CHEMISTRY LETTERS, pp. 1061-1064, 1988.

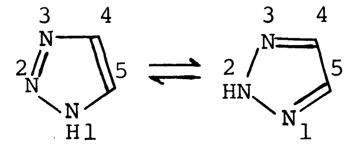
Freezing of Equilibrium of 1,2,3-Triazole and 3(5)-Methylpyrazole by Complex Formation with 1,1-Bis(2,4-dimethylphenyl)but-2-yn-1-ol, and X-Ray Crystal Structure of the Complexes

Fumio TODA,* Koichi TANAKA, Jose ELGUERO,† Zafra STEIN,†† and Israel GOLDBERG*††
Department of Industrial Chemistry, Faculty of Engineering,
Ehime University, Matsuyama 790
†Instituto de Quimica Medica, Madrid, Spain
††School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv
University, 69978 Ramat-Aviv, Israel

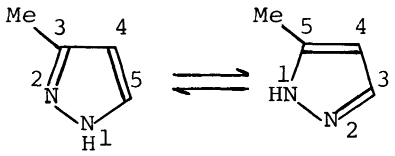
From an equilibrium mixture of two tautomers, 1*H*- and 2*H*-1,2,3-triazole, the relatively unstable 1*H*-isomer was isolated in pure state as a 1:1 complex with 1,1-bis(2,4-dimethylphenyl)but-2-yn-1-ol. The two equilibrating tautomers of almost the same stability, 3- and 5-methyltriazole, were also isolated in pure state as a 1:1:1 complex of these and the host compound.

1,2,3-Triazole (**1**) and 3(5)-methylpyrazole (**2**) exist as an equilibrium mixture of two tautomers of not much different stability, 1*H*- (**1a**) and 2*H*-1,2,3-triazole (**1b**), and 3- (**2a**) and 5-methylpyrazole (**2b**), respectively.[1,2] However, the structures of these tautomers have not been studied because of difficulty in obtaining the tautomers in pure state. We succeeded in freezing the equilibrium by complexation with 1,1-bis(2,4-dimethylphenyl)but-2-yn-1-ol (**3**) to isolate relatively unstable **1a** in pure state as its 1:1 complex (**4**) with **3**. We also succeeded in isolating both **2a** and **2b** in pure state as a 1:1:1 complex (**5**) of **2a**, **2b**, and **3**. These are the first isolations of tautomers of almost the same stability, although isolation of more stable 1,2,4-triazacyclopenta-3,5-diene (**6a**) from its equilibrium with less stable 1,2,4-triazacyclopenta-2,5-diene (**6b**) by complexation with **3** has been reported.[3)]

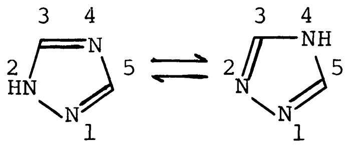
Complexations of **1** and **2** with **3** were carried out as follows: when a solution



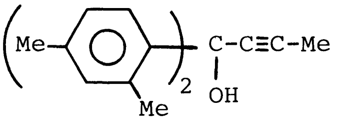
1a **1b**



2a **2b**



6a **6b**



3

of **1** (1 g, 14.5 mmol) and **3** (1 g, 3.6 mmol) in ether-petroleum ether (1:1) (5 ml) was kept at room temperature for 12 h, a 1:1 complex (**4**) of **1a** and **3** was formed as colorless prisms (1.1 g, 3.2 mmol, 89% yield based on **3**), mp 84-89 °C. Similarly, when a solution of **2** (1 g, 12.2 mmol) and **3** (1 g, 3.6 mmol) in cyclohexane (5 ml) was kept at room temperature for 12 h, a 1:1:1 complex (**5**) of **2a**, **2b**, and **3** was formed as colorless prisms (1.3 g, 2.9 mmol, 81% yield based on **3**), mp 60-63 °C. The host:guest ratios in **4** and **5** were determined by ^{1}H NMR spectra in $CDCl_3$.

