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SiC_2 Revisited in a DFT Light

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For the first time various pure and hybrid density functionals with three larger basis sets have been used to study the troublesome and the most forensic molecule, SiC_2. It is concluded that BLYP and B3LYP functionals have failed to predict the cyclic form of SiC_2 as the most stable structure over its linear counterpart even with the most flexible basis set, 6-311+G(3df). On the contrary, the other two pure density functionals of Perdew, Perdew and Wang with larger basis sets correctly identify the minimum energy structure. Finally, the two hybrid functionals B3P86 and B3PW91 predict the cyclic isomer of SiC_2 to be more stable than the linear and the increase in the size of the basis set increases the stability of the former. The energy difference between the cyclic and the linear structures, 2.89 kcal/mol, obtained in B3PW91/6-311+G(3df) is better than that of MBPT(2) using the largest 120 CGTO basis set. This difference in energy is better than that of most of the highly sophisticated ab initio levels. Besides, it just deviates 1.03 and 0.62 kcal/mol from the two accurate levels in ab initio, CBS-Q and G2, respectively. The linear structure is shown to be a transition state in all the functionals with the two larger basis sets. The geometries obtained at B3P86 and B3PW91 levels using 6-311+G(3df) basis set excellently agree with the experimental values. The controversial ν_3 vibrational mode obtained in the abovesaid hybrid functionals with the same large basis set coincides better with the experimental value than any of those obtained using ab initio methodologies. Some LYP-containing functionals result in a more stable bent structure on the SiC_2 pinwheel surface lying between the linear and cyclic structures, but in some other functionals this bent structure is shown to be a transition state. Finally, no such bentlike structure of the SiC_2 molecule has been found in B3P86 and B3PW91 levels with the 6-311+G(3df) basis set.

1. Introduction

It took more than 70 years to arrive at a concrete conclusion about the structure of, not a gigantic organic compound, but a simple triatomic molecule with 26 electrons, the so-called SiC_2. Schaefer group made three attempts during the past 13 years to find out the exact energy difference (ΔE) between the linear and the cyclic structures of the SiC_2 molecule.[1−3] The history of the SiC_2 molecule is very interesting. The blue-green absorption bands of the SiC_2 system were first reported in 1926 by Merrill[4] and Sanford[5] in the spectra of certain carbon-rich stars. But the first identification was made only after 30 years. In 1956, Kleman[6] gave the first identification of SiC_2 in the laboratory, and it took another 25 years to gain knowledge about the ground-state electronic structure of the SiC_2 molecule. The first historic evidence of its cyclic nature was proposed by Grev and Schaefer[1] in 1983 through ab initio theory which contradicted the earlier reports of its linear nature. Simultaneously, Michalopoulos et al.[7] proved the existence of the cyclic nature of SiC_2 as the ground-state experimentally. Nielsen et al.[3] visited the SiC_2 field with all the available improved ab initio methodologies and concluded that the global minimum of SiC_2 is a T-shaped C_{2v} (cyclic) structure connected monotonically to a linear transition state which is 5.8 kcal/mol higher in energy, thus ruling out any metastable linear isomer. In the meantime, numerous works have been carried out on this important molecule to find out the correct energy difference.[8]

Almost all the levels of theory existing in ab initio have made use of all the available basis sets on the SiC_2 molecule. The conclusions from the earlier studies[1,3,9−11] are as follows. (a) At the SCF level of theory, the linear structure is the global minimum (∼5 kcal/mol), but a carefully optimized basis set may forecast the cyclic form to be slightly more stable (1.2 kcal/mol). (b) At MP2 with DZ(d) basis set, the ΔE ($E_{\text{cyclic}} - E_{\text{linear}}$) value is underestimated though it identifies the cyclic ground state, and the increase in the size of the basis set increases the ΔE value. But the larger basis set (cc-pV5Z) overestimates the energy difference. (c) The increase in the order of the Moller−Plesset perturbation theory gives different results. The ΔE value obtained at the MP3/DZ(d) level is less than the MP2/DZ(d) value. The MP4 comes out with the linear ground-state structure. (d) Quadruple excitation provides additional stabilization for the cyclic form, but sizable triples destabilization of cyclic SiC_2 is also documented, and finally, again linear is the minimum energy state. (e) Correlation through configuration interaction also gives an unpredictable result. The CISD/DZ(d) predicts the linear SiC_2 as the global minimum state. (f) The coupled cluster approximation is unable to succeed strongly in identifying the correct ground-state structure. At CCSD/DZ-(d), ΔE is -1.636 kcal/mol but the inclusion of triples reduces the ΔE value to -0.151 kcal/mol. The TZ(d) basis set further worsens the situation in almost all the levels.

