

Crystallographic Studies and Physicochemical Properties of π -Electron Compounds. XVII.* The Structure of *p*-Nitrophenylacetic Acid

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Abstract. $C_8H_7NO_4$, $M_r = 181.15$, orthorhombic, *Pbca*, $a = 15.096$ (1), $b = 7.1500$ (5), $c = 15.923$ (2) Å, $V = 1718.7$ (1) Å³, $Z = 8$, $D_m = 1.41$, $D_x = 1.40$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 9.94$ cm⁻¹, $F(000) = 752$, room temperature, final $R = 0.065$ for 882 unique intensities. The molecules form centrosymmetric hydrogen-bonded cyclic dimers with $O \cdots O = 2.613$ (6) Å. No disorder is observed. The displacement between the planes of COOH groups, d , is 0.093 (6) Å. To explain the influence of the lattice forces on this displacement, STO-3G model calculations for dimers of formic acid with different d values have been performed. A variation in d of up to 0.2 Å does not significantly change the energy of the dimer (about 2 kJ mol⁻¹). Hence a variety of d values for the crystal structures of carboxylic acid dimers may result from packing forces.

Introduction. Lower aliphatic acids, such as formic (Holtzberg, Post & Fankuchen, 1953) and acetic acid (Jönsson, 1971), do not form dimers in the crystalline state, but consists of linear chains joined together by hydrogen bonds. However, in the gaseous state, electron diffraction studies (Almenningen, Bastiansen & Motzfeldt, 1969; Derissen, 1971) reveal that both these acids form dimers. Moreover, if the methyl H atoms of acetic acid are substituted by F or Cl, the modified acid forms dimers in crystals (Nahringbauer, Lundgren & Andersen, 1979; Kanters, Roelofsen & Feenstra, 1976). The crystal chemistry of carboxylic acids has been reviewed extensively (Leiserowitz, 1976).

The structures of the more-complex *p*-substituted phenylacetic and phenoxyacetic acids are known, for example: 4-chlorophenoxyacetic acid (Kennard,

Smith & White, 1981), 4-(benzyloxy)phenylacetic acid (Bats & Canenbley, 1984a), 4-(phenoxyethyl)phenylacetic acid (Bats & Canenbley, 1984b). Disorder is observed in the carboxyl group in the first compound. The structure of 4-(benzyloxy)phenylacetic acid has two independent molecules in the asymmetric unit, one of which is disordered. In all cases the molecules form centrosymmetric dimers *via* hydrogen bonding by the carboxyl groups.

A relationship has been given between the geometrical parameters of the carboxyl group (Borthwick, 1980). The effect on the disorder of the displacement between the planes of the carboxyl groups has also been studied (Grabowski & Krygowski, 1984, 1989).

Experimental. Pale prismatic crystals of *p*-nitrophenylacetic acid (*p*-NPAA) were grown from an ethanol solution. Orthorhombic symmetry was determined from oscillation and Weissenberg photographs. A crystal (0.30 × 0.25 × 0.25 mm) was mounted on a Syntex P2₁ single-crystal diffractometer. D_m was measured at 293 K by flotation in a chloroform–bromoform mixture. Systematic absences: $0kl$, k odd, $h0l$, l odd, $hk0$, h odd, indicate space group *Pbca*. The cell constants were determined by least-squares treatment of 15 reflections with 2θ values between 17.7 and 29°. The intensities were collected at room temperature using graphite-monochromatized Cu $K\alpha$ radiation; $2\theta \leq 110^\circ$, $h 0 \rightarrow 16$, $k 0 \rightarrow 7$, $l 0 \rightarrow 17$. No significant variation was observed for two standard reflections. 1113 unique intensities were collected of which 882 were classified as observed [$I > 1.962\sigma(I)$, $\sigma(I)$ from counting statistics]. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved by routine application of *SHELX76* (Sheldrick, 1976). The H

* Part XVI: Maurin & Krygowski (1987).

