

STRUCTURE, ENERGY CHARACTERISTICS, AND ELECTRONIC SPECTRA OF TWO ISOELECTRONIC RADICALS, HCN₂ AND H₂C₂N: A THEORETICAL STUDY

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The molecular structure of the title radicals was investigated by means of the CNDO/2 and MINDO/2 methods. Calculations suggest that both radicals might exist in two isomeric forms (cyclic and open). Thermodynamic characteristics of the H₂C₂N isomerization were calculated. Electronic spectra of both radicals were obtained using limited configuration interaction treatment based on the Del Bene and Jaffé SCF method. Calculation and observation agree satisfactorily for the HCN₂ radical. A comment is made on the role of isomerism when electronic spectra are studied theoretically.

Predictions of structural and spectroscopic features, based on quantum chemical methods, have reached sufficient reliability and accuracy to be used for most chemical purposes (for a comprehensive review, see refs^{1,2}). It has become easy to fill certain gaps in our knowledge by calculation. Examples are furnished by the isoelectronic HCN₂ and H₂C₂N radicals; an additional reason for the theoretical treatment of these radicals is the desire to evaluate experimental data on highly unstable systems.

The HCN₂ radical was observed among products of the flash photolysis of diazomethane^{3,4} and of a mixture of cyanogen and ammonia⁵. Herzberg and Warsop³, by an analysis of the fine structure of one band of the electronic spectrum of HCN₂, obtained some of its structural characteristics; Ogilvie⁴ was able to assign one line of its vibrational spectrum. Formation of H₂C₂N was observed in products of radiolysis of acetonitrile⁶⁻¹⁰ or cyanoacetic acid by γ -irradiation¹¹. Electronic spectral characteristics for HCN₂ were obtained by semiempirical calculations¹² based on experimental data of geometry³. Molecular geometry of cations associated with the radicals (HCN₂⁺, H₂C₂N⁺) was optimized within the framework of the INDO method¹³. Zhuravleva¹⁴ studied spin densities of the H₂C₂N radical using Hückel's molecular orbitals. Isotropic coupling constants¹⁵, the effects of the geometry change and substitution on the electronic structure¹⁶ and ionization potential¹⁷ of the H₂C₂N radical were studied theoretically. In these calculations, assumed or partially optimized geometry was used.

A systematic study of properties of both radicals, based on completely optimized geometries, is still missing. It is our aim to fill this gap as completely as possible. It turned out^{1,2} that the CNDO/2 and MINDO/2 methods are, with small radicals,

both successful and economical. Hence it seems justified to use them for optimization of geometrical structure, establishing stationary points on the respective energy hypersurfaces, and analyzing relationships between local energy minima found on the hypersurfaces. Moreover, modified methods (CNDO/S and INDO/S) were used for calculating electronic spectra of the radicals.

CALCULATIONS

No *a priori* assumption was made concerning geometry or symmetry point group of the radicals under study. The CNDO/2 (ref.¹⁸) and MINDO/2 (ref.¹⁹) methods were combined with the Longuet-Higgins and Pople²⁰ open-shell procedure for the nondegenerate ground state and with the restricted open-shell "half-electron" method^{21,22} for doubly degenerate ground state. A systematic search of stationary points was performed for CNDO/2 and MINDO/2 energy functions. For this purpose an automatic procedure reported by McIver and Komornicki²³ and Páncf²⁴ was used, which connects explicit formulas for the first derivatives of the total energy with the iterative variable metric method. Schemes of the established stationary points are given in Fig. 1. Matrices of the second derivatives of energy were set up (by means of the finite difference method²⁵) at all stationary points of the energy hypersurfaces. These values gave (in a conventional way²⁵) eigenvalues and eigenvectors of the force constant matrix (FCM) which allowed us to distinguish real minima, saddle points, and higher type stationary points of the energy hypersurface. Simultaneously a vibrational $G \times F$ matrix analysis^{26,27} supplied us with frequencies of the normal vibrational modes in the harmonic approximation. The stationary points found, with their nature and symmetry point groups, energy and geometry characteristics, are summarized in Tables I and II. The data concerning local minima of energy hypersurfaces permitted us to calculate partition functions in the rigid rotator and harmonic oscillator (RRHO) approximations²⁸ and, moreover, to describe the thermodynamics of equilibria between the individual isomers of the given radical. The ideal gas approximation was used in these calculations. Finally, limited configuration interaction¹² based on the Del Bene and Jaffé²⁹ (DBJ) molecular orbitals was performed for all stable forms (energy hypersurface minima) of the radicals.

