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Crystal Structure of Hydrazone Form of 1-Butyl-3-cyano-6-hydroxy-4-methyl-5-(2-nitrothiazolylazo)-2(1H)-pyridone

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ABSTRACT

The crystal structure of 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-nitrothiazolylazo)-2(1H)-pyridone ($C_{14}H_{14}N_6O_4S$, mol. wt. 362.37 a.m.u.) has been determined from X-ray diffraction data: monoclinic $P2_1/n$, a = 12.949(6) Å, b = 5.912(3) Å, c = 21.149(10) Å, β = 90.23(5)°, V = 1613(2) Å^3, Z = 4, D_c = 1.49 g cm^{-3}, F(000) = 752, μ(MoK$_\alpha$) = 2.2 cm^{-1}, λ(MoK$_\alpha$) = 0.71073 Å. The molecular structure is that of the hydrazone tautomer with an N–N distance of 1.341(9) Å. The entire molecule is essentially planar except for the nitro and the butyl groups. The tautomeric form is stabilized by a strong intramolecular hydrogen bond [N···O = 2.615(9) Å]. © *1997 Elsevier Science Ltd. All rights reserved*

Keywords: Azo dye, hydrazone, pyridone, thiazolylazotautomerism.

INTRODUCTION

Disperse monoazo dyes prepared from enol-type coupling components exhibit azo-hydrazone tautomerism. Numerous investigations have been carried out and a variety of techniques have been used to establish the correct structure in solution.[1–4] Cheng *et al.*[5] and Cee *et al.*[6] reported the existence of some azopyridone form structures in the crystal form of the dyes or in solutions. Although there have been several crystallographic studies of monoazo disperse dyes,[7–14] the crystal structure of azopyridone-type derivatives has not yet been described.

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One of us (N.E.) has reported the synthesis of thiazolylazopyridones and benzothiazolylazopyridones and found the existence of a hydrazone–common anion equilibrium in solution. In continuation of this work we now report the crystal structure of the hydrazone form of 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-nitrothiazolylazo)-2(1H)-pyridone and discuss the solid-state tautomer, the nature of the intramolecular hydrogen bonding, and the effects of the substituents on the molecular geometry.

EXPERIMENTAL

The title compound, prepared by Ertan and Eyduran,[15] was recrystallized from chloroform as orange needles. Intensity data were collected on an

TABLE 1
Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Compound	$C_{14}H_{14}N_6O_4S$
Colour/shape	orange/needle
Formula wt.	362.37
Space group	$P2_1/n$
Temp. (°C)	23
Cell constants (no. of reflections > θ used)	12 reflections > 5°
a (Å)	12.949(6)
b (Å)	5.912(3)
c (Å)	21.149(10)
β (deg)	90.23(5)
Cell vol. (Å^3)	1619(2)
Formula units/unit cell	4
D_{calc} (g cm^{-3})	1.49
μ_{calc} (cm^{-1})	2.2
Diffractometer/scan	Enraf–Nonius CAD4/ω–2θ
Range of relative transm. factors,%	89.3–99.9
Radiation, graphite monochromator	MoK$_\alpha$ $\lambda = 0.71073$ Å
Max crystal dimensions (mm)	0.16×0.08×0.64
Scan width	0.7 + 1.5 tan θ
Standard reflections	3 measured every 60 min
Decay of standards	2.9%
Reflections measured	2563
2θ range (deg)	2 to 45.6
Range of h,k,l	$-14 \leq h \leq 0$, $-6 \leq k \leq 0$, $-23 \leq l \leq 23$
Reflections observed	656 [$F_o \geq 3\sigma(F_o)$]
Corrections applied	Lorentz-pol., linear-decay, empirical-absorption
Structure solution	Direct methods
No. of parameters varied	229
Weights	$4F_o/\sigma(F_o)$
GOF	1.29
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0424
R_w	0.0429
Largest feature final diff. map (eÅ^{-3})	0.20

Enraf–Nonius CAD4 diffractometer equipped with MoK_α(0.71073 Å) radiation using the $\omega-2\theta$ scan technique.[16] The raw data were corrected for absorption using the ψ-scan data. The structure was solved by direct methods and refined by full-matrix least squares minimizing $\sum w (F_o - F_c)$.[17] Hydrogen atoms bonded to carbon atoms were placed in the calculated position and not refined. The hydrogen atom bonded to N4 atom was located

