of the C18 methyl group result in a previously unobserved conformation of the C20 carbonyl group. See Duax, Griffin & Rohrer (1981).

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Acta Cryst. (1989). C**45**, 2016–2018

Structure of 4-Nitrobenzaldehyde

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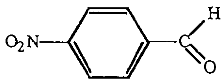
(*Received* 11 *May* 1989; *accepted* 13 *July* 1989)

Abstract. $C_7H_5NO_3$, $M_r = 151{\cdot}1$, monoclinic, $P2_1$, $a = 6{\cdot}2076\,(3)$, $b = 5{\cdot}0968\,(4)$, $c = 10{\cdot}6723\,(7)$ Å, $\beta = 95{\cdot}222\,(5)°$, $V = 336{\cdot}3\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}492$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 9{\cdot}74$ cm^{-1}, $F(000) = 156$, $T = 297\,(1)$ K, $R = 0{\cdot}040$ for 1191 reflections with $I > 3\sigma(I)$ (1372 unique observations). The carbonyl O atom exhibits a slight disorder, having 10% occupancy in a site nearly coincident with the aldehydic H atom. The molecule shows only small deviations from overall planarity, with mean deviation 0·014 Å and largest individual deviations 0·032 (1) and −0·022 (2) Å for the O atoms of the nitro group. The N—O distances are 1·213 (2) and 1·227 (2) Å, and the C═O distance for the major conformer is 1·204 (2) Å.

Experimental. The compound (I) was prepared by reducing 4-nitrobenzoyl chloride with tributyltin deuteride (Lusztyk, Lusztyk, Maillard & Ingold, 1984; Four & Guibe, 1981). Crystals for analysis were grown in benzene/hexane (6/1). Deuterium substitution was desired on the aldehydic H atom for observation in low-temperature zero-field NMR spectroscopy. Torsion angles were needed for the NMR study, so the structure of (I) was determined.



(I)

Intensity data for (I) were obtained on an Enraf–Nonius CAD-4 diffractometer with a graphite incident-beam monochromator using Cu $K\alpha$ radiation. The ω–2θ scans were made at variable rate, 0·66–3·30° min^{-1}. Absorption corrections were based on ψ scans. Details of data collection and structural refinement are given in Table 1. The structure was solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The structure was refined by full-matrix least squares with Enraf–Nonius *SDP* (Frenz, 1985), where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight, w, was defined as $4F_o^2\mathrm{Lp}^2/[S^2(C + R^2B) + (0{\cdot}020F_o^2)^2]$, S = scan rate, C = integrated count, R = scan time/background time, and B = background count. Atomic scattering factors, including those for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). Except as described below, the C, N and O atoms were refined anisotropically. H atoms were located by difference maps and refined isotropically. The aldehydic H atom initially refined to a position 1·2 Å from C7, with a negative isotropic thermal parameter. This observation was interpreted as a slight disorder (~10%) of the carbonyl O3 atom. Atom O3 was assigned occupancy 90% and refined anisotropically. O3′ was placed in a position related to O3 by 180° rotation about the C4—C7 bond, assigned occupancy 10%, and refined isotropically. Refinement of the occupancies was unsuccessful, and the values used were chosen to yield reasonable thermal parameters for O3. The aldehydic H atom was placed in a calculated position 0·95 Å from C7 and fixed with occupancy 90% and $B = 1{\cdot}3 \times B_{\mathrm{eq}}$ of C7. An extinction parameter, g, was refined where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c. The refinement converged with $R =$

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Table 1. *Experimental details*

Crystal	Very pale yellow 0·15 × 0·30 × 0·38 mm Capillary mounted
Unit-cell determination	25 reflections $25 < \theta < 30°$
Standards	400, 020, 006
R_{int}	0·015, Friedel equivalents not averaged
Corrections	Background, Lorentz, polarization Empirical absorption [0·9171–0·9962 on (I)]
2θ range (°)	4–150 (full sphere)
hkl	$h = -7$ to 7 $k = -6$ to 6 $l = -13$ to 13
Reflections	2887 total 1372 unique 1191 with $I > 3\sigma(I)$
Parameters refined	119
R, wR, R (all)	0·040, 0·056, 0·048
Goodness of fit, S	2·671
Maximum shift/e.s.d.	0·14
Max., min. $\Delta\rho$ (e Å $^{-3}$)	0·26, −0·30
H atoms	Refined, isotropic
Extinction	1·5 (2) × 10^{-5}

