CCCLXXXIX.—*Melting Points of the Substituted Amides of Dibasic Acids.*

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The members of homologous series usually show a fairly regular variation in physical properties as each series is ascended. The mono- and the di-basic acids are exceptions, as their melting points rise and fall alternately. Biach (*Z. Physik*, 1904, **50**, 43) pointed out that this alternation is really quite general, as it appears in at least sixteen series of compounds. By plotting the melting points against the number of carbon atoms in the chain, two distinct curves, not necessarily exhibiting rise and fall, are obtained in each case, and those compounds containing an even number of carbon atoms lie on the higher curve. This phenomenon, evident even in the paraffins, appears to be due to something inherent in the carbon chain itself.

Robertson (J., 1908, **93**, 1033; 1919, **115**, 1210) has shown that the amides and substituted amides of the monobasic fatty acids exhibit this irregularity to an even more marked extent than the acids themselves. The investigations did not extend to dibasic acids, and it is to the study of the corresponding compounds of these that this work is confined.

EXPERIMENTAL.

The method of preparation of these substances was much the same as that described in Robertson's papers (*loc. cit.*).

The acids were from Kahlbaum, except the three highest members which were prepared by Lumsden and Walker's method (J., 1901, **79**, 1191).

All the melting-point determinations were made by the capillary-tube method in a castor-oil bath, and are uncorrected. The same standardised thermometer was used throughout.

The compounds not containing bromine were analysed by Kjeldahl's method, and the bromo-derivatives by the chromic acid method (Robertson, J., 1915, **107**, 902).

In Table I are the redetermined values of the melting points of compounds which were already known.

TABLE I.

Compound.	Formula.	M. p.	Previous observers.
Malonanilide	$C_{15}H_{14}O_2N_2$	224°	225°, 230°
Malono-*o*-toluidide	$C_{17}H_{18}O_2N_2$	189	193
Malono-*p*-toluidide	$C_{17}H_{18}O_2N_2$	247	248, 250
Succinanilide	$C_{16}H_{16}O_2N_2$	227	226
Succino-*p*-toluidide	$C_{18}H_{20}O_2N_2$	260	256
Succino-*o*-toluidide	$C_{18}H_{20}O_2N_2$	231	100 *
Glutaranilide	$C_{17}H_{18}O_2N_2$	223	223, 214
Adipanilide	$C_{18}H_{20}O_2N_2$	235	235, 233, 240
Pimelanilide	$C_{19}H_{22}O_2N_2$	152	155
Suberanilide	$C_{20}H_{24}O_2N_2$	182	183, 187
Subero-*p*-toluidide	$C_{22}H_{28}O_2N_2$	219	218
Azelanilide	$C_{21}H_{26}O_2N_2$	184	185
Sebacanilide	$C_{22}H_{28}O_2N_2$	200	198

* This is probably the melting point of succino-*o*-toluidic acid.

In Table II are the m. p.'s and analyses of the new compounds prepared in connexion with this work.

TABLE II.

Compound.	Formula.	M. p.	% N found.	% N calc.
n-Nonanedicarboxyamide	$C_{11}H_{22}O_2N_2$	173°	12·8	13·1
n-Decanedicarboxyamide	$C_{12}H_{24}O_2N_2$	189	12·0	12·3
n-Nonanedicarboxyanilide	$C_{23}H_{30}O_2N_2$	156	7·45	7·65
n-Decanedicarboxyanilide	$C_{24}H_{32}O_2N_2$	191	7·3	7·4
n-Undecanedicarboxyanilide	$C_{25}H_{34}O_2N_2$	158	7·0	7·1
Glutaro-*o*-toluidide	$C_{19}H_{22}O_2N_2$	222	9·2	9·0
Adipo-*o*-toluidide	$C_{20}H_{24}O_2N_2$	222	8·2	8·6
Pimelo-*o*-toluidide	$C_{21}H_{26}O_2N_2$	174	8·2	8·3
Subero-*o*-toluidide	$C_{22}H_{28}O_2N_2$	185	7·8	7·9
Azelo-*o*-toluidide	$C_{23}H_{30}O_2N_2$	171	7·6	7·65
Sebaco-*o*-toluidide	$C_{24}H_{32}O_2N_2$	179	7·5	7·4
n-Nonanedicarboxy-*o*-toluidide	$C_{25}H_{34}O_2N_2$	164	7·0	7·1
n-Decanedicarboxy-*o*-toluidide	$C_{26}H_{36}O_2N_2$	164	7·2	6·9
n-Undecanedicarboxy-*o*-toluidide	$C_{27}H_{38}O_2N_2$	142	6·7	6·6
Glutaro-*p*-toluidide	$C_{19}H_{22}O_2N_2$	218	8·7	9·0
Adipo-*p*-toluidide	$C_{20}H_{24}O_2N_2$	241	8·3	8·6
Pimelo-*p*-toluidide	$C_{21}H_{26}O_2N_2$	206	8·2	8·3
Azelo-*p*-toluidide	$C_{23}H_{30}O_2N_2$	198	7·5	7·65
Sebaco-*p*-toluidide	$C_{24}H_{32}O_2N_2$	201	7·2	7·4
n-Nonanedicarboxy-*p*-toluidide	$C_{25}H_{34}O_2N_2$	191	7·4	7·1
n-Decanedicarboxy-*p*-toluidide	$C_{26}H_{36}O_2N_2$	165	7·0	6·9
n-Undecanedicarboxy-*p*-toluidide	$C_{27}H_{38}O_2N_2$	156	6·5	6·6

In Table III are the m. p.'s and analyses of the new bromo compounds.

