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THE CRYSTAL STRUCTURE OF 1-(2-THIAZOLYLAZO)-2-NAPHTHOL

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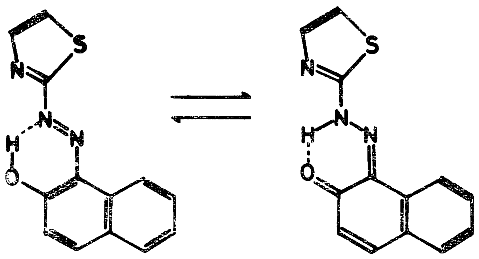
Crystal and molecular structure of 1-(2-thiazolylazo)-2-naphthol has been determined by X-ray analysis. Evidence for the coexistence of the azo and hydrazone tautomer was obtained.


Azo Hydrazone

In recent years, 1-(2-thiazolylazo)-2-naphthol (H-TAN) has received considerable attention as an analytical reagent.$^{1,2)}$ As a part of serial studies on the structures of metal chelates of H-TAN, an X-ray analysis of H-TAN has been undertaken. The main purpose of the investigation is to establish the configuration of the ligand molecule so as to elucidate the structural change in chelate ring formation. Another interest lies in the tautomerism of this compound. IR spectrum study suggested an azo-hydrazone tautomerism, but explicit interpretation was not made.$^{3)}$

The crystals of H-TAN were obtained from an ethanol solution by slow evaporation. The crystal data are: $C_{13}H_9N_3OS$, M.W. 255.2, monoclinic, $a = 17.662(5)$, $b = 28.296(7)$, $c = 4.693(2)$ Å, $\beta = 91.60(3)°$, $V = 2320.6$ Å^3, $Z = 8$, $D_m = 1.44$, $D_x = 1.445$ g/cm^3, $\mu = 2.64$ cm^{-1} (for MoKα), space group $P2_1/c$. Intensities for about 6000 independent reflections with 2θ value up to 55° were measured on a Rigaku computer-controlled four-circle diffractometer using MoKα radiation(ω-2θ scan). 2150 of these had intensities greater than 3σ(I) and were regarded as observed. They were corrected for Lorentz and polarization factors but corrections for absorption and extinction were not applied.

The structure was solved by symbolic addition procedures. In the calculation of E factors, the unobserved reflections were assigned $I_{min}/3$ where I_{min} is the lowest observable intensity. After four cycles of the symbolic addition procedure, signs of 374 reflections were determined. An E-map using these terms revealed the positions of all 36 non-hydrogen atoms. The coordinates of the hydrogen atoms were obtained by a difference synthesis. Least-squares refinements, with anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms respectively, were carried out and an R value was reduced to 0.051 for the 2150 observed reflections.

There are two crystallographically independent molecules(hereafter referred to as A and B) in an asymmetric unit. Both molecules show broadly similar shape, but the structural details are different from each other in the behavior of the phenolic hydrogens, planarity of the molecules and distribution of the bond lengths.

Fig. 1 shows a projection of the molecules along the a-axis. Contours of the difference synthesis, corresponding to the hydrogen atoms attached to oxygen, are superposed. The contour interval is 0.1 $eÅ^{-3}$, starting at 0.1 $eÅ^{-3}$. It is likely that the phenolic hydrogens(or hydrazone hydrogens) are disordered especially in B. In A molecule, a large peak is observed at 1.1 Å from O and at 1.7 Å from N_2, indicating that the azo tautomer is predominant. On the other hand, the contours of B are elongated in the direction of N_2. The peak position, being in good agreement with that determined by the least-squares method, lies at 1.2 Å from O and at 1.5 Å from N_2. A structure factor calculation was carried out assuming that the elongated peak is due to the phenolic and imino hydrogens in a ratio of 3 to 2, but R value was hardly improved. Since the thermal ellipsoids for N_1, N_2, C_1, C_2 and O atoms of the molecule B suggested partial disorder in the structure, it is reasonable to assume that the azo and hydrazone tautomers coexist and that the equilibrium position is located more toward the azo form. The N_2 atom is linked to the phenolic O by intramolecular hydrogen bonding(O-H··N or O··H-N), O····N distances being 2.55 and 2.56 Å in A and B, respectively.

