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A theoretical investigation on intramolecular hydrogen-atom transfer in curcumin

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Abstract

Intramolecular H-atom-transfers (IHTs) in curcumin (enol) and its mimic, 1,6-heptadiene-3,5-dione (enol), in ground state and excited state were investigated by ab initio and CIS methods in this paper. It is revealed that double *ortho*-methoxy-phenolic rings have little effect on the IHT barrier of curcumin, and the IHT barrier of curcumin in ground state is much lower than those of other IHT models, such as 9-hydroxyphenalen-1-one and perylenequinonoid pigments. More interestingly, the IHT barrier of 1,6-heptadiene-3,5-dione (enol) in the singlet excited state is nearly 25 kJ/mol higher than that in the ground state, which is very unique in IHT phenomenon. The unexpected IHT behavior of 1,6-heptadiene-3,5-dione (enol) is explained in terms of O–O distance, charge variation of H-atom, and flexibility of the structure.
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1. Introduction

Curcumin (Fig. 1) is a natural phenolic pigment found in the rhizomes of curcuma longa, an Indian spice known as turmeric [1,2]. Various remarkable pharmacological activities, such as anti-inflammatory, anti-carcinogenic and anti-proliferative activities, have been recognized for the pigment [3–9]. In addition, curcumin has been considered as an excellent free radical scavenger, which was mainly attributed to the methoxy phenolic moiety [10–18].

The excellent photosensitizing activity of curcumin has been known for a long while. It can induce photo-killing of bacteria and has also been used as skin protector against melanoma and other skin diseases [19–22]. As the photo-toxicity was found to increase in the presence of oxygen, it was proposed that the formation of reactive oxygen species (ROS), like hydroxyl radical, singlet oxygen, superoxide radical, etc. was mainly responsible for its activity.

The excited photophysics of curcumin is mainly controlled by the diketone moiety. The β-diketone moiety of curcumin undergoes keto-enol tautomerism, where an intramolecular H-atom-transfer (IHT) takes place between the two oxygen atoms of the diketo group [23–25]. Since IHT is one of the most basic chemical reactions, it has aroused much interest [26–28]. It has been found that some excellent photosensitizers, such as perylenequinones and anthraquinones [29–32], exhibit IHT in ground and excited states. However, little is known about the IHT in curcumin. In this paper, ab initio and CIS methods have been employed to investigate the IHT of curcumin and its mimic, 1,6-heptadiene-3,5-dione (enol) (Fig. 1), in the ground and excited states. The results will shed light on the curcumin's IHT mechanisms and give more insight into the important chemical reaction, H-atom-transfer.

2. Methods

Initial structures for all isomers and transition states were obtained with the semi-empirical AM1 method [33]. Using

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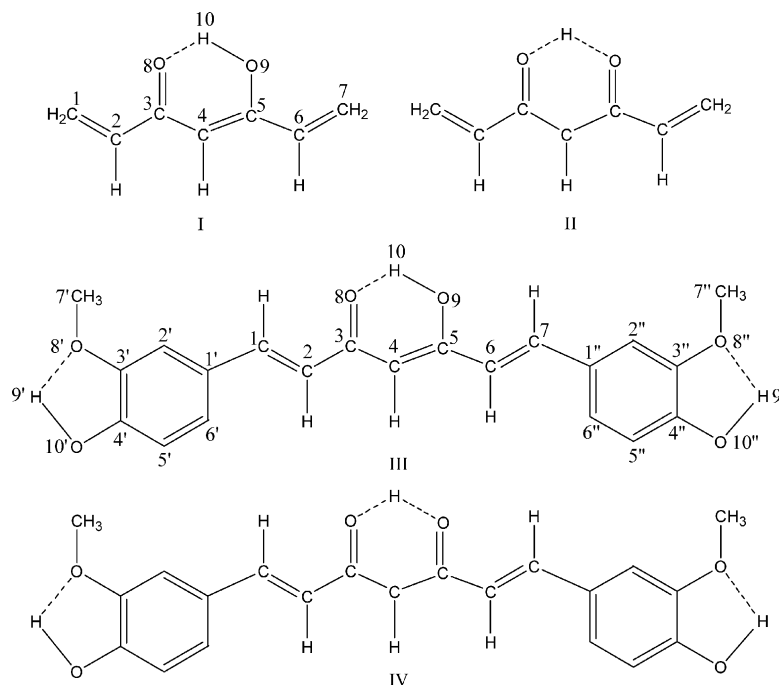*E-mail address:* zhanghy@sdut.edu.cn (H.-Y. Zhang).

