# Molecular Packing Modes. Part IX.[1] Crystal and Molecular Structures of Pentafluorobenzoic Acid and Mesitoic Acid

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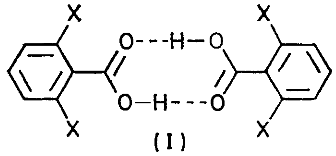
The crystal structure of pentafluorobenzoic acid has been solved from 1598 three-dimensional counter data, and refined by least-squares to $R$ 0·04. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: $a = 7·925$, $b = 8·637$, $c = 6·262$ Å, $\alpha = 97·55$, $\beta = 89·65$, and $\gamma = 121·86°$. Values of $\sigma$ for bond lengths are 0·002 Å. The angle between the planar pentafluorophenyl group and the carboxy-group is 29·8°. The molecules form cyclic hydrogen-bonded dimers (OH ··· O 2·668 Å) in which the C–OH and C=O bond lengths are 1·278 and 1·221 Å.

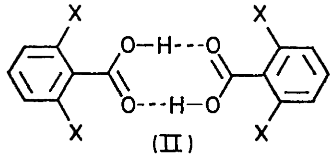
The structure of mesitoic acid was refined similarly to $R$ 0·05 for 2060 reflections. Crystals are monoclinic, space group $C2/c$, $Z = 8$, in a unit cell of dimensions: $a = 15·142(1)$, $b = 7·026(1)$, $c = 17·439(1)$ Å, $\beta = 89·35(1)°$. The mean $\sigma$ values of the heavy- and hydrogen-atom co-ordinates are 0·001 and 0·03 Å. The angle between the mesityl and carboxy-groups is 48·4°. The molecules form cyclic hydrogen-bonded pairs (OH ··· O 2·640 Å) in which the C–O bond lengths are nearly equal (1·275 and 1·248 Å).

The molecular dimensions and the packing arrangements of both structures are discussed.

THE structural analyses of pentafluorobenzoic acid and mesitoic acid were undertaken as part of a study on the packing modes of carboxylic acids. Specifically we wished to consider those benzoic acids in which the intramolecular environment of each of the oxygen atoms of the carboxy-group was identical: in molecules of such a type there exist two equivalent orientations (I) and (II) mutually indistinguishable unless incorporated into a geometrical framework such as a crystal lattice. The question then arises as to what extent intermolecular forces could determine the degree of orientational disorder of the carboxy-dimer, *i.e.* the random incorporation of (I) or (II) at a centrosymmetric lattice point in the crystal.

Pentafluorobenzoic acid (III) was chosen as the C–F ··· O interaction was assumed to be weak, in comparison say to the C–H ··· O interaction, and so


(I)


(II)

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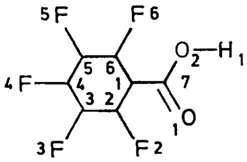
[1] Part VIII, V. Benghiat and L. Leiserowitz, preceding paper.

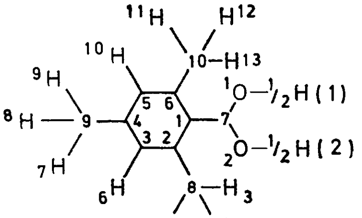
would exert little influence on the orientation of the carboxy-dimer.

In mesitoic acid (IV), the van der Waals radii of the *ortho*-substituted methyl groups were considered to be sufficiently large to prevent any close approach of neighbouring atoms to the cyclic acid pair, and so isolate it from intermolecular contacts.

On completion of the structural determination of mesitoic acid we learned that the crystal structure had been studied by Florencio and Smith.[2]



(III)



(IV)

EXPERIMENTAL

Crystals of (III), m.p. 103—104 °C, were obtained by slow evaporation of a light petroleum–toluene solution. The triclinic crystals exhibited the {100}, {001}, $\{1\bar{1}0\}$, and $\{\bar{1}20\}$ forms.

(IV), m.p. 149—150 °C, was crystallised by slow evaporation of n-pentane solution. The monoclinic crystals showed the {100}, {110}, {331}, and {001} forms.

*Crystal Data.*—(i) *Pentafluorobenzoic acid* (III). $C_7HF_5O_2$, $M = 212{\cdot}1$. Triclinic, $a = 7{\cdot}925(1)$, $b = 8{\cdot}637(1)$, $c = 6{\cdot}262(1)$ Å, $\alpha = 97{\cdot}55(1)$, $\beta = 89{\cdot}65(1)$, $\gamma = 121{\cdot}86(1)°$, $U = 359{\cdot}8$ Å$^3$, $D_m = 1{\cdot}94$, $Z = 2$, $D_c = 1{\cdot}957$, $F(000) = 208$. Space group $P\bar{1}$. $\mu(\text{Cu-}K_\alpha) = 21$ cm$^{-1}$.

(ii) *Mesitoic acid* (IV). $C_{10}H_{10}O_2$, $M = 162{\cdot}2$. Monoclinic, $a = 15{\cdot}142(1)$, $b = 7{\cdot}026(1)$, $c = 17{\cdot}439(1)$ Å, $\beta = 89{\cdot}35(1)°$, $U = 1855{\cdot}3$ Å$^3$, $D_m = 1{\cdot}16$, $Z = 8$, $D_c = 1{\cdot}161$, $F(000) = 688$. Space group $C2/c$ from systematic absences: $hkl$ for $h + k$ odd, $h0l$ for $l$ odd. $\mu(\text{Cu-}K_\alpha) = 6{\cdot}6$ cm$^{-1}$.

The cell constants of both compounds were determined by a least-squares analysis of high-angle spectra ($2\theta > 120°$) measured on a General Electric goniostat with Cu-$K_\alpha$ radiation.

*Data Collection.*—Crystals of (III) were hygroscopic and so the specimen, of dimensions 0·38 × 0·32 × 0·44 × 0·50 mm (bounded by faces 001, 00$\bar{1}$, 100, $\bar{1}$00, $\bar{1}$10, 1$\bar{1}$0, $\bar{1}$20, 1$\bar{2}$0), was sealed in a Lindemann glass capillary. The diffraction data $I(hkl)$ were measured on a General Electric goniostat by the stationary-crystal–stationary-counter technique with nickel-filtered Cu-$K_\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The intensity and background were each measured for a period of 10 s; for the background measurement the Eulerian cradle was offset in $\omega$ by 1°. 1598 Independent reflections were recorded including 206 reflections which were treated as unobserved.

A crystal of (IV) of dimensions 0·47 × 0·46 × 1·28 × 0·33 mm (bounded by faces $\bar{1}$00, 100, 1$\bar{1}$0, $\bar{1}$10, 110, $\bar{1}\bar{1}$0, 001, 00$\bar{1}$), was mounted along $a^*$ on the General Electric goniostat. The data $I(hkl)$ and $I(h\bar{k}l)$ were collected by a similar procedure to that already described. To minimise the effect of extinction, the strong reflections were measured with a second smaller crystal; 2060 independent, including 73 unobserved, reflections were measured.

