Vibrational Zero-Point Energies of Iodo Compounds

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Abstract

In this study, the contribution of the bond C–I has been derived and incorporated in empirical formula to calculate zero-point energies (ZPE) of Iodo compounds. The calculated ZPE for 38 molecules containing this bond correlate well with experimental values. The comparison of these results with semiempirical (AM1) ZPE appears very satisfactory .

Introduction

The zero point energies (ZPE) of polyatomic molecules can be experimentally determined via equation (1):

$$ZPE = \frac{1}{2} \sum_{i}^{k} h v_i \qquad (1)$$

Where h Planck's constant, V_i is the frequency of fundamental vibration i, and k the normal modes of vibrations .

Normal vibrations are usually determined by IR and Raman spectroscopy. This method has some difficulties, especially, for large molecules because of the existence of overtones and combination frequencies in their molecular spectra. Ab initio calculations are also used in determining the frequencies of normal modes of compounds. This method have several difficulties. Firstly, It overestimates the frequencies by about 10% [1]. Secondly, ab initio calculations require sophisticated computers and need long computing times especially for large molecules.

As a consequence of the above difficulties, empirical methods had been developed to calculate the ZPE's of organic compounds . Flanigen et al, [2] derived a simple empirical formula for the calculation of the ZPE of a hydrocarbon, equation (2):

$$ZPE = 2n + 7m \quad (kcal/mol) \qquad (2)$$

Where n, m are the number of carbon and hydrogen atoms, respectively. Later, Schulman and Disch [3] have developed another empirical formula for the calculation to the ZPE,s of hydrocarbons, equation (3) :

$$ZPE\ (n,m) = 3.88n\ +\ 7.12m - 6.19 \quad (kcal/mol) \qquad (3)$$

Where n and m are the number of carbon and hydrogen atoms, respectively, 3.88 is the increment of carbon atom, 7.12 is the increment of hydrogen atom and 6.19 is a constant.

Ibrahim, Fatafiata and AbdulHussain [4-6] used Schuman and Disch formula to calculate the ZPE,s of other organic compounds by deriving increment for N, O, Cl, F, S, Br and I atoms.

Rahal et al, [7-8] established an empirical relationship making it possible to calculate the ZPE of organic compounds. This relationship was determined by relating ZPE to the nature and type of bonds forming the molecule. The empirical formula found is written as follows :

$$ZPE_{(empirical)} = \sum_{i}^{p} N_i BC_i - 2.09 \qquad (kcal/mol) \qquad (4)$$

with p the number of bonds in the molecule, N the number of bonds of type i and BC, the contribution of the bond i to the ZPE.

This equation makes it possible to calculate the ZPE of compounds containing the bonds C-H, N-H, O-H, S-H, C-O, C-C, C-N, C-S, N-N, C-F, C-Cl, C-Br, C=C, C=N, C=O, C=S, C≡C, and C≡N. It has been applied to more than 80 chemical systems belonging to different categories of compounds (alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, ketones, aldehydes, acids, esters, alcohols, ethers, amines, amides, nitriles, thio compounds, chloro compounds, fluoro compounds, aromatics, etc.). The correlation between the experimental and empirical ZPE values is virtually linear for the non-aromatic compounds while for aromatic compounds, the empirical values have to be adjusted using the equation (5):

$$ZPE = 1.08\ ZPE\ (empirical) - 1.07 \qquad (kcal/mol) \qquad (5)$$

This correction is due to the fact that in the aromatic nucleus the CC bonds are identical by resonance, while the model supposes the presence of three C-C bonds and three C=C bonds.

In this study, we determine the contribution of the C-I bond in order to calculate the ZPE of iodo compounds. The results obtained have been compared to the experimental values on the one hand, and to the values obtained using semi-empirical (AM1) calculations on the other hand.

Computational details

The semiempirical calculations were carried out using the (AM1) method [9] implemented in the Gaussian 09 program [10] and Pentium IV PC at Baghdad University. Zero-point vibrational energy was calculated after optimising the geometry on the basis of normal vibration frequencies.

Results and Discussion

The derivation of bond contribution for any type bond requires molecules have reliable ZPE values. The set molecules used in the derivation of C-I bond contribution with their experimental ZPE values are recorded in Table (1). The experimental ZPE values are calculated from the reported vibrational spectra for chosen organic iodo compounds belong to different organic classes of compounds such as acyclic, cyclic, saturated and unsaturated. Other functional groups such as OH are also present in the chosen molecules. The chosen

compounds can be also divided into mono-, di- and tetra- iodo compounds. Thus , the chosen molecules include various classes of iodo compounds.