Fig. 1. Molecular structures of 1,6-heptadiene-3,5-dione (enol) (I), curcumin (enol) (III) and corresponding transition states (II and IV).

these structures as starting points, the geometries in the ground state were then fully optimized at the restricted Hartree–Fock level with different basis sets including 6-31G, 6-31G(d) and 6-31G(d,p). The configuration interaction single-excitations (CIS) method with the spin-restricted Hartree–Fock reference ground state was employed to optimize the singlet-excited-state geometries [34]. The effectiveness of the CIS method has been verified in previous studies that it provided a qualitatively correct characterization on the excited-state-IHT process [35,36]. All located transition states exhibited one normal imaginary frequency with a transition vector corresponding to the motion of H-atom during the IHT process. All of the calculations were achieved with GAUSSIAN 98 package of programs [37].

3. Results and discussion

The IHT barriers of curcumin (enol) and its mimic, 1,6-heptadiene-3,5-dione (enol), in the ground state and excited state were calculated on different basis sets and were listed in Tables 1 and 2. It can be found that the barriers do not sensitively depend on the basis set, especially the difference between 6-31G and 6-31G(d) is approximately 1 kJ/mol. This implies that the medium basis set could give acceptable IHT barriers, which will be of significance in studying the IHT of larger molecules

3.1. IHT in ground state

As shown in Table 1, the IHT barriers of curcumin are about 20 kJ/mol, much lower than those of other typical IHT

models, such as 9-hydroxyphenalen-1-one (9-HPO) and perylenequinonoid pigments (PQPs), in which the IHT barriers are 35–40 kJ/mol [38–42]. Therefore, the IHT in curcumin will be much faster than those in 9-HPO or PQDs. In addition, it is interesting to note that the IHT barriers of 1,6-heptadiene-3,5-dione (enol) calculated by different methods are 2–3 kJ/mol lower than those of curcumin (Table 1), suggesting that the IHT barrier of curcumin is little influenced by both *ortho*-methoxy phenolic rings. Therefore, it seems the IHT in curcumin is localized at the six-number ring of C3, C4, C5, O8, O9 and H10, which is supported by the geometries and Mulliken charge

Table 1
Different-methods-calculated total electronic energies (TE, in hartree) and zero point vibrational energies (ZPVEs, in hartree) of 1,6-heptadiene-3,5-dione (enol) (I), curcumin (enol) (III) and corresponding transition states (TS) in the ground state and the derived IHT barriers (ΔE, in kJ/mol) of I and III

Molecule	TE	ZPVE	ΔE
I[a]	−419.2441936	0.1458130	
TS(I)[a]	−419.2291801	0.1408900	26.84
III[a]	−1255.5022110	0.4017400	
TS(III)[a]	−1255.4885840	0.3968130	23.19
I[b]	−419.4135305	0.1452240	
TS(I)[b]	−419.3985948	0.1401690	26.30
III[b]	−1255.9981832	0.4002530	
TS(III)[b]	−1255.9843119	0.3951780	23.45
I[c]	−419.4328547	0.1448280	
TS(I)[c]	−419.4200718	0.1398920	20.95
III[c]	−1256.0474698	0.3992170	
TS(III)[c]	−1256.0357032	0.3942520	18.21

[a] Calculated by HF/6-31G.
[b] Calculated by HF/6-31G(d).
[c] Calculated by HF/6-31G(d,p).

Table 2

Different-methods-calculated total electronic energies (TE, in hartree) and zero point vibrational energies (ZPVEs, in hartree) of 1,6-heptadiene-3,5-dione (enol) (I) and corresponding transition state (II) in the singlet excited state and the derived IHT barriers (ΔE, in kJ/mol)

	TE	ZPVE	ΔE
I[a]	−419.2355819	0.1419600	
II[a]	−419.2107454	0.1368770	52.22
I[b]	−419.4040772	0.1408800	
II[b]	−419.3802325	0.1363970	51.15
I[c]	−419.4232097	0.1404900	
II[c]	−419.4022287	0.1360940	43.86

[a] Calculated by CIS/6-31G.
[b] Calculated by CIS/6-31G(d).
[c] Calculated by CIS/6-31G(d,p).

populations of ground state and transition state. As shown in Table 3, during the IHT processes, the bond lengths of C3–C4, C4–C5, C5–O9, O9–H10, O8–H10 and C3–O8 varied drastically, while the lengths of other bonds change

Table 3

HF/6-31G(d,p)-calculated ground-state bond lengths (R, in Å), bond angles (A, in degree) and dihedral angles (D, in degree) of curcumin (enol) and corresponding transition state

