broad range, 1·78 to 1·91 Å. The lengths of the two C—S bonds in the present crystal, 1·806 (3) and 1·862 (3) Å, lie in this range. There is no abnormally short intermolecular distance in this crystal.

Table 2. *Bond lengths (Å) and angles (°)*

S—C(1)	1·806 (3)	S—C(4)	1·862 (3)
O—C(3)	1·200 (4)	N—C(1)	1·461 (4)
N—C(3)	1·374 (4)	N—C(19)	1·427 (4)
C(1)—C(2)	1·581 (4)	C(1)—C(4)	1·488 (4)
C(2)—C(3)	1·545 (4)	C(2)—C(7)	1·529 (4)
C(2)—C(13)	1·518 (4)	C(4)—C(5)	1·511 (5)
C(4)—C(6)	1·522 (5)	C(7)—C(8)	1·382 (5)
C(7)—C(12)	1·397 (5)	C(8)—C(9)	1·412 (5)
C(9)—C(10)	1·382 (6)	C(10)—C(11)	1·378 (7)
C(11)—C(12)	1·397 (6)	C(13)—C(14)	1·391 (5)
C(13)—C(18)	1·393 (5)	C(14)—C(15)	1·397 (5)
C(15)—C(16)	1·369 (6)	C(16)—C(17)	1·387 (6)
C(17)—C(18)	1·390 (5)	C(19)—C(20)	1·376 (5)
C(19)—C(24)	1·402 (5)	C(20)—C(21)	1·384 (5)
C(21)—C(22)	1·405 (6)	C(22)—C(23)	1·362 (6)
C(23)—C(24)	1·386 (5)		
C(1)—S—C(4)	47·8 (1)	C(1)—N—C(3)	94·7 (2)
C(1)—N—C(19)	136·7 (3)	C(3)—N—C(19)	128·3 (3)
S—C(1)—N	122·2 (2)	S—C(1)—C(2)	128·8 (2)
S—C(1)—C(4)	68·1 (2)	N—C(1)—C(2)	88·5 (2)
N—C(1)—C(4)	124·5 (3)	C(2)—C(1)—C(4)	129·9 (3)
C(1)—C(2)—C(3)	83·7 (2)	C(1)—C(2)—C(7)	113·3 (2)
C(1)—C(2)—C(13)	116·6 (2)	C(3)—C(2)—C(7)	111·7 (2)
C(3)—C(2)—C(13)	113·1 (2)	C(7)—C(2)—C(13)	114·6 (3)
O—C(3)—N	132·0 (3)	O—C(3)—C(2)	134·8 (3)
N—C(3)—C(2)	93·2 (2)	S—C(4)—C(1)	64·1 (2)
S—C(4)—C(5)	117·4 (2)	S—C(4)—C(6)	113·0 (2)
C(1)—C(4)—C(5)	119·7 (3)	C(1)—C(4)—C(6)	119·0 (3)
C(5)—C(4)—C(6)	114·2 (3)	C(2)—C(7)—C(8)	121·9 (3)
C(2)—C(7)—C(12)	118·5 (3)	C(8)—C(7)—C(12)	119·6 (3)
C(7)—C(8)—C(9)	120·0 (3)	C(8)—C(9)—C(10)	119·6 (4)
C(9)—C(10)—C(11)	120·7 (4)	C(10)—C(11)—C(12)	119·8 (4)
C(7)—C(12)—C(11)	120·2 (4)	C(2)—C(13)—C(14)	119·5 (3)
C(2)—C(13)—C(18)	121·5 (3)	C(14)—C(13)—C(18)	119·0 (3)
C(13)—C(14)—C(15)	119·9 (3)	C(14)—C(15)—C(16)	120·8 (4)
C(15)—C(16)—C(17)	119·8 (4)	C(16)—C(17)—C(18)	120·0 (4)
C(13)—C(18)—C(17)	120·5 (3)	N—C(19)—C(20)	118·4 (3)
N—C(19)—C(24)	121·2 (3)	C(20)—C(19)—C(24)	120·3 (3)
C(19)—C(20)—C(21)	120·1 (3)	C(20)—C(21)—C(22)	120·0 (4)
C(21)—C(22)—C(23)	119·1 (4)	C(22)—C(23)—C(24)	121·8 (4)
C(19)—C(24)—C(23)	118·6 (3)		
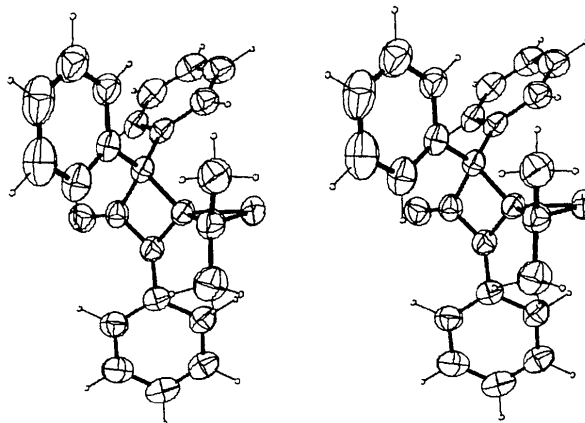
Fig. 1. A stereoscopic view of the molecule.

