The von Auwers' Boiling Point Rule. A New Approach

By **George M. Kellie** and **Frank G. Riddell**,* Department of Chemistry, The University, Stirling

An empirical approach to the determination of relationships between b.p.s and chemical constitution in a homologous series of compounds is described. Molar volumes are shown to be similarly useful in structural and stereochemical studies. The relationships derived should be useful for predicting b.p.s and assignment of stereochemistry in several series of compounds. Large discrepancies between observed and predicted values in certain 1,3-dioxans are taken as indicators of twist conformations.

FROM the early years of this century many chemists have felt that there might exist a simple relationship between the chemical structure of the molecules of a compound and its bulk physical properties such as b.p., density, refractive index, *etc*. Since most of these properties are, in general, readily measurable, several attempts have been made to use them for structure determination. Notable examples are the parachor introduced by Sugden,[1] and the famous von Auwers' rule,[2] which relates to b.p.s. Since then a large number of b.p. rules have been proposed,[3-6] a typical example being that put forward by Allinger,[4] which states, ' With respect to *cis*- and *trans*-isomers in cyclic systems, that isomer which has the higher b.p., higher index of refraction, and higher density, is the isomer which possesses the least stable configuration.'

van Bekkum and his co-workers critically examined many of these rules,[6] and concluded that none of them was without some distinct limitation. Since the demise of these rules many powerful techniques for the investigation of configuration and conformation have come to the fore, notably n.m.r. spectroscopy. As a consequence little attention has been paid to the evaluation of bulk physical properties as an indicator of the stereochemistry of a compound.

We have recently reported [7] that for a series of similar cyclic compounds, the b.p.s (TB) may be expressed by equation (1) where $\mathrm{TB_p}$ is the b.p. of the parent compound

$$\mathrm{TB} = \mathrm{TB_p} + \Sigma t_i \qquad (1)$$

in the series, and the t_i values are incremental factors relating to structure.

We rationalise this rule as follows. For a liquid boiling under equilibrium conditions, the free energy difference between vapour and liquid must be zero, therefore equation (2) applies where ΔH_{vap} and ΔS_{vap} are the

$$\Delta H_{\text{vap}} = T\mathrm{B}\Delta S_{\text{vap}} \qquad (2)$$

enthalpy and entropy of vaporisation. Trouton's rule states that the entropy of vaporisation is constant for a series of non-polar liquids.[8] If ΔH_{vap} is a linear function of the type and orientation of substituents present in a homologous series, then the b.p.s should be a linear function too, and therefore equation (1) follows.

We first examined this relationship for the 12 members of the methylbenzene series (Table 1). A least squares

---

[1] (*a*) S. Sugden, *J. Chem. Soc.*, 1924, 22; (*b*) O. R. Quale, *Chem. Rev.*, 1953, **53**, 439.

[2] K. von Auwers, *Annalen*, 1920, **420**, 84.

[3] A. Skita, *Ber.*, 1923, **56**, 1014.

[4] N. L. Allinger, *J. Amer. Chem. Soc.*, 1957, **79**, 3443.

[5] A. E. van Arkel, *Rec. Trav. chim.*, 1932, **51**, 1018; 1934, **53**, 546.

[6] H. van Bekkum, A. van Veen, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1961, **80**, 1310.

[7] G. M. Kellie and F. G. Riddell, *J.C.S. Chem. Comm.*, 1972, 42.

[8] See W. J. Moore, ' Physical Chemistry,' Longmans, London, 1965, p. 105.

analysis of the b.p.s in terms of two parameters, a methyl group incremental factor, and an *ortho*-group incremental factor which had best fit values +29·1 and +1·8° respectively, gave a plot with standard deviation 2·6° and a correlation coefficient of 0·998.

