Mendeleev Commun., 1998, 8(4), 138–139

Ab initio study of the structure of, and double proton exchange in, 1,4-dihydroxy-2,3-diformylbuta-1,3-diene

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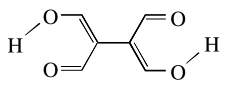
Concerted low-energy barrier (3.7 kcal mol^{-1}) double proton exchange in 1,4-dihydroxy-2,3-diformylbuta-1,3-diene has been predicted using *ab initio* [MP2(fc)/6-31G] calculations.**

Particular attention has been given to the study of the kinetics and mechanism of the intramolecular two proton migration in oxalic acid,[1] oxalamidine,[2] azophenine,[3,4] 2,2′-bipyridyl-3,3′-diole[5,6] and other similar compounds.[7,8] Both theoretical and experimental investigations[1–8] showed that all the dyotropic rearrangements studied follow a two-step mechanism involving sequential proton transfer with inclusion of a zwitterionic intermediate. No unambiguous experimental or theoretical evidence for the realization of the concerted (one-step) double proton transfer within a molecule have hitherto been presented. In the present work we report on *ab initio* [MP2(fc)/6-31G**][9] calculations of a concerted low-energy barrier (3.7 kcal mol^{-1}) degenerate rearrangement of 1,4-dihydroxy-2,3-diformylbuta-1,3-diene **1** due to intramolecular double proton transfer.

According to the MP2(fc)/6-31G** calculations, a planar structure **1** ($\lambda = 0$; hereafter λ designates the number of negative eigenvalues at a given stationary point) with C_{2h}-symmetry corresponds to the most stable form of the 1,4-dihydroxy-2,3-diformylbuta-1,3-diene. A possible *cis*-(*Z*)-conformer **3** is 2.6 kcal mol^{-1} less favourable than **1**. Unlike **1**, the isomer **3** is acoplanar (C_2-symmetry) with the dihedral C=C–C=C angle equal to 61.6°.

Calculated molecular structures, geometry and energy parameters of the structures **1**–**3** are given in Figure 1 and Table 1.



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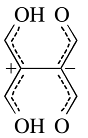

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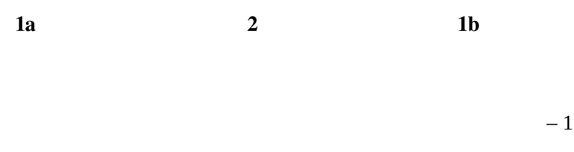
The symmetric structure **2** of D_{2h}-symmetry corresponds to a true saddle point ($\lambda = 1$) on the potential energy surface (PES) of $C_6H_6O_4$. A possible zwitterionic intermediate **4** that would result from single-proton transfer does not correspond to a stationary point. Optimizations starting from the zwitterionic configuration **4** with C_{2v} and C_1 symmetries lead to structures **2** and **1**, respectively. Thus, there exists only the concerted proton exchange pathway **1a** ⇌ **2** ⇌ **1b** in 1,4-dihydroxy-2,3-diformylbuta-1,3-diene which implies occurrence of the multicentered transition state structure **2** with a very low energy of 3.7 kcal mol^{-1} relative to **1**. The three-centre hydrogen bridges in **2** are nearly linear (deviation from linearity is *ca.* 12°). The H···O=C angle of 112.6° lies within the limits of the optimal values for proton transfer along the hydrogen bond.[10] Accounting for zero-point energy corrections in **1** and **2** leads to the conclusion that the bicyclic structure **2** with hydrogen atoms centered in the middle of the O···O bridge possesses lower total energy as compared with **1**. A similar phenomenon of the vibrational stabilisation of the structure with symmetrical hydrogen bridges has been discussed[11] recently with reference to experimental data for the IHI system.[12]



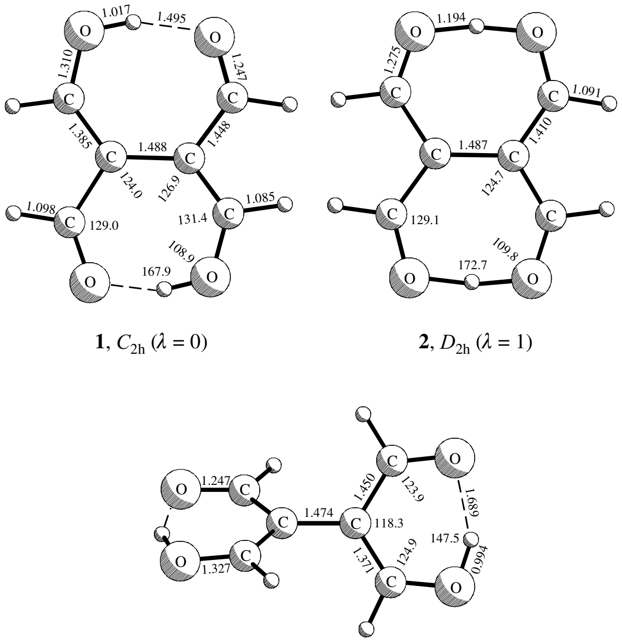
1a **2** **1b**

Table 1 Total energies (E_{tot} in hartree), relative energies (ΔE in kcal mol^{-1}), the number of negative hessian eigenvalues (λ), harmonic zero-point correction (ZPE in hartree), relative energy including harmonic zero-point correction (ΔE_{ZPE} in kcal mol^{-1}), reaction enthalpy (ΔH in kcal mol^{-1}) and the smallest or imaginary vibration frequency ($\omega_1/i\omega$ in cm^{-1}) for the structures **1**–**3** calculated by the MP2(fc)/6-31G** method.

Structure	E_{tot}	ΔE	λ	ZPE	ΔE_{ZPE}	ΔH	($\omega_1/i\omega$)
1, C_{2h}	-531.63149	0	0	0.11877	0	0	22.7
2, D_{2h}	-531.62561	3.68	1	0.11193	-0.60	-0.91	i1189.5
3, C_2	-531.62732	2.62	0	0.11813	2.21	2.47	46.1

Thus, our calculations corroborate the assumption about the crucial influence of the stereochemical conditions on the proton transfer mechanism. Structure 1,4-dihydroxy-2,3-diformylbuta-1,3-diene appears to be the first example of a dyotropic molecule in which one-step low-barrier double proton exchange confirmed at the MP2-level is possible.

This work was supported by the Russian Foundation for Basic Research (grant nos. 98-03-33169a and 96-15-97476).



1, C_{2h} ($\lambda = 0$)

2, D_{2h} ($\lambda = 1$)

Dihedral angle CCCC 61.6°
3, C_2 ($\lambda = 0$)

Figure 1 Geometry parameters of structures **1**–**3** calculated by the MP2(fc)/6-31G** method. Bond lengths and angles are given in angströms and degrees, respectively.

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Received: Moscow, 14th May 1998
Cambridge, 8th June 1998; Com. 8/03649G