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REGULAR ARTICLE

Computational methods for analysis of an unsaturated carbocycle: heptafulvene

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Abstract With respect to geometric optimizations, harmonic vibrational frequencies and single point conformational energies, various computational methods [HF, MP2, CCSD(T), BD(T), CASSCF, CASPT2, and DFT] were evaluated for their suitability to describe the heptafulvene system. We found that a significant number of basis sets lead to wrong predictions of folded minima, when ab initio methods including dynamic electron correlation are used. Possible explanations for these inconsistencies, such as wave function instabilities, near linear dependences of the basis sets and inadequate inclusion of polarization functions in the basis set, are discussed. Such concerns are likewise important for other classes of π-conjugated compounds, such that the results are expected to be of interest not only for heptafulvenes.

Keywords Ab initio calculations · Carbocycles · Density functional calculations · Hydrocarbons · Quantum chemistry

1 Introduction

Heptafulvene (**1**, Fig. 1) is a fully unsaturated seven-membered carbocycle consisting of a cross-conjugated eight π-electron system, including one semi-cyclic carbon–carbon double bond [1, 2]. This π-system shares physico-chemical similarities with heptalene (**2**) and heptafulvalene (**3**) [3]. These compounds, in turn, comprise heptafulvene substructures, so theoretical investigations of heptafulvene **1** can lead to further understanding of the properties of both heptalenes and heptafulvalenes. Further, many substituted heptafulvenes are known in the literature [4], and heptafulvene substructures are found in many complex-conjugated polycyclic molecules [5, 6]. Therefore, an investigation of the parent heptafulvene **1** can be expected to reveal facts that will be important for a whole family of related molecules.

The physico-chemical properties and other theoretical aspects of heptafulvenes have frequently been the focus of computational investigations [7–17]. Fundamental pioneering work was conducted by Krygowski et al. [7, 15], Radom et al. [10], Schleyer et al. [16], and Tidwell et al. [13, 16], among others. In silico analyses are particularly important in the field of heptafulvene chemistry, because many derivatives suffer from limited stability, complicating their synthesis and experimental analysis [1, 2, 4]. This is especially true for the highly unstable parent heptafulvene **1**, the simplest known representative of this compound class [1]. It is a pure hydrocarbon that consists of only the eight carbon atoms, essential to build the basic heptafulvene skeleton. Most of the previous computational investigations of heptafulvene used restricted mono-determinantal methods, such as Hartree–Fock (HF) [7–13], second-order Møller–Plesset perturbation theory (MP2) [9–13], or density functional theory (DFT) method [7, 8, 10, 14–16]. For these analyses, Pople-type basis sets, such as the 6-31G(d,p) set, have most typically been employed.

Generally, one of the central questions in the field of fulvene chemistry is the polarization of the semi-cyclic double bond [18]. Likewise, among the theoretical approaches to heptafulvene, the polarization of the semi-cyclic bond

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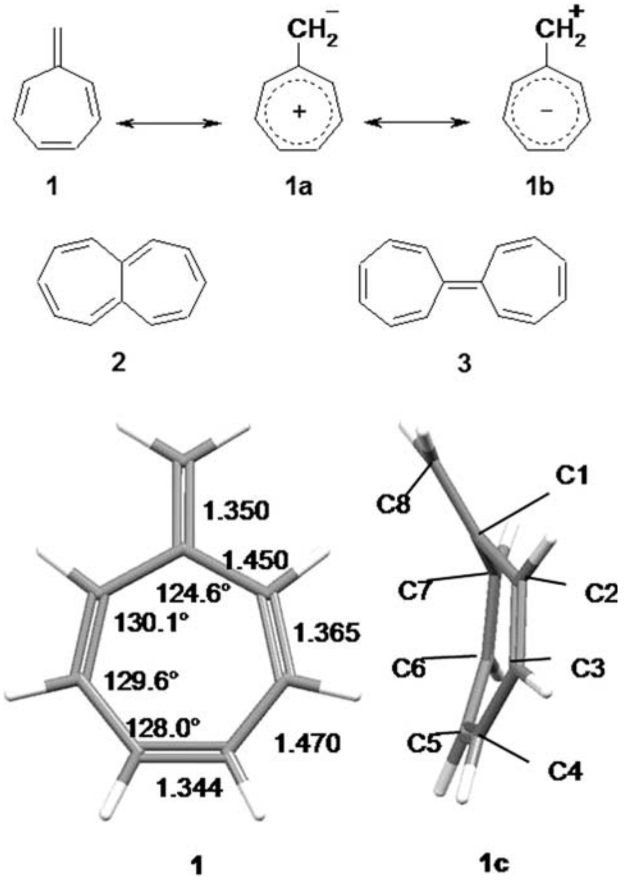

