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Crystal structure of 3-(4-azidophenyl)pentane-2,4-dione, $C_{11}H_{11}N_3O_2$

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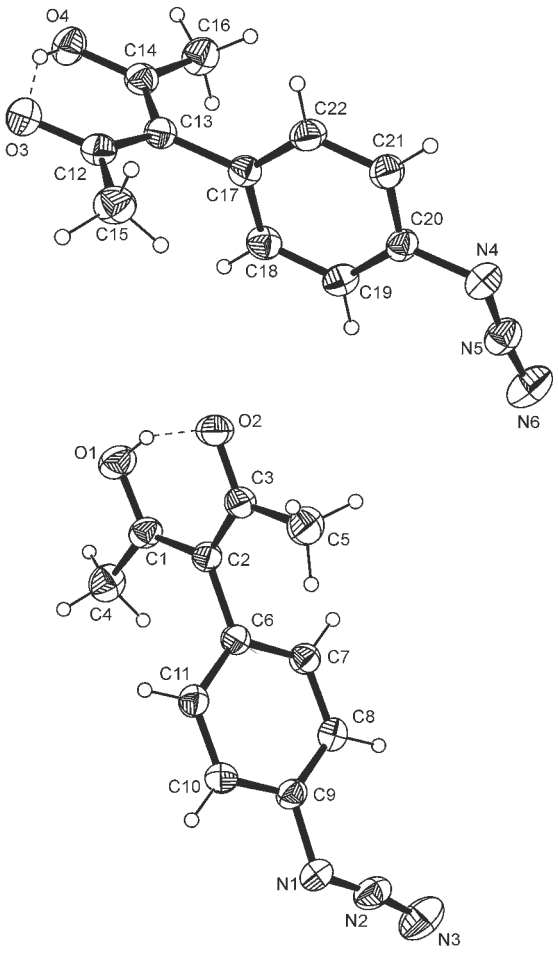

Abstract

$C_{11}H_{11}N_3O_2$, triclinic, $P\bar{1}$ (no. 2), a = 7.4695(7) Å, b = 10.6088(6) Å, c = 14.0710(9) Å, α = 92.586(5)°, β = 101.138(3)°, γ = 91.651(5)°, V = 1092.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.053, $wR_{ref}(F^2)$ = 0.141, T = 233 K.

Source of material

The title compound was prepared from 3-(4-nitrophenyl)-pentane-2,4-dione [1] by reduction, diazotization and substitution. The synthesis of the nitro and amino compounds has been described earlier [2], but it was not reproducible. Therefore, the synthesis of the nitro compound was conducted in analogy to an improved procedure [3]. Also, an improved reduction to the amino compound using $SnCl_2$ was employed in analogy to a published procedure [4]. In the next step, the respective diazonium hexafluorophosphate was prepared using aqueous sodium nitrite in the presence of hexafluorophosphoric acid. Finally, aqueous sodium azide was applied for the conversion to the desired product. The overall yield of this four-step process was 12 %. Suitable crystals were obtained from diethyl ether. IR and NMR spectra are available in the CIF.

Experimental details

The hydrogen atoms at O1 or O2 and O3 or O4 of the acetylacetonyl groups were calculated in the form of a 1 : 1 disorder model with occupancy of 0.5 for each hydrogen position. The hydrogen atoms were allowed to rotate about the C—O bonds. Furthermore, the crystal structure was analyzed for additional symmetry, but none was found.

Discussion

The new bifunctional intermediate represents an interesting building-block for the construction of metal-organic frameworks (MOFs) [5]. The MOFs are versatile carriers for catalysts [6], gases [7] and drugs [8]. The 1,3-dicarbonyl moiety lends itself to strong chelation of metal cations, whereas the azide group offers the opportunity for further functionalization by promising 'click chemistry', such as cycloadditions [9].

