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On the Electronic Structure of N_2H_2. A Possible Triplet Ground State in Diazines

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Within the frame of closed-shell and restricted open-shell *ab initio* SCF calculations 1,1-dihydrodiazine $H_2N{=}N$ has a triplet ground state, $^3A_2$. This result, though not unsuspected from simple valence theory, is critically discussed and possible chemical implications are briefly mentioned.

Key words: Diazine – Triplet ground state – Singlet-triplet separation – Cheletropic cleavage

Introduction

The electronic structure of *cis*- and *trans*-diimide and of 1,1-dihydrodiazine has already been the subject of a number of theoretical investigations [1–6]. These molecules, though difficult or even impossible to isolate, are of particular interest for more than academic reasons: They are isoelectronic with such chemically important species as oxygen, formaldehyde and ethylene. *Cis*- and *trans*-diimide are the parent molecules of the chemically important class of the azo compounds [3, 7, 8]. The aminonitrenes, related to 1,1-dihydrodiazine, undergo cheletropic reactions liberating nitrogen [9–11]. Although all isomers of N_2H_2 are thermodynamically unstable with respect to N_2 and H_2 [4], some spectroscopic data on N_2H_2 is known [4, 12–14] which confirms the existence of the *trans* form.

In the present note we wish to report that within the frame of closed-shell and restricted open-shell SCF calculations [15] 1,1-dihydrodiazine has a triplet ground state. This coincides with the situation assumed to prevail in general in nitrenes [16]. We also compare the singlet-triplet splitting of the $(n\pi^*)$ and $(\pi\pi^*)$ excited states of the different N_2H_2 isomers. The lowest excited states of *cis*- and *trans*-diimide are $^3(n\pi^*)$, $^1(n\pi^*)$, and $^3(\pi\pi^*)$. In this context we will not consider the higher excited states, with the exception of $^1(\pi\pi^*)$.

Calculations

The *ab initio* calculations were performed with the program IBMOL-5 [17] using a Gaussian-type basis. For all three isomers the geometry was considered as planar and, as in Ref. [3], the following values were adopted: $r(\mathrm{NN}) = 1.240$ Å, $r(\mathrm{NH}) = 1.021$ Å, $\sphericalangle$ (NNH) $= 112°39'$. The orbital basis consisted for the calcula-

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* The *ab initio* calculations were performed at the IBM Research Center, San Jose, California.

tions listed under I in a nitrogen 11 *s*, 7 *p* derived set and a hydrogen 6*s* set [18] contracted to a (5, 3/2) set (see Tables 1 a and 1 b). The computations designated by II started from the same contracted basis, augmented by polarization functions in the plane of the molecule, p_x and p_y, of exponent $\alpha = 1.000$ on each hydrogen atom, and by diffuse s, p_x, p_y, p_z functions of exponent $\alpha = 0.030$ on each nitrogen atom.

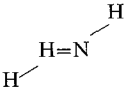
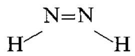
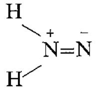
Table 1 a. Orbital exponents of the uncontracted bases [18]

s_N	p_N	s_H
22800.2	82.7715	82.702833
3413.45	19.3820	12.418535
776.383	5.99713	2.825682
219.966	2.14355	0.798266
71.7952	0.820810	0.258165
25.8175	0.316980	0.089859
9.92954	0.118820	
3.94843		
1.11085		
0.436520		
0.160920		

Table 1 b. Contraction coefficients listed in the sequence corresponding to Table 1 a. Most values are taken from atomic SCF calculations [18]

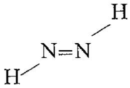
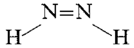
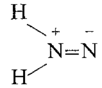
	s_N		p_N		s_H
χ_1	0.000221	χ'_1	0.002359	χ''_1	0.002004
	0.001715		0.017447		0.015333
	0.008908		0.074625		0.075518
	0.036023		0.212116		0.256733
	0.115506	χ'_2	1.00000	χ''_2	0.497645
	0.277557	χ'_3	0.397308		0.296084
χ_2	0.423141		0.167249		
	0.271130				
χ_3	1.00000				
χ_4	1.00000				
χ_5	1.00000				

Table 2. Comparison of the total energy in a.u. of the lowest closed-shell SCF state

Calculation			
I	−109.96338	−109.94822	−109.94019
II	−109.98092	−109.96639	−109.95317
WFA GLO in situ[a] adjusted [4]	−109.93017	−109.92913	−109.92233
WFA Extended GLO[a] [4]	−109.95274	−109.94423	−109.94145

[a] Geometry determined by energy minimization. See Ref. [4].

