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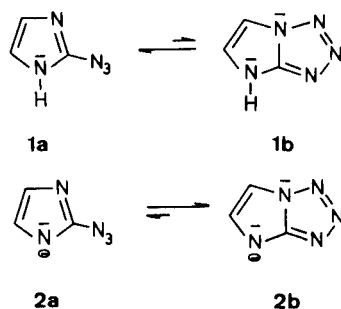
Calculations are reported for the cyclization of 2-azidoimidazole and its anion to the corresponding pentaazapentalenes using the recently developed MNDO semiempirical SCF-MO method. The bicyclic anion is predicted to be 16.9 kcal/mole relatively more stable than the neutral bicyclic molecule. The shifting of the equilibrium to the tetrazole form in the case of the anion is mainly attributed to the delocalization of the negative charge on the tetrazole moiety of the bicyclic system.

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In the past years, molecular orbital calculations by HMO (1), PPP (2), and CNDO/2 (2) methods have been carried out to elucidate the assumed aromaticity of the aza analogues of pentalene dianion. More recently, as an alternative approach to the problem, it has been suggested that the study of the azido/tetrazole equilibrium in the azole series may provide some information on the relative thermodynamical stability of the *N*-bridged azapentalenes, a stability which will be largely related to the higher or lower aromaticity of these bicyclic systems (3).

Despite the great number of azidoazines known in which the tetrazole form predominates in the equilibrium (4), in the azole series, with very few exceptions (3-5), the tetrazole form can hardly be detected, suggesting that the aromaticity of the 3a-azapentalenic systems is not so large as claimed.

On the other hand, although the possible equilibrium between 2-azidoimidazole (**1a**) (6) and imidazo[1,2-*d*]tetrazole **1b**, as mentioned above, is shifted to the azide form, the equilibrium between the corresponding anions **2a** and **2b** is shifted to the tetrazole form (3,5a,7). This remarkable fact may suggest that the azapentalenic system **1b** would be less aromatic than the imidazole **1a**, while the anion **2b**, being perhaps more comparable to the pentalene dianion, constitutes, in contrast, a highly aromatic system.



In order to support or to discard this assertion we have carried out semiempirical SCF-MO calculations on the cyclization of 2-azidoimidazole and its anion to the tetrazole forms.

#### Theoretical Procedure.

We have been unable until now to study azidoazoles and the corresponding *N*-bridged poliazapentalenes using the most current semiempirical SCF-MO methods (*e.g.*, CNDO/2, INDO, and MINDO/3) because these methods have been based on the neglect of one centre differential overlap approximation (8). Since the repulsion between lone pairs of electrons are underestimated in this approximation, procedures as those mentioned above lead to calculated energies that are too negative in the case of molecules where adjacent atoms have unshared pairs of electrons in hybrid atomic orbitals.

This problem is substantially avoided in the more rigorous NDDO approximation (8), and a suitable version of this (MNDO) has recently been developed (9). All the calculations we report here have been carried out using the MNDO method.

The equilibrium geometries were found by minimizing the energy with respect to all geometrical values; no assumptions were made. Minimum energy reaction paths (MERP) were determined by the usual reaction coordinate method (10), the energy being minimized with respect to all other geometrical parameters for successive increments in the reaction coordinate. The transition states, located approximately from the MERP's, were refined by minimizing the scalar gradient (11). It was established that each such structure was a true transition state by diagonalizing the force matrix and thus determining that it had one, and only one, negative eigenvalue (11).

#### Results and Discussion.

Table I shows the optimized geometrical parameters for

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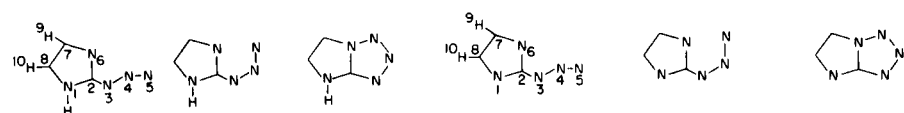
the azidoimidazoles **1a** and **2a**, the corresponding imidazotetrazoles **1b** and **2b**, and the transition states TS<sub>1</sub> and TS<sub>2</sub> for their interconversion. All these structures are calculated to be planar. As seen in Table I, the azido group is found to have a non-linear geometrical structure. This result is consistent with experimental structural work (12) and with an *ab initio* calculation on hydrogen azide (13). Of the many possible stable conformers of **1a** arising from rotation about bond C2-N3, the lowest energy conformer calculated has the azide nitrogens arrangement shown in Table I. A second stable conformer was located for **1a**, corresponding to a rotation of 180° about that bond, but this proved to be 7.9 kcal/mole less stable than the former.

