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Electron-Density Distribution in Crystals of *p*-Nitrobenzene Derivatives

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Abstract

The electron-density distributions in five nitrobenzene derivatives have been examined by the multipole expansion method based on X-ray diffraction data measured with Mo $K\alpha$ radiation ($\lambda = 0.70926 \text{ \AA}$) at 120 K. *p*-Dinitrobenzene, $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$, (I), $M_r = 168.1$, monoclinic, $P2_1/n$, $a = 10.941(2)$, $b = 5.3813(5)$, $c = 5.6684(4) \text{ \AA}$, $\beta = 92.116(8)^\circ$, $V = 333.51(7) \text{ \AA}^3$, $Z = 2$, $D_x = 1.67 \text{ Mg m}^{-3}$, $\mu = 0.135 \text{ mm}^{-1}$, $R = 0.030$ for 2045 unique reflections. 4-Nitrobenzoic acid, $\text{C}_7\text{H}_5\text{NO}_4$, (II), $M_r = 167.1$, monoclinic, $A2/a$, $a = 12.857(1)$, $b = 5.0272(2)$, $c = 20.997(2) \text{ \AA}$, $\beta = 97.072(8)^\circ$, $V = 1346.8(2) \text{ \AA}^3$, $Z = 8$, $D_x = 1.65 \text{ Mg m}^{-3}$, $\mu = 0.130 \text{ mm}^{-1}$, $R = 0.030$ for 3930 reflections. 4-Nitrobenzamide, $\text{C}_7\text{H}_6\text{N}_2\text{O}_3$, (III), $M_r = 166.1$, monoclinic, $P2_1/c$, $a = 7.393(2)$, $b = 6.8005(9)$, $c = 13.814(2) \text{ \AA}$, $\beta = 90.88(1)^\circ$, $V = 694.4(2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.59 \text{ Mg m}^{-3}$, $\mu = 0.119 \text{ mm}^{-1}$, $R = 0.033$ for 3811 reflections. 4-Nitrobenzaldehyde oxime, $\text{C}_7\text{H}_6\text{N}_2\text{O}_3$, (IV), $M_r = 166.1$, monoclinic, $P2_1/c$, $a = 6.2336(6)$, $b =$

$4.8377(5)$, $c = 24.352(2) \text{ \AA}$, $\beta = 94.87(8)^\circ$, $V = 731.7(1) \text{ \AA}^3$, $Z = 4$, $D_x = 1.51 \text{ Mg m}^{-3}$, $\mu = 0.113 \text{ mm}^{-1}$, $R = 0.043$ for 2493 reflections. 4-Nitroaniline, $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$, (V), $M_r = 138.1$, monoclinic, $P2_1/n$, $a = 12.122(2)$, $b = 6.0276(9)$, $c = 8.487(1) \text{ \AA}$, $\beta = 92.72(1)^\circ$, $V = 619.4(2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.48 \text{ Mg m}^{-3}$, $\mu = 0.107 \text{ mm}^{-1}$, $R = 0.040$ for 2573 reflections. Single-crystal neutron diffraction studies were also made for (I) at 120 K, and for (II) at both 120 and 302 K. For the nitro group, the N—O bonding electrons and the lone pairs of the O atoms are clearly observed. The π -donating nature of the amino group in (V) can be seen by the polarization of the electron density of the benzene ring. The carboxyl H atom in (II) and the oxime H atom in (IV) have pronounced positive effective charges, which are reflected in the relatively large thermal parameters in the X-ray conventional refinement using neutral-atom scattering factors. Neutron diffraction study of (II) indicated that the disorder of the COOH group due to the double proton transfer is 11(3)% at 302 K and is not observed at 120 K within experimental error.

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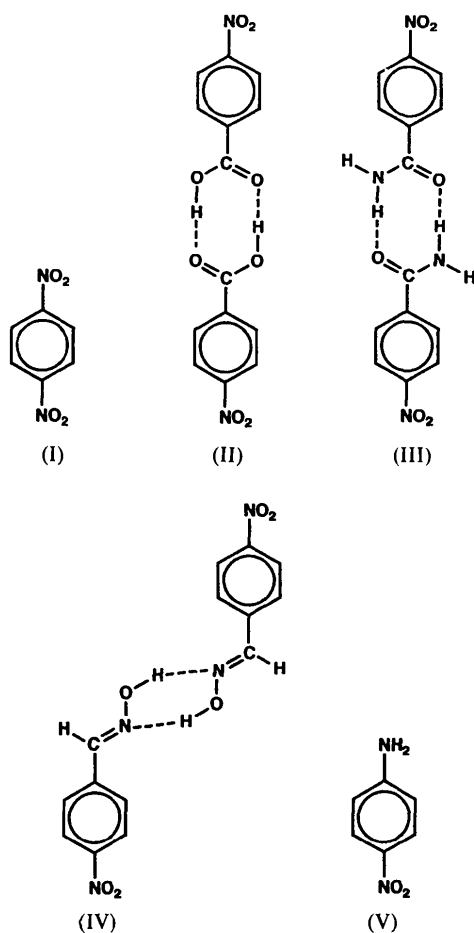
Introduction

The N—O bonding electron of the nitrite ion was observed in crystals of $\text{LiNO}_2 \cdot \text{H}_2\text{O}$ (Ohba, Kikkawa & Saito, 1985) and NaNO_2 (Okuda, Ohba, Saito, Ito & Shibuya, 1990), and was reproduced by *ab initio* molecular orbital calculations using a double-zeta basis set with polarization function (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). Although the $X-N$ difference map of 4-nitropyridine *N*-oxide reported by Coppens & Lehmann (1976) showed very small excess density on the N—O bond axes, this peculiarity was later attributed to the cut-off of the high-order reflections (Hansen & Coppens, 1978). In order to investigate the electron distribution of the nitro group further, both X-ray and neutron diffraction studies have been carried out for *p*-dinitrobenzene, (I). Nitroaniline derivatives receive much attention as organic non-linear optical materials, and the charge density in crystals of 2-methyl-4-nitroaniline has been investigated by Howard, Hursthouse, Lehmann, Mallinson & Frampton (1992) to reveal that the molecular dipole moment is enhanced in the crystal field. One of the aims of this

study is to investigate the electron polarization of the benzene ring in 4-nitroaniline, (V).