TABLE 1

Methylbenzene b.p.s

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C) [b]
0	80·1	80·1
1	110·6	109·2
1,2	144·4	140·2
1,3	139·1	138·4
1,4	138·3	138·4
1,3,5	164·7	167·5
1,2,4	169·4	169·4
1,2,3	176·1	171·2
1,2,3,4	205·0	202·2
1,2,3,5	198·0	200·4
1,2,4,5	196·8	200·4
1,2,3,4,5	231·8	233·2
1,2,3,4,5,6	265·0	266·0

[a] Values at 760 mmHg from ref. 9. [b] Calculated using parameters given in the text.

Encouraged by this result we analysed the known b.p.s of 29 methylcyclohexanes. Five parameters were employed for the least-squares analysis which had the following best fit values; equatorial, +19·1°; axial, +23·0°; geminal, −5·7°; equatorial–equatorial vicinal, +4·2°; equatorial–axial vicinal, +3·1°. The standard deviation here is 1·7° and the correlation coefficient is 0·997 (Table 2).

TABLE 2

Methylcyclohexane b.p.s

Substituents	Obs. b.p. (°C)[a]	Calc. b.p. (°C) [b]
0	81	81
1	101	100
1,1	120	117
cis-1,2	130	127
trans-1,2	123	122
cis-1,3	120	119
trans-1,3	124	123
cis-1,4	124	123
trans-1,4	119	119
1,1,3	136	136
1,1,4	135	136
r-1-*c*-3,5	139	138
r-1-*c*-3-*t*-5	142	142
r-1-*c*-2,3	151	150
r-1-*c*-2-*t*-3	151	149
r-1-*t*-2-*c*-3	146	144
r-1-*c*-2,4	146	146
r-1-*c*-2-*t*-4	146	146
r-1-*t*-2-*c*-4	145	145
r-1-*t*-2,4	142	141
1,1,3,3	155	153
1,1,4,4	153	153
cis-1,1,3,5	152	155
trans-1,1,3,5	156	159
r-1-*c*-2,3,5	169	169
r-1-*t*-2,4-*c*-5	161	163
r-1-*t*-2-*c*-4,5	165	168
r-1-*c*-2-*t*-4,5	170	173
r-1-*c*-2,4,5	170	173

[a] Values at 760 mmHg from refs. 10 and 11. [b] Calculated using parameters given in the text.

The success of equation (1) in these instances implies that our assumption that the heat of vaporisation is a linear function of substituents is correct. This clearly merits a closer examination. The major attractive forces to be overcome when a non-polar liquid boils are dispersion forces, which depend upon how closely molecules can pack together, and hence on molar volumes. Since each additional group of the same constitution (*e.g.* methyl) added to the parent molecule is expected to add a similar and constant molar volume increment, it should also add a constant b.p. increment. Now because Trouton's rule only applies to non-polar liquids, this extrapolation from molar volumes to b.p.s should only hold for non-polar liquids. For molecules with groups pushed close together, such as an axial methyl and the two *syn*-axial hydrogens in a cyclohexane derivative, the molar volume increment should be smaller; the molecules will consequently be more closely packed, have larger intermolecular forces, and the compound should have a greater b.p. Thus one expects the b.p. incremental factor for an axial methyl group in cyclohexane (+23·0°) to be slightly larger than for an equatorial methyl group (+19·1°).

TABLE 3

Methylbenzene molar volumes

Substituents	Obs. V_{m} [a]	Calc. V_{m} [b,c]
0	88·7	88·7
1	106·3	105·9
1,2	120·6	119·9
1,3	122·9	122·8
1,4	123·3	122·8
1,3,5	138·9	139·8
1,2,3	134·4	134·4
1,2,4	137·2	136·9
1,2,3,4	148·3	148·1
1,2,3,5	150·8	151·0
1,2,4,5	151·2	151·0
1,2,3,4,5	161·7	162·2

[a] Values in $\mathrm{cm^3\ mol^{-1}}$ from ref. 9. [b] Calculated using a methyl group incremental factor (17·0 $\mathrm{cm^3\ mol^{-1}}$) and an *ortho*-group incremental factor (−2·9 $\mathrm{cm^3\ mol^{-1}}$). [c] Standard deviation 0·5 $\mathrm{cm^3\ mol^{-1}}$; regression coefficient 0·999.

