The Crystal and Molecular Structure of 1-(2-Thiazolylazo)-2-naphthol

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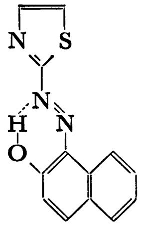
The crystal structure of 1-(2-thiazolylazo)-2-naphthol, $C_{13}H_9N_3OS$, has been determined from three-dimensional X-ray data collected by counter methods. The crystals are monoclinic with space group $P2_1/a$; cell dimensions: $a=17.721(1)$, $b=28.366(2)$, $c=4.699(1)$ Å, $\beta=91.78(1)°$, and $Z=8$. The structure was solved by the symbolic addition procedure and refined by the least-squares method to give an R value of 0.051 for 2150 observed reflections. There are two crystallographically independent molecules in an asymmetric unit; both of the molecules show a generally similar shape and size, but their structural details differ in planarity and distribution of the bond lengths. Both molecules have the azo and hydrazone character, but the equilibrium is shifted toward the azo tautomer.

The compound 1-(2-thiazolylazo)-2-naphthol (abbreviated as Htan) forms colored complexes with various metals, and has therefore been used as an analytical reagent. As part of a series of investigations of the structure of Htan and its metal chelates, the X-ray determination of Htan has been undertaken. The main purpose of the investigation is to establish the configuration of the ligand molecule; this will help to elucidate the structural change involved in the chelate ring formation.



Htan

There is also interest in the tautomerism of this compound. It is well known that the azo and hydrazone tautomers frequently coexist in *ortho*-azophenol compounds.[1-5] An IR spectral study has suggested the azo-hydrazone tautomerism of Htan;[6] however, an explicit interpretation has never been made. Since the phenomenon of the tautomerism seemed to be important for understanding the reactions of this compound with metals, a detailed analysis of the structure has been undertaken. A preliminary note of this work has already been published.[7]

Experimental

The crystals of Htan were obtained from an ethanolic solution by slow evaporation. A crystal of dimensions 0.15 × 0.3 × 0.4 mm was chosen for data collection. The crystal data are summarized in Table 1. The cell parameters were determined by the least-squares procedure from the 2θ values of 40 reflections measured on a diffractometer using monochromated Cu $K\alpha$ radiation. The density was determined by flotation in an aqueous solution of sodium iodide.

Table 1. Crystal data

$C_{13}H_9N_3OS$	M. W. 255.3
Monoclinic	Space group $P2_1/a$
$a=17.721(1)$ Å	$D_m=1.44$ g cm^{-3}
$b=28.366(2)$ Å	$D_x=1.436$ g cm^{-3}
$c=4.699(1)$ Å	$Z=8$
$\beta=91.78(1)°$	$\mu=2.64$ cm^{-1} (for Mo $K\alpha$)
$V=2360.8$ Å^3	

The integrated intensities of the reflections were measured on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. The ω-2θ scan technique was employed at a scan speed of 4°/min in ω, and scanning was repeated up to four times when the $\sigma(|F|)$ due to the counting statistics was larger than 3% of $|F|$. The scan width was determined according to the formula $1.5°+0.6°\times\tan\theta$. Background was counted for 10 s at both sides of each peak. Three standard reflections were measured every fifty reflections during the data collection. The intensities of unique reflections with 2θ values less than 55° were collected and a total of 2150 reflections with $|F|>3\sigma(|F|)$ were obtained. The data were corrected for Lorentz and polarization factors, but no correction was made for absorption ($\mu r<0.1$).

Solution of the Structure and Refinement

The structure was determined by the symbolic addition procedure.[8] The distribution and statistics of $|E|$'s agree well with the theoretical values for the centrosymmetric case. Signs of 386 reflections could be determined by the usual symbolic addition procedure using three origin reflections and three symbols, and the resulting E map revealed the location of all 36 non-hydrogen atoms. Several cycles of least-squares refinement of the coordinates and isotropic temperature factors resulted in an $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ of 0.092. Anisotropic thermal parameters were then introduced for all non-hydrogen atoms, and the R factor was reduced to 0.075. All the hydrogen atoms were located on the difference map. This map also revealed that the phenolic hydrogen atoms (H(O) and H(O′)) are disordered or oscillate violently, especially the H(O′) atom; the contour lines corresponding to the H(O′) are elongated toward both O′ and N(2′) atoms. A second difference map, computed after three cycles of refinement in which all the hydrogen atoms except H(O) and H(O′) were included with an isotropic temperature factor, showed the same tendency. Then various least-squares calculations were made, assuming the internal hydrogen bonding of the double minimum type [O–H(O)···H(N)–N]. For example, when the occupancy factors [H(O) to H(N) ratio] of 7 to 3 and 6 to 4, estimated from the N(1)–N(2) and C(2)–O distances, were given to A (unprimed molecule) and B (primed molecule) respectively, R dropped to 0.052. However, the lowest R value, 0.051, was obtained when the single minimum model of the type O–H(O)···N(2) was assumed. Unit weight was given to all 2150 reflections. The atomic scattering factors used for S, O, N, and C were taken from International Tables for X-ray Cry-

