ELSEVIER

Dyes and Pigments, Vol. 32, No. 4, pp. 237–244, 1996

PII:S0143-7208(96)00028-9 0143-7208/96 $15.00+0.00

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

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(Received 9 February 1996; accepted 1 April 1996)

ABSTRACT

The structural results clearly indicate that 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-thiazolylazo)-2(1H)-pyridone, ($C_{14}H_{15}N_5O_2S$), exists primarily as the hydrazone tautomer in the solid state. The molecule is nearly planar not regarding the butyl group. Some of the bond lengths and angles are distorted due to π-electron delocalization and strain. A strong intramolecular N-H···O hydrogen bond was found [N···O = 2.53(1) Å]. The crystallographic parameters are as follows: triclinic $P\bar{1}$, a = 5.972(4) Å, b = 7.732(5) Å, c = 17.348(9) Å, α = 85.62(5)°, β = 79.24(6)°, γ = 78.41(7)°, V = 770.4(9) Å^3, Z = 2, D_c = 1.37 g cm^{-3}, μ(MoK$_\alpha$) = 2.1 cm^{-1}, R = 0.045, G.O.F. = 1.78.

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] On the other hand, there have been only a few crystallographic studies of these compounds. Cheng *et al.*,[5] and Cee *et al.*,[6] reported that some azopyridone structures existed in the crystal form of the dyes or in solutions.

In previous work,[7] we have reported the synthesis of thiazolylazopyridones and benzothiazolylazopyridones and found the existence of hydrazone–common anion equilibrium in solution. In the solid state IR spectra of the dyes, the presence of two carbonyl bands suggested that these compounds exist as the hydrazone form in the solid state. In continuation of this work

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we now report the crystal structure of the hydrazone form of 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-thiazolylazo)-2(1H)-pyridone and discuss the effects of the substituents on the molecular geometry.

EXPERIMENTAL

The synthesis and purification of the dye has been previously reported.[7] Recrystallization from chloroform gave orange needles (λ_{max} (ethanol) = 430 nm; m.p. = 212–213°C).

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

Compound	$C_{14}H_{15}N_5O_2S$
Color/shape	orange/needle
For. wt.	317.37
Space group	$P\bar{1}$
Temp., °C	23
Cell constants (no. reflections > θ used)	14 reflections > 2°–18°
a, Å	5.972 (4)
b, Å	7.732 (5)
c, Å	17.348 (9)
α, deg	85.62 (5)
β, deg	79.24 (6)
γ, deg	78.41 (7)
Cell vol, Å^3	770.4 (9)
Formula units/unit cell	2
D_{calc}, g cm^{-3}	1.37
μ_{calc}, cm^{-1}	2.1
Diffractometer/scan	Enraf Nonius CAD4/ω-2θ
Range of relative transm. factors, %	88.3–99.5
Radiation, graphite monochromator	M_oK_α λ = 0.71073 Å
Max crystal dimensions, mm	0.08×0.10×0.60
Scan width	1.4 + 1.5 tan θ
Standard reflections	3 measured every 60 min
Decay of standards	1.4%
Reflections measured	1747
2θ range, deg	5.6–44.0
Range of h, k, l	$0 \leq h \leq 5$, $-7 \leq k \leq 7$, $-17 \leq l \leq 17$
Reflections observed	441 [$F_o \geq 3\sigma$ (F_o)]
Corrections applied	Lorentz-pol., linear-decay, empirical-absorption
Source of structure factors used	*International Tables for X-Ray Crystallography* Vol. IV[10]
Structure solution	Direct methods
Treatment of hydrogen atoms	Located and not refined except H6
No. of parameters varied	202
Weights	$4F_o/\sigma(F_o)$
G.O.F.	1.78
$R = \Sigma \parallel F_o\| - \|F_c\| / \Sigma\|F_o\|$	0.045
R_w	0.051
Largest feature final diff. map, eÅ^{-3}	0.20

