

Electron-Density Distribution in Crystals of 4-Chloroaniline, 4-Chlorobenzoic Acid and 1-Chloro-2,4-dinitrobenzene at 110 K

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Abstract

$T = 110$ (2) K, Mo $K\alpha_1$, $\lambda = 0.70926$ Å. 4-Chloroaniline, C_6H_6ClN , (I), $M_r = 127.6$, orthorhombic, $Pnma$, $a = 8.5940$ (7), $b = 7.2438$ (4), $c = 9.1913$ (6) Å, $V = 572.19$ (7) Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, $\mu = 0.539$ mm⁻¹, $F(000) = 264.6$, $R = 0.026$ for 2784 unique reflections with multipole refinement. 4-Chlorobenzoic acid, $C_7H_5ClO_2$, (II), $M_r = 156.6$, triclinic, $P\bar{1}$, $a = 14.3681$ (6), $b = 6.1324$ (3), $c = 3.7782$ (2) Å, $\alpha = 87.463$ (6), $\beta = 100.498$ (5), $\gamma = 92.943$ (4)°, $V = 326.69$ (3) Å³, $Z = 2$, $D_x = 1.59$ Mg m⁻³, $\mu = 0.504$ mm⁻¹, $F(000) = 160.3$, $R = 0.027$ for 4775 reflections. 1-Chloro-2,4-dinitrobenzene, $C_6H_3ClN_2O_4$, (III), $M_r = 202.6$, orthorhombic, $Pccn$, $a = 8.7346$ (12), $b = 10.9404$ (4), $c = 15.6406$ (5) Å, $V = 1494.6$ (2) Å³, $Z = 8$, $D_x = 1.80$ Mg m⁻³, $\mu = 0.487$ mm⁻¹, $F(000) = 817.5$, $R = 0.034$ for 4087 reflections. By using an oriented-atom model, the positive peak on the C–Cl bond axis could be observed clearly with height nearly the same as those of the single C–C and C–N bonding peaks. For nitro and carboxyl groups, the sp^2 lone-pair peaks of the terminal O atoms disappeared and the N–O and C–O bonding peaks were emphasized when the reference density was changed from the independent-atom model to the oriented-atom model.

Introduction

The polarization of spherical electron density of Cl⁻ caused by metal-complex formation is expected to be larger than that of F⁻ because of the smaller electronegativity of Cl. In fact, charge-distribution studies of KMF_3 , [$M = Co$: Kijima, Tanaka & Marumo (1981); Mn and Ni: Kijima, Tanaka & Marumo (1983); Fe: Miyata, Tanaka & Marumo (1983); Cu: Tanaka & Marumo (1983); a reinvestigation for $M = Mn, Fe, Co$ and Ni: Maslen & Spadaccini (1989)] have shown no excess electron density on the metal–F bond axes. On the other hand, significant density was observed on the metal–Cl bond axis for $K_2[PdCl_4]$ (Takazawa, Ohba & Saito, 1988), although none or only small amounts of excess electron density was reported for several other chlorometal complexes, *cis*-[Fe(bpy)₂Cl₂][FeCl₄]

(Figgis, Reynolds & White, 1985), Cs_2CoCl_4 (Figgis, Reynolds & White, 1987), $(NH_4)_3[ZnCl_4]Cl$ (Ohba, Shiokawa & Saito, 1987), and $K_2[PdCl_6]$ (Takazawa, Ohba & Saito, 1988). The comparison of the charge distribution around the ligands, F⁻ and Cl⁻, is prevented by the relatively high noise level, which is a disadvantage in the charge-density study of the metal complexes. Since one of the extremes of the coordination bond might be a covalent bond, it is instructive to compare the electron-density distribution in the C–Cl bond with that in the C–F bond. For the C–F bond in tetrafluoroterephthalonitrile, only a very small deformation density was observed (Dunitz, Schweizer & Seiler, 1983; Seiler, Schweizer & Dunitz, 1984). This result has attracted considerable attention and was attributed to the unsuitability of the independent-atom model (IAM) for valence-electron-rich atoms for studying the nature of the chemical bond (Spackman & Maslen, 1985; Hall, 1986) and the oriented-atom model (OAM) was introduced (Schwarz, Valtazanos & Ruedenberg, 1985). The alternative promolecule consists of oriented atomic ground states and neutral atoms in hybridization. By using the OAM, the effect of hybridization is removed from the deformation-density maps to elucidate the nature of the chemical binding. In the present study, the C–Cl bond has been investigated based on the OAM, which is constructed with spherical-harmonic functions (Hansen & Coppens, 1978). The C–F bond will be reported in a future paper.

