Original Article

Investigation of the Jahn-Teller Effect on Intramolecular Hydrogen Bonding in Dimer Compounds of Methanoic Acid and Analog Containing S and Se Atoms

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Abstract

Based on the studies in the field of chemical and the origin of the equilibrium geometric structure, any system tends to reach its stable state. Therefore, the unstable states of molecular systems with high symmetry configuration are inclined towards the low symmetry and become stable. In fact, this effect is an important factor in the symmetry breaking of the molecules and solid-state systems. The vibronic coupling between the base and excited states along the core movements are assumed as distortions which alter the configuration of the system from a high-symmetry flat geometric structure to a low-symmetry distorted equilibrium structure with low symmetry. The distortion significantly affects the prediction of the systems' molecular spectrum and molecular properties, as the electrical, magnetic, and conductance properties, as well as other properties, can be changed. Based on what was said, the current study aimed to investigate the Pseudo Jahn-Teller Effect (PJTE) on the distortion of hydrogen bonding of dimmer compounds of Methanoic acid and the analog containing the S and Se atoms. The results show that the dimmer of compounds 1 to 3 in the high-symmetry form of D_{2h} has a high virtual frequency in b_3g symmetry. The results of TD-DFT studies also indicate that the distortions of the high-symmetry compounds 1 to 3 and their alteration into symmetric forms C_{2h} occur due to the PJTE $(Ag+B_3g) \otimes b_3g$. In this regard also, the energy distance of composite reference electron levels (Δ) is reduced from compound 1 to compound 3. Finally, the correlation between the structural parameters and the stability energy of PJTE in compounds 1 to 3 has been investigated.

Keywords: Pseudo Jahn-Teller Effect, hydrogen bond, intramolecular distortion, computational chemistry, Gaussian software

Introduction

In chemistry, the chemical stability is addressed in a specialist manner, which is meant to be the thermodynamic stability. The thermodynamic stability occurs when a system is in its lowest energy state or chemical equilibrium with the environment. The chemical stability might be dynamic in a way that the length of the bonds and angles in the molecules change so much that the molecule reaches stability with the lowest energy. Every system is inclined to maintain this type of stability until an unlimited time unless changes are applied to the system. In this case, the system is out of the stability state and naturally tends to regain stability [1].

In some specific chemical compounds, the hydrogen bonding has been scientifically worthy of research and scrutiny due to its special importance in the chemical and biochemical phenomena and the structure of nature. The intramolecular hydrogen bonding exists in many organic molecules and biomolecules such as the sugars, hormones and proteins. Also, this bonding determines the configuration of many of the molecules and it is due to the presence of the same bonding that the proteins have a unique configuration. An important parameter in the division of the systems containing hydrogen bonding is the power of these bonding. This power is structurally determined by the distance between the two electronegative atoms (A … B), the hydrogen bond length (H … B), covalent bond length (A—H), and bond angle (A^H^B), as well as the thermodynamic parameters such as the enthalpy of formation (ΔH_f), entropy of formation (Δsf), and Gibbs free energy [2, 3]. These empirical experienced methods cannot measure the hydrogen bonding power, or at least, their applicability is limited. The more useful and comprehensive methods in this regard are the theoretical and computational methods in which the molecule can be

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optimized terms of the energy, in any electron or structure state. These methods, which are necessary for measuring intramolecular hydrogen bonding energy, have been also widely used after the arrival of high-tech and superfast computers to the market [4].

The Jahn-Teller Effect is a general approach to understanding the molecules and crystals properties, and it is one of the most wonderful phenomena of modern chemistry and physics. Regarding the recent achievements in the field of usage in molecular systems, the Jahn-Teller Effect, in addition to the provision of numerous solutions for the structural, spectral, and magnetic problems, has been used for explanation of the properties of new compounds such as the Fullerenes which have a high conductivity. The new usages of the Jahn-Teller Effect can be seen in reactivity and mechanism of chemical reactions [4].

One of the prominent criteria of the Jahn-Teller Effect is that when it is not needed, it disappears. The simplest Jahn-Teller problem is the doubled alignment effect of electron term E with the binary vibration alignment e which is shown as $E \otimes e$. This effect is hidden in the non-linear molecular system with an electron formation in which the aligned orbitals are not occupied symmetrically, and it tends to somehow reduce the alignment in electron formation. It means that it tends to generate a gap between the aligned orbitals so that the symmetry would be reduced, and higher stability would be achieved [5].

This subject is the base for inference and justification of distortion in many of mediator metals complexes such as the tetragonal distortion of octahedral complexes. In many of the octahedral complexes, due to asymmetry of the electron formation alignments, the regular octagonal structure with symmetry Oh is not the most stable structure for them. Therefore, the complexes lose their regular octagonal formation and their symmetry is reduced, getting a tetragonal formation (tetrahedral or two-pyramid two-square) to attain more stability [6].