TABLE 2
Final Fractional Atomic Coordinates and Thermal Parameters (Å^2) $B_{eq} = \sum_i \sum_j B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$

Atom	*x/a*	*y/a*	*z/a*	B_{eq}
S1′	0.3127(2)	−0.9419(5)	0.9999(1)	3.77(6)
O1	−0.0080(4)	−0.498(1)	0.9126(3)	4.3(2)
O2	0.0939(5)	0.110(1)	0.7984(3)	4.5(2)
O3	0.4667(5)	−0.243(1)	0.0526(3)	7.2(2)
O4	0.3636(5)	−0.479(1)	0.0976(3)	7.1(2)
N1	0.0404(5)	−0.200(1)	0.8522(3)	2.4(2)
N2	0.3580(6)	0.133(1)	0.7854(4)	4.9(2)
N3	0.2013(5)	−0.620(1)	0.9305(3)	2.8(2)
N3′	0.1260(5)	−0.095(1)	0.0203(3)	3.1(2)
N4	0.1359(5)	−0.761(1)	0.9599(3)	3.1(2)
N5	0.3795(5)	−0.311(1)	0.0664(4)	5.1(2)
C2	0.1175(7)	−0.060(2)	0.8262(4)	3.3(2)
C2′	0.1802(7)	−0.933(2)	0.9941(4)	2.8(2)
C3	0.2254(6)	−0.132(1)	0.8373(4)	2.3(2)
C4	0.2539(6)	−0.317(2)	0.8708(4)	2.7(2)
C4′	0.1969(6)	−0.238(2)	0.0490(4)	3.3(2)
C5	0.1707(6)	−0.449(2)	0.8976(4)	2.8(2)
C5′	0.2945(6)	−0.188(2)	0.0433(4)	3.0(2)
C6	0.0614(6)	−0.389(2)	0.8883(4)	2.9(2)
C10	−0.0667(6)	−0.146(2)	0.8354(4)	3.4(2)
C11	−0.0981(7)	−0.225(2)	0.7697(4)	4.3(3)
C12	−0.1055(7)	−0.479(2)	0.7641(4)	4.7(3)
C13	−0.1271(7)	−0.552(2)	0.6970(4)	6.3(3)
C14	0.2979(6)	0.020(1)	0.8089(4)	3.3(2)
C15	0.3633(6)	−0.382(2)	0.8764(4)	4.0(3)
H1	0.070(5)	−0.74(1)	0.957(3)	3.9*
H2	0.175	−0.366	0.073	4.6*
H3	0.370	−0.514	0.902	5.1*
H4	0.391	−0.410	0.836	5.1*
H5	0.400	−0.261	0.896	5.1*
H6	−0.076	0.013	0.837	4.5*
H7	−0.111	−0.217	0.865	4.5*
H8	−0.048	−0.173	0.740	5.5*
H9	−0.163	−0.161	0.759	5.5*
H10	−0.160	−0.530	0.790	5.6*
H11	−0.042	−0.545	0.778	5.6*
H12	−0.132	−0.712	0.694	7.9*
H13	−0.190	−0.485	0.683	7.9*
H14	−0.072	−0.500	0.671	7.9*

Starred atoms were refined isotropically.

in a difference map and its positional parameters were refined. A final refinement with anisotropic temperature factors for non-hydrogen atoms converged to $R = 0.042$. Crystal data and a summary of intensity data collection and structure refinement are given in Table 1. Final fractional atomic coordinates and thermal parameters are listed in Table 2.

Bond lengths, bond angles and some selected torsion angles are given in Table 3. Figure 1 shows a view of the molecule and Fig. 2 shows the crystal packing diagram as drawn by the ORTEP program.[18] A list of structure factors and geometric parameters involving H-atoms may be obtained from the authors of this paper.

