

## The Crystal Structure of Benzoylacetato Boron Difluoride

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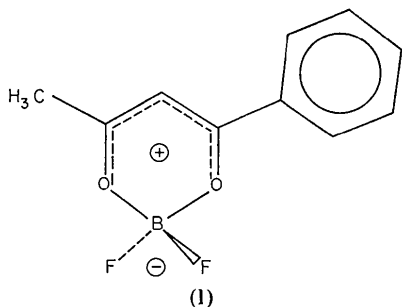
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Crystals of benzoylacetato boron difluoride are orthorhombic, probably *Pnam*, with (at  $-180^{\circ}\text{C}$ )  $a=12.466$  (6),  $b=10.940$  (5),  $c=6.875$  (12) Å,  $Z=4$ . Three-dimensional intensity data were recorded at  $-180^{\circ}\text{C}$  with a four-circle diffractometer and scintillation counter. The approximate structure was determined by symbolic addition procedures, and was refined by block-diagonal least-squares methods to a final  $R$  index of 0.04. The compound is a chelate, with the boron atom in a symmetrical, approximately tetrahedral environment. The residual electron density reveals the presence of bonding and lone-pair electrons.

### Introduction

The complexes of acetylaceton derivatives with boron difluoride have long been considered to be chelates, with the boron atom tetrahedrally coordinated, and this view is supported by a recent spectroscopic study (Brown & Bladon, 1969). The X-ray analysis of benzoylacetato boron difluoride (I) was undertaken in order to provide further confirmation of this point. The crystal structures of many metal chelates of acetylaceton have been reported, and the structural characteristics of some of these have been summarized by Lingafelter & Braun (1966). It was considered of interest also to compare these characteristics with those found in the present study.



During preliminary examination it became apparent that the material was well suited for accurate analysis, such as would permit a meaningful study of the distribution of valence electrons. The major difficulty for such undertakings is, of course, the tendency of the refinement procedure to conceal the defects of the model. Thus deviations from the usually assumed spherical symmetry of the atomic scattering factors tend to be absorbed in the structural parameters, particularly those describing thermal motion. The difficulty is sometimes avoided by determining the nuclear

parameters by neutron crystal-structure analysis, and using these to calculate the structure factors which define the electron density of the model (Coppens, Sabine, Delaplane & Ibers, 1969). It was hoped to achieve much the same result by refining the atomic parameters with high-angle reflexions only, on the assumption that these would be but little affected by the redistribution of valence electrons resulting from bonding. The intensity data were measured at a low temperature, both to reduce the thermal motion, and to increase the yield of high-angle reflexions. On completion of the work it was discovered that the crystal structure had been determined also by P.-T. Cheng and S. C. Nyburg, essentially as a chemical analysis of an unknown compound.

### Experimental

Crystal data:  $\text{C}_{10}\text{H}_9\text{BF}_2\text{O}_2$ , F.W. 210.0  
Orthorhombic,  $a=12.466$  (6),  $b=10.940$  (5),  $c=6.875$  (12) Å,  $V=937.6$  Å<sup>3</sup>,  $D_m=1.426$  g.cm<sup>-3</sup> (by flotation, at  $20^{\circ}\text{C}$ ),  $Z=4$ ,  $D_x=1.487$  g.cm<sup>-3</sup>,  $\mu=12.5$  cm<sup>-1</sup> (all measurements except  $D_m$  at  $-180^{\circ}\text{C}$ , using Cu  $K\alpha$ , for which  $\lambda_{\alpha 1}=1.54050$  Å,  $\lambda_{\alpha 2}=1.54433$  Å. Cell dimensions at  $20^{\circ}\text{C}$ :  $a=12.545$  (6),  $b=10.940$  (5),  $c=7.113$  (4) Å.

Space group  $Pna2_1$  or *Pnam*, from precession and Weissenberg photographs. Systematic absences,  $h0l$  when  $h$  odd;  $0kl$  when  $k+l$  odd. *Pnam* is consistent with the proposed structure. Molecular symmetry: mirror plane.

