Molecular Orbital Theory of the Electronic Structure of Organic Compounds

IV. A CNDO/S-CI SCF MO Study on the Lower Electronic States of Large Molecules. Singlet-triplet Transitions of Dioxodiazacycloalkanes

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The semiempirical molecular orbital CNDO/S-CI spectral parameterization has been used to elucidate the lower triplet electronic states of a series of dioxodiazacycloalkanes. The $1^3B_2(n_0\pi^*)$ and $1^3A_2(n_0\pi^*)$ triplet spectroscopic states involve intramolecular charge transfer from the oxygen to the carbon atom of the carbonyl group, which is supported by electron density calculations of these excited states. The solvation energy was incorporated in the calculations.

Introduction

In previous papers some ground state molecular properties of a restricted set of dioxodiazacycloalkanes (Fig. 1) [1] and of the cyclol and bicyclic lactam derived from I ($m=n=3$) [2] have been obtained with the CNDO/2 and INDO SCF semiempirical methods. More recently, a detailed analysis of the lower spectroscopic states associated with the singlet-singlet electronic transitions of I using the CNDO/S-CI methodology [3] was performed [4].

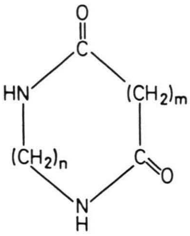

Fig. 1. Dioxodiazacycloalkanes (I) computed. $m=2, 3$; $n=2, 3, 4, 5$. Molecular symmetry group is C_{2v} for I ($m=2$, $n=2$; $m=2$, $n=4$) and C_s for I ($m=2$, $n=3$; $m=2$, $n=5$; $m=3$, $n=2$; $m=3$, $n=3$; $m=3$, $n=4$).

This lent credence to the applicability of the CNDO/S-CI parameterization and led us to a consistent account of the electronic spectra of these molecules in terms of the closely related electronic states. The trends in the electronic states were related to trends found in the ground state molecular orbitals (MO's). Thus, the interplay of the experimental and computed transition energies could lead to a better characterization of the excited states if an analysis of the triplet states of I could be performed. To this end a description of the lower singlet-triplet electronic transition of I upon the application of the CNDO/S-CI procedure will be presented.

Computational Procedure

Complete computational details were given in [4]. In the present work we follow the same line of reasoning except for the fact that we have choosen the Pariser-Parr interpolation method [5] instead of the Nishimoto-Mataga approximation [6] for the calculation of the two-center electron repulsion integrals. In fact, it has generally been concluded that when these integrals are used with the CNDO/S parameterization, the Nishimoto-Mataga integrals give better estimates of singlet states, while the Pariser approximation is better suited for the calculation of triplet states [7, 8].

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In the Hartree-Fock scheme the singlet-triplet transition is given by the expression

$$\Delta E = e_j - e_i - J_{ij}\,, \tag{1}$$

where e_i and e_j are the energies of the initial and final orbitals, and J_{ij} is the molecular Coulomb integral.

The molecules indicated in Fig. 1 will be identified as (m, n) where m and n are the numbers of methylene groups of the carboxylic and amine moieties, respectively. The spectroscopic CNDO/S-CI technique developed by Jaffé and co-workers [3] and used by us in our initial investigation [4] was obtained from the QCPE [9]. The program was modified to suit local input-output requirements and to facilitate changing dimension statements. Excited states were generated from the ground state occupied and virtual orbitals through a configuration interaction procedure between the 40 lowest-energy, singly excited states. The restriction to singly excited states means that essentially the IVO-method was used.

Results and Discussion

As long as the Pariser-Parr approximation to the two-center Coulomb repulsion integrals is used, the eigenvectors will differ from those previously computed using the Mataga method [4]. However, the same ordering and symmetry pattern was observed in the present calculations. Therefore, the ordering and energies of selected occupied and virtual orbitals that play a part in the computed electronic transitions as given by the ground state and virtual orbitals correlation will be omitted from the present discussion.

In discussing the MO's resulting from these computations it is convenient to view each molecule as divided between a carbonyl portion and a donor portion attached to the carbonyl group, in this case the lone pairs on nitrogen and oxygen.