It is seen from inspection of Table I, that in passing from the azides **1a** and **2a** to the corresponding transition states, the major effect is the N3-N4-N5 bond angle closure and the stretching of the bonds N3-N4 and N4-N5, reflecting the change in hybridization of atom N4. On the other hand, in the transition state the forming N5-N6 bond is very long (*ca.* 2 Å), and there is only a slight stretching of bond C2-N6, whereas the C2-N3 bond length is close to its value in the azide forms. These features suggest that the geometry of the imidazole moiety is only slightly perturbed in the transition state, whereas the rehybridization at the atom N4 is rather substantial.

Table II gives the calculated heats of formation. The predicted potential barrier height for the cyclizations **1a** → **1b** and **2a** → **2b** are 39.1 and 34.1 kcal/mole, respectively. It should be noted that the calculated difference in the potential barrier height is not significant enough to explain the fact that the tetrazole form **1b** is not experimentally detected. On the other hand, the heats of reaction are calculated to be -8.8 and -25.7 kcal/mole, respectively. Undoubtedly, these values seem too negative, but taking into account the entropic term that should favour the open structures, the discrepancy between the calculated heats of reaction and the experimental facts is not very large. It is worth noting that the thermodynamic stabilization of the bicyclic molecule, with respect to the corresponding azide form, is 16.9 kcal/mole larger for **2b** as compared with the neutral compound **1b**. This extra stabilization of **2b** with respect to **1b** seems to suggest a larger aromatic character of the former molecule. An alternative explanation would be a possible larger delocalization of the negative charge in the bicyclic anion **2b** with respect to the azide form **2a**.

Table III shows the calculated distributions of formal charge. In keeping with the geometric changes noted in passing from the azidoazoles **1a** and **2a** to the corresponding transition states, there is substantial electronic rearrangement at the azido moiety. The main effect of this is

Table I  
Optimized Geometries



	<b>1a</b>	TS <sub>1</sub>	<b>1b</b>	<b>2a</b>	TS <sub>2</sub>	<b>2b</b>
r(Å)						
N1-C2	1.390	1.371	1.375	1.372	1.363	1.360
C2-N3	1.406	1.404	1.360	1.416	1.420	1.385
N3-N4	1.266	1.307	1.327	1.245	1.280	1.307
N4-N5	1.125	1.183	1.280	1.139	1.197	1.292
N5-N6		1.949	1.347		2.043	1.344
C2-N6	1.351	1.367	1.415	1.376	1.381	1.423
N6-C7	1.394	1.389	1.416	1.371	1.372	1.400
C7-C8	1.392	1.396	1.386	1.417	1.416	1.406
C8-N1	1.405	1.415	1.418	1.373	1.383	1.386
C7-H9	1.083	1.082	1.081	1.082	1.080	1.077
C8-H10	1.080	1.080	1.083	1.082	1.082	1.085
N1-N11	0.995	0.995	0.995			
θ (degrees)						
N1-C2-N6	111.3	110.8	107.6	115.4	114.2	111.3
C2-N3-N4	116.1	105.4	104.6	116.8	108.0	105.8
N3-N4-N5	193.2	129.5	115.4	196.2	130.4	115.5
N3-C2-N6	128.9	116.2	106.6	124.8	115.7	104.5
C2-N6-C7	105.6	106.9	109.2	103.2	105.3	107.4
N6-C7-C8	110.7	108.7	105.7	109.1	106.9	103.8
C7-C8-N1	105.6	106.9	109.9	109.5	110.7	113.7
C8-N1-C2	107.0	106.7	107.7	102.9	102.9	103.8
N6-C7-H9	120.2	121.7	122.4	121.9	122.8	123.5
C7-C8-H10	132.5	131.8	129.8	128.9	128.3	126.5
C8-N1-H11	126.1	126.8	126.5			

Table II  
Calculated Heats of Formation

	<b>1a</b>	TS <sub>1</sub>	<b>1b</b>	<b>2a</b>	TS <sub>2</sub>	<b>2b</b>
$\Delta H_f$ (kcal/mole)	101.4	140.5	92.6	67.3	101.4	41.6

Table III  
Calculated Distributions of Formal Charge (a)

