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Is a triplet HC₄N molecule linear?

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Recently a series of HC_nN molecules have been observed by the radio astronomical observations in Taurus Molecular Cloud 1.¹ Some of the species have also been observed in the laboratory by microwave spectroscopy.² Molecules with even number *n* are especially of interest from a theoretical point of view, since they have (diradical and carbene) candidates for most probable structures.³ The authors recently reported the stability ladder of various conformers of HC₂N molecules by the use of SDCI+Q level of theory with the atomic natural orbital (ANO) basis set.⁴ Although the study on the HC₄N molecule is desired, no calculations have been reported to date.

We performed the geometrical surveys of the two (1 and 2) candidates of triplet HC₄N molecule and determined the energy difference between them. Optimized parameters are shown in Fig. 1, which were obtained by the use of the second-order Moller-Plesset perturbation method (MP2)⁵ with the Dunning *d*95** basis set.⁶ Calculated rotational constants are 2.281 GHz for the linear conformer and 104.824, 2.442, and 2.387 GHz for the bent one.

The energy differences were determined by the SDCI level of theory.⁷ Natural orbitals obtained in the CASSCF calculations⁸ (10 electrons in 10 orbitals) were used. Five 1s orbitals and the corresponding virtual orbitals were deleted in the SDCI calculations; thus 159 orbitals were cor-

related. We used a C_{2v} point group for the linear conformer 1 and a C_s for the bent 2. Numbers of the configuration are 465,721 and 912,780 for 1 and 2, respectively. General contraction scheme of ANO basis set [5s3p2d1f(C and N)/3s2p1d(H)]⁹ was used. (The calculations with a less extended basis set, [4s2p1d/2s1p], were also performed.)

Table I lists the total energies of the two conformers and their energy difference; the CASSCF and ACPF¹⁰ values are included for comparison. The triplet-bent conformer 2 is slightly more stable at the MP2/*d*95** (−0.95), CASSCF (−0.77), and SDCI (−0.36 kcal/mol) levels of theory. However, the triplet-linear conformer 1 is more stable at the SDCI with the Davidson correction (SDCI+Q)¹¹ (1.66) and ACPF (1.43 kcal/mol) levels of theory.

The present results on HC₄N molecule differ from those on HC₂N, where triplet-bent conformer is more stable than the triplet-linear at *all* the levels of theory.⁴ The energy difference obtained with the SDCI+Q/[5s3p2d1f/3s2p1d] method is −1.3 kcal/mol in HC₂N.

We should note the following two theoretical results before finally judging the most stable structure of HC₄N. (i) Multireference SDCI calculations in HC₂N stabilized more the *bent* conformer.⁴ (ii) Further basis set extensions may reduce the energy difference as shown in Table I. Thus, the SDCI+Q energy difference in HC₄N (1.66 kcal/

TABLE I. Calculated total energies (in hartrees) and their energy differences (in kcal/mol).^a

	CASSCF	SDCI	SDCI+Q	ACPF
[4s2p1d/2s1p]				
<i>Triplet</i>				
linear(1)	−206.547 264	−206.901 867	−207.006 846	−206.995 645
Δ <i>E</i> ^b	0.00	0.00	0.00	0.00
bent(2)	−206.548 136	−206.901 588	−207.003 270	−206.992 447
Δ <i>E</i> ^b	−0.55	0.17	2.24	2.01
<i>Singlet</i>				
bent(3)	(−206.354 603) ^c	−206.881 973	−206.985 752	−206.974 660
Δ <i>E</i> ^b		12.5	13.2	13.2
[5s3p2d1f/3s2p1d]				
<i>Triplet</i>				
linear(1)	−206.569 343	−207.029 170	−207.153 727	−207.140 448
Δ <i>E</i> ^b	0.00	0.00	0.00	0.00
bent(2)	−206.570 566	−207.029 745	−207.151 084	−207.138 174
Δ <i>E</i> ^b	−0.77	−0.36	1.66	1.43
<i>Singlet</i>				
bent(3)	(−206.376 096) ^c	−207.008 709	−207.132 679	−207.119 437
Δ <i>E</i> ^b		12.8	13.2	13.2

^aThe results on the singlet-bent 3 were included for comparison; SCF MO's were used in the SDCI calculations.

^bRelative energies to the conformer 1. Positive values indicate the linear form being more stable.

^cTotal energies at the Hartree-Fock level.

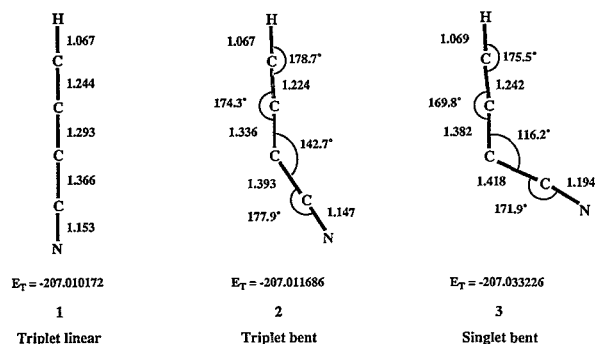


FIG. 1. Geometrical parameters optimized with the MP2/d95** method. Bond lengths in angstrom. Bond angles in degrees. Total energies (in hartrees) are also listed.

mol) may decrease at more elaborated levels of theory.

The MP2 geometrical parameters of the singlet-bent conformer **3** are also shown in Fig. 1; calculated rotational constants are 39.026, 2.753, and 2.572 GHz. Although its MP2 total energy is lower than the others (as shown in the figure) due to the spin-contaminations of the triplet species, the triplet-linear **1** is by 13.2 kcal/mol more stable than the singlet-bent **3** at the SDCI+Q level of theory with the $[5s3p2d1f/3s2p1d]$ ANO basis set.

Dipole moments calculated at the SDCI level of theory are 1.6091, 1.5497, and 1.6634 a.u. in the **1**, **2**, and **3** conformers, respectively.

The present theoretical calculations indicate clearly that the triplet-linear conformer **1** competes with the bent form **2** as a probable candidate of HC_4N .

The calculations were performed at the Computer Center of Tokyo Metropolitan University by the use of IBM 3090/300J and IBM RS6000 computers. MOLCAS¹² and GAUSSIAN90¹³ programs were used. The authors thank Professor B. O. Roos who provided us with the MOLCAS2 program.

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