

glacial acetic acid: yield 40 g., m. p. 178–183°. Two recrystallizations left 15 g. of picrates (m. p. 201–203°). Next, the crude viscous bases ( $n_D^{25}$  1.6096) liberated from the picrates were dissolved in a 1:1 alcohol-ether solution and a slight excess of concentrated sulfuric acid was added. The resulting acid sulfates after three recrystallizations from alcohol melted at 265–267° with decomposition. A base melting at 82–82.5° was liberated from the acid sulfate which after two recrystallizations from petroleum ether melted at 83.5–84°; yield of pure base, 0.7 g. The pure picrate of the base melted at 228.5–229.5°. From another fraction boiling at 340° ( $n_D^{25}$  1.6504), an additional quantity of the base was recovered, bringing the total yield up to 1.9 g.

*Anal.* of base. Calcd. for  $C_{15}H_{13}N$ : C, 86.95; H, 6.23; N, 6.76. Found: C, 86.97; H, 6.30; N, 7.00.

*Anal.* of picrate. Calcd. for  $C_{21}H_{15}O_7N_4$ : C, 57.79; H, 3.67; N, 12.84. Found: C, 58.10; H, 3.83; N, 12.97.

**Isolation of a  $C_{15}H_{13}N$  Transformer-Oil Base.**—The bases, recovered from the residues after separation of the  $C_{15}H_{13}N$  compound, were combined and processed through degassing of their sulfurous acid solution into 8 fractions of bases. To each fraction in alcohol was added a slight excess of concentrated nitric acid. Precipitates in fractions 5, 6, 7 and 8 followed immediately and appeared in very small amount in the first four fractions after seeding and prolonged stirring. The combined nitrates were recrystallized from water containing a trace of nitric acid. The base liberated from the salt melted at 86–87°. The melting point, 228–229°, of the picrate prepared from the base remained unchanged after recrystallization from glacial acetic acid.

The very slight solubility of the nitrate in water at 100°, which is approximately 1 part in 100, offers a selective method for the isolation of this base. This claim is emphasized by the isolation of only 0.6 g. of this substance, or 0.59%, calculated from the quantity of the complex mixture of bases processed.

The slight difference in melting points of this base and the  $C_{15}H_{13}N$  compound, as well as the slight difference in melting points of the corresponding picrates, suggested an identity of the two bases. However, the melting point of a mixture of the two picrates showed a depression of 30°. Furthermore, the  $C_{15}H_{13}N$  base possesses a pronounced sweet odor, whereas the  $C_{15}H_{15}N$  base is odorless.

*Anal.* of base.<sup>17</sup> Calcd. for  $C_{15}H_{13}N$ : C, 86.84; H, 6.83; N, 6.32. Found: C, 87.86; H, 6.88; N, 6.60.

*Anal.* of picrate. Calcd. for  $C_{22}H_{15}N_5O_7$ : C, 58.66; H, 4.02; N, 12.44. Found: C, 58.62; H, 4.04; N, 12.46.

### Summary

Fractional degassing of base acid sulfites as described in the preceding paper by Roberts and Bailey has been employed in isolation, from the 300° range of kero bases, of two quinoline homologs, 2,3-dimethyl-8-*n*-propylquinoline and 2,3,4,8-tetramethylquinoline. The structures of these products have been established through degradation and synthesis.

Two other bases of undetermined structure of the compositions  $C_{13}H_{15}N$  and  $C_{14}H_{17}N$  were separated from bases boiling in the neighborhood of 295°.

Two high-boiling bases,  $C_{15}H_{13}N$  and  $C_{16}H_{15}N$ , which are probably of the acridine or naphthoquinoline types, have been isolated from transformer-oil base fractions through employment of selective salts and fractional degassing of base acid sulfites.

(17) The determination of carbon in the free base is obviously in error, but lack of material prevented a duplicate analysis.

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## A System Correlating Molecular Structure of Organic Compounds with their Boiling Points. I. Aliphatic Boiling Point Numbers

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Several systems have been devised for correlating different physical properties of organic compounds with their molecular structure and two are particularly valuable tools in organic chemistry—molecular refraction and the parachor. Unfortunately, however, these methods give no information about certain types of isomerism and the parachor often involves considerable experimental difficulties. Consequently it would be most desirable to have available another method which correlated molecular structure with

an easily determined physical property which would be sensitive to types of isomerism not shown by other methods. The boiling temperature of a compound is probably more dependent upon molecular structure, and more easily determined usually, than any other physical property; and yet no attempt has been made to devise a system for correlating the molecular structure of all types of organic compounds with their boiling points. Large numbers of expressions have been devised for correlating the boiling points of members of

homologous series with the molecular weight or other similar property, but no general system has been made available for correlating all types of compounds. Such a system would be especially valuable for determining the structures of unknown substances, for calculating the boiling points of substances from their structure, and for studying the effect of one group upon another in the molecule.

