Low-temperature X-ray study of benzoid-quinoid tautomerism in crystals of 2-(*N*,*N*-diphenylhydrazinoethylidene)-3(2*H*)-benzo[*b*]thiophenone

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An X-ray investigation of 2-(*N*,*N*-diphenylhydrazinoethylidene)-3(2*H*)-benzo[*b*]thiophenone was performed at room and low (−80 °C) temperatures. It was established that the structure of this compound in the crystalline state at ~20 °C is intermediate between the ketoenehydrazine and hydroxyhydrazone forms, while at −80 °C the molecular structure is completely transformed to the hydroxyhydrazone form. This confirms the dynamic nature of hydrogen atom disordering in the molecule at ~20 °C.

Key words: 2-(*N*,*N*-diphenylhydrazinoethylidene)-3(2*H*)-benzo[*b*]thiophenone, molecular structure; tautomerism; dynamic disordering in crystal.

An X-ray study of 2-(*N*,*N*-diphenylhydrazinoethylidene)-3(2*H*)-benzo[*b*]thiophenone (**1**) has previously[1] been performed. Based on the analysis of the bond lengths in the aminoenone fragment of **1** (Table 1), the conclusion was drawn that its molecular structure is intermediate between the possible tautomeric hydroxy (**A**) and keto (*E*-**B**) forms (Scheme 1).[1–3]

This is confirmed by the comparison of bond lengths in the aminoenone fragment of compound **1** with the corresponding bond lengths in related molecules **2** and **3**, which crystallize as ordered **A**- and *E*-**B**-tautomers, respectively[2,3] (see Table 1).

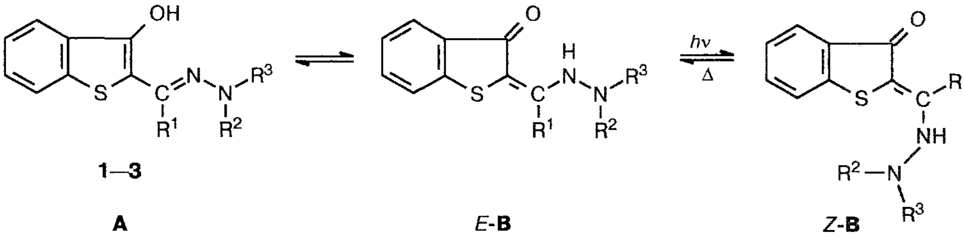
It has been established by a photochemical study of hydrazones in solution and in the solid state that, unlike compounds **2** and **3**, compound **1** has no solvato- or photochromic properties.[4]

The analysis of the results obtained makes it possible to suggest that the observed molecular structure of **1** is a superposition of the **A** and *E*-**B** forms with disordering of the H atom over two positions (OH— and NH—).[1] To answer the question about the nature of this disordering, compound **1** was studied at two different temperatures (20 °C and −80 °C) by X-ray analysis.

Experimental

Compound **1** is crystallized as yellow plates with monoclinic syngony. The main crystallographic parameters: at 20 °C a = 7.550(7) Å, b = 16.539(5) Å, c = 16.068(9) Å, γ = 116.75(5)°, V = 1791(6) Å^3, d = 1.328 g cm^{-3}; at −80 °C a = 7.455(7) Å, b = 16.310(5) Å, c = 16.160(9) Å, γ = 115.65(5)°, V = 1771(6) Å^3, d = 1.343 g cm^{-3}. The space group is $P2_1/b$,

Scheme 1



1—3

A *E*-**B** *Z*-**B**

1: R^1 = Me; R^2 = R^3 = Ph
2: R^1 = R^2 = Me; R^3 = Ph
3: R^1 = H; R^2 = R^3 = Ph

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Table 1. Bond lengths (*d*/Å) in aminoenone fragments of molecules **1—3**

Compound	O—C(2)	C(2)—C(1)	C(1)—C(9)	C(9)—N(1)	N(1)—N(2)
1[1]	1.326(5)	1.386(5)	1.415(4)	1.308(4)	1.423(6)
1a	1.315(4)	1.387(5)	1.422(4)	1.311(5)	1.430(5)
1b	1.347(3)	1.357(4)	1.464(4)	1.297(3)	1.455(4)
2[2]	1.264(2)	1.441(2)	1.357(2)	1.348(2)	1.385(2)
3[3]	1.351(1)	1.357(2)	1.439(2)	1.282(1)	1.377(1)

Note. See Fig. 1 for the numeration of atoms. The data for conformer **1a** were obtained at 20 °C, the data for conformer **1b** were obtained at −80 °C.

