C13^i—C11—C12	112.47 (14)	B4—C1—B3	62.42 (11)
C13^i—C11—C1	124.10 (14)	C2—C1—B3	59.69 (10)
C12—C11—C1	123.35 (14)	C21—C2—B7	124.53 (14)
F12—C12—C13	115.08 (14)	C21—C2—B11	122.13 (13)
F12—C12—C11	121.18 (14)	B7—C2—B11	61.88 (12)
C13—C12—C11	123.72 (14)	C21—C2—B6	115.65 (13)
F13—C13—C12	114.59 (14)	B7—C2—B6	112.38 (14)
F13—C13—C11^i	121.63 (15)	B11—C2—B6	61.86 (11)
C12—C13—C11^i	123.78 (14)	C21—C2—B3	119.61 (13)
C26—C21—C2	120.83 (10)	B7—C2—B3	61.70 (11)
C22—C21—C2	119.10 (10)	C21—C2—C1	117.22 (12)
C11—C1—B4	120.65 (13)	B6—C2—C1	60.43 (9)
C11—C1—B5	120.76 (13)	B3—C2—C1	60.53 (10)
B4—C1—B5	62.83 (12)	B12—B8—B9	59.77 (13)
B5—C1—B6	62.13 (11)	B5—B9—B10	59.63 (11)
C2—C1—B6	59.74 (10)	B11—B12—B10	59.81 (12)

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

The C atoms of the phenyl ring were constrained to form a regular hexagon (C—C = 1.395 Å), whilst those of the haloaryl ring were refined freely. The H atoms of the phenyl ring were set in idealized positions (C—H = 1.08 Å) with a common displacement parameter (U_{iso} = 0.089 Å^2). The positions of the cage H atoms were allowed to refine with a separate common displacement parameter (U_{iso} = 0.059 Å^2 at convergence).

Data reduction: *CADABS* (Gould & Smith, 1986). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1305). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Nitrobenzaldehyde

Joseph A. King Jr* and Garold L. Bryant Jr†

General Electric Company, Corporate Research and Development, Schenectady, NY 12301, USA. E-mail: kingja@crd.ge.com

Abstract

The title compound, $C_7H_5NO_3$, constitutes the simplest aromatic nitrocarbonyl system whose class of structures is commonly investigated for photochromic behavior. The nitro and aldehyde groups of p-nitrobenzaldehyde are coplanar with the plane of the arene ring.

Comment

As part of our continuing interest in the intramolecular interaction of carbonyl groups with nitro-substituted aromatic systems (King & Bryant, 1990; Bryant & King, 1995), p-nitrobenzaldehyde, (I), was examined at low temperature by single-crystal X-ray diffraction. The *para* data was compared with that of *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) in order to contrast steric effects for ground-state modeling work. The modeling work was initiated, in part, in order to gain a better understanding of the geometrical limitations involved in photochromism for this class of compounds (Margerum & Miller, 1971). The *para* isomer was necessary for this structural comparison.
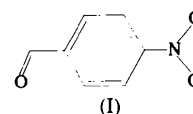
(I)

The nitro and aldehyde groups of p-nitrobenzaldehyde are coplanar with the plane of the arene ring. The carbonyl bond length is 1.197 (6) Å and the O(3)—N—O(2) bond angle is 120.0 (7)°. The aldehyde group of p-nitrobenzalydehyde was disordered. The general structure is unexceptional. A comparison of bond lengths and angles between the *ortho* and *para* isomers is given in Table 1. In contrast to the *para* isomer, the functional groups in *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) exhibit a slight canting of the nitro and aldehyde groups from coplanarity with the arene ring; the torsional angles are C(6)—C(1)—N(1)—O(1) = −151.1 (1), C(7)—C(2)—C(1)—N(1) = 9.5 (1)

† Present address: Pharmacia and Upjohn Inc., Structural, Analytical and Medicinal Chemistry, MS 7255-209-102.1, Kalamazoo, MI 49001, USA.

and C(1)—C(2)—C(7)—O(3) = $-152.8(1)°$. One O atom on the nitro group is oriented towards the carbonyl C atom of the aldehyde. The intramolecular internuclear distance for the proximal O atom [O(1)] to C(7) is 2.700 Å; the aldehydic $H \cdots O(1)$ distance is 2.712 Å while the $N \cdots C(7)$ internuclear distance is 2.967 Å. The carbonyl C—O bond distance is slightly longer than that of the *para* isomer, but still normal at 1.200 (9) Å.