The deviations of atoms from the mean planes of H-TAN are characterized as follows: Molecule A is twisted along the N_1-C_1 bond and the angle between the planes of thiazole and the naphthol ring is 4.2°. Molecule B is slightly folded at N_2 atom and the plane of the thiazole ring makes an angle of 3.5° with the plane of the naphthol ring.

Bond lengths and angles are shown in Fig. 2. The average standard deviations are about 0.005, 0.006, 0.007, 0.008, 0.05 and 0.06 Å for S-C, N-N, C-O, C-C, C-H and O-H, respectively, and about 0.3, 0.4 and 0.5° for C-S-C, C-N-N and C-C-C, respectively. Observed N_1-N_2 distances of 1.279 and 1.307 Å in A and B respectively lie between the standard distance of the azo -N=N-(1.24 Å) and that of the hydrazone -NH-N=(1.38 Å). The former is rather close to the value corresponding to the azo tautomer than to the value corresponding to the hydrazone. Similarly, observed C-O distances of 1.324 and 1.317 Å are between the standard distance of phenolic C-OH(1.39 Å) and that of the quinoid C=O(1.22 Å), being slightly closer to the value corresponding to the phenol (azo) than to the value corresponding to the quinone(hydrazone). The fact that 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 suggests some hydrazone character of B. This tendency agrees well with the evidence from the characteristic features of the difference synthesis.

Thus X-ray evidence shows that the azo and hydrazone tautomers coexist in the crystal of H-TAN and that the azo tautomer is more predominant. The coexistence of the two tautomers is further supported by the results for 1-phenylazo-2-naphthol obtained by spectroscopic methods[4-6] and MO calculations.[7]

The crystal structure projected along the c-axis is shown in Fig. 3 together with intermolecular distances. All distances are consistent with van der Waals contacts, and there is no evidence for intermolecular hydrogen bonding. The planes of A and B are inclined at about 45° from the (001) plane and interplanar distance is about 3.4 Å for both cases. In the crystal structure of 1-(2-thiazolylazo)-6-bromo-2-naphthol,[8] the features of molecular configuration are similar to those of H-TAN, but the molecular arrangement is somewhat different. The structures of metal chelates of this reagent will be reported elsewhere.

