

Electron-Density Distribution in Fluorobenzene Derivatives

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Abstract

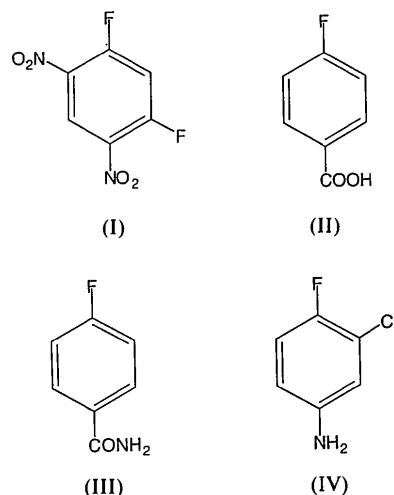
The electron-density distribution in four fluorobenzene derivatives has been studied at 120 (2) K. Mo $K\alpha$ radiation was used throughout ($\lambda = 0.71073 \text{ \AA}$). 1,5-Difluoro-2,4-dinitrobenzene, $C_6H_2F_2N_2O_4$, (I), $M_r = 204.1$, orthorhombic, $Pbca$, $a = 10.804$ (3), $b = 13.007$ (4), $c = 10.381$ (2) \AA , $V = 1458.8$ (7) \AA^3 , $Z = 8$, $D_x = 1.86 \text{ Mg m}^{-3}$, $\mu = 0.178 \text{ mm}^{-1}$, $F(000) = 816$, $R = 0.034$ for 2581 unique reflections with multipole refinement. 4-Fluorobenzoic acid, $C_7H_5FO_2$, (II), $M_r = 140.1$, monoclinic, $P2_1/n$, $a = 26.733$ (5), $b = 6.2947$ (9), $c = 3.7257$ (6) \AA , $\beta = 94.88$ (2)°, $V = 624.7$ (2) \AA^3 , $Z = 4$, $D_x = 1.49 \text{ Mg m}^{-3}$, $\mu = 0.121 \text{ mm}^{-1}$, $F(000) = 288$, $R = 0.037$ for 1710 reflections. 4-Fluorobenzamide, C_7H_6FNO , (III), $M_r = 139.1$, monoclinic, $P2_1/a$, $a = 9.584$ (2), $b = 7.601$ (3), $c = 8.903$ (2) \AA , $\beta = 92.67$ (3)°, $V = 647.9$ (3) \AA^3 , $Z = 4$, $D_x = 1.43 \text{ Mg m}^{-3}$, $\mu = 0.109 \text{ mm}^{-1}$, $F(000) = 288$, $R = 0.049$ for 1529 reflections. 3-Chloro-4-fluoroaniline, C_6H_5ClFN , (IV), $M_r = 145.6$, orthorhombic, $Pbca$, $a = 14.608$ (5), $b = 15.757$ (6), $c = 5.303$ (2) \AA , $V = 1220.6$ (8) \AA^3 , $Z = 8$, $D_x = 1.59 \text{ Mg m}^{-3}$, $\mu = 0.538 \text{ mm}^{-1}$, $F(000) = 592$, $R = 0.039$ for 2090 reflections. The deformation densities on the halogen-carbon bond axes were investigated, based on the oriented-atom model. The electron accumulation on the C–F bond is sharper than that on the C–Cl bond, indicating the more compact distribution of the $2p$ orbitals of the F atom compared to the $3p$ orbitals of the Cl atom. The pronounced positive effective charge of the carboxylic H atom of (II) was estimated by κ refinement and molecular orbital calculations.

Introduction

In the electron-density study of tetrafluoroterephthalodinitrile, a very low deformation density was observed on the C–F bond axis (Dunitz, Schweizer & Seiler, 1983; Seiler, Schweizer & Dunitz, 1984; Hirshfeld, 1984). It was rationalized that the independent-atom model (IAM) assumes more than

two electrons in the bonding region involving the valence-rich atoms and the electron accumulation by the covalent bond is underestimated. An alternative promolecule, the oriented-atom model (OAM), was proposed by Schwartz, Valtazanos & Ruedenberg (1985) to take into account the hybridization of the atomic orbitals. The electron density of the C–Cl bond axis in crystals of 4-chloroaniline, 4-chlorobenzoic acid and 1-chloro-2,4-dinitrobenzene was investigated based on the OAM (Takazawa, Ohba & Saito, 1989). In this paper, fluorobenzene derivatives have been investigated to compare the bonding electron of the C–F bond with that of the C–Cl bond.