TABLE 3

Bond Lengths (Å), Bond Angles (deg), and some Selected Torsion Angles (deg)

S1′–C2′	1.720(9)	N3′–C4′	1.38(1)
S1′–C5′	1.738(9)	N4–C2′	1.37(1)
O1–C6	1.22(1)	N5–C5′	1.40(1)
O2–C2	1.20(1)	C2–C3	1.48(1)
O3–N5	1.23(1)	C3–C4	1.35(1)
O4–N5	1.21(1)	C3–C14	1.44(1)
N1–C2	1.41(1)	C4–C5	1.45(1)
N1–C6	1.38(1)	C4–C15	1.47(1)
N1–C10	1.47(1)	C4′–C5′	1.30(1)
N2–C14	1.14(1)	C5–C6	1.47(1)
N3–N4	1.341(9)	C10–C11	1.52(1)
N3–C5	1.29(1)	C11–C12	1.51(1)
N3′–C2′	1.31(1)	C12–C13	1.51(1)
C2′–S1′–C5′	85.7(4)	C4–C3–C14	123.3(7)
C2–N1–C6	123.7(7)	C3–C4–C5	115.9(7)
C2–N1–C10	116.4(7)	C3–C4–C15	120.9(8)
C6–N1–C10	119.7(7)	C5–C4–C15	123.1(8)
N4–N3–C5	123.0(7)	N3′–C4′–C5′	117.7(8)
C2′–N3′–C4′	105.9(7)	N3–C5–C4	113.9(7)
N3–N4–C2′	116.2(6)	N3–C5–C6	123.5(8)
O3–N5–O4	123.5(8)	C4–C5–C6	122.5(8)
O3–N5–C5′	117.9(8)	S1′–C5′–N5	120.5(6)
O4–N5–C5′	118.6(7)	S1′–C5′–C4′	111.7(7)
O2–C2–N1	120.3(8)	N5–C5′–C4′	127.7(9)
O2–C2–C3	123.9(8)	O1–C6–N1	121.2(7)
N1–C2–C3	115.8(7)	O1–C6–C5	121.8(8)
S1′–C2′–N3′	119.0(7)	N1–C6–C5	117.0(7)
S1′–C2′–N4	118.2(6)	N1–C10–C11	113.8(7)
N3′–C2′–N4	122.7(7)	C10–C11–C12	113.2(8)
C2–C3–C4	125.0(7)	C11–C12–C13	111.7(8)
C2–C3–C14	111.7(7)	N2–C14–C3	176.8(9)
C2–N1–C10–C11	78.2(9)		
C6–N1–C10–C11	−97.8(9)		
C5–N3–N4–C2′	−178.7(8)		
N4–N3–C5–C4	179.0(7)		
N3–N4–C2′–N3′	−173.4(8)		