	Curcumin (enol)	Transition state
$R(C_1–C_2)$	1.33	1.33
$R(C_2–C_3)$	1.48	1.47
$R(H_{10}–O_8)$	1.76	1.18
$R(O_8–C_3)$	1.22	1.27
$R(C_3–C_4)$	1.45	1.40
$R(C_4–C_5)$	1.36	1.40
$R(C_5–O_9)$	1.32	1.27
$R(O_9–H_{10})$	0.96	1.18
$R(O_8–O_9)$	2.60	2.32
$R(C_5–C_6)$	1.46	1.47
$R(C_6–C_7)$	1.33	1.33
$R(C_{1'}–C_{2'})$	1.40	1.40
$R(C_{2'}–C_{3'})$	1.38	1.38
$R(C_{3'}–C_{4'})$	1.40	1.40
$R(C_{4'}–C_{5'})$	1.38	1.38
$R(C_{5'}–C_{6'})$	1.38	1.38
$R(C_{6'}–C_{1'})$	1.39	1.39
$R(C_{3'}–O_{8'})$	1.36	1.36
$R(O_{8'}–C_{7'})$	1.40	1.40
$R(O_{8'}–H_{9'})$	2.13	2.13
$R(C_{4'}–O_{10'})$	1.34	1.34
$R(O_{10'}–H_{9'})$	0.95	0.95
$R(C_{1'}–C_1)$	1.47	1.47
$R(C_7–C_{1''})$	1.47	1.47
$R(C_{1''}–C_{2''})$	1.40	1.40
$R(C_{2''}–C_{3''})$	1.38	1.38
$R(C_{3''}–C_{4''})$	1.40	1.40
$R(C_{4''}–C_{5''})$	1.38	1.38
$R(C_{5''}–C_{6''})$	1.38	1.38
$R(C_{6''}–C_{1''})$	1.39	1.39
$R(C_{3''}–O_{8''})$	1.36	1.36
$R(O_{8''}–C_{7''})$	1.40	1.40
$R(O_{8''}–H_{9''})$	2.13	2.13
$R(C_{4''}–O_{10''})$	1.34	1.34
$R(O_{10''}–H_{9''})$	0.95	0.95
$A(C_1C_2C_3)$	120.46	121.11
$A(C_2C_3C_4)$	117.01	120.75

Table 3 (continued)

	Curcumin (enol)	Transition state
$A(H_{10}O_8C_3)$	100.64	102.92
$A(O_8C_3C_4)$	121.99	119.98
$A(C_3C_4C_5)$	121.75	117.05
$A(C_4C_5O_9)$	122.97	119.98
$A(C_5O_9H_{10})$	108.40	102.92
$A(O_9H_{10}O_8)$	144.26	157.16
$A(C_4C_5C_6)$	121.67	120.75
$A(C_5C_6C_7)$	122.57	121.11
$A(C_{6'}C_{1'}C_{2'})$	118.43	118.45
$A(C_{1'}C_{2'}C_{3'})$	120.92	120.91
$A(C_{2'}C_{3'}C_{4'})$	119.89	119.89
$A(C_{3'}C_{4'}C_{5'})$	119.61	119.62
$A(C_{4'}C_{5'}C_{6'})$	120.33	120.33
$A(C_{5'}C_{6'}C_{1'})$	120.82	120.81
$A(C_{6'}C_{1'}C_1)$	123.62	123.63
$A(C_{1'}C_1C_2)$	128.13	127.89
$A(C_6C_7C_{1''})$	127.28	127.89
$A(C_7C_{1''}C_{6''})$	123.61	123.63
$A(C_{6''}C_{1''}C_{2''})$	119.93	119.89
$A(C_{1''}C_{2''}C_{3''})$	120.92	120.91
$A(C_{2''}C_{3''}C_{4''})$	118.40	118.40
$A(C_{3''}C_{4''}C_{5''})$	120.82	120.81
$A(C_{4''}C_{5''}C_{6''})$	120.36	120.33
$A(C_{5''}C_{6''}C_{1''})$	119.26	119.62
$D(C_1C_2C_3C_4)$	179.96	180.00
$D(O_8C_3C_4C_5)$	0.03	0.00
$D(C_3C_4C_5O_9)$	−0.02	0.00
$D(C_4C_5O_9H_{10})$	0.00	0.00
$D(C_5O_9H_{10}O_8)$	0.00	0.00
$D(O_9H_{10}O_8C_3)$	0.00	0.00
$D(H_{10}O_8C_3C_4)$	0.00	0.00
$D(C_4C_5C_6C_7)$	179.86	−180.00
$D(C_{2'}C_{3'}O_{8'}C_{7'})$	−0.01	0.01
$D(C_{4'}C_{3'}O_{8'}H_{9'})$	0.00	0.00
$D(C_{3'}C_{4'}O_{10'}H_{9'})$	0.00	0.30
$D(C_{1'}C_1C_2C_3)$	−180.00	180.00
$D(C_5C_6C_7C_{1''})$	179.84	−180.00
$D(C_{2''}C_{3''}O_{8''}C_{7''})$	0.09	−0.01
$D(C_{4''}C_{3''}O_{8''}H_{9''})$	0.00	0.00
$D(C_{3''}C_{4''}O_{10''}H_{9''})$	−0.03	0.00

