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Quantum-chemical Simulation of Migration of Proton and Methoxycarbonyl Group in Amidinylcyclopentadiene Derivatives*

N. N. Kharabaev[1], R. N. Borisenko[2], G. A. Dushenko[1], I. E. Mikhailov[1], and V. I. Minkin[1]

[1]*Research Institute of Physical and Organic Chemistry at Rostov State University, Rostov-on-Don, 344090 Russia*
[2]*Rostov State University of Building and Construction, Rostov-on-Don, 344090 Russia*

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Abstract—A quantum-chemical simulation by MNDO method of probable migration mechanisms of proton and methoxycarbonyl group in a series of amidinylcyclopentadiene derivatives, which takes into consideration methoxycarbonyl and aryl substituents attached respectively to the cyclopentadienyl and amidine moieties, provided a theoretical confirmation of 1,4-shift occurrence for the methoxycarbonyl group in quantitative agreement with the experimental evaluation of the barrier in this reaction.

We synthesized lately bifunctional chiral ligands from the cyclopentadiene series with a donor amidine substituent in the side chain $C_5(CO_2Me)_4$[ArNC(Ar')-NHAr], and their precursors, amidinylcyclopentadiene-*N*-ylides $C_5(CO_2Me)_4$[ArNC(Ar')N(CO_2Me)Ar] [1–3]. By the X-ray diffraction study, ^{1}H and ^{13}C NMR spectroscopy we established that the compounds had zwitter-ionic structure with delocalization of the positive charge in the amidine triade, and the negative charge in the cyclopentadiene fragment. The chiral properties of the above compounds suggested that they may be regarded as promising ligands for metal-complex catalysts for asymmetric syntheses [2, 3]. In the amidinylcyclopentadienes migration of a methoxycarbonyl group between the cyclopentadiene (Cp) and amidine (Am) moieties [ΔG (353 K) 27.6–28.8 kcal × mol^{-1}] [1] was revealed a reversible intramolecular.

Scheme 1.

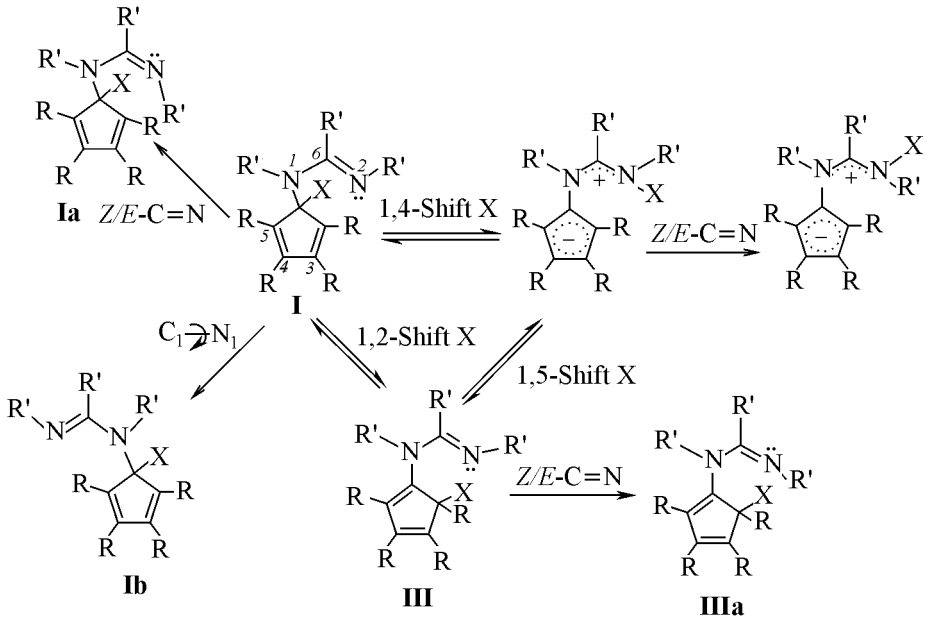

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Table 1. Total energy difference Δ(**I, II**) for isomers **I, II** (X = H, R = COOMe), the corresponding barriers to prototropy δ(**I** → **II**), δ(**II** → **I**), kcal mol^{-1}, and interatomic distances d_1(C^1–N^2), r_1(C^1–X), r_2(N^2–X) in TS(**I** → **II**), Å