Table 1. Final positional parameters (fractional $\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for heavy atoms with estimated standard deviations in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C1	2974 (3)	1419 (6)	7801 (3)	661 (26)
C2	2465 (3)	1252 (6)	8515 (2)	638 (25)
C3	1545 (2)	1310 (6)	8471 (2)	604 (24)
C4	1150 (3)	1566 (7)	7700 (3)	748 (29)
C5	1647 (3)	1768 (7)	6982 (3)	750 (30)
C6	2555 (3)	1699 (6)	7055 (2)	647 (25)
C7	1004 (3)	1081 (6)	9258 (3)	751 (30)
C8	594 (2)	2845 (6)	9575 (2)	614 (25)
N	3093 (3)	1912 (6)	6289 (3)	932 (31)
O1	2731 (3)	2314 (7)	5643 (2)	1521 (38)
O2	3881 (3)	1655 (7)	6337 (2)	1275 (34)
O3	228 (2)	2692 (4)	10305 (2)	724 (19)
O4	588 (2)	4310 (4)	9164 (2)	797 (20)

Table 2. Valence angles ($^\circ$) for *p*-nitrophenylacetic acid

O3—C8—O4	123.0 (4)	O3—C8—C7	114.2 (4)
O4—C8—C7	122.7 (4)	C8—C7—C3	114.5 (4)
C7—C3—C4	121.4 (4)	C7—C3—C2	119.8 (4)
C4—C3—C2	118.7 (4)	C3—C2—C1	120.8 (4)
C2—C1—C6	118.3 (4)	C1—C6—C5	122.8 (4)
C6—C5—C4	118.0 (4)	C5—C4—C3	121.2 (4)
C1—C6—N	118.8 (4)	C5—C6—N	118.4 (4)
C6—N—O2	118.4 (5)	C6—N—O1	118.9 (5)
O1—N—O2	122.6 (4)		

atoms were located from a $\Delta\rho$ map. Final refinement on *F*, including isotropic thermal parameters of the H atoms, was carried out by full-matrix least-squares analysis and led to $R = 0.0648$, $wR = 0.0771$, $S = 1.250$ $\{w = 1.0/[\sigma^2 F_o + 10^{-4}(F_o)^2]\}$; scattering factors for the non-H atoms were taken from Doyle & Turner (1968), and for H atoms from Stewart, Davidson & Simpson (1965), $\Delta/\sigma \leq 0.005$, average value 0.001. The heights of the peaks in the final difference Fourier map varied from -0.36 to 0.32 e \AA^{-3} .

Discussion. Atomic coordinates are listed in Table 1.* A projection of the molecule with the bond lengths is presented in Fig. 1, and the valence angles are given in Table 2.

As the interactions between the substituents are weak, the phenyl ring in the *p*-NPAA molecule exhibits no significant distortion from the expected geometry. The COO planes in dimers are not exactly coplanar, with the displacement between them $d = 0.093 \text{ \AA}$. According to Jeffrey & Sax (1963) the displacement in dimers of carboxylic acids in the

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52272 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

crystalline state is a result of crystal packing forces. To check this hypothesis, the energies of formic acid dimers were calculated for increasing values of *d*. The geometry parameters have been refined in the energy optimization for each fixed value of *d*. For this work, *ab initio* SCF MO calculations with the STO-3G basis set (Hefre, Stewart & Pople, 1969) as incorporated in the GAUSSIAN80 program (Binkley, Whiteside, Krishnan, Seeger, DeFrees, Schlegel, Topiol, Kahn & Pople, 1980) have been employed. Fig. 2 shows the dependence of $\Delta E = E(d) - E(\text{opt})$ on *d*; it is seen that for low values of *d* (up to 0.2 \AA) the energy loss (ΔE) is very small, about 2 kJ mol^{-1} . ΔE values plotted against *d* were taken as the difference between $E(d)$ and $E(\text{opt})$, i.e. for an optimal geometry of the dimer. Thus, in the subtraction, most of the systematic errors caused by too low

