Theoret. chim. Acta (Berl.) 17, 120—130 (1970)

Configuration Mixing Involving σ and π Orbitals

II. The Effect of Doubly Excited Configurations on the Energy Values in the CNDO Method

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Received December 17, 1969

The effect (on the energy of the different states) of including doubly excited configurations in a σ- plus π-configuration interaction treatment, is studied within the CNDO/2 framework. For moderately large molecules the problem of the choice of the type (σ or π) of configurations taken into account is examined. When possible, comparison is made with similar non empirical calculations.

L'effet (sur l'énergie des différents états) de l'introduction de configurations diexcitées dans une interaction de configuration σ plus π, est étudié dans le cadre de la méthode CNDO/2. Pour des molécules de taille moyenne le problème du choix du type σ ou π des configurations est examiné. Les résultats obtenus sont comparés aux calculs non-empirique similaires disponibles.

Im Rahmen der CNDO/2 Methode wird der Einfluß (auf die Energien verschiedener Zustände) des Einschlusses doppelt angeregter Konfigurationen in einer σ- und π-Konfigurationswechselwirkungs-Behandlung studiert. Für nicht allzu große Moleküle wird das Problem der Wahl der Art (σ oder π) der berücksichtigten Konfigurationen untersucht. Soweit möglich, werden die Resultate mit denen ähnlicher nichtempirischer Rechnungen verglichen.

Introduction

Within the framework of a semiempirical method which introduces all the valence electrons, namely CNDO/2, we have shown [1] that a configuration mixing treatment among *all* the (σ and π) singly-excited configurations (CIS) calculates molecular spectra which are qualitatively very different in most cases from the corresponding results obtained in the virtual orbital approximation (VO) without configuration mixing.

For the small molecules C_2H_4, H_2CO, HCOOH, $HCONH_2$, where all such configurations could be included, a considerable lowering of the first $\pi \rightarrow \pi^*$ transition by mixing with $\sigma \rightarrow \sigma^*$ configurations was obtained, together with an appreciable improvement of the calculated value of the corresponding oscillator strength. On the contrary the first $\pi\pi^*$ triplet was found very little affected by the mixing so that the singlet-triplet separation became more reasonable than in the VO approximation. Meanwhile, the mixing among $\sigma \leftrightarrow \pi$ jumps appeared relatively small, so that the number of $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions below the first $\pi \rightarrow \pi^*$ transition was appreciably decreased, but not suppressed. These results were qualitatively identical to those obtained in non-empirical calculations for C_2H_4 [2] and H_2CO [3].

In the polyenes the lowering of the first $\pi \rightarrow \pi^*$ singlet decreased along the series, whereas the effect on the $\sigma \leftrightarrow \pi$ states increased. In benzene and pyridine the different $\pi \rightarrow \pi^*$ transitions mixed differently with $\sigma \rightarrow \sigma^*$ jumps the first one being the less modified, thus leaving a number of parasit $\sigma \leftrightarrow \pi$ transitions below it.

No definite conclusion could be reached as to the respective locations of transition energies in CNDO before examining the effect of introducing configurations of higher degrees of excitation in the scheme, especially the doubly excited configurations.

Indeed the role of doubly excited configurations in CI calculations had been studied in the π electron approximation both in non-empirical [4-6] and in Pariser-Parr-type calculations [5–15]. The results have shown that the introduction of doubly excited states could change considerably not only the numerical values of the energy of the different states of the molecule, but sometimes even the ordering of the π excited states, like in benzene [4, 5, 9, 13, 14] and butadiene [6, 10, 16]. More recently, the non-empirical treatment of formic acid by Peyerimhoff and Buenker [17] and of *trans*-butadiene by Buenker and Whitten [18], including configuration mixing up to quadruple excitation of σ as well as π-electrons have confirmed that taking into account double excitations is necessary in order to obtain a calculated spectrum which is qualitatively stable.

We present in this paper a detailed study of the effect of σ and π doubly excited configurations, both on the ground state energy and on the ordering of the excited states for the two sets of molecules already studied in our previous paper.

