

## A charge density study of the effect of irradiation on the $\alpha$ -form of *p*-nitrophenol

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**Abstract.** Careful investigation of the structure and charge density of the  $\alpha$  polymorph of *p*-nitrophenol has been carried out following prolonged irradiation by visible light. Though the change in colour from yellow to red is remarkable, the molecular geometry and the intermolecular hydrogen contacts exhibit only minor changes. However, a charge density analysis in comparison with the pristine  $\alpha$  and  $\beta$  polymorphs has brought out significant differences in the charge distribution in the intra- and intermolecular bonding regions. The deformation density map of the  $\alpha$  form reveals many differences in the bonding regions of the molecule before and after irradiation. Charge migration from the nitro and the hydroxyl groups to the phenyl ring of the molecule occurs on irradiation, resembling more the charge distribution in the light stable  $\beta$  form. The molecular dipole moment in the irradiated crystal is significantly lower compared to that before irradiation. Relief maps of the negative Laplacian in the hydrogen bond region also show less polarization of the oxygen lone pairs after irradiation.

**Keywords.** Crystal structure; charge density; *p*-nitrophenyl; polymorphism; photoirradiation.

### 1. Introduction

The experimental charge density method using X-ray diffraction to study chemical bonding in the solid state is becoming increasingly popular amongst chemists in recent years<sup>1,2</sup>. There have been a number of studies on a variety of materials of interest in quantum chemistry and medicine. Cameron and his coworkers<sup>3</sup>, for instance, experimentally examined charge densities in aziridinyl, benzene and phosphazene rings and compared them with the theoretical values. Topological analysis of the charge distribution in maleate salts<sup>4,5</sup> has shown that short hydrogen bonds possess some covalent character. Charge density studies on L-dopa<sup>6</sup>, vitamin C<sup>7</sup> and DL-aspartic acid<sup>8</sup> have been reported recently. Some workers have analysed non-centrosymmetric crystals of importance in nonlinear optics<sup>9,10</sup>. Recently, Coppens and coworkers<sup>11</sup> have carried out charge density studies on long-lived metastable excited states in nitrosyl complexes using synchrotron radiation.

We have been interested in investigating charge densities of organic crystals in relation to chemical reactivity and polymorphic forms. Recently, we reported a detailed investigation on the  $\beta$  and  $\alpha$  polymorphs of *p*-nitrophenol using the charge density

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method<sup>12</sup>. The study showed that there exists significant differences in the intra- and intermolecular charge densities of the two forms particularly in the hydrogen bond region. The  $\alpha$  form, which is thermodynamically stable, was found to have more favourable intermolecular hydrogen bonding.

The  $\alpha$  form is known to undergo a topochemically controlled photochemical transformation<sup>13</sup>, manifesting itself in an irreversible colour change of the crystal from yellow to red. The origin of the colour change is however not clear and could be due to a side reaction. The  $\beta$  modification is light stable at room temperature. Thus *p*-nitrophenol provides an interesting example of polymorphism, where one polymorph is thermodynamically unstable and the other photochemically so. Based on ENDOR experiments Atherton *et al*<sup>14</sup> have suggested the possible presence of hydroxycyclopentadienyl-like radicals in the red  $\alpha$  crystals. However, the study is not conclusive. We have carried out charge density analysis of the irradiated crystal to examine the effect of photoirradiation on the crystal structure as well as the topography of the charge distribution of *p*-nitrophenol in the  $\alpha$  form, using low temperature X-ray diffraction measurements. We have not studied the transformation or followed the time dependence of the extent of transformation because of the difficulty in ascertaining the nature of the reaction. We have carried out our study only to see if there are discernible changes in the single crystal due to irradiation. Our charge density analysis has revealed significant changes in the intra- and intermolecular regions following irradiation, although the crystal and molecular structures show small variations.

## 2. Experimental

Pale yellow crystals of the  $\alpha$  form were grown from benzene solution and exposed to indirect sunlight for two weeks, during which time their colour slowly changed to deep red. A high quality crystal was chosen after detailed examination under an optical microscope. X-ray diffraction intensities were measured by  $\omega$  scans using Siemens three-circle diffractometer attached to a CCD area detector and a graphite monochromator for the MoK $\alpha$  radiation (50 kV, 40 mA). The crystal was cooled on the diffractometer using a stream of cold nitrogen gas from a vertical nozzle and held at 110 K throughout the data collection.

