

$\text{Br}^-(26^{\text{ii}}) = 2,32 (7) \text{ \AA}$; l'angle correspondant $\text{Br}(26^{\text{ii}})-\text{H}(271^{\text{i}})-\text{O}(27^{\text{i}}) = 155 (6)^\circ$; et $\text{O}(27^{\text{i}})-\text{Br}(26^{\text{vi}}) = 3,379 (5) \text{ \AA}$; l'hydrogène $\text{H}(270^{\text{i}})$ se trouve engagé dans cette liaison: $\text{H}(270^{\text{i}})-\text{Br}^-(26^{\text{vi}}) = 2,58 (7) \text{ \AA}$; l'angle correspondant $\text{Br}(26^{\text{vi}})-\text{H}(270^{\text{i}})-\text{O}(27^{\text{i}}) = 149 (6)^\circ$.

Les molécules forment des feuillets parallèles au plan (001). Au sein de ces feuillets la cohésion est assurée par des contacts de type de van der Waals: $\text{C}(19^{\text{i}})-\text{O}(14^{\text{iii}}) = 3,341 (8) \text{ \AA}$ [$\text{H}(191^{\text{i}})-\text{O}(14^{\text{iii}}) = 2,47 (7) \text{ \AA}$]; $\text{C}(12^{\text{i}})-\text{C}(5^{\text{iv}}) = 3,36 (3) \text{ \AA}$ [$\text{H}(120^{\text{i}})-\text{C}(5^{\text{iv}}) = 2,44 (8) \text{ \AA}$]; $\text{O}(27^{\text{i}})-\text{C}(21^{\text{iv}}) = 3,435 (9) \text{ \AA}$ [$\text{O}(27^{\text{i}})-\text{H}(211^{\text{iv}}) = 2,47 (6) \text{ \AA}$] et par une liaison hydrogène $\text{O}(27^{\text{i}})-\text{O}(14^{\text{v}}) = 2,800 (7) \text{ \AA}$ [$\text{O}(27^{\text{i}})-\text{H}(140^{\text{v}}) = 2,09 (7) \text{ \AA}$]. Deux feuillets voisins sont liés par contact de van der Waals $\text{C}(24^{\text{i}})-\text{O}(16^{\text{vii}}) = 2,980 (9) \text{ \AA}$ [$\text{H}(240^{\text{i}})-\text{O}(16^{\text{vii}}) = 2,81 (7) \text{ \AA}$].

Les auteurs remercient les laboratoires Roger Bellon qui leur ont fourni l'échantillon étudié.

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Structural Studies of Benzene Derivatives.

V.* The Crystal and Molecular Structure of *p*-Fluorobenzoic Acid

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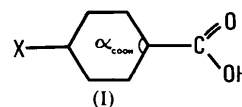
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Abstract

The molecular geometry of *p*-fluorobenzoic acid has been accurately determined by X-ray diffraction from 1017 independent counter intensities. The crystals are monoclinic, space group $P2_1/n$, with $a = 26.567 (7)$, $b = 6.382 (2)$, $c = 3.820 (1) \text{ \AA}$, $\beta = 93.81 (2)^\circ$, $Z = 4$, and are isostructural with those of *p*-chloro- and *p*-bromobenzoic acids. The refinement gave a final R of 0.0416. The C hexagon has mm symmetry within experimental error. The strongly σ -electron-withdrawing F substituent gives rise to marked distortions from $6/mmm$ symmetry: the internal angle at the *ipso* atom, α_F , is $124.0 (2)^\circ$, and the two adjacent C-C bonds are about 0.02 \AA shorter than the central C-C bonds of the ring. The internal angle *ipso* to the carboxy group, α_{COOH} , is $119.9 (2)^\circ$.

Introduction

In the preceding paper of this series (Colapietro & Domenicano, 1978) it was shown that in *para*-substituted benzoic acids (I) the nature of the *para* substituent has a small, but definite, effect on the endocyclic angle at the carboxy group, α_{COOH} . To provide the structural data needed for a study of this effect we are currently determining the molecular geometry of several *para*-substituted benzoic acids. This paper describes the molecular structure of *p*-fluorobenzoic acid.