Carboxylic acids usually exist in crystals as cyclic hydrogen-bond dimers. The potential energy of the protons in the hydrogen bond has a double minimum with a low-energy barrier, and the kinetics of the proton transfer have been investigated using IR and NMR spectra (Hayashi, Oobatake, Nakamura & Machida, 1991; Takeda, Tsuzumitani & Chatzidimitriou-Dreismann, 1992, and references therein) as well as *ab initio* calculations (Hayashi, Umemura, Kato & Morokuma, 1984; Shida, Barbara & Almlöf, 1991). An X-ray study of fluoromalonic acid revealed that the disorder of the carboxyl group due to the double proton transfer markedly decreases on cooling from 293 to 123 K (Roelofsen, Kanters, Kroon, Doesburg & Koops, 1978). Even the thermodynamic parameters of the proton transfer in the solid state can be estimated by X-ray measurement at various temperatures (Destro, 1991). However, using neutron diffraction it is feasible to investigate the positional disorder of the H atoms. In the study of the electron-density distributions in crystals of 4-chlorobenzoic acid (Takazawa, Ohba & Saito, 1989) and 4-fluorobenzoic acid (Kubota & Ohba, 1992) at 120 K, abnormally large thermal parameters of the carboxyl H(O) atoms were obtained by high-order refinement. This fact was tentatively attributed to the positive effective charge of the acid H atom based on the κ refinement and *ab initio* MO calculations (Kubota & Ohba, 1992). However, the possibility of disorder of the COOH group could by no means be excluded. Crystals of 4-fluorobenzoic acid and 4-chlorobenzoic acid easily lose their crystallinity by undergoing cutting or cooling. 4-Nitrobenzoic acid is suitable for further investigations including neutron diffraction. Not only 4-nitrobenzoic acid, (II), but also 4-nitrobenzamide, (III), and 4-nitrobenzaldehyde oxime, (IV), form dimers by cyclic hydrogen bonds. (III) and (IV) are good references for (II), because there is little possibility of proton transfer in (III) and (IV).

The papers of crystal structure determination or redetermination are (I) Di Rienzo, Domenicano & Di Sanseverino (1980); (II) Colapietro & Domenicano (1977); (III) Di Rienzo, Domenicano & Foresti Serantoni (1977); (IV) Bachechi & Zambonelli (1973); and (V) Colapietro, Domenicano, Marciante & Portalone (1982).



Experimental

X-ray data collection

Crystals were grown from acetone solutions for (I) and (II), from ethanol solutions for (III) and (V), and from benzene solution for (IV). X-ray diffraction

Table 1. *Experimental details of the X-ray study*

	(I)	(II)	(III)	(IV)	(V)
Crystal size (mm)	0.5 × 0.5 × 0.4	0.5 × 0.5 × 0.4	0.7 × 0.4 × 0.25	0.5 × 0.3 × 0.3	0.3 × 0.3 × 0.3
2 θ_{\max} (°)	110	120	120	80	90
Range of h , k and l	0 ≤ h ≤ 19 -9 ≤ k ≤ 9 -10 ≤ l ≤ 10 (4 < 2 θ ≤ 80°) 0 ≤ h ≤ 26 0 ≤ k ≤ 13 -13 ≤ l ≤ 13 (80 < 2 θ ≤ 110°)	-23 ≤ h ≤ 23 -9 ≤ k ≤ 9 0 ≤ l ≤ 38 (4 < 2 θ ≤ 80°) -31 ≤ h ≤ 31 0 ≤ k ≤ 12 0 ≤ l ≤ 51 (80 < 2 θ ≤ 120°)	-13 ≤ h ≤ 13 0 ≤ k ≤ 12 -25 ≤ l ≤ 25 (4 < 2 θ ≤ 80°) 0 ≤ h ≤ 18 0 ≤ k ≤ 16 -33 ≤ l ≤ 33 (80 < 2 θ ≤ 120°)	-8 ≤ h ≤ 8 -6 ≤ k ≤ 6 0 ≤ l ≤ 34 (4 < 2 θ ≤ 80°) -11 ≤ h ≤ 11 0 ≤ k ≤ 8 0 ≤ l ≤ 44 (60 < 2 θ ≤ 80°)	-21 ≤ h ≤ 21 -10 ≤ k ≤ 10 0 ≤ l ≤ 15 (4 < 2 θ ≤ 80°) -24 ≤ h ≤ 24 0 ≤ k ≤ 12 0 ≤ l ≤ 16 (80 ≤ 2 θ ≤ 90°)
Variation of five standard reflections*	0.95-1.00	0.99-1.01	0.88-1.00	1.00-1.01	0.99-1.00
Measured reflections	6780	14351	10530	6581	9143
Observed reflection†	3514	6519	6727	3816	4566
Unique reflections (R_m)	2045 (0.014)	3930 (0.017)	3811 (0.020)	2493 (0.022)	2573 (0.023)
Transmission factors	0.94-0.95	0.94-0.96	0.095-0.97	0.97-0.98	0.97-0.98
High-order refinement					
Parameters refined	63	129	133	133	115
R	0.042	0.043	0.048	0.058	0.054
wR	0.055	0.051	0.056	0.072	0.060
S	1.98	1.69	1.89	2.18	1.82
Multipole refinement					
Parameters refined	162	330	337	337	286
R	0.030	0.030	0.033	0.043	0.040
wR	0.032	0.028	0.033	0.053	0.038
S	1.07	1.01	1.11	1.65	1.15
κ refinement					
Parameters refined	—	139	—	143	—
R	—	0.041	—	0.053	—
wR	—	0.049	—	0.063	—
S	—	1.34	—	1.94	—

* $\sum(F_o/F_{o,initial})/S$.† $F_o > 3\sigma(F_o)$.

intensities were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation by θ -2 θ -scan technique with scan speed 6° min⁻¹ in θ . Crystals were kept at 120 K with a stream of cold nitrogen gas. Experimental conditions and refinement information are listed in Table 1. Lattice constants were determined based on 24 2 θ values (54 < 2 θ < 74°) with $\lambda(\text{Mo } K\alpha_1) = 0.70926 \text{ \AA}$. Five standard reflections were measured every 100 measurements. Reflection data with $|F_o| > 3\sigma(|F_o|)$ were recognized as observed. An absorption correction was made by the Gauss numerical integration method (Busing & Levy, 1957).

Refinement

High-order refinement was performed with the program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weight $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Atomic coordinates and anisotropic thermal parameters of non-H atoms were refined with $(\sin\theta/\lambda)_{\max} = 0.6 \text{ \AA}^{-1}$, and H atoms were refined isotropically based on all the reflections. An extinction correction did not reduce the R values. Complex neutral-atom scattering factors for non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Scattering factors of H atoms were those of Stewart, Davidson & Simpson (1965). Calculations were performed with FACOM M-380R and M-1600/8 computers of

Keio University. Positional parameters are given in Table 2, and bond lengths and bond angles in Table 3.*

Multipole refinement was carried out with the program *MOLLY* (Hansen & Coppens, 1978). The radial function was $r^n \exp(-\zeta r)$, where $n_l = 2, 2, 3$ and 4 (for $l = 1, 2, 3$ and 4, respectively) for non-H atoms, 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 of the unit cell was constrained to be neutral. The positional, thermal, multipole and radial (κ) parameters of non-H atoms were refined based on all the reflections. The κ refinement (Coppens *et al.*, 1979) was also carried out for (II) and (IV) to estimate the effective charge of the carboxyl and oxime H(O) atoms (see Table 6). Valence-electron populations, thermal parameters, and κ parameters of non-H atoms were refined based on all the reflections. The atomic coordinates were fixed at those of high-order refinement. Chemical twofold symmetry was assumed for the nitrobenzene moiety, and a common effective charge was assigned for the benzene H atoms.