TABLE 2. POSITIONAL AND THERMAL PARAMETERS

(a) Fractional atomic coordinates for the non-hydrogen atoms

	x	y	z		x	y	z
S	0.1994(1)	0.0125(1)	−0.0166(3)	S′	0.2008(1)	0.2967(2)	−0.3010(11)
O	0.2341(2)	0.1798(1)	0.4676(9)	O′	0.1158(2)	0.4517(1)	0.7121(8)
N(1)	0.1597(2)	0.0899(1)	0.3437(9)	N(1′)	0.1133(2)	0.3528(1)	0.8596(9)
N(2)	0.2196(3)	0.1010(1)	0.2085(9)	N(2′)	0.1615(2)	0.3793(1)	0.9965(9)
N(3)	0.3002(2)	0.0735(2)	−0.1381(9)	N(3′)	0.2600(3)	0.3782(2)	1.3353(10)
C(1)	0.1384(3)	0.1229(2)	0.5362(11)	C(1′)	0.0675(3)	0.3731(2)	0.6608(11)
C(2)	0.1712(3)	0.1660(2)	0.5953(12)	C(2′)	0.0692(3)	0.4220(2)	0.5846(11)
C(3)	0.1406(4)	0.1971(2)	0.7955(11)	C(3′)	0.0201(3)	0.4384(2)	0.3621(12)
C(4)	0.0772(3)	0.1862(2)	0.9297(12)	C(4′)	−0.0297(3)	0.4102(2)	0.2299(12)
C(5)	0.0383(3)	0.1431(2)	0.8819(11)	C(5′)	−0.0356(3)	0.3609(2)	0.3011(11)
C(6)	−0.0276(3)	0.1319(2)	1.0255(12)	C(6′)	−0.0885(3)	0.3320(2)	0.1594(12)
C(7)	−0.0624(4)	0.0897(2)	0.9827(13)	C(7′)	−0.0921(4)	0.2851(2)	0.2285(14)
C(8)	−0.0333(4)	0.0578(2)	0.7915(15)	C(8′)	−0.0440(3)	0.2665(2)	0.4354(14)
C(9)	0.0298(3)	0.0681(2)	0.6461(13)	C(9′)	0.0078(3)	0.2940(2)	0.5764(12)
C(10)	0.0680(3)	0.1110(2)	0.6841(11)	C(10′)	0.0139(3)	0.3425(2)	0.5146(11)
C(11)	0.2429(3)	0.0667(2)	0.0221(11)	C(11′)	0.2083(3)	0.3566(2)	1.1915(11)
C(12)	0.2539(3)	−0.0017(2)	−0.2641(12)	C(12′)	0.2747(3)	0.3019(2)	1.4948(12)
C(13)	0.3118(3)	0.0340(2)	−0.3010(11)	C(13′)	0.2978(3)	0.3467(2)	1.5083(14)

