A Multireference Coupled-Cluster Potential Energy Surface of Diazomethane, CH_2N_2

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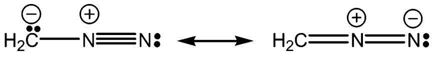
The intrinsically multireference dissociation of the C−N bond in ground-state diazomethane (CH_2N_2) at different angles has been studied with the multireference Brillouin−Wigner coupled-cluster singles and doubles (MRBWCCSD) method. The morphology of the calculated potential energy surface (PES) in C_s symmetry is similar to a multireference perturbational (CASPT3) PES. The MRBWCCSD/cc-pVTZ $H_2C{-}N_2$ dissociation energy with respect to the asymptotic $CH_2(\tilde{a}^1A_1) + N_2(X^1\Sigma_g^+)$ products is $D_e = 35.9$ kcal/mol, or a zero-point corrected $D_0 = 21.4$ kcal/mol with respect to the ground-state $CH_2(\tilde{X}^3B_1) + N_2(X^1\Sigma_g^+)$ fragments.

1. Introduction

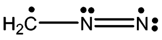
Diazomethane (CH_2N_2) is a well-known organic compound that was discovered more than a century ago (1894).[1] Despite its toxicity and explosiveness, it has for a long time been used in organic synthesis as a means of very efficient and facile acid, alcohol, and phenol methylation.[1] Recent studies have also indicated its probable formation in the N_2-rich ice surfaces of Triton (a moon of Neptune) and Pluto.[2,3]

The various isomers of CH_2N_2, mainly diazomethane, diazirine, and cyanamide, have been largely studied in the past, both experimentally and theoretically.[4,5] Indeed, by 1962, the experimental geometrical structures of diazomethane and diazirine were already known.[6,7] From a chemical point of view, diazomethane is one of the many molecules for which a single "conventional" Lewis structure cannot be written. In literature, it is usually referred to as a closed-shell "1−3 dipolar resonance hybrid" of the form[8,9]



$$H_2\overset{\ominus}{\ddot{C}}{-}\overset{\oplus}{N}{\equiv}N\colon \longleftrightarrow H_2C{=}\overset{\oplus}{N}{=}\overset{\ominus}{N}\colon \qquad (1)$$

but, a singlet biradical form has also been proposed by Walsh and Goddard:[10]

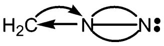


$$H_2\dot{C}{-}\ddot{N}{=}\dot{N}\colon \qquad (2)$$

a conjecture strongly opposed by Gerratt and co-workers in the light of spin-coupled calculations.[11] Instead, it is proposed that the in situ central nitrogen atom is in a "hypervalent" state with a valence number of five:

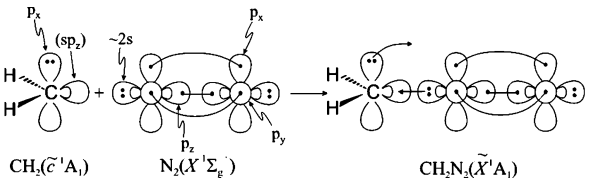
$$H_2C{=}N{\equiv}N\colon \qquad (3)$$

A somehow similar point of view has been put forth by Papakondylis and Mavridis[4] who, with the help of multireference perturbation calculations proposed a similar "five-bond" picture of the central N, without the need though of employing any virtual "hypervalent" state of N:



(4)

This bonding picture is based on the actual spectroscopic states of the fragments that participate in the formation of the $\tilde{X}^1A_1$ state of diazomethane, $CH_2 + N_2$. The in situ CH_2 finds itself in its $\tilde{c}^1A_1$ excited state, whereas the N_2 moiety remains in its ground $X^1\Sigma_g^+$ state according to the following valence-bond Lewis (vbL) diagrams:



(5)