* Lists of structure factors and anisotropic thermal parameters determined by X-ray high-order refinement and neutron studies have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71244 (66 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0633]

Table 2. Positional parameters ($\times 10^5$ for non-H atoms; $\times 10^4$ for H atoms) and equivalent isotropic temperature factors ($\times 10$) determined by X-ray high-order refinement

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B/B_{\text{eq}} (\text{\AA}^2)$
(I) p-Dinitrobenzene				
O(1)	12327 (4)	46411 (9)	38947 (9)	20 (1)
O(2)	22211 (4)	48358 (8)	6472 (8)	20 (1)
N	14335 (3)	39430 (6)	18830 (7)	13 (1)
C(1)	6864 (3)	18934 (6)	8987 (7)	11 (1)
C(2)	-3256 (4)	11346 (7)	21224 (7)	13 (1)
C(3)	10316 (4)	8109 (7)	-12015 (7)	13 (1)
H(2)	-542 (9)	1934 (17)	3586 (15)	26 (2)
H(3)	1725 (9)	1338 (20)	-1967 (17)	28 (2)
(II) 4-Nitrobenzoic acid				
O(1)	54615 (3)	24345 (9)	4750 (2)	12 (1)
O(2)	37692 (3)	15392 (9)	1501 (2)	13 (1)
O(3)	38294 (4)	118395 (11)	25303 (3)	17 (1)
O(4)	22730 (4)	117915 (9)	19921 (3)	15 (1)
N	31834 (4)	110042 (8)	20978 (2)	11 (1)
C(1)	41549 (3)	50094 (9)	8992 (2)	9 (1)
C(2)	49063 (3)	64648 (9)	12938 (2)	11 (1)
C(3)	45925 (3)	84384 (9)	16940 (2)	11 (1)
C(4)	35234 (3)	89143 (8)	16796 (2)	9 (1)
C(5)	27619 (3)	75167 (10)	12888 (2)	11 (1)
C(6)	30849 (3)	55278 (9)	8961 (2)	10 (1)
C(7)	45230 (3)	28804 (8)	4891 (2)	9 (1)
H(0)	4063 (9)	119 (23)	-92 (6)	34 (3)
H(2)	5627 (7)	6134 (19)	1281 (5)	16 (2)
H(3)	5100 (7)	9440 (18)	1964 (4)	13 (2)
H(5)	2038 (7)	7861 (20)	1296 (5)	16 (2)
H(6)	2570 (8)	4535 (19)	620 (5)	19 (2)
(III) 4-Nitrobenzamide				
O(1)	53948 (6)	85375 (6)	40021 (3)	13 (1)
O(2)	81567 (8)	-3318 (7)	22024 (3)	16 (1)
O(3)	96082 (7)	-9987 (7)	35346 (3)	15 (1)
N(1)	65934 (7)	79621 (6)	54857 (3)	12 (1)
N(2)	86568 (6)	843 (6)	30308 (3)	11 (1)
C(1)	69553 (6)	55117 (6)	42019 (3)	9 (1)
C(2)	66260 (7)	50778 (7)	32241 (3)	11 (1)
C(3)	71774 (7)	32961 (7)	28329 (3)	11 (1)
C(4)	80736 (6)	19731 (7)	34368 (3)	9 (1)
C(5)	84271 (7)	23551 (7)	44080 (3)	11 (1)
C(6)	78551 (7)	41429 (7)	47910 (3)	10 (1)
C(7)	62587 (6)	74514 (6)	45642 (3)	9 (1)
H(2)	5970 (14)	6017 (17)	2831 (7)	24 (2)
H(3)	6952 (13)	2970 (16)	2140 (7)	17 (2)
H(5)	9003 (14)	1423 (16)	4787 (8)	26 (2)
H(6)	8102 (12)	4294 (14)	5472 (6)	14 (2)
H(1N)	6099 (14)	9067 (17)	5712 (7)	27 (2)
H(2N)	7168 (15)	7187 (19)	5919 (8)	33 (3)
(IV) p-Nitrobenzaldehyde oxime				
O(1)	-23368 (28)	98458 (36)	2500 (7)	19 (1)
O(2)	58679 (24)	-20463 (33)	18022 (7)	17 (1)
O(3)	33573 (25)	-27527 (33)	23504 (6)	17 (1)
N(1)	-6722 (26)	80617 (32)	4449 (7)	14 (1)
N(2)	40871 (24)	-15563 (31)	19630 (7)	12 (1)
C(1)	2055 (25)	44946 (31)	11171 (6)	11 (1)
C(2)	-4895 (25)	31951 (35)	15847 (7)	13 (1)
C(3)	7853 (25)	12125 (33)	18656 (7)	12 (1)
C(4)	27553 (24)	5688 (31)	16736 (6)	10 (1)
C(5)	34930 (25)	18308 (36)	12095 (7)	13 (1)
C(6)	22004 (27)	38090 (34)	9304 (7)	13 (1)
C(7)	-12521 (29)	65320 (38)	8360 (7)	14 (1)
H(2)	-1852 (28)	3618 (37)	1720 (8)	21 (4)
H(3)	353 (28)	353 (35)	2190 (8)	20 (4)
H(5)	4799 (31)	1307 (39)	1113 (9)	28 (4)
H(6)	2667 (27)	4651 (37)	620 (8)	21 (4)
H(7)	-2712 (31)	6730 (39)	940 (9)	28 (4)
H(0)	-1675 (35)	10947 (47)	-27 (10)	45 (6)
(V) p-Nitroaniline				
O(1)	42936 (10)	62280 (19)	86791 (14)	20 (1)
O(2)	44682 (10)	91418 (16)	72148 (13)	20 (1)
N(1)	81436 (12)	31702 (22)	44838 (17)	20 (1)
N(2)	47391 (8)	72228 (16)	76079 (12)	13 (1)
C(1)	73046 (8)	41267 (18)	52358 (12)	13 (1)
C(2)	67915 (8)	30185 (16)	64737 (13)	13 (1)
C(3)	59467 (8)	40232 (16)	72543 (12)	12 (1)
C(4)	56041 (9)	61556 (14)	67976 (13)	11 (1)

