

## Correlation between Topological Features & Critical Constants of Alkanes, Aliphatic Monoalcohols & Alkylbenzenes

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Critical temperatures, critical pressures and critical volumes of 49 alkanes, 13 aliphatic monoalcohols and 21 alkylbenzenes have been correlated with their topological features quantified in terms of connectivity indices. The calculated values have been compared with the experimental values and the values estimated by other methods.

Critical constants,  $T_c$ ,  $P_c$  and  $V_c$  are generally difficult to measure experimentally but these quantities are important in determining the phase conditions of a substance in reactors and mass transfer equipments. Therefore, development of methods for estimating realistic values of critical properties is quite useful.

Spencer and Daubert<sup>1</sup> have evaluated various methods<sup>2-5</sup> for the estimation of critical constants and found that the method of Nokay<sup>6</sup>, giving an average error of <0.5%, was the best for estimating critical temperature ( $T_c$ ). The methods of Lydersen<sup>7</sup> and Forman and Thodos<sup>8</sup> were recommended for the estimation of critical pressure ( $P_c$ ) with an average error of 3-4%. For a series of homologous compounds the critical volumes ( $V_c$ ) were best estimated, with an average deviation of 2%, by the method of Reidel<sup>9</sup>.

The present paper attempts to correlate critical properties of alkanes, aliphatic monoalcohols and alkylbenzenes with their topological features quantitated in terms of connectivity indices<sup>10</sup> of different orders and types.

### Method

For calculation of the connectivity indices associated with a molecule, numerical values ( $\delta^0$ ) are assigned to each vertex of the hydrogen suppressed graph (HSG) representing topology of the non-hydrogen atoms of the molecule<sup>11</sup>. A connectivity index,  ${}^m\chi_t$ , is then defined as the algebraic sum of contributions  $C_i$  of all the subgraphs,  ${}^m g_i$ , of order  $m$  and type  $t$ ;  $m$  and  $t$  refer to the number and arrangements, respectively, of the vertices involved in the contributing subgraphs. The contribution of each subgraph is computed from Eq. (1).

$$C_i = \prod_{j=1}^{m+1} (\delta_j^0)^{-1/2} \quad \dots(1)$$

In the simplest version,  $\delta^0$  is taken to be  $\delta^v$ , which is equal to the number of edges converging at a vertex, and the resulting indices are termed simple connectivity indices ( ${}^m\chi^s$ ). However, for quantification of structural features like heterocity, cyclisation and bond multiplicity,  $\delta^v$  values are used for  $\delta^0$ . For first row atoms  $\delta^v$  is equal<sup>12</sup> to the difference between valence shell electrons of the atom and the hydrogen suppressed at that vertex<sup>13,14</sup>. The indices thus obtained are called valence connectivity indices ( ${}^m\chi^v$ ).

For 2,3-dimethylhexane, for instance, the HSG and  $\delta^v$  values assigned to different vertices are given in Fig. 1. The calculation of various  ${}^m\chi_t^v$  indices (for all possible types (1-12) up to fifth order) associated with this molecule is exemplified in Table 1.

### Computations

#### Connectivity indices

The visual perception and counting of contributing subgraphs becomes difficult in case of higher order and branched type<sup>14</sup> connectivity indices. A FORTRAN program KNKTVT† which requires only the connection matrix as the input was developed and used in the present calculations. The program computes all the path connectivity terms upto highest order possible

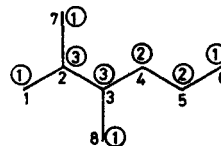
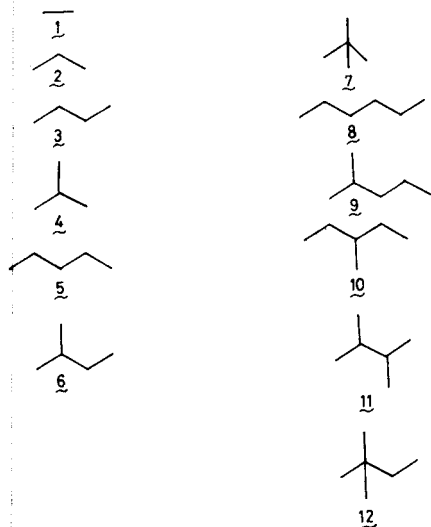


Fig. 1—Hydrogen-suppressed graph, numbering of vertices and  $\delta^v$  values (encircled) for 2,3-dimethylhexane

† Unpublished work.


