Molecular Orbital Theory of the Electronic Structure of Organic Compounds

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

Horacio Grinberg * and Norma Sbarbati Nudelman *

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

Julio Marañón *, Oscar M. Sorarrain **, and Carlos F. Gómez

Laboratorio de Física Teórica, Departamento de Física, Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, La Plata, Argentina

Z. Naturforsch. **36a**, 494—501 (1981); received January 7, 1981

The semiempirical molecular orbital CNDO/S-CI spectral parameterization has been used to elucidate the lower electronic states of a series of dioxodiazacycloalkanes. The a_1, b_1, and a' occupied molecular orbitals lie predominantly on the oxygen, while a_2, b_2, and a'' are largerly nonbonding orbitals delocalized on the nitrogen and oxygen atoms. The two lowest unoccupied virtual orbitals are predicted to be of b_2, a_2, and a'' symmetry. These orbitals are strongly localized on the $C=0$ group. The resulting $1\,B_2(n_0\,\pi^*)$ and $1\,A_2(n_0\,\pi^*)$ 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. Although the calculated transition energies may not allow for absolute comparisons with experimental values, it appears that the introduction of self-consistency together with solvation energy and configuration interaction, when the elements of the interaction matrix are properly evaluated, lead to a fairly good interpretation of the singlet-singlet transitions. The lowest energy singlet excited state calculated for each structure is comprised almost entirely of the $n\pi^*$ configuration.

Introduction

In previous papers some ground state molecular properties of a restricted set of dioxodiazacycloalkanes (Fig. 1) [1] and those of the cyclol and bicyclic lactam derived from I ($m=n=3$) [2] upon the application of the CNDO/2 and INDO SCF semiempirical methods were described.

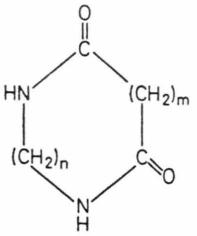

Fig. 1. Dioxodiazacycloalkanes (I) computed. $m=2$, 3: $n=2, 3, 4, 5$. Molecular symmetry group is C_{2v} for $I\,(m=2, n=2;\ m=2, n=4)$ and C_s for $I\,(m=2, n=3;\ m=2, n=5;\ m=3, n=2;\ m=3, n=3;\ m=3, n=4)$.

The results were encouraging enough for a reasonable description of a set of molecules having the same molecular symmetry and functional groups.

In the present study we extend our ground state molecular calculations of I in order to investigate the properties associated with the lower electronic states and singlet-singlet transitions.

In the past, theoretical studies of the spectra resulting from $\pi^* \leftarrow \pi$ transitions in various compounds have been based largely upon the Pariser-Parr-Pople SCF-CI scheme [3, 4]. This method, which is limited to pi electrons, has been used extensively and with a great deal of success. However, since this method deals explicitly only with those orbitals which are antisymmetric with respect to the molecular plane and treats all others as part of a nonpolarizable core, it is not applicable to the study of the $\pi^* \leftarrow n$ transitions.

In our search for a method which would satisfactorily predict both $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ electronic transitions, our findings of the above mentioned

---

* MCIC CONICET. República Argentina.

** MCIC CIC, Provincia de Buenos Aires, República Argentina.

Reprint requests should be addressed to Dr. Horacio Grinberg, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Ciudad Universitaria, 1428 Buenos Aires, Argentina.

0340-4811 / 81 / 0500-0494 $ 01.00/0. — Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

properties of I based on elucidation of the electronic structure using the "spectroscopic" CNDO/S parameterization of Del Bene and Jaffe [5] as modified by Jaffe and co-workers for the study of $\pi^* \leftarrow n$ transitions [6] will be reported. It is one of the best methods available at present to study the electronic transitions of large molecules, enabling us to follow the general NDO procedure and making it possible to use a standard hamiltonian which is applicable to a wide range of problems, minimally including optical spectra, multiplet splittings, oscillator strengths, excited state charge and bond order matrices. This technique has been successfully applied to the interpretation of both $\pi^* \leftarrow \sigma$ and $\pi^* \leftarrow \pi$ transitions in the electronic spectra of a large number of monosubstituted aromatics [5] including the singlet and triplet spectra of a series of nitroaromatics [7] and more recently, to the electronic structure study of some methyl and phenyl substituted pyryliums [8], N-alkylation effects on the electronic structure of carbazol [9] and electronic spectra of biomolecules [10].

Computational Procedures

The method of calculation can be divided in two parts:

(i) the determination of the CNDO MO's by means of an SCF calculation and

(ii) the generation of the spectroscopic states by configuration interaction.

Thus, our procedure was to calculate the ground state electronic wave functions of the molecular systems in the CNDO/S MO approximation and then construct electronic excited states in the virtual-orbital configuration interaction (CI) approximation.

