

2766 measured reflections
 2684 independent reflections
 1680 reflections with
 $I > \sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

Refinement on F
 $R = 0.044$
 $wR = 0.048$
 $S = 1.64$
 1680 reflections
 167 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = \sigma_F^{-2}$
 $(\Delta/\sigma)_{\text{max}} = < 0.01$

6 standard reflections
 every 150 reflections
 intensity variation: $\pm 3.0\%$
 (average maximum
 relative intensity)

$\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 $5.8(8) \times 10^{-7}$
 Scattering factors from
 Stewart, Davidson &
 Simpson (1965) and
 Cromer & Waber (1974)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C15	1.322 (2)	C9—C15	1.491 (2)
O2—C15	1.219 (2)		
C10—C9—C15	117.3 (2)	C9—C15—O2	125.3 (2)
C14—C9—C15	122.8 (1)	C15—O1—H	109 (1)
C9—C15—O1	113.8 (1)	O1—C15—O2	120.9 (1)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H...O2 ⁱ	1.02 (2)	1.66 (3)	2.675 (2)	173 (2)

Symmetry code: (i) $1 - x, -y, 1 - z$.

Scan widths were $(1.40 + 0.35 \tan \theta)^\circ$ in ω , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group $C2/c$ (No. 15); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the H-atom positions. In later stages of refinement, ring H atoms H1—H3, H6—H8 and H10 were made canonical with a C—H distance of 0.98 \AA and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the associated C atom. Atoms H4, H5 and H were refined isotropically. The maximum effect of extinction was 10.0% of F_o for 114. The maximum positive residual peak was located near the midpoint of the C13—C14 bond; the maximum negative peak was located near the center of the central ring.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Support provided to LJJ by PPG Industries is gratefully acknowledged. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1046). Services for accessing these data are described at the back of the journal.

References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Burtner, R. R. & Cusic, J. W. (1943). *J. Am. Chem. Soc.* **65**, 262–267.
 Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72–98. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 Fitzgerald, L. J. & Gerkin, R. E. (1997a). *Acta Cryst.* **C53**, 71–73.
 Fitzgerald, L. J. & Gerkin, R. E. (1997b). *Acta Cryst.* **C53**, 1080–1082.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kay, M. I., Okaya, Y. & Cox, D. E. (1971). *Acta Cryst.* **B27**, 26–33.
 Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1991). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
 Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1997). **C53**, 1267–1270

Benzophenone-3,3',4,4'-tetracarboxylic Acid Dihydrate†

LAWRENCE J. FITZGERALD AND ROGER E. GERKIN

Department of Chemistry, The Ohio State University,
 Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.
 ohio-state.edu

(Received 10 February 1997; accepted 22 April 1997)

Abstract

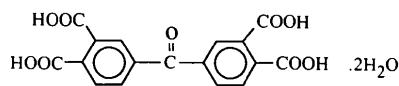
The title compound, $C_{17}H_{10}O_9 \cdot 2H_2O$, crystallizes in the centrosymmetric space group $P2_1/a$ but does not exhibit strong eight-membered cyclic dimer hydrogen bonds about centers of symmetry or otherwise. A richly three-dimensional hydrogen-bonding network is observed, however, which arises from 19 hydrogen bonds per asymmetric unit; it includes a 14-membered cyclic dimer about a center of symmetry and hydrogen-bonding rings of 18 and 30 members involving the acid molecule and a water molecule, both also about centers of symmetry. The carboxyl H and O atoms are ordered in each of the carboxyl groups. The configuration of the benzophenone core is quite similar to that in benzophenone itself and the configuration of the adjacent

† Alternative name: 4-(3,4-dicarboxybenzoyl)phthalic acid dihydrate.

carboxyl groups is quite similar to that in phthalic acid and naphthalene-2,3-dicarboxylic acid.

Comment

This is one of a series of reports on hydrogen bonding in aromatic polycarboxylic acids. The title compound, (I), crystallizes in the centrosymmetric space group $P2_1/a$ but, as discussed below, does not form strong eight-membered cyclic dimer hydrogen bonds about centers of symmetry or otherwise.