(b) Anisotropic thermal parameters for the non-hydrogen atoms ($\times 10^4$)
The anisotropic thermal parameters are in the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}		B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	44(1)	11(1)	584(8)	−4(1)	50(4)	−18(2)	S′	41(1)	11(1)	552(8)	1(1)	0(4)	−5(2)
O	50(2)	13(1)	749(27)	−9(2)	82(12)	−46(7)	O′	47(2)	11(1)	603(23)	−5(2)	−20(10)	7(6)
N(1)	35(2)	10(1)	394(22)	3(2)	−13(10)	−2(6)	N(1′)	27(2)	12(1)	442(23)	2(2)	−10(10)	−1(6)
N(2)	36(2)	10(1)	421(23)	0(2)	−30(10)	−14(6)	N(2′)	31(2)	10(1)	506(25)	0(2)	−12(10)	14(7)
N(3)	31(2)	13(1)	534(26)	−2(2)	29(11)	22(7)	N(3′)	36(2)	14(1)	690(30)	−5(2)	−76(13)	−7(8)
C(1)	36(2)	10(1)	399(26)	5(2)	−14(12)	−21(7)	C(1′)	25(2)	11(1)	466(28)	2(2)	17(12)	−18(8)
C(2)	40(2)	11(1)	502(30)	3(2)	−5(14)	−10(8)	C(2′)	34(2)	12(1)	450(28)	5(2)	29(12)	−4(8)
C(3)	58(3)	11(1)	644(37)	−5(3)	28(17)	−38(9)	C(3′)	43(2)	13(1)	538(33)	4(2)	35(15)	44(9)
C(4)	54(3)	12(1)	537(33)	6(2)	39(16)	−23(8)	C(4′)	31(2)	18(1)	559(33)	10(2)	−7(14)	2(9)
C(5)	35(3)	11(1)	460(29)	9(2)	−31(13)	5(8)	C(5′)	27(2)	16(1)	494(31)	2(2)	24(12)	−4(9)
C(6)	42(3)	16(1)	565(33)	14(3)	30(15)	−13(9)	C(6′)	30(2)	23(1)	575(34)	−3(3)	−10(14)	−8(10)
C(7)	44(3)	19(1)	685(39)	5(3)	87(16)	13(11)	C(7′)	41(3)	23(1)	664(40)	−16(3)	−37(16)	−44(11)
C(8)	47(3)	16(1)	887(46)	−10(3)	91(18)	−38(11)	C(8′)	45(3)	14(1)	787(43)	−10(3)	54(17)	−38(10)
C(9)	41(3)	12(1)	657(36)	2(2)	18(15)	−20(9)	C(9′)	37(2)	13(1)	608(34)	−1(2)	31(14)	−13(9)
C(10)	34(2)	9(1)	439(28)	7(2)	−31(12)	−15(7)	C(10′)	28(2)	12(1)	441(27)	3(2)	22(12)	2(8)
C(11)	34(2)	11(1)	399(27)	3(2)	−24(12)	−3(8)	C(11′)	32(2)	13(1)	462(29)	2(2)	11(12)	4(8)
C(12)	48(3)	12(1)	511(30)	8(2)	−13(15)	−34(8)	C(12′)	46(3)	16(1)	551(33)	9(3)	−2(15)	2(10)
C(13)	32(2)	17(1)	483(30)	9(2)	−20(13)	−20(9)	C(13′)	37(2)	20(1)	698(37)	3(3)	−31(16)	−21(11)

(c) Positional and thermal parameters for the hydrogen atoms

	x	y	z	B		x	y	z	B
H(3)	0.168(3)	0.223(2)	0.827(10)	5.0(12)	H(3′)	0.024(3)	0.470(2)	0.316(10)	5.9(12)
H(4)	0.059(2)	0.207(2)	1.081(9)	4.8(11)	H(4′)	−0.064(3)	0.421(2)	0.067(10)	4.8(12)
H(6)	−0.049(3)	0.154(2)	1.165(11)	6.3(14)	H(6′)	−0.120(3)	0.345(2)	−0.003(12)	6.8(15)
H(7)	−0.105(3)	0.082(2)	1.090(10)	5.6(12)	H(7′)	−0.126(3)	0.265(2)	0.133(10)	5.4(13)
H(8)	−0.058(3)	0.026(2)	0.754(11)	6.0(13)	H(8′)	−0.046(3)	0.232(2)	0.481(11)	6.2(13)
H(9)	0.049(2)	0.048(2)	0.513(10)	4.8(11)	H(9′)	0.039(3)	0.285(2)	0.734(10)	4.9(13)
H(12)	0.261(3)	−0.032(2)	−0.354(11)	6.8(15)	H(12′)	0.289(3)	0.275(2)	1.601(10)	4.9(12)
H(13)	0.355(2)	0.035(1)	−0.439(9)	3.9(10)	H(13′)	0.335(3)	0.361(2)	1.632(11)	6.5(14)
H(O)	0.245(3)	0.155(2)	0.310(13)	9.0(17)	H(O′)	0.148(3)	0.429(2)	0.877(13)	9.1(17)

stallography,[9] for H, those of Stewart, Davidson, and Simpson were used.[10] The final atomic parameters based on the single minimum model are listed in Table 2. The observed and calculated structure factors are compared in Table 3.*

