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Two Azabenzotriazines

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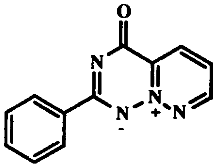
Abstract

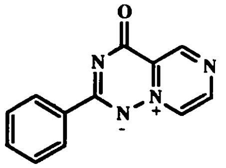
The structures of 2-phenylpyridazino[2,1-*f*][1,2,4]triazin-4-one (I) and 2-phenylpyrazino[3,2-*f*][1,2,4]triazin-4-one (II) were determined. The geometries of both compounds are similar. The bond distances between the carbonyl C and adjacent C atoms were rather long [1.463(6) (I) and 1.476(6) Å (II)]. The dihedral angles between the triazine and phenyl rings were close to 0° [2.77 (I) and 3.22° (II)].

Comment

The X-ray crystallographic analyses of the title compounds were undertaken to determine the structures of the products obtained from the reaction of 1-benzoylimino-pyridazine and -pyrazine with carbamoyl radicals, generated by the decomposition of $(NH_4)_2SO_2$ in formamide. A few examples of similar compounds, including azanaphthalene derivatives with six-membered mesoionic structures, are known (Sato & Yoshiie, 1976). The pyridazino- and pyrazinotriazine rings are almost planar, with maximum displacements out of the least-squares plane of 0.054 Å for C1 (I) and 0.038 Å for N2 (II). This planarity and the endocyclic bond distances indicate extensive delocalization of π electrons which also extends over O11 for both compounds. The endocyclic bond distances as well as the C1–C6 distances of 1.463(6) (I) and 1.476(6) Å (II), which are close to a single-bond distance, indicate the contribution of canonical forms (I) and (II) shown below. The dihedral angles between the heterocycles and the phenyl rings are small [2.77 (I) and 3.22° (II)].



(I)



(II)

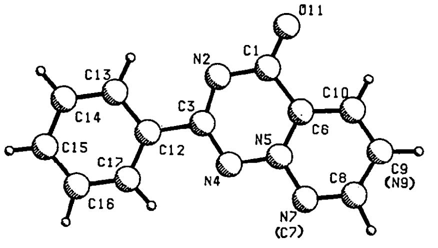


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing showing the atomic numbering of the molecules.

Experimental

Compound (I)

Crystal data

$C_{12}H_8N_4O$
$M_r = 224.22$
Monoclinic
$P2_1/n$
$a = 19.057$ (7) Å
$b = 7.473$ (3) Å
$c = 7.286$ (3) Å
$\beta = 94.76$ (3)°
$\theta = 28.0$–30.0°

$V = 1033.9$ (7) Å^3
$Z = 4$
$D_x = 1.440$ Mg m^{-3}
Cu $K\alpha_1$
$\lambda = 1.5405$ Å
$\mu = 0.763$ mm^{-1}
$T = 297$ K
Needle
0.40 × 0.08 × 0.06 mm
Clear

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1870 measured reflections
1541 independent reflections
958 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.063$
$\theta_{\rm max} = 60$°
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 150 reflections
intensity variation: <3%

Refinement

Refinement on F^2
Final $R = 0.058$
$wR = 0.065$
$S = 1.030$
958 reflections
186 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.043F^2]$

$(\Delta/\sigma)_{\rm max} = 0.132$
$\Delta\rho_{\rm max} = 0.184$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.291$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$C_{12}H_8N_4O$
$M_r = 224.22$
Monoclinic
$P2_1/n$

$V = 1034.3$ (5) Å^3
$Z = 4$
$D_x = 1.440$ Mg m^{-3}
Cu $K\alpha_1$
$\lambda = 1.5405$ Å

0108-2701/92/061152-03$06.00

$a = 14.452\ (2)$ Å
$b = 10.257\ (1)$ Å
$c = 7.048\ (3)$ Å
$\beta = 98.11\ (2)°$
$\theta = 28.0–30.5°$

$\mu = 0.763\ \text{mm}^{-1}$
$T = 297$ K
Prism
$0.25 \times 0.13 \times 0.02$ mm
Clear

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1241 measured reflections
1030 independent reflections
900 observed reflections $[F > 3\sigma(F)]$

$R_{\text{int}} = 0.026$
$\theta_{\text{max}} = 60°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 7$
3 standard reflections monitored every 150 reflections intensity variation: <3%

Refinement

Refinement on F^2
Final $R = 0.062$
$wR = 0.054$
$S = 1.380$
900 reflections
186 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.070F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.155$
$\Delta\rho_{\text{max}} = 0.220$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.343$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

For both compounds: Data collection: *AFD* (Rigaku Corporation, 1985*a*) Cell refinement: *AFD*. Data reduction: *RCRYSTAN* (Rigaku Corporation, 1985*b*). Program(s) used to solve structure: *SAPI85* (Yao, Zheng, Qian, Han, Gu & Fan, 1985). Program(s) used to refine structure: *RCRYSTAN*. Molecular graphics: *ACV* (Stardent Computer Inc., 1990). Software used to prepare material for publication: *XPACK* (Yamaguchi, 1987).