In terms of the Jahn-Teller Effect, several studies have been done, especially, Liehr And Ballhausen investigated the Jahn-Teller problem $E \otimes e$ by the vibrational- electron reactions of the quadratic terms. In 1961-63, Bersuker [7] reported the fission of the lowest vibrational- electron energy levels due to the system tunneling between the distorted aligned configurations and their effects on the ESR's [8].

In 1964, O'Brien showed the vibrational- electron energy levels in the $E \otimes e$ problem by linear terms' vibrational-electron coupling and the quadratic terms and calculated it numerically. In 1965, Ham [9] generalized the idea of vibronic reduction factors. Important progress in the Jahn-Teller theory is the performance of Jahn-Teller cores interactions, especially the regular Jahn-Teller cores in the crystals which are known as the interactional Jahn-Teller effect [10].

Kanamori [11] in 1960, investigated such interactional phenomena in Jahn-Teller crystals while Elliot et al., [12] necessarily used this important method in the rare element of zircon. In 1966, Bersuker [13] firstly proposed the vibrational-electron theory for ferromagnetic compounds as the interactional Jahn-Teller Effect, while the idea of the interaction between the Jahn-Teller cores in the crystals and ordering the Jahn-Teller distortions was quite understandable and physically clear.

Garcia-Fernandez and Bersuker in 2010, revealing the PJTE which is excited by the electron levels, showed that the solids and the multi-atom systems with partially filled aligned layers $e^{۲}$ and $t^{۳}$, form a new group in terms of magnetic and dielectric stabilities. Garcia-Fernandez et al. in 2010 provided some results for PJTE in the Cis-Trans conformational compounds. They showed how the high-symmetry molecular geometrical formation $D_{۲d}$ with the binary bonding and electron configuration $e^{۲}$ (e is the binary alignment of molecular orbital) transforms into the point group $D_{۲h}$ through different distortions of PJTE and the rotational transformation $(b_۱)$ $(D_{۲d} \rightarrow D_{۲h})$.

The geometric formation with symmetry $D_{۲h}$ is categorized as the cis-trans intra-plate ei and chair and boat off-plate $(e_۰)$ formations. The other reactions of the PJTE are initiated with E levels that gave high energy. The understanding of these formations depends on the position of the excited levels E and the parametric values of PJTE [14].

In 2011, Gorinchog et al. investigated the JTE and PJTE on the systems with partial loads. The new method of instability and structural transformations in the molecular systems occurs due to relatively weak interaction between the molecular systems. These transformations lead to the distortions due to the JTE, PJTE, and RTE by the use of Orbital Charge Transfers (OCT) that transform the intramolecular vibrational-electron coupling [15].

Based on what was mentioned, and the studies conducted previously, and regarding the importance of JTE and the fact that hydrogen bonding as one of the effective factors on human life, the intramolecular hydrogen bonding in dimeric compounds of methanoic acid (1) and analogs containing S (2) and Se (3) atoms were investigated with PJTE analysis.

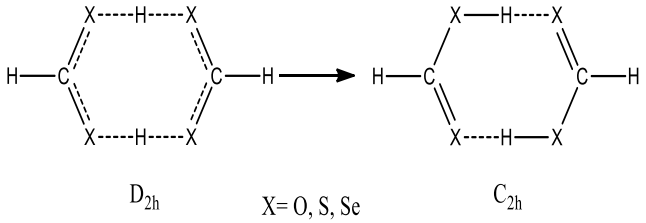

Figure 1: the transformation of the formation with the D_{2h} symmetry in dimeric methanoic acid and the analog containing S and Se atoms into the formation C_{2h} ($D_{2h} \rightarrow C_{2h}$) by the use of calculations at the theoretical level B3LYP/6-311++G** (X=O, S, Se).

It is estimated that the PJTE describes the transformations of the high-symmetry structures D_{2h} to low-symmetry structures C_{2h} for the following compounds (figure 1). It was revealed that the compounds 1 to 3 have a high-symmetry D_{2h} and they are transformed into configuration C_{2h}.

In the current study, the very important issue of mixing the base electron state with the excited electron state for applying the normal coordinates describing the transformation of high-symmetry to the low-symmetry has been investigated. The main reason for the transformation of the formations is the PJTE which is created through the combination of the base states with the excited states. Because the base electron state of these compounds is non-aligned, it is natural that all the observed formation changes in a linear configuration with the highest symmetry are due to the PJTE. Generally, the PJTE is used for non-aligned states of any systems, the JTE is used for aligned states of the non-linear molecules, and the RTE is used for aligned states of the linear molecules [16].

Empirical Chapter:

The Computational Method:

First, the molecular shape which is written based on the Z_{matrix}, is drawn and numbered based on the related symmetry. The structure of the optimized molecule and the negative frequency are calculated by the Gaussian Software 03 & 98. Then, the DFT (B3LYP) hybrid-based method with the bases series 6-311++G** is used for all the related compounds.