At the boiling point of a substance the kinetic energy of the molecules in the liquid state equals the energy associated with the attractive forces tending to hold the molecules together plus the energy required to do the necessary work against the external pressure. Since the latter energy is constant at a given pressure for all types of molecules and since the molecular attractive forces are primarily dependent upon (1) the kind, (2) the number, and (3) the arrangement of the atoms in the molecule, the boiling point of the substance may also be considered to be primarily dependent upon the kind, number, and arrangement of the atoms in the molecule. The kind and number of the atoms in the molecule, *i. e.*, the molecular formula, may be determined by qualitative and quantitative analyses together with molecular weight estimations; consequently, the effect of the structure upon the boiling point of a compound may be studied in this way. The boiling point of a compound is affected by such factors as dipole moment, hydrogen bonds, association, etc.; but, since these effects are also dependent upon the kind, number and arrangement of the atoms in the molecule they will be accounted for to a large extent. The boiling point is, of course, greatly affected by the pressure; but, by using pressures at or near the normal pressure in the following considerations, that factor has been largely eliminated.

There is no known relationship between the boiling point of a compound and atomic values such as atomic weight, atomic volume, atomic refraction, and atomic parachor; consequently, it was necessary to choose numbers for the atoms and groups in molecules which may be used with boiling point data. It was also necessary to devise an expression for equating the two. The absolute boiling temperature of members of an homologous series of organic compounds may be expressed as a function of the molecular weight raised to a fractional power using Walker's<sup>1</sup> formula,  $T = aM^b$ ,

(1) Walker, *J. Chem. Soc.*, **65**, 193 (1894).

where  $T$  is the absolute boiling point,  $M$  the molecular weight, " $a$ " a constant characteristic of each homologous series and of a different value for each series, and " $b$ " another similar constant. The value of " $b$ " does not vary greatly from a value of one-third for most series and it becomes apparent that boiling point data may be expressed as a function of the sum of the atomic values chosen for use with boiling points raised to the one-third power. These atomic values and the expression for equating them with boiling point data were obtained in the following way.

Practically all organic compounds may be considered to be derivatives of the normal paraffin hydrocarbons or of hydrogen. Consequently, the normal paraffin hydrocarbons and hydrogen were taken to be the basis of the system. Next, various values were assigned to carbon and hydrogen and the absolute boiling points of hydrogen and the normal paraffin hydrocarbons plotted against the cube root of the sum of the different atomic numbers assigned to carbon and hydrogen. In this way it was possible to choose those values of carbon and hydrogen which cause the boiling point of molecular hydrogen to coincide most closely with the straight line of the hydrocarbon plot, thus making it possible to compare derivatives of hydrogen and of the normal paraffin hydrocarbons. The best values of carbon and hydrogen are 0.8 and 1.0 unit, respectively, and may be called the atomic boiling point numbers (b. p. n.) for these atoms. Also the equation for the hydrogen-hydrocarbon plot may be used for correlating the boiling points of derivatives of hydrogen and the normal hydrocarbons with the boiling points of those substances themselves. Two forms of this equation are given below in which B. P. is the boiling point in degrees centigrade and B. P. N. (molecular boiling point number) is the sum of the individual atomic and group boiling point numbers expressing the structure of the molecule.

$$B. P. = 230.14 \sqrt[3]{B. P. N.} - 543 \quad (1)$$

$$\text{Log } B. P. N. = 3(\text{log } (B. P. + 543) - 2.3620) \quad (2)$$

The boiling point number (B. P. N.) of derivatives of hydrogen or of the normal hydrocarbons may be considered to be composed of two parts: that due to the hydrogen atom or the hydrocarbon residue and that due to the characteristic atom or group. The latter value may be determined readily as the difference between the boiling number for the hydrogen atom or the hydrocarbon residue and the molecular boiling point number

determined from the boiling point. For example, the branched chain hydrocarbons are considered to be alkyl derivatives of the normal hydrocarbons and the molecular boiling point number the sum of the atomic boiling point numbers for the hydrogen and carbon atoms in the normal chain plus the boiling point number which has been determined for the alkyl group. The boiling point number of the methyl group was determined from the following data, which demonstrates the method. The boiling point of 2-methylbutane is  $28^{\circ}$ , which gives an observed B. P. N. of 15.27. In the butane chain there are four carbon atoms which contribute 3.2 and nine hydrogens which contribute 9.0 units. The difference of 3.07 units is to be attributed to the side chain methyl group. As an approximation a value of 3.05 has been adopted as the b. p. n. of the side chain methyl group which gives a calculated B. P. N. of 15.25 and a boiling point of  $27.75^{\circ}$ . The b. p. n. of several of the alkyl groups together with a number of the characteristic groups present in aliphatic