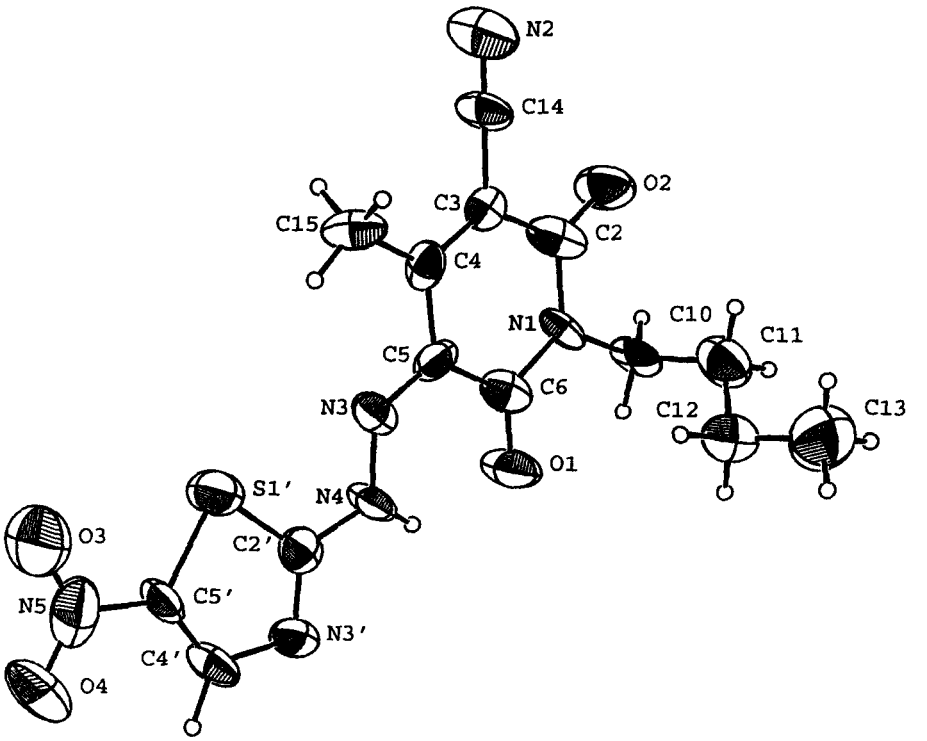


Fig. 1. ORTEP drawing of the compound with 50% probability thermal ellipsoids and the numbering scheme. H-atoms are shown as circles of arbitrary small diameter.

RESULTS AND DISCUSSION

As shown in Scheme 1, there are two possible tautomeric forms for the title compound, the diketohydrazone form (**Ia**) and the azohydroxypyridone form (**Ib**).

Comprehensive IR studies show that this dye exists completely in the hydrazone form in the solid state and predominantly in the hydrazone form in $CHCl_3$.[15]

The structural results for this compound support these findings. The location of the H-atom on N4 rather than O1 and the lengths of the N3–N4, N3–C5, and C6–O1 bonds indicate that the molecule exists as the diketohydrazone form (**Ia**) in the solid state. The N3–C5 [1.29(1) Å] and C6–O1 [1.22(1) Å] bond lengths are consistent with the double bond character expected in the hydrazone form.[11] These values are comparable to those in some related compounds.[7–10] The significant difference between the lengths of N3–C5, 1.29(1) Å and N4–C2′, 1.37(1) Å is also a sensitive indicator of the hydrazone character.

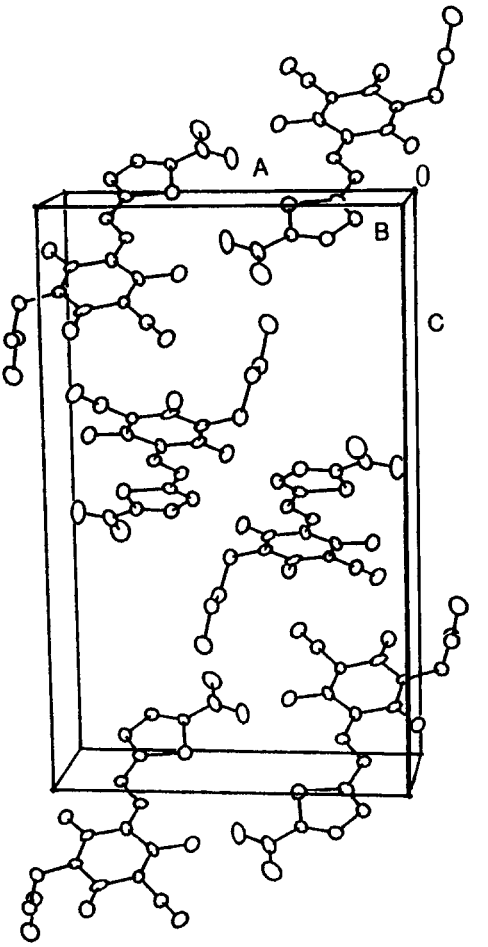
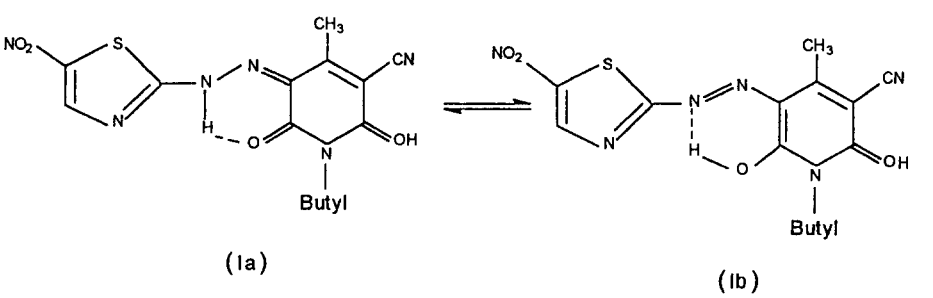


Fig. 2. The overall packing diagram of the molecule.