Neutron study

Single-crystal neutron diffraction measurements for (I) and (II) were carried out at the Research Reactor Institute, Kyoto University, with $\lambda = 1.015 \text{ \AA}$ using a Cu(220) monochromator. The flux of the incident beam was $10^5 \text{ neutrons cm}^{-2} \text{ s}^{-1}$. (I): A crystal of dimensions $ca 5 \times 4 \times 3 \text{ mm}$ was attached to the top of an aluminium rod and kept at 120 K in a liquid N_2 cryostat. The ω - and θ - 2θ -step scan techniques gave the same integrated intensities as well as peak half-widths for reflections with $2\theta = 60^\circ$, a typical peak half-width being 1.1° in θ . The intensity measurements were carried out up to $2\theta = 90^\circ$ by the ω -step scan technique and 357 unique reflections were obtained. Symmetry-related reflections were measured for 14 strong reflections to check the data quality ($R_{\text{int}} = 0.017$). Correction for absorption was neglected. The coordinates and anisotropic thermal parameters of all the atoms were refined by the program *RADIEL*. The scattering lengths were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV): O 5.804, N 9.380, C 6.657, H $-3.789 (\times 10^{-13} \text{ cm})$. Extinction was corrected isotropically in the type I Lorentzian approximation (Becker & Coppens, 1974, 1975). $R(F) = 0.029$, $wR(F) = 0.035$, $S = 2.55$, number of reflections/number of parameters (N/P) = 357/74, $y_{\text{min}} (F_o/F_c) = 0.83$. Atomic coordinates are listed in Table 4. In order to calculate the X - N deformation density, a multipole refinement was carried out based on all the X-ray data with the positional parameters determined by neutron study.

(II): Neutron diffraction intensities were measured by an ω -step scan technique with a crystal of dimensions $16.5 \times 14 \times 3.5 \text{ mm}$. At 120 K, 467 reflections were measured up to $2\theta = 80^\circ$, and 439 reflections were observed with $|F_o| > 8\sigma(|F_o|)$. At 302 K, 1005 reflections were measured up to $2\theta = 95^\circ$, and 747 reflections were observed. The lattice constants at room temperature reported by Colapietro & Domenicano (1977) were utilized: $a = 12.918 (2)$, $b = 5.042 (2)$, $c = 21.298 (6) \text{ \AA}$, $\beta = 96.66 (2)^\circ$. Non-H atoms were refined anisotropically and the H atoms isotropically. An anisotropic extinction correction of type I was applied (Becker & Coppens, 1974, 1975). The positional disorder of the H(O) atom was taken into account. The site-occupancy ratio of the two possible positions, H(O1) and H(O2), was refined with a common thermal parameter. The position of

Table 3. Bond lengths (Å) and bond angles (°) determined by X-ray high-order refinement

(I) *p*-Dinitrobenzene

O(1)—N	1.2281 (6)	O(1)—N—O(2)	124.28 (4)
O(2)—N	1.2283 (6)	O(1)—N—C(1)	117.76 (4)
N—C(1)	1.4705 (5)	O(2)—N—C(1)	117.96 (4)
C(1)—C(2)	1.3894 (6)	N—C(1)—C(2)	118.23 (3)
C(1)—C(3)	1.3901 (6)	N—C(1)—C(3)	118.32 (3)
C(2)—C(3)	1.3912 (6)	C(2)—C(1)—C(3)	123.44 (3)
		C(1)—C(2)—C(3)	118.39 (4)
		C(1)—C(3)—C(2)	118.17 (4)

(II) 4-Nitrobenzoic acid

O(1)—C(7)	1.2312 (6)	O(3)—N—O(4)	124.48 (5)
O(2)—C(7)	1.3155 (6)	O(3)—N—C(4)	117.57 (5)
O(3)—N	1.2268 (7)	O(4)—N—C(4)	117.95 (4)
O(4)—N	1.2296 (7)	C(2)—C(1)—C(6)	120.80 (4)
N—C(4)	1.4698 (6)	C(2)—C(1)—C(7)	118.26 (4)
C(1)—C(2)	1.3993 (6)	C(6)—C(1)—C(7)	120.94 (4)
C(1)—C(6)	1.3994 (6)	C(1)—C(2)—C(3)	120.00 (4)
C(1)—C(7)	1.4870 (6)	C(2)—C(3)—C(4)	117.93 (4)
C(2)—C(3)	1.3917 (6)	N—C(4)—C(3)	118.39 (4)
C(3)—C(4)	1.3918 (6)	N—C(4)—C(5)	118.35 (4)
C(4)—C(5)	1.3884 (6)	C(3)—C(4)—C(5)	123.26 (4)
C(5)—C(6)	1.3915 (6)	C(4)—C(5)—C(6)	118.27 (4)
O(2)—H(0)	0.98 (1)	C(1)—C(6)—C(5)	119.73 (4)
O(2)...O(1 ⁱⁱ)	2.6479 (6)	O(1)—C(7)—O(2)	123.54 (4)
		O(1)—C(7)—C(1)	121.85 (4)
		O(2)—C(7)—C(1)	114.61 (4)

(III) 4-Nitrobenzamide

O(1)—C(7)	1.2414 (6)	O(2)—N(2)—O(3)	123.43 (5)
O(2)—N(2)	1.2301 (6)	O(2)—N(2)—C(4)	118.07 (4)
O(3)—N(2)	1.2274 (6)	O(3)—N(2)—C(4)	118.51 (4)
N(1)—C(7)	1.3388 (6)	C(2)—C(1)—C(6)	119.69 (4)
N(2)—C(4)	1.4689 (6)	C(2)—C(1)—C(7)	116.76 (4)
C(1)—C(2)	1.4002 (6)	C(6)—C(1)—C(7)	123.53 (4)
C(1)—C(6)	1.3981 (6)	C(1)—C(2)—C(3)	120.72 (4)
C(1)—C(7)	1.5045 (6)	C(2)—C(3)—C(4)	118.12 (4)
C(2)—C(3)	1.3903 (7)	N(2)—C(4)—C(3)	118.52 (4)
C(3)—C(4)	1.3883 (7)	N(2)—C(4)—C(5)	118.74 (4)
C(4)—C(5)	1.3874 (6)	C(3)—C(4)—C(5)	122.74 (4)
C(5)—C(6)	1.3942 (7)	C(4)—C(5)—C(6)	118.46 (4)
O(1)...N(1 ⁱⁱⁱ)	2.8913 (7)	C(1)—C(6)—C(5)	120.27 (4)
		O(1)—C(7)—N(1)	121.74 (4)
		O(1)—C(7)—C(1)	119.28 (4)
		N(1)—C(7)—C(1)	118.98 (4)