Approximations and Notations

Like in our previous work and for the reasons already explained [1] we are utilizing CNDO/2 *with the original parametrization* of Pople, Santry, and Segal [19]. The limitation of the number of configurations introduced is made independently for the singly and doubly excited states. For the single excitations our previous scheme [1] has not been modified. For the double excitations we fix a number of "frozen" electrons and a number of empty orbitals which will not be used. Then we build all the doubly excited configurations which can be constructed with the non "frozen" electrons going to all the empty allowed orbitals. Since, in the present work, we are interested only in planar molecules, we take advantage of this fact to treat separately the states which are of the ground state symmetry and those corresponding to $\sigma \leftrightarrow \pi$ transitions. The present treatment will be denoted by CISD. CIS. and CISD results always correspond to the same number of single excitations. When we indicate a transition as being $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$, we indicate the single configuration which has the highest weight in the calculated state. All the energies are given in electron volts *with respect to the* SCF *ground state taken as zero energy.*

Results and Discussion

We present two groups of results. The first one includes four small molecules for which we can introduce *all* the singly excited configurations in the CISD treatment and which have a small number of π doubly excited configurations.

The second group is made of benzene, pyridine and butadiene. In large molecules the deepest π-orbital is often below several σ-orbitals and one could be induced to neglect it if the choice of the orbitals considered was made only on energy criteria. In fact, we shall see that for these molecules, the problem of the choice of the configurations according to their σ or π nature is quite important. On the other hand, by comparison of our results with those of pure π-calculations, we shall examine the role of $\sigma \rightarrow \sigma^*$ excitations on the calculated spectrum.

1. Small Molecules

Ethylene

The ground state energy is lowered by 1.3 eV. Among the doubly-excited configurations, the $\pi\pi \rightarrow \pi^*\pi^*$ jump has the largest coefficient (0.118). All the other values are less than 0.05 but extremely scattered with no clearcut regularity, 40 configurations among the 196 included having coefficients above 0.01. Thus, if the doubly-excited π-configuration alone is introduced, the lowering of the ground state is only 0.39 eV, that is roughly 30% of the total lowering.

Among the excited singlets it appears that the $\sigma \rightarrow \pi$ states are much more affected than the $\pi \rightarrow \pi^*$ singlet which remains practically unchanged by inclusion of the doubly excited configurations, while the $\sigma \rightarrow \sigma^*$ singlets are appreciably lowered. Thus, the final image of the distribution of the states after CISD is analogous to that obtained in the VO approximation, all states, including the ground state being translated down to lower energies with some shrinking of the scale among the excited states.

The singlet-triplet separation is slightly decreased and comes somewhat closer to the experimental value.

Formaldehyde

The ground state of this molecule undergoes the largest energy lowering of all the cases studied: 2.45 eV. This strong effect is probably not entirely due to the fact that all the doubly excited configurations were included in this case. Like in ethylene, the $\pi\pi \rightarrow \pi^*\pi^*$ configuration has the largest weight. Taken alone, it gives 26% of the total energy gain.

All the excited states undergo a large lowering in energy upon the introduction of the double excitations (over 1.6 eV). The most modified state is the $n \rightarrow \sigma^*$ which now lies below the $\sigma \rightarrow \pi^*$. This crossing-over leads to qualitative agreement with most experimental attributions of the second band of the formaldehyde spectrum [20, 21]. Thus, we now find the order:

$$n\pi^* < n\sigma^* < \sigma\pi^* < \sigma\sigma^* < \pi\pi^* .$$

As to the third band it appears that the calculation would disagree with experiment if the suggestion was correct [19] that it has the same polarisation as the second one: no state of this symmetry is found before 11.56 eV above the $\pi \rightarrow \pi^*$ state.

Table 1. *Energies of the ground and excited states after configuration mixing referred to the* SCF *ground state energy. The type refers to the configuration having the largest weight. For each molecule, the number of σ and π orbitals included in* CISD *is indicated under the name. The first group of states represent singlets, the second one triplets*