 Table 1—Various  $m\chi_i^s$  Indices Possible in 2,3-Dimethylhexane upto 5th Order

Representative subgraph	$m_g$	$m$	$r^s$	Value
1	7	1		3.68073
2	8	2		3.00997
3	7	3		1.88208
4	2	3	1	0.56903
5	4	4		0.78867
6	5	4	1	1.20710
7	0	4	11	—
8	2	5		0.33333
9	2	5	1	0.33333
10	1	5	2	0.16666
11	1	5	12	0.23570
12	0	5	11	—

 (a) See ref. 14 for rational nomenclature of  $\chi$ -indices

in an HSG and all the branched connectivity indices upto 7th order.

### Regression analysis

Following the stepwise procedure of Dixon<sup>15</sup> a computer program STPRGR was developed and used. The program had provision for deletion of a once-included variable at a later step depending upon a pre-defined threshold partial  $F$ -value.

All the values of critical constants, were taken from literature<sup>16</sup>. The set of independent variables included nine simple connectivity indices, viz.  ${}^0\chi$ ,  ${}^1\chi$ ,  ${}^2\chi$ ,  ${}^3\chi$ ,  ${}^3\chi_1$ ,  ${}^4\chi$ ,  ${}^4\chi_1$ ,  ${}^{1/0}\chi$ ,  ${}^{1/1}\chi$  for alkanes. For alcohols and alkylbenzenes corresponding valence connectivity indices were used. The regression analysis was terminated after inclusion of three variables. During the present work the intercorrelation between the included variables was not considered.

## Results and Discussion

### Alkanes

Limiting the procedure of stepwise regression analysis upto three steps, the three-variable correlations (3-4) were obtained for critical temperature, critical pressure and critical volume, respectively, for a set of 49 alkanes ranging from  $C_4$  to  $C_{20}$ .

$$T_c/K = 24.433 {}^0\chi - \frac{348.782}{{}^1\chi} - 11.017 {}^2\chi + 531.913$$

$$r = 0.998; s = 6.03; F_{3,45} = 3215 (p < 0.005) \quad \dots(2)$$

$$P_c/\text{atm} = -2.747 {}^1\chi + \frac{74.661}{{}^0\chi} + 2.821 {}^3\chi + 19.932$$

$$r = 0.993; s = 0.79; F_{3,45} = 1001 (p < 0.005) \quad \dots(3)$$

$$V_c/\text{cm}^3 \text{ mol}^{-1} = 162.834 {}^1\chi + 57.823 {}^2\chi - 61.764 {}^0\chi + 95.096$$

$$r = 0.999; s = 11.49; F_{3,45} = 6232 (p < 0.005) \quad \dots(4)$$

The average predicted deviation is less than 1%, 3% and 1.5%, respectively, for  $T_c$ ,  $P_c$  and  $V_c$ . The predictions are better than those obtained by the group contribution method of Lydersen<sup>16</sup>. It can be argued that the deviation of 1% in  $T_c$  is almost double the deviation obtained by Nokay's<sup>1,6</sup> method. The present approach, however, does not involve any series-specific constants or other physicochemical parameters.

The unitless connectivity indices can be easily calculated from the hydrogen-suppressed topology of a molecule. For  $P_c$  and  $V_c$  the present results are comparable to the best ones available.

The values calculated from these equations are compared with experimental values in Table 2.

### Alkylbenzenes

For  $T_c$ ,  $P_c$  and  $V_c$  of a series of 21 alkylbenzenes the two-variable correlations did not show any significant statistical improvement on inclusion of a third variable. The two-variable equations obtained are:

$$T_c/K = 50.454 {}^3\chi^r - \frac{181.759}{{}^1\chi^r} + 619.830$$

$$r = 0.979; s = 8.49; F_{2,18} = 212 (p < 0.005) \quad \dots(5)$$

$$P_c/\text{atm} = \frac{32.848}{{}^1\chi^r} + \frac{90.229}{{}^0\chi^r} + 6.631$$

$$r = 0.991; s = 0.75; F_{2,18} = 510 (p < 0.005) \quad \dots(6)$$

$$V_c/\text{cm}^3 \text{ mol}^{-1} = 81.626 {}^1\chi^r + 21.638 {}^0\chi^r + 26.807$$

