Monatshefte für Chemie 132, 223–233 (2001)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

An *ab initio* Study of the Rotamers and Rotations of Propane-1,3-dial by DFT and SCF Calculations

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Summary. Eight planar rotamers of the enol form of malonaldehyde were considered at the HF (*Hartree-Fock*) and DFT (density functional theory) levels with 6-311G** and D95** (*Dunning/Huzinaga* full double-ζ) basis sets with the aim to establish the most stable of them and to find the energy barriers of their conversions. The results show that the rotamer with an intramolecular hydrogen bond is the most stable one. High energy barriers were ascertained for the conversions including rotations around a CC double bond. Most of the reactions connected with breaking of the hydrogen bond display strongly asymmetric energy barriers. Their transition states were determined as first-order saddle points because of one imaginary frequency in the IR spectrum related with a negative energy gradient.

Keywords. *ab initio* Calculations; Density Functional Theory; Malonaldehyde; Rotamers; Transition states.

Introduction

Propane-1,3-dial (**1**, malonaldehyde) is a compound with interesting properties with respect to the possibility to exist in two forms (enol and diketone). It is the simplest representative of the β-diketones and is unstable at ambient temperature and pressure. Therefore, mainly theoretical investigations are known so far for this compound including different methods and programs. In the past, predominantly semiempirical quantum chemical methods such as AM1, MNDO [1–3], and, to a minor extent, *ab initio* methods [4–8] have been used. Recently, however, *ab initio* techniques have improved the results for the electronic structure and the different modes of motions of molecules; hence they are preferred in this work. Our recently published papers [9, 10] report on the keto-enol equilibrium of **1** using the self-consistent field theory (SCF) and the 6-311G** basis set. In Ref. [9], the rotations have been performed varying a specific dihedral angle for the given rotamer from 0 to 180°. Therefore, the transition states of the separate rotations are unknown. The energy barriers were found as the difference between the point with highest energy and that corresponding to certain rotamers.

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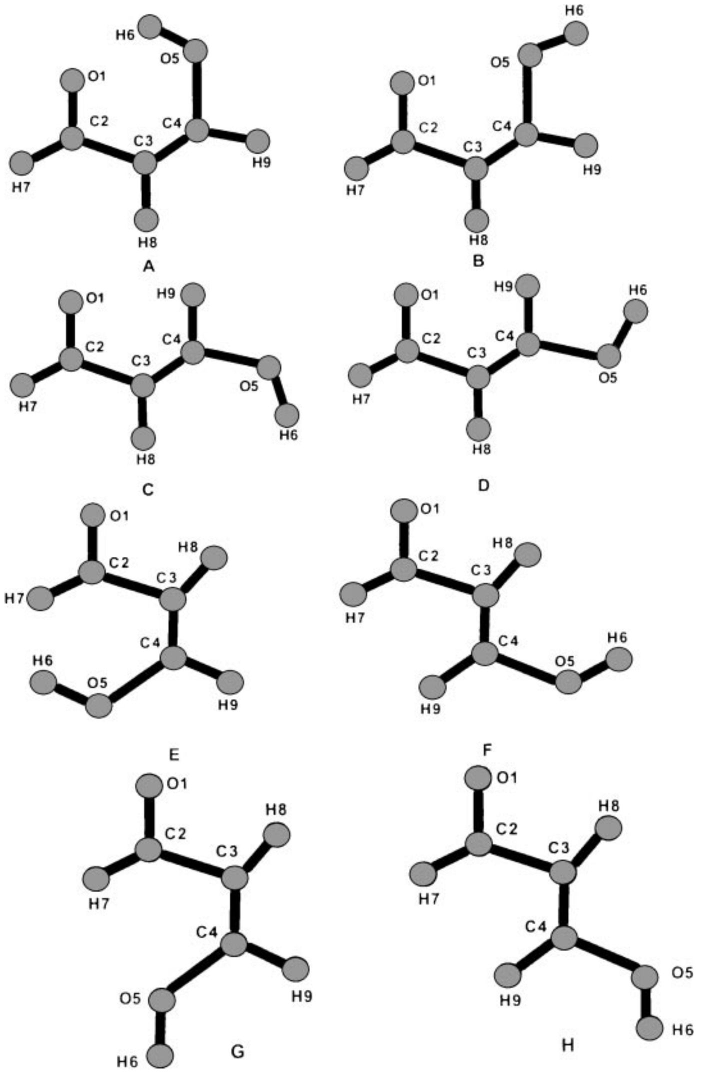
A theoretical study of the structure and the force constants of **1**, acetylacetone, and some other methyl derivatives of **1** has been presented by *Chiavassa et al.* [11, 12]. The geometry and the force constants have been used to build the force field of **1** with a complete set of 24 internal coordinates [11]. The proton transfer in the ground and first excited triplet states have been investigated by means of *ab initio* calculations to deduce the energy barriers of the reaction in different states and between the three enol forms of **1** [13, 14]. It has been shown that the energies of the excited states are strongly affected by inclusion of electron correlation. Excitation energies are markedly reduced, especially for the 6-311G** basis, as are the spacings between the levels [14].