R^2	R^3	R^4	R^5	R'	Δ(I, II)	δ(I → II)	δ(II → I)	d_1(TS)	r_1(TS)	r_2(TS)
H	H	H	H	H	–17.2	48.4	31.2	2.405	1.521	1.238
R	H	H	H	H	–11.8	45.0	33.2	2.403	1.495	1.260
R	R	H	H	H	–6.8	43.3	36.5	2.403	1.467	1.284
R	R	R	H	H	–1.9	40.6	38.7	2.403	1.453	1.299
R	R	R	R	H	+4.7	39.3	44.0	2.405	1.436	1.320
R	R	R	R	Ph	+3.8	31.9	35.7	2.398	1.414	1.322

Table 2. Bond lengths, Å, and bond angles, deg, in isomers **I**–**III** and TS(**I** → **II**), (**II** → **III**) (R = COOMe, R' Ph)

X = H	I	TS (**I** → **II**)	**II**	TS (**II** → **III**)	**III**
C^1–C^2	1.550	1.485	1.424	1.501	1.545
C^2–C^3	1.369	1.391	1.429	1.487	1.535
C^3–C^4	1.488	1.464	1.421	1.387	1.370
C^4–C^5	1.370	1.390	1.429	1.469	1.486
C^5–C^1	1.547	1.492	1.436	1.388	1.379
C^1–N^1	1.469	1.462	1.443	1.433	1.422
N^1–C^6	1.424	1.399	1.364	1.405	1.433
C^6–N^2	1.301	1.323	1.361	1.329	1.298
α			125.3	120.7	124.2
α_1	121.0	112.1	122.2	117.0	119.5
α_2	115.6	109.7	119.4	115.9	114.4
d_1	2.744	2.398	2.805		
d_2			3.603	2.554	3.492
X = COOMe					
d_1	2.806	2.556	2.996		
d_2			3.567	2.738	3.657

Note that the said experimental findings were not supported by theoretical investigations with the use of quantum-chemical calculation of the electronic structure and the presumable migration paths of X (X = H, COOMe) in the amidinylcyclopentadienes (Scheme 1).

In this connection the goal of this study was a quantum-chemical investigation of the electronic and molecular structure of presumable isomers in the amidinylcyclopentadiene series presented in Scheme 1, and also of the corresponding transition states (TS) **I** → **II**, **I** → **III**, **III** → **II** of X migration (X = H, COOMe) at variation of the radicals R and R' in Cp- and Am-moieties respectively as factors affecting the reaction in question.

The first stage of the quantum-chemical simulation of prototropy in the systems under consideration can be the analysis of the ground states of the presumable isomers and the corresponding TS for the simplest with respect to calculation amidinylcyclopentadiene derivatives with R = R' = H.

Thus the estimation of relative positions of isomers **I** and **II** (R = R' = H, X = H) with respect to total energy was carried out both by semiempirical MNDO procedure and nonempirical restricted Hartree–Fock (RHF) method in 6-31G** basis with accounting for electron correlation along perturbation theory of Møller–Plesset of the second order (MP2), and from both calculations resulted that isomer **I** is more energetically favored than isomer **II**. The total energy difference of isomers **I** and **II** amounted to 17.2 kcal mol^{-1} (MNDO), 24.4 kcal mol^{-1} (RHF 6-31G**), and with accounting for electron correlation on MP2 level for the points corresponding to total energy minima of isomers **I** and **II** in the framework of RHF 6-31G** this value was 14.4 kcal mol^{-1}.

(Both nonempirical and semiempirical calculations were performed with the use of GAMESS software [4]).

