Crystal structure of bis(phthalazino)azine, $C_8H_6N_3$

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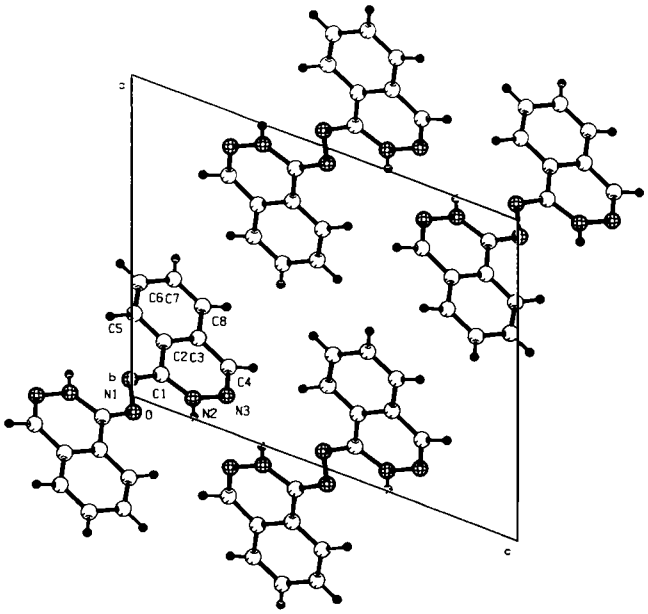
Received January 15, 2002, accepted and available on-line March 21, 2002; CCDC-No. 1267/794



Abstract

$C_8H_6N_3$, monoclinic, $P12_1/c1$ (No. 14), $a = 10.847(3)$ Å, $b = 4.706(1)$ Å, $c = 14.058(4)$ Å, $\beta = 110.57(1)°$, $V = 671.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.046$, $wR_{ref}(F^2) = 0.120$, $T = 293$ K.

Source of material

The compound was isolated as a by-product, in the recrystallization of the 1,4-dihydrazinophthalazine, obtained by the reaction of 1,2-dicyanobenzene and hydrazine.

Discussion

As a part of a work on the ligand behaviour and reactivity of azines, [1] here we report the characterization of the bis(phthalazino)azine. The crystal structure of the title compound is depicted in the figure. The distance C4—N3 is equal to 1.289(4) Å, clearly indicating a double bond. The bond lengths N2—N3, N2—C1 and C1—N1 are 1.360(3) Å, 1.373(4) Å and 1.296(3) Å, respectively; these data suggest a single bond between the endocyclic nitrogen atoms N2 and N3, while the double bond is assigned to C1—N1. In the final stage of the refinement, an hydrogen atom located 0.90(3) Å from N2 confirms this assumption. The hetero cycle is pratically planar, C2 and N2 atoms show the largest deviation from the plane, –0.016(3) Å and 0.016(2) Å, respectively. It forms with the phenyl ring a dihedral angle of 2.4(1)°. In the crystal structure of the methyl derivative, the bis(2-methylphthalazino)azine [2], an analogous arrangement was found; the bond distances and endocyclic bond angles are in agreement with those determined in the present work. The significant differences are at the esocyclic angles at C1: in particular ∠N1–C1–N2 and ∠N1–C1–C2 are 112.5° and 132.7° vs 123.0(2)° and 121.0 (2)° in the present work. This is probably due to the presence at N2 of the methyl instead of the hydrogen substituent. Moreover, in the bis(2-methylphthalazino)azine the methyl substituted nitrogen is *trans* to the azine bond, while in the bis(phthalazino)azine an intramolecular hydrogen bond stabilizes the *cis* isomer. The H2 hydrogen is, in effect, involved in a bifurcated hydrogen bond: one hydrogen bond is intramolecular, i.e. N2–H2N···N1A, with N1A symmetry related atom (d(N2···N1A) = 2.569(3) Å; d(H2N···N1A) = 2.24(3) Å, ∠N2–H2N–N1A = 101(2)°), and the other is intermolecular, N2–H2N···N3(i): d(N2···N3(i)) = 3.106(4) Å; d(H2N···N3(i)) = 2.23(3) Å; ∠N2–H2N–N3(i) = 146(2)°; (i) = 2–x, 1/2–y, 1/2–z.