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Tetrafluorophthalic Acid (TFAC), $C_8H_2F_4O_4$

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Abstract. $M_r = 238·1$, monoclinic, $P2_1/n$, $a = 11·450$ (3), $b = 5·559$ (1), $c = 13·775$ (2) Å, $\beta = 107·52$ (1)°, $V = 836·1$ Å³, $Z = 4$, $D_x = 1·89$, $D_m = 1·82$ Mg m⁻³, $\mu(Cu\,K\alpha) = 1·93$ mm⁻¹, $T = 294$ K, Ni-

filtered Cu K radiation ($\lambda_{K\alpha_1} = 1.54051$ Å); the structure was solved with direct methods and refined to $R = 0.033$ for 1417 reflections. Bond lengths ($\sigma = 0.002$ Å) and angles ($\sigma = 0.1°$) are normal. The F atoms are slightly out of the plane of the benzene ring, and the two carboxyl groups are inclined 81.0 and 13.4° to this plane. The structure is stabilized by hydrogen bonding, with only one carbonyl oxygen, O(2), acting as the hydrogen-bond acceptor for both hydrogen bonds.

Introduction. The present study is related to our continuing investigation of phase transitions in the tetra*halo*phthalic anhydrides, TXPA (X = F, C ≡ Cl, B ≡ Br, I). The structures of the room-temperature phases of TCPA, TBPA, and TIPA have been completed (Sake Gowda & Rudman, 1982*a,b*) and it was our intention to study the remaining member of the series, TFPA. The latter compound was synthesized from TFAC and crystallized from a heptane–benzene solution. After studying several TFPA crystals selected from the bottom of the beaker and which decomposed rapidly upon exposure to the air, a crystal picked off the side of the beaker was mounted. This crystal (with different unit-cell parameters) was stable in air and data were collected from it. Midway through the structure solution it became apparent that the crystal was a twinned TFAC crystal, rather than TFPA. Realizing, at this point, that TFPA hydrolyzes readily in air to TFAC, we decided to study TFAC as well as TFPA. The structure of TFAC is reported here, while the structure of TFPA, based on data collected from a single crystal of TFPA mounted inside a capillary tube under dry conditions, is currently under investigation and will be reported elsewhere.

Experimental. TFAC from PCR Research Chemicals, Inc. (Gainesville, FL 32602, USA); D_m: trichloroethane–iodomethane mixture; white prisms (from toluene) $0.11 \times 0.16 \times 0.20$ mm; Syntex $P2_1$-F diffractometer, lattice parameters from 20 reflections ($30° < 2\theta < 60°$). Data collection: 2922 ($h,\pm k,\pm l$ with $2\theta \leq 115°$, $h,k,\pm l$ with $115° < 2\theta \leq 135°$, $h_{max} = 13$, $|k_{max}| = 6$, $|l_{max}| = 15$), automatic recentering every 633 reflections, three standard reflections every 102 reflections (3.5% variation), 1508 independent, 1417 with $F > 3\sigma(F)$, Lp correction, absorption and decay not applied; $P2_1/n$, general positions: $\pm$ (x,y,z; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) from systematic absences $0k0$, $k\neq2n$ and $h0l$, $h+l\neq2n$; direct methods (*MULTAN*; Declercq, Germain, Main & Woolfson, 1973; 128 $E>1.67$, 125 ψ_0, $E < 0.12$), anisotropic full matrix, H (from ΔF synthesis isotropic, based on F; final cycle: 153 parameters, $\Delta/\sigma_{max} = 0.03$, $\Delta/\sigma_{av} = 0.002$; R, R_w (defined in Sake Gowda & Rudman, 1982*a*): 0.033 and 0.049; $S = 2.53$, $w^{-1} = \sigma^2(F) + (0.015F_o)^2$, $\sigma(F) = \sigma(F^2)/(2F)$, $\sigma(F^2)$ based on counting statistics ($R = 0.034$, $R_w = $