Several planar conformers are possible for **1** (Scheme 1) where the rotamer with an intramolecular hydrogen bond has been proved to be the most stable one [1]. Its extraordinary stability is related to the formation of a cyclic pseudoaromatic



Scheme 1

structure. The relative stability of the other rotamers is not known. Since some of the rotamers may play an important role in keto-enol conversions, it is of interest to know their properties in detail.

The first task of our work was to find transition states of different rotations of the enol forms of **1** and to estimate the energy barriers of all examined rotations by means of DFT and SCF methods at 6-311G** and D95** basis sets [15]. Then the results obtained by combinations of the methods and basis sets HF/6-311G**, BLYP/6-311G**, and B3LYP/D95** were compared. BLYP is a combination of *Becke* exchange and LYP correlation functional, whereas B3LYP is a combination between *Becke*'s 3-parameter hybrid functional and the LYP correlation functional.

Results and Discussion

As mentioned above, all rotamers of the enol form of **1** were optimized in their singlet ground states with zero charge, and interaction between separated molecules were neglected. The results from all methods and basis sets show that the rotamer A is the most stable one, probably because of the stabilization of the intramolecular hydrogen bond. The results for the energies are presented in Table 1.

Best results were obtained using B3LYP/D95**; the values are different from those obtained by BLYP/6-311G**, and far apart from those provided by HF/6-311G**. With all methods and basis sets it was established that the rotamers are planar and of low symmetry (C_S).

Since rotamer A is the most stable one, it was interesting to predict its IR spectrum. Unfortunately, we could not compare the results with experimental ones

Table 1. Electron energies and zero-point level energies of the rotamers of **1**; all relative energies (in a. u.) were calculated as the difference between the energy of the corresponding rotamer and the energy of rotamer A; *ZPC* = zero-point correction

Rotamer	Relative energies (E) and zero-point corrected relative energies ($E^\circ = E + ZPC$)		
	HF/6-311G**	BLYP/6-311G**	B3LYP/D95**
A E	0.0 (−265.70629)	0.0 (−267.16520896)	0.0 (−267.2105511)
E°	0.0 (−265.633143)	0.0 (−267.10002)	0.0 (−267.143049)
B E	0.0185	0.0227	0.0239
E°	0.0173	0.0220	0.0232
C E	0.0090	0.0148	0.0158
E°	0.0081	0.0144	0.0153
D E	0.0110	0.0164	0.0174
E°	0.0097	0.0157	0.0168
E E	0.0131	0.0171	0.0174
E°	0.0121	0.0164	0.0169
F E	0.0079	0.0136	0.0140
E°	0.0068	0.0130	0.0134
G E	0.0125	0.0189	0.0192
E°	0.0112	0.0181	0.0184
H E	0.0114	0.0163	0.0171
E°	0.0099	0.0154	0.0162