The MO's that are most important in the computed electronic transitions are the lowest unoccupied MO's, i.e. $b_2(\pi^*)$, $a_2(\pi^*)$, and $a''(\pi^*)$, and the highest occupied orbitals of symmetry a_1, b_1, and a', which are labeled $a_1(n_0)$, $b_1(n_0)$, $a'(n_0)$ according to the molecular symmetry group.

The solvent effect as computed from the expression [10]

$$E_{\text{sol}} = 1/2\,(1 - D^{-1}) \sum_{p,q} Q_p Q_q (pp/qq)\,, \tag{2}$$

where D is the dielectric constant [11], Q_p is the net charge on the p center evaluated at each excited state from expression (3) (see below) and (pp/qq) are the bicentric atomic integrals, was introduced in each spectroscopic state before and after CI was performed. The corresponding correlation of these excited states is given in Figure 2. Solvents used were chloroform-acetic acid for (2,2), water-DMF for (2,3), and acetic acid for the rest of the molecules [12].

Since the atomic charge densities in the different excited states vary widely, the solvation energy shows no regular variation, i.e. an inversion of certain spectroscopic levels was detected when the participation of the solvent was allowed for. Therefore, in order to avoid spurious crossings, the correlation as given in Fig. 2 was limited to the lower lying triplet excited states, and hence the subsequent discussion will be restricted to this problem.

As long as the low-energy $\pi^* \leftarrow n$ transitions in these compounds cannot be explained on the basis of the amount of interaction of the nonbonding pairs, we must look elsewhere for an explanation. A clue can be obtained from our previously reported results [4]. However, before discussing the $\pi^* \leftarrow n$ triplet transitions in the light of Fig. 2, it should be recalled that every attempt to explain spectroscopic results on the basis of MO energy diagrams can be dangerous for two reasons [13]:

(1) Observed spectroscopic states are frequently mixtures of a number of spin configurations, and hence the transitions leading to such states cannot be identified by simple one-electron excitations as implied in MO diagrams;

(2) MO diagrams do not take into account electron repulsions in the excited state.

Even with these limitations, the MO diagrams of our previous findings [4] did definitely indicate a very important trend. Thus, it was evident that the order of the $\pi^* \leftarrow n$ transition energies was determined by three important factors: the amount of interaction of the nonbonding electrons, the extent of delocalization of these electrons, and the relative energies of the MO's.

Neglecting the solvent effect, the lowest energy triplet excited states calculated for each structure (1^3A_2, 1^3B_2, $1^3A''$, $2^3A''$) is comprised almost entirely of the $n\pi^*$ configuration. Thus, the (2,2)