Controversy has surrounded the ground-state interactions of the *ortho*-nitro group with both the aldehyde carbonyl and its associated H atom. Early work with this class of compounds focused on whether or not anomalous IR absorption shifts resulted from intramolecular hydrogen bonding or from steric interactions between the aldehyde and the nitro groups (Forbes, 1962). This dispute led to a structural analysis of *o*-nitrobenzaldehyde by both single-crystal X-ray (Coppens & Schmidt, 1964) and by neutron diffraction (Coppens, 1964). These later structural works indicated that the O atom of the nitro group was much too distant from the aldehyde for hydrogen bonding. Thus, both the IR and crystallographic work led to the conclusion that simple steric repulsion between the *ortho*-nitro and the aldehyde groups account for their rotation from coplanarity with the arene ring; the crystal structure of the *p*-nitrobenzaldehyde indicates the aldehyde and the nitro moieties to be coplanar with the arene ring (this work).

Recent work with *ortho*-substituted nitroaryl systems (King & Bryant, 1990; Bryant & King, 1995) indicate dipole–dipole effects may contribute heavily towards the relative orientation of the two groups. Both the aldehyde and nitro groups have substantial dipole moments; benzaldehyde has a dipole moment of 4.01 D and the aldehyde group has a dipole moment of 2.96 D oriented at an angle of 146° relative to the arene ring (Gordon & Ford, 1972). A dipole–dipole interaction would manifest itself as a reorientation of one of the nitro group's N—O bonds towards the carbonyl C atom of the aldehyde. This type of interaction would induce a shift in the carbonyl stretching frequency (ν_{co}) to lower energy. In fact, the N—O bond orientation towards the carbonyl C atom (Coppens & Schmidt, 1964) and the lower energy IR shift are observed (Forbes, 1962). Fig. 1 illustrates the molecule with the numbering scheme employed. Fig. 2 illustrates the projected packing of the molecule viewed down the *b* axis.
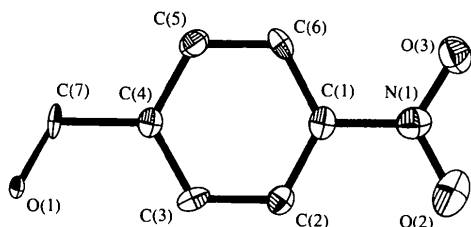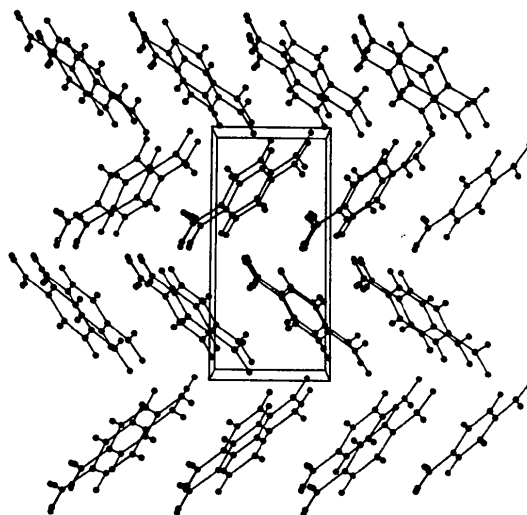

Fig. 2. Projected packing plot of (I) viewed down the *b* axis.

Experimental

The title compound was obtained from Aldrich and recrystallized from pentane–ether at 253 K. Crystals were sealed in glass capillary under dry nitrogen due to moisture sensitivity.

Crystal data

$C_7H_5NO_3$	Mo $K\alpha$ radiation
$M_r = 151.1$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 17
$P2_1$	reflections
$a = 6.209(2)$ Å	$\theta = 3.915–14.02°$
$b = 5.023(1)$ Å	$\mu = 0.116$ mm^{-1}
$c = 10.457(3)$ Å	$T = 160.95$ K
$\beta = 95.35(3)°$	Needle
$V = 324.7(2)$ Å^3	$0.30 \times 0.12 \times 0.08$ mm
$Z = 2$	Colorless
$D_x = 1.546$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $R3mV$ upgrade of Nicolet $P3F$ diffractometer	$R_{int} = 0.0116$
	$\theta_{max} = 27.5°$
	$h = -1 \rightarrow 8$
Wycoff scans	$k = -6 \rightarrow 6$
Absorption correction: none	$l = -13 \rightarrow 13$
908 measured reflections	3 standard reflections monitored every 47 reflections
832 independent reflections	
763 observed reflections	intensity decay: 7%
$[F > 2.0\sigma(F)]$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.39$ e Å^{-3}
$R = 0.0589$	$\Delta\rho_{min} = -0.33$ e Å^{-3}
$wR = 0.0755$	Extinction correction: none

Fig. 1. Thermal ellipsoid plot of (I) (50% probability).

$S = 4.39$
763 reflections
103 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.114$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Bond-length and angle comparison between p- and o-nitrobenzaldehydes*

	N—O	N—C	C_{co}—C_{aryl}	C—O	C_{aryl}—C_{co}—O_{co}	O—N—O
ortho*	1.226 (10)	1.468 (8)	1.490 (9)	1.200 (9)	122.2 (6)	125.0 (6)
	1.234 (6)					
para	1.236 (7)	1.446 (8)	1.521 (6)	1.197 (6)	116.3 (8)	120.0 (6)
	1.248 (6)					

* Coppens & Schmidt (1964).