The two fragments are connected with a dative σ-bond stemming from one of the N_2 lone pairs to the empty CH_2 p_σ orbital, and a π−"back-transfer" conjugative interaction from the doubly occupied p_π orbital of CH_2 to the π system of N_2. The $-N_2$ triple bond remains practically intact as it lengthens by only ∼0.035 Å as compared with the free N_2 bond length.[4]

The characteristics of the chemically important dissociation of diazomethane to the CH_2 and N_2 fragments

$$CH_2N_2(\tilde{X}^1A_1) \rightarrow CH_2(\tilde{a}^1A_1) + N_2(X^1\Sigma_g^+) \qquad (6)$$

have caught the attention of the scientific community for more than half a century. It was early realized that this process had an energy barrier in C_{2v} symmetry, attributed to a Woodward−Hoffmann nonfavored dissociation.[12] As early as 1976, Lievin and Verhaegen pointed out the participation of the highly excited $\tilde{c}^1A_1$ state of CH_2 to the existing barrier and its involvement to the diazomethane equilibrium structure.[12,13] Even though their calculations along the $CH_2 + N_2$ singlet potential energy surface (PES) were rather minimal, these authors suggested that the

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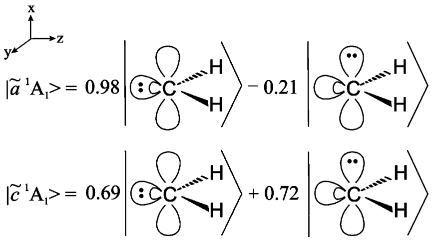
TABLE 1: Energies, Bond Lengths, Angles, and Energy Gaps of the Four Lowest-Lying States of CH_2 at the (CASPT3, MRBWCCSD, MRCI, MRCI+Q and MRACPF)/cc-pVTZ Levels of Theory

	E (E_h)	R_{C-H} (Å)	∠H−C−H (deg)	T_e (kcal/mol)
$\tilde{X}^3B_1$				
CASPT3	−39.074522	1.078	133.7	0
MRBWCCSD	−39.074928^a			0
MRCI	−39.074542	1.0787	133.3	0
MRCI+Q	−39.078511^b			0
MRACPF	−39.077245	1.0788	133.4	0
MRCI^c	−39.140113	1.0751	133.66	0
expt^d		1.07530	133.9308	0
$\tilde{a}^1A_1$				
CASPT3	−39.057323	1.110	101.5	10.79
MRBWCCSD	−39.060832^a			8.85
MRCI	−39.058916	1.1109	101.6	9.81
MRCI+Q	−39.063085^b			9.68
MRACPF	−39.061759	1.1107	101.7	9.72
MRCI^c	−39.125487	1.1061	102.20	9.178
expt		1.107 ± 0.002^e	102.4 ± 0.4^e	9.354^d
$\tilde{b}^1B_1$				
CASPT3	−39.019908	1.074	142.6	34.27
MRBWCCSD	−39.019484^a			34.79
MRCI	−39.019619	1.076	141.8	34.46
MRCI+Q	−39.024768^b			33.72
MRACPF	−39.023148	1.075	142.5	33.95
MRCI^c	−39.087831	1.0723	142.44	32.807
expt^f		1.086	139.3	
expt^g		1.053	140 ± 15	
$\tilde{c}^1A_1$				
CASPT3	−38.972117	1.068	173.9	64.26
MRBWCCSD	−38.974976^a			62.72
MRCI	−38.976951	1.066	173.9	61.23
MRCI+Q	−38.982550^b			60.22
MRACPF	−38.980791	1.068	171.3	60.53
MRCI^c	−39.046391	1.0657	171.92	58.811

[a] At the CASPT3-optimized geometry. [b] At the MRCI-optimized geometry. [c] All-electron calculation/d-aug-cc-pCV6Z basis, ref 24, [c] Reference 25. T_0 value converted to T_e using the zero-point energy difference from ref 26. [d] Reference 27. [e] Reference 28. [f] Reference 29.