(IV) *p*-Nitrobenzaldehyde oxime

O(1)—N(1)	1.401 (3)	O(1)—N(1)—C(7)	111.1 (2)
O(2)—N(2)	1.231 (2)	O(2)—N(2)—O(3)	123.9 (2)
O(3)—N(2)	1.226 (3)	O(2)—N(2)—C(4)	118.2 (2)
N(1)—C(7)	1.282 (3)	O(3)—N(2)—C(4)	118.0 (2)
N(2)—C(4)	1.464 (2)	C(2)—C(1)—C(6)	120.2 (2)
C(1)—C(2)	1.402 (3)	C(2)—C(1)—C(7)	117.2 (2)
C(1)—C(6)	1.400 (3)	C(6)—C(1)—C(7)	122.6 (2)
C(1)—C(7)	1.470 (3)	C(1)—C(2)—C(3)	120.4 (2)
C(2)—C(3)	1.388 (3)	C(2)—C(3)—C(4)	118.4 (2)
C(3)—C(4)	1.386 (3)	N(2)—C(4)—C(3)	118.6 (2)
C(4)—C(5)	1.396 (3)	N(2)—C(4)—C(5)	118.9 (2)
C(5)—C(6)	1.392 (3)	C(3)—C(4)—C(5)	122.5 (2)
O(1)—H(O)	0.98 (3)	C(4)—C(5)—C(6)	118.7 (2)
N(1)...O(1 ⁱⁱⁱ)	2.819 (3)	C(1)—C(6)—C(5)	119.8 (2)
		N(1)—C(7)—C(1)	122.1 (2)

(V) *p*-Nitroaniline

O(1)—N(2)	1.234 (2)	O(1)—N(2)—O(2)	122.0 (1)
O(2)—N(2)	1.244 (2)	O(1)—N(2)—C(4)	119.4 (1)
N(1)—C(1)	1.355 (2)	O(2)—N(2)—C(4)	118.6 (1)
N(2)—C(4)	1.433 (2)	N(1)—C(1)—C(2)	121.0 (1)
C(1)—C(2)	1.414 (2)	N(1)—C(1)—C(6)	120.1 (1)
C(1)—C(6)	1.415 (2)	C(2)—C(1)—C(6)	118.8 (1)
C(2)—C(3)	1.385 (2)	C(1)—C(2)—C(3)	120.7 (1)
C(3)—C(4)	1.400 (1)	C(2)—C(3)—C(4)	119.1 (1)
C(4)—C(5)	1.397 (1)	N(2)—C(4)—C(3)	119.6 (1)
C(5)—C(6)	1.377 (2)	N(2)—C(4)—C(5)	119.2 (1)
		C(3)—C(4)—C(5)	121.2 (1)
		C(4)—C(5)—C(6)	119.6 (1)
		C(1)—C(6)—C(5)	120.6 (1)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $1-x, 2-y, 1-z$; (iv) $-x, 2-y, -z$.

Table 4. Positional parameters, equivalent isotropic temperature factors ($\times 10$), and site occupation (SO) parameters determined by neutron study

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / <i>B</i> _{eq} (Å ²)	SO
(I) at 120 K					
O(1)	0.1232 (3)	0.4648 (5)	0.3886 (4)	27 (1)	
O(2)	0.2222 (3)	0.4835 (5)	0.0650 (4)	25 (1)	
N	0.1432 (1)	0.3946 (3)	0.1880 (2)	20 (1)	
C(1)	0.0687 (2)	0.1888 (4)	0.0901 (3)	17 (1)	
C(2)	-0.0327 (2)	0.1127 (4)	0.2122 (3)	19 (1)	
C(3)	0.1030 (2)	0.0809 (5)	-0.1199 (3)	19 (1)	
H(2)	-0.0559 (5)	0.2043 (11)	0.3730 (8)	34 (1)	
H(3)	0.1826 (5)	0.1457 (10)	-0.2079 (8)	34 (1)	
(II) at 120 K					
O(1)	0.5450 (4)	0.246 (2)	0.0470 (2)	21 (4)	
O(2)	0.3770 (3)	0.149 (2)	0.0139 (3)	23 (4)	
O(3)	0.3827 (4)	1.189 (2)	0.2528 (3)	23 (4)	
O(4)	0.2275 (4)	1.178 (2)	0.1998 (3)	25 (4)	
N	0.3181 (2)	1.100 (1)	0.2099 (2)	20 (3)	
C(1)	0.4157 (3)	0.504 (2)	0.0903 (2)	16 (3)	
C(2)	0.4905 (3)	0.647 (2)	0.1293 (2)	19 (4)	
C(3)	0.4588 (3)	0.847 (2)	0.1695 (2)	19 (4)	
C(4)	0.3528 (3)	0.891 (2)	0.1683 (2)	17 (1)	
C(5)	0.2759 (3)	0.749 (2)	0.1288 (2)	21 (3)	
C(6)	0.3084 (3)	0.551 (2)	0.0898 (2)	19 (1)	
C(7)	0.4528 (3)	0.285 (2)	0.0487 (2)	18 (1)	
H(0)	0.4076 (7)	0.011 (4)	-0.0093 (5)	29 (2)	
H(2)	0.5730 (7)	0.600 (4)	0.1282 (5)	30 (2)	
H(3)	0.5155 (7)	0.959 (4)	0.2000 (5)	28 (2)	
H(5)	0.1941 (7)	0.798 (4)	0.1306 (5)	30 (2)	
H(6)	0.2500 (7)	0.443 (4)	0.0596 (5)	29 (2)	
(II) at 302 K					
O(1)	0.5456 (3)	0.243 (2)	0.0481 (2)	35 (4)	
O(2)	0.3800 (3)	0.157 (3)	0.0144 (3)	40 (4)	
O(3)	0.3814 (4)	1.179 (3)	0.2507 (3)	54 (6)	
O(4)	0.2290 (4)	1.174 (3)	0.1989 (3)	36 (4)	
N	0.3187 (2)	1.094 (2)	0.2083 (1)	33 (2)	
C(1)	0.4161 (3)	0.500 (2)	0.0900 (2)	26 (2)	
C(2)	0.4904 (3)	0.641 (2)	0.1293 (2)	33 (3)	
C(3)	0.4585 (3)	0.838 (2)	0.1688 (2)	31 (3)	
C(4)	0.3535 (3)	0.885 (2)	0.1673 (2)	28 (3)	
C(5)	0.2778 (3)	0.750 (2)	0.1285 (2)	36 (3)	
C(6)	0.3104 (3)	0.554 (2)	0.0893 (2)	33 (3)	
C(7)	0.4525 (3)	0.284 (2)	0.0489 (2)	30 (3)	
H(O1)	0.4084 (9)	0.015 (6)	-0.0093 (6)	44 (2)	0.89 (3)
H(O2)*	0.5711	-0.390	0.5232	44	0.11
H(2)	0.5727 (7)	0.595 (5)	0.1285 (5)	47 (2)	
H(3)	0.5150 (7)	0.948 (5)	0.1995 (4)	45 (2)	
H(5)	0.1971 (7)	0.796 (5)	0.1294 (4)	47 (2)	
H(6)	0.2530 (7)	0.447 (5)	0.0605 (4)	47 (2)	

* Atomic coordinates of H(O2) were fixed and the thermal parameter was constrained to be equal to that of H(O1).