(I)

A view of the hydrated molecule is shown in Fig. 1. As listed in Table 2, there are 19 hydrogen bonds in this structure, which appear to fall naturally into two groups: a group of six bonds having $O_d \cdots O_a$ distances ranging from ~ 2.57 to 2.80 Å with $O-H \cdots O$ angles ranging from ~ 163 to 179° ; and a group of 13 bonds having $O_d \cdots O_a$ distances ranging from ~ 2.92 to 3.30 Å with $O-H \cdots O$ angles ranging from ~ 89 to 155° . The hydrogen bonding can then be characterized as follows. Three of the carboxylic H atoms interact with water O-atom acceptors and the fourth carboxylic H atom interacts with a carboxylic O atom, O8, acting as acceptor to form four of the bonds in the first group described above; the remaining two bonds of the first group involve water atom O10 as donor with carboxylic atoms O4 and O6 as acceptors. Thus, water atom O11 is the only donor atom not participating in one of the first group of hydrogen bonds, but it does participate in six of those in the second group. Furthermore, carboxylic atom O2 is the only acceptor atom not involved in one of the first group of bonds, but it participates in four of the second group. A point of particular interest, noted above, is that eight-membered cyclic dimer hydrogen bonding is not a prominent feature in this structure. The only occurrence involves the carboxyl group at C9 and the cyclic dimer formed (about the center at $\frac{1}{2}, 0, 0$) is weak, with the $O_d \cdots O_a$ distance $3.300(2)$ Å and with the hydrogen bonds almost perpendicular to the planes of the carboxyl groups. As is made clear by the data in Table 2, the hydrogen bonding overall is richly three-dimensional with molecules of all symmetry types being linked, for example, through hydrogen bonds to and from the water molecules. The results of hydrogen-bond graph-set analysis (Bernstein, Davis, Shimoni & Chang, 1995) for the subset of eight hydrogen bonds giving the single 'best' interaction for each of the eight donors [entries 1, 4, 5, 8, 9, 11, 14 and 17 in Table 2, hereafter referred to as (a), (b), ..., (h), respectively] for the first- and second-level graph sets are presented in Table 3. The first-level pattern $R_2^2(14)$ arises from

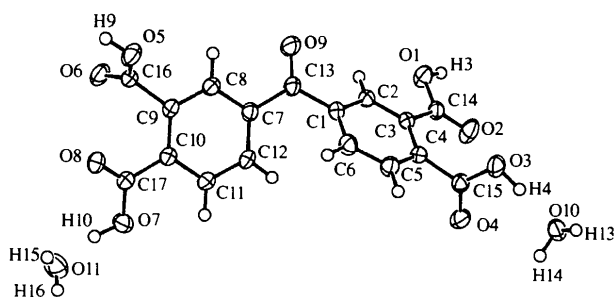


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all non-H atoms; H atoms have been drawn artificially small.

a 14-membered (acid molecule) cyclic dimer about a center of symmetry. The second-level patterns $R_4^4(18)$ and $R_4^4(30)$ arise from hydrogen-bonding rings of 18 and 30 members involving the acid molecule and a water molecule, both also about centers of symmetry.

In each of the four carboxyl groups, the H atom is ordered as are the O atoms, as shown by the relevant data in Table 2.

The benzenoid rings in (I) are very nearly planar: for the first (C1–C6), the maximum deviation of an atom from the best-fit plane describing them is $0.016(2)$ Å and the average deviation is $0.011(2)$ Å; for the second (C7–C12), the respective values are $0.015(2)$ and $0.010(2)$ Å. For comparison, we have chosen benzophenone itself (Fleischer, Sung & Hawkinson, 1968), for which the corresponding average deviations are 0.008 and 0.005 Å (our calculation). In (I), the dihedral angle between these two best-fit planes is $49.46(7)^\circ$, while in benzophenone it is 56° as given by Fleischer, Sung & Hawkinson (1968). Thus, the presence and interactions of the carboxyl groups and water molecules do not cause a major change in the configuration of the molecular core. Moreover, in each case, atoms C1, C7, C13 and O9 (present numbering) lie very nearly in a plane, the maximum deviations of an atom from the best-fit plane describing them being $0.009(2)$ Å for (I) and 0.002 Å (our calculation) for benzophenone.

