Computational modeling of the mechanisms and stereochemistry of circumambulatory rearrangements of formylcyclopropene and 4-hydroxycyclobutenyl cation†

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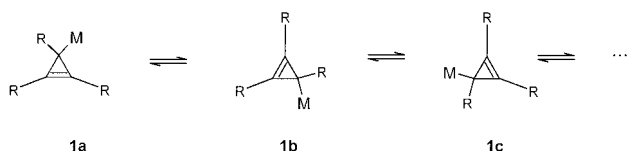Institute of Physical and Organic Chemistry, Rostov University, 194/2 Stachka St, Rostov on Don 344090, Russia

ABSTRACT: MP2(fc)/6-31G** calculations on the ground and transition state structures for intramolecular rearrangements of formylcyclopropene found that circumambulation of the ring by a formyl group occurs through a high-energy ($\Delta E = 42.6$ kcal mol^{-1}) intermediate with a structure similar to bicyclo[1.1.0]oxide zwitterion. By passing through two successive transition state structures this intermediate rearranges also to topomers of monoepoxide of cyclobutadiene (Dewar furan). Another intramolecular rearrangement of formylcyclopropene leading to inversion of stereochemical configuration at the sp^3-carbon centre is associated with a one-step transposition reaction which involves a CC bond scission. The energy barrier to the circumambulatory rearrangement of formylcyclopropene can be considerably decreased by protonation of the carbonyl group resulting in formation of the homoaromatic 4-hydroxycyclobutenyl cation. Exo and endo conformers of this cation are susceptible to low-energy barrier (10.1 and 10.3 kcal mol^{-1}, correspondingly) circumambulatory rearrangement due to migration of a hydroxymethylene group along the periphery of the three-membered ring. The rearrangement occurs as a non-concerted two-step reaction involving intermediacy of bisected exo and endo conformers of hydroxycyclopropenylcarbinyl cation, and results in inversion of stereochemical configuration at the migrating carbon centre. Homoaromaticity of 4-hydroxycyclobutenyl cation is manifested by the predicted high energy barrier (13.1 kcal mol^{-1}) against its planar inversion. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: *ab initio* calculations; circumambulatory rearrangements; energy barriers; homoaromaticity

INTRODUCTION

Whereas circumambulatory (merry-go-round, walk) rearrangements due to migration of organometallic[1] or main-group-element centred[2] groups around the periphery of the five-membered cyclopentadiene ring have been amply studied, those related to the smallest unsaturated carbocyclic system of cyclopropene **1** have received thus far much less attention.

In contrast with rearrangements of cyclopentadienes, most of which occur as a sequence of 1,5-sigmatropic shifts of a migrating group, the rearrangements of cyclopropenes containing such readily ionizable substituents as M = Cl,[3a] N$_3$,[3b] NCS and SCN[3c] proceed according to random ionization –recombination mechanisms facilitated by the aromatic stability of the formed cyclopropenium cation. An exception to this trend is a low-energy barrier ($\Delta G^{\#}_{298} = 17.8$ kcal mol^{-1}, toluene-d$_8$) circumambulatory rearrangement of S-(1,2,3-triphenylcyclopropenyl)-O-ethyldithiocarbonate **1** [R = Ph, M = SC(OEt) = S], which is most probably governed by a non-dissociative 3,3-sigmatropic shift mechanism.[4] At the same time MNDO/PM3 calculations show that the 1,3-sigmatropic shift mechanism is highly energy unfavourable compared with both 3,3-sigmatropic shift and ionization–recombination reaction routes.

Of special interest are the rearrangements of the derivatives of cyclopropene **1** with migrating groups M = −X = Y containing π-bonds. As previous semiempirical[5] (MINDO/3, MNDO/PM3 and AM1) and *ab initio*[5b] calculations of the C$_3$H$_3$NO and C$_3$H$_3$PO potential energy surfaces (PES) have revealed, secondary orbital interactions between such types of migrants and the basal ring

provide for the existence of several different channels of intramolecular rearrangements. According to MNDO/PM3 and RHF/6-31G** calculations,[5b] the relative energy of the bicyclic structure **2c** (X = N), corresponding to the transition state for the 1,3-shift of a nitroso group over the cyclopropene ring, is as high as 61.8 and 68.4 kcal mol^{-1}, respectively. However, an account for electron correlation at the MP2(full)/6-31G** level of approximation results in substantial stabilization of **2c** and even changes the nature of the stationary point pertinent to **2c**. The energy of **2c** relative to the ground state structure **2a** ($\Delta E = 35.3$ kcal mol^{-1}) was predicted to be too high for the rearrangements detectable by dynamic NMR. The calculations[5] also predicted that substitution in the three-membered ring of **2** only slightly affected the value of the energy barrier to the 1,3-sigmatropic shift circumambulatory rearrangement. A much stronger effect is caused by substitution of a nitrogen atom in the migrating group by phosphorus. At the RHF/6-31G** level of approximation, the local minimum of the structure **2c** on the C_3H_3PO PES lies only 5.1 kcal mol^{-1} higher than the minimum of **2a** (X = P).

2a   2c   2b
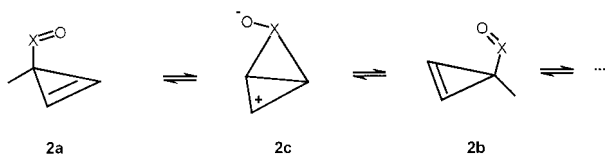
In this paper, we report on a computational modelling of the mechanism and energetics of the intramolecular rearrangements of another isoelectronic analogue of **2**, formylcyclopropene, **3**. The possibility of catalysis of the circumambulatory rearrangement of **3** through its protonation has been considered and the mechanism and stereochemistry of topomerization of the thus formed non-classical 4-hydroxycyclobutenyl cation, **13**, studied.

EXPERIMENTAL

The *ab initio* calculations were performed on a workstation IBM RS/6000 with the Gaussian 94 programme package.[6] The standard polarized split valence basis set and second-order Møller-Plesset (MP2) perturbation theory in a frozen core (fc) approximation were used for geometry optimization of all the structures corresponding to minima or transition state (TS) structures on potential energy surfaces. Stationary points were characterized by analysing the Hessian force constant matrices.