By using the least squares method and Eq. (4) can derive C-I bond contribution to calculate ZPE value. The contribution of C-I bond as well as the contributions already established [7-8] for the other bonds are given in Table (2). The derived C-I bond contribution value is 1.6344 kcal/mol. To test the reliability of the generalized empirical formula, it is applied to 38 iodo compounds of various classes (iodoalkanes, iodoalkenes, iodoalkynes, iodoaromatics, etc.). The results in Table (1) show that the calculated values correlate well with the experimental values. The correlation between the experimental and empirical values list in Fig (1), standard deviation, SD, is 0.681, slope is close to unity 1.013 , correlation coefficient is 099979 and average error is 0.47. This means the developed C-I bond contribution could reproduce the experimental ZPE values for an iodo organic compounds.

The Table (1) shows that there is little difference between the experimental values of ZPE and those calculated empirically, less than 1.3 kcal/mol in all cases except tert-Butyl iodide was 2.29 kcal/mol. The standard deviation, SD, average error, slope and correlation coefficient will be improved to 0.579, 0.42, 1.011 and 0.99984 respectively if the tert-Butyliodide value is neglected Fig (2).

The same Iodo compounds are calculated by using the semi empirical (AM1) method. The results are corrected by a factor of 0.96 Table (1). The standard division, SD, slope, average error, and correlation coefficient are 0.824, 1.011, 0.646 and 0.99963 respectively Fig (3).

The comparison between the semi empirical (AM1) values and empirical estimation values shows that the empirical estimation values are closer to experimental values.

Conclusion

In this study the zero point energy ZPE values of iodo organic compounds are calculated using the contribution of the C-I bond determined. The results obtained are compared with the experimental results available and with the results obtained using the semi-empirical method (AM1). The empirical method provides a simple and quick method of calculating ZPE values of iodo compounds.

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Table (1): Comparison of calculated (empirical, AM1) zero-point energy with experimental values.

Formula	Molecular	ZPE (Kcal/mol)			DIF (Kcal/mol)[a]		Ref
		Exp.	Emp.	AM1[b]	Emp.	AM1	
CH3I	Methyliodide	22.02	22.31	21.65	-0.29	0.37	[11]
CHI3	Iodoform	10.90	10.40	10.25	0.50	0.65	[12]
CCl3I	Trichloroiodomethane	5.36	6.16	5.76	-0.80	-0.40	[11]
CF3I	Triiodoflurooiodomethane	8.69	9.47	9.17	-0.78	-0.48	[13]
CH2I2	Diiodomethan	16.30	16.35	16.12	-0.05	0.18	[13]
CI4	Carbontetraiodide	3.42	4.45	4.16	-1.03	-0.74	[11]
ICN	Cyanogeniodide	4.70	4.36	5.31	0.34	-0.61	[14]
C2BrI	Bromoiodoacetylene	5.75	5.94	6.48	-0.19	-0.73	[14]
C2ClI	Chloroiodoacetylene	6.11	6.16	6.91	-0.05	-0.80	[14]
C2H3OI	Acetyliodide	28.16	28.32	28.30	-0.16	-0.14	[13]
C2H4I2	1,2-Diiodoethane	33.60	33.60[c]	33.39	0.00	0.21	[15]
C2H5I	Ethyliodide	39.60	39.56	39.14	0.04	0.46	[16]
C2H5OI	Iodoethanol	43.16	41.96	42.28	1.20	0.88	[17]
C2HI	Iodoacetylene	10.95	11.54	11.96	-0.59	-1.01	[18]
C2I2	Diiodoacetylene	5.55	5.59	6.34	-0.04	-0.79	[14]
C2I4	Tetraiodoethene	6.86	7.10	7.69	-0.24	-0.83	[19]
C3H3I	Methyliodoacetylene	28.33	28.79	28.70	-0.46	-0.37	[20]
C3H3I	Iodopropadiene	28.16	27.61	28.41	0.55	-0.25	[14]
C3H3I	Propargyliodide	28.00	28.79	28.70	-0.79	-0.70	[21]
C3H5I	Iodocyclopropane	43.51	43.71	43.81	-0.20	-0.30	[22]
C3H5I	3-iodopropene	42.74	42.21	42.61	0.53	0.13	[11]
C3H6I2	1,3-Diiodopropane	50.98	50.85	50.63	0.13	0.35	[17]
C3H7I	1-Propyliodide	56.80	56.81	56.48	-0.01	0.32	[11]
C3H7I	Isopropyliodide	56.63	56.81	56.30	-0.18	0.33	[17]
C3H7OI	2-iodoethylmethyllether	59.95	60.13	59.83	-0.18	0.12	[23]
C3NI	Iodocyanoethyne	10.97	10.85	12.29	0.12	-1.32	[14]
C4H8I2	1,4-Diiodobutane	68.23	68.10	67.92	0.13	0.31	[20]
C4H9I	1-Iodobutane	74.10	74.06	73.85	0.04	0.25	[24]
C4H9I	tert-Butyliodide	76.35	74.06	73.25	2.29	3.10	[20]
C4HI	Iododiacetylene	17.33	18.03	18.82	-0.70	-1.49	[17]
C4O3I2	Diiodomalaicanhydride	21.84	21.24	23.16	0.60	-1.32	[24]
C5H11I	1-Iodopentane	91.37	91.31	91.09	0.06	0.28	[20]
C5H3I	1-Iodo-1,3-Pentadiyne	34.51	35.28	35.51	-0.77	-1.00	[25]
C6H10ClI	1,4-chloroiodocyclohexane	91.38	90.08	91.72	1.30	-0.34	[26]
C6H10I2	1,4-diiodocyclohexane	90.62	89.51	91.18	1.11	-0.56	[21]
C6H10IBr	1,4-iodobromocyclohexane	91.05	89.86	91.29	1.19	-0.24	[27]
C6H4I2	1,2-Diiodobenzene	48.10	48.29[c]	49.40	-0.19	-1.30	[28]
C6H5I	Iodobenzene	54.68	54.72[c]	55.57	-0.04	-0.89	[28]