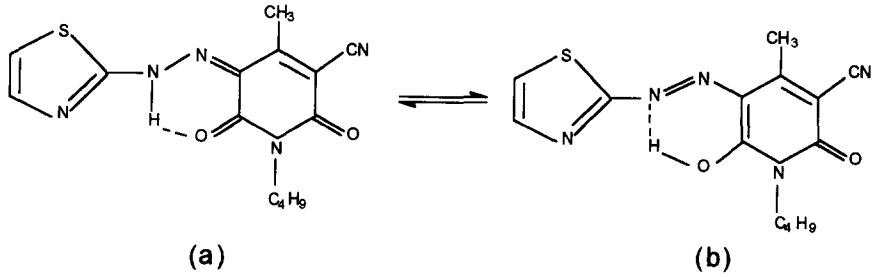
The X-ray diffraction data collection was performed on an Enraf-Nonius CAD4 diffractometer equipped with MoK_α (0.71073 Å) radiation using ω-2θ scan technique. The raw data were corrected for absorption using the ψ-scan data. The structure was solved by direct methods using SIMPEL:(MolEN).[8] All non-hydrogen atoms rather than two C-atoms were located in the first electron density synthesis and refined by full-matrix least squares minimizing $\Sigma W(F_o - F_c)$. The missing C-atoms and H-atom bonded to N4 were found in a difference Fourier map and refined. The other H-atoms were generated in idealized positions 0.95 Å from the bonded C-atom and not refined. Final refinement with anisotropic temperature factors for non-H atom converged to $R = 0.045$. Crystal data and 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 and selected geometric parameters in Table 3. Figure 1 shows a view of the molecule as drawn by the ORTEP[9] program and Figs 2 and 3 show the crystal packing arrangement and the unit cell as drawn by the PLUTO program.[11] A list of structure factors, hydrogen atom coordinates and geometric parameters involving H-atoms may be obtained from the authors of this paper.

TABLE 2
Fractional atomic coordinates and thermal parameters (Å^2)

Atom	x/a	$B_{eq} = 4/3\ \Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ y/b	z/c	B_{eq}
S1′	0.0156 (7)	0.1808 (6)	0.3762 (3)	5.8 (1)
O1	0.628 (1)	−0.183 (1)	0.1614 (5)	5.4 (3)
C5	0.644 (2)	−0.171 (2)	0.2971 (8)	3.7 (4)
N1	0.949 (2)	−0.331 (2)	0.2031 (6)	4.7 (3)
N3	0.439 (2)	−0.065 (1)	0.3133 (6)	4.4 (3)
C3	0.997 (2)	−0.329 (2)	0.3365 (8)	5.2 (4)
N4	0.311 (2)	−0.009 (2)	0.2591 (6)	5.0 (3)
C4	0.781 (2)	−0.228 (2)	0.3584 (8)	4.7 (4)
C15	0.668 (2)	−0.171 (2)	0.4409 (8)	5.2 (5)
N3′	0.968 (2)	0.155 (1)	0.2312 (7)	5.4 (4)
C6	0.729 (2)	−0.223 (2)	0.2151 (8)	3.9 (4)
C2	0.089 (2)	−0.383 (2)	0.2555 (8)	4.4 (4)
C14	0.128 (2)	−0.377 (2)	0.4001 (9)	5.7 (5)
C10	0.038 (2)	−0.390 (2)	0.1275 (9)	5.9 (5)
O2	0.288 (1)	−0.472 (1)	0.2434 (6)	6.5 (3)
C2′	0.098 (2)	0.100 (2)	0.2835 (9)	5.4 (5)
N2	0.243 (2)	−0.419 (2)	0.4467 (8)	8.0 (5)
C5′	0.768 (2)	0.289 (2)	0.3454 (9)	6.6 (5)
C11	0.179 (2)	−0.262 (2)	0.0759 (8)	5.6 (5)
C4′	0.770 (2)	0.269 (2)	0.2694 (9)	7.3 (5)
C12	0.237 (3)	−0.305 (3)	−0.009 (1)	9.5 (6)
C13	0.407 (3)	−0.199 (3)	−0.056 (1)	12.2 (8)

RESULTS AND DISCUSSION

As shown in Scheme 1, for the title compound there are two possible tautomeric forms, namely, the diketohydrazone form (a) and the azohydroxypyridone form (b).