RESULTS AND DISCUSSION

Rearrangements of formylcyclopropene

The mechanism of the photochemical rearrangement of

acylcyclopropenes has been the subject of detailed experimental[7] and theoretical[8] investigation. In a recent work,[8b] the topology and energetics of the PES of the lowest excited singlet and triplet states were analysed along several possible reaction coordinates using CAS-SCF calculations in a 6-31G* basis set. Although no question of the ground state rearrangement of the parent acylcyclopropene **3** has been directly addressed, calculations on the bicyclic structure **4** potentially related to a transition state or an intermediate of various rearrangements of **3** have been performed. According to these calculations, **4** represents a high-energy (89.9 kcal mol^{-1}) transition state linking **3** to a biradical intermediate on the reaction coordinate leading to furan.

An objective of our study was to obtain a deeper insight into the part of the ground state C_4H_4O PES relevant to circumambulatory and transposition rearrangements of formylcyclopropene using a higher level of approximation than those previously employed.

Table 1 presents the main results of our MP2(fc)/6-31G** calculations of energies of the principal structures involved into rearrangements of formylcyclopropene as portrayed by Scheme 1. The geometries of these structures are shown in Fig. 1 and Fig. 2.

The bisected exo-conformer of formylcyclopropene, **3** (exo), is 0.9 kcal mol^{-1} energy-preferable to its endo-isomer **3** (endo). The conformers interconvert by passing through the eclipsed transition state structure **5**, overcoming the energy barrier of 6.7 kcal mol^{-1} to rotation of a formyl group about the C(2)–C(4) bond. Only one exo-isomer of the bicyclic intermediate **4** exists on the MP2(fc)/6–31G** PES, whereas at the RHF/6-31G** level of approximation local minima corresponding to both exo- and endo- forms of **4** have been found on the C_4H_4O PES. Because of the flatness of the PES in the region of the structure **4** we were unable to locate a transition state structure directly connecting **4** to **3** (exo). It was found, indeed, that variation in the C(2)–C(3) bond distance in the range of 1.60–1.68 Å results in only 0.01 kcal mol^{-1} change in the total energy. Therefore, the energy barrier to circumambulation of cyclopropene ring by a formyl group **3a** $\rightleftharpoons$ **3b** may be reasonably well approximated by the energy (42.6 kcal mol^{-1}) of the intermediate **4** relative to **3** (exo). This energy barrier is apparently too high to be surmounted in the course of a thermally driven rearrangement observed on the NMR time scale.

It might be expected that exo conformer of **4** is capable of undergoing ring inversion isomerization into its endo form. The calculations employing intrinsic reaction coordinate (IRC) technique[10] showed that planarization of **4** resulted in its conversion not to endo conformer of **4**, but to the energy-preferable isomer **8** (Dewar furan) and involved passage through two successive transition state structures **6** and **7**. That the rearrangement tends to end up in the formation of **8** is clearly seen from the
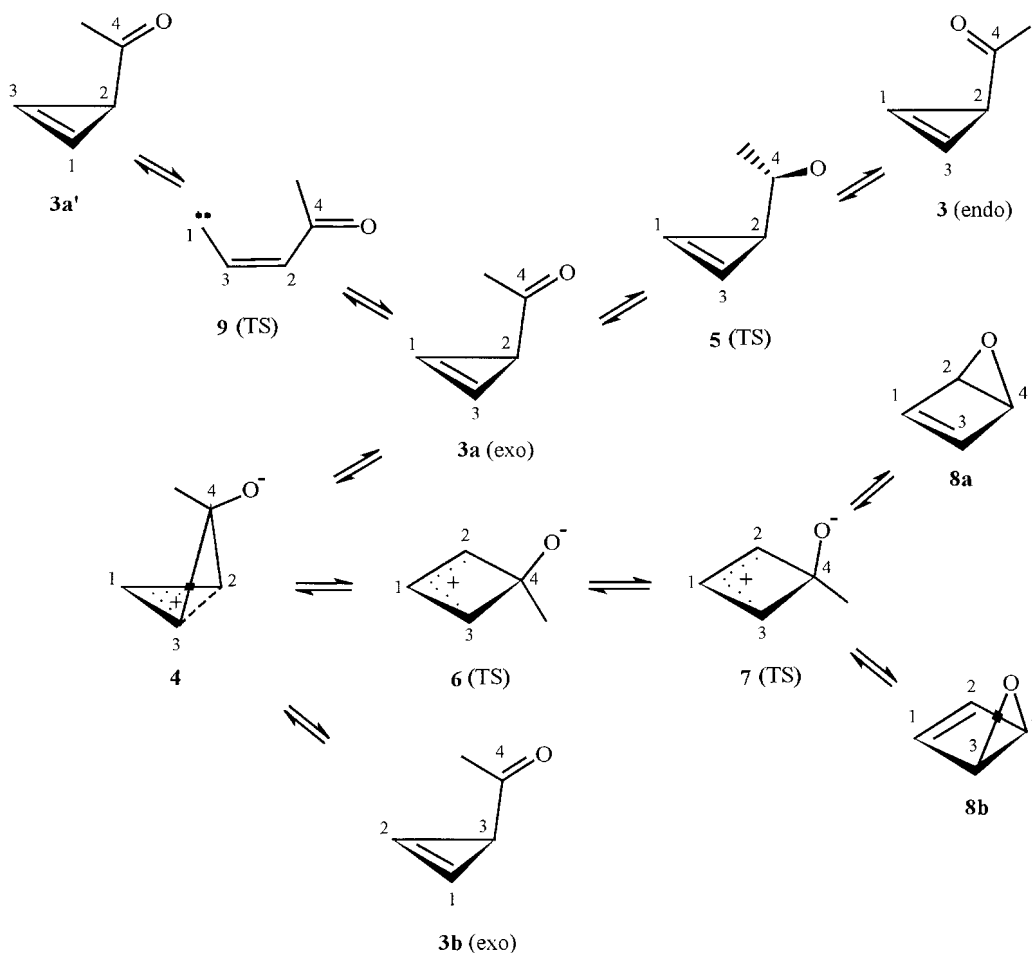
Scheme 1