Crystal structures have been reported for (II) (Colapietro, Domenicano & Ceccarini, 1979) and (III) (Takaki, Taniguchi & Sakurai, 1965). Structures of (I) and (IV) were determined in the present study.



Experimental

Data collection

Preliminary intensity measurements were performed at 297 (1)–298 (1) K to check the crystal quality. For both (I) and (IV), systematic absences ($0kl$, k odd; $h0l$, l odd; $hk0$, h odd) indicated the space group to be $Pbca$. Their structures were solved

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Table 1. *Experimental details*

	(I)	(II)	(III)	(IV)
Crystal size (mm)	0.33 × 0.47 × 0.45	0.40 × 0.40 × 0.30	0.30 × 0.25 × 0.20	0.50 × 0.50 × 0.40
Scan mode	θ - 2θ	ω	θ - 2θ	θ - 2θ
Scan speed ($^{\circ}$ min $^{-1}$)	6	6	6	6
$2\theta_{\max}$ ($^{\circ}$)	80	80	70	90
Range of h, k and l	$0 \leq h \leq 15$ $-18 \leq k \leq 18$ $-14 \leq l \leq 14$ ($4 < 2\theta \leq 60^{\circ}$) $0 \leq h \leq 21$ $0 \leq k \leq 22$ $0 \leq l \leq 18$ ($60 < 2\theta \leq 80^{\circ}$)	$-37 \leq h \leq 37$ $0 \leq k \leq 8$ $-5 \leq l \leq 5$ ($4 < 2\theta \leq 60^{\circ}$) $-48 \leq h \leq 48$ $0 \leq k \leq 11$ $0 \leq l \leq 6$ ($60 < 2\theta \leq 80^{\circ}$)	$0 \leq h \leq 13$ $-10 \leq k \leq 10$ $-12 \leq l \leq 12$ ($4 < 2\theta \leq 60^{\circ}$) $0 \leq h \leq 15$ $-12 \leq k \leq 12$ $-14 \leq l \leq 14$ ($60 < 2\theta \leq 70^{\circ}$)	$-20 \leq h \leq 20$ $-22 \leq k \leq 22$ $0 \leq l \leq 7$ ($4 < 2\theta \leq 60^{\circ}$) $0 \leq h \leq 29$ $0 \leq k \leq 31$ $0 \leq l \leq 10$ ($60 < 2\theta \leq 90^{\circ}$)
Variation of standard reflections*	1.00–1.01	1.00–1.01	0.98–1.02	0.98–1.01
Measured reflections	14752	5901	6045	10503
Observed reflections†	7010	2933	2802	5505
Unique reflections (R_{int})	2581 (0.024)	1710 (0.021)	1529 (0.032)	2090 (0.026)
Number and range of 2θ for cell parameters	24 (20–30 $^{\circ}$)	24 (21–29 $^{\circ}$)	24 (20–30 $^{\circ}$)	20 (20–30 $^{\circ}$)
Transmission factor	0.93–0.95	0.95–0.97	0.97–0.98	0.77–0.81
Refinement A				
($\sin\theta/\lambda$) $_{\max}$ (\AA^{-1})	0.65	0.60	0.5	0.6
Parameters refined	135	111	115	102
R	0.052	0.057	0.068	0.054
wR	0.039	0.045	0.053	0.034
S	1.7	2.0	1.9	1.6
Refinement B				
Parameters refined	347	268	275	256
R	0.034	0.035	0.043	0.042
wR	0.020	0.029	0.030	0.023
S	1.0	1.2	1.3	1.1
Refinement C				
Parameters refined		128		
R		0.054		
wR		0.057		
S		1.8		

* $\sum(|F_o|/|F_o|_{\text{initial}})/n$ (the number of standard reflections n was 4 or 5).† $|F_o| > 3\sigma(|F_o|)$.

by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Intensities at 120 K were measured on a Rigaku AFC-5 four-circle diffractometer with a nitrogen-gas cooling unit and graphite-monochromatized Mo $K\alpha$ radiation. Experimental conditions and refinement information are given in Table 1.

