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METHODS FOR THE ENUMERATION OF ISOMERS

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Isomers of alkyl derivatives including alkanes were first counted by Cayley, then by Henze and Blair, using recurrence formulas for labelled trees with restrictions of vertex degrees. An elegant procedure makes use of Pólya's theorem, as presented at this meeting by professor O. E. Polansky.

Some further applications of Pólya's theorem for cyclic graphs are presented : isotope-isomers of labelled compounds (generalizing suitably the figure-counting series), isomers of the porphyrins (correcting D. Blackman's figures from J. Chem. Educ. 1973, 50, 258), substituted or hetero-analogues of valence-isomers of annulenes. In the last class, coisomeric cubic multigraphs are those which have the same cycle index, e. g. benzene and benzprismane, or diademane and triquinacene (ignoring stereoisomerism).

Enumerations of all possible monocyclic aromatic systems may be effected either directly or using Pólya's theorem. If adjacency restrictions are imposed on the three kinds of atoms forming such rings, the problem becomes more complicated ; it has been subjected to a recent mathematical analysis and solved for a few particular cases.

Condensed benzenoid polycyclic hydrocarbons may be enumerated using their modified dual graphs (involving angular coordinates for vertices). So far this was done separately for branched and non-branched cata-condensed systems, but it was not yet possible to solve rigorously the problem for

peri-condensed systems (only by a computer algorithm was it possible to count such systems). The problem can be generalized to systems of mathematical interest (the cell growth problem) or of chemical significance (non-benzenoid condensed hydrocarbons).

The enumeration of valence-isomers of annulenes is equivalent to enumerating cubic multigraphs. An algorithm was devised, because the mathematically rigorous treatment proved too difficult to be applied to chemically interesting cases. Efforts were made to adapt this algorithm for valence-isomers of benzoannulenes.

Enumerations of stereoisomers are interesting for the organic and coordinative chemistry, or for rationalizing rotamers evidenced by variable-temperature NMR. The enumerations of the geometric configurations of annulenes superimposable on the graphite lattice, and of the conformations of large-ring cycloalkanes superimposable on the diamond lattice made use of three and four spatial coordinates, respectively, for the orientation of edges.

The ultimate problem, to enumerate all constitutional isomers (cyclic and acyclic) with a given molecular formula was initially dealt with by means of a recurrent algorithm for multigraphs of degree four or less, and was recently developed by Lederberg, Masinter and their coworkers into an efficient computer program.