shape of the transition vector related to the structure **7** (Fig. 2). This structure represents the transition state for the oxygen-walk rearrangement of monoepoxide of cyclobutadiene (Dewar furan) associated with migration of an oxygen around the four-membered ring. Such rearrangement that leads to scrambling carbon centres in the four-membered ring has not yet been observed for derivatives of Dewar furan, **8**, but this type of thermal walk rearrangement of derivatives of Dewar thiophene occurring on the NMR time scale is known.[11] The peculiar topology of this part of the C_4H_4O PES (two

directly connected saddle points without a minimum between them), shown in Fig. 3, is not an artefact of the calculations and has been previously documented for a number of other reactions.[12]

Another reaction channel of intramolecular rearrangements of formylcyclopropene is associated with the one-step transposition reaction **3a** = **3a′** that leads to inversion of stereochemical configuration at the tetrahedral carbon centre and occurs through a planar transition state structure, **9**. It is formed via an energy-consumable ($\Delta E = 51.8 \, \text{kcal mol}^{-1}$) scission of a CC bond in the

Table 1. Total energies (E_{tot}), zero-point energies (ZPE), relative energies (ΔE) and values of the imaginary normal mode frequencies (ν_{im}) for the structures **3–9** located at the MP2(fc)/6-31G** PES of C_4H_4O

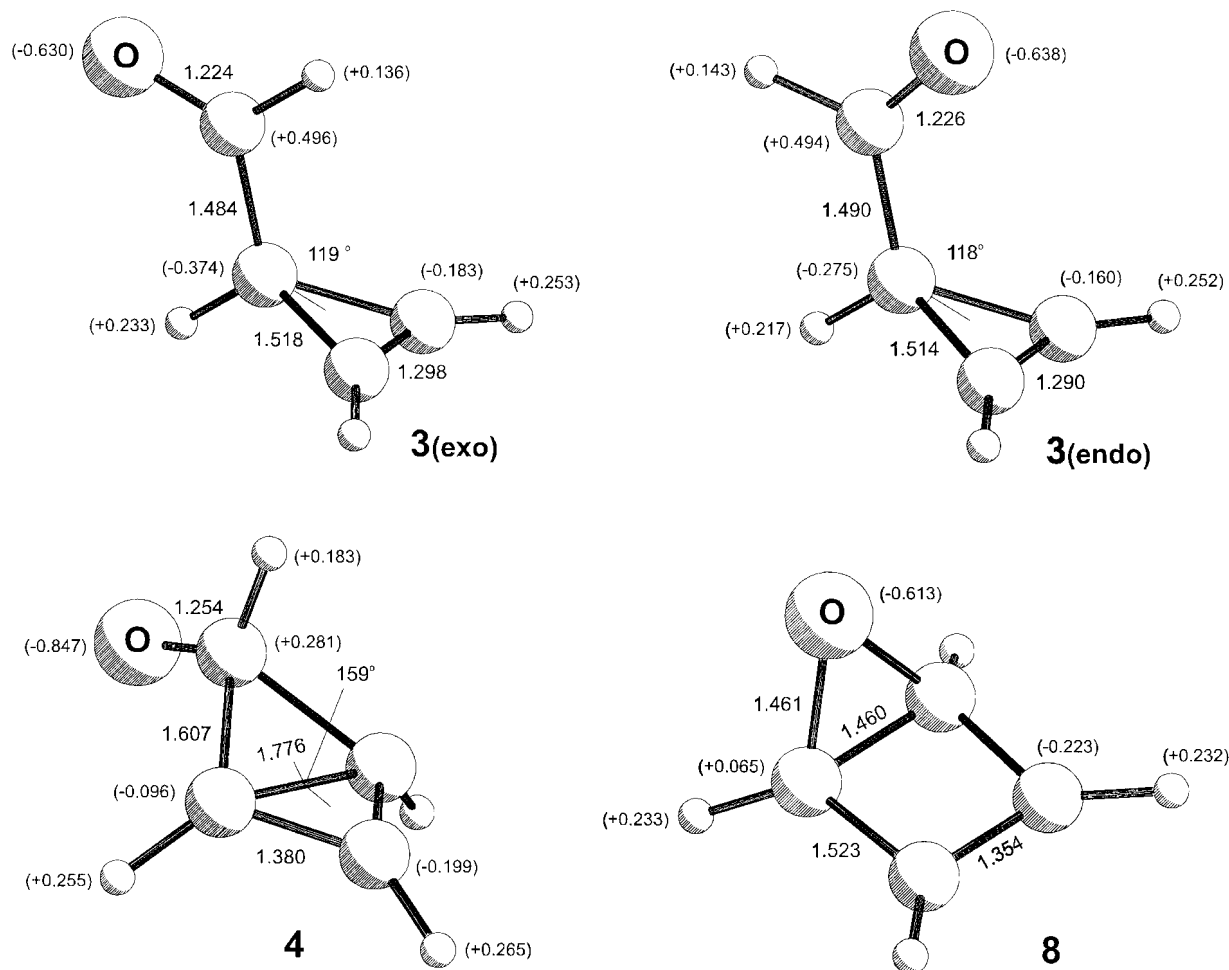| Structure	E_{tot} (a.u)	ZPE (a.u)	ν_{im} (cm^{-1})	ΔE (kcal mol^{-1})
3(exo)	−229.264816	0.066717	—	0
3(endo)	−229.263351	0.066644	—	0.9
4	−229.195519	0.065365	—	42.6
5	−229.253645	0.066213	175	6.7
6(TS)	−229.192257	0.066304	208	45.3
7(TS)	−229.195248	0.067002	460	43.8
8	−229.234040	0.068797	—	20.6
9(TS)	−229.179947	0.064468	290	51.8