Table 2. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in the structure of **1** at −80 °C

Atom	*x*	*y*	*z*
S	2160(2)	4869(1)	9664(1)
O	4335(5)	6672(2)	11419(2)
N(1)	3992(6)	5126(2)	12014(3)
N(2)	4194(5)	4615(2)	12671(2)
C(1)	3006(6)	5274(3)	10680(3)
C(2)	3650(6)	6197(3)	10725(3)
C(3)	3563(6)	6601(3)	9935(3)
C(4)	4218(7)	7505(3)	9769(3)
C(5)	4059(8)	7779(3)	8957(4)
C(6)	3229(8)	7121(4)	8336(3)
C(7)	2595(7)	6221(3)	8504(3)
C(8)	2745(6)	5940(3)	9340(3)
C(9)	3115(6)	4704(3)	11309(3)
C(10)	2463(6)	4003(3)	13101(3)
C(11)	888(8)	4210(3)	13251(3)
C(12)	−767(8)	3586(4)	13693(3)
C(13)	−864(8)	2780(4)	13963(3)
C(14)	751(9)	2594(3)	13802(4)
C(15)	2358(7)	3198(3)	13370(3)
C(16)	6008(7)	5117(3)	13094(3)
C(17)	6166(7)	4976(3)	13944(3)
C(18)	7925(9)	5452(4)	14351(3)
C(19)	9594(8)	6074(4)	13946(4)
C(20)	9443(8)	6221(3)	13105(4)
C(21)	7670(8)	5756(3)	12692(3)
C(22)	2427(7)	3745(3)	11168(3)
H(1)	533(7)	367(5)	820(6)
H(1')	431(8)	81(5)	299(5)
H(2)	477(8)	802(3)	1012(3)
H(3)	460(8)	844(2)	890(3)
H(4)	322(6)	733(2)	776(3)
H(5)	199(6)	573(3)	809(3)
H(6)	128(6)	490(2)	1307(2)
H(7)	−205(6)	374(3)	1388(4)
H(8)	−213(6)	228(4)	1426(3)
H(9)	39(6)	195(3)	1400(2)
H(10)	361(5)	313(3)	1310(2)
H(11)	490(5)	448(3)	1431(3)
H(12)	805(6)	532(2)	1483(3)
H(13)	1087(5)	661(3)	1420(3)
H(14)	1084(6)	679(3)	1277(3)
H(15)	742(6)	587(2)	1216(2)
H(16)	249(6)	360(2)	1051(2)
H(17)	309(7)	351(2)	1147(2)
H(18)	140(9)	322(2)	1124(2)

$Z = 4$, M = 358.46, $C_{22}H_{18}N_2SO$. Intensities of 1785 (*hk*0—*hk*16) and 1525 (*hk*0—*hk*15) independent reflections with $I > 3\sigma(I)$ in the range of $2.8° < \theta < 59.7°$ and $2.2° < \theta < 76.2°$ at 20 °C and −80 °C, respectively, were measured on a DAR-UM diffractometer (Cu-Kα irradiation) from a 0.7×0.08×0.15 mm^3 crystal.

The structure was solved by the direct method by the SHELX-86[5] complex and refined by the full-matrix LSM in the anisotropic approximation (SHELXTL-76).[6] The H atoms were revealed by difference Fourier synthesis, and only the position parameters were refined for them. The coordinates of atoms in the structure of **1** at the low temperature are presented in Table 2. The final values of the *R*-factors for compound **1** are 0.052 and 0.075 at 20 °C and −80 °C, respectively.

