# A NOVEL TOPOLOGICAL INDEX AND ITS CORRELATION WITH THE NMR CHEMICAL SHIFTS OF VARIOUS COMPOUNDS

Lin-Feng Li, Xiao-Zeng You* and Tian-Ming Yao

Coordination Chemistry Institute and the State Key Laboratory of
Coordination Chemistry, Nanjing University, Nanjing 210 008, P. R. China

## ABSTRACT:

Based on the donor-acceptor (D-A) interaction of the frontier orbitals, a novel topological (graph-theoretical) index $H_l$ was proposed through a four-energy-level interaction model. Topological indices of various compounds containing elements of IIIA, IVA, VA, and VIA groups and the transition metals in the periodic table were calculated. It has been found that there are good correlations between the $H_l$'s and their corresponding experimental nuclear magnetic resonance (NMR) chemical shifts for the studied compounds. Brief discussion was made on the topological index proposed here.

Keywords: Topological index, NMR chemical shifts, main group elements

## INTRODUCTION:

It is well known that the molecular properties are largely dependent of the associated structure. In some cases, as a good first-order approximation, some molecular properties may rely mainly upon the molecular shape, constitutions and the connectivities of its atoms, which are so-called the topological structure. In order to quantitatively analyze such relations between them, a kind of numerical descriptor of the molecular graph, i.e., the topological (graph-theoretical) index, is necessary to be employed. Since the early proposal of Wiener index [1] in 1947 and its successful application in correlation with various physicochemical properties of a series of alkanes, a lot of topological indices [2-8] have been introduced to represent one or two characters of a graph. Among them, Randic connectivity index [4] and its derivatives [9,10] have been most extensively used. However, almost all of the above indices are preliminarily designed to characterize the graph deduced from the organic compounds, so the applications of them are somewhat limited.

Recently some extensions were made to the Randic index by explicitly introducing the electronic structure information, such as the Hückel resonance integral parameters [11], into a molecular graph to get so-called chromograph. Unfortunately, the utilities of these extensions are still confined to a certain set of compounds, because the parameters required in the calculation are not readily available. Quite a few of indices are available now for the investigation of inorganic compounds [12 13]. Therefore, a topological index $H_l$ based on the four-energy-level interaction level [14] was proposed as a new application of the chromograph in this field. This index is associated with the local edge invariants corresponding to edges symbolizing chemical bonds. It has been proved to be effective and efficient in the study of the Mössbauer isomer shifts of $SnX_nY_{4-n}$ (X, Y are halogens) [14], the enthalpies of formation for various compounds [15], and the diamagnetic susceptibilities of alkyl-IVA group organometallic halides [16].

In the present paper, this topological treatment was applied to investigate another interesting chemical property, i.e., the nuclear magnetic resonance (NMR) chemical shifts $\delta$ of various compounds containing elements of IIIA, IVA, VA, and VIA groups and the transition metals. This study has covered most of the magnetic resonance sensitive nuclei in the periodic table. The good correlation coefficient for the relation between $H_1$ and $\delta$ showed that the new topological index $H_1$ is also quite useful in the systematic study of NMR information.

## METHODS:

Lall *et al.* [11] and Xin *et al.* [17] once introduced a kind of index based on the vertex or edge weighted Randic index:

$$H=\left(\sum_i \frac{1}{e^{\Delta_i}\sqrt{p_i q_i}}\right)^2 \qquad (1)$$

where the summation runs over all edges in a molecular graph, $p_i$, $q_i$ are the degrees of the vertices which form the *i*th edge, $\Delta_i$ is a kind of physical parameter used to incorporate the electronic information. In Lall's treatment, $\Delta_i$ was taken as Hückel resonance parameter. While in Xin's treatment, eq 2 was adopted:

$$\Delta_i = I_i(1) - A_i(2) \qquad (2)$$

$I_i$ and $A_i$ are the experimental first-order ionization energy and the electron affinity of the atoms connected by the *i*th edge (see Table 1). Through the first-order series expansion of the exponential term in eq 1, it can be obtained that:

$$H_1 = \left(\sum_i h_i\right)^2 = \left(\sum_i \frac{1}{(1+\Delta_i)\sqrt{p_i q_i}}\right)^2 \qquad (3)$$

where $h_i$ is the contribution of the *i*th bond.

