

CXCII.—*The Diacyl Derivatives of Benzidine and p-Phenylenediamine.*

By FRANCIS JOSEPH ANTHONY BROGAN.

AN alternation in melting point such as that shown by successive members of the normal fatty acid series has been found by Robertson (J., 1908, **93**, 1033; 1919, **115**, 1210) to occur to a more marked extent in the amides and various substituted amides; for the odd and the even members of each series, two distinct curves, more or less parallel, were obtained when the melting points were plotted against the number of carbon atoms in the acid chain. To explain this alternation of physical properties, the theory of alternating polarities has been put forward.

The melting points of two series of diacyl diamines, prepared by condensing the normal fatty acid chlorides with benzidine and *p*-phenylenediamine, respectively, have now been determined.

The diacyl diamines, with the exception of the diacetyl compounds, were prepared by the general method described by Robertson (*loc. cit.*). Dipropionyl- and dibutyryl-*p*-phenylenediamine could not be isolated, owing probably to their extreme solubility, but small amounts of the monoacyl compounds were obtained by adding light petroleum to aqueous-alcoholic solutions of the crude products. Recrystallisation of the crude product from aniline also gave the monoacyl compound.

The diacetyl compounds were prepared from acetic anhydride and the base in aqueous-alcoholic solution by Cain's method (J., 1909, **95**, 714). A considerable proportion of monoacyl compound also was formed.

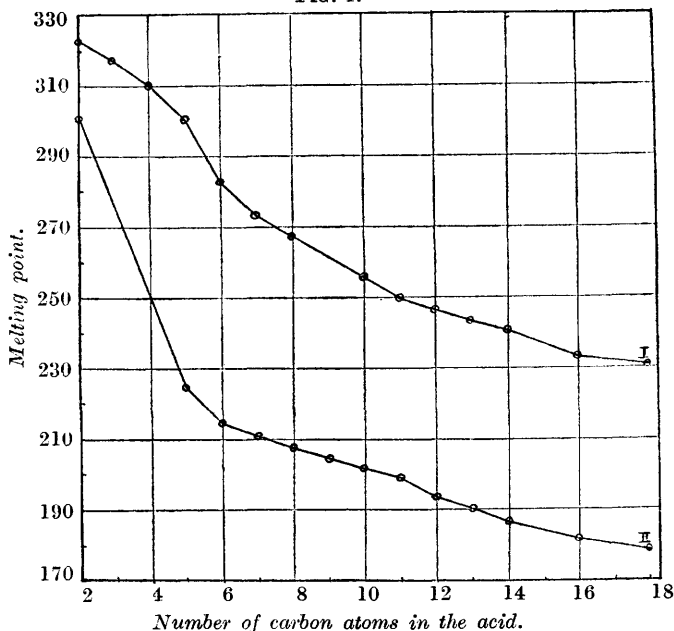
The crude products were recrystallised until the melting points were constant. The benzidine compounds, with the exception of the first three or four members of the series, are sparingly soluble in most of the common solvents. Alcohol was found to be the most suitable solvent for most of them, but the rate of solution was very slow, and prolonged boiling with a large volume of alcohol was necessary. Diacetylbenzidine crystallised well from aniline. The dipropionyl and dibutyryl compounds were very soluble in alcohol, and required to be precipitated by water. The four highest members were recrystallised from amyl acetate or acetic acid. The *p*-phenylenediamine derivatives, with the exceptions mentioned below, were recrystallised from alcohol, the solubility being much greater than that of corresponding compounds in the benzidine series. The diacetyl compound was recrystallised from nitrobenzene, and the two highest members from amyl acetate.

The new compounds prepared in this investigation, with their formulæ, melting points, and analytical results, are tabulated below.