The material consisted of colourless prisms [110] which were readily cleaved, normal to  $c$ , to give approximately equidimensional specimens. Two such fragments were used in data collection, one of volume 0.008 mm<sup>3</sup>, and the other of 0.001 mm<sup>3</sup>. A nominal specimen temperature of  $-180^{\circ}\text{C}$  (subsequently measured by substituting a thermocouple for the specimen) was maintained by immersion of the specimen in a stream (directed vertically downwards) of cold gaseous nitrogen which was itself surrounded by an envelope of dry nitrogen at room temperature. The specimen

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was protected against abrupt temperature changes by being mounted within, but not touching a thin-walled Lindemann glass capillary. The cell and intensity data were measured with a manually set four-circle diffractometer and scintillation counter, using nickel-filtered Cu  $K\alpha$  radiation with pulse-height discrimination. For intensity measurements the  $\theta$ - $2\theta$  scan method was used, with  $2^\circ$  scans for  $2\theta < 100^\circ$ ,  $3^\circ$  for  $100^\circ \leq 2\theta < 145^\circ$ , and  $4^\circ$  for  $145^\circ \leq 2\theta < 165^\circ$ . The background intensity was measured at the beginning and end of each scan. Both specimens were mounted with (110) parallel to the  $\phi$  axis; this mounting allowed all independent reflexions to be measured with  $\chi \leq 49^\circ$ , thus reducing temperature fluctuations caused by turbulent flow of nitrogen around the protective capillary. The relative temperature was monitored during data collection by frequent measurement of  $2\theta$  for the reflexion 008. The  $c$  dimension is extremely sensitive to temperature (the mean coefficient of expansion is  $0.00017/^\circ\text{C}$ ) and the observed fluctuations have been included in the uncertainty quoted for this dimension.

The larger specimen was used for the bulk of the intensity data measurement. Reflexions were considered to be observed only if the net count exceeded 4 (deca-) counts and 0.1 times the corresponding background count. Attenuating filters were used to keep counting rates within the linear response range of the detector. The intensities measured with this specimen were corrected for absorption with a program, written by Ahmed, which uses the Busing & Levy (1957) approximation; corrections ranged from 1.19 to 1.29. In order to reduce possible extinction errors, the 33 most intense reflexions were remeasured for the smaller specimen. These measurements were not corrected for absorption. The weaker members were used to establish a scale factor with the main set, and the 6 strongest were accepted as definitive measurements. Within the limiting sphere ( $2\theta = 165^\circ$ ;  $\sin\theta/\lambda = 0.64$ ) 965 of 1123 accessible reflexions were observed above background. In the region  $\sin\theta/\lambda > 0.5$  470 of 574 were observed.

### Structure determination

The space group was initially assumed to be  $Pnam$ , and the approximate structure was readily deduced by symbolic addition procedures, using the program of Ahmed, Hall, Pippy & Huber (1966). This structure was refined by block-diagonal least-squares methods, using the program of Ahmed *et al.* (1966). This program minimizes  $\sum w\Delta F^2$ . The weight  $w$  was taken to be  $w_1 w_2 w_3$ , where  $w_1$  is the reciprocal of the variance of  $F_o$ , and is calculated from the intensity counts as:  $w_1 = 4L_p(\text{Total count} - \text{background count})/(\text{Total count} + \text{background count})$  (Ahmed *et al.*, 1966) and

$$\begin{aligned} w_2 &= 1 && \text{for } F_o < 7 \\ &= 7/F_o && \text{for } F_o \geq 7 \\ w_4 &= 4 \sin^2 \theta && \text{for } \sin^2 \theta < 0.25 \\ &= 1 && \text{for } 0.25 \leq \sin^2 \theta < 0.80 \\ &= (1.8 - \sin^2 \theta) && \text{for } \sin^2 \theta \geq 0.8 \end{aligned}$$

The functions  $w_2$  and  $w_3$  were chosen to ensure reasonable constancy of  $w\Delta F^2$  with  $F_o$  and with  $\sin^2\theta$ .