Fig. 1 Difference synthesis

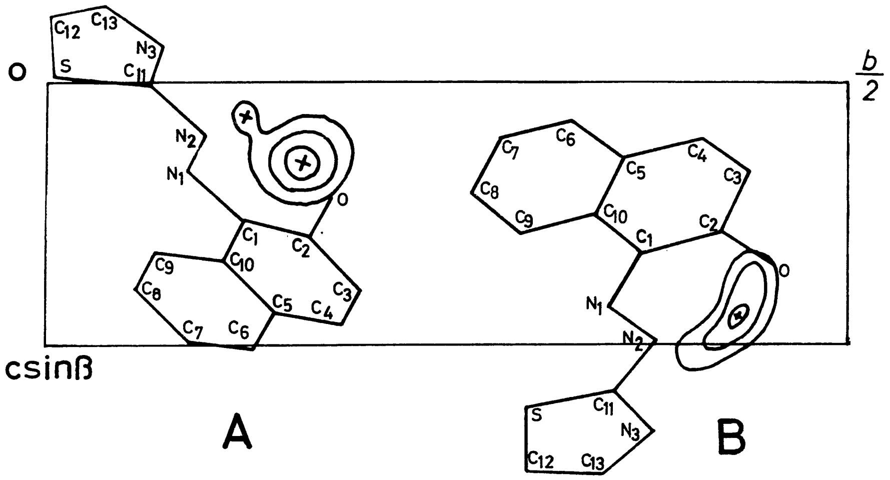


Fig. 2 Bond lengths and angles

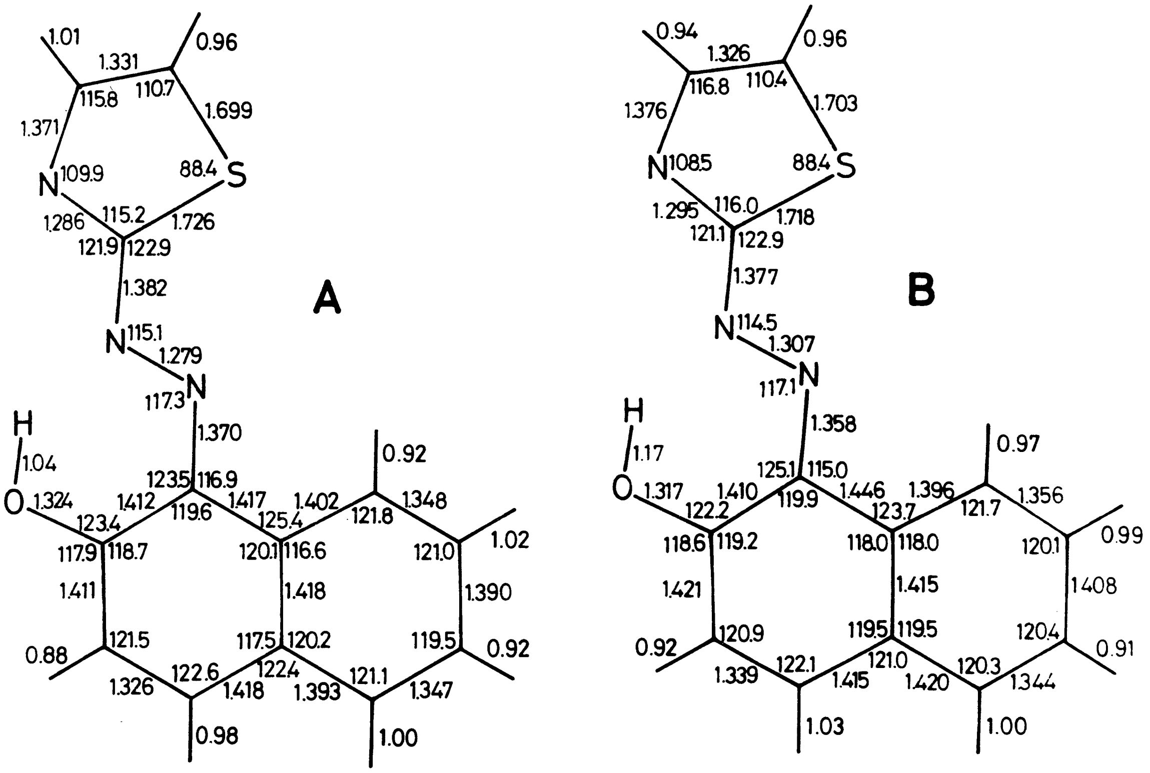
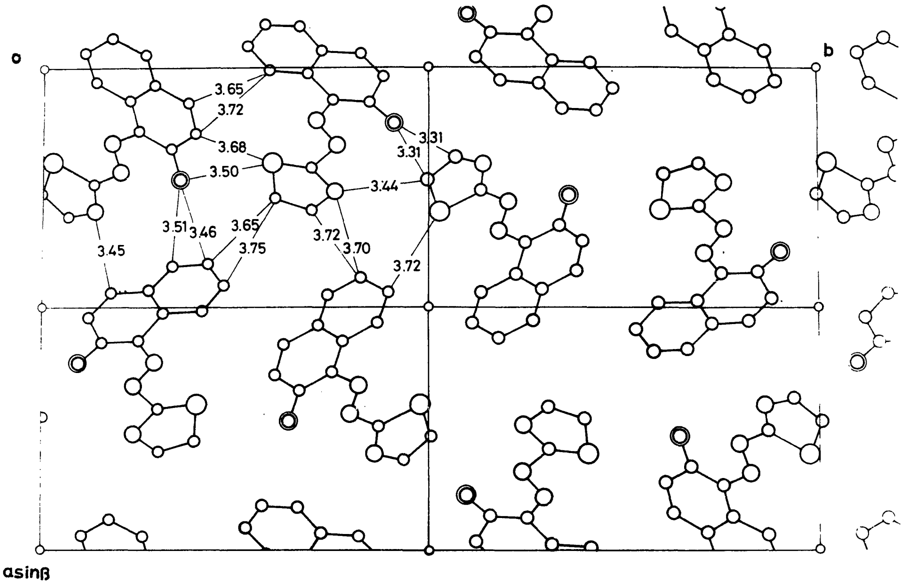


Fig. 3 Crystal structure projected along the c-axis



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