	CIS		CISD	
	E(eV)	Type	E(eV)	Type
Ethylene	0		-1.33	
4σ, 1π	10.60	$\sigma\pi^*$	9.70	$\sigma\pi^*$
$4\sigma^*$, $1\pi^*$	12.17	$\pi\pi^*$	11.46	$\pi\sigma^*$
	12.22	$\sigma\pi^*$	11.80	$\sigma\pi^*$
	12.42	$\pi\sigma^*$	12.00	$\pi\sigma^*$
	13.08	$\pi\sigma^*$	12.07	$\pi\pi^*$
	15.03	$\sigma\sigma^*$	13.24	$\sigma\sigma^*$
	8.33	$\pi\pi^*$	8.33	$\pi\pi^*$
Formaldehyde	0		-2.45	
5σ, 1π	4.61	$n\pi^*$	3.00	$n\pi^*$
$3\sigma^*$, $1\pi^*$	9.43	$\sigma\pi^*$	7.38	$n\sigma^*$
	11.27	$n\sigma^*$	8.24	$\sigma\pi^*$
	11.44	$\pi\pi^*$	9.18	$\sigma\sigma^*$
	14.04	$\sigma\sigma^*$	11.18	$\pi\sigma^*$
			11.28	$\sigma\sigma^*$
	5.02	$n\pi^*$	3.00	$n\pi^*$
	7.63	$\pi\pi^*$	6.09	$\pi\pi^*$
Formic acid	0		-2.16	
3σ, 2π	5.58	$n\pi^*$	4.15	$n\pi^*$
$4\sigma^*$, $1\pi^*$	7.21	$\pi\sigma^*$	5.16	$\pi\sigma^*$
	8.90	$\sigma\pi^*$	6.07	$\sigma\sigma^*$
	9.49	$\pi\pi^*$	7.83	$\pi\pi^*$
	10.01	$\sigma\sigma^*$	8.16	$\sigma\pi^*$
	5.58	$n\pi^*$	4.15	$n\pi^*$
	6.29	$\pi\pi^*$	5.40	$\pi\pi^*$
Formamide	0		-1.27	
3σ, 2π	5.91	$n\pi^*$	5.04	$n\pi^*$
$4\sigma^*$, $1\pi^*$	7.72	$\pi\sigma^*$	6.80	$\pi\sigma^*$
	9.66	$\sigma\sigma^*$	7.35	$\sigma\sigma^*$
	9.93	$\pi\pi^*$	8.55	$\pi\pi^*$
	10.22	$\sigma\pi^*$	8.80	$\pi\sigma^*$
	10.78	$n\sigma^*$		
	5.91	$n\pi^*$	5.04	$n\pi^*$
	6.99	$\pi\pi^*$	6.32	$\pi\pi^*$

No transition in this molecule can really be qualified as being $\pi \rightarrow \pi^*$ in CISD: the $\sigma\pi$ mixing is so strong that no configuration is found to have a weight above 50% in this type of state.

For the triplets we see that the $n \rightarrow \pi^*$ transition is more lowered than the corresponding singlet, with an opposite behaviour for the $\pi \rightarrow \pi^*$ states.

The numerical agreement of the transition energies with the experimental ones is again not improved by inclusion of double excitations since, except the first $n \rightarrow \sigma^*$ state, all the excited states are less lowered than the ground state.

Table 2. *Comparison of* NE *and* CNDO *results for formic acid using* 2σ, 2π, $2\sigma^*$, $1\pi^*$ *orbitals in the* CISD *treatment. Comparison is made with the* VO *approximation (no* CI *included). Energies like in Table 1*

VO			CISD		
Type	NE [17]	CNDO	Type	NE [17]	CNDO
	0	0		−0.95	−0.91
$n \to \pi^*$	6.24	5.91	$n \to \pi^*$	4.85	5.05
$\sigma \to \pi^*$	10.02	9.81	$\pi \to \pi^*$	8.74	9.76
$\pi \to \pi^*$	11.88	13.03	$\sigma \to \pi^*$	9.50	9.69
$\pi \to \pi^*$	15.07	18.01	$\pi \to \pi^*$	12.87	15.78
$\pi \to \sigma^*$	15.07	9.42	$\pi \to \sigma^*$	13.89	5.84
$n \to \sigma^*$		11,69	$n \to \sigma^*$	14.43	7.14
$\pi \to \pi^*$	5.55	7.53	$n \to \pi^*$	4.31	5.05
$n \to \pi^*$	5.58	5.91	$\pi \to \pi^*$	4.92	6.10

Formic Acid

The ground state is lowered by as much as 2.16 eV in spite of the fact that not all diexcited configurations were included. The π double excitations yield (alone) 30% of the ground state energy gain. The $2\pi 2\pi \to 3\pi^* 3\pi^*$ jump has the largest coefficient (0.103) in the ground state wave function, but 64 configurations out of 160 have a coefficient larger than 0.01. The order of the transitions given by CIS is modified in such a way that only one $\sigma \leftrightarrow \pi$ state remains between $n \to \pi^*$ and $\pi \to \pi^*$. But, like in formaldehyde the first in-plane polarized transition is more $\sigma \to \sigma^*$ than $\pi \to \pi^*$.