Absorption corrections [3] were applied to both compounds in the data reduction routines. Treatment of data and the weighting scheme have been described previously.[4]

*Structure Determination and Refinement.*—The molecular structure of (III) was assumed to consist of a planar hydrogen-bonded dimer from which 36 plausible packing arrangements were generated by SEARCH.[5] One of these models achieved the lowest $R$ of 0·37 when tested in a rigid-body least-squares programme with a limited number of low-order reflections. This model was further refined by the rigid-body method in which the restriction on molecular planarity was relaxed, and the carboxy- and phenyl groups were allowed to rotate independently about the exocyclic C–C bond; $R$ was reduced to 0·22. The model was further refined with individual atomic positional and anisotropic thermal parameters. The final $R$ was 0·040 and $R'$ 0·008 [$R' = \Sigma w(kF_o^2 - |F_c|^2)^2/\Sigma wk^4F_o^4$]. A difference-Fourier synthesis, based on all nonhydrogen atoms was computed in the plane at the carboxy-acid pair, and clearly located the hydroxylic hydrogen (Figure 1).

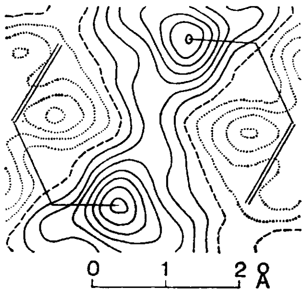


FIGURE 1 Pentafluorobenzoic acid: electron-density difference-Fourier synthesis in the plane of the carboxy-dimer. Full, dashed, and dotted lines correspond to positive, zero, and negative contours at intervals of 0·05 eÅ$^{-3}$

An $E$ map, based on 150 reflections of mesitoic acid with signs determined by the symbolic addition method,[6] revealed all the carbon and oxygen positions. This model was refined to $R$ 0·13. At this stage the hydrogen atoms of the three methyl groups were located on electron-density difference-Fourier maps (Figure 2); these hydrogen atoms, together with the two aromatic hydrogen atoms, which were inserted at chemically reasonable positions, were refined with isotropic temperature factors whereupon $R$ dropped to 0·052. The C–O bond lengths being nearly equal (1·287 and 1·257 Å), 'half hydrogens' were attached to each of the oxygen atoms at 1 Å along the O · · · O line, and their positional and thermal parameters refined. From the final least-squares refinement cycle the two 'half hydrogens,' $\frac{1}{2}$H(1) and $\frac{1}{2}$H(2), were located 1·1 and 0·9 Å from their nearest oxygen atoms with a temperature factor of 0·14 Å$^2$. The two corresponding C–O bond lengths were then 1·275 and 1·248 Å. A difference-Fourier synthesis, based on all but the 'half hydrogens' was computed in the plane of the carboxy-dimer (Figure 3) and showed a disordered electron-density distribution. The final agreement factors for the 2060 reflections were $R$ 0·050 and $R'$ 0·009.

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[2] F. Florencio and P. Smith, *Acta Cryst.*, 1970, *B*, **26**, 659.

[3] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[4] S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1967, 290.

[5] D. Rabinovich and G. M. J. Schmidt, *Nature*, 1966, **211**, 1391.

[6] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

The observed and calculated structure factors of the final cycle of each compound are listed in Supplementary Publication No. SUP 20329 (5 pp., 1 microfiche).* The scattering factor curves used for hydrogen, carbon and oxygen, and fluorine were taken from refs. 7—9.

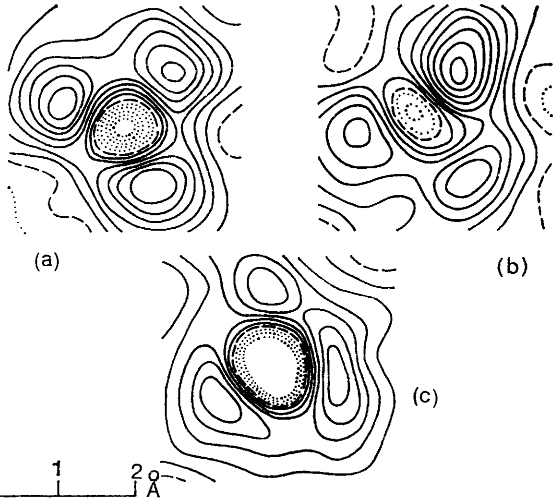

FIGURE 2 Mesitoic acid: electron-density difference-Fourier maps showing the methyl hydrogen atoms of the three methyl groups, contoured at intervals of 0·05 eÅ$^{-3}$

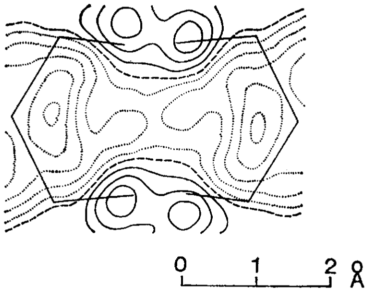

FIGURE 3 Mesitoic acid: electron-density difference-Fourier synthesis in the plane of the carboxy-dimer, contoured at intervals of 0·05 eÅ$^{-3}$

## RESULTS AND DISCUSSION

Tables 1 and 2 list the experimental positional and thermal parameters of pentafluorobenzoic acid and mesitoic acid, together with their estimated standard deviations.

*Molecular Shape*.—Pentafluorobenzoic acid is not planar; the carboxy-group is twisted out of the plane of the benzene ring by 29·8° (Table 3). By comparison, in the mono-*ortho*-substituted fluorobenzoic acid[10] the angle is 6·7°. The intramolecular O ··· F contacts in pentafluorobenzoic acid are 2·675 [O(1) ··· F(2)] and 2·655 Å [O(2) ··· F(6)]; in *o*-fluorobenzoic acid the O(carbonyl) ··· F distance is 2·585 Å. The benzene ring itself is quite planar and the fluorine substituents show small deviations from its best plane (Table 3).

