A direct conversion of cis- cyclohexane-1, 2, 3, 4 -tetracarboxylic 1:2,3:4-dianhydride to its trans-isomer

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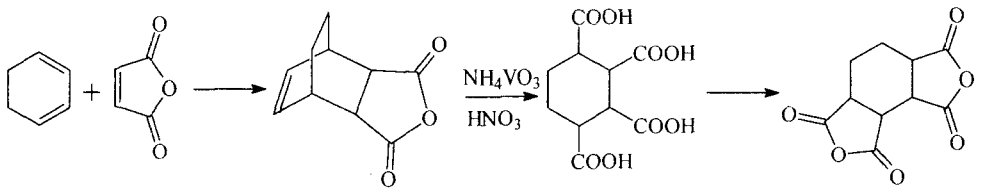
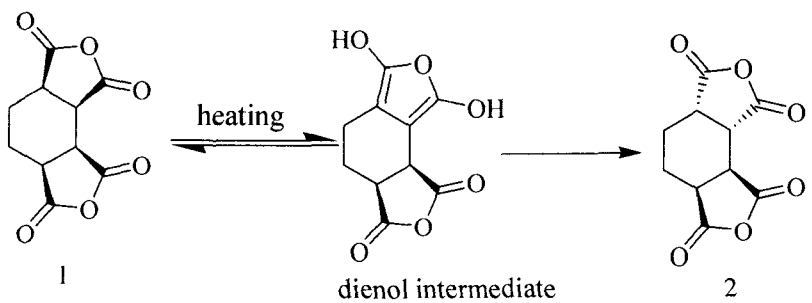
A direct synthetic method of trans-cyclohexane-1, 2, 3, 4 -tetracarboxylic 1:2,3:4 -dianhydride(2) was established by thermal isomerization of cis-tetracarboxylic dianhydride (1), the crystal structures of 1 and 2 were determined by single crystal X-ray diffraction.

A considerable effort has been made towards aliphatic polyimides,[1] a class of polymers known for their solubility and colorlessness and their potential applications including use as liquid crystal orientation layers, light-guide, or high-temperature low dielectric materials.[2] Recently, we are greatly interested in the polyimides from isomeric aliphatic dianhydrides. We synthesized compound **1** by the following steps.



In an attempt to purify cis-cyclohexane 1,2,3,4-tetracarboxylic-1:2,3:4-dihydride (**1**), we found a thermal isomerization of **1** to trans-cyclohexane dianhydride(**2**). We herein report a facile conversion of **1** to **2** and the crystal structures of **1** and **2**.



Scheme 1 possible thermal isomerization mechanism.

Cyclohexane-1-exo, 2-exo, 3-exo, 4-exo-tetracarboxylic acid(**3**) was prepared by literature's method[3]. The single crystals of **1** were formed by treatment **3** with acetic anhydride in refluxing for 2 hours, followed by standing at room temperature for 12 hours. The crystal structure of **1** is shown in Figure **1**.

Interestingly, vacuum sublimation of **1** afforded a mixture of **1** and **2** , a small amount of pure **2** was obtained at the beginning of the slow sublimation of **1**. Recrystallizaton of **2** with acetic anhydride give its single crystal. The crystal structure of **2** is shown in Figure **2.**

