

# Quantum-chemical study of the properties of the excited states of organic molecules

## III. Excited states of $N_2O$ , $HN_3$ , and $H_2CCO$

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Received 1 February 1983

Accepted for publication 10 November 1983

*Dedicated to Academician V. Kellö, in honour of his 65th birthday*

Electron transition energies have been calculated for three 16-electron molecules  $N_2O$ ,  $HN_3$ ,  $H_2CCO$  in semiempirical CNDO/S, INDO, and MINDO/2 parametrizations. INDO results are closest to experimental values. Spectroscopically parametrized CNDO/S and MINDO/2 methods strongly underestimate transition energies although the order of transitions remains in principle correct. But the CNDO/S method is not able to differentiate states following *e.g.* from  $\pi \rightarrow \pi^*$  excitation of linear  $N_2O$  molecule.

В рамках полуэмпирических параметризаций CNDO/S, INDO и MINDO/2 были рассчитаны энергии электронных переходов для трех 16-электронных молекул  $N_2O$ ,  $HN_3$  и  $H_2CCO$ . Результаты INDO самые близкие к экспериментальным данным. Параметризация MINDO/2 и спектроскопическая параметризация CNDO/S дает заниженные величины энергий переходов, хотя энергетический порядок переходов остается правильным. CNDO/S метод, в свою очередь, неспособен отличить состояния возникающие, например, из  $\pi \rightarrow \pi^*$  эксцитации линейной  $N_2O$  молекулы.

Three molecules, ketene, azoimide, and nitrogen oxide are interesting as models for studying photochemical dissociation. The three molecules show diffuse spectral bands in the region of valence electron transitions [1, 2]. The diffusion is caused by the photochemical activity of transitions and leads to difficulties encountered by assigning bands to individual transitions.

Our aim is to discuss applicability of semiempirical quantum-chemical methods for computing electronic spectra of the three molecules, especially for reproducing the energy of transitions as compared with experimental values and *ab initio* results.

## Calculations

Calculations were done in standard semiempirical INDO [3], CNDO/S [4], and MINDO/2 [5, 6] parametrizations. The MINDO/2 parametrization was used with the aim to calculate dissociation curves: MINDO/2 was parametrized to heats of formation and should properly define the relative energy for a reactant and dissociation products, which cannot be expected in other two parametrizations.

Twenty lowest occupied monoexcited configurations were included into configuration interaction which was then extended by four pair biexcited configurations together with the ground state configuration. Computations were done in experimental geometries of the ground state (Table 1).

Table 1

Geometries of the investigated molecules

Molecule	Symmetry	Bond lengths				Bond angles	Ref.
		$R/(10^{-10} \text{ m})$					
H <sub>2</sub> CCO	C <sub>2v</sub>	CO	1.16	CC	1.315	∠ HCH 122.3°	[1]
		CH	1.079				
N <sub>2</sub> O	C <sub>∞v</sub>	NN	1.128			∠ NNO 180°	[1]
		NO	1.184				
N <sub>3</sub> H (H—N <sub>1</sub> —N <sub>2</sub> —N <sub>3</sub> )	C <sub>s</sub>	N <sub>1</sub> N <sub>2</sub>	1.24	N <sub>2</sub> N <sub>3</sub>	1.12	∠ HNN 112.5°	[9]
		NH	1.02			∠ NNN 180°	

## Results and discussion

Each of the three discussed molecules (N<sub>2</sub>O, HN<sub>3</sub>, H<sub>2</sub>CCO) has 16 valence electrons. In view of the geometrical and orbital structure they represent transition from the linear structure of N<sub>2</sub>O characterized in MO description by the doubly degenerated  $\pi$  orbitals through N<sub>3</sub>H, where the linear structure of N—N—N chromophore is disturbed by an out-of-line hydrogen atom which causes splitting of  $\pi$  levels to pairs of orbitals  $a'$  and  $a''$  in C<sub>s</sub> symmetry, to H<sub>2</sub>CCO where the effect of the two hydrogen atoms on the still more remarkable splitting to orbitals  $b_1$  and  $b_2$  in C<sub>2v</sub> symmetry (Fig. 1) occurs. The order and orbital energies in the figure were calculated by MINDO/2 method. Two highest occupied and two lowest virtual orbitals for N<sub>2</sub>O are degenerated  $2\pi$  and  $3\pi$  orbitals, respectively, while in the other two molecules the corresponding couples of orbitals are split. The order

