



Accurate structural parameters and binding energy of the \tilde{X}^1A_1 state of diazomethane through coupled-cluster calculations



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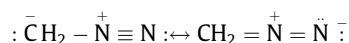
ABSTRACT

Through coupled-cluster CCSD(T) calculations combined with extended correlation consistent basis sets, we have determined accurate structural parameters of the ground \tilde{X}^1A_1 state of the H_2CN_2 molecule. In particular, the hitherto doubtful dissociation energy H_2C-N_2 has been pinpointed to $D_0^0 = 27.3$ kcal/mol with respect to $CH_2(\tilde{X}^3B_1) + N_2(X^1\Sigma_g^+)$.

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1. Introduction

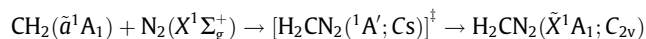
Diazomethane is a well known chemical reagent used in organic synthesis mainly due to its methylating properties. It was isolated some 120 years ago [1] and corresponds to one of the six experimentally known CH_2N_2 structural isomers, namely, cyanamide (H_2NCN), carbodiimide ($HNCNH$), diazomethane ($H_2C=N=N$), isocyanamide (H_2NNC), nitrilimine ($HNNCH$), and diazirine ($c-H_2CN_2$) [2]. The diazomethane compound is highly toxic and explosive under certain conditions [3,4]. Besides its useful synthetic agility diazomethane's discovery bequeathed to the chemical society a serious, though constructive, conundrum concerning the nature of the bond between two legendary molecules: the rock-stable N_2 ($X^1\Sigma_g^+$, $D_0^0 = 225.05$ kcal/mol) [5] and the $CH_2(\tilde{X}^3B_1)$ moiety [6]. With no doubt the conventional allocation of bonds in H_2CN_2 , a closed shell system (\tilde{X}^1A_1), fails dismally. Most attempts to interpret its bonding nature involves the wide spread idea of 'chemical resonance' as a *deus ex machina*. Even to our days diazomethane is referred to as a 1,3 bipolar hybrid composed of, at least, two zwitterionic resonance structures,



Of course an arbitrary large number of such structures can be drawn depending, more or less, on one's disposition. It is our strong conviction that the resonance concept is an *ad hoc* approach which grew explosively due to our past inability to perform accurate quantum mechanical calculations even for 'small' molecules and conceptual-interpretational problems inherent in the quantum world [7]. Nowadays a large number of ab initio studies on

H_2CN_2 are available in the literature; see references [8,9,11] and references therein. According to the literature of the last 15 years it seems that the bonding H_2C-N_2 mechanism has been fully clarified since 1999 [9] (but see below).

The authors of Ref. [9] carried out multireference perturbation calculations (CASPT2 and CASPT3) in conjunction with triple zeta polarized valence correlation consistent (cc-pVTZ) basis sets. The $CH_2 + N_2 \rightarrow H_2CN_2$ reaction mechanism proposed can be envisaged as a two step process,



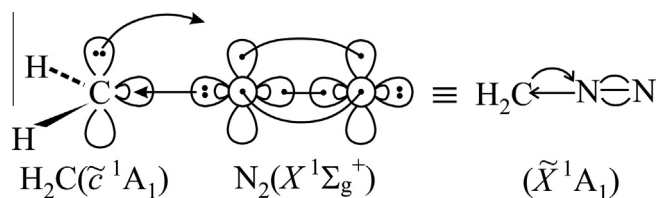
where the first step referring to $[H_2CN_2(^1A'; Cs)]^\ddagger$ represents a perpendicular π attack of $N_2(X^1\Sigma_g^+)$ on the \tilde{a}^1A_1 state of CH_2 (see the valence bond-Lewis (vbL) diagram of reference [9]), followed by a (barrierless) opening of the 90° $\angle CNN$ angle leading finally to the linear ($\angle CNN = 180^\circ$) equilibrium C_{2v} geometry. The second step ('opening') takes place through the participation of the third \tilde{c}^1A_1 state of CH_2 . Therefore the most economical and consistent way to represent the bonding in H_2CN_2 is shown in Scheme 1, where the curved C-to-N arrow represents a π interaction ('conjugation') between the CH_2 and N_2 molecules.