0.049 for all unique data); final ΔF map featureless, $F(000) = 472$, lattice parameters calculated with *CELREF* (Adelphi University Library of Crystallographic Programs); all other calculations with the Syntex *XTL* programs [which utilize atomic scattering factors based on the analytical expressions found in *International Tables for X-ray Crystallography* (1974)] with the exception of the rigid-body calculations that were carried out using *TLS6* (Schomaker & Trueblood, 1968); anomalous-dispersion corrections for F and O were included. The final fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1 and follow the atom numbering scheme shown in Fig. 1.*

Twinned crystal. The twinned crystal of TFAC described in the *Introduction* had lattice parameters $a = 7.514$ (1), $b = 5.561$ (1), $c = 10.199$ (1) Å, $\beta = 101.06$ (1)°, $V = 418.2$ Å^3, with systematic absences $0k0$, $k=2n+1$, consistent with space groups $P2_1$ and $P2_1/m$, $Z=2$. A crystal with maximum dimensions $0.24 \times 0.16 \times 0.16$ mm was mounted and intensities of 1632 reflections were measured, from which 784 observed unique reflections were used in the refinement. *MULTAN*, least-squares, and difference Fourier methods were used to determine and refine the structure. Refinement was halted (and the study of the untwinned structure reported here was initiated) when the twinned model was refined to $R = 0.073$ and

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* Lists of structure factors, anisotropic thermal parameters, rigid-body tensors, interatomic angles, and the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38176 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters of TFAC in fractional coordinates* (F, O, C $\times 10^5$, H $\times 10^3$) *and* $B_{eq}(= \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j)$

Also shown are the deviations, $\Delta(\times 10^3$ Å), of atoms from the least-squares plane calculated through the benzene ring, whose equation is (X,Y,Z in Å): $0.6765X - 0.6588Y - 0.3291Z + 3.3177 = 0$.

|	x	y	z	$B_{eq}(\text{Å}^2)$	Δ
F(1)	−17653 (10)	48205 (22)	2661 (8)	4.95	−5 (1)
F(2)	96 (12)	80212 (23)	5876 (9)	5.02	−31 (1)
F(3)	18082 (10)	81911 (20)	23912 (9)	4.20	14 (1)
F(4)	17388 (9)	52141 (18)	39077 (7)	3.75	−30 (1)
O(1)	7079 (10)	810 (20)	39596 (9)	2.92	1014 (1)
O(2)	−6633 (10)	24377 (19)	43414 (8)	2.78	−1184 (1)
O(3)	−17387 (11)	−3743 (21)	24026 (9)	3.74	395 (1)
O(4)	−28327 (12)	14111 (24)	9687 (9)	3.99	−84 (1)
C(1)	−9738 (14)	32113 (26)	19360 (11)	2.39	7 (2)
C(2)	−9273 (15)	48179 (30)	11772 (12)	2.92	−4 (2)
C(3)	16 (17)	64821 (30)	13325 (13)	3.02	−5 (2)
C(4)	9050 (15)	65877 (28)	22429 (13)	2.76	8 (2)
C(5)	8663 (14)	50311 (27)	30137 (11)	2.51	−2 (2)
C(6)	−518 (14)	33630 (25)	28766 (11)	2.22	−5 (2)
C(7)	−573 (13)	18640 (25)	37865 (10)	2.31	−108 (2)
C(8)	−18869 (14)	12429 (27)	17988 (11)	2.57	119 (2)
H(O1)	66 (2)	−57 (4)	447 (2)	5.2 (5)	
H(O4)	−330 (2)	0.2 (46)	94 (2)	5.7 (6)	
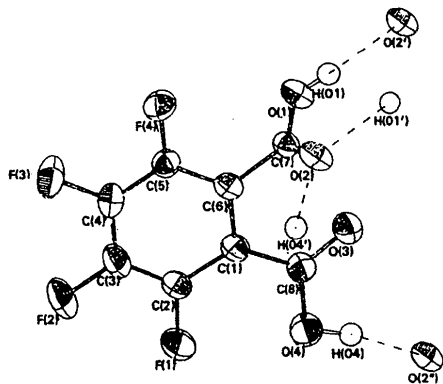
Fig. 1. *ORTEP* (Johnson, 1965) drawing of TFAC, showing hydrogen bonding of carboxyl groups. The symmetry operations for H(O1′), H(O4′), O(2′) and O(2″) are given in Table 2.