**Table 1** The first-order ionization energy (I) and electron affinity (A) of the adopted atoms in current work [a] (unit: KJ/mol)

| atom | I | A | atom | I | A |
|---|---|---|---|---|---|
| C | 1086.4 | 122.0 | N | 1402.3 | 6.754 |
| Si | 786.5 | 120.0 | P | 1011.8 | 74.0 |
| Ge | 762.2 | 116.0 | O | 1314.0 | 141.0 |
| Sn | 708.6 | 121.1 | S | 999.6 | 200.4 |
| Pb | 715.5 | 100.0 | F | 1681.0 | 332.0 |
| B | 800.6 | 23.0 | Cl | 1251.1 | 348.7 |
| Al | 577.6 | 44.0 | Br | 1139.9 | 324.5 |
| Ga | 578.8 | 36.0 | I | 1008.4 | 295.0 |
| In | 558.3 | 34.0 | Mo | 685.0 | 96.0 |
| Tl | 558.3 | 34.0 | Pt | 870.0 | 205.3 |
| H | 1312.0 | 72.9 | Nb | 664.0 | 86.161 |

[a] Ref.18

The above formulation may be explained in terms of a *two-energy-level* interaction model as illustrated in Scheme 1(a). In this kind of treatment, only the bonding between the highest occupied atomic orbital (HOAO) of atom **1** and the lowest unoccupied atomic orbital (LUAO) of atom **2** is considered. However, under the real chemical circumstance, the bonding of two atoms to form a bond (the edge in a molecular graph) involves at least four frontier orbitals: both HOAOs and LUAOs of atom **1** and **2**. From the chemical point of view, the new treatment includes the feed-back interaction of electrons, which may also be important in some cases. For example, for molecule $BF_3$, in addition to the formation of the partially charge transferred $\sigma$ bond between B and F, the lone pair of fluorine also feeds back to the vacant 2p orbital of boron to enhance the bonding [19]. Thus a new formula is given as follows to incorporate both kinds of interactions:

$$\Delta_i = \alpha[I_i(1) - A_i(2)] + (1-\alpha)[I_i(2) - A_i(1)] \qquad (4)$$

where α is the adjustable parameter to reflect the difference between the two kinds of interactions. The first term shows the electron transfer interaction from HOAO of atom **1** to LUAO of atom **2**, while the last term represents the feed-back interaction from HOAO of atom **2** to LUAO of atom **1**. This kind of interaction model, as illustrated in Scheme 1(b), was called *four-energy-level* interaction model. To avoid further empirical hypothesis in the evaluation of α, it is taken as 0.5 in all calculations, which means the weight of two kinds of interactions to form the edge in a graph is assumed as being equally important. Although such a postulate does not always hold (*vide infra*), the effectiveness of the assumption and the advantage of the model proposed here have been proved in previous investigations [14-16].

(a) (b)

**Scheme 1** (a) *two-energy-level* and (b) *four-energy-level* interaction models in the topological treatment.

## RESULTS AND DISCUSSION:

### *Correlation with the NMR shifts of group IVA elements.*

$^{13}C$ is one of the most extensively studied nucleus in NMR spectroscopy. The electronic structure and bonding of the carbon-contained compounds have been broadly investigated. A lot of interpretations and experimental data of the NMR shifts can now be found in the literature. Therefore it is possible to explore the applicability of the new topological index $H_1$ in this area. The $H_1$'s of halogen substituted methanes are shown in Table 2a). It can be seen that good linear relations with correlation coeffici-ents>0.9, were found between $H_1$'s and the $^{13}C$ NMR shifts of the mono-, di-, tri- and tetra-substituted methanes respectively. It is worthwhile to note that there is no overall linear relation for all these halogen substituted methanes. This may be due to the fact that the hydrogen-carbon bonding is quite different from those of halogen-carbon, because no lone pairs and thus no feed-back electrons are available for the hydrogen. If the overall correlations are needed, an adjustable α in eq 4 should be introduced.