The scattering-factor curves used were those of Hanson, Herman, Lea & Skillman (1964) for non-hydrogen atoms, and that of Stewart, Davidson & Simpson (1965) for hydrogen. The hydrogen atoms, initially located in a difference map, were refined isotropically, and the other atoms anisotropically. A correction for secondary extinction was calculated in the manner described by Pinnock, Taylor & Lipson (1956) and was applied to the three most intense reflexions; the structure amplitudes of 002, 120 and 004 were thereby increased 9%, 2%, and 1% respectively. Further details of the refinement are given in Table 1. A second refinement of the parameters of the non-hydrogen atoms was then undertaken, using only the high-angle reflexions. The intention was, as men-

Table 1. Details of refinement

	Full data ( $\sin\theta/\lambda < 0.64$ )	High-angle data ( $0.5 < \sin\theta/\lambda < 0.64$ )
Number of accessible reflexions	1123	574
Number of observed reflexions	965	470
Number of observed reflexions omitted from least-squares*	15	10
Final $R$ index (Observed reflexions only)	0.038	0.041
Coordinate shift in final cycle:		
maximum	0.0003 Å	0.0005 Å
average	0.0001	0.0001
Final scale factor for $F_o$	0.5547	0.5586

\* These are weak reflexions for which the calculated amplitudes are less than threshold.

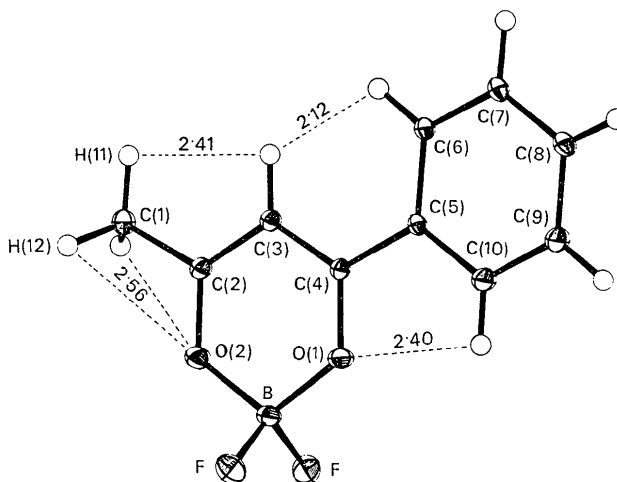


Fig. 1. The molecule viewed at  $60^\circ$  to the mirror plane. The hydrogen atoms are represented by open circles, and the other atoms by thermal ellipsoids of 50% probability. The dotted lines indicate some non-bonded contacts of interest.

tioned above, to reduce errors resulting from the incorrect assumption of spherically-symmetrical scattering factors. Details of this refinement also are given in Table 1, and the parameters resulting from both refinements in Table 2.

### Assessment of analysis

The agreement between observed and calculated structure amplitudes (Table 3) is satisfactory, and there can be no doubt of the essential correctness of the proposed structure. It will be noted, however, that for atoms lying in the crystallographic mirror plane, the out-of-plane thermal motion is somewhat greater than the in-plane motion. While such behaviour does not seem unreasonable, it could conceivably indicate a lower molecular symmetry than that assumed. Four possibilities can be recognized:

1. The space group is  $Pna2_1$ , and the molecule has only an approximate plane of symmetry. The elongation

of some atoms results from the incorrect assumption that the space group is  $Pnam$ .

- The space group is  $Pnam$ ; the molecule has only an approximate plane of symmetry, but the structure is spatially disordered, so that the apparent molecule is a superposition of enantiomorphs.
- The structure is disordered, as in 2, but rapid interconversion of enantiomorphs occurs.
- The molecule has a true plane of symmetry, and the structure is essentially as described.

For cases 1, 2, and 3, the implied deviation from mirror symmetry is rather small, as none of the atoms concerned could lie more than 0.2 Å from the mean plane. It therefore seems unlikely that an enantiomorph could maintain a unique conformation for long, and interconversion would almost certainly occur. Cases 1 and 2 can therefore be disregarded. The distinction between 3 and 4 is somewhat arbitrary, and probably cannot be inferred.