Figure 1. MP2(fc)/6-31G** optimized geometrical parameters (distances in Å and angles in degrees) and NBO charge distributions[9] of the conformers of formylcyclopropene **3** (exo) and **3** (endo), bicyclic intermediate **4** and Dewar furan, **8**

three-membered ring of **3**. As follows from the geometry of the transition state structure **9** [double C–O and C(2)–C(3) bonds], it should be assigned to a singlet 1,5-biradical rather than 1,1-biradical (carbene) type (Fig. 2). A similar transition state structure has been located on the reaction path of the rearrangement of nitrosocyclopropene **1** (R = H, M = NO) to azacyclobutadiene-N-oxide.[5b] A planar type **9** structure has been identified by calculations[8b] as not a transition state but a biradicaloid intermediate on the ground state C_4H_4O PES in the region of the $^3(\pi\ \pi^*)/S_0$ triplet/singlet crossing point related to the ring-fission mechanism of the photorearrangement of formylcyclopropene to furan.

The calculations performed lead to the conclusion of a very low migratory aptitude of a formyl group in the cyclopropene ring. One should not, therefore, expect that the circumambulatory rearrangement of **3** or its derivatives can be observed by the use of dynamic NMR spectroscopy. It is well known, however, that an appreciable acceleration of the rearrangements related to intramolecular migration of acyl groups can be achieved under conditions of general or specific acid

catalysis.[13] Protonation of the carbonyl oxygen causes significant lowering of the energy level of the π^*_{co} orbital and thus amplifies its interaction with π-system of the rest of a molecule. The same and even stronger effects are brought about by complexation with strong Lewis acids. Manifestation of this effect is exemplified by a large decrease (8–10 kcal mol^{-1}) in the energy barrier to circumambulatory rearrangements of 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes **10**, which were suggested to proceed through formation of the intermediate adducts with aluminium trichloride possessing the structure of the bicyclo[3.1.0]hexenyl zwitterions **11**.[1c,14]
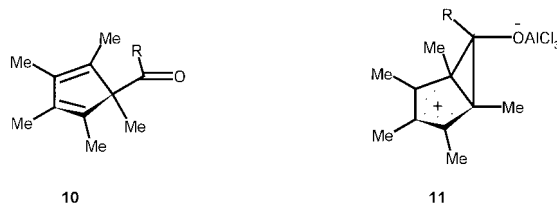
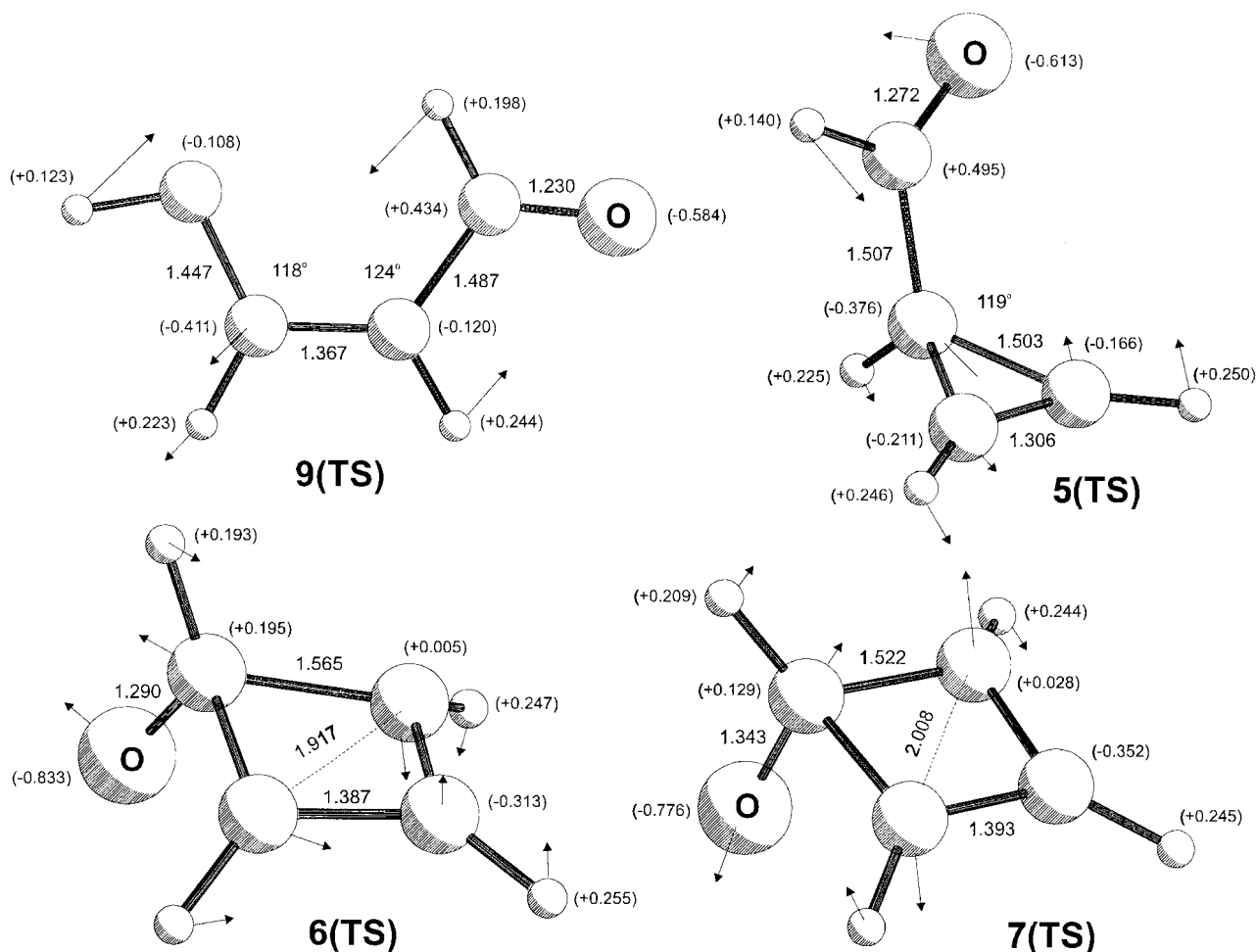It may, therefore, be expected that, by analogy with acylcyclopentadienes, protonated acylcyclopropenes ex-

Figure 2. MP2(fc)/6-31G** optimized geometrical parameters (distances in Å and angles in degrees), NBO charge distributions[9] and the transition vectors corresponding to the normal vibration mode of v_{im} (Table 1) of the transition state structures involved in the rearrangements of formylcyclopropene, as shown in Scheme 1

hibit greater fluxionality than their conjugated bases **3**. To explore theoretically this possibility we have carried out MP2(fc)/6-31G** calculations of the structure and reaction paths for circumambulatory rearrangement of the protonated formylcyclopropene.

