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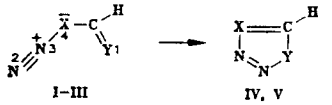
CALCULATION OF THE CYCLIZATION OF 2-DIAZOETHANIMINE TO 1H-1,2,3-TRIAZOLE BY THE MINDO/3 METHOD

V. A. Bakulev and I. P. Gloriozov

UDC 547.791'235.2'233.2:519.25

It is shown that the MINDO/3 approximation can be used for the calculation of the cyclization of 2-diazoethanimine and its 2-aza analog. It was found that, as in the case of the azidoimine, the formation of the new bond during cyclization results from reaction of the unshared electron pair at the nitrogen atom of the imino group with the terminal nitrogen atom of the diazo group.

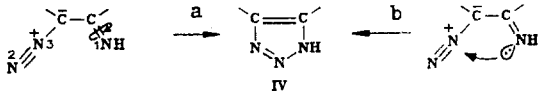
The nitrogen analogs of α-diazocarbonyl compounds, i.e., α-diazoimines, are highly reactive substances which undergo cyclization to isomeric 1H-1,2,3-triazoles even under the conditions of production. They are intermediate compounds in the generation of iminoketenes and iminocarbenes and also in the synthesis of imidazoles and triazoles [1-3]. Study of the relationships governing the cyclization of α-diazoimines therefore opens up prospects for a greater understanding of the rearrangements of five-membered heterocycles and the directed synthesis of various derivatives of 1,2,3-triazole, including those possessing strong biological activity [4].



I-III IV, V

I, IV X=CH, Y=NH; II, V X=N, Y=NH; III X=CH, Y=CH_2

At the same time there are a series of unresolved questions in the chemistry of these compounds. For example, it is not clear why the α-diazoimines (I) undergo cyclization more quickly than the azidoimines (II) while they, in turn, undergo cyclization much more quickly than the derivatives of vinydiazomethane (III) [1, 5-7]. It is also unclear as to how the cyclization of the diazoimines takes place, i.e., by an electrocyclic mechanism (a) or, like the azidoimine (II), without rotation about the C=N bond (b) [8].



IV

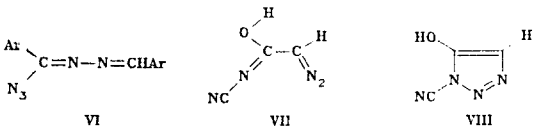
In order to answer these questions we undertook a calculation for the cyclization of 2-diazoethanimine (I) to 1H-1,2,3-triazole (IV) by the MINDO/3 method using the VIKING programs [9]. However, it is well known that the methods of the CNDO family, which satisfactorily describe the characteristics of azapentalene aromatic compounds, have proved inadequate for the study of azido–tetrazole isomerization [8]. This is why the cyclization of azidoazomethine (II), which is the aza analog of the diazoimine (I), was studied by the ab initio method in the STO-3G basis set [8]. In this connection in order to determine the suitability of the adopted method for solution of the problem we first undertook a calculation for the cyclization

S. M. Kirov Urals Polytechnical Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 504-507, April, 1989. Original article submitted January 21, 1987; revision submitted May 4, 1988.

 0009-3122/89/2504-0420$12.50

of the azidoimine (II) and compared the results with the data in [8]. As reaction coordinate we used the distance between the terminal nitrogen atoms, since the $N_{(1)}$–$N_{(2)}$ bond is the only bond which is formed as a result of the cyclization. The initial geometry of the azide (II) and the tetrazole (V) was taken from [8]. We then optimized the bond angles and the bond lengths between the nonhydrogen atoms for 13 structures along the reaction coordinate. In addition, for the initial [azidoimine (II)] and final [tetrazole (V)] structures we optimized all the parameters, including the dihedral angles and the $N_{(1)}$–$N_{(2)}$ bond, and for the intermediate structures with $r_{N_{(1)}\text{-}N_{(2)}}$ values of 247.5 and 200 pm, we optimized the values of all the dihedral angles between the heavy atoms and the $N_{(4)}C_{(5)}N_{(1)}H$ angle.

It was found that all the structures are planar. This agrees with the data from nonempirical calculations [8] and indicates that rotation about the $N_{(1)}$–$C_{(5)}$ bond does not occur with approach of the $N_{(1)}$ and $N_{(2)}$ atoms, and the $N_{(1)}$–$N_{(2)}$ bond is consequently formed on account of interaction between the unshared electron pair of $N_{(1)}$ and the terminal nitrogen atom of the azido group. The calculated activation energy of the cyclization amounted to 27.6 kcal/mole, which is close to the experimental value for imidoyl azide (VI) (23.1 kcal/mole [4]) but is somewhat larger than the value obtained by the nonempirical method (12.3 kcal/mole [8]). However, the value obtained for the enthalpy of reactions (–13.3 kcal/mole) differs significantly from the results in [8] (–47.3 kcal/mole). We therefore undertook an additional MINDO/3 calculation of the heats of formation of the cyanoimide of 2-diazoacetic acid (VII) and its cyclic isomer (VIII). The choice of these subjects was based on the fact that unlike the diazoimine (I) the diazoimine (VII) is more stable than its cyclic isomer (VIII).