The parameters derived from the two refinements

Table 2. Final atomic parameters and their *e.s.d.*'s

The first row for each atom gives the values from the full-data refinement and the second (non-hydrogen atoms only) those from the high-angle refinement. The fractional coordinates are  $\times 10^3$  for non-hydrogen and  $\times 10^4$  for hydrogen. General equivalent positions are  $\pm [x, y, z; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, \bar{z}; \bar{x}, \bar{y}, \frac{1}{2} + z]$ . Thermal parameters are  $U_{ij} \times 10^4$ , where  $T.F. = \exp [-2\pi^2 (U_{11}a^2h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$ .  $D_i$  are the r.m.s. displacements (in Å  $\times 10^3$ ) along the principal axes of the vibration ellipsoids. The thermal parameters,  $B$ , for the hydrogen atoms are Debye-Waller factors, in Å<sup>2</sup>.

Atom	x	y	z	U <sub>11</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>22</sub>	U <sub>23</sub>	U <sub>33</sub>
C(1)	10409(16) 10410(16)	-39395(17) -39425(18)	25000 25000	154(9) 138(8)	24(7) 16(7)	0 0	92(8) 80(7)	0 0	308(11) 297(10)
C(2)	13348(15) 13335(15)	-26255(17) -26265(16)	25000 25000	113(9) 105(7)	-14(7) -7(6)	0 0	121(8) 93(7)	0 0	148(8) 161(8)
C(3)	5815(14) 5779(15)	-16947(17) -16927(17)	25000 25000	94(8) 97(7)	-10(7) -2(6)	0 0	105(8) 90(7)	0 0	184(9) 178(8)
C(4)	9177(14) 9210(14)	-4865(16) -4845(16)	25000 25000	107(7) 98(6)	-7(7) -2(6)	0 0	111(8) 81(7)	0 0	113(8) 123(7)
C(5)	1811(14) 1811(14)	5684(17) 5711(17)	25000 25000	114(8) 91(7)	13(6) 14(5)	0 0	101(8) 81(7)	0 0	127(8) 133(7)
C(6)	-9344(15) -9359(15)	4090(16) 4055(16)	25000 25000	135(8) 105(6)	-1(7) 10(6)	0 0	92(8) 87(7)	0 0	139(9) 152(8)
C(7)	-16088(15) -16131(16)	14205(17) 14215(17)	25000 25000	121(8) 120(7)	17(7) 28(6)	0 0	139(8) 113(7)	0 0	138(8) 139(7)
C(8)	-11808(16) -11819(17)	25926(17) 25960(17)	25000 25000	145(9) 116(8)	44(7) 29(6)	0 0	126(8) 122(7)	0 0	184(9) 185(8)
C(9)	-737(17) -724(18)	27585(18) 27632(19)	25000 25000	169(9) 138(8)	-16(7) -3(6)	0 0	104(8) 91(7)	0 0	301(11) 308(11)
C(10)	6032(15) 6059(16)	17535(18) 17530(18)	25000 25000	123(8) 117(7)	-10(7) -2(6)	0 0	129(8) 101(7)	0 0	263(10) 272(10)
O(1)	19376(10) 19386(12)	-2127(12) -2118(14)	25000 25000	86(6) 89(6)	-12(4) -8(4)	0 0	101(5) 108(5)	0 0	317(8) 301(8)
O(2)	23619(11) 23629(12)	-24056(12) -24062(14)	25000 25000	112(6) 102(6)	14(5) 14(4)	0 0	124(6) 121(6)	0 0	312(8) 304(8)
B	28061(16) 28077(16)	-11485(20) -11470(19)	25000 25000	91(9) 88(7)	21(8) 0(7)	0 0	137(9) 135(8)	0 0	197(10) 193(9)
F	34162(6) 34195(8)	-9942(8) -9944(9)	85774(13) 85264(14)	188(3) 188(3)	13(3) 13(3)	33(3) 31(3)	219(4) 215(4)	27(3) 25(3)	181(4) 169(4)