Rearrangements of 4-hydroxycyclobutenyl cation

The calculations show that protonation of formylcyclopropene, **3**, occurs at the carbonyl oxygen and gives four isomeric cations, of which the exo-conformer of 4-hydroxycyclobutenyl cation **13a** represents the most stable form. It is 8.1 kcal mol^{-1} energy-preferable to the endo conformer, **13b**, and 3.7 kcal mol^{-1} more stable than the bisected exo-conformer of cyclopropenylcarbinyl cation, **15a**. It is noteworthy that the bisected endo-cyclopropenylcarbinyl isomeric form is predicted to be slightly (3.2 kcal mol^{-1}) energy-favourable compared with the corresponding endo-cyclobutenyl structure, **13b** (Table 2). Calculated geometries and charge

distribution in the cations **13a,b** and **15a,b** are illustrated in Fig. 4.

The structure of 4-hydroxycyclobutenyl cation may be analysed in terms of three basic forms, **A–C**, related to cyclobutenyl, bicyclo-[1.1.0]butyl and homocyclopropenyl structural types, respectively.
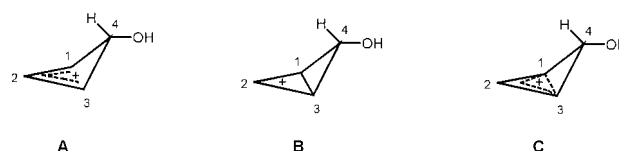
Much like the parent cyclobutenyl cation, the cation **13** has a pronounced homoaromatic character (the structure **C**), which is defined by nearly equal charges on the atoms C(1), C(2) and C(3), as well as a sufficiently short C(1)–C(3) distance. This distance is intermediate between the corresponding bond length in bicyclobutane (1.47 Å) and the C(1)–C(3) separation (1.99 Å) in the almost planar transition state structure, **16**, for ring inversion of 4-
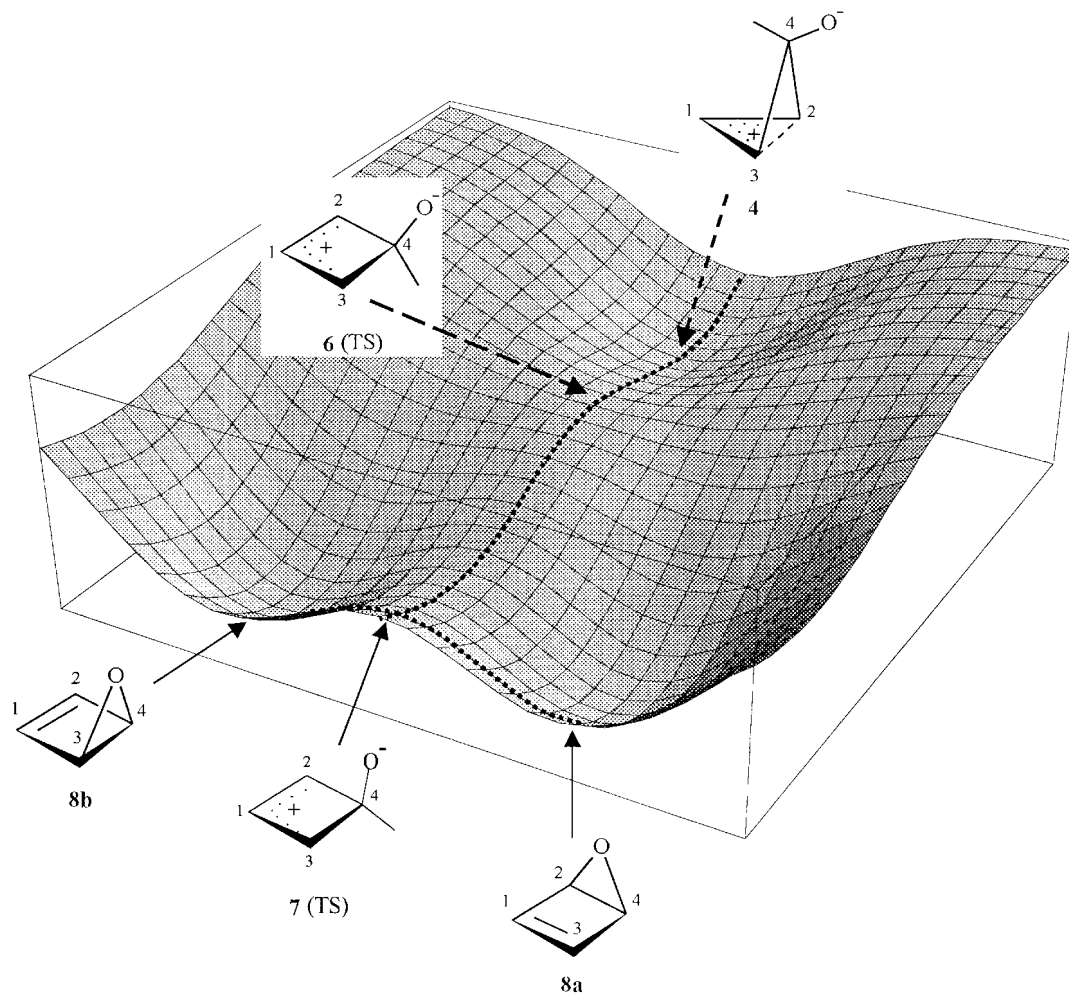
Figure 3. A part of the C_4H_4O PES related to conversion of the intermediate **4** to topomers of Dewar furan, **8**

