

A CYCLIC TRIMER OF 4-VINYLPYRIDINE

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Although the co-ordinated polymerization of 2-vinylpyridine leads to the formation of crystallizable macromolecules, the polymerization of 4-vinylpyridine gives always non-crystallizable linear high polymers (1):

Supposing that this lack of crystallization could be attributed to some steric hindrances and could be obviated, even though partially, by decreasing the molecular weight of the macromolecules, we investigated on the thermal degradation of poly-4-vinylpyridines. These researches confirmed that no linear crystallizable polymers of 4-vinylpyridine, even though having low molecular weight, can be obtained, and demonstrated that, among the degradation products of poly-4-vinylpyridine obtained by both radicalic and anionic polymerization, a crystalline product was always present, corresponding to a sym-tri(4-pyridyl)cyclohexane, that is to say a cyclic head-to-tail trimer of 4-vinylpyridine (°).

It was also found that particularly high yields of cyclic trimer can be obtained when the degradation (at 250-300°C) was carried out by using, instead of the polymer, some of its salts (e.g. poly-4-vinylpyridinium hydrochloride).

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(°) As far as we know, the formation of a cyclic trimer by degradation of linear macromolecules having a hydrocarbon chain, has never been described.

As a consequence of the above-mentioned researches, it can be inferred that the most suitable procedure for the preparation of the said trimer by a poly-4-vinylpyridine degradation, has to include: a) the preparation of the polymer of 4-vinylpyridine; b) the preparation and degradation of poly-4-vinylpyridinium hydrochloride; c) the isolation of the cyclic trimer from the degradation products.

a) Preparation of poly-4-vinylpyridine

As an example, a typical anionic co-ordinated polymerization run of 4-vinylpyridine is hereinafter described.

$(C_2H_5)_2NMgI$  (2.2 g) and anhydrous toluene ( $100\text{ cm}^3$ ) are introduced, under nitrogen atmosphere, in a  $250\text{ cm}^3$  capacity three-necked flask, equipped by mechanical stirrer, dropping funnel, and thermostatic oil-bath at  $60^\circ\text{C}$ . After stirring for 15 min., a recently distilled solution of 20 g anhydrous 4-vinylpyridine in  $50\text{ cm}^3$  toluene is slowly added. After 5 hrs. at  $60^\circ\text{C}$ , n-butanol ( $5\text{ cm}^3$ ) is added; the flask content is poured in a 3 litres capacity separatory funnel, and water (1 litre) and conc. HCl ( $30\text{ cm}^3$ ) are added; the toluene layer is removed. Chloroform ( $800\text{ cm}^3$ ) and a solution of  $NH_4Cl$  (30 g) and of conc.  $NH_3$  ( $150\text{ cm}^3$ ) in  $400\text{ cm}^3$  of water are added to the aqueous layer. The lower phase, consisting of a chloroform solution of poly-4-vinylpyridine, is evaporated until  $30\text{--}50\text{ cm}^3$  and polymer is precipitated by pouring in n-heptane (about  $50\text{ cm}^3$ ). After drying 15.5 g of polymer are weighed; intrinsic viscosity in dimethylformamide at  $30^\circ\text{C}$ :  $0.2 \cdot 100\text{ cm}^3/\text{g}$ .

b) Preparation and Degradation of Poly-4-vinylpyridinium Hydrochloride

In a 500 cm<sup>3</sup> capacity flask, poly-4-vinylpyridine (15.5g) is dissolved in chloroform (250 cm<sup>3</sup>) and gaseous hydrochloric acid is let in at room temperature, under stirring, until hydrochloric acid is no longer absorbed.

The white precipitate is dried at reduced pressure (1-2 mmHg) at 50-60 °C.

The poly-4-vinylpyridinium hydrochloride thus obtained is heated, by a Wood alloy bath, at 280 °C for 3 hrs. at a reduced pressure (14 mmHg). Hydrochloric acid and 4-vinylpyridine monomer are evolved.

c) Isolation of the crystalline product

The final degradation product is dissolved in chloroform (100 cm<sup>3</sup>) and treated twice in a separatory funnel, first with aqueous ammonia, then with distilled water, until the Cl<sup>-</sup> ion absence. The chloroform solution is then dried (by removing the chloroform-water azeotrope) and slowly added to n-heptane (about 300 cm<sup>3</sup>). A semi-solid product, mostly consisting of linear low-molecular-weight polymers of 4-vinylpyridine, is separated. A light yellow crystalline product, mostly consisting of the desired compound, is further separated from the remaining solution, by addition of n-heptane (about 600 cm<sup>3</sup>). After filtering and drying it amounts to 9.5 g; purification by crystallization from methylethylketone is the carried out.

By using poly-4-vinylpyridine (23 g) obtained by radical induced polymerization ( in benzene solution at 80 °C; azobisisobutyronitrile as initiator) and by following the procedure described in b) and c), 8.2 g of crude crystalline product are obtained.

d) Properties and structure of the Crystalline Product

The pure product melts at 228.5 °C; it is soluble in chloroform, methylene chloride, aromatic hydrocarbons, alcohols, and ketones; slightly soluble in ethyl ether, insoluble in cold aliphatic or cycloaliphatic hydrocarbons. Analysis gives a nitrogen content of 13.03 % (calc. for 4-vinylpyridine = 13.32 %). By cryoscopy in nitrobenzene solution, 312 is found as for the molecular weight. Therefore the substance examined is a trimer of 4-vinylpyridine (calc. molecular weight: 315.4), to which either a linear or a cyclic structure might be attributed.

