

geometrically as indicating that the lamella consists of beaded strings running parallel with the fibre direction and shifted irregularly with regard to one another within this direction. On the assumption that the globular units have a dimension of 21 Å. in the fibre axis—which seems reasonable in view of the molecular weight of 33,000 and the dimension of 45 Å. in the side-chain direction—this interpretation could explain the diffuse layer-line reflexion.

We are still unable to say why both groups of new reflexions, those at the equator and those at the meridian, exclude one another. Furthermore, we wish to emphasize that the other interpretations offered are still somewhat hypothetical. Our investigations are being continued.

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¹ Kratky, O., Schauenstein, E., and Sekora, A., *Nature*, **165**, 319 (1950).

² Kratky, O., Schauenstein, E., and Sekora, A., *Nature*, **165**, 527 (1950).

³ Coleman, D., and Howitt, F. O., *Proc. Roy. Soc., A*, **190**, 145 (1947).

⁴ Kratky, O., Schauenstein, E., and Sekora, A., *Nature*, [166, 1031 (1950)].

⁵ Zahn, H., and Kratky, O. (unpublished experiments).

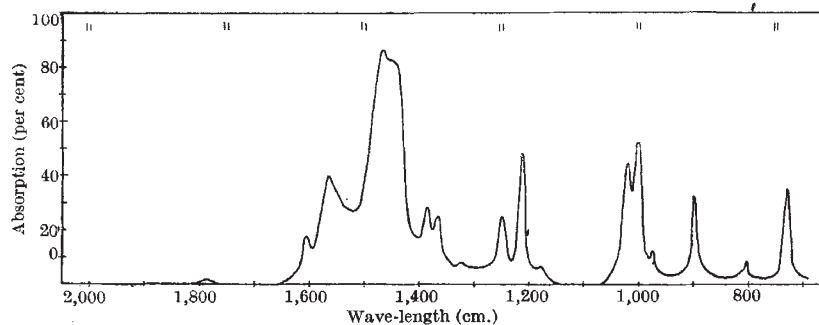
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Isolation of 2:3:5:6-Tetramethylpyridine from Coal Tar

DURING AN investigation of the nitrogenous bases extracted by sulphuric acid from the 'benzol absorbing oil' fraction of coal tar, a solid base has been isolated which has been proved to be 2:3:5:6-tetramethylpyridine, a compound which has not hitherto been reported as a constituent of coal tar.

The solid separated out from a fraction (b. 130–132°C./100 mm.) obtained by high-efficiency fractional distillation (efficiency approximately 100 theoretical plates) of certain purified coal-tar base samples. After repeated crystallization of this solid from petroleum ether, a product was obtained which consisted of small white glistening platelets with a pleasant odour and a melting point of 76°C. From this pure product the picrate (m.p. 176°C.), the picrolonate (m.p. 259–260°C., decomp.) and the methiodide (m.p. 178°C.) were prepared.

The distillation-range and melting point of this base, as well as the melting points of the derivatives prepared, were found to be identical with those of a tertiary base of the formula $C_9H_{13}N$, which was isolated from the mixed pyridine bases in shale oil in these laboratories by Messrs. R. J. Benzie and J. N. Milne¹, and mixed melting points showed no lowering. Benzie and Milne suggested tentatively that this compound was 2:3:5:6-tetramethylpyridine on the basis of a comparison of its dissociation constant with those of other methylated pyridines, and this was further supported by analogy of the tetramethylpyridines to the tetramethylbenzenes.



There are few references in the literature to the preparation of this compound. Oparina², however, obtained a solid tertiary base in the reaction products on passing a mixture of formaldehyde, methyl ethyl ketone and ammonia over alumina in a heated copper tube. This solid base melted at 73–74°C. and its picrate melted at 173–174°C. This work has been repeated in this College by R. T. Smith, who obtained a solid product which on purification melted at 76°C. and the picrate of which melted at 176°C. The mode of preparation of this compound strongly indicates the 2:3:5:6 configuration. Mixed melting points of the base isolated from coal tar and its picrate with these products showed no lowering.

Oparina³ has recently repeated his earlier work² and obtained a product which melted at 81°C. and the picrate of which melted at 173.5°C. On partial oxidation of this free base with permanganate, he obtained 2:6-dimethylpyridine-3:5-dicarboxylic acid, which on distillation with lime yielded 2:6-dimethylpyridine. Oxidation with excess permanganate yielded a crude tetracarboxylic acid which on heating lost carbon dioxide to give an acid melting at 308–309°C. From the mother liquors of the oxidation the 3:5-dicarboxylic acid and 2:5-dimethylpyridine-3:6-dicarboxylic acid were obtained.

This work proves quite conclusively that the product obtained by Oparina was 2:3:5:6-tetramethylpyridine, and, on the grounds that their reaction conditions were almost identical, it can be assumed that the product obtained by Smith was also 2:3:5:6-tetramethylpyridine, in spite of discrepancies in the melting points.

The infra-red absorption spectrograms for the three samples of solid base obtained in this College, which were prepared by Mr. J. L. Hales, of the Department of Scientific and Industrial Research, using saturated solutions in carbon tetrachloride/carbon disulphide mixture and a 50-μ cell, were found to be identical and to follow the graph reproduced herewith. The graph is corrected for solvent bands.

This evidence, together with the evidence of the mixed melting points, is sufficient to prove that these three samples are identical and thus that the solid base isolated from coal tar was 2:3:5:6-tetramethylpyridine.

A complete account of this work will be published at a later date.

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