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REGULAR ARTICLE

A theoretical study on CH_2N_2 isomers: structure and energetics

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Abstract Five CH_2N_2 isomers, namely cyanamide, carbodiimide, diazomethane, isocyanamide and nitrilimine, have been investigated at a high level of accuracy. The singles and doubles coupled-cluster method including a perturbational correction for connected triple excitations, CCSD(T), in conjunction with correlation-consistent basis sets ranging in size from triple to quintuple zeta have been employed. Extrapolation to the complete basis set limit has been used with treatments of core-valence correlation effects in order to accurately predict structures, relative energies as well as N–H and C–H bond dissociation energies. The latter required to also investigate the HNNC radical with the same methodology used for CH_2N_2 isomers, while HCNN and HNCN data are available in the literature by the same authors (Puzzarini and Gambi in J Chem Phys 122:064316, 2005). For all the species studied, harmonic vibrational frequencies have also been evaluated at the CCSD(T) level in order to obtain zero-point corrections to total energies.

Keywords CH_2N_2 non-cyclic isomers · Molecular structure · Energetics

Dedicated to Professor Vincenzo Barone and published as part of the special collection of articles celebrating his 60th birthday.

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1 Introduction

Cyanamide (H_2NCN) and its tautomer carbodiimide (HNCNH), diazomethane (H_2CNN) and isocyanamide (H_2NNC) with their tautomer nitrilimine (HNNCH), together with the three-membered ring diazirine (c-H_2CN_2), are the six experimentally known CH_2N_2 isomers and the most stable species on the singlet potential energy surface of the CH_2N_2 system. These are important molecules entering several chemical processes. Cyanamide is of considerable interest because in addition to its industrial [1] and agricultural uses is also a key molecule in prebiotic [2] synthesis and is one of the species that have been detected in the interstellar medium [3]. Carbodiimides are important reactants for peptides and nucleotide reactions [4], whereas diazomethane provided chemists with a versatile synthetic reagent, especially in the methylation of acids and alcohols [5]. Due to the easy generation of carbenes by thermolysis or photolysis, diazirine has extensively been used for preparations and mechanistic studies [6]. Relevant to the present investigation is that its molecular structures and energetics have been recently investigated at high level of theory by the authors themselves [7]. Isocyanamide is subject to fast rearrangement to cyanamide, but despite its unstable nature, valence ionization spectra [8] and rotation-inversion spectra in the millimeter-wave region have been observed [9]. Because of its character as reactive intermediate, there is very little direct experimental evidence on the structure of nitrilimine [10, 11], the first matrix-spectroscopic identification of HCNNH being reported only 15 years ago [12].

The HCN_2 radicals, which can be obtained by the removal of a hydrogen atom from the CH_2N_2 isomers, are highly reactive transient species that play an important role in various fields such as atmospheric processes, especially

in relation to combustion products. Relevant to these reactions are the diazomethyl (HCNN) and cyanomidyl (HNCN) radicals, whose energetics and structural properties have been recently investigated at high level of theory [13]. The diazomethyl radical can be obtained from the C–H bond cleavage of diazomethane or from the N–H cleavage of nitrilimine. As far as the cyanomidyl radical is concerned, it can be generated by N–H bond cleavage of cyanamide or carbodiimide. Finally, from the N–H bond breaking in isocyanamide or the C–H cleavage of nitrilimine, the HNNC (isocyanomidyl) radical can be obtained. Although considered feasible [12], the latter has never been experimentally detected. On the other hand, its presence in the electronic spectra of cyanogen radical reactions has been suggested by Basco et al. [14].

In this work, the five isomeric non-cyclic species, namely cyanamide, carbodiimide, diazomethane, isocyanamide and nitrilimine, have been accurately investigated by means of state-of-the-art computational techniques. Calculations were also extended to the HNNC radical in order to determine all possible N–H and C–H dissociation energies.

The manuscript is organized as follows. In the next section, the methodology used is explained together with the corresponding quantum-chemical details. Thereafter, the results are reported and discussed with emphasis on molecular structures of the species investigated (Sect. 3.1) and the corresponding energetics (Sect. 3.2).

2 Computational details

Throughout the present study, the coupled-cluster method with single and double excitations with a perturbative treatment of connected triples [CCSD(T)] has been used [16, 17]. This method has been found suitable for describing the systems under investigation, as confirmed by the values of the coupled-cluster T_1 diagnostic [18, 19] (i.e., 0.01–0.03, where the largest value applies to the open-shell case). Test computations, carried out at the multi-configuration self-consistent field (MCSCF) [20, 21] level, showed that all the species considered are well described by a single-reference wave function. Correlation-consistent basis sets, the valence cc-pVnZ (n = T,Q,5) [22] sets, have been used in conjunction with the CCSD(T) method in the frozen-core approximation. All the computations have been carried out with the MOLPRO suite of programs [15].

For all the species considered, geometry optimizations have been performed using numerical gradients, as implemented in MOLPRO [15, 23, 24]. The step sizes used were 0.0005 Å for bond lengths and 0.1 degrees for bond angles. As for convergence criteria, both the maximum component of the gradient and the maximum component of the step have been constrained to be less than 1.0×10^{-6} a.u.

