{\cdot}45$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}93$ cm^{-1}, $F(000) = 496$, $T = 295$ K, $R = 6{\cdot}8\%$ for 2649 reflections, $S = 1{\cdot}59$. (2): *N,N'*-Diethylperylene-3,4:9,10-bis(dicarboximide), $C_{28}H_{18}N_2O_4$, $M_r = 446{\cdot}5$, orthorhombic, *Pcca*, $a = 34{\cdot}333$ (40), $b = 16{\cdot}659$ (11), $c = 6{\cdot}906$ (2) Å, $V = 3949{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}50$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 7{\cdot}84$ cm^{-1}, $F(000) = 1856$, $T = 295$ K, $R = 21{\cdot}6\%$ for 417 reflections, $S = 2{\cdot}71$. (3): *N,N'*-Bis(2,6-xylyl)perylene-3,4:9,10-bis(dicarboximide), $C_{40}H_{26}N_2O_4$, $M_r = 598{\cdot}7$, monoclinic, $P2_1/c$, $a = 19{\cdot}929$ (15), $b = 7{\cdot}770$ (8), $c = 25{\cdot}197$ (17) Å, $\beta = 50{\cdot}42$ (8)°, $V = 3007{\cdot}2$ Å^3, $Z = 4$, $D_m = 1{\cdot}33$, $D_x = 1{\cdot}32$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}04$ cm^{-1}, $F(000) = 1248$, $T = 295$ K, $R = 6{\cdot}6\%$ for 3530 reflections, $S = 1{\cdot}65$. All compounds were synthesized to verify the possible correlation between the colours of the pigments and their crystal packings. All molecules show a flat perylenetetracarboxylic diimide portion with bent side chains. The mutual arrangement of neighbours in the stacks is determined by the substituents. The exchange of π electrons of these neighbours determines the different colours of the crystals.

Introduction. The present investigation is part of studies carried out on perylenetetracarboxylic diimide pigments (Graser & Hädicke, 1980, 1984). The crystal structures of the pigments reported here show distinct differences in their crystal packings compared with those in the preceding paper (Hädicke & Graser, 1986).



	R	Colour of crystals
(1)	$CH_2-CH_2-CH_3$	black
(2)	CH_2-CH_3	red
(3)		red

Experimental. All substances were recrystallized from nitrobenzene. Densities measured with a pycnometer. Crystal sizes: (1) 0·45 × 0·15 × 0·015 mm, (2) 0·20 ×

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