hydroxycyclobutenyl cation (Scheme 2). These characteristics were considered[15] the basic attributes of homoaromaticity. Another reliable index of homoaromaticity is the value of energy barrier to ring inversion[15a,b] (homoaromatization energy[16]). For the parent cyclobutenyl cation considered to be a prototype for homoaromatic character,[15a,17] an experimental value of this

barrier obtained by the dynamic ^{1}H NMR method is $8.4 \pm 0.5\,\mathrm{kcal\,mol^{-1}}$,[15b] which is in accord with a theoretical MP2 (full)/6-31G* estimate (10.2 kcal mol^{-1}).[15a] The energy barriers to the ring inversion in exo- and endo-hydroxycyclobutenyl cations, **13a** and **13b**, have been calculated to be 13.1 and 5.0 kcal mol^{-1}, respectively (the average value is 9.05 kcal mol^{-1}),

Table 2. MP2(fc)/6-31G** calculated total energies (E_{tot}), zero-point energies (ZPE), relative energies (ΔE) and values of the imaginary normal mode frequencies (v_{im}) for the structures **13–17**

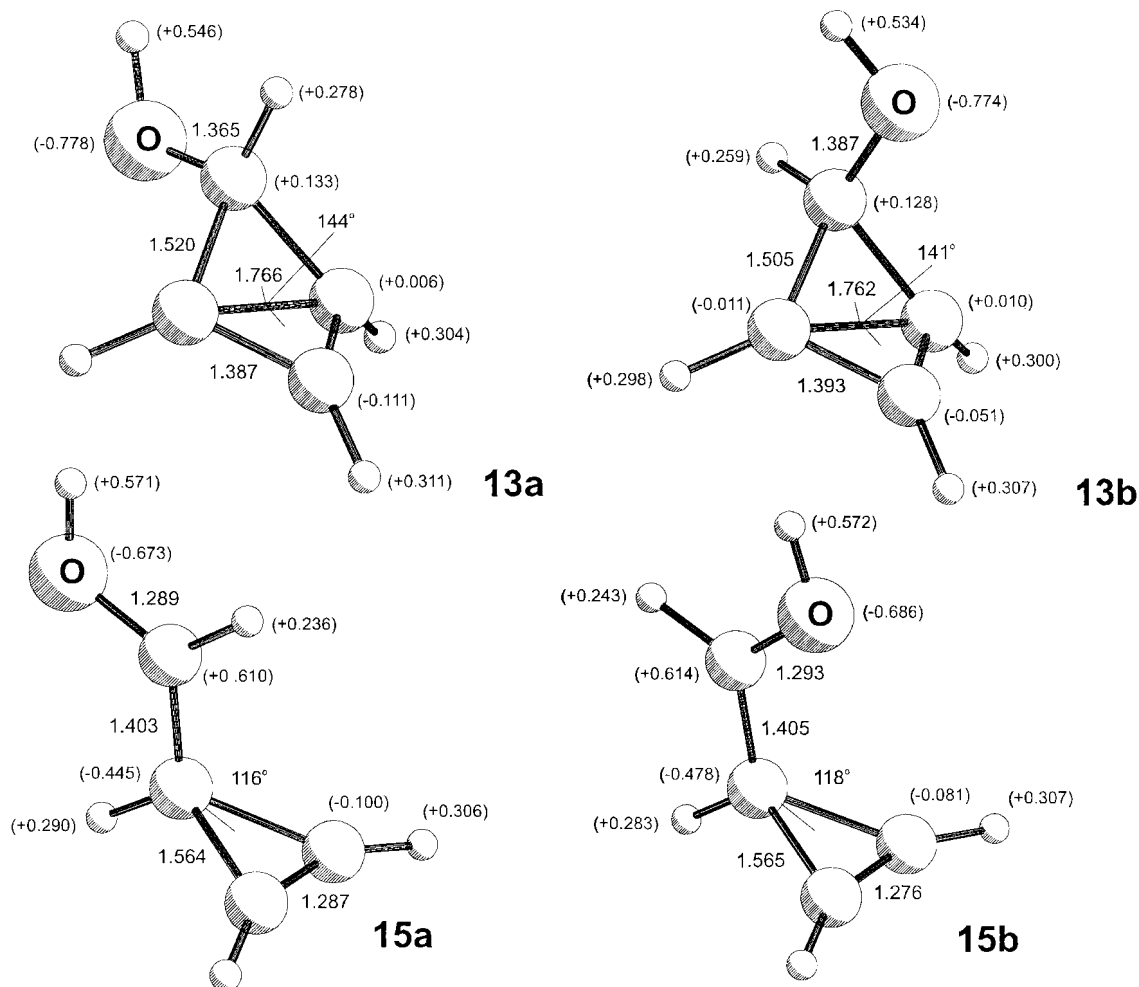| Structure	E_{tot} (a.u)	ZPE (a.u)	v_{im} (cm^{-1})	ΔE (kcal mol^{-1})
13a	−229.601643	0.081079	—	0
14a	−229.584232	0.079728	272	10.1
15a	−229.594571	0.079893	—	3.7
13b	−229.588671	0.081039	—	8.1
14b	−229.570761	0.079475	431	18.4
15b	−229.592529	0.079720	—	4.9
16	−229.580431	0.080800	267	13.1
17	−229.568111	0.079626	266	20.1

Figure 4. MP2(fc)/6-31G** optimized geometrical parameters (distances in Å and angles in degrees) and NBO charge distributions[9] of the conformers of 4-hydroxycyclobutenyl, **13a** and **13b**, and the conformers of hydroxycyclopropenylcarbinyl, **15a** and **15b**, cations

which points to significant homoaromatic character of the 4-hydroxycyclobutenyl cation.