Refinement

High-order refinement (refinement *A*) was performed with the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) after absorption correction by the Gauss numerical integration method (Busing & Levy, 1957). Positional and anisotropic thermal parameters of non-H atoms were refined ($\Delta/\sigma < 0.30$) based on high-order reflections and H atoms were refined isotropically based on all the reflection data. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weight $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. No extinction correction was applied. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed with a FACOM M-780/10 computer of Keio University. Positional parameters

of non-H atoms are given in Table 2 and bond lengths and bond angles in Table 3.*

Multipole refinement (refinement *B*) was carried out with the program *MOLLY* (Hansen & Coppens, 1978). Multipoles were included up to hexadecapole for F and Cl, up to octapole for C, N and O, and a monopole and a bond-directed dipole for H atoms. The radial function was $r^{n_l} \exp(-\zeta r)$, where $n_l = 4, 4, 6$ and 8 (for multipole y_{lm} with $l = 1, 2, 3$ and 4 , respectively) for F and Cl, $n_l = 2, 2$ and 3 for C, N and O, and $n_l = 1$ for H. The core and valence scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The total charge in the unit cell was constrained to be zero. The H parameters and thermal, multipole and radial (κ) parameters of non-H atoms were refined based on all the reflections. Positional parameters of non-H atoms were fixed at those of refinement *A*.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters (refinement *A*) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55330 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0604]

Table 2. Positional parameters ($\times 10^4$, $\times 10^5$ for Cl) and equivalent isotropic temperature factors ($\times 10$)
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq} (\AA^2)
(I)				
F(1)	-277 (2)	4016 (1)	2873 (2)	21 (1)
F(2)	2301 (2)	5394 (1)	-269 (2)	22 (1)
O(1)	1532 (2)	1251 (1)	2584 (2)	17 (1)
O(2)	220 (2)	2168 (2)	3656 (2)	21 (1)
O(3)	4238 (2)	4217 (2)	-884 (2)	26 (1)
O(4)	3681 (2)	2615 (2)	-1031 (2)	21 (1)
N(1)	989 (2)	2061 (1)	2797 (2)	14 (1)
N(2)	3584 (2)	3493 (2)	-592 (2)	15 (1)
C(1)	678 (2)	3886 (1)	2086 (2)	13 (1)
C(2)	1302 (1)	2946 (1)	1996 (1)	11 (1)
C(3)	2248 (1)	2830 (1)	1110 (1)	11 (1)
C(4)	2594 (1)	3655 (1)	350 (1)	11 (1)
C(5)	1997 (2)	4600 (1)	473 (2)	14 (1)
C(6)	1025 (2)	4714 (1)	1325 (2)	16 (1)
(II)				
F	2154 (1)	7116 (4)	6088 (7)	27 (1)
O(1)	625 (1)	91 (3)	-44 (7)	19 (1)
O(2)	110 (1)	2435 (4)	2284 (7)	21 (1)
C(1)	977 (1)	3203 (3)	2795 (5)	13 (1)
C(2)	1470 (1)	2528 (4)	2448 (6)	16 (1)
C(3)	1872 (1)	3858 (4)	3553 (7)	18 (1)
C(4)	1764 (1)	5823 (5)	4968 (7)	18 (1)
C(5)	1281 (1)	6534 (4)	5358 (6)	17 (1)
C(6)	884 (1)	5188 (4)	4266 (6)	15 (1)
C(7)	556 (1)	1784 (4)	1575 (6)	14 (1)
(III)				
F	785 (2)	8556 (3)	4505 (3)	31 (1)
O	1231 (2)	1418 (2)	1057 (2)	15 (1)
N	-1096 (2)	1800 (2)	720 (2)	15 (1)
C(1)	262 (2)	3963 (2)	2147 (2)	11 (1)
C(2)	1365 (2)	4141 (3)	3217 (2)	14 (1)
C(3)	1540 (2)	5684 (3)	4031 (3)	18 (1)
C(4)	611 (2)	7050 (3)	3727 (3)	18 (1)
C(5)	-488 (3)	6929 (3)	2662 (3)	19 (1)
C(6)	-663 (2)	5359 (3)	1886 (3)	14 (1)
C(7)	160 (2)	2293 (3)	1267 (2)	12 (1)
(IV)				
Cl	50411 (3)	33506 (3)	-16808 (12)	18 (1)
F	4943 (1)	4535 (1)	2517 (4)	20 (1)
N	8368 (1)	3116 (1)	1213 (4)	16 (1)
C(1)	7525 (1)	3530 (1)	1427 (4)	12 (1)
C(2)	6805 (1)	3306 (1)	-162 (4)	12 (1)
C(3)	5941 (1)	3654 (1)	209 (4)	12 (1)
C(4)	5796 (1)	4227 (1)	2139 (4)	13 (1)
C(5)	6505 (1)	4474 (1)	3697 (4)	16 (1)
C(6)	7370 (1)	4125 (1)	3350 (5)	15 (1)