There are two independent molecules in the asymmetric unit. No strong intermolecular interactions are observed. The azide groups are rotated out of the phenyl ring plane. They both deviate from linearity and exhibit an N1–N2–N3 and N4–N5–N6 angle of 171°. The almost planar pentane-2,4-dione moieties are obviously not in conjugation with the aromatic ring and adopt almost perpendicular conformations with an interplanar phenyl / C1–C2–C3 angle of 78° and a phenyl / C12–C13–C14 angle of 85°, respectively. Not unexpectedly, they exist in the enol form. A slight alternation of bond lengths was observed in the enolic β-diketone moiety, being between formal single and double bonds. Thus, bond lengths are 1.309(3), 1.391(3), 1.415(4), and 1.282(3) Å in the sequence O1–C1–C2–C3–O2, and 1.295(3), 1.411(4), 1.395(3) and 1.298(3) Å for O3–C12–C13–C14–O4, comparable to previously reported 3-phenylpentane-2,4-diones [10-12]. The enol groups exhibit strong intramolecular hydrogen bonds (O1···O2 distance 2.460 Å, O3···O4 distance 2.464 Å). The enol hydrogens are delocalized due to a dynamic fluctuation between the oxygen atoms and were calculated with 0.5 occupancies (only one shown). Interestingly, attempted refinement without restraints resulted in the following bond lengths: d(O1—H) = 1.11(5) Å, d(O2—H) = 1.43(5) Å, d(O3—H) = 1.24(6) Å, d(O4—H) = 1.32(6) Å, and a slightly higher R value. In this alternative model, the enolic hydrogen atoms move to the center midway between the oxygens, as discussed earlier [12,13]. However, the electron density was deemed too small to warrant refinement as an enol hydrogen. Therefore, we favor the interpretation of this structure as a pair of rapidly interconverting tautomers.

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Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.04 × 0.2 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.94 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ/ω
$2\theta_{max}$:	47.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5448, 3416
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2245
$N(param)_{refined}$:	298
Programs:	SHELXS-97 [14], SHELXL-97 [15]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1O)	2*i*	0.50	0.2852	0.8817	0.4859	0.102
H(2O)	2*i*	0.50	0.3821	0.8323	0.4837	0.095
H(3O)	2*i*	0.50	0.4017	0.6700	0.0015	0.094
H(4O)	2*i*	0.50	0.2973	0.6252	0.0054	0.094
H(4A)	2*i*		0.2571	1.1669	0.6155	0.104
H(4B)	2*i*		0.2421	1.0834	0.7044	0.104
H(4C)	2*i*		0.0843	1.0751	0.6110	0.104
H(5A)	2*i*		0.7137	0.7036	0.6518	0.106
H(5B)	2*i*		0.7922	0.8425	0.6841	0.106
H(5C)	2*i*		0.8067	0.7831	0.5807	0.106
H(7)	2*i*		0.5033	0.8483	0.8148	0.059
H(8)	2*i*		0.6659	0.9288	0.9635	0.061
H(10)	2*i*		0.8319	1.2281	0.8340	0.067
H(11)	2*i*		0.6711	1.1477	0.6858	0.063
H(15A)	2*i*		0.8581	0.6467	0.0983	0.101
H(15B)	2*i*		0.8149	0.6823	0.2019	0.101
H(15C)	2*i*		0.7960	0.7842	0.1220	0.101
H(16A)	2*i*		0.0976	0.4035	0.0970	0.096
H(16B)	2*i*		0.1888	0.4530	0.2037	0.096
H(16C)	2*i*		0.2830	0.3475	0.1494	0.096
H(18)	2*i*		0.5052	0.6174	0.3299	0.063
H(19)	2*i*		0.6670	0.5329	0.4683	0.063
H(21)	2*i*		0.8823	0.2850	0.3012	0.068
H(22)	2*i*		0.7195	0.3700	0.1643	0.066

