Hooker, T. M., Bayley, P. M., Radding, W. & Schellman, J. A. (1974). *Biopolymers*, **13**, 549–566.
IUPAC–IUB Commission on Biochemical Nomenclature (1970). *Biochemistry*, **9**, 3471–3479.
Kopple, K. D. & Marr, D. H. (1967). *J. Am. Chem. Soc.* **89**, 6193–6200.
Kopple, K. D. & Ohnishi, M. (1969). *J. Am. Chem. Soc.* **91**, 962–970.
Lin, C. F. & Webb, L. E. (1973). *J. Am. Chem. Soc.* **95**, 6803–6811.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Acta Cryst. (1995). C**51**, 2581–2583

3-Hydroxy-2,6-dinitroacetophenone: an Unusual Substitution Pattern Resulting from Nitration of 3-Hydroxyacetophenone

M. Lurdes S. Cristiano and Robert A. W. Johnstone

Department of Chemistry, University of Liverpool, Liverpool L69 3BX, England

Michael J. Pratt

Du Pont (UK) Ltd, Coal Road, Leeds LS14 2AL, England

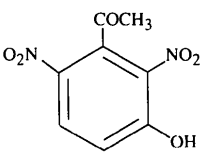
(*Received* 17 *October* 1994; *accepted* 6 *June* 1995)

Abstract

Nitration of 3-hydroxyacetophenone gives 2,6-dinitro-3-hydroxyacetophenone, $C_8H_6N_2O_6$, in which the nitro groups have entered the sterically least favourable positions in the aromatic nucleus. None of the expected substitution in the 4-position was observed. The two nitro groups flanking the carbonyl side chain are different in that one is in the plane of the aryl ring but the other is twisted well out of the plane.

Comment

During nitration of 3-hydroxyacetophenone to obtain the previously reported 2-nitro-3-hydroxyacetophenone (Butenandt, Hallmann & Beckmann, 1957), a substantial quantity of a new compound was also isolated. ^{1}H NMR spectroscopy showed that there were two *ortho* H atoms and, by using additivity rules for chemical shifts (Gordon & Ford, 1972), it seemed that the H atoms occupied the 4,5-positions in the aromatic ring indicating that an unexpected substitution had occurred. However, this prediction was not sufficiently clear-cut to distinguish it from the alternative expected structure with H atoms at the 5,6-positions. X-ray analysis gave the true structure (I) and showed that the NMR prediction had been correct. The relatively high yield of nitration products is unusual in that one nitro group joined the aryl ring *ortho* to the carbonyl and *para* to hydroxyl while the other joined *ortho* to both carbonyl and hydroxyl (a position of sterically restricted access); no nitration was observed in the expected position, *ortho* to hydroxyl and *para* to carbonyl, where there is no steric constraint. This substitution pattern violates the normal rules for electrophilic substitution into a simple aromatic ring (March, 1985) since sterically hindered nitration is highly unfavourable. There are a few examples in the literature exhibiting a similar '*ortho*' effect of carbonyl (Ingold, 1954; Rubenstein, 1925; Raiford & Wells, 1935; Ginsburg, 1951). The present result is another even more extreme example of substitution which appears to be governed by transition-state energies rather than the 'normal' ground-state considerations for electrophilic aromatic substitution (Kruse & Cha, 1982).



(I)

The structure of the title compound is also unusual in that one nitro group alongside the carbonyl lies planar with the aryl ring whilst the other nitro adjacent to the carbonyl is twisted almost at right angles to it. The aromatic ring remains substantially planar.

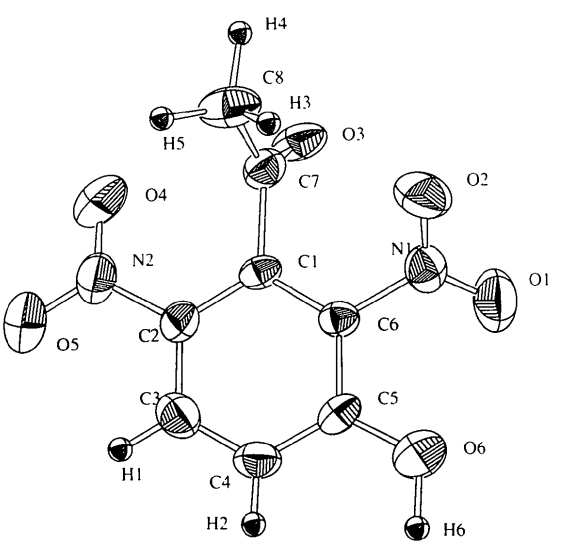


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids.

Experimental

Addition of conc. nitric acid (s.g. 1.42; 10 ml) in conc. sulfuric acid (8 ml) to 3-hydroxyacetophenone (20 g) in conc. sulfuric acid (59 ml) at 253 K, followed by stirring for 15 min gave, after chromatography on silica gel, some starting material (5.2 g), 2-nitro-3-hydroxyacetophenone (6.5 g; 33% yield) and 2,6-dinitro-3-hydroxyacetophenone (6.1 g; 25% yield). The latter was recrystallized from ethanol as yellow needles (m.p. 455–456 K).