Initially, the unit cell parameters and the orientation matrix of the crystal were determined using  $\sim 60$  reflections from 25 frames collected over a small  $\omega$  scan of 7.5°. A hemisphere of reciprocal space was then collected in two shells using SMART software<sup>15</sup> with  $2\theta$  settings of the detector at 32° and 70°. The data reduction was performed using the SAINT program<sup>15</sup> and the orientation matrix along with the detector and the cell parameters were refined for every 40 frames on all the measured reflections. The crystal structure was determined using the SHELXTL program<sup>16</sup>. The cell parameters and other structural features showed only minor changes, compared to those before irradiation. Some of the important changes following irradiation are listed in table 1 along with the corresponding features in the  $\beta$  structure.

Charge density analysis was carried out based on multipole expansion of the electron density centred at the nucleus of the atom<sup>17</sup>. Accordingly, the aspherical atomic density can be described in terms of spherical harmonics,

$$\rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + \rho_{\text{valence}}(r) + \rho_{\text{def}}(r).$$

**Table 1.** Important structural differences between the different forms of *p*-nitrophenol.

		Irradiated $\alpha$	$\alpha$	$\beta$
<i>Unit cell parameters</i>	a	6.1414(1)	6.1664(1)	3.6812(3)
	b	8.8032(2)	8.8366(2)	11.1152(9)
	c	11.5013(2)	11.5435(2)	14.6449(12)
	$\beta$	103.338(1)	103.390(1)	92.802(2)
	<i>Space group</i>	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
	$\rho$ (g/cm <sup>3</sup> )	1.527	1.510	1.544
<i>Bond lengths (Å)</i>				
	N–O(2)	1.229(2)	1.237(1)	1.235(1)
	N–O(3)	1.247(2)	1.251(1)	1.238(1)
	$\angle$ C–C–O inequality (°)	5.57	5.48	6.24
	$\angle$ C–C–N inequality (°)	0.96	1.2	0.31
<i>Deviation from the plane of benzene ring (Å)</i>				
	O(1)	0.0296	0.03	0.046
	H(1)	0.293	0.319	0.030
	N	0.049	0.045	0.001
	O(2)	0.044	0.043	0.221
	O(3)	0.087	0.088	0.079
<i>Shortest intermolecular hydrogen contact O(1)–H(1)···O(3)</i>				
	O(1)···O(3)	2.825(1)	2.832(1)	2.832(1)
	H(1)···O(3)	1.881(1)	1.890(1)	1.909(1)
	$\angle$ O–H···O	167.1(1)	166.39(5)	160.55(6)

Thus for each atom,

$$\rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=0} \kappa'^3 R_l(\kappa' \zeta r) \sum_{m=0} \sum_{p=\pm 1} P_{lmp} Y_{lmp}(\theta, \varphi),$$

with the origin at the atomic nucleus. The population coefficients,  $P_{lmp}$ , are to be refined along with the  $\kappa$  and  $\kappa'$  parameters which control the radial dependence of the valence shell density. The analysis was carried out in several steps<sup>12</sup>.

A high order refinement of the data was first performed using reflections with  $\sin\theta/\lambda \geq 0.6 \text{ \AA}^{-1}$  and  $F_0 \geq 10\sigma$ . Multipolar refinement for the charge density analysis ( $R = 0.37$ ,  $wR = 0.043$ ,  $S = 0.9$ ,  $N_{\text{ref}}/N_v = 18$ ) was carried out using the XDLSM routine of the XD package<sup>18</sup>. The XDPROP routine was used to calculate the total electron density  $\rho(r)$ , the deformation density  $\Delta\rho$  and the Laplacian  $\nabla^2\rho$  at the bond critical points (CPs). These results are listed in table 2 for comparison with the pristine  $\alpha$  and the  $\beta$  forms. Pseudoatomic charges and the dipole moments obtained using XDPROP are listed in table 3. Intermolecular hydrogen contacts as determined by the PARST<sup>19</sup> program were also analysed using the XDPROP routine and the results are given in table 4.

### 3. Results and discussion

#### 3.1 Structural aspects

In figure 1 we show the molecular packing diagrams of the  $\alpha$  form before and after irradiation. The adjacent nonparallel molecules subtend an angle of  $74.58^\circ$  compared to

**Table 2.** Analysis of the bond critical points for the irradiated  $\alpha$  (top row),  $\alpha$  (middle row) and  $\beta$  (bottom row) forms.