In order to obtain the ground state energy and other properties of a molecule, the CNDO MO's were populated according to the "molecular Aufbau principle". In all cases of interest in this study, a closed-shell singlet-ground state resulted. The virtual orbitals which are not populated in the ground state are of importance in the calculation of spectroscopic data. Thus, the energy required to promote an electron from orbital i to virtual orbital j is given by the expression [11]

$$E = e_j - e_i - J_{ij} + 2\,K_{ij}\,, \qquad (1)$$

where e_i and e_j are the energies of the initial and final orbitals, and J_{ij} and K_{ij} are the molecular Coulomb and exchange integrals. The expression given refers to the energy associated with a singlet-singlet transition, since these are the only transitions which will be treated in detail in this paper. The CI calculation was restricted to the 40 lowest singly excited states.

All molecules given in Fig. 1 will be identified as (m, n) where m and n are the number of methylene groups of the carboxylic and amine moieties, respectively. The atomic coordinates and atom numbering system used are given in [1].

The closed-shell "spectroscopic" CNDO/S program was obtained from the Quantum Chemistry Program Exchange [12]. The program was modified to suit local input-output requirements and to facilitate changing dimension statements.

The program provides for the choice of several approximations to the two-center Coulomb repulsion integrals, γ_{AB}, the most common of which are the Pariser [13, 14], and Nishimoto-Mataga integrals [15]. 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 [16, 17]. Both methods have been used interchangeably in the literature depending on the properties of interest. Since the primary concern here is in reproducing the electronic excitation spectra, we have chosen arbitrarily to use the Nishimoto-Mataga Coulomb integrals throughout.

Results and Discussion

Ground State and Virtual Orbitals Correlation

Figure 2 shows the ordering and energies of selected occupied and virtual orbitals that play a part in the computed electronic transitions. Their relative localization, symmetries, and atomic orbital composition are given in Table 1.

In discussing the molecular orbitals 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 molecular orbitals that are most important in the computed electronic transitions are the lowest

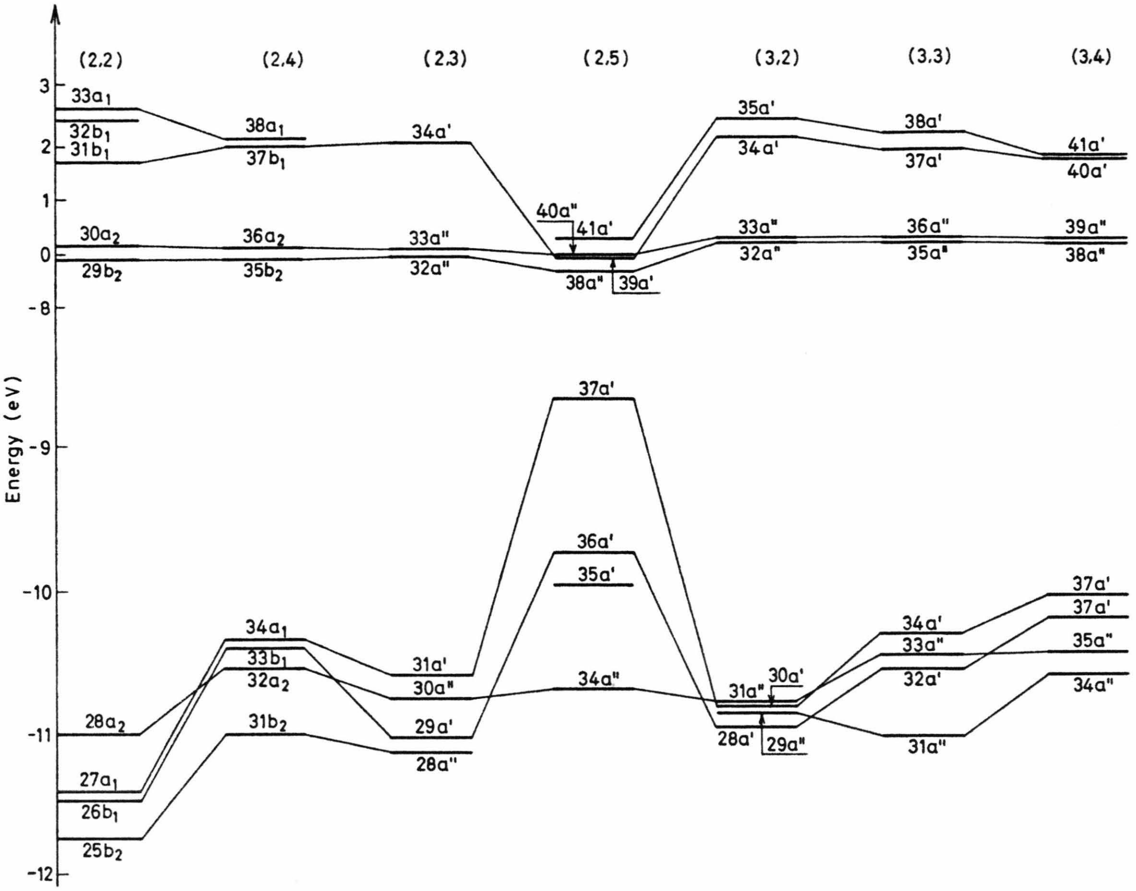

Fig. 2. CNDO/S eigenvalues correlation diagram for selected occupied and virtual orbitals of dioxodiazacycloalkanes (I). Energies of occupied and virtual molecular orbitals are not at the same scale. See Table 1 for the symmetry of the different molecular orbitals.

