QUANTUM-CHEMICAL STUDY OF THE ELECTROPHILICITIES OF YNAMINO AND YNAZIRIDINO ESTERS

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The geometries, conformations, and electron structures of the methyl esters of dimethylamino- and (1-aziridino)propiolic acid were studied by means of the MNDO method. It was shown that the energies of the lowest vacant molecular orbital may serve as a measure of the electrophilicities of these compounds. The increased electrophilicity of the ynaziridino ester is associated with the greater pyramidal character of the nitrogen atom in the aziridine ring.

It is known [1] that ynamines are strong nucleophiles and react readily with reagents of the electrophilic type. Nucleophilic addition to ynamines is uncharacteristic and, as a rule, proceeds satisfactorily only under acid-catalysis conditions [2].

In contrast to ynamino esters [4], the ynaziridino esters that we recently synthesized [3] display increased reactivities with respect to nucleophiles [5]. The difference in the rates of nucleophilic addition of amines to the triple bond of the two types of compounds constitutes evidence for this.

$$(CH_n)_2N-C\equiv C-COOCH_3$$

I, II I n=2; II n=3

Thus ynaziridine I readily adds a second molecule of aziridine even at 0°C [5], while 2 days at 37°C are required to accomplish a similar reaction in the case of ynamine II [4]. Substantial differences in the rates of addition to the investigated substrates also occur in the case of other amines [4, 5].

In order to ascertain the reasons for the difference in the reactivities of I and II we calculated their conformations and electron structures by the MNDO method [6] with complete optimization of the geometries of the molecules.

According to the calculations, the methoxycarbonyl group in both ynamine II and ynaziridine I is planar; the methyl group is cis-oriented with respect to the carbonyl oxygen atom. This mutual orientation of the methoxycarbonyl and amino groups in which the unshared pair of electrons (UPE) of the nitrogen atom lies in the plane of the π_z bond formed by the p_z orbitals of the $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ atoms (Figs. 1-3) corresponds to the energy minimum. Thus in the ground state (GS) of I and II (conformer A) the UPE of the nitrogen atom is conjugated with the carboxy group through the $C\equiv C$ bond. The two maxima on the energy curve (Figs. 2 and 3) correspond to transition states (TS) B and C, in which the UPE of the nitrogen atom is orthogonal to the π_z plane and is not conjugated with the carboxy group. The maximum barrier to rotation about the $C_{(1)}-N$ bond in ynamine II is somewhat higher than in ynaziridine I (1.51 and 0.57 kcal/mole, respectively); however, the magnitude of these barriers to rotation is small, which constitutes evidence for the ease of the transition from the GS to the TS.

The nitrogen atom in the GS of II is almost planar, while in the TS* the angle of pyramidal character (ϕ) is 8.8° (Table 1). The $C_{(1)}-N$ bond in the GS of ynamine II is

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*Since transition states B and C virtually do not differ with respect to their geometrical characteristics and electron structures, we will use one TS in the subsequent discussion.

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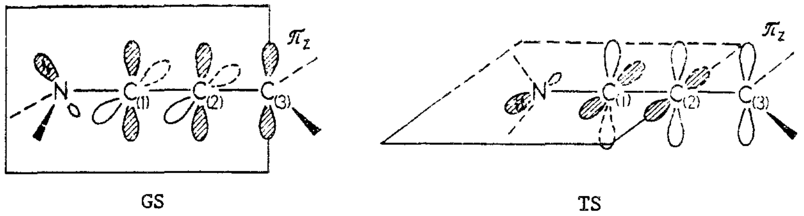

Fig. 1. Ground state (GS) and transition state (TS) of I and II.

