References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.

Anulewicz, R. & Maciejewska, D. (1996). *Pol. J. Chem.* **70**, 742–751.

Bocelli, G. & Cantoni, A. (1992). *Acta Cryst.* C**48**, 961–963.

Freeman, H. C. & Hutchinson, N. D. (1979). *Acta Cryst.* B**35**, 2051–2054.

Gillespie, R. J. (1963). *J. Chem. Educ.* **40**, 295.

Kálmán, A. & Argay, Gy. (1983). *J. Mol. Struct.* **102**, 391–402.

Krygowski, T. M. (1993). *J. Chem. Inf. Comput. Sci.* **33**, 70–78.

Kuma (1991). *Kuma KM-4 Software*. Version 5.0. Kuma Diffraction, Wrocław, Poland.

Maciejewska, D. (1995). *Pol. J. Chem.* **69**, 1628–1641.

Maciejewska, D. & Skulski, L. (1993). *Pol. J. Chem.* **67**, 1059–1066.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual*. Release 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2945-2946

(Z)-2-(Benzoyl-*aci*-nitro)-2-phenylacetonitrile

Douglas R. Powell, Peter E. Hanson and Samuel H. Gellman

Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706-1396, USA. E-mail: powell@chem.wisc.edu

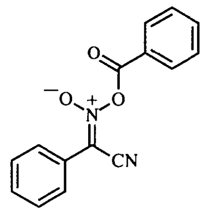
(*Received 24 June 1996; accepted 5 September 1996*)

Abstract

The *aci*-nitro group of the title compound, $C_{15}H_{10}N_2O_3$, is almost coplanar with the phenylacetonitrile moiety [O11—N10···C1—C2 8.3 (2)°] and is almost perpendicular to the benzoyl group [O11—N10—O12—C13 84.7 (2)°]. The C—N=O angle of the *aci*-nitro group is distorted due to steric interaction with the neighboring *ortho*-H atom of the phenyl ring.

Comment

As part of an investigation of acyl-group transfer agents, carboxylic nitronic anhydrides (Nielsen, 1989) were examined. The title compound, (I), is an effective acylating agent under mild conditions (Thurston & Shriner, 1937). Its structure was determined in order to establish the conformation of the anhydride juncture.



(I)

The title compound exhibits a shortened C—N bond [C7—N10 1.318 (2) Å] and unequal N—O bond lengths [N10=O11 1.232 (2) and N10—O12 1.453 (2) Å] characteristic of an *aci*-nitro group (Nielsen, 1989). The difference in the O—N—C angles [O11=N10—C7 130.3 (2) and O12—N10—C7 114.00 (14)°] probably arises from non-bonded repulsion between the phenyl *ortho*-H2 atom and O11. Similar bond-angle distortions were seen in two silyl nitronates (Colvin *et al.*, 1980) and in *aci*-nitrodiphenylmethane (Bock *et al.*, 1993).

The title molecule assumes a conformation with two separate planar regions. The sp^2 character of the C7 atom causes the *aci*-nitro and phenylacetonitrile groups to form one almost planar region of the molecule as shown by the O11—N10···C1—C2 torsion angle of −8.3 (2)°. The benzoyl group is almost perpendicular to the *aci*-nitrophenylacetonitrile group as shown by the O11—N10—O12—C13 torsion angle of 84.7 (2)°. The roughly 90° orientation of the benzoyl plane with respect to the *aci*-nitro plane may reduce dipolar and/or steric repulsions between the carbonyl and both the *aci*-nitro and acetonitrile groups. There are no unusually short intermolecular contacts.

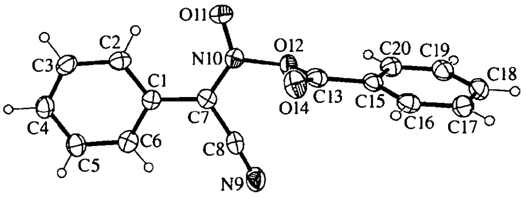


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids.

Experimental

The title compound was prepared according to the method of Thurston & Shriner (1937). Crystals were grown by vapor diffusion from a solution of 1,2-dichloroethane using pentane as the precipitant. Spectroscopic data: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (*m*, 4H), 7.72 (*tt*, J = 8.94, 1.3 Hz, 1H), 7.56 (*m*, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 162.3 (C), 135.2 (CH), 132.1 (CH), 130.4 (CH), 129.2 (CH), 129.1 (CH), 127.8 (CH), 125.3 (C), 124.7 (C), 111.3 (C); IR (thin film): 2230, 1761, 1606, 1449, 1340, 1318, 1250, 1223, 975 cm^{-1}; HRMS (EI): calculated for $C_{15}H_{10}N_2O_3$ 266.0691, found 266.0691; m.p. (recrystallized from hexane) 389 K.