Crystal data for *p*-halobenzoic acids have been presented by Toussaint (1952). Crystals of *p*-fluoro-, *p*-bromo- and *p*-iodobenzoic acids are monoclinic, space

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* Part IV: Colapietro & Domenicano (1978).

group $P2_1/a$, $Z = 4$, with closely related cell dimensions ($a = 26.5\text{--}30.5$, $b = 6.4\text{--}6.0$, $c = 3.8\text{--}4.2$ Å, $\beta = 95\text{--}97^\circ$). Crystals of *p*-chlorobenzoic acid are triclinic, space group $P\bar{1}$, $Z = 2$; the unit cell, however, may be derived from that of the previous compounds by halving the a parameter. Analyses have been reported for *p*-chlorobenzoic acid (Miller, Paul & Curtin, 1974) and *p*-bromobenzoic acid (Ohkura, Kashino & Haisa, 1972): the results show that the two compounds are isostructural. The same crystal structure is anticipated for *p*-fluoro- and *p*-iodobenzoic acids.

Experimental

Colourless tablets of *p*-fluorobenzoic acid were grown by evaporation of a benzene solution of the commercial product (Fluka). Preliminary oscillation and Weissenberg photographs confirmed the crystal data given by Toussaint (1952). The $P2_1/n$ unit cell adopted here is obtained from that of Toussaint through the matrix $(\bar{1}0\bar{1}/0\bar{1}0/001)$. A crystal, $ca\ 0.37 \times 0.41 \times 0.76$ mm, was mounted on a Syntex $P2_1$ diffractometer. The cell parameters were refined by a least-squares method from the measured θ values for 15 accurately centred reflexions, lying in the θ range $18\text{--}20.5^\circ$ and well distributed in reciprocal space (Table 1).

Intensities were collected at room temperature in the $\theta\text{--}2\theta$ scan mode with Si-monochromatized Mo $K\alpha$ radiation. The scanning interval was from $2\theta(K\alpha_1) - 1.0^\circ$ to $2\theta(K\alpha_2) + 1.4^\circ$. The scanning speed was varied according to the intensity, from a minimum of 0.025 to a maximum of 0.49° s^{-1} . The background was measured for $\frac{1}{4}$ of the scanning time at each end of the scan. A recentring routine was run every 500 reflexions. 2592 reflexions in the θ range $1.5\text{--}32.5^\circ$ were measured; only 1017 of them, having $I \geq 4\sigma(I)$, were considered as non-zero and used in all subsequent calculations.* Three standard reflexions, monitored

* The reflexions 011 and 111 were too intense to be measured accurately and were excluded from the data set.

Table 1. *Crystal data*

p-Fluorobenzoic acid, $C_7H_5FO_2$, FW = 140.12. Monoclinic, space group $P2_1/n$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$), $Z = 4$. M.p. = $182\text{--}184^\circ\text{C}$.

$a = 26.567$ (7) Å ^a	$V = 646.2$ (3) Å ³
$b = 6.382$ (2)	$D_c = 1.440$ Mg m ⁻³
$c = 3.820$ (1)	$D_m = 1.437^b$
$\beta = 93.81$ (2) ^c	

(a) Measured at 293 K with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). E.s.d.'s are given in parentheses as units in the last digit.

(b) Measured at 298 K by flotation in a mixture of carbon tetrachloride and *n*-hexane.

every 100 reflexions, showed a regular, time-dependent decrease of the intensity (17% during the entire data collection). This was due to decomposition of the crystal, which gradually turned opaque. The intensities were corrected for the decrease and for Lorentz and polarization effects, but not for absorption (μ for Mo $K\alpha$ is 0.134 mm^{-1}). A secondary-extinction correction was applied during the final stages of refinement.