The κ refinement [refinement C (Coppens *et al.*, 1979)] was carried out for (II) and for 4-chlorobenzoic acid [compound (II'); Takazawa *et al.* (1989)] to estimate the effective charge of the carboxylic H atom. Valence-electron populations, positional and thermal parameters of H atoms and κ parameters of non-H atoms were refined based on all the reflections. For (II), positional and thermal parameters of non-H atoms were refined based on high-order reflections. For (II'), thermal parameters of non-H atoms were refined based on all the reflections as described in a previous paper (Takazawa *et al.*, 1989), where the κ refinement had not been carried out. The valence-electron population of the Cl atom was fixed at the theoretical value of the molecular orbital calculation, since a refinement gave positive effective charge to the Cl atom. A constraint of twofold symmetry was adopted for the effective charges of the benzene C atoms and the charges of

Table 3. Bond lengths (\AA) and bond angles ($^\circ$)

(I)			
F(1)—C(1)	1.327 (3)	O(1)—N(1)—O(2)	123.6 (2)
F(2)—C(5)	1.330 (2)	O(1)—N(1)—C(2)	117.7 (2)
O(1)—N(1)	1.226 (2)	O(2)—N(1)—C(2)	118.8 (2)
O(2)—N(1)	1.227 (3)	O(3)—N(2)—O(4)	125.1 (2)
O(3)—N(2)	1.216 (3)	O(3)—N(2)—C(4)	118.7 (2)
O(4)—N(2)	1.234 (4)	O(4)—N(2)—C(4)	116.2 (2)
N(1)—C(2)	1.460 (2)	F(1)—C(1)—C(2)	121.8 (2)
N(2)—C(4)	1.464 (2)	F(1)—C(1)—C(6)	117.5 (2)
C(1)—C(2)	1.399 (2)	C(2)—C(1)—C(6)	120.7 (2)
C(1)—C(6)	1.387 (2)	N(1)—C(2)—C(1)	122.6 (1)
C(2)—C(3)	1.383 (2)	N(1)—C(2)—C(3)	117.6 (1)
C(3)—C(4)	1.383 (2)	C(1)—C(2)—C(3)	119.7 (1)
C(4)—C(5)	1.394 (2)	C(2)—C(3)—C(4)	119.6 (1)
C(5)—C(6)	1.381 (3)	N(2)—C(4)—C(3)	117.8 (1)
		N(2)—C(4)—C(5)	121.7 (1)
		C(3)—C(4)—C(5)	120.4 (1)
		F(2)—C(5)—C(4)	121.2 (2)
		F(2)—C(5)—C(6)	118.4 (2)
		C(4)—C(5)—C(6)	120.3 (2)
		C(1)—C(6)—C(5)	119.1 (2)
(II)			
F—C(4)	1.360 (4)	C(2)—C(1)—C(6)	120.5 (2)
O(1)—C(7)	1.246 (3)	C(2)—C(1)—C(7)	119.1 (2)
O(2)—C(7)	1.309 (4)	C(6)—C(1)—C(7)	120.4 (2)