**Table 2a)** $H_1$ and δ of $^{13}C$.

| Compds | $H_1(\times10^{-6})$ | $\delta_{exp}$[a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $CH_3F$ | 3.205 | 74.10 | 76.8 |
| $CH_3Cl$ | 3.592 | 23.80 | 19.2 |
| $CH_3Br$ | 3.692 | 8.90 | 4.32 |
| $CH_3I$ | 3.824 | −21.80 | −15.3 |
| $\delta=553.74+148.808\times10^6 H_1$ | | | R=−0.990 |
| $CH_2Cl_2$ | 3.909 | 52.85 | 59.5 |
| $CH_2ClBr$ | 4.013 | 38.75 | 36.1 |
| $CH_2Br_2$ | 4.118 | 20.30 | 12.3 |
| $CH_2I_2$ | 4.399 | −55.10 | −51.1 |
| $\delta=942.44-225.86\times10^6 H_1$ | | | R=−0.990 |
| $CHCl_3$ | 4.238 | 77.40 | 89.3 |
| $CHCl_2Br$ | 4.347 | 56.05 | 58.1 |
| $CHClBr_2$ | 4.456 | 33.25 | 27.0 |
| $CHBr_3$ | 4.567 | 11.05 | −4.7 |
| $CHI_3$ | 5.015 | −141.00 | −132.8 |
| $\delta=1301.34-285.98\times10^6 H_1$ | | | R=−0.991 |
| $CF_4$ | 2.959 | 69 [b] | 53.1 |
| $CF_3Cl$ | 3.331 | 33 [b] | 35.1 |
| $CF_2Cl_2$ | 3.726 | 8 [b] | 16.0 |
| $CFCl_3$ | 4.143 | 0 [b] | −4.1 |
| $CF_3Br$ | 3.427 | 21 [b] | 30.5 |
| $CF_2Br_2$ | 3.930 | −7 [b] | 6.0 |
| $CFBr_3$ | 4.468 | −7 [b] | −19.8 |
| $\delta=196.126-48.332\times10^6 H_1$ | | | R=−0.911 |

[a] Ref.20 [b] Ref.21.

The theory of $^{29}$Si chemical shifts is not as well-advanced as that of $^{13}$C. Early attempts to explain the data were mostly at a qualitative level [21]. It is known that the difference between Si and C is the availability of their d orbitals in the formation of a chemical bond. Then the feed-back donation of the lone pair electrons of the halogen to the 3d orbital of silicon (so called dπ-pπ bonding) may also be different from that of carbon. As a result, the coefficients of the regression equations to represent their correlations with the topological indices employed here are different. But the linear relation between their $H_1$'s and chemical shifts δ's can still be obtained for $SiX_nY_{4-n}$ (X,Y=Halogen, n=0-4) as depicted in Table 2b). This fact further qualifies the capability of our topological index in the study of NMR spectroscopy.

**Table 2b)** $H_1$ and δ of $^{29}$Si.

| Compds | $H_1(\times10^{-6})$ | $-\delta_{exp}$ $^a$(ppm) | $-\delta_{cal}$ (ppm) |
|---|---|---|---|
| $SiBrClI_2$ | 7.605 | 181.9 | 185.2 |
| $SiBrCl_2I$ | 7.133 | 98.9 | 101.3 |
| $SiBrCl_3$ | 6.675 | 34.3 | 19.9 |
| $SiBrI_3$ | 8.093 | 280.1 | 272.0 |
| $SiBr_2ClI$ | 7.333 | 122.8 | 136.9 |
| $SiBr_2Cl_2$ | 6.869 | 50.7 | 54.4 |
| $SiBr_2I_2$ | 7.812 | 212.3 | 222.1 |
| $SiBr_3Cl$ | 7.066 | 69.8 | 89.4 |
| $SiBr_3I$ | 7.537 | 149.5 | 173.1 |
| $SiBr_4$ | 7.266 | 92.7 | 124.9 |
| $SiClI_3$ | 7.882 | 245.9 | 234.5 |
| $SiCl_2I_2$ | 7.400 | 151.5 | 148.8 |
| $SiCl_3I$ | 6.935 | 75.4 | 66.1 |
| $SiCl_4$ | 6.484 | 20.0 | −14.05 |
| $SiI_4$ | 8.378 | 351.7 | 322.7 |
| $\delta=1166.90-177.79\times10^6 H_1$ | | | R=−0.981 |

[a] Ref.23.