Bond	$\rho$	$\nabla^2\rho$	$\varepsilon$	$\Delta\%$	$d$
C(1)–C(2)	2.11(3)	-18.1(1)	0.28	8.8C(2)	0.021
	2.08(5)	-18.1(1)	0.27	1.5C(2)	0.011
	2.21(5)	-22.4(2)	0.26	5.6C(2)	0.014
C(2)–C(3)	2.19(3)	-19.8(1)	0.21	2.1C(3)	0.015
	2.09(5)	-18.0(1)	0.22	1.3C(3)	0.005
	2.20(5)	-21.7(1)	0.24	4.0C(2)	0.009
C(3)–C(4)	2.05(3)	-17.5(1)	0.22	2.5C(4)	0.013
	2.01(5)	-17.8(1)	0.21	5.3C(3)	0.012
	2.24(5)	-23.0(2)	0.18	12.7C(3)	0.016
C(4)–C(5)	2.14(3)	-18.9(1)	0.26	2.1C(4)	0.018
	2.20(5)	-19.4(1)	0.22	1.1C(5)	0.014
	2.34(6)	-23.4(2)	0.19	5.1C(5)	0.019
C(5)–C(6)	2.10(3)	-20.8(1)	0.22	12.8C(6)	0.018
	2.10(5)	-18.0(1)	0.18	3.9C(5)	0.007
	2.35(6)	-24.2(2)	0.17	0.3C(5)	0.018
C(6)–C(1)	2.17(3)	-21.6(1)	0.27	4.1C(1)	0.009
	2.04(5)	-18.4(1)	0.24	6.4C(6)	0.008
	2.27(6)	-22.3(2)	0.22	6.4C(6)	0.013
C(2)–H(2)	1.87(5)	-17.1(1)	0.04	23.1H(2)	0.021
	1.89(4)	-21.0(1)	0.07	20.0H(2)	0.017
	1.89(5)	-16.6(2)	0.04	23.9H(2)	0.015
C(3)–H(3)	1.88(6)	-18.5(2)	0.09	30.3H(3)	0.006
	1.97(4)	-20.2(1)	0.10	24.6H(3)	0.007
	2.01(4)	-19.0(2)	0.12	20.9H(3)	0.015
C(5)–H(5)	1.93(5)	-20.1(1)	0.09	18.1H(5)	0.002
	1.97(4)	-20.3(1)	0.06	18.5H(5)	0.007
	1.96(4)	-19.9(2)	0.09	18.5H(5)	0.014
C(6)–H(6)	1.85(5)	-17.1(1)	0.09	24.0H(6)	0.007
	1.82(3)	-17.7(1)	0.13	20.0H(6)	0.017
	1.96(4)	-19.6(2)	0.14	19.3H(6)	0.015
O(1)–C(1)	2.12(5)	-17.5(2)	0.13	17.4C(1)	0.027
	2.09(6)	-21.1(3)	0.05	22.9C(1)	0.027
	2.32(6)	-20.0(3)	0.04	35.4C(1)	0.022
O(1)–H(1)	2.40(10)	-42.4(7)	0.04	55.9H(1)	0.020
	2.91(6)	-45.2(6)	0.09	46.5H(1)	0.041
	2.68(11)	-36.4(4)	0.14	47.7H(1)	0.026
N–C(4)	1.80(3)	-12.3(1)	0.22	19.1C(4)	0.006
	1.78(5)	-14.0(2)	0.29	25.5C(4)	0.016
	1.91(5)	-12.5(2)	0.20	17.2C(4)	0.018
O(2)–N	3.15(6)	-2.3(2)	0.16	4.5N	0.004
	3.49(8)	-8.7(3)	0.14	2.1N	0.009
	3.14(14)	2.5(4)	0.08	1.8N	0.025
O(3)–N	3.18(6)	3.3(2)	0.12	1.2O(3)	0.006
	3.39(8)	5.0(3)	0.20	0.6O(3)	0.006
	3.03(8)	10.6(5)	0.25	0.6N	0.031

$\rho$  ( $\text{e}\text{\AA}^{-3}$ ) is the electron density,  $\nabla^2\rho$  ( $\text{e}\text{\AA}^{-5}$ ) is the Laplacian,  $\varepsilon$  is the ellipticity,  $\Delta$  is the bond polarity in %,  $d$ ( $\text{\AA}$ ) is the perpendicular distance between the critical point and the internuclear vector