Fig. 1 Molecular structures of heptafulvene (**1**), heptalene (**2**) and heptafulvalene (**3**) as well as some of the geometric parameters [bond angles (°); bond lengths (Å)] of **1** obtained by microwave spectroscopy [22]

has been the subject of particularly intense discussion [13, 15]. Negative polarization of the exocyclic carbon atom in **1** could be described by contributing structure **1a**, and positive polarization by structure **1b** (Fig. 1) [14]. Depending on which of these two mesomeric structures contributes more significantly to the resonance hybrid of **1**, the seven-membered ring of heptafulvene can be characterized as aromatic (six π electrons, **1a**) or antiaromatic (eight π electrons, **1b**). It must be stressed, however, that the properties of heptafulvene are best described as non-aromatic [7, 19, 20], and many authors reported only a very slight polarization toward a zwitterionic character [21]. This interpretation is supported by the small dipole moment of heptafulvene, which is only 0.477 D [22]. Most of the previous theoretical investigations arrived at the conclusion that heptafulvene has only a weakly aromatic character. However, based on calculations of nuclear magnetic properties, a slight antiaromatic character of **1** has also been inferred [9], because calculations of nucleus-independent chemical shifts (NICS) [23] of **1** give positive values [7, 9, 11]. It was stressed, however, that these might be better interpreted as paratropicity of the ring instead of antiaromaticity [11]. Thus, **1** might belong to a unique class of compounds that are paratropic but non-antiaromatic systems [24].

Another topic that has led to controversial discussions is the conformational preference of the heptafulvene ring system [3, 10, 25–27]. A planar equilibrium structure was determined for **1** [22], but folded conformations, analogous to geometry **1c** in Fig. 1, have been found for some of its derivatives. The magnitude of the conformational energies of **1** is strongly related to the torsion potential between conjugated double bonds. Therefore, the conformational analysis of heptafulvenes might give interesting insights into the properties of π-conjugated compounds, in general.

In this paper, we report an evaluation of the suitability of various computational methods for the physico-chemical characterization of heptafulvenes. Despite the numerous theoretical analyses published so far, to the best of our knowledge, the adequacy of different computational methods has not yet been investigated systematically. We have compared data obtained with different computational methods to experimental data, and focused solely on calculations of the parent heptafulvene.

Few experimental data are available that could serve as a comparison to evaluate computational results. In Fig. 1, some of the experimentally determined geometric parameters are presented. These bond lengths and bond angles were obtained via microwave spectroscopy of **1** [22]. This spectroscopic analysis revealed further that heptafulvene has a planar equilibrium conformation with a low frequency out-of-plane bending mode of 70 ± 11 cm^{-1}.

2 Computational details

All methods used in these investigations are based on the Born–Oppenheimer approximation, one of the well-known assumptions of quantum chemistry [28], which states that the motion of electrons and nuclei can be decoupled due to the great difference in their masses. A possible breakdown of this (adiabatic) approximation was not considered.