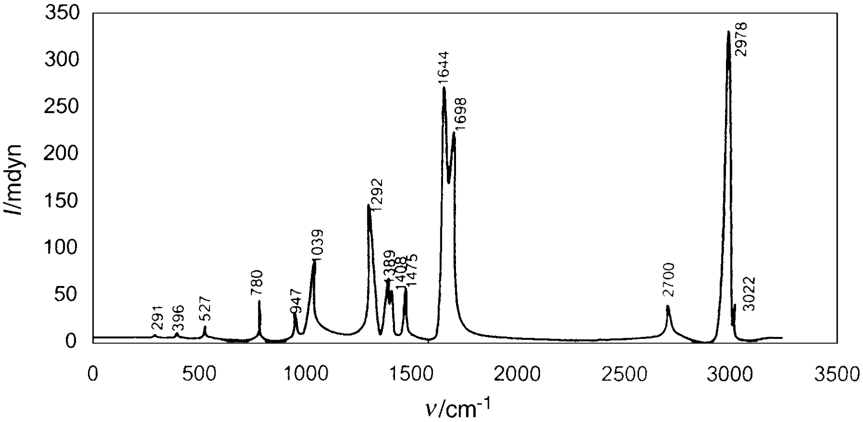


Fig. 1. Simulated IR spectrum of rotamer A of **1**

because it was mentioned above that **1** doesn't exist in a free state. The simulated IR spectrum obtained from B3LYP as the best method is presented in Fig. 1.

The most intensive line at 2978 cm^{-1} corresponds to the HO bond vibration. The H-bond shifts the characteristic OH vibration toward smaller wavenumbers as compared with primary hydroxyl derivatives where this vibration is found in a broad interval at about 3400 cm^{-1}. It should be mentioned that the frequencies from the calculations were not multiplied with any coefficient.

The low value for the OH vibration in our case proved the strong influence of the H-bond. The double-split line is due to C=O and C=C stretching vibrations, where the high frequency line is assigned to the symmetric vibration and the lower one to the asymmetric one. The small peaks at 1389, 1408, and 1475 cm^{-1} correspond to ν(C=O and C=C), ν(C–O), and $\delta(CCH_3)$ vibrations, and the last line to ν(C–O) and $\delta(H_8CCH_9)$. The third-most intensive line consists of pure ν(C–O), and the peaks at 1039, 947, and 780 cm^{-1} represent the deformational vibrations $\delta(H_6OCH_9)$, a mixed vibration, and $\delta(CCH_8)$. The difference between ν_{as}(C=O) and ν_{as}(C=C) is smaller for frequencies obtained with the B3LYP and HF calculations (1712 cm^{-1}, $\Delta\nu = 14\,cm^{-1}$) than for those provided by B3LYP and BLYP (1612 cm^{-1}, $\Delta\nu = 77\,cm^{-1}$). For ν_s(C=O) and ν_s(C=C), the differences were 74 and 62 cm^{-1} (HF: 1570 cm^{-1}; BLYP: 1582 cm^{-1}) and inverse to those stated before. Bearing in mind that ν(C=O) varies in a broad interval, the obtained results can be considered satisfactory.

In the present work the intermediate complexes of the rotational reactions A↔B, A↔C, A↔E, C↔D, E↔F, E↔G, F↔H, and G↔H were calculated. The energies of the transition states and energy barriers of the rotations are presented in Table 2. It can be seen that conversions related with a rotation about a partial double bond have high energy barriers for the forward and reverse reactions, because in these rotations a rather big fragment of the molecule is involved. The double bond is situated in the middle of the molecule, and during the rotation the conjugation of π-electrons breaks, thus increasing the potential energy. The disturbance of the conjugation is connected with a shortening of the C=C and C=O bonds, whereas the single bonds decrease in order and get longer. This is not valid for rotations related

Table 2. Energy characteristics of the transition states and the separate rotations of **1**