Scheme 1.

An important feature of (**Ia**) is the strong intramolecular hydrogen bond between the hydrazone hydrogen and carbonyl oxygen. The lengths of N4–H1 and O1···H1 are 0.86(6) and 1.98(6) Å with that of N4···O1 being 2.622(9) Å. The O1–C6–C5–N3–N4–H1 ring completed by the hydrogen bond is essentially planar, with the hydrogen atom deviating 0.033 Å from the least-squares plane. The entire molecule is nearly planar except for the nitro and butyl groups. The dihedral angle between the planes of the pyridone ring and the OCCNNH chelate ring is 1.79(3)°. The thiazolyl ring plane slightly deviates from coplanarity with a N3–N4–C2′–N3′ torsion angle of −173.4(8)°. The nitro group is twisted out of the plane of this ring by 4.5(7)°; the butyl group is nearly perpendicular to the plane of the pyridone ring with a torsion angle of −97.8(9)° for C6–N1–C10–C11. According to the results reported previously, the presence of the predominant hydrazone tautomer and intramolecular hydrogen bonding account for the observed planarity.[9–14]

All intermolecular contacts were examined. With the exceptions of the short O2–H11 [2.727(6) Å] and N2–H4 [2.937(6) Å] (H4 and H11 at x, $y+1$, z) distances, the minimum intermolecular distances conform to normal van der Waals interactions. As shown in Fig. 2, the molecules are disposed on top of each other in an antiparallel fashion with a displacement which avoids superposition of the pyridone rings.

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REFERENCES

1. Lyčka, A. & Mustroph, H., *J. Prakt. Chem.*, **331** (1989) 11.
2. Peng, Q., Li, M., Gao, K. & Cheng, L., *Dyes and Pigments*, **14** (1990) 89.
3. Shawali, A. S., Harb, N. M. S. & Badahdah, K. O., *J. Heterocycl. Chem.*, **22** (1985) 1397.
4. Hawkes, G. E., Randall, E. W., Elguero, J. & Marzin, C. J., *J. Chem. Soc., Perkin Trans.*, **2** (1977) 1024.
5. Cheng, L., Chen, X., Gao, K., Hu, J. & Griffiths, J., *Dyes and Pigments*, **7**(5) (1986) 373.
6. Cee, A., Horakova, B. & Lyčka, A., *Dyes and Pigments*, **9** (1988) 357.
7. Mez, H. C., *Ber. Bunsenges. Phys. Chem.*, **72** (1968) 389.
8. Grainger, C. T. & McConnell, J. F., *Acta Crystallogr., Sect. B*, **25** (1969) 1962.
9. Guggenberger, L. J. & Teufer, G., *Acta Crystallogr., Sect. B*, **31** (1975) 785.

10. Desiraju, G. R., *J. Chem. Soc., Perkin Trans. 2*, **7** (1983) 1025.
11. Pendergrass, D. B., Jr, Paul, I. C. & Curtin, D. Y., *J. Am. Chem. Soc.*, **94** (1972) 8730.
12. McIntosh, S. A., Freeman, H. S. & Singh, P., *Text. Res. J.*, **59** (1989) 389.
13. Ide, S., Kendi, E. & Ertan, N., *J. Chem. Cryst.*, **24** (1994) 743.
14. Ojala, W. H., Gleason, W. B., Richardson, T. I. & Loverien, R. E., *Acta Crystallogr., Sect. C*, **50** (1994) 1615.
15. Ertan, N. & Eyduran, F., *Dyes and Pigments*, **27** (1995) 313.
16. Enraf–Nonius, *CAD4 Software*, Version 1.1, Enraf–Nonius, Delft, The Netherlands, 1993.
17. Fair, C.K., *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*, Enraf–Nonius, Delft, The Netherlands, 1990.
18. Johnson, C.K., *ORTEP. Report ORNL-5138*, Oak Ridge National Laboratory, TN, U.S.A., 1976.