Crystal data of $C_{20}H_{22}O\cdot C_2H_3N_3$ (**4**) are as follows: FW = 347.5, monoclinic, space group $P2_1/c$, a = 13.796(4), b = 10.886(3), c = 14.772(5) Å, β = 114.76(2)°, V = 2014.6 Å^3, D_c = 1.146 gcm^{-3} for Z = 4, μ =0.67 cm^{-1}, $F(000)$ = 744. Crystal data of $C_{20}H_{22}O\cdot(C_4H_6N_2)_2$ (**5**) are as follows: FW = 442.6, monoclinic, space group $P2_1/n$, a = 12.317(2), b = 13.866(5), c = 15.260(6) Å, β = 92.97(2)°, V = 2603.3 Å^3, D_c = 1.129 g cm^{-3} for Z = 4, μ = 0.65 cm^{-1}, $F(000)$ = 952.

Diffraction data of **4** and **5** were measured at ca. 18 °C on a CAD-4 diffractometer equipped with a graphite monochromator, using MoKα (λ = 0.7107 Å) radiation and the θ-2θ scan technique. For **4**, 2880 unique reflections were collected to θ_{max} = 25° at a constant 3° min^{-1} scan rate, scan range $\Delta\theta = 1.1+0.3\tan\theta°$. For the less stable crystal, 2248 unique data were measured to θ_{max} = 21° at a constant 5° min^{-1} scan rate, scan range $\Delta\theta = 0.9 + 0.3\tan\theta°$. The crystals were checked for deterioration, monitoring the intensities of three standard reflections from different zones of the reciprocal space. In both crystals an appropriate correction of data was required to account for the linear (in time) decrease of the intensities of the standards, 7.5% in **4** and 20% in **5**, during the experiment. The data sets were not corrected for absorption or secondary extinction effects. The overall precision of the structural results is affected by the poor quality of the analyzed crystals.

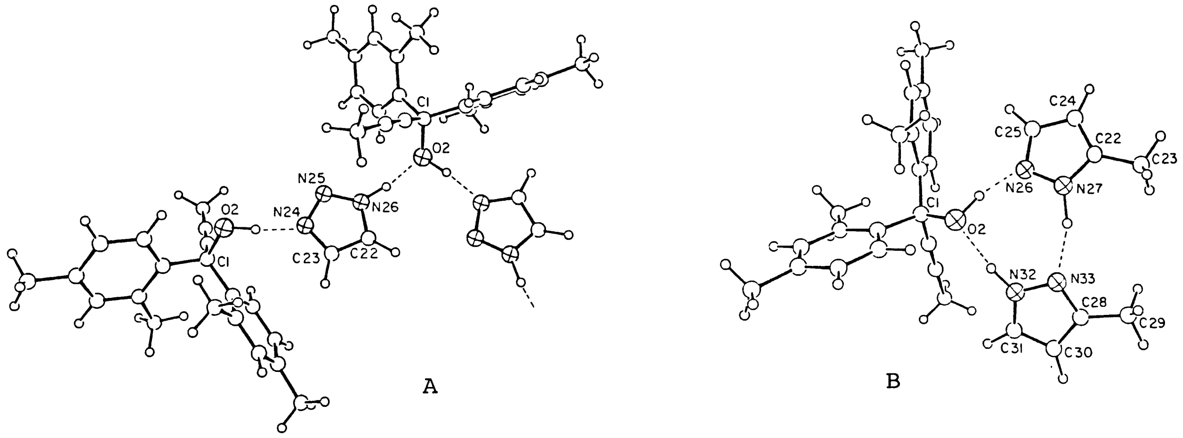


Fig. 1. View of the molecular structures and hydrogen bonding patterns in **4** (A) and **5** (B). All guest molecules are very close to planarity in the respective structures.

The crystal structure4) of **4** is isomorphous to that found for the closely related 1:1 complex of **6a** and **3**.3) It consists of continuous chains of hydrogen bonded moieties, each triazole guest almost symmetrically interacting with two adjacent host molecules (Fig. 1). This pattern, location of the proton near N26, and the covalent parameters within the guest molecule indicate that one of the two possible tautomeric forms of **1**, namely **1a**, predominates in this structure. The distribution of the observed distances[C22-C23 1.361(10), C23-N24 1.326(10), N24-N25 1.310(7), N25-N26 1.321(9), and N26-C22 1.315(9) Å] suggests a considerable degree of delocalization within the planar and symmetric molecule. The geometry of the hydrogen bonds is described by the following parameters: O2-H2 1.06, O2•••N24 2.715, H2•••N24 1.66 Å, O2-H2•••N24 172°; N26-H26 1.04, N26•••O2 2.841, H26•••O2 1.82 Å, N26-H26•••O2 166°. The central N25 is not involved in hydrogen bonding.