Here again, CISD does not decrease the calculated values of the transition energies since it lowers more the ground state than the excited states.

For formic acid we have performed another calculation reported in Table 2, limiting the configuration mixing in the same fashion as in a recent non-empirical calculation [17], taking into account two σ and two π occupied levels with two σ and one π empty levels. This more limited calculation provides thus an oppurtunity to study the role of the CNDO hypothesis in the effect observed. The comparison of the CNDO and NE results, shows very neatly that the action of CISD is the same in both. The energies have rather different numerical values (except for the $n \to \pi^*$ state), but they are lowered by about the same quantity in the two calculations. The major difference is the presence in CNDO of two low-lying $\pi \to \sigma^*$ and $\sigma \to \sigma^*$ states which are located at much higher energies in the NE results. As already noted for ethylene and formaldehyde in CIS, we see from Table 2 that CNDO gives smaller singlet-triplet splitting than NE methods, a result maintained in the CISD approximation.

Formamide

The ground state of this molecule is lowered by only 1.28 eV, the smallest value among the small molecules considered. The π double excitations alone yield 41% of this lowering. Like in formic acid, many configurations have a coefficient larger than 0.01 (53 out of 167) but none of them reaches over 0.05.

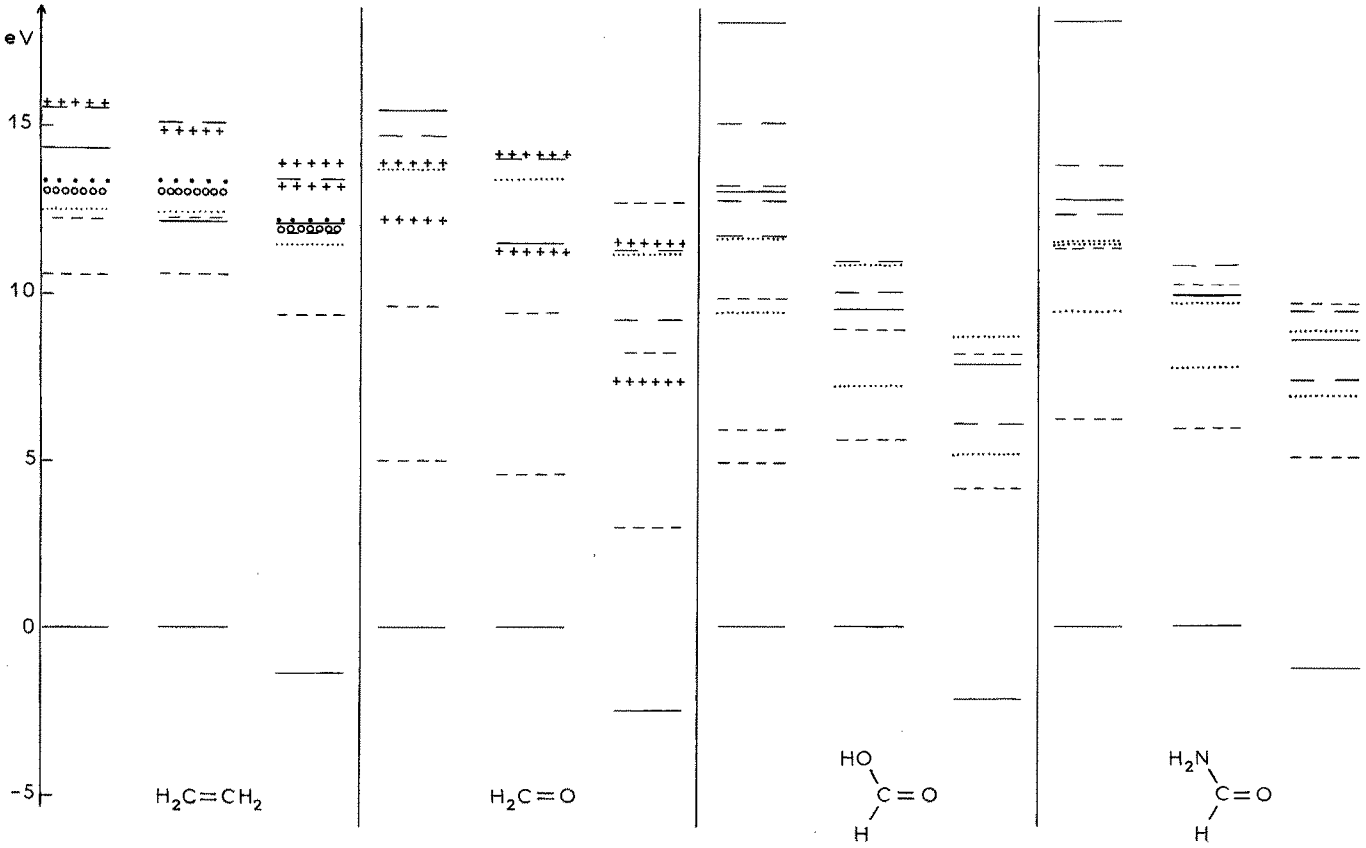

Fig. 1. ——— Ground state or $\pi\to\pi^*$, — — — — $\sigma\to\pi^*$ or $n\to\pi^*$, — — — $\sigma\to\pi^*$ *not* interacting with the preceding ones, ………… $\pi\to\sigma^*$, ooooooooooo $\pi\to\sigma^*$ *not* interacting with the preceding ones, •••••• $\pi\to\sigma^*$ *not* interacting with the preceding ones, —— —— $\sigma\to\sigma^*$ interacting with the $\pi\to\pi^*$, + + + + + $\sigma\to\sigma^*$ *not* interacting with the $\pi\to\pi^*$

Here again the largest coefficient corresponds to a $\pi \rightarrow \pi^*$ double excitation, but, this time involving the deepest π orbital, in contrast with the results seen in HCOOH.

