Pergamon

Tetrahedron Letters 39 (1998) 2843–2846

TETRAHEDRON
LETTERS

Unexpected isomerization of maleic acid to fumaric acid on co-crystallization with 4,4'-bipyridine

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Received 25 November 1997; revised 3 February 1998; accepted 6 February 1998

Abstract: Co-crystallization of maleic acid, **1**, with 4,4'-bipyridine, **2**, in acetone, chloroform, ethylacetate and methanol gives a hydrogen bonded 2:1 adduct of **1** with **2** (monoclinic space group, C2/c, a=24.056(8), b=6.891(2), c=11.474(6)Å, β=116.10(4)°). Co-crystallization in dimethylformamide and dimethylsulfoxide, however, yields a 1:1 adduct of fumaric acid with **2** (triclinic space group P$\bar{1}$, a=3.875(1), b=8.906(1), c=10.016(1)Å, α=109.60(1)°, β=98.64(1)°, γ=96.64(1)°).

We have been investigating the structures of hydrogen bonded adducts obtained by the co-crystallization of aliphatic dicarboxylic acids with molecules containing two donor sites with the expectation of forming interesting hydrogen bonded supramolecular assemblies.[1,2] As part of the study, we recently examined the structures of the adducts obtained from the co-crystallization of maleic acid, **1**, with 4,4'-bipyridine, **2**, in different solvents. Co-crystallization of **1** with **2** in acetone, chloroform, ethylacetate and methanol gave the expected adduct, but co-crystallization in dimethylformamide and dimethylsulfoxide gave an adduct where **1** had isomerized to fumaric acid. We report the essential results related to this unexpected *cis* → *trans* isomerization in this contribution.

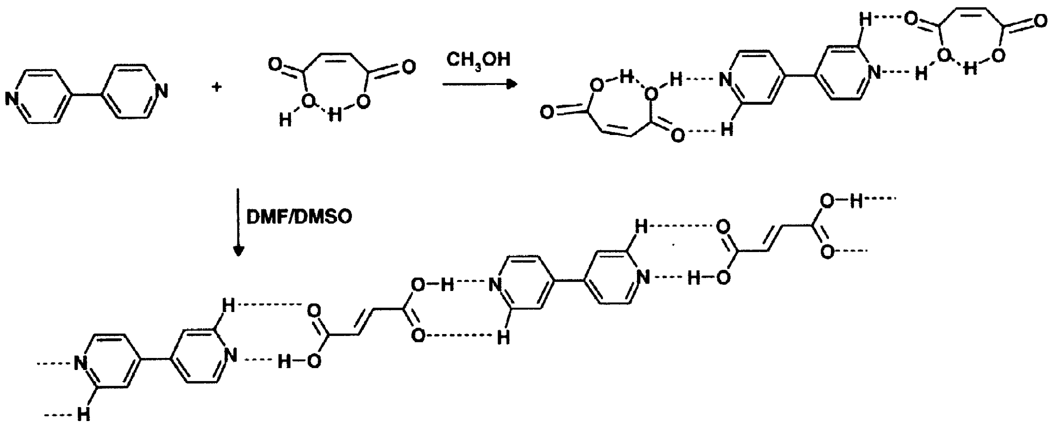

Chart 1

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PII: S0040-4039(98)00313-X

In Fig. 1 we show the structure[3] of the 2:1 adduct of maleic acid, **1**, with 4,4'-bipyridine, **2** obtained by co-crystallization in methanol solvent. The composition and structure of the adduct crystallized from acetone, chloroform, ethylaceate were identical. In the structure shown in Fig. 1, the strong intramolecular O-H...O bond of **1** is unperturbed. Each maleic acid molecule forms an intermolecular O-H...N bond with **2** (H...N, 1.81(2)Å; O...N, 2.61(1)Å) and the C-H bonds of 4,4'-bipyridine interact with the oxygens of **1** forming C-H...O bonds with H...O and C...O distances in the ranges 2.26 - 2.57Å and 3.21 - 3.26Å respectively (also see Chart 1). The 4,4'-bipyridine molecule in the adduct is non-planar with the two pyridine rings forming an angle of 23°.

