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Tautomerism of peroxyacetic acid derivatives: a quantum chemical study*

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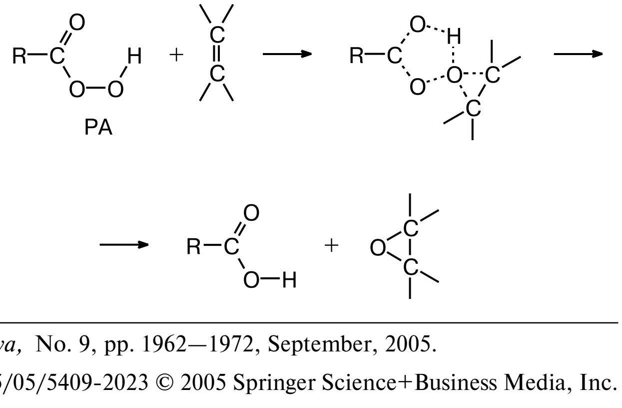
The electronic and molecular structures and the relative stabilities of organic peracids $\mathrm{X{=}C(R){-}COOH}$ and their cyclic tautomers, dioxiranes $\mathrm{HX{-}C(R){-}\overline{C{-}O{-}O}}$, with R = Me, CF_3; X = O, NH, were studied using the *ab initio* Hartree—Fock method and the density functional theory (B3LYP version) as well as at the MP2-MP4 Møller—Plesset levels of perturbation theory. Geometry optimization was performed by the UHF and B3LYP methods with the 6-31G** basis set and at the MP2/cc-pvtz level of theory. The acyclic form of the peracid is more stable than the cyclic dioxirane form irrespective of the nature of the substituent. The energy difference between these tautomers increases as the CF_3 and NH groups are replaced by Me and O, respectively. Parameters of the activation barrier to tautomeric conversion increase in parallel with enhancement of the electron-accepting properties of both substituents. The transition state of tautomeric interconversion, which is topologically similar to the acyclic structure of the carbonyl oxide derivative $\mathrm{R(HX)C{=}O^{+}{-}O^{-}}$, was found and characterized taking peroxyacetic acid as an example. The characteristic features of the transition state are an intramolecular "multicenter" H-bond and the charge distribution that is inconsistent with the canonical structure mentioned above. An appropriate reaction coordinate for the transformation of the quasi-tetrahedral dioxirane structure into a planar peroxyacetic acid structure is provided by the dihedral angle. Deprotonated anionic systems are characterized by much smaller differences between the relative stabilities of the open and closed forms of isomers and by much lower activation barriers to isomeric conversions.

Key words: peroxyacetic acid, dioxiranes, tautomerism, energy barrier, quantum chemical calculations.

Interest in the chemistry of peroxide compounds is first of all due to the role of these compounds in synthetic chemistry and industry.[1—3] For instance, both peroxo and hydroperoxo complexes of transition metals (vanadium, molybdenum, titanium, *etc.*) are used as oxidants not only in research practice but also in industrial catalysis. Consideration of reactions mechanisms of organic peracids involves not only free-radical routes but also the pathways involving polar reactions of the "open" forms of the peracids (PA-forms) or its cyclic isomers (D-forms).[4,5]

For instance, the mechanism of olefin epoxidation with organic peracids (Prilezhaev reaction), which was first proposed in 1950, involves an attack of the terminal electrophilic oxygen atom of the peroxy group on the atoms of the olefin double bond[6] (Scheme 1).

Scheme 1



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* Dedicated to Academician A. L. Buchachenko on the occasion of his 70th birthday.

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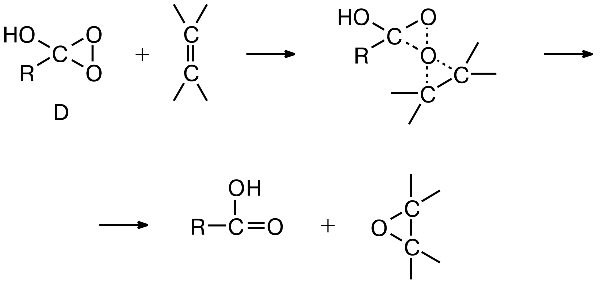
Meanwhile, epoxidation with peracids is usually carried out in basic (buffer) solutions in order to minimize the yield of hydroxylation products. In such solutions the role of active epoxidizing agents can probably be played by both the cyclic form of the peracid (D-form, Scheme 2) and by its anionic forms (PI- and DI-forms, respectively).

Scheme 2

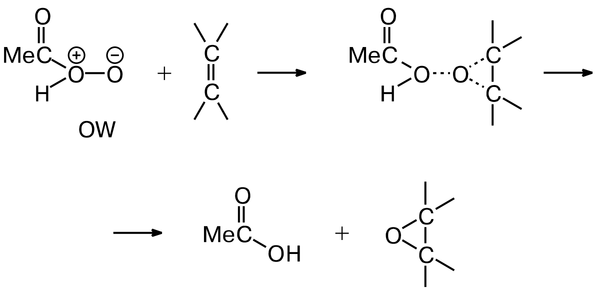


D

The involvement of the dioxirane form, D, of the peracid in the epoxidation reaction was first reported in 1982.[7] The ability of more or less stable dioxiranes to act as active epoxidizing agents was also reported.[3,8]

In addition to the schemes mentioned above the possibility has been discussed[8] of the reactions including epoxidation involving yet another form of the peracid, namely, an acyl derivative of water oxide (OW-form) (Scheme 3).

Scheme 3



OW

Tautomeric conversions between these forms of peroxides involving changes from cyclic to acyclic structure seem to be directly related to the reactivity of these compounds. Using quantum chemical modeling methods, it is possible to treat the problems in this field in terms of the electronic structure of reactants, products, and corresponding transition states.

A number of quantum chemical studies on peroxides are available.[9—24] The emphasis was placed on investigation of the oxidation reactions of various compounds and first of all olefins (ethylene) with peracids (*e.g.*, peroxyformic acid). Other forms of peroxides, in particular, dioxiranes (the simplest of them, H_2CO_2, was studied in detail) as well as transition-metal peroxo complexes were also considered. At the same time, relations between the specific features of tautomerism in peroxides and the reasons for actually observed selective or, *vice versa*, multichannel character of the oxidation reactions, peculiar features of proton and oxygen transfer, *etc.* are still poorly studied. In this connection there is a need in performing a comparative analysis of the reactivity of various peroxides, from hydrogen peroxide to transition-metal peroxo complexes, in the framework of a unified approach.