The overcrowding of the carboxy-group and the *o*-methyl substituents in mesitoic acid is relieved primarily by an out-of-plane twist of 48·4° while from the crystal structure analysis of *o*-toluic acid[11] the molecule is described as approximately planar (atomic co-ordinates were not listed). The benzene ring of mesitoic acid is planar to within 0·01 Å (Table 3). The displacement of the carboxy-carbon C(7) from this plane (0·06 Å) is significant and is most likely to be due to the overcrowding of the carboxy-group and the *o*-methyl substituents. The deviation of 0·03 Å of the *p*-methyl carbon C(9) from the ring-plane may be due to intramolecular forces

TABLE 1

Atomic co-ordinates (fractional) and standard deviations referred to axes *a*, *b*, *c*

(*a*) Pentafluorobenzoic acid

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 0·19530(18) | 0·21005(17) | 0·10211(20) |
| O(2) | 0·11307(19) | −0·06174(17) | 0·19119(22) |
| C(1) | 0·39251(22) | 0·20416(21) | 0·37744(24) |
| C(2) | 0·56698(22) | 0·36987(21) | 0·35430(23) |
| C(3) | 0·72766(21) | 0·45416(21) | 0·50690(25) |
| C(4) | 0·71656(23) | 0·37608(24) | 0·68742(25) |
| C(5) | 0·54671(24) | 0·21388(23) | 0·71596(24) |
| C(6) | 0·38700(22) | 0·12930(22) | 0·56273(24) |
| C(7) | 0·22098(21) | 0·11394(21) | 0·20939(24) |
| F(2) | 0·58668(14) | 0·45355(14) | 0·18346(15) |
| F(3) | 0·89156(14) | 0·61280(15) | 0·47795(18) |
| F(4) | 0·86892(15) | 0·45810(16) | 0·83479(16) |
| F(5) | 0·53370(18) | 0·13706(16) | 0·89138(16) |
| F(6) | 0·22505(15) | −0·02676(14) | 0·60234(17) |
| H(1) | −0·0077(57) | −0·1222(49) | 0·0914(57) |

(*b*) Mesitoic acid

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 0·41806(6) | 0·54952(12) | 0·43075(5) |
| O(2) | 0·45940(7) | 0·27930(12) | 0·48536(6) |
| C(1) | 0·33525(7) | 0·27337(13) | 0·40104(5) |
| C(2) | 0·35173(7) | 0·10144(13) | 0·36254(6) |
| C(3) | 0·28131(8) | 0·01004(15) | 0·32643(6) |
| C(4) | 0·19624(8) | 0·08073(17) | 0·32885(6) |
| C(5) | 0·18193(8) | 0·25077(16) | 0·36714(6) |
| C(6) | 0·24958(7) | 0·35052(13) | 0·40288(5) |
| C(7) | 0·40897(7) | 0·37142(14) | 0·44208(6) |
| C(8) | 0·44291(9) | 0·01482(21) | 0·35702(10) |
| C(9) | 0·12038(12) | −0·02355(33) | 0·29126(11) |
| C(10) | 0·22780(10) | 0·53429(17) | 0·44383(8) |
| ½H(1) | 0·4713(39) | 0·6060(85) | 0·4654(33) |
| ½H(2) | 0·5021(43) | 0·3458(85) | 0·5056(41) |
| H(3) | 0·4890(12) | 0·1067(27) | 0·3401(10) |
| H(4) | 0·4705(15) | −0·0302(32) | 0·4128(13) |
| H(5) | 0·4431(11) | −0·0999(29) | 0·3208(11) |
| H(6) | 0·2920(9) | −0·1048(20) | 0·2993(8) |
| H(7) | 0·0650(17) | 0·0161(34) | 0·3212(15) |
| H(8) | 0·1240(16) | 0·0005(35) | 0·2351(16) |
| H(9) | 0·1291(17) | −0·1661(42) | 0·2958(14) |
| H(10) | 0·1217(10) | 0·2873(19) | 0·3726(7) |
| H(11) | 0·1646(12) | 0·5445(22) | 0·4583(9) |
| H(12) | 0·2467(11) | 0·6416(25) | 0·4124(10) |
| H(13) | 0·2553(10) | 0·5341(25) | 0·4969(12) |

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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[9] A. J. Freeman, *Acta Cryst.*, 1959, **12**, 261.

[10] J. Krausse and H. Dunken, *Acta Cryst.*, 1966, **20**, 67; G. Ferguson and K. M. S. Islam, *Acta Cryst.*, 1966, **21**, 1000.

[11] C. Katayama, A. Furusaki, and I. Nitta, *Bull. Chem. Soc. Japan*, 1967, **40**, 1293.

TABLE 2

Observed thermal parameters and standard deviations (Å$^2$) referred to axes *a*, *b*, *c*

(*a*) Pentafluorobenzoic acid

| Atom | $u^{11}$ | $u^{22}$ | $u^{33}$ | $u^{12}$ | $u^{23}$ | $u^{13}$ |
|---|---|---|---|---|---|---|
| O(1) | 0·0556(7) | 0·0508(7) | 0·0630(8) | 0·0210(6) | 0·0041(6) | −0·0217(6) |
| O(2) | 0·0531(7) | 0·0403(7) | 0·0747(9) | 0·0098(6) | 0·0007(6) | −0·0234(6) |
| C(1) | 0·0357(6) | 0·0371(7) | 0·0393(7) | 0·0147(6) | 0·0022(6) | −0·0022(5) |
| C(2) | 0·0381(7) | 0·0396(8) | 0·0375(7) | 0·0166(6) | 0·0063(6) | −0·0000(5) |
| C(3) | 0·0327(7) | 0·0401(8) | 0·0481(8) | 0·0113(6) | 0·0013(7) | −0·0003(6) |
| C(4) | 0·0408(7) | 0·0508(9) | 0·0445(8) | 0·0235(7) | −0·0028(7) | −0·0098(6) |
| C(5) | 0·0536(9) | 0·0503(9) | 0·0383(7) | 0·0301(8) | 0·0074(7) | −0·0009(6) |
| C(6) | 0·0403(7) | 0·0371(8) | 0·0453(6) | 0·0145(6) | 0·0073(6) | 0·0034(6) |
| C(7) | 0·0365(7) | 0·0376(8) | 0·0455(8) | 0·0135(6) | 0·0023(6) | −0·0047(6) |
| F(2) | 0·0546(6) | 0·0477(6) | 0·0456(5) | 0·0159(4) | 0·0160(4) | 0·0001(4) |
| F(3) | 0·0369(5) | 0·0482(6) | 0·0693(6) | 0·0033(4) | 0·0063(5) | 0·0000(4) |
| F(4) | 0·0518(6) | 0·0757(8) | 0·0578(7) | 0·0294(6) | −0·0054(6) | −0·0236(5) |
| F(5) | 0·0834(8) | 0·0656(7) | 0·0464(5) | 0·0415(6) | 0·0179(5) | −0·0021(5) |
| F(6) | 0·0550(6) | 0·0458(6) | 0·0609(6) | 0·0075(5) | 0·0181(5) | 0·0043(5) |

