Fig. 3. Ring–ring interactions across a centre of symmetry. (a) Molecules A; (b) molecules B.

much larger deviations of $0 \cdot 119$ $(0 \cdot 124)$ and $0 \cdot 185$ $(0 \cdot 188)$ Å respectively, also towards the other ring. The pyridine ring points with $C(4)$ towards the benzene ring; the nearest approaches of $H(4)$ to the benzene ring are $H(4) \cdots C(11)$ $2 \cdot 69$ $(2 \cdot 77)$ Å and $H(4) \cdots C(12)$ $2 \cdot 65$ $(2 \cdot 69)$ Å. There are hydrogen bonds of lengths $2 \cdot 949$ (5) and $2 \cdot 897$ (4) Å between $N(8A)$ and $O(22A)$ $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ and between $N(8B)$

and $O(22B)$ $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ respectively. These hydrogen bonds connect the molecules to form chains of molecules A and of molecules B in the $[101]$ direction as illustrated in Fig. 2. The packing of the molecular chains is such that alternating layers of molecules A and of molecules B parallel to $(10\bar{1})$ can be distinguished. The interaction between the chains in a layer is between the 1-methoxy-3,5-dimethylbenzene groups across centres of symmetry. The overlap of these groups is indicated in Fig. 3; the ring-to-ring distances are $3 \cdot 38$ and $3 \cdot 48$ Å for molecules A and B respectively.

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Structure of Tetrafluoro-p-benzoquinone (p-Fluoranil) at 120 K

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Abstract. $C_6F_4O_2$, $M_r = 180 \cdot 0$, monoclinic, $P2_1/c$, $a = 6 \cdot 524$ (2), $b = 5 \cdot 354$ (3), $c = 8 \cdot 825$ (3) Å, $\beta = 106 \cdot 93$ $(3)°$, $V = 294 \cdot 88$ Å^3, $Z = 2$, $D_m = 1 \cdot 90$, $D_x(298\,\text{K}) = 1 \cdot 90$ g cm^{-3}, Mo$K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 3 \cdot 36$ cm^{-1}, $F(000) = 176$, $T = 120$ K, final $R = 0 \cdot 043$ $(wR = 0 \cdot 065)$ for 1046 reflections. Fluoranil exhibits distinct, albeit small, deviations from planarity. The departure from D_{2h} symmetry is discussed in terms of intramolecular interactions. The results are compared with those from room-temperature X-ray and electron diffraction studies.

Introduction. The molecular structures of a number of substituted p-benzoquinones, $C_6O_2X_4$ $(X = H, CH_3, F$

and Cl) have been determined by electron (Hagen & Hedberg, 1973, 1978; Schei, Hagen, Trætteberg & Seip, 1980) and X-ray diffraction (Trotter, 1960; Chu, Jeffrey & Sakurai, 1962; Rabinovich, Schmidt & Ubell, 1967; van Weperen & Visser, 1972; Meresse, Courseille & Chanh, 1974; van Bolhuis & Kiers, 1978). The results of wide ranges of molecular structure determinations generally agree within experimental errors, although, of course, the concept of chemical bond lengths is implicitly defined in different ways by the two methods. Whereas this is also true for most of the p-benzoquinone systems studied hitherto, there are significant differences between the parameters of the p-fluoranil structures as determined by Schei et al.

(1980) (electron diffraction) and Meresse *et al.* (1974) (X-ray diffraction).

The electron diffraction results are based on the assumption that the molecule is planar (D_{2h} symmetry), although it was recognized that deviations too small to be detected by the method are not unlikely. As we are interested both in establishing any tendency to non-planarity, and in more detailed comparisons with the gas-phase results than is possible from room-temperature data alone, we report here the crystal and molecular structure of p-fluoranil at 120 K.

