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Publisher: Taylor & Francis

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Philosophical Magazine Series 5

Publication details, including instructions
for authors and subscription information:
<http://www.tandfonline.com/loi/tphm16>

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Published online: 28 Apr 2009.

To cite this article: Thomas Carnelley D.Sc. (1882) XIII. Chemical symmetry,
or the influence of atomic arrangement on the physical properties of
compounds , Philosophical Magazine Series 5, 13:79, 112-130, DOI:
[10.1080/14786448208627154](http://dx.doi.org/10.1080/14786448208627154)

To link to this article: <http://dx.doi.org/10.1080/14786448208627154>

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solidification supervened ; while the analogous structure developed by the desiccation of homogeneous masses of moist clay, mud, or starch appears to be produced by a similar strain consequent upon shrinkage from loss of moisture. In a similar manner, the tense superficial capillary film of the water, when it experiences the sudden molecular impulse due to the emergence of the elastic pulse, is ruptured along lines more or less symmetrically disposed on the surface of the water ; and the liquid beneath is projected through these lines or points of least resistance.

Berkeley, California, Oct. 25, 1881.

XIII. *Chemical Symmetry, or the Influence of Atomic Arrangement on the Physical Properties of Compounds.* By THOMAS CARNELLEY, D.Sc., Professor of Chemistry in Firth College, Sheffield*.

TWO years ago I published in this Magazine (Oct. 1879) a paper on the Influence of Atomic Weight, in which I endeavoured to trace the connexion between the atomic weights of the elements and their properties and those of their compounds. In the present paper I wish to consider this subject from a different point of view, viz. the influence which the atomic position or arrangement has on the properties of compounds.

This is a subject which has lately absorbed a great deal of attention, more especially as regards the connexion between the refractive indices of compounds and the arrangement of their constituent atoms in the molecule; and it will be my object to give as brief and as clear a sketch as possible of the chief results which have been obtained up to the present, tracing the influence which atomic arrangement has on (1) the melting-point, (2) the solubility, (3) the heat of formation, (4) the heat of combustion, (5) the action of polarized light, (6) the specific refraction, and (7) the tinctorial properties of chemical compounds. For this purpose I shall necessarily limit myself entirely to the consideration of carbon compounds, and to those which are isomeric with one another.

Those compounds are said to be isomeric which, though having the same percentage composition and the same molecular weight, have very different physical and chemical properties. This difference in properties must evidently depend on the different arrangement or linking together of atoms in the molecules of the several compounds. Thus, acetic acid

* Communicated by the Author, being the Opening Address of the Session to the Owens College Chemical Society, Nov. 18, 1881.

and methyl formate have both exactly the same composition, viz. $C_2H_4O_2$, and yet have very different properties,—the former being a well-characterized acid, which on cooling solidifies in the form of large transparent plates, which melt at $+17^\circ$ and boil at $118^\circ C.$, it possesses a pungent sour smell, and is highly corrosive; whilst the latter is a colourless liquid which has not yet been obtained in the solid state, and boils as low as $33^\circ.4$, or about 85° below the isomeric acetic acid, from which it also differs notably in emitting a pleasant ethereal smell. Since both compounds have exactly the same composition, this remarkable difference in properties can only be caused by the atoms being arranged differently in the two bodies; and that the atoms *are* differently arranged, we know from the various chemical decompositions which the two compounds undergo. This difference in atomic arrangement is represented by the following graphical formulæ:—

Acetic acid.

Methyl formate.

In the former the two carbon atoms are directly united, whilst in the latter they are combined indirectly by means of oxygen.

I. INFLUENCE OF ATOMIC ARRANGEMENT ON THE MELTING-POINT.

It seems strange that scarcely any attempt has been made to trace the connexion between the composition and melting-points of carbon compounds, notwithstanding that the melting-points of a very large number of such compounds have been determined. The most noteworthy of these attempts is that of Baeyer, in regard to the melting-points of the fatty acids, and that of Körner, who states that, amongst aromatic compounds, what are called para-derivatives usually melt higher than the corresponding ortho- and meta-derivatives.