Methodologically, quantum chemical analysis of peroxides should be started with the study of tautomerism of organic peroxides (peroxyacetic acid derivatives). The key problems to be solved are as follows:

1) determination of the total number of tautomers and their relative stabilities; analysis of possible tautomeric conversions including the search for realistic "reaction coordinates" (for all compounds); and elucidation of specific features of proton transfer;

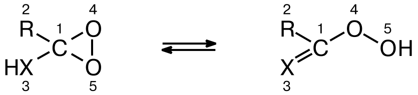
2) investigation of the substituent effects on the stabilities of various tautomers and on the parameters of activation barriers;

3) analysis of the relative stabilities of isomers in corresponding ionic (deprotonated) systems; and

4) comparative analysis of tautomerism in the PA $\rightleftarrows$ D, PA $\rightleftarrows$ OW, and D $\rightleftarrows$ OW systems, in the theoretically well-studied system "hydrogen peroxide—water oxide" (HO—OH $\rightleftarrows$ H_2O—O),[9—11] and in transition-metal peroxo complexes (taking vanadium(v) complexes as examples).

In this work we studied organic cyclic compounds, dioxiranes D**1**—D**4**, and their acyclic tautomers, hydroperoxides PA**1**—PA**4** (Scheme 4).

Scheme 4



D**1**—D**4** PA**1**—PA**4**

Compound	R	X	Compound	R	X
1	Me	NH	**3**	Me	O
2	CF_3	NH	**4**	CF_3	O

For comparison, we also considered hydrogen peroxide and water oxide. The structures and properties of isomers of vanadium(v) peroxo complexes and the possibility for other tautomeric forms of the organic and inorganic peroxides mentioned above to exist will be reported elsewhere.

Calculation Procedure

The electronic structures, geometric parameters, and relative stabilities of tautomers and transition states of tautomeric reactions were mainly calculated using the density functional theory (B3LYP/6-31G** approximation). A number of systems were also calculated using other *ab initio* computational schemes, namely, the RHF (or UHF) and the MP2-MP4 Møller—Plesset levels of perturbation theory, with two basis sets. In all cases, full geometry optimization was performed at the RHF(UHF)/6-31G**, B3LYP/6-31G**, and MP2/cc-pvtz levels. Search for and calculations of the transition states were carried out using the QST2 procedure. The electronic structure and the nature of chemical bonds were analyzed by the natural bonding orbital (NBO) method. Calculations were carried out using the GAUSSIAN-98 program package.[25]

We evaluated the calculation procedures employed in this work taking the $H_2O_2 \rightarrow H_2OO$ tautomerism as an example, which was studied in detail by different quantum chemical methods earlier.[9—11] It was found[10,11] that B3LYP/6-31G** calculations correctly reproduce the key energy characteristics and geometric parameters obtained for this system using more rigorous quantum chemical methods including MP4/SDTQ, QCISD(T), CCSD, and CASSCF. For instance, the activation barriers we calculated were 53.5 and 3.4 kcal mol^{-1}, being comparable with the results obtained by the methods mentioned above (51.4—58.0 and 2.7—4.2 kcal mol^{-1}, respectively). The O—O bond lengths in H_2O_2, H_2OO, and in the transition state (1.456, 1.557, and 1.627 Å, respectively) were calculated with the same accuracy as that obtained by the more rigorous methods (1.44—1.48, 1.53—1.58, and 1.61—1.66 Å, respectively); the H—O—O bond angles differed by at most 2° (see Refs. 9—11).

In choosing computational procedures we were also guided by the results of a study[23] concerned with the analysis of the applicability of the B3LYP approximation with the minimal basis sets of the 6-31G type in studying the oxidation reaction involving related organic peroxides. A comparison of the results obtained by different methods (MP2(4), DFT, QCISD(T), CCSD(T)) showed[23] that the B3LYP and MP2(4) calculations, even with the minimal basis set (6-31G*), provide efficient means for the description of the energy characteristics and geometries of reactants, products, and transition states. In particular, in contrast to the MP2(4) procedures and similarly to the more rigorous CCSD(T) and QCISD(T) methods the B3LYP approximation, irrespective of the basis set, leads to the so-called *spiro*-form of the transient structure, which is significant for detailed consideration of the mechanisms of the epoxidation reactions mentioned above. At the same time the B3LYP approximation systematically underestimates the activation barriers (on the average, by $\Delta E_a \approx 4$ kcal mol^{-1}) compared to the more rigorous methods.[23] This drawback is also characteristic of the MP2 calculations, although to somewhat lesser extent. MP4 corrections are usually small (1—2 kcal mol^{-1}). Nevertheless, the use of these methods and first of all the cost-efficient B3LYP approach seems to be quite appropriate for comparative description of peroxides including transition-metal peroxo complexes.

Results and Discussion

Electronic structures and geometries of peroxyacetic acid tautomers

Table 1 lists the total energies of the tautomers of peroxyacetic acid **3** (E_{total}) and the transition state (E_{TS}), the activation barriers calculated with respect to the energies of the D**3** and PA**3** forms (ΔE_D and ΔE_{PA}, respectively), and the relative stabilities of the tautomers (ΔE_r). Based on comparison of these data, one can draw the following conclusions.

First of all it should be noted that in the ground state the acyclic form PA**3** is much more stable than the cyclic form D**3** (Scheme 5). Different approximations lead to quite similar ΔE_r values (14—19 kcal mol^{-1}).