Scheme 1.

TABLE 3
Selected Geometric Parameters (Å,°)

S1′–C2′	1.72 (2)	C3–C14	1.45 (2)
S1′–C5′	1.70 (1)	N4–C2′	1.39 (2)
O1–C6	1.19 (2)	C4–C15	1.52 (2)
C5–N3	1.32 (1)	N3′–C2′	1.30 (2)
C5–C4	1.45 (2)	N3′–C4′	1.41 (2)
C5–C6	1.48 (2)	C2–O2	1.23 (1)
N1–C6	1.40 (1)	C14–N2	1.14 (2)
N1–C2	1.33 (2)	C10–C11	1.55 (2)
N1–C10	1.39 (2)	C5′–C4′	1.34 (2)
N3–N4	1.31 (2)	C11–C12	1.49 (2)
C3–C4	1.37 (2)	C12–C13	1.51 (3)
C3–C2	1.47 (2)		
C2′–S1′–C5′	86.3 (7)	O1–C6–C5	126. (1)
N3–C5–C4	120. (1)	O1–C6–N1	120. (1)
N3–C5–C6	118. (1)	C5–C6–N1	114. (1)
C4–C5–C6	122. (1)	N1–C2–C3	117. (1)
C6–N1–C2	128. (1)	N1–C2–O2	127. (1)
C6–N1–C10	117. (1)	C3–C2–O2	116. (1)
C2–N1–C10	115. (1)	C3–C14–N2	176. (1)
C5–N3–N4	122. (1)	N1–C10–C11	113. (1)
C4–C3–C2	123. (1)	S1′–C2′–N4	123. (1)
C4–C3–C14	114. (1)	S1′–C2′–N3′	119.3 (1)
C2–C3–C14	123. (1)	N4–C2′–N3′	117. (1)
N3–N4–C2′	116. (1)	S1′–C5′–C4′	113. (1)
C5–C4–C3	117. (1)	C10–C11–C12	113. (1)
C5–C4–C15	117. (1)	N3′–C4′–C5′	115. (1)
C3–C4–C15	127. (1)	C11–C12–C13	113. (1)
C2′–N3′–C4′	106. (1)		
C5–N3–N4–C2′	179.36 (1.17)		
N3–N4–C2′–N3′	− 179.46 (1.15)		
C4–C5–N3–N3′	179.56 (1.15)		
C6–N1–C10–C11	89.62 (1.45)		

The structural results show that the compound exists as the hydrazone tautomer (a) rather than as the azo tautomer (b). The location of the H-atom on N4 rather than O1, and the C5-C6 and the C6-O1 bond lengths, support this idea. The distances for N3-N4 and N3-C5 are slightly shorter and longer, respectively, than the expected bonds in the hydrazone form. The N-N and N-C bond lengths [1.31(2) and 1.32(1) Å, respectively] are close to those observed in 4-(2-bromophenylhydrazono)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one,[12] 2-(2-methylphenylazo)-1,3-indandione,[13] and 2-phenylazo-1,3-indandione.[14] The above observations indicate very remarkable electron delocalization, as we would also anticipate due to the greater electron withdrawal by the pyridone ring.

An important feature of the molecule is the strong intramolecular hydrogen bond formed between the hydrazone hydrogen H(N4) and the 6-carbonyl group.