Attention has been directed almost exclusively to the boiling-points. Now the boiling-points are by no means so suitable for tracing the influence of atomic arrangement as the melting-points, since they are far from being such a fixed property as the latter; for, as is well known, the boiling-point is raised or lowered considerably by even small alterations in the pressure, whilst under ordinary circumstances the melting-

point of a pure compound is practically fixed and constant, and hence depends solely on the nature of the compound, whilst the boiling-point depends not only on the nature of the compound, but also on the superincumbent pressure; and, further, given alterations of pressure by no means produce corresponding alterations in the boiling-points of different compounds. It is therefore far easier to trace the connexion between melting-point and atomic arrangement than the connexion between boiling-point and atomic arrangement.

Such considerations as these induced me, about three years ago, to commence the study of the influence of composition and atomic arrangement on the melting-points of organic compounds. And for this purpose I have made complete lists of all the melting- and boiling-points which have been determined up to the present date. This tabulation has taken three years, and was finished only a few weeks ago. During this time I have collected not far short of 30,000 melting- and boiling-points, about one half of which are melting-points. The systematic arrangement of this enormous quantity of data is now in progress; and I have already been able to trace certain relations between them, which I hope will throw light on the influence of atomic arrangement. Some of these I now propose to describe; but at the same time I wish to say that, though these conclusions have been verified in a very large number of cases, I have not yet been able to test them in every possible case, because the systematic tabulation of my lists of melting-points is not yet completed.

Of the compounds of carbon, the aromatic compounds are perhaps the most important, and are certainly the most interesting. These compounds may all be considered as derived from benzene.

Benzene has the formula C_6H_6 ; and its constitution is generally represented as follows:—

or it consists of a closed ring of six atoms of carbon united alternately with one and two combining-powers, whilst the fourth combining-power of each carbon atom is combined with hydrogen.

The aromatic compounds are derived from this ring by

replacing one or more of the atoms of hydrogen by the atoms or groups of atoms of other elements.

The ring

is called the benzene ring, or the benzene nucleus; and the carbon atoms in this ring we will number, for sake of distinction, as in the figure.

Now suppose we replace one atom of hydrogen by an atom of another element, say bromine; then we can only get one derivative, for an identical compound is obtained no matter which of the six atoms of hydrogen is replaced by the atom of bromine, thus:—

But when we replace two atoms of hydrogen by two like atoms of another element, or by two like groups of elements, then no less than three different isomeric bodies may be obtained; viz.—

Ortho- or 1.2-dibrom-
benzene.

Meta- or 1.3-dibrom-
benzene.

Para- or 1.4-dibrom-
benzene.

It has been observed for some time past, that para-compounds always melt higher than ortho- and meta-compounds; whereas, as regards the ortho- and meta-compounds, the former sometimes melt higher, and sometimes lower, than the latter.

Now the arrangement of the atoms in the para-compounds is symmetrical, whilst in the ortho- and meta-compounds the

arrangement is asymmetrical; *i. e.* if we imagine the para-compound to be suspended from a point in the centre of the benzene ring, then the molecule would balance in any position, whilst this would not be the case with the ortho- and meta-compounds. Or, in other words, the centre of gravity of the molecule of the para-compounds corresponds more nearly with the centre of figure of the molecule than is the case with the ortho- and meta-compounds. This fact led me to conclude that a similar rule might hold good, not only with the primary derivatives of benzene, but also in the case of all isomeric compounds of carbon; and this appears to be true in a very large number of instances. I have therefore ventured to conclude, "*That of two or more isomeric compounds, those whose atoms are the MORE SYMMETRICALLY and the MORE COMPACTLY arranged melt higher than those in which the atomic arrangement is asymmetrical or in the form of long chains*"*.