Rotation	Relative Energies			E_{forward} ($\text{kJ} \cdot \text{mol}^{-1}$)			E_{reverse} ($\text{kJ} \cdot \text{mol}^{-1}$)			$E^{\circ}_{\text{forward}}$ ($\text{kJ} \cdot \text{mol}^{-1}$)			$E^{\circ}_{\text{reverse}}$ ($\text{kJ} \cdot \text{mol}^{-1}$)		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
A↔B	0.0060	0.0050	0.0059	64	87	85	15	27	23	56	80	79	11	23	18
A↔C	0.0751	0.0633	0.0700	245	240	254	221	201	212	236	230	244	215	192	204
A↔E	0.0072	0.0065	0.0065	67	90	87	32	46	41	61	85	82	30	42	38
C↔D	0.0016	0.0018	0.0023	28	39	34	23	35	30	24	34	30	20	30	26
E↔F	0.0872	0.0650	0.0754	242	200	222	256	209	231	235	191	213	249	200	222
E↔G	0.0012	0.0012	0.0014	16	32	28	18	27	23	13	28	24	15	23	20
G↔H	0.1032	0.0750	0.0882	286	222	251	289	228	257	278	212	242	281	218	248
F↔H	0.0 (−265.68805)	0.0 (−267.137266)	0.0 (−267.184007)	27	38	33	18	31	25	23	33	29	15	27	21

All relative energies (in a. u.) were calculated as the difference between the energy of the most stable transition state and the energy of corresponding state; 1 HF/6-311G** 2 BLYP/6-311G** 3 B3LYP/D95**

with the change of the dihedral angle H(6)O(5)C(4)C(3), because they include the motion of H(6) only. Therefore, they have the lowest energy barriers.

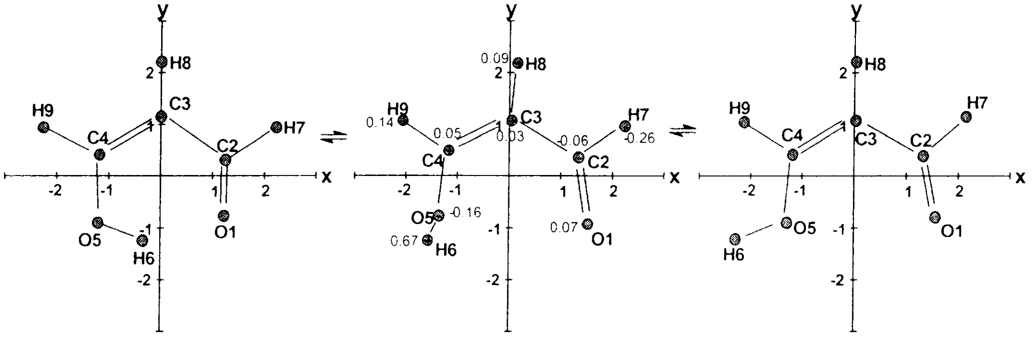
Rotations A↔B, C↔D, E↔G, F↔H

All rotations are connected with a change in the H(6)O(5)C(4)C(3) dihedral angle from 0 to 180° or with the rotation round the C–O bond which includes only the movement of H(6). The first rotation corresponds to a breaking of the intramolecular hydrogen bond, and since it forms the unstable rotamer B, the barrier is strongly asymmetric. According to B3LYP results, the barrier of the reverse reaction is about 3.6 times lower than that of the forward one. Comparatively low and symmetric, however, is the energy barrier of the rotation C↔D because of the small difference in the energies of both rotamers (about $4\,\text{kJ} \cdot \text{mol}^{-1}$ calculated with B3LYP and BLYP, app. $5\,\text{kJ} \cdot \text{mol}^{-1}$ with HF). Although the two DFT results suggest different values for the absolute energies of the rotamers, the calculated relative energy differences are nearly the same (see also Table 2).

The A↔B conversion (Fig. 2) leads to a breaking of the O···H bond as confirmed by the values of this distance in enol A, transition state, and enol B of 1.6118, 3.1982, and 3.8639 Å. The angle H(6)O(5)C(4)C(3), which is the main reaction coordinate, changes from 0° in enol A through 103.23° in the transition state to 180° in enol B (B3LYP).