| Atom | $U$ |
|---|---|
| H(1) | 0·147(14) |

(*b*) Mesitoic acid

| Atom | $u^{11}$ | $u^{22}$ | $u^{33}$ | $u^{12}$ | $u^{23}$ | $u^{13}$ |
|---|---|---|---|---|---|---|
| O(1) | 0·1076(7) | 0·0579(5) | 0·1132(7) | −0·0244(4) | 0·0168(5) | −0·0371(6) |
| O(2) | 0·0860(6) | 0·0645(5) | 0·0977(6) | −0·0122(4) | 0·0121(4) | −0·0293(5) |
| C(1) | 0·0664(6) | 0·0475(5) | 0·0552(5) | −0·0046(4) | 0·0038(4) | −0·0015(4) |
| C(2) | 0·0697(6) | 0·0506(5) | 0·0622(5) | −0·0020(4) | 0·0014(4) | 0·0057(4) |
| C(3) | 0·0837(7) | 0·0554(6) | 0·0620(6) | −0·0059(5) | −0·0104(5) | 0·0051(5) |
| C(4) | 0·0756(6) | 0·0711(5) | 0·0580(5) | −0·0124(5) | −0·0061(5) | −0·0056(0) |
| C(5) | 0·0660(6) | 0·0693(6) | 0·0614(5) | 0·0015(5) | −0·0003(5) | −0·0035(5) |
| C(6) | 0·0725(6) | 0·0496(5) | 0·0545(5) | 0·0016(4) | 0·0005(4) | −0·0002(4) |
| C(7) | 0·0710(6) | 0·0512(5) | 0·0660(6) | −0·0072(4) | 0·0057(4) | −0·0057(5) |
| C(8) | 0·0757(8) | 0·0689(7) | 0·1087(11) | 0·0086(6) | −0·0076(7) | 0·0113(7) |
| C(9) | 0·0938(13) | 0·1145(11) | 0·0992(9) | −0·0252(10) | −0·0311(9) | −0·0164(0) |
| C(10) | 0·0943(9) | 0·0546(6) | 0·0814(8) | 0·0083(6) | −0·0081(6) | 0·0042(7) |

| Atom | $U$ | Atom | $U$ | Atom | $U$ | Atom | $U$ |
|---|---|---|---|---|---|---|---|
| $\frac{1}{2}$H(1) | 0·143(20) | H(5) | 0·094(6) | H(8) | 0·142(9) | H(11) | 0·077(5) |
| $\frac{1}{2}$H(2) | 0·140(24) | H(6) | 0·055(4) | H(9) | 0·152(10) | H(12) | 0·082(5) |
| H(3) | 0·090(6) | H(7) | 0·138(9) | H(10) | 0·057(4) | H(13) | 0·086(5) |
| H(4) | 0·121(7) | | | | | | |

involving methyl hydrogen to aromatic hydrogen contacts.

*Rigid-body Motion Analysis.*—The thermal motion analysis (Schomaker and Trueblood)[12] was carried out, not on the entire molecule of pentafluorobenzoic acid, but on the more rigid $C_6F_5C$ fragment, the oxygen atoms being excluded. The results are given in Table 4.

TABLE 3

Equations of planes in the form $Ax + By + Cz + D = 0$ where $x$, $y$, $z$ are fractional atomic co-ordinates; distances (10$^3$ Å) of relevant atoms from the planes are given in square brackets

(*a*) Pentafluorobenzoic acid

Plane (I):

C(1)—(6) $5{\cdot}9781x - 6{\cdot}6965y - 2{\cdot}5448z - 0{\cdot}0158 = 0$

[O(1) −515, O(2) 587], C(1) 3, C(2) −5, C(3) 3, C(4) 0, C(5) −2, C(6) 0, C(7) 10, F(2) −13, F(3) −6, F(4) −13, F(5) −11, F(6) −24]

Plane (II):

C(1), C(7), O(1), O(2) $-5{\cdot}7937x + 3{\cdot}1350y + 4{\cdot}2176z + 0{\cdot}0420 = 0$

[O(1) −1, O(2) −1, C(1) −1, C(7) 2, H(1) 89]

(*b*) Mesitoic acid

Plane (I):

C(1)—(6) $-2{\cdot}2727x - 3{\cdot}5601y + 14{\cdot}7376z - 4{\cdot}1388 = 0$

[O(1) −766, O(2) 888, C(1) 5, C(2) 5, C(3) −10, C(4) 6, C(5) 4, C(6) −9, C(7) 60, C(8) −17, C(9) 30, C(10) 0]

Plane (II):

C(1), C(7), O(1), O(2) $-9{\cdot}2536x + 1{\cdot}3190y + 13{\cdot}5295z - 2{\cdot}6849 = 0$

[O(1) −1, O(2) −1, C(1) −1, C(7) 2, $\frac{1}{2}$H(1) 50, $\frac{1}{2}$H(2) −34]

There is, in general, fairly good agreement between the observed and calculated thermal parameters $u^{ij}$ which were expressed in terms of the inertial frame of the $C_6F_5C$ fragment (Table 4). However, the root-mean-square discrepancy of $\Delta u^{ij}$ is 0·0032 Å$^2$ which is large compared with the mean $\sigma$ of the observed $u^{ij}$ (0·0008 Å$^2$). These values suggest that the $C_6F_5C$ fragment does not behave as an ideal rigid body; the exocyclic C–F and C–C bonds undergoing independent vibrations. An excess libratory motion of the carboxy-group was indicated by the positive discrepancies [$u^{33}$ (obs.) — $u^{33}$ (calc.)] of the oxygen atoms.

Similarly, the rigid-body analysis of mesitoic acid was carried out on the $C_6Me_3C$ fragment, the oxygens being excluded. The results are listed in Table 4.

The agreement between the observed and calculated thermal parameters $u^{ij}$ is fairly good. The root-mean-square discrepancy $\Delta u^{ij}$ is 0·0025 Å$^2$, while the mean $\sigma$ of the observed $u^{ij}$ [Table 2(*b*)] is 0·0007 Å$^2$. As in pentafluorobenzoic acid, the observed and calculated $u^{ij}$ indicate that the carboxy-group is not rigidly attached to the ring.

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[12] V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, *B*, **24**, 63.