Structure determination and refinement

The positional parameters of the non-H atoms of *p*-chlorobenzoic acid (Miller, Paul & Curtin, 1974) were used as a starting model, after a suitable change of the reference system [transformation matrix $(\frac{1}{2}00/010/-\frac{1}{2}01)$]. A structure factor calculation based on this model gave $R = 0.49$. Notwithstanding the high initial value, R was reduced to 0.074 by block-diagonal least-squares refinement (first in the isotropic, then in the anisotropic approximation). Further refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms (which had all been located on a difference map), converged to $R = 0.047$. Inspection of the structure factor list revealed that F_o for the most intense reflexions was systematically lower than F_c . A plot of $\log(I_c/I_o)$ vs I_c was essentially linear, and gave a value of 1.76×10^{-5} for the secondary-extinction coefficient, g (Stout & Jensen, 1968). The I_o values were corrected accordingly.

The final refinement was by a full-matrix least-squares procedure, minimizing $\sum w(|F_o| - K|F_c|)^2$; the number of observations per refined parameter was $1017/111 = 9.16$. Three different weighting schemes were tested: $w = 1.0$ (refinement 1), $w = \sin \theta/\lambda$ (refinement 2), and $w = 1/(a + b|F_o| + c|F_c|^2)$, with $a = 9.0$, $b = 1.0$, $c = 0.107$ (refinement 3). The final R and R_w were 0.0413 and 0.0361 for refinement 1, 0.0413 and 0.0435 for refinement 2, 0.0416 and 0.0558 for refinement 3, with all final shifts less than 0.1σ .

The atomic parameters from refinement 3 are given in Tables 2 and 3.* This refinement, although affording a slightly higher R , gave a lower dispersion for the mean values of the minimized function over ranges of either F_o or $\sin \theta/\lambda$. Comparison of the molecular geometries obtained through the three refinements shows that the differences between corresponding bond distances and angles in the heavy-atom skeleton never exceed 2σ . Although the individual differences are far from significant, the geometry of the C hexagon from refinement 3 is appreciably closer to perfect C_{2v} (mm)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34079 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final coordinates for non-hydrogen atoms ($x \times 10^5$; y , $z \times 10^4$)

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	x	y	z
F	21427 (6)	6972 (3)	6107 (4)
O(1)	6375 (6)	73 (2)	86 (4)
O(2)	1060 (6)	2374 (3)	2165 (5)
C(1)	9736 (7)	3137 (3)	2825 (4)
C(2)	14698 (8)	2488 (4)	2520 (5)
C(3)	18649 (8)	3788 (5)	3632 (6)
C(4)	17519 (9)	5696 (4)	5003 (5)
C(5)	12721 (9)	6393 (4)	5359 (5)
C(6)	8776 (8)	5087 (3)	4250 (5)
C(7)	5531 (7)	1762 (3)	1605 (5)

Table 3. Final coordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	x	y	z	B (\AA^2)
H(O)	-20 (1.5)	131 (6)	114 (9)	8.7 (10)
H(2)	153 (1)	118 (4)	158 (6)	2.9 (5)
H(3)	218 (1)	336 (4)	350 (7)	4.4 (6)
H(5)	120 (1)	777 (4)	632 (6)	4.0 (6)
H(6)	53 (1)	557 (4)	437 (6)	4.1 (6)

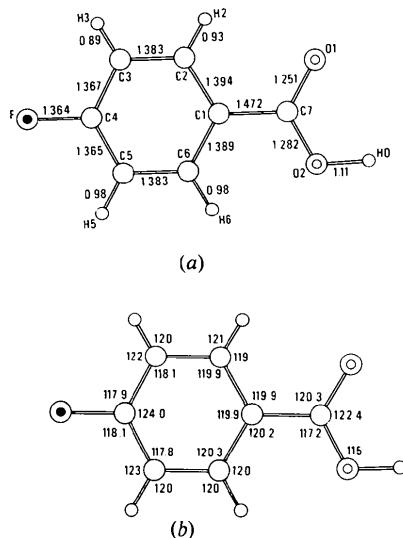


Fig. 1. Molecular geometry of *p*-fluorobenzoic acid: (a) bond lengths (\AA), (b) bond angles ($^\circ$). E.s.d.'s (calculated from the e.s.d.'s in the atomic parameters given in Tables 2 and 3) are 0.003 \AA for C-C, C-O and C-F bonds, 0.03 \AA for C-H bonds, 0.04 \AA for the O-H bond, 0.2 $^\circ$ for angles not involving H atoms, 1.5-2.0 $^\circ$ for angles involving H atoms.

symmetry than those from the other refinements. As with *p*-methoxybenzoic acid (Colapietro & Domenicano, 1978), the internal angles at the *ipso* atoms of the benzene ring are unaffected by the weighting scheme.