Geometry calculations of the PA- and D-tautomers indicate a planar structure of the nearest environment of the C(1) atom in the PA-form and a non-planar (quasi-tetrahedral) structure of this fragment in the D-form. In agreement with these results, NBO data showed that the C(1) atom forms with the neighboring atoms two ordinary bonds, C(1)—C(2) and C(1)—O(4), and one multiple bond, C(1)=O(3), in the former case and four ordinary bonds, namely, C(1)—C(2), C(1)—O(3), C(1)—O(4), and C(1)—O(5) in the latter. Each of these bonds

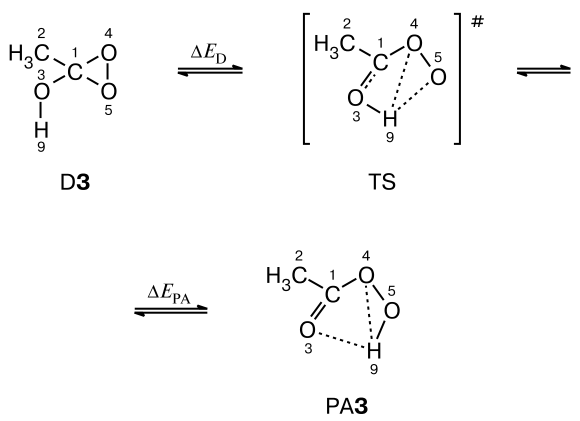
Table 1. Total energies (E_{total}), activation barriers (ΔE_D, ΔE_{PA}), and relative stabilities (ΔE_r) of peroxyacetic acid tautomers

Computational procedure	$-E_{total}$/a.u.			ΔE_D	ΔE_{PA}	ΔE_r
	D**3**	TS	PA**3**	kcal mol^{-1}		
UHF//UHF[a]	302.543641	302.497236	302.571836	29.12	46.81	17.69
MP4(SDTQ)//UHF[a]	303.415334	303.346610	303.438409	43.12	57.60	14.48
B3LYP//UHF[a]	304.183604	304.124413	304.212501	37.14	55.28	18.14
B3LYP//B3LYP[a]	304.188371	304.135630	304.217684	33.10	51.49	18.39
B3LYP//B3LYP + ZPE[a]	304.123148	304.072132	304.152544	32.01	50.46	18.45
RHF//RHF[b]	302.649061	302.597294	302.679556	32.48	51.62	19.14
MP2//MP2[b]	303.702068	303.632079	303.724387	43.92	57.92	14.00
MP3//MP2[b]	303.705182	303.639042	303.728675	41.50	56.25	14.74

[a] Calculated with the 6-31G** basis set. Geometry optimization was performed by the UHF(RHF) method (rows 1—3), in the B3LYP approximation (rows 4,5), and at the MP2 level of theory (rows 7,8).

[b] Calculated with the cc-pvtz basis set.

Scheme 5



(σ-component in the case of the multiple bond) is composed of the hybrid sp-orbitals of the neighboring atoms with a considerable contribution of the s-component (at least 19%). The averaged characteristics of the hybrid orbitals of the atom C(1) in the PA- and D-tautomers obtained from the NBO analysis appeared to be similar to the conventional sp^2 and sp^3 values (2.15 and 2.38, respectively). The contributions of the polarization d-orbitals of the carbon and oxygen atoms are small (<3%).

The O—O interatomic distances in the PA- and D-tautomers are different (Table 2). For instance, the O—O bond length in the PA-tautomer is nearly the same as in H_2O_2 (≈1.44 Å), whereas in the D-tautomer it approaches the value calculated[9–11] for H_2O—O (≈1.53 Å). The formation of these bonds is primarily determined by p-orbitals of oxygen atoms, although for the PA-form the s-orbitals contribute significantly (≈10%). This seems to be the reason for the distinctions between the O—O interatomic distances (see above). The calculated geometric parameters of the PA-tautomer are consistent with the available X-ray diffraction data for various organic peracids O=C(R)—OOH.[26,27] Calculations correctly reproduce the planar arrangement of the nearest neighbors of the C atom and the key bond lengths and bond angles, in particular, the O—OH bond length, which most often lies between 1.43 and 1.47 Å (see Refs 9, 10). It should also be noted that the O(4)—O(5) bond length in the D-form, obtained from our calculations is similar to that in dioxiranes RR´CO_2 (R = H, Me), being in agreement with the microwave and X-ray diffraction data[28,29] and with the results of calculations.[13–15]

Both tautomers have an additional intramolecular H-bond (see Table 2). In each structure, there are two shortened contacts O(3)—O(4)/O(5) (d ≈ 2.35 Å for the D-form and d ≈ 2.25 and ≈ 2.50 Å for the PA-form). Because of this, the H atom is in the field produced by three oxygen atoms, *i.e.*, in fact these H-bonds are multicenter in character (see Scheme 5). The O—H bond in the PA-form is slightly longer than the corresponding bond in the D-form (Δd ≈ 0.02 Å), which is similar to the "typical" length of a terminal bond. At the same time two other H...O contacts in the PA-form (d ≈ 1.85 Å) are

Table 2. Calculated interatomic distances (d) and bond angles (ω) in the molecules of dioxirane (D**3**), peroxyacetic acid (PA**3**), and in the transition state (TS)

Parameters	D**3**		TS		PA**3**				Experiment[a]
	B3LYP/ 6-31G**	MP2/ cc-pvtz	B3LYP/ 6-31G**	MP2/ cc-pvtz	B3LYP/ 6-31G**	MP2/ cc-pvtz	B3LYP/ 6-311++G**[a]	MP2/ 6-311++G**[a]	
Bond				d/Å					
C(2)—C(1)	1.502	1.491	1.486	1.477	1.503	1.494	1.500	1.499	
C(1)—O(3)	1.361	1.358	1.316	1.305	1.216	1.212	1.209	1.212	≈1.22
C(1)—O(4)	1.397	1.392	1.288	1.287	1.354	1.351	1.355	1.357	≈1.33
C(1)—O(5)	1.397	1.392	1.976	1.932	2.304	2.284			
O(4)—O(5)	1.522	1.530	1.537	1.501	1.442	1.437	1.439	1.437	≈1.47
O(3)...O(4)	2.355	2.349	2.290	2.283	2.247	2.245			
H(9)...O(4)	2.413	2.397	2.271	2.233	1.881	1.867			
O(3)...O(5)	2.355	2.349	2.424	2.373	2.531	2.510			
O(3)**H(9)	0.970	0.966	0.988	0.992	1.851	1.818			
H(9)**O(5)	2.413	2.397	1.957	1.862	0.989	0.983	0.984	0.981	≈1.00
Angle				ω/deg					
C(2)—C(1)—O(3)	112.2	112.0	116.6	117.0	127.0	127.1	127.2	127.3	
C(2)—C(1)—O(4)	118.5	118.4	119.6	118.8	111.1	110.7	111.6	110.8	≈113
C(2)—C(1)—O(5)	118.5	118.4							
O(3)—C(1)—O(4)	117.3	117.3	123.4	123.5	121.9	122.2	121.8	122.3	
O(3)—C(1)—O(5)	117.3	117.3							
C(1)—O(4)—O(5)	57.0	56.7	88.3	87.4	110.9	110.0			

[a] Data taken from Ref. 24.

much shorter than in the D-form ($d \approx 2.40$ Å). Therefore, such a multicenter (bifurcate) H-bond in the acyclic form should be stronger than in the cyclic form, which favors an additional stabilization of the former tautomer.