The title chlorobenzene derivatives were selected because they have melting points higher than 323 K and have centrosymmetric structures. Original papers for structure determination are (I) Trotter, Whitlow & Zobel (1966), (II) Miller, Paul & Curtin (1974) and (III) Gopala Krishna (1960). A redetermination of (I) was performed by Ploug-Sørensen & Andersen (1985) and that of (II) by Colapietro & Domenicano (1982) in order to investigate asymmetries of the benzene ring induced by the π -electron-withdrawing or -releasing substituents. It is noted that *p*-dichlorobenzene is not suitable for the present study because of a sluggish phase transition at 279 K (Ghelfenstein & Szwarc, 1971).

Experimental

Preliminary intensity measurements were performed at 297 K to check the suitability of the compounds for electron-density study. Crystals were ground into spheres where possible. The C—C bonding peaks of the benzene ring could be observed with heights (I) 0.24–0.27, (II) 0.27–0.39 and (III) 0.16–0.28 $e \text{ \AA}^{-3}$ after a conventional refinement with R values (I) 0.035, (II) 0.047 and (III) 0.050, respectively. Mean B_{eq} values are (I) 3.4, (II) 3.6 and (III) 3.9 \AA^2 , almost independent of the melting points, (I) 343, (II) 516 and (III) 324 K. Intensities at 110 K were then measured on a Rigaku AFC-5 four-circle diffractometer with a stream of cold nitrogen gas; graphite-monochromatized Mo $K\alpha$ radiation; θ – 2θ scan, scan speed 6° min^{-1} in θ , scan width $(1.3 + 0.5 \tan \theta)^\circ$, detector aperture $1.55 \times 1.55^\circ$ and collimator 1.0 mm \varnothing . Polarization factor was assumed to be $K = \cos 2\theta_{\text{M}}$ (Jennings, 1984). Other experimental conditions and refinement information are as follows.

(I): A sphere of 0.617 (6) mm in diameter; $0 \leq h \leq 12$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$ ($2\theta \leq 60^\circ$); $0 \leq h \leq 18$, $0 \leq k \leq 15$, $-19 \leq l \leq 19$ ($60 < 2\theta \leq 100^\circ$); $0 \leq h \leq 20$, $0 \leq k \leq 17$, $0 \leq l \leq 22$ ($100 < 2\theta \leq 120^\circ$). 5 standard reflections varied within 2%; 9381 reflections measured, 6459 reflections observed with $|F_o| > 3\sigma(|F_o|)$, 2784 unique ($R_{\text{int}} = 0.015$); lattice constants based on 20 2θ values ($60 < 2\theta < 72^\circ$). After absorption correction with $\mu r = 0.17$, conventional refinement was performed with the program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). Function $\sum w(|F_o| - |F_c|)^2$ was minimized with weight $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. The molecules are arranged perpendicularly to the mirror plane and half of it is independent. Positions of all the H atoms were confirmed by difference synthesis with height $0.6 < \Delta\rho < 0.7 e \text{ \AA}^{-3}$. After the high-order refinement with $(\sin\theta)/\lambda > 0.7 \text{ \AA}^{-1}$ (refinement A), the Cl atom was surrounded with high residual density. Thus, only the atomic coordinates of non-H atoms were determined based on the high-order reflections, and their anisotropic thermal parameters were refined based on all the reflections (refinement B). With the introduction of an isotropic secondary-extinction parameter g (Zachariasen, 1967), the R value reduced from 0.036 to 0.035 for 2784 unique reflections. Smallest extinction factor $\gamma(F_o^2/F_c^2)$ was 0.88 for 202, $g = 0.08 (2) \times 10^{-4}$, $wR = 0.043$, $S = 1.7$, reflection/parameter (N/P) was 50.6, and $\Delta/\sigma < 0.1$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Calculation was performed with FACOM M-380R computer of this university. Multipole refinement was also carried out with the program *MOLLY* (Hansen & Coppens, 1978). Multipoles were included up to hexadecapole for Cl, up to octapole for the other non-H atoms, 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 $l = 1, 2, 3$ and 4, respectively) for Cl, $n_l = 2, 2$ and 3 for the other 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). Total charge of the unit cell was constrained to be neutral. The parameters of H atoms and thermal, multipole, radial (κ) and shielding (ζ) parameters of non-H atoms were refined based on all the reflections (refinement C). Final $R = 0.026$, $wR = 0.026$, $S = 1.0$, $y_{\text{min}} = 0.82$, $g = 0.13 (1) \times 10^{-4}$, $\Delta/\sigma = 0.3$, $N/P = 18.4$.*