To check this analysis of the situation we next analysed the molar volumes of the benzene and cyclohexane derivatives by a similar procedure (Tables 3 and 4). Even better agreement was obtained than for the b.p.s. The magnitudes of the parameters found are about what would be expected. From the methyl incremental factors it follows that the radius of a spherical methyl group on benzene is 190 pm, and equatorial on cyclohexane is 197 pm, close to the accepted value of *ca.* 200 pm. The smaller radius in the former case probably arises from the shorter methyl–ring carbon bond. It is now possible to use these experimentally determined radii to check whether the experimentally determined overlap volumes are realistic. For two spherical *o*-methyl groups on a benzene ring of side 139 pm, with a

---

[9] 'Handbook of Tables for Organic Compound Identification,' ed. Z. Rappoport, Chemical Rubber Company, Cleveland, 1967.

[10] G. Mann, M. Muhlstadt, and J. Braband, *Tetrahedron*, 1968, **24**, 3607.

[11] G. Mann, H. Werner, M. Muhlstadt, and W. Engewald, *Tetrahedron*, 1971, **27**, 3223.

C–CH_3 bond length of 150 pm, and a methyl group of radius 190 pm, the overlap volume is 5·0 cm^3 mol^{-1}. This is somewhat larger than the observed value (2·9 cm^3 mol^{-1}). One would however, expect the observed value of this parameter to be lower than that calculated for several reasons: (i) the function describing the overlap volume of two spheres is sensitive to small changes in geometry; (ii) methyl groups are not spherical, and a spherical model will exaggerate overlap; (iii) although methyl groups are not conical, a cone with three dimples is a better model than a sphere, this would reduce the overlap and allow some ' cogwheeling '; (iv) the molecule can distort to relieve this interaction. A similar argument applies to the cyclohexane series. Overlap of two spherical equatorial methyl groups of radius 197 pm separated by 294 pm gives a calculated overlap of 5·7 cm^3 mol^{-1}, again larger than the observed value of 2·2 cm^3 mol^{-1}. There is probably more opportunity in this case for the molecule to reduce its non-bonded interactions by distortion, and so reduce the overlap. As expected an axial methyl group in cyclohexane, hindered by two *syn*-axial hydrogens, shows a smaller volume increment than an equatorial methyl.

TABLE 4

Methylcyclohexane molar volumes

Substituents	Obs. V_m [a]	Calc. V_m [b,c]
0	107·9	107·9
1	127·6	127·1
1,1	143·7	143·1
cis-1,2	140·9	140·9
trans-1,2	144·6	144·1
cis-1,3	146·5	146·3
trans-1,3	143·0	143·1
cis-1,4	143·3	143·1
trans-1,4	147·2	146·3
1,1,3	162·1	162·4
1,1,4	163·5	162·4
r-1-*c*-2,3	158·2	157·8
r-1-*t*-2,3	156·4	157·9
r-1-*t*-2-*c*-3	161·6	161·2
r-1-*c*-2,4	160·4	160·1
r-1-*c*-2-*t*-4	160·4	160·1
r-1-*t*-2-*c*-4	160·2	160·2
r-1-*t*-2,4	161·2	162·3
r-1-*c*-3,5	164·0	165·5
r-1-*c*-3-*t*-5	163·5	163·4

[a] Values in cm^3 mol^{-1} from ref. 12. [b] Calculated using the following incremental factors: equatorial Me = 19·2; axial Me = 16·0; equatorial–axial vicinal Me_2 = −2·3; equatorial–equatorial vicinal Me_2 = −2·2 cm^3 mol^{-1}. [c] Standard deviation 0·7 cm^3 mol^{-1}; regression coefficient 0·998.