little. On the other hand, the Mulliken charge populations indicate that the charges on the atoms of two *ortho*-methoxy phenolic rings keep the same during the IHT process, while the charges on the atoms of the six-number ring change a lot (Fig. 2). Thus, it is clear that both *ortho*-methoxy phenolic rings do not participate in the IHT of curcumin. As we failed to optimize the excited-state structures of curcumin, this finding provides an opportunity to investigate the excited-state IHT of curcumin by using 1,6-heptadiene-3,5-dione (enol) as a model.

3.2. IHT in singlet excited state

As the enol group gets more acidic and keto group gets more basic in singlet excited state than in ground state [43], there is a common notion that IHT between double oxygens will be facilitated in singlet excited state For instance, the IHT barriers of model compounds decrease by
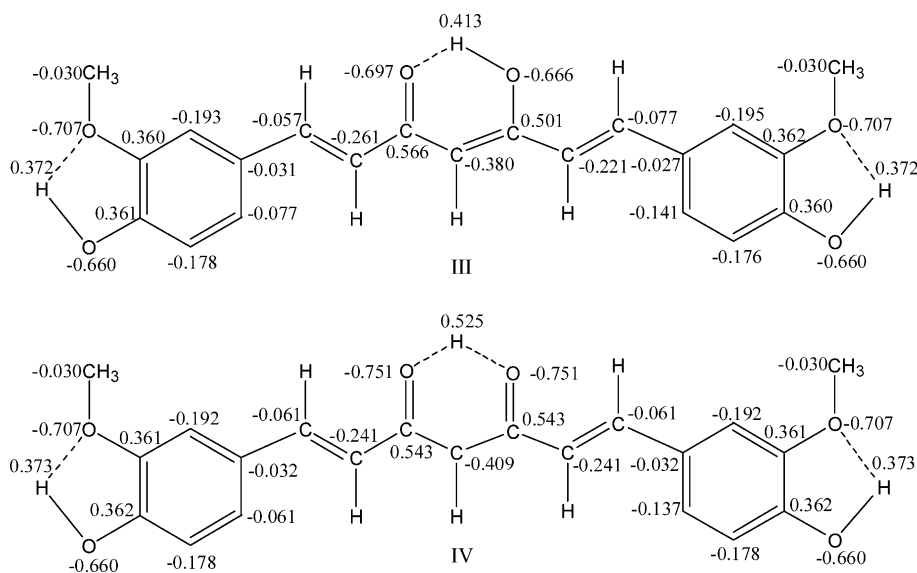
Fig. 2. Mulliken charge populations at atoms of curcumin (enol) (III) and its transition state (IV) in the ground state (S_0), calculated by HF/6-31G (d,p).

10–30 kJ/mol in singlet excited state [32,39,41], in comparison with those in ground state. However, as shown in Table 2, the IHT barriers of 1,6-heptadiene-3,5-dione (enol) in the excited state are 40–50 kJ/mol, approximately 25 kJ/mol higher than those in ground state, just opposite to the common notion. It is thus very interesting to explore the reason underlying the abnormal IHT barrier of 1,6-heptadiene-3,5-dione (enol).

According to the IHT theory, the O–O distance is critical in determining the IHT barrier, that is, the shorter the distance is, the lower the barrier [44–46]. In contrast to the O–O distance in PQPs [39], the O8–O9 distance in excited state of 1,6-heptadiene-3,5-dione (enol) (2.81 Å, Table 4) is longer than that in ground state (2.68 Å, Table 4), which provides a partial explanation to the unexpected IHT barrier of 1,6-heptadiene-3,5-dione (enol). Furthermore, the abnormal behavior of IHT can be explained in terms of the charge variation on the H-atom during the IHT process, because it has been revealed that IHT barrier correlates well with the charge variation of H-atom, i.e. the higher the charge increment at the H-atom is, the higher the barrier [39–42,47]. From Table 5, it can be seen that the H-atom-charge increment during the IHT of 1,6-heptadiene-3,5-dione in excited state (35.5%) is unequivocally higher than