The contradiction in detecting the correct ground state is documented in other ab initio levels also. At the G2 level,[12] ΔE is -3.51 kcal/mol, while the correct ΔE is -5.8 kcal/mol.

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The highest level of theory, cc-pVTZ CCSD(T), used by Nielsen et al.[3] predicts that the cyclic SiC_2 is more stable than the linear by 3.82 kcal/mol with the overestimation of the Si−C bond length by 0.01 Å and some underestimation of the ν_3 mode frequency. After a marathon effort, Nielsen et al.[3] obtained the ΔE value as −5.8 cal/mol. The only well comparable ΔE value of −5.2 kcal/mol had been obtained at QCISD/6-311+G(3df).[13]

In almost all the levels except QCISD/6-311+G(3df), the problem is not only restricted to the ΔE value alone but extended to R(Si−C) and ν_3 values also. As Sadlej et al.[10] concluded, "... would require a highly correlated calculation, most likely by methods such as CCSDT with larger basis sets probably not less than 150 CGTOs", larger basis sets with highly correlated levels may be very important. But after Nielsen et al.'s success in predicting the correct ΔE value, they were forced to conclude that "... a discrepancy greater than 0.01 Å between the theory and the experiment remains to be resolved for R(Si−C)".[3] The above facts indirectly pinpoint that higher level ab initio methodologies with the largest basis set are necessary to predict the exact ΔE value for a molecule like SiC_2, but with some unavoidable structural/vibrational discrepancies. If this situation arrives/continues for a larger molecule there will be no solution other than to handle the problem with Density Functional Theory (DFT), for its less computational difficulty. So in the present investigation we have aimed at making use of various pure and hybrid density functionals to overcome the existing disparity between the theory and the experiment in the SiC_2 case. Moreover, a molecule like SiC_2 is a good platform to analyze the various density functional models in predicting the ΔE as well as other important parameters.

Nowadays, DFT plays a prominent role in studying the chemistry of the molecules. It has been already shown in many occasions that the results obtained from the hybrid DFT methods are highly comparable in quality with experimental values.[14−18] The results produced particularly at the B3LYP level are better than those obtained from MP2, MP3, and even MP4 and are in quite close agreement with the experimental values. In some case, the results generated at hybrid density functionals are of the same quality as CCSD or G2 levels. So it would be better to utilize these hybrid functionals to study the SiC_2 molecule since the computational cost for these functionals is less than that of the high level ab initio calculations.

We report below a detailed analysis of the difference in energies, geometries, and vibrational frequencies of the cyclic and the linear isomers of SiC_2 molecule at different available levels of sophistication both with respect to the three larger basis sets and various pure and hybrid density functionals. The present investigation is also extended to MP2 with two larger basis sets and the complete basis set ab initio model.[19]

2. Computational Methodology

All the calculations were performed with the Gaussian 94 computational packages.[20]

Both pure and hybrid DFT calculations have been carried out. In pure DFT methods, the exchange functional is Becke's gradient-corrected (B)[21] and the correlation functional is the gradient-corrected correlation, by Lee, Yang, and Parr (LYP),[22] by Perdew (P86),[23] and by Perdew and Wang (PW91).[24] So by notation, these three functionals are BLYP, BP86, and BPW91, respectively. The hybrid DFT methods include a mixture of Hartree−Fock exchange and DFT exchange correlation. They are Becke's three-parameter functional[25] which has the form $AE_x^{\text{slater}} + (1 - A)E_x^{\text{HF}} + B\Delta E_x^{\text{Becke}} + E_c^{\text{VWN}} + C\Delta E_c^{\text{nonlocal}}$, where the nonlocal correlation is provided by any one of the expressions of Lee−Yang−Parr,[22] Perdew 86,[23] or Perdew−Wang 91.[24] These three hybrid methods are B3LYP, B3P86, and B3PW91 by notation. The constants A, B, and C are those determined by Becke by fitting the results in the G1 molecular set.[26] The MP2 level of theory has also been used. Since the basis set improvement has played a dominant role in the earlier studies on the SiC_2 molecule, the present investigation also includes the complete basis set (CBS-Q)[19] model. It starts with the geometry optimization at the MP2 level with the zero-point energy computed at the HF level of theory. Then the energy is evaluated at the MP2 level of theory with a larger basis set and CBS extrapolation to correct the energy through the second order. Two additional calculations have been used to approximate the contributions of higher orders {MP4(SDQ)/6-31G(d,p) and QCISD/6-31+G†}. There are also empirical corrections for spin contamination and a size-consistent higher-order correction.