Table 2. *Positional parameters and equivalent isotropic thermal parameters with their e.s.d.'s*

$$B_{\mathrm{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
O1	0·8343 (2)	1	0·5287 (1)	5·76 (3)
O2	1·1274 (2)	0·9633 (5)	0·6488 (2)	6·73 (4)
O3	0·6646 (2)	−0·0252 (4)	0·9788 (1)	4·58 (3)
O3′	0·372 (1)	0·018 (2)	0·8500 (8)	2·2 (1)*
N	0·9408 (2)	0·8963 (4)	0·6159 (1)	4·04 (3)
C1	0·8448 (2)	0·6871 (5)	0·6860 (2)	3·34 (3)
C2	0·6368 (3)	0·6070 (4)	0·6469 (2)	3·87 (4)
C3	0·5477 (2)	0·4081 (5)	0·7143 (2)	3·84 (3)
C4	0·6650 (2)	0·2974 (4)	0·8189 (2)	3·42 (3)
C5	0·8743 (2)	0·3830 (5)	0·8543 (2)	3·84 (4)
C6	0·9662 (2)	0·5779 (4)	0·7878 (2)	3·87 (4)
C7	0·5668 (3)	0·0828 (4)	0·8908 (2)	3·82 (4)

* Refined isotropically

0·04014, $wR = 0·05595$, $S = 2·671$, while refinement of the alternate enantiomorph yielded $R = 0·04021$, $wR = 0·05600$, $S = 2·674$.

Final positional and equivalent isotropic thermal parameters for the former refinement are given in Table 2,* bond lengths, bond angles and torsion angles are shown in Table 3. Fig. 1 shows the molecule and the atomic numbering scheme.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

O1—N	1·213 (2)	C2—H2	1·00 (2)
O2—N	1·227 (2)	C3—C4	1·395 (2)
O3—C7	1·204 (2)	C3—H3	0·97 (1)
O3′—C7	1·290 (6)	C4—C5	1·390 (2)
N—C1	1·461 (2)	C4—C7	1·497 (2)
C1—C2	1·382 (2)	C5—C6	1·374 (2)
C1—C6	1·382 (2)	C5—H5	1·01 (2)
C2—C3	1·387 (2)	C6—H6	0·96 (2)
O1—N—O2	122·2 (2)	C3—C4—C5	119·8 (2)
O1—N—C1	119·5 (1)	C3—C4—C7	119·9 (1)
O2—N—C1	118·4 (1)	C5—C4—C7	120·3 (1)
N—C1—C2	118·4 (1)	C4—C5—C6	120·6 (1)
N—C1—C6	118·5 (1)	C4—C5—H5	122 (1)
C2—C1—C6	123·1 (1)	C6—C5—H5	117 (1)
C1—C2—C3	117·7 (1)	C1—C6—C5	118·4 (1)
C1—C2—H2	117 (1)	C1—C6—H6	119 (1)
C3—C2—H2	125 (1)	C5—C6—H6	123 (1)
C2—C3—C4	120·5 (1)	O3—C7—O3′	122·3 (4)
C2—C3—H3	117 (1)	O3—C7—C4	122·2 (2)
C4—C3—H3	122 (1)	O3′—C7—C4	115·4 (3)
O1—N—C1—C2	2·5 (3)	C3—C4—C7—O3	177·2 (2)
O1—N—C1—C6	−177·7 (2)	C3—C4—C7—O3′	−1·3 (6)
O2—N—C1—C2	−178·3 (2)	C5—C4—C7—O3	−1·4 (3)
O2—N—C1—C6	1·4 (3)	C5—C4—C7—O3′	−179·9 (5)

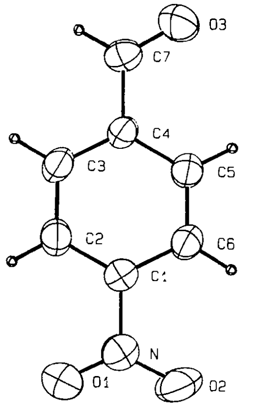

Fig. 1. *ORTEP* (Johnson, 1965) diagram showing 40% ellipsoids.