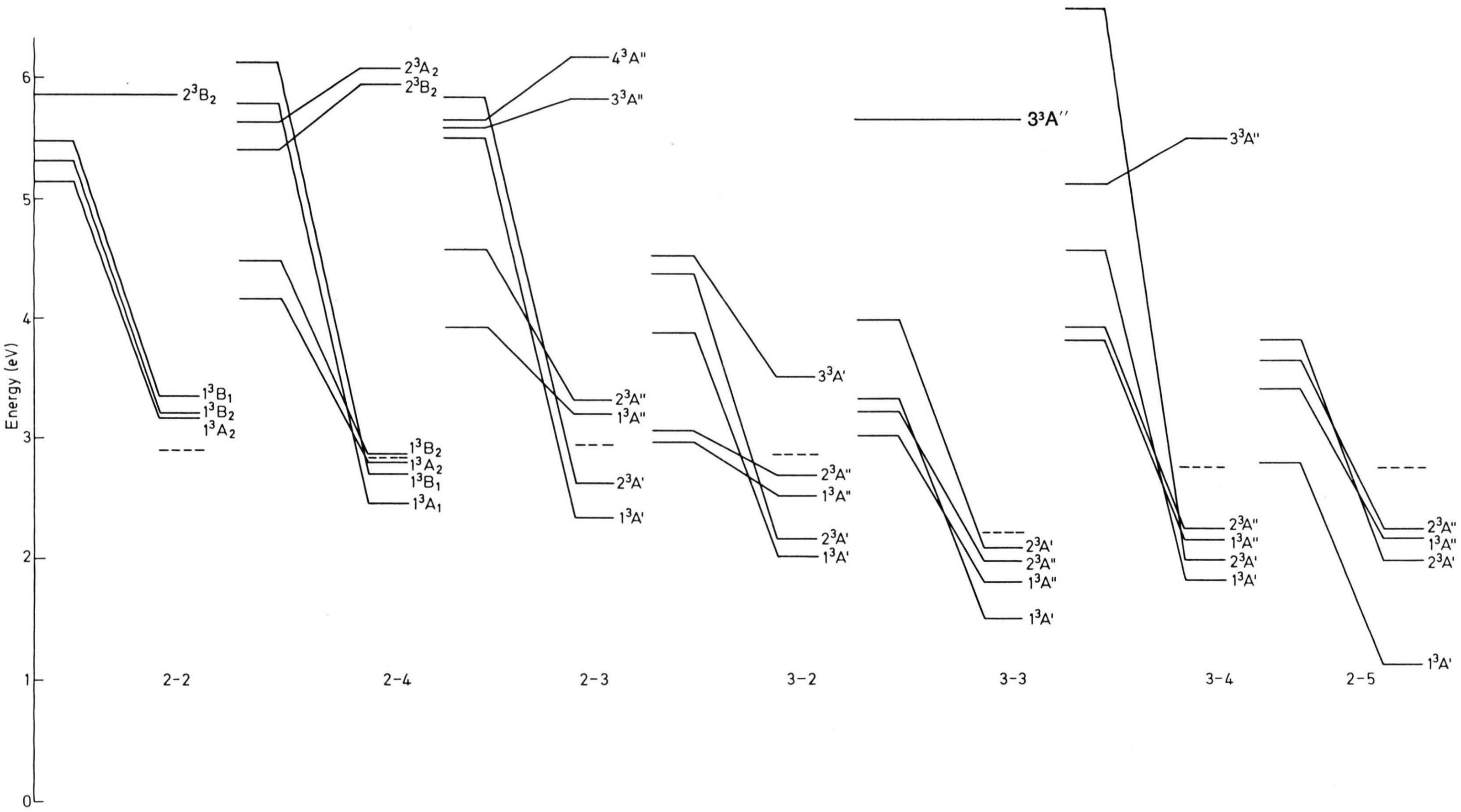

Fig. 2. Singlet-triplet correlation diagram of the lower electronic states of dioxodiazacycloalkanes (I). The symmetry of the spectroscopic states is given by the direct product of the symmetry of the molecular orbitals involved in the transition. See Ref. [4] for the symmetry of the different molecular orbitals. Experimental energies are shown in broken lines.

triplet electronic transitions near 3 eV result from the transitions $b_2 \leftarrow a_1$, $a_2 \leftarrow b_1$, $b_2 \leftarrow b_1$ which in turn lie at higher energies than the corresponding transitions in (2,4). The same transition energy pattern is observed for $1^3A''$, $2^3A''$ excited states of the lower symmetry compounds involving the $\pi^*_{c=0} \leftarrow n_0$ transition.

Excitations at lower wavelength ($^3A_1$ and $^3A'$ symmetry) are mainly due to the $\pi^*_{c=0} \leftarrow \pi_N$, π_0 transitions. These assignments are consistent with the experimental fact that the carbonyl bands are blue-shifted by the formation of a hydrogen bond with acetic acid as the proton donor, because these hypsochromic shifts characterize the absorption bands due to the $\pi^* \leftarrow n$ transitions [14].

The triplet $\sigma\pi^*$ states are calculated to be at the same energy as the singlet $\sigma\pi^*$ states of the same molecular configuration, since exchange integrals vanish in the CNDO approximation.

The $\pi\pi^*$ exchange integrals which are included in the CNDO approximation, are expected to be much larger than the $\sigma\pi^*$ exchange integral. The $^3B_2(n_0\pi^*)$ singlet-triplet splitting is calculated to be 0.5 eV. Since the $^3A_2(n_0\pi^*)$ is similar to the $^3B_1(\pi\pi^*)$, it probably also has a splitting on the order of 0.5 eV. Thus, the incorporation of $\sigma\pi^*$ exchange, although it would increase the energy of the $1^3B_2(n_0\pi^*)$ and $1^3A_2(n_0\pi^*)$ by about 0.5 eV, would not change the order of the first three triplet states.