Three types of basis sets, 6-31+G(d), 6-311+G(2d), and 6-311+G(3df), have been used for pure and hybrid density functional calculations, and the last two basis sets have been employed for MP2 calculation. The zero-point energy (ZPE) correction has also been made by calculating the vibrational frequencies which is also useful to identify the nature of the isomers.

3. Results and Discussion

The calculated geometrical parameters and the relative energy $\Delta E(E_{\text{cyclic}} - E_{\text{linear}})$ have been summarized in Table 1 along with the experimental values.[27] The results obtained in almost all the pure density functionals deviate much from the experimental values. By far the worst, the BLYP/6-31+G(d) level overestimates the Si−C bond length by more than 0.04 Å for the cyclic structure, but the increase in the size of the basis set reduces the difference. This deviation is found to be small in the other two pure functional calculations. A maximum difference of 0.01 Å is obtained in the case of C−C bond length for the same structure at the BLYP/6-31+G(d) level. Some difference in bond lengths is documented in hybrid functionals with the smallest basis set (6-31+G(d)). But with the largest basis set (6-311+G(3df)) all the pure and hybrid functionals provide results which are very much in unison with the experimental values. An excellent agreement is arrived at both B3P86 and B3PW91 functionals with 6-311+G(3df) basis set. But as described by Nielsen et al.,[3] a discrepancy greater than 0.01 Å in R(Si−C) between the theory and the experiment again appeared in the B3LYP/6-311+G(3df) level. Such deviation has not been observed at the MP2/6-311+G(3df) level, but instead, it reappeared for the R(C−C) case. This deviation at the B3LYP level may be due to the small overestimation of the dipole moment (0.12 D for the cyclic structure), while the same parameter obtained using the other two hybrid functionals with the same 6-311+G(3df) basis set is excellently coincides with the experimental value.

The difference in bond length is also evident from the Mulliken charges. Based on both ab initio[28] and experimental grounds,[29,30] SiC_2 is a highly ionic molecule of the form $Si^{+\delta}$ $(C_2^{-\delta})$ with $\delta = 0.34$ e. Though some deviation from the above value is documented in both B3P86 and B3PW91 calculations with the 6-311+G(3df) basis set, more deviations have been recorded only in B3LYP calculation. Here it is worthwhile to note that, in the case of benzene, the LYP-containing correlation functional fails to reach the uniform electron gas limit.[31,32] The Si−C bond length obtained at the highest level of theory (aug-cc-pVTZ CCSD(T)) has a 0.016 Å difference[3] with the

TABLE 1: Structures and Relative Energies of SiC_2[f]

	linear		cyclic			ΔE	
level of theory[e]	R(Si−C)	R(C−C)	R(Si−C)	R(C−C)	Θ(C−Si−C)	before ZPE	after ZPE
BLYP/A	1.720	1.300	1.876	1.282	40.0	5.10	4.54
BLYP/B	1.714	1.288	1.868	1.270	39.8	2.90	2.91
BLYP/C	1.710	1.288	1.861	1.270	39.9	2.35	2.46
B3LYP/A	1.671	1.270	1.857	1.271	40.0	3.21	2.61
B3LYP/B	1.696	1.276	1.851	1.260	39.8	0.82	0.68
B3LYP/C	1.693	1.276	1.844	1.260	40.0	0.16	0.20
BP86/A	1.718	1.302	1.867	1.284	40.2	1.96	1.70
BP86/B	1.712	1.291	1.861	1.273	40.0	−0.33	−0.20
BP86/C	1.709	1.291	1.854	1.273	40.2	−0.98	−0.78
B3P86/A	1.698	1.287	1.848	1.271	40.2	0.31	−0.09
B3P86/B	1.693	1.277	1.843	1.261	40.0	−2.17	−2.11
B3P86/C	1.689	1.277	1.835	1.261	40.2	−2.93	−2.78
BPW91/A	1.717	1.301	1.864	1.283	40.3	1.47	1.25
BPW91/B	1.711	1.289	1.859	1.273	40.0	−0.87	−0.71
BPW91/C	1.708	1.289	1.851	1.272	40.2	−1.57	−1.34
B3PW91/A	1.700	1.289	1.850	1.272	40.2	0.27	−0.10
B3PW91/B	1.695	1.278	1.845	1.263	40.0	−2.25	−2.19
B3PW91/C	1.692	1.278	1.838	1.262	40.2	−3.04	−2.89
MP2/B	1.707	1.288	1.848	1.278	40.5	−2.55	−2.64
MP2/C	1.701	1.288	1.835	1.278	40.8	−5.64	−5.56[a]
CBS-Q						−3.92	
G2[b]						−3.51	
expt[c]			1.832	1.269	40.4	−5.40[d]	

