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ALTERNATION IN MELTING-POINT IN HOMOLOGOUS SERIES

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Abstract—The "alternation" in m.p. in homologous series is discussed. In particular four series of derivatives of methyl n-alkylketones are studied and the "alternations" shown diagrammatically.

THE preparation and purification of a series of methyl n-alkylketones and of four series of crystalline derivatives has already been briefly reported.[1] It is now desired to emphasize the interesting changes in the m.p.–composition curves in each series of derivatives (Figs I and II).

With compounds where $n = 1 - 5$, in $MeCO(CH_2)_nH$, all four series show large variations in m.p.: of these early members the m.ps are of course primarily dependent on the properties of the reagent (a substituted hydrazine in each case), but every additional methylene group up to 5 exerts a significant effect. When the length of the chain is further increased, either (a) the new methylene groups have only minor, variable effects on the m.p., as in the simicarbazones where the structure is permanently dominated by the "head" of the molecule, $H_2N{\cdot}CO{\cdot}NH{\cdot}N{:}CMe{\cdot}(CH_2)_4{\cdot}$, the longer chain merely increasing one dimension of the unit cell; or (b) the longer chain can bring into the m.p.–composition diagram the characteristics of simple raliphatic homologous series: namely, either smooth increase in the m.p. with added methylene groups, or "alternation" of m.p. Thus the thiosemicarbazones exhibit (after $n = 3$) "abnormal" alternation, the "odd" carbon chain derivatives having higher m.ps than the neighbouring even members. *p*-Nitrophenylhydrazones and 2,4-dinitrophenylhydrazones show "normal" alternation of m.p.

Similar phenomena are of course found in other series, but the matter is confused by recordings in the literature of m.ps of impure specimens, or of metastable polymorphous forms, or possibly by the occurrence of *cis*, *trans*- isomerism (at least in derivatives of unsaturated ketones and aldehydes[2]). There are also many gaps in the records for most series: few investigators have taken the trouble to work with a long series of carefully purified homologues. A fairly complete series is that of the 2,4-dinitrophenylhydrazones of the n-aldehydes:[3] from hexaldehyde onwards these derivatives have m.ps lying between 104° and 110°, except for an unexpected drop to 96° for that of nonaldehyde. The semicarbazones of the n-aldehydes, from butyraldehyde to stearaldehyde, have m.ps lying between 98–110°. Thus both series show little rise in m.p. with increase of chain-length.

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* This work is dedicated to the memory of Professor H. Stephen.

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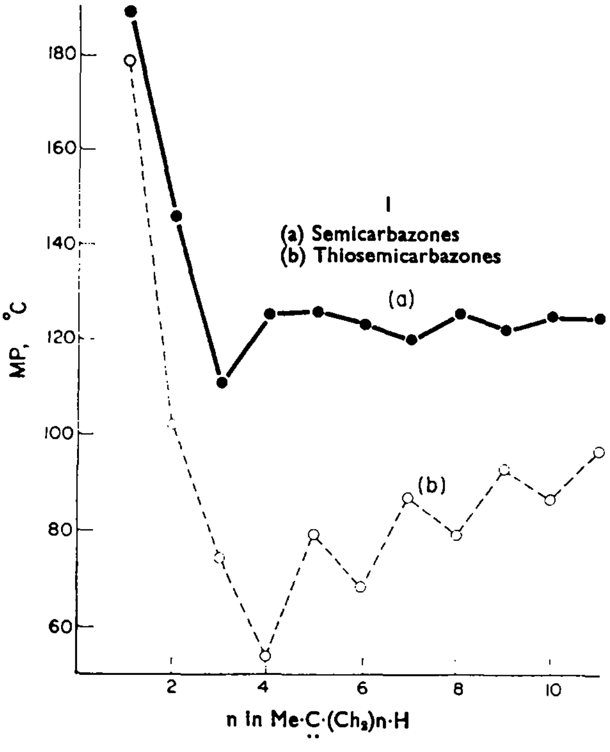
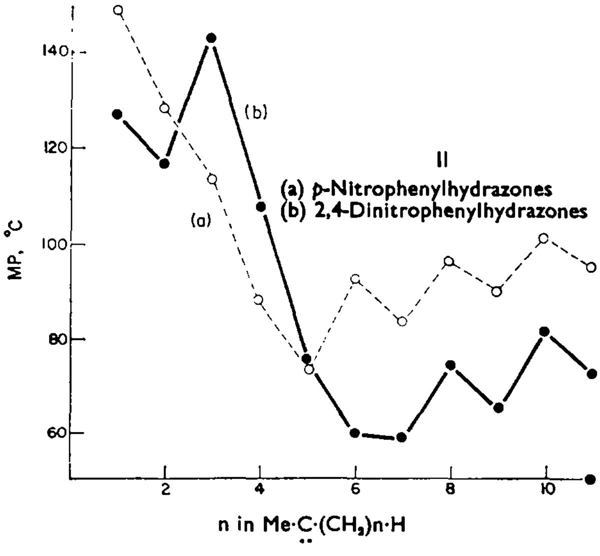
[2] F. J. Wilson and I. M. Heilbron, *J. Chem. Soc.* **103**, 377 (1913).

[3] P. E. G. Moult, Part II Thesis, Oxford University (1955).





Replacement of the substituted-hydrazine "end" of these derivatives by a larger and non-polar group does not lead to simplification. Thus the α- and the β- n-alkylnaphthalenes and the α- and the β-acylnaphthalenes display all the variety listed above, in their m.p.–composition curves. Some of the β-acyl naphthalenes crystallize with one molecule per unit cell, some with two or four molecules.

Many years before, in 1928, some light was thrown on the phenomenon of alternation of m.ps in homologons series when Caspari[4] showed that, in the classical example of the α,ω-dicarboxylic acids, the "odd" and the "even" members differ in their crystal structure: the "odd" have four molecules to the unit-cell, while the "even" require only two molecules. In 1931 Smith[5,8] showed that ethyl palmitate and ethyl stearate were dimorphous (as later the ethyl esters of all the acids, C_{13} to C_{20}, were found to be). There is for example, a transparent form of ethyl palmitate of m.p. 19·3° and with ester of more than 95% purity, an opaque form of m.p. 24·2°. Malkin[6] made a thorough investigation of these esters with X-ray methods and found that the transparent forms had the main axis (the chain) perpendicular to the end plane of the crystal, while the opaque forms had "tilted" chains. In the m.p.–composition curves for the ethyl esters of the n-C_{13} to C_{20} acids, the transparent forms yield a smooth curve, but the opaque forms show alternation in m.p. More generally, it appears that those homologous series like the higher paraffins, all the methyl n-alkyl ketones or the n-alcohols, which yield smooth curves, or mildly zig-zagging lines, either have transparent crystals or change their crystal-form during heating to the m.p. Kolp and Lutton[7] identified three crystal-forms of n-hexadecyl alcohol.[8] The transparent forms are "liquid crystals" in which the chain rotates; they would therefore not be expected to show "alternation" of m.p. which is a property of the solid state. Malkin[6] shows diagrammatically a possible explanation of "alternation" of m.p. in crystals with "tilted" chains, but the subject of crystal structure in homologous series would repay a modern investigation.

[4] W. A. Caspari, *J. Chem. Soc.* 3235 (1928).

[5] J. C. Smith, *Nature* **127**, 201 (1931).

[6] T. Malkin, *J. Chem. Soc.* 2796 (1931).

[7] D. G. Kolp and E. S. Lutton, *J. Amer. Chem. Soc.* **73**, 5593 (1951).

[8] J. C. Smith, *J. Chem. Soc.* 802 (1931).