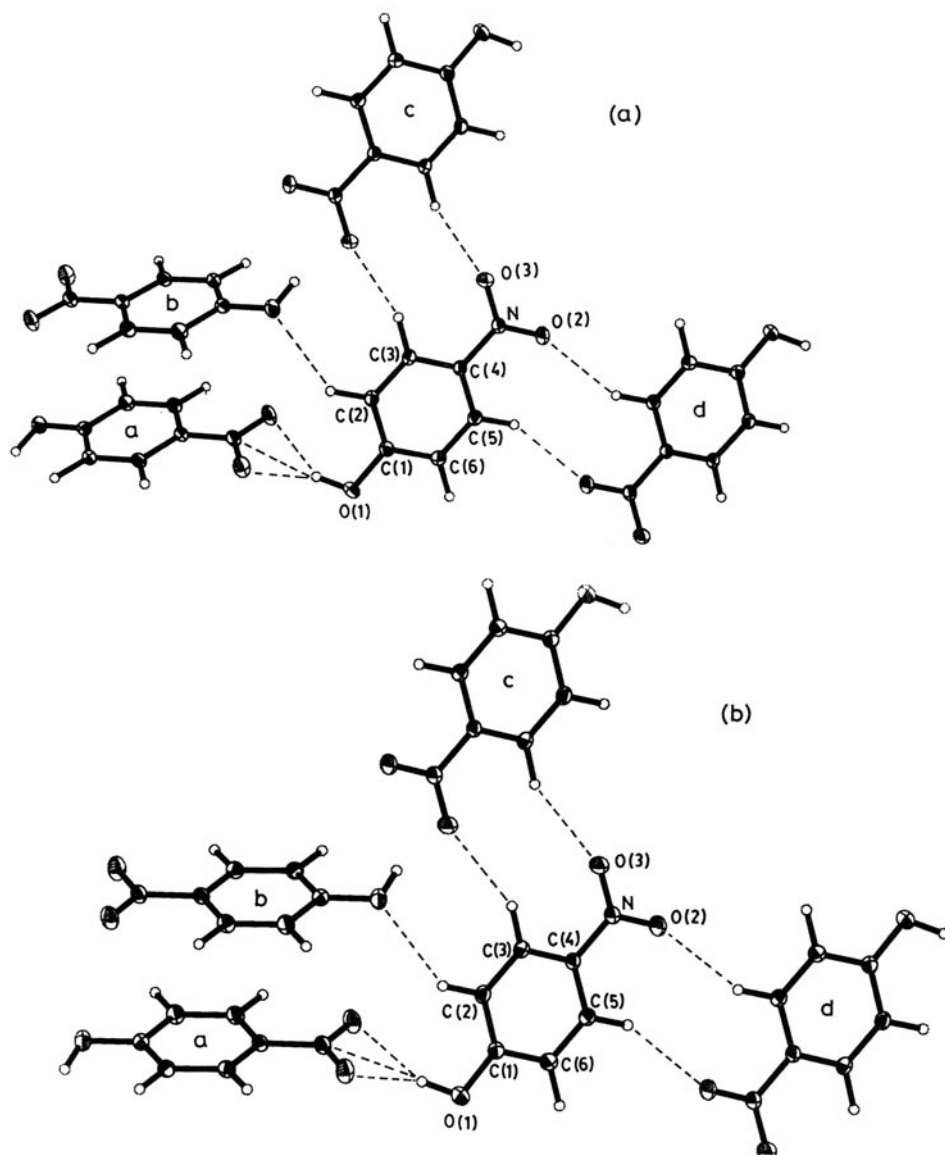
**Table 3.** Pseudoatomic charges and dipole moments.

Atom	Irradiated $\alpha$	$\alpha$	$\beta$
O(1)	-0.08(7)	-0.29(10)	-0.09(9)
O(2)	-0.10(8)	-0.36(10)	-0.14(9)
O(3)	-0.04(9)	-0.30(10)	-0.22(9)
N	-0.25(20)	-0.60(22)	-0.47(21)
C(1)	-0.06(8)	0.29(13)	0.00(13)
C(2)	-0.08(7)	0.32(12)	-0.01(12)
C(3)	-0.15(7)	0.30(13)	-0.08(13)
C(4)	0.00(7)	0.21(11)	-0.49(13)
C(5)	-0.13(7)	0.20(13)	-0.06(12)
C(6)	0.04(7)	0.30(12)	-0.10(12)
H(1)	0.33(6)	0.03(11)	0.46(6)
H(2)	0.11(5)	0.03(11)	0.32(7)
H(3)	0.20(5)	-0.02(11)	0.30(7)
H(5)	0.11(5)	-0.06(11)	0.30(7)
H(6)	0.12(5)	0.02(10)	0.27(8)
Dipole moment (debye)	9.9	18.0	21.5