[a] ZPE at MP2/6-311+G(2d)//MP2/6-311+G(3df). [b] Reference 12. [c] Reference 27. [d] Reference 13. [e] A = 6-31+G(d); B = 6-311+G(2d); C = 6-311+G(3df). [f] Bond lengths in Å, bond angles in degrees, and $\Delta E(E_{\text{cyclic}} - E_{\text{linear}})$ in kcal/mol.

experimental value. But B3P86 and B3PW91 hybrid density functionals with the most flexible basis set provide more reliable geometrical parameters. Similar in the linear structure too, the calculated R(Si−C) values in pure density functional models deviate from the experimental value. But the geometrical parameters obtained in the hybrid density functionals agree well with that of the QCISD/6-311+G(3df) level.[13] Thus, from all the above facts it could be concluded as described by Jursic that “. . . this is an excellent agreement between the very CPU-expensive ab initio methods and the modest CPU-demanding hybrid DFT methods”. In fact, the values obtained at hybrid functionals are much better than those obtained in many high-level ab initio methods.

The B3LYP functional completely failed in predicting the minimum energy structure of SiC_2 with all the basis sets. It predicts the linear structure to be energetically more stable than the cyclic even with the most flexible basis set, 6-311+G(3df), after ZPE correction. In most of the earlier cases, B3LYP succeeded in predicting the difficult parameters with greater accuracy. This peculiar behavior of the B3LYP functional in the case of SiC_2 may be due to the small overestimation of the dipole moment and the δ value and hence the poor geometry. A similar trend has also been noticed in the pure LYP-containing functional. The linear is more stable than the cyclic by 2.61 kcal/mol at B3LYP with the smallest basis set, but with the largest basis set ΔE is just 0.2 kcal/mol. BLYP/6-31+G(d) favors the linear by 4.45 kcal/mol, while with 6-311+G(3df) basis set it decreases the ΔE value to 2.46 kcal/mol. It is gratifying to note that the other two pure functionals with the two larger basis sets correctly identify the cyclic as the more stable structure. The 6-31+G(d) basis set is not at all sufficient to identify the global minimum structure in both BP86 and BPW91 functionals. So it is obvious that the increase in the size of the basis set plays a vital role in identifying the most stable structure. Comparing the two pure functionals BP86 and BPW91, the ΔE value calculated at the latter functional is higher than that at the former. The cyclic structure is more stable than the linear by 1.34 kcal/mol at the BPW91/6-311+G(3df) level. This value is well comparable with many of the highly correlated ab initio results. For example, the ΔE values calculated at the MP4/DZ+P (including single, double, and quadruple substitution), CCSD/DZ+P, CCSD+T(CCSD)/DZ+P, and CISD/DZ+P levels are −1.44, −1.78, −0.13, and −1.13 kcal/mol, respectively.[11] Again, ΔE values are −0.23 and −1.6 kcal/mol at MP4 and CCSD+T(CCSD), respectively, with a larger basis set (6s5p1d/6s4p1d).[11]

The two hybrid functionals B3P86 and B3PW91 with the smallest basis set provide poor results. Though the ZPE correction is very small, it plays a key role in predicting the global minimum structure at some level of calculations. Both the B3P86 and B3PW91 functionals with 6-31+G(d) basis set declare the linear structure is more stable than the cyclic structure before ZPE correction, but the inclusion of the correction reverses the trend. The results obtained with the 6-311+G(2d) basis set are well comparable in quality with the results of the 6-311+G(3df) basis set. The difference in ΔE values between these two basis sets is about 0.7 kcal/mol in both B3P86 and B3PW91 functionals. So it is obvious that the basis set of at least 6-311+G(2d) quality is very important to predict the reliable ΔE values but further enhancement of the basis set shows no noticeable improvement. The cyclic structure is more stable than the linear by 2.78 and 2.89 kcal/mol in B3P86 and B3PW91 functionals, respectively, with the 6-311+G(3df) basis set. Even though these values are below the values obtained by Nielsen et al.[3] and by Rose et al.,[13] qualitatively they are much better than those obtained in various high-level ab initio methodologies. So it is not contradictory to say that both the hybrid functionals are better and are of higher quality than many other high-level ab initio calculations. In fact, computational cost of these two functionals is less compared to that of ab initio methods. But to reach the final goal with DFT, i.e., to find out the exact ΔE value, the time is needed for some better functionals rather than the enhancement of the basis sets.