unoccupied molecular orbital, the $b_2(\pi^*)$, $a_2(\pi^*)$, and $a''(\pi^*)$, and the highest occupied orbitals of symmetry a_1, b_1, and a' which are labeled the $a_1(n_0)$, $b_1(n_0)$, $a'(n_0)$ according to the molecular symmetry group [12].

Table 1 shows that there are obvious similarities in orbital composition throughout the series. The a_1, b_1, and a' occupied molecular orbitals lie predominantly on the oxygen, while the a_2, b_2, and a'' are largely non-bonding orbitals delocalized on the nitrogen and oxygen atoms. However, the contribution as given in Table 1 is not too large and thus the CNDO/S description of the electron lone pairs in this study is in general agreement with the many previous all valence electron SCF calculations which have predicted the electron lone pairs to be partially delocalized throughout the molecule [5, 18 – 22]. It is found that this localization can vary over wide ranges depending on the parameters used in the calculation. The two oxygen atom lone pairs are best represented by the in-plane eigenvectors $a_1(n_0)$, $b_1(n_0)$, and $a'(n_0)$, where there is 0.22 e – 0.74 e of charge associated with this heteroatomic center.

These calculations predict the heteroatom nonbonding lone pair (0.22 e in 26 b_1, 0.35 e in 27 a_1 orbitals) localized in the oxygen σ molecular orbitals to be shifted to the higher energies 33 b_1 and 34 a_1 orbitals (relative localization 0.32 e and 0.34 e respectively) on going from (2, 2) to (2, 4) (see Figure 2).

It is interesting to note that while the CNDO/S parameterization imparts sufficient charge localization at the oxygen in $a_1(n_0)$, $b_1(n_0)$, and $a'(n_0)$ orbitals so as to result in a lone pair classification, the closest approach to this concept is predicted for

Table 1. CNDO/S (Nishimoto-Mataga integrals) eigenvectors[a] and relative localization[b] for selected eigenvalues of dioxodiazacycloalkanes.

(2,2)		(2,3)		(2,4)		(2,5)	
Orbital	Localization	Orbital	Localization	Orbital	Localization	Orbital	Localization
$25b_2$	N′s (0.27) O′s (0.19)	$28a''(b_2)$	N′s (0.32) O′s (0.24)	$31b_2$	N′s (0.30) O′s (0.14)	$34a''$	N′s (0.49) N′s (0.13)
$26b_1$	O′s (0.22)	$29a'(b_1)$	O′s (0.74)	$32a_2$	N′s (0.18)	$35a'$	O′s (0.48)
$27a_1$	O′s (0.35)	$30a''(a_2)$	N′s (0.46) O′s (0.14)	$33b_1$	O′s (0.32)	$36a'$	O′s (0.63)
$28a_2$	N′s (0.21) O′s (0.14)	$31a'(a_1)$	O′ (0.71)	$34a_1$ $35b_2$	O′s (0.34) C=O (0.45)	$37a'$ $38a''$	--- C=O (0.81)
$29b_2$	C=O (0.45	$32a''(b_2)$	C=O (0.79)	$36a_2$	C=O (0.43)	$39a'$	--
$30a_2$	C=O (0.44)	$33a''(a_2)$	C=O (0.79			$40a''$	C=O (0.43)
(3,2)		(3,3)		(3,4)			
Orbital	Localization	Orbital	Localization	Orbital	Localization		
$28a'$	O′s (0.69)	$31a''$	N′s (0.46) O′s (0.46)	$34a''$	O′s (0.44)		
$29a''$	N′s (0.24) O′s (0.35)	$32a''$	O′s (0.74)	$35a''$ $36a'$	N′s (0.29) O′s (0.62)		
$30a'$	O′s (0.64)	$33a''$	N′s (0.31) O′s (0.24)	$37a'$	O′s (0.64)		
$31a''$	N′s (0.29) O′s (0.35)	$34a'$	O′s (0.50)	$38a''$	C=O (0.84)		
$32a''$	C=O (0.85)	$35a''$	C=O (0.86)	$39a''$	C=O (0.84)		
$33a''$	C=O (0.85)	$36a''$	C=O (0.86)				

[a] In (2,3), (2,5), (3,2), (3,3), and (3,4), the C_s symmetry labels a' and a'' correlate to the C_{2v} symmetry labels, a_1, b_1, and a_2, b_2, respectively. The C_{2v} label is given in parentheses next to symmetry label to which it correlates such as exemplified for (3,3). σ- and π-eigenvectors transform as a_1, b_1, a' and a_2, b_2, a'' respectively.