H(O2) was calculated from H(O1) by rotation around the C(1)—C(7) bond axis by 180°. Since the site-occupation parameter of H(O2) became negative in the structure analysis at 120 K, disorder was assumed to be absent. At 120 K, $R(F) = 0.071$, $wR(F) = 0.087$, $S = 4.97$, $N/P = 439/126$, $y_{\min} = 0.33$. At 302 K, $R(F) = 0.085$, $wR(F) = 0.102$, $S = 4.44$, $N/P = 747/130$, $y_{\min} = 0.30$.

Theoretical calculation

Mulliken population analyses (Mulliken, 1955) were carried out by an *ab initio* SCF method using an STO-6G basis set with the program system MOLYX (Nambu, Nakata & Iwata, 1989) on a MIPS RS3230 computer at Keio University. The bond lengths and bond angles were symmetrized and H-atom positions idealized. Electron populations in

Table 5. Electron populations in the $2p_z$ (π) orbitals and effective charges of the groups in *p*-dinitrobenzene (I) and *p*-nitroaniline (V) derived from Mulliken population analyses

Carbon $2p_z$	(I)	(V)
C(-nitro)	1.048	1.154
C(-amino)	—	0.900
C(-C-nitro)	0.968	0.933
C(-C-amino)	—	1.098
Effective charge		
NO ₂	-0.224	-0.278
NH ₂	—	-0.212
C ₆ H ₄	+0.448	+0.490

Table 6. Effective atomic charges of 4-nitrobenzoic acid (II) and 4-nitrobenzaldehyde oxime (IV)

	(II)		(IV)	
	κ refinement	Theory	κ refinement	Theory
O(1)	-0.33 (2)	-0.275	-0.03 (4)	-0.214
O(2)	-0.12 (2)	-0.305	-0.20 (2)*	-0.202
O(3)	-0.16 (2)*	-0.198	-0.20 (2)*	-0.202
O(4)	-0.16 (2)*	-0.199	—	—
N(1)	+0.31 (2)*	+0.161	+0.03 (4)	-0.124
N(2)	—	—	+0.27 (4)*	+0.160
C(1)	-0.24 (2)	-0.012	-0.09 (4)	+0.023
C(2)	+0.10 (2)	-0.049	-0.10 (3)	-0.061
C(3)	-0.06 (2)	-0.051	-0.10 (3)	-0.045
C(4)	-0.13 (3)	+0.078	-0.15 (4)	+0.075
C(5)	-0.06 (2)	-0.043	-0.10 (3)	-0.054
C(6)	+0.10 (2)	-0.045	-0.10 (3)	-0.046
C(7)	+0.32 (3)	+0.323	0.07 (5)	+0.024
H(2)	+0.04 (2)	+0.094	+0.12 (2)	+0.078
H(3)	+0.04 (2)	+0.099	+0.12 (2)	+0.100
H(5)	+0.04 (2)	+0.100	+0.12 (2)	+0.099
H(6)	+0.04 (2)	+0.094	+0.12 (2)	+0.090
H(7)	—	—	+0.12 (2)	+0.081
H(O)	+0.25 (3)	+0.229	+0.25 (5)	+0.218

* These N and O atoms are of the nitro group.

the $2p_z$ (π) orbitals of the benzene C atoms for (I) and (V) are listed in Table 5. The effective atomic charges for (II) and (IV) are shown in Table 6.

Results and discussion

Substitution effect

Bond lengths and bond angles determined by X-ray high-order refinement are listed in Table 3. The influence of the nitro group on the internal angle α of the benzene ring has already been investigated in detail (Colapietro, Domenicano, Marciante & Portalone, 1982). The ipso angle α is large when the nitro group is *para* to a strong π -acceptor, as in *p*-dinitrobenzene [(I), 123.44 (3)^o] and 4-nitrobenzoic acid [(II), 123.26 (4)^o]. Lower values of α occur with a strong π -donor, as in 4-nitroaniline [(V), 121.2 (1)^o]. In (V), the Ph—NO₂ bond distance is 1.433 (2) Å, which is significantly shorter than those in (I)–(IV), from 1.464 (2) to 1.471 (1) Å. This fact indicates the effects of through-conjugation in (V) with the substantial contribution of the quinonoid canonical form (Colapietro *et al.*, 1982).

Fig. 1 shows the observed deformation densities through the benzene ring, where one can scarcely see