Otherwise, the action of double excitations on the calculated spectrum is very analogous to that observed for formic acid, the final order of the transitions being:

$$n \rightarrow \pi^* < \pi \rightarrow \sigma^* < n \rightarrow \sigma^* < \pi \rightarrow \pi^*$$

whereas VO and CIS gave different orders for these two molecules. Here again CISD does not improve the numerical agreement of the transition energies with experiment.

Summing up the conclusions reached for the four small molecules, one may say that they have a number of common features:

a) The $\pi \rightarrow \pi^*$ double excitations have the highest weight in the ground state but they are responsible for only a fraction of its energy lowering.

b) The weight of the ground state configuration in the final ground state remains above 90% everywhere.

c) As a rule, the ground state is more sensitive to the inclusion of the double excitations than the excited states, a feature which has been noted years ago in the π electron approximation [6, 22].

d) The $\sigma \rightarrow \sigma^*$ states do not obey this rule and this seems due to the strong interaction between $\sigma \rightarrow \sigma^*$ single excitations and the $\sigma\pi \rightarrow \sigma^*\pi^*$ double excitations. It is true that double excitations interact very strongly with the $\pi \rightarrow \pi^*$ configurations [23] but we see here that they interact still more with the $\sigma \rightarrow \sigma^*$-ones, so as to give rise to strong $\sigma\pi$ mixing which thus can produce a crossing-over of the two states when they are not too far apart.

e) The $\sigma \leftrightarrow \pi$ transitions are less affected by the double excitations than the others, except for ethylene in which symmetry forbids mixing in the $\pi \rightarrow \pi^*$ state.

f) As to the numerical agreement with experiment, the $\pi \rightarrow \pi^*$ transitions remain much too large and the good value observed after CIS for $n \rightarrow \pi^*$ transitions is destroyed by CISD.

The evolution of the calculated singlets in the four small molecules considered, from VO to CIS to CISD, is schematized in Fig. 1.