In this work the structure of the PA-form was calculated at three levels of theory (see Calculation Procedure). The results of our computations can be compared with those obtained by the same methods with the 6-31G** and 6-311++G** basis sets.[24] A comparison shows that for this form the individual bond lengths and bond angles including the geometric parameters of the intramolecular bond vary only slightly dependng on the computational method employed, especially the methods with inclusion of electron correlation (see Table 2). All methods quite correctly reproduce the experimental molecular geometry.[24] Besides, calculations at all levels of theory including UHF/6-31G** lead to almost the same energy of transition (4—6 kcal mol^{-1}) of the H(9)—O(5)—O(4)—C(1) fragment to the conformationally excited states characterized by *trans*-conformation with the same length of the H(9)—O(4) contact (≈1.8 Å); Scheme 5 shows the ground-state *cis*-conformation of the fragment. This energy can be considered as an estimate of the energy gain upon the formation of the multicenter bond instead of the two-center bond in the PA-form. Calculations also provide a similar description of the intramolecular H-bond including its geometry, although the multicenter character of this bond was ignored.[24]

Analysis of the electron density distribution in the tautomers using the canonical and natural bonding orbitals (B3LYP/6-31G** and MP3/cc-pvtz) showed that the degree of charge redistribution on going from D to PA is low in both cases in spite of differences. In the framework of the NBO analysis the charge redistribution is more pronounced and shows that cleavage of the O(3)—H(9) bond in the D-tautomer is followed by partial transfer of the electron density localized in the region of this bond to almost all atoms of the PA-tautomer except the O(4) atom. This is accompanied by an increase in the charge difference between the O(5) and O(4) atoms (−0.5 and −0.3, respectively) with the highest degree of electron density transfer to the region of the new O(5)—H(9) bond.

As mentioned above, a characteristic feature of the dioxirane form of peroxyacetic acid in the ground state is quasi-tetrahedral coordination of the nearest environment of the C(1) atom (the C(2)C(1)O(3) and C(1)O(4)O(5) planes are almost perpendicular to each other). At the same time noteworthy is that calculations at all levels of theory predict significant distortions of the tetrahedral angles and first of all a dramatic decrease in the O(4)—C(1)—O(5) bond angle (to $\omega \approx 65°$) and an increase in the other bond angles by $\Delta\omega \approx 10°$ compared to the tetrahedral value (see Table 2).

This character of distortions can be interpreted in terms of the theory of the Jahn—Teller effect, which describes removal of the orbital degeneration as a result of vibronic interaction in the system.[30] Then, distortion of the tetrahedral coordination in the dioxirane molecule should be treated as a consequence of the presence of unfilled electron shell, T^4 (T is the degenerate highest occupied MO for the idealized tetrahedral geometry of dioxirane), with two missing electrons compared to the "classical" tetrahedral systems with the T^6 configurations, *e.g.*, CX_4 (X is a halogen), hypothetical molecule $C(OH)_4$ (OH is a quasi atomic substituent), tetraoxy anions of main-group elements of the SiO_4^{4-} or $Si(OH)_4$ type, *etc.* Using the terminology specific to consideration of vibronic interactions in molecular systems,[30,31] one can conclude that here we face a $[T-(e+t)-S]$ vibronic problem, where e and t are the vibrational modes of the E and T_2 symmetry, respectively, for tetrahedral coordination and S is the substitution operator in the vibronic Hamiltonian, which describes the "heteroligand" character of the tautomer in question.

Consideration of a simpler problem (no substitution) for a hypothetical system CO_4^{2-} (T_2^4 configuration) in the linear vibronic coupling approximation with separate inclusion of the stretching and bending modes showed that we can expect significant (first of all, angular) distortions involving mutual approach of two "neutral" oxygen atoms and withdrawing of two "negatively charged" oxygen atoms. Further analysis in terms of the theory of substituent effects,[31] which provides a means for the description of changes in the system´s geometry upon the replacements of O— by R(Me) and O— by OH, showed that the character of the angular distortions remains unchanged and one should expect only relatively small changes in the system´s geometry (including the bond angles), which are determined by the electronegative substituents mentioned above. Of course, based on this pure qualitative interpretation, we can only say that the expected Jahn—Teller distortions on the one hand and the geometric implications of the presence of the dioxirane ring with comparable C—O and O—O bond lengths on the other hand complement each other.

Of course, the description of the peculiar features of the molecular structure of dioxirane by a strongly distorted quasi-tetrahedral system with (two) missing π-electrons is not unique. Dioxirane can also be treated as a π-complex of a singlet (triplet) carbene with singlet (triplet) dioxygen; correspondingly, its structure can be analyzed from this point of view. However, the first interpretation can be somewhat better consistent with the results of quantum chemical calculations, which indicate the presence of four "normal" σ-bonds in the dioxirane structure (see above).

Specific features of the transition state

Calculations of the energy parameters and geometry of the transition state of tautomeric conversion of peracetic acid D → TS → PA (or *vice versa*) led to a planar configuration of the transition state (see Tables 1 and 2), which in this respect is similar to the structure of the PA-form. Of course, there is also a number of significant distinctions between their geometries. First of all noteworthy is that, similarly to the D-form, the H(9) proton remains covalently bound to the O(3) atom, although the O(3)—H(9) bond in the transition state is longer ($\Delta d \approx$ 0.02 Å) than in the D-form (see Table 2). Besides, the C(1)—O(3) bond in the transition state appeared to be much longer ($\Delta d \approx$ 0.1 Å) than in the PA-form, whereas the C(1)—C(2) bond and the C—H bonds in the Me radical vary to a much lesser extent. The C(1)—O(3) and C(1)—O(4) bond lengths in the transition state are similar (see Table 2), being intermediate between the ordinary and multiple carbon—oxygen bond lengths. It is interesting that NBO analysis predicts an increase in the multiplicity of the C(1)—O(3) rather than C(1)—O(4) bond in the transition state as in the PA-form, although both components of the former bond in the transition state are of higher polarity, especially the π-component. Yet another salient feature of the TS compared to the PA-form is an appreciable elongation of the O(4)—O(5) bond ($\Delta d \approx$ 0.1 Å according to B3LYP/6-31G** and 0.06 Å according to MP2/cc-pvtz calculations) (see Table 2). It should also be noted that the TS is topologically similar to the structure of a carbonic acid oxide $R(HX)C{=}O^{+}{-}O^{-}$; however, the charge distribution obtained in this work (−0.4 on the first and −0.5 on the second oxygen atom) is inconsistent with this canonical structure.