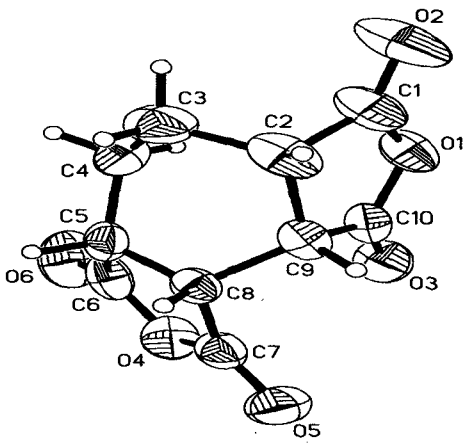


Figure 1 X-ray crystal structure of 1

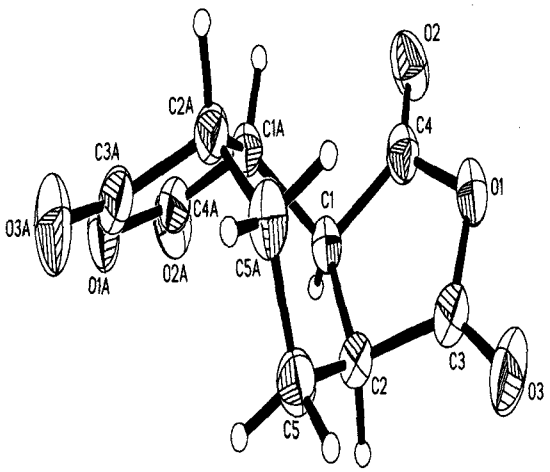


Figure 2 X-ray crystal structure of 2

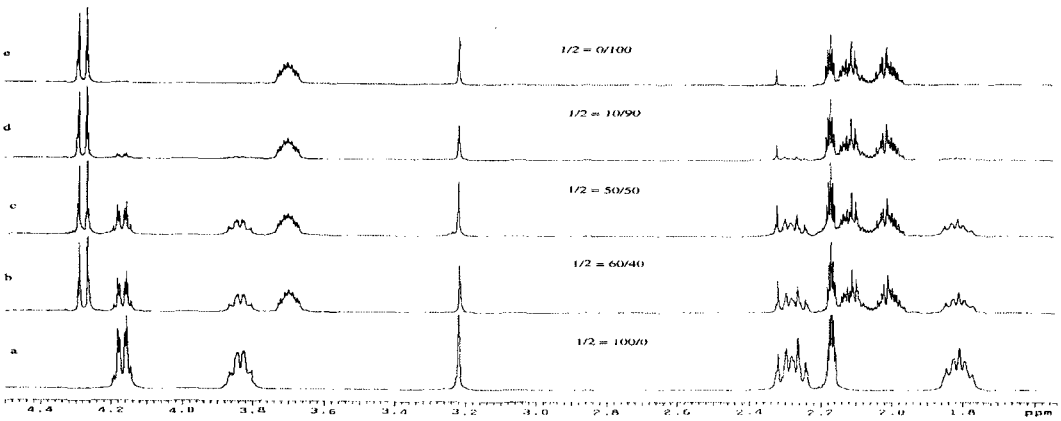


Figure 3 ^{1}H NMR spectra (400MHz) at 25℃ of in d_6-acetone

(a) compound 1; (b) treatment 1 with acetic anhydride in refluxing for 2.5 hours; (c) treatment 1 with acetic anhydride in refluxing for 3 hours; (d) treatment 1 with acetic anhydride in refluxing for 3.5 hours; (e) treatment 1 with acetic anhydride in refluxing for over 4 hours.

To investigate this conversion, the compound **1** was heated in a vacuum sealed tube for 8 hours at 230^{0}C, the resulting product was characterized by ^{1}H NMR， compounds **1** and **2** with a ratio of 1:9

were finally obtained. When treatment of compound **1** in refluxing acetic anhydride, followed by ^1H NMR, the compound **2** was exclusively formed after 4 hours as shown in Figure **3**. However, none of **2** was observed when heating **1** in refluxing xylene for 4 hours. This indicated that the conversion of **1** to **2** probably underwent a enolization which would be catalyzed by a trace of carboxylic acid in acetic anhydride. The intermediate of thermal isomerization was dienol, which is a planar structure and easy to converse its more stable trans-configuration(**Scheme 1**). The compound **2** is a more thermal stable product which cannot be converted to **1** at the temperature of refluxing acetic anhydride. However, at elevated temperature , compound **2** partialy convert to **1** (10%) in a vacuum sealed tube heating(230^0C). The higher temperature (>230^0C) will lead to the decomposition of product..

Quantum chemical calculations were performed on **1** and **2** using the semiempircal AMI[4]method by input their crystal data. All calculations were computed by using MOPAC of the option of SYBYL version 6.1. As our expected, **2** (-219.71 kcal•mol^{-1}) is lower than **1** (-216.16 kcal•mol^{-1}) in the final heat of formation.

In conclusion, a new facile method of synthesizing **2** by thermal isomerization of **1** was found. The present experimental results and the computational results fit well together. The more flexiblity of the cyclohexane ring, which has special electronic and steric effect, will contribute to thermal isomerization. Furthermore, our experimental results and computational results have provided a new mechanistic picture of thermal isomerization that will be a guide to other alicyclic dianhydrides.. Thermal isomerization in polyimides from these isomeric dianhydrides will be expected.

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Notes and references

§ *crystal data* for **1** : C10H8O6, M=224.16, monoclinic, a= 7.270(2), b=10.296(2), c=12.868(3) Å, U=955.1(3) $Å^3$, T=293(2) K, space group $P2_1/n$, Z=3, μ (M_O-K α)=0.099 mm^{-1}, 2443 reflections measured, 1683 unique (R_{int} = 0.0216) which were used in all calculations. The final $Wr(F^2)$ was 0.784(all data).

for **2** : C10H8O6, M=224.16, monoclinic, a=13.342(2), b=6.6980(10), c=10.214(2) Å, U=889.0(3) $Å^3$, T=293(2) K, space group $C2/c$, Z=4, μ (M_O-K α)=0.142 mm^{-1}, 1170 reflections measured, 785 unique (R_{int} = 0.0135) which were used in all calculations. The final $Wr(F^2)$ was 0.989(all data).

Note: All data were recorded using Siemens P4 four-circle diffractometer ω/2θ scans Absorption correction: empirical via Ψ scans(XSCANS; Siemens,1994a)

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