The triplet state energies, without the large positive contribution of the exchange integral to the $\pi\pi^*$ state, which is found for the singlet states, follow the same ordering as that of the occupied MO's from which they arise. Thus, the trends in the energies of the $1^3B_2(n_0\pi^*)$, $1^3A_2(n_0\pi^*)$, and $1^3A''(\sigma\pi^*)$ are the same as those given for their singlet counterparts. The in-plane polarization of the 1^3A_1, 1^3B_1, $1^3A'$ spectroscopic states involved in the $\pi\pi^*$ transitions probably result from intensity stealing from transitions that occur at higher energies of the same molecular configuration induced by a combination of solvent perturbation and non planarity of the amide group in the excited state.

The triplet spectroscopic state 1^3B_1 is computed to occur at 3.849 and 2.726 eV for the molecules (2,2) and (2,4), respectively, when the solvent effect is incorporated (Figure 2). The associated electronic transitions $b_2 \leftarrow a_2$, $a_2 \leftarrow b_2$ are predicted to be of relatively high intensity since they are $\pi^* \leftarrow \pi$. The same trend is observed for the spectroscopic state 1^3A_1. Here the computed energy (neglecting the solvent effect) is also calculated to be lower for (2,4) than for (2,2).

The computed triplet transitions between 2 and 3 eV for the other molecules (C_s symmetry) in the series result from transitions to the a'' states which arise from transitions from the $a'(n_0)$ to the $a''(\pi^*)$ orbitals at energies below 4.5 eV (Figure 2).

The electronic transitions of A' symmetry ($a'' \leftarrow a''$) involve lone pairs on nitrogen and oxygen. The stabilization of the $a''(\pi^*)$ is less than that of the $a''(\pi)$. This results in the $1^3A'(\pi\pi^*)$ being calculated in the narrow energy range 1.18—3.23 eV (Fig. 2) along the series, except for (2,5) where the spectroscopic transition is of the type $a' \leftarrow a'$ with a high CI composition (0.9).

From Fig. 2 it can be observed that the first two triplet spectroscopic states are much lowered by CI, since only 45—50% of the composition of these excited states can be attributed to one molecular configuration. The $a_1(\sigma)$ MO remains close in energy to the $b_2(n_0)$ even though the $a_1(\sigma)$ no longer contains a high percentage of nitrogen lone pair character. In particular, since the $1^3A_2(n_0\pi^*)$ and $1^3B_2(n_0\pi^*)$ both result from a transition from MO's that are predominantly on the oxygen to a MO $b_2(\pi^*)$ containing about 45% C=0 character [4], transitions to these states result in charge transfer from the oxygen to the carbon atom of the carbonyl group. Transitions to the $b_2(\pi^*)$ and $a_2(\pi^*)$ (symmetries A_1 and B_1) also involve carbonyl, oxygen to carbon charge transfer, but to a lesser degree since the $a_2(\pi)$ and $b_2(\pi)$ eigenvectors possess more nitrogen character [4]. The same trend is observed for the $1^3A''$ and $2^3A''$ excited states of the lower symmetry compounds.

These excited state properties can be rationalized by analazing the charge densities of the amide group atoms in the various triplet spectroscopic states. In the virtual orbital approximation to the excited state wave functions the atomic charge densities in the excited state are given by [3]

$$q(A)^*_i = q(A)^\circ + \sum_{m=1}^{l} \sum_{r=1}^{n} C'^2_{im}(C^2_{k'r} - C^2_{jr}), \quad (3)$$

where $q(A)^\circ$ is the ground state charge density on atom A, C'_{im} is the CI coefficient for the contribution to the ith state of the mth electronic configura-

Table 1. CNDO/S-CI electron density difference for excited triplets (Pariser-Parr integrals) from ground state[a].