Without dwelling (at the moment) on a possible type of the reaction coordinate of the D → TS → PA tautomeric conversion, it should be noted that, irrespective of the computational procedure employed, the potential energy profile can be conditionally divided into two regions. One of them corresponds to the opening of the dioxirane ring $\overline{C{-}O{-}O}$, which is accompanied by a change in the coordination of the C(1) atom from quasi-tetrahedral to planar triangular, while the other corresponds to proton transfer from the O(3) atom to the O(5) or O(4) atom.

Based on the results of analysis of the molecular structure of both tautomers and TS, it is logical to consider the following four most possible reaction pathways, namely, 1) consecutive elongation of the C(1)—O(5) bond in the D-form; 2) an increase in the C(1)—O(4)—O(5) bond angle; 3) a decrease in the dihedral angle, φ, between the C(1)O(4)O(5) and O(3)C(1)O* planes (O* is the midpoint of the O(4)—O(5) bond) (Fig. 1); and 4) proton transfer along intramolecular H-bond O(3)...O(5) upon an increase in the O(3)—C(1)—H(9) angle (Fig. 2).

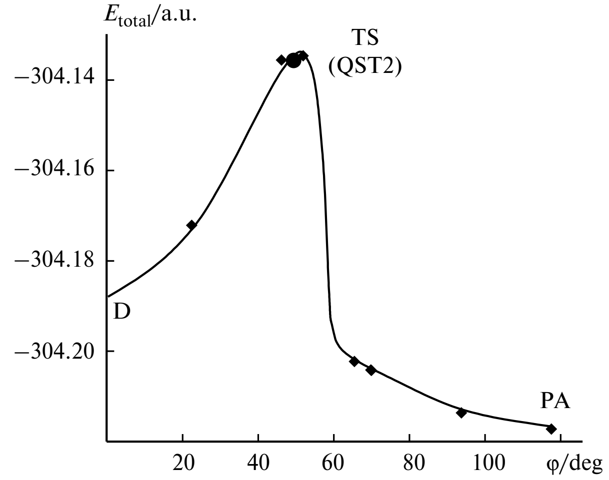


Fig. 1. Potential energy profile of D → TS → PA conversion obtained by varying the dihedral angle (φ) between the C(1)O(4)O(5) and O(3)C(1)O* planes (O* is the midpoint of the O(4)—O(5) bond). The atomic numbering scheme is given in Scheme 5.

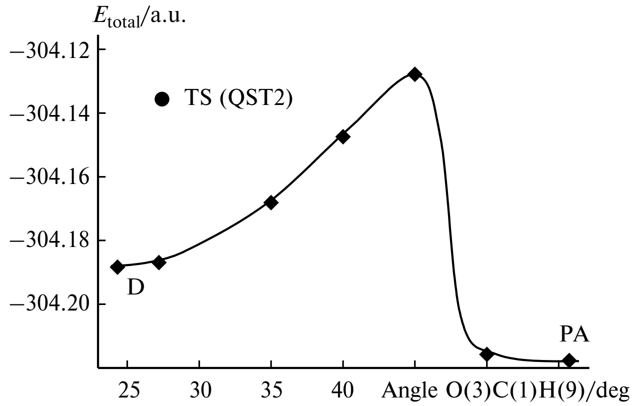


Fig. 2. Potential energy profile of D → PA conversion obtained by varying the O(3)—C(1)—H(9) angle (proton transfer along the intramolecular H-bond O(3)...O(5)). The atomic numbering scheme is given in Scheme 5.

B3LYP/6-31G** calculations showed that the first two routes starting from the D-form do not lead to the PA-form at all. Analysis of the reaction pathways leading to formation of other peroxyacetic acid tautomers will be reported elsewhere.

The one-dimensional potential profile of the D → PA conversion obtained by varying the dihedral angle φ provided that other atoms in the system are relaxed is shown in Fig. 1. The system moves along this coordinate in the immediate vicinity of the transition state ($E \approx$ 0.6 kcal mol^{-1}), which provides almost monotonic changes in the bond lengths and bond angles including the geometric parameters of the intramolecular H-bond. In this case with some restrictions one can assume a "single-mode" character of the reaction coordinate with a jumpwise proton transfer (at $\varphi \approx 49°$). However, here it

Table 3. Activation barriers (ΔE_D/kcal mol^{-1}) and relative stabilities (ΔE_r/kcal mol^{-1}) of tautomeric peroxyacetic acid derivatives

Computational procedure[a]	D**1**		D**2**		D**3**		D**4**	
	ΔE_D	ΔE_r	ΔE_D	ΔE_r	ΔE_D	ΔE_r	ΔE_D	ΔE_r
UHF//UHF	21.60	8.68	29.50	3.34	29.12	17.69	36.09	12.88
MP4(SDTQ)//UHF	35.99	5.95	46.67	0.08	43.12	14.48	57.45	10.29
B3LYP//UHF	30.59	9.28	40.17	4.42	37.14	18.13	51.89	14.02
B3LYP//B3LYP	27.62	9.32	35.58	6.02	33.09	18.39	45.69	14.08

[a] Calculated with the 6-31(d,p)G basis set. Geometry optimization was performed by the UHF method (rows 1—3) and in the B3LYP approximation (row 4).

seems to be more appropriate to mention only a concerted character of the relaxation of the atoms of the non-hydrogen molecular skeleton and of proton transfer to the final state.

The potential profile of the D → PA conversion, obtained by varying the O(3)—C(1)—H(9) angle, corresponds to proton transfer along the O(3)...O(5) H-bond (see Fig. 2). Compared to the preceding profile, this one has quite a different character and does not pass through the TS even approximately.