TABLE 5

Methylcyclopropane b.p.s

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C) [b,c]
0	−33	−33
1	5	1
1,1	21	23
cis-1,2	37	35
trans-1,2	29	31
1,1,3	56	53
r-1-*c*-2,3	66	68
r-1-*c*-2-*t*-3	60	60

[a] Values at 760 mmHg from refs. 9 and 13. [b] Calculated using the following incremental factors: methyl group (34°), *gem*-dimethyl (−11°), and *trans*-1,2-vicinal dimethyl (−4°). [c] Regression coefficient 0·994; standard deviation 3°.

We next turned our attention to b.p. analysis in other homologous series. The observed and calculated values are reported in Tables 5—8. For the cyclo-propanes, -pentanes, -hexanes, and -heptanes, the decreasing factor by which a methyl group increases the b.p. is probably due to the decreasing proportionate molar volume increment due to each additional methyl group. For cyclopropane, the introduction of a methyl group causes a proportionately much larger effect than does the same change in cycloheptane.

TABLE 6

Methylcyclopentane b.p.s

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C) [b,c]
0	49	49
1	72	70
1,1	88	86
cis-1,2	100	96
trans-1,2	92	91
cis-1,3	92	91
trans-1,3	91	91
1,1,2	114	112
1,1,3	105	107
r-1-*t*-2-*c*-3	110	112
r-1-*t*-2-*c*-4	109	112
r-1-*c*-2-*t*-3	118	117
r-1-*c*-2-*t*-4	117	117
r-1-*c*-2,4	118	117
cis-1,1,3,4	133	133
trans-1,1,3,4	122	122
1,1,3,3	118	117
r-1-*c*-2,3,4	147	148
r-1-*t*-2,3-*c*-4	134	133
cis-1,1,2,3	136	138

[a] Values at 760 mmHg from refs. 9 and 13. [b] Calculated using the following incremental factors: methyl group (21°), *gem*-dimethyl (−5°), *cis*-vicinal dimethyl (5°), and 1,3-*cis*-dimethyl (−6°). [c] Regression coefficient 0·997; standard deviation 2°.

TABLE 7

Methylcycloheptane b.p.s

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C) [b,c]
0	118	118
1	136	136
1,1	152	153
cis-1,2	161	161
trans-1,2	157	157
cis-1,3	153	153
trans-1,3	153	153
cis-1,4	154	153
trans-1,4	154	153

[a] Values at 760 mmHg from ref. 14. [b] Calculated using the following incremental factors: methyl group (18°), *cis*-1,2-vicinal dimethyl (8°), and *trans*-1,2-vicinal dimethyl (4°). [c] Regression coefficient 0·996; standard deviation 1°.

In our post-rationalisation of our b.p. equation (1) we noted that Trouton's rule does not apply to polar liquids. This is because polar molecules will adopt preferred

---

[12] K. Altenberg, *Z. phys. Chem. (Leipzig)*, 1966, **231**, 274.

[13] ' Rodd's Chemistry of the Carbon Compounds,' ed. S. Coffey, Elsevier, London, 1967.

[14] G. Mann, M. Muhlstadt, R. Muller, E. Kern, and W. Hadeball, *Tetrahedron*, 1968, **24**, 6941.

orientations with respect to each other in the liquid phase due to dipolar interactions, and hence ΔS_{vap} will no longer be a constant for this series. If, however, ΔS_{vap} varies in a predictable manner, then our approach may still be valid, because the substituent effects chosen may also reflect dipolar effects. We tested this in the chlorobenzene series (Table 8) using four parameters, a chloro-effect and three directional parameters, *ortho*, *meta*, and *para*. A satisfactory fit was obtained.