The crystal structure4) of **5** is composed of isolated units of the 1:1:1 complex of **2a**, **2b**, and **3** (Fig. 1). The observed molecular dimensions indicate that the molecule assigned by C22-N27 atoms corresponds to **2b** with proton at N27 [C22-C23 1.48(2), C22-C24 1.34(2), C24-C25 1.37(2), C25-N26 1.31(2), N26-N27 1.32(2), and N27-C22 1.36(2) Å], while that labeled by C28-N33 corresponds to **2a** with proton at N32 [C28-C29 1.48(2), C28-C30 1.39(2), C30-C31 1.35(2), C31-N32 1.32(2), N32-N33 1.35(2), and N33-C28 1.33(2) Å]. The three components form a cyclic arrangement of hydrogen bonds, each one of them acting simultaniously as a proton donor to and as a proton acceptor from a different species. The corresponding parameters are: O2-H2 1.11, O2•••N26 2.73, H2•••N26 1.66 Å, O2-H2•••N26 159°; N27-H27 1.16, N27···N33 2.91, H27···N33 1.78 Å, N27-H27···N33 163°; N32-H32 1.06, N32···O2 2.89, H32···O2 1.94 Å, N32-H32···O2 171°.

The crystal packing arrangement of **5** is illustrated in Fig. 2. There are no hydrogen bonds between adjacent units of the complex. This explains the lower melting point of **5** as compared to that of **4**, and the tendency of the crystals to deteriorate rather quickly.

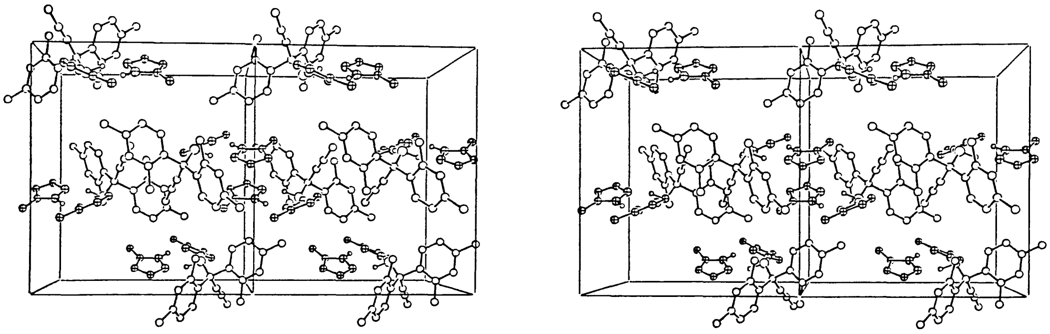


Fig. 2. Stereoview of the molecular packing in **5** projected along a axis. **2a** and **2b** molecules are marked by crossed circles; in the crystal they are located in pseudo cage-type voids formed between the host moieties, around the inversion centers at (0,0.5,0) and (0.5,0,0.5).

References

1) J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, "The Tautomerism of Heterocycles," Academic Press, New York (1976).

2) J. Elguero, "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford (1984).

3) F. Toda, K. Tanaka, J. Elguero, L. Nassimbeni, and M. Niven, Chem. Lett., 1987, 2317.

4) The two structures were solved by a combination of direct methods and Fourier techniques (MULTAN-80). Their refinements were carried out by full-matrix least-squares (SHELX-76), including the positional and anisotropic thermal parameters of all the nonhydrogen atoms. Most hydrogens were included in the structure factor computations in calculated positions, the methyls being treated as rigid groups. Those involved in hydrogen bonds were located directly in difference-Fourier maps. The final refinements were based only on observations above the intensity threshold of $3\sigma(I)$, using experimental weights $w = \sigma(F)^{-2}$, and minimizing $w(\Delta F)^2$. Due to the low data-to-parameters ratio in **5**, the phenyl rings in this structure were refined as regular hexagons of constrained geometry. The final difference-Fourier maps showed no indication of incorrectly placed or missing atoms, the highest peak and deepest trough not exceeding 0.27 eÅ^{-3}. At convergence, the discrepancy factors are: For **4**, R = 0.072 and wR = 0.074 for 1239 reflections above the intensity threshold, goodness-of-fit = 1.23e. For **5**, R = 0.075 and wR = 0.070 for 904 observations, g.o.f. = 1.16e. The atomic coordinates of the two complexes have been deposited with the Cambridge Crystallographic Data Centre.

(Received March 24, 1988)