Since a hierarchical sequence of bases has been considered, the systematic trend of the optimized geometrical parameters can be exploited to estimate the complete basis set (CBS) limit. As demonstrated by the recent study from one of the author [25], it can be assumed that the convergence behavior of the structural parameters mimics that of the energy. The consolidated $1/n^3$ extrapolation form [26] has been used to describe the convergence of the correlation contribution, and $n = 4$ (which stands for cc-pVQZ) and $n = 5$ (for cc-pV5Z) have been employed. The extrapolated correlation contributions have then been added to the corresponding Hartree–Fock self-consistent field (SCF) geometrical parameters optimized employing the cc-pV6Z basis, as this level of theory is expected to provide the CBS SCF limit. The extrapolated structures obtained in such a way will be denoted as r(CBS) in the reminder of the text. As concerns total energies, an approach similar to that employed for structural parameters has been followed to derive the CBS limit. In detail, the correlation contribution has been extrapolated to the complete basis limit by means of the n^{-3} formula [26, 27]:

$$\Delta E^{\mathrm{corr}}(n) = \Delta E^{\mathrm{corr}}_{\infty} + A' n^{-3}, \tag{1}$$

and added to the SCF CBS limit, evaluated as follows [28, 29]

$$E^{\mathrm{SCF}}(n) = E^{\mathrm{SCF}}_{\infty} + B' \exp(-C' n). \tag{2}$$

To take into account the effects of core-valence (CV) correlation, geometry optimizations have been carried out also including all electrons in the correlation treatment. The weighted core-valence correlation-consistent cc-pwCVQZ basis set [30] has been used in this step. In regards to the geometrical parameters, making use of the additivity approximation, the core-correlation corrections have been added to the extrapolated structures r(CBS) as:

$$\begin{aligned}(\mathrm{CBS} + \mathrm{CV}) = {} & r(\mathrm{CBS}) + r(\mathrm{wCVQZ, all}) \\ & - r(\mathrm{wCVQZ, valence}),\end{aligned} \tag{3}$$

where r(wCVQZ, all) and r(wCVQZ, valence) are the geometries optimized at the CCSD(T)/cc-pwCVQZ level correlating all and only valence electrons, respectively. Analogously, for total energies, the CV corrections have been calculated as

$$\Delta E_{\mathrm{CV}} = E_{\mathrm{core+val}} - E_{\mathrm{val}}, \tag{4}$$

where $E_{\mathrm{core+val}}$ is the CCSD(T) total energy obtained by correlating all electrons, and E_{val} is the CCSD(T) total energy obtained in the frozen-core approximation, both in the cc-pwCVQZ basis set.

In a similar way, the effects of diffuse functions (aug) in the basis set have been considered for both geometry and energy:

$$\Delta r_{\text{aug}} = r(\text{CCSD(T)/aug-cc-pVTZ}) - r(\text{CCSD(T)/cc-pVTZ}) \quad (5)$$

and

$$\Delta E_{\text{aug}} = E(\text{CCSD(T)/aug-cc-pVTZ}) - E(\text{CCSD(T)/cc-pVTZ}). \quad (6)$$

These corrections have then been added to the corresponding CBS+CV values in order to obtain the best estimated equilibrium structures and energies.

Isomerization from cyanamide to carbodiimide and from diazomethane to nitrilimine has also been investigated. Geometry optimizations of the connecting transition states have been carried out at the CCSD(T) method in conjunction with triple- and quadruple-zeta basis sets. As mentioned for the investigation of minimum structures, test computations have been carried out to check the suitability of the coupled-cluster method in describing these transition states. Furthermore, to have all the information required for studying the C–H and N–H dissociation energies, the tetratomic HNNC radical species has also been studied at the coupled-cluster level employing the same methodology mentioned above. Being HNNC an open-shell species, the variant denoted R/UCCSD(T) [31–33] has been employed. This is based on restricted open-shell Hartree–Fock (ROHF) orbitals but spin unrestricted in the solution of the CCSD equations. For the other tetratomic species involved, we refer to our previous investigation reported in Ref. [13].

Finally, to obtain the zero-point vibrational (ZPV) corrections to total energy within the harmonic approximation,

$$E_{\text{ZPV}}^{\text{harm}} = \frac{1}{2}\sum_i d_i \omega_i, \quad (7)$$

harmonic frequencies for all the species investigated have been computed at the CCSD(T)/cc-pVQZ level of theory in the frozen-core approximation. The harmonic force fields have been evaluated in a cartesian coordinate representation at the corresponding optimized geometry, and as in the case of energy gradients, the hessian matrix was calculated numerically [23, 24] by finite differences. Following the

Table 1 Equilibrium geometries and energies of nitrilimine, HCNNH (^1A), computed at the coupled-cluster level of theory employing different basis sets

	N–H (Å)	N–N (Å)	C–N (Å)	C–H (Å)	∠HNN (deg.)	∠NNC (deg.)	∠NCH (deg.)	T_1^a (∠HNNC) (deg.)	T_2^a (∠NNCH) (deg.)	Energy (Hartree)
MP2/6-311+G(2df,2p)[b]	1.020	1.256	1.181	1.067	108.6	170.3	144.48	−137.2	227.4	
QCISD/6-311G**[b]	1.022	1.244	1.204	1.081	107.1	169.1	128.9	−130.6	219.8	
B3LYP/6-311+G(d,p)[c]	1.023	1.242	1.189	1.076	109.5	169.8	133.0	−137.2	227.3	
CASSCF/3-21G(d)[d]	1.016	1.233	1.205	1.073	109.2	166.8	127.2	−131.4	219.9	
B3LYP/6-311++G(3df,2p)[e]	1.0216	1.2379	1.1858	1.0744	109.86	169.75	132.48	−135.52	224.81	
aug-cc-pVTZ	1.0226	1.2506	1.2001	1.0772	108.15	168.50	130.08	−131.85	220.83	−148.4707934
cc-pVTZ	1.0219	1.2477	1.2019	1.0771	107.95	168.66	129.09	−130.84	220.01	−148.4587066
cc-pVQZ	1.0203	1.2457	1.1969	1.0758	108.25	168.85	130.10	−131.12	220.23	−148.5027860
cc-pV5Z	1.0202	1.2457	1.1956	1.0754	108.37	168.88	130.49	−131.32	220.38	−148.5165868
cc-pwCVQZ(f.c.)	1.0204	1.2454	1.1965	1.0758	108.25	168.83	130.09	−131.22	220.32	−148.5061322
cc-pwCVQZ(all)	1.0190	1.2431	1.1930	1.0738	108.45	169.10	130.89	−131.97	221.17	−148.6733044
CBS[f]	1.0202	1.2457	1.1952	1.0752	108.42	168.89	130.65	−131.45	220.48	−148.5290394
CBS+CV[g]	1.0188	1.2434	1.1917	1.0732	108.62	169.16	131.45	−132.20	221.33	−148.6962117
CBS+CV+aug[h]	1.0195	1.2463	1.1899	1.0733	108.82	169.00	132.44	−133.21	222.15	−148.7082985

Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates values (CBS+CV and CBS+CV+aug) are also reported

'f.c.' and 'all' mean CCSD(T) calculations correlating only valence and all electrons, respectively

[a] Dihedral angles

[b] Ref. [42]

[c] Ref. [11]

[d] Ref. [43]

[e] Ref. [41]

[f] CBS geometry and energy. See text

[g] CV correction added to the corresponding CBS limit. See text

[h] Best estimated geometry and energy. See text

standard notation, in Eq. 7, d_i and ω_i are the degeneracy and the harmonic frequency of the ith vibrational normal mode, respectively.

3 Results and discussion

3.1 Molecular structure

The equilibrium geometries and energies of the five CH_2N_2 isomers investigated in the present study as obtained at the CCSD(T) level employing different basis sets are summarized in Tables 1, 2, 3, 4 and 5. For all the molecules, the extrapolation to the CBS limit has been carried out as explained in the methodology section, and the results are also listed in Tables 1, 2, 3, 4 and 5. The subsequent inclusion of the core-correlation and diffuse-function corrections provided our best estimated values (denoted CBS+CV+aug).

From the results of Tables 1, 2, 3, 4 and 5, it is first observed that the valence correlation limit is nearly reached at the CCSD(T)/cc-pV5Z level; in fact, the discrepancies between r(V5Z) and r(CBS) are in all cases smaller than 0.0005 Å for bonds and in general smaller than 0.2 degrees for angles. The largest deviations are presented by dihedral angles; for instance, for the denoted T_2 angle of cyanamide, a discrepancy as large as 0.57 degrees is observed (see Table 4). As far as core-valence corrections are concerned, they are small but not negligible, that is, they are of the order of 0.001–0.004 Å for bond lengths and 0.1–0.3 degrees for angles. Once again, the largest effect is noted for the T_2 angle of cyanamide, for which a correction of 0.6 degrees is observed. With a few exception, the effects of the inclusion of diffuse functions in the basis set are small,

Table 2 Equilibrium geometries and energies of diazomethane, CH_2NN ($^1A_1$), computed at the coupled-cluster level of theory employing different basis sets

	C–H (Å)	C–N (Å)	N–N (Å)	∠HCN (deg.)	∠CNN (deg.)	T[a] (∠HNNN) (deg.)	Energy (Hartree)
B3LYP/6-311+G(d,p)[b]	1.078	1.295	1.137	118.0	180.0	180.0	
CASPT3/cc-pVTZ[c]	1.071	1.303	1.128	117.2	180.0	180.0	
CCSD(T)/aug-cc-pVTZ[d]	1.0760	1.3030	1.1434	117.35	180.0	180.0	
MRCI/cc-pVTZ[e]	1.068	1.295	1.125	117.4	180.0	180.0	−148.417234
B3LYP/6-311++G(3df,2p)[f]	1.0758	1.2910	1.1323	117.98	180.0	180.0	
aug-cc-pVTZ	1.0761	1.3029	1.1434	117.37	180.0	180.0	−148.5093657
cc-pVTZ	1.0751	1.3027	1.1426	117.39	180.0	180.0	−148.4987697
cc-pVQZ	1.0746	1.2996	1.1395	117.36	180.0	180.0	−148.5418702
cc-pV5Z	1.0745	1.2991	1.1389	117.34	180.0	180.0	−148.5552657
cc-pwCVQZ(f.c.)	1.0745	1.2993	1.1392	117.36	180.0	180.0	−148.5452495
cc-pwCVQZ(all)	1.0732	1.2965	1.1370	117.42	180.0	180.0	−148.7124624
CBS[g]	1.0745	1.2990	1.1388	117.34	180.0	180.0	−148.5674199
CBS+CV[h]	1.0732	1.2962	1.1366	117.40	180.0	180.0	−148.7346327
CBS+CV+aug[i]	1.0742	1.2964	1.1374	117.38	180.0	180.0	−148.7452287
Experiment[j] r_s	1.077	1.300	1.139	116.95	180.0	180.0	
Experiment[m] r_0/r_s	1.075	1.300	1.140	117.0	180.0	180.0	

Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates values (CBS+CV and CBS+CV+aug) are also reported

'f.c.' and 'all' mean CCSD(T) calculations correlating only valence and all electrons, respectively

[a] Dihedral angle

[b] Ref. [11]

[c] Ref. [44]

[d] Ref. [45]

[e] Ref. [46]

[f] Ref. [41]

[g] CBS geometry and energy. See text

[h] CV correction added to the corresponding CBS limit. See text

[i] Best estimated geometry and energy. See text

[j] Refs. [50, 51]

[m] Refs. [52, 53]. For more details, see original papers

Table 3 Equilibrium geometries and energies of carbodiimide, HNCNH (^1A), computed at the coupled-cluster level of theory employing different basis sets