Atom	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	Atom	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>
C(1)	91 87	127 119	175 172	C(8)	95 95	134 122	136 136
C(2)	101 95	115 104	122 127	C(9)	100 95	132 117	173 176
C(3)	94 94	105 99	135 133	C(10)	107 100	117 108	162 165
C(4)	101 90	107 99	108 111	O(1)	89 85	104 105	178 174
C(5)	96 85	110 100	112 115	O(2)	101 97	115 113	176 174
C(6)	95 91	116 105	118 123	B	95 94	117 116	140 139
C(7)	105 94	117 118	122 121	F	122 120	138 138	157 155

Atom	x	y	z	B
H(3)	-159(19)	-190(22)	2500	1.110(5)
H(6)	-1257(21)	-418(24)	2500	1.916(5)
H(7)	-2421(20)	1331(22)	2500	1.210(5)
H(8)	-1627(19)	3309(23)	2500	1.410(5)
H(9)	251(20)	3583(24)	2500	1.610(5)
H(10)	1373(20)	1882(24)	2500	1.710(5)
H(11)	286(24)	-4054(29)	2500	3.210(7)
H(12)	1402(16)	-4340(18)	1350(30)	3.010(4)



from the high-angle refinement are regarded as the more reliable, but it is reassuring to find that the differences are so small. The quoted e.s.d.'s were derived from the diagonal elements of the inverse matrix, and, to the extent that there are no significant differences between chemically equivalent bond distances in either refinement, appear to be realistic.

Table 4. Bond lengths and angles

(a) Bond lengths and e.s.d.'s for the two refinements, averaged where appropriate.

	Full data	Mean	High-angle data	Mean
C(1)—C(2)	1.482 (3) Å		1.485 (3) Å	
C(2)—C(3)	1.386 (3)	1.386	1.390 (3)	1.389
C(3)—C(4)	1.387 (3)		1.389 (3)	
C(4)—C(5)	1.475 (3)		1.478 (3)	
C(5)—C(6)	1.401 (3)	1.393	1.404 (3)	1.396
C(6)—C(7)	1.390 (3)		1.396 (3)	
C(7)—C(8)	1.389 (3)		1.393 (3)	
C(8)—C(9)	1.392 (3)		1.395 (3)	
C(9)—C(10)	1.386 (3)		1.391 (3)	
C(10)—C(5)	1.399 (3)		1.397 (3)	
C(2)—O(2)	1.303 (2)	1.304	1.306 (3)	1.304
C(4)—O(1)	1.306 (2)		1.303 (2)	
B—O(1)	1.490 (2)	1.487	1.490 (3)	1.488
B—O(2)	1.483 (3)		1.485 (3)	
B—F	1.372 (2)		1.376 (2)	
C—H		0.98 (0.95 to 1.02)		

(b) Bond angles and e.s.d.'s for the high-angle refinement

C(1)—C(2)—C(3)	123.1 (2)°	F—B—F	110.8 (2)°
C(1)—C(2)—O(2)	114.8 (2)	C(3)—C(4)—C(5)	123.5 (2)
C(5)—C(4)—O(1)	115.4 (2)	C(5)—C(4)—O(1)	115.4 (2)
C(3)—C(2)—O(2)	122.0 (2)	C(4)—C(5)—C(6)	121.2 (2)
C(3)—C(4)—O(1)	121.2 (2)	C(4)—C(5)—C(10)	119.1 (2)
C(2)—C(3)—C(4)	119.4 (2)	C(5)—C(6)—C(7)	119.8 (2)
C(2)—O(2)—B	122.6 (2)	C(6)—C(7)—C(8)	120.1 (2)
C(4)—O(1)—B	123.4 (2)	C(7)—C(8)—C(9)	120.2 (2)
O(1)—B—O(2)	111.4 (2)	C(8)—C(9)—C(10)	119.9 (2)
O(1)—B—F	108.6 (2)	C(9)—C(10)—C(5)	120.3 (2)
O(2)—B—F	108.6 (2)	C(10)—C(5)—C(6)	119.7 (2)

Angles involving hydrogen: trigonal, 118 to 122°;  
tetrahedral, 108 to 113°.