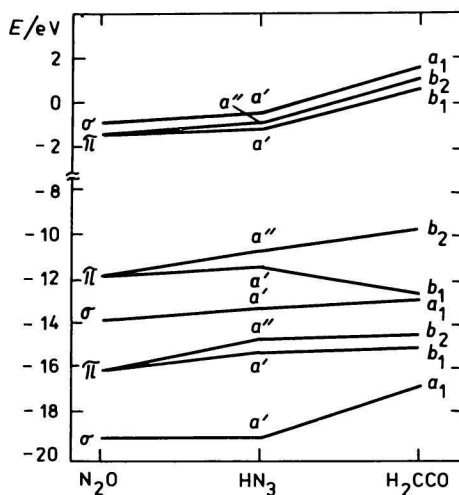


Fig. 1. Correlation of MO energies for isoelectron molecules  $\text{N}_2\text{O}$ ,  $\text{HN}_3$ ,  $\text{H}_2\text{CCO}$ .

of orbitals  $\dots 3\sigma^2 1\pi^4 4\sigma^2 2\pi^4 3\pi^0 5\sigma^0$  is in MINDO/2 also retained for  $\text{HN}_3$  and  $\text{H}_2\text{CCO}$  if we consider splitting of  $\pi$  orbitals of nonlinear molecules. The general trend — a decrease in values of orbital energies in the order  $\text{H}_2\text{CCO}$ ,  $\text{HN}_3$ ,  $\text{N}_2\text{O}$  qualitatively corresponds with the sum of electronegativities of heavy atoms of the studied molecules. The order of orbital energies for  $\text{N}_2\text{O}$  computed by MINDO/2 method agrees with *ab initio* calculations [7] in the basis of 18 contracted GF from 75 primitive GF but, for other molecules, calculations differ in determining the energy order of the lower occupied orbitals. The values for the respective orbital energies given in Table 2 indicate stabilization of virtual orbitals in MINDO/2 method, and on the other hand, mainly for  $\text{N}_2\text{O}$ , high values of orbital energies for occupied (mainly  $\sigma$ ) orbitals. Since the difference in orbital energies is an important contribution to the calculated transition energies, one can expect that the computed energies of the excited states will be lower than experimental values. Table 3 contains the values for excitation energies we calculated by MINDO/2, CNDO/S or INDO methods, available experimental data, and published results obtained by nonempirical computations. The order of the lowest excited states calculated by MINDO/2 method agrees with the order determined by more laborious *ab initio* methods and with experimental data. For azoimide, no accurate computations are available for excited states and assignment [2] was based on semiempirical Mulliken—Wolfsberg—Helmholtz EHT calculations. A change in the order of the  ${}^1A'$  ( ${}^1\Delta$ ) and  ${}^1A''$  ( ${}^1\Delta$ ) states in monoexcited CI with respect to CI with mono- and pair biexcited configurations is connected with greater stabilization of the  ${}^1A'$  state as a result of an interaction with biexcited configurations.

The CNDO/S is unable to remove degeneration of the  ${}^3\Sigma^+$ ,  ${}^3\Delta$ ,  ${}^3\Sigma^-$ ,  ${}^1\Sigma^-$ ,  ${}^1\Delta$  and  ${}^1\Pi$ ,  ${}^3\Pi$  states for the linear  $\text{N}_2\text{O}$  molecule because monocentric bielectronic

Table 2

Numerical values of orbital energies ( $E/eV$ ) for the highest occupied and lowest virtual orbitals  
(Only valence orbitals are numbered)

N <sub>2</sub> O			HN <sub>3</sub>				H <sub>2</sub> CCO			
MO	MINDO/2	<i>ab initio</i> [17]	MO	MINDO/2	<i>ab initio</i> [10]	exp IP [11]	MO	MINDO/2	<i>ab initio</i> [12]	<i>ab initio</i> [13]
5 $\sigma$	- 1.00	10.72					5a <sub>1</sub>	1.55	17.69	2.72
3 $\pi$	- 1.54	1.90	3a''	- 0.87			3b <sub>2</sub>	1.16	10.07	4.90
			7a'	- 0.90			3b <sub>1</sub>	0.67	8.16	2.18
2 $\pi$	-12.19	-14.46	2a''	-10.57	-11.08	10.70	2b <sub>2</sub>	- 9.69	- 6.80	-12.79
			6a'	-11.19	-12.74	11.60	2b <sub>1</sub>	-12.84	-11.70	-15.51
4 $\sigma$	-14.04	-20.06	5a'	-13.30	-18.54	15.47	1b <sub>2</sub>	-14.88	-14.42	-17.96
			4a'	-15.21	-19.41	16.70	4a <sub>1</sub>	-12.87	-15.78	-19.05
1 $\pi$	-16.35	-22.89	1a''	-14.89	-19.42	17.40	1b <sub>1</sub>	-15.81	-17.69	-19.59
3 $\sigma$	-19.36	-23.36	3a'	-19.44	-22.83	20.10	3a <sub>1</sub>	-17.17	-19.86	-21.22