	N–H (Å)	C–N (Å)	∠HNC (deg.)	∠NCN (deg.)	T[a] (deg.)	Energy (Hartree)
CCSD(T)/cc-pVQZ+CV(cc-pCVTZ)[b]	1.0098	1.2242	117.84	170.62	44.59	
MP2/cc-pVQZ[c]	1.008	1.225	119.0	170.0	46.5	
CCSD/6-31G(d,p)[c]	1.102	1.233	116.9	170.5	46.8	
B3LYP/6-311++G(3df,2p)[d]	1.0105	1.2185	120.34	170.83	44.6	
aug-cc-pVTZ	1.0127	1.2302	117.38	170.25	44.53	−148.5564791
cc-pVTZ	1.0119	1.2300	116.70	170.57	44.62	−148.5438347
cc-pVQZ	1.0104	1.2264	117.50	170.53	44.59	−148.5888910
cc-pV5Z	1.0102	1.2257	117.78	170.50	44.59	−148.6028899
cc-pwCVQZ(f.c.)	1.0104	1.2261	117.51	170.54	44.59	−148.5922566
cc-pwCVQZ(all)	1.0090	1.2232	117.90	170.65	44.60	−148.7596429
CBS[e]	1.0102	1.2255	117.88	170.48	44.59	−148.6155649
CBS+CV[f]	1.0088	1.2226	118.27	170.59	44.60	−148.7829513
CBS+CV+aug[g]	1.0096	1.2228	118.95	170.27	44.51	−148.7955957
Experiment r_s[h]	1.0074	1.2242	118.63	170.63	44.50	

Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates values (CBS+CV and CBS+CV+aug) are also reported

'f.c.' and 'all' mean CCSD(T) calculations correlating only valence and all electrons, respectively

[a] The two dihedral angles $\angle H_1NCN$ and $\angle NCNH_2$ are defined as T + 180.0 degrees and T − 180.0 degrees, respectively

[b] Ref. [47]

[c] Ref. [48]

[d] Ref. [41]

[e] CBS geometry and energy. See text

[f] CV correction added to the corresponding CBS limit. See text

[g] Best estimated geometry and energy. See text

[h] Ref. [54]

the corrections being smaller than 0.001 Å for bonds and smaller than 0.5 degrees. From a comparison among the five isomers, we note that, while the N–H and C–H distances vary a little from one species to another, the N–N and C–N bond lengths may change significantly depending on the corresponding bond order. Before proceeding with commenting on the comparison of our results with previous theoretical investigations and available experimental data, a few comments on the expected accuracy of our molecular structures are warranted. On the basis of the magnitude of the various contributions and the literature on this topic (see for example Refs. [13, 34–40]), the accuracy of CBS+CV and CBS+CV+aug type geometries is expected to be of the order of 0.001–0.002 Å for distances and of about 0.05–0.1 degrees for angles. These can be considered as conservative estimates, which also account for the approximations made and for neglecting higher-order correlation effects.

From Tables 1, 2, 3, 4 and 5, it is evident that all isomers considered have been previously studied at different levels of theory [11, 41–48], but we report the first systematic investigation of their molecular structure. As in most cases the method and/or the basis set used are inferior to ours, a detailed comparison of these results to ours is not too meaningful. We only note an overall agreement. As concerns experiment, data are available only for diazomethane, carbodiimide and cyanamide [49–52, 54]. In all cases, we note a good agreement, and in particular, the recent, thorough investigation of the molecular structure of cyanamide, which provided the corresponding equilibrium geometry [49], allows us to confirm the accuracy estimate discussed above.

The results for the molecular structure of the HNNC radical, investigated following the methodology presented in the previous section, are given in Table 6. Concerning the convergence to the CBS limit, the magnitude of the CV corrections and the accuracy of the final CBS+CV geometry, we note that the conclusions drawn above for the five CH_2N_2 isomers also apply to this molecule, even if they are not straightforwardly applicable to open-shell species as for the latter the situation is more involved from a theoretical point of view.

As mentioned in the methodology section, the transition states along the isomerization path from cyanamide to carbodiimide and from diazomethane to nitrilimine have been optimized at the CCSD(T)/cc-pVTZ and CCSD(T)/

Table 4 Equilibrium geometries and energies of cyanamide, NH_2CN ($^1A'$), computed at the coupled-cluster level of theory employing different basis sets

	N–H (Å)	N–C (Å)	C–N (Å)	∠HNC (deg.)	∠NCN (deg.)	T_1^a (∠HNCH) (deg.)	T_2^a (∠NCNH) (deg.)	Energy (Hartree)
MP2/cc-pVQZ[b]	1.007	1.347	1.169	113.4	176.8			
B3LYP/6-311++G(3df,2p)[c]	1.0093	1.3392	1.1545	115.9	177.32	111.83	−111.83	
aug-cc-pVTZ	1.0109	1.3565	1.1658	113.05	176.81	128.26	−116.10	−148.5625089
cc-pVTZ	1.0101	1.3578	1.1655	112.47	176.79	126.55	−116.99	−148.5509322
cc-pVQZ	1.0086	1.3531	1.1621	113.07	176.86	128.33	−116.24	−148.5950219
cc-pV5Z	1.0084	1.3520	1.1615	113.28	176.93	129.04	−115.51	−148.6087072
cc-pwCVQZ(f.c.)	1.0086	1.3528	1.1618	113.09	176.86	128.40	−115.81	−148.5984090
cc-pwCVQZ(all)	1.0073	1.3493	1.1593	113.39	176.96	129.34	−115.26	−148.7658267
CBS[d]	1.0083	1.3517	1.1613	113.35	176.98	129.33	−114.94	−148.6211350
CBS+CV[e]	1.0070	1.3482	1.1588	113.65	177.08	130.27	−114.39	−148.7885527
CBS+CV+aug[f]	1.0078	1.3469	1.1591	113.23	177.10	132.08	−113.50	−148.8001294
Experiment r_e, I (semi-exp)[g]	1.0063(1)	1.3475(4)	1.1594(4)	112.69(2)	[176.96]			
Experiment r_e, II (semi-exp)[g]	1.0059(1)	1.3470(2)	1.1594(2)	112.74(2)	178.22(17)			
Experiment r_m^{1L} [g]	1.0065(15)	1.3450(8)	1.1620(8)	112.62(14)	[180.0]			

Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates values (CBS+CV and CBS+CV+aug) are also reported 'f.c.' and 'all' mean CCSD(T) calculations correlating only valence and all electrons, respectively

[a] Dihedral angle

[b] Ref. [48]

[c] Ref. [41]

[d] CBS geometry and energy. See text

[e] CV correction added to the corresponding CBS limit. See text

[f] Best estimated geometry and energy. See text

[g] Ref. [49]. Angle between the N–C bond and the ∠(HNH) bisector: 42.64(32) [r_m^{1L}], 43.35(2) [r_e (semi-exp),I] and 42.78(9) [r_e (semi-exp),II] degrees

cc-pVQZ levels of theory. Harmonic frequency calculations confirmed the transition state character of the optimized geometries. The corresponding results are collected in Table 7. We note that in both cases, the transition state is a cyclic, non-planar form. For the first isomerization, the N–C–N frame is close to linearity and one H connects the two nitrogens. For the second one, the C–N–N frame is strongly bent, forming an angle close to 90 degrees. According to Ref. [55], the accuracy of molecular structures optimized at the CCSD(T)/cc-pVQZ is expected to be of the order of 0.002–0.004 Å for distances and 0.1–0.3 degrees for angles. From the energy values reported in Tables 1, 2, 3, and 4, the barriers to isomerization have been derived. We note that in both cases, the barrier is high, and therefore, we expect that the isomerization hardly happens.

3.2 Energetics

On the basis of the total energies summarized in Tables 1, 2, 3, 4 and 5, the relative stability of the five isomers can be discussed. By including the results for diazirine [7] (the extrapolation to the CBS limit has been repeated following the methodology introduced above), the relative energies of the most stable CH_2N_2 isomers have been obtained. These are reported in Table 8 with respect to cyanamide, which is the lowest-lying isomer, and schematized in Fig. 1. First of all, the stability order, given as energetic order, is:

$$\text{cyanamide} < \text{carbodiimide} < \text{diazomethane} < \text{diazirine} < \text{isocyanamide} < \text{nitrilimine},$$

where cyanamide is only ∼3 kcal/mol stabler than carbodiimide, but as discussed above, the two isomers are separated by a barrier as high as ∼80 kcal/mol. The other isomers are definitely less stable, with diazomethane ∼32 kcal/mol higher in energy, diazirine ∼43 kcal/mol, isocyanamide ∼45 kcal/mol and nitrilimine ∼56 kcal/mol. There is thus a small energy difference between diazirine and isocyanamide, but there is no direct path connecting these two isomers. From Table 8, we note that the convergence to the CBS limit is smooth, and the CCSD(T)/cc-pV5Z results are already converged; in fact, the differences between the latter and the CBS values are smaller than 0.2 kcal/mol. By enlarging the basis set, there is not an unique trend: the energy difference increases for

Table 5 Equilibrium geometries and energies of isocyanamide, NH_2NC ($^1A'$), computed at the coupled-cluster level of theory employing different basis sets

	N–H (Å)	N–N (Å)	N–C (Å)	∠HNN (deg.)	∠NNC (deg.)	T_1^a (∠*HNNH*) (deg.)	T_2^a (∠CNNH) (deg.)	Energy (Hartree)
B3LYP/6-311+G(d,p)[b]	1.016	1.356	1.173	109.3	174.1	120.0		
B3LYP/6-311++G(3df,2p)[c]	1.0146	1.3547	1.1676	109.29	174.23	120.05	−120.05	
aug-cc-pVTZ	1.0159	1.3700	1.1788	107.41	174.22	116.28	−122.28	−148.4917144
cc-pVTZ	1.0148	1.3692	1.1789	107.29	174.33	115.85	−123.47	−148.4800091
cc-pVQZ	1.0133	1.3648	1.1751	107.62	174.40	116.65	−122.24	−148.5240210
cc-pV5Z	1.0132	1.3638	1.1744	107.75	174.42	116.95	−121.84	−148.5374871
cc-pwCVQZ(f.c.)	1.0134	1.3643	1.1746	107.64	174.34	116.67	−122.19	−148.5273196
cc-pwCVQZ(all)	1.0120	1.3607	1.1719	107.87	174.55	117.19	−119.27	−148.6941112
CBS[d]	1.0132	1.3635	1.1740	107.80	174.43	117.13	−121.70	−148.5497324
CBS+CV[e]	1.0118	1.3599	1.1713	108.03	174.64	117.65	−118.78	−148.7165009
CBS+CV+aug[f]	1.0129	1.3607	1.1712	108.15	174.53	118.08	−117.59	−148.7282062

Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates values (CBS+CV and CBS+CV+aug) are also reported

'f.c.' and 'all' mean CCSD(T) calculations correlating only valence and all electrons, respectively

[a] Dihedral angle

[b] Ref. [11]

[c] Ref. [41]

[d] CBS geometry and energy. See text

[e] CV correction added to the corresponding CBS limit. See text

[f] Best estimated geometry and energy. See text

Table 6 Equilibrium geometries and energies of isocyanomidyl radical, HNNC ($^2A''$), computed at the coupled-cluster level of theory employing different basis sets

