CHEMISTRY LETTERS, pp. 2317-2320, 1987.

Freezing of Equilibrium of 1,2,4-Triazole by Complex Formation with 1,1-Di(2,4-dimethylphenyl)but-2-yn-1-ol, and X-Ray Crystal Structure of the Complex

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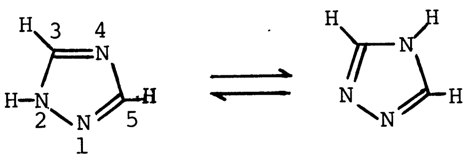
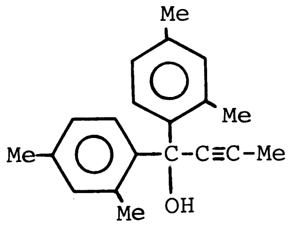
Of the two tautomeric isomers of 1,2,4-triazole, 1,2,4-triazacyclopenta-3,5-diene and 1,2,4-triazacyclopenta-2,5-diene, the former was isolated as a 1:1 complex with the title host compound. X-Ray analysis of the complex reveals that the two molecular components are linked by hydrogen bonds with the triazole molecules lying in channels running parallel to the *b* axis, cutting *a* near 0 and *c* near 1/4.

Since 1,2,4-triazole (**1**) exists as an equilibrium mixture of the two tautomers,[1,2] 1,2,4-triazacyclopenta-3,5-diene (**1a**) and 1,2,4-triazacyclopenta-2,5-diene (**1b**), it is difficult to isolate one tautomer in pure state and study its structure. We tried to freeze the equilibrium by complexing with 1,1-di(2,4-dimethylphenyl)but-2-yn-1-ol (**2**), and succeeded in isolating **1a** in pure state as a 1:1 complex (**3**) with **2**.



1a **1b**



2

Complexation of **1** and **2** was carried out as follows: When a solution of **1** (0.25 g, 3.62 mmol) and **2** (1.00 g, 3.60 mmol) in MeOH (3 ml) was kept at room temperature for 12 h, **3** was formed as colorless prisms (1.10 g, 3.17 mmol, 88% yield), mp 101-102 °C. The 1:1 ratio of **1** and **2** in **3** was determined by measuring its ^{1}H NMR spectrum in $CDCl_3$.

Crystal data of $C_{20}H_{22}O \cdot C_2H_3N_3$ (**3**) are as follows: F·W = 347.46, monoclinic, space group $P2_1/c$, a = 13.721(4), b = 10.970(3), c = 14.801(7)Å, β = 114.90(3)°, V = 2021(1)Å^3, D_c = 1.14 g cm^{-3} for Z = 4, MoKα radiation (monochromatized) λ = 0.7107Å, μ = 0.67 cm^{-1}, F(000) = 744. A single crystal of dimensions 0.28 x 0.41 x 0.41 mm^3 was irradiated using an Enraf-Nonius CAD4 diffractometer. The unit cell was obtained by least-squares analysis of the setting angles of 24 reflections $16 \le \theta \ge 17^\circ$. Data were collected in the w-2θ mode with variable scan width (0.95 + 0.35tanθ)° and aperture width (1.12 + 1.05tanθ)mm and a variable scan speed, with a maximum recording time of 40s. Θ-range scanned = 1-25°. Intensity and orientation control was carried out periodically. Crystal decay, 1.2%. Total number of unique reflections collected = 2920. Data were Lp processed and an empirical absorption correction applied.3)