The ΔE values calculated at the MP2/6-311+G(2d) and MP2/6-311+G(3df) levels are −2.64 and −5.56 kcal/mol, respec-

TABLE 2: Unscaled Vibrational Frequencies for SiC_2 in cm^{-1}

level of theory[d]	linear	cyclic
BLYP/A	154, 752, 1848	43i, 748, 1765
BLYP/B	74i, 753, 1844	91, 750, 1765
BLYP/C	26i, 759, 1855	159, 760, 1722
B3LYP/A	161, 792, 1927	115i, 785, 1838
B3LYP/B	81i, 791, 1921	58i, 784, 1832
B3LYP/C	19i, 797, 1928	125, 795, 1837
BP86/A	128, 758, 1852	151, 767, 1764
BP86/B	105i, 758, 1846	174, 766, 1760
BP86/C	79i, 763, 1855	217, 776, 1766
B3P86/A	143, 800, 1938	98, 804, 1845
B3P86/B	105i, 798, 1929	133, 801, 1835
B3P86/C	70i, 803, 1935	194, 811, 1840
BPW91/A	124, 760, 1857	170, 773, 1768
BPW91/B	107i, 760, 1851	188, 771, 1764
BPW91/C	84i, 765, 1859	233, 781, 1769
B3PW91/A	138, 797, 1931	100, 802, 1838
B3PW91/B	106i, 795, 1922	133, 798, 1828
B3PW91/C	74i, 800, 1929	195, 809, 1832
MP2/B	57i, 722, 1891	67, 796, 1733
MP2[a]	73i, 781, 1894	186, 819, 1729
expt[b]		160, 824, 1741
expt[c]		196, 841, 1746

[a] MP2/6-311+G(2d)//MP2/6-311+G(3df). [b] Reference 33. [c] Reference 30. [d] A = 6-31+G(d); B = 6-311+G(2d); C = 6-311+G(3df).

tively. These values indicate that the MP2 calculations are still far from being basis set converged. In addition, it further increases the ΔE value while increasing the size of the basis set.[3] One point from Nielson et al.[3] worth mentioning is that one needs to go well beyond the second-order level of theory to mostly cancel the basis set incompleteness error by inexactness of the electron correlation treatment. In comparing the two accurate ab initio levels G2 and CBS-Q, the latter comes out with the more reliable ΔE value.

It is important to note that some bent transition-state and L-shaped minima are documented at a relatively high level of theory in Nielsen et al.'s work.[3] So in the present study, computations have been made to find out the existence of these two structures (we call it just bent structure), if it really exists on the SiC_2 pinwheel surface. All the density functionals which were used for the cyclic and linear structure calculations have been utilized for this purpose. The bent structure has been found to be more stable than the cyclic structure in some LYP-containing functional calculations. Briefly, the bent structure is more stable than the cyclic by 3.25, 2.36, 1.62, 0.32, and 0.96 kcal/mol at BLYP/6-311+G(2d), BLYP/6-311+G(3df), B3LYP/6-311+G(2d), B3LYP/6-311+G(3df), and BP86/6-311+G(2d) levels, respectively. The geometry obtained for the bent structure in B3LYP/6-311+G(3df) is $R(\mathrm{Si-C}) = 1.697$ Å, $R(\mathrm{C-C}) = 1.277$ Å, and $\theta(\mathrm{Si-C-C}) = 117.7°$. This bent structure turns out to be a transition state in the BPW91/6-311+G(2d), B3P86/6-311+G(2d), B3PW91/6-31+G(d), and B3PW91/6-311+G(2d) levels. In all the other levels we could not find such a bent structure. So, as described by Nielsen et al.,[3] these stationary points are spurious.

The vibrational frequencies (without anharmonic correction) calculated at all the levels have been presented in Table 2. Calculations have been done not only to provide the frequencies or to correct ZPE but also to identify the transition-state structure. This is of great importance, since many high-level ab initio theories have failed to identify the linear structure as the transition state. From the present study, the linear structure is shown to be a transition state in all the functionals with the two larger basis sets.