The above bonding mechanism has been experimentally confirmed through time resolved IR laser pulsed spectroscopy by Windhorn et al. [10]. Further Brillouin-Wigner coupled cluster singles and doubles (MRBWCSD/cc-pVTZ) calculations published by Kerkines et al. [11] in 2005, are in complete accord with the bonding conclusions of reference [9].

It should be stated at this point, however, that in a very recent ab initio work by Barbosa and Monteiro [8] the above bonding scenario is disputed, albeit 'mildly'. It is claimed by these authors that a more complete bonding description of H_2C-N_2 , is a hybrid of two structures, the one presented in reference [9], $H_2C \overset{\curvearrowright}{\pi} N \equiv N$, and an open singlet biradical ($H_2\bar{C} - \bar{N} = \bar{N} :$) with the in situ CH_2 and

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Scheme 1.

N_2 fragments in the \tilde{X}^3B_1 and $B^3\Pi_g$ states, respectively. Incidentally the $B^3\Pi_g$ state of N_2 lies 7.39 eV above the $X^1\Sigma_g^+$ ground state and with a bond distance of 1.216 Å as compared to 1.098 Å of $X^1\Sigma_g^+$ [5] and 1.139 in $H_2CN\equiv N$ (*vide infra*), thus rendering its participation to the bonding problematic. The latter biradical structure has been proposed in 1975 by Walch and Goddard on the basis of GVB-PP (6/12)/DZ calculations [12]. We disagree with the Barbosa–Monteiro [8] suggestion; not only the previously presented bonding mechanism has been confirmed experimentally [10], but it has also been excluded on purely theoretical grounds; see reference 9 and references therein.

The purpose of this short communication is twofold. (a) To show that a single reference treatment is absolutely adequate to describe the diazomethane equilibrium structure, and (b) to obtain an essentially indisputable equilibrium geometry, electric dipole moment, and, especially the still controversial H_2C-N_2 binding energy. Indeed, there are serious discrepancies among the existing experimental H_2C-N_2 binding energies [13–17], whereas theoretical values including ours [9,11] cannot be considered as accurate enough.

To that end we have performed single reference coupled cluster singles + doubles + quasiperturbative connected triples (CCSD(T)) calculations [18–20], combined with extended correlation consistent basis sets, cc-pVnZ with $n = T, Q, 5, 6$ [21,22]. Core electrons ($\sim 1s^2$ on C and N) were kept frozen except if stated otherwise. For the total energy as well as the binding energy we have estimated complete basis set (CBS) limits using the well tested single exponential [23] and mixed exponential-Gaussian [24] extrapolation formulae. The reported CBS numbers are the arithmetic mean values of the two CBS limits. Geometrical parameters were obtained by full optimization at the CCSD(T)/cc-pVnZ ($n = T, Q, 5$) levels, whereas harmonic frequencies by diagonalization of the corresponding Hessian matrices at the same levels of theory. Dipole moments were calculated through the finite field approach by applying a 5×10^{-6} a.u. electric field.

All electron correlated calculations were performed using the core-valence cc-pCV6Z [25] for C and N and the cc-pV6Z basis set for the H atom. No further corrections, that is scalar relativistic and basis set superposition effects were deemed as necessary. It should be noted, also, that for reasons of completeness, the role of iterative triples has been examined through CCSDT calculations employing triple and quadruple cc-basis sets (*vide infra*).

With the exception of the CCSDT calculations done by the NWChem code [26], the MOLPRO2012.1 [27] suite of programs was used through all calculations.

2. Results and discussion

Our numerical results are condensed in Table 1. As we can see all geometrical parameters calculated at the CCSD(T)/cc-pV5Z level are in excellent agreement with the experimental values [28,29] and identical to the values obtained by Puzzarini and Gambi [2] at the same level. The latter authors showed that CBS limit extrapolation has negligible effect on the geometrical parameters, thus the quintuple-zeta geometry was employed for the CCSD(T)/cc-pV6Z/cc-pCV6Z calculations. The excellent agreement with experiment as well as the fact that the leading CASSCF coefficient (Hartree–Fock) is $C_{HF} = 0.98$ [9], justify completely our single reference CCSD(T) equilibrium computational approach.