Table 3

Calculated and experimental numerical values of excitation energies ( $E/eV$ )

Nitrogen oxide						
Excited state	MINDO/2 CI—S <sup>a</sup>	CNDO/2 CI—S <sup>a</sup>	INDO [14] c	MINDO/2 CI—SD <sup>b</sup>	<i>ab initio</i> CI [15]	exp [15]
<sup>3</sup> Σ <sup>+</sup>	1.096	2.85	3.5	1.62	5.4	5.6
<sup>3</sup> Δ	1.57	2.85	4.0	2.06	6.0	6.2
<sup>3</sup> Σ <sup>-</sup>	1.98	2.85	4.1	2.47	6.5	—
<sup>1</sup> Σ <sup>-</sup>	1.98	2.85	4.2	2.46	6.6	—
<sup>3</sup> Π	2.00	8.26	6.1	2.50	—	—
<sup>1</sup> Δ	2.38	2.85	4.3	2.85	6.8	6.85
<sup>1</sup> Π	2.87	8.26	7.0	3.36	—	8.52
<sup>1</sup> Σ <sup>+</sup>	4.08	9.66	10.9	4.56	—	9.6

Azoimide					
Excited state	MINDO/2 CI—S <sup>a</sup>	CNDO/S CI—S <sup>a</sup>	INDO CI—S <sup>a</sup>	MINDO/2 CI—SD <sup>b</sup>	exp [2]
<sup>1</sup> A''( <sup>1</sup> Σ <sup>-</sup> )	1.63	2.24	4.57	2.24	4.7
<sup>1</sup> A'( <sup>1</sup> Δ)	2.13	4.06	6.23	2.65	6.56
<sup>1</sup> A''( <sup>1</sup> Δ)	2.07	3.88	6.76	2.77	6.20
<sup>1</sup> A''( <sup>1</sup> Π)	2.25	7.99	7.39	2.93	7.29
<sup>1</sup> A'( <sup>1</sup> Π)	2.67	7.28	8.51	3.31	7.94
<sup>1</sup> A'( <sup>1</sup> Σ)	3.61	8.00	9.81	4.23	8.84

Ketene							
Excited state	MINDO/2 CI—S <sup>a</sup>	CNDO/S CI—S <sup>a</sup>	INDO CI—S <sup>a</sup>	MINDO/2 CI—SD <sup>b</sup>	<i>ab initio</i> MC SCF [10]	<i>ab initio</i> SCF + CI [13]	exp [17, 18]
<sup>3</sup> A <sub>2</sub>	2.06	3.33	4.83	2.46	3.79	4.00	3.35
<sup>1</sup> A <sub>2</sub>	2.43	3.33	5.11	2.83	3.99	4.27	3.84
<sup>1</sup> B <sub>2</sub>	4.15	6.29	9.95	4.56	6.40	9.71	5.82
<sup>1</sup> A <sub>1</sub>	4.32	6.17	9.77	4.59	—	—	—
<sup>1</sup> A <sub>2</sub>	6.20	7.91	12.89	5.52	—	—	—

a) Twenty monoexcited configurations were included into CI. b) CI as in a) extended by a configuration of the ground state and by 4 pair biexcited configurations between the two highest occupied and the two lowest virtual orbitals. c) Transition energies computed by the *Segal* method [19].

exchange integrals are neglected. Transition energies calculated by the MINDO/2 method are very low as compared with expected values obtained experimentally: the closest values are those for ketene. But neither spectroscopically parametrized CNDO/S method gives much better results for these relatively small molecules. This is probably due to the fact that it was parametrized for the electronic spectra of larger  $\pi$  systems — derivatives of benzene compounds. The values obtained in INDO parametrizations for  $N_2O$  and  $N_3H$  molecules are nearest to the experimental results, the best results for ketene are obtained in the CNDO/S parametrization. However, only the MINDO method itself could satisfactorily describe the energy of the bond breaking during the reactions studied since it was parametrized for heats of formation of molecules. Although the INDO method yields better transition energies for the mentioned molecules, one cannot expect acceptable relative values for energies of a reactant and products. The INDO method, similarly to the CNDO/2 method usually significantly overestimates bond energies [8].

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Translated by A. Rebrová