For the comparative studies presented here, we employed the most frequently used computational methods based on the molecular orbital (MO) theory and DFT. Besides to the simple HF self-consistent field (SCF) method, we used DFT methods and post-SCF methods in order to include dynamic electron correlation after the orbital determining (SCF) step. As representatives of the post-HF methods, we used the second-order Møller–Plesset perturbation theory (MP2) and the coupled cluster (CC) method. Non-dynamic (static) electron correlation was considered by the complete active space SCF (CASSCF) approach. Moreover, an inclusion of dynamic electron correlation was also combined with multi-configurational wave functions using the second-order multireference (Rayleigh Schrödinger) perturbation theory (CASPT2). References and detailed descriptions of these methods and the different basis sets are presented in more detail in the later sections. In the discussions, the HF, DFT, and MP2 methods are regarded as a group of "computationally less expensive methods". The phrase "electron correlated", without further specification, refers to dynamic electron correlation. The basis sets employed use either pure d-functions (5D) or Cartesian d-functions (6D), according to the default settings of the Gaussian03 [29] program package. These default Gaussian settings were also used in the calculations performed with the MOLPRO [30] package. Hence, the default setting of the MOLPRO package was changed to Cartesian functions for Pople's 6-31G basis set. All the basis sets use pure f-functions.

Unless stated otherwise, all the MP2, CC, and multi-configurational methods were performed under the frozen-core (fc) approximation, meaning that the 1s orbitals on carbon were kept inactive. Some calculations, chosen at random, were repeated with the full inclusion of all the electrons (e.g., MP2=full), in order to check for differences in the fc calculations. Unless these calculations revealed important differences, they are not explicitly reported, but none of these tests indicated an inadequacy of the fc approximation.

Except in the CCSD geometric optimizations, the nature of all the stationary points as minima or saddle points on the potential energy surface (PES) was determined by analyzing the harmonic vibrational frequencies using the same level of theory as used in the respective geometric optimizations. In the case that imaginary frequencies were encountered, these are explicitly mentioned. The energies presented do not include a correction for zero point vibrational energies. All computational methods were used in their restricted form (e.g., RHF, RMP2, RCCSD).

The coupled cluster single point (SP) calculations for the determination of the T_1 and D_1 diagnostic values and the CASPT2 calculations (all use the RS2C command) were computed with the MOLPRO program package [30]. All other calculations were performed with the Gaussian03 suite of programs (G03) [29]. Unless noted otherwise, the tight convergence criteria were used in all the Gaussian calculations in the SCF (SCF=tight: 10^{-8} Hartree on the density) as well as to determine convergence of geometric optimizations [OPT=tight: maximum force and root mean square (RMS) force of 1.5×10^{-5} and 1×10^{-5} Hartree Bohr^{-1}, respectively, and maximum and RMS displacements of 6×10^{-5} and 4×10^{-5} Bohr, respectively]. All the DFT calculations were performed with a pruned (99,590) integration grid (Int=UltraFine).

Cartesian coordinates of all the geometrically optimized structures and electronic energies obtained by geometric optimizations and SP calculations are presented in the Online Resource.

3 Results and discussion

3.1 Geometric optimizations of heptafulvene

First, we focus on geometric optimizations of **1** in the planar C_{2v} conformation, which has been experimentally shown to be the equilibrium structure [22]. In Tables 1, 2 and 3, the geometric parameters obtained at various levels of theory are compared to data obtained by microwave spectroscopy. Included are the single-determinantal SCF HF method as well as the second-order Møller–Plesset perturbation theory (MP2) [31], and the CC approach [32]. Both of the latter methods include dynamic electron correlation and are based on a restricted single determinant HF wave function. Both single as well as double excitations were included in the coupled cluster calculations (CCSD) [33].

Furthermore, geometric optimizations were performed with the Kohn–Sham DFT method, employing the four functionals B3LYP [34–37], B1B95 [34, 38], M053 [39], and M05-2X [40]. All of these are hybrid functionals, which incorporate HF exchange. The inclusion of HF exchange was advisable, as pure DFT methods often perform poorly for conjugated π systems [41]. The well-known B3LYP functional belongs to the class of hybrid generalized gradient approximation (GGA) functionals that incorporate electron spin density and the gradient of the density. The B1B95, the M05, and the M05-2X functionals are hybrid meta-GGA functionals that additionally depend on the kinetic energy density. The choice to include these four specific functionals in our studies was based on the following considerations. The B3LYP is a functional of the first generation. Although comparative studies have shown that it is often outperformed by newer functionals [42], it is the most popular one and it has been used frequently since its introduction. Like B3LYP, the B1B95 functional is based on Becke's B88 exchange functional. This is combined with Becke's B95 correlation functional. The B1B95 functional is also relatively old, but is repeatedly proving successful in comparative studies of various functionals [43, 44]. Therefore, it is regarded as a good choice for a general purpose functional.