(II): An as-grown crystal of $0.44 \times 0.25 \times 0.43$ mm; $-30 \leq h \leq 30$, $-13 \leq k \leq 13$, $0 \leq l \leq 8$ ($2\theta \leq 100^\circ$). 5 standard reflections varied within 1%; 7527 reflections measured, 5259 reflections observed; lattice constants based on 50 2θ values ($60 < 2\theta < 70^\circ$). After absorption correction ($0.79 < A < 0.90$) and averaging equivalent reflections ($R_{\text{int}} = 0.011$), 4775 unique reflections were obtained. By introducing an isotropic secondary-extinction parameter in a conventional refinement (refinement B), R was reduced from 0.039 to 0.038 for 4775 unique reflections, $g = 0.17 (1) \times 10^{-4}$, $y_{\text{min}} = 0.59$ for 011. $wR = 0.040$, $S = 1.6$, $N/P = 47.4$, $\Delta/\sigma < 0.1$. Multipole refinement was also carried out, $R = 0.027$, $wR = 0.028$, $S = 1.0$, $y_{\text{min}} = 0.57$, $g = 0.16 (1) \times 10^{-4}$, $\Delta/\sigma < 0.3$, $N/P = 15.6$.*

(III): A sphere 0.577 (6) mm in diameter; $0 \leq h \leq 8$, $-10 \leq k \leq 10$, $-15 \leq l \leq 15$ ($2\theta \leq 40^\circ$); $0 \leq h \leq 15$, $0 \leq k \leq 19$, $-28 \leq l \leq 28$ ($40 < 2\theta \leq 80^\circ$); $0 \leq h \leq 18$, $0 \leq k \leq 23$, $0 \leq l \leq 33$ ($80 < 2\theta \leq 100^\circ$). Variation of 5 standards within 1%, 13 745 reflections measured, 8208 reflections observed, 4087 unique ($R_{\text{int}} = 0.021$); lattice constants based on 18 2θ values ($58 < 2\theta < 68^\circ$). After absorption correction with $\mu r = 0.14$, a conventional refinement (refinement B) was performed. Extinction parameter did not reduce the R value. $R = 0.044$, $wR = 0.048$, $S = 1.7$ for 4087 observed unique reflections, $N/P = 31.4$, $\Delta/\sigma < 0.05$. Multipole refinement was also carried out without extinction parameter, $R = 0.034$, $wR = 0.032$, $S = 1.2$, $\Delta/\sigma < 0.5$ for non-H atoms, $N/P = 11.0$.*

Results and discussion

There are no significant alterations in crystal structures compared to the previous studies, although the present

* Lists of structure factors (refinement C), anisotropic thermal parameters, shifts of the atoms from the best plane through the benzene ring, effective atomic charges, positional and thermal parameters and bond lengths and angles involving H atoms and observed deformation densities based on the oriented-atom model for (I), (II) and (III) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51777 (94 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^5$) and equivalent isotropic temperature factors (Hamilton, 1959)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} ($\text{\AA}^2 \times 10$)
(I)				
Cl	53053 (2)	25000	70635 (2)	13 (1)
C(1)	12070 (9)	25000	39501 (7)	12 (1)
C(2)	18485 (6)	8337 (7)	44485 (6)	12 (1)
C(3)	30948 (6)	8293 (7)	54158 (5)	12 (1)
C(4)	37144 (8)	25000	58898 (7)	10 (1)
N	140 (11)	25000	29338 (12)	18 (1)
(II)				
Cl	42828 (2)	78716 (4)	82727 (8)	17 (1)
C(1)	18449 (4)	33400 (10)	36577 (18)	10 (1)
C(2)	27753 (4)	27422 (11)	37446 (21)	11 (1)
C(3)	35313 (4)	41289 (12)	51854 (22)	13 (1)
C(4)	33436 (4)	61192 (11)	64974 (20)	12 (1)
C(5)	24242 (5)	67442 (11)	64378 (22)	12 (1)
C(6)	16717 (4)	53355 (10)	50147 (21)	12 (1)
C(7)	10464 (4)	18595 (10)	20775 (20)	11 (1)
O(1)	11775 (4)	1874 (10)	5425 (22)	15 (1)
O(2)	2056 (4)	24485 (12)	23984 (27)	18 (1)
(III)				
Cl	26764 (5)	4752 (3)	-6779 (2)	15 (1)
C(1)	35728 (16)	10736 (11)	2063 (7)	10 (1)
C(2)	31762 (15)	7424 (10)	10415 (7)	9 (1)
C(3)	38079 (16)	13228 (11)	17471 (6)	10 (1)
C(4)	48890 (14)	22236 (11)	15981 (7)	10 (1)
C(5)	53570 (17)	25449 (12)	7786 (6)	11 (1)
C(6)	46809 (17)	19738 (12)	824 (7)	11 (1)
N(1)	20324 (15)	-2127 (11)	12112 (7)	11 (1)
N(2)	55038 (16)	29071 (11)	23274 (7)	12 (1)
O(1)	21029 (20)	-11548 (11)	7901 (9)	17 (1)
O(2)	10993 (19)	-60 (12)	17758 (10)	17 (1)
O(3)	48618 (27)	27684 (15)	30169 (7)	20 (1)
O(4)	65855 (18)	35959 (14)	22033 (10)	17 (1)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