From the results of calculations it also follows that the intramolecular H-bonds in both tautomers should be strongly different from conventional two-center H-bonds. Based on the O(3)...O(4) and O(3)...O(5) interatomic distances listed in Table 2, one could suggest a strong low-barrier intramolecular H-bond with two-well (or even single-well) local proton potential. However, in fact the barrier was found to be high ($\Delta E \approx 18$ kcal mol^{-1}) (see Fig. 2). Besides, studies of all three structures (D, TS, and PA) revealed no correlation between the O...O and O—H bond lengths, which is characteristic of conventional two-center H-bonds.[32,33]

Thus, there are grounds to believe that the actual reaction coordinate is complex in character and differs from the coordinate of proton transfer along the intramolecular H-bond (O(3)...O(5)). From this point of view the transition state of the D → PA tautomeric conversion found in this work is significantly different from the transition state of the reaction $H_2O_2 \rightarrow H_2O—O$, where it confirms the proton character of the reaction coordinate (1,2 H-shift). This, in particular, provides an explanation for high activation barrier ($\Delta E \approx 50$ kcal mol^{-1}) in the latter case (this was obtained by different methods[9—11]) owing to long proton-transfer distance (≥1.5 Å).

Substituent effects

Neutral systems

Problems related to the substituent effects will be discussed using the results of B3LYP/6-31G** calculations only, because the case in point is mainly the relative changes in the energy characteristics and geometry upon variation of substituents, which are identically described by different methods.

First, we will consider how the nature of the radical R (R = Me, CF_3) in position 2 (R-substitution) and the group X (X = O, NH) in position 3 (X-substitution) affect the heights of the activation barriers (ΔE_D, ΔE_{PA}) and the relative stabilities (ΔE_r) of tautomers (the atomic and substituent numbering schemes are given in Scheme 4). Replacement of the NH_2 group by OH in dioxiranes and of the =NH group in the peracid amide by the =O atom causes a simultaneous increase in the both parameters of the barrier (ΔE_D and ΔE_{PA}) and in ΔE_r, whereas replacement of Me group by CF_3 group increases only ΔE_D and ΔE_{PA} but decreases ΔE_r (Table 3).

Now consider structural implications of R-substitution for different tautomers using the calculated lengths of the bonds formed by the C(1) atom and the O(4)—O(5) bonds (Table 4). We will compare the geometry of D**1** with D**2**, D**3** with D**4**, and PA**1** with PA**2** and PA**3** with PA**4** (see Table 4). Changes in these bond lengths in both forms obey a similar pattern, being somewhat different only quantitatively. Replacement of Me group by a stronger electron-acceptor group CF_3 in D**1** and D**3** or in PA**1** and PA**3** leads to shortening of the C(1)—X(3) and C(1)—O(4)/O(5) bonds and to lengthening of the C(1)—C(2) bond. Identical qualitative changes in the ge-

Table 4. Bond lengths in tautomers of peroxyacetic acid derivatives obtained from B3LYP/6-31G** calculations

Bond	*d*/Å			
	D**1** (PA**1**)	D**2** (PA**2**)	D**3** (PA**3**)	D**4** (PA**4**)
C(1)—C(2)	1.510 (1.504)	1.536 (1.530)	1.502 (1.503)	1.534 (1.537)
C(1)—X(3)	1.382 (1.273)	1.371 (1.266)	1.361 (1.216)	1.347 (1.208)
C(1)—O(4)/O(5)	1.409	1.396	1.397	1.384
C(1)—O(4)	(1.355)	(1.342)	(1.354)	(1.339)
O(4)—O(5)	1.516 (1.446)	1.520 (1.443)	1.522 (1.442)	1.526 (1.440)

ometry upon replacement of a stronger donor substituent by a stronger acceptor substituent are characteristic of a number of molecules and clusters of the type $ML_{n-k}Y_k$, where M is the atom of a main-group element in the highest oxidation state and L and Y are monodentate substituents with different electronegativities. Examples can be provided by fluoro-substituted methanes, silanes, and some related systems.[34,35] It is this character of distortions that follows from analysis of the substituent effects in the framework of the vibronic theory of heteroligand systems[31] for tetrahedral and planar triangular molecular systems of main-group elements.[36] Therefore, one can expect that this approach, even in its simplest form (σ-approximation, frontier orbital approximation, *etc.*) can be applied to obtain a qualitative description of the substituent effects in the organic peroxides under study, although these molecules have more complex structures first of all due to the presence of different substituents in both types of tautomers.

Analysis of the results of the equilibrium geometry calculations for both tautomeric forms and the conclusions drawn in the model study[31] show that replacement of Me by CF_3 leads to shortening and thus stabilization of the stronger bonds, C(1)—X(3) and C(1)—O(4)/O(5), and at the same time to lengthening and therefore weakening of the weaker bonds, C(1)—C(2). This effect is somewhat more pronounced for the D-forms, which suggests that this type of substitution makes the D-form relatively more stable. This effect seems to be responsible for the decrease in ΔE_r for the CF_3-derivatives compared to the corresponding values for the Me-substituted ones (at the same X). Small changes in the lengths of the bonds mentioned above ($\Delta d \leq 0.02$ Å) obtained in the calculations (see Table 4) correspond to small changes in the relative stabilities ($\Delta E_r \leq 4$ kcal mol^{-1}) (see Table 3).

Now we will consider structural implications of X-substitution and compare the geometries of the D**1** and D**3**, D**2** and D**4**, as well as those of the PA**1** and PA**3**, and PA**2** and PA**4** forms (see Table 4). Assuming that the $—NH_2$ and =NH groups are less electronegative than —OH and =O, respectively, from the model study one should expect shortening (strengthening) of all bonds, except C(1)—X(3), in both tautomers. The results of the equilibrium geometry calculations for both forms are by and large consistent with these expectations, but the changes in the bond lengths were found to be very small (≤0.01 Å), probably owing similar orbital electronegativities of the $—NH_2$ and —OH groups and =NH and =O, especially in the latter case.

Interpretation of the influence on the C(1)—X(3) bond in the case of X-substitution in peroxides is somewhat more complicated. In contrast to R-substitution, where the changes in the C(1)—C(2) bond length allow one to assess the effect of substituent on the behavior of the substituent itself, here a new bond is formed between carbon and oxygen (instead of carbon—nitrogen bond). The electronic characteristics and structural parameters of the new bond can be significantly different. This differs the model substituent (with different electronegativity only), whose effect is considered by the perturbation theory, from a real one. Taking account of inhomogeneous ("heteroligand") character of the peroxides in question, in this case it is more appropriate to employ the results of the MO calculations with full geometry optimization without using additional (in our case, "too artificial") systems with homogeneous substituents.