**Table 4.** Intermolecular hydrogen bond critical points.

Bond	Bond length	$\angle$ donor-H...acceptor	$\rho$	$\nabla^2\rho$
<i>Irradiated <math>\alpha</math></i>				
O(2)...H(1 <sup>a</sup> )	2.466(2)	131.75(1)	0.03(1)	0.946(1)
O(3)...H(1 <sup>a</sup> )	1.881(1)	167.10(1)	0.11(4)	3.07(3)
N...H(1 <sup>a</sup> )	2.466(1)	157.48(9)	0.03(1)	0.948(1)
O(1)...H(2 <sup>b</sup> )	2.498(1)	132.2(1)	0.039(9)	0.804(2)
O(3)...H(3 <sup>c</sup> )	2.603(1)	130.60(8)	0.030(4)	0.499(2)
O(2)...H(5 <sup>d</sup> )	2.392(1)	145.96(8)	0.018(7)	0.600(3)
$\alpha$				
O(2)...H(1 <sup>a</sup> )	2.461(1)	133.24(5)	0.016(3)	0.897(8)
O(3)...H(1 <sup>a</sup> )	1.890(1)	166.39(5)	0.19(3)	2.43(4)
N...H(1 <sup>a</sup> )	2.467(1)	159.46(5)	0.016(13)	0.897(8)
O(1)...H(2 <sup>b</sup> )	2.509(1)	132.14(4)	0.029(9)	0.814(6)
O(3)...H(3 <sup>c</sup> )	2.617(1)	130.74(4)	0.035(5)	0.562(2)
O(2)...H(5 <sup>d</sup> )	2.406(1)	145.71(4)	0.040(10)	0.890(9)
Symmetry codes: (a) $x+1, -y+1/2, z+1/2$ ; (b) $-x, y-1/2, -z-1/2$ ; (c) $-x+1, -y+1, -z$ ; (d) $-x+2, -y, -z$				
$\beta$				
O(2)...H(2 <sup>a</sup> )	2.382(1)	143.34(6)	0.076(14)	1.147(10)
O(3)...H(1 <sup>a</sup> )	1.909(1)	160.55(6)	0.11(3)	4.66(5)
O(1)...H(3 <sup>b</sup> )	2.345(1)	157.26(6)	0.039(13)	0.66(1)
O(2)...H(5 <sup>c</sup> )	2.400(1)	139.89(5)	0.007(8)	0.257(4)
Symmetry codes: (a) $x-1/2, -y+1/2+1, z+1/2$ ; (b) $-x+1/2, y-1/2, z+1/2+1$ ; (c) $-x-1, -y+1, -z+2$				

74.73° in the pristine  $\alpha$  form. The value of this angle in the  $\beta$  form is 29.26°<sup>20,21</sup>. The intermolecular hydrogen contacts also appear unaffected following irradiation. There are



**Figure 1.** Molecular packing diagrams of (a) pristine and (b) irradiated crystals of the  $\alpha$  form.

nine contacts as in the pristine  $\alpha$  form (see figure 1) with the O(3)···H(1) contact at  $\sim 1.88$  Å being the shortest ( $\angle O(3)\cdots H(1)-O(1) \approx 167^\circ$ ). It is interesting that the N and O(2) atoms of the same nitro group make weak contacts with H(1) at  $\sim 2.47$  Å. As though to favour such an interaction, the H(1) atom is displaced from the phenyl plane by 0.29 Å. This value is 0.03 Å less than that found before irradiation. Other atoms N, O(2), O(3) and O(1) exhibit small displacements of 0.05, 0.05, 0.09 and 0.03 Å respectively, regardless of irradiation. In the  $\beta$  form however, the H(1) atom remains in the plane of the

phenyl ring and it is the O(2) atom which shows the maximum displacement (0.22 Å). We find six hydrogen contacts in this structure with O(3)··H(1) as the main contact similar to that in the  $\alpha$  structure except that the bond angle in this case is  $\approx 160^\circ$ .