After working out this subject at some length, I noticed that Mr. Henry Watts had already observed, in the third Supplement of his well-known 'Dictionary of Chemistry,' that "the more symmetrical the constitution of a benzene derivative, the greater is the resistance which it offers to the passage from the solid to the liquid state," or, in other words, the higher the melting-point. Subsequently, however, in a note to a paper by Neville and Winther (Journ. Chem. Soc. xxxvii. p. 450), Mr. Watts emphatically says that he intended this rule to apply only and solely to the derivatives of benzene containing but six atoms of carbon; whilst I believe that it holds good, with a very few exceptions, in the case of all carbon compounds whatever.

Let us now illustrate this rule by a number of examples taken almost at random. In the following tables the compounds are generally, though not always, arranged in the order of symmetry, those to the left being the most symmetrical. In the case where two compounds are equally symmetrical, that which is most compact is placed to the left.

I.

Tetramethyl methane.	Normal pentane.	Dimethylethyl methane.
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ <p>m.p. = -20.</p>	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ <p>Liquid.</p>	$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_2 \cdot \text{CH}_3 \\ \quad \diagdown \quad \diagup \\ \text{CH}_3 - \text{C} - \text{H} \end{array}$ <p>Liquid.</p>

* In the examples given below of this and of all the rules stated subsequently, the exceptions are in every case marked with an asterisk.

II.

III.

Normal butyl benzene.

Isobutyl benzene.

IV.

Hexamethyl benzene.	Dipropyl benzene.	Triethyl benzene.
m.p. = 150.	Liquid.	$C_6H_5 \cdot (C_2H_5)_3$ Liquid.
Amylmethyl benzene.	Propylisopropyl benzene.	Hexyl benzene.
$C_6H_4 \cdot CH_3 \cdot C_6H_{11}$ Liquid.	$C_6H_4 \cdot C_3H_7 \cdot CH(CH_3)_2$ Liquid.	$C_6H_5 \cdot C_6H_{13}$ Liquid.

V.

Diphenyl methane.	Tolylphenyl.	Tolylphenyl.
m.p. = 26.5.	m.p. = -2.	Liquid.

VI.

1.4; 1.4 Ditolyl.	Dibenzyl.	1.2; 1.4 Ditolyl.
$CH_3 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_3$ m.p. = 121.	$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$ m.p. = 52.	$CH_3 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_3$ Liquid.
Benzyltoluene.	Phenylxylene.	Diphenyl ethane.
$C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$ Liquid.	$C_6H_5 \cdot C_6H_3(CH_3)_2$ Liquid.	$CH_3 \cdot CH(C_6H_5)_2$ (?)

VII.

Derivatives of Ethane.

		Ethylene.	Ethylidene.
		CH_2C-CH_2X	H_3C-CHX_2
Dibromide	Br.Br	m.p. = 9	Liquid.
Diiodide	I.I	73	"
Chloriodide	Cl.I	Solid in freezing-mixture.	"
Bromiodide	Br.I	m.p. = 28	"
Diphenide	Ph.Ph	52 (dibenzyl)	"
Sulphide	S''	112	95
Iodopropionic acid	COOH.I	82	Liquid.
Succinic acid . . .	COOH.COOH	180	129

VIII.

		$XHC=CHX.$	$H_2C=CX_2.$
Diphenide	Ph. Ph	120 (stilbene)	Liquid.
Titolide	$C_7H_7.C_7H_7$	176 (dimethyl stilbene)	Liquid.

IX.

Derivatives of Benzene.