Crystal data

$C_{15}H_{10}N_2O_3$
$M_r = 266.25$
Orthorhombic
Pbca
$a = 8.6150\,(10)$ Å
$b = 9.9540\,(10)$ Å
$c = 29.684\,(2)$ Å
$V = 2545.5\,(4)$ Å^3
$Z = 8$
$D_x = 1.389$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 39 reflections
$\theta = 10.4$–$27.4°$
$\mu = 0.821$ mm^{-1}
$T = 113\,(2)$ K
Prism
0.40 × 0.35 × 0.10 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical (*SHELXTL-Plus*; Sheldrick, 1995)
$T_{\min} = 0.76$, $T_{\max} = 0.91$
3432 measured reflections
1718 independent reflections
1585 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.067$
$\theta_{\max} = 57°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 32$
3 standard reflections monitored every 100 reflections intensity decay: 6.54%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.102$
$S = 1.12$
1718 reflections
182 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.7415P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.012$

$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0017 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
C1	0.1591 (2)	0.3964 (2)	0.02829 (6)	0.0250 (4)
C2	0.2664 (2)	0.4654 (2)	0.00152 (6)	0.0303 (5)
C3	0.2645 (2)	0.4498 (2)	−0.04461 (6)	0.0327 (5)
C4	0.1579 (2)	0.3657 (2)	−0.06503 (6)	0.0303 (5)
C5	0.0511 (2)	0.2976 (2)	−0.03895 (6)	0.0304 (5)
C6	0.0511 (2)	0.31280 (15)	0.00726 (6)	0.0286 (5)
C7	0.1519 (2)	0.4081 (2)	0.07727 (6)	0.0262 (5)
C8	0.0222 (2)	0.3557 (2)	0.10162 (6)	0.0268 (5)
N9	−0.0867 (2)	0.31711 (15)	0.11965 (5)	0.0386 (5)
N10	0.2587 (2)	0.46793 (15)	0.10193 (5)	0.0324 (4)
O11	0.3795 (2)	0.5251 (2)	0.09063 (5)	0.0492 (4)
O12	0.23154 (14)	0.45896 (11)	0.15015 (4)	0.0320 (4)
C13	0.1613 (2)	0.5747 (2)	0.16693 (6)	0.0282 (5)
O14	0.1225 (2)	0.66530 (12)	0.14278 (4)	0.0377 (4)
C15	0.1423 (2)	0.5649 (2)	0.21614 (6)	0.0253 (5)
C16	0.0531 (2)	0.6625 (2)	0.23741 (6)	0.0305 (5)
C17	0.0366 (2)	0.6603 (2)	0.28356 (6)	0.0349 (5)
C18	0.1076 (2)	0.5611 (2)	0.30880 (6)	0.0358 (5)
C19	0.1950 (2)	0.4629 (2)	0.28773 (6)	0.0340 (5)
C20	0.2126 (2)	0.4641 (2)	0.24143 (6)	0.0312 (5)

Table 2. *Geometric parameters (Å, °)*

C1—C6	1.396 (2)	N10—O12	1.453 (2)
C1—C2	1.399 (2)	O12—C13	1.394 (2)
C1—C7	1.460 (2)	C13—O14	1.199 (2)
C2—C3	1.378 (2)	C13—C15	1.473 (2)
C3—C4	1.383 (3)	C15—C16	1.391 (2)
C4—C5	1.380 (2)	C15—C20	1.392 (2)
C5—C6	1.380 (2)	C16—C17	1.378 (3)
C7—N10	1.318 (2)	C17—C18	1.382 (3)
C7—C8	1.429 (3)	C18—C19	1.383 (3)
C8—N9	1.146 (2)	C19—C20	1.383 (2)
N10—O11	1.232 (2)		
C6—C1—C7	117.66 (15)	C7—N10—O12	114.00 (14)
C2—C1—C7	123.7 (2)	C13—O12—N10	111.80 (12)
N10—C7—C8	115.5 (2)	O14—C13—O12	121.9 (2)
N10—C7—C1	124.0 (2)	O14—C13—C15	127.7 (2)
C8—C7—C1	120.53 (15)	O12—C13—C15	110.35 (14)
N9—C8—C7	176.5 (2)	C16—C15—C20	120.0 (2)
O11—N10—C7	130.3 (2)	C16—C15—C13	117.72 (15)
O11—N10—O12	115.62 (14)	C20—C15—C13	122.3 (2)

The Laue-unique and Friedel-related data were collected. The H-atom positions, which were initially determined by geometry, were refined by a riding model, with isotropic displacement parameters set equal to 1.2 times the equivalent value for the bonded C atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

The authors thank the Exxon Education Foundation and the National Science Foundation Presidential Young Investigator Program (CHE-9157510) for support. Funds to purchase the X-ray instrument and computer were provided by the NSF (CHE-9105497) and the University of Wisconsin.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1280). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bock, H., Dienelt, R., Schödel, H., Havlas, Z., Herdtweck, E. & Herrmann, A. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1758–1760.

Colvin, E. W., Beck, A. K., Bastani, B., Seebach, D., Kai, Y. & Dunitz, J. D. (1980). *Helv. Chim. Acta*, **63**, 697–710.

Nielsen, A. T. (1989). *Nitrones, Nitronates and Nitroxides*, edited by S. Patai & Z. Rappoport, pp. 1–138. New York: John Wiley and Sons.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1995). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thurston, J. T. & Shriner, R. L. (1937). *J. Org. Chem.* **2**, 183–194.