(I)			
Cl—C(4)	1.7416 (7)	C(2)—C(1)—N	120.67 (5)
C(1)—C(2)	1.4038 (6)	C(1)—C(2)—C(3)	120.83 (4)
C(1)—N	1.3870 (12)	C(2)—C(3)—C(4)	119.49 (4)
C(2)—C(3)	1.3920 (7)	Cl—C(4)—C(3)	119.61 (4)
C(3)—C(4)	1.3921 (6)	C(2)—C(1)—C(2)	118.59 (6)
		C(3)—C(4)—C(3')	120.76 (6)
(II)			
Cl—C(4)	1.7352 (7)	C(2)—C(1)—C(6)	120.18 (5)
C(1)—C(2)	1.3985 (9)	C(2)—C(1)—C(7)	119.51 (6)
C(1)—C(6)	1.3984 (9)	C(6)—C(1)—C(7)	120.31 (5)
C(1)—C(7)	1.4793 (8)	C(1)—C(2)—C(3)	120.07 (6)
C(2)—C(3)	1.3893 (9)	C(2)—C(3)—C(4)	118.87 (6)
C(3)—C(4)	1.3944 (11)	Cl—C(4)—C(3)	119.23 (5)
C(4)—C(5)	1.3903 (10)	Cl—C(4)—C(5)	118.80 (6)
C(5)—C(6)	1.3920 (9)	C(3)—C(4)—C(5)	121.97 (6)
C(7)—O(1)	1.2392 (10)	C(4)—C(5)—C(6)	118.72 (6)
C(7)—O(2)	1.3064 (9)	C(1)—C(6)—C(5)	120.19 (6)
		C(1)—C(7)—O(1)	121.55 (6)
		C(1)—C(7)—O(2)	115.44 (6)
		O(1)—C(7)—O(2)	123.01 (6)
(III)			
Cl—C(1)	1.7188 (12)	Cl—C(1)—C(2)	122.7 (1)
C(1)—C(2)	1.399 (2)	Cl—C(1)—C(6)	118.3 (1)
C(1)—C(6)	1.394 (2)	C(2)—C(1)—C(6)	119.0 (1)
C(2)—C(3)	1.388 (2)	C(1)—C(2)—C(3)	121.7 (1)
C(3)—C(4)	1.385 (2)	C(1)—C(2)—N(1)	121.4 (1)
C(4)—C(5)	1.391 (2)	C(3)—C(2)—N(1)	116.9 (1)
C(5)—C(6)	1.387 (2)	C(2)—C(3)—C(4)	117.6 (1)
C(2)—N(1)	1.470 (2)	C(3)—C(4)—C(5)	122.4 (1)
C(4)—N(2)	1.466 (2)	C(3)—C(4)—N(2)	118.8 (1)
N(1)—O(1)	1.225 (2)	C(5)—C(4)—N(2)	118.7 (1)
N(1)—O(2)	1.223 (2)	C(4)—C(5)—C(6)	119.0 (1)
N(2)—O(3)	1.225 (2)	C(1)—C(6)—C(5)	120.3 (1)
N(2)—O(4)	1.224 (2)	C(2)—N(1)—O(1)	117.8 (1)
		C(2)—N(1)—O(2)	116.9 (1)
		O(1)—N(1)—O(2)	125.3 (1)
		C(4)—N(2)—O(3)	117.0 (1)
		C(4)—N(2)—O(4)	118.3 (1)
		O(3)—N(2)—O(4)	124.7 (1)