[b] The values in parentheses are the sum of the squares of the coefficients for the indicated atom or group in the normalized eigenvector. Molecular orbitals localized on heteroatoms are lone pairs; those localized on the C=O group are π^* orbitals.

the a' occupied orbitals in molecules with C_s symmetry, where the atomic orbital composition is larger than 60% (see Table 1).

The first ionization potential is predicted to be of a_2 symmetry in (2, 2), $a_1(n_0)$ in (2, 4, and $a'(n_0)$ in the rest of the molecules, except in (3, 2) where it is predicted to be of a'' symmetry mainly localized on both heteroatoms.

The calculated progressive $b_2(n)$, $a_2(n)$ orbital energies in (2, 2) and (2, 4) are in order since the increased electronegative character of nitrogen and oxygen would intuitively be expected to exert a more strongly perturbing influence on the in-plane b_1 and a_1 orbitals. In addition there is a small asymmetry induced in the $b_2(n)$ occupied orbital of both molecules due to the nitrogen. In the $25\,b_2$ and $28\,a_2$ orbitals of (2, 2), for example, the nitrogens have slightly larger atomic orbital coefficients than the oxygen centers, while in the $32\,a_2$ orbital of (2, 4) no participation of the oxygen lone pair was detected.

As showed in Table 1 the lowest unoccupied virtual orbitals are predicted to be of b_2 and a_2 symmetry for (2, 2) and (2, 4) respectively, and of a'' symmetry for the rest of the molecules. All these orbitals are strongly localized on the C=O group (more than 45% of relative localization) and will be of importance in discussing charge transfer properties in excited states.

The trends in the orbital energies of MO's of $a_1(n_0)$, $b_1(n_0)$, and $a'(n_0)$ symmetry can be related to the series: (2, 2), (2, 3), (2, 4), and (2, 5). The orbitals localized on the oxygen are all destabilized across this series (see Figure 2).

Excited States Properties

In order to compare these calculations with the experimental spectra, the solvent effect as computed from the expression [23].

$$E_{\mathrm{sol}} = 1/2\,(1 - D^{-1}) \cdot \Big[\sum_{p} Q_p^2 (p\,p/p\,p) + 2 \sum_{p<q} Q_p Q_q (p\,p/q\,q) \Big], \tag{2}$$

where D is the dielectric constant [24], Q_p is the net charge on the p center evaluated at each excited state from expression (3) (see below) and $(p\,p/q\,q)$ 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 3. The experimental energies are shown in broken lines and are taken from a previous paper [25]. Solvents used were chloroform-acetic acid for (2, 2), water-DMF for (2, 3), and acetic acid for the rest of the molecules.

In the course of the present analysis, it was observed that when the participation of the solvent was allowed for, an inversion of certain spectroscopic levels resulted. Therefore, in order to avoid spurious crossings, the correlation as given in Fig. 3 was limited to the lower lying excited states and hence the subsequent discussion will be restricted to this problem.

The lowest energy singlet excited states calculated for each structure ($1\,A_2$, $1\,B_2$, $1\,A''$, $2\,A''$) is comprised almost entirely of the $n\pi^*$ configuration. Thus, for (2, 2) singlet electronic transitions near 2 eV result from the transitions $b_2 \leftarrow a_1$, $a_2 \leftarrow b_1$, $a_2 \leftarrow a_1$, $b_2 \leftarrow b_1$ which in turn lie at higher energies than the corresponding transitions in (2, 4). The theoretical absorption bands of (2, 2) and (2, 4) at 2.48 – 2.51 eV and 2.18 – 2.19 eV respectively, are then assigned to the $\pi^*_{C=O} \leftarrow n_O$ transition. The same transition energies pattern is observed for the $1\,A''$, $2\,A''$ excited states of the lower symmetry compounds involving the $\pi^*_{C=O} \leftarrow n_O$ transition.

Excitations at lower wavelength (B_1 and A' symmetry) are mainly due to the $\pi^*_{C=O} \leftarrow \pi_N, \pi_O$ transitions. These assignments are consistent with the previous experimental facts that carbonyl bands are blue-shifted by the formation of a hydrogen bond with acetic acid as a proton donor, because these hypsochromic shifts characterize the absorption bands due to the $\pi^* \leftarrow n$ transitions [26].

Since the excited state in question is predominantly expressed by the single excited $\pi^*_{C=O} \leftarrow n_O$ electronic configuration (for which the CI composition is larger than 0.9), it is understood that the a_2, b_2 vibrations predominantly generate the a_2, b_2 character in the nonbonding orbital (n_O), making this transition vibronically allowed too [27].