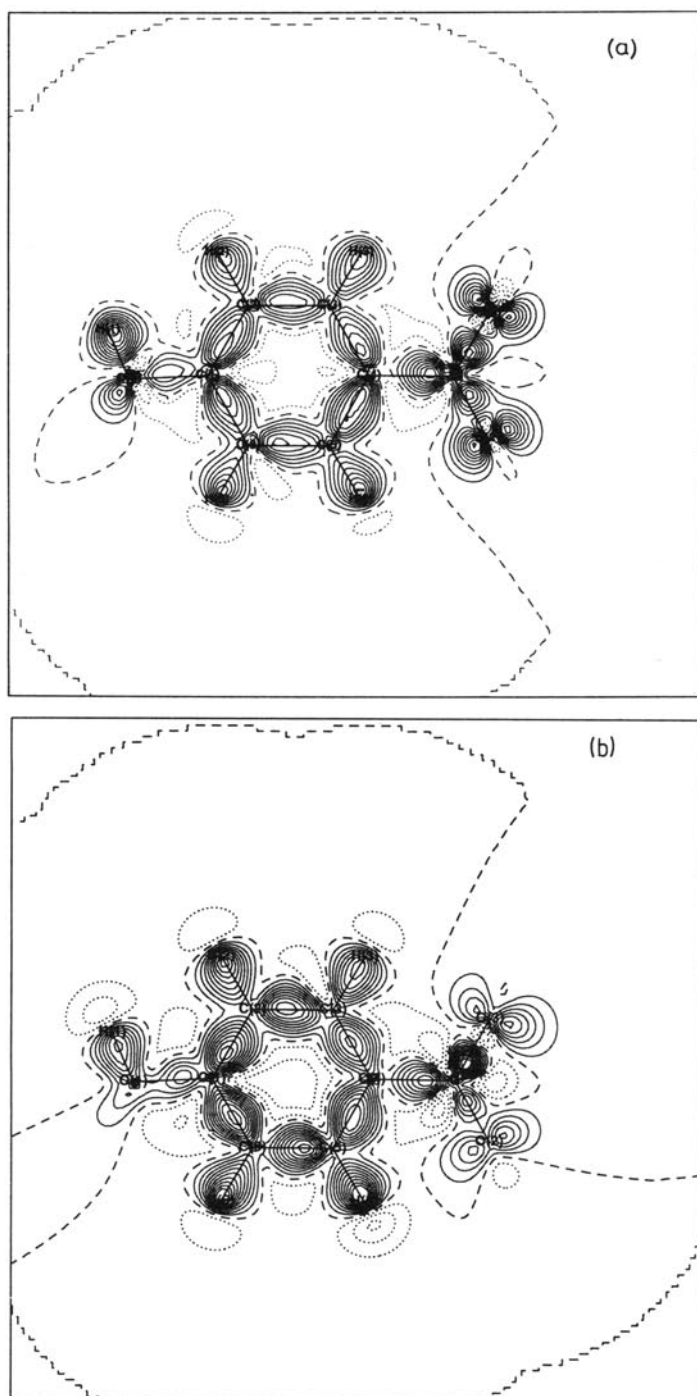
### 3.2 Charge density analysis

We shall first compare the intermolecular bonding in the pristine  $\alpha$  and irradiated crystals. The static deformation density,  $\Delta\rho$ , was obtained as the difference between the total density and the spherical density without the thermal smearing, and the maps before and after irradiation of the  $\alpha$  form are shown in figure 2 in the plane of the benzene ring. The deformation density due to bonding builds up as concentric contours in the regions of the C–C bonds of the benzene ring, the C–N bond, and the N–O bonds of the nitro group, as well as in the C–O and the O–H bonds of the hydroxyl group. The lone pairs of the oxygen atoms are also clearly seen in figure 2. The residual density map obtained as the difference between the calculated and the experimental densities was featureless, the magnitude of the random peaks being less than  $0.12 \text{ e}\text{\AA}^{-3}$ .

The intramolecular CPs are found to be (3, -1) type, characteristic of a covalently bonded molecular system<sup>22</sup>. The  $\rho_{\text{CP}}$  of the six C–C bonds in the benzene ring vary in a rather narrow range, 2.05–2.19  $\text{e}\text{\AA}^{-3}$  (see table 2) the mean value being  $2.13 \text{ e}\text{\AA}^{-3}$ . Following Cremer and Kraka<sup>23</sup>, this corresponds to a mean bond order of 1.77, akin to those in aromatic rings. This value may be compared with that obtained before irradiation (1.70) and also that of the  $\beta$  form (2.02)<sup>12</sup>. The ellipticity,  $\epsilon$ , is slightly higher in the irradiated crystal (0.24) as compared to the pristine  $\alpha$  polymorph ( $\sim 0.21$ ), but much lower than the theoretical value of 0.33. The homonuclear bonds are a little polarized, some up to 12% due to the perturbation caused by the two functional groups. The mean density in the C–H bond regions of the benzene ring is very similar to those obtained with the two polymorphs ( $\sim 1.9 \text{ e}\text{\AA}^{-3}$ ) and is close to the theoretical density of  $1.85 \text{ e}\text{\AA}^{-3}$ . The polarity of the C–H bonds,  $\Delta$ , is expected to be 26.6% towards hydrogen. We obtained a mean  $\Delta$  value of 23.9%; a value of  $\sim 21\%$  had been obtained for the pristine  $\alpha$  and  $\beta$  forms.