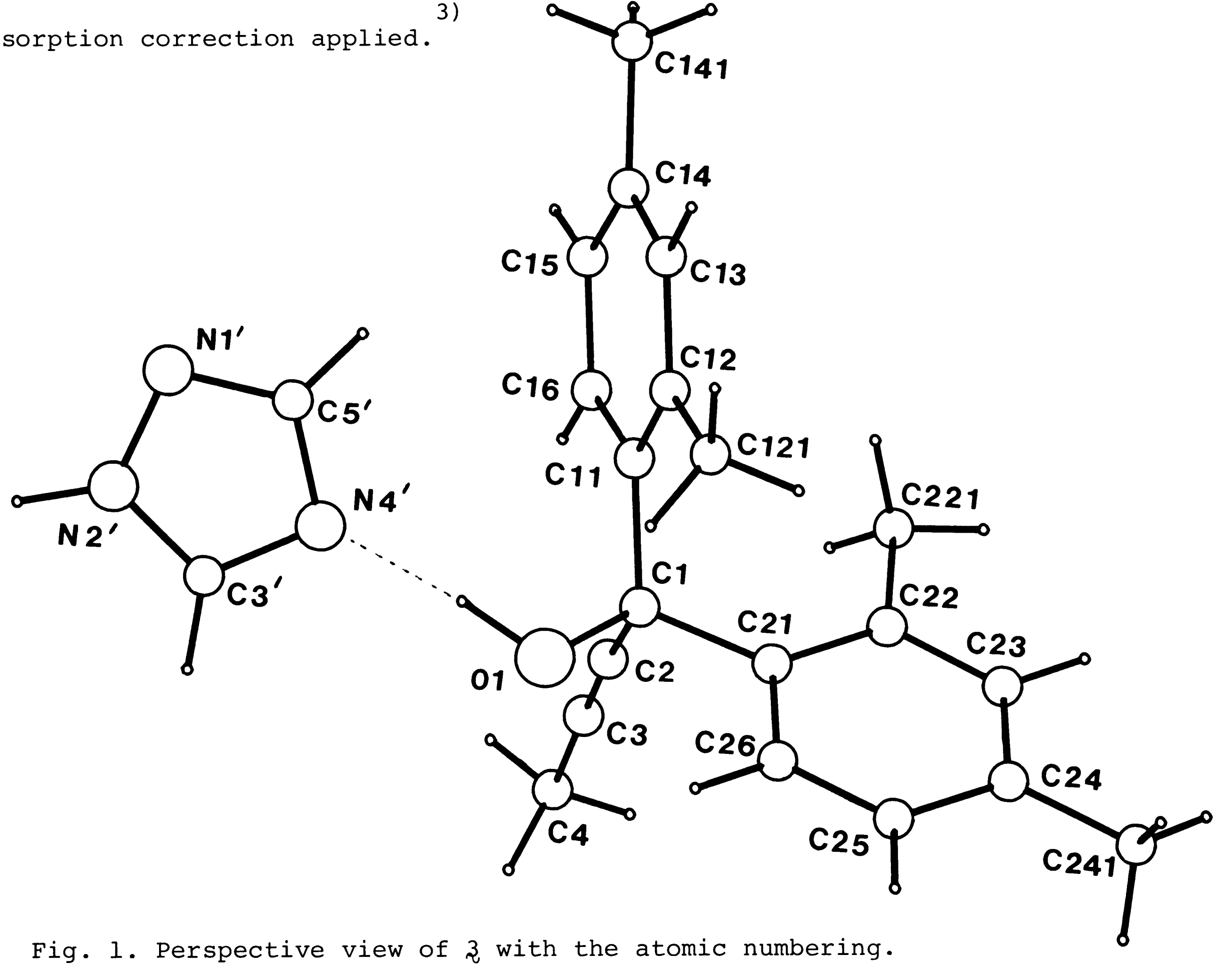


Fig. 1. Perspective view of **3** with the atomic numbering.

The structure was solved using 2132 reflections with $I_{rel} \geq 2\sigma I_{rel}$ and the direct methods package SHELXS-86.[4] Refinement was carried out using SHELX-76.[5] In the final refinements, all non-hydrogen atoms were treated anisotropically and all hydrogens isotropically. Methyls were modelled as rigid groups with a single temperature factor; triazole and phenyl hydrogens were located in a difference map, but were ultimately placed in calculated positions at 1.00Å from their parent atoms, again with a single temperature factor. The hydroxyl hydrogen was located in a difference map and constrained to ride at 1.00(2)Å from O1 and at 1.60(2)Å from N4' (with which it is involved in H-bonding), its temperature factor the same as that of the methyl hydrogens. Final data are as follows: R = 0.047, Rw = 0.046, $w = (\sigma^2 F)^{-1}$, for 255 parameters.[6]

Molecular parameters for the host molecule (**2**) are as expected and require no comment. The crystallographic result establishes that the triazole (**1**) is protonated at N2', with N-N, 1.342(4)Å; N=C, 1,306(4), 1.311(4)Å; N-C, 1.319(5), 1.346(5)Å, indicating some degree of delocalization. There are two types of close contacts between **1a** and **2** of **3**:

1. $\underbrace{\mathrm{O1} \xrightarrow{1.04(2)\,\text{Å}} \mathrm{H1} \xrightarrow{1.66(2)\,\text{Å}} \mathrm{N4'}}_{2.697(4)\,\text{Å}}$ O-H····N angle, 172(3)°

2. $\underbrace{\mathrm{N2'} \xrightarrow{1.000(3)\,\text{Å}} \mathrm{H2'} \xrightarrow{1.1819(3)\,\text{Å}} \mathrm{O1}}_{2.813(3)\,\text{Å}}$ N-H····O angle, 172.4(3)°

(O1 through -x, y-1/2, -z+1/2)

As illustrated in Fig. 1, **1a** and **2** are held together by a hydrogen bond N4'····H-O, so that the resulting aggregate faithfully represents the 1:1 stoichiometry of **3**. The exclusive inclusion of **1a** by **2** agrees with the finding that **1a** is more stable than **1b** in the solid phase at -155 °C,[1] and that **1a** exists predominantly in the vapor phase.[2]

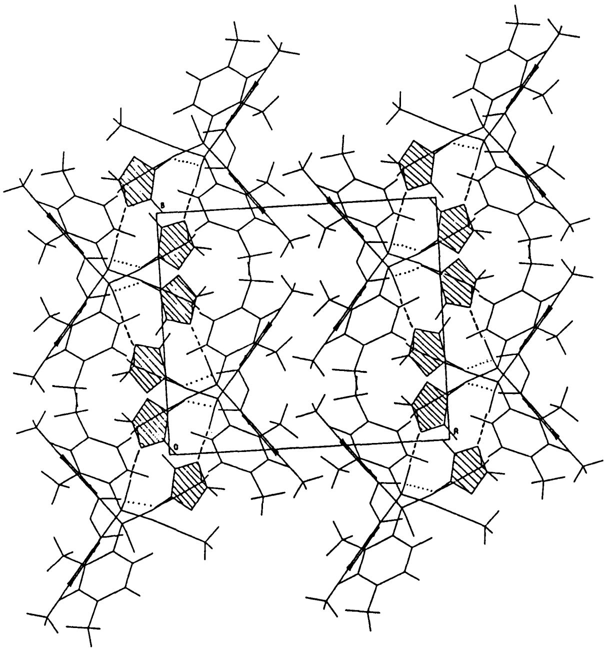


Fig. 2. View of the molecular packing down c. Molecules of **1a** are shaded; dashed lines indicate the O1-H1····N4' hydrogen bonds; dotted lines indicate the N2'-H2'····O1 hydrogen bonds.

The mode of molecular packing in **3** is shown in Figs. 2 and 3.

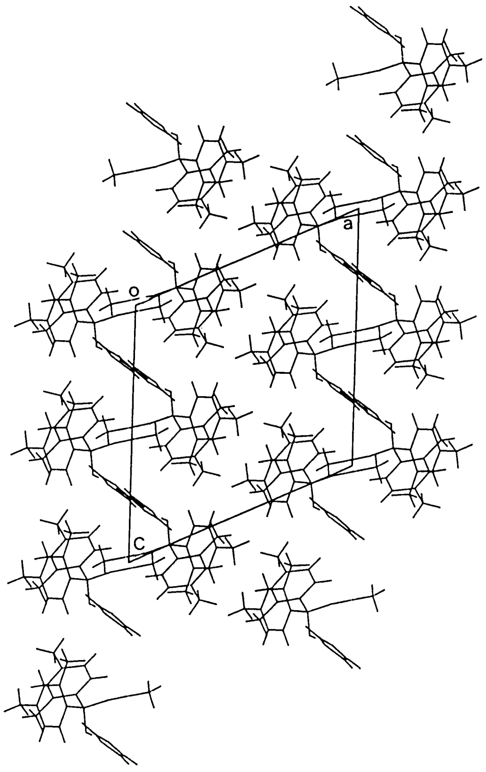


Fig. 3. View of the molecular packing down b, showing the channels containing the triazole molecules. (No hydrogen bonding indicated.)

References

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6) The atomic coordinates for this work have been deposited with the Cambridge Crystallographic Data Centre. A table of structure factors is available from the last author (MN).

(Received September 2, 1987)