formation of diazomethane can be thought of as a two-step barrierless process in C_s symmetry involving a perpendicular π-attack of N_2 to CH_2 ($\tilde{a}^1A_1$) followed by relaxation of the system to a C_{2v} geometry with the active participation of the CH_2 $\tilde{c}^1A_1$ state, and an opening of the ∠HCH angle from ∼102 to ∼126°.[12] This was verified and vividly exhibited in the complete active space third-order perturbation theory (CASPT3) PES by Papakondylis and Mavridis[4] with a correlation-consistent basis set of triple-ζ quality, cc-pVTZ.[14] The reason for the preferred barrierless approach of N_2 to CH_2 can be convincingly understood by examining the composition of the $\tilde{a}^1A_1$ and $\tilde{c}^1A_1$ valence complete active space (CAS) wave functions of CH_2:



(7)

The “0.98” configuration of the CH_2 $\tilde{a}^1A_1$ state hinders the approach of N_2 along the C_2 axis, explaining the presence of the energy barrier along this path. On the other hand, the “0.72” configuration of the incoming $\tilde{c}^1A_1$ state favors bonding along the C_2 axis, rationalizing the actual formation of a C_{2v} geometry stable CH_2N_2 species.[4] Therefore, even the qualitative description of the diazomethane dissociation would require at least a two-reference wave function, while a single-reference method would dramatically fail in this respect. For instance, utilization of the “0.98” configuration as a reference wave function should lead to an unbound C_{2v} CH_2N_2 system, while the use of the “0.21” configuration should, if calculable, lead to a *barrierless* potential energy curve in C_{2v} symmetry. Indeed, Boldyrev et al. mention that no barrier is found at the single reference MP2 level of theory,[15] apparently due to the participation of the “0.72” component in the ground $^1A_1$ state of CH_2N_2.

In light of the above, we believe that the multireference character of the CH_2N_2 dissociation process along its ground-state PES could provide a good testing ground for the newly developed MRBWCCSD method.

2. Methodology

The MRBWCCSD method is a size-consistent and approximately size-extensive multireference coupled-cluster method based on the use of the Brillouin−Wigner resolvent. In the present problem, the size-nonextensivity error ranges from 20 to 40 μE_H; thus, the results are practically size-extensive. Details of the MRBWCCSD ansatz have been extensively discussed previously.[16−20] The Hartree−Fock ground-state electronic configuration of diazomethane in C_s symmetry is

$$\tilde{X}^1A' = (\text{core})^6(4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(1a'')^2(2a'')^2(9a')^2 \quad (8)$$

where “core” denotes the total of six 1s-like electrons of C, N and N, respectively. The reference space for the MRBWCCSD calculations contains the (9a′) and (10a′) orbitals; therefore, it