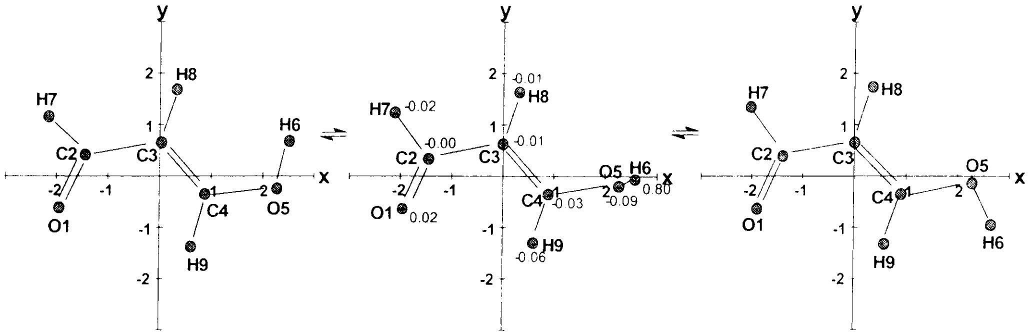
Rotamer C could be obtained from rotamer A by a rotation around the C=C double bond. Rotamer C easily transforms into rotamer D (Fig. 3) by rotation about the C–O single bond or by a change of the dihedral angle H(6)O(5)C(4)C(3) from 0° in enol C through 88.72° in the transition state to 180° in rotamer D according to B3LYP calculations. The other two methods give the same results for the main reaction coordinate H(6)O(5)C(4)C(3).

The other two rotations are connected with a maximal removal of H(6) from C(3) and O(1), rendering the probability for through-space H transfer between O(5) and C(3) very small. Therefore, a keto-enol conversion connected with a motion



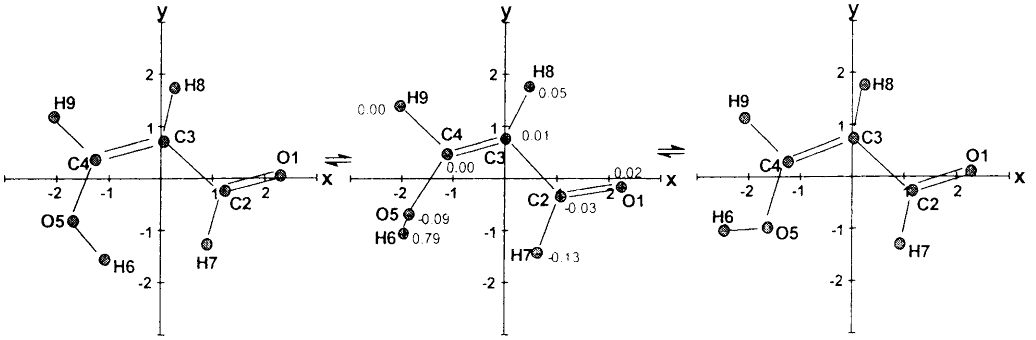
ROTAMER A TRANSITION STATE (TS) ROTAMER B

Fig. 2. Rotation A→B



ROTAMER C TRANSITION STATE (TS) ROTAMER D

Fig. 3. Rotation C→D



ROTAMER E TRANSITION STATE (TS) ROTAMER G

Fig. 4. Rotation E→G

of H(6) through the space in rotamers G and H cannot occur. The angles H(6)O(5)C(4)C(3) in the transition states according to B3LYP calculations are 86.59° for E↔G and 89.84° for F↔H.

All transition states have a non-planar structure and were determined as first order saddle points. In the calculated IR spectrum of each compound there were 38