Although electric dipole moments ($n = T, Q, 5, 6$) given in Table 1 are in good agreement with the 1.50 ± 0.01 D experimental value [28,29], the largest discrepancy being less than 0.1 D, the monotonic increase with the basis set cardinality prompted us to examine the role of the iterative triples through CCSDT/cc-pVTZ calculations. At this level $\langle \mu_e \rangle = 1.488$ D, practically identical to the corresponding CCSD(T) value $\mu_e = 1.486$ D, confirming the robustness of the CCSD(T) approach. Including the $\sim 1s^2$ core electrons of C and N at the sextuple basis level, CCSD(T)/cc-pCV6Z//CCSD(T)/cc-pV5Z, the dipole moment is shifted by +0.005 D, $\mu_e = 1.572$ D. Now the (TQ56)–CBS limit gives $\mu_e = 1.568 \pm 0.010$ D. Adding to the latter value the core effect we finally end up with $\mu_e = 1.573 \pm 0.010$ D a difference of +0.07 D away from the experimental value. This systematic difference from experiment, albeit small, suggests an experimental re-investigation of μ_e .

We focus now to the H_2C-N_2 numerical binding energy problem; clearly the available experimental values are in conflict (Table 1). Moreover, most of them are upper limits and, also, it is not quite clear what end products of CH_2 these values refer to, that

Table 1
Total energies E (E_h), bond distances r_{C-H} , r_{C-N} , r_{N-N} (Å), angle θ_{HCH} (degrees), dipole moment μ_e (D), and binding energies D_e and D_0 (kcal/mol), with respect to the \tilde{X}^3B_1 and \tilde{a}^1A_1 states of $CH_2 + N_2$ ($X^1\Sigma_g^+$), of the H_2CN_2 molecule at the RCCSD(T)/cc-pVnZ, $n = T, Q, 5, 6$ level of theory.

n^a	$-E$	r_{C-H}	r_{C-N}	r_{N-N}	θ_{HCH}	μ_e^b	D_e^0 (\tilde{X}^3B_1) ^c	D_0^0 (\tilde{X}^3B_1) ^c	D_e (\tilde{a}^1A_1) ^d	D_0 (\tilde{a}^1A_1) ^d
T	148.49877	1.0751	1.3027	1.1426	125.2	1.486	29.69	24.18	39.82	33.87
Q	148.54187	1.0750	1.2996	1.1395	125.3	1.539	31.65	24.76	41.14	35.23
5	148.55527	1.0745	1.2990	1.1389	125.3	1.550	32.18	26.71	41.44	35.55
6 ^e	148.56000					1.567	32.34	26.87	41.49	35.60
∞ (CBS)	148.5644					1.568 ± 0.010	32.4	26.9	41.5	35.6
CV6 ^f	148.73498					1.572	33.0	27.5	42.6	36.7
Expt. ^g		1.077	1.300	1.139	126.1	1.50 ± 0.01	<44 ^h , <35 ⁱ , <41.7 ^j , 25 ^k			

^a Basis set cardinality number.

^b Calculated by the finite field method; field strength 5×10^{-6} a.u. The polarity of the molecule is $(^-)CH_2-N_2^{(+)}$.

^c Binding energy with respect to $CH_2(\tilde{X}^3B_1) + N_2(X^1\Sigma_g^+)$.

^d Binding energy with respect to $CH_2(\tilde{a}^1A_1) + N_2(X^1\Sigma_g^+)$.

^e All numbers reported in the $n = 6$ entry have been obtained with the geometry and harmonic frequencies at the $n = 5$ level.

^f CCSD(T) calculation correlating all core electrons and using the cc-pCV6Z basis set at the CCSD(T)/cc-pV5Z optimized geometry.

^g Geometrical parameters and dipole moment are from Refs. [28,29].

^h Electron impact, Refs. [14,15].

ⁱ Pyrolysis, Ref. [13].

^j Photodissociation measurements, Ref. [17].

^k Flash photolysis, Ref. [16].

is \tilde{X}^3B_1 or \tilde{a}^1A_1 . The ground state potential energy profile of H_2C-N_2 adiabatically correlates to $CH_2(\tilde{a}^1A_1) + N_2(X^1\Sigma_g^+)$, the ground $CH_2(\tilde{X}^3B_1) + N_2(X^1\Sigma_g^+)$ asymptote being 8.998 kcal/mol [30] lower.