By gaining insight into the structure of protonated formylcyclopropene as a derivative of the non-classic cyclobutenyl cation, we are faced with the long-debated problem of the mechanism and stereochemistry of fast circumambulatory rearrangements of its derivatives.[1c,18] A tetra-*tert*-butyl derivative of 4-hydroxycyclobutenyl cation, **12**, was previously prepared by oxydation of tetra-*tert*-butyltetrahedrane[19] and shown to undergo low-energy-barrier ($\Delta G^{\#} \cong 15\,\mathrm{kcal\,mol^{-1}}$) rearrangements due to a sequence of 1,2-sigmatropic shifts of the CHOH group around the perimeter of the cyclopropene ring. Although no direct experimental evidence of stereo-chemical outcome of the rearrangement was available, weighty arguments were presented in favour of the mechanism with inversion of the configuration at the migrating carbon centre. Thus, the value of the ^{13}C NMR chemical shift of the migrating sp3-carbon atom in the cation **12** remains constant in a wide range of solution

temperature, which evidences the participance of only one (exo) isomer of the cation **12** in the reaction course. The reaction pathway with retention of stereochemical configuration at the migrating centre would require interconversion of exo- and endo-conformers at each step of the rearrangement.
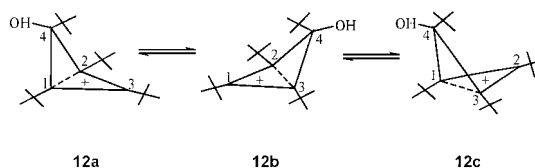
This conclusion seems to be in accord with that of RHF/4-31G calculations[18b,c] on the stereochemical course of the circumambulatory rearrangement of the unsubstituted cyclobutenyl cation. The rearrangement was attributed to a one-step concerted 1,2-sigmatropic shift reaction occurring with violaton of the Woodward–Hoffmann rules. However, these calculations left open
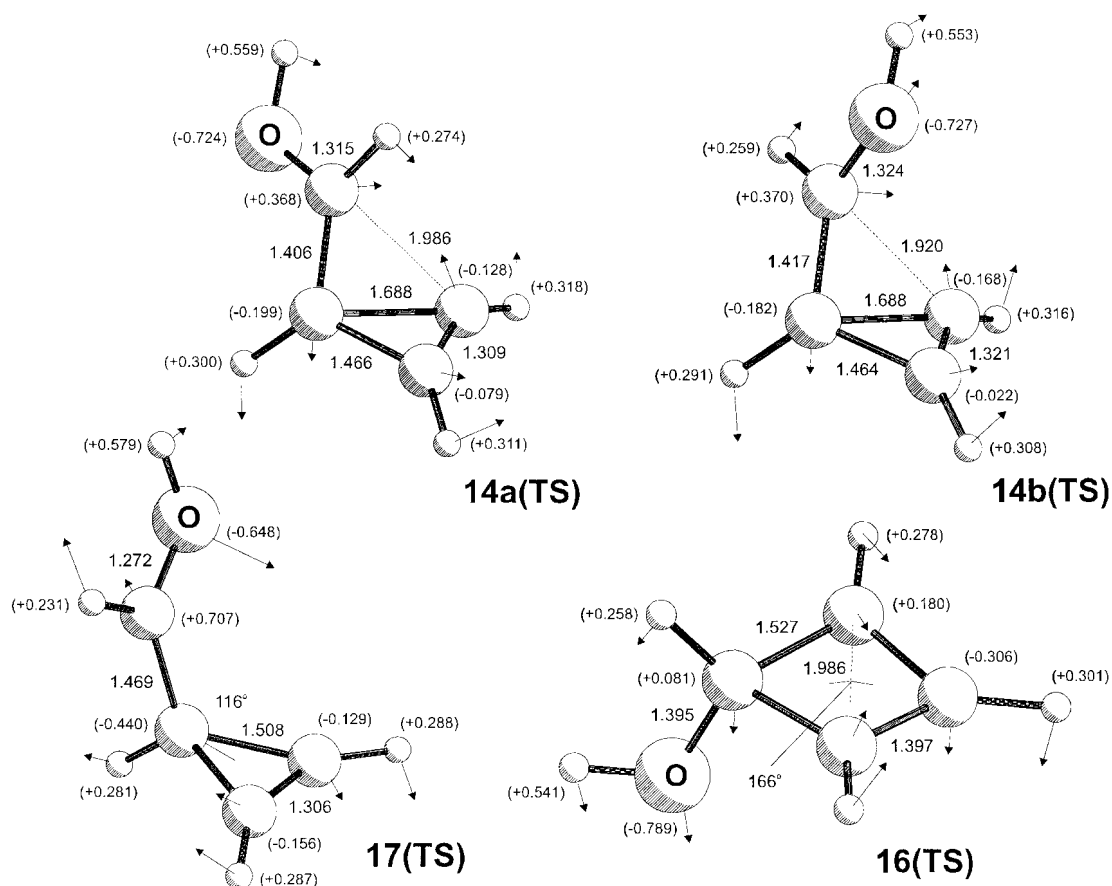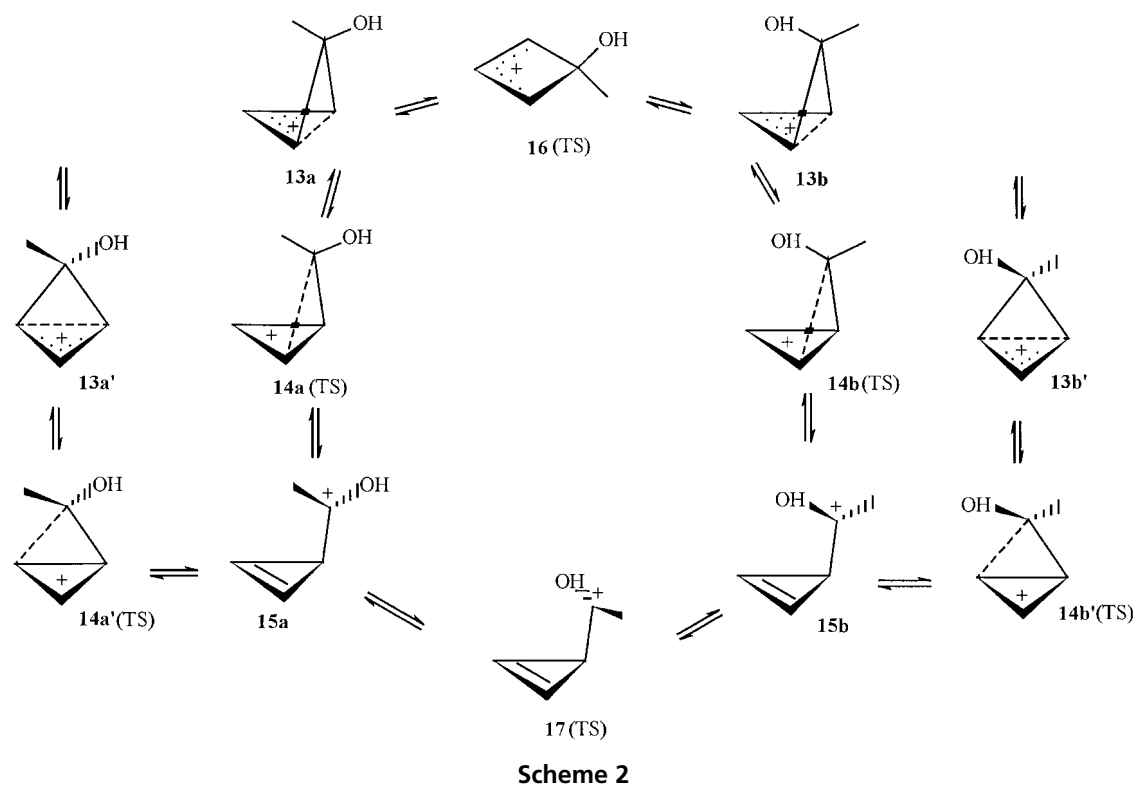
Scheme 2