TABLE 8

Chlorobenzene b.p.s

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C) [b,c]
0	80	80
1	137	137
1,2	179	180
1,3	173	173
1,4	173	173
1,3,5	208	207
1,2,3	218	219
1,2,4	213	213
1,2,3,4	254	250
1,2,3,5	246	244
1,2,4,5	245	244
1,2,3,4,5	277	280

[a] Values at 760 mmHg from ref. 9. [b] Calculated using the following incremental factors: chloro-parameter (51°), *ortho*-parameter (−3°), *meta*-parameter (−9°), and *para*-parameter (−9°). [c] Regression coefficient 0·997; standard deviation 3°.

TABLE 9

Methyl-1,3-dioxan b.p.s

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C)
0	105	105
2	110	108
4	114	115
5	118	121,[c] 118 [d]
5,5	127	134
cis-4,6	126	130
trans-4,6	137	139
cis-2,4	119	118
cis-2,5	121	120
trans-2,5	127	124
2,2	125	119
4,4	133	135
4,4,6	143	140
r-2-*c*-4,6	129	132
r-2-*c*-4-*t*-6	138	142
r-4-*c*-5-*t*-6	157	155,[c] 152 [d]
r-4-*c*-5,6	148	146
r-4-*t*-5-*c*-6	148	143
2,5,5	132	136
2,2,4	132	129
cis-2,4,4,6	139	142
r-2-*c*-4-*t*-5,6	159	158
cis-2,4,5,5	147	147
cis-2,2,4,6	138	144
2,2,5,5	145	148
r-2-*c*-4,5,6	149	148
r-2-*c*-4,6-*t*-5	149	145
trans-4,5,5,6	173	168
cis-4,5,5,6	159	159
cis-2,4,4,5	156	153
2,2,5	137	135,[c] 132 [d]

[a] Values at 760 mmHg determined by us [15] or an average of published figures.[16–24]. [b] Calculated using the following incremental factors; 2-equatorial Me (3°), 2-axial Me (11°), 4-equatorial Me (10°), 4-axial Me (33°), 5-equatorial Me (16°), 5-axial Me (13°), 4-*gem*-Me_2 (−14°), 4,6-diequatorial Me_2 (4°), and 4-equatorial-6-axial Me_2 (−9°). [c] Calculated for 5-equatorial methyl. [d] Calculated for 5-axial methyl.

Finally we applied our molar volume and b.p. correlations to some 1,3-dioxans (Tables 9—11). To obtain the substituent parameters we considered only those compounds known to exist in chair conformations.[25,26] Calculation of the molar volume for *trans*-2,2,4,6-tetramethyl-1,3-dioxan showed the molecule to have an anomalously large molecular volume (Found: 161·1. Calc.: 156·7 $cm^3\ mol^{-1}$). Since molecules go from a chair to a twist conformation to relieve strains

TABLE 10

Observed and calculated b.p.s for 1,3-dioxans suspected of existing in non-chair conformations

Substituents	Obs. b.p. (°C) [a]	Calc. b.p. (°C) [b]
trans-2,2,4,6	132	153
2,2,4,4,6	147	155
2,2-*r*-4-*c*-5-*t*-6	152	169 [c]
2,4,4,6,6	150	152
4,4,6,6	154	150
2,2,4,4,5 [d]	147	165 [c]

[a] Values at 760 mmHg determined by us.[15] [b] Calculated for chair conformations. [c] Calculated for 5-methyl equatorial. [d] Value from ref. 23.

TABLE 11

Methyl-1,3-dioxan molar volumes

Substituents	Obs. V_m [a]	Calc. V_m [b,c]
0	85·4	85·4
4	104·6	104·6
5,5	121·4	122·1
cis-4,6	124·4	123·7
trans-4,6	120·9	121·0
4,4,6	140·1	140·1
2	105·5	105·0
cis-2,4	124·0	124·1
2,5,5	142·2	141·7
r-2-*c*-4,6	142·5	143·2
r-2-*c*-4-*t*-6	140·5	140·5
cis-2,4,4,6	159·7	159·6
2,2	121·0	121·2
2,2,4	140·1	140·3
2,2,5,5	158·1	157·9
cis-2,2,4,6	159·8	159·5
2,4,4,6,6 [d]	176·0	176·0
4,4,6,6 [d]	155·7	156·5
trans-2,2,4,6 [d]	161·1	156·7