C(1)—C(2)	1.401 (4)	C(1)—C(2)—C(3)	119.8 (2)
C(1)—C(6)	1.395 (3)	C(2)—C(3)—C(4)	117.9 (3)
C(1)—C(7)	1.478 (3)	F—C(4)—C(3)	118.2 (2)
C(2)—C(3)	1.396 (4)	F—C(4)—C(5)	118.1 (3)
C(3)—C(4)	1.385 (4)	C(3)—C(4)—C(5)	123.7 (3)
C(4)—C(5)	1.386 (4)	C(4)—C(5)—C(6)	117.8 (2)
C(5)—C(6)	1.391 (4)	C(1)—C(6)—C(5)	120.2 (2)
O(1)—O(2)	2.609 (3)	O(1)—C(7)—O(2)	122.7 (3)
		O(1)—C(7)—C(1)	121.7 (2)
		O(2)—C(7)—C(1)	115.6 (2)
(III)			
F—C(4)	1.344 (3)	C(2)—C(1)—C(6)	119.7 (2)
O—C(7)	1.244 (3)	C(2)—C(1)—C(7)	118.0 (2)
N—C(7)	1.331 (3)	C(6)—C(1)—C(7)	122.3 (2)
C(1)—C(2)	1.396 (3)	C(1)—C(2)—C(3)	120.6 (2)
C(1)—C(6)	1.395 (3)	C(2)—C(3)—C(4)	118.1 (2)
C(1)—C(7)	1.492 (3)	C(3)—C(4)—C(5)	123.0 (2)
C(2)—C(3)	1.385 (3)	F—C(4)—C(3)	118.3 (2)
C(3)—C(4)	1.386 (3)	F—C(4)—C(5)	118.7 (2)
C(4)—C(5)	1.387 (4)	C(4)—C(5)—C(6)	117.9 (2)
C(5)—C(6)	1.385 (3)	C(1)—C(6)—C(5)	120.7 (2)
		N—C(7)—C(1)	117.9 (2)
		O—C(7)—C(1)	119.9 (2)
		O—C(7)—N	122.2 (2)
(IV)			
Cl—C(3)	1.721 (2)	N—C(1)—C(2)	119.8 (2)
F—C(4)	1.352 (2)	N—C(1)—C(6)	120.8 (2)
N—C(1)	1.398 (2)	C(2)—C(1)—C(6)	119.1 (2)
C(1)—C(2)	1.393 (2)	C(1)—C(2)—C(3)	120.0 (2)
C(1)—C(6)	1.404 (3)	C(1)—C(3)—C(2)	120.1 (1)
C(2)—C(3)	1.390 (2)	C(1)—C(3)—C(4)	119.7 (1)
C(3)—C(4)	1.381 (3)	C(2)—C(3)—C(4)	120.1 (2)
C(4)—C(5)	1.381 (2)	F—C(4)—C(3)	119.1 (2)
C(5)—C(6)	1.390 (2)	F—C(4)—C(5)	120.1 (2)
		C(3)—C(4)—C(5)	120.8 (2)
		C(4)—C(5)—C(6)	119.4 (2)
		C(1)—C(6)—C(5)	120.5 (2)

Symmetry code (i) -x, -y, -z.

the benzene H atoms were assumed to be the same. The effective atomic charges determined by the κ refinement are listed in Table 4.

Theoretical calculation

Molecular orbital calculations and Mulliken population analyses (Mulliken, 1955) for 4-fluorobenzoic acid (II) and 4-chlorobenzoic acid (II') were carried out by using an STO-6G basis set with programs *MOLYX* (Nambu, Nakata & Iwata, 1989) and *GAUSSIAN88* (Frisch *et al.*, 1988). The H-atom

Table 4. *Effective atomic charges of 4-fluorobenzoic acid (II) and 4-chlorobenzoic acid (II')*