2. Large Molecules

Benzene and Pyridine

As already mentionned in the introduction, the large molecules present a problem of orbital choice for the generation of the diexcited configurations: if the orbitals were included in the CISD calculation according to the ordering of their energies, we would have been limited to 3σ, 2π, $2\pi^*$ and $3\sigma^*$ orbitals. The results of this interaction for benzene (Table 3, column 3) and for pyridine (Table 4, column 3) show no effect on the positions of the "*u*" excited states. The situation is not changed if one includes more σ orbitals, (and consequently less π) except that, now, even the ground state does not mix with the excited configurations introduced (Table 3, column 4). But, on the contrary, when increasing

Table 3. *Energies of the states of benzene (eV, with respect to the* SCF *ground state)*

Orbitals included in CISD treatment	$\sigma+\pi$ CI					π CI			
	0 (CIS)[a]	$3\sigma 2\pi$	4σ	3π	$3\pi 2\sigma$	CIS		CISD	
		$3\sigma^* 2\pi^*$	$4\sigma^*$	$3\pi^*$	$3\pi^* 2\sigma^*$	NE [15]	CNDO	NE [15]	CNDO
$^1A_{1g}$	0	− 0.86	− 0.17	− 1.07	− 1.14	0	0	−1.90	− 1.07
$^1B_{2u}$	10.15	10.12	10.15	8.25	8.22	7.15	10.15	4.03	8.25
$^1B_{1u}$	10.11	10.10	10.11	9.79	9.76	8.31	10.26	7.80	9.93
$^1E_{1u}$	12.73	12.65	11.94	11.94	11.90	10.93	14.13	9.39	13.02
$^1E_{2g}$	14.26	13.57	13.29	13.51	13.26	12.66	16.17	7.98	13.51
$^3B_{1u}$	7.59	7.59			7.23	3.60	7.59	3.35	7.25
$^3E_{1u}$	9.23	9.21			8.17	5.73	9.23	4.15	8.19

[a] In CIS we introduce 58 singly excited configurations. This choice is kept constant for all CISD $\sigma+\pi$ calculations.

the number of π-orbitals at the expense of the σ-orbitals, thus introducing all the π- and π^*-orbitals, all the states are appreciably lowered, and this even when suppressing entirely the σ-orbitals (Table 3, columns 5 and 6). Thus *within the limitation imposed by the size of our computer*, the π double excitations appear as responsible of almost the totality of the ground state as well as of the excited states lowering, a feature rather different from the situation encountered in small molecules.

The calculated spectrum is then in *qualitative* agreement with the experimental attribution of the different excitations [24, 25]. This was not obtained with π CI calculations using non-empirical repulsion integrals [9, 15] where the double excitations lower the position of the E_{2g} singlet enough to bring it below the ${}^1B_{1u}$ state. Since the Coulomb integrals used in CNDO are equally non-empirical, we wondered if this difference in results could be due to our introducing the $\sigma \rightarrow \sigma^*$ excitations which interact mainly with the B_{1u} and E_{1u} states: we thus ran again CIS and CISD with no σ-orbitals in the CI treatment, but again we found the order:

$${}^1B_{2u} < {}^1B_{1u} < {}^1E_{1u} < {}^1E_{2g}$$

(see Table 3, columns 8 and 10).

This difference in location of the E_{2g} state in NE and CNDO computations is probably related to the fact that the action of double excitations is much stronger in NE than in CNDO (compare columns 7 and 9 of Table 3): since the E_{2g} state is the most modified by CI, it appears very low in the NE approach. It is interesting that a CISD calculation with all the π double excitations gives no $\sigma \rightarrow \pi^*$ transition below the ${}^1B_{2u}$ state, the lowest one occuring at 9.28 eV. In the CIS treatment we obtained four such low-lying $\sigma \leftrightarrow \pi$ bands. The results for pyridine are very similar to those of benzene. Clearly, the ordering of the excited states is improved by the introduction of double excitations, but the numerical agreement with experiment is not.