[a] Values in $cm^3\ mol^{-1}$ at 20° from ref. 24. [b] Calculated using the following incremental factors; 2-equatorial methyl (19·5), 2-axial methyl (16·2), 4-equatorial methyl (19·1), 4-axial methyl (16·4), and 5-*gem*-dimethyl (36·7 $cm^3\ mol^{-1}$). [c] Regression coefficient 0·999, standard deviation 0·4 $cm^3\ mol^{-1}$. [d] Compounds suspected of existing in non-chair conformations. These were not included in the analysis.

---

[15] G. M. Kellie, Ph.D. Thesis, Stirling, 1972.

[16] F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, 1970, **92**, 3050.

[17] E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, 1968, **90**, 3444.

[18] F. G. Riddell and M. J. T. Robinson, *Tetrahedron*, 1967, **23**, 3417.

[19] K. Pihlaja, *Acta Chem. Scand.*, 1968, **22**, 716.

[20] K. Pihlaja, *Acta Chem. Scand.*, 1971, **25**, 451.

[21] L. Pihlaja and P. Ayras, *Acta Chem. Scand.*, 1970, **24**, 531.

[22] K. Pihlaja, *Soumen Kemi*, 1969, **842**, 74.

[23] K. Pihlaja, personal communication.

[24] K. Pihlaja, *Ann. Univ. Turkuensis*, 1967, Ser. A1, No. 114.

[25] G. M. Kellie and F. G. Riddell, *J. Chem. Soc.* (*B*), 1971, 1030.

[26] K. Pihlaja, G. M. Kellie, and F. G. Riddell, *J.C.S. Perkin II*, 1972, 252.

present due to proximity of groups, molecules in twist conformations should have anomalously large molecular volumes. If this compound had a chair conformation with 2,4-*syn*-diaxial methyl grouping the molar volume would have been lower than that calculated. This result confirms that *trans*-2,2,4,6-tetramethyl-1,3-dioxan has a non-chair conformation.[25,26] The b.p. analysis shows three compounds with anomalously low b.p.s (*i.e.* high molecular volumes). This evidence reinforces our previous assignment of non-chair conformations to these compounds. Those dioxans with a 4,6-*syn*-diaxial interaction do not show anomalies, and hence probably have chair conformations.

The molar volume incremental factors for 1,3-dioxan (Table 11) are as expected. Equatorial and axial methyl groups at positions 2 and 4 show almost identical values to those found for cyclohexane with equatorial methyls showing larger incremental factors than axial methyls. Unfortunately our data did not allow separation of the axial and equatorial parameters at C(5).

The uneven nature of the b.p. substituent parameters for the 1,3-dioxans must reflect not only the molar volume changes, but also alterations to the packing and alignment of the molecules in the liquid phase. Hindrance to dipolar attractions and ordering will vary with position and direction of the introduced substituent.

It is not at all remarkable that we have found these correlations, for the whole of modern chemistry rests on the supposition that behaviour patterns can be extrapolated in a homologous series. What is important is that two factors emerge. First, we have a predictive approach to molar volumes and b.p.s which will allow confirmation or even assignment of stereochemistry in compounds yet to be synthesised.* Secondly, our approach can yield conformational information of a fundamental nature, purely by detection of anomalies in molar volumes or in b.p.s.

EXPERIMENTAL

Least squares analyses were performed on an Elliot 4130 computer using the program described in refs. 15 and 25.

We thank Professor J. M. G. Cowie for discussions and the S.R.C. for a maintenance grant (to G. M. K.).

[4/1939 *Received, 23rd September*, 1974]

---

* With a preliminary set of data we were able to confirm the stereochemical assignments in ref. 11 on the basis of their b.p.s.