		Para X X	Meta X X	Ortho X X
Dichlorobenzene.....	Cl. Cl	53	L at -18	L at -14
Dibromobenzene.....	Br. Br	89	-28	-1
Diiodobenzene	I. I	127	40	94
Dicyanobenzene	CN. CN	222	158	
Chloriodobenzene	Cl. I	56	...	L
Bromiodobenzene	Br. I	92	L	L
Dihydroxybenzene	OH. OH	172	99	112
Disulphydrobenzene.....	SH. SH	98	27	
Dinitrobenzene	$NO_2.NO_2$	171	90	118
Diamidobenzene	$NH_2.NH_2$	140	63	99
Nitrobromobenzene	$NO_2.Br$	126	56	41.5
Nitrochlorobenzene	$NO_2.Cl$	83	44	32
Nitroiodobenzene	$NO_2.I$	171	36	49
Amidobromobenzene	$NH_2.Br$	64	18	31
Amidochlorobenzene	$NH_2.Cl$	70	L	Labove-14
Amidoiodobenzene	$NH_2.I$	60	25	
Amidonitrobenzene	$NH_2.NO_2$	146	110	71
Dimethylbenzene	$CH_3.CH_3$	15	L	L
Diphenylbenzene	Ph. Ph	205	1.3 or 1.2 L	L
Tolylidipenylmethane	Me. (CHPh ₂)	71	59.5 or L	L or 59.5
Methyl chlorobenzene	Me. Cl	6.5	L	L
Methyl bromobenzene	Me. Br	28	L	L
Methyl iodobenzene	Me. I	35	L	L
Methyl amidobenzene	Me. NH ₂	45	L	L
Phenyl chlorobenzene	Ph. Cl	75	...	4
Phenyl bromobenzene	Ph. Br	89	...	L
Phenyl amidobenzene	Ph. NH ₂	50	...	48
Di-(amidomethyl)benzene	$(CH_2.NH_2).(CH_2.NH_2)$	99	89	
Hydroxy-carboxyl benzene	OH. COOH	210	200	156
Methoxy-carboxylbenzene	$OCH_3.COOH$	175	106	99
Ethoxy-carboxylbenzene	$OEt.COOH$	195	137	20
Fluo-carboxyl benzene	F. COOH	182	123	
Chloro-carboxyl benzene	Cl. COOH	234	152	137
Bromo-carboxyl benzene	Br. COOH	250	155	148
Iodo-carboxyl benzene	I. COOH	267	185	159
Hydroxy-potassium-sul- phobenzene.....	OH. SO ₃ K	not at 260	200	240
Bromhydroxybenzene	OH. Br	64	32	L
Nitro-carboxyl benzene	COOH. NO ₂	240	141	143
Amido-carboxyl benzene	COOH. NH ₂	187	174	144

X. Triderivatives of Benzene.

		Symmetrical.	Consecutive.	Asymmetrical.
		1. 3. 5	1. 2. 3	1. 2. 4
Trichlorobenzene	Cl. Cl. Cl	64	54	16
Tribromobenzene	Br. Br. Br	119	87	44
Methyl dibromobenzene	CH ₃ . Br. Br	39	27	L
Nitrodibromobenzene {	NO ₂ . Br. Br.	104	...	62
	Br. Br. NO ₂	...	59	...
	Br. NO ₂ . Br	...	83	85
Nitrodichlorobenzene {	NO ₂ . Cl. Cl	65	...	32
	Cl. Cl. NO ₂	...	...	43
	Cl. NO ₂ . Cl	...	...	55
Nitrochlorobromoben- zene	NO ₂ . Cl. Br	83	...	47
	Cl. NO ₂ . Br	...	...	69
	Br. NO ₂ . Cl	...	...	50
Amidodibromobenzene {	NH ₂ . Br. Br	57*	...	79
	Br. NH ₂ . Br	...	...	52
	Br. Br. NH ₂	...	...	80
Amidodichlorobenzene {	NH ₂ . Cl. Cl	51*	24	63
	Cl. NH ₂ . Cl	...	...	50
	Cl. Cl. NH ₂	...	...	71
Dibromobenzoic acid ...	COOH. Br. Br	209	...	...
	Br. Br. COOH	...	...	228*
	Br. COOH. Br	...	...	151
Dinitrobenzoic acid ...	COOH. NO ₂ . NO ₂	205	...	179
	NO ₂ . COOH. NO ₂	...	202	140