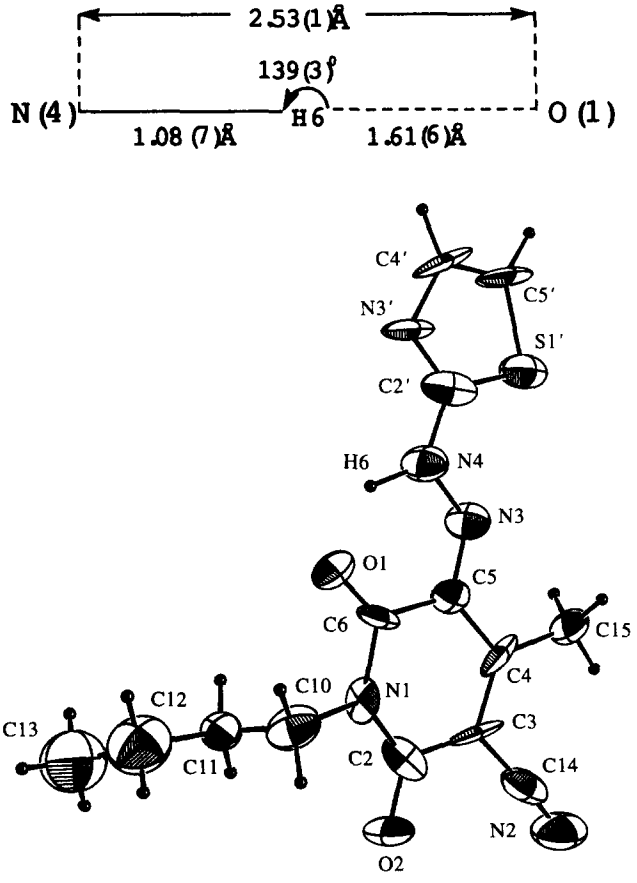


Fig. 1. Ortep drawings of the compound with 50% probability thermal ellipsoids and the numbering scheme. H-atoms are shown as circles of arbitrary small diameter.

The short O1···H6 and N4···O1 distances suggest the presence of a hydrogen bond.

The N4-N3-C5-C6-O1-H6 ring completed by the H6-O1 hydrogen bond is nearly planar, with a maximum deviation from the least squares plane defined by all atoms of 0.086 Å (H6). The pyridone ring is effectively coplanar with the azo group and the thiazolyl ring. The angle between the planes of the pyridone ring and the thiazolyhydrazone group is $5.7(3)^0$. The butyl group is twisted out of the plane of the pyridone ring by $83.1(9)^0$; the cyano substituent is essentially planar. These structural features are shared by a number of the disperse dyes.[12–16] We should mention at this point that the presence of the predominant hydrazone tautomer and intramolecular hydrogen bonding account for the observed planarity.

The packing arrangement of the hydrazone form of 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-thiazolylazo)-1(H)-pyridone is shown in Fig. 2. We looked in detail at the stacking for unusual intermolecular interactions between parallel molecules. The shortest contacts between nonhydrogen and hydrogen atoms N2···H5 (x+1, y, z) and O1···H9 (x−1, y, z) were 2.58(2) and 2.57(1) Å, respectively. Except for these weak-intermolecular contacts all other minimum intermolecular distances (in Å) in the structure (*S*1′···O2, 3.82; O2···C6, 3.51; C15···N2, 3.46; C2···N4, 3.43; O2···O1, 3.38; *S*1′···H4,