Table 4
Theoretically calculated bond lengths (R, in Å), bond angles (A, in degree) and dihedral angles (D, in degree) of 1,6-heptadiene-3,5-dione (enol) (I) and corresponding transition state (II) in ground and singlet excited states

	I[a]	II[a]	I[b]	II[b]
$R(H_{10}–O_8)$	1.78	1.18	2.06	1.19
$R(O_8–C_3)$	1.22	1.26	1.26	1.28
$R(C_3–C_4)$	1.45	1.40	1.46	1.44
$R(C_4–C_5)$	1.35	1.40	1.34	1.44
$R(C_5–O_9)$	1.32	1.26	1.34	1.28
$R(O_9–H_{10})$	0.96	1.18	0.94	1.19
$R(O_8–O_9)$	2.62	2.32	2.81	2.34
$A(H_{10}O_8C_3)$	100.67	102.99	100.69	103.37
$A(O_8C_3C_4)$	122.25	120.28	119.93	117.11
$A(C_3C_4C_5)$	121.65	116.69	127.18	117.79
$A(C_4C_5O_9)$	123.52	120.28	125.66	117.11
$A(C_5O_9H_{10})$	108.78	102.99	112.31	103.37
$A(O_9H_{10}O_8)$	143.13	156.77	134.24	156.60
$D(O_8C_3C_4C_5)$	0.01	0.00	0.00	10.52
$D(C_3C_4C_5O_9)$	0.03	0.00	0.00	10.52
$D(C_4C_5O_9H_{10})$	0.02	0.00	0.01	−17.55
$D(C_5O_9H_{10}O_8)$	0.00	0.00	−0.30	10.12
$D(O_9H_{10}O_8C_3)$	0.00	0.00	0.00	10.12
$D(H_{10}O_8C_3C_4)$	0.00	0.00	0.00	−17.55

[a] Ground state, calculated by HF/6-31G (d,p).
[b] Singlet excited state, calculated by CIS/6-31G (d,p).

Table 5

Mulliken charge populations at atoms of 1,6-heptadiene-3,5-dione (enol) (I) and corresponding transition state (II) in the ground state (S_0) and singlet excited state (S_1), calculated by HF/6-31G (d,p) and CIS/6-31G (d,p), respectively.

atom	S_0		S_1	
	I	II	I	II
O8	−0.673	−0.733	−0.675	−0.744
O9	−0.655	−0.733	−0.659	−0.744
H10	0.412	0.527	0.392	0.531

that during the IHT in ground state (27.9%), in good agreement with the higher IHT barrier in the former state. Whereas in PQPs, the H-atom-charge increment during the IHT in excited state is lower than that in ground state [39,47].

Comparing the structure of 1,6-heptadiene-3,5-dione (enol) with those of PQPs, it can be found that they hold the same IHT center, namely, a six-number ring consisting of three carbons, two oxygens and one H-atom. However, PQPs have a rigid conjugation system, which will limit the IHT in a plane, but 1,6-heptadiene-3,5-dione (enol) has no such a structure. As a result, although the IHT in ground state of 1,6-heptadiene-3,5-dione (enol) may occur in a plane, the IHT in excited state may be out of the plane, because the double bond can get flexible in excited state [48]. This is supported by the distorted geometry of 1,6-heptadiene-3,5-dione (enol) in excited-transition state. As shown in Table 4, the dihedral angles of excited-transition state are around $\pm 10°$, in contrast to those in ground state that are zero. Apparently, the flexibility of excited state provides deeper insight into the unique IHT behavior of 1,6-heptadiene-3,5-dione (enol). We hope this novel finding will spur the interest of experimentalists, who can verify it by transient spectrum technique.

4. Conclusion

HF and CIS methods with different basis sets have been employed to study the IHT of curcumin (enol) and its mimic, 1,6-heptadiene-3,5-dione (enol), in the ground state and excited state. It was revealed that the IHT behaviors of curcumin or 1,6-heptadiene-3,5-dione (enol) are much different from those of other IHT models, such as 9-HPO and PQPs. First, the IHT barriers in ground state of the former molecules are rather lower than those of the latters. Second, the IHT barrier of 1,6-heptadiene-3,5-dione (enol) in the singlet excited state is much higher than that in the ground state, which is opposite to the IHT of PQPs. The unexpected IHT behavior of 1,6-heptadiene-3,5-dione (enol) can be understood in terms of O–O distance, charge variation of H-atom, and flexibility of the structure. As double *ortho*-methoxy-phenolic rings have little effect on the IHT barrier of curcumin, we believe that the reversed

IHT barrier in excited state also can be observed for curcumin.

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