The frequencies ν_2(Si−C stretch) and ν_3(antisymmetric bend) have not been unambiguously assigned yet.[30,33] Much controversy over these two modes has been observed in the literature. The two recent experiments provide two different values (160.4 and 196.4 cm^{-1}) for the ν_3 mode,[30,35] so it is better to analyze the vibrational frequencies by DFT methods. In the present study, we have not made any scaling for the calculated frequencies as it is a hard topic still for DFT frequencies and the final conclusion is yet to come out.[16,17,34] Further, various functionals and different types of basis sets have been used, and hence a uniform scaling is not possible in the present study.

It is observed that the quality of the ν_3 mode improves while increasing the size of the basis set. The values (194 and 195 cm^{-1}) obtained at B3P86 and B3PW91 with 6-311+G(3df) basis set are in excellent agreement with the experiment (196.4 cm^{-1}), but B3LYP with the same basis set underestimates this mode by over 70 cm^{-1}. The same ν_3 mode calculated at QCISD/6-311+G(3df) and CCSD(T)/aug-cc-pVTZ levels is 152 and 137 cm^{-1}, respectively.[13,3] This fact once again confirms that the vibrational frequencies calculated through hybrid density functionals are in better agreement with the experimental results than either MP2 or even CCSD values.[16,17] The varying performance of the B3LYP functional in calculating the vibrational frequencies has also been noticed in some sulfur-containing molecules,[17] where the B3P86 functional has outclassed MP2 and B3LYP.

The Si−C stretching frequency (ν_2) obtained at B3P86 and B3PW91 functionals with the 6-311+G(3df) basis set agrees better with the experimental value than that of B3LYP. The differences in the ν_2 mode between the experiment and those obtained from B3P86/6-311+G(3df), B3PW91/6-311+G(3df), QCISD/6-311+D(3df), and CCSD(T)/aug-cc-pVTZ levels of theories are 30, 32, 20, and 43 cm^{-1}, respectively. But surprisingly, all the hybrid density functionals overestimate the ν_1(C−C) stretching frequency by around 100 cm^{-1}. This may be due to the omission of anharmonic corrections. A geometric progression correlation factor may also be very much essential to obtain the reliable value. So for the higher frequency mode, scaling is very important for the DFT frequencies to obtain the expected accuracy. After scaling (0.97) as suggested by Altmann et al.[17] for B3P86 frequencies, the calculated values are 188, 787, and 1785 cm^{-1}. These values coincide better with the experimental values than any of the earlier ab initio values. The unscaled frequencies obtained at both B3P86 and B3PW91 hybrid density functionals using the 6-311+G(3df) basis set coincide well with the values of QCISD/6-311+G(3df) for the linear structure. Thus, the frequencies obtained using these two hybrid functionals with proper corrections would be the most reliable values. The present study reveals that the B3P86 and B3PW91 functionals have outdone the B3LYP functional in all the departments, which is probably linked to better geometries arising from DFT calculation with the former two functionals. The MP2/6-311+G(2d)//MP2/6-311+G(3df) level provides a reliable vibrational spectra, but MP2/6-311+G(2d) underestimates the crucial ν_3 bending mode for the cyclic structure.

4. Conclusions

Though the complete and the most surprising failure of both the pure and the hybrid LYP-containing density functionals are documented in predicting the energy difference between the cyclic and the linear structures of the SiC_2 molecule, most of the other functionals precisely identify the cyclic structure as the global minimum state for the SiC_2 molecule. The energy difference obtained in B3P86 and B3PW91 hybrid functionals has ∼3 kcal/mol deviation from the exact ΔE value but is far better than many high-level ab initio calculations and is very close to the values obtained at CBS-Q and G2 ab initio theories. Some LYP-containing functionals come out with the bent as the most stable structure. There is an excellent correspondence between the predictions of the geometrical parameters at B3P86 and B3PW91 functionals and the experiment. A deviation of 0.01 Å in the R(Si−C) bond length is appeared in the B3LYP/6-311+G(3df) level of calculation. The linear structure has been shown to be a transition state in all the functionals with the two larger basis sets. Finally, it could be concluded that both B3P86 and B3PW91 functionals with larger basis sets may provide reliable results, but one should be cautious on the B3LYP functional. From the above facts, it is worth mentioning that DFT is better than many computationally costlier higher ab initio levels but it still requires a promising functional to overtake all the available ab initio methodologies to handle the crucial situations like the ΔE of SiC_2. The day will come soon and the milestone to be reached is not far ahead; as Parr described, "DFT will be the real gold mine".

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