	H–N (Å)	N–N (Å)	N–C (Å)	∠HNN (deg.)	∠NNC (deg.)	Energy (Hartree)
MP2/cc-pVTZ(all)[a]	1.021	1.298	1.180	105.6	173.9	
B3LYP/6-311++G(3df,2p)[b]	1.0281	1.2870	1.1879	107.37	171.44	
CCSD(T)/aug-cc-pVTZ[c]	1.024	1.297	1.191	106.1	171.6	
aug-cc-pVTZ	1.0284	1.3037	1.1961	105.86	171.72	−147.8364668
cc-pVTZ	1.0276	1.3035	1.1959	105.66	172.22	−147.8262512
cc-pVQZ	1.0260	1.2990	1.1924	105.97	172.14	−147.8674980
cc-pV5Z	1.0258	1.2981	1.1918	106.07	172.11	−147.8803260
cc-pwCVQZ(f.c.)	1.0261	1.2987	1.1920	105.97	172.11	−147.8708520
cc-pwCVQZ(all)	1.0248	1.2957	1.1893	106.14	172.24	−148.0370570
CBS[d]	1.0257	1.2978	1.1916	106.11	172.10	−147.8920230
CBS+CV[e]	1.0244	1.2948	1.1889	106.28	172.23	−148.0582280
CBS+CV+aug[f]	1.0252	1.2950	1.1891	106.48	171.73	−148.0684436

Extrapolated geometries and energies to valence correlation limit (CBS) and best estimates values (CBS+CV and CBS+CV+aug) are also reported

'f.c.' and 'all' mean (R/U)CCSD(T) calculations correlating only valence and all electrons, respectively

[a] Ref. [56]

[b] Ref. [41]

[c] Ref. [57]

[d] CBS geometry and energy. See text

[e] CV correction added to the corresponding CBS limit. See text

[f] Best estimated geometry and energy. See text

Table 7 CCSD(T) optimized geometries and energies for the carbodiimide–cyanamide transition state (TS1) and the nitrilimine–diazomethane transition state (TS2)

	H_1–N_2 (Å)	N_2–C_3 (Å)	C_3–N_4 (Å)	N_4–H_5 (Å)	$\angle H_1N_2C_3$ (deg.)	$\angle N_2C_3N_4$ (deg.)	$\angle C_3N_4H_5$ (deg.)	T_1^a (deg.)	T_2^a (deg.)	Energy[b] (cyanamide) (kcal/mol)	Energy[b] (carbodiimide) (kcal/mol)
TS1											
cc-pVTZ	1.7722	1.2186	1.3417	1.0215	40.35	188.09	108.54	75.43	186.37	83.8	79.3
cc-pVQZ	1.7418	1.2130	1.3337	1.0196	41.71	187.93	109.24	99.33	187.93	83.7 (79.1)	79.8 (76.2)
	H_1–C_2 (Å)	C_2–N_3 (Å)	N_3–N_4 (Å)	N_4–H_5 (Å)	$\angle H_1C_2N_3$ (deg.)	$\angle C_2N_3N_4$ (deg.)	$\angle N_3N_4H_5$ (deg.)	T_1^a (deg.)	T_2^a (deg.)	Energy[b] (diazomethane) (deg.)	Energy[b] (nitrilimine) (deg.)
TS2											
cc-pVTZ	1.1086	1.4321	1.2551	1.1543	103.16	88.87	104.10	−98.56	−7.47	81.5	56.4
cc-pVQZ	1.1072	1.4271	1.2513	1.1582	103.36	88.79	103.87	−98.64	−7.56	82.2 (79.1)	57.7 (54.5)

[a] For TS1: $T_1 = \angle H_1N_2C_3N_4$ and $T_2 = \angle N_2C_3N_4H_5$. For TS2: $T_1 = \angle H_1C_2N_3N_4$ and $T_2 = \angle C_2N_3N_4H_5$

[b] Relative energy with respect to the isomer given below. In parentheses, the ZPV corrected value is given

Table 8 Relative energy (kcal/mol) of CH_2N_2 isomers with respect to cyanamide at the coupled-cluster level of theory employing different basis sets

	Carbodiimide	Diazomethane	Diazirine	Isocyanamide	Nitrilimine
B3LYP/6-311++G(3df,2p)[a]	−1.59	28.37	45.07	44.39	51.78
cc-pVQZ	3.85	33.35	42.38	44.55	57.88
cc-pV5Z	3.65	33.54	42.46	44.69	57.81
CBS	3.50	33.71	42.53	44.81	57.79
CBS+CV	3.51	33.84	43.22	45.21	57.94
CBS+CV+ZPV[b]	2.60	32.14	42.67	44.95	56.39
CBS+CV+aug	2.84	34.45	–	45.13	57.62
CBS+CV+aug+ZPV[b]	1.94	32.75	–	44.87	56.07

CBS, CBS+CV and CBS+CV+aug values are also reported

[a] ZPV correction included, Ref. [41]

[b] ZPV corrections at the CCSD(T)/cc-pVQZ level within the harmonic approximation

diazomethane, diazirine and isocyanamide, while it decreases for carbodiimide and nitrilimine. CV corrections are in all cases positive, but for their extent, a general conclusion cannot be drawn; in fact, they vary from being negligible, 0.01 kcal/mol, in the case of carbodiimide to being relevant, 0.7 kcal/mol, for diazirine. In all cases, inclusion of diffuse functions in the basis set leads to corrections smaller than 1 kcal/mol: they range from about 0.3 kcal/mol for nitrilimine to about 0.9 kcal/mol for isocyanamide. While they are positive for diazomethane and isocyanamide, they are negative for carbodiimide and nitrilimine. To the best of our knowledge, the comparison to previous theoretical calculations is limited to those at the B3LYP/6-311++G(3df,2p) level of Ref. [41]. Differences of some kcal/mol are observed, and in the latter work, a wrong stability order was obtained with carbodiimide predicted stabler than cyanamide and isocyanamide stabler than diazirine. In view of the high-level calculations carried out in the present investigation, we consider our results more reliable.