$$r = 0.998; s = 5.17; F_{2,18} = 1923 (p < 0.005) \quad \dots(7)$$

Table 2—Observed and Calculated Critical Constants of Alkanes

Compound	$T_c/K$		$P_c/\text{atm.}$		$V_c/\text{cm}^3\text{mol}^{-1}$	
	Obs	Calc (Eq. 2)	Obs	Calc (Eq. 3)	Obs	Calc (Eq. 4)
<i>n</i> -Butane	425.2	422.1	37.5	38.0	255	254
2-Methylpropane	408.1	398.9	36.0	36.0	263	256
<i>n</i> -Pentane	469.5	473.2	33.3	33.4	311	312
2-Methylbutane	460.4	463.1	32.9	33.4	308	304
2,2-Dimethylpropane	433.8	434.4	31.6	31.0	303	316
<i>n</i> -Hexane	507.3	511.4	29.9	30.1	368	370
2-Methylpentane	496.5	503.9	30.0	29.7	367	364
3-Methylpentane	504.7	508.5	30.8	31.1	367	355
2,2-Dimethylbutane	488.7	490.8	30.7	30.2	359	359
2,3-Dimethylbutane	499.9	498.5	30.9	30.9	358	351
<i>n</i> -Heptane	540.3	542.3	27.0	27.5	426	428
2-Methylhexane	530.3	536.6	27.2	27.3	428	422
3-Methylhexane	535.6	540.4	28.1	28.1	418	415
3-Ethylpentane	540.8	543.9	28.6	28.7	416	409
2,2-Dimethylpentane	520.9	526.0	28.4	27.0	404	420
2,3-Dimethylpentane	537.8	536.5	29.2	29.0	405	403
2,4-Dimethylpentane	520.3	530.3	27.4	26.7	420	417
3,3-Dimethylpentane	536	533	30	29.	411	404
2,2,3-Trimethylbutane	531.5	523.1	29.8	29.0	394	403
<i>n</i> -Octane	568.6	568.7	24.6	25.3	486	486
2-Methylheptane	559.6	564.1	24.8	25.1	488	480
3-Methylheptane	565	568	25.6	26.1	478	473
4-Methylheptane	563	567	25.6	25.5	476	475
3-Ethylhexane	567	571	26.4	26.3	466	469
2,2-Dimethylhexane	552	555	25.6	25.0	466	478
2,3-Dimethylhexane	566	565	26.6	26.5	461	463
2,4-Dimethylhexane	555	563	25.8	25.7	466	468
2,5-Dimethylhexane	552	559	24.6	25.1	478	474
3,3-Dimethylhexane	564	561	27.2	26.6	450	465
3,4-Dimethylhexane	571	568	27.4	27.5	452	455
2-Methyl-3-ethylpentane	568	568	27.4	26.7	450	458
3-Methyl-3-ethylpentane	578	567	28.9	28.3	435	452
2,2,3-Trimethylpentane	567	557	28.2	27.3	437	455
2,2,4-Trimethylpentane	543.6	550	25.4	24.4	482	473
2,3,3-Trimethylpentane	576	560	29.0	28.3	433	449
2,3,4-Trimethylpentane	568	561	27.6	27.2	477	451
2,2,3,3-Tetramethylbutane	544	546	24.5	28.0	480	452
<i>n</i> -Nonane	594.6	592	22.5	23.4	543	545
<i>n</i> -Decane	617.6	614	20.8	21.7	602	603
<i>n</i> -Undecane	640	634	19.2	20.2	660	661
<i>n</i> -Dodecane	659	652	17.9	18.9	718	719
<i>n</i> -Tridecane	677	670	17	18	780	777
<i>n</i> -Tetradecane	694	688	16	16	830	836
<i>n</i> -Pentadecane	710	704	15	15	890	894
<i>n</i> -Hexadecane	717	721	14	14	950	952
<i>n</i> -Heptadecane	735	737	13	13	1000	1010
<i>n</i> -Octadecane	756	753	13	12	1100	1068
<i>n</i> -Nonadecane	760	768	12	11	1100	1127
<i>n</i> -Eicosane	775	783	11	10	1200	1185

Equations (5) and (6) predict  $P_c$  and  $V_c$  for alkylbenzenes more accurately than the corresponding Eqs (3) and (4) for alkanes. The predictions are also better than or comparable to the best estimated values. The correlation with  $T_c$  is not as satisfactory. It has

been reported<sup>17</sup> that for the alkyl benzenes the higher order connectivity indices are important for correlations with their physicochemical properties. May be here also higher order connectivity indices correlate better. We have limited the independent

