Quantitative relationship of diamagnetic susceptibility with molecular connectivity in hydrocarbons

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The diamagnetic susceptibility of hydrocarbons is found to be parallel to Kier's first order valence molecular connectivity index $^1X^v$. The regression analysis reveals a significant linear correlation between diamagnetic susceptibility x_M and $^1X^v$.

Kier and Hall have shown that the molecular connectivity index $^1X^v$ can be correlated with several physicochemical and biological properties of the molecules. The molecular connectivity has several versions. They are calculated from a hydrogen suppressed graph of molecules. The simplest as well as the most extended version, the first-order valence connectivity[1-3], $^1X^v$ is given by Eq. (1),

$$^1X^v = \Sigma \, (\delta_i^v \delta_j^v)^{-1/2} \qquad \ldots (1)$$

where the sum is overall connections or edges in the hydrogen suppressed graph. δ_i^v and δ_j^v are the numbers assigned to each atom reflecting the number of atoms adjacent or connected to atoms i and j, which are formally bonded.

The atom connectivity term δ_i^v is defined as,

$$\delta_i^v = \frac{Z_i^v - h_i}{Z - Z_i^v - 1} \qquad \ldots (2)$$

Z_i^v = no. of valence electrons of atom i, Z = atomic no. of atom i and h_i = no. of hydrogen atoms attached to atom i.

Experimental

The diamagnetic susceptibility depends upon the specific orientation of atoms in a molecule and the electronic environment generated. It is generally known[4] that the diamagnetic susceptibility of many organic compounds may be predicted theoretically by assuming that they are more or less additive. It has been shown for various homologous series of organic compounds that the molar susceptibilities of the compounds in one such series is a linear function of the number of methylene groups. Among the various semiempirical

theories for the diamagnetic susceptibilities of organic molecules, the best theory was proposed by Pascal[5]. According to him, the molar susceptibility of an organic compound is represented by Eq. (3),

$$x_M = \Sigma \, n_A \, x_A + \Sigma \, \alpha \qquad \ldots (3)$$

where n_A is the number of atoms of susceptibility x_A in the molecule and α is a correction depending on the nature of the bonds between the atoms. What it amounts to is that the molar susceptibility x_M of an organic molecule is written as a sum of atomic contributions. The diamagnetic susceptibility and the molecular connectivity both are more or less dependent on their atomic contributions and the nature of the bonds between the atoms. Therefore, it becomes obvious that the diamagnetic susceptibility must be in some way related with molecular connectivity.

Table 1 — Diamagnetic susceptibility and $^1X^v$ values of hydrocarbons

Compound	$^1X^v$	x_M Exp.	x_M Calc.	Ref.
Methane	0.00	12.40	17.05	5
		17.40*		11
Propane	1.40	38.60	47.84	6
		39.60*		5
		40.50		11
Butane	1.90	50.30	58.84	5
		57.40*		11
2-Methylpropane	1.70	50.50	54.44	5
		51.70		6
		56.30*		11
Pentane	2.40	61.50	69.84	11
		63.30*		11
2-Methylbutane	2.24	63.00*	66.32	11
		64.40		4
2,2-Dimethylpropane	2.00	63.00*	61.04	6
		63.10		11
Hexane	2.90	73.63	80.84	12
		74.30*		4,7,8
2-Methylpentane	2.74	75.26	77.32	4
3-Methylpentane	2.77	75.52	77.98	4
2,2-Dimethylbutane	2.55	76.24	73.14	4
2,3-Dimethylbutane	2.61	76.22	74.46	4
Heptane	3.41	85.24	92.06	4,9
		85.83*		12
2-Methylhexane	3.04	86.24	83.92	4,9
3-Methylhexane	3.27		88.98	
3-Ethylpentane	3.30		89.64	
2,2-Dimethylpentane	3.05	86.97	84.14	4,9
2,3-Dimethylpentane	3.14	87.51	86.12	4,9
2,4-Dimethylpentane	3.08	87.48	84.80	4,9
3,3-Dimethylpentane	3.10		85.24	
2,2,3-Trimethylbutane	2.93	88.36	81.50	4,9
Octane	3.90	96.63	102.34	4,9
		96.93*		12

Table 1 — Diamagnetic susceptibility and $^1X^v$ values of hydrocarbons — Contd

Compound	$^1X^v$	x_M		Ref.
		Exp	Calc.	
3-Methylheptane	3.77	97.99	99.98	4,9
4-Methylheptane	3.77		99.98	
3-Ethylhexane	3.80		100.64	
2,3-Dimethylhexane	3.64	98.77	97.12	4,9
2,4-Dimethylhexane	3.61		96.46	
2,5-Dimethylhexane	3.58	98.15	95.80	4,9
3,3-Dimethylhexane	3.60		96.24	
3,4-Dimethylhexane	3.67	99.06	97.78	4
2,2,3-Trimethylpentane	3.46	99.86	93.16	4,9
2,2,4-Trimethylpentane	3.39	98.34	91.62	4,9
2,3,3-Trimethylpentane	3.48		93.60	
2-Methyl-3-ethylpentane	3.67		97.78	
3-Methyl-3-ethylpentane	3.45	99.90	92.94	9
2,2,3,3-Tetramethylbutane	3.25		88.54	
Nonane	4.40	108.10	113.84	4,9,10
4-Methyloctane	4.18	109.60	108.99	10
Decane	4.90	119.51	124.84	4,10
4-Methylnonane	4.80	121.40	122.86	10
2,6-Dimethyloctane	4.66	122.50	119.56	10
Undecane	5.40	131.80	135.84	10
2,4-Dimethylnonane	5.16	134.70	130.56	10
3,4-Dimethylnonane	5.21	134.70	131.66	10
3,5-Dimethylnonane	5.21	134.50	131.66	10
Dodecane	5.90		146.83	
Tridecane	6.40		157.87	
Tetradecane	6.90		168.83	
Pentadecane	7.40		179.82	
Hexadecane	7.90	187.63	190.83	4

* The experimental values (if more than one) are the ones that are used for regression analysis values.

The resulting theoretical and experimental values of diamagnetic susceptibilities are expressed in term of 10^{-6} cgs units on $4\pi \times 10^{-9}$ SI units.

Results and discussion

The molecular connectivity $^1X^v$ values are calculated for some hydrocarbons using Eqs (1) and (2) and are listed in Table 1. The diamagnetic susceptibility values are taken from literature[6-14].

The level of significance of this linear correlation between diamagnetic susceptibility (x_M) and $^1X^v$ is shown by Eq. (4),

$$x_M = 21.997 \,^1X^v \,(\pm 0.513) + 17.047 \qquad \ldots (4)$$

$$n = 36, r = 0.991, s = 4.289, F(1,34) = 1836.983.$$

In regression analysis, the statistical parameters, n = the number of data points, r = the correlation coefficient, s = the standard deviation and F = the ratio between the variance of calculated and observed data, exhibits very high level of significance of the correlations.

The diamagnetic susceptibility values reproduced from Eq. (4) are found to be in good agreement with the experimental ones. These correlations can be used to predict the diamagnetic susceptibilities of any hydrocarbon by simply calculating $^1X^v$.

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