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters $(\mathring{A}^2)$*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	−0.1557 (7)	0.0000	−0.8147 (4)	0.020 (1)
C(2)	−0.0333 (6)	−0.1163 (15)	−0.7133 (4)	0.018 (1)
C(3)	−0.1249 (7)	−0.3210 (16)	−0.6474 (4)	0.021 (1)
C(4)	−0.3361 (7)	−0.3982 (9)	−0.6818 (4)	0.017 (1)
C(5)	−0.4572 (6)	−0.2809 (17)	−0.7881 (4)	0.023 (1)
C(6)	−0.3653 (7)	−0.0821 (15)	−0.8557 (4)	0.020 (1)
N(1)	−0.0595 (6)	0.2095 (15)	−0.8852 (4)	0.027 (1)
O(2)	0.1283 (7)	0.2823 (18)	−0.8485 (4)	0.054 (1)
O(3)	−0.1645 (5)	0.3286 (15)	−0.9738 (3)	0.032 (1)
C(7)	−0.4374 (7)	−0.6224 (15)	−0.6101 (4)	0.016 (1)
O(1)	−0.3346 (5)	−0.7241 (16)	−0.5207 (3)	0.015 (1)
O(1B)	−0.6294 (19)	−0.681 (4)	−0.6482 (11)	0.010 (0)

Table 3. *Geometric parameters $(\mathring{A}, °)$*

C(1)—C(2)	1.375 (6)	C(4)—C(7)	1.521 (8)
C(1)—C(6)	1.395 (6)	C(5)—C(6)	1.377 (9)
C(1)—N(1)	1.446 (7)	N(1)—O(2)	1.248 (6)
C(2)—C(3)	1.389 (9)	N(1)—O(3)	1.236 (7)
C(3)—C(4)	1.382 (6)	C(7)—O(1)	1.197 (6)
C(4)—C(5)	1.412 (6)	C(7)—O(1B)	1.256 (13)
C(2)—C(1)—C(6)	123.0 (4)	C(4)—C(5)—C(6)	119.4 (4)
C(2)—C(1)—N(1)	118.5 (4)	C(1)—C(6)—C(5)	118.4 (4)
C(6)—C(1)—N(1)	118.4 (4)	C(1)—N(1)—O(2)	118.3 (5)
C(1)—C(2)—C(3)	118.3 (4)	C(1)—N(1)—O(3)	121.4 (4)
C(2)—C(3)—C(4)	120.0 (4)	O(2)—N(1)—O(3)	120.0 (7)
C(3)—C(4)—C(5)	120.7 (5)	C(4)—C(7)—O(1)	119.1 (4)
C(3)—C(4)—C(7)	120.3 (4)	C(4)—C(7)—O(1B)	116.3 (8)
C(5)—C(4)—C(7)	118.8 (4)	O(1)—C(7)—O(1B)	124.6 (9)

Data collection: Siemens *R3m/V* software. Cell refinement: *SHELXTL-Plus* (Sheldrick, 1990). Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: manual.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1179). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Linear Tripeptide L-Alanylglycyl-L-alanine

G. Sreekanta Padiyar and T. Parthasarathy Seshadri

*Department of Physics, Indian Institute of Science, Bangalore 560 012, India. E-mail: gspadiya@physics.iisc.ernet.in*

Abstract

L-Alanylglycyl-L-alanine, $C_8H_{15}N_3O_4$, exists as zwitterion in the crystal with the N terminus protonated and the C terminus in an ionized form. Both the peptide units are in *trans* configurations and deviate significantly from planarity. Backbone torsion angles are $\psi_1 = 172.7\,(2)$, $\omega_1 = -178.2\,(2)$, $\varphi_2 = 91.7\,(2)$, $\psi_2 = -151.9\,(2)$, $\omega_2 = -176.9\,(2)$, $\varphi_3 = -71.3\,(2)$, $\psi_{31} = -7.0\,(3)$ and $\psi_{32} = 172.4\,(2)°$. The protonated NH_3^+ group forms three hydrogen bonds with atoms of symmetry-related molecules.

Comment

Accurate geometric parameters of simple peptides are extensively utilized in theoretical conformational studies of polypeptides and proteins. In addition, knowledge of the hydrogen-bonding scheme and van der Waals contacts in simple peptides will aid understanding of the secondary structures of polypeptides and proteins. We report here the crystal structure of L-alanylglycyl-L-alanine, AGA.
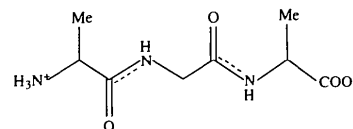
AGA

The atomic numbering and molecular conformation of the AGA molecule are shown in Fig. 1. AGA exists as a zwitterion with terminal NH_3^+ and COO^- groups. Both peptide units (C1A, C1', N2, C2A and O1; C2A,