TABLE 4

The components of the tensors and the unit vectors along their principal axes are referred to the axial systems of inertia (***M****ᵢ*) defined below. The calculation is referred to the origin which symmetrises ***S*** and reduces the trace of ***T***. The co-ordinates (Å) of this origin in the inertial system with its origin at the centre of mass, are:

| | $m_1$ | $m_2$ | $m_3$ |
|---|---|---|---|
| (*a*) Pentafluorobenzoic acid | 0·221 | −0·825 | −0·145 |
| (*b*) Mesitoic acid | 0·627 | −0·169 | −0·241 |

(*a*) Pentafluorobenzoic acid

Covariant components of the $\boldsymbol{M}_i$ set

| | $x_1$ | $x_2$ | $x_3$ |
|---|---|---|---|
| $\boldsymbol{M}_1$ | 1·0555 | 5·4331 | −4·1870 |
| $\boldsymbol{M}_2$ | 5·0902 | −0·3456 | 3·9053 |
| $\boldsymbol{M}_3$ | 5·9814 | −6·7054 | −2·5344 |

Tensor elements $\times 10^5$

| Tensor | 11 | 22 | 33 |
|---|---|---|---|
| ***L***/radian² | 330(32) | 641(39) | 379(21) |
| ***T***/Å² | 3633(107) | 3216(103) | 3945(165) |
| ***S***/radian × Å | −21(47) | 0(44) | 21(64) |

| Tensor | 12 | 23 | 13 |
|---|---|---|---|
| ***L***/radian² | −75(22) | −101(29) | 14(28) |
| ***T***/Å² | −305(92) | 112(111) | 7(113) |
| ***S***/radian × Å | −33(43) | −46(21) | −76(24) |

| | Root-mean-square amplitudes | Principal axes | | |
|---|---|---|---|---|
| | | $m_1$ | $m_2$ | $m_3$ |
| ***L***/deg. | 4·8 | 0·1851 | −0·9364 | 0·2983 |
| | 3·5 | 0·5572 | −0·1500 | −0·8167 |
| | 3·1 | 0·8095 | 0·3174 | 0·4940 |
| ***T***/Å | 0·199 | −0·1737 | 0·2137 | 0·9613 |
| | 0·194 | −0·8717 | 0·4208 | −0·2510 |
| | 0·174 | −0·4582 | −0·8816 | 0·1132 |

(*b*) Mesitoic acid

Covariant components of the $\boldsymbol{M}_i$ set

| | $x_1$ | $x_2$ | $x_3$ |
|---|---|---|---|
| $\boldsymbol{M}_1$ | 11·4056 | 3·3662 | 7·7110 |
| $\boldsymbol{M}_2$ | 9·5804 | −5·0242 | −5·3081 |
| $\boldsymbol{M}_3$ | 2·7235 | 3·5766 | −14·7137 |

Tensor elements $\times 10^5$

| Tensor | 11 | 22 | 33 |
|---|---|---|---|
| ***L***/radian² | 749(35) | 561(23) | 457(17) |
| ***T***/Å² | 5722(86) | 5790(91) | 4174(131) |
| ***S***/radian × Å | −38(45) | −156(49) | 194(67) |

| Tensor | 12 | 23 | 13 |
|---|---|---|---|
| ***L***/radian² | −84(37) | 36(24) | 84(30) |
| ***T***/Å² | 868(80) | 469(93) | −46(101) |
| ***S***/radian × Å | 85(38) | 54(22) | 20(19) |

| | Root-mean-square amplitudes | Principal axes | | |
|---|---|---|---|---|
| | | $m_1$ | $m_2$ | $m_3$ |
| ***L***/deg. | 5·1 | −0·9315 | 0·3045 | −0·1992 |
| | 4·3 | −0·1884 | −0·8718 | −0·4521 |
| | 3·7 | −0·3113 | −0·3836 | 0·8694 |
| ***T***/Å | 0·258 | −0·6691 | −0·7324 | −0·1257 |
| | 0·224 | −0·7178 | 0·5933 | 0·3644 |
| | 0·200 | −0·1923 | 0·3340 | −0·9227 |

The bond lengths of both structures corrected for libratory motion are shown in Figure 4.

*Bond Lengths and Bond Angles.*—The bond lengths and bond angles of pentafluorobenzoic acid are shown in Figure 4. Their mean σ values are 0·002 Å and 0·14° respectively. A measure of precision of these bond parameters may also be derived from a comparison of the ' chemically equivalent ' halves of the $C_6F_5C$ group, leading to a mean ' scatter ' of 0·003 Å and 0·1°.

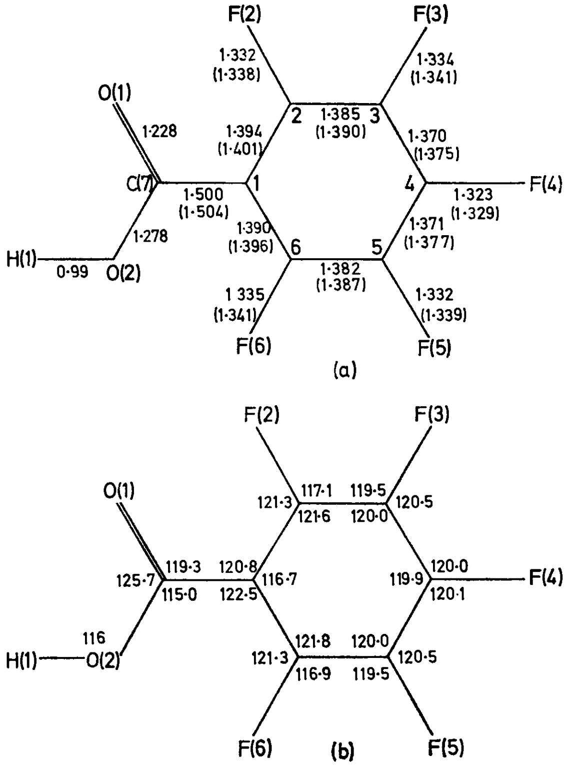

FIGURE 4 Pentafluorobenzoic acid: (a) bond lengths (Å), with values corrected for thermal vibration in parentheses; and (b) bond angles (°)

The benzene ring, which conforms to *m* symmetry about the line C(1) · · · C(4), shows a systematic trend in bond lengths. The bonds adjacent to the carboxy-group [C(1)–C(2) and C(1)–C(6)], are the longest, mean **1·392 Å**; the length of the adjoining bonds C(2)–C(3) and C(6)–C(5), is **1·384 Å**; and the remaining bonds C(3)–C(4) and C(4)–C(5) are the shortest (**1·371 Å**). This trend could hardly be an artefact caused by the libratory motion of the molecule for the bond lengths show the same variation after correction for rigid-body motion (Figure 4). These differences in aromatic bond lengths may be due, in the main, to non-bonded repulsions between the carboxylic oxygens and the phenyl ring, which induce a stretching of the C(1)–C(2) and C(1)–C(6) bonds. The role of non-bonded repulsions between adjacent atoms in determining bond lengths has been strongly stressed,[13] and bond length variation in a number of overcrowded compounds [14,15] has been interpreted along these lines.

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[13] L. S. Bartell, *Tetrahedron*, 1962, **17**, 177.
[14] A. W. Hanson, *Acta Cryst.*, 1962, **15**, 956.
[15] M. Mathew, *Acta Cryst.*, 1968, *B*, **24**, 530.