Table 3—Observed and Calculated Critical Constants of Alkylbenzenes

Compound	T <sub>c</sub> /K		P <sub>c</sub> /atm.		V <sub>c</sub> /cm <sup>3</sup> mol <sup>-1</sup>	
	Obs	Calc (Eq. 5)	Obs	Calc (Eq. 6)	Obs	Calc (Eq. 7)
Benzene	562.1	562.6	48.6	49.1	260	265
Methylbenzene	592.0	591.9	41.6	40.8	316	319
1,4-Dimethylbenzene	618.8	616.9	33.9	35.3	378	372
1,3-Dimethylbenzene	616.8	614.6	34.7	35.3	376	372
1,2-Dimethylbenzene	631.6	627.5	35.7	35.2	369	372
Ethylbenzene	617.1	621.8	36.9	35.4	374	380
1,3,5-Trimethylbenzene	637.3	632.5	32.	31	430	425
1,2,4-Trimethylbenzene	649.0	647.6	32	31	430	426
1,2,3-Trimethylbenzene	664.5	658.4	31	31	430	426
Isopropylbenzene	635.9	639.6	31.2	31.6	440	430
4-Ethyl-1-methylbenzene	636.2	643.2	31	31	430	433
3-Ethyl-1-methylbenzene	636.2	641.3	31	31	430	433
2-Ethyl-1-methylbenzene	653.2	649.0	31	31	430	434
<i>n</i> -Propylbenzene	638.4	637.2	31.2	31.7	440	436
1,2,3,5-Tetramethylbenzene	662.2	674.6	28.4	28.2	481	480
1,2,4,5-Tetramethylbenzene	676	677	28.6	28.2	481	480
<i>n</i> -Butylbenzene	661	658	28.4	28.8	498	492
1-Methyl-4-isopropylbenzene	658.7	659.5	27.7	28.5	476	483
Isobutylbenzene	657.9	647.4	30.1	28.7	477	484
Pentamethylbenzene	691.2	713.6	25.8	25.9	532	534
Hexamethylbenzene	767.2	749.3	23.5	24.0	586	589

Table 4—Observed and Calculated Critical Constants of Aliphatic Monoalcohols

Compound	T <sub>c</sub> /K		P <sub>c</sub> /atm.		V <sub>c</sub> /cm <sup>3</sup> mol <sup>-1</sup>	
	Obs	Calc (Eq. 8)	Obs	Calc (Eq. 9)	Obs	Calc (Eq. 10)
Methanol	513.2	513.5	78.5	79.5	118	116
Ethanol	516.3	513.5	63.0	60.6	167	170
2-Propanol	508.2	513.5	47.0	48.2	220.4	221.3
1-Propanol	536.7	532.0	51.0	50.1	218.2	220.0
1-Butanol	563.0	559.1	43.6	43.0	274.6	274.7
2-Methylpropanol	547.7	532.4	42.2	42.4	272.2	271.0
2-Methyl-2-propanol	506.2	513.5	39.2	40.0	274.5	274.8
2-Butanol	536.0	551.1	41.4	42.4	269.0	268.1
2-Methyl-2-butanol	544.9	543.5	38.3	38.1	319	319
1-Pentanol	582.9	583.8	37.4	37.7	333	331
1-Heptanol	638.5	632.3	29.4	29.7	443	442
1-Octanol	658.7	656.5	26.5	26.4	498	497
2-Octanol	637.3	645.0	27.0	26.3	494	496

variables to  ${}^4\chi_1$  only in this study. The agreement between observed and calculated values for individual cases is satisfactory (Table 3).

#### Aliphatic monoalcohols

For a series of 13 aliphatic alcohols, Eqs (8) to (10), respectively, were obtained for T<sub>c</sub>, P<sub>c</sub> and V<sub>c</sub>. The level of significance of each correlation is given in the parentheses.

$$T_c/K = 19.623 {}^4\chi^v + 83.068 {}^3\chi^v - 62.503 {}^4\chi^v + 513.464$$

$$r = 0.990, s = 8.78; F_{3,9} = 142 (p < 0.005) \quad \dots(8)$$

$$P_c/\text{atm} = \frac{75.644}{{}^0\chi^v} - 2.554 {}^0\chi^v + 4.164 {}^4\chi^v + 30.942$$

$$r = 0.998, s = 1.17; F_{3,9} = 615 (p < 0.005) \quad \dots(9)$$

$$V_c/\text{cm}^3 \text{ mol}^{-1} = 78.706 {}^1\chi^v + 26.950 {}^2\chi^v + 36.914 {}^4\chi^v + 80.621$$

$$r = 0.9999, s = 1.79; F_{3,9} = 17246 (p < 0.005) \quad \dots(10)$$

The three-variable equation (Eq. 10) in terms of  ${}^1\chi^v$ ,  ${}^2\chi^v$  and  ${}^4\chi^v$ , predicts V<sub>c</sub> very accurately. The average error is < 0.6% which is far better than 2.7% reported by Vetere<sup>18</sup>. The predicted maximum absolute deviation is ~2.5 cm<sup>3</sup> mol<sup>-1</sup>. To the best of our knowledge literature data to compare the quality of

correlations (9) and (8) are not available. The values of  $T_c$ ,  $P_c$  and  $V_c$  calculated from these equations are compared with experimental values in Table 4.

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