In (I), the dihedral angles between the carboxyl-group planes and the best-fit planes of the benzenoid rings are $6.5(1)$ and $84.80(8)^\circ$ for the C1–C6 ring and $68.33(7)$ and $21.9(1)^\circ$ for the C7–C12 ring. The corresponding single (due to symmetry) value for phthalic acid is $34.5(16)^\circ$ (Ermer, 1981; our calculation) or 34.3° (Küppers, 1981). In (I), the planes of adjacent carboxyl groups form dihedral angles of $84.6(2)$ and $69.0(2)^\circ$ with each other, respectively. The corresponding values for phthalic acid are $55.6(1)^\circ$ (Ermer, 1981; our calculation) or $54.8(2)^\circ$ (Küppers, 1981; our calculation). Thus, in both substances, there is a substantial angle between planes of adjacent carboxyl groups. We have previously described the same observation for naphthalene-2,3-dicarboxylic acid (Fitzgerald & Gerkin, 1992).

All intramolecular distances and angles in (I) fall within normal ranges. In particular, the potentially crowded atoms H6 and H12 are found 2.38 (3) Å apart, the Bondi (1964) van der Waals radius sum being 2.40 Å. The closest intermolecular approach, excluding pairs of atoms within directly hydrogen-bonded groups, is between C15 and H13^x [symmetry code: (x) $\frac{1}{2} + x, -\frac{1}{2} - y, z$] and falls short of the Bondi radius sum by 0.10 Å. No other approach is significantly less than the corresponding Bondi sum. In particular, the closest intermolecular approaches to the carbonyl O atom, O9, are by H12ⁱⁱ and H6ⁱⁱ [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$] but are more than 0.1 Å greater than the Bondi sum.

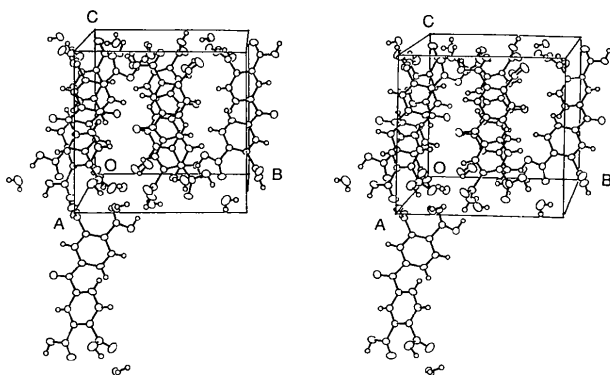


Fig. 2. ORTEP (Johnson, 1976) packing diagram of the title compound. Displacement ellipsoids are drawn at the 50% probability level for all non-H atoms; H atoms have been drawn artificially small.

Experimental

Benzophenone-3,3',4,4'-dianhydride (Aldrich Chemical Company) was suspended in water and reacted with excess NaOH. The reaction mixture was treated with Norit-A decolorizing carbon, filtered and acidified with a slight excess of dilute HCl. Evaporation of the resulting solution produced numerous clear plates, one of which was cut to provide the experimental sample.

Crystal data

C₁₇H₁₀O₉ · 2H₂O

M_r = 394.29

Monoclinic

*P*2₁/*a*

a = 11.497 (2) Å

b = 12.507 (2) Å

c = 11.789 (2) Å

β = 101.64 (2)°

V = 1660.2 (5) Å³

Z = 4

D_x = 1.577 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 14.7–15.0°

μ = 0.127 mm⁻¹

T = 296 K

Cut plate

0.54 × 0.46 × 0.12 mm

Colorless

Data collection

Rigaku AFC-5S diffractometer

2θ-ω scans

Absorption correction: none

4182 measured reflections

3993 independent reflections

3331 reflections with

I > 0.1σ(*I*)