The scattering factors of Cromer & Mann (1968) were used for F, O and C, and of Hanson, Herman, Lea & Skillman (1964) for H.

The full-matrix least-squares refinements were carried out on the Univac 1106 computer of the University of Rome, all other calculations on the HP 21MX mini-computer of the CNR Research Area. Local crystallographic programs (Carruthers & Spagna, 1975; Cerrini & Spagna, 1977) were used.

Results and discussion

Bond lengths and angles calculated from the atomic parameters of refinement 3 are given in Fig. 1; no corrections have been applied for the effects of thermal motion. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all atoms from this plane are given in Table 4. Torsion angles are reported in Table 5.

The benzene ring

The symmetry of the C ring is C_{2v} (mm) within experimental error (Fig. 1 and Table 4), as in *p*-nitrobenzoic acid (Colapietro & Domenicano, 1977). The most significant distortions from D_{6h} ($6/mmm$) symmetry are caused by the strongly σ -electron-with-

Table 4. Deviations from planarity

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes):

$$-1.2293x - 2.5975y + 3.4888z = 0.0523.$$

The e.s.d.'s in the atomic positions are 0.0015-0.0025 \AA for the non-H atoms, 0.037 \AA for H(O), 0.025 \AA for the other H atoms.

Displacements (\AA) of atoms from the plane

C(1)*	0.001	C(6)*	-0.001	H(O)	-0.03
C(2)*	0.000	C(7)	0.018	H(2)	0.00
C(3)*	-0.002	O(1)	0.120	H(3)	-0.03
C(4)*	0.002	O(2)	-0.073	H(5)	0.01
C(5)*	0.000	F	-0.004	H(6)	0.04

* Atoms defining the least-squares plane.

Table 5. Torsion angles ($^\circ$)

Signs have been given according to the convention of Klyne & Prelog (1960). E.s.d.'s are given in parentheses as units in the last digit.

O(1)-C(7)-C(1)-C(2)	-4.7 (3)
O(1)-C(7)-C(1)-C(6)	174.7 (2)
O(2)-C(7)-C(1)-C(6)	-5.2 (3)
O(2)-C(7)-C(1)-C(2)	175.4 (2)

drawing F substituent and consist of: (i) a shortening (by ca 0.017 Å, 6σ) of C(3)–C(4) and C(4)–C(5) with respect to the central C–C bonds of the ring;* (ii) an increase from 120° (by 4.0°, 20σ) of the C(3)–C(4)–C(5) angle, α_F ; and (iii) a decrease from 120° (by ca 2.0°, 10σ) of the C(2)–C(3)–C(4) and C(4)–C(5)–C(6) angles, β_F . The distortions are in good agreement with those observed by Nygaard, Bojesen, Pedersen & Rastrup-Andersen (1968) in a microwave study of fluorobenzene ($\Delta C-C = -0.012$ Å, $\Delta\alpha_F = 3.4$, $\Delta\beta_F = -2.1^\circ$), and also compare well with those occurring in the naphthalene nucleus upon F substitution (Meresse, Courseille, Leroy & Chanh, 1975).

Of special interest is the internal angle at the *ipso* atom, α_x , a parameter that may be measured accurately by X-ray diffraction analysis and appears to be a suitable indicator of the electronic properties of the substituent (Domenicano, Mazzeo & Vaciago, 1976). Values of α_F observed by this technique in a number of *para*-substituted derivatives of fluorobenzene are reported in Table 6. The weighted mean value, 123.3 (2)°, is in excellent agreement with the $123.4 \pm 0.4^\circ$ obtained for fluorobenzene (Nygaard *et al.*, 1968). Several α_F values in Table 6, including that for *p*-fluorobenzoic acid, deviate significantly from the mean, which may be indicative of a structural effect of the *para* substituent.