The calculated enthalpy of formation of the diazo compound (VII) (–28.6 kcal/mole) is lower than that of the triazole (VIII) (–20.1 kcal/mole). This agrees with experimental data on the position of equilibrium between these substances [1].

During study of the cyclization of the diazoimine (I) we also used the $N_{(1)}$–$N_{(2)}$ distance as reaction coordinate. All the bond lengths and bond angles at the heavy atoms and also the dihedral $C_{(4)}C_{(5)}N_{(1)}H$ were optimized for 14 values of this distance in the range of 354-122 pm. In addition, a full optimization of the geometry was undertaken for the initial and final structures. For the point at 200 pm, which corresponds to the structure with the maximum energy, the calculated norm of the gradient amounted to 2 eV/nm^2. During its minimization to 0.04 eV/nm^2 the geometry of the molecule changed little, and $r_{N_{(1)}\text{-}N_{(2)}}$ in particular changed to 198.9 pm; as in the initial structure, all the atoms remained in one plane. However, the length of the $C_{(4)}$–H and $C_{(5)}$–H bonds increased from 108 to 109.9 and 111.6 pm, respectively. After this diagonalization of the matrices of the second derivatives of the total energy with respect to the Cartesian coordinates of the atoms led to one negative eigenvalue, and this indicated the presence of a saddle point [10]. The eigenvector corresponding to this force constant and representing the reaction coordinate in the form of a linear combination with respect to the Cartesian coordinates of the atoms of the molecular system has a major contribution (with coefficient 0.9777) from the component X of the $N_{(2)}$ atom. (The origin of the coordinates was established at the $N_{(1)}$ atom, and the OX axis was directed from $N_{(1)}$ to $N_{(2)}$.) This confirms the accuracy of the choice of $N_{(1)}$–$N_{(2)}$ distance as reaction coordinate.

The calculated lengths of the $N_{(1)}$–$N_{(2)}$, $N_{(2)}$–$N_{(3)}$, $N_{(3)}$–$C_{(4)}$, $C_{(4)}$–$C_{(5)}$, and $N_{(1)}$–$C_{(5)}$ bonds and the angles $N_{(2)}N_{(3)}C_{(4)}$, $N_{(3)}C_{(4)}C_{(5)}$, and $C_{(4)}C_{(5)}N_{(1)}$ for the diazoimine (I), the transition state, and the triazole (IV) have the following values: 343, 112, 129, 145, 129 pm and 179.9, 119.9, 120.0°; 199, 113, 132, 144, 128 pm and 134.1, 105.7, 111.4°; 122, 124, 138, 139, 138 pm and 110.8, 103.5, 103.5°.

For eight values of the reaction coordinates we undertook calculations of the charges, the π-atomic population, and the bond orders by the CNDO/2 method, since this method reproduces the experimentally determined dipole moments of organic compounds more accurately [11]. The results of these calculations for the most important structures are given in Fig. 1.

The data from the calculations showed that all the atoms remain in one plane during cyclization. The transition state is closer in electronic structure to the molecule of the ini-

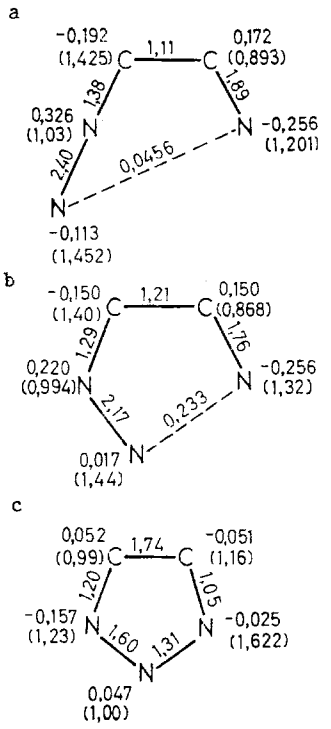


Fig. 1. The cyclization of 2-diazoethanimine. The charges at the atoms (π-electron density) and the bond orders of the structures with $r_{N_{(1)}\text{-}N_{(2)}}$ equal to 325 (a), 200 (b), and 122 pm (c).

tial diazo compound, and the π-system changes little before the attainment of the transition state. As the order of the $N_{(1)}$–$N_{(2)}$ increases there is a rearrangement of the -π-electron system of the molecule; an electron pair directed perpendicularly to the plane of the ring is formed at $N_{(1)}$, as a result of the decrease in the π-electron density at the $N_{(2)}$ and $C_{(4)}$ atoms a π-bond is formed between the $C_{(4)}$ and $C_{(5)}$ atoms, and the electron density at $N_{(1)}$ and $N_{(2)}$ and the positive charge at $N_{(3)}$ are decreased.

