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CONFORMATION OF SYM-TRI(4-PYRIDYL)CYCLOHEXANE BY NMR ANALYSIS

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G. Natta and co-workers (1) have shown that by anionic co-ordinated polymerization processes it is possible to obtain crystallizable linear high polymers of 2-vinylpyridine. In the case of 4-vinylpyridine the same process gives amorphous polymers which cannot be crystallized.

Recently more work has been carried out with the purpose of studying whether one could obtain a crystalline polymer of 4-vinylpyridine by lowering its molecular weight.

It has been found that among the thermal degradation products of poly-4-vinylpyridines, obtained by both radicalic and anionic polymerization, a crystalline substance was always present (2).

The chemical analysis revealed that such a substance consisted of a 4-vinylpyridine trimer. Because the infrared spectrum had not shown the existence of terminal groups, a cyclic structure was postulated for that substance.

Therefore we thought it was interesting to study by nuclear magnetic resonance method the structure and in particular the conformation of that crystalline substance. The NMR spectrum was run on the compound in a saturated solution at room temperature in $CDCl_3$, using tetramethylsilane (TMS) as internal reference.

We have used a Varian HR 100 spectrometer, working at the fixed frequency of 100 Mc/sec.

Five multiplets have been observed (fig.1) with chemical shift (with respect to TMS) of 8.55; 7.20; 3.00; 2.25; 1.80 ppm. and relative intensities 2 2 1 1 1 respectively. The chemical shifts have been measured at the center of the bands.

The bands at 8.55 and 7.2 ppm. have been assigned to the "a" and "b" protons of the pyridine group (fig.2)(3); the former band is broad with respect to the latter because of the coupling with nitrogen (4). Thus the 8.55 ppm. peak is attributed to the protons in "a". The pair of bands show a spectrum of the A_2X_2 type (4).

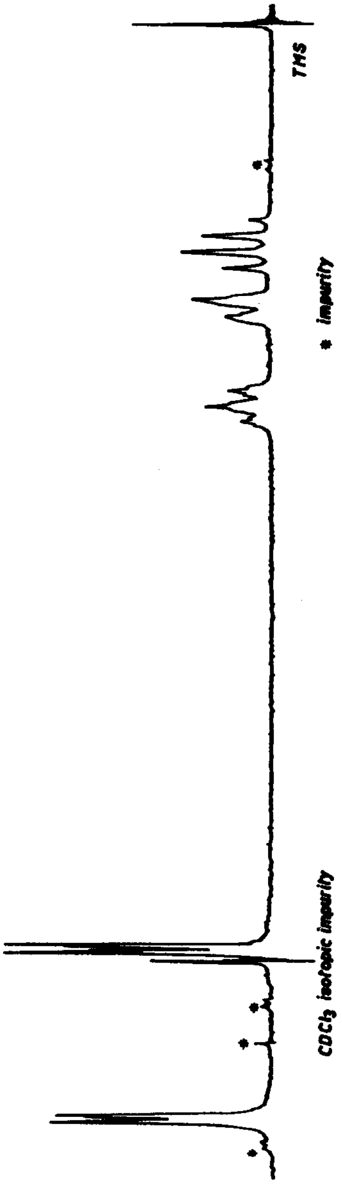

FIG.1

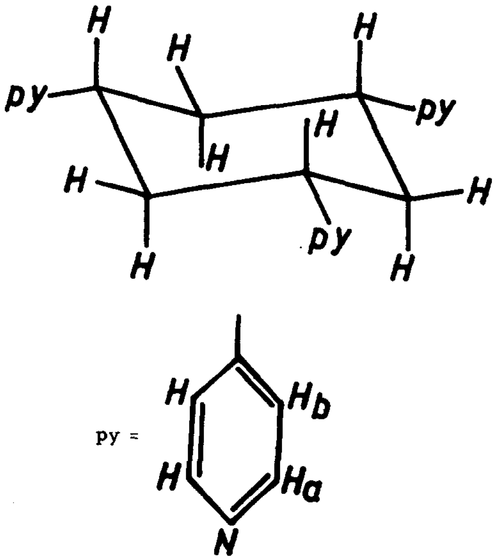

FIG.2

The band at 3 ppm appears as a main symmetric triplet with splitting of 12.5 cps. Each of the components is itself a triplet. On the basis of the value of the chemical shift, it was attributed to the protons placed on the C atom, to which the pyridine ring is attached.

The other two bands at 2.25 and 1.8 ppm have therefore been attributed to the hydrogen atoms of the CH_2 groups, which occur with distinct peaks because of their equatorial and axial positions.

The first of these two bands appears as a broad doublet, the second as a quartet having sharp components. This is due to the strong coupling between gem-hydrogens: J_{gem} = 12.5 cps. Moreover it is found that the first band has broad components and the second one has sharp components. On the basis of this finding and by observing the value of the chemical shift (5, 6), we assign the first of these bands to equatorial hydrogen atoms and the second one to the axial CH_2.

Finally, one can also say that the tertiary hydrogen atoms of the cyclohexane ring are in axial position, because they are strongly coupled to the adjacent axial hydrogen atoms (6). In this way we can explain the main triplet at 3 ppm, and also the quartet at 1.8 ppm, being $J_{ax-ax} = 12.5$ cps. Moreover the minor triplets occurring in the band at 3 ppm and in the band at 2.25 ppm due H_{ax}, H_{eq} the interactions with $J_{ax,eq} = 2$ cps can be explained with this assignment.

Therefore we propose that the most probable structure of sym-tri(4-pyridyl)cyclohexane is that described in fig.2, where the pyridine groups are 1, 3,5 equatorial positions.

This structure corresponds to the cis isomer.

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References

1) G.Natta, G.Mazzanti, P.Longi, G.Dall'Asta, F.Bernardini, J.Polymer Sci. 51, 487 (1961).
2) P.Longi, I.W.Bassi, F.Greco, M. Cambini, in press.
3) W.G.Schneider, H.J.Bernstein, J.A.Pople, Can.J.Chem. 35, 1487 (1957)
4) J.A.Pople, W.G.Schneider, H.J.Bernstein, High Resolution Nuclear Magnetic Resonance, p.140, p.392, McGraw Hill
5) Lemieux et al., J.Am.Chem.Soc. 80, 6098 (1958)
6) Lemieux et al., J.Am.Chem.Soc. 80, 2237 (1958).