compounds have been determined and may be found in Table II. In Table I have been listed most of the paraffin hydrocarbons for which boiling points at atmospheric pressures have been recorded, the boiling point and the corresponding B. P. N., the calculated B. P. N., and the amount of the deviation from the calculated. Where the boiling point was recorded in the literature as a range of temperature the midpoint of the range has been taken as the boiling point. Many of the boiling points appearing in Table I were obtained at pressures considerably less than standard. This, of course, introduces quite a little error and undoubtedly accounts for, in part, the low boiling points recorded for many of the higher boiling compounds. Another source of inaccuracy is that introduced by the use of some boiling points that have been corrected and many that have not. In addition, the differences in technique in taking the boiling point must cause serious discrepancies. For example, compounds 43 and 44 in section B of Table I, 2,4,7-trimethyloctane

TABLE I  
BOILING POINT NUMBERS FOR THE PARAFFIN HYDROCARBONS

Substance	B. p., $^{\circ}$ C.	B. P. N. (obsd.)		B. P. N. (calcd.)	Deviation
A. Normal Hydrocarbons					
0 Hydrogen	-252.8	2.005	0.0 + 2	= 2.0	+0.005
1 Methane	-161.5	4.555	.8 + 4	4.8	-.245
2 Ethane	-88.3	7.71	1.6 + 6	7.6	+.11
3 Propane	-44.5	10.16	2.4 + 8	10.4	-.24
4 Butane	-0.45	13.10	3.2 + 10	13.2	-.10
5 Pentane	+36.2	15.94	4.0 + 12	16.0	-.06
6 Hexane	69	18.80	4.8 + 14	18.8	= .0
7 Heptane	98.52	21.66	5.6 + 16	21.6	+.06
8 Octane	125.8	24.54	6.4 + 18	24.4	+.14
9 Nonane	150.72	27.38	7.2 + 20	27.2	+.18
10 Decane	174	30.24	8.0 + 22	30.0	+.24
11 Hendecane	195.84	33.08	8.8 + 24	32.8	+.28
12 Dodecane	214.5	35.66	9.6 + 26	35.6	+.06
13 Tridecane	234	38.48	10.4 + 28	38.4	+.08
14 Tetradecane	246	40.29	11.2 + 30	41.2	-.91
15 Pentadecane	270	44.16	12.0 + 32	44.0	+.16
16 Hexadecane	287	47.00	12.8 + 34	46.8	+.20
17 Heptadecane	303	49.67	13.6 + 36	49.6	+.07
18 Octadecane	317	52.18	14.4 + 38	52.4	-.22
19 Nonadecane	330	54.58	15.2 + 40	55.2	-.62
B. Methyl Derivatives					
1 2-Methylpropane	-10.2	12.40	2.4 + 7 + 3.05	=12.45	-0.05
2 2,2-Dimethylpropane	+9.5	13.84	2.4 + 6 + 6.1	14.50	-.66
3 2-Methylbutane	28	15.27	3.2 + 9 + 3.05	15.25	+.02
4 2,2-Dimethylbutane	49	17.02	3.2 + 8 + 6.1	17.30	-.28
5 2,3-Dimethylbutane	58.1	17.82	3.2 + 8 + 6.1	17.30	+.52
6 2,2,3-Trimethylbutane	80.9	19.92	3.2 + 7 + 9.15	19.35	+.57
7 2,2,3,3-Trimethylbutane	106.8	22.50	3.2 + 6 + 12.2	21.40	+1.10
8 2-Methylpentane	60	17.99	4.0 + 11 + 3.05	18.05	-0.06
9 3-Methylpentane	64	18.35	4.0 + 11 + 3.05	18.05	+.30

TABLE I (Concluded)