The M05 and M05-2X functionals have been introduced only recently [39, 40]. Both are highly parameterized—the M05 also for metals. The M05-2X is a high-nonlocality functional that includes double the amount of nonlocal (HF) exchange, compared to the M05 functional. Both of

Table 1 Mean unsigned errors (MUEs, %) of all carbon–carbon bond lengths of **1**, geometrically optimized at different levels of theory

Basis set	HF[a]	B3LYP[a]	B1B95[a]	M05[a]	M05-2X[a]	MP2[a]	CCSD[a]	CASSCF[a]
STO-3G	2.03	1.19	1.05	1.08	1.14	1.76	2.29	1.26
3-21G	1.58	1.08	1.05	1.08	1.07	1.01	1.18	0.94
6-31G(d)	1.44	1.02	0.99	1.01	1.00	0.96	0.91	0.88
6-31G(d,p)	1.45	1.02	1.00	1.01	1.00	0.96	0.91	0.88
combi1[b]	1.42	1.07	1.04	1.06	1.00	1.01	–	0.91
combi2[c]	1.36	1.00	0.98	1.00	0.94	0.95	–	0.87
6-31+G(d,p)	1.34	1.02	1.00	1.02	0.96	0.97	0.91	0.88
6-31+G(2d,p)	1.42	1.02	0.99	1.01	0.99	0.95	–	0.87
6-31++G(d,p)	1.34	1.02	1.00	1.02	0.96	–	–	–
cc-pVDZ	1.31	1.02	0.99	1.01	0.95	1.11	0.90	0.88
combi3[d]	1.29	1.04	1.01	1.03	0.97	1.16	–	0.89
combi4[e]	1.26	1.02	0.99	1.01	0.95	1.19	–	0.87
aug-cc-pVDZ	1.25	1.02	0.99	1.01	0.95	1.22	0.89	0.87
6-311G(d,p)	1.47	1.03	1.03	1.01	1.06	0.96	0.90	–
6-311++G(d,p)	1.42	1.03	1.01	1.01	1.02	–	–	–
cc-pVTZ	1.56	1.02	1.09	1.03	1.16	–	–	–
aug-cc-pVTZ	1.55	1.02	1.08	1.02	1.02	–	–	–

[a] Unsigned errors (UEs) of all the eight carbon–carbon bond lengths were obtained by a comparison of calculated bond lengths with the corresponding values experimentally obtained [21]. The presented MUEs represent the arithmetic means of all eight UEs of **1** given as percent (%) of the average carbon–carbon bond length of **1**, determined experimentally

[b] 6-31+G(d,p) on C8 and 6-31G(d,p) on all other atoms

[c] 6-31++G(d,p) on H2 and H7, 6-31+G(d,p) on C2, C7, and C8, and 6-31G(d,p) on all other atoms

[d] aug-cc-pVDZ on C8 and cc-pVDZ on all other atoms

[e] aug-cc-pVDZ on H2, H7, C2, C7, and C8, and cc-pVDZ on all other atoms

these functionals have proved to be advantageous in certain cases that are typically challenging for DFT [45]. In calculations on heptafulvenes, a typical shortcoming of DFT is its tendency to overpolarize conjugated π systems and to describe such organic molecules as too metal-like. Typical examples are the torsion potentials of butadiene, styrene, or biphenyl [41, 46] for which the M05 and M05-2X functionals performed significantly better than many other functionals [47]. The conformational energies of heptafulvene, discussed below, are among the foci of this investigation. These energies depend strongly on the dihedral angles between conjugated double bonds. Therefore, the performance of the M05 and M05-2X functionals is especially interesting for the conformational analysis of heptafulvenes.