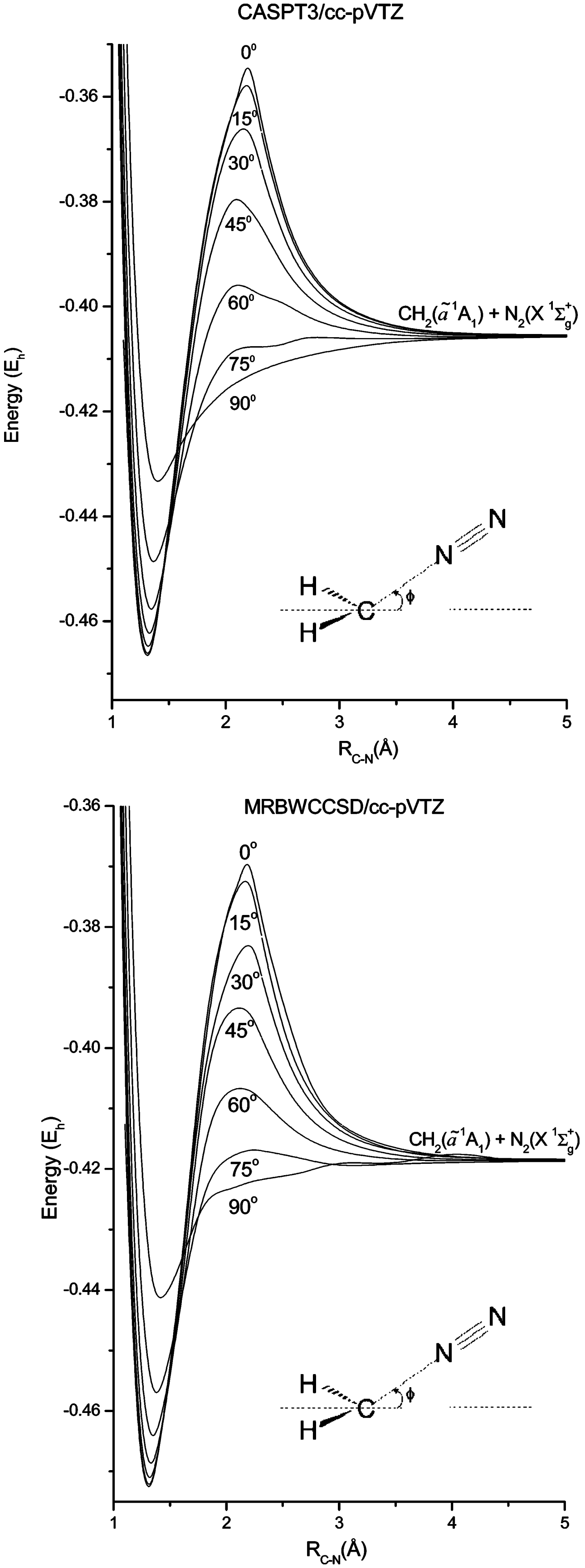


Figure 1. Potential energy curves of the $CH_2(\tilde{a}^1A_1)$ approach to N_2($X^1\Sigma_g^+$) for different ϕ angles at CASPT3/cc-pVTZ and MRBWCCSD/cc-pVTZ levels of theory. All energies have been shifted by +148 E_h.

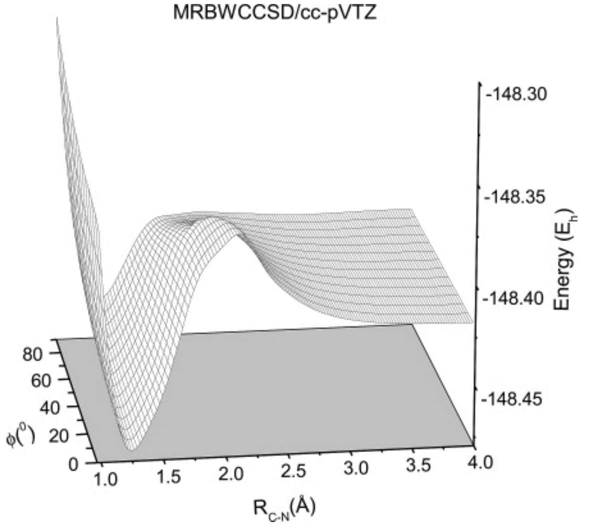


Figure 2. Three-dimensional illustration of the MRBWCCSD potential energy curves of Figure 1.