Experimental. Yellow acicular crystals (D_m by flotation) with approximate dimensions $0.55 \times 0.33 \times 0.20$ mm were grown by slowly subliming (5 days) a commercial product (Aldrich Chemical Co. Ltd, UK) *in vacuo* at 295 K onto a cold finger (278 K). Data were collected in the ω–2θ scan mode out to $\theta = 40°$ at 120 K using an Enraf–Nonius CAD-4 automatic diffractometer fitted with a cooling device, and graphite-monochromated Mo $K\alpha$ radiation; 25 independent reflections with $10 \leq 2\theta \leq 30°$ were selected for least-squares determination of cell constants. Sublimation was insignificant. Of the 1833 independent reflections measured, 1046 reflections were classified as observed, *i.e.* $I_{net} > 3.0\sigma(I)$.

The structure was refined with starting parameters from the room-temperature structure (Meresse *et al.*, 1974). All calculations were carried out using *CRYSTALS*, Issue 9 (Watkin, Carruthers & Betteridge, 1985). Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The structure was corrected for absorption and refined by full-matrix least squares on F. The final stage of the refinement was to assign each reflection a weight (Carruthers & Watkin, 1979), $w = 1/\sum_r^n A_r T_r(X)$, where n is the number of coefficients, A_r, for a Chebyshev series, T_r is the polynomial function, and X is $F_o/F_o(\text{max})$. The values of A_r which gave similar values of $w(F_o - F_c)^2$ over ranges of $(\sin\theta)/\lambda$ and F_o were 8.3, 10.5 and 2.1. Final $R = 0.043$, $wR = 0.065$. At convergence r.m.s. shift/e.s.d. < 0.1 and the highest peak in the difference Fourier map $= 0.5$ e Å^{-3}. The atomic positions and equivalent isotropic temperature factors are given in Table 1,* and Table 2 contains the interatomic distances* and valence angles. No correction for secondary extinction.

Discussion. The p-fluoranil molecule is shown in Fig. 1 together with the atom numbering. In addition to the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44059 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature parameters* ($\text{Å}^2 \times 10^4$) *with estimated standard deviations in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	494 (2)	2154 (2)	1022 (1)	163
C(2)	2170 (2)	362 (2)	928 (1)	180
C(3)	1709 (2)	−1626 (2)	−32 (1)	180
O(4)	905 (2)	4003 (2)	1854 (1)	217
F(5)	4137 (2)	844 (2)	1828 (1)	273
F(6)	3186 (2)	−3241 (2)	−158 (1)	255

Table 2. *Bond distances* (Å) *and angles* (°), *with estimated standard deviations in parentheses*

	This work*	Meresse *et al.* (1974)†	Schei *et al.* (1980)‡
C(1)–O(4)	1·215 (2)	1·210 (5)	1·211 (3)
C(1)–C(2)	1·475 (2)	1·447 (7)	1·489 (3)
C(1)–C(3)	1·476 (2)	1·465 (7)	1·489 (3)
C(2)–F(5)	1·323 (1)	1·334 (6)	1·323 (3)
C(2)–C(3)	1·339 (2)	1·310 (7)	1·339 (6)
C(3)–F(6)	1·323 (2)	1·329 (6)	1·323 (3)
C(2)–C(1)–O(4)	121·8 (1)	122·6 (4)	121·6 (4)
C(3)–C(1)–O(4)	121·3 (1)	122·0 (5)	121·6 (4)
C(3)–C(1)–C(2)	116·9 (1)	115·4 (4)	116·8 (4)
C(3)–C(2)–F(5)	122·3 (1)	122·1 (5)	122·3 (4)
C(1)–C(2)–F(5)	116·4 (1)	115·5 (4)	116·1 (4)
C(1)–C(2)–C(3)	121·3 (1)	122·5 (4)	121·6 (4)
C(2)–C(3)–F(6)	122·5 (1)	123·4 (4)	122·3 (4)
C(1)–C(3)–F(6)	115·7 (1)	114·5 (4)	116·1 (4)
C(1)–C(3)–C(2)	121·8 (1)	122·1 (5)	121·6 (4)

* X-ray diffraction at 120 K.
† X-ray diffraction at room temperature.
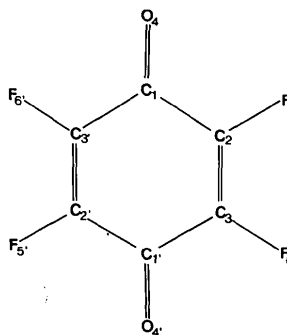‡ Electron diffraction results assuming D_{2h} symmetry.