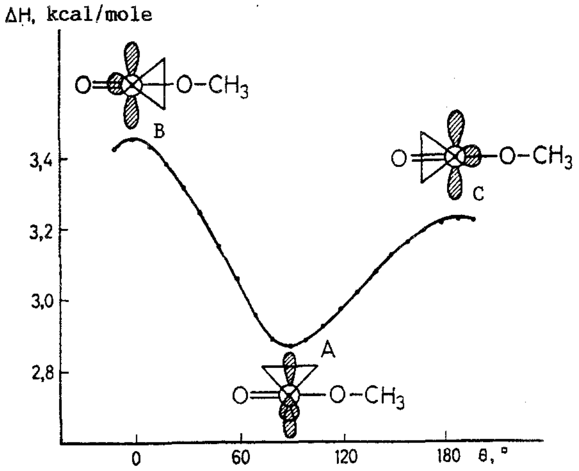

Fig. 2. Dependence of the heat of formation (ΔH) of I on the dihedral angle (θ) between the axis of the UPE of the nitrogen atom and the C=O bond.

TABLE 1. Optimized Geometrical Parameters of I and II (angles, deg; bond lengths, Å)

Compound	Ground state A				Transition states B and C			
	φ^*	$N—C_{(1)}$	$C_{(1)}—C_{(2)}$	$C_{(2)}—C_{(3)}$	φ^*	$N—C_{(1)}$	$C_{(1)}—C_{(2)}$	$C_{(2)}—C_{(3)}$
I	57,5	1,36	1,20	1,43	57,5	1,36	1,20	1,43
II	0,3	1,34	1,20	1,43	8,8	1,36	1,20	1,43

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*The angle of pyramidal character of the nitrogen atom. It was calculated from the formula $\phi = 360 - \Sigma\sigma$, where $\Sigma\sigma$, is the sum of the bond angles at the nitrogen atom.

shorter than in the TS; this constitutes evidence for stronger p—π conjugation in the GS of II.

A distinctive feature of the geometry of ynaziridine I is the nonplanar configuration of the nitrogen atom in both the GS and the TS. The angle of pyramidal character is 57.5°, which is much greater than in II. The length of the $C_{(1)}$—N bond in the ynaziridine does not change on passing from the GS to the TS and is equal to 1.36 Å (Table 1).

The charges on the atoms of I and II that are most important for the study of the reactivities are presented in Table 2. From the data in Table 2 one may conclude that a correlation between the charge distributions in the I and II molecules and their reactivities is absent, since the most electropositive carbonyl $C_{(3)}$ atom is not the center of nucleophilic attack by amines.

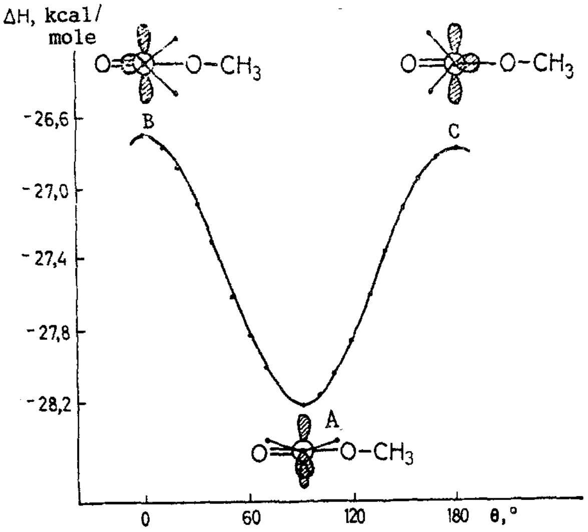

Fig. 3. Dependence of the heat of formation (ΔH) of II on angle θ.

TABLE 2. Charges on the Atoms of I and II

Compound	Ground state A				Transition state			
	N	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	N	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$
I	−0,201	0,060	−0,187	0,504	−0,199	0,059	−0,188	0,505
II	−0,322	0,100	−0,228	0,511	−0,312	0,096	−0,226	0,511

TABLE 3. Energy (E_{LVMO}, eV) and Form of the Lowest Vacant Molecular Orbital (LVMO) in the I and II Molecules (the squares of the coefficients of the atomic orbitals for the corresponding atoms are given)