	Substance	B. P., °C.	B. P. N. (obsd.)		B. P. N. (calcd.)		Deviation
10	2,2-Dimethylpentane	80.5	19.89	4.0 + 10 +	6.1	20.10	-0.21
11	2,3-Dimethylpentane	89.7	20.77	4.0 + 10 +	6.1	20.10	+ .67
12	2,4-Dimethylpentane	83.9	20.21	4.0 + 10 +	6.1	20.10	+ .11
13	3,3-Dimethylpentane	86	20.42	4.0 + 10 +	6.1	20.10	+ .32
14	2,2,3-Trimethylpentane	110.6	22.91	4.0 + 9 +	9.15	22.15	+ .76
15	2,2,4-Trimethylpentane	98.5	21.66	4.0 + 9 +	9.15	22.15	- .49
16	2,3,3,4-Tetramethylpentane	130	25.01	4.0 + 8 +	12.2	24.20	+ .81
17	2-Methylhexane	90	20.81	4.8 + 13 +	3.05	20.85	- .04
18	3-Methylhexane	91.8	20.98	4.8 + 13 +	3.05	20.85	+ .13
19	2,2-Dimethylhexane	106.5	22.48	4.8 + 12 +	6.1	22.90	- .42
20	2,3-Dimethylhexane	113.9	23.24	4.8 + 12 +	6.1	22.90	+ .34
21	2,4-Dimethylhexane	110	22.84	4.8 + 12 +	6.1	22.90	- .06
22	2,5-Dimethylhexane	109.2	22.76	4.8 + 12 +	6.1	22.90	- .14
23	3,3-Dimethylhexane	111.5	23.00	4.8 + 12 +	6.1	22.90	+ .10
24	3,4-Dimethylhexane	116.5	23.54	4.8 + 12 +	6.1	22.90	+ .64
25	2,3,5-Trimethylhexane	129	24.90	4.8 + 11 +	9.15	24.95	- .05
26	2,2,3,4-Tetramethylhexane	156.6	28.10	4.8 + 10 +	12.2	27.0	+1.10
27	2-Methylheptane	116	23.48	5.6 + 15 +	3.05	23.65	-0.17
28	3-Methylheptane	118.8	23.77	5.6 + 15 +	3.05	23.65	+ .12
29	4-Methylheptane	118	23.69	5.6 + 15 +	3.05	23.65	+ .04
30	2,4-Dimethylheptane	130	25.01	5.6 + 14 +	6.1	25.70	- .69
31	2,5-Dimethylheptane	135	25.57	5.6 + 14 +	6.1	25.70	- .13
32	2,6-Dimethylheptane	134.5	25.52	5.6 + 14 +	6.1	25.70	- .18
33	3,3-Dimethylheptane	137.5	25.86	5.6 + 14 +	6.1	25.70	+ .16
34	2,4,6-Trimethylheptane	143	26.49	5.6 + 13 +	9.15	27.75	-1.26
35	3,3,5-Trimethylheptane	159.2	28.40	5.6 + 13 +	9.15	27.75	+0.65
36	3-Methyloctane	142.5	26.43	6.4 + 17 +	3.05	26.45	- .02
37	4-Methyloctane	141.5	26.31	6.4 + 17 +	3.05	26.45	- .14
38	2,4-Dimethyloctane	152.5	27.60	6.4 + 16 +	6.1	28.50	- .90
39	2,5-Dimethyloctane	156	28.03	6.4 + 16 +	6.1	28.50	- .47
40	2,6-Dimethyloctane	158.5	28.32	6.4 + 16 +	6.1	28.50	- .18
41	2,7-Dimethyloctane	160	28.50	6.4 + 16 +	6.1	28.50	= .0
42	3,6-Dimethyloctane	159.5	28.44	6.4 + 16 +	6.1	28.50	- .06
43	2,4,7-Trimethyloctane	167.5	29.43	6.4 + 15 +	9.15	30.55	-1.08
44	2,6,7-Trimethyloctane	158.5	28.32	6.4 + 15 +	9.15	30.55	-2.23
45	2,2,7,7-Tetramethyloctane	188	32.05	6.4 + 14 +	12.2	32.60	-0.55
46	5-Methylnonane	165	29.12	7.2 + 19 +	3.05	29.25	- .13
47	2,6-Dimethylnonane	174.5	30.31	7.2 + 18 +	6.1	31.30	- .99
48	2,6-Dimethyldecane	194.5	32.91	8.0 + 20 +	3.05	34.10	-1.19
49	2,6,9-Trimethyldecane	207	34.61	8.0 + 19 +	9.15	36.15	-1.54
C. Ethyl Derivatives							
1	2-Ethylpentane	93.3	21.13	4.0 + 11 +	5.5	20.50	+0.63
2	2-Methyl-3-ethylpentane	114	23.27	4.0 + 10 +	3.05 + 5.5	22.55	+ .72
3	3-Methyl-3-ethylpentane	118.8	23.78	4.0 + 10 +	3.05 + 5.5	22.55	+1.23
4	3,3-Diethylpentane	139.2	26.04	4.0 + 10 +	11.0	24.80	+1.24
5	3-Ethylhexane	118.9	23.79	4.8 + 13 +	5.5	23.30	+0.49
6	4-Ethylheptane	139	26.02	5.6 + 15 +	5.5	26.10	- .08
7	6-Methyl-7-ethyldecane (729 mm.)	241	39.54	9.6 + 24 +	3.05 + 5.5	42.15	-2.61
D. Propyl Derivatives							
1	2-Methyl-5-propyloctane	189	32.18	6.4 + 16 +	3.05 + 7.0	32.45	-0.27
2	5-Propylnonane	196	33.11	7.2 + 19 +	7.0	33.20	- .09
3	4-Methyl-6-propylhendecane (729 mm.)	235.5	38.71	8.8 + 22 +	3.05 + 7.0	40.85	-2.14
4	6-Propyldecane (729 mm.)	242	39.68	9.6 + 25 +	7.0	41.60	-1.92
E. Butyl Derivatives							
1	5-Butylnonane	218	36.15	7.2 + 19 +	9.7	35.90	+0.25