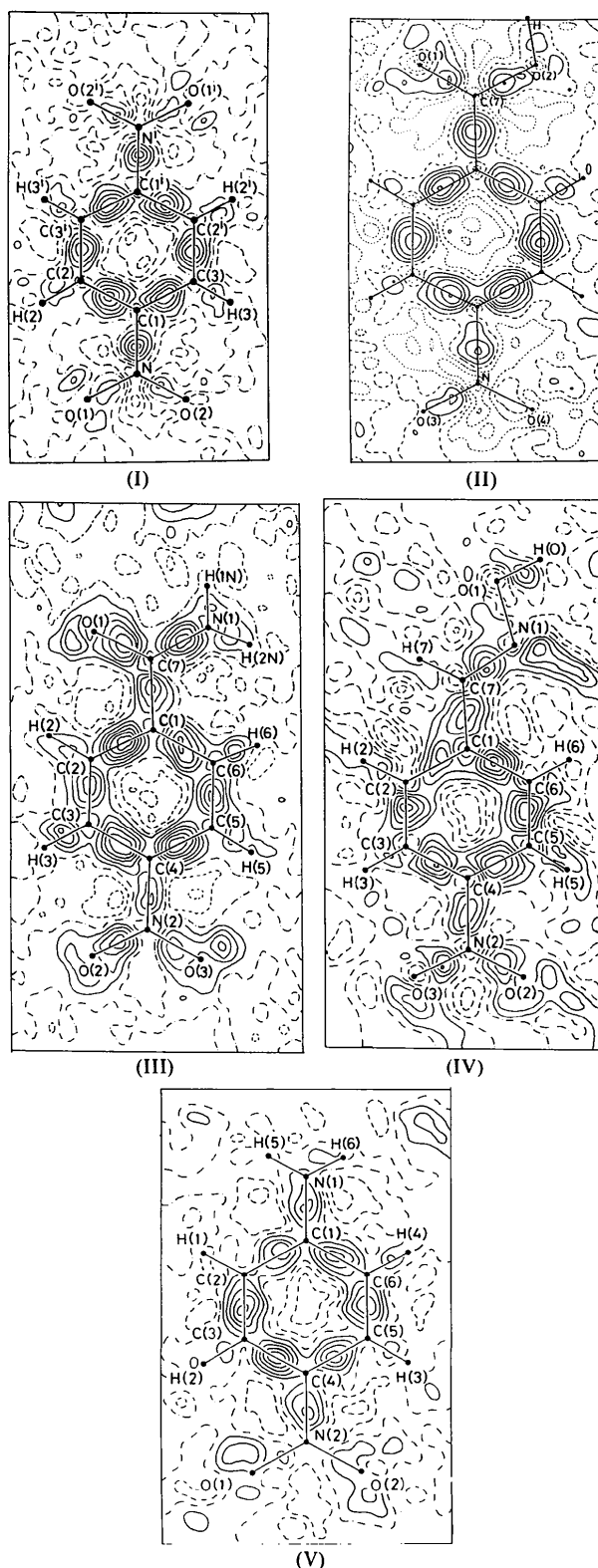


Fig. 1. Observed deformation densities through the benzene ring after high-order refinement. Contour intervals at $0.1 \text{ e} \text{ \AA}^{-3}$, negative contours broken, zero contours chain-dotted.

the substitution effects on the benzene ring. Sections of the deformation densities through the C—C bond and perpendicular to the benzene ring of (V) are shown in Fig. 2. Electron-density distribution in the

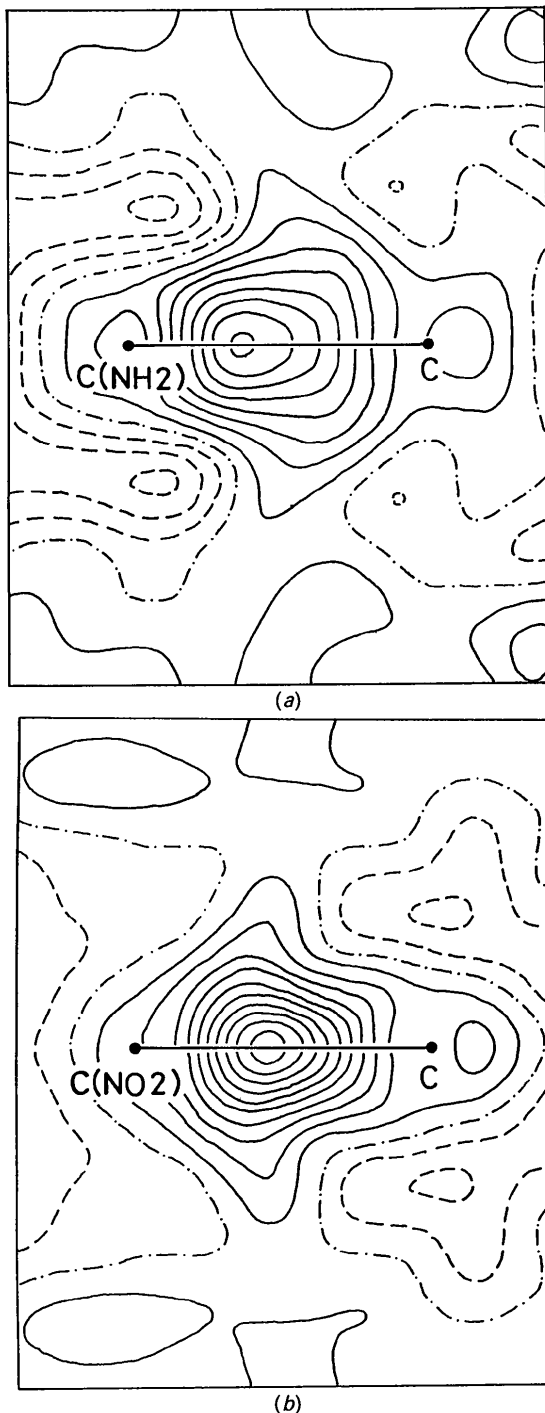


Fig. 2. Averaged deformation densities through the C—C bond axis and perpendicular to the benzene ring of (V) for (a) C(1)—C(2) and C(1)—C(6) axes, and (b) C(3)—C(4) and C(5)—C(4) axes. Contour intervals at $0.1 \text{ e } \text{Å}^{-3}$.

π region is unsymmetric along the C—C bond axes. The polarization of electron distribution accords with the π -donating and accepting characters of the amino and nitro groups, respectively. Molecular orbital calculations support the experimental results. The carbon $2p_z$ (π) orbital population is smallest for the C atom bonded to NH_2 and is largest for the C atom next to the NO_2 group (see Table 5).

The dihedral angles between the nitro and the benzene planes are (I) 10.2 (1), (II) 14.8 (1), (III) 7.9 (1), (IV) 3.7 (2) and (V) 2.2 (1) $^\circ$. The observed deformation density on the nitro plane of (I) after the high-order refinement, and X - N multipole model deformation density are shown in Fig. 3. The N—O bonding and sp^2 lone-pair peaks of the O atoms are clearly observed. The peak height of the N—O bonding electron is much lower than those of the C—C and C—N bonds, because more than two electrons are subtracted in the N—O bonding region based on the independent-atom model. When the oriented atom model is used for reference densities, the elec-

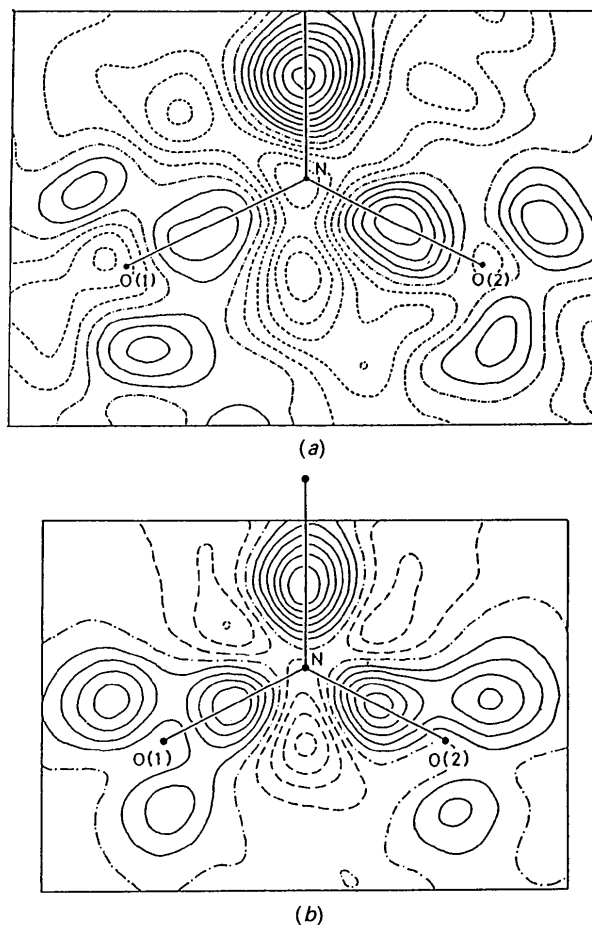


Fig. 3. Deformation density in the nitro plane of (I). (a) Observed density after high-order refinement, and (b) X - N multipole model deformation density. Contour intervals at $0.05 \text{ e } \text{Å}^{-3}$.

tron accumulation on the N—O bond axis can be seen remarkably as was illustrated for 1-chloro-2,4-dinitrobenzene (Takazawa, Ohba & Saito, 1989) and NaNO₂ (Okuda, Ohba, Saito, Ito & Shibuya, 1990).