	(II)			(II')	
	κ refinement	Theory		κ refinement	Theory
	Monomer	Dimer*		Monomer	
F or Cl	-0.18 (2)	-0.143	-0.143	-0.133†	-0.133
O(1)	-0.62 (3)	-0.297	-0.360	-0.56 (3)	-0.293
O(2)	-0.47 (3)	-0.317	-0.361	-0.33 (3)	-0.319
C(1)	-0.14 (3)	-0.035	-0.038	-0.17 (5)	-0.021
C(2)	+0.04 (2)	-0.035	-0.034	+0.05 (3)	-0.041
C(3)	-0.24 (3)	-0.090	-0.092	-0.17 (3)	-0.057
C(4)	+0.19 (3)	+0.156	+0.158	+0.19 (5)	+0.045
C(5)	-0.24 (3)	-0.091	-0.092	-0.17 (3)	-0.057
C(6)	+0.04 (2)	-0.038	-0.034	+0.05 (3)	-0.043
C(7)	+0.68 (3)	+0.323	+0.334	+0.65 (6)	+0.329
H(2)	+0.10 (1)	+0.087	+0.086	+0.06 (1)	+0.091
H(3)	+0.10 (1)	+0.081	+0.081	+0.06 (1)	+0.087
H(5)	+0.10 (1)	+0.079	+0.079	+0.06 (1)	+0.085
H(6)	+0.10 (1)	+0.085	+0.090	+0.06 (1)	+0.089
H(O)	+0.53 (3)	+0.234	+0.280	+0.35 (2)	+0.237

* Basis-set superposition error was corrected.

† This parameter was fixed at the theoretical value.

positions were idealized. The dimer of (II) connected by cyclic hydrogen bonds (see Fig. 1) was also calculated in order to investigate the effect of the hydrogen bonds on the atomic charges. The basis-set superposition error in the effective atomic charges was corrected by calculating the molecular orbitals of the monomer with the basis set of the dimer (Boys & Bernardi, 1970). The effective charges are given in Table 4. The calculation was carried out on a workstation, MIPS RS3230, in Keio University and on a HITAC M680 computer at the Computer Center of the Institute for Molecular Science.

Results and discussion

Molecular and crystal structure

The internal bond angles of the benzene ring at the F atom in monohalogeno compounds 123.7 (3) (II) and 123.0 (2)° (III), indicate the electron-withdrawing character of F (Liebman, Greenberg & Dolbier, 1988). In (I), intramolecular steric repulsions between the nitro group and the F atom at the *ortho* position cause the imbalance of the C–C–F and the C–C–NO₂ bond angles as reported for 1-fluoro-2,4-dinitrobenzene (Wilkins & Small, 1991).

Crystals of (II) easily lose their crystallinity by undergoing cutting or cooling, because dimers of the molecule are arranged in two-dimensional sheets nearly parallel to (001) and the layers slip relative to each other. The contraction of the unit cell of (II), which resulted from lowering the temperature from 278 to 120 K, showed anisotropy, *i.e.* a larger contraction was observed for the *c* axis, from 3.8172 (4) to 3.7257 (6) Å, than for the other axes.

Deformation density

With the multipole model of deformation density, $\Delta\rho_{MM-IAM}$ ($=\rho_{\text{calc,multipole}} - \rho_{\text{calc,IAM}}$), excess elec-

tron density is not observed regularly on the C–F and C–Cl bond axes, as shown in Fig. 1. Fig. 2 shows the model deformation densities based on the OAM, $\Delta\rho_{MM-OAM}$ ($=\rho_{\text{calc,multipole}} - \rho_{\text{calc,OAM}}$). The reference density for the OAM was calculated from the real spherical-harmonic functions as described previously (Takazawa *et al.*, 1989) with the assumption that the electron population of the bonding atomic orbitals is unity. Accordingly, the difference densities on the C–F and C–Cl bond axes increase when the reference density changes to that for the OAM from that for the IAM. Positive deformation density on the extension of the C–F bond indicates that the electron population of the $2p_x$ orbital of F along the C–F bond is greater than unity. This accords with the result of the molecular orbital cal-

