double bond in the side chain, C(20)—C(21), with the carbonyl group is defined by the torsional angle C(20)—C(15)—C(16)—O(24) 44·8 (3)° [*cf.* value 46·2 (3)° in senecionine].

The bond lengths and angles are in good agreement with those reported for comparable structures. The bonds in the unsaturated ring have a mean length of 1·381 (5) Å with the two C—N bonds having a mean length of 1·370 (5) Å. These values are indicative of extensive electron delocalization around the ring as observed in other pyrrole moieties (English, McGillivray & Smal, 1980; Acheson, Ferris, Critchley & Watkin, 1980). The considerable distortion of the exocyclic angles from standard trigonal values, C(3)—N(4)—C(5) 137·0 (3)° and C(1)—C(8)—C(7) 142·4 (3)°, is a consequence of the flattening of the pyrrolizidine nucleus. The central C—C bond in the C=C—C=O grouping of 1·491 (5) Å is similar to the value 1·493 (5) Å in the parent alkaloid, and the C—H lengths in the molecule range in value from 0·91 (4) Å [C(18)—H(18*c*)] to 1·05 (4) Å [C(9)—H(9*b*)]. As in senecionine, there is no indication of intramolecular hydrogen bonding.

The mode of packing in the crystal (Fig. 2) is quite different from that observed in senecionine. In the latter the α-OH substituent is involved in intermolecular H-bonding interactions with the N atom. In dehydrosenecionine, the α-OH group forms hydrogen bonds with the carbonyl O of the secondary-ester system, O(24), of a molecule related by the twofold screw axis ($x = \frac{1}{4}$, $y = 0$). These interactions link the molecules into helices along the *c* axis. The O(23)···O(24), O(23)—H(23) and H(23)···O(24) distances are 2·941 (3), 0·91 (4) and 2·07 (4) Å respectively and the O(24)···H(23)—O(23) angle is 160 (3)°.

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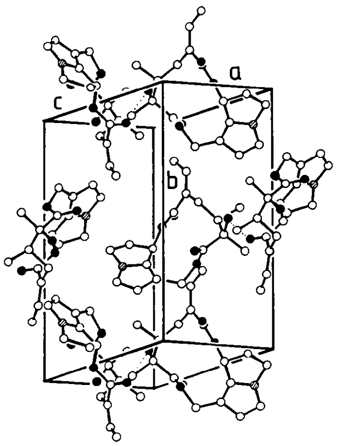

Fig. 2. The molecular packing in the crystal.

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Structure of Perylene–Chloranil* Molecular Complex (1:1), $C_{20}H_{12}.C_6Cl_4O_2$

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Abstract. $M_r = 498{\cdot}19$, triclinic, $P\bar{1}$, $a = 8{\cdot}602\ (1)$, $b = 9{\cdot}635\ (2)$, $c = 7{\cdot}234\ (2)$ Å, $\alpha = 102{\cdot}67\ (2)$, $\beta = 111{\cdot}17\ (2)$, $\gamma = 64{\cdot}38\ (1)°$, $V = 502{\cdot}7$ Å^3, $Z = 1$, $D_m = 1{\cdot}64$, $D_x = 1{\cdot}645$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 6·13 cm^{-1}, $F(000) = 252$, $T = 294 \pm 1$ K, $R = 0{\cdot}046$ for 1803 observed reflections.

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* Chloranil is 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione.

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Perylene and chloranil molecules occupy centers of symmetry to form a mixed-stack structure along the *c* axis. Both molecules are planar and all the chemically equivalent bonds have compatible lengths.

Introduction. Polycyclic aromatic hydrocarbons are generally characterized as good π-electron donors, and therefore easily form complexes with some electron-acceptor molecules. Most of those which have so far been analyzed structurally have an alternating stacked structure. However, several recent reports described a segregated-stack structure for perylene or fluoranthene cations possessing high electrical conductivity (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980; Alcácer, Novais, Perdroso, Flandrois, Coulon, Chasseau & Gaultier, 1980; Enkelmann, Morra, Kröhnke, Wegner & Heinze, 1982). This suggests the specific character of these hydrocarbons, molecules of which have a partially conjugated system.

In relation to the previous report on the structural study of perylene–2,5-dibromo-3,6-dichloro-*p*-benzoquinone(BCQ) (Kozawa & Uchida, 1979), we are here concerned with the perylene–chloranil complex.