XI. Tetraderivatives of Benzene.

Order of symmetry.		m.p.	1.	2.	3.	4.	5.	6.
1.	Br. Br. Br. Br	138	Br	Br	...	Br	Br	
2.	" " " "	99	Br	...	Br	Br	Br	
1.	Cl. Cl. Cl. Cl	138	Cl	Cl	...	Cl	Cl	
2.	" " " "	50	Cl	...	Cl	Cl	Cl	
3.	" " " "	46	Cl	Cl	Cl	Cl		
1.	NH ₂ . Br. NO ₂ . Br	202	NH ₂	Br	...	NO ₂	...	Br
2.	" " " "	127	NH ₂	Br	...	Br	...	NO ₂
1.	NH ₂ . Cl. Cl. NO ₂	100	NH ₂	Cl	...	NO ₂	...	Cl
2.	" " " "	66	NH ₂	Cl	...	NO ₂	Cl	NO ₂
1.	CH ₃ . Cl. Cl. Cl	138	CH ₃	Cl	...	Cl	Cl	
2.	" " " "	27-35	CH ₃	...	Cl	Cl	Cl	
3.	" " " "	46*	CH ₃	Cl	Cl	Cl		
1.	CH ₃ . Br. Br. Br	112	CH ₃	Br	...	Br	Br	
2.	" " " "	88	CH ₃	...	Br	Br	Br	Br
3.	" " " "	66	CH ₃	Br	...	Br	Br	
4.	" " " "	59	CH ₃	Br	Br	...	...	Br
5.	" " " "	52	CH ₃	Br	Br	...	Br	
6.	" " " "	44	CH ₃	Br	Br	Br		

Note.—When all the side chains are of one kind the form

is the most symmetrical, and always has the highest melting-point. But when the side chains are not all of the same kind, then there seems to be a struggle between the three forms

and between

and

XII.

Pentaderivatives of Benzene.

m.p. = 116.

m.p. = 111.

m.p. = 107.

XIII.

Hexaderivatives of Benzene.

XIV.

XV.

X = Cl m.p. = 6.5
X = Br m.p. = 28
X = I m.p. = 35

Liquid.
Liquid.
Liquid.

Liquid.
Liquid.
Liquid.

Liquid.
Liquid.
Liquid.

XVI.

XVII.

m.p. = 79.	Liquid.	Liquid.	Liquid.	Liquid.

XVIII.

m.p. = 29.	Liquid.

XIX.

Diamidobenzene.			Phenylhydrazine.
1.4	1.3	1.2	$C_6H_5 \cdot NH \cdot NH_2$
m.p. = 140	63	99	23

XX.

Amidotoluene, $CH_3 \cdot C_6H_4 \cdot NH_2$.			Benzylamine.	Methylaniline.
1.4	1.3	1.2	$C_6H_5 \cdot CH_2 \cdot NH_2$.	$C_6H_5 \cdot NHCH_3$.
m.p. = 45.	Liquid.	Liquid.	Liquid.	Liquid.

XXI.

XXII.

XXIII.

XXIV.

XXV.

Diamidostilbene.

m.p. = 170*.

* This, though nearly, is not quite so symmetrical as (1.4; 1.4) azotoluene.

Azotoluene (1.4; 1.4).

m.p. = 144.

Azotoluene (1.2; 1.2).

m.p. = 137.

Ethenyldiphenylamidine.

m.p. = 132.

Phenylacetophenyl-
amidine.

m.p. = 128.

Benzenyltolylamidide.

m.p. = 99.

Ethenylisodiphenylamidine.

m.p. = 63.

Azotoluene (1.3; 1.3).

m.p. = 54.

The influence of symmetry on the melting-point is still further shown by the following table, which contains the melting-points of the *most* symmetrical modification of a few of the mono-, di-, tri-, tetra-, penta-, and hexa-derivatives of benzene; from which it will be seen that the melting-points of the mono- and penta-derivatives are comparatively always very low, whilst those of the other derivatives are high; the reason being that benzene cannot form symmetrical mono- and penta-derivatives, whereas a symmetrical form of a di-, tri-, tetra-, and hexa-derivative is always possible.