### Molecular structure

Details of the molecular structure are given in Table 4 and in Figs. 1 and 2. The compound is seen to be a true chelate, with the boron atom in a symmetrical, approximately tetrahedral environment. In Fig. 2 the bond lengths of the acetylacetonone nucleus are compared with the mean values reported for metal chelates (Lingafelter & Braun, 1966). The C—O distance is

considerably longer than that found in metal chelates, indicating less double-bond character; the B—O distance is quite short, suggesting largely covalent charac-

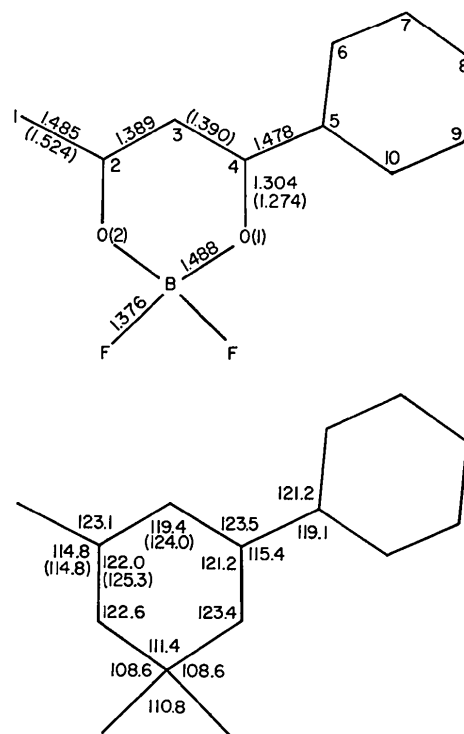


Fig. 2. Selected bond lengths and angles, averaged where appropriate. Values in parentheses are mean values for the acetylacetonone nucleus in metal chelates (Lingafelter & Braun, 1966).

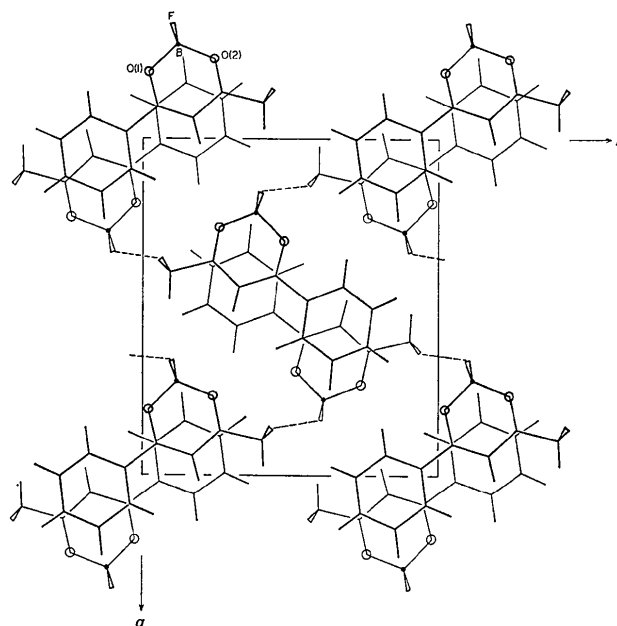


Fig. 3. The structure viewed along *c*. The dotted lines indicate a fluorine-hydrogen contact of length 2.37 Å.

ter. The distances C(2)–C(3) and C(3)–C(4) are consistent with aromaticity, and the distance C(4)–C(5) is as expected for a single bond linking two aromatic systems. An unexpected and puzzling feature of the present compound is the distance C(1)–C(2) of 1.485 (3) Å; this may be compared with the more reasonable value of 1.524 Å found for the metal chelates. Thermal motion could, of course, cause an apparent shortening of this bond, but the effect could hardly be appreciable. A correction for ‘riding motion’ (Busing & Levy, 1964) – probably an overestimate in this situation – could increase the distance by only 0.005 Å. It must be concluded that this distance is in fact unusually short.