Description of the Structure and Discussion

The structure consists of two chemically similar but crystallographically independent molecules (referred to as A and B). The configuration of these molecules viewed normal to the naphthalene plane is shown in Fig. 1. The thermal ellipsoids are drawn at 50% probability. Both molecules show a generally similar shape and size, but some structural details are different, as described below. Each azo group adopts a *trans* conformation, and the phenolic oxygen atom, O, is linked to the azo nitrogen atom, N(2), by intramolecular hydrogen bonding; the O···N(2) distances are 2.548(6) and 2.556(6) Å for A and B, respectively. N(1) and N(3) are in *trans* positions with respect to the C(11)–N(2) bond. A similar conformation was observed for a bromo-derivative of Htan, 1-(2-thiazolylazo)-6-bromo-2-naphthol.[11] This will imply that the observed conformation is the most stable one for these molecules. A relatively short non-bonded distance of 2.87 Å, as shown in Fig. 2a, is observed between N(1) and S (and N(1′) and S′).

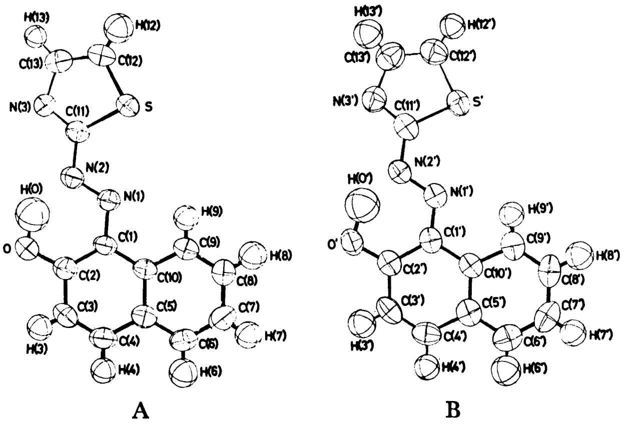
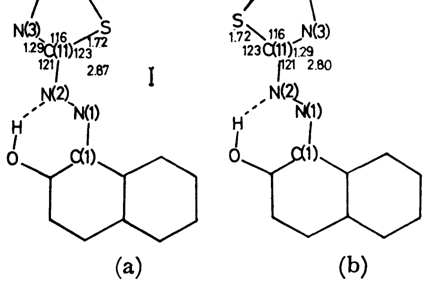


Fig. 1. The molecular structures viewed normal to each naphthalene plane. The thermal ellipsoids are drawn at 50% probability.



(a) (b)

Fig. 2. Two possible planar configurations for Htan. (a) *trans* (b) *cis* (N(1)–N(2)–C(11)–N(3)).

If the thiazole ring is rotated by 180° around the C(11)–N(2) bond, that is, when N(1) and N(3) are in *cis* positions, the N(1)···N(3) distance will be about 2.80 Å (Fig. 2b). Inspection of MO calculations for this molecule[12] reveals that such a conformation is less stable in view of the electrostatic interaction, because the formal charges on N(1) and N(3) are both negative. On the other hand, the N(1)···S interaction in the observed conformation (Fig. 2a) is of the attractive type, since the formal charges on N(1) and S are negative and positive, respectively.

Bond lengths and angles are shown in Table 4 with their e.s.d.'s. The most significant differences between A and B are in the N(1)–N(2) and C(1)–C(10) distances; the other distances of both molecules agree well, within the limit of three times their corresponding e.s.d.'s.

The observed N(1)–N(2) distance of 1.278(7) Å lies between the standard distance of the azo form (–N=N–), 1.24±0.01 Å,[13–18] and that of the hydrazone form (–NH–N=), 1.39±0.01 Å,[16,19,20] and is closer to the value corresponding to the azo form. On the other hand, the observed value of 1.306(7) Å for N(1′)–N(2′) is almost intermediate between the azo and hydrazone

Table 4. Bond lengths and angles

(a) Bond lengths (l/Å)