The angle α_{COOH} is 119.9 (2)°, near to the upper limit of the 118.1–120.4° range observed in several

* A part of this shortening may however be due to thermal motion effects in the crystal.

para-substituted benzoic acids (Colapietro & Domenicano, 1978). The small lengthening of C(1)–C(2) and C(1)–C(6), compared to the central C–C bonds of the ring, is just at the border of significance ($2-4\sigma$).

The F substituent

The F atom lies on the C(1)···C(4) line within experimental error. The length of C(4)–F, 1.364 (3) Å, is in good agreement with the length of the corresponding bond in the other *para*-substituted fluorobenzenes of Table 6. It also compares fairly well with the value obtained for fluorobenzene by microwave spectroscopy, 1.354 ± 0.006 Å (Nygaard *et al.*, 1968), and with the values reported by Meresse *et al.* (1975) for 1,5-difluoronaphthalene, 1.354 (3) Å, and 1,8-difluoronaphthalene, 1.362 (2) and 1.357 (2) Å. Markedly shorter C–F bonds, 1.32–1.34 Å, have been reported for molecules containing more than one F substituent per benzene ring, *e.g.* *m*-difluorobenzene (Van Schaick, Geise, Mijlhoff & Renes, 1973), pentafluorobenzoic acid (Benghiat & Leiserowitz, 1972), decafluorobiphenyl (Gleason & Britton, 1976), and hexafluorobenzene (Almenningen, Bastiansen, Seip & Seip, 1964).

The COOH substituent

Bond lengths and angles in the carboxy group are similar to those observed in *p*-methoxybenzoic acid

Table 6. C–F lengths (Å) and α_F angles (°) in *para*-substituted fluorobenzenes

E.s.d.'s, σ , are given in parentheses as units in the last digit. Values of C–F and α_F differing from the respective mean values by more than 3 σ are marked with an asterisk. Only compounds with $\sigma(\alpha_F) \leq 0.5^\circ$ have been included in this table.

No.	Compound	Reference	C–F	α_F
1	8-[4-(4-Fluorophenyl)-3-pentenyl]-1-phenyl-1,3,8-triazaspiro[4.5]decan-4-one	<i>a</i>	1.368 (5)	121.6 (4)*
2	<i>N</i> -{1-[3-(<i>p</i> -Fluorobenzoyl)propyl]-4-piperidyl}propionanilide	<i>b</i>	1.358 (6)	123.4 (5)
3	<i>B,B</i> -Bis(<i>p</i> -fluorophenyl)boroxazolidine	<i>c</i>	1.369 (4)	121.9 (3)*
			1.367 (4)	121.8 (3)*
4	4,4'-Difluorodiphenyl sulphone	<i>d</i>	1.351 (5)	123.7 (4)
			1.348 (5)	123.2 (4)
5	3-Cyclohexylimino-2-(<i>p</i> -fluorophenyl)-4,4-bis(trifluoromethyl)-1-azetine	<i>e</i>	1.361 (6)	124.0 (4)
6	1'-[4-(4-Fluorophenyl)-4-oxobutyl]-1,4'-bipiperidine-4'-carboxamide	<i>f</i>	1.356 (2)	123.3 (2)
7	1-[4-(3-Chlorophenyl)-1-(4-fluorophenyl-4-oxobutyl)-4-piperidinylcarbonyl]pyrrolidine	<i>g</i>	1.373 (6)	124.7 (5)
8	Bis(1,4-difluorobenzene)vanadium(0)	<i>h</i>	1.363 (3)	123.6 (3)
			1.360 (3)	123.4 (3)
9	4'-Fluoro-4-[4-(2-pyridyl)-1-piperazinyl]butyrophenone	<i>i</i>	1.355 (3)	124.7 (3)*
10	5-Chloro-1-[3-[4-(4-fluorobenzoyl)piperidino]propyl]-1,3-dihydro-2 <i>H</i> -benzimidazol-2-one	<i>j</i>	1.360 (3)	123.6 (3)
11	<i>p</i> -Fluorobenzonitrile	<i>k</i>	1.360 (2)	123.0 (2)
12	<i>p</i> -Fluorobenzoic acid	<i>l</i>	1.364 (3)	124.0 (2)*
	Weighted mean values	<i>m</i>	1.360 (1) 1	123.3 (2) 1