In Table 1, following the usual convention, D_e^0 and D_0^0 values are with respect to the \tilde{X}^3B_1 state of CH_2 while D_e and D_0 refer to its first \tilde{a}^1A_1 excited state. D_e^0 and D_0^0 values were obtained by using the calculated harmonic frequencies for the $n = T, Q, 5$ cardinalities while the quintuple-zeta harmonic frequencies were employed in all other cases. It is useful at this point to give all $n = 5$ calculated harmonic frequencies, nine for $H_2CN_2(\tilde{X}^1A_1)$, three for each state of $CH_2(\tilde{X}^3B_1, \tilde{a}^1A_1)$, and one for N_2 (in cm^{-1}): (3340.8, 3206, 2147.2, 1443.5, 1187.7, 1120.9, 567.7, 415.2, 371.6), [(3373.2, 3144.4, 1097.8), (2999.1, 2924.8, 1400.5)], and 2358.6, respectively. Thus the zero point energy (ZPE) correction at this level is $ZPE = \sum_{i=1}^9 \omega_i/2(H_2CN_2) - \sum_{i=1}^3 \omega_i/2(CH_2) - \omega_e/2(N_2) = 5.47$ and 5.89 kcal/mol for the \tilde{X}^3B_1 and the \tilde{a}^1A_1 states of CH_2 , respectively.

Using the $n = Q, 5, 6$ results for the total and binding energies we obtained CBS limit values as described in the previous section. For the total energy our CBS limit differs by ~ 3 mE_h from the Puzzarini and Gambi ($n = T, Q, 5$) CBS value [2].

Concerning the binding energies we can see that all values converge to the $n = 6$ level. From Table 1 we have $D_0^0(\tilde{X}^3B_1) = 26.9$ kcal/mol and $D_0(\tilde{a}^1A_1) = 35.6$ kcal/mol at the (Q56)-CBS limit. These values are by ~ 3 kcal/mol greater than our previously reported CASPT3/cc-pVTZ corresponding numbers [9].

In order to explore the effect of the core electrons we performed all electron correlated CCSD(T) calculations using the core-valence cc-pCV6Z basis sets on C and N, CCSD(T)/cc-pCV6Z//cc-pV5Z. The total energy, $E = -147.73498 E_h$, is by $\sim 0.022 E_h$ lower than the corresponding CCSD(T)/cc-pCVQZ energy reported by Puzzarini and Gambi [2]. As we can see the $n = 6$ D_e^0 and D_e values increase by 0.66 and 1.11 kcal/mol, respectively, to $D_e^0 = 33.0$ and $D_e = 42.6$ kcal/mol. Taking into account the core effects we obtain the CBS(+core) limits, $D_e^0 = 32.4 + 0.66 = 33.06$ and $D_e = 42.61$ kcal/mol. Subtracting the ZPE corrections we obtain $D_0^0 = 33.06 - 5.47 = 27.6$ and $D_0 = 42.61 - 5.89 = 36.7$ kcal/mol. Using, as well, the experimental frequencies of $N_2(X^1\Sigma_g^+)$ [5], $CH_2(\tilde{X}^3B_1)$ [30], and $H_2CN_2(\tilde{X}^1A_1)$ [31–34] we obtain $ZPE = 5.27$ kcal/mol, thus $D_0^0(\tilde{X}^3B_1) = 27.8$ kcal/mol.

Once more the validity of the non-iterative inclusion of triple excitations (CCSD(T)) concerning the dissociation energy, was tested using the CCSDT method in conjunction with the quadruple cc-basis set. At this level we obtain $E(\text{CCSDT}) = -148.54142 E_h$ while $D_e = 40.93$ and $D_e^0 = 31.19$ kcal/mol, smaller by 0.21 and 0.46 kcal/mol as contrasted to the 41.14 and 31.65 kcal/mol values at the CCSD(T)/cc-pVQZ (Table 1), respectively. These small differences are below the conventional chemical accuracy, ~ 1 mE_h.

In the light of the above, our final recommended dissociation energy $D_0^0(\tilde{X}^3B_1) = 27.8 - 0.5 = 27.3$ kcal/mol. We believe that this is a definitive number and relatively consistent with the experimental flash photolysis value of ~ 25 kcal/mol by Braun et al. [16].

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