The calculations period depends on the density function theory. Undoubtedly, the Time-dependent Density Functional Theory (TD-DFT) is one of the most prevalent instruments for investigation of the excited states of the molecular systems which have been used for electron configuration of enol forms of methanoic acid dimer and the analog containing S and Se.

The results of B3LYP.6-311++G** and TD-DFT show that the main role in changing the high-symmetry configurations (D_{2h}) to the low-symmetry configuration (C_{2h}) for these compounds belongs to the PJTE which is created by the combination of the basic and excited states. The energy difference (Δ) and the stability energy of PJTE between the reference states and ΔE_{el} in the $D_{2h} \rightarrow C_{2h}$ formation change were also investigated.

Results and Discussion:

Investigation of the Pseudo Jahn-Teller Effect on the Distortion of Methanoic Acid Dimer Compound

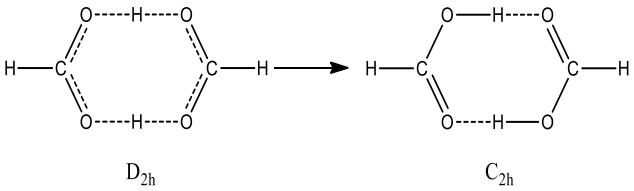

Figure 2: the symmetric D_{2h} formation change of methanoic acid to ($C_{2h} \rightarrow D_{2h}$) C_{2h} formation by the use of calculations in the theoretical level B3LYP.6-311++G**

The structural properties of the methanoic acid dimer are investigated by the use of theoretical level B3LYP.6-311++G**. The results indicated that the structure of methanoic acid dimer has a high symmetry (D_{2h}) and it has a low symmetry in point group C_{2h}. The main reason behind these formation changes is the PJTE which is created by a combination of basic state Ag, which is non-level, with the excited state (B_{3g}) through the displacement of b_{3g}. the PJTE problem is in the form of $(Ag+B_{3g}) \otimes b_{3g}$.

As is seen, in changing the geometric structure from D_{2h} to C_{2h}, the excited states of the methanoic acid dimer are in the form of B_{2g} ،Au ،B_{3u} ،B_{1g} ،B_{3g} ،B_{2u} and B_{1u}. The electron energy of some excited states for the methanoic acid dimer which has been calculated in the theoretical level B3LYP.6-311++G** are presented in Table (1). In this state, the levels B_{1u} and B_{2u} are high-energy excited states which do not intervene in the mutual pseudo-Jahn-Teller effects.

Table 1: The investigation of excited states energy (ev) for methanoic acid dimer and the analog containing S and Se in the symmetric change ($C_{2h} \rightarrow D_{2h}$)

	B_{2u}	Au	B_{3u}	B_{1g}	B_{3g}	B_{2u}	**B_{3g}**
$C_2O_4H_4$	6.25	6.56	6.68	6.93	7.48	7.90	–
$C_2S_4H_4$ (1)	2.76	3.04	3.25	3.52	3.64	3.98	4.62
$C_2S_4H_4$ (2)	2.80	3.08	3.29	3.56	3.68	–	–
$C_2Se_4H_4$ (1)	2.27	2.47	2.70	2.90	3.03	3.34	–
$C_2Se_4H_4$ (2)	2.28	2.48	2.71	2.91	3.04	3.35	–

The energy difference (ΔE) between the basic state and excited state (B_{3g}) in a formation with high-symmetry in the methanoic acid dimer (with the orbital compositions [Homo – 3(B_{1g}) → Lumo + 1 (B_{2g}), Homo – 2 (Au) → Lumo (B_{3u})]) is 7.48eV. Figure (3) shows the energy of the basic state and excited states as well as the distortions of high-symmetry formation due to the PJTE.

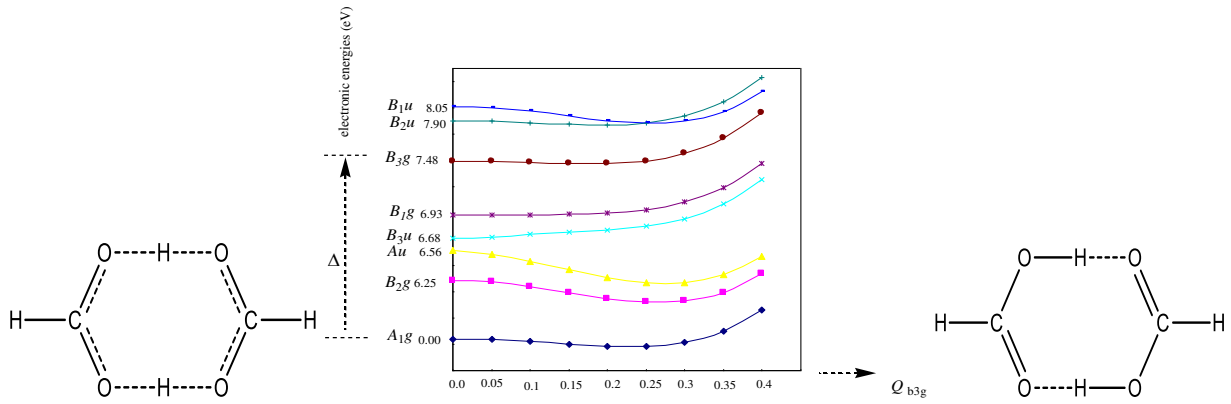

Figure 3: the calculated primary energy level (the basic and excited states) in the methanoic acid dimer and their distortions due to the PJTE