TABLE II  
 ALIPHATIC BOILING POINT NUMBERS

Derivative	B. p. n.	Derivative	B. p. n.
A. Alkyl Radical	R—	B. Chlorides	Cl—
1 Methyl	3.05	1 RCH <sub>2</sub> Cl	7.5
2 Ethyl	5.5	2 R <sub>2</sub> CHCl	6.5
3 Propyl	7.0	3 R <sub>3</sub> CCl	6.0
4 Butyl	9.7		
C. Alcohols	—OH	D. Ethers	—O—
1 CH <sub>3</sub> OH	12.8	1 CH <sub>3</sub> OCH <sub>3</sub>	3.8
2 RCH <sub>2</sub> OH	10.8	2 RCH <sub>2</sub> OCH <sub>3</sub> , R <sub>2</sub> CHOCH <sub>3</sub> , R <sub>3</sub> COCH <sub>3</sub>	2.9
3 R <sub>2</sub> CHOH	8.8	3 RCH <sub>2</sub> OCH <sub>2</sub> R, R <sub>2</sub> CHOCH <sub>2</sub> R, R <sub>3</sub> COCH <sub>2</sub> R	2.0
4 R <sub>3</sub> COH	6.8	4 R <sub>2</sub> CHOCHR <sub>2</sub> , R <sub>3</sub> COCHR <sub>2</sub>	1.1
		5 R <sub>3</sub> COCR <sub>3</sub>	(0.2?)
E. Aldehydes	=O	F. Ketones	=O
1 HCHO, CH <sub>3</sub> CHO	8.8	1 CH <sub>3</sub> COCH <sub>3</sub>	8.5
2 RCH <sub>2</sub> CHO	8.2	2 RCH <sub>2</sub> COCH <sub>3</sub>	8.0
3 R <sub>2</sub> CHCHO	7.6	3 R <sub>2</sub> CHCOCH <sub>3</sub> , RCH <sub>2</sub> COCH <sub>2</sub> R	7.5
4 R <sub>3</sub> CCHO	7.0	4 R <sub>3</sub> CCOCH <sub>3</sub> , R <sub>2</sub> CHCOCH <sub>2</sub> R	7.0
		5 R <sub>3</sub> CCOCH <sub>2</sub> R, R <sub>2</sub> CHCOCHR <sub>2</sub>	6.5
		6 R <sub>3</sub> CCOCH <sub>2</sub> R	(6.0?)
		7 R <sub>3</sub> CCOCH <sub>3</sub>	(5.5?)
G. Acids	—COOH	H. Esters	—OO—
1 HCOOH, CH <sub>3</sub> COOH	20.0	1 HCOOCH <sub>3</sub> , CH <sub>3</sub> COOCH <sub>3</sub>	9.4
2 RCH <sub>2</sub> COOH	19.3	2 RCH <sub>2</sub> COOCH <sub>3</sub> , CH <sub>3</sub> COOCH <sub>2</sub> R	8.5
3 R <sub>2</sub> CHCOOH	18.6	3 R <sub>2</sub> CHCOOCH <sub>3</sub> , RCH <sub>2</sub> COOCH <sub>2</sub> R, HCOOCHR <sub>2</sub> , CH <sub>3</sub> COOCHR <sub>2</sub>	7.6
4 R <sub>3</sub> CCOOH	17.9	4 R <sub>3</sub> CCOOCH <sub>3</sub> , R <sub>2</sub> CHCOOCH <sub>2</sub> R, RCH <sub>2</sub> COOCHR <sub>2</sub> , HCOOCR <sub>3</sub> , CH <sub>3</sub> COOCR <sub>3</sub>	6.7
		5 R <sub>3</sub> CCOOCH <sub>2</sub> R, R <sub>2</sub> CHCOOCHR <sub>2</sub> , RCH <sub>2</sub> COOCR <sub>3</sub>	5.8
		6 R <sub>3</sub> CCOOCHR <sub>2</sub> , R <sub>2</sub> CHCOOCR <sub>3</sub>	4.9
		7 R <sub>3</sub> CCOOCR <sub>3</sub>	4.0
I. Primary Amines	—NH <sub>2</sub>	J. Secondary Amines	—NH—
1 CH <sub>3</sub> NH <sub>2</sub>	8.4	1 CH <sub>3</sub> NHCH <sub>3</sub>	6.0
2 RCH <sub>2</sub> NH <sub>2</sub>	7.3	2 RCH <sub>2</sub> NHCH <sub>3</sub>	5.0
3 R <sub>2</sub> CHNH <sub>2</sub>	6.2	3 R <sub>2</sub> CHNHCH <sub>3</sub> , RCH <sub>2</sub> NHCH <sub>2</sub> R	4.0
4 R <sub>3</sub> CNH <sub>2</sub>	5.1	4 R <sub>3</sub> CNHCH <sub>3</sub> , R <sub>2</sub> CHNHCH <sub>2</sub> R	3.5
		5 R <sub>3</sub> CNHCH <sub>2</sub> R, R <sub>2</sub> CHNHCHR <sub>2</sub>	3.0
K. Tertiary Amines	=N—		
1 CH <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	2.5		
2 RCH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	2.0		
3 R <sub>2</sub> CHN(CH <sub>3</sub> ) <sub>2</sub> , (RCH <sub>2</sub> ) <sub>2</sub> NCH <sub>3</sub>	1.5		
4 R <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub> , (R <sub>2</sub> CH) <sub>2</sub> NCH <sub>3</sub> , (RCH <sub>2</sub> ) <sub>3</sub> N	1.25		
L. Cyanides	—CN	M. Isocyanides	—NC
1 CH <sub>3</sub> CN	15.2	1 CH <sub>3</sub> NC	13.3
2 RCH <sub>2</sub> CN	14.0	2 RCH <sub>2</sub> NC	12.2
3 R <sub>2</sub> CHCN	12.8	3 R <sub>2</sub> CHNC	11.1
4 R <sub>3</sub> CCN	11.6	4 R <sub>3</sub> CNC	10.0