Fig. 1 View of the molecule with atom numbering.

bond parameters found in this study the corresponding values from the previous X-ray and electron diffraction determinations are included in Table 2. Comparison of these results shows that there is excellent agreement (all parameters are equal within experimental error) between the present work and the electron diffraction results. However, a similar comparison between these models and the room-temperature X-ray solution is not as impressive. (We note that the latter appears to give overly precise bond angles, the more so when one

considers the standard deviations of the bond lengths. We have therefore recalculated the bond lengths, angles and e.s.d.'s for the room-temperature structure.) The advantage in determining the structure at 120 K is reflected by significantly smaller standard deviations in the bond lengths. A similar observation has been made for p-chloranil where the low-temperature crystal structure (van Weperen & Visser, 1972) agrees better with the electron diffraction results than it does with the room-temperature structure (Chu *et al.*, 1962). In particular, the C=C bonds of the electron diffraction solution of p-fluoranil are now confirmed and reproduced by this work. It has previously been pointed out that the chloro derivatives of p-benzoquinone have a tendency to non-planarity, the chlorine and oxygen atoms bonded to neighbouring carbon atoms alternating 0·05 Å above and below the best plane through the carbon atoms (van Weperen & Visser, 1972). This feature, although not so dominant, is also exhibited by fluoranil. Thus, the perpendicular distances (Å) of the O and F atoms of the asymmetric unit from the best plane through the six carbon atoms are O4 = −0·036 (2), F5 = −0·006 (2), F6 = +0·019 (2). The corresponding values for the room-temperature solution, calculated here to be O4 = +0·033 (7), F5 = −0·001 (7), F6 = +0·011 (7), are indistinguishable within the experimental errors.

It is well known that aggregation often results in different degrees of deviations from the free-molecule geometries. Nevertheless, the non-planarity of the substituents observed in the solid state for the chloro derivative has been ascribed (van Weperen & Visser, 1972) to intramolecular interactions between the substituents and hence must also extend to the free

molecule. Whereas the non-bonded halogen–oxygen and halogen–halogen distances in chloranil are significantly shorter than the sum of the van der Waals radii the same is only true to a lesser extent for p-fluoranil. Therefore, it is not unexpected that the observed deviations from planarity are more pronounced in p-chloranil. Furthermore, the planar model used in the electron diffraction study gives bond lengths and angles which accord with the present X-ray diffraction results.

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endo,endo-5,9-Dibromo-cis-transoid-cis-13,oxatricyclo[8.2.1.0²,⁶]tridecane

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Abstract. $C_{12}H_{18}Br_2O$, $M_r = 338·09$, monoclinic, $P2_1/c$, $a = 6·352$ (1), $b = 12·002$ (1), $c = 16·378$ (3) Å, $\beta = 97·17$ (1)°, $V = 1238·8$ Å³, $Z = 4$, $D_x = 1·81$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 6·45$ mm⁻¹, $F(000) = 336$, $T = 296$ K, final $R = 0·033$ for 1690 unique observed reflections. A surprising tricyclic tetrahydrofuran derivative was obtained, *via* trans-annular π-cyclization and O-heterocyclization, by methoxybromination reaction of (E,Z,Z)-cyclododeca-1,5,9-triene. The compound has two five-membered rings with an envelope conformation and one eight-membered ring with a distorted crown conformation.