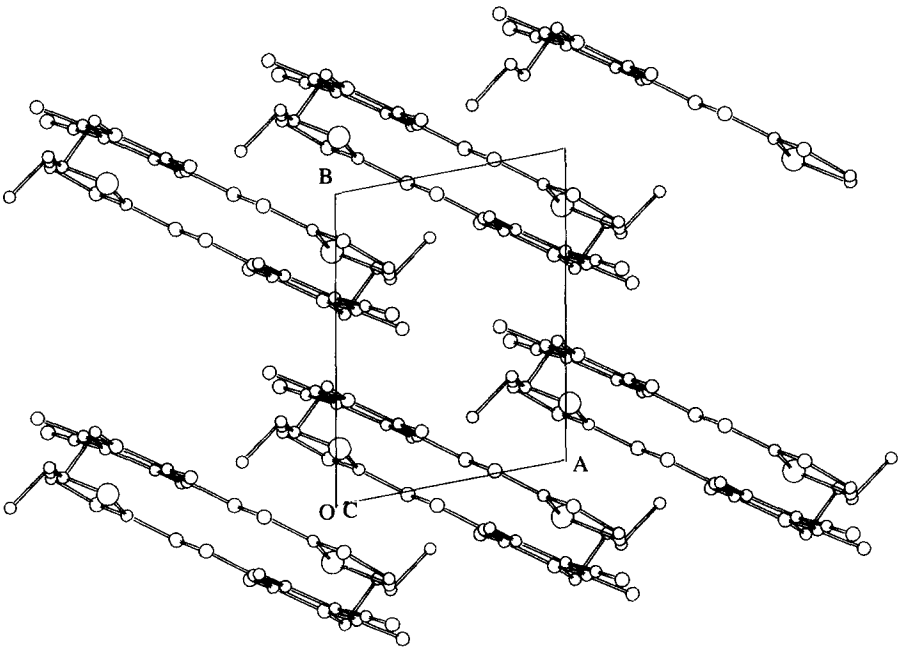


Fig. 2. The crystal packing viewed along C (hydrogen atoms have been omitted).

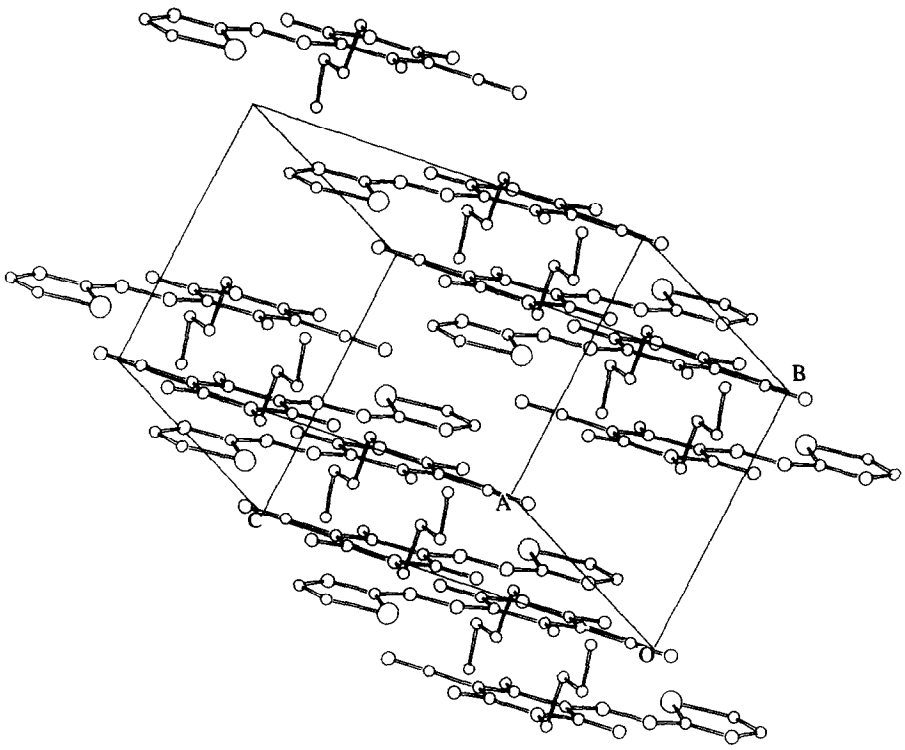


Fig. 3. The overall packing diagram of the molecule.

3.14; *C*5′···H4, 3.13; H9···H6, 2.75) conform to normal Van der Waals interactions. As shown in Fig. 3, the molecules are disposed on top of each other in an antiparallel fashion with a displacement which avoids superposition of the pyridone rings.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the purchase of CAD4 diffractometer under Grant DPT/TBAG-1 of The Scientific and Technical Research Council of Turkey.

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