RESULTS AND DISCUSSIONS

As expected for systems with relatively numerous internal degrees of freedom, more than one stationary point has been found on energy hypersurfaces of both radicals. (More specifically, four on each hypersurface.) For purposes of the present study, we were particularly interested in the local minima. Saddle points (*i.e.* stationary points whose FCM possesses just one negative eigenvalue), *i.e.* activated complexes²⁵, would be useful when describing kinetic behaviour. Finally higher type of stationary points (FCM with more than one negative eigenvalue) have not yet been used in theories of chemical reactivity.

Unfortunately, no generally applicable rule is available which would permit us to determine *a priori*, for a given hypersurface, the number of its stationary points.

Therefore, when searching for them by means of automatic geometry optimization procedures, it is necessary to change systematically coordinates of the initial (starting) geometry. Even when this is done very carefully, we cannot be sure of finding all stationary points. This of course also applies to our data presented in Table I and II. We believe, however, that, because of care devoted to the search, all local minima have been found. Remarkably enough, no saddle point was found: this is peculiar because there exist on both hypersurfaces two minima, which should imply^{25,30} the existence of at least one saddle point for mediating the transition between structures belonging to the minima. The failure to find saddle points might have another reason than lack of investigation of some parts of the energy hypersurface. It must be remembered that the energy functions used are not quite correct; for non-degenerate and degenerate frontier orbitals different approximations were used, presented in ref.²⁰ and refs^{21,22}, respectively. This lack of consistency might even lead to two energy hypersurfaces. Fortunately, this problem is not crucial in this work.

Both semiempirical methods used (Table I and II) with these radicals give similar results. More specifically, of the two local minima, the one which is associated with a ring system (*I* or *V*) is, for both systems, a more stable isomer. With respect to a recent study³¹, this might be considered as a special case of so-called isomerism of reaction components. Thermodynamic characteristics of the energetically most favourable isomerization ($V \rightleftharpoons VI$; MINDO/2) are given in Table III. Clearly, even at ordinary laboratory temperature (and strictly equilibrium conditions) the cyclic structure *V* represents the predominant component in the ideal gas phase. As to the structure of radicals formed (HCN_2 and $\text{H}_2\text{C}_2\text{N}$) by means of flash photolysis or γ -radiolysis, the data on stability of the individual isomers (even if they were quite accurate) might be misleading. The reason is that these methods generate radicals under conditions that are far from equilibrium.

The CNDO/2 and MINDO/2 results (Table I and II) possess common features and also some significant differences. This concerns geometry characteristics, energetics, and even types of corresponding stationary points (see structures *II*, *IV* and *VII*). Except for C—H and N—H bond lengths, there is a fair agreement between CNDO/2 and MINDO/2 bond lengths and angles. MINDO/2 bond lengths of these bonds are (in agreement with former work¹⁹) overestimated although with the radicals under study it is less than the 10 pm usually assumed. This circumstance and the already established^{18,32} quality of the CNDO/2 geometries prompted us to use CNDO/2 in further calculations in this study.

Another failure^{32,33} of the MINDO/2 method might be illustrated by the results obtained in a study of structure *II*. This concerns incorrect configuration found on the N-atom which sometimes leads to a wrong prediction of the point symmetry group^{32,33}. MINDO/2 is unable to reproduce the bent arrangement of the H, N' and C atoms with the structure *II* as found by means of CNDO/2. This failure manifests itself by the absence of the type *II* minimum on the MINDO/2 energy hypersurface

TABLE I

Structural and Energy Characteristics of Stationary Points Found on CNDO/2 and MINDO/2 Energy Hypersurfaces of the HCN₂ Radical

Structure ^a	Group of symmetry	Method	Type of stationary point ^b	ΔE^c kJ mol ⁻¹	Geometrical characteristics ^d 10 ⁻¹⁰ m or °
I	C _{2v}	CNDO/2	M	0.0	$d(\text{C}-\text{H}) = 1.097$; $d(\text{C}-\text{N}) = 1.329$; $\angle \text{NCN} = 61.3$
		MINDO/2	M	0.0	$d(\text{C}-\text{H}) = 1.162$; $d(\text{C}-\text{N}) = 1.318$; $\angle \text{NCN} = 54.1$
II	C _s	CNDO/2	M	453.4	$d(\text{N}'-\text{H}) = 1.070$ (1.034) ^e ; $d(\text{C}-\text{N}') = 1.304$; $d(\text{N}'-\text{N}'') = 2.520$ (2.470) ^e ; $\angle \text{HN}'\text{C} = 106.1$ (116.5) ^e ; $\angle \text{N}'\text{CN}'' = 177.8$ ^f
		MINDO/2	see structure I) ^d		
III	C _{∞v}	CNDO/2	H	672.1	$d(\text{C}-\text{H}) = 1.086$; $d(\text{C}-\text{N}') = 1.237$; $d(\text{N}'-\text{N}'') = 1.208$
		MINDO/2	H	55.4	$d(\text{C}-\text{H}) = 1.147$; $d(\text{C}-\text{N}') = 1.225$; $d(\text{N}'-\text{N}'') = 1.045$
IV	C _{∞v}	CNDO/2	H	586.4	$d(\text{N}'-\text{H}) = 1.045$; $d(\text{C}-\text{N}') = 1.261$; $d(\text{C}-\text{N}'') = 1.232$
		MINDO/2	M	85.5	$d(\text{N}'-\text{H}) = 1.089$; $d(\text{C}-\text{N}') = 1.229$; $d(\text{C}-\text{N}'') = 1.212$