Symmetry code: (i) $x, \frac{1}{2}-y, z$.

study reduced the e.s.d.'s in the atomic parameters to less than half with lower *R* values than the latest structural references in the *Introduction*. Positional parameters of non-H atoms are given in Table 1 derived from high-order refinement. They were fixed in multipole refinement but those of H atoms were allowed to alter. The C—H, N—H and O—H bond lengths were elongated by the multipole refinement. In particular, C—H bond distances changed from 0.90 (1)–0.98 (1) to 0.96 (1)–1.07 (1) \AA , which may be due to the introduction of the bond-directed dipole for H atoms. Bond lengths and bond angles are listed in Table 2. Although both chloro and nitro substituents tend to enlarge the internal *ipso* angle (α) of the benzene ring (Colapietro & Domenicano, 1982), α_{Cl} of (III) is less than 120°. This seems to be an effect of the nitro groups in *ortho* and *para* positions, which may be related to the shorter C—Cl bond length of (III), 1.7188 (12) \AA , than those of (I), 1.7416 (7) \AA , and (II), 1.7352 (7) \AA . It is noted that the C—Cl bond lengths of *p*-dichlorobenzene are 1.746 (4), 1.737 (6) and 1.749 (3) \AA for α , β and γ phases at 100 K (Wheeler & Colson, 1975). The dihedral angles of the substituents to the benzene ring are 6.8 (1)° for the carboxyl group C(7)O(1)O(2) in (II) and 42.6 (1) and 13.1 (1)° for the nitro groups N(1)O(1)O(2) and N(2)O(3)O(4) in (III).

Fig. 1(a) shows the conventional deformation density, $\Delta\rho_{conv} (= \rho_{obs} - \rho_{calc, IAM})$, through the benzene ring of (I) after refinement $A\{[(\sin\theta)/\lambda]_{max} = 1.22 \text{\AA}^{-1}$ for (I) and 1.08 \AA^{-1} for (II) and (III)}. High positive contours appeared around the Cl atom and an elongated peak or double peaks were observed on the C—C bond axis. These features were common in (I), (II) and (III) and seemed to be a result of an underestimate of the thermal parameters by the high-order refinement. When the thermal parameters of non-H atoms were refined with all the observed reflections (refinement *B*), they increased by ca 5, 6 and 8% for (I), (II) and (III), respectively. As shown in Fig 1(b), the positive densities around the Cl atom disappeared, the elongated peak on the C—C bond became spherical, and the double peaks changed into a single peak. Thus sufficient $(\sin\theta)/\lambda$ range is needed to determine the thermal parameters although the thermal parameters should be determined based on only high-order reflections to avoid the bias by the deformation of the valence-electron distribution. One of the solutions of this problem is achieved by the

multipole refinement (refinement C). The observed deformation density could be reproduced by the multipole-expansion method as shown in Fig. 2, which is $\Delta\rho_{\text{MM-IAM}} (= \rho_{\text{calc, multipole}} - \rho_{\text{calc, IAM}})$. The considerable improvement of the model densities was indicated by the decrease in R values by as much as 0.01 over those of the conventional refinement. The observed deformation density on the C–Cl bond axis, (I) 0.12 (7), (II) 0.22 (4) and (III) 0.27 (6) $\text{e} \text{ \AA}^{-3}$, is hardly detected as in the case of the C–F bond (Dunitz, Schweizer & Seiler, 1983; Seiler, Schweizer & Dunitz, 1984; Hirshfeld, 1984). This is because IAM assumed more than two electrons in the halogen–carbon bond. To overcome this type of problem, the oriented-atom model (OAM) was proposed. In the present study, OAM was created with real spherical-harmonic functions (see *Appendix*) so that an atomic orbital in the bond direction is occupied by one electron. The observed and calculated deformation densities with respect to OAM are the same.* Fig. 3 shows the model deformation density, $\Delta\rho_{\text{MM-OAM}} (= \rho_{\text{calc, multipole}} - \rho_{\text{calc, OAM}})$, which is noise free. The peak heights on the C–Cl bond axis in the model maps increased from (I) 0.08 to 0.29, (II) 0.15 to 0.28, (III) 0.16 to 0.53 $\text{e} \text{ \AA}^{-3}$ when the reference density was changed from IAM to OAM. The peak height in (III) is larger than in the others, which may be due to the electron concentration in accord with the shorter C–Cl bond length.