$R_w = 0.098$ with 32 atoms and 208 variable parameters (F and O were refined with anisotropic thermal parameters) in space group $P2_1$. No further work on this twinned crystal is contemplated.

Discussion. The distances and angles observed in TFAC (Table 2) fall within the normal range observed in similar compounds (*e.g.* potassium tetrafluorophthalate, Sake Gowda & Rudman, 1983). The planarity of halogenated benzene rings is of interest (*viz* Sake Gowda & Rudman, 1982*a*). Although the F atoms are found within 0.02 Å of the plane of the benzene ring, they lie significantly off this plane in a manner similar to that found in TCPA, TBPA, and TIPA (that is, with three atoms on the same side of the plane). The carboxyl groups are inclined to this plane, with the group centered on C(7) inclined at an angle of 81.0° and that centered on C(8) making an angle of 13.4°.

The hydrogen bonding in this dicarboxylic acid follows the usual pattern in that the acceptor atom is the carbonyl oxygen, but it is unusual in that O(2), which is the atom furthest from the least-squares plane through the benzene ring (Table 1), is the acceptor atom for *both* hydrogen bonds, while O(3) which is closer to this plane does not participate in the hydrogen bonding at all. This is shown schematically in Fig. 1 and in the (more crowded) packing diagram (Fig. 2). The angle H(O4′)···O(2)···H(O1′) is 116 (1)°. Thus, the C(7) carboxyl group forms the common hydrogen-bond dimer across a center of symmetry and also accepts the hydrogen bond from the C(8) carboxyl group on a different molecule. A three-dimensional hydrogen-bonded network results in which three of the four O atoms on each molecule are involved in four hydrogen-bond linkages (two acceptor and two donor) to three other molecules. Consequently, the fluorobenzene moieties are concentrated in one portion of the unit cell while the hydrogen-bonded carboxyl moieties are concentrated in another portion of the unit cell.

Table 2. *Interatomic distances* (Å) *in TFAC*

(*a*) Intramolecular

	Uncorrected	Corrected*
F(1)–C(2)	1·331 (2)	1·338
F(2)–C(3)	1·338 (2)	1·344
F(3)–C(4)	1·334 (2)	1·339
F(4)–C(5)	1·336 (2)	1·343
C(1)–C(2)	1·388 (2)	1·394
C(2)–C(3)	1·377 (3)	1·383
C(3)–C(4)	1·366 (2)	1·373
C(4)–C(5)	1·381 (2)	1·387
C(5)–C(6)	1·372 (2)	1·378
C(6)–C(1)	1·406 (2)	1·414
C(1)–C(8)	1·486 (2)	1·492
C(6)–C(7)	1·507 (2)	1·513
C(7)–O(1)	1·297 (2)	1·304
C(7)–O(2)	1·219 (2)	1·225
C(8)–O(3)	1·202 (2)	1·207
C(8)–O(4)	1·321 (2)	1·328
O(1)–H(O1)	0·81 (3)	
O(4)–H(O4)	0·95 (3)	
F(1)···F(2)	2·636 (2)	
F(2)···F(3)	2·710 (2)	
F(3)···F(4)	2·685 (1)	
F(1)···O(4)	2·595 (2)	

(*b*) Shortest intermolecular distances for F and O

F(1)···H(O1)	2·84 (3)	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$
F(2)···F(2)	2·727 (2)	$-x, 2-y, -z$
F(3)···O(1)	3·000 (2)	$x, 1+y, z$
F(4)···H(O4)	2·82 (2)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
O(1)···O(2′)	2·741 (2)†	$-x, -y, 1-z$
O(2)···H(O4′)	1·818 (25)†	$-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
···H(O1′)	1·937 (25)†	$-x, -y, 1-z$
O(3)···C(8)	2·875 (2)	$-\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
O(4)···O(2″)	2·754 (2)†	$-\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$

* Schomaker & Trueblood (1968).
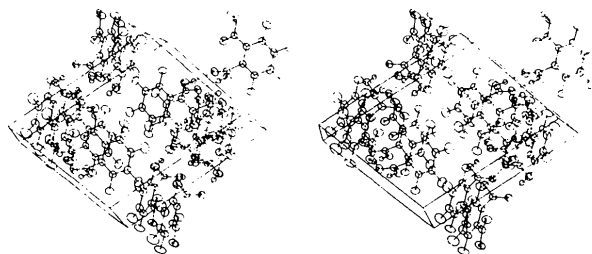† Hydrogen-bonded distances. Angles O(1)–H(O1)···O(2′) 174 (3)°; O(4)–H(O4)···O(2″) 170 (2)°.