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*i*	0.2278(3)	0.9409(2)	0.5043(1)	0.056(1)	0.079(2)	0.061(1)	–0.004(1)	–0.007(1)	–0.001(1)
O(2)	2*i*	0.4745(3)	0.7923(2)	0.5038(1)	0.070(2)	0.060(1)	0.056(1)	–0.0039(9)	0.009(1)	–0.0066(9)
O(3)	2*i*	0.5042(3)	0.7048(2)	0.0202(1)	0.072(1)	0.061(1)	0.055(1)	0.002(1)	0.012(1)	0.0084(9)
O(4)	2*i*	0.2296(3)	0.5722(2)	0.0240(1)	0.054(1)	0.070(1)	0.059(1)	0.0069(9)	–0.002(1)	0.0088(9)
N(1)	2*i*	0.8790(3)	1.1408(2)	0.9988(2)	0.073(2)	0.062(2)	0.055(2)	0.001(1)	–0.012(1)	0.003(1)
N(2)	2*i*	0.8660(3)	1.0947(2)	1.0765(2)	0.052(2)	0.081(2)	0.057(2)	0.014(1)	–0.001(1)	–0.010(1)
N(3)	2*i*	0.8712(4)	1.0630(3)	1.1523(2)	0.085(2)	0.141(3)	0.053(2)	0.015(2)	0.012(2)	0.002(2)
N(4)	2*i*	0.9070(3)	0.3481(2)	0.4780(2)	0.056(2)	0.072(2)	0.048(2)	0.002(1)	0.003(1)	0.006(1)
N(5)	2*i*	0.8763(3)	0.3740(2)	0.5599(2)	0.047(2)	0.073(2)	0.059(2)	–0.012(1)	0.001(1)	0.010(1)
N(6)	2*i*	0.8663(4)	0.3886(3)	0.6389(2)	0.075(2)	0.123(2)	0.052(2)	–0.010(2)	0.005(2)	0.010(2)
C(1)	2*i*	0.3093(4)	0.9832(2)	0.5912(2)	0.045(2)	0.060(2)	0.054(2)	–0.007(1)	0.004(1)	0.005(1)
C(2)	2*i*	0.4727(3)	0.9344(2)	0.6370(2)	0.045(2)	0.046(1)	0.047(2)	–0.004(1)	0.005(1)	0.005(1)
C(3)	2*i*	0.5525(4)	0.8381(2)	0.5880(2)	0.056(2)	0.049(2)	0.047(2)	–0.004(1)	0.008(1)	0.003(1)
C(4)	2*i*	0.2150(4)	1.0860(3)	0.6342(2)	0.054(2)	0.079(2)	0.073(2)	0.014(2)	0.008(2)	0.004(2)
C(5)	2*i*	0.7317(4)	0.7874(3)	0.6297(2)	0.073(2)	0.071(2)	0.067(2)	0.022(2)	0.011(2)	–0.002(2)
C(6)	2*i*	0.5705(3)	0.9881(2)	0.7338(2)	0.040(2)	0.045(1)	0.049(2)	0.003(1)	0.007(1)	0.002(1)
C(7)	2*i*	0.5707(4)	0.9252(2)	0.8182(2)	0.049(2)	0.050(2)	0.049(2)	–0.002(1)	0.009(1)	0.003(1)
C(8)	2*i*	0.6678(4)	0.9727(2)	0.9071(2)	0.052(2)	0.054(2)	0.049(2)	0.005(1)	0.010(1)	0.009(1)
C(9)	2*i*	0.7673(3)	1.0851(2)	0.9122(2)	0.046(2)	0.053(2)	0.047(2)	0.008(1)	–0.000(1)	–0.002(1)
C(10)	2*i*	0.7664(4)	1.1505(2)	0.8300(2)	0.054(2)	0.051(2)	0.058(2)	–0.006(1)	0.001(1)	0.001(1)
C(11)	2*i*	0.6699(4)	1.1025(2)	0.7416(2)	0.054(2)	0.050(2)	0.050(2)	–0.002(1)	0.006(1)	0.009(1)
C(12)	2*i*	0.5866(4)	0.6533(2)	0.0976(2)	0.056(2)	0.050(2)	0.048(2)	0.002(1)	0.011(1)	–0.004(1)
C(13)	2*i*	0.4963(3)	0.5618(2)	0.1430(2)	0.044(2)	0.045(1)	0.048(2)	0.004(1)	0.007(1)	0.000(1)
C(14)	2*i*	0.3173(4)	0.5227(2)	0.1014(2)	0.049(2)	0.051(2)	0.050(2)	0.007(1)	0.007(1)	–0.003(1)
C(15)	2*i*	0.7808(4)	0.6952(3)	0.1330(2)	0.063(2)	0.069(2)	0.067(2)	–0.015(2)	0.011(2)	0.001(2)
C(16)	2*i*	0.2125(4)	0.4229(3)	0.1414(2)	0.051(2)	0.072(2)	0.067(2)	–0.008(1)	0.005(1)	0.008(1)
C(17)	2*i*	0.5958(3)	0.5046(2)	0.2320(2)	0.038(1)	0.047(1)	0.049(2)	–0.002(1)	0.007(1)	–0.001(1)
C(18)	2*i*	0.5823(4)	0.5503(2)	0.3236(2)	0.050(2)	0.054(2)	0.055(2)	0.007(1)	0.014(1)	–0.002(1)
C(19)	2*i*	0.6789(4)	0.5003(2)	0.4067(2)	0.050(2)	0.062(2)	0.045(2)	–0.000(1)	0.010(1)	–0.003(1)
C(20)	2*i*	0.7930(3)	0.4020(2)	0.3978(2)	0.039(2)	0.050(2)	0.048(2)	–0.006(1)	–0.000(1)	0.006(1)
C(21)	2*i*	0.8067(4)	0.3530(2)	0.3073(2)	0.057(2)	0.057(2)	0.052(2)	0.014(1)	0.004(1)	–0.003(1)
C(22)	2*i*	0.7092(4)	0.4041(2)	0.2258(2)	0.056(2)	0.060(2)	0.046(2)	0.009(1)	0.005(1)	–0.007(1)

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