For both compounds, the ω-scan width was $(1.3 + 0.14\tan\theta)°$ and the scan speed 16° min^{-1}. Refinement was by full-matrix least-squares methods.

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

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.3833 (1)	0.5969 (6)	0.7598 (5)	0.052 (1)
N2	0.4435 (1)	0.6753 (4)	0.7145 (4)	0.050 (1)
C3	0.5017 (1)	0.5792 (5)	0.7305 (4)	0.041 (1)
N4	0.5111 (1)	0.4103 (4)	0.7869 (4)	0.045 (1)
N5	0.4502 (1)	0.3284 (4)	0.8251 (4)	0.042 (1)
C6	0.3864 (1)	0.4079 (5)	0.8119 (5)	0.043 (1)
N7	0.4619 (1)	0.1563 (4)	0.8771 (4)	0.054 (1)
C8	0.4054 (2)	0.0644 (6)	0.9110 (5)	0.054 (1)
C9	0.3375 (2)	0.1307 (6)	0.8965 (5)	0.054 (1)
C10	0.3288 (2)	0.3039 (6)	0.8485 (5)	0.051 (1)
O11	0.3263 (1)	0.6750 (4)	0.7579 (5)	0.085 (1)
C12	0.5680 (1)	0.6672 (5)	0.6849 (4)	0.043 (1)
C13	0.5669 (2)	0.8467 (6)	0.6321 (5)	0.057 (1)
C14	0.6273 (2)	0.9319 (8)	0.5865 (6)	0.070 (2)
C15	0.6897 (2)	0.8375 (9)	0.5936 (6)	0.072 (2)
C16	0.6917 (2)	0.6613 (8)	0.6449 (6)	0.065 (1)
C17	0.6320 (2)	0.5762 (7)	0.6895 (6)	0.055 (1)

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

C1—O11	1.233 (4)	N5—C6	1.349 (4)
C1—N2	1.353 (5)	N5—N7	1.354 (4)
C1—C6	1.463 (6)	C6—C10	1.388 (5)
N2—C3	1.319 (5)	N7—C8	1.319 (5)
C3—N4	1.335 (5)	C8—C9	1.382 (6)
C3—C12	1.486 (5)	C9—C10	1.347 (6)
N4—N5	1.361 (4)		

O11—C1—N2	123.8 (4)	N7—N5—N4	111.1 (2)
O11—C1—C6	118.5 (3)	N5—C6—C10	117.5 (3)
N2—C1—C6	117.6 (3)	N5—C6—C1	117.5 (3)
C3—N2—C1	117.8 (3)	C10—C6—C1	125.0 (3)
N2—C3—N4	129.3 (3)	C8—N7—N5	115.3 (3)
N2—C3—C12	117.6 (3)	N7—C8—C9	125.0 (4)
N4—C3—C12	113.1 (3)	C10—C9—C8	117.3 (4)
C3—N4—N5	113.1 (3)	C9—C10—C6	120.4 (3)
C6—N5—N7	124.5 (3)	C13—C12—C3	119.5 (3)
C6—N5—N4	124.5 (3)		

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (II)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.5439 (3)	−0.2566 (5)	0.3516 (7)	0.048 (2)
N2	0.5779 (2)	−0.1344 (3)	0.3324 (5)	0.047 (1)
C3	0.5177 (3)	−0.0407 (4)	0.2706 (6)	0.042 (1)
N4	0.4253 (2)	−0.0493 (3)	0.2175 (5)	0.044 (1)
N5	0.3908 (2)	−0.1718 (3)	0.2297 (5)	0.040 (1)
C6	0.4424 (3)	−0.2755 (4)	0.2970 (6)	0.041 (1)
C7	0.2970 (3)	−0.1878 (5)	0.1705 (7)	0.047 (2)
C8	0.2604 (3)	−0.3082 (5)	0.1805 (7)	0.051 (2)
N9	0.3089 (2)	−0.4138 (4)	0.2498 (5)	0.055 (1)
C10	0.3994 (3)	−0.3948 (4)	0.3079 (7)	0.048 (2)
O11	0.5934 (2)	−0.3501 (3)	0.4084 (5)	0.066 (1)
C12	0.5551 (3)	0.0928 (4)	0.2545 (7)	0.047 (2)
C13	0.6492 (4)	0.1179 (5)	0.3155 (8)	0.061 (2)
C14	0.6862 (5)	0.2406 (7)	0.3021 (10)	0.081 (3)
C15	0.6280 (5)	0.3420 (7)	0.2304 (9)	0.083 (3)
C16	0.5354 (5)	0.3199 (6)	0.1716 (9)	0.076 (3)
C17	0.4978 (4)	0.1947 (5)	0.1812 (7)	0.057 (2)

Table 4. *Geometric parameters* (Å, °) *for* (II)