Compound	Ground state				Transition state			
	E_{LVMO}	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	E_{LVMO}	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$
I	0,189	0,298	0,150	0,305	0,084	0,292	0,180	0,240
II	0,555	0,303	0,101	0,312	0,311	0,300	0,173	0,283

According to the theory of boundary molecular orbitals [7], the nucleophilic addition can be regarded as a reaction with charge transfer from the highest occupied molecular orbital (HOMO) to the lowest vacant molecular orbital (LVMO) of the electrophile. The level of the energy of the LVMO may then serve as a measure of the relative electrophilic capacities of I and II. It follows from an analysis of the form of the boundary orbitals that the LVMO of I and II is an antibonding orbital of the π_Z^* type; ynaziridine I has the lower E_{LVMO} energy and, consequently, increased electrophilicity (Table 3), in agreement with the experimental data on the reactivities of I and II [4, 5]. In addition, according to the calculations, in the transition from the GS to the TS the energy of the LVMO decreases significantly for both ynamine II and ynaziridine I. An analysis of the form of the LVMO in I and II (Table 3) shows that in the case of the TS the strongest electrophilic center is located at the $C_{(1)}$ atom, while in the GS the electrophilicities of the $C_{(1)}$ and $C_{(3)}$ atoms are approximately the same. However, according to the experimental data [5, 8], the addition of amines to the investigated substrates is realized exclusively in the $C_{(1)}$ position. The regiospecificity of nucleophilic addition can be explained by assuming that I and II react with nucleophiles in the TS, which has a lower LVMO and higher electrophilicity of the $C_{(1)}$ atom. Consequently, the rotation about the $C_{(1)}$—N bond, in which the UPE of the

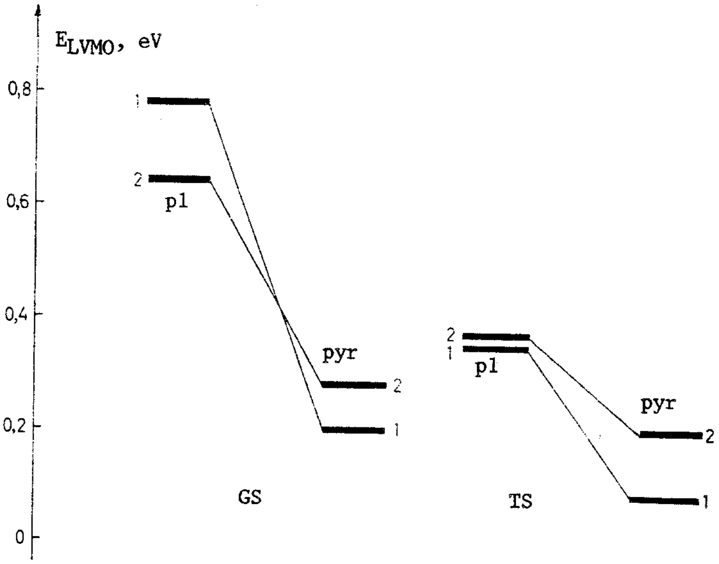

Fig. 4. Relationship between the energy of the LVMO of I and II and the configuration of the nitrogen atom: 1) E_{LVMO} of ynaziridine I; 2) E_{LVMO} of ynamine II (the abbreviations "pl" and "pyr" pertain to the planar and pyramidal configurations of the nitrogen atom, respectively).

nitrogen atom deviates from conjugation with the carboxy group, should enter into the coordinate of the reaction of I and II with the amine, and the decrease in E_{LVMO} is the driving force of this process.

The marked difference in the E_{LVMO} in I and II (Table 3) makes it possible to assume that the energy of the LVMO is associated with the configuration of the nitrogen atom. This is confirmed by calculation of I and II for two rigidly fixed configurations of the nitrogen atom, viz., planar and pyramidal (Fig. 4). Thus, for both the ynaziridine and the ynamine the transition from the planar configuration of the nitrogen atom to the pyramidal configuration in both the GS and the TS is accompanied by a significant decrease in the level of the energy of the LVMO. It is noteworthy that a greater ΔE_{LVMO} energy jump is observed in the GS than in the TS with a change in the configuration of the nitrogen atom.