Thus, of the two possible mechanisms for the cyclization of the diazoimine (I), as also the azide (II), mechanism b is preferred according to the data from the calculations. A new σ-bond is formed during the reaction of the unshared pair of the $N_{(1)}$ atom with the terminal nitrogen atom of the diazo group $N_{(2)}$. The electrophilicity of the $N_{(2)}$ atom is explained by its high coefficient (0.78) at the lowest unoccupied molecular orbital. The calculated activation energy and enthalpy of reaction are 22.5 and −15.8 kcal/mole, and this is close to the values of these parameters for the cyclization of the azide (II). The lower activation energy for the cyclization of the diazo compound (I) compared with the azide (II) agrees with experimental data on the higher rate of cyclization of the derivatives (I) [5, 8].

The data from the calculations showed that the isoionic substitution of the $N_{(3)}$ atom by a carbon atom does not lead to a change of mechanism and has little effect on the energetics of the process. This enabled us to apply the arguments in [8] about the relative cyclization rates of the azide (II) and vinyl azide to the diazo compounds (I) and (III). Rotation about the $C_{(1)}$–$C_{(5)}$ bond is necessary for the cyclization of vinyldiazomethane, and this requires an additional expenditure of energy. The more ready cyclization of the diazoimine (I) compared with vinyldiazomethane (III) is therefore explained by the presence of the unshared electron pair, lying in the plane of the molecule, at the nitrogen atom of the imino group.

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DEPENDENCE OF THE REACTIVITY OF FIVE-MEMBERED HETEROCYCLES ON THEIR STRUCTURE. 3.* PROTON AFFINITY OF AZOLES AND OXAZOLES

V. G. Andrianov, M. A. Shokhen, and A. V. Eremeev

UDC 541.6:547.7:519.25

The proton affinity (PA) of a number of azoles and oxazoles was calculated by MNDO and STO-3G ab initio methods. In spite of the fact that these methods predict poorly the absolute values of the PA, a good correlation between the PA values calculated by STO-3G and the experimental values of PA as well as pK_a values exists. Correlation of the experimental values with MNDO results are much worse.

Various semiempirical and nonempirical quantum mechanical methods are used for calculation of proton affinity (PA) values. We use the nonempirical method with the limited basis of STO-3G orbitals in our calculations of PA of azoles and aminoazoles. These use the geometry which is optimized by the semiempirical MNDO method [2]. Recently, reports have appeared whose authors suggest that a similar method does not permit the changes in PA of amines to be predicted correctly [3]. In order to verify the reliability of results obtained by various methods, we compared experimental and calculated values of PA for azoles and oxazoles. The values of PA which were calculated by us by MNDO and ab initio STO-3G are given in Table 1. Experimental data from the literature and results of calculations in the 6-31** basis accounting for configuration interaction based on the geometry optimized for STO-3G [4] are also given.

The PA value was determined as the difference of the absolute energies of the initial and protonated forms of the molecules. The STO-3G basis is known for a number of reasons to overestimate the PA [5], but the MNDO method, on the other hand, underestimates the PA due to underestimation of the value of enthalpy of proton formation [6]. The values of PA on the 6-31** basis are nearer to the experimental, but the error is still too large (up to 9 kcal/mole [4]) to compare directly the experimental and calculated values. However, as a rule, the succession of changes in PA for the series studied proves to be more important than the absolute value for characterization of the reactivity. In order to evaluate the accuracy of the prediction of PA change in a series of azoles and oxazoles by various methods, we used regression coefficients in equations which relate the experimental and calculated PA values (Table 1):

$$PA_{exp} = 91.1 + 0.764\,PA_{MNDO} \quad (r = 0{,}941;\ s = 3.0;\ F = 38;\ n = 7); \tag{1}$$

$$PA_{exp} = 27.9 + 0.688\,PA_{STO\text{-}3G} \quad (r = 0.990;\ s = 1.2;\ F = 242;\ n = 7); \tag{2}$$

$$PA_{exp} = 49.5 + 0.754\,PA_{6\text{-}31^{**}} \quad (r = 0{,}993;\ s = 1.1;\ F = 334;\ n = 7). \tag{3}$$

As seen from the correlation coefficients and mean square deviations, the PA calculated in the STO-3G and 6-31** bases correlate with the experimental values with practically identical accuracy. Thus, the limited STO-3G basis is practically as good as the extensive 6-31**

*For Communication 2, see [1].

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 508-511, April, 1989. Original article submitted September 10, 1987; revision submitted April 12, 1988.