Experimental. From apparently monoclinic dark-blue crystals grown from a diethyl ether solution of the constituents in the ratio 1:1, a hexangular prismatic triclinic crystal (0·3 × 0·30 × 0·35 mm) was selected photographically. D_m measured by flotation in aqueous K_2HgI_4. Hilger & Watts Y290 diffractometer, Zr-filtered Mo $K\alpha$; cell dimensions from least-squares refinement of the setting angles of 12 reflections (27·6° > θ > 23·9°); intensity data by ω–2θ step-scan mode, scan speed 1·2° (2θ) min^{-1}, scan width 0·8° (ω), $2\theta_{\max} = 55°$, $0 \le h \le 11$, $-11 \le k \le 12$, and $-9 \le l \le 8$; standard reflections (010, $13\bar{1}$, and $21\bar{2}$) monitored every 50 measurements: intensity variation within ±4%. No systematic extinction, 2458 unique reflections collected, 1804 observed [$F_o \ge 3\sigma(F)$]; Lorentz and polarization corrections, no absorption correction. Structure solved by heavy-atom method, refined by anisotropic full-matrix least squares, $\sum w(|F_o| - k|F_c|)^2$, $w = 1{\cdot}0$; H (from difference map) isotropic, $B = 4{\cdot}0$ Å^2. In the final cycle, reflection $21\bar{2}$ given zero weight as being affected by extinction ($F_o = 130$, $F_c = 161$), $R = 0{\cdot}046$, $wR = 0{\cdot}046$, $S = 1{\cdot}969$.* $(\Delta/\sigma)_{\max} = 0{\cdot}51$ [*x* of H(1)] and $(\Delta/\sigma)_{\mathrm{av}} = 0{\cdot}06$. In the final difference map, $\rho_{\max} = 0{\cdot}3$ and $\rho_{\min} = -0{\cdot}2$ e Å^{-3}. Scattering factors including anomalous dispersion of the Cl atom from *International Tables for X-ray Crystallography* (1974). HITAC M200H computers at the Computer Centre of the University of Tokyo with the *UNICS* (1967) program system.

Discussion. Final atomic coordinates are given in Table 1. Molecular packing in the crystal, shown in Fig. 1, is the same as that of perylene–BCQ (Kozawa & Uchida, 1979). The donor and acceptor molecules occupy centers of symmetry, and alternately stack along the *c* axis to form characteristic π–π^*-type electron-donor–electron-acceptor complexes. The molecular overlapping of perylene and chloranil is the same as that found in perylene–BCQ and perylene–fluoranil (Hanson, 1963). The perylene and chloranil molecules are virtually planar; only C(9) and C(11) deviate by about 2·9σ and 2·6σ from the planes, respectively. The mean separation between the two planes (in the region of overlap) is 3·33 Å and the dihedral angle between the

Table 1. *Positional parameters* (×10^4; *for* H, ×10^3) *and equivalent isotropic thermal parameters* (Å^2), *with e.s.d.'s in parentheses*

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Cl(1)	2711 (1)	1442 (1)	2973 (1)	3·55 (3)
Cl(2)	3856 (1)	−2188 (1)	2367 (1)	3·61 (2)
O	−985 (3)	3055 (2)	494 (4)	3·60 (2)
C(1)	1290 (4)	596 (3)	1374 (4)	3·50 (9)
C(2)	1773 (4)	−936 (3)	1115 (4)	2·39 (10)
C(3)	−529 (4)	1671 (3)	274 (5)	2·42 (9)
C(4)	−2779 (4)	4223 (3)	4327 (5)	2·48 (10)
C(5)	−3908 (4)	3596 (4)	2945 (5)	3·20 (11)
C(6)	−3388 (4)	1989 (3)	2682 (5)	2·70 (10)
C(7)	−1749 (4)	1005 (3)	3795 (4)	2·11 (9)
C(8)	−1178 (4)	−695 (3)	3539 (4)	2·17 (9)
C(9)	−2288 (4)	−1387 (4)	2165 (5)	2·82 (10)
C(10)	−1737 (5)	−3006 (4)	1916 (5)	3·19 (12)
C(11)	−87 (5)	−3930 (4)	3040 (5)	3·13 (12)
C(12)	1080 (4)	−3283 (3)	4482 (4)	2·58 (10)
C(13)	546 (4)	−1646 (3)	4747 (4)	2·14 (9)
H(4)	−308 (6)	533 (5)	448 (7)	
H(5)	−502 (6)	427 (5)	212 (7)	
H(6)	−424 (6)	157 (5)	167 (7)	
H(9)	−348 (6)	−77 (5)	131 (7)	
H(10)	−254 (6)	−347 (5)	91 (7)	
H(11)	24 (6)	−501 (5)	292 (7)	