Related literature. The crystal structure of 4-nitrobenzoic acid shows a 13·7° dihedral angle between the nitro group and the plane of the ring owing to a twist about the C—N bond (Colapietro & Domenicano, 1977). Similar displacement from the plane of the ring has been found in the β modification of 4-nitrophenol (Coppens & Schmidt, 1965). A neutron diffraction study of 2-nitrobenzaldehyde to examine possible intramolecular hydrogen bonding found neither substituent of the *ortho*-substituted benzaldehyde to be coplanar with the ring (Coppens, 1964). The crystal structure of 2-nitrobenzaldehyde has been determined (Coppens & Schmidt, 1964).

The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and of the Louisiana Educational Quality Support Fund is gratefully acknowledged.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles involving H, H-atom parameters, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52120 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1989). C**45**, 2018–2020

Structure of a Functionalized Tetrahydrobenzothiophene

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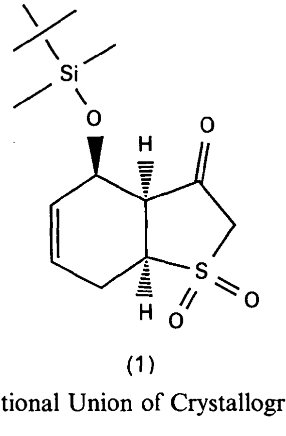
(*Received* 30 *May* 1989; *accepted* 13 *July* 1989)

Abstract. (±)-4-(*tert*-Butyldimethylsiloxy)-3a,4,7,7a-tetrahydrobenzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide, $C_{14}H_{24}O_4SSi$, $M_r = 316{\cdot}49$, monoclinic, $P2_1/n$, $a = 7{\cdot}1431\,(7)$, $b = 19{\cdot}643\,(2)$, $c = 12{\cdot}528\,(1)$ Å, $\beta = 104{\cdot}810\,(8)°$, $V = 1699{\cdot}4\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}24$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}597$ cm^{-1}, $F(000) = 680$, $T = 298$ K, $R = 0{\cdot}0566$ for 2733 reflections $[F_o \geq 4\sigma(F_o)]$. The two rings are *cis*-fused with the cyclohexene ring in the half-chair conformation while the thiophene moiety has the envelope conformation. The endocyclic bond angles of the cyclohexene ring are enlarged, especially at the bridgehead C atoms, C3a and C7a, which have angles 116·0 (2) and 116·8 (2)°, respectively. There are several close intramolecular contacts: C3···O11 2·614 (3), O10···O11 3·137 (3), O10···C7 3·073 (4) Å. Adjacent molecules related by $1-x$, $1-y$, $2-z$ stack so that the carbonyl O and C atoms of one molecule lie directly over the carbonyl C and O atoms of the second molecule. The C···O distance is 3·023 (3) Å in this intermolecular interaction.

Experimental. (1) was synthesized *via* an intermolecular Diels–Alder reaction of the *tert*-butyldimethylsiloxydiene of crotonaldehyde and the appropriate enone obtained from 3-sulfolene. The structure was obtained to confirm the regiochemistry and the stereochemistry of this process. Full details will be described elsewhere (Martin & Daniel, 1989). Crystals of (1) were obtained by slow evaporation from ethyl acetate. The data crystal was a colorless needle of approximate dimensions 0·18 × 0·23 × 0·76 mm. The data were collected on a Nicolet *P*3 diffractometer using a graphite monochromator. Lattice parameters were obtained from the least-squares refinement of 50 reflections with $21{\cdot}3 < 2\theta < 29{\cdot}2°$. The data were collected using the ω-scan technique (8446 reflections, of which 3913 were unique, $R_{\rm int} = 0{\cdot}0185$), with a 2θ range from 4·0–55·0° and a 1·2° ω scan at 5–10° min^{-1} ($h = 0\rightarrow10$, $k = -26\rightarrow26$, $l = -17\rightarrow17$). Four reflections ($\bar{2}0\bar{2}$, 080, 112, $\bar{2}\bar{3}1$) were remeasured every 196 reflections to monitor instrument and crystal stability (maximum correction on I was <2%). The data were also corrected for Lp effects and absorption (based on crystal shape; transmission-factor range 0·9315–0·9615). Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (1180 reflections). Data reduction, absorption and decay correction were performed using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick, 1987). The structure was solved by direct methods (Sheldrick, 1987) and refined by full-matrix least squares (Sheldrick, 1976). In all, 277 parameters were refined. The non-H atoms were refined with anisotropic thermal parameters. All H-atom positions were obtained from a ΔF map and refined with isotropic thermal parameters. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0{\cdot}5kI^{-1/2}\{[\sigma(I)]^2 + (0{\cdot}02I)^2\}^{1/2}$. The intensity,



(1)