is a 2-electron/2-orbital complete active space (CAS) with the resulting CASSCF wave function composed of four singlet determinants (three singlet configuration functions). This reference space is adequate to correctly describe the two-configuration character of both ã and $\tilde{c}^1A_1$ states of CH_2. For purpose of comparison, the PES has also been calculated at the CASPT3 level employing the same CAS reference space, while the MRBWCCSD calculations are performed at the optimized geometries of the aforementioned CASPT3 surface. Note that the present CASPT3 calculation employs a smaller reference space than in ref 4 where a 12-electron/12-orbital reference space was used, the results, however, are practically the same (vide infra). Geometrical and energetical parameters for diazomethane were also calculated at the multireference configuration interaction level (MRCI), as well as the MRCI+Davidson correction (MRCI+Q) and multireference averaged coupled-paired functional (MRACPF) levels of theory. For reasons of uniformity, the cc-pVTZ basis has been employed in all methods.[14] For the MRBWCCSD calculations, we have used a version of the ACES II program extended for MRBWCCSD calculations;[21,22] the CASPT3, MRCI, MRCI+Q, and MRACPF results were obtained with the MOLPRO 2002 package.[23]

3. Results and Discussion

According to the results of Table 1, the first four low-lying states of CH_2 are described satisfactorily in all levels of theory as compared to either experiment or with the very large MRCI/d-aug-cc-pCV6Z calculations of Kalemos et al.[24] Note that the "renowned" $\tilde{a}^1A_1 \leftarrow \tilde{X}^3B_1$ energy gap of methylene is better predicted with MRBWCCSD (underestimated by 0.5 kcal/mol) than, for instance, by CASPT3 which, in turn, overestimates it by about 1.5 kcal/mol.

The CASPT3/cc-pVTZ-optimized bond length of N_2 is r_e = 1.1048 Å, in very good agreement with the experimental value of 1.0977 Å.[30] The CASPT3 and MRBWCCSD energies at the CASPT3 r_e are −109.36754 and −109.35775 E_h, respectively.

Figure 1 depicts different "slices" of the CASPT3 and MRBWCCSD ground-state PES of CH_2N_2 along the r_{C-N} and ϕ ("attack angle") coordinates. A three-dimensional representation of the MRBWCCSD curves is illustrated in Figure 2. A detailed explanation of the shape of the surface has already been given,[4] therefore only the main points will be summarized here. Ultimately, the surface shape is determined by the wave function composition (eq 7) of the $\tilde{a}^1A_1$ and $\tilde{c}^1A_1$ states of CH_2 and their relevant energy difference. The largest barrier, but also the

TABLE 2: Geometry and Energetics of CH_2N_2 at Various Multireference Levels of Theory (cc-pVTZ basis)

	CASPT3	CASPT3[a]	MRCI	MRCI+Q	MRACPF	MRBWCCSD	expt[b]
E (E_h)	−148.46979	−148.46935	−148.417234	−148.480411[c]	−148.482457	−148.47570[d]	
D_e (kcal/mol)[e]	40.3	38.2	36.6	38.5[c]	38.6	35.9[d]	
D_0 (kcal/mol)[f]	23.9	21.6	21.2	23.2[c]	23.3	21.4[d]	≤35,[g] ≤44,[h] ≤41.7,[i] 25[j]
barrier height (kcal/mol)[k]	34.5	∼26	36.2	34.8[c]	34.4	32.7[d]	
r_{C-N} (Å)	1.300	1.303	1.295		1.301		1.300
r_{N-N} (Å)	1.129	1.128	1.125		1.139		1.139
r_{C-H} (Å)	1.072	1.071	1.068		1.074		1.077
∠HCH(deg)	125.4	125.6	125.2		125.1		126.2
ϕ(deg)	0.0	0.0	0.0		0.0		0.0
∠NNC(deg)	180.0	180.0	180.0		180.0		180.0

[a] Reference 4. Basis set: cc-pVTZ, CAS active space: 12 electrons/12 orbitals. [b] Experimental geometrical values from ref 6. [c] Calculated at the MRCI optimized geometry. [d] Calculated at the CASPT3 optimized geometry, see text for details. [e] D_e values with respect to the *adiabatic* $CH_2(\tilde{a}^1A_1)$ + $N_2(X^1\Sigma_g^+)$ fragments. [f] D_0 values with respect to the *ground state* $CH_2(\tilde{X}^3B_1)$ + $N_2(X^1\Sigma_g^+)$ fragments; see text for details. [g] Pyrolysis, ref 31. [h] Electron impact, ref 32. [i] Photodissociation measurements, ref 33. [j] Flash photolysis, ref 34. [k] Barrier height with respect to the $CH_2(\tilde{a}^1A_1)$ + $N_2(X^1\Sigma_g^+)$ dissociation limit.