Benzidine derivs.	M. p.	% N found.	<i>p</i> -Phenylenediamine derivs.	M. p.	% N found.
Dipropionyl, C ₁₈ H ₂₀ O ₂ N ₂	317°	9.3	Divaleryl, C ₁₆ H ₂₄ O ₂ N ₂	225°	10.3
Dibutyryl, C ₂₀ H ₂₄ O ₂ N ₂	310	8.4	Dihexoyl, C ₁₆ H ₂₈ O ₂ N ₂	215	9.1
Divaleryl, C ₂₂ H ₂₈ O ₂ N ₂	301	7.7	Diheptoyl, C ₂₀ H ₃₂ O ₂ N ₂	211	8.3
Dihexoyl, C ₂₄ H ₃₂ O ₂ N ₂	283	7.3	Dioctoyl, C ₂₂ H ₃₆ O ₂ N ₂	208	7.7
Diheptoyl, C ₂₆ H ₃₆ O ₂ N ₂	274	6.7	Dinonoyl, C ₂₄ H ₄₀ O ₂ N ₂	205	7.0
Dioctoyl, C ₂₈ H ₄₀ O ₂ N ₂	268	6.4	Didecyl, C ₂₆ H ₄₄ O ₂ N ₂	202	6.6
Didecyl, C ₃₂ H ₄₈ O ₂ N ₂	256	5.5	Diundecyl, C ₂₈ H ₄₈ O ₂ N ₂	199	6.5
Diundecyl, C ₃₄ H ₅₂ O ₂ N ₂	250	5.4	Dilauryl, C ₃₀ H ₅₂ O ₂ N ₂	194	5.9
Dilauryl, C ₃₆ H ₅₆ O ₂ N ₂	247	4.9	Ditridecyl, C ₃₂ H ₅₆ O ₂ N ₂	190	5.6
Ditridecyl, C ₃₈ H ₆₀ O ₂ N ₂	243	4.9	Dimyristyl, C ₃₄ H ₆₀ O ₂ N ₂	187	5.3
Dimyristyl, C ₄₀ H ₆₄ O ₂ N ₂	241	4.6	Dipalmityl, C ₃₈ H ₆₈ O ₂ N ₂	182	4.8
Dipalmityl, C ₄₄ H ₇₂ O ₂ N ₂	233	4.3	Distearyl, C ₄₂ H ₇₆ O ₂ N ₂	178	4.5
Distearyl, C ₄₈ H ₈₀ O ₂ N ₂	231	4.1			

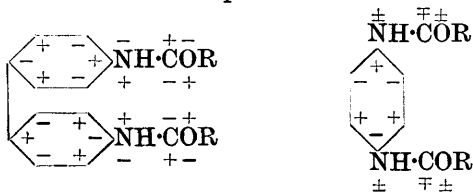
The results are shown graphically in the diagram, in which the melting points are plotted against the number of carbon atoms in the substituting acid. The general nature of the curves is typical, in so far as they fall fairly sharply at first and then more regularly with increase of molecular weight, but alternation is entirely absent. It is remarkable also that no minimum melting point is reached even at the eighteenth member, although a slight flattening is apparent about this point. Robertson's results indicate that the melting points become higher and the minimum occurs later as the molecule becomes heavier.

FIG. 1.



I. Benzidine derivatives. II. *p*-Phenylenediamine derivatives.

An examination of the polarity of the diacyl benzidines and *p*-phenylenediamines reveals the fact that a system of "crossed polarities" similar to that existing in the dibasic acids with an even number of carbon atoms is present.



This, together with the highly symmetrical nature of the molecule, would contribute to the structural stability of the acid, and thus tend to make the melting point high. The heaping up of like charges as in the odd dibasic acids, which may be supposed to make the crystalline arrangement less stable, and the melting points lower than those of the even acids, does not occur in the above compounds; this may explain the absence of alternation.

In conclusion, I wish to thank Professor Robertson for valuable advice and criticism in connexion with this research.

VICTORIA UNIVERSITY COLLEGE,
WELLINGTON, N.Z.

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