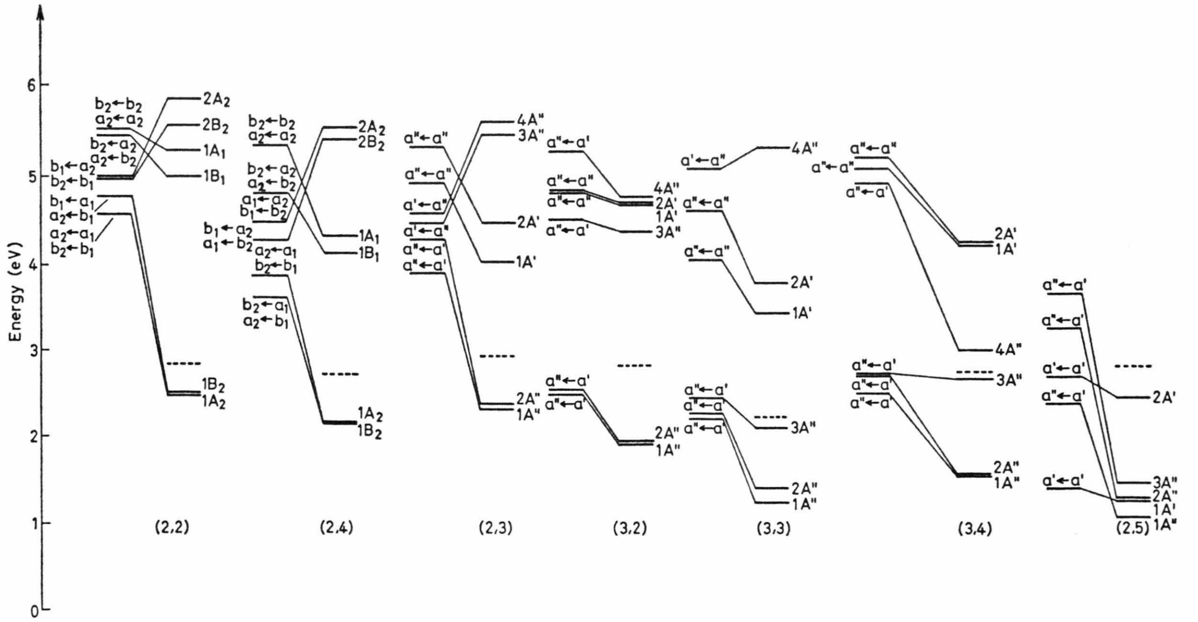

Fig. 3. Singlet-singlet correlation diagram of the lower electronic states of dioxodiazacycloalkanes (I). The symmetry of the spectroscopic states is given by the direct product of the symmetry of the molecular orbitals involved in the transition. See Table 1 for the symmetry of the different molecular orbitals. Experimental energies are shown in broken lines.

These electronic transitions are expected to be of low intensity ($\lg \varepsilon = 1.54$ and 2.75 for (2, 2) and (2, 4) respectively) [25], since the n_0 and π^* orbitals are perpendicular to each other (the oscillator strengths of $\sigma\pi^*$ states are computed to be zero in the CNDO approximation). It should be mentioned that a more complicated situation arises in the lower symmetry compounds (C_s symmetry) involving the carbonyl chromophore. In this case the intensity for the vibronic $\pi^* \leftarrow n_0$ transition, being locally electronic dipole forbidden, consists of both the electronically allowed part and the electronically forbidden, vibronically allowed part.

The singlet spectroscopic state $1\,B_1$ is computed to occur at 4.971 and at 4.110 eV for the molecules (2, 2) and (2, 4) respectively when the solvent effect is incorporated (Figure 3). 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 $1\,A_1$. Here the computed energy (neglecting the solvent effect) is also calculated to be lower for (2, 4) than for (2, 2). These transitions are much more intense ($f = 0.20$, 0.349) owing to the favorable geometry of the a_2 and b_2 eigenvectors.

The computed singlet transitions above 1.5 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 3). Neglecting the solvent effect, the first two spectroscopic states are very similar to their counterparts in molecules (2, 2) and (2, 4). Since the relative disposition of these spectroscopic states as given in Fig. 3 is determined by the molecular orbital energies, the trends in the energies of the excited states is discussed in terms of the same ordering of molecules within the series. Thus, since the $a'(n_0)$ and $a''(\pi^*)$ molecular orbitals are stabilized about the same amount in going through the series, the $1\,A''(n_0\pi^*)$ and $2\,A''(n_0\pi^*)$ are computed to occur at about the same energy 1.20 – 2.0 eV, through the series.

The electronic transitions above 3 eV from the ground state ($a'' \leftarrow a''$) 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 $1\,\mathrm{A}'(\pi\pi^*)$ being calculated in the narrow energy range 3.46 – 4.06 eV (Fig. 3) along the series, except for (2, 5) where the spectroscopic transition is of the type $a' \leftarrow a'$ with a high CI composition (0.95).