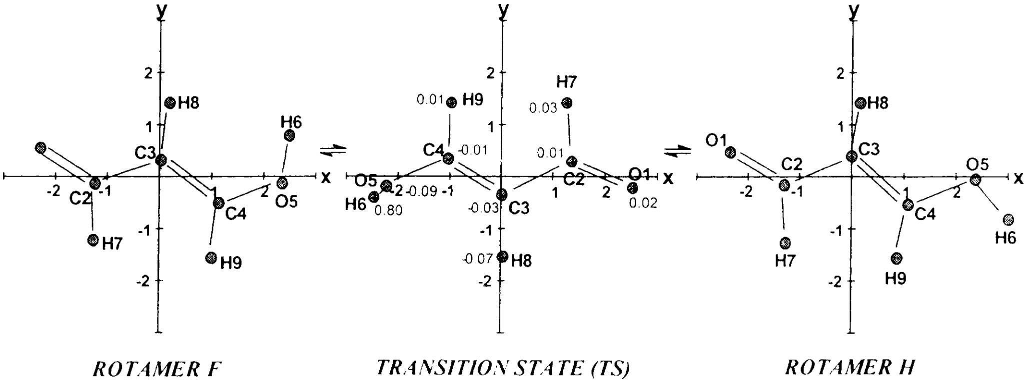


Fig. 5. Rotation F→H

Table 3. Imaginary frequencies (cm^{-1}) and distances (Å) for the transition states of **1**

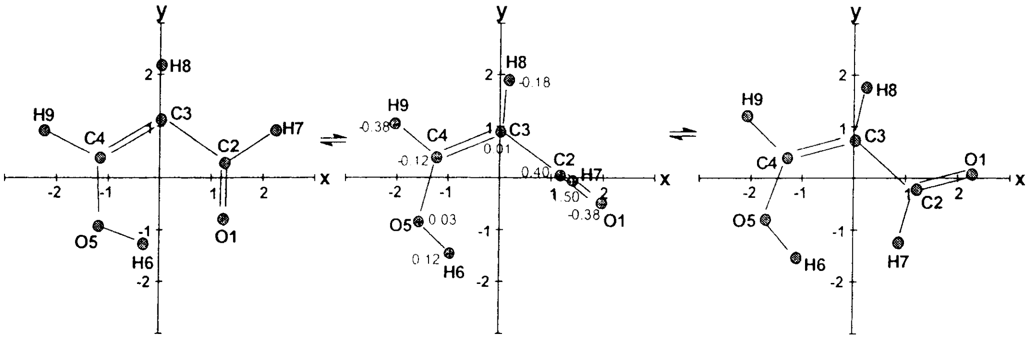
Rotation	HF/6-311G**			BLYP/6-311G**			B3LYP/D95**		
	IF	$C_3 \cdots H_6$	$O \cdots H$	IF	$C_3 \cdots H_6$	$O \cdots H$	IF	$C_3 \cdots H_6$	$O \cdots H$
A↔B	−397	2.9061	3.2000	−600	2.9369	3.1560	−552	2.9433	3.1982
A↔C	−589	2.3567	3.3668	−1359	2.3636	3.7127	−1434	2.3289	3.5874
A↔E	−172	2.5112	3.1148	−248	2.5290	3.0929	−227	2.5236	3.0890
C↔D	−431	2.7793	4.6187	−597	2.8580	4.7322	−545	2.8395	4.7038
E↔F	−837	2.3310	4.3361	−1385	2.3622	4.3063	−1671	2.3283	4.3427
E↔G	−240	2.7595	4.2548	−527	2.8547	4.4291	−481	2.8412	4.3998
G↔H	−1206	3.1717	5.2668	−1722	3.2062	5.3545	−2688	3.2026	5.3554
F↔H	−397	2.7939	5.0831	−566	2.8618	5.1926	−509	2.8500	5.1733

real frequencies and one imaginary eigenvalue (Table 3) which can be connected with the reaction coordinate. According to classical theory, the transition state has one vibrational mode less than the initial or final compound. Therefore, the motion from the transition state toward the enols is connected with a negative gradient of the potential energy. The distances O···H and C(3)···H(6) in Table 3 are approximately the same as ascertained with the three methods.