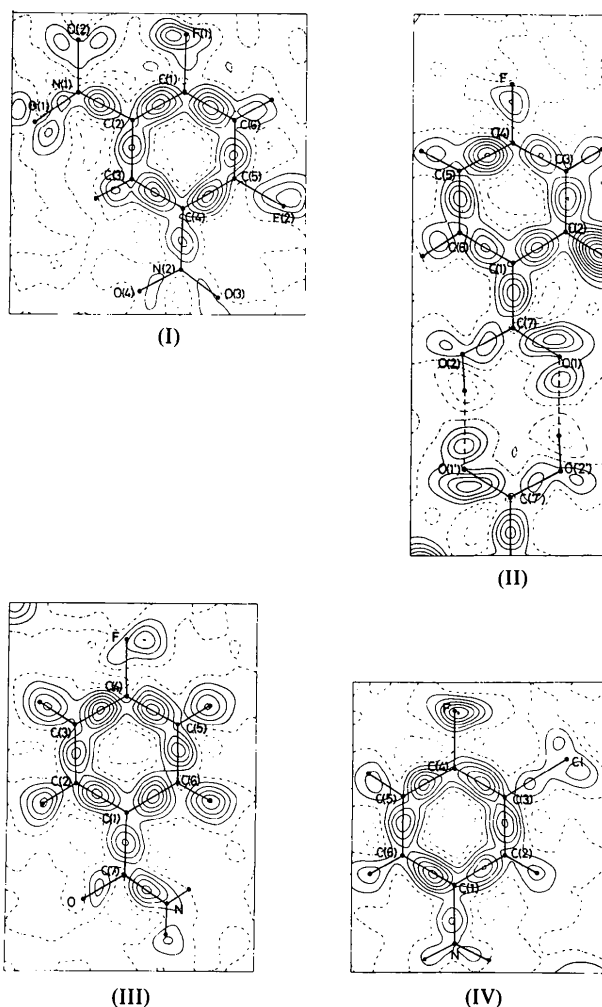


Fig. 1. Multipole-model deformation densities based on the independent-atom model (IAM) through the benzene ring after refinement B. Contour intervals at 0.1 e Å⁻³, negative contours broken, zero contours chain-dotted.

culations showing that the electron population of $2p_x$ (F) is 1.297 for 4-fluorobenzoic acid. As it is known that the peak height of the deformation density depends on the experimental resolution and the magnitude of thermal vibration of the molecule, a direct comparison of the deformation densities in two crystals sometimes loses its physical meaning. However, the direct comparison between the C–F and C–Cl bonds is allowed for compound (IV). Deformation density on the C–F bond axis is more contracted than that on the C–Cl bond, indicating a more compact distribution of the $2p$ orbitals of the F atom compared to the $3p$ orbitals of the Cl atom. No correlation was found between the peak height of the bonding electron and the C–F bond length, which ranges from 1.327 (3) to 1.360 (4) Å.

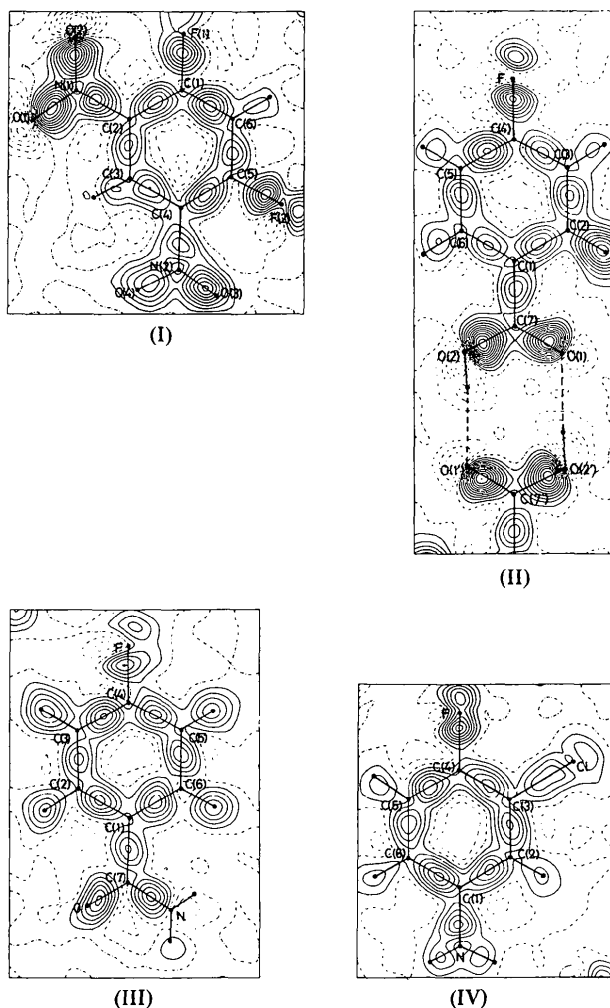


Fig. 2. Multipole-model deformation densities based on the oriented-atom model (OAM) through the benzene ring after refinement *B*. Contour intervals at $0.1 \text{ e } \text{Å}^{-3}$, negative contours broken, zero contours chain-dotted.