There is no splitting of the quasidegeneracy of the $1\,B_2$ and $1\,A_2$ states in (2, 2) and (2, 4) by allowing the solvent effect as given by the expression (2) (Figure 3). Although the same phenomenon was observed in the rest of the molecules (C_s symmetry) a small split (0.16 eV) of the $1\,A''$ and $2\,A''$ levels was observed for (3, 3).

The splitting of the quasi-degeneracy of the $1\,A_2$ and $2\,A_2$ states in (2, 2) and (2, 4) by 3.8 and 4.4 eV respectively by inclusion of CI, results in the $2\,A_2$ state going to much higher energy. The degeneracy of the $1\,A_1$ and $3\,B_2$ which are $\pi\pi^*$ and $n_0\pi^*$ states respectively, is however, only split by 0.45 eV in (2, 2) when the CI is admitted.

From Fig. 3 it can be observed that the first two singlet spectroscopic states are very lowered by CI, since only 45 – 50% of the composition of these excited states can be attributed to one molecular configuration. In particular, since the $1\,B_2(n_0\pi^*)$ and $1\,A_2(n_0\pi^*)$ 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 (see Table 1), 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 $a_2(\pi^*)$ (symmetry 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 possesses more nitrogen character (Table 1). The same trend is observed for the $1\,A''$ and $2\,A''$ excited states of the lower symmetry compounds.

These excited states properties can be rationalized by analyzing the charge densities of the amide group atoms in the various spectroscopic states. In the virtual orbital approximation to the excited state wave functions the atomic charge densities in the excited state are given by [5].

$$q(A)_i{}^* = q(A)^0 + \sum_{m=1}^{l} \sum_{r=1}^{n} C_{im}'^2 \,(C_{k'r}^2 - C_{jr}^2)\,, \quad (3)$$

where $q(A)^0$ is the ground state charge density, C_{im}' is the CI coefficient for the contribution to the ith state of the mth electronic configuration resulting 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 orbital on atom A in molecular orbitals j and k', respectively.

Results of the CNDO/S CI atomic electron density differences for excited singlets from ground state of the atoms involved in intramolecular charge transfer are compared in Table 2.

The oxygen atom is predicted to be the most basic heteroatom in both the ground and excited states. The hydrogen atom attached to nitrogen is predicted to be somewhat acidic in $1\,B_2$, $1\,A_2$, $1\,A''$, $2\,A''$ excited states whereas the carbonyl carbon becomes more basic in the lower excited states than in the ground state. 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 $1\,B_2$, $1\,A_2$, $1\,B_1$, $1\,A'$, $2\,A''$, $1\,A'$, and $2\,A'$ excited states than in the ground state, while the contrary occur for the $1\,A_1$ and $3\,A''$ excited states.

Conclusions

This study has demonstrated that CNDO/S calculations provide a quantitative basis for the understanding of various ground and excited singlet state properties of the seven dioxodiazacycloalkanes considered. The nature of the low-lying singlet states was further elucidated through a detailed study of the calculated CI wavefunctions thus providing an excellent opportunity to examine the nature of the lone pair electrons in these excited states.

Table 2. CNDO/S-Cl electron density difference for excited singlets from ground state[a].