The thermodynamic parameters values ΔG ،ΔH ،ΔS, and ΔE_{el} of this compound which have been calculated by the B3LYP.6-311++G** method are shown in Table (2). The results obtained from this method show that the ΔE_{el} of the methanoic acid dimer is 7.31 Kcalmol^{-1}.

Table 2: the calculated thermodynamic functions (enthalpy, Gibbs free energy (hartree) and entropy and the basic energy as well as their changes) in the temperature 25°C and 1-atmosphere pressure for methanoic acid dimer and the analog containing S and Se atoms by the use of the calculations in the theoretical level B3LYP.6-311++G**

Geometries	H (Hartree)	S	G	ΔH[a]	ΔS[a]	ΔG[a]	E_{el}	ΔE_{el}
1-C_2-O_4-H_4.TD 0.0	-379.597474	74.264	-379.632759	0.004122	0.0000	0.007145	-379.6678864	**0.0116519**
				(2.59) b		(4.48) b		**(7.31)b**
1- C_2-O_4-H_4. TD 0.25	-379.601596	80.625	-379.639904	0.0000	6.361	0.0000	-379.6795383	**0.0000**
				(0.0) b		(0.0) b		**(0.00)b**
2-C_2-S_4-H_4.TD 0.0	-1671.401113	84.467	-1671.441246	0.014871	0.000	0.023595	-1671.4564347	**0.0228048**
				(9.33)b		(14.81) b		**(14.31)b**
2-C_2-S_4-H_2. TD 0.4	-1671.415984	102.828	-1671.464841	0.0000	18.361	0.000	-1671.4792395	**0.0000**
				(0.00)b		(0.0) b		**(0.00)b**
3-C_2-S_4-H_4. TD 0.0	-1671.401113	84.467	-1671.441246	0.001348	0.0000	0.003425	-1671.4564347	**0.0022277**
				(0.85)b		(2.15) b		**(1.40)b**
3-C_2-S_4-H_4. TD 0.4	-1671.402461	88.839	-1671.444671	0.0000	4.372	0.0000	-1671.4586624	**0.0000**
				(0.00)b		(0.0) b		**(0.00)b**
4-C_2-Se_4-H_4. TD 0.0	-9684.722764	96.708	-9684.768713	0.010471	0.0000	0.018529	-9684.7746346	**0.017806**
				(6.57)b		(11.63) b		**(11.17)b**
4-C_2-Se_4 –H_4 TD 0.3	-9684.733235	113.668	-9684.787242	0.0000	16.96	0.000	-9684.7924406	**0.0000**
				(0.00)b		(0.0) b		**(0.00)b**
5-C_2-Se_4-H_4. TD 0.0	-9684.722764	96.708	-9684.768713	0.002999	0.0000	0.005175	-9684.7746346	**0.0039233**
				(1.88)b		(3.25) b		**(2.46)b**
5-C_2-Se_4-H_4 .TD 0.3	-9684.725763	101.286	-9684.773888	0.0000	4.578	0.000	-9684.7785579	**0.0000**
				(0.00)b		**(0.0) b**		**(0.00)b**

a: compared to the more stable form; b: per kcal mol^{-1}

The methanoic acid dimer, after being optimized by theoretical level B3LYP.6-311++G**, would have angle and distance values in the symmetry $_{h2}$D as follows:

<COH = 32.7°, <OCC = 126.6°

$R_{O...H}$ = 1.209° A, R_{C-O} = 1.261° A, R_{C-H} = 1.095° A

Which can be compared to the calculated geometric parametric by C_{2h}. The angles and distances values are as follows:

<CO–H = 110.5°, <COO = 126.2°, <CO…H = 31.3°

$R_{O–H}$ = 0.99° A, $R_{O...H}$ = 1.701° A, $R_{C=O}$ = 1.314° A, $R_{C=O}$ = 1.219° A, $R_{C–H}$ = 1.096° A

The comparison of these two configurations with the symmetries D_{2h} and C_{2h} shows that the lengths of ($_{O–H}$) bonds in a formation with symmetry C_{2h} are not equal, however, they are equal in the symmetry D_{2h}. The reason behind inequality between the lengths of ($_{O–H}$) bonds in the symmetry C_{2h} is the PJTE.