The molecule is required to have a plane of symmetry, containing all the non-hydrogen atoms except fluorine. As mentioned earlier, there can be no assurance that the observed molecule is not a superposition of enantiomorphs, but even if it were, the deviation from mirror symmetry would have to be rather small. In view of the steric forces involved, this is rather surprising [although the example of biphenyl demonstrates that considerable crowding can be tolerated in a planar system (Trotter, 1961; Hargreaves & Rizvi, 1962)]. Thus H(3) and H(6) lie only 2.12 (3) Å apart and their mutual repulsion causes the angle C(4)C(5)C(6) to be 2.1 (3)° larger than C(4)C(5)C(10). This distortion is probably limited by an opposing repulsion between H(10) and O(1); the separation of these atoms is only 2.40 (4) Å and the residual electron density (to be discussed) suggests some deformation of the lone-pair distribution. A corresponding repulsion involving O(2) is minimized by the orientation adopted by the methyl group.

The molecular packing is illustrated in Fig. 3. The molecules overlap each other with a separation of their mean planes of 3.44 Å. Intermolecular contacts appear to be normal except for F...H(12') (Fig. 3). Although the separation here is only 2.37 Å there seems to be no possibility of binding forces stronger than van der Waals. It is possible that intermolecular repulsive forces are concentrated at this contact.

### The residual electron density

A difference Fourier synthesis was computed using only the data for which  $\sin\theta/\lambda \leq 0.5$ . The structure factors were, however, calculated using the parameters derived from the high-angle refinement ( $\sin\theta/\lambda > 0.5$ ). [The scale factor applied to  $F_o$  is clearly important. Fortunately the value indicated by least-squares analysis was rather insensitive to the data set used, differing by only 0.7% for the two modes of refinement (Table 1). An intermediate value of 0.557 was used for the difference synthesis.] It was assumed that the high-angle data would be but little affected by the distribution of valence electrons, and that their inclusion would contribute little but noise to the difference map. The validity of this assumption has, however, been questioned by O'Connell, Rae & Maslen (1966), who

describe the scattering by valence electrons as ‘predominantly a higher-angle effect’. The difference map showed many interesting features, plausible identifiable as bonding and lone-pair electrons. However, in order to test the primary assumptions, another difference synthesis was computed, using only those data for which  $\sin\theta/\lambda > 0.5$ . Virtually all of the physically meaningful features observed in the low-angle map appeared here also. Peaks attributable to bonding electrons had, on average, about 40% of the height observed in the low-angle map. It may be concluded that the omission of high-angle terms is not justified, and that the high-angle refinement cannot (as was hoped) be entirely free of the effects of asphericity. It is nevertheless considered to be worth while to exam-