Molecule[b] (m, n)	State	N	C	O	H
(2,2)	$1\,B_2$	$-1.8 \cdot 10^{-3}$	$2.8 \cdot 10^{-1}$	$-1.6 \cdot 10^{-1}$	$-3.6 \cdot 10^{-3}$
	$1\,A_2$	$-4.2 \cdot 10^{-3}$	$2.8 \cdot 10^{-1}$	$-1.5 \cdot 10^{-1}$	$-4.0 \cdot 10^{-3}$
	$1\,B_1$	$-1.8 \cdot 10^{-1}$	$3.1 \cdot 10^{-1}$	$-3.6 \cdot 10^{-2}$	$0.9 \cdot 10^{-3}$
	$2\,B_2$	$-8.4 \cdot 10^{-2}$	$3.1 \cdot 10^{-1}$	$-1.4 \cdot 10^{-1}$	$4.4 \cdot 10^{-2}$
	$1\,A_1$	$-1.9 \cdot 10^{-1}$	$2.3 \cdot 10^{-1}$	$4.6 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$
(2,4)	$1\,B_2$	$-4.4 \cdot 10^{-2}$	$3.2 \cdot 10^{-1}$	$-2.2 \cdot 10^{-1}$	$-6.9 \cdot 10^{-3}$
	$1\,A_2$	$-4.5 \cdot 10^{-2}$	$3.2 \cdot 10^{-1}$	$-2.2 \cdot 10^{-1}$	$-6.9 \cdot 10^{-3}$
	$1\,B_1$	$-1.6 \cdot 10^{-1}$	$3.1 \cdot 10^{-1}$	$-2.3 \cdot 10^{-2}$	$0.8 \cdot 10^{-3}$
	$1\,A_1$	$-1.7 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$3.6 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$
	$2\,B_2$	$-1.3 \cdot 10^{-1}$	$6.2 \cdot 10^{-2}$	$8.9 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$
(3,2)	$1\,A''$	$-7.1 \cdot 10^{-3}$	$5.7 \cdot 10^{-1}$	$-4.2 \cdot 10^{-1}$	$-2.9 \cdot 10^{-3}$
	$2\,A''$	$-2.7 \cdot 10^{-3}$	$6.7 \cdot 10^{-2}$	$-2.7 \cdot 10^{-2}$	$-2.3 \cdot 10^{-3}$
	$1\,A'$	$-9.6 \cdot 10^{-2}$	$1.7 \cdot 10^{-1}$	$-3.4 \cdot 10^{-2}$	$0.8 \cdot 10^{-3}$
	$2\,A'$	$-1.3 \cdot 10^{-1}$	$4.6 \cdot 10^{-1}$	$-7.6 \cdot 10^{-2}$	$0.7 \cdot 10^{-3}$
	$3\,A''$	$6.8 \cdot 10^{-3}$	$4.2 \cdot 10^{-1}$	$8.7 \cdot 10^{-2}$	$-1.8 \cdot 10^{-2}$
(2,3)	$1\,A''$	$-3.0 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	$-2.9 \cdot 10^{-1}$	$-3.7 \cdot 10^{-3}$
	$2\,A''$	$-2.4 \cdot 10^{-2}$	$3.1 \cdot 10^{-2}$	$-2.5 \cdot 10^{-1}$	$-3.4 \cdot 10^{-3}$
	$1\,A'$	$-1.6 \cdot 10^{-1}$	$2.9 \cdot 10^{-2}$	$-3.7 \cdot 10^{-2}$	$5.5 \cdot 10^{-2}$
	$2\,A'$	$-1.9 \cdot 10^{-1}$	$3.2 \cdot 10^{-2}$	$-7.4 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$
	$3\,A''$	$-1.2 \cdot 10^{-1}$	$6.0 \cdot 10^{-2}$	$-1.1 \cdot 10^{-1}$	$1.9 \cdot 10^{-2}$
(2,5)	$1\,A''$	$-7.7 \cdot 10^{-2}$	$3.3 \cdot 10^{-1}$	$-2.0 \cdot 10^{-1}$	$7.6 \cdot 10^{-3}$
	$2\,A''$	$-7.4 \cdot 10^{-2}$	$3.3 \cdot 10^{-1}$	$-1.9 \cdot 10^{-1}$	$-7.7 \cdot 10^{-3}$
	$1\,A'$	$-1.1 \cdot 10^{-2}$	$-3.1 \cdot 10^{-3}$	$-1.9 \cdot 10^{-2}$	$1.4 \cdot 10^{-3}$
	$2\,A'$	$1.9 \cdot 10^{-2}$	$3.4 \cdot 10^{-3}$	$-9.8 \cdot 10^{-3}$	$5.7 \cdot 10^{-3}$
	$3\,A''$	$2.1 \cdot 10^{-2}$	$3.0 \cdot 10^{-1}$	$5.9 \cdot 10^{-3}$	$-5.3 \cdot 10^{-4}$
(3,3)	$1\,A''$	$-1.4 \cdot 10^{-2}$	$6.3 \cdot 10^{-1}$	$-3.8 \cdot 10^{-1}$	$-1.1 \cdot 10^{-2}$
	$2\,A''$	$-2.7 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$-1.8 \cdot 10^{-1}$	$-3.3 \cdot 10^{-3}$
	$1\,A'$	$-1.1 \cdot 10^{-1}$	$5.3 \cdot 10^{-2}$	$-1.3 \cdot 10^{-1}$	$2.1 \cdot 10^{-4}$
	$2\,A'$	$-1.3 \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$	$-5.6 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$
	$3\,A''$	$-0.4 \cdot 10^{-1}$	$7.1 \cdot 10^{-2}$	$-1.5 \cdot 10^{-1}$	$1.6 \cdot 10^{-2}$
(3,4)	$1\,A''$	$-1.8 \cdot 10^{-2}$	$5.6 \cdot 10^{-1}$	$-2.6 \cdot 10^{-1}$	$-0.1 \cdot 10^{-1}$
	$2\,A''$	$-2.3 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$	$-1.5 \cdot 10^{-1}$	$-6.9 \cdot 10^{-3}$
	$1\,A'$	$-7.2 \cdot 10^{-2}$	$1.8 \cdot 10^{-1}$	$-0.9 \cdot 10^{-1}$	$0.9 \cdot 10^{-4}$
	$2\,A'$	$-7.0 \cdot 10^{-2}$	$4.1 \cdot 10^{-1}$	$-0.6 \cdot 10^{-1}$	$2.9 \cdot 10^{-4}$
	$3\,A''$	$-2.3 \cdot 10^{-2}$	$0.8 \cdot 10^{-1}$	$-0.8 \cdot 10^{-1}$	$-1.0 \cdot 10^{-2}$

[a] Carbon and hydrogen atoms are those of the amide group. [b] See Figure 1.