Investigation of the PJTE on the distortion of the Analog Containing S Atom Methanoic Acid Dimer

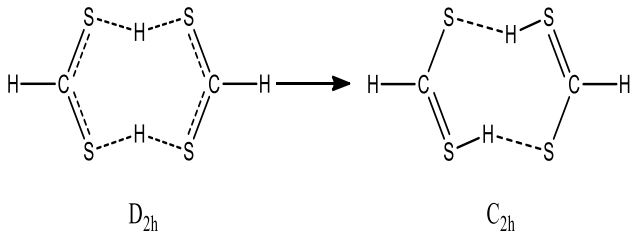

Figure 4: the change in the formation with the symmetry D_{2h} for the analog with S atoms in the methanoic acid dimer in the form of (D_{2h} →C_{2h}) C_{2h} by the use of calculations in the theoretical level B3LYP.6-311++G**

The initial quantum mechanics calculations in the theoretical level B3LYP.6-311++G** showed that the structure of compound 2 has a high symmetry D_{2h} and in the group point C_{2h} it has a low symmetry. These distortions in the high-symmetry formation are created due to the PJTE which is the only source of instability for high-symmetry formations in the level and non-level states. The distortions occur due to a combination of the basic state (Ag) with the excited state (B_{3g}) through the displacement of (b_{3g}), and a combination of the basic state (Ag) with the excited state (Au) through the displacement of (Au). It should be noted that after optimizing the molecule and calculating its negative frequencies, two states with negative frequencies were observed and two series of calculations for each negative frequency must be done. The JPTE of compound 2 leads to problems (Ag+B_{3g}) ⊗ b_{3g} and (Ag+Au)⊗au.

As seen in Figures (5) and (6), in changing the geometric structure D_{2h} to C_{2h}, the excited states of Methane Dithioic Acid are in the form of ‘A_u ‘B_{3g} ‘B_{1g} ‘B_{3g} ‘B_{2u} ‘B_{3g} in the first state and ‘A_u ‘B_{3u} ‘B_{1g} ‘B_{3g} in the second state. The electron energy of some excited states for the structure of Methane Dithioic Acid which has been calculated in the theoretical level B3LYP.6-311++G** is provided in Table (2). The last excited state (B_{3g}) with high energy (4.62 eV) in Figure (5) intervenes in the creation of PJTE.

The basic state with low energy is changed from the symmetric state D_{2h} to the electron formation C_{2h} with lower symmetry and more stability through Q transfers and combines with the excited state B_{3g} (first state) and excited state A_u (second state) that are going up, and lead to the formation of PJTE. The energy difference between the reference states in the two intended states with symmetries B_{3g} and A_u in compound (5) (along with the orbital compositions

1) [Homo – 3 (B_{1g}) → Lumo + 2 (B_{2g}), Homo – 1(B_{3g}) → Lumo+2(A_{1g})]

2) [Homo –1 (B_{3g}) → Lumo (B_{3u})] is 4.62eV and 3.08eV, respectively. Based on the obtained results, in the intended composition with symmetry A_u, regarding the decrease in energy difference between the basic and excited states, we expect its PJTE energy to be higher. However, the effects of other factors make it unnoticed. Figures (5) and (6) show the basic and excited states energies and the distortions in the high-symmetry formations due to the PJTE.

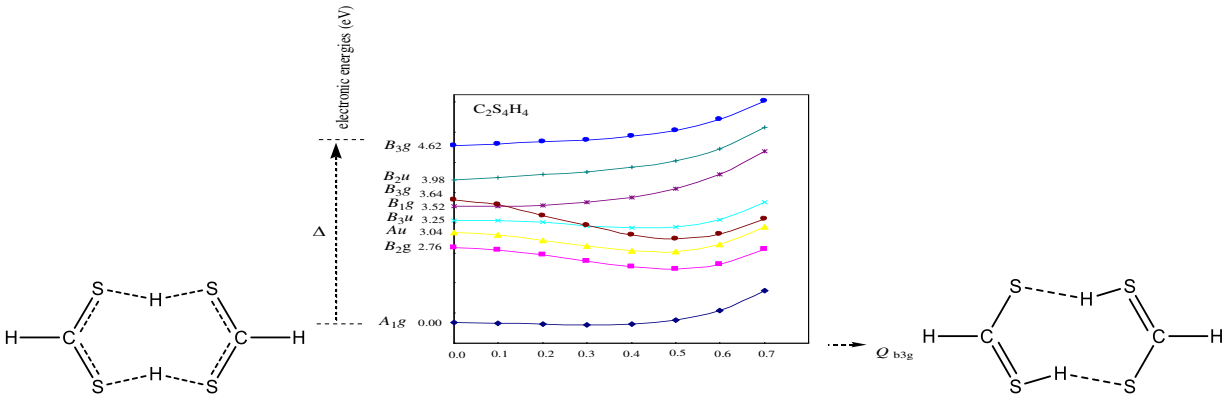

Figure 5: the calculated primary energy levels (the basic state and excited state B_{3g}) in the analog containing S atom of methanoic acid dimer and their changes due to the PJTE (first state)