and 2,6,7-trimethyloctane, have very similar structures and should have very similar boiling points; however, their recorded boiling points differ by nine degrees and, judging by their calculated boiling point numbers, both of the recorded boiling points are much too low. In spite of these difficulties in obtaining accurate boiling point

data, the deviation is less than 5% in all cases except three and for two of these the boiling point was determined at 729 mm. Consequently, it appears quite likely that the general use of boiling point numbers as guide in obtaining boiling points would lead to more accurately determined and better standardized boiling points appearing in the

literature. It is, of course, unfortunate that the boiling points of so few ethyl, propyl, and higher radical derivatives have been recorded at atmospheric pressure and it may be desirable later, as a consequence, to alter slightly the values assigned to these radicals when more boiling points have been recorded.

When two methyl groups are attached to the same carbon atom it would be expected, because of the steric effect, that the b. p. n. of the second methyl group would be less than the first. This is correct for the 2,2-dimethyl paraffins, such as 2,2-dimethylpropane (Table I, Sec. B, 2) and their derivatives, but does not apply to the 3,3-dimethyl derivatives such as 3,3-dimethylpentane (13), etc. The introduction of several methyl groups into the center of the carbon chain produces a marked exaltation of the boiling point. This is shown particularly by such compounds as 2,2,3,3-tetramethylbutane (7) or 2,3,3,4-tetramethylpentane (16). Young,<sup>2</sup> while studying the properties of 2,3-dimethylbutane (5) and 2,5-dimethylhexane (22), first noticed this behavior. The cause of this exaltation may be due to the relation of the structure of these molecules to the packing effect in the liquid state. Whether this is the cause or not, the new method of correlating boiling point data makes it possible to observe and study the various effects of structure upon the boiling point in a very striking manner. Since the maximum deviation from the calculated B. P. N. of these compounds is only about 5%, no corrective factor has been devised for the present, but for making more accurate calculations the effect of related groups upon the B. P. N. should be considered.

The introduction of other atoms or groups, in contrast with the introduction of alkyl groups, produces a very marked change in the b. p. n. depending upon the position (as well as the number) of the atoms or groups substituted into the molecule. In Table II various characteristic atoms and groups are listed giving the b. p. n. for the different positions that may be taken. For example, the values given for the b. p. n. of chlorine in the primary, secondary, and tertiary positions are 7.5, 6.5, and 6.0, respectively, and show the steric effect of the surrounding atoms in a striking manner. It is possible that the depression of the b. p. n. is due in part to a change in the dipole

moment of such compounds, but insufficient data are available to make a decision. With molecular chlorine, hydrogen chloride, and methyl chloride data are available (Table III) and the change in b. p. n. corresponds to the change in dipole moment; however, the effect must be complicated by the steric effect in such a series.

TABLE III

Substance	B. p., °C.	Obsd. B. P. N.	B. p. n. of chlorine	Dipole moment × 10 <sup>18</sup>
Chlorine	-33.7	10.48	5.24	0.0
Hydrogen chloride	-83.7	7.95	6.95	1.28
Methyl chloride	-23.7	11.49	7.69	1.86

The boiling point of a substance may be calculated from its structure in the following way provided, of course, that the b. p. n. of the various structural components are known. In Table IV the boiling points of the eight chloropentanes have been calculated and compared with the observed.