The first conclusion to be drawn is that the $1\,B_2$, $1\,A_2$, $1\,A''$, $2\,A''$ bands for the heterocyclic molecules are correlated pictorially with single electron jumps between n_0 and π^* orbitals. Thus, neglecting the solvent effect, a low intensity transition to the $1\,A_2(n_0\pi^*)$, $1\,B_2(n_0\pi^*)$, $1\,A''(n_0\pi^*)$, and $2\,A''(n_0\pi^*)$ states occur at $3-4$ eV. When the solvation effect is incorporated the energies of these states range from 1.3 to 2.5 eV, which improved the correlation with the experimental spectra.

Secondly, there is an important observation to be made about the importance of configuration interaction. In spite of the absence of degeneracies in the heterocycles, heavy interaction occurs between states wherever it is allowed by symmetry.

Lastly it can be seen that although the transition energies calculated in this study may not yield absolute comparisons with experimental values, it appears that the introduction of self-consistency together with solvation energy and configuration interaction, when the elements of the interaction matrix are properly evaluated, lead to a fairly good interpretation of the singlet-singlet transitions. 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 $C=0$ bond distance due to the excitation of the lone pair electron to the $\pi^*_{C=0}$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 *.

Acknowledgements

This work has been made possible by grants in aid from CONICET, República Argentina, and CIC (Provincia de Buenos Aires), República Argentina. J. M. and O. M. S. are grateful to the Organization of American States for a research grant in support of this work.

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

[1] J. Marañón, O. Sorarrain, H. Grinberg, S. Lamdan, and C. H. Gaozza, Z. Naturforsch. **31a**, 1677 (1976).
[2] J. Marañón, O. Sorarrain, H. Grinberg, S. Lamdan, and C. H. Gaozza, Tetrahedron, **34**, 53 (1978).
[3] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).
[4] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953).
[5] J. Del Bene and H. H. Jaffe, J. Chem. Phys. **48**, 1807 (1968); ibid. **48**, 4050 (1968); ibid. **49**, 1221 (1968).
[6] R. L. Ellis, G. Kuehnlenz, and H. H. Jaffe, Theor. Chim. Acta **26**, 131 (1972).
[7] J. J. Mikula, R. W. Anderson, L. E. Harris, and E. W. Stuebing, J. Mol. Spectrosc. **42**, 350 (1972); L. E. Harris, J. Chem. Phys. **58**, 5615 (1973).
[8] R. W. Bigelow, J. Chem. Phys. **66**, 4861 (1977); ibid. **67**, 4498 (1977).
[9] R. W. Bigelow and G. P. Ceasar, J. Phys. Chem. **83**, 1790 (1979).
[10] V. I. Danilov, V. I. Pechenaya, and N. V. Zheltovsky, Int. J. Quantum Chem. **17**, 307 (1980).
[11] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
[12] Calculations were performed on a IBM 360/50 computer with a QCPE program CNDO/S-CI. The modified closed-shell CNDO/S-CI program (QCPE N° 315) was obtained from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47401. The molecular symmetry groups were automatically generated from the cartesian coordinates.
[13] R. G. Parr, J. Chem. Phys. **20**, 1499 (1952).
[14] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 767 (1953).
[15] K. Nishimoto and N. Mataga, Z. Phys. Chem. Frankfurt **12**, 335 (1957).
[16] C. A. Masmanidis, H. H. Jaffe, and R. L. Ellis, J. Phys. Chem. **79**, 2052 (1975).
[17] H. M. Chang and H. H. Jaffe, Chem. Phys. Lett. **23**, 146 (1973).
[18] W. Adam and A. Grimison, Tetrahedron **21**, 3417 (1965).
[19] R. Hoffmann, J. Chem. Phys. **40**, 2745 (1964).
[20] J. E. Bloor and D. L. Breen, J. Amer. Chem. Soc. **89**, 6835 (1967).
[21] E. Clementi, J. Chem. Phys. **46**, 4731, 4737 (1967).
[22] G. Hojer, S. Meza, and M. E. Ruiz, Acta Chem. Scand. **27**, 1860 (1973).
[23] I. Jano, C. R. Acad. Sci. Paris **261**, 103 (1965).
[24] The dielectric constants used to calculate the solvation energy are intended to be the limiting values at low frequencies, the so-called static values. Solvents used are given in [25].
[25] H. Grinberg, S. Lamdan, and C. H. Gaozza, J. Heterocyclic Chem. **12**, 763 (1975).
[26] For instance, G. J. Brealey and M. Kasha, J. Amer. Chem. Soc. **77**, 4462 (1955).
[27] J. M. Hollas, E. Gregrek, and L. Goodman, J. Chem. Phys. **49**, 1745 (1968).