Figure 5. MP2(fc)/6-31G** optimized geometrical parameters (distances in Å and angles in degrees), NBO charge distributions and the transition vectors corresponding to the normal vibration mode of v_{im} (Table 2) of the transition state structures involved in the rearrangements of 4-hydroxycyclobutenyl cation, as shown in Scheme 2

the questions on the nature of the stationary points pertinent to the transition state or intermediate structures for both alternative reaction paths as well as on the concertedness of the rearrangement.

In the present computational study we addressed the following questions: (i) what is the theoretical expectation for energy barriers of the circumambulatory rearrangements of the conformers of 4-hydroxycyclobutenyl cation **13a** and **13b;** (ii) whether circumambulatory rearrangement of 4-hydroxycyclobutenyl cation occurs as a concerted (one-step) reaction or if it is a two-step reaction with inclusion of the isomeric hydroxycyclopropenylcarbinyl cations **15** as the intermediates; (iii) can the alternative reaction pathway with retention of stereochemical configuration at the migrating carbon centre of **13** be energy-competitive through either low-energy barrier conformational isomerizations of the hydroxycyclopropenylcarbinyl cations or planar inversion of the cations **13**? In order to answer these questions, critical parts of the $C_4H_5O^+$ potential energy surface depicted by Scheme 2 were investigated. To estimate the opportunities of interconversions of exo- and endo-isomers of 4-hydroxycyclobutenyl cation **13**, the energy profiles for rotation of the hydroxy group about the C–C bond in the intermediate hydroxycyclopropenylcarbinyl cations **15** and also for planar inversion of the four-membered ring in the cations **13** were computationally studied.

Scheme 2 features all basic structures corresponding to local minima on the $C_4H_5O^+$ PES that take part in the degenerate circumambulatory rearrangements of exo- (**13a**, **13a′**) and endo- (**13b**, **13b′**) conformers of the 4-hydroxycyclobutenyl cation, including intermediates and transition state structures (marked as TS) involved. Energy characteristics of the calculated transition state structures are given in Table 2, and their geometries and atomic charges are presented in Fig. 5. As stems from the calculations, displacement of the migrating carbon centre along the three-membered ring in endo-, **13a**, and exo-, **13b**, conformers of 4-hydroxycyclobutenyl cation occurs non-concertedly and is realized as a two-step reaction that involves intermediate formation of conformers, respectively **15a** and **15b**, of bisected hydroxycyclopropenylcarbinyl cation.

The energy barriers to a 1,2-shift of a hydroxymethylene group ($10.1 \, \text{kcal mol}^{-1}$ in **13a** and $10.3 \, \text{kcal mol}^{-1}$ in **13b**) are in reasonable agreement with the experimental estimate[19] of free activation energy ($\cong 15 \, \text{kcal mol}^{-1}$) for the circumambulatory rearrangement of tetra-*tert*-butyl derivative, **12**, of the parent cation, **13a**. The eclipsed conformer of hydroxycyclopropenylcarbinyl cation **17**, whose existence as a local minimum or transition state on the reaction pathway of the rearrangement would result in retention of stereochemical configuration at the migrating carbon, lies outside of this pathway. The structure **17** has been identified as the transition state for the conformational isomerization of the intermediates

15a and **15b** caused by rotation around the exocyclic C–C bond. Accounting for the rather high energy barrier ($16.4 \, \text{kcal mol}^{-1}$) required for this isomerization, one may conclude that this type of intersection of two reaction pathways associated with retention and inversion of configuration at the migrating carbon centre has a low probability. Another intersection of the reaction pathways through the ring inversion mechanism **13a** ⇌ **16** ⇌ **13b** also requires the surmounting of an energy barrier higher than that calculated for the circumambulatory rearrangement **13a** ⇌ **14a** ⇌ **15a** ⇌ **14a′** ⇌ **5a′**. It may, therefore, be concluded that the circumambulatory rearrangement of exo-isomer **13a** of 4-hydroxycyclobutenyl cation occuring with inversion of stereochemical configuration at the migtrating carbon centre represents its lowest-energy-barrier intramolecular rearrangement. The rearrangement proceeds as a two-step reaction with exo- conformer, **15a**, of hydroxycyclopropenylcarbinyl cation as the intermediate on the reaction pathway.

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