	<b>1a</b>	TS <sub>1</sub>	<b>1b</b>	<b>2a</b>	TS <sub>2</sub>	<b>2b</b>
N1	-0.219	-0.195	-0.234	-0.267	-0.252	-0.294
C2	0.137	0.112	0.121	-0.060	-0.064	0.042
N3	-0.245	-0.197	-0.169	-0.174	-0.174	-0.252
N4	0.250	0.054	-0.033	0.231	-0.004	-0.093
N5	0.025	0.160	-0.024	-0.186	0.090	-0.168
N6	-0.273	-0.335	-0.189	-0.325	-0.350	-0.168
C7	-0.042	0.012	0.021	-0.151	-0.118	-0.153
C8	-0.070	-0.072	0.010	-0.165	-0.156	-0.055
H9	0.106	0.114	0.134	0.049	0.059	0.083
H10	0.109	0.113	0.119	0.049	0.050	0.058
H11	0.223	0.234	0.245			

(a) See Table I for the numeration of the atoms.

Table IV  
Calculated  $\pi$  Charge Densities ( $q_i^\pi$ ) and Bond Orders ( $p_{ij}^\pi$ ) (a)

	<b>1a</b>	TS <sub>1</sub>	<b>1b</b>	<b>2a</b>	TS <sub>2</sub>	<b>2b</b>
$q_i^\pi$ N1	1.635	1.637	1.705	1.263	1.274	1.354
C2	0.986	0.930	0.978	1.139	1.076	1.006
N3	1.581	1.506	1.308	1.451	1.397	1.358
N4	1.108	1.044	1.079	1.137	1.093	1.102
N5	1.247	1.325	1.230	1.415	1.501	1.354
N6	1.281	1.398	1.539	1.297	1.375	1.509
C7	1.031	1.016	1.094	1.142	1.143	1.270
C8	1.131	1.142	1.066	1.149	1.141	1.045
$q_{ij}^\pi$ N1-C2	0.513	0.532	0.434	0.625	0.646	0.589
C2-N3	0.301	0.405	0.655	0.260	0.302	0.520
N3-N4	0.547	0.575	0.559	0.654	0.699	0.632
N4-N5	0.018	0.797	0.770	0.704	0.670	0.702
N5-N6		0.189	0.423		0.149	0.394
C2-N6	0.716	0.655	0.508	0.610	0.592	0.507
N6-C7	0.538	0.509	0.365	0.639	0.598	0.431
C7-C8	0.796	0.815	0.867	0.662	0.693	0.737
C8-N1	0.449	0.421	0.396	0.642	0.616	0.604

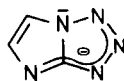
(a) See Table I for the numeration of the atoms.

an increase of the formal charge on atom N5, while atom N4 becomes less positive; in the transition state the former nitrogen is the atom with the largest positive charge. After passing the activated complex there is a build-up of elec-

tron density at the azido moiety, leading to a total negative charge on this group of 0.226 and 0.513 electrons in the bicyclic products **1b** and **2b**, respectively. This charge is mostly transferred from the imidazole ring. This

effect is particularly remarkable in the cyclization of the anion **2a**. In fact, the imidazole moiety as a whole carries a negative charge of about 0.870 electrons in the azide form **2a**, while in the tetrazole form the charge on the imidazole group is only 0.487 electrons.

In order to investigate the possible analogy between the ten  $\pi$ -electron system of the bicyclic molecules **1b** and **2b** and the aromatic isoelectronic pentalene dianion, we have calculated the  $\pi$ -charge densities and bond orders shown in Table IV. An examination of the  $\pi$ -electrons distribution in **1b** suggests that this is adequately represented by the classical valence bond structure **1b**. In fact, the C7-C8, N4-N5, and C2-N3 bonds of **1b** possess a considerable amount of double bond character. Regarding the bicyclic anion **2b**, although the C7-C8 and N4-N5 bonds still have the largest bond orders, the calculated bond orders of the C2-N3 and N1-C2 bonds are less and larger, respectively, than those in **1b**. Therefore, as it could be expected, the calculated geometry, formal charge distribution, and  $\pi$ -electrons distribution of **2b** show that this species can be satisfactorily represented by the structure **3**.



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In summary, it is felt that there is sufficient evidence to support the role of the more efficient delocalization of the negative charge on the nitrogen atoms of the tetrazole ring (mainly on N3 and N5) as the principal cause for the experimentally observed shifting of equilibrium **2a**  $\rightleftharpoons$  **2b** to the tetrazole form.

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