^a See Fig. 1; ^b M means a local minimum on the energy hypersurface, H means a higher type of its stationary point (the FCM possesses more than one negative eigenvalue); ^c Relative total energy with respect to the assumed absolute minimum of the energy hypersurface; in the case of MINDO/2 method based on ΔH_f^0 , 298.15 terms; ^d Within the frame of MINDO/2 the structure II passes into the structure IV; ^e Experimental values³ if available are given in parentheses; ^f The H and N'' atoms are mutually *trans* oriented.

TABLE II
Structural and Energy Characteristics of Stationary Points Found on CNDO/2 and MINDO/2 Energy Hypersurfaces of the H₂C₂N Radical

Structure ^a	Group of symmetry	Method	Type of stationary point ^b	ΔE^c kJ mol ⁻¹	Geometrical characteristics ^d 10 ⁻¹⁰ m or °
V	C _{2v}	CNDO/2	M	0.0	$d(\text{C}-\text{H}) = 1.098$; $d(\text{C}-\text{C}) = 1.324$; $\angle \text{CNC} = 56.6$; $\angle \text{CCH} = 157.5$
		MINDO/2	M	0.0	$d(\text{C}-\text{H}) = 1.171$; $d(\text{C}-\text{C}) = 1.305$; $\angle \text{CNC} = 56.1$; $\angle \text{CCH} = 158.6$
VI	C _{2v}	CNDO/2	M	303.1	$d(\text{C}'-\text{H}) = 1.109$; $d(\text{C}'-\text{C}^*) = 1.347$; $d(\text{C}^*-\text{N}) = 1.215$; $\angle \text{HC}'\text{H} = 115.2$
		MINDO/2	M	22.0	$d(\text{C}'-\text{H}) = 1.186$; $d(\text{C}'-\text{C}^*) = 1.334$; $d(\text{C}^*-\text{N}) = 1.198$; $\angle \text{HC}'\text{H} = 115.5$
VII	C _{∞v}	CNDO/2	H	537.0	$d(\text{C}'-\text{H}) = 1.090$; $d(\text{N}-\text{H}) = 1.044$; $d(\text{C}'-\text{C}^*) = 1.244$; $d(\text{C}^*-\text{N}) = 1.275$
		MINDO/2	M	1.5	$d(\text{C}'-\text{H}) = 1.155$; $d(\text{N}-\text{H}) = 1.086$; $d(\text{C}'-\text{C}^*) = 1.224$; $d(\text{C}^*-\text{N}) = 1.247$
VIII	D _{∞h}	CNDO/2	H	955.6	$d(\text{C}-\text{H}) = 1.085$; $d(\text{C}-\text{N}) = 1.247$
		MINDO/2	H	285.4	$d(\text{C}-\text{H}) = 1.143$; $d(\text{C}-\text{N}) = 1.228$

^a See Fig. 1; ^b M means a local minimum on the energy hypersurface, H means a higher type of its stationary point (the FCM possesses more than one negative eigenvalue); ^c Relative total energy with respect to the assumed absolute minimum of the energy hypersurface; in the case of MINDO/2 method based on ΔH_f^0 , 298.15 terms.

(Fig. 1 and Table I). Structure *IV* is, within the framework of MINDO/2, a minimum which is in contrast with the CNDO/2 result. This is easily understandable, however, in the light of the findings described in ref.³². The difference in CNDO/2 and MINDO/2 predictions for the stationary point *VII* (Table II) may be rationalized along similar lines.