**Table 2c)** $H_1$ and δ of $^{73}$Ge.

| Compds | $H_1(\times10^{-6})$ | $-\delta_{exp}$ $^a$(ppm) | $-\delta_{cal}$ (ppm) |
|---|---|---|---|
| $GeBrClI_2$ | 7.823 | 601 | 595.2 |
| $GeBrCl_2I$ | 7.331 | 316 | 309.0 |
| $GeBrCl_3$ | 6.854 | 47 | 31.6 |
| $GeBrI_3$ | 8.332 | 901 | 891.2 |
| $GeBr_2ClI$ | 7.540 | 407 | 430.6 |
| $GeBr_2Cl_2$ | 7.056 | 130 | 149.1 |
| $GeBr_2I_2$ | 8.039 | 708 | 720.8 |
| $GeBr_3Cl$ | 7.261 | 219 | 268.3 |
| $GeBr_3I$ | 7.752 | 513 | 553.9 |
| $GeBr_4$ | 7.469 | 312.1 | 389.3 |
| $GeClI_3$ | 8.112 | 808 | 763.3 |
| $GeCl_2I_2$ | 7.610 | 518 | 471.3 |
| $GeCl_3I$ | 7.124 | 213 | 188.7 |
| $GeCl_4$ | 6.655 | −30.9 | −84.1 |
| $GeI_4$ | 8.630 | 1080.7 | 1064.6 |
| $\delta=3953.81-581.49\times10^6 H_1$ | | | R=−0.993 |

[a] Ref.24.

**Table 2d)** $H_1$ and δ of $^{119}$Sn.

| Compds | $H_1(\times10^{-6})$ | $-\delta_{exp}$ $^a$(ppm) | $-\delta_{cal}$ (ppm) |
|---|---|---|---|
| $SnCl_4$ | 7.188 | 150 | 79.0 |
| $SnBr_4$ | 8.105 | 638 | 723.6 |
| $SnI_4$ | 9.424 | 1701 | 1650.7 |
| $SnCl_3Br$ | 7.412 | 263 | 236.5 |
| $SnCl_2Br_2$ | 7.639 | 385 | 396.0 |
| $SnClBr_3$ | 7.871 | 508 | 559.1 |
| $\delta=1166.90-177.79\times10^6 H_1$ | | | R=−0.981 |
| $MeSnCl_3$ | 5.440 | −6.3 | −42.5 |
| $MeSnBr_3$ | 6.037 | 170 | 253.9 |
| $MeSnI_3$ | 6.886 | 699.5 | 675.5 |
| $MeSnCl_2I$ | 5.903 | 202 | 187.4 |
| $MeSnClI_2$ | 6.385 | 436 | 426.8 |
| $\delta=2743.77-496.56\times10^6 H_1$ | | | R=−0.984 |

[a] Ref.21.

Because of technique difficulties, fewer data are available for $^{73}$Ge NMR spectroscopy. Naturally there is little theoretical work on the chemical shifts. Here the $H_1$'s and δ's of a series of compounds $GeX_nY_{4-n}$ (X,Y=Cl,Br,I; n=0-4) are listed in Table 2c). An excellent linear relation with the correlation coefficient 0.993 is existent between the topological index $H_1$ and $^{73}$Ge NMR chemical shifts, which shows that the newly proposed topological index $H_1$ on the basis of the *four-energy-level* interaction model are suitable in the electrotopological description of current kind of compounds.

As regards to $^{119}$Sn NMR, two sets of compounds $SnX_nY_{4-n}$ (n=0-4) and $MeSnX_nY_{3-n}$ (n=0-3; X,Y=Halogen) are studied here. Several qualitative rules of the shielding of tin in various compounds were obtained in the previous theoretical studies [21]. Each factor does not influence the shielding in an additive manner. However, when various factors of a molecule are combined together as a whole, it can be additive. In this way, the topological index $H_I$ is expected to correlate quite well with the chemical shifts of both sets of compounds (see Table 2d).

The good correlation is also demonstrated in Table 2e) between the indices $H_I$ and the chemical shifts of $^{207}Pb$ in compounds $Me_3PbX$ (X=halogen).

**Table 2e) $H_I$ and δ of $^{207}Pb$.**

| Compds | $H_I(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $Me_3PbCl$ | 2.579 | 432 | 444.1 |
| $Me_3PbBr$ | 2.710 | 367 | 346.0 |
| $Me_3PbI$ | 2.889 | 203 | 211.9 |
| $\delta=2382.73-751.73\times10^6 H_I$ | | | R=−0.988 |

[a] Ref.21.