R_{int} = 0.014

θ_{max} = 27.5°

h = 0 → 14

k = 0 → 16

l = -15 → 15

6 standard reflections

every 150 reflections

intensity variation: ±1.8%

(average maximum relative intensity)

Refinement

Refinement on *F*

R = 0.054

wR = 0.049

S = 1.49

3331 reflections

310 parameters

All H atoms refined

w = 1/σ_{*F*}²

(Δ/σ)_{max} < 0.01

Δρ_{max} = 0.29 e Å⁻³

Δρ_{min} = -0.22 e Å⁻³

Extinction correction:

Zachariasen (1963, 1968)

Extinction coefficient:

7.0(12) × 10⁻⁷

Scattering factors from

Stewart, Davidson & Simpson (1965) (H), and Cromer & Waber (1974) (C, O)

Table 1. Selected geometric parameters (Å, °)

O1—C14	1.320 (2)	O5—C16	1.312 (2)
O2—C14	1.201 (2)	O6—C16	1.201 (2)
O3—C15	1.311 (2)	O7—C17	1.314 (2)
O4—C15	1.211 (2)	O8—C17	1.209 (2)
O9—C13—C1	120.0 (2)	O4—C15—C4	122.0 (2)
O9—C13—C7	120.4 (2)	O5—C16—C9	112.2 (2)
C1—C13—C7	119.6 (2)	O6—C16—O5	125.1 (2)
O1—C14—O2	123.5 (2)	O6—C16—C9	122.6 (2)
O1—C14—C3	113.7 (1)	O7—C17—C10	114.3 (2)
O2—C14—C3	122.7 (2)	O8—C17—O7	123.5 (2)
O3—C15—O4	123.2 (2)	O8—C17—C10	122.1 (2)
O3—C15—C4	114.6 (2)		

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
O1—H3...O10 ⁱ	0.92 (3)	1.78 (3)	2.705 (2)	179 (2)
O1—H3...O8 ⁱⁱ	0.92 (3)	2.98 (3)	3.270 (2)	100 (2)
O1—H3...O11 ⁱⁱⁱ	0.92 (3)	3.00 (3)	3.126 (2)	89 (2)
O3—H4...O10	0.96 (3)	1.73 (3)	2.686 (2)	172 (3)
O5—H9...O8 ^{iv}	0.88 (3)	1.85 (3)	2.727 (2)	178 (3)
O5—H9...O4 ^v	0.88 (3)	2.88 (3)	2.992 (2)	89 (2)
O5—H9...O6 ^{vi}	0.88 (3)	2.94 (3)	3.300 (2)	106 (2)
O7—H10...O11	0.99 (3)	1.59 (3)	2.571 (2)	171 (3)
O10—H13...O4 ^{vii}	0.87 (3)	1.90 (3)	2.766 (2)	170 (2)
O10—H13...O5 ^{viii}	0.87 (3)	2.96 (3)	3.268 (2)	103 (2)
O10—H14...O6 ^{ix}	0.91 (3)	1.92 (3)	2.797 (2)	163 (3)
O10—H14...O8 ^x	0.91 (3)	2.83 (3)	3.220 (2)	108 (2)
O10—H14...O4	0.91 (3)	2.99 (3)	3.243 (2)	98 (2)
O11—H15...O2 ^{xi}	0.79 (6)	2.41 (7)	2.921 (2)	123 (6)
O11—H15...O4 ^{xii}	0.79 (6)	2.45 (6)	3.189 (3)	155 (6)
O11—H15...O2 ^{xiii}	0.79 (6)	2.85 (6)	3.146 (3)	105 (5)
O11—H16...O2 ^{xiv}	0.74 (5)	2.51 (5)	2.921 (2)	118 (5)
O11—H16...O3 ^{xv}	0.74 (5)	2.51 (5)	3.181 (3)	152 (5)
O11—H16...O2 ^{xvi}	0.74 (5)	2.91 (5)	3.146 (2)	102 (5)

Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $1 - x, -y, -z$; (v) $x - \frac{1}{2}, -\frac{1}{2} - y, z$; (vi) $-x, -y, 1 - z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (viii) $x - \frac{1}{2}, -\frac{1}{2} - y, 1 + z$; (ix) $\frac{1}{2} + x, -\frac{1}{2} - y, z - 1$.