Molecules (II) form dimers by hydrogen bonds between the carboxyl groups, $\text{O}(1) \cdots \text{O}(2) (-x, -y, -z) = 2.6117(9) \text{ \AA}$. In the conventional deformation map, there are peaks of 0.48 (4)–0.51 (4) $\text{e} \text{ \AA}^{-3}$ on the

* See deposition footnote.

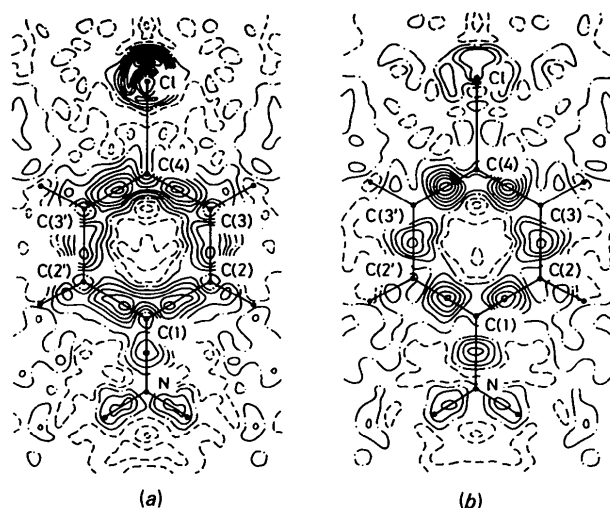


Fig. 1. Conventional deformation densities through the benzene ring of (I) after (a) refinement A and (b) refinement B. Contour intervals at $0.1 \text{ e} \text{ \AA}^{-3}$, negative contours broken, zero contours chain-dotted.

C–O bond axis and oxygen lone-pair peaks of 0.20 (4)–0.45 (4) $\text{e} \text{ \AA}^{-3}$. In the multipole-model deformation density based on OAM [Fig. 3(II)], the positive peak on the C–O bond axis increased and the lone-pair peaks disappeared in comparison with Fig. 2(II). This is because sp^2 hybridization was assumed for O atoms in OAM and four electrons were subtracted in the lone-pair region but only one electron in the C–O bond direction. The concentrated positive density on the C–O bond axis suggests polarization of the electron density (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). In the conventional deformation density map of the nitro groups in (III), the peak of the N–O bond is detected with height 0.21 (6)–0.42 (6) $\text{e} \text{ \AA}^{-3}$. Lone-pair peaks of 0.13 (6)–0.38 (6) $\text{e} \text{ \AA}^{-3}$ are observed around

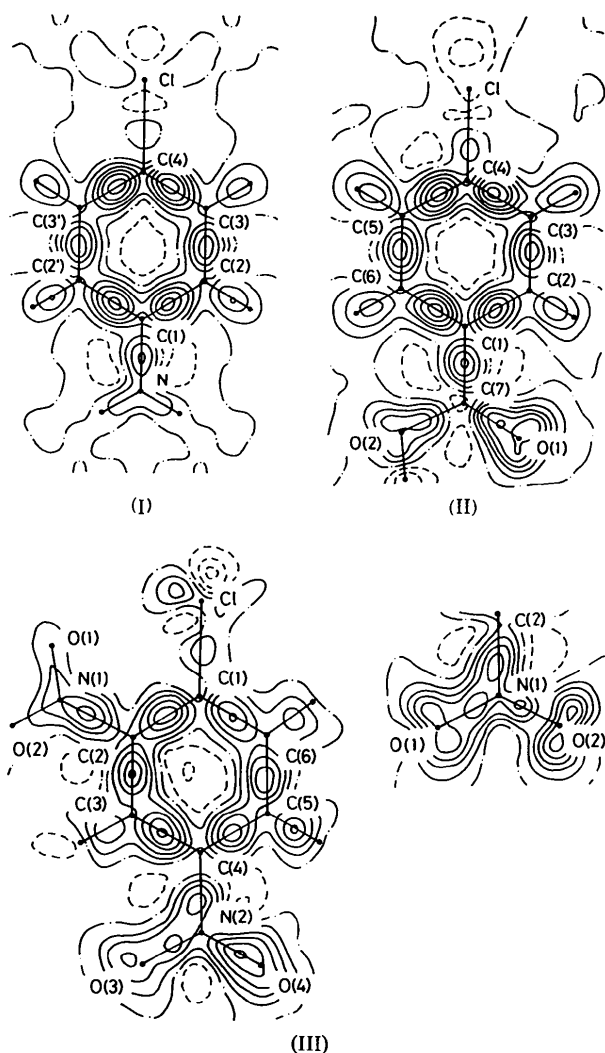


Fig. 2. Multipole-model deformation densities based on the independent-atom model (MM-IAM) through the benzene ring after refinement C. Contour intervals at $0.1 \text{ e} \text{ \AA}^{-3}$. The section through the $\text{N}(1)\text{O}(1)\text{O}(2)$ plane is also shown because the dihedral angle to the benzene ring is $42.6(1)^\circ$.