With regard to the fluorine substituents, all the C–F bonds, except the *para*-substituted C(4)–F bond, are equal in length to within 0·002 Å. The mean C–F bond length (1·331) compares well with the literature value (1·328 Å).[16] The bond lengths of the carboxy-group are discussed later.

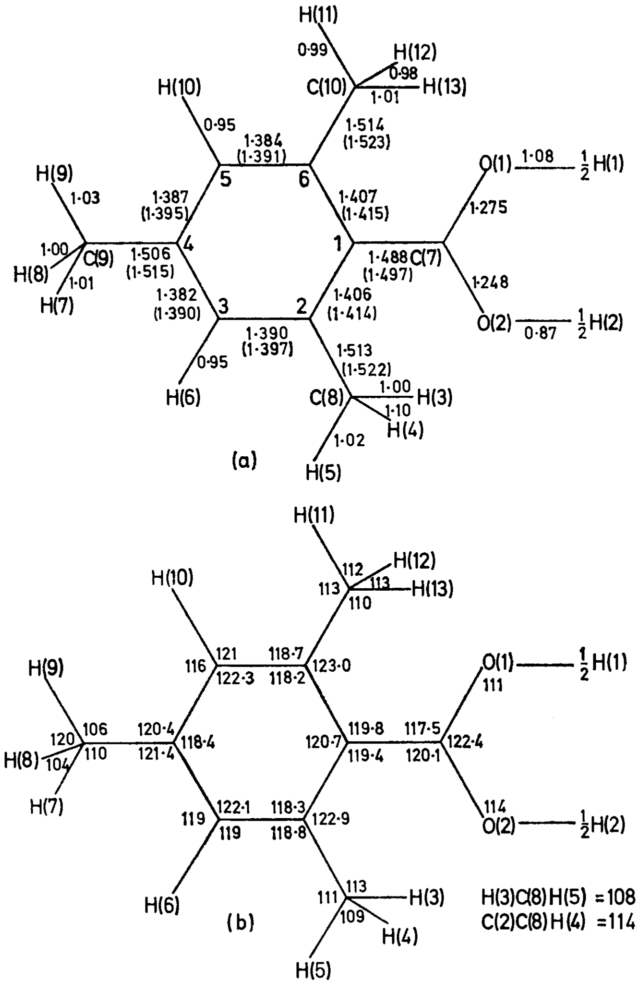


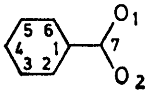
FIGURE 5 Mesitoic acid: (a) bond lengths (Å), with values corrected for thermal vibration in parentheses; and (*b*) bond angles (°) [C(4)–C(9)–H(8) 107, H(7)–C(9)–H(9) 110, H(11)–C(10)–H(13) 99, and C(6)–C(10)–H(12) 109°]

The bond lengths and bond angles of mesitoic acid are shown in Figure 5. The $\sigma$ values for heavy atoms only are 0·002 Å and 0·10°. The corresponding values involving a hydrogen atom are 0·03 Å and 1·5°. A comparison of the ' chemically equivalent ' halves of the carbon skeleton leads to a mean ' scatter ' in bond length and angle of 0·004 Å and 0·15°.

The aromatic bonds adjacent to the carboxy-group, mean 1·406 Å, are 0·02 Å longer than the other ring bonds which in themselves match to within their mean by 0·004 Å. This variation in aromatic bond length is probably significant and, as in pentafluorobenzoic acid, may be attributed to the non-bonded repulsions between the carboxy-group and the neighbouring phenyl atoms inducing a stretching of the C(1)–C(2) and C(1)–C(6) bonds. Indeed, for the same reason, we may account for the fact that the *ortho*-C–$CH_3$ methyl bonds are 0·009 Å longer than the *para*-C–$CH_3$ methyl bond. The symmetric and tetrahedral nature of the methyl groups is illustrated by the mean C–H bond length and bond angle at the methyl carbon of 1·02 Å and 109°, and their respective ' scatters ' of 0·03 Å and 5°.

TABLE 5

Molecular dimensions of a number of methyl-substituted benzoic acids



| Bond | 2,4,6-triMe | 2,4,6-triMe [a] | 2,6-diMe [b] | 3,4,5-triMe [c] |
|---|---|---|---|---|
| C(7)–O(1) | 1·275 Å | 1·286 Å | 1·276 Å | 1·287 Å |
| C(7)–O(2) | 1·248 | 1·250 | 1·226 | 1·251 |
| C(1)–C(7) | 1·488 | 1·491 | 1·525 | 1·472 |
| C(1)–C(2) | 1·407 | 1·382 | 1·403 | 1·400 |
| C(6)–C(1) | 1·406 | 1·395 | 1·399 | 1·397 |
| C(2)–C(3) | 1·384 | 1·398 | 1·399 | 1·394 |
| C(5)–C(6) | 1·390 | 1·402 | 1·395 | 1·400 |
| C(3)–C(4) | 1·387 | 1·390 | 1·396 | 1·391 |
| C(4)–C(5) | 1·382 | 1·380 | 1·394 | 1·410 |
| C(6)–$CH_3$ | 1·513 | 1·538 | 1·519 | |
| C(2)–$CH_3$ | 1·514 | 1·547 | 1·531 | |
| C(4)–$CH_3$ | 1·506 | 1·533 | | 1·526 |
| C(3)–$CH_3$ | | | | 1·523 |
| C(5)–$CH_3$ | | | | 1·516 |
| O–H · · · O | 2·640 | 2·648 | 2·673 | 2·628 |
| Plane angle [d] | 48°27′ | 48°29′ | 53°31′ | 5°6′ |

[a] Ref. 2. [b] Ref. 17. [c] Ref. 18. [d] Angle between the benzene and carboxy-group planes.

Table 5 lists the bond lengths of mesitoic acid determined by Florencio and Smith [2] as well as those of the present analysis. The bond lengths of 2,6-dimethylbenzoic acid [17] and 3,4,5-trimethylbenzoic acid [18] are also included.

*Carboxy-pair and Packing*.—The molecules of pentafluorobenzoic acid form hydrogen-bonded pairs (O–H · · · O, 2·668 Å) as shown in the packing diagram (Figure 6). These hydrogen-bonded carboxy-groups are not fully coplanar, being offset 0·09 Å.

The C=O and C–OH bond lengths (1·228 and 1·278 Å) and the presence of the hydroxy-hydrogen on the difference-Fourier electron-density map (Figure 1) indicate that the carboxy-pair does not exhibit appreciable orientational disorder in the crystal lattice, the lack of which must be attributed to intermolecular forces in view of the *mm* symmetry of the $C_6F_5C$ fragment. An examination of the packing normal to the best plane of the carboxy-dimer [Figure 6(a)] reveals

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[16] *Chem. Soc. Special Publ.*, No. 11, 1958.