*Correlation with the NMR shifts of groups IIIA elements.*

**Table 3a) $H_I$ and δ of $^{11}B$.**

| Compds | $H_I(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $BCl_3$ | 4.242 | 46.5 | 54.1 |
| $BBr_3$ | 4.717 | 38.7 | 31.5 |
| $BI_3$ | 5.383 | −7.9 | −0.2 |
| $BBrCl_2$ | 4.397 | 44.7 | 46.7 |
| $BICl_2$ | 4.607 | 36.1 | 36.7 |
| $BBr_2Cl$ | 4.556 | 42.3 | 39.2 |
| $BClI_2$ | 4.988 | 18.1 | 18.6 |
| $BClBrI$ | 4.769 | 31.6 | 29.0 |
| $BBr_2I$ | 4.934 | 26.3 | 21.2 |
| $BBrI_2$ | 5.156 | 11.0 | 10.6 |
| $\delta=255.954-47.584\times10^6 H_I$ | | | R=−0.959 |
| $Me_3NBF_3$ | 2.666 | 10.1 | 9.1 |
| $Me_3NBF_2Cl$ | 3.096 | 16.8 | 17.6 |
| $Me_3NBF_2Br$ | 3.211 | 20.2 | 19.9 |
| $Me_3NBF_2I$ | 3.367 | 23.7 | 22.9 |
| $Me_3NBFCl_2$ | 3.559 | 25.1 | 26.7 |
| $Me_3NBFClBr$ | 3.682 | 29.0 | 29.1 |
| $Me_3NBFClI$ | 3.849 | 31.0 | 32.4 |
| $Me_3NBFBr_2$ | 3.808 | 32.6 | 31.6 |
| $Me_3NBFBrI$ | 3.977 | 34.2 | 34.9 |
| $Me_3NBCl_3$ | 4.054 | 34.5 | 36.5 |
| $Me_3NBFI_2$ | 4.150 | 40.1 | 38.4 |
| $Me_3NBCl_2Br$ | 4.186 | 38.8 | 39.1 |
| $Me_3NBCl_2I$ | 4.363 | 44.2 | 42.6 |
| $Me_3NBClBr_2$ | 4.319 | 42.9 | 41.7 |
| $Me_3NBClBrI$ | 4.499 | 45.1 | 45.2 |
| $Me_3NBBr_3$ | 4.553 | 45.4 | 46.3 |
| $Me_3NBClI_2$ | 4.683 | 50.3 | 48.9 |
| $Me_3NBBr_2I$ | 4.638 | 47.8 | 47.9 |
| $Me_3NBBrI_2$ | 4.824 | 52.1 | 51.7 |
| $Me_3NBI_3$ | 5.014 | 54.2 | 55.4 |
| $\delta=-43.411+19.706\times10^6 H_I$ | | | R=−0.996 |

[a] for $BX_3$ in Ref.25; for $Me_3NBX_3$ in Ref.26.

**Table 3b) $H_I$ and δ of $^{27}Al$.**

| Compds | $H_I(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $[AlI_4]^-$ | 10.256 | −28.0 | −8.5 |
| $[AlI_3Cl]^-$ | 9.593 | 21.7 | 25.1 |
| $[AlI_2Cl_2]^-$ | 8.953 | 59.4 | 57.6 |
| $[AlBr_4]^-$ | 8.766 | 80.0 | 67.1 |
| $[AlICl_3]^-$ | 8.334 | 86.2 | 89.0 |
| $[AlCl_4]^-$ | 7.738 | 100.0 | 119.3 |
| $[AlBrCl_3]^-$ | 7.989 | 99.0 | 106.6 |
| $[AlBr_2Cl_2]^-$ | 8.244 | 93.0 | 93.6 |
| $[AlBr_3Cl]^-$ | 8.503 | 87.2 | 80.5 |
| $[AlIBrCl_2]^-$ | 8.595 | 79.0 | 75.8 |
| $[AlI_2BrCl]^-$ | 9.223 | 47.7 | 43.9 |
| $[AlI_2Br_2]^-$ | 9.497 | 37.0 | 30.0 |
| $[AlI_3Br]^-$ | 9.873 | 8.0 | 10.9 |
| $[AlIBr_3]^-$ | 9.128 | 60.6 | 48.7 |
| $[AlIBr_2Cl]^-$ | 8.859 | 69.3 | 62.4 |
| $\delta=512.129-50.766\times10^6 H_I$ | | | R=−0.967 |

[a] Ref.27.