Hydrogen bonds

The —COOH, —CONH₂ and —CH=NOH groups in (II), (III) and (IV) are hydrogen bonded with each other in crystallographically centrosymmetric pairs. The O...O distance in 4-nitrobenzoic acid (II) is 2.6479 (6) Å at 120 K, which is a little longer than those in 4-fluorobenzoic acid, 2.609 (3) Å (Kubota & Ohba, 1992), and 4-chlorobenzoic acid, 2.6117 (9) Å (Takazawa, Ohba & Saito, 1989). From these O...O distances, the strength of the hydrogen bond is classified into a medium type (Emsley, 1984). However, the activation energies for proton transfer and proton tunneling of (II) were estimated at only 2.5 and 1.0 kJ mol⁻¹, respectively, by NMR techniques (Imaoka, Takeda & Chihara, 1988). The geometry optimization of the formic acid dimer by *ab initio* MO calculations indicated that the O...O distance decreases by 0.2–0.3 Å in the transition state (Hayashi, Umemura, Kato & Morokuma, 1984; Shida, Barbara & Almlöf, 1991). This is an important mechanism which reduces the energy barrier in the double-minimum potential.

The κ refinement and theoretical calculations for (II) and (IV) indicate that the H(O) atoms have positive effective charges, +0.22–0.25 e (see Table 6). The relatively large thermal parameters of the H(O) atoms obtained from the X-ray high-order refinement are the result of the electron deficiency around the H(O) atoms. The neutron study of (II) at 120 K revealed that the H(O) proton has almost the same thermal parameter as those of the benzene-ring protons. The abnormally large thermal parameter of the carboxyl H atom of oxalic acid dihydrate at 15 K obtained from the X-ray high-order refinement, $B = 5.5$ (5) Å², corresponds to the effective charge of +0.35 (2) e, which was derived from multipole refinement (Zobel, Luger, Dreissig & Koritsanszky, 1992). For 4-fluorobenzoic acid, the effective atomic charge of H(O) was estimated at +0.53 (3) e by the κ refinement, although *ab initio* molecular orbital calculation indicates that the effective charge is +0.234 and +0.280 for the monomer and hydrogen-bond dimer, respectively (Kubota & Ohba, 1992). The over-estimation of positive effective charge of H(O) for 4-fluorobenzoic acid suggests that the disorder of the carboxyl group is not negligible in this crystal even at 120 K. In comparison with the O—H bonds in (II) and (IV), the N—H bonds in (III) are less ionic, which can be judged from the thermal parameters of H(N) in Table 2.

Proton transfer

4-Nitrobenzoic acid shows polymorphism. The crystals grown from solution are monoclinic *A2/a* as in the present study, and those obtained by sublimation are the *P2₁/c* modification (Groth, 1980; Imaoka, Takeda & Chihara, 1988). The kinetics of the double proton transfer in the *P2₁/c* crystals were investigated based on the temperature dependence of the IR spectra and the proton spin-lattice relaxation times (Nagaoka, Terao, Imashiro, Saika, Hirota & Hayashi, 1983). The differences in enthalpy ΔH and entropy ΔS between the two possible configurations of the hydrogen-bond dimer were reported as $\Delta H = 0.63 \pm 0.08$ kJ mol⁻¹, and $\Delta S = -13 \pm 4$ J mol⁻¹ deg⁻¹. The *A2/a* modification was also investigated using NMR spectra (Imaoka, Takeda & Chihara, 1988). The ΔH is estimated at *ca* 1 kJ mol⁻¹ from the spin-lattice relaxation times in the temperature range from 20 to 40 K (Takeda, 1993). The population of the minor configuration was determined by the neutron study to be 0.11 (3) at 302 K, suggesting that $\Delta G (= \Delta H - T\Delta S)$ at 302 K is 5.2 ± 1 kJ mol⁻¹. Assuming that $\Delta H = 1$ kJ mol⁻¹, ΔS is calculated to be -14 J mol⁻¹ deg⁻¹, which is accidentally equal to that for the *P2₁/c* modification. From the thermodynamic data, the population of the minor configuration at 120 K is expected to be 0.06. However, the population could not be refined properly based on the neutron diffraction data.

In the course of this study, the authors thought it unusual that the thermal ellipsoids of the carboxyl O atoms look normal for 4-fluorobenzoic acid at 120 K although the positions of the O atoms are expected to be disordered by the proton transfer. Accordingly, hypothetical crystal structure analyses were carried out. Artificial structure factors of (II) were calculated for several disordered levels of the carboxyl group, and the disordered structures were refined by assuming a single position of the O atom at each site. The disorder was conveniently created by rotating the carboxyl group by 180° with respect to the Ph—COOH bond axis. The refined thermal ellipsoids of the O atoms look normal, although the bias of the disorder appears in the elongation of the ellipsoid. The geometry of the COO moiety follows the observed tendency that the smaller the difference between the two C—O bond lengths (with higher disordered level), the smaller the difference between the two C—C—O bond angles (Borthwick, 1980; Fitzgerald & Gerkin, 1992). A similar phenomenon was reported for X-ray analyses of (*E*)-stilbenes. The reasonably small *R* factors, the normal appearance of the thermal ellipsoids, but the unusually short distance of the ethylene bond and strong temperature dependence of the molecular geometry have been

assigned to be artefacts of dynamic disorder in the crystals (Ogawa, Suzuki, Sakurai, Kobayashi, Kira & Toriumi, 1988; Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992).

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Classification of the Isostructurality of Organic Molecules in the Crystalline State*

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Abstract

Since its discovery by Mitscherlich in 1819, the isomorphism of crystals has been interpreted in various, sometimes controversial ways. This can be attributed to the fact that the word isomorphous refers only to the external similarities between crystalline substances. Identical or quasi-identical packing

motifs of related organic substances should therefore be distinguished by a more appropriate terminology. For organic substances, in contrast with inorganic crystals, where the recommended term is isotypic, the term isostructural is unambiguous. The present work attempts to classify the main forms as isostructural and homeostructural. Within the former class, there are two subclasses distinguished by the degree of isostructurality. Special attention is also paid to the isostructurality of molecular associates (e.g. clath-

* Dedicated to Dr Kálmán Sasvári on the occasion of his 80th birthday.