largest depth in the PES is observed at $\phi = 0°$, i.e., along the C_2 axis. The perpendicular attack ($\phi = 90°$) is, as mentioned already, barrierless, but the C−N bond is "weaker" than in any other ϕ orientation. As expected, for intermediate ϕ values (15−75°) the bonding situation becomes a "crossbreed" of the two extreme cases, $\phi = 0°$ and $\phi = 90°$. The participation of the $\tilde{c}^1A_1$ state of CH_2 becomes evident for $r_{C-N} < 2.3$ Å and is corroborated by the change in wave function composition after the energy maximum, and the sudden opening of the ∠HCH angle from 102 to 126°. Obviously, the involvement of the $\tilde{c}^1A_1$ state is maximized at $\phi = 0°$.

As shown in Figure 1, the PES morphologies are very similar in both MRBWCSSD and CASPT3 methods. The only qualitative difference between the two methods is that the MRBWCCSD perpendicular ($\phi = 90°$) attack of N_2 to $CH_2(\tilde{a}^1A_1)$ is not predicted to be barrierless, but it exhibits a small barrier of 1.1 kcal/mol. It is possible though that this is an artifact of the calculation since the MRBWCCSD calculations are performed on the CASPT3-optimized geometry.

Relevant numerical data for CH_2N_2 are collected in Table 2. The calculated equilibrium geometry in all levels of theory is in very good agreement with the experimental one. The H_2C-N_2 MRBWCCSD binding energy with respect to the adiabatic $CH_2(\tilde{a}^1A_1) + N_2(X^1\Sigma_g^+)$ dissociation channel is $D_e = 35.9$ kcal/mol, with the corresponding MRACPF value being 38.6 kcal/mol. Since literature experimental data refer to dissociation to the ground-state $CH_2(\tilde{X}^3B_1) + N_2(X^1\Sigma_g^+)$ channel, our MRBWCCSD calculated binding energy with respect to the ground-state fragments, taking into account the zero-point energy of 5.6 kcal/mol,[4] is $D_0 = 21.4$ kcal/mol. The corresponding CASPT3, MRCI, MRCI+Q, and MRACPF D_0 values are 21.6, 21.2, 23.2, and 23.3 kcal/mol. There are many different experimental upper bound estimates in the literature regarding the binding energy of the H_2C-N_2 bond.[31−33] Even though the purpose of this paper is not to extract the most accurate D_e value of CH_2N_2, we note that all our values are in fair agreement with the work of Braun et al., $D_0 = 25$ kcal/mol.[34] Finally, all the methods used in the present work predict a barrier to dissociation of 33−35 kcal/mol.

4. Concluding Remarks

The potential energy surface of diazomethane (CH_2N_2) in its ground state along the r_{C-N} and ϕ ("attack" angle of N_2 to CH_2 on the C_s plane) coordinates was studied with the CASPT3 and the MRBWCCSD methods, and energetics were contrasted to the MRCI, MRCI+Q and MRACPF methods. The inherent multireference character of the surface due to the two-configurational description of the CH_2 $\tilde{a}^1A_1$ and $\tilde{c}^1A_1$ states, and the involvement of the latter to the formation of stable diazomethane could adequately be described by the MRBWCCSD method. Guided by the latest successful tests of the method, as well as the very recent inclusion of triple excitations in the MRBWCCSD ansatz,[35] we will continue examining its capabilities as a multireference coupled-cluster alternative to conventional approaches for the description of small and medium-sized chemical systems, specifically in cases where single-reference coupled cluster methods are problematic.

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