	Benzene.	Mono-derivative.	Di-derivative.	Tri-derivative.	Tetra-derivative.	Penta-derivative.	Hexa-derivative.
Position of side chains...	0	1	1.4	1.3.5	1.2.4.5	1.2.3.4.5	1.2.3.4.5.6
The side chains being—							
CH ₃	7	Liquid	15	Liquid	80	50	164
Cl	7	{ Liquid at -40	53	63.5	138	74	226
Br	7	b. -20	89	119	140	a 240	a 310
I	7	Liquid	127				
NO ₂	7	Liquid	171				
NH ₂	7	-8	147				

Influence of Compactness, or number of Side Chains on the Melting- and Boiling-points.

Lothar Meyer has pointed out, in his 'Modern Theories of Chemistry,' p. 280, "that, of any number of isomeric compounds, those are the most volatile in which there are the greatest number of side chains, or in which the main chain of atoms is most branched, and therefore in which the main chain is the shortest."

From the observation of a great number of compounds, I cannot help concluding that a rule the exact reverse of the above holds good as regards the melting-point, viz. *that those isomeric compounds melt the highest in which there are the greatest number of side chains.* This has already been indicated to some extent above, where it has been pointed out that the greater the compactness of the molecule the higher the melting-point. The above rules may be illustrated as follows:—

	Boiling-point.	Melting-point.
Pentanes. { <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> $\begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \text{} \\ \text{CH}_3 \diagup \text{CHCH}_2\text{CH}_3 \text{} \\ \text{CH}_3 \diagdown \\ \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \text{} \\ \\ \text{CH}_3 \end{array}$ </div>	38 30 9.5	Liquid. Liquid. -20
Octanes. { <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> $\begin{array}{l} \text{CH}_3 - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_3 \diagup \text{CH} - \text{CH}_2\text{CH}_2 - \text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array} \text{} \\ \text{CH}_3 \diagdown \\ \text{CH}_3\text{CH}_3 \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \text{} \\ \quad \\ \text{CH}_3\text{CH}_3 \end{array}$ </div>	125 108 105	Liquid. Liquid. 96-97

Table (continued).

	Boiling-point.	Melting-point.
Pentyl alcohols. $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \dots\dots\dots \\ \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH} \dots\dots\dots \\ \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH} \dots\dots\dots \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH} \dots\dots\dots \\ \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH} \dots\dots\dots \end{array} \right.$	117 109 97 84	Liquid. Liquid. Liquid. 25
Heptyl chlorides. $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \dots\dots\dots \\ \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl} \dots\dots\dots \\ \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \dots\dots\dots \end{array} \right.$	159 136 	Liquid. Liquid. 136
Butyric acids. $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \dots\dots\dots \\ \text{CH}_3\text{CH}(\text{CH}_3)\text{COOH} \dots\dots\dots \end{array} \right.$	162 154	0 L (?) *
Valeric acids. $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \dots\dots\dots \\ \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH} \dots\dots\dots \\ \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH} \dots\dots\dots \\ \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{COOH} \dots\dots\dots \end{array} \right.$	184 175 173 164	Liquid. Liquid. Liquid. 35.4
Butyl cyanides. $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \dots\dots\dots \\ \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CN} \dots\dots\dots \\ \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CN} \dots\dots\dots \end{array} \right.$	140 127 105	Liquid. Liquid. 15-16

Table (continued).

	Boiling-point.	Melting-point.
Dipropargyl, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$	85	Liquid.
Benzene,	81	7
Amyl benzene, $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}_2.\text{CH} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$...	193	Liquid.
Propyldimethyl benzene, $\text{C}_6\text{H}_5 \left\{ \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \right. \text{CH}_2.\text{CH}_2.\text{CH}_3$...	188	Liquid.
Diethylmethyl benzene, $\text{C}_6\text{H}_5 \left\{ \begin{smallmatrix} \text{CH}_2.\text{CH}_3 \\ \text{CH}_2.\text{CH}_3 \end{smallmatrix} \right. \text{CH}_3$...	$\left\{ \begin{smallmatrix} 178 \\ 198-200 \end{smallmatrix} \right\}$	Liquid.
Pentamethyl benzene, $\text{C}_6\text{H} \left\{ \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \right.$	225*	50