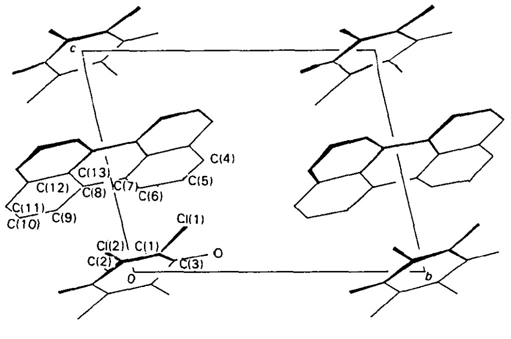

Fig. 1. Projection of the molecular arrangement onto the *bc* plane.

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38609 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England

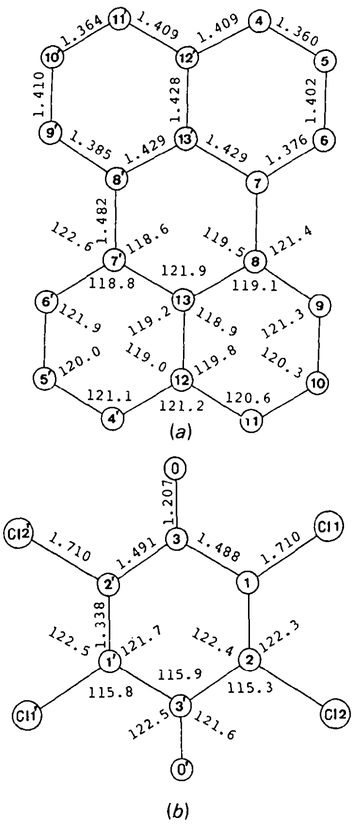

Fig. 2. Bond lengths (Å) and bond angles (°). (*a*) Perylene; mean e.s.d.'s are 0·006 Å and 0·3° respectively. (*b*) Chloranil; mean e.s.d.'s are 0·005 Å and 0·3° respectively.

two planes is 4·3°; these values are intermediate between those of perylene–fluoranil (3·23 Å and 1·8°) and perylene–BCQ (3·35 Å and 4·9°). The inclination angles of the perylene plane toward the a, b and c axes are 46·7, 18·7 and 64·3°, and those of the chloranil plane are 42·4, 17·9 and 68·6°, respectively. The shortest contact distances between adjacent columns are: 2·57 (10) Å for H(9)(x, y, z) and H(6)($-x-1, -y, -z$), 2·57 (7) Å for O(x, y, z) and H(11)($x, y+1, z$) and 2·87 (7) Å for Cl(2)(x, y, z) and H(4)($x+1, y-1, z$). Though the standard deviations of the values for the H atoms are too large for them to be discussed extensively, the value of the last one suggests the possibility of weak hydrogen-bond formation between the columns. Fig. 2 shows the bond distances and angles of the constituent molecules. The geometry of perylene is similar to that in perylene–BCQ and perylene–fluoranil.

In the perylene skeleton, all the chemically equivalent C—C bond lengths are compatible. The largest difference, 0·009 Å (1·3σ), involves C(6)—C(7) and C(8)—C(9). The mean length of C(6)—C(7) is 1·381 Å, and this is remarkably shorter than that of neutral perylene, 1·397 Å (Camerman & Trotter, 1964), or that of perylene cation, 1·419 Å (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980). In relation to this fact, C(7)—C(8) at 1·482 Å is longer than that of neutral perylene (1·471 Å). Then, considering the π-electron system, the perylene in this complex is close to a binaphthalene system (Cruickshank, 1957). The geometrical parameters of chloranil are quite close to those found in the TTF–chloranil complex (Mayerle, Torrance & Crowley, 1979) rather than those of neutral chloranil (Ueda, 1961; Chu, Jeffrey & Sakurai, 1962; van Weperen & Visser, 1972), or chloranil anion (Konno, Kobayashi, Marumo & Saito, 1973; Zanotti & Del Pra, 1980).

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