Rotations A↔C, A↔E, E↔F, G↔H

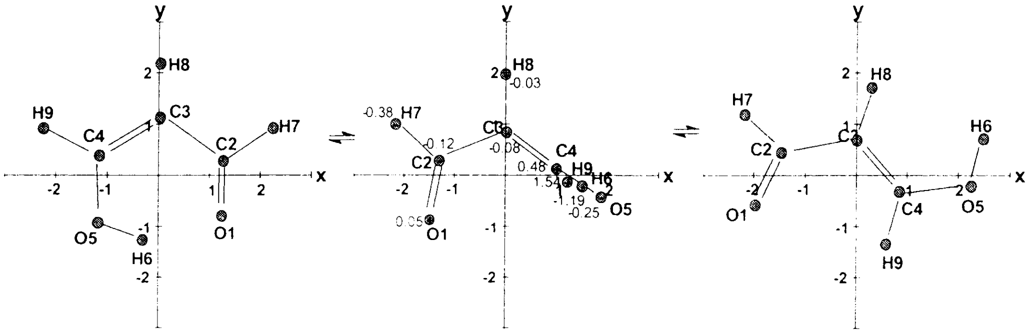
A↔C, E↔F, and G↔H are connected with a rotation around the partial double bond. The A↔E rotation around the approximate single bond results in an energy barrier which is lower than the first three. The A↔E rotation is connected with rotating the fragment –C(H)=O and generates a rotamer which is the *s-trans* isomer of rotamer A (Fig. 6). According to the B3LYP method, the angle O(1)C(2)C(3)C(4) changes from 0° to 180° in rotamer E and passes through a transition state with 96.06°.

The other rotations are connected with a movement of the rather large fragment =C(H)–OH which enhances the reaction energy. The mechanisms of the reactions are illustrated in Figs. 7–9.



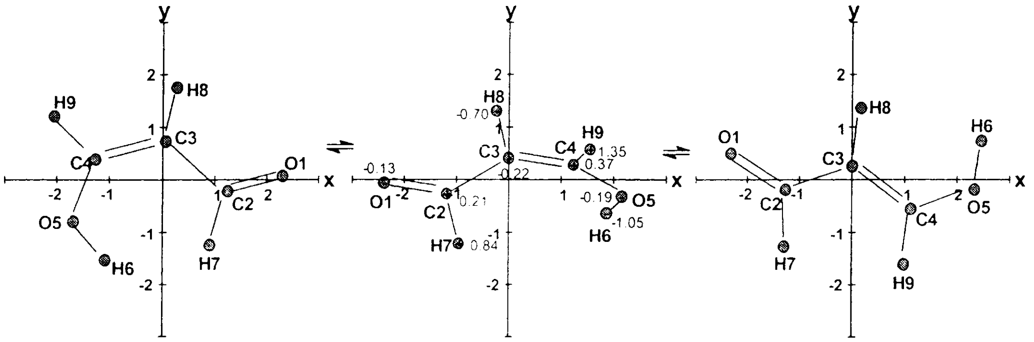
ROTAMER A *TRANSITION STATE (TS)* *ROTAMER E*

Fig. 6. Rotation A→E



ROTAMER A *TRANSITION STATE (TS)* *ROTAMER C*

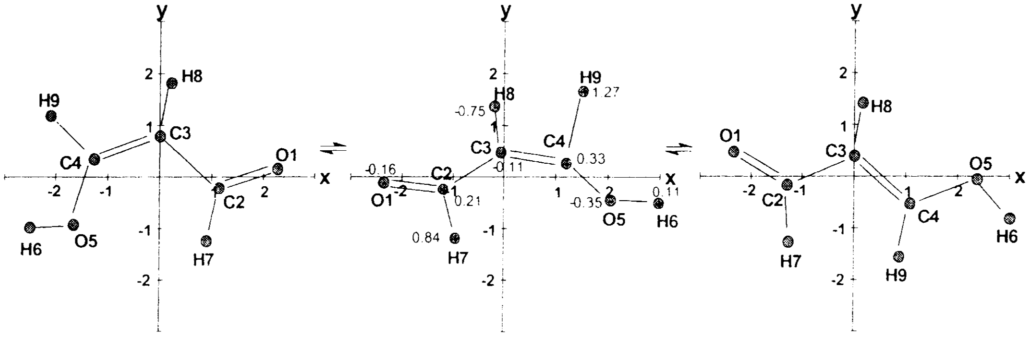
Fig. 7. Rotation A→C



ROTAMER E *TRANSITION STATE (TS)* *ROTAMER F*

Fig. 8. Rotation E→F

In Table 2, energies of the transition states and energy barriers of the rotations are given where *E* designates energy barriers estimated as the difference between the energies of the transition states and the corresponding enols, whereas E° relates to those found as the difference between the zero-point levels of the same molecular systems. For the examined rotations, the barriers were found to be high and nearly