Molecule[b] (*m*, *n*)	State	C	O	N	H
(2, 2)	1^3A_2	$2.9 \cdot 10^{-1}$	$-1.9 \cdot 10^{-1}$	$-0.2 \cdot 10^{-2}$	$-0.3 \cdot 10^{-2}$
	1^3B_2	$2.9 \cdot 10^{-1}$	$-1.9 \cdot 10^{-1}$	$-0.8 \cdot 10^{-1}$	$-0.3 \cdot 10^{-2}$
	1^3A_1	$3.2 \cdot 10^{-1}$	$-0.4 \cdot 10^{-1}$	$-2.1 \cdot 10^{-1}$	0.0
	1^3B_1	$3.2 \cdot 10^{-1}$	$-0.3 \cdot 10^{-1}$	$-2.2 \cdot 10^{-1}$	0.0
	2^3A_1	$2.9 \cdot 10^{-1}$	$-0.3 \cdot 10^{-1}$	$-0.6 \cdot 10^{-1}$	$0.4 \cdot 10^{-1}$
(2, 4)	1^3A_1	$3.4 \cdot 10^{-1}$	$-0.9 \cdot 10^{-2}$	$-2.2 \cdot 10^{-1}$	0.0
	1^3B_1	$3.4 \cdot 10^{-1}$	$-0.7 \cdot 10^{-2}$	$-2.0 \cdot 10^{-1}$	0.0
	1^3A_2	$3.3 \cdot 10^{-1}$	$-2.4 \cdot 10^{-1}$	$-4.3 \cdot 10^{-2}$	$-0.5 \cdot 10^{-2}$
	1^3B_2	$3.3 \cdot 10^{-1}$	$-2.4 \cdot 10^{-1}$	$-4.2 \cdot 10^{-2}$	$-0.5 \cdot 10^{-2}$
	2^3B_2	$0.5 \cdot 10^{-1}$	$-0.8 \cdot 10^{-2}$	$-1.7 \cdot 10^{-1}$	$1.3 \cdot 10^{-2}$
(2, 3)	$1^3A'$	$3.1 \cdot 10^{-1}$	$-1.7 \cdot 10^{-2}$	$-2.6 \cdot 10^{-1}$	0.0
	$2^3A'$	$3.6 \cdot 10^{-1}$	$-0.4 \cdot 10^{-1}$	$-0.2 \cdot 10^{-1}$	$-0.2 \cdot 10^{-2}$
	$1^3A''$	$3.4 \cdot 10^{-1}$	$-2.6 \cdot 10^{-1}$	$-0.2 \cdot 10^{-1}$	$-0.2 \cdot 10^{-2}$
	$2^3A''$	$2.8 \cdot 10^{-1}$	$-2.7 \cdot 10^{-1}$	$-1.6 \cdot 10^{-1}$	$1.6 \cdot 10^{-2}$
	$3^3A''$	$5.4 \cdot 10^{-2}$	$-0.9 \cdot 10^{-1}$	$-1.8 \cdot 10^{-1}$	$0.2 \cdot 10^{-1}$
(3, 2)	$1^3A'$	0.6	$0.3 \cdot 10^{-2}$	$-1.3 \cdot 10^{-1}$	$0.1 \cdot 10^{-1}$
	$2^3A'$	$0.4 \cdot 10^{-1}$	$-1.7 \cdot 10^{-1}$	$-1.5 \cdot 10^{-1}$	0.0
	$1^3A''$	$4.4 \cdot 10^{-2}$	$-1.5 \cdot 10^{-3}$	$-1.5 \cdot 10^{-3}$	$-0.7 \cdot 10^{-4}$
	$2^3A''$	$6.1 \cdot 10^{-1}$	$-4.6 \cdot 10^{-1}$	$-0.3 \cdot 10^{-2}$	$-0.2 \cdot 10^{-2}$
	$3^3A''$	$4.9 \cdot 10^{-2}$	$-1.5 \cdot 10^{-1}$	$-1.6 \cdot 10^{-1}$	$1.2 \cdot 10^{-2}$
(3, 3)	$1^3A'$	$1.5 \cdot 10^{-1}$	$-8.6 \cdot 10^{-2}$	$-1.8 \cdot 10^{-1}$	0.0
	$1^3A''$	$1.5 \cdot 10^{-2}$	$-1.8 \cdot 10^{-1}$	$-2.6 \cdot 10^{-2}$	$-2.4 \cdot 10^{-3}$
	$2^3A''$	$6.6 \cdot 10^{-1}$	$-3.4 \cdot 10^{-1}$	$2.5 \cdot 10^{-3}$	$-7.5 \cdot 10^{-3}$
	$2^3A'$	$5.3 \cdot 10^{-1}$	$-2.6 \cdot 10^{-2}$	$-2.1 \cdot 10^{-1}$	0.0
	$3^3A'$	$5.5 \cdot 10^{-1}$	$-3.2 \cdot 10^{-2}$	$-3.7 \cdot 10^{-2}$	0.0
(2, 5)	$1^3A'$	$-0.3 \cdot 10^{-2}$	$-1.1 \cdot 10^{-2}$	$-0.9 \cdot 10^{-2}$	$0.9 \cdot 10^{-3}$
	$1^3A''$	$3.4 \cdot 10^{-1}$	$-2.9 \cdot 10^{-2}$	$-3.0 \cdot 10^{-1}$	0.0
	$2^3A''$	$3.3 \cdot 10^{-1}$	$-2.0 \cdot 10^{-1}$	$-0.7 \cdot 10^{-1}$	$-0.6 \cdot 10^{-2}$
	$2^3A'$	$1.7 \cdot 10^{-2}$	$-1.7 \cdot 10^{-2}$	$0.9 \cdot 10^{-2}$	$0.4 \cdot 10^{-2}$
	$3^3A'$	$3.4 \cdot 10^{-1}$	$-2.9 \cdot 10^{-2}$	$-3.1 \cdot 10^{-1}$	0.0
(3, 4)	$1^3A'$	$1.2 \cdot 10^{-1}$	$-1.1 \cdot 10^{-1}$	$-1.6 \cdot 10^{-1}$	0.0
	$2^3A'$	$5.8 \cdot 10^{-1}$	$-0.4 \cdot 10^{-2}$	$-1.2 \cdot 10^{-1}$	0.0
	$1^3A''$	$5.6 \cdot 10^{-1}$	$-3.1 \cdot 10^{-1}$	$-0.1 \cdot 10^{-1}$	$-1.0 \cdot 10^{-2}$
	$2^3A''$	$1.1 \cdot 10^{-1}$	$-1.7 \cdot 10^{-1}$	$-2.0 \cdot 10^{-1}$	$-0.7 \cdot 10^{-2}$
	$3^3A''$	$5.7 \cdot 10^{-2}$	$-1.0 \cdot 10^{-1}$	$-0.8 \cdot 10^{-1}$	$0.8 \cdot 10^{-2}$