At the second stage of simulation into the systems considered were introduced the Cp-fragment substituents R = COOMe. Their effect turned out to be so significant that the total energy levels of the compared isomers **I** and **II** were reversed. Actually, as show the calculations by MNDO procedure, at gradually increasing number of COOMe groups in the Cp-fragment the difference between total energies of isomers **I** and **II** decreased, and in tetramethoxycarbonyl derivatives of the Cp-fragment isomer **II** becomes more favorable by energy than isomer **I** (Table 1). In Table 1 alongside the total energy difference Δ(**I, II**) = E(**I**)–E(**II**) for isomers (**I**, X = H) and (**II**, X = H) and barriers to prototropy $\delta(\mathbf{I}\rightarrow\mathbf{II})$ = E(TS)–E(**I**), $\delta(\mathbf{II}\rightarrow\mathbf{I})$ = E(TS)–E(**II**) are given also some interatomic distances $d_1(C^1\text{–}N^2)$, $r_1(C^1\text{–}X)$, $r_2(N^2\text{–}X)$ characteristic of TS ($\mathbf{I}\rightarrow\mathbf{II}$). Note that the interatomic distance $d_1(C^1\text{–}N^2)$ in TS ($\mathbf{I}\rightarrow\mathbf{II}$) is virtually not affected by the substituents in the Cp-fragment, and this distance is a characteristic parameter of the given TS.

Therewith in the series of the considered model compounds the position of migrating proton in the transition state regularly shifted in the direction of carbon atom of the Cp-fragment as the protons in the five-membered ring were substituted by COOMe groups (Table 1).

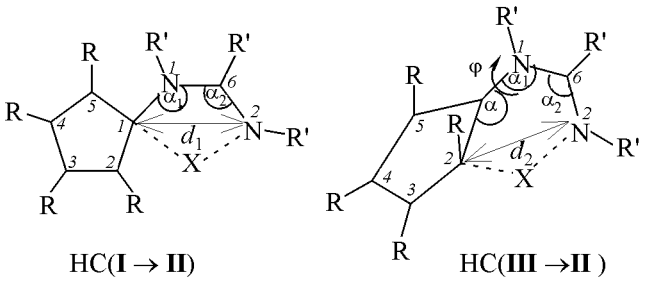
The value $r_1(C^1\text{–}X)$ in TS ($\mathbf{I}\rightarrow\mathbf{II}$) changes in this series in parallel with the barrier to prototropy $\delta(\mathbf{I}\rightarrow\mathbf{II})$, and the variation of $r_2(N^2\text{–}X)$ in the same series occurs in the same direction as $\delta(\mathbf{II}\rightarrow\mathbf{I})$ value (Table 1), i.e. the geometrical and energy parameters of prototropy reaction vary consistently in the series of model systems studied.

The R' substituents in the Am-fragment also notably affect the barrier to prototropy. As showed calculations by MNDO procedure the barriers to reactions ($\mathbf{I}\rightarrow\mathbf{II}$) and ($\mathbf{II}\rightarrow\mathbf{I}$) became significantly lower on replacing R' = H in the Am-fragment of the models under consideration by R' = Ph (Table 1).

Thus the quantum-chemical simulation of prototropy along the reaction path ($\mathbf{I}\rightarrow\mathbf{II}$) shows that introducing substituent R = COOMe instead of R = H in the Cp-fragment results in considerable leveling of the barriers $\Delta(\mathbf{I}\rightarrow\mathbf{II})$ and $\Delta(\mathbf{II}\rightarrow\mathbf{I})$ of the reaction, and replacement of substituent R' = H by R' = Ph in the Am-fragment favors notable lowering of the prototropy barriers $\delta(\mathbf{I}\rightarrow\mathbf{II})$ and $\delta(\mathbf{II}\rightarrow\mathbf{I})$.

In view of the significant role played by substituents R and R' in the Cp- and Am-moieties respectively all the subsequent quantum-chemical investigation of migration either of proton or COOMe group along reaction paths ($\mathbf{I}\rightarrow\mathbf{II}$), ($\mathbf{I}\rightarrow\mathbf{III}$), and ($\mathbf{III}\rightarrow\mathbf{II}$), and also the study of conformational isomers **Ia, b, IIa, IIIa** were carried out with the use of MNDO procedure for models containing all radicals in CP-fragment R = COOMe, and in Am-fragment R' = Ph.