Furthermore, geometric optimizations were performed using a multi-configurational SCF (MCSCF) method. Here, the CASSCF approach was employed. All of the CASSCF calculations reported here are characterized as CASSCF(8,8) calculations. In these calculations, all of the eight π electrons and all of the four bonding and four antibonding π MOs are included in the active space. In the C_{2v} point group, these π orbitals are only represented by the irreducible representations a2 and b1. In contrast, all the occupied orbitals with a1 and b2 symmetry are σ orbitals.

All computational methods were performed in combination with various basis sets. Minimal basis sets (STO-3G) [48] were used as well as Pople's split-valence (3-21G [49], 6-31G [50]) basis sets up to triple-split-valence quality (6-311G) [51]. Here, we regard the 6-311G basis set as a triple-split set, rather than a triple-ζ set although the latter classification has been sometimes used in the past [52]. Furthermore, the class of Dunning's correlation consistent plus polarization basis sets (cc-pV*n*Z) has been used for geometric optimization [53, 54]. These sets have been used as double-ζ (cc-pVDZ) or triple-ζ (cc-pVTZ) quality basis sets.

For an improved description of molecules, it is important that not only the atoms are described well, but also the basis set must have enough flexibility to account for the atomic deformations that occur when a molecule is formed. This, in turn, is achieved by basis set augmentation with diffuse and polarization functions. The use of such diffuse (e.g., aug-, +, ++) or polarization (e.g., d, 2d, df, p) functions is indicated according to common convention. The use of diffuse functions is regarded as especially

Table 2 Mean unsigned errors (MUEs, %) of all intracyclic bond angles of **1**, geometrically optimized at different levels of theory

Basis set	HF[a]	B3LYP[a]	B1B95[a]	M05[a]	M05-2X[a]	MP2[a]	CCSD[a]	CASSCF[a]
STO-3G	0.54	0.51	0.51	0.53	0.48	0.37	0.33	0.32
3-21G	0.51	0.53	0.51	0.53	0.47	0.45	0.39	0.33
6-31G(d)	0.52	0.64	0.62	0.67	0.54	0.53	0.42	0.37
6-31G(d,p)	0.52	0.64	0.62	0.67	0.54	0.51	0.41	0.37
combi1[b]	0.52	0.65	0.64	0.68	0.55	0.52	–	0.37
combi2[c]	0.53	0.65	0.64	0.69	0.56	0.55	–	0.38
6-31+G(d,p)	0.51	0.64	0.63	0.67	0.55	0.51	0.41	0.37
6-31+G(2d,p)	0.49	0.62	0.61	0.65	0.52	0.54	–	0.36
6-31++G(d,p)	0.51	0.64	0.63	0.67	0.54	–	–	–
cc-pVDZ	0.50	0.64	0.62	0.67	0.53	0.53	0.41	0.37
combi3[d]	0.49	0.60	0.59	0.65	0.49	0.46	–	0.36
combi4[e]	0.48	0.60	0.59	0.65	0.49	0.51	–	0.35
aug-cc-pVDZ	0.49	0.62	0.60	0.66	0.50	0.52	0.40	0.37
6-311G(d,p)	0.50	0.63	0.61	0.66	0.52	0.51	0.41	–
6-311++G(d,p)	0.50	0.62	0.60	0.65	0.51	–	–	–
cc-pVTZ	0.49	0.63	0.60	0.67	0.51	–	–	–
aug-cc-pVTZ	0.49	0.62	0.59	0.66	0.66	–	–	–

[a] Unsigned errors (UEs) of all the seven intracyclic bond angles were obtained by a comparison of calculated angles with the corresponding angles experimentally obtained [21]. The presented MUEs represent the arithmetic means of all the seven UEs of **1** given as percent (%) of the average intracyclic bond angle of a planar heptagon (128.57°)