Crystal data

$C_8H_6N_2O_6$
$M_r = 226.15$
Monoclinic
$P2_1/c$
$a = 7.813\ (2)$ Å
$b = 12.708\ (3)$ Å
$c = 9.392\ (2)$ Å
$\beta = 101.14\ (2)°$
$V = 915.0\ (4)$ Å^3
$Z = 4$
$D_x = 1.641$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 13.10–18.93°$
$\mu = 0.135$ mm^{-1}
$T = 24.0$ K
Prism
0.450 × 0.300 × 0.300 mm
Yellow

Data collection

Rigaku AFC-6S diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical refined from ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.95$, $T_{max} = 1.00$
1815 measured reflections
1688 independent reflections
937 observed reflections $[I > 4\sigma(I)]$
$R_{int} = 0.008$
$\theta_{max} = 24.98°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 150 reflections
intensity decay: 0.01%

Refinement

Refinement on F
$R = 0.0656$
$wR = 0.0766$
$S = 2.982$
937 reflections
145 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.0408$
$\Delta\rho_{max} = 0.619$ e Å^{-3}
$\Delta\rho_{min} = -0.310$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^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}
O1	1.0350 (6)	0.7770 (4)	0.1465 (4)	0.0771
O2	0.8398 (6)	0.7066 (4)	−0.0168 (5)	0.0757
O3	0.5906 (4)	0.8915 (3)	−0.0453 (4)	0.0512
O4	0.5662 (6)	1.0191 (4)	−0.3214 (5)	0.0732
O5	0.7383 (6)	1.0923 (4)	−0.4417 (5)	0.0984
O6	1.2748 (5)	0.8441 (4)	0.0055 (5)	0.0709
N1	0.9482 (6)	0.7750 (4)	0.0263 (5)	0.0455
N2	0.7092 (7)	1.0321 (4)	−0.3476 (6)	0.0594
C1	0.8277 (6)	0.9010 (4)	−0.1650 (5)	0.0306
C2	0.8557 (7)	0.9764 (4)	−0.2632 (5)	0.0387
C3	1.0243 (7)	1.0046 (5)	−0.2768 (6)	0.0473
C4	1.1648 (7)	0.9604 (4)	−0.1895 (6)	0.0434
C5	1.1429 (6)	0.8883 (4)	−0.0858 (6)	0.0394
C6	0.9723 (6)	0.8584 (4)	−0.0768 (5)	0.0323
C7	0.6456 (7)	0.8639 (4)	−0.1508 (6)	0.0408
C8	0.5505 (7)	0.7907 (5)	−0.2638 (7)	0.0603

Table 2. *Selected geometric parameters* (Å, °)

O1—N1	1.200 (6)	C1—C2	1.376 (7)
O2—N1	1.226 (6)	C1—C6	1.376 (6)
O3—C7	1.206 (6)	C1—C7	1.529 (7)
O4—N2	1.200 (6)	C2—C3	1.395 (7)
O5—N2	1.224 (6)	C3—C4	1.358 (8)
O6—C5	1.331 (6)	C4—C5	1.372 (7)
N1—C6	1.472 (7)	C5—C6	1.404 (7)
N2—C2	1.446 (7)	C7—C8	1.497 (8)
O1—N1—O2	123.6 (5)	C2—C3—C4	120.4 (5)
O1—N1—C6	118.9 (5)	C3—C4—C5	120.5 (5)
O2—N1—C6	117.5 (5)	O6—C5—C4	123.5 (5)
O4—N2—O5	122.9 (6)	O6—C5—C6	118.2 (5)
O4—N2—C2	119.4 (5)	C4—C5—C6	118.2 (5)
O5—N2—C2	117.7 (5)	N1—C6—C1	119.0 (4)
C2—C1—C6	117.3 (4)	N1—C6—C5	118.5 (5)
C2—C1—C7	123.0 (5)	C1—C6—C5	122.4 (5)
C6—C1—C7	119.7 (5)	O3—C7—C1	117.9 (5)
N2—C2—C1	119.7 (5)	O3—C7—C8	123.8 (5)
N2—C2—C3	119.1 (5)	C1—C7—C8	118.2 (5)
C1—C2—C3	121.0 (5)		
O1—N1—C6—C1	−138.4 (5)	O4—N2—C2—C1	7.0 (8)
O1—N1—C6—C5	44.4 (7)	O4—N2—C2—C3	−169.3 (6)
O2—N1—C6—C1	41.9 (7)	C2—C1—C6—C5	−0.9 (7)
O2—N1—C6—C5	−135.4 (5)	C2—C1—C7—C8	76.1 (7)
O3—C7—C1—C2	−107.4 (6)	C3—C4—C5—C6	2.7 (8)
O3—C7—C1—C6	72.5 (6)	C6—C1—C7—C8	−104.0 (6)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