Clearly, X-substitution in the PA- and D-tautomers is accompanied by formation of carbon—oxygen bonds instead of carbon—nitrogen bonds, the former being much shorter (stronger) than the latter. According to calculations, this effect is much more pronounced in the PA-forms, because here "shortening" of the C(1)—X(3) bond (*i.e.*, the difference between the C=O and C=N bond lengths) is much larger ($\Delta d \approx 0.06$ Å) than in the corresponding D-forms ($\Delta d \approx 0.02$ Å); besides, in the former case we deal with stabilization of the multiple bond (see Table 4). This indicates that enhancement of the electron-accepting properties of the X-substituent leads to higher relative stability of the PA-form. Therefore, it is not surprising that the relative stability, ΔE_r, increases on going from the nitrogen- to oxygen-containing peroxides even with different R (see Table 3).

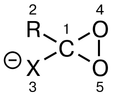
Moreover, we can assume that stabilization of the PA-form in the presence of a more electron-accepting X-substituent will dominate over the reverse effect of stabilization of the D-forms in the case of analogous R-substitution because of the high strengthening of the C=X multiple bond in the PA-forms predicted by calculations in the former case (see above).

If the arguments listed above are reasonable and the behavior of the C(1)—X(3) bond in the course of a tautomeric conversion does determine the energy characteristics of the conversion, is it logical to expect a correlation between (parallel changes in) the tautomerization energies (ΔE_r) and the differences between the C(1)—X(3) bond lengths in the corresponding D- and PA-forms of the organic peroxides mentioned above. (The squared Δd_{CX} difference multiplied by the corresponding force constant k_{CX} characterizes the contribution of the changes in this bond to the energy of geometric relaxation.) Indeed, such a correlation does occur (see Tables 3 and 4), although has a pure qualitative character. Nevertheless, it also remains when we consider the changes in other bonds (first of all, C(1)—O(4) and O(4)—O(5)) ignoring the differences between the force constants of the different bonds. It is important that Δd_{CX} appears to be an exclusive structural parameter, which changes in parallel to the ΔE_r values in the case of the D → PA conversions of the peroxides under study. This again emphasizes the determining role of the changes in the strongest bond, C(1)—X(3), in both forms on the tautomerization energy.

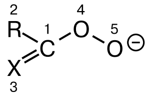
The effect of substitution at any position on the changes in the O(4)—O(5) bond lengths in both forms is very small (≤0.005 Å). With a given type of substitution, changes in the key bond angles and dihedral angles are also small (≤5°). In the case of the D → PA conversion such changes in each pair of tautomers are not small but almost identical; therefore, it seems likely that their effect on the isomerization energy can be ignored.

Ionic (deprotonated) derivatives

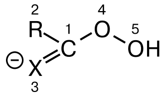
The approach[31] employed in this work allows peculiar features of the structures of ionic systems (DI and PI) to be considered in a dual fashion. On the one hand, it is natural to compare them with corresponding neutral systems (*i.e.*, DI with D and PI with PA). On the other hand, it is important to compare them with each other in exactly the same way as it was done above for the neutral systems (*i.e.* DI with each other and PI too).



DI**1**—DI**4**



PI**1**—PI**4**



PI**1**′, PI**2**′

	1	**2**	**3**	**4**	**1**′	**2**′
R	Me	CF_3	Me	CF_3	Me	CF_3
X	NH	NH	O	O	NH	NH

In the former case from the model consideration it follows that deprotonation, *i.e.*, formal electropositive replacement of the —NH_2 group by —NH^- group and of the —OH group by —O^- in the D-forms and of the —OOH group by —OO^- group in the PA-forms should destabilize them. Destabilization of the cyclic forms is expected to be significant, because it is related to weakening of three out of four bonds, namely, C(1)—O(4)/O(5) and C(1)—C(2), and to strengthening of only one bond, C(1)—X(3). At least equally high destabilization is also expected in the case of the acyclic forms, because here two out of three bonds, C(1)=X(3) and C(1)—C(2), are weakened while only one bond, C(1)—O(4), is strengthened. Rather, the destabilization can probably be even more pronounced. If, as above, we consider weakening of the multiple bond, C(1)=X(3), as a stronger destabilizing effect, it is quite natural to expect a decrease in the relative stability difference between the corresponding ionic cyclic (DI) and acyclic (PI) isomers provided that they are stable (Table 5).

Table 5. Bond lengths in deprotonated peroxyacetic acid derivatives obtained from B3LYP/6-31G** calculations

Bond	d/Å			
	DI**1** (PI**1**) [PI**1**′]	DI**2** (PI**2**) [PI**2**′]	DI**3** (PI**3**)	DI**4** (PI**4**)
C(1)—C(2)	1.525	1.539	1.540	1.548
	(1.516)	(1.531)	(1.535)	(1.540)
	[1.520]	[1.515]		
C(1)—X(3)	1.323	1.313	1.249	1.242
	(1.302)	(1.294)	(1.230)	(1.225)
	[1.233]	[1.230]		
C(1)—O(4)/O(5)	1.500	1.482	1.489	1.467
C(1)—O(4)	(1.319)	(1.309)	(1.315)	(1.304)
	[1.495]	[1.476]		
O(4)—O(5)	1.510	1.512	1.510	1.513
	(1.457)	(1.441)	(1.442)	(1.434)
	[1.443]	[1.448]		

This trend, along with the expected structural changes in both types of anions (containing —NH^- or —O^-) compared to the corresponding neutral systems, is consistent with the results of B3LYP/6-31G** calculations of the equilibrium geometry (see Tables 4 and 5). In order to compare the nitrogen-containing forms PI**1** and PI**2** with the corresponding oxygen-containing forms PI**3** and PI**4**, we considered configurations with broken intramolecular H-bonds. Indeed, the results of calculations indicate a significant destabilization of acyclic forms compared to the corresponding cyclic ones where the determining role is played by the changes in the C(1)—X(3) bond, namely, in the PA-form this *multiple* bond is lengthened while in the D-form this *ordinary* bond is shortened. Therefore, it is not surprising that the total energies of the cyclic and acyclic ionic forms in all systems considered approach one another and the ΔE_r values decrease to 2—4 kcal mol^{-1}, being changed irregularly.