Table 3. First- and second-level graph-set descriptors involving hydrogen bonds designated (a)–(h) as described in the text

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
(a)	D	R ₂ ² (18)			C ₄ ¹ (18)	C ₄ ¹ (28)		
(b)		D			C ₄ ¹ (12)	C ₄ ¹ (30)		
(c)			R ₂ ² (14)					
(d)				D			C ₄ ¹ (30)	C ₄ ¹ (30)
(e)					D	R ₄ ¹ (30)		
(f)						D		
(g)							D	R ₂ ² (4)
(h)								D

Scan widths were $(1.20 + 0.35 \tan \theta)^\circ$ in ω , with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry indicated space group $P2_1/a$ (No. 14) and since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. Refined C—H distances range from 0.92 (2) to 0.99 (2) Å, with a mean value of 0.96 Å; refined O—H distances are given in Table 2. The refined water molecule angles are 106 (2) and 91 (4)°. The maximum effect of extinction was 7.2% of F_o for 202. The maximum positive residual peak was located near the midpoint of the C1—C13 bond; the maximum negative peak was located ~ 1.2 Å from C16 and ~ 1.6 Å from C9.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Support provided to LJJ by PPG Industries is gratefully acknowledged. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1049). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Ermer, O. (1981). *Helv. Chim. Acta*, **64**, 1902–1909.
- Fitzgerald, L. J. & Gerkin, R. E. (1992). *Acta Cryst.* **C48**, 1971–1975.
- Fleischer, E. B., Sung, N. & Hawkinson, S. (1968). *J. Phys. Chem.* **72**, 4311–4312.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Küppers, H. (1981). *Cryst. Struct. Commun.* **10**, 989–991.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1997). **C53**, 1270–1273

1:1 Molecular Complex of 2-Amino-5-nitropyridine and 3-Nitro-2-pyridone

VELICHKA VELIKOVA, KRASIMIR KOSSEV AND OLYANA ANGELOVA

Bulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography, Rakovski str. 92, 1000 Sofia, Bulgaria. E-mail: jmacicek@bgcict.acad.bg

(Received 25 February 1997; accepted 16 April 1997)

Abstract

The 2-amino-5-nitropyridine molecule of the title complex, C₅H₅N₃O₂·C₅H₄N₂O₃, is planar, while the nitro group in 3-nitro-2-pyridone is tilted away from the mean plane by 27.9 (3)°. The C—C bond distance between the substituted atoms in the pyridone ring, 1.439 (3) Å, is slightly lengthened due to the electron-withdrawing effect of the adjacent carbonyl and nitro groups. The molecules are linked into centrosymmetric tetramers which are stacked in layers along the *c* axis. The layers are held together by weak C—H···O hydrogen bonds and van der Waals interactions.

Comment

2-Amino-5-nitropyridine derivatives (Lehn, 1987; Nicoud & Twieg, 1987), its adducts (Masse, 1995; Hu, Shi, Huang, Li & Yang, 1994) and salts (Watanabe, Noritake, Hirose, Okada & Kurauchi, 1993; Pecaut & Masse, 1993) have been intensively examined in relation to their application as non-linear optical materials. We attempted to use a one-stage procedure for 2-aminopyridine nitration with a mixture of concentrated sulfuric and nitric acids (Lewis & Winfield, 1955), which usually gives a mixture of 3-nitro- and 5-nitro-2-aminopyridines in a ratio of 1:5 to 1:8 (Shoefield, 1967; Smith, 1985). The attempts to separate the two isomers by repeated fractionation from ethanol were unsuccessful because of the presence of an unknown phase. The structure analysis showed that under the experimental conditions