The agreement between the calculated and observed boiling points in Table IV is good with the exception of the last compound which belongs to the class of 2,2-dimethyl derivatives which, as pointed out above, show a marked depression of the boiling point. Furthermore, this compound shows the greatest depression of any examined thus far and the amount is usually less than half as much. If several tenths of a unit were subtracted to account for the behavior of the 2,2-dimethyl derivatives, the calculated boiling point would more closely approximate the observed value and this should be done in making more accurate calculations.

In calculating the structure of a substance such as an alkyl chloride from its boiling point, certain limitations are encountered. In the first place, there is no way to distinguish between those isomers in which the characteristic group is merely shifted along the carbon chain, *i. e.*, 2- or 3-chloropentane and 1- or 4-chloro-2-methylbutane which are listed in Table IV. In the second place the branched compounds have a second variable, *i. e.*, the position of the alkyl group. This requires that either the position of the alkyl group be known or that of the characteristic group. Since it is possible, usually, to determine the position of the characteristic group but not the position of the alkyl groups attached to the carbon chain, the new method becomes of especial value in determining the structure of hydrocarbon radi-

(2) Young, *J. Chem. Soc.*, **77**, 1144 (1900); see also van Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921).

TABLE IV

Substance	B. P. N. (calcd.)	B. p. (calcd.)	B. p. (obsd.)	B. P. N. (obsd.)
1 1-Chloropentane	4.0 + 11 + 7.5 = 22.5	106.7	108.35	22.67
2 2-Chloropentane	4.0 + 11 + 6.5 = 21.5	96.9	96.7	21.48
3 3-Chloropentane	4.0 + 11 + 6.5 = 21.5	96.9	97.3	21.54
4 1-Chloro-2-methylbutane	3.2 + 8 + 3.05 + 7.5 = 21.75	99.4	98.3	21.64
5 2-Chloro-2-methylbutane	3.2 + 8 + 3.05 + 6.0 = 20.25	84.3	86.0	20.41
6 3-Chloro-2-methylbutane	3.2 + 8 + 3.05 + 6.5 = 20.75	89.4	91.0	20.91
7 4-Chloro-2-methylbutane	3.2 + 8 + 3.05 + 7.5 = 21.75	99.4	99.6	21.77
8 1-Chloro-2,2-dimethylpropane	2.4 + 5 + 6.10 + 7.5 = 21.0	92.0	84.4	20.26

calcs. This will be found of greatest value in the determination of the structure of hydrocarbons which have no characteristic group.

The data given in Table IV may be used in the following way to determine the nature of the hydrocarbon radical. Taking the observed boiling point of the first compound of 108.35° a B. P. N. (observed) of 22.67 is obtained. Knowing that the compound has a molecular formula of C<sub>5</sub>H<sub>11</sub>Cl we may calculate the B. P. N. for the normal chloride, which always has the greatest B. P. N. by at least 0.75 unit. The calculated B. P. N. is 22.50, which tells us at once that the chloride boiling at 108.35° is *n*-pentyl chloride. The second compound boiling at 96.7° has a B. P. N. of 21.48, which is very nearly one unit less than the normal chloride, indicating that the compound is a secondary chloride with a straight chain. However, a side chain methyl group would lower the B. P. N. by 0.75 unit giving a B. P. N. of 21.75 which might be confused with the secondary chlorides when the boiling points were not carefully obtained. This difficulty is readily cleared up by determining whether compound 2 is a primary or secondary chloride. If it is shown to be a secondary chloride then it must be either 2- or 3-chloropentane and cannot have the branched chain structure. Compound 3 will, of course, yield the same results as 2. The fourth compound is a primary chloride and subtracting the value of the primary chlorine (7.5) from the observed B. P. N. of 21.64 there are 14.14 units to be attributed to the hydrocarbon radical. The normal pentyl chain has a value of 15.0, which indicates that compound 4 has a side chain methyl group which lowers the B. P. N. by 0.75 to the calculated value of 14.25. Again, there are two possible structures which satisfy these conditions, *i. e.*, 1-chloro-2-methylbutane and 4-chloro-2-methylbutane, compounds 4 and 7 in Table IV.

The fifth compound is a tertiary chloride and, subtracting 6.0 from the observed B. P. N. of

20.41, the boiling point number of the alkyl radical is found to be 14.41. This value, being approximately 0.75 unit less than the normal pentyl radical, indicates the presence of a branched chain methyl group and only 2-chloro-2-methylbutane fulfils the conditions. However, if the carbon chain were longer, it would not be possible to locate the particular carbon atom to which both the chlorine and methyl were attached. The sixth compound is a secondary chloride and the b. p. n. of the alkyl radical is again 14.41 and a derivative of isopentane. The only secondary chlorine derivative of isopentane is 3-chloro-2-methylbutane. The eighth compound is a primary chloride and the b. p. n. of the alkyl group 12.76. This value indicates that there are more than one branched chain methyl groups, in fact the depression of 2.24 units indicates the presence of three. However, that is impossible with five carbon atoms and using the rule that the 2,2-dimethyl derivatives have low boiling points, the compound may be identified as neopentyl chloride.