Table 3. Calculations I, II, and WFA [4] give energies in eV of the open-shell SCF states relative to the lowest closed-shell SCF state. The results listed under RHK [3] were obtained by a limited CI calculation

Calculation	State						
I	$^3(n\rightarrow\pi^*)$	^3B_g	1.678	$^3B_2$	2.127	$^3A_2$	−0.171
	$^1(n\rightarrow\pi^*)$	^1B_g	3.017	$^1B_2$	3.659	$^1A_2$	1.273
	$^3(\pi\rightarrow\pi^*)$	^3B_u	3.697	$^3B_1$	3.656	$^3A_1$	5.566
	$^1(\pi\rightarrow\pi^*)$	^1B_u	12.435	$^1B_1$	12.441	$^1A_1$	5.732
II	$^3(n\rightarrow\pi^*)$		1.755		2.198		−0.090
	$^1(n\rightarrow\pi^*)$		3.077		3.722		1.328
	$^3(\pi\rightarrow\pi^*)$		3.689		3.651		5.430
	$^1(\pi\rightarrow\pi^*)$		11.263		11.372		5.593
RHK [3]	$^3(n\rightarrow\pi^*)$	^3B_g	3.01	$^3B_2$	2.07		
	$^1(n\rightarrow\pi^*)$	^1B_g	3.92	$^1B_2$	3.36		
	$^3(\pi\rightarrow\pi^*)$	^3B_u	6.53	$^3B_1$	6.45		
WFA [4]	$^3(n\rightarrow\pi^*)$	^3B_g	3.223		—		
	$^1(n\rightarrow\pi^*)$	^1B_g	3.838		—		

With the purpose of assessing the influence of methyl substitution on the energy of the ($n\pi^*$) states some semi-empirical SCF–CI calculations within the CNDO approximation are included (see Table 4). The difference between the parametrizations *a* and *b* concerns solely the core matrix elements. In case *a* they are determined following Wratten [19], in case *b* they are increased in their absolute value so as to depress the energy of the lower σ orbitals [8, 20].

Results and Conclusions

In our calculation the geometry of the molecules was assumed fixed and no search for the minimum of the SCF energy with respect to the geometric parameters was undertaken. Nevertheless, with our orbital basis II the total ground state energy of *cis*- and *trans*-diimide turns out to be between 0.01 and 0.03 Hartrees lower than the better values listed in Ref. [4], which, though obtained using a Gaussian lobe basis, correspond to minima of the respective potential curves. We believe that minimization of the SCF energies with respect to geometry should not basically affect at least our qualitative conclusions. The finding that in $H_2\overset{+}{N}=\overset{-}{N}$ the SCF energy of the $^3A_2$ state lies below the one of the closed-shell $^1A_1$ state is not unsuspected. This situation is in some sense analogous to the one encountered in the oxygen molecule. The $2b_1$ (n) and $2b_2$ (π^*) orbitals of the diazine are related to the highest filled e_{1g} (π_y^* and π_z^*) orbitals of oxygen (see Fig. 1). Because of the breakdown in cylindrical symmetry the degeneracy is of course lifted in the diazine. But the orbital energy gap is not as large as in the other N_2H_2 isomers. The different environments of the two nitrogen atoms in the diazine leads to a relative localization of the molecular orbitals on one side or another of the molecule. In

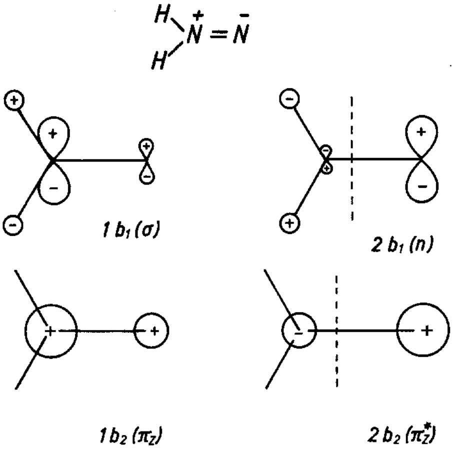


Fig. 1. Qualitative picture of orbitals for 1,1-dihydrodiazine

the lower $1b_1$ orbital this localization takes place on the $^{\mathrm{H}}_{\mathrm{H}}\!\!>\!\mathrm{N}$ side, as this favors H–N bonding. In $2b_1$ the localization must, for orthogonality reasons, be on the other nitrogen. The very large orbital coefficients of $2b_1(n)$ on this latter nitrogen atom, i.e., the "one-sidedness" of the MO, concomitantly reduces the antibonding effect of the node bisecting the N–N axis. The resulting molecular orbital may therefore be rated as quite characteristically nonbonding.