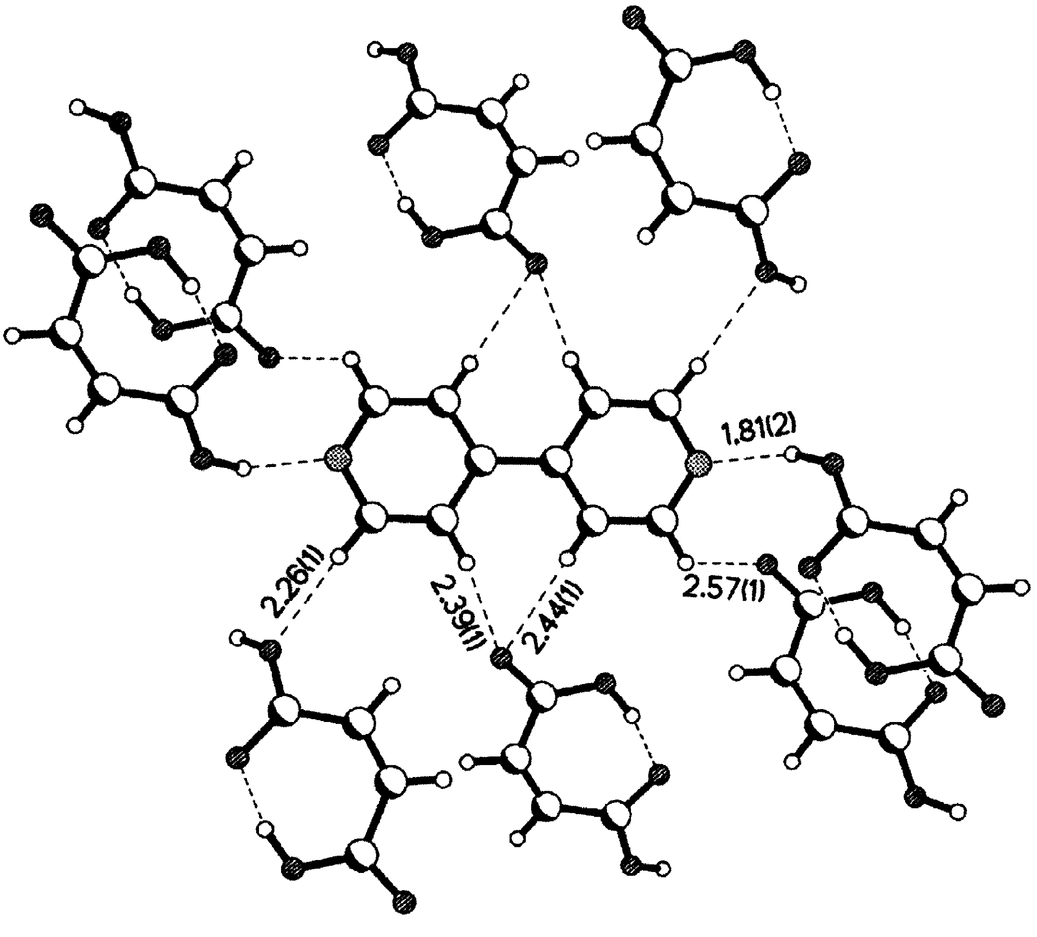

Fig. 1: Structure of the 2:1 adduct of maleic acid, **1**, with 4,4'-bipyridine, **2**.

When **1** was co-crystallized with **2** in dimethylformamide (DMF) or dimethylsulfoxide (DMSO) solvent, however, we obtained a 1:1 adduct[4] with the structure shown in Fig. 2. We see that **1** has isomerized into fumaric acid in the adduct. In this adduct, each fumaric acid molecule forms two intermolecular O-H...N bonds (H...N, 1.69(2)Å; O...N, 2.63(1)Å) as well as two C-H...O bonds (H...O, 2.49(1)Å; C...O, 3.35(1)Å) with **2**. This imposes a center of inversion and results in the planarity of the 4,4'-bipyridine molecule. The *cis* → *trans* isomerization found here is rather unusual, considering that the isomerization of maleic acid is normally induced by interaction with other compounds by thermal or photochemical means.[5-7]