From the total energies reported in Tables 1, 2, 3, 4, 5, and 6 and those available in Ref. [13], the C–H and N–H equilibrium dissociation energies corresponding to the following reactions can be evaluated:

$$H_2NCN \rightarrow HNCN + H, \quad (8)$$

$$HNCNH \rightarrow HNCN + H, \quad (9)$$

$$H_2CNN \rightarrow HCNN + H, \quad (10)$$

$$HCNNH \rightarrow HCNN + H, \quad (11)$$

$$HCNNH \rightarrow HNNC + H, \quad (12)$$

$$H_2NNC \rightarrow HNNC + H. \quad (13)$$

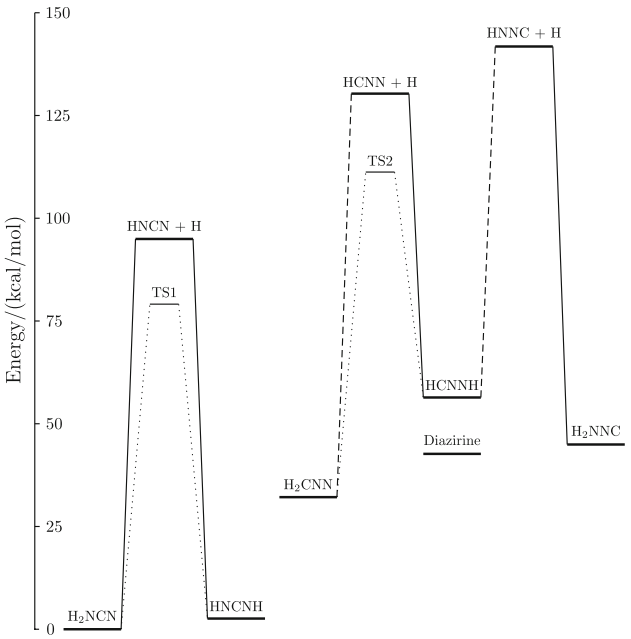

Fig. 1 Relative energy levels for the CH_2N_2 isomers with respect to cyanamide. Transition states TS1 and TS2 are also reported (*dotted lines*). The dissociation limit involving HCNN, HNCN and HNNC radicals is indicated: C–H bond cleavage in dashed line and N–H bond breaking in continuous line. All data taken from Tables 7, 8, and 9

The results obtained are collected in Table 9. Here, we mention that for HCNN and HNCN, the required extrapolations of the total energies reported in Ref. [13] have been carried out following the methodology presented above. The total energies extrapolated to the CBS limit have been employed in order to determine the complete basis set limit of the dissociation energies. First of all, we note that by enlarging the basis set, the dissociation energy increases. As noted for relative energies, the convergence is smooth and essentially reached at the CCSD(T)/cc-pV5Z level, the differences with respect to the CBS limit being smaller than 0.4 kcal/mol. Subsequently, by adding the core-valence corrections to the CBS limit, best estimates of the equilibrium dissociation energies have been derived. CV corrections are positive and of the order of 0.4–0.6 kcal/mol. For the two reactions involving the dissociation to HNNC+H, the effect of additional diffuse functions in the basis set can be also estimated. The corresponding corrections are positive and on the order of 1 kcal/mol. On the basis of the above discussion and of the literature on this topic (see, for example, Refs. [37–39, 55]), our best estimated dissociation energies are expected to fulfill the chemical accuracy, that is, they are expected to have an accuracy better than 1 kcal/mol. The addition of the appropriate zero-point differences evaluated from the harmonic frequencies (Eq. 7) provides the D_0 dissociation energies, which are also reported in Table 9. As expected, ZPV corrections lower the dissociation energies, and they are important corrections to be taken into account for this property as they amount to 7–9 kcal/mol. As well known, the use of the harmonic approximation overestimates the ZPV corrections; in the present case, the relevant term is the anharmonic contribution connected to C–H or N–H bonds which can be estimated on the order of −0.3 to −0.5 kcal/mol. Concerning the literature, to the best of our knowledge, there are no experimental data to compare with, while the theoretical values are limited to those at the B3LYP/6-311++G(3df,2p) level deducible from the energies obtained in Ref. [41]. In view of the limited accuracy of the B3LYP/6-311++G(3df,2p) level pointed out when discussing relative energies (see Table 8), the corresponding results are not collected in Table 9.

4 Concluding remarks

The structural and energetics of cyanamide, carbodiimide, diazomethane, isocyanamide and nitrilimine as well as of the HNNC radical have been accurately investigated using the CCSD(T) method with systematic treatments of basis

Table 9 C–H and N–H dissociation energies (kcal/mol) for the five CH_2N_2 isomers considered

	cc-pVQZ	cc-pV5Z	CBS	CBS+CV	CBS+CV+ZPV[a]	CBS+CV+aug	CBS+CV+aug+ZPV[a]
C–H dissociation							
$H_2CNN \rightarrow HCNN + H$	105.04	105.34	105.46	105.93	98.18		
$HCNNH \rightarrow HNNC + H$	84.93	85.51	85.98	86.59	78.62	87.87	79.90
N–H dissociation							
$H_2NCN \rightarrow HCNN + H$	103.09	103.51	103.79	104.16	94.96		
$H_2NNC \rightarrow HNNC + H$	98.25	98.63	98.96	99.32	90.05	100.36	91.10
$HCNNH \rightarrow HCNN + H$	80.52	81.07	81.38	81.82	73.93		
$HNCNH \rightarrow HNCN + H$	99.24	99.86	100.29	100.65	92.36		

[a] ZPV corrections at the CCSD(T)/cc-pVQZ level within the harmonic approximation

set truncation errors, and core-valence correlation and diffuse-function effects. Where available the present results are in excellent agreement with experiment. As far as molecular structures are concerned, the accuracy obtained in the present study is estimated to be 0.001–0.002 Å for bond lengths and 0.05–0.1 degrees for angles. The relative and dissociation energies derived are estimated to fulfill the so-called chemical accuracy, that is, they are expected to be affected by uncertainties of the order of 1 kcal/mol.