Fig. 2. Stereoview of a unit cell of TFAC. The O atoms are labelled as 1, 2, 3, and 4.

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Structure of Morpholinium 4-Morpholinecarboxylate, $C_4H_{10}NO^+.C_5H_8NO_3^-$

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Abstract. $M_r = 218.14$, triclinic, $P\bar{1}$, $a = 9.421$ (4), $b = 9.932$ (4), $c = 6.408$ (4) Å, $\alpha = 102.10$ (4), $\beta = 94.45$ (4), $\gamma = 105.00$ (3)°, $V = 560.68$ Å³, $Z = 2$, $D_x = 1.293$, $D_m = 1.290$ (1) Mg m⁻³, $T = 296$ K, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.095$ mm⁻¹. The structure was solved by direct methods and refined to residuals $R = 0.065$ and $R_w = 0.045$ for the 2635 most intense reflections collected with Mo $K\alpha$ radiation on an automated diffractometer. The compound is formed in the reaction of CO_2 and morpholine. Both rings are in chair form with normal bond distances and angles. Hydrogen bonds linking two cations and two anions in rings are formed between the ammine H atoms of the cations and the carboxy groups on the anions. The O atoms in the morpholine rings do not participate in hydrogen bonding.

Introduction. Morpholinium 4-morpholinecarboxylate is formed in the reaction of morpholine and CO_2; the compound can be obtained in good yield by adding dry ice to morpholine. The original preparation was by Knorr (1898) who bubbled CO_2 gas through morpholine, and there are just two later references (Murray, 1959; Hunter & Glenn, 1953) which, in patents, describe it as a rust inhibitor and an activator for the rubber vulcanization accelerator thiazyl sulfide, respectively. Very recently Brown & Gray (1981) describe the crystal structure performed essentially simultaneously with this work, but with a distinctly different unit-cell volume (549.96 *vs* 560.68 Å³ in this work). As a consequence their calculated crystal density, 1.317 Mg m⁻³, is higher than either our observed or calculated densities; our densities are in good agreement. Transformation of the lattice parameters reported by Brown & Gray by

$$\mathbf{a}' = -\mathbf{b}$$
$$\mathbf{b}' = \mathbf{c} - \mathbf{a}$$
$$\mathbf{c}' = -\mathbf{c}$$

to bring them into registration with those found here gives $a' = 9.366$, $b' = 9.876$, $c' = 6.365$ Å, $\alpha' = 102.81$, $\beta' = 94.07$, $\gamma' = 104.79°$, $V = 549.96$ Å³. The agreement with our results is quite poor and the differences are far in excess of the estimated standard deviations. Since their axial lengths are all shorter than ours by 0.6 – 0.7% the difference is probably systematic. Similarly their atom coordinates (Brown & Gray, 1982) are transformed to be in accord with ours (Table 1) by

$$x' = y$$
$$y' = x$$
$$z' = x + z - \tfrac{1}{2}.$$

A comparison of their transformed coordinates† with ours shows that the average difference in (x,y,z) between the two results is essentially zero [$\overline{\varDelta x} = 0.0002$ (9), $\overline{\varDelta y} = 0.0002$ (18) and $\overline{\varDelta z} = -0.0003$ (21)], but many individual differences are quite large (maximum $= 0.0035$). Thus there are considerable variations in the bond distances between the two studies [$\overline{\varDelta b} = 0.002$ (19) Å], most due to differences in atom coordinates.

Because of these differences between the two studies and the greater precision in our data, we present our structural data for morpholinium 4-morpholinecarboxylate.

Experimental. Crystals obtained from morpholine solution; the compound was apparently formed in the reaction of the solvent with CO_2 in the atmosphere; because the compound easily sublimed at room temperature, a suitable crystal was placed in a glass capillary which was then sealed; precession photographs and subsequent axial photographs on the diffractometer yielded only $\bar{1}$ Laue symmetry, a Delaunay reduction of the lattice parameters also did not yield any higher symmetry; setting angles for 15

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† See deposition footnote.