ROTAMER G *TRANSITION STATE (TS)* *ROTAMER H*

Fig. 9. Rotation G→H

symmetric according to all methods; only the barrier of A↔E was found to be lower. In this case it should be considered that it occurs by rotation around an approximate single bond, although in this process the intramolecular hydrogen bond breaks. The barrier is also strongly asymmetric because of the great difference in the energies of the two rotamers taking part in the reaction. The most symmetric barrier is that of G↔H with a small difference of about $6\,\mathrm{kJ \cdot mol^{-1}}$ (B3LYP) between the barrier of the reverse and forward reactions.

The transition states of this rotations were found analogously to the transition states of the previous four rotations using the FREQ (computing force constants and the resulting vibrational frequencies) and QST3 (searching for a transition structure) options available in the GAUSSIAN98 program. They were determined as first-order saddle points by analyzing calculated IR spectra for each transition state. Each calculation gave 38 real frequencies and one imaginary eigenvalue in which the corresponding eigenvector shows a motion of a fragment between both enol forms involved in the reaction. The imaginary eigenvalue is very useful from a theoretical point of view, because it is connected with a negative potential energy gradient and indicates that the given structure is not an energy minimum. All transition states are non-planar with low symmetry (C_1) and possess a strongly strained structure due to a disturbance of the conjugation.

Knowing the stability of the rotamers and the barriers of the rotations, the theoretical composition of **1** could be predicted as a first step of the keto-enol equilibrium study. Thus, rotamer A will predominate, and the keto-enol reaction will occur between A and the dialdo form of **1**. Other rotamers will exist in very small amounts, and it would be meaningless to include them in further keto-enol calculations. As has been established before by means of HF/6-311G** calculations, the other interesting rotamer for a keto-enol study is rotamer E [10], but its transition state was determined as a second order saddle point. This means that from this point the reaction can proceed in more than two directions and will lead to different products. This transition state is an intermediate complex of more than one reaction and thus additionally complicates the mechanism of the keto-enol equilibration.

Conclusions

The best results for the enol forms and the keto form of **1** were obtained using DFT and especially B3LYP methods combined with the double-ζ basis set D95**. The results obtained with HF/6-311G** calculations are quite different from those of DF calculations, but they provide a good starting position for higher levels. HF methods are time saving and give – in our case – sufficient results for the electronic structure of the compounds.

The transition states of the rotations were determined as first order saddle points. The calculated IR spectrum of each transition state gave 38 real vibrations and one imaginary eigenvalue with eigenvectors corresponding to a fluctuation between both rotamers taking part in the reaction and leading to only one of the rotamers, rendering other reactions impossible. Whereas the rotamers are flat and belonging to the C_S point group, the transition states are non-planar and have the lowest possible symmetry (C_1). They are also strongly strained, and especially those connected with a disturbance of the π-conjugation existing in the flat rotamers and the rotation around a C=C double bond are strongly destabilized.

From all eight examined rotamers, A is the most stable one because of its intramolecular hydrogen bond which additionally stabilizes the molecule and forms a pseudoaromatic ring. The energies of the reactions A↔B, A↔C, and A↔E correspond to a breaking of the intramolecular hydrogen bond and lead to products with higher energy.

The rotation G↔H was found to have the highest energy value for the reverse reaction, but the barrier is nearly symmetric because of the similar energies of the involved rotamers. Strongly asymmetric barriers are associated with rotations connected with a breaking of the hydrogen bond: A↔B, A↔E and, to a minor extent, A↔C. The lowest energy barriers are connected to rotations around the C–O bond and the formation of a rotamer with the same OCCCO conformation.

Since rotamer A is the most stable one, it will predominate and will take part in a keto-enol conversion to a larger extent than others. At different conditions, however, other rotamers might participate as well.

Acknowledgements

V. B. Delchev thanks the Austrian Ministry of Science and Transport for a grant.

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Received July 6, 2000. Accepted (revised) September 7, 2000