[17] R. Ance, S. Martinez-Carrera, and S. Garcia-Blanco, *Acta Cryst.*, 1967, **23**, 1010.

[18] F. H. Cano, S. Martinez-Carrera, and S. Garcia-Blanco, *Acta Cryst.*, 1970, *B*, **26**, 972.

differences in environment of the carbonyl- and hydroxy-oxygen atoms, in particular the contact approach directly above the plane of the dimer. However, we are not able, at this stage, to state with any degree of certainty which are the decisive intermolecular contacts maintaining the orientation of the carboxy-dimer. Intermolecular distances are listed in Table 6.

The molecules of mesitoic acid form cyclic pairs linked by O–H · · · O hydrogen bonds (2·640 Å) (Figure 7). These hydrogen-bonded carboxy-groups are not fully coplanar, being offset 0·10 Å. The observed lengths of

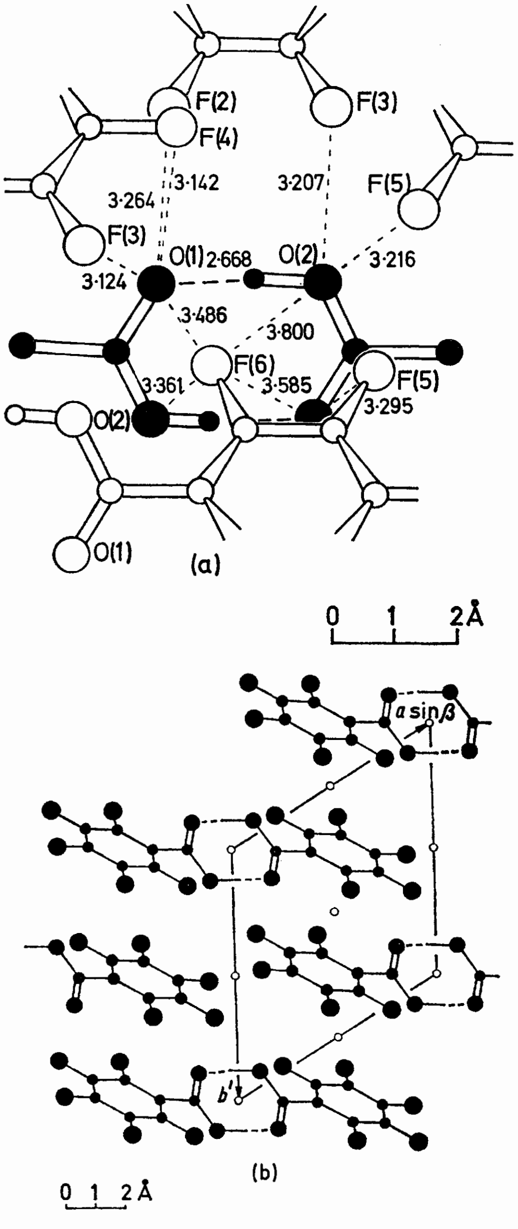

**Figure** 6 Pentafluorobenzoic acid: (a) packing environment about the shaded centrosymmetric hydrogen-bonded carboxy-pair, showing some intermolecular distances (Å). (b) Packing arrangement seen along [001]. $b' = b \sin \alpha$

TABLE 6

Interatomic distances ($\leq$3·70 Å)

(*a*) Pentafluorobenzoic acid

| | |
|---|---|
| $A$(000) * $A$(000) | |
| O(1) · · · O(2) | 2·230 |
| O(1) · · · F(2) | 2·675 |
| O(1) · · · C(1) | 2·357 |
| O(1) · · · C(2) | 2·875 |
| O(2) · · · F(6) | 2·655 |
| O(2) · · · C(1) | 2·345 |
| O(2) · · · C(6) | 2·849 |
| C(7) · · · F(2) | 2·859 |
| C(7) · · · F(6) | 2·891 |
| C(7) · · · C(2) | 2·516 |
| C(7) · · · C(6) | 2·533 |
| F(2) · · · F(3) | 2·647 |
| F(3) · · · F(4) | 2·709 |
| F(4) · · · F(5) | 2·709 |
| F(5) · · · F(6) | 2·643 |
| $A$(000) $\bar{A}$(102) | |
| F(5) · · · F(5) | 2·691 |
| $A$(000) $A(\bar{1}\bar{1}0)$ | |
| O(2) · · · F(3) | 3·207 |
| F(6) · · · F(3) | 2·826 |
| $A$(000) $A(00\bar{1})$ | |
| O(1) · · · F(6) | 3·585 |
| O(1) · · · F(5) | 3·295 |
| O(2) · · · F(5) | 3·509 |
| C(7) · · · F(5) | 3·109 |
| F(2) · · · F(5) | 2·912 |
| F(2) · · · F(4) | 3·105 |
| $A$(000) $\bar{A}$(000) | |
| O(1) · · · O(2) | 2·668 |
| $A$(000) $\bar{A}$(001) | |
| O(2) · · · F(6) | 3·361 |
| $A$(000) $\bar{A}$(101) | |
| O(2) · · · F(5) | 3·216 |
| O(2) · · · F(4) | 3·484 |
| $A$(000) $\bar{A}$(111) | |
| O(1) · · · C(3) | 3·326 |
| O(1) · · · C(4) | 3·338 |
| O(1) · · · F(3) | 3·124 |
| O(1) · · · F(4) | 3·142 |
| C(7) · · · F(3) | 3·344 |
| $A$(000) $\bar{A}$(211) | |
| C(3) · · · F(3) | 3·363 |
| C(4) · · · F(3) | 3·225 |
| F(3) · · · F(3) | 3·242 |
| F(3) · · · F(4) | 2·946 |
| $A$(000) $\bar{A}$(212) | |
| F(4) · · · F(4) | 2·682 |
| $A$(000) $\bar{A}$(110) | |
| O(1) · · · F(2) | 3·264 |
| F(2) · · · F(2) | 3·081 |

* Co-ordinates of equivalent positions:

$A$ $x, y, z$ $\bar{A}$ $-x, -y, -z$

$A(pqr)$ Denotes fractional co-ordinates $p + x, q + y, r + z$.