	A (Unprimed atoms)	B (Primed atoms)
S–C(11)	1.728(6)	1.719(6)
S–C(12)	1.700(6)	1.702(6)
O–C(2)	1.325(7)	1.317(7)
N(1)–N(2)	1.278(6)	1.306(6)
N(1)–C(1)	1.371(7)	1.359(7)
N(2)–C(11)	1.382(7)	1.378(7)
N(3)–C(11)	1.285(7)	1.294(7)
N(3)–C(13)	1.372(8)	1.375(8)
C(1)–C(2)	1.412(8)	1.409(7)
C(1)–C(10)	1.416(8)	1.446(7)
C(2)–C(3)	1.413(9)	1.423(8)
C(3)–C(4)	1.323(9)	1.337(9)
C(4)–C(5)	1.418(8)	1.419(8)
C(5)–C(6)	1.395(8)	1.419(9)
C(5)–C(10)	1.418(8)	1.415(8)
C(6)–C(7)	1.345(9)	1.347(10)
C(7)–C(8)	1.389(10)	1.410(10)
C(8)–C(9)	1.348(9)	1.354(9)
C(9)–C(10)	1.405(8)	1.396(8)
C(12)–C(13)	1.332(9)	1.326(9)
C(3)–H(3)	0.88(5)	0.91(5)
C(4)–H(4)	0.97(5)	1.02(4)
C(6)–H(6)	1.00(5)	0.98(6)
C(7)–H(7)	0.93(5)	0.90(5)
C(8)–H(8)	1.02(5)	0.99(6)
C(9)–H(9)	0.92(5)	0.96(5)
C(12)–H(12)	0.95(6)	0.96(5)
C(13)–H(13)	1.00(4)	0.93(6)
O–H(O)	1.04(6)	1.17(6)
N(2)···H(O)	1.66(6)	1.50(6)
O···N(2)	2.548(6)	2.556(6)

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* Table 3 is kept as Document No. 7629 at the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo.

(b) Bond angles ($\varphi/°$)

	A (Unprimed atoms)	B (Primed atoms)
C(11)–S–C(12)	88.3(3)	88.3(3)
N(2)–N(1)–C(1)	117.2(4)	117.1(4)
N(1)–N(2)–C(11)	115.2(4)	114.6(4)
C(11)–N(3)–C(13)	109.9(5)	108.4(5)
N(1)–C(1)–C(2)	123.4(5)	125.0(5)
N(1)–C(1)–C(10)	116.8(5)	114.9(4)
C(2)–C(1)–C(10)	119.8(5)	120.1(5)
O–C(2)–C(1)	123.6(5)	122.3(5)
O–C(2)–C(3)	117.8(5)	118.6(5)
C(1)–C(2)–C(3)	118.6(5)	119.1(5)
C(2)–C(3)–C(4)	121.4(6)	120.9(6)
C(3)–C(4)–C(5)	122.8(6)	122.2(6)
C(4)–C(5)–C(6)	122.5(5)	121.0(5)
C(4)–C(5)–C(10)	117.5(5)	119.4(5)
C(6)–C(5)–C(10)	120.0(5)	119.7(5)
C(5)–C(6)–C(7)	121.2(6)	120.2(6)
C(6)–C(7)–C(8)	119.5(6)	120.4(6)
C(7)–C(8)–C(9)	120.9(7)	120.1(6)
C(8)–C(9)–C(10)	121.8(6)	121.9(6)
C(1)–C(10)–C(5)	120.0(5)	118.3(5)
C(1)–C(10)–C(9)	123.4(5)	123.9(5)
C(5)–C(10)–C(9)	116.6(5)	117.8(5)
S–C(11)–N(2)	122.8(4)	122.8(4)
S–C(11)–N(3)	115.3(4)	116.1(4)
N(2)–C(11)–N(3)	121.9(5)	121.1(5)
S–C(12)–C(13)	110.7(5)	110.4(5)
N(3)–C(13)–C(12)	115.8(5)	116.9(6)
O–H(O)–N(2)	146(5)	140(5)

forms, but is slightly closer to the value corresponding to the azo form.

The C(2)–O and C(2′)–O′ distances of 1.325(7) and 1.317(7) Å observed for A and B respectively are congruent with neither the standard distance of the phenolic form (C–OH), 1.38±0.01 Å,[21,22] nor with that of the quinoid form (C=O), 1.22±0.01 Å.[21,23,24] The distances lie intermediate between these two values, but are slightly closer to the value corresponding to the phenolic C–OH distance.

Somewhat similar behaviors were observed in 1-(*p*-nitrophenylazo)-2-naphthol,[25] 4-chloro-2,5-dimethoxyanilide of 1-(2,5-dichlorophenylazo)-2-hydroxy-3-naphthoic acid,[26] and 1,2-naphthoquinone 1-(2-nitro-4-chlorophenylhydrazone).[27] In these compounds N–N (–N=N– or –NH–N=) and C–O (C=O or C–OH) distances range from 1.32 to 1.34 Å and from 1.25 to 1.26 Å, respectively. These reported values correspond more nearly to the hydrazone tautomer than to the azo tautomer.

In view of the bond length distribution for Htan, azo-like (phenol) character is predominant rather than the hydrazone-like (quinone) character in both A and B. However, B has more of a hydrazone-like character than A, since the N(1)–N(2) and C(1)–C(10) are longer and C(2)–O and N(1)–C(1) are shorter in B than in A.