the terminal O atoms. The multipole-model deformation density based on OAM [Fig. 3(III)] shows the same feature as for the carboxyl group, *i.e.* the lone-pair peaks disappeared and the N—O bonding electron density increased with respect to Fig. 2(III). The effective charge of the N and O atoms ranges from -0.25 (13) to -0.43 (14) and from -0.23 (7) to -0.31 (7) *e*, respectively.

APPENDIX

The oriented atomic densities are calculated as follows.

(i) Cl atom

The angular components of the wave function of Cl for $3s$, $3p_x$, $3p_y$ and $3p_z$ orbitals can be expressed with

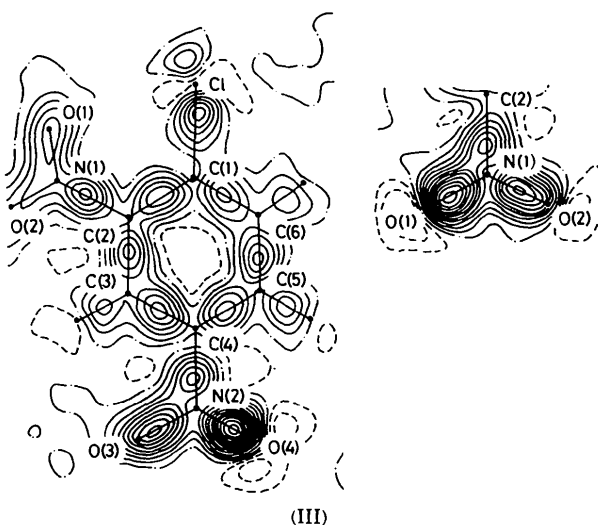
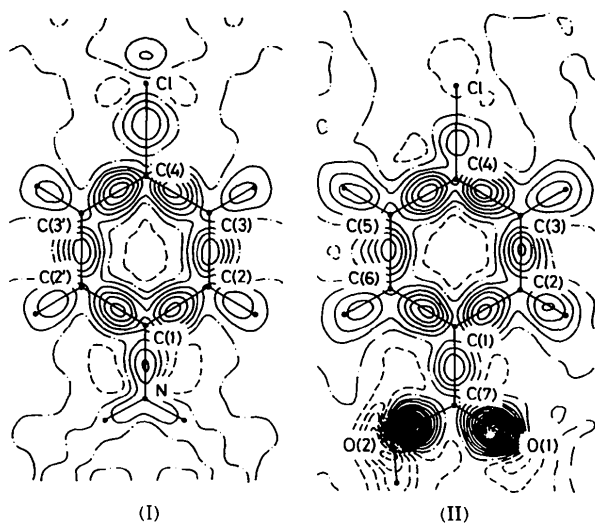


Fig. 3. Multipole-model deformation densities based on the oriented-atom model (MM-OAM) through the benzene ring after refinement C. Contour intervals at $0.1 \text{ e } \text{Å}^{-3}$. The section through the N(1)O(1)O(2) plane is also shown.

real spherical-harmonic functions, y_{00} , y_{11+} , y_{11-} and y_{10} . If P_s , P_x , P_y and P_z are the electron populations of the valence orbitals, we have the valence density

$$\rho_{\text{val}} = [R(\mathbf{r})]^2 [P_s(y_{00})^2 + P_x(y_{11+})^2 + P_y(y_{11-})^2 + P_z(y_{10})^2], \quad (A1)$$

where $R(\mathbf{r})$ is a radial function expressed by $r^n \exp(-\zeta r)$ (Hansen & Coppens, 1978). Since the spherical-harmonic functions form a complete set, their products can be expressed as a linear combination of spherical harmonics (Rae, 1978). Thus, we have

$$\begin{aligned} \rho_{\text{val}} &= [R(\mathbf{r})]^2 [P_{00}y_{00} + P_{20}y_{20} + P_{22+}y_{22+}], \\ P_{00} &= (P_s + P_x + P_y + P_z) (1/4\pi)^{1/2} M_{00}, \\ P_{20} &= (2P_z - P_x - P_y) (1/20\pi)^{1/2} M_{20}, \\ P_{22+} &= (P_x - P_y) (3/20\pi)^{1/2} M_{22+}, \end{aligned} \quad (A2)$$