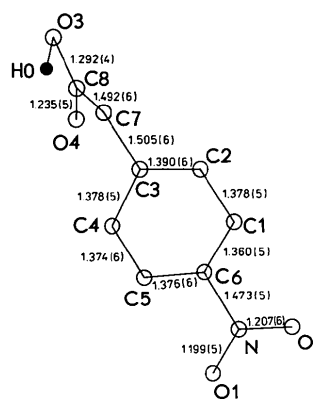


Fig. 1. Projection of the molecule along the *b* axis: atomic numbering and bond lengths (\AA) with estimated standard deviations are given.

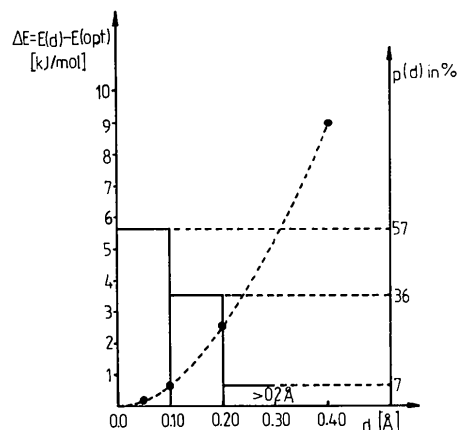


Fig. 2. Dependence of ΔE vs *d*: $\Delta E = E(d) - E(\text{opt})$, where $E(d)$ denotes the energy of the optimized geometry of the dimer of formic acid for the fixed value of *d* and $E(\text{opt})$ is the energy of the dimer of formic acid for optimized geometry (included *d*); $d = 0$ is chosen as optimal value.

a basic set in the calculations are expected to be reduced.

Taking into account the value of *d* for 16 crystal structures of carboxylic acids analyzed elsewhere (Grabowski & Krygowski, 1984, 1989) it is clear that an increase in *d* associated with an increase in $\Delta E(d)$ results in a decrease in the probability, $p(d)$, of finding dimers that could realize such a situation. Fig. 2 illustrates this clearly; for *d* values between 0 and 0.1 Å, $p(d) = 0.57$; for *d* values between 0.1 and 0.2 Å, $p(d) = 0.36$; and for *d* > 0.2 Å, $p(d) = 0.07$. This supports the hypothesis of Jeffrey & Sax (1963), since the greater the energy loss of the dimer, the lower is the probability of finding it.

There is no disorder for the carboxyl group of *p*-NPAA. According to Dieterich, Paul & Curtin (1974) the disorder exists if there is an equalization of the C=O and C—O(H) bond lengths and of the appropriate valence angles of the carboxyl group. Fig. 1 and Table 2 show that the difference between the bond lengths of the carboxyl groups is 0.057 Å and the difference between the angles O4—C8—C7 and O3—C8—C7 is 8.5°, *i.e.* that the geometry of the COOH group is not affected by disorder.

The angle between the best plane of the benzene ring and the plane of the NO₂ group is 7.25°; the angle between the plane of the COOH group and the plane of the benzene ring is 69.90°. The latter value is not caused by the lattice forces but rather by hybridization of C3, C7 and C8 atoms of the molecule (Fig. 1). The torsional angles O3—C8—C7—C3, O4—C8—C7—C3, C2—C3—C7—C8 and C4—C3—C7—C8 are 171.5, 10.2, 105.9 and -74.6°, respectively.

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Structure of 4,4'-Dimethylbenzophenone

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Abstract. C₁₅H₁₄O, *M_r* = 210.28, orthorhombic, *P*2₁2₁2₁, *a* = 7.957 (1), *b* = 12.169 (2), *c* = 12.268 (2) Å, *V* = 1187.89 (3) Å³, *Z* = 4, *D_x* =

1.176 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.68 cm⁻¹, *T* = 293 K, *F*(000) = 448, *R* = 0.049 for 1184 independent reflections with *I* > 1.5σ(*I*). The

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