Replacement of substituents in the case of R- and X-substitutions in the deprotonated (cyclic and acyclic) anions should lead to exactly the same qualitative changes in the structural parameters as in the corresponding neutral systems. According to calculations, this holds for the R-substitution. The changes in the corresponding bond lengths appeared to be nearly the same (see Table 5). A somewhat different situation was revealed for the X-substitution in both types of anions. First of all, calculations led to "incorrect" behavior of the R-group, where one should expect shortening rather than elongation of the C(1)—C(2) bond in the case of the DI**2** → DI**4**, PI**1** → PI**3**, and PI**2** → PI**4** conversions. As a pretext, note that in all cases the elongation of the C(1)—C(2) bond is small (<0.01 Å). Therefore, the inconsistency mentioned above is insignificant, especially taking into account that it concerns relatively weak bonds. The main reason for these discrepancies is that the model approach[31] treats bulky Me and CF_3 groups as monatomic substituents, thus ignoring possible changes in their internal structure on substitution (by the way, possible formation of intramolecular H-bonds is also ignored).

Besides, stabilization of both types of anions in the case of X-substitution due to formation of the carbon—nitrogen bond instead of the carbon—oxygen bond is of different character compared to neutral systems in spite of all similarities. If in the neutral systems such a substitution to a greater extent stabilizes the acyclic form, both forms of anions are stabilized nearly equally (although in the DI-forms we still deal with the ordinary bond while in the PI-forms we deal with the multiple bond), the more so two C(1)—O(4)/O(5) bonds in the DI-forms are additionally stabilized. If, as above, we assume that the stabilization effect predominates, this method of description also leads to "levelling" of the relative stabilities of both anionic forms, which was predicted by calculations.

Clearly, the nitrogen-containing open forms can have two other isomers, namely, the proton-transfer forms **PI1**´ and **PI2**´ (see Table 5). Their comparison with the **PI1** and **PI2** isomers, respectively, in the framework of the model approach shows that in each case we deal with a double substitution. First, =NH group is replaced by a more electron-donor substituent, $=N^-$, and then $—OO^-$ is replaced by a more electron-accepting substituent, —OOH. Then, one can expect shortening of the C(1)=X(3) bond and lengthening of the C(1)—O(4) and C(1)—C(2) bonds in the former and shortening of the C(1)=X(3) and C(1)—C(2) bonds and elongation of the C(1)—O(4) bond in the latter case. The overall effect is apparent, consisting in shortening of the C(1)=X(3) bond and lengthening of the C(1)—O(4) bond (the C(1)—C(2) bond behaves ambiguously). Considering the shortening of the multiple bond as preferred effect, it is logical to expect stabilization of the "new" PI-isomers compared to the "old" ones.

Indeed, calculations substantiated (see Table 5) that the **PI1** → **PI1**´ and **PI2** → **PI2**´ conversions are followed by shortening of the C(1)=X(3) multiple bond by 0.04 Å and lengthening of the C(1)—O(4) ordinary bond by 0.14 Å, the stabilization energy of the new PI-isomers being equal to 5—6 kcal mol^{-1}. This again emphasizes a realistic character of the proposed correlation between the isomerization energy and the changes in the strongest bonds, C(1)—X(3), in the isomers.

From the results of calculations of the deprotonated anions it also follows that the activation barriers to the isomeric conversions become much lower than those obtained for the corresponding neutral systems (in particular, by 1—1.5 eV for the DI**3** → TS´ → PI**3** conversion: $\Delta E = 10.8$ and $\Delta E = 12.8$ kcal mol^{-1} (*cf.* the data listed in Table 1). Here, owing to the lack of hydrogen atom and corresponding shortening of the $C(1)—O^-(3)$ bond in dioxirane DI**3** (1.25 Å) the energy expenditure for relaxation of this bond on going to TS´ (1.22 Å) and PI**3** (1.23 Å) is smaller than in the case of the D**3** → TS → PA**3** conversion (*cf.* the data listed in Table 2). Relaxations of other geometric parameters in the corresponding anionic and neutral systems obey nearly identical patterns. A similar effect, although being somewhat more pronounced, also occurs in the case of the DI**4** → TS″ → PI**4** conversion; here, this effect is even stronger (2—2.5 eV).

Note that qualitative conclusions about the structure of isomers, specific features of the transition states, and substituent effects in the organic systems under study depend only slightly on the computational procedure employed. Discrepancies between the individual interatomic distances and bond angles in reactants, products, and transition states obtained in the course of the RHF(UHF), B3LYP, and MP2 geometry optimizations are insignificant except for the O—O interatomic distance in the TS, which seems to be too overestimated in the calculations without inclusion of electron correlation (by 0.1 Å). The energy parameters ΔE_D (ΔE_{PA}) and ΔE_r depend on the computational procedure employed in a more complex fashion (see Table 3). If we restrict ourselves to the B3LYP calculations only, the ΔE_D (ΔE_{PA}) values differ by less than 10% while the ΔE_r values differ to even lesser extent.

From the results of our calculations it follows that the acyclic forms of the PA and D tautomers of organic peroxides are more stable than the cyclic forms at any R and X. On the contrary, the dioxirane forms of isomers of the organic peroxides $RR'CO_2$ (R = H, R´ = H, OH) are more stable, $\Delta E_r \approx 1$ eV (see Ref. 3). It should be emphasized that the open forms of the type-I and type-II peroxides are different: in the former case this is a peracid, *i.e.*, the PA-form, whereas in the latter case this is the carbonyl oxide form. The existence of the carbonyl oxide form of the type-I peroxides (as well as the form with the structure of water oxide[8,12,13,24], see above) and the salient features of its tautomerism in the case of conversions into the D- and PA-forms require a separate study.

The key feature of the transition state of tautomeric conversion D → PA is a "two-step" character of this process. The first step involves flattening of the quasi-tetrahedral dioxirane structure while the second step involves relaxation of the "non-hydrogen" skeleton to the final state accompanied by proton transfer. It was also found that in the case of tautomerism it is appropriate to use the change in the dihedral angle on going from the quasi-tetrahedral to planar structure as the reaction coordinate and that the potential energy profile along this coordinate provides a reasonable description of both steps of the tautomeric conversion.

In studying the effect of substituents on the activation barrier parameters it was found that they increase as the electron-accepting properties of both substituents are enhanced. Analysis of a more complex dependence of the tautomerisation energy on the nature of the substituent revealed a correlation between the changes in this energy and the key characteristics of structural rearrangement upon substitution at both positions, the changes in the C(1)—X(3) bond playing the predominant role.

Analysis of the electronic and molecular structures of deprotonated anionic systems showed that the relative stability differences between the open and closed forms of isomers dramatically decrease. We also found a lowering of the activation barrier, which seems to be due to the absence, in this case, of the proton transfer step in the course of isomerization.

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