where the M_{lm} 's are the ratio of normalization factors for wave function and density function (Stevens & Coppens, 1979). For the oriented atomic density of Cl with C—Cl bond along y , $P_y = 1$ and $P_s = P_x = P_z = 2$. Then,

$$P_{00} = 7, P_{20} = (1/27)^{1/2}, P_{22+} = 1/\pi.$$

(ii) C, N and O atoms in sp^2 hybridization

The wave functions are expressed as follows,

$$\begin{aligned} (h_1): & \left(\frac{1}{3}\right)^{1/2} y_{00} + \left(\frac{2}{3}\right)^{1/2} y_{11+}, \\ (h_2): & \left(\frac{1}{3}\right)^{1/2} y_{00} - \left(\frac{2}{3}\right)^{1/2} y_{11+} + \left(\frac{1}{3}\right)^{1/2} y_{11-}, \\ (h_3): & \left(\frac{1}{3}\right)^{1/2} y_{00} - \left(\frac{2}{3}\right)^{1/2} y_{11+} - \left(\frac{1}{3}\right)^{1/2} y_{11-}, \\ (2p_z): & y_{10}, \end{aligned} \quad (A3)$$

where orbital h_1 is parallel to the local x axis and z is the out-of-plane direction (Eyring, Walter & Kimball, 1944). If P_1 , P_2 , P_3 and P_z are the occupancies of the valence orbitals, we obtain the following relations.

$$\begin{aligned} P_{00} &= (P_1 + P_2 + P_3 + P_z) (1/4\pi)^{1/2} M_{00}, \\ P_{11+} &= (2P_1 - P_2 - P_3) (1/18\pi)^{1/2} M_{11+}, \\ P_{11-} &= (P_2 - P_3) (1/6\pi)^{1/2} M_{11-}, \\ P_{20} &= (3P_z - P_1 - P_2 - P_3) (1/45\pi)^{1/2} M_{20}, \\ P_{22+} &= (2P_1 - P_2 - P_3) (1/60\pi)^{1/2} M_{22+}, \\ P_{22-} &= (P_3 - P_2) (1/20\pi)^{1/2} M_{22-}. \end{aligned} \quad (A4)$$

For C atoms, we assume that $P_1 = P_2 = P_3 = P_z = 1$. Thus,

$$P_{00} = 4, P_{lm}(l \neq 0, m \neq 0) = 0,$$

which is identical to the independent-atom density.

For N atoms in nitro groups, h_1 , h_2 and h_3 are σ -bonding orbitals ($P_1 = P_2 = P_3 = 1$) and P_z equals two in order to keep the atomic charge neutral.

Therefore,

$$P_{00} = 5, P_{20} = (4/27)^{1/2},$$

and the other P_{lm} 's are zero.

For O atoms, the bonding axis is taken to be $x(P_1 = 1)$, and the population of the lone-pair orbitals is assumed to be two ($P_2 = P_3 = 2$) and π -bonding-orbital population P_z is one, then

$$P_{00} = 6, P_{11+} = -\left(\frac{1}{6}\right)^{1/2}, P_{20} = -(16/243)^{1/2}, \\ P_{22+} = -2/3\pi, P_{11-} = P_{22-} = 0.$$

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Investigation of the Intermolecular Potential Hypersurface of *N,N*-Dimethyl-*p*-nitroaniline

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Abstract

Atom–atom potentials are used to calculate the lattice energy of *N,N*-dimethyl-*p*-nitroaniline for a selection of space-group symmetries. The aim is to demonstrate the viability of computer models to select crystal forms of interest in nonlinear optical applications.

Introduction

The critical problem of designing new molecules to produce crystals with large second-order susceptibilities

is the indeterminacy of their crystal form. If synthetic effort is to be used efficiently then it is important to include in the initial design as much information as possible on the factors influencing the crystalline form of the proposed molecule.

This study investigates the applicability of a semi-empirical atom–atom potential, as a representation of the intermolecular interaction, to the problem of determining influences on the selected molecular arrangement.

The molecule *N,N*-dimethyl-*p*-nitroaniline (DIM-NAN) (Mak & Trotter, 1965) satisfies the requirements for producing a high first hyperpolarizability, β , and was chosen as representative of a large class of substituted benzene molecules examined by various

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