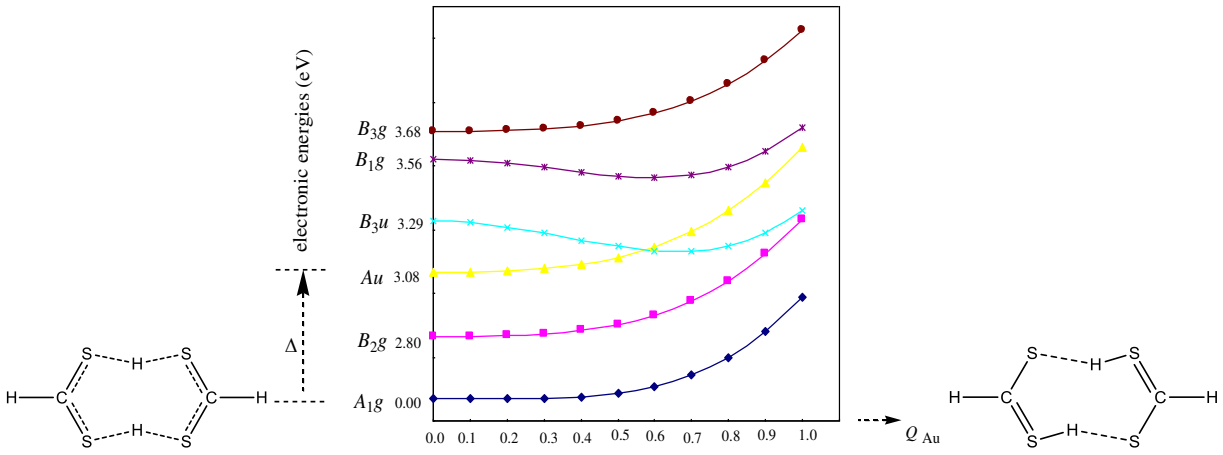

Figure 6: the calculated primary energy levels (the basic state and excited state A_u) in the analog containing S atom of methanoic acid dimer and their changes due to the PJTE (second state)

The thermodynamic parameters values ΔG ،ΔH ،ΔS, and ΔE_{el} of the intended compound which have been calculated by the B3LYP.6-311++G** method, are presented in Table (2).

The results obtained from this method show that ΔE_{el} of the analog containing S atom of the methanoic acid dimer with symmetry B_{3g} is 14.31 Kcal.moll, and it is 1.40 Kcal.moll with the symmetry A_u, which indicates that the compound with symmetry A_u has lower PJTE stability energy.

The geometric parameters (the values of the angles and distances) calculated for compound 2 with the symmetry D_{2h}, after being optimized by the theoretical level B3LYP.6-311++G**, are as follows:

<CSH = 37°, <SCS = 133.2°

R_{S-H} = 1.670° A, R_{S-C} = 1.679° A, R_{C-H} = 1.090° A

(it should be noted that in both states (A_u and B_{3g}), the values of the angles and distances are equal)

The values of the angles and distances with the symmetry $_{h2}C$

are as follows:

<CS–H = 98.4°, <SCS = 130.6°, <CS…H = 41.2°

R_{S-C} = 1.732° A, $R_{S=C}$ = 1.636° A, R_{S-H} = 1.363° A, $R_{S...H}$ = 2.615° A

The comparison between these two configurations with symmetries D_{2h} and C_{2h} shows that the (S…H) bonds length in the formation with the symmetry D_{2h} is equal in the tow sates A_u and B_{3g}, however, in the formation with symmetry C_{2h}, the lengths are not equal, which is due to the PJTE.

Investigation of the PJTE on the distortion of the Analog Containing Se Atom Methanoic Acid Dimer

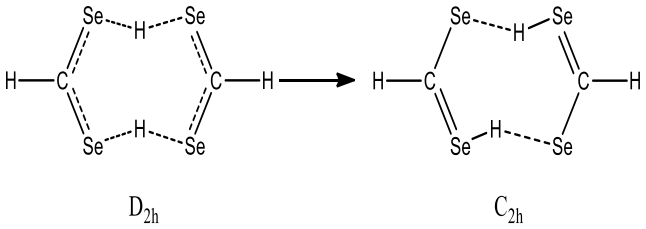

Figure 7: the change in the formation with the symmetry D_{2h} for the analog with Se atoms in the methanoic acid dimer in the form of(D_{2h} →C_{2h}) C_{2h} by the use of calculations in the theoretical level B3LYP.6-311++G**

As was mentioned in for the previous compounds, the structure of compound 3 has a high symmetry D_{2h} while it has a low symmetry in the point group C_{2h}. The main reason behind these distortions is PJTE. Because after the optimization by the theoretical level B3LYP.6-311++G**, the negative frequency can be seen in the two-point groups A_u and B_{3g}, these distortions occur due to the combination of the basic state (A_{1g}) with the excited state (B_{3g}) by displacement of b_{3g}, and the combination of basic of the basic state (A_{1g}) with the excited state (A_u) by displacement of A_u (i.e.