References: (a) Koch & Evrard (1973). (b) Koch & Evrard (1974). (c) Rettig & Trotter (1974). (d) Sime & Woodhouse (1974). (e) Gieren, Burger & Thenn (1974). (f) Declercq, Germain & Koch (1975). (g) Michel, Evrard, Schiltz, Durant & Koch (1976). The e.s.d.'s have been calculated from the e.s.d.'s of the atomic parameters quoted in the paper. (h) Radonovich, Zuerner, Efner & Klabunde (1976). (i) Koch, Germain, Declercq & Van Meerssche (1977). (j) Koch, Declercq, Germain & Van Meerssche (1977). (k) Britton & Gleason (1977). (l) This work. (m) Mean values and their 'external' () and 'internal' [] standard errors have been calculated as in part I of this series (Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977).

(Colapietro & Domenicano, 1978). As in that case, the moderate differences occurring in the lengths of the two C—O bonds and in the values of the two C—C—O angles (Fig. 1), as well as the rather high B value for H(O) (8.7 \AA^2), suggest some degree of rotational disorder in the carboxy group. The substituent is coplanar with C(1), but is twisted by 5° about C(1)—C(7) (Table 5).

The crystal structure

As generally found with aromatic carboxylic acids the molecules are hydrogen bonded in dimers across centres of symmetry. The O(2)—H(O)···O(1') hydrogen bond is characterized by the following parameters: distances O(2)···O(1') = $2.618(2)$, O(2)—H(O) = $1.11(4)$, H(O)···O(1') = $1.51(4) \text{ \AA}$; angle O(2)—H(O)···O(1') = $176(3)^\circ$.*

As in the isostructural *p*-chloro and *p*-bromo analogues, the dimers are arranged in stacks along c . The overlap of dimers within a stack is shown in Fig. 2. The ring-to-ring separation between adjacent dimers in a stack is 3.489 \AA , compared with 3.486 and 3.550 \AA in *p*-chloro- and *p*-bromobenzoic acid, respectively.

In the crystal structure of *p*-chlorobenzoic acid a short Cl···Cl contact occurs between adjacent stacks of dimers, approximately along the axis of C(4)—Cl (Miller, Paul & Curtin, 1974). The contact distance is markedly shorter than the Cl···Cl separation within a stack (3.44 vs 3.86 \AA). A similar, though less marked, effect occurs in *p*-bromobenzoic acid, with Br···Br separations of 3.91 and 3.98 \AA , respectively (Ohkura, Kashino & Haisa, 1972). No short F···F contacts, however, are observed in *p*-fluorobenzoic acid, where the F···F inter- and intra-stack separations are practically equal (3.83 vs 3.82 \AA). These distances greatly exceed the van der Waals separation of 2.70 \AA , derived by doubling the van der Waals radius for F (Pauling, 1960).

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* The symmetry operation relating O(1') to O(1) is $-x, -y, -z$.

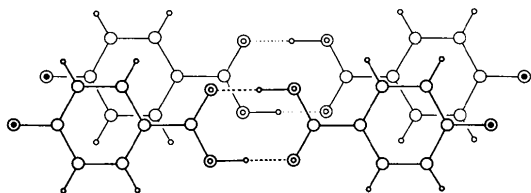


Fig. 2. Crystal structure of *p*-fluorobenzoic acid: overlap of dimers in a stack projected on to the least-squares plane through the two carboxy groups of a dimer.

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