The C(1)–O(1) bond connecting the hydroxyl group to the benzene ring is associated with  $\rho_{\text{CP}}$  values of  $2.12 \text{ e}\text{\AA}^{-3}$  corresponding to a bond order of 1.25. The pristine  $\alpha$  and  $\beta$  forms exhibit C–O bond orders of 1.23 and 1.43 respectively. The bond is polarized towards C(1) with  $\Delta = 17.4\%$  in the irradiated crystal while the polarization is much higher in both, the pristine  $\alpha$  (22.9%) and the  $\beta$  forms (35.4%). The O(1)–H(1) bond region also exhibits noticeable differences (table 2). The  $\rho_{\text{CP}}$  value in the  $\alpha$  form upon irradiation decreases remarkably from 2.91 to  $2.40 \text{ e}\text{\AA}^{-3}$ . The  $\beta$  form exhibits a moderate density of  $2.68 \text{ e}\text{\AA}^{-3}$ . We notice that in all the cases, the CPs in the C(1)–O(1)–H(1) region deviate significantly ( $d \approx 0.03 \text{ \AA}$ ) from the intermolecular vectors due to the bending of the orbitals, which is also reflected in the inequality of the C–C–O bond angles, a feature common to many other phenolic compounds<sup>24</sup>.

The C(4)–N bond linking the nitro group to the benzene ring in the  $\alpha$  form remains essentially unchanged on irradiation (bond order  $\approx 0.94$ ) though bonding within the nitro group varies significantly. The irradiated crystal exhibits moderate densities of 3.15 and  $3.18 \text{ e}\text{\AA}^{-3}$  in the N–O(2) and N–O(3) bond regions respectively as compared to the pristine  $\alpha$  form ( $3.49$  and  $3.39 \text{ e}\text{\AA}^{-3}$  respectively) and the  $\beta$  form ( $3.14$  and  $3.03 \text{ e}\text{\AA}^{-3}$  respectively). We notice from table 2 that some of the Laplacians in the nitro group are small positive numbers in contrast to the negative values observed in general for covalently bonded systems. This may be due to the higher ionicity of the nitro bonds.

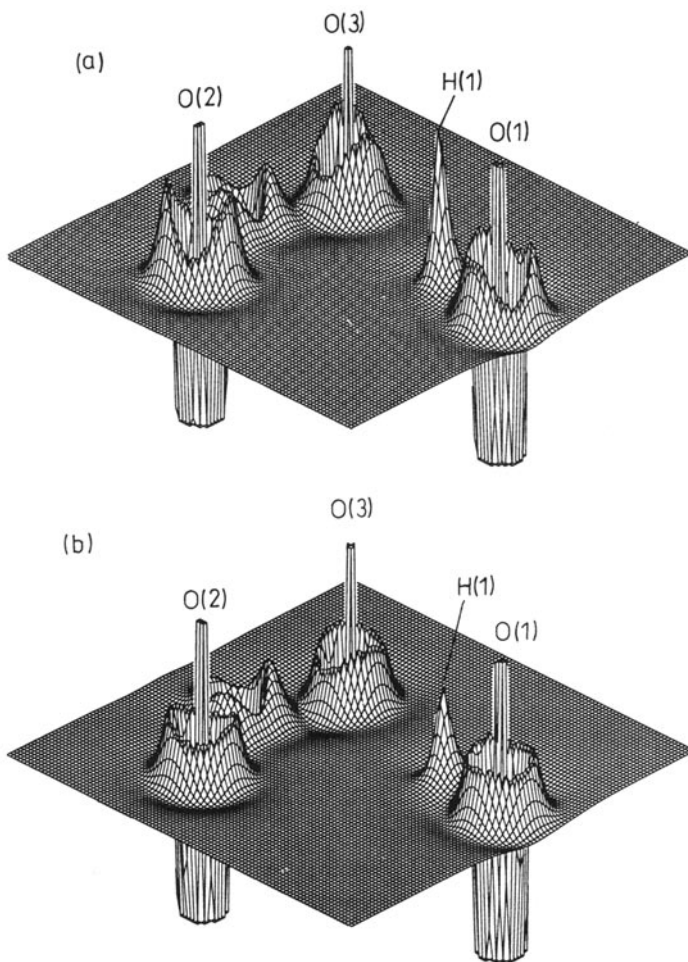


**Figure 2.** Static deformation density in the plane of the benzene ring for (a) pristine and (b) irradiated  $\alpha$  crystals. Contour intervals at  $0.075 \text{ e}\text{\AA}^{-3}$ .



In table 3 we list the pseudoatom charges in the different forms. The group charges of  $\text{NO}_2$  and  $\text{OH}$  of the irradiated crystal are  $-0.39$  and  $0.25$  respectively. These values are quite different from those before irradiation ( $-1.26$  and  $-0.26$  respectively) as well as from those of the  $\beta$  form<sup>12</sup> ( $-0.83$  and  $0.37$  respectively). The charge distribution appears to be less polarized after irradiation. As a result, the molecular dipole moment is relatively low in the irradiated crystal ( $9.9$  debye, see table 3) though somewhat larger than in the free molecule. The experimental value of dipole moment of the free molecule<sup>25</sup>, as well as that calculated by us<sup>26</sup> are around  $5.5$  debye. This enhancement of the dipole moment clearly arises from the charge densities in the condensed state<sup>10</sup>.