A larger array of reflections (1785 > 1311) was obtained and a lower value of the *R*-factor (0.052 < 0.059) was achieved at room temperature than in the previously described data.[1]

Results and Discussion

The geometric parameters of molecule **1** at room temperature (Fig. 1, see Table 1) coincide within the limits of the experimental error with the published data.[1]

The molecular structure of **1** at −80 °C is not intermediate (disordered). The distribution of bond lengths in the aminoenone fragment of molecule **1** unambiguously corresponds to hydroxy form **A**, which is observed for structure **3** (see Table 1). The angle of rotation of the diphenylamino group of the substituent around the N(1)—N(2) bond changes as the temperature decreases: 51.4(2)° at −80 °C and 55.2(2)° at 20 °C. The rotations of the phenyl rings around the N(2)—C(10) and N(2)—C(16) bonds also noticeably change and are 55.9(1)° and 17.8(1)° at −80 °C and 54.2(1)° and 18.3(1)°

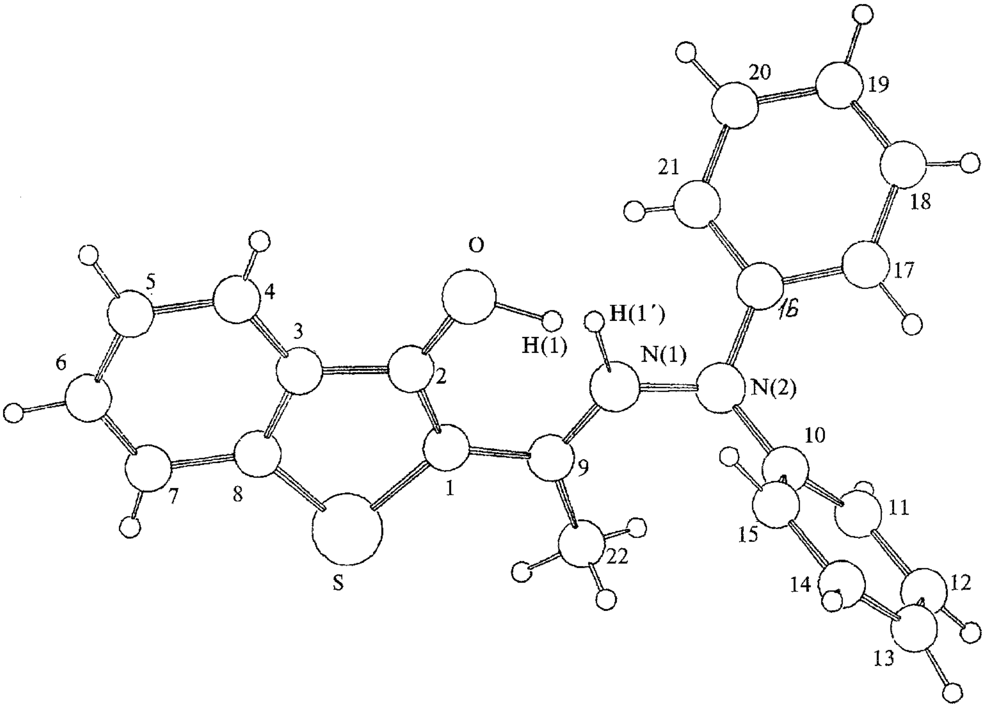

Fig. 1. General view of molecule **1b**. The two possible positions of the H(1) atom, H(1) and H(1') at 20 °C are shown; only the H(1) position is observed at −80 °C. The numbers correspond to the numeration of C atoms.

at 20 °C. The N(2) atom of the amino group at −80 °C retains the trigonal-pyramidal coordination and deviates by 0.27 Å from the plane of the adjacent atoms. Its unpaired electron pair has a *syn*-orientation with respect of the C(22) methyl group. The sum of the valence angles at the N(2) atom is equal to 349.7(2)°.

Only one peak, occupying the position at the O atom (the O—H(1) bond length is 0.92 Å; the C(2)—O—H(1) angle is equal to 102.7°), was found for the H(1) atom at −80 °C in the difference Fourier synthesis. The parameters of the >C—OH...N intramolecular hydrogen bond formed are the following: 2.605(4) Å for N(1)...O, 1.85(2) Å for H(1)...N(1), and the O—H(1)—N(1) angle is 138(1)°.

It is worthy of note that the N(1)—N(2) bond is considerably longer at −80 °C (up to 1.455(4) Å compared to 1.430(5) Å at −20 °C) and the N(1)—C(9)—C(22) valence angle increases from 123.7(1)° at 20 °C to 126.0(1)° at −80 °C.

Thus, the structural data testify that the decrease in temperature results in a shift of the tautomeric equilibrium in crystal **1** to hydroxy form **B**, which confirms the previous assumption about the dynamic nature of the distribution of the H(1) hydrogen atom over two positions.

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