The b. p. n. for the various oxygen containing groups in aliphatic compounds are listed in Table II. The introduction of alkyl groups about the characteristic group lowers the b. p. n. more or less depending upon the group. The hydroxyl is affected the most, the depression being 2.0 units per alkyl group and the ketones the least where 0.5 is the observed value. The effect is probably due to the steric effect of the alkyl groups. In spite of the well-known irregularity of the alcohols, the maximum deviation from the calculated B. P. N., out of 53 alcohols examined, was 2.71 with 4-decanol while at least half of the alcohols showed a deviation of less than 1.0. The ethers behaved more regularly: the greatest variation observed being 0.72 with diisobutyl ether, while more than half deviated less than 0.2 from the calculated. Decanal, among the aldehydes, gave the greatest deviation with a value 1.31 too low. The majority of aldehydes showed a deviation of

less than 0.6. Among the ketones 2-pentadecanone was too low by 1.9 while half of them deviated by 0.4 or less. The B. P. N. of decanoic acid was found to be farthest from the calculated and was 1.57 while half of the acids examined had deviations less than 0.4 unit. Among the esters methyl caprate was too low by 2.28 and half deviated by as much as 0.4 unit.

The amines, cyanides, and isocyanides have been studied among the aliphatic nitrogen compounds. The b. p. n.'s for the various substitution products containing these characteristic groups may also be found in Table II. Using those values satisfactory results are obtained with the exception of tri-*n*-heptylamine for which a boiling point about 20° too low has been reported. This seems entirely out of line with the other tertiary amines and further investigation may show that a value nearer 350° is correct. The amine that gave the next widest variation from the calculated was di-( $\alpha$ -methylheptyl)-amine with 2.32. It also is high boiling and its boiling point may have been determined incorrectly. With at least half of the amines the deviation amounts to less than 0.4 unit. Among the alkyl cyanides decane nitrile gave the greatest variation of 1.42, while over half of them deviated less than 0.3. Out of ten isocyanides

ethyl isocyanide deviated the most with 0.94 while half deviated 0.6 or less.

Other groups of compounds are being studied in the same way and a general survey of the field has been contemplated. The author will welcome data, suggestions, and criticism in the hope that the new method will become a particularly useful tool in organic chemistry and that many new relationships affecting the behavior of compounds will be the result. In developing the method the author is especially indebted to the late Professor E. P. Kohler and to Professors L. Pauling and H. Gilman for many valuable suggestions and encouragement.

### Summary

A method has been devised for correlating the structure of organic compounds with their boiling point. Boiling point numbers for a variety of atoms, groups, and molecules have been obtained and the accuracy discussed. Methods for calculating the boiling point of a compound from its structure and the structure from the boiling point have been outlined. The combined effect of several groups in the molecule upon the boiling point has been discussed.

SALT LAKE CITY, UTAH

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY AND FROM THE DEPARTMENT OF PEDIATRICS, HARVARD MEDICAL SCHOOL]

## The Viscosities of Solutions of the Proteins of Horse Serum<sup>1</sup>

BY KATHLEEN R. FAHEY AND ARDA ALDEN GREEN

The viscosity of solutions of proteins is known to vary widely with the character of these solutes. Some, in sufficiently dilute solution, obey approximately the classical Einstein law relating viscosity and concentration. Thus Loeb,<sup>2</sup> in studying egg albumin, observed agreement with the Einstein equation; and Daniel and Cohn<sup>3</sup> noted that "the viscosity of such a protein as egg albumin is not very different from that of glycine when both solutes occupy the same volume fraction of solution. . . . Hemoglobin and serum albumin, whose molecules—according to Svedberg—are larger and not quite spherical, are, however, more viscous than demanded by the coefficient of Ein-

stein's equation. None the less, hemoglobin like egg albumin obeys Poiseuille's law relating viscosity to pressure. A great many protein molecules are, however, highly asymmetrical in shape, and give rise both to anomalous viscosity and to double refraction of flow, in this respect resembling the long chain polymers studied by Staudinger and his collaborators."

The serum protein fractions as then separable were studied carefully by Harriette Chick<sup>4</sup> twenty-five years ago. She investigated their viscosities as affected by temperature and by concentrations of protein, salt and hydrogen ions. She reported, "In all cases, increase in protein concentration is accompanied by a disproportionately great in-

(1) This study was supported in part by a grant from the Commonwealth Fund of New York.

(2) Loeb, *J. Gen. Physiol.*, **4**, 73 (1921-1922).

(3) Daniel and Cohn, *This Journal*, **58**, 415 (1936).

(4) H. Chick, *Biochem. J.*, **8**, 261 (1914); H. Chick and E. Lubrzynska, *ibid.*, **8**, 59 (1914).