The lone pairs on the oxygen atoms of the nitro group occur as  $(3, -3)$  critical points in the deformation density<sup>6</sup> and show significant differences in the three cases. The mean total density at lone-pair CPs is  $\sim 6.97 \text{ e}\text{\AA}^{-3}$  in the irradiated crystal compared to  $\sim 7.6 \text{ e}\text{\AA}^{-3}$  and  $\sim 5.5 \text{ e}\text{\AA}^{-3}$  in the pristine  $\alpha$  and  $\beta$  forms respectively<sup>2</sup>. We also find that the lone-pair lobes move slightly closer to the nucleus by  $\approx 0.02 \text{ \AA}$ <sup>8</sup> after irradiation.



**Figure 3.** Relief map of the negative Laplacian in the plane of the hydrogen bond for (a) pristine and (b) irradiated  $\alpha$  crystals. Range,  $-250$  to  $250 \text{ e}\text{\AA}^{-5}$ .

We have carried out critical point analysis along the hydrogen contacts and found the presence of small densities associated with small, positive Laplacians. These observations imply a closed-shell interaction typical of intermolecular hydrogen bonding<sup>23</sup>. The structural features of the intermolecular hydrogen bonding remained almost unchanged after irradiation. The  $\alpha$  form exhibits a density of  $0.19 \text{ e}\text{\AA}^{-3}$  with the shortest contact (O(3)···H(1)). Following irradiation, the density decreases to  $0.11 \text{ e}\text{\AA}^{-3}$  much like that obtained for the same contact in the  $\beta$  form. There are some differences in weaker contacts as well (see table 4). An interesting feature in the  $\alpha$  structure is that a common critical point is present with a density of  $\sim 0.016 \text{ e}\text{\AA}^{-3}$  for the N···H(1) and O(2)···H(1) contacts, providing evidence for the participation of the entire nitro group in hydrogen bonding with H(1). The density at the common critical point increases marginally after irradiation. These intermolecular hydrogen bond interactions may be best represented using relief maps of the negative Laplacian<sup>2</sup>. We show such maps in figure 3, for the  $\alpha$  form before and after irradiation, in the plane of the oxygen atoms of the nitro and the hydroxyl groups involved in the intermolecular bonding. We see from the figure that the oxygen lone-pair lobes are polarized in the direction of the hydrogen atom. We find that the relief map resembles that of the pristine  $\alpha$  form in that the hydroxyl group appears to have rotated and moved closer to the nitro group compared to the situation in the  $\beta$  form<sup>12</sup>. However, the lone-pair polarization as well as the magnitude of the hydrogen peak is much less, similar to the  $\beta$  form.

The main conclusions from the present study are as follows.

- (1) The structure of the parent  $\alpha$  form of *p*-nitrophenol shows only marginal changes on turning red. Small differences are observed in the intermolecular hydrogen contacts.
- (2) On the contrary, the deformation density map of the irradiated crystal modification of the  $\alpha$  form more closely resembles that of the  $\beta$  form than that of the pristine  $\alpha$  form. The densities at the bond CPs in the nitro group region are much like the values obtained with the  $\beta$  form. The density on the hydroxyl bond is far less than that observed before irradiation.
- (3) The density at the oxygen lone-pairs decreases following irradiation and the contours resemble those in the  $\beta$  form.
- (4) The relief map of the negative Laplacian shown in figure 3, however, resembles that of the pristine  $\alpha$  form mainly because of the structural similarities. The hydrogen atom is slightly out of plane as in the  $\beta$  structure. It appears that the  $\alpha$  form essentially retains its geometrical structure even after prolonged irradiation, but undergoes subtle changes in the topography of the molecular charge density somewhat resembling that found in the light stable  $\beta$  form.
- (5) The charge appears to migrate outwardly from the benzene ring to the nitro and the hydroxyl groups when the crystal structure changes from  $\beta$  to  $\alpha$ . On irradiation, the charge migrates inward and the distribution becomes more across the whole molecule. The dipole moment is also much smaller (9.9 debye).

Study of *p*-nitrophenol using charge-density indicates that the molecule in the heat stable  $\alpha$  structure tends to be less polar on photoirradiation with the charge distribution resembling more that of the light stable  $\beta$  structure.

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