The azo-hydrazone tautomerism of Htan was better established by the location of the relevant hydrogen

Table 5. Least-squares planes

Plane 1	entire molecular plane	A
Plane 2	naphthalene ring plane	
Plane 3	thiazole ring plane	
Plane 4	entire molecular plane	B
Plane 5	naphthalene ring plane	
Plane 6	thiazole ring plane	

(a) equations of planes (a, b, c*)

Plane 1	$0.5431x-0.4202y+0.7270z=1.625$
Plane 2	$0.5357x-0.4203y+0.7324z=1.638$
Plane 3	$0.5867x-0.3738y+0.7184z=1.882$
Plane 4	$-0.6853x+0.1958y+0.7014z=3.466$
Plane 5	$-0.6956x+0.2099y+0.6871z=3.575$
Plane 6	$-0.6639x+0.1812y+0.7255z=3.556$

(b) Deviations of atoms from planes (l/Å)

	A		
	1	2	3
S	0.083*	0.044	−0.002*
O	0.042*	0.010	0.180
N(1)	−0.004*	−0.028	−0.035
N(2)	−0.024*	−0.060	0.012
N(3)	−0.079*	−0.135	−0.001*
C(1)	−0.005*	−0.021*	−0.021
C(2)	0.029*	0.009*	0.095
C(3)	0.033*	0.023*	0.107
C(4)	0.002*	0.002*	0.006
C(5)	−0.018*	−0.013*	−0.098
C(6)	−0.038*	−0.020*	−0.190
C(7)	−0.013*	0.008*	−0.246
C(8)	0.009*	0.021*	−0.234
C(9)	0.006*	0.006*	−0.168
C(10)	−0.010*	−0.014*	−0.101
C(11)	−0.015*	−0.059	0.002*
C(12)	0.044*	−0.010	0.002*
C(13)	−0.043*	−0.105	−0.001*

	B		
	4	5	6
S	0.003*	−0.109	0.004*
O	0.047*	0.048	−0.108
N(1)	0.028*	−0.019	−0.071
N(2)	0.055*	0.001	−0.021
N(3)	0.003*	−0.092	0.002*
C(1)	0.022*	0.005*	−0.124
C(2)	0.014*	0.021*	−0.160
C(3)	−0.045*	−0.017*	−0.278
C(4)	−0.055*	−0.012*	−0.301
C(5)	−0.016*	0.004*	−0.236
C(6)	−0.015*	0.013*	−0.258
C(7)	0.003*	0.008*	−0.215
C(8)	0.017*	−0.007*	−0.152
C(9)	0.021*	−0.012*	−0.125
C(10)	0.006*	−0.004*	−0.164
C(11)	0.023*	−0.061	−0.004*
C(12)	−0.058*	−0.196	−0.004*
C(13)	−0.043*	−0.169	−0.002*

* Only the atoms with asterisks were used in the plane calculation.

(c) Angles between planes (φ/°)

	1	2	3	4	5
2	0.8				
3	3.7	4.2			
4	87.0	86.2	88.6		
5	88.3	87.6	90.0	1.4	
6	84.8	84.1	86.5	2.2	3.5

atoms. The positions of H(O) and H(O′), which were located from the difference map (higher than 0.3 e Å^{-3}), were refined by the least-squares method as mentioned above. The observed O–H(O) and O′–H(O′) distances are 1.04(6) and 1.17(6) Å respectively (the N(2)···H(O) and N(2′)···H(O′) distances are 1.65(6) and 1.55(6) Å respectively), indicating O–H(O)···N(2) [and O′–H(O′)···N(2′)] hydrogen bonding. This fact is sufficient to establish the azo form as the predominant tautomer in both A and B. It can also be seen from the hydrogen positions that B has more of a hydrazone-like character than A.

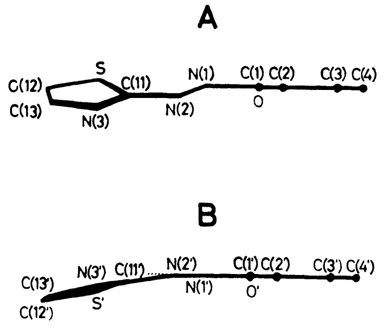
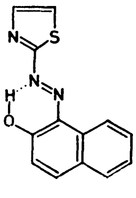
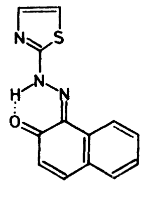


Fig. 3. Side view of the A and B molecules. The vertical scale is approximately eight times greater than the horizontal scale.