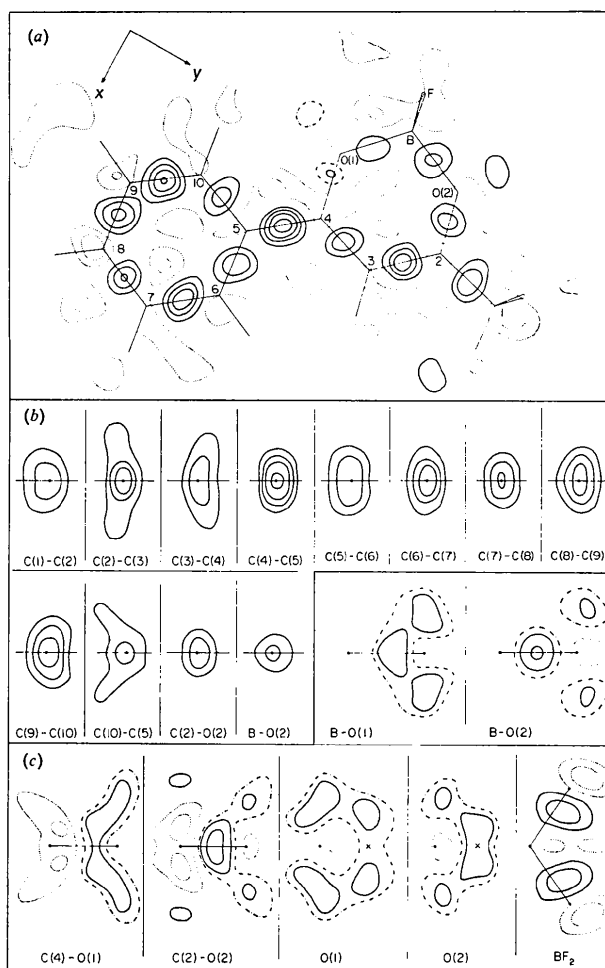


Fig. 4. Selected sections of the difference Fourier map. The dotted contours are at  $-0.1$  and  $-0.2$   $e.\text{\AA}^{-3}$ , the chain contour (given only where needed to indicate specific features) at  $0.05$   $e.\text{\AA}^{-3}$ , and the solid contours at  $0.1$  to  $0.4$   $e.\text{\AA}^{-3}$ . (a) Section in the mirror plane. (b) Sections normal to, and bisecting, specified bonds. (c) Sections normal to the mirror plane and, in most cases, containing the specified bond. Sections O(1) and O(2) contain the appropriate oxygen atom and, (denoted by X), the point where the presumed lone-pair distribution meets the mirror plane.

ine the residual density in some detail. It is believed that features lying at some distance from the atomic centres (*i.e.* bonding and lone-pair electrons) should have at least qualitative significance, although features near the atomic centres (indicative, for example, of possible charge migration) are less likely to be meaningful.

The definitive difference synthesis was computed with essentially all terms included, omitting only the 002 reflexion (for which the extinction correction was regarded as unreliable) and those weak reflexions previously omitted from the least-squares refinements (Tables 1 and 3). Selected sections of the difference map are shown in Fig. 4. All bonds joining non-hydrogen atoms have concentrations of density at or near their midpoints, thus confirming the covalent character of, in particular, the B–O bonds. The peaks are most pronounced for the C–C bonds, and tend to be somewhat elongated in the direction normal to the plane of symmetry. However, the degree of elongation cannot be used to distinguish between the aromatic and the nominally single bonds. All non-hydrogen atoms are found to lie in or close to regions of negative density. The situation in the neighbourhood of the oxygen atoms is quite interesting. Near O(2) there is a concentration of density in the mirror plane, at about the trigonal position. This is rather poorly localized, extending out of the plane in an arc enclosing O(2) with local maxima above and below the atom. These maxima tend to merge also with the overlap electrons of the C–O bonds. A similar, but more extreme situation is found near O(1). Here the concentration at the mirror plane is actually split into two peaks and the maxima above and below the atom are enhanced, merging with the overlap electrons of both the adjacent bonds. A possible reason for the difference of distribution about the two oxygen atoms is to be found in their environment of non-bonded hydrogen contacts. H(10) lies in the mirror plane only 1.9 Å from the point where the peak near O(1) meets this plane. The splitting of the peak, and the enhancement of the peaks above and below O(1) would be consistent

with repulsion between the lone pairs and the electron cloud of H(10). The contacts of O(2) with H(12) and H(12') are much longer – the distance of these atoms from the corresponding peak near O(2) is 2.6 Å – and any repulsion would tend to consolidate rather than split the peak. (As mentioned earlier, the orientation of the methyl group may be fixed by the oxygen-hydrogen repulsion.) In spite of the apparent difference in the electron-density distributions about O(1) and O(2), there is no detectable difference in the lengths of their corresponding adjacent bonds.

Computer programs used in this work are those of Ahmed *et al.*, (1966), and of C. K. Johnson (*ORTEP*, thermal ellipsoid plot). The specimen material was provided by Dr N. M. D. Brown.

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