The authors thank Du Pont, the Eschenmoser Trust and JNICT (Portugal) for financial support (MLSC) and Mr James V. Barkley for expert technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Butenandt, A., Hallmann, G. & Beckmann, R. (1957). *Chem. Ber.* **90**, 1120–1124.
Ginsburg, D. (1951). *J. Am. Chem. Soc.* **73**, 702–704.
Gordon, A. J. & Ford, R. A. (1972). *The Chemist's Companion*, pp. 261–262. New York: Wiley.
Ingold, C. K. (1954). *Structure and Mechanism in Organic Chemistry*, pp. 261–263. Ithaca: Cornell Univ. Press.
Kruse, L. I. & Cha, J. K. (1982). *J. Chem. Soc. Chem. Commun.* pp. 1333–1336.
March, J. (1985). *Advanced Organic Chemistry*, pp. 459–460. New York: Wiley.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Raiford, L. C. & Wells, E. H. (1935). *J. Am. Chem. Soc.* **57**, 2500–2503.
Rubenstein, L. (1925). *J. Chem. Soc.* **127**, 1998–2004.

Acta Cryst. (1995). C**51**, 2583–2584

Homochiral Methyl (*S*)-2-Benzoyloxy-4-bromo-4-methylpentanoate

JOANNE P. SHAW, ENG WUI TAN AND ALLAN G. BLACKMAN

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand

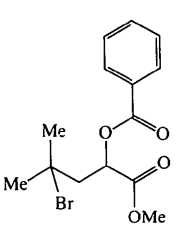
(*Received* 24 *April* 1995; *accepted* 22 *June* 1995)

Abstract

The stereochemistry at position 2 of the title compound, $C_{14}H_{17}BrO_4$, has been confirmed as *S*.

Comment

The title compound, methyl (*S*)-2-benzoyloxy-4-bromo-4-methylpentanoate, (I), was investigated as part of a study of the regioselective bromination of 2-hydroxy-4-methylpentanoic acid derivatives (Shaw, Tan & Blackman, 1995). X-ray structure analysis was undertaken in order to confirm that the stereochemistry at the 2 position (*i.e.* atom C5) was unaffected by the bromination reaction.



(I)

The compound crystallized as large blocks; the smallest of these was used for data collection as, despite repeated attempts, suitable smaller crystals could not be obtained. Cutting the crystal also destroyed the crystal mosaicity. Despite the fact that there may have been some reflections for which the crystal was not bathed in a uniform beam, the quality of the data does not appear to have been affected, as evidenced by the excellent results. We have previously used similarly large crystals without deleterious effects (Shaw, Tan & Blackman, 1995).

Refinement in the orthorhombic space group $P2_12_12_1$ showed the presence of only one enantiomer. The stereochemistry at atom C5 was found to be *S*, with the correct choice of 'handedness' verified by the value of the Flack (1983) parameter [$\chi = -0.01\,(2)$]. All bond lengths and angles within the identical fragments of (I) and methyl (*S*)-2-benzenesulfonyloxy-4-bromo-4-methylpentanoate are the same within three e.s.d.'s, with the exception of the O3—C5—C7 angle [107.2 (3) *versus* 111.6 (4)° in the latter] (Shaw, Tan & Blackman, 1995).

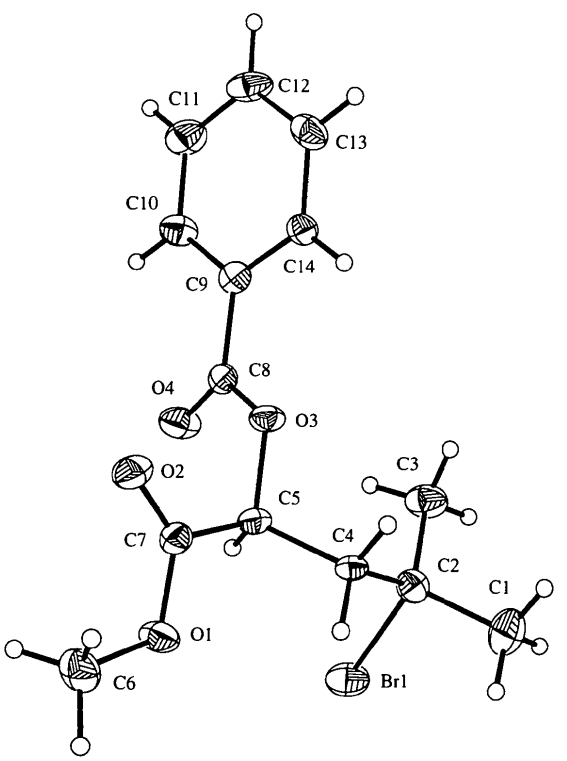


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (I) showing displacement ellipsoids at the 50% probability level.

Experimental

A mixture of methyl (*S*)-2-benzoyloxy-4-methylpentanoate (1.11 g, 4.4 mmol) and *N*-bromosuccinimide (1.18 g, 6.6 mmol) in benzene (100 ml) was heated at reflux under