a $ZPE_{(experimental)} - ZPE_{(calculated)}$.

b Values adjust by 0.96 .

c Adjust value by Eq. (5)

Table (2)

Contribution of each bond to ZPE (in Kcal/mol)

Bond	Bond contribtion (BC$_i$)
C-H	7.5877[a]
N-H	7.2013[a]
O-H	7.2964[a]
S-H	5.6921[a]
C-O	2.6985[a]
C-C	2.0751[a]
C-N	4.1409[a]
C-S	1.4403[a]
N-N	6.8372[a]
C-F	3.3078[a]
C-Cl	2.2051[a]
C=C	2.6501[a]
C=N	3.8852[a]
C=O	3.9343[a]
C=S	2.7319[a]
C≡C	4.4125[a]
C≡N	4.8169[a]
C-Br	1.9837[b]
C-I	1.6344[c]

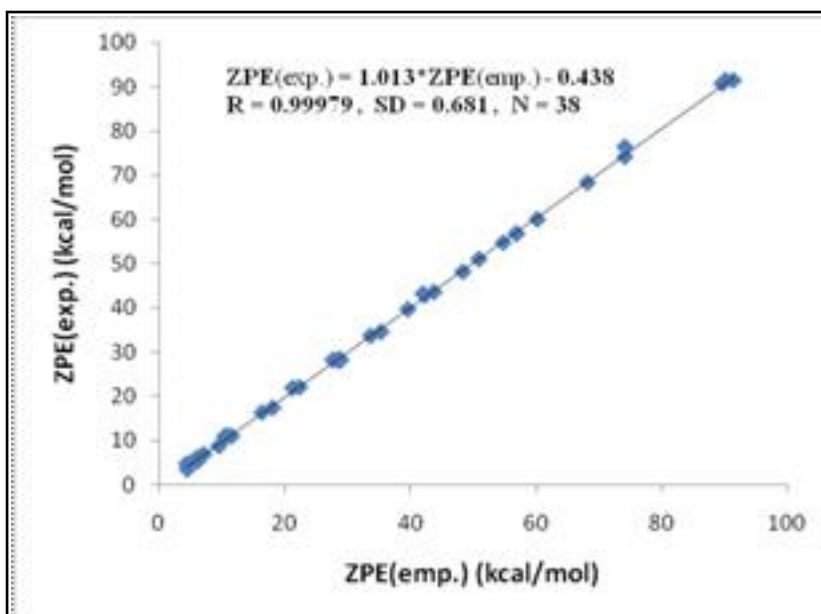*a Ref [7].*

b Ref [8].

c This study.