Table 1. Data collection and handling.

Crystal:	colourless tablet, size 0.10 × 0.25 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.92 cm^{-1}
Diffractometer, scan mode:	Bruker AMX Smart 1000, $\omega/2\theta$
$2\theta_{max}$:	53.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3708, 1388
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 598
$N(param)_{refined}$:	125
Programs:	SHELXS-97 [3], SHELXL-97[4], ORTEP [5], PLUTO [6]

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

Atom	Site	x	y	z	U_{iso}
H(5)	4e	0.779(2)	0.140(5)	0.557(2)	0.066(8)
H(8)	4e	0.614(2)	–0.414(5)	0.255(2)	0.068(8)
H(6)	4e	0.602(2)	–0.175(5)	0.530(2)	0.076(9)
H(2N)	4e	0.994(3)	0.410(6)	0.339(2)	0.072(9)
H(7)	4e	0.522(3)	–0.452(6)	0.386(2)	0.10(1)
H(4)	4e	0.771(2)	–0.200(4)	0.185(2)	0.053(6)

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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}
N(1)	4*e*	0.9509(2)	0.4088(4)	0.5047(1)	0.046(1)	0.047(1)	0.047(1)	–0.004(1)	0.017(1)	0.000(1)
N(2)	4*e*	0.9370(2)	0.2722(5)	0.3407(1)	0.059(2)	0.058(2)	0.045(1)	–0.009(1)	0.022(1)	–0.008(1)
N(3)	4*e*	0.8903(2)	0.1122(5)	0.2549(1)	0.066(2)	0.078(2)	0.047(1)	–0.007(1)	0.021(1)	–0.013(1)
C(1)	4*e*	0.8990(2)	0.2550(5)	0.4240(2)	0.043(2)	0.040(1)	0.042(1)	0.006(1)	0.015(1)	0.002(1)
C(2)	4*e*	0.7938(2)	0.0548(5)	0.4163(2)	0.038(1)	0.041(1)	0.045(1)	0.005(1)	0.009(1)	0.006(1)
C(5)	4*e*	0.7409(3)	0.0246(6)	0.4932(2)	0.053(2)	0.056(2)	0.055(2)	–0.001(2)	0.020(1)	0.006(1)
C(8)	4*e*	0.6390(3)	–0.2958(6)	0.3165(2)	0.050(2)	0.057(2)	0.064(2)	–0.004(2)	0.002(2)	–0.002(2)
C(3)	4*e*	0.7432(2)	–0.1054(5)	0.3277(2)	0.041(2)	0.051(2)	0.052(2)	0.005(1)	0.007(1)	0.003(1)
C(6)	4*e*	0.6386(3)	–0.1628(7)	0.4796(2)	0.054(2)	0.079(2)	0.074(2)	–0.000(2)	0.027(2)	0.023(2)
C(4)	4*e*	0.7988(3)	–0.0679(6)	0.2503(2)	0.062(2)	0.074(2)	0.053(2)	–0.010(2)	0.016(2)	–0.016(2)
C(7)	4*e*	0.5878(3)	–0.3184(7)	0.3910(2)	0.050(2)	0.070(2)	0.078(2)	–0.010(2)	0.007(2)	0.017(2)

References

1. Amadei, E.; Carcelli, M.; Ianelli, S.; Cozzini, P.; Pelagatti, P.; Pelizzi, C.: Ligand behaviour and reactivity of phenyl-2-pyridylketone azine. Structure of two polymorphic forms of the azine and a copper complex of the 3-phenyltriazolo[1,5-α]pyridine. J. Chem. Soc., Dalton Trans. (1998) 1025-1029.
2. Litvinov, I. A.; Buzykin, B. I.: Bis(2-methylphthalazion)azine. Zh. Obshch. Khim. **66** (1996) 1741.
3. Sheldrick, G. M.: SHELXS-97, a program for automatic solution of crystal structures. University of Göttingen, Germany 1997.
4. Sheldrick, G. M.: SHELXL-97, a program for refining crystal structures. University of Göttingen, Germany 1997.
5. Johnson, C. K.: ORTEP, Rep. ORNL-3794, Oak Ridge, TN, USA 1965.
6. Motherwell, W. D. S.: PLUTO, University of Cambridge, UK 1976.