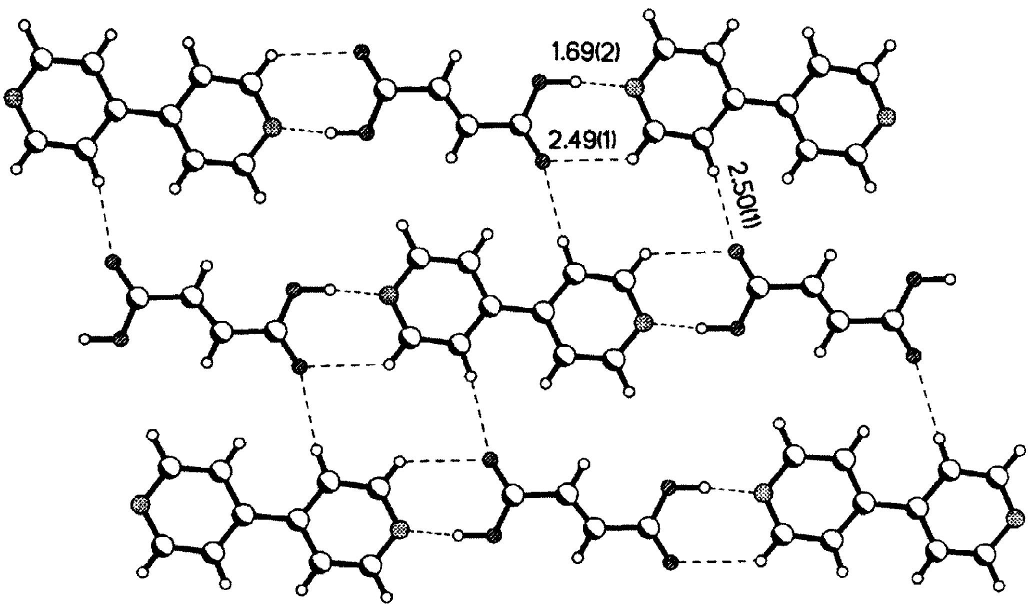

Fig. 2: Structure of the 1:1 adduct of fumaric acid with 4,4'-bipyridine.

It appears that the role of the highly polar DMF (DMSO) solvent is primarily to break the intramolecular hydrogen bond in **1**. The bipyridine molecule being a good nucleophile adds on to the hydrogen-bond free maleic acid forming a zwitterionic species which then isomerizes to the *trans* form, followed by the elimination of the bipyridine molecule. That bipyridine plays the crucial role in the *cis* → *trans* isomerization is supported by our finding that refluxing **1** in DMF or DMSO solvent does not give fumaric acid. Interestingly, based on NMR studies, we find that the isomerization occurs in solution phase as well.

References and Notes:

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2) Aakeroy C. B.; Seddon, K. R. Chem. Soc. Rev. 1993, 397.
3) Crystal Data for co-crystals of **1** and **2**: $2(C_4H_4O_4)$: $(C_{10}H_8N_2)$, M=388.33, monoclinic, space group C2/c, a=24.056(8), b=6.891(2), c=11.474(6)Å, β=116.10(4)°, V=1708.1(1)Å^3, Z=4, ρ_{calcd}=1.510, $\mu(MoK_\alpha)$=0.121mm^{-1}, F(000)=808, λ=0.71073, T=293K, Smart CCD area detector, Siemens, The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least squares on F^2 (SHELX-93; G. M. Sheldrick, Gottengen, 1993) to R_1=0.030 and wR_2=0.082. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically except the carboxyl hydrogen atom which is fixed in a calculated position. Residual density, min/max -0.133/0.135e.Å^{-3}.
4) Crystal Data for co-crystals of fumaric acid and **2** : $C_4H_4O_4$: $C_{10}H_8N_2$, M=272.26, triclinic, space group $P\bar{1}$, a=3.875(1), b=8.906(1), c=10.016(1)Å, α=109.60(1)°, β=98.64(1)°, γ=96.64(1)° V=316.8(1)Å^3, Z=1, ρ_{calcd}=1.427, μ(MoKα)=0.107mm^{-1}, F(000)=142, λ=0.71073, T=293K, Smart CCD area detector, Siemens, R_1=0.048 and wR_2=0.106. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically. Residual density, min/max -0.186/0.166e.Å^{-3}.
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