**Table 3c) $H_I$ and δ of $^{71}Ga$.**

| Compds | $H_I(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $[GaCl_4]^-$ | 7.639 | 251 | 311.3 |
| $[GaCl_3Br]^-$ | 7.886 | 212 | 234.3 |
| $[GaBr_2Cl_2]^-$ | 8.136 | 168 | 156.3 |
| $[GaClBr_3]^-$ | 8.389 | 119 | 77.5 |
| $[GaBr_4]^-$ | 8.648 | 68 | −3.3 |
| $[GaI_4]^-$ | 10.107 | −500 | −458.1 |
| $\delta=2692.80-311.76\times10^6 H_I$ | | | R=−0.983 |

[a] Ref.28.

Atom in group III is a kind of electron-deficient one, where the existence of vacant p orbital will greatly affect its bonding with other atoms. For example, unlike other compounds in the series of $BX_nY_{3-n}$ (n=0-3) as listed in Table 3a), the predicted chemical shift of $BF_3$ is 131.1 ppm, which is largely deviated from the experimental value 10.0 ppm. This may be due to the difference between B-F and other boron-halogen bonds [19], which arises from the extent of the feed-back bonding of vacant p orbital in this system. Nevertheless, the feed-back pπ-pπ bonding in the boron halides can be greatly reduced while the adduct is formed [19]. As a consequence, the large deviation found previously in the case of $BF_3$ may be removed. In fact, it has been demonstrated by our results about the shifts of the boron halide adducts with ammonia. An excellent linear relation was obtained for the chemical shifts of the compounds including $Me_3NBF_3$, $Me_3NBF_2Cl$ and so on. Now the calculated δ's are in good agreement with the experimental ones (see Table 3a).

Other nuclei such as $^{27}Al$, $^{71}Ga$, $^{115}In$ and $^{205}Tl$ have also been investigated by NMR spectroscopy. As shown in Table 3b), 3c), 3d) and 3e), the chemical shifts of various compounds of them are also in good linear relations with the topological indices $H_1$'s.

*Correlation with the NMR shifts of group VA elements.*

For an atom in group VA, the number of valence electrons is greater than that of its valence orbitals. the bonding of them with other atoms may be quite different. As illustrated in Table 4, different but similar linear regression equation was obtained in correlation with the NMR shifts of various phosphorus compounds by means of the presently used topological index $H_1$. The fact certifies the wide suitability of the novel topological index.

*Correlation with the NMR shifts of group VIA elements.*

The presently studied topological index can be applied to investigate the NMR information of $^{17}O$, $^{77}Se$ and $^{125}Te$ as well. As shown in Table 5a), 5b) and 5c), good linear relations with correlation coefficients R=0.997, 0.928 and 0.954 respectively for $OPX_nY_{3-n}$ (n=0-3), SeOXY and $H_2TeX_6$ were existing between their δ's and $H_1$'s.

*Correlation with the NMR shifts of transition metals.*

Table 3d) $H_1$ and δ of $^{115}In$.

| Compds | $H_1(\times 10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $[InCl_4]^-$ | 7.839 | 440 | 501.4 |
| $[InBr_4]^-$ | 8.888 | 180 | 76.4 |
| $[InI_4]^-$ | 10.411 | –583 | –540.7 |
| $\delta=3676.15-405.04\times 10^6 H_1$ | | | R=–0.985 |

[a] Ref.27.

Table 3e) $H_1$ and δ of $^{205}Tl$.

| Compds | $H_1(\times 10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $Me_2TlF$ | 1.889 | 3413 | 3416.5 |
| $Me_2TlBr$ | 2.618 | 3575 | 3560.2 |
| $Me_2TlI$ | 2.847 | 3594 | 3605.3 |
| $\delta=3044.01+197.19\times 10^6 H_1$ | | | R=–0.991 |

[a] Ref.27.