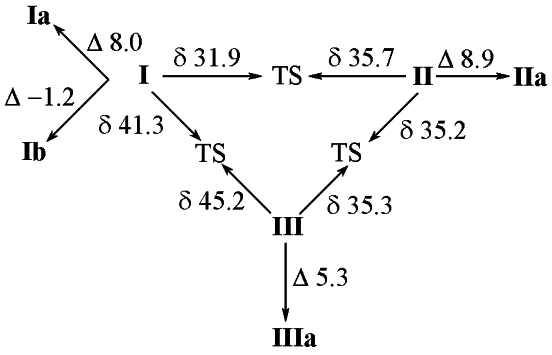
The proton transfer in the systems in question notably affects both electronic and molecular structure of Cp- and Am-moieties. Electron redistribution at the prototropic reaction along the path ($\mathbf{I}\rightarrow\mathbf{II}$) may be characterized for instance by the change of the electron charge on the Am-fragment: q_{Am}(**I**) –0.133, q_{Am}(II) 0.752 a.u. (R = COOMe, R' = Ph). Judging from the calculated geometrical parameters of the models **I, II** (R = COOMe, R' = Ph) in isomer **II** the bond lengths within the Cp-cycle and the bond lengths C^7–N ($C^6\text{–}N^1$, $C^6\text{–}N^2$) in the Am-fragment were leveled off. A similar trend was observed for prototropy ($\mathbf{III}\rightarrow\mathbf{II}$) (Table 2), and also for migration of the COOMe group along the same reaction paths ($\mathbf{I}\rightarrow\mathbf{II}$) and ($\mathbf{III}\rightarrow\mathbf{II}$).



HC($\mathbf{I}\rightarrow\mathbf{II}$) HC($\mathbf{III}\rightarrow\mathbf{II}$)

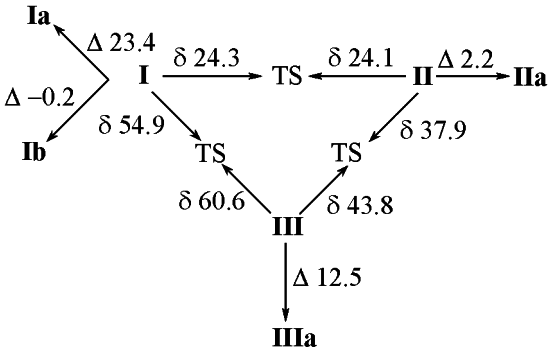
The mechanism of proton migration along the path ($\mathbf{I}\rightarrow\mathbf{II}$) can be deduced from the comparison of calculated geometrical parameters listed in Table 2 for isomers **I, II** and TS ($\mathbf{I}\rightarrow\mathbf{II}$) corresponding by its structure to an H-chelate ring with atoms C^1 and N^2 as centers of prototropy [$d_1(C^1\text{–}N^2)$ defines the size of the reaction "claw"]. Thus the mechanism consists in primary narrowing of the reaction "claw" (decrease in the bond angles α_1, α_2) in going from the state **I** to TS (d_1 is reduced approximately by 0.4 Å) and further transition from TS into state **II** with opening of the said "claw" and proton fixation at the nitrogen atom N^2, and vice versa in the prototropy along the path ($\mathbf{II}\rightarrow\mathbf{I}$). The prototropy barriers $\delta(\mathbf{I}\rightarrow\mathbf{II})$ and $\delta(\mathbf{II}\rightarrow\mathbf{I})$ originate mostly from the value and energy of the necessary deformation of the H-chelate ring for transition from state **I** into TS and from state **II** into TS respectively.

Scheme 2.



X = H, R = COOMe, R' = Ph.

Scheme 3



X = COOMe, R = COOMe, R'= Ph.

Unlike the above mechanism of proton migration along the path (**I** → **II**), another possible mechanism of proton migration between the Cp- and Am-fragments, namely along the path (**I** → **III** → **II**) with participation of the C^2 atom of the Cp-fragment, includes TS (**I** → **III**) localized in the Cp-moiety, and TS (**III** → **II**), corresponding to a six-membered H-chelate ring. Therewith the size of the reaction "claw" $d_2(C^2–N^2)$ for isomer **II** playing the role of the initial state of reaction (**II** → **III**) is considerably larger than the value $d_1(C^1–N^2)$ for the same isomer **II** as the initial state of reaction (**II** → **I**) (Table 2). However TS (**II** → **III**) or (**III** → **II**) characterized by significant narrowing of the reaction "claw" [d_2 in TS (**II** → **III**) (**III** → **II**) is reduced by ~1 Å as compared with isomers **I** and **II**] is realized due to combination of reduction in the bond angles α, α_1, α_2 with a considerable relative rotation of Cp- and Am-fragments around the $C^1–N^1$ bond. According to calculations the reciprocal position of Cp- and Am-fragments in isomers **II** and **III** is nearly orthogonal (η 99°), and in TS (**II** → **III**) or (**III** → **II**) the angle is η 42°.