C1—O11	1.228 (5)	N5—C6	1.346 (5)
C1—N2	1.360 (6)	N5—C7	1.370 (6)
C1—C6	1.476 (6)	C6—C10	1.379 (6)
N2—C3	1.326 (6)	C7—C8	1.349 (7)
C3—N4	1.338 (6)	C8—N9	1.344 (6)
C3—C12	1.482 (7)	N9—C10	1.328 (6)
N4—N5	1.358 (5)		

O11—C1—N2	123.4 (4)	N4—N5—C7	116.7 (3)
O11—C1—C6	119.5 (4)	N5—C6—C10	119.2 (4)
N2—C1—C6	117.1 (4)	N5—C6—C1	117.9 (4)
C3—N2—C1	118.1 (3)	C10—C6—C1	122.8 (4)
N2—C3—N4	128.7 (4)	C8—C7—N5	118.3 (4)
N2—C3—C12	117.7 (4)	N9—C8—C7	124.5 (4)
N4—C3—C12	113.6 (4)	C10—N9—C8	115.7 (4)
C3—N4—N5	113.9 (3)	N9—C10—C6	123.1 (4)
C6—N5—N4	124.2 (3)	C17—C12—C3	121.3 (4)
C6—N5—C7	119.1 (4)	C13—C12—C3	119.9 (4)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54973 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1002]

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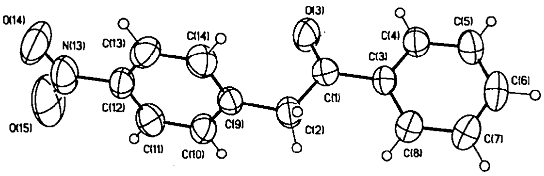

Fig. 1. General view (*SHELXTL-Plus*; Sheldrick, 1987) of the molecule showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

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Structure of 2-(4-Nitrophenyl)-1-phenylethanone

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Abstract

The plane through the two central bridging C atoms and the carbonyl O atom is nearly coplanar with the phenyl ring [6.6(1)°], and forms a dihedral angle of 78.91(9)° with the plane of the six-membered ring of the 4-nitrophenyl group and a dihedral angle of 82.6(1)° with the nitro group. The carbonyl C atom in the bridging group is sp^2 hybridized; the bond angles are 117.9(2), 121.0(2) and 121.0(2)° and the C—C—C bond angle at the methylene C atom of the bridge is 114.1(2)°. The bond distances in this molecule are in the expected range indicating almost no interaction between the carbonyl group and the 4-nitrophenyl moiety.

Comment

The structure determination of the title compound was undertaken in order to obtain more structural information about deoxybenzoin derivatives and the effects of substituents in different positions on their conformations. This information is significant because this skeleton forms a part of many natural compounds and the title compound can easily be transformed into the corresponding carbanion by removal of one proton from the methylene group. These carbanions are of great interest as intermediate species in many chemical reactions. We are interested in the structural and electronic effects of the replacement of the methylene H atoms by O atoms.

Experimental

Crystal data

$C_{14}H_{11}NO_3$
$M_r = 241.25$
Monoclinic
$P2_1/c$
$a = 14.662\ (4)$ Å
$b = 10.790\ (2)$ Å
$c = 7.749\ (2)$ Å
$\beta = 104.55\ (2)°$
Cell parameters from 20 reflections
$\theta = 7.50–14.35°$
$V = 1186.6\ (5)$ Å^3
$Z = 4$
$D_x = 1.350$ Mg m^{-3}
Mo $K\alpha$
$\lambda = 0.71073$ Å
$\mu = 0.09$ mm^{-1}
$T = 293\ (1)$ K
0.60 × 0.40 × 0.24 mm
Colourless

Data collection

Nicolet *R*3*m*/*V* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1981 measured reflections
1425 independent reflections
1068 observed reflections [$F > 4.0\sigma(F)$]
$R_{\text{int}} = 0.028$
$\theta_{\max} = 22.5°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 9$
6 standard reflections frequency: 150 min intensity variation: 0%

Refinement

Refinement on F
Final $R = 0.044$
$wR = 0.048$
$S = 1.21$
1068 reflections
164 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F) + 0.0010F^2]$
$(\Delta/\sigma)_{\max} = 0.027$
$\Delta\rho_{\max} = 0.1$ e Å^{-3}
$\Delta\rho_{\min} = -0.1$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Nicolet *R*3*m*/*V* software, release 4.11. Cell refinement: Nicolet *R*3*m*/*V* software. Data reduction: Nicolet *R*3*m*/*V* software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXTL-Plus*, *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987).

The title compound was obtained from deoxybenzoin and HNO_3 according to Womack, Campbell & Dodds (1938). The product was purified by multifold recrystallization from anhydrous ethanol (m.p. 418–419 K). The IR spectrum of the title compound shows a band at 1687 cm^{-1} in the carbonyl stretching region while the corresponding Raman band is at 1694 cm^{-1}. Intensity data were collected with variable scan speed 3.5–15.0°