1) [Homo – 3 (B_{1g}) → Lumo + 1 (B_{2g}), Homo – 2(Au) → Lumo (B_{3u})]

2) [Homo –1 (B_{3g}) → Lumo (B_{3u})])

The PJTE of compound 3 leads to the problems $(Ag+B_{3g})$ ⊗b_{3g} and (Ag+Au) ⊗ au.

Figure (8) shows the energies of the basic and excited states with symmetry B_{3g} and the distortions in high-symmetry

formations that occur due to the PJTE. Figure (9) shows the energies of the basic and excited states with symmetry A_u.

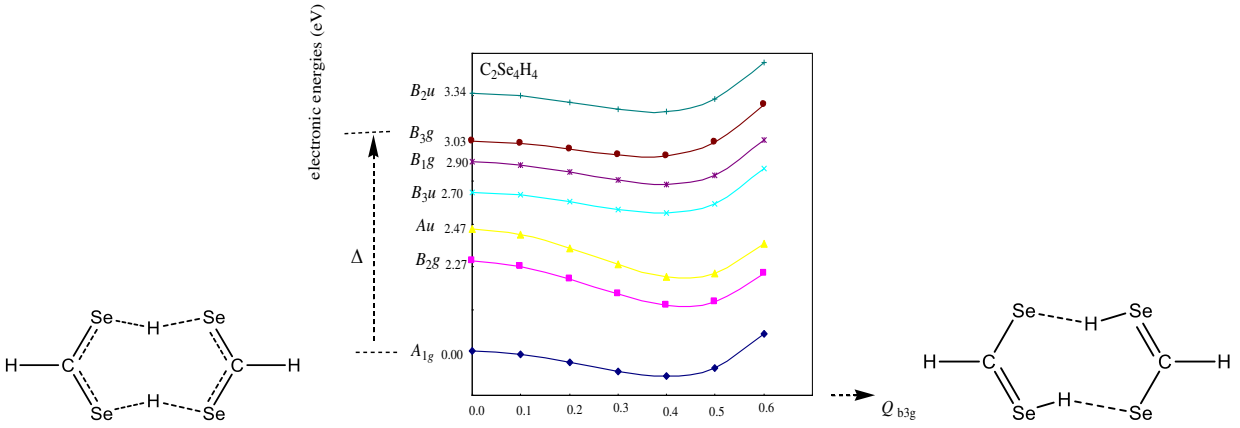

Figure 8: the calculated primary energy levels (the basic state and excited state B_{3g}) in the analog containing Se atom of methanoic acid dimer and their changes due to the PJTE (first state)

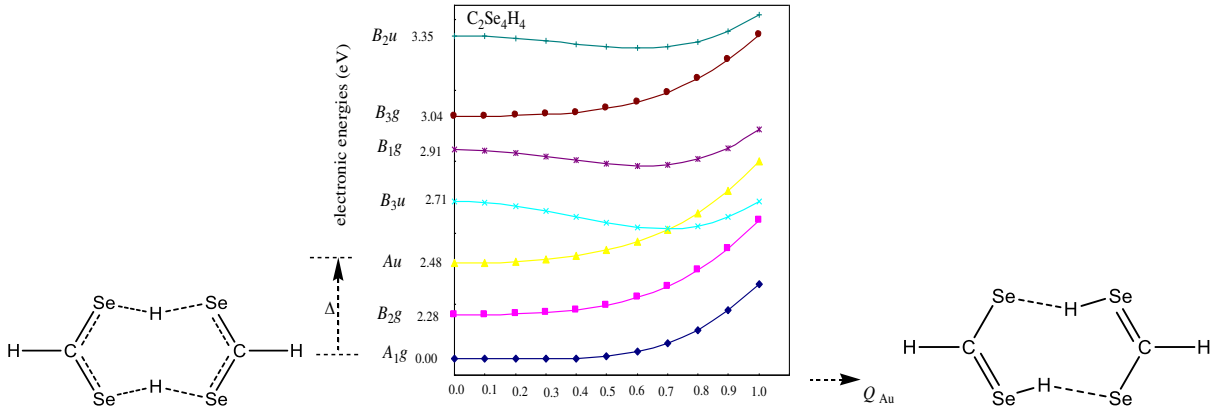

Figure 9: the calculated primary energy levels (the basic state and excited state A_u) in the analog containing Se atom of methanoic acid dimer and their changes due to the PJTE (second state)

The energy difference between the basic state and the excited state (B_{3g}) (Figure 8) and the basic state and excited state (A_u) (Figure 9) is 3.03eV and 2.48eV. Regarding the decrease in energy difference of the compound in symmetry A_u, we expect the PJTE to be higher, but it is not so.