Table 4. *Energies of the states in pyridine (eV, with respect to* SCF *ground state) first group: singlets; second group: triplets*

CIS	CISD	
	$3\sigma 2\pi$ $3\sigma^* 2\pi^*$	$2\sigma 3\pi$ $2\sigma^* 3\pi^*$
0	−0.92	−1.27
6.06 $n \rightarrow \pi^*$	5.56 $n \rightarrow \pi^*$	5.62 $n \rightarrow \pi^*$
8.52 $n \rightarrow \pi^*$	7.67 $n \rightarrow \pi^*$	7.62 $n \rightarrow \pi^*$
9.41 $\sigma \rightarrow \pi^*$	9.33 $\sigma \rightarrow \pi^*$	7.74 $\pi \rightarrow \pi^*$
9.86 $\pi \rightarrow \pi^*$	9.81 $\pi \rightarrow \pi^*$	8.90 $\sigma \rightarrow \pi^*$
9.87 $\pi \rightarrow \pi^*$	9.85 $\pi \rightarrow \pi^*$	9.49 $\pi \rightarrow \pi^*$
11.39 $\sigma \rightarrow \sigma^*$	10.92 $\sigma \rightarrow \sigma^*$	10.86 $\sigma \rightarrow \sigma^*$
12.42 $\pi \rightarrow \pi^*$	11.66 $\pi \rightarrow \pi^*$	11.35 $\pi \rightarrow \pi^*$
6.06 $n \rightarrow \pi^*$		5.76 $n \rightarrow \pi^*$
7.16 $\pi \rightarrow \pi^*$		6.72 $\pi \rightarrow \pi^*$

Table 5. *Trans-butadiene*

State	π double excitations only as in NE (Ref. [18])						CNDO	
	VO		CIS		CISD		$(3\sigma, 2\pi, 2\pi^*, 3\sigma^*)$	
	NE	CNDO	NE	CNDO	NE	CNDO	CIS	CISD
^1A_g	0	0	0	0	-1.62	-0.77	0	-0.99
^1B_u	9.04	11.26	9.03	11.12	8.72	10.91	10.11	9.92
^1A_g	11.34	14.30	10.99	14.30	6.09	11.61	13.23	11.44
^1A_g	12.29	16.85	12.64	16.85				
^1B_u	14.58	19.47	14.59	19.62				
^1A_u	9.72	9.91	9.72	9.91	9.20	9.59	9.32	9.04
^3B_u	4.18	7.30	2.98	6.73	2.73	6.14	6.37	6.14

Trans-Butadiene

In the π approximation the calculated spectrum of trans-butadiene has been found to depend strongly on the extent of the CI treatment [6, 10, 16, 18]. All the previous calculations (non-empirical or Pariser-Parr-type) which have included double and higher excitations have obtained the forbidden $^1A_{1g} \to {}^1A_{1g}^*$ band at a lower energy than the $N \to V$ absorption. On the contrary, we obtain here a B_{1u} singlet lower than the first A_{1g} excited singlet, and this whether introducing σ excitations or not (Table 5). From this point of view, butadiene behaves like benzene and pyridine and not like the small molecules: here again (compare columns 6 and 9 with 8 and 10 in Table 5), the π double excitations are much more important than the σ ones, and this is true for the ground state as well as for the excited states. Moreover, comparing the results of Buenker and Whitten [18] with CNDOCISD with the same choice of configurations we observe, like in benzene, that the action of CI is much smaller in CNDO than in NE computations for the A_{1g} singlets. In contrast to the NE results, one $\sigma \to \pi^*$ state remains below B_u.

Conclusions

It is clear from the present study that double excitations have a non-negligible effect on the energies of the different states in the CNDO approximation. The ground state as well as the excited states are mixed to a large extent with this type of excitations.

Within the limitations of the present calculation it appears that a CISD treatment improves the ordering of the different states and that most of the parasit low $\sigma \leftrightarrow \pi$ transitions found in CIS disappear when double excitations are introduced. Unfortunately, the numerical agreement between calculated and measured transition energies is still poor.

At the end of this investigation, a number of questions can be raised: 1) What is the role of the particular CNDO/2 parametrization in the results? 2) If the doubly excited configurations really have such an important effect on the ground state energy, what are the consequences on the computed ground state observables? 3) In the large molecules in particular, what is the effect of the neglected configurations?

In the next paper of this series, we shall report on an investigation of the modified CNDO procedure of Del Bene and Jaffé [26] and the two other questions will be dealt with separately.

Acknowledgement. The help of J. P. Daudey in the programming part of this work has been of extreme value and is gratefully acknowledged.

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