Based on the OAM, the bonding electrons of the N–O bonds in the nitro groups of (I), the C–O bond in the carboxylic acid of (II) and the C–O bond in the amide group of (III) appeared clearly. Since the OAM assumes two electrons in the lone-pair orbitals of (I) nitro and (II) carboxylic O atoms, the lone-pair region became featureless.

Effective atomic charge

Effective atomic charges of 4-fluorobenzoic acid (II) and 4-chlorobenzoic acid (II') are listed in Table 4. Although a quantitative comparison of the experimental and theoretical values is limited by the unsatisfactory accuracy of the result of the κ refinement, the general tendencies of the charge distributions agree with each other. The halogen atom is negative and the C(4) atom bonded to the halogen has a positive charge. In the carboxylic group, the O atoms are significantly negative and the C(7) and H(O) atoms are strongly positive. The O...O hydrogen-bond distances in (II) and (II') are 2.609 (3) and 2.612 (1) Å, respectively. The theoretical calculation for (II) indicated that the charge distribution in the COOH group is not drastically changed by the cyclic hydrogen bonds. A molecular orbital (MO) calculation for (IV) was also carried out to confirm the negative effective charges of the halogen atoms, -0.138 and -0.119 for the F and Cl atoms, respectively.

The B_{eq} value of the carboxylic H(O) atom of (II) was estimated to be $10.0 (8) \text{ Å}^2$ in refinement *A*, which is abnormally large compared to that of an H atom in the benzene ring, $1.8 (3)$ – $2.8 (4) \text{ Å}^2$. This tendency was also observed for (II'): $B_{\text{eq}} = 5.6 (5) \text{ Å}^2$ for H(O) and $1.6 (2)$ – $3.1 (3) \text{ Å}^2$ for benzene H atoms (Takazawa *et al.*, 1989). The κ refinement (refinement *C*) indicated the positive effective charge of the H(O) atom to be $0.35 (2)$ – $0.53 (3)$, which is larger than that of a benzene H atom, $0.06 (1)$ – $0.10 (1)$. Therefore, the large thermal parameter of the H(O) atom in refinement *A* may be an artifact resulting from the use of the scattering factors of the neutral H atom. Molecular orbital calculations support this explanation.

However, the possibility of orientational disorder of the carboxylic group can by no means be excluded (Leiserowitz, 1976; Roelofsen, Kanters, Kroon, Doesburg & Koops, 1978). There is a good linear correlation between the difference between the two C–O bond lengths and the difference between the two C–C–O bond angles for carboxylic groups (Dieterich, Paul & Curtin, 1974; Borthwick, 1980). Structural data of (II) correspond to a plot in the middle of the correlation line: on the H(O) side, the C–O bond length is longer by $0.063 (4) \text{ Å}$ and the C–C–O bond angle is smaller by $6.1 (2)^\circ$ than on the

other side. Thermal ellipsoids of the carboxylic O atoms are normal and elongated perpendicular to the C–O bond axis. The ordered oxygen and disordered hydrogen structure can be explained in terms of tunneling of the H atom in a symmetric double-minimum potential (Fitzgerald, Gallucci & Gerkin, 1991). Split-atom refinement of the disordered H atom based on X-ray diffraction data (*e.g.* Roelofsen *et al.*, 1978) may not be sound because the electron density of the H atom cannot be distinguished from that of the oxygen lone pairs (see Fig. 1). Neutron diffraction measurement is required to investigate this phenomenon. A neutron study on benzoic acid failed because of twinning of the crystals grown from the melt (Feld, Lehmann, Muir & Speakman, 1981).

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