In studying the problem of the tautomerism, it is of interest to see the planarity of the molecules. The equations of the best planes through various sets of atoms in the respective molecules are presented in Table 5(a). The displacement of atoms from the planes and the angles between these planes are given in Tables 5(b) and 5(c). A view of the molecules which illustrates the planarity is shown in Fig. 3. The vertical scale is approximately eight times greater than the horizontal scale. Naphthol and thiazole rings of both molecules are planar within the experimental error. The A and B molecules are roughly planar within the deviations of ±0.08 and ±0.06 Å respectively, and each breaks the planarity in a different way, as can be seen in Figs. 1 and 3. The molecule A is twisted along the N(1)–C(1) bond, with 4.2° as the angle between the planes of the thiazole and naphthol rings. On the other hand, the molecule B is slightly folded at the N(2) atom and the thiazole ring plane makes an angle of 3.5° with the naphthol ring plane. The slight rotation along the N(1)–C(1) bond will indicate the single bond character, and accordingly the pronounced azo-like character in A. The slight pyramidal configuration $(\mathrm{C}(11')\text{–}\mathrm{N}(2'){<}\genfrac{}{}{0pt}{}{\mathrm{N}(1')}{\mathrm{H}(\mathrm{O}')})$ around the N(2′) atom is indicative of some hydrazone-like character in B.

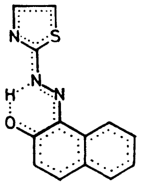
From the X-ray evidence mentioned above, the following two models can be proposed for the real molecular structure of Htan. The first is to assume that the azo (I) and hydrazone (II) tautomers coexist in the crystals of Htan, but the azo tautomer predominates.

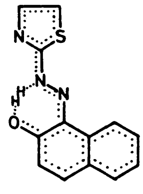

(I)


(II)

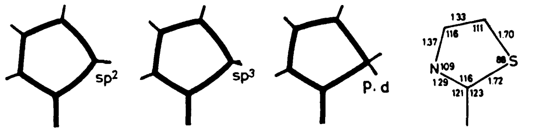
Accordingly the molecules as a whole are disordered; the azo and hydrazone tautomers occupy statistically two slightly different positions with unequal probability. Elongation of the thermal ellipsoids, especially in the molecule B, along the N(1)–N(2), N(1)–C(1), C(2)–O, *etc.*, suggests this model. However, it seems that more elongated ellipsoids should appear in such a case.

The second is that there exists only one type of molecule, whose electronic structure is intermediate between the azo and hydrazone tautomer, but the contribution of the azo form is more pronounced. If the potential curve of the hydrogen bonding is of the single minimum type (IIIa), the hydrogen atom would vibrate violently in the potential well. If the potential is of the double minimum type (IIIb), only the hydrogen atoms would be disordered. X-Ray evidence cannot distinguish these two cases. The potential well is clearly not the symmetric double minimum nor the symmetric single minimum type.


(IIIa)


(IIIb)

The average values of bond distances and angles in the thiazole ring are: S–C(11)=1.724, S–C(12)=1.701, N(3)–C(11)=1.290, N(3)–C(13)=1.374, and C(12)–C(13)=1.329 Å. C(11)–S–C(12)=88.3, C(11)–N(3)–C(13)=109.2, S–C(11)–N(3)=115.7, S–C(12)–C(13)=110.6, and N(3)–C(13)–C(12)=116.4°. Both S–C(11) and S–C(12) distances are significantly shorter than the standard distance of the paraffinic C–S bond, 1.817(5) Å.[28] This indicates that both C–S bonds have some double bond character and that the hybridization state of S is not sp^3.



(a)　(b)　(c)　(d)

Fig. 4. Framework molecular models (a, b, c) for thiazole and observed geometry (d). For S atom (a) sp^2, (b) sp^3 and (c) p (or d_{xy}) orbital skeleton was used.

Figure 4 shows the molecular models of a thiazole ring in which the valence state of S is assumed to be (a) sp^2, (b) sp^3, and (c) p (or some other orthogonal orbitals like d_{xy}). The observed distribution of bond angles, (d), corresponds more to that of model (c) than to (a) or (b). This may suggest that the valence state of S is not sp^2 either. In the case of thiophene, the C–S distance and the C–S–C angle are reported to be 1.718 Å and 92.2(1)° respectively,29) and the d-electron orbitals are thought to be involved in the hybridization.30) The observed values of C–S bond length and C–S–C angle for Htan are very close to the values for thiophene. Therefore, d-electron orbitals may be connected with the hybridization in the case of thiazole as well. If the hybridization state is purely sp^2 or sp^3, and if the accuracy of the analysis is high enough, lone pair electrons will appear in a residual map. An attempt to locate the relevant lone pair electrons for the sulfur atom in the final difference map failed; A more detailed analysis will be necessary to discuss this problem.