Table 4 $H_1$ and δ of $^{31}P$.

| Compds | $H_1(\times 10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $PCl_3$ | 3.536 | 220 | 242.3 |
| $PCl_2F$ | 3.083 | 224 | 198.3 |
| $PClF_2$ | 2.662 | 176 | 157.2 |
| $PF_3$ | 2.271 | 97 | 119.2 |
| $\delta=-101.824+97.329\times 10^6 H_1$ | | | R=–0.899 |
| $PMeF_2$ | 1.710 | 245 | 244.3 |
| $PMeCl_2$ | 2.424 | 192 | 195.1 |
| $PMeBr_2$ | 2.621 | 184 | 181.5 |
| $\delta=362.24-68.943\times 10^6 H_1$ | | | R=–0.996 |
| $PMe_2F$ | 1.229 | 186 | 184.2 |
| $PMe_2Cl$ | 1.521 | 96.5 | 104.9 |
| $PMe_2Br$ | 1.598 | 90.5 | 83.8 |
| $\delta=518.50-271.943\times 10^6 H_1$ | | | R=–0.989 |

[a] Ref.29.

**Table 5a) $H_l$ and δ of $^{17}O$.**

| Compds | $H_l(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $OPF_3$ | 3.162 | 66 | 74.2 |
| $OPCl_3$ | 4.418 | 216 | 219.9 |
| $OPBr_3$ | 4.763 | 259.2 | 259.9 |
| $OPCl_2Br$ | 4.531 | 232 | 232.9 |
| $OPCl_2F$ | 3.976 | 177 | 168.6 |
| $OPClBr_2$ | 4.647 | 245 | 246.4 |
| $OPClF_2$ | 3.558 | 127 | 120.1 |

$\delta=292.627+116.011\times10^{6}H_l$ $R=-0.997$

[a] Ref.30.

**Table 6a) $H_l$ and δ of $^{93}Nb$.**

| Compds | $H_l(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $[NbF_6]^-$ | 6.385 | −1620 | −1546.8 |
| $[NbF_5Cl]^-$ | 7.057 | −1270 | −1295.7 |
| $[NbF_5Br]^-$ | 7.241 | −1230 | −1227.1 |
| $[NbF_4Cl_2]^-$ | 7.763 | −1080 | −1032.1 |
| $[NbF_3Cl_3]^-$ | 8.503 | −780 | −755.9 |
| $[NbF_4Br_2]^-$ | 8.151 | −755 | −887.4 |
| $[NbF_2Cl_4]^-$ | 9.276 | −530 | −467.2 |
| $[NbF_3Br_3]^-$ | 9.114 | −405 | −527.6 |
| $[NbFCl_5]^-$ | 10.083 | −250 | −166.9 |
| $[NbCl_6]^-$ | 10.924 | 0 | 148.0 |
| $[NbF_2Br_4]^-$ | 10.132 | 5 | −147.7 |
| $[NbCl_5Br]^-$ | 11.152 | 126 | 233.2 |
| $[NbFBr_5]^-$ | 11.203 | 375 | 252.4 |
| $[NbClBr_5]^-$ | 12.089 | 616 | 582.9 |
| $[NbBr_6]^-$ | 12.329 | 735 | 672.5 |
| $[NbCl_4Br_2]^-$ | 11.383 | 249.5[b] | 319.3 |
| $[NbCl_3Br_3]^-$ | 11.616 | 374.5[b] | 406.3 |
| $[NbCl_2Br_4]^-$ | 11.851 | 494.5[b] | 494.2 |

$\delta=-3930.467+373.357\times10^{6}H_l$ $R=0.992$

[a] Ref.32. [b] averaged for *trans*- and *cis*-compds.

**Table 5b) $H_l$ and δ of $^{77}Se$.**

| Compds | $H_l(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $SeOF_2$ | 2.881 | 1378 | 1390.1 |
| $SeOFCl$ | 3.418 | 1478.6 | 1448.0 |
| $SeOCl_2$ | 4.002 | 1479 | 1511.1 |
| $SeOBr_2$ | 4.320 | 1559 | 1545.4 |

$\delta=1079.05+107.95\times10^{6}H_l$ $R=-0.928$

[a] Ref.31.

**Table 5c) $H_l$ and δ of $^{125}Te$.**

| Compds | $H_l(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $H_2TeCl_6$ | 9.570 | 1430 | 1493 |
| $H_2TeBr_6$ | 10.715 | 1356 | 1248 |
| $H_2TeI_6$ | 12.340 | 857 | 901.4 |

$\delta=3537.06-213.58\times10^{6}H_l$ $R=-0.954$

[a] Ref.32.