(*b*) Mesitoic acid

| | |
|---|---|
| $A$(000) † $A$(000) | |
| O(1) · · · H(13) | 2·73 |
| O(1) · · · O(2) | 2·211 |
| O(1) · · · H(12) | 2·69 |
| O(1) · · · C(10) | 2·894 |
| O(1) · · · C(6) | 2·945 |
| O(1) · · · C(1) | 2·364 |
| C(7) · · · C(10) | 2·973 |
| C(7) · · · C(8) | 2·960 |
| O(2) · · · C(8) | 2·918 |
| O(2) · · · C(2) | 2·954 |
| O(2) · · · C(1) | 2·374 |
| O(2) · · · H(4) | 2·52 |
| O(2) · · · H(3) | 2·85 |
| C(5) · · · H(9) | 2·54 |
| C(5) · · · H(8) | 3·02 |
| C(4) · · · H(8) | 2·04 |
| C(4) · · · H(7) | 2·09 |
| C(4) · · · H(9) | 2·04 |
| $A$(000) $A(0\bar{1}0)$ | |
| C(4) · · · H(12) | 3·49 |
| C(3) · · · H(12) | 3·04 |
| $A$(000) $B(0\bar{1}0)$ | |
| C(8) · · · H(10) | 3·15 |
| $A$(000) $A$(010) | |
| O(1) · · · H(3) | 3·08 |
| O(1) · · · H(5) | 3·15 |
| $A$(000) $\bar{D}$(000) | |
| O(1) · · · H(8) | 2·97 |
| C(4) · · · H(6) | 3·15 |
| C(5) · · · H(6) | 3·11 |
| C(1) · · · H(8) | 2·93 |
| $A$(000) $B$(000) | |
| O(1) · · · H(9) | 2·96 |
| C(7) · · · H(9) | 3·34 |
| $A$(000) $B(\bar{1}\bar{1}0)$ | |
| C(9) · · · H(3) | 3·39 |
| $A$(000) $A$(010) | |
| O(1) · · · H(4) | 3·08 |
| O(1) · · · H(5) | 3·15 |
| O(1) · · · C(8) | 3·535 |
| $A$(000) $\bar{B}$(011) | |
| C(10) · · · H(13) | 3·21 |
| $A$(000) $\bar{A}$(101) | |
| O(2) · · · H(4) | 2·702 |
| $A$(000) $\bar{A}$(111) | |
| O(1) · · · O(2) | 2·640 |
| $A$(000) $\bar{B}$(001) | |
| O(2) · · · C(5) | 3·371 |
| O(2) · · · H(10) | 2·82 |
| O(2) · · · H(11) | 3·12 |
| C(1) · · · C(10) | 3·600 |
| C(1) · · · H(13) | 3·13 |
| C(3) · · · H(13) | 3·15 |
| C(2) · · · H(13) | 3·10 |

† Co-ordinates of equivalent positions:

$A$ $x, y, z$ $C$ $x, -y, \frac{1}{2} + z$

$B$ $\frac{1}{2} + x, \frac{1}{2} + y, z$ $D$ $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

Where $\bar{A}$ is $\bar{x}, \bar{y}, \bar{z}$ *etc.*; $A(pqr)$ denotes fractional co-ordinates $p + x, q + y, r + z$.

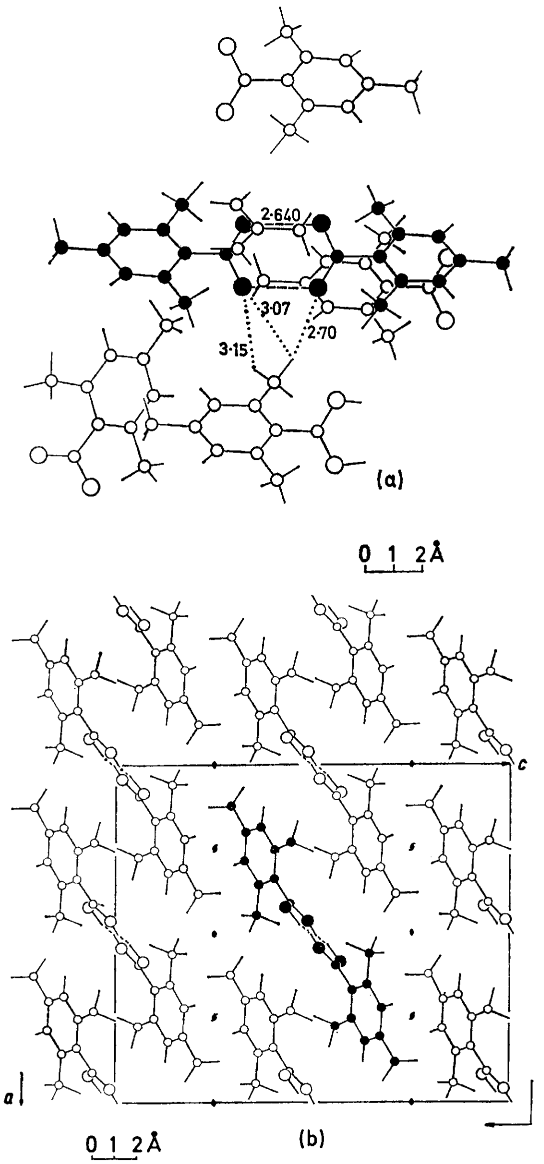

Figure 7 Mesitoic acid: (a) packing environment seen perpendicular to the best plane of the carboxylic acid dimer of the shaded molecules showing some intermolecular contacts (Å). (b) Packing arrangement seen along [010]

the C–O bonds (1·248, 1·275 Å), and the difference-Fourier electron-density map in the plane of the carboxy-group indicate that the carboxy-pair displays partial orientational disorder in the crystal lattice. This effect is most likely to be due to the presence of the *o*-methyl groups which are related by approximate two-fold symmetry, and which would provide similar contact geometry (Figure 8) for the carboxy-group in its two equivalent orientations (I) and (II). Furthermore, the oxygen atoms are partially shielded from intermolecular contacts [Table 6(*b*)] by the *o*-methyl groups. The extent of shielding is dependent upon the degree of coplanarity of the carboxy-group with the benzene ring; the larger the angle of twist, the more exposed are the oxygen atoms.

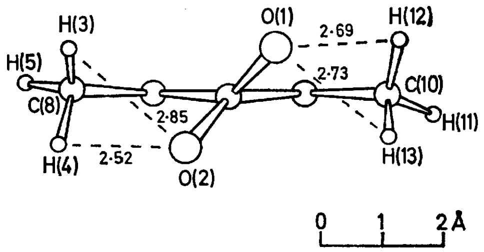

Figure 8 Mesitoic acid: environment of the carboxy-group as seen along the molecular pseudo-two-fold axis; O · · · H intramolecular contacts (Å) are given

The angle of twist in 2,6-dimethylbenzoic acid is 53·5° and yet its C–O bond lengths (Table 5) are 1·276 and 1·226 Å which indicate less orientational disorder than in mesitoic acid. Perhaps this is correlated with the somewhat greater angle of twist of the carboxy-group in the former. In addition the methyl hydrogens in 2,6-dimethylbenzoic acid were not determined and so we are not aware of the extent to which the two methyl groups are related by molecular two-fold symmetry, and hence its effect on the stabilisation of the orientation of the carboxy-group.

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