TABLE III.

Compound.	Formula.	M. p.	% Br found.	% Br calc.
Succino-*p*-bromoanilide	$C_{16}H_{14}O_2N_2Br_2$	284°	37·4	37·5
Glutaro-*p*-bromoanilide	$C_{17}H_{16}O_2N_2Br_2$	256	36·6	36·4
Adipo-*p*-bromoanilide	$C_{18}H_{18}O_2N_2Br_2$	268	35·5	35·3
Pimelo-*p*-bromoanilide	$C_{19}H_{20}O_2N_2Br_2$	240	34·3	34·1
Subero-*p*-bromoanilide	$C_{20}H_{22}O_2N_2Br_2$	248	33·0	33·2
Azelo-*p*-bromoanilide	$C_{21}H_{24}O_2N_2Br_2$	225	32·1	32·3
Sebaco-*p*-bromoanilide	$C_{22}H_{26}O_2N_2Br_2$	225	31·1	31·4
n-Nonanedicarboxy-*p*-bromoanilide	$C_{23}H_{28}O_2N_2Br_2$	215	30·5	30·5
n-Decanedicarboxy-*p*-bromoanilide	$C_{24}H_{30}O_2N_2Br_2$	213	29·5	29·7
n-Undecanedicarboxy-*p*-bromoanilide	$C_{25}H_{32}O_2N_2Br_2$	202	28·9	29·0

Remarks.—Acids. The differences in melting point of adjacent members are considerably greater than those between the corresponding monobasic acids, and the two curves tend to converge. A minimum is obtained at the fifth member (Fig. 1).

Amides. The curves resemble those of the acids, as the terminal groups are somewhat similar. The melting points are on the average 70° higher, and the differences between corresponding members more marked (Fig. 1).

Anilides. The introduction of a phenyl group causes a striking change in the nature of the curves (Fig. 2), that of the odd series showing greater irregularity than its fellow, and less marked alternation results (*i.e.*, the curves lie closer together). Alternation appears to exhibit an unusual arrangement in fours.

o-*Toluidides* (Fig. 3). There is a marked similarity between these and the two following series, with substituted phenyl groups in the chain. A pronounced maximum is attained at the fifth member. The relative variation between the odd and the even series decreases slightly. The initial irregularity is apparently due to the unsymmetrical arrangement of the *o*-tolyl ring distorting the molecule, particularly when the chain is short and the end groups are in close proximity.

Fig. 1.

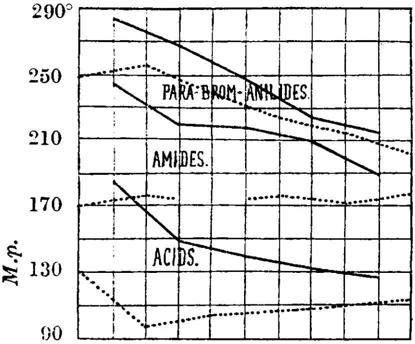
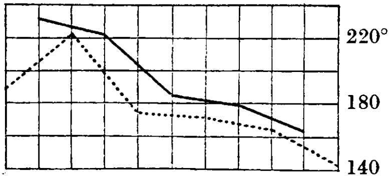


Fig. 3. o-*Toluidides.*



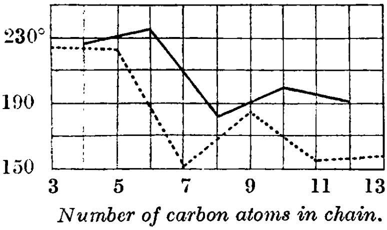


Fig. 2. *Anilides.*

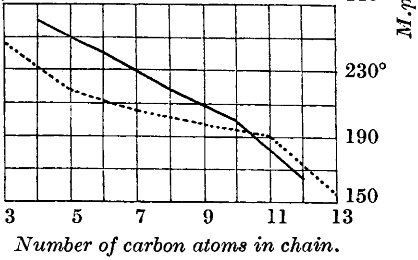


Fig. 4. p-*Toluidides.*

p-*Toluidides* (Fig. 4). The curves show slightly greater variation and the molecule is symmetrical, causing irregularity to be absent.

p-*Bromoanilides* (Fig. 1). The bromine atom has the most marked influence of all the substituents, producing curves almost devoid of irregularity.

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