

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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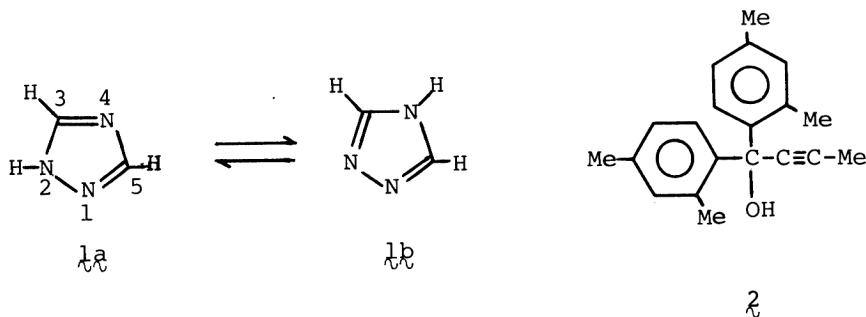
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Of the two tautomeric isomers of 1,2,4-triazole, 1,2,4-triazacyclopenta-3,5-diene and 1,2,4-triazacyclopenta-2,5-diene, the former was isolated as a 1:1 complex with the title host compound. X-Ray analysis of the complex reveals that the two molecular 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.



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

Crystal data of $\text{C}_{20}\text{H}_{22}\text{O}\cdot\text{C}_2\text{H}_3\text{N}_3$ (ν) are as follows: $F\cdot W = 347.46$, monoclinic, space group $P2_1/c$, $a = 13.721(4)$, $b = 10.970(3)$, $c = 14.801(7)\text{\AA}$, $\beta = 114.90(3)^\circ$, $V = 2021(1)\text{\AA}^3$, $D_c = 1.14\text{ g cm}^{-3}$ for $Z = 4$, $\text{MoK}\alpha$ radiation (monochromatized) $\lambda = 0.7107\text{\AA}$, $\mu = 0.67\text{ cm}^{-1}$, $F(000) = 744$. A single crystal of dimensions $0.28 \times 0.41 \times 0.41\text{ mm}^3$ was irradiated using an Enraf-Nonius CAD4 diffractometer. The unit cell was obtained by least-squares analysis of the setting angles of 24 reflections $16 <\theta> 17^\circ$. Data were collected in the $w-2\theta$ mode with variable scan width $(0.95 + 0.35\tan\theta)^\circ$ and aperture width $(1.12 + 1.05\tan\theta)\text{ mm}$ and a variable scan speed, with a maximum recording time of 40s. θ -range scanned = $1-25^\circ$. Intensity and orientation control was carried out periodically. Crystal decay, 1.2%. Total number of unique reflections collected = 2920. Data were I_p processed and an empirical absorption correction applied.³⁾