As to energy characteristics, MINDO/2 (except systems where the method predicts a wrong symmetry group) is superior³² to CNDO/2. Meanwhile CNDO/2 values permit a qualitative evaluation^{18,34} of reaction enthalpies, there is frequently good agreement¹⁹ between MINDO/2 and experimental ΔH_{298}^0 terms. This circumstance has been taken into consideration in the calculations presented in Table III. CNDO/2 structural and vibrational data were used for evaluation of the partition functions (RRHO approximations), while enthalpies are of MINDO/2 origin. Let us conclude this paragraph by saying that at present structures *I*, *II* and *V*, *VI* are important for comparison with experimental data.

Let us attempt now to correlate calculation and observation. It is well known^{35,36} that semiempirical methods tend to overestimate the stability of small rings. We have to estimate the consequences of this failure for calculated results obtained for structures *I* and *V*. For example, the MINDO/2 value of $\Delta H_{f,298}^0$ for cyclopropane is 95 kJ mol⁻¹ lower³² than the observed value. If this value is used to correct characteristics of *I* and *V*, it turns out that either comparable stability of *I* and *II* (and also of *V* and *VI*) is to be expected, or even that open-chain isomers might be more stable than the cyclic. *Ab initio* calculations with sufficiently extensive basis sets will help decide this question.

Some experimental data for the radical *II* are available in the literature^{3,4}. A comparison between CNDO/2 and observed³ structural characteristics is encouraging (Table I). The agreement in bond lengths is perfect but the difference associated with the HN'C bond angle amounts to about 10°. A deeper analysis of experimental data³ offers an explanation. A complete description of the planar struc-

TABLE III

Calculated Thermodynamic Characteristics of Equilibrium Isomerization $\text{H}_2\text{C}_2\text{N} (\text{V}; \text{g}) \rightleftharpoons \text{H}_2\text{C}_2\text{N} (\text{VI}; \text{g})$ in Ideal Gas Phase

ΔH_0^0 kJ mol ⁻¹	$\Delta H_{298.15}^0$ kJ mol ⁻¹	$\Delta S_{298.15}^0$ J mol ⁻¹ K ⁻¹	log K_p	$1 - \alpha^a$ %
20.9	22.0	3.4	-3.7	99.98

^a α denotes degree of conversion of title reaction.

ture *II* requires five independent internal coordinates. However, Herzberg and Warsop³ had at their disposal just three rotational constants, obtained by means of analysis of the fine structure of one electronic band of HCN_2 . Therefore, they had to make a tentative assumption of linearity in the $\text{N}'\text{C}\text{N}''$ chain. Our CNDO/2 calculation shows that this assumption is only approximate, the N'' atom being slightly out of the $\text{N}'\text{—C}$ line, so that the H and N'' atoms are trans oriented (Fig. 1 and Table I). Using this information we may now reinterpret the values of the principal moments of inertia taken from ref.³ Starting from the orientation of the principal axes³ in structure *II*, it becomes evident that the shift of the N'' atom in accordance with the CNDO/2 results requires an increase of the $\text{HN}'\text{C}$ angle in order to keep the principal moments of inertia constant. The H atom shift (accompanying the N'' atom shift) has to be, with respect to the ratio of masses of H and N, larger than the N'' atom shift. Evidently, the discrepancy between calculated and observed values of the $\text{HN}'\text{C}$ angle tends to confirm the good quality of CNDO/2 geometry.

Our information on the vibrational spectrum of HCN_2 is poorer than that concerning structure. Ogilvie⁴ assigned the band at 861 cm^{-1} to the HCN_2 radical but did not specify the corresponding vibrational motion. The radical was generated by means of photolysis of diazomethane in inert gas matrices at 4 K. The CNDO/2 results, however, do correspond to the free-space approximation. The CNDO/2 frequencies at 937 cm^{-1} and 1001 cm^{-1} with the isomers *I* and *II*, respectively, are the closest to the observed value. If the poor quality of the unscaled CNDO/2 vibrational frequencies^{37,38} is considered, it is hardly possible to make any structural conclusion based on these results.

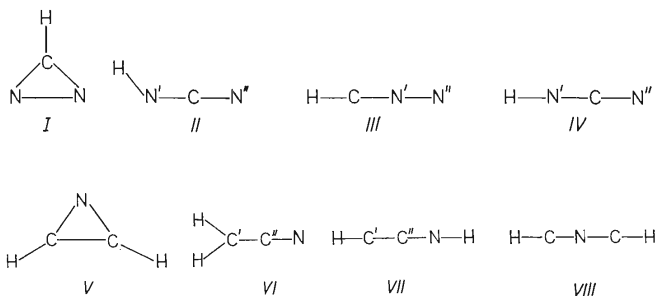


FIG. 1

Schemes of Stationary Points Found on the CNDO/2 and MINDO/2 Energy Hypersurfaces of the HCN_2 (*I–IV*) and $\text{H}_2\text{C}_2\text{N}$ (*V–VIII*) Isoelectronic Radicals