Trimer having linear structure should have to contain groups, such as  $-\text{CH}_3$  or  $-\text{CH}=\text{CH}-$  or  $>\text{C}=\text{CH}_2$ . On the contrary, I.R. spectrum of the trimer (fig. 1) does not show any bands which can be attributed to the said groups (°°).



Fig. 1 - I.R. absorption spectrum of 1e, 3e, 5e-tri(4-pyridyl)cyclohexane in the molten state.

(°°) The position of the absorption bands of the above mentioned groups ( $7.28\mu$  for  $-\text{CH}_3$ ,  $10.34\mu$  for trans  $-\text{CH}=\text{CH}-$  and  $11.07\mu$  for  $>\text{C}=\text{CH}_2$ ) was determined from the I.R. absorption spectra of 4-picoline, trans-4-propenylpyridine and 4-isopropenylpyridine. The weak band at  $7.26\mu$  of fig. 1 must be attributed to the pyridine ring rather than to the methyl group (2).

We can therefore conclude for a cyclic structure of the trimer, that is to say (in the very likely hypothesis of a head-to tail enchainment of the monomeric units) for the structure of sym-tri(4-pyridyl)cyclohexane.

The exactness of this hypothesis has been proved by X-ray examination of the trimer in the solid state (3) and by examination of the nuclear magnetic resonance spectrum of the trimer in a  $\text{CDCl}_3$  saturated solution (4).

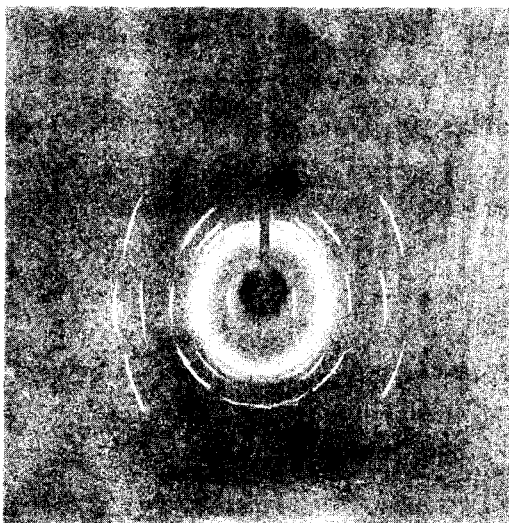


Fig. 2 - X-ray diffraction spectrum ( $\text{CuK}\alpha$ ) of 1e, 3e, 5e-tri(4-pyridyl)cyclohexane in the solid state.

In particular, interpretation of the X-ray diffraction spectrum (fig. 2) ( $^{\circ\circ\circ}$ ) gives a rhombohedral unit cell, wherein constants referred to a hexagonal system of axes, are:  
 $a = b = 17.50 \pm 0.10 \text{ \AA}$ ;  $c = 4.65 \pm 0.05 \text{ \AA}$  (most probable space group:  $R3$ ).

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( $^{\circ\circ\circ}$ ) Such a spectrum was made on a stretched fibre obtained from a 1:1 mixture of commercial polystyrene and cyclic trimer of 4-vinylpyridine.

Since three molecules of the trimer are present in the unit cell, it can be calculated, as for its density, a  $1.27 \text{ g/cm}^3$  value quite near to the experimental one of  $1.28 \text{ g/cm}^3$ .

Taking into consideration the unit cell symmetry and any possible packing of the molecules, it can be concluded that a cyclic structure has to be attributed to the trimer, and the three pyridine rings are arranged in the equatorial belt of the cyclohexane "chair" configuration (fig. 3).

Based on the structure factors obtained by the steric configuration of fig. 3, a good agreement is found between the calculated and observed intensities.

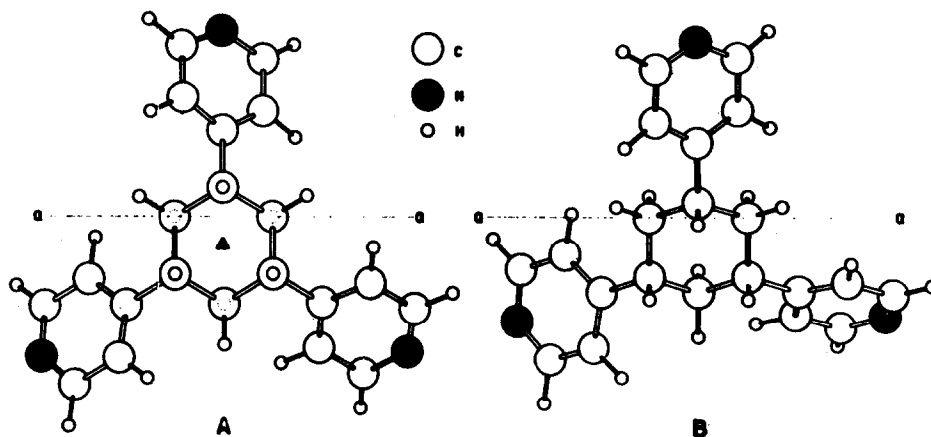


Fig. 3 - Steric configuration of 1e, 3e, 5e-tri(4pyridyl)cyclohexane.

(A = projection of the trimer molecule on (001) plane;

B = the same rotated about a.....a through a  $30^\circ$  angle).

#### References

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