The results obtained illustrate the well-known (in organic chemistry) concept of p—π conjugation. In fact, the possibility of conjugation of the UPE of the nitrogen atom with the carboxy group (through the C≡C bond) is a factor that is critical in the determination of the reactivities of the investigated compounds. Conjugation is weaker, the greater the pyramidal character of the nitrogen atom [the smaller the corresponding integral of $N—C_{(1)}$ overlap in the π system]. A change in the planar character of the nitrogen atom therefore has a pronounced effect on the reactivities of the compounds (a decrease in the energy of the LVMO). Furthermore, conjugation is maximal in the GS and is absent in the TS, which is again manifested in the corresponding change in the reactivity.

The following conclusions can be drawn from the results obtained. The energies of the LVMO, the calculated values of which are in good agreement with the experimentally observed reactivities, can serve as a measure of the relative electrophilicities of I and II. Rotation about the $N—C_{(1)}$ bond, as a result of which the UPE of the nitrogen atom deviates from conjugation with the carbonyl group, enters into the coordinate of the reaction of I and II with the nucleophile. In I and II the electrophilicity of the triple bond is higher, the greater the pyramidal character of the nitrogen atom in the substituent attached to the triple bond.

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AZIRIDINYL KETONES AND THEIR CYCLIC ANILS.

9.* SUBSTITUTED 1,3-DIAZABICYCLO[3.1.0]HEX-3-ENES

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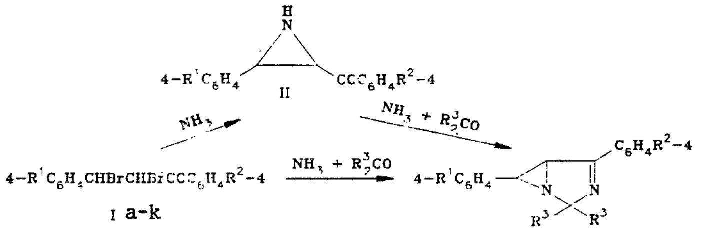
Aryl-substituted 1,3-diazabicyclo[3.1.0]hex-3-enes were obtained by the reaction of α,β-dibromodihydrochalcones with ammonia and formaldehyde (or acetone). Their structures were confirmed by spectral methods and x-ray diffraction analysis.

The interest in substituted 1,3-diazabicyclo[3.1.0]hex-3-enes is due to their photochromic properties [2-5]. It has been proposed that compounds with a p-nitrophenyl group in the 6 position of the two-ring system, for which the most profound changes in color are characteristic, be used to obtain light-sensitive materials, including materials for recording photographic and holographic images [6-11]. In the present research we set out to study the structure and the effect of various substituents on the properties of 1,3-diazabicyclo[3.1.0]hex-3-ene.

The method for the synthesis of the desired heterocycle proposed in [2, 6] was based on the reaction of aldehydes (or ketones) and ammonia with aziridinyl ketones II, which, in turn, are obtained from α,β-dibromodihydrochalcones I. The process can be accomplished in one step without isolation of aziridinyl ketones II; to obtain high yields ammonia should be passed into a suspension of dibromide I in methanol until the dibromide has dissolved completely, and the aldehyde or acetone should be added to the reaction system only after this while continuing saturation of the solution with ammonia:



II

I a-k

IIIa-e,g; IVa,b,e-k

I, III, IV **a,c** $R^1=H$, **b,d** $R^1=Br$, **e – k** $R^1=NO_2$; **a,b,e** $R^2=H$, **f** $R^2=Cl$, **c,d,g** $R^2=Br$, **h** $R^2=NO_2$, **i** $R^2=CH_3$, **j** $R^2=OCH_3$, **k** $R^2=C_6H_5$; III $R^3=H$, IV $R^3=CH_3$

It was noted that the addition of formaldehyde (or acetone) at the start of the reaction leads to a decrease in the yield and contamination of the desired III and IV with

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*See [1] for Communication 8.

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