	Melting-point.		Melting-point.
Propyl terephthalate	31°	and Isopropyl terephthalate	56°
Butyl	„	Liquid, and Isobutyl	„
Butyl hippurate	40·5,	and Isobutyl hippurate	45·5

So great indeed is the influence of the compactness of the molecule, that it sometimes overbalances the influence of increase of atomic weight : thus

		Melting-point.
Methyl terephthalate	$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COO.CH}_3 \\ \text{COO.CH}_3 \end{smallmatrix}$	140
Ethyl	„ $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COO.CH}_2.\text{CH}_3 \\ \text{COO.CH}_2.\text{CH}_3 \end{smallmatrix}$	44
Propyl	„ $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COO.CH}_2.\text{CH}_2.\text{CH}_3 \\ \text{COO.CH}_2.\text{CH}_2.\text{CH}_3 \end{smallmatrix}$...	31
Butyl	„ $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COO.CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3 \\ \text{COO.CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3 \end{smallmatrix}$	Liquid.

		Melting-point.
Methyl hippurate	$(C_8H_8NO).COO.CH_3$	80.5
Ethyl	„ $(C_8H_8NO).COO.CH_2.CH_3$	60.5
Butyl	„ $(C_8H_8NO).COO.CH_2.CH_2.CH_2.CH_3$	40.5

Isobutylhippurate $(C_8H_8NO).COO.CH_2.CH \begin{smallmatrix} \swarrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$... 45.5

Isoamyl „ $(C_8H_8NO).COO.CH_2.CH_2.CH \begin{smallmatrix} \swarrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$ 27.5

It will now be necessary to make a few remarks in regard to the examples which have been given in illustration of what is thought to be a true connexion between atomic structure and melting-point, and more especially as regards the influence of symmetry. It would, of course, be easy to support any theory if we merely gave those examples which were favourable and excluded all those which were adverse. This, however, has not been done in the examples which have been given above. For the purpose of this paper there were taken quite at random somewhere about 300 cases to which the rule of symmetry could be applied; and of these 278 were in agreement with the rule, whilst 22 were exceptions; the latter amounted therefore to only 7 per cent., which proves that the rule is of almost general application. Many of the exceptions may possibly be due to the constitution or arrangement of the atoms not having been correctly determined, and might thus on close examination be shown to agree with the rule.

The following are some of the most marked exceptions included in the above 22, and which are undoubtedly real exceptions, since the constitution is known with a considerable degree of certainty:—

Isomeric Pyrotartaric Acids.

No. 4, which is more symmetrical than No. 2 and No. 3, is less compact; and perhaps this is the cause of the low melting-point.

Bayer has shown that, if we compare the melting-points of homologous series, we find that the melting-point is materially influenced by odd and even numbers, in such a way that those compounds containing an even number of carbon atoms melt higher than the neighbouring compounds containing an odd number, thus:—

	Melting-point.			Melting-point.	
	Even.	Odd.		Even.	Odd.
CH_2O_2	...	8·6	$C_2H_2O_4$	200	
$C_2H_4O_2$	+17		$C_3H_4O_4$	...	132
$C_3H_6O_2$	...	b. -21	$C_4H_6O_4$	180	
$C_4H_8O_2$	+1		$C_5H_8O_4$	...	97
$C_5H_{10}O_2$	...	b. -16	$C_6H_{10}O_4$	148	
$C_6H_{12}O_2$	-2		$C_7H_{12}O_4$	...	103
$C_7H_{14}O_2$	...	-10·5	$C_8H_{14}O_4$	140	
$C_8H_{16}O_2$	+16		$C_9H_{16}O_4$	...	106
$C_9H_{18}O_2$	...	+12	$C_{10}H_{18}O_4$	127	
$C_{10}H_{20}O_2$	+30		$C_{11}H_{20}O_4$	...	108
<hr/>			<hr/>		
$C_{16}H_{32}O_2$	+62		$C_{17}H_{32}O_4$	...	132
$C_{17}H_{34}O_2$	...	+60			
$C_{18}H_{36}O_2$	+69				

[To be continued].