If the thiazole sulfur atom does not have lone pair electrons pointing to the bisector of C(11)–S–C(12), the sulfur atom will not participate in any chelate ring formation. Actually, there is no example of the participation of the thiazole sulfur atom in metal binding. X-Ray determinations of Fe(II)-, Co(III)-, Ni(II)-, Cu(II)-, and Pd(II)-chelates of the 1-(2-thiazolylazo)-2-naphtholato (tan) group have established that tan is coordinated to the metal through the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring, and the thiazole nitrogen atom so as to form two five-membered chelate rings.31–35)

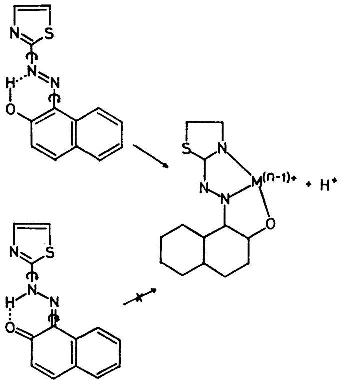


Fig. 5. Conformational changes on chelate ring formation.

Comparison of the structures of Htan and tan indicates that both thiazole and naphthol rings are rotated by 180° around the N(2)–C(11) and N(1)–C(1) bonds, as illustrated by Fig. 5. It should be noted that the rotation around the N(1)–C(1) bond will not usually occur when the N(1)–C(1) is a double bond (*i.e.* hydrazone form). Thus the reaction of the type $\text{Htan} + M^{n+} \longrightarrow M^{(n-1)+}\text{-tan} + H^+$ will occur through the azo tautomer.

The crystal structure projected along the c axis is shown in Fig. 6. Intermolecular distances shorter than 3.5 Å are given in Table 6. All distances are consistent with the van der Waals contacts, and there is no evidence of intermolecular hydrogen bonding.

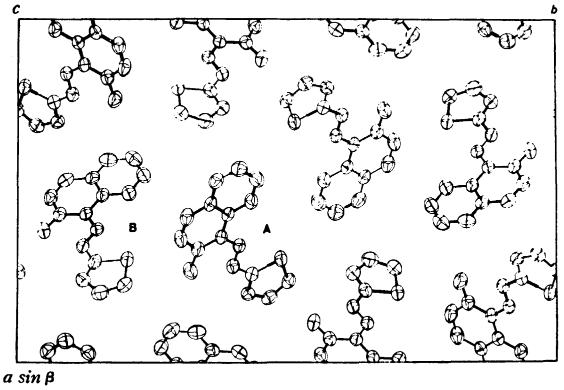


Fig. 6. Crystal structure projected along the c axis. The thermal ellipsoids are drawn at 50% probability.

Table 6. Interatomic distances shorter than 3.5 Å

		Symmetry operation	Distance (l/Å)
O	S′	1	3.50
O	C(7′)	3	3.46
N(1)	N(2)	1	3.44
N(1)	C(5)	2	3.37
N(1)	C(13)	1	3.48
N(2)	N(3)	1	3.43
N(2)	C(2)	2	3.50
N(2)	C(13)	1	3.36
N(3)	C(4′)	3	3.45
C(1)	C(4)	2	3.49
C(1)	C(11)	1	3.34
C(11)	C(13)	1	3.48
C(12)	O′	4	3.31
C(12)	N(3′)	5	3.44
C(13)	O′	4	3.31
N(1′)	C(5′)	1	3.40
N(2′)	C(2′)	1	3.46
N(2′)	C(3′)	1	3.50
N(2′)	C(13′)	2	3.50
C(1′)	C(4′)	1	3.39
C(1′)	C(11′)	2	3.40
C(6′)	C(9′)	2	3.43

Symmetry operations
1 (x y $1+z$) 4 ($\frac{1}{2}-x$ $\frac{1}{2}+y$ $-z$)
2 (x y $1-z$) 5 ($\frac{1}{2}-x$ $\frac{1}{2}+y$ $1-z$)
3 ($\frac{1}{2}+x$ $\frac{1}{2}-y$ z)

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