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References

1. Maier-Greiner UH, Klaus BA, Estermeier LM, Hartmann GR (1991) Angew Chem Int Ed Engl 30:1314
2. Turner BE, Kislayakov AG, List HS, Kaifu N (1975) Astrophys J 201:149
3. Matthews HE, Sears T (1986) Astrophys J 300:766
4. Williams A, Ibrahim IT (1981) Chem Rev 81:589
5. Streitwieser A Jr, Heathcock CH (1985) Introduction to organic chemistry, 3rd edn. Macmillan Publishing Company, New York
6. Liu, MTH (eds) (1987) The chemistry of diazirines, vol I and II. CRC Press, Boca Raton
7. Puzzarini C, Gambi A (2004) Chem Phys 306:131
8. Cambi R, von Niessen W, Schirmer J (1984) Chem Phys 86:389
9. Schäfer E, Winnewisser M (1982) Ber Bunsenges Chem Phys 86:780
10. Bertrand G, Wentrup C (1994) Angew Chem Int Ed Engl 33:527
11. Goldberg N, Fiedler A, Schwarz H (1994) Helv Chim Acta 77:2354
12. Maier G, Eckwerk J, Bothur A, Reisenauer HP, Schmidt C (1996) Liebigs Ann 1041
13. Puzzarini C, Gambi A (2005) J Chem Phys 122:064316
14. Basco N, Yee KK (1968) Chem Commun (Lond) 150
15. Werner H-J, Knowles PJ, Lindh R, Manby FR, Schütz M, Celani P, Korona T, Rauhut G, Amos RD, Bernhardsson A, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Lloyd AW, McNicholas SJ, Meyer W, Mura ME, Nicklass A, Palmieri A, Pitzer R, Schumann U, Stoll H, Stone A J, Tarroni R, Thorsteinsson T (2006) MOLPRO, version 2006.1, a package of ab initio programs
16. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 156:479
17. Hampel C, Peterson KA, Werner HJ (1992) Chem Phys Lett 190:1
18. Lee TJ, Taylor PR (1989) Int J Quantum Chem Symp 23:199
19. Lee TJ, Scuseria GE (1995) In: Langhoff SR (ed) Quantum mechanical electronic structure calculations with chemical accuracy. Kluwer, Dordrecht, p 47
20. Werner H-J, Knowles PJ (1985) J Chem Phys 82:5053
21. Knowles PJ, Werner H-J (1985) Chem Phys Lett 115:259
22. Dunning TH Jr (1989) J Chem Phys 90:1007
23. Eckert F, Pulay P, Werner H-J (1997) J Comp Chem 18:1473
24. El Azhary A, Rauhut G, Pulay P, Werner H-J (1998) J Chem Phys 108:5185
25. Puzzarini C (2009) J Phys Chem 113A:14530
26. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106:9639
27. Halkier A, Helgaker T, Jørgensen P, Klopper W, Koch H, Olsen J, Wilson AK (1998) Chem Phys Lett 286:243
28. Feller D (1992) J Chem Phys 96:6104
29. Feller D (1993) J Chem Phys 98:7059
30. Peterson KA, Dunning TH Jr (2002) J Chem Phys 117:10548
31. Scuseria GE (1991) Chem Phys Lett 176:27
32. Watts JD, Gauss J, Bartlett RJ (1993) J Chem Phys 98:8718
33. Knowles PJ, Hampel C, Werner H-J (1994) J Chem Phys 99:5219
34. Puzzarini C (2005) J Chem Phys 123:024313
35. Puzzarini C, Cazzoli G, Gambi A, Gauss J (2006) J Chem Phys 125:054307
36. Puzzarini C, Cazzoli G, Baldacci A, Baldan A, Michauk C, Gauss J (2007) J Chem Phys 127:164302
37. Puzzarini C (2008) Chem Phys 346:45
38. Puzzarini C, Barone V (2010) Int J Quantum Chem 110:637
39. Puzzarini C (2010) Int J Quantum Chem 110:2483
40. Puzzarini C, Barone V (2011) Phys Chem Chem Phys 13:7158
41. Du B, Zhang W (2006) Int J Quantum Chem 106:1827
42. Wong MW, Wentrup C (1993) J Am Chem Soc 115:7743
43. Kuhler K, Palmer RT, Wittkamp BL, Hoffmann MR (1996) J Mol Struct (THEOCHEM) 360:41
44. Papakondylis A, Mavridis A (1999) J Phys Chem A 103:1255
45. Dixon DA, de Jong WA, Peterson KA, McMahon TB (2005) J Phys Chem A 109:4073
46. Kerkines ISK, P. Carsky P, A. Mavridis A (2005) J Phys Chem A 109:10148
47. Koput J, Jabs W, Winnewisser M (1998) Chem Phys Lett 295:462
48. Tordini F, Bencini A, Bruschi M, De Gioia L, Zampella G, Fantucci P (2003) J Phys Chem A 107:1188
49. Kraśnicki A, Kisiel Z, Jabs W, Winnewisser BP, Winnewisser M (2011) J Mol Spectrosc 267:144
50. Cox AP, Thomas LF, Sheridan J (1958) Nature (Lond) 181:1000
51. Sheridan J (1962) Adv Mol Spectrosc Proc IVth Int Meet Mol Spectrosc 1:139
52. Harmony MD, Laurie VW, Kuczkowski RL, Schwendeman RH, Ramsay DA, Lovas FJ, Lafferty WJ, Maki AG (1979) J Phys Chem Ref Data 8:619
53. Moore CB (1963) J Chem Phys 39:1884
54. Jabs W, Winnewisser M, Belov SP, Lewen F, Maiwald F, Winnewisser G (1999) Molec Phys 97:213
55. Helgaker T, Jørgensen P, Olsen J (2000) Electronic-structure theory. Wiley, Chichester
56. Kurosaki Y, Takayanagi T (1999) J Phys Chem A 103:9323
57. Berman MR, Tsuchiya T, Gregušová A, Perera SA, Bartlett RJ (2007) J Phys Chem A 111:6894