The von Auwers' Boiling Point Rule. A New Approach

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Summary An empirical approach to the determination of relationships between boiling points and chemical constitution, in a homologous series of compounds, which should be of use in structural and conformational studies, is described.

IT has long been thought that there should be a relationship between chemical constitution and properties such as boiling points. This idea has been expressed in many forms,[1-5] the most famous being the von Auwers rule.[1-3]

We have found that for a series of similar compounds the boiling points may be expressed[6] by equation (1).

$$TB = TB_p + \Sigma ti \quad (1)$$

TB_p is the boiling point of the parent compound in the series and ti's are incremental factors related to structure.

This expression was first tested for the methyl benzenes. A least-squares analysis of boiling points was performed in terms of two parameters;[7] a methyl group incremental factor (+29·1°) and an *ortho* group incremental factor (+1·8°). The fit between observed and calculated boiling points using these two parameters has a standard deviation of 2·6° and a correlation coefficient of 0·998.[8]

We then analysed the boiling points of the methyl cyclohexanes known to exist in chair conformations in terms of 5 parameters: equatorial methyl (+19·1°), axial methyl (+23·0), geminal dimethyl (−5·7°), equatorial–equatorial vicinal dimethyl (+4·2°), equatorial–axial vicinal dimethyl (+3·1°). The standard deviation of this fit is 1·7°, the correlation coefficient is 0·997, the maximum deviation is 3°, and the number of examples taken was 30.[8,9]

The significant difference between equatorial and axial group incremental factors caused us to look next at the methyl substituted 1,3-dioxans. We analysed the boiling points of those compounds with chair conformations in terms of nine parameters. The larger numbers of parameters is determined by the lower symmetry of the 1,3-dioxan ring. The values obtained were 2-equatorial (+2·6°), 2-axial (+11·4°), 4-equatorial (+10·4°), 4-axial

(+33·2°), 5-equatorial (+16·1°), 5-axial (+12·8°), 4-geminal (−13·8°), 4-equatorial-6-equatorial (+3·9°), 4-equatorial 6-axial (−9·4°). The standard deviation of this fit is 3·5° and the regression coefficient 0·97. The maximum deviation was 7° from a selection of 31 examples.

TABLE

1,3-*Dioxans suspected of existing in non-chair conformations*

Substituents	Observed boiling point[a]	Calculated boiling point
2,2-*trans*-4,6	132	153
2,2,4,4,6	147	155
2,2,r-4-*cis*-5-*trans*-6 ..	152	169
2,4,4,6,6	150	152
4,4,6,6	154	150
2,2,4,4,5	147	165

[a] The values were our choice of literature values confirmed in many cases in our laboratory.

Our interest in non-chair conformations of the 1,3-dioxan ring prompted calculation of boiling points for compounds thought to exist in non-chair conformations. Considerable discrepancies between observed and calculated boiling points were noted for 3 of these compounds. This confirms our earlier assignment of non-chair conformations to these compounds (Table).

The fact that boiling points can be analysed empirically in terms of substituent effects, although interesting, is not unduly remarkable as it has been suspected for a long time.[1-5] It is more important to recognise that the von Auwers[1-3] and other boiling points rules[4,5] have been replaced by a new, if at present rather blunt, method for structural and conformational assignments.

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