We notice that the improvement of the orbital basis, on going from I to II, reduces the SCF energy difference between $^3A_2$ and $^1A_1$. Furthermore it cannot be ruled out that electron correlation will push $^1A_1$ below $^3A_2$. Nevertheless it is conceivable that the $^3A_2$ state might remain within thermal accessibility from the $^1A_1$ ground state. However, we know of no simple way of assessing this possibly crucial difference in electron correlation energy.

The results of SCF–CI–CNDO calculations have been included for two reasons. Firstly, to assess the influence of methyl groups on the $(n\pi^*)$ state energies. Secondly, to see in general where the average $^{3,1}(n\pi^*)$ state energies come to lie with respect to the lowest closed-shell (ground) states. Within the ZDO approximation the singlet-triplet splitting cannot, of course, be computed. Table 4 shows these average energies to be very comparable to the *ab initio* SCF values, but in general to lie somewhat higher. As our semiempirical conclusions are incomplete without an attempt to estimate the magnitude of the singlet-triplet separation, and for the sake of a general comparison, we include the results of Table 5. The "simplified estimate" applies to $(n\pi^*)$ and $(\pi\pi^*)$ configurations described by MO's of the form:

$$\text{i)}\quad \pi_z = \frac{1}{\sqrt{2(1+S)}}(p_{z1}+p_{z2}), \qquad \pi_z^* = \frac{1}{\sqrt{2(1-S)}}(p_{z1}-p_{z2}),$$

$$n \equiv \pi_y^* = \frac{1}{\sqrt{2(1-S)}}(p_{y1}-p_{y2});$$

$$\text{ii)}\quad \pi_z = p_{z1}, \qquad \pi_z^* = p_{z2}, \qquad n = p_{y2}.$$

Table 4. Energies in eV of the ($n \rightarrow \pi^*$) states in N_2H_2 and $N_2(CH_3)_2$ as obtained by semiempirical SCF–CI–CNDO calculations. The singlet and triplet states are degenerate because of the ZDO approximation

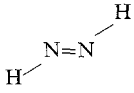
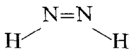
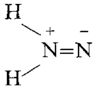
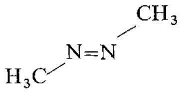
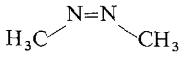
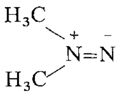
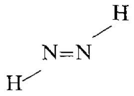
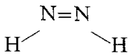
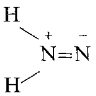
Parametrization			
a	3.10	4.07	1.77
b	2.90	3.83	1.43
			
a	2.37	3.21	1.94
b	2.29	3.14	1.59

Table 5. Singlet-triplet separation in eV. Values for the "simplified estimate" are based on functions as indicated in the text under i) and ii)

Calculation	State			
I	($n \rightarrow \pi^*$) ($\pi \rightarrow \pi^*$)	1.34 8.74	1.53 8.78	1.44 0.17
II	($n \rightarrow \pi^*$) ($\pi \rightarrow \pi^*$)	1.32 7.57	1.52 7.72	1.42 0.16
RHK [3]	($n \rightarrow \pi^*$)	0.91	1.29	
WFA [4]	($n \rightarrow \pi^*$)	0.62		
"simplified estimate"[a]	($n \rightarrow \pi^*$) ($\pi \rightarrow \pi^*$)	i) 1.98 10.91		ii) 2.24 1.38

[a] Sahni, R. C., Cooley, J. W.: Tables for Molecular Integrals, TN D-146 II. Use of the Mulliken approximation for integrals not listed therein.

The AO's are nitrogen Slater-type orbitals of exponent 1.950. If, as indicated, we take the results of Table 4 as averages of the respective singlet and triplet energies and apply our "simplified estimate" to then, then in 1,1-dihydrodiazine the lowest ${}^3A_2$ state lies at about *a)* 0.65 eV, *b)* 0.31 eV above the closed-shell ${}^1A_1$ state. For the dimethyl compound the corresponding values are *a)* 0.82 eV, *b)* 0.47 eV. This admittedly sketchy second procedure would indicate that the thermal accessibility of the lowest triplet state in diazines is rather unlikely.

The possible chemical consequence of a very low lying triplet state in diazines might be, for instance, that the cheletropic cleavage [9–11] of cyclic compounds of the type shown below leads to diradical formation:

To determine unambiguously the course of such a reaction requires apparently much more elaborate computations on one hand, or suitable experiments on the other.

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