As seen in Figure (8), in changing the geometric structure from D_{2h} to C_{2h}, the excited states of compound 3 are as follows: B_{2g} ،A_u ،B_{1g} ،B_{3g}، and B_{2g}, and the excited states of Figure (9) include B_{2g} ،A_u ،B_{3u} ،B_{1g} ،B_{3g} ،B_{2g}. The electron energy of some excited states for the structure of compound 3 in the two symmetries B_{3g} and A_u which have been calculated in the theoretical level B3LYP.6-311++G** (eV) are presented in table (5). In the excited state B_{3g} with the energy of 3.03eV (Figure 8), compared to the excited state A_u with the energy of 2.48eV (Figure 9), there is a PJTE which is seen in Table (1).

The calculated thermodynamic parameters ΔG ،ΔH ،ΔS, ΔE_{el} of the intended compound with the theoretical method B3LYP.6-311++G** are presented in Table (2). The results obtained from this method show that ΔE_{el} of the compound 3 for the symmetry B_{3g} is 11.17 kcal mol⁻ and it is 2.46 kcal mol⁻ which show that the intended compound with symmetry A_u has a lower PJTE in spite of the decrease in energy difference between the basic and excited states.

The values of the angles and distances calculated for compound 3 with the symmetry D_{2h} for both negative frequencies (B_{3g} and A_u) are as follows after being optimized by the theoretical level B3LYP.6-311++G**:

<CSeH = 37.5°, <SeCSe = 134.2°

$R_{Se...H}$ = 1.809° A, R_{CSe} = 1.820° A, R_{C-H} = 1.088° A

The comparison between these two configurations with the symmetries D_{2h} and C_{2h} shows that the lengths of (Se…H) bonds in a formation with symmetry D_{2h} in the two negative frequencies (A_u and B3g) are equal, but they are not equal in the formation C_{2h} which is due to the PJTE.

The results of the B3LYP.6-311++G** calculations for the compounds 1, 2, and 3, show that the main reason behind the formation changes in configurations with high symmetry D_{2h} to configuration with low symmetry C_{2h} is the PJTE. The combination of the basic state A_g and the excited state B_{3g} leads to the PJTE problem $(Ag+B_3g)\otimes b_3g$ Another configuration is the combination of the basic state A_g with the excited state A_u which leads to the PJTE problem $(Ag+Au)\otimes au$. The energy difference (ΔE) between the reference states is reduced from compound 1 to compound 3 (i.e. 7.48, 3.08-4.62, and 2.48-3.03 eV for the compounds 1, 2, and 3, respectively). Therefore, we expect that the PJTE for these formations changes $D_{2h} \rightarrow C_{2h}$ would increase from compound 1 to compound 3. But, since other factors such as the changes in electron energy of the basic state in the symmetric formation $D_{2h} \rightarrow C_{2h}$ and the electron-vibrational coupling constant (J_{e-v}) and the initial force constant from compound 1 to compound 3 must be taken into consideration, so the PJTE stability energy would not be increased.

The comparison between the two configurations with the symmetries D_{2h} and C_{2h} shows that the lengths of (O-H), (S…H), and (Se…H) in a formation with symmetry D_{2h} in all three compounds 1, 2, and 3, are the same. Therefore, these compounds are symmetric, but in a formation with symmetry C_{2h}, the lengths of (O-H), (S…H), and (Se…H) bonds are different in the intended formations. Therefore, these compounds are asymmetric due to the PJTE and all three compounds contain Intermolecular hydrogen bonds.

Conclusion:

The results obtained from the calculation in the theoretical level B3LYP.6–311++G** indicate that the PJTE describe the change in the structures with high symmetry D_{2h} to the structures with low symmetry C_{2h}, for the following compounds:

- methanoic acid dimer (compound 1)
- analog containing S atoms of the methanoic acid dimer (compound 2)
- analog containing Se atoms of the methanoic acid dimer (compound 3)

It was revealed that the formations containing hydrogen bonds in compounds 1 to 3 have a high-symmetry D_{2h} configuration and they are changed from the basic state and high-symmetry D_{2h} into the excited and low-symmetry C_{2h} configuration. It brings about the decrease in electron energy of the electron configuration of the basic states and the increase in the electron energy of the electron configuration of the excited states. In the current study, it was argued that the combination of the electron basic state with the electron excited state for application of the normal coordinates can describe the change from the high symmetry to the low symmetry. Therefore, the distortion of high-symmetry D_{2h} formation has a hydrogen bond, and it is as $(Ag+B_3g)\otimes b_3g$ in the compounds 1 to 3. Also, the energy difference from 1 to 3 (i.e. 7.48, 3.08-4.62, and 2.48-3.03 eV for the methanoic acid dimer, and analogs with S and Se atoms, respectively) is decreased. In addition, the investigation of the PJTE for $D_{2h} \rightarrow C_{2h}$ formation changes shows that the PJTE stability energy is reduced from 1 to 3, and is increased from 1 to 2·

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