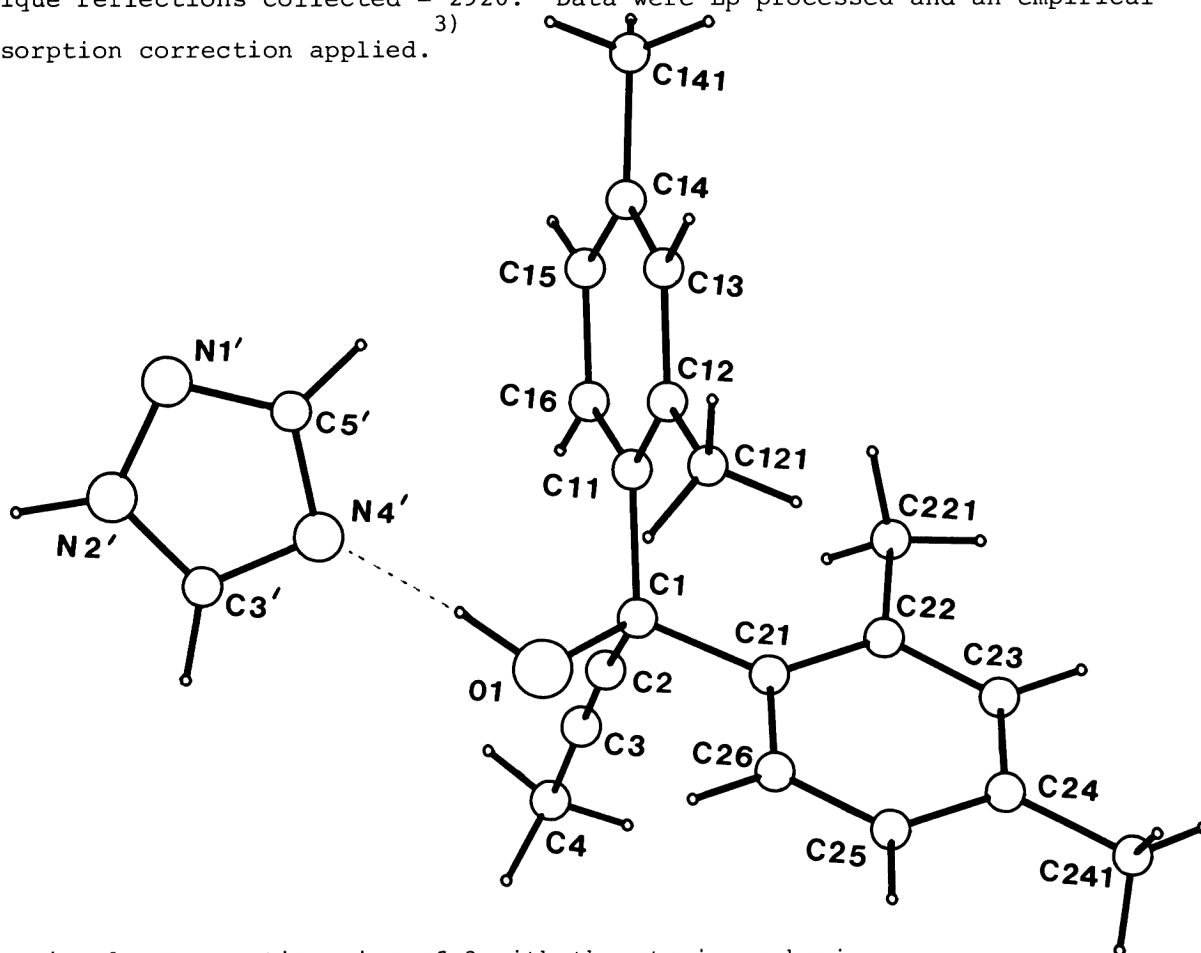


Fig. 1. Perspective view of ν with the atomic numbering.

The structure was solved using 2132 reflections with $I_{rel} > 2\sigma I_{rel}$ and the direct methods package SHELXS-86. Refinement was carried out using SHELX-76. 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 1.00\AA from their parent atoms, again with a single temperature factor. The hydroxyl hydrogen was located in a difference map and constrained to ride at $1.00(2)\text{\AA}$ from O1 and at $1.60(2)\text{\AA}$ 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: $R = 0.047$, $R_w = 0.046$, $w = (\sigma^2 F)^{-1}$, for 255 parameters.

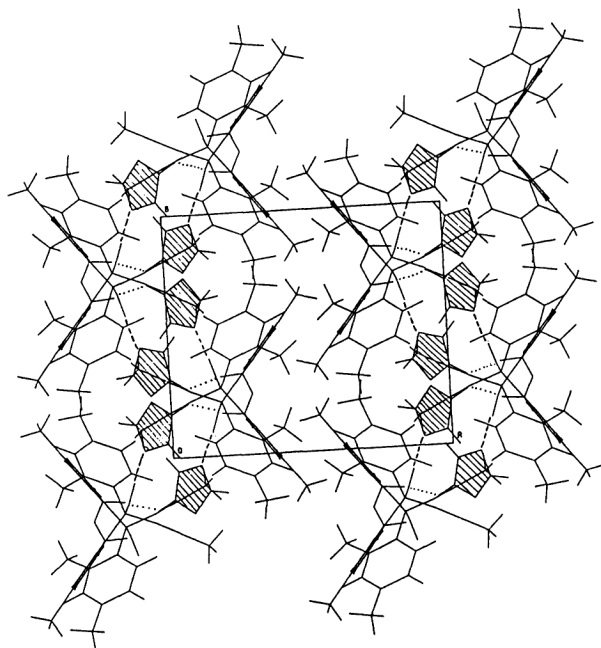
Molecular parameters for the host molecule ($\mathcal{2}$) are as expected and require no comment. The crystallographic result establishes that the triazole ($\mathcal{1}$) is protonated at N2', with N-N, $1.342(4)\text{\AA}$; N=C, $1.306(4)$, $1.311(4)\text{\AA}$; N-C, $1.319(5)$, $1.346(5)\text{\AA}$, indicating some degree of delocalization. There are two types of close contacts between $\mathcal{1a}$ and $\mathcal{2}$ of $\mathcal{3}$:

1. $O1 \xrightarrow[2.697(4)\text{\AA}]{1.04(2)\text{\AA}} H1 \xrightarrow[2.697(4)\text{\AA}]{1.66(2)\text{\AA}} N4'$ O-H.....N angle, $172(3)^\circ$
2. $N2' \xrightarrow[2.813(3)\text{\AA}]{1.000(3)\text{\AA}} H2' \xrightarrow[2.813(3)\text{\AA}]{1.1819(3)\text{\AA}} O1$ N-H.....O angle, $172.4(3)^\circ$

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

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

Fig. 2. View of the molecular packing down c . Molecules of $\mathcal{1a}$ are shaded; dashed lines indicate the $O1-H1 \cdots N4'$ hydrogen bonds; dotted lines indicate the $N2'-H2' \cdots O1$ hydrogen bonds.



The mode of molecular packing in \mathfrak{z} is shown in Figs. 2 and 3.

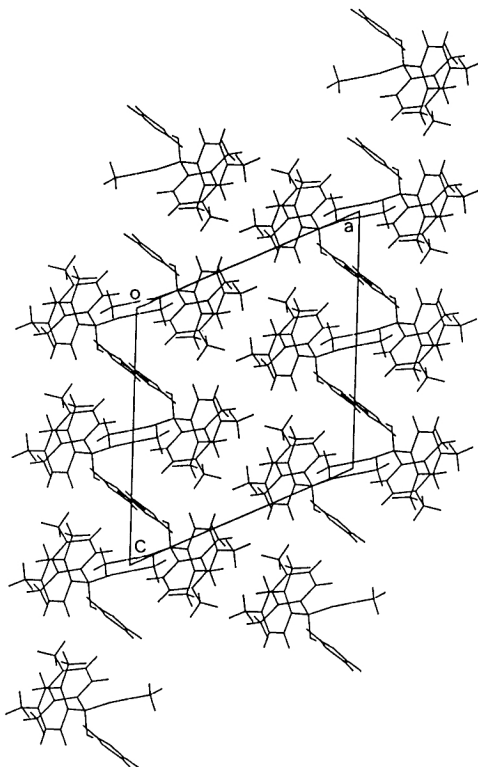


Fig. 3. View of the molecular packing down *b*, showing the channels containing the triazole molecules. (No hydrogen bonding indicated.)

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).

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