TABLE IV
 Calculated Wavenumbers $\tilde{\nu}$ and Oscillator Strengths f of γ Transitions in Electronic Spectrum of the HCN₂ Radical

No	Cyclic isomer (I) ^a				Open isomer (II) ^a			
	CNDO-DBJ		INDO-DBJ		CNDO-DBJ		INDO-DBJ	
	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	log f	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	log f	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	log f	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	log f
1	16.52	-2.78	15.84	-2.98	13.56	-2.96	12.28	-2.71
2	38.20	forbidden	35.61	forbidden	30.68	-3.43	28.33	-2.26
3	39.31	-3.74	37.28	-1.95	32.55	-4.38	31.53	-2.39
4	43.06	-1.96	38.50	forbidden	33.18	-1.99	37.79	-4.90
5	43.68	forbidden	45.58	-4.14	36.79	-6.08	39.04	-4.46
6	51.03	forbidden	49.25	forbidden	40.54	-2.34	41.03	-4.42
7	51.79	forbidden	52.45	-2.05	40.70	forbidden	42.03	-3.21
8	56.13	-3.08	52.69	forbidden	43.94	-3.48	44.29	-3.14
9	58.95	-1.41	62.80	-1.43	46.78	-3.67	52.73	-3.72
10	63.56	-1.69	66.69	-2.02	60.17	-1.96	56.82	-2.01

^a See Fig. 1.

TABLE V
 Calculated Wavenumbers $\tilde{\nu}$ and Oscillator Strengths f of Transitions in Electronic Spectrum of the $\text{H}_2\text{C}_2\text{N}$ Radical

No	Cyclic isomer (VI) ^a				Open isomer (VII) ^a			
	CNDO-DBJ		INDO-DBJ		CNDO-DBJ		INDO-DBJ	
	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	$\log f$	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	$\log f$	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	$\log f$	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	$\log f$
1	8.77	-2.25	7.76	-2.39	22.20	forbidden	26.42	forbidden
2	31.63	forbidden	31.62	forbidden	29.79	forbidden	30.33	-4.41
3	37.26	forbidden	33.05	-2.08	30.20	-2.99	34.90	-2.33
4	37.74	-2.15	38.37	forbidden	37.19	forbidden	35.49	forbidden
5	41.17	forbidden	38.94	forbidden	38.70	forbidden	36.69	-3.54
6	45.71	forbidden	47.13	-1.72	39.07	-3.52	44.00	forbidden
7	49.18	-1.69	49.08	forbidden	42.61	-2.27	45.66	forbidden
8	50.49	-2.70	55.02	-2.56	42.88	forbidden	48.92	forbidden
9	52.68	-1.36	57.16	-1.26	50.11	-1.47	49.14	-1.54
10	59.83	-1.59	58.61	forbidden	61.86	forbidden	53.63	-2.40

^a See Fig. 1.

Calculated electronic spectral data for isomers *I* and *II* obtained by CNDO/S and INDO/S procedures are in agreement (Table IV). Experimentally, a band at 29100 cm^{-1} has been ascribed³ to the structure *II*. The second and third calculated transitions of *II* might be assigned to the observed band at 29100 cm^{-1} . There is no calculated transition with *I* in this region, which is a supporting argument for the adequate quality of the methods used. It is reasonable to believe that the spectroscopic calculations for the structure *I* (Table IV) and the structures *V* and *VI* (Table V) will prove useful in analyzing spectra of the HCN_2 and $\text{H}_2\text{C}_2\text{N}$ radicals, which might be obtained in near future.

Let us add that both CNDO/S and INDO/S calculations were based on CNDO/2 optimal molecular geometries. This is correct because it is well known³² that CNDO/2 and INDO optimal geometries are very close to each other. Moreover, it is apparent that even passing from the experimental³ to the CNDO/2 geometry (this study) does not manifest itself significantly in calculated transition energies of structure *II* (see results of ref.¹²).

The results presented in Table IV suggest that even if the photolysis of diazomethane, leading to the structure *II* (as shown in ref.³), would also yield isomer *I*, no significant overlap of both spectra in the region studied³ would appear. Nevertheless occurrence of isomerism even with small radicals, found in this paper, is a warning that electronic spectra of these systems have to interpret with caution. Strictly speaking, for the comparison with experimental absorption curves, not only calculated spectra of pure isomers but also superposition spectra in form of a weighted average should be used³¹. Weight factors derived along the lines recommended in ref.³¹ would be, however, applicable only when the spectra were recorded under (nearly) equilibrium conditions.

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