Fig. (1) Comparison between experimental ZPE's and empirical values calculated using Eq.(4)
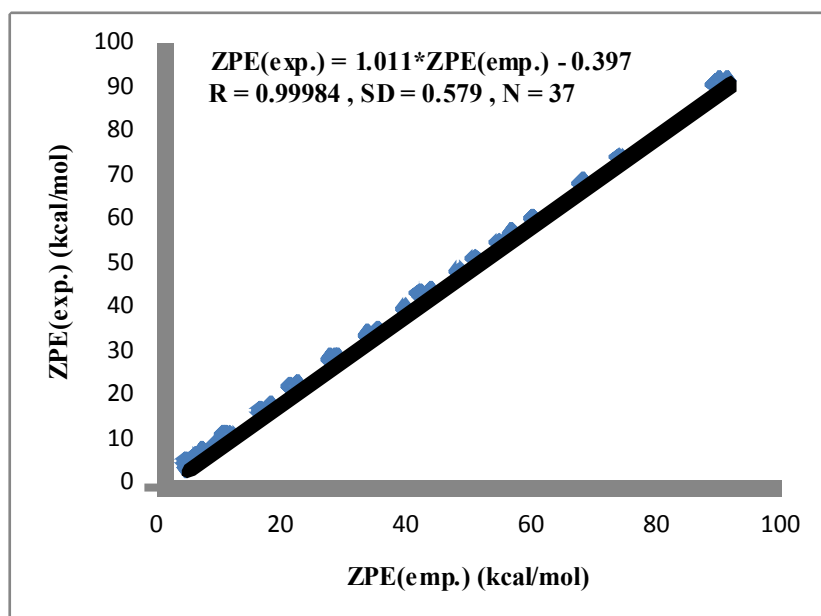

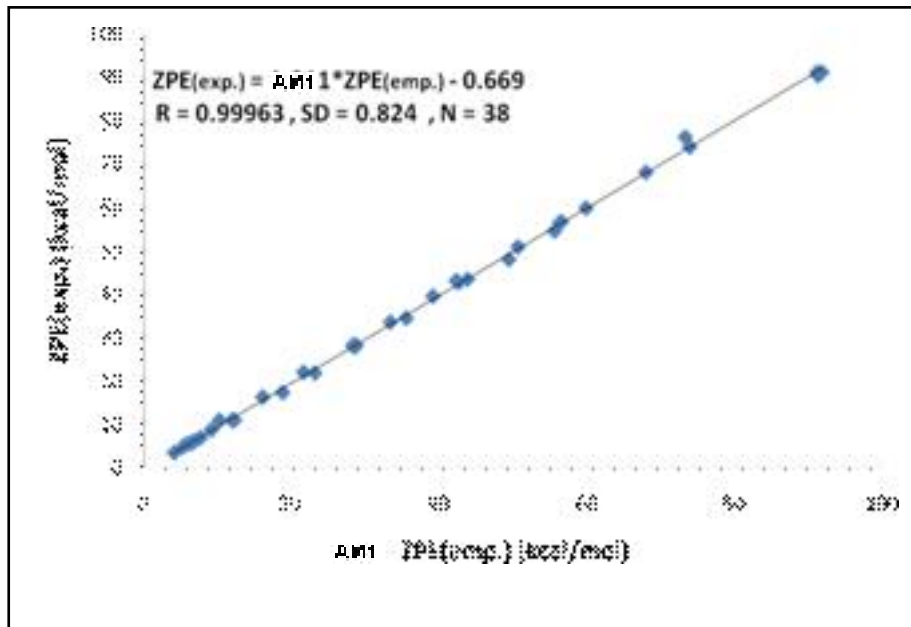**Fig. (2) Comparison between ZPE's experimental and empirical values except tert-Butyl iodide value's**

ZPE(exp.) = AM1*ZPE(emp.) - 0.669
R = 0.99963 , SD = 0.824 , N = 38

Fig. (3) Comparison between experimental ZPE's and theortical (AM1) ZPE

طاقات نقطة الصفر لمركبات اليود

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الخلاصة

في هذه الدراسة ، اشتقت مساهمة الاصرة C-I وضمت مع مساهمات الاواصر المشتقة سابقا في الصيغة الوضعية لمركبات اليود ، و حسبت طاقات نقطة الصفر لمركبات اليود من خلال مساهمات الاواصر المشتقة ، ووجد ان العلاقة بين قيم طاقة نقطة الصفر المحسوبة لـ 38 جزيئة تحتوي هذه الاصرة مع القيم التجريبية هي علاقة جيدة ، وكذلك مقارنة هذه النتائج مع قيم طاقات نقطة الصفر المحسوبة بـ (AM 1) Semiempirical تبدو مقنعة جدا .