Thus the mechanism of proton migration along the path (**III** → **II**) or (**II** → **III**) unlike that by the path (**I** → **II**) or (**II** → **I**) consist not only in deformation of bond angles in the H-chelate ring at formation of the corresponding TS, but also in simultaneous considerable reduction of the dihedral angle η between the planes of Cp- and Am-fragments by rotation around the $C^1–N^1$ bond.

The statements concerning the spatial mechanism of proton migration in the molecules under study between Cp- and Am-moieties along reaction paths (**I** → **II**) or (**II** → **I**) and (**III** → **II**) or (**II** → **III**) as show quantum-chemical calculations correspond completely also to the migration of COOMe group along the same routes.

The results of calculation of total energy *E* difference Δ for the compared isomer pairs [e.g, for isomers **I, II** Δ(**I, II**) = *E*(**I**)–*E*(**II**)] and also the barriers to migration δ for X (X = H, COOMe) along the reaction paths (**I** → **II**), (**II** → **III**), (**I** → **III**) are given in Schemes 2 and 3 where Δ defines the change in the total energy *E* of isomers along the arrow (+ sign corresponds to increase in *E*). The Δ and δ values are given in Schemes 2 and 3 in kcal mol^{-1}.

According to the quantum-chemical calculations the values of barriers to prototropy occurring between Cp- and Am-moieties along reaction paths (**I** → **II**) or (**II** → **I**) and (**III** → **II**) or (**II** → **III**) are similar, but the calculation of the corresponding values for migration of COOMe group in the amidinylcyclopentadienes under study (R = COOMe, R' = Ph) shows a considerable difference in the compared barriers to this reaction, and the energetically favorable reaction path is (**I** → **II**) or (**II** → **I**) where the barrier is δ 24.3 kcal × mol^{-1} [for the path (**II** → **I**) δ is 24.1 kcal mol^{-1}].

As seen from Schemes 2 and 3 the barrier to migration of proton and COOMe group along the path (**I** → **III**), i.e. in reaction localized on Cp-fragment only, is considerably higher than for migration of X = H and X = COOMe between Cp- and Am-fragments along the paths (**I** → **II**) or (**II** → **I**) and (**III** → **II**) or (**II** → **III**), and the comparison of the reaction paths (**I** → **II**) and (**I** → **III** → **II**) with participation of isomer **I** in X migration (X = H, COOMe) between Cp- and Am-fragments supports that preferable is the path (**I** → **II**).

It should be especially noted that the quantitatively estimated by semiempirical MNDO method barriers to migration of the methoxycarbonyl group in the model amidinylcyclopentadiene systems with consideration of four methoxycarbonyl substituents in the cyclopentadiene ring and of three aryl substituents in the amidine fragment are in good agreement with

the corresponding experimental evaluation of the barrier of this reaction equal to 27.6–28.8 kcal mol^{-1} [1].

The analysis of relative energies of conformational isomers **Ia, Ib, IIa, IIIa** (R = COOMe and R' = Ph) which were not active in X migration in these systems showed that these isomers virtually always were not more energetically feasible than the considered reactive isomers **I–III** although the difference in some cases (**Ib**, X = H, COOMe; **IIa**, X = COOMe) is sufficiently small to regard them as equally probable with respect to the corresponding isomers (**I**, X = H, COOMe; **II**, X = COOMe). Thus the quantum-chemical simulation of presumable mechanisms for migration of proton or COOMe group in amidinylcyclopentadienes provided a possibility, firstly, of establishing on a level of fragment calculations a significant role played by all substituents both in Cp- and Am-fragments, and, secondly, to obtain qualitative notion of the geometrical aspect for the presumable mechanisms of the reaction in question and quantitative agreement of the calculated barrier to migration of the methoxycarbonyl group in the systems under study with the results of the corresponding experimental investigations.

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