**Table 6b) $H_l$ and δ of $^{95}Mo$.**

| Compds | $H_l(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $[MoO_4]^{2-}$ | 5.142 | 0 | −5.7 |
| $[MoSO_3]^{2-}$ | 5.856 | 497 | 510.7 |
| $[MoS_2O_2]^{2-}$ | 6.617 | 1066 | 1061.1 |
| $[MoS_3O]^{2-}$ | 7.425 | 1654 | 1654.6 |
| $[MoS_4]^{2-}$ | 8.279 | 2258 | 2263.3 |

$\delta=-3724.98+723.307\times10^{6}H_l$ $R=-0.9999$

[a] Ref.34.

**Table 6c) $H_l$ and δ of $^{195}Pt$.**

| Compds | $H_l(\times10^{-6})$ | $\delta_{exp}$ [a] (ppm) | $\delta_{cal}$ (ppm) |
|---|---|---|---|
| $H_2PtCl_6$ | 9.748 | 0 | −353.4 |
| $H_2PtCl_5Br$ | 9.940 | 284 | 73.7 |
| $H_2PtCl_4Br_2$ | 10.133 | 579 | 503.1 |
| $H_2PtCl_3Br_3$ | 10.328 | 882 | 936.9 |
| $H_2PtCl_2Br_4$ | 10.526 | 1190 | 1377.4 |
| $H_2PtClBr_5$ | 10.725 | 1522 | 1820.2 |
| $H_2PtBr_6$ | 10.926 | 1860 | 2267.4 |
| $H_2PtI_6$ | 12.600 | 6300 | 5991.7 |

$\delta=-22035.4+2224.29\times10^{6}H_l$ $R=-0.989$

[a] Ref.35.

Because of the difficulties encountered in the theoretical calculation of the shielding for the transition metallic compounds, little work was done in this field [33]. Here the good results can also been obtained in the application of $H_l$ in the correlation with the NMR shifts of such compounds. The calculated δ's are listed in Table 6a), 6b) and 6c) for compounds $[NbX_nY_{6-n}]^-$ (X,Y=halogen;n=0-6), $[MO_nS_{4-n}]^-$ (M=Mo, W) and $H_2PtX_6$ respectively. As regards to the chemical shifts of these molecules, correlation coefficients R exceed 0.98 for each series. The validity of $H_l$ is thus testified extensively for the quantitative interpretation of the NMR shifts of transition metals.

### *Discussion*

Many empirical rules are suggested in the study of the NMR spectroscopy. Most of them are based on the assumption that each substitutent will contribute separately to the overall chemical shifts of the nucleus. As a matter of fact, each group does not contribute a fixed increment to the shielding of a nucleus. The contribution of each group is dependent upon other substituents bonded to the nucleus concerned. Therefore, the pairwise additive consideration is necessary [37]. Through expansion of eq 3, it can be derived as follows:

$$H_1 = \sum_i h_i^2 + 2\sum_{i<j} h_i h_j \tag{6}$$

It can be seen from this expression that the novel topological index $H_1$ can be easily decomposed into additive factors which depend on pairs of bonds. For instance, $H_1$'s of $[AlX_nY_{4-n}]^-$ (X=Cl, Br, I) can separated into the contribution from the following bond pairs, (Cl,Cl), (Br,Br), (I,I), (Cl,Br), (Cl,I), (Br,I). In this way, the good correlations with the NMR shifts of our topological index can be expected. The general fitness of $H_1$ is proved by the studies on compounds containing atoms of different groups in the periodic table.

Some exceptions have also been found in a set of compounds, such as $BF_3$, because the value of α in eq 4 is fixed. This may not be able to reflect the difference of two kinds of interactions in a given bond. So further researches are necessary in this field.

*Conclusion*

In summary, the novel topological index $H_1$ given in the paper is reasonable in the correlation with the NMR chemical shifts of various compounds containing most of the elements in the periodic table. By combining the electronic information with the topological form in a molecule, the novel topological index $H_1$ is able to provide a satisfactory description of a molecular graph. Other correlation analyses [16 18] on various chemical or physical properties have shown that the index $H_1$ is a good candidate for the topological description of both organic and inorganic compounds.

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