[a] Carbon and hydrogen atoms are those of the amide group.

[b] See Figure 1.

tion which arises from the excitation of an electron from orbital j to virtual orbital k' and C_{jr} and $C_{k'r}$ are the coefficients of the rth atomic orbital on atom A in molecular orbitals j and k', respectively. In this work, the sum over m includes the 40 lowest energy electronically excited configurations, and the sum over r is again over the atomic orbitals on atom A.

Results of the CNDO/S-CI atomic electron density differences for excited triplets from the ground state of the atoms involved in intramolecular charge transfer are compared in the Table 1.

They follow the same general trend as found for the singlet states [4]. Particularly, the decrease of charge on the carbon is accompanied by a corresponding increase in electron density on the hydrogen atom in 1^3A_2, 1^3B_2, $1^3A''$, and $2^3A''$ excited electronic states. Thus the electronic repulsions which result from the π-system are relieved by a delocalization of electrons from the ring onto the hydrogen atoms through the σ framework.

The oxygen atom is predicted to be the most basic heteroatom in both the ground and triplet excited states. These results predict the nitrogen to bear a slight negative charge and the oxygen atom, while still the most negatively charged site in the molecule, to be less basic in the 1^3A_1, 1^3B_1, $1^3A'$, $2^3A'$, $1^3A''$, and $2^3A''$ excited states than in the ground state.

Conclusions

This study has demonstrated that CNDO/S calculations provide a reasonable description of various triplet state properties of the seven dioxodiazacycloalkanes considered. In particular, this method provided an excellent opportunity to examine the nature of the "lone pair" of electrons in this kind of molecules. It was further found that transitions to the π^* states result in intramolecular charge transfer from the oxygen to the carbon atom of the carbonyl group. This probably causes a lengthening of the C=) bond distance due to the excitation of the lone pair electron to the $\pi^*_{C=O}$ orbital.

It is hoped that this study will further serve as a reference for the investigation of ring contractions via cyclol in excited states. Work along these lines is underway and will be published at a later time*.

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* *Note added in proof*: Additional material associated with this work (extensive singlet-triplet correlations, solvation energy for the various spectroscopic triplet states, etc.) is available upon request.

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