[b] 6-31+G(d,p) on C8 and 6-31G(d,p) on all other atoms

[c] 6-31++G(d,p) on H2 and H7, 6-31+G(d,p) on C2, C7, and C8, and 6-31G(d,p) on all other atoms

[d] aug-cc-pVDZ on C8 and cc-pVDZ on all other atoms

[e] aug-cc-pVDZ on H2, H7, C2, C7, and C8, and cc-pVDZ on all other atoms

necessary for the adequate description of loosely bound electrons, as in anions or involved in weak interactions. However, we included diffuse functions in some of these basis sets, to investigate how such basis sets perform in the calculations on heptafulvene. For example, the analysis of certain heptafulvene derivatives might require diffuse functions in order to analyze weak interactions. Furthermore, it was unclear whether diffuse functions might be necessary, because hypothetically the contributing structure **1a** can be formulated (Fig. 1). This zwitterionic form has a negative charge on the exocyclic carbon atom. Accordingly, we wondered if diffuse functions might be important in order to describe the contribution of this structure (**1a**).

In addition to these standard basis sets, we also report calculations in which different basis sets were used on different atoms of **1**. The purpose of these combinations of basis sets was to include diffuse functions only on specific atoms. Such combined sets might be advantageous for the computation of weak interactions at specific positions of the heptafulvene ring system [55]. In addition, the inclusion of diffuse functions on the exocyclic carbon atom (C8) was of interest, in order to evaluate the contribution of resonance structure **1a** to the overall description of **1**. This partial structure includes a negative charge on a single atom (C8), which might require diffuse functions for an accurate description. These combined basis sets are called *combi1*–*combi4*, and are defined in the following way. The basic basis set in *combi1* and *combi2* is the 6-31G(d,p) set. In addition, the 6-31+G(d,p) set was used for C8 in *combi1* and for C2, C7, and C8 in *combi2*. Furthermore, the 6-31++G(d,p) set was used for H2 and H7 in *combi2*. The basic basis set in *combi3* and *combi4* is the cc-pVDZ basis set. In addition, the aug-cc-pVDZ set was used for C8 in *combi3* and for H2, H7, C2, C7, and C8 in *combi4*.

In order to reproduce the microwave spectroscopic geometric parameters with geometric optimizations, heptafulvene was constrained to be planar and to belong to the C_{2v} point group. The geometric parameters of the resulting stationary points have been arranged in the following groups: the bond lengths of all carbon–carbon bonds (Table 1) and all intracyclic bond angles (Table 2). All values are presented as mean unsigned errors (MUEs) in percent (%).

3.2 Carbon–carbon bond lengths

The comparison of the MUEs of carbon–carbon bond lengths obtained at different levels of theory in Table 1 shows that the HF method is the least suitable

Table 3 Wave numbers (cm^{-1}) of the lowest frequency out-of-plane bending mode of heptafulvene at different levels of theory

Basis set	HF[a]	B3LYP[a]	B1B95[a]	M05[a]	M05-2X[a]	MP2[a,b]	CASSCF[a]
STO-3G	42.3	71.1	68.4	65.8	56.4	62.0	56.9
3-21G	37.1	63.3	52.2	58.0	39.4	i33.4	56.7
6-31G(d)	47.5	73.5	66.1	65.2	43.0	13.7	63.9
6-31G(d,p)	45.7	72.4	64.7	64.3	53.4	i19.5	62.8
combi1[c]	39.8	67.0	59.8	58.3	48.3	i37.2	59.8
combi2[d]	33.1	61.6	55.3	52.8	41.9	i58.5	56.6
6-31+G(d,p)	28.6	62.9	55.2	53.1	38.9	i153.0	56.3
6-31+G(2d,p)	42.8	66.7	60.1	56.7	47.7	i24.3	60.8
6-31++G(d,p)	24.4	62.6	55.0	52.7	38.0	–	–
cc-pVDZ	54.0	74.0	67.3	65.3	57.8	45.3	66.5
combi3[e]	50.5	70.2	64.1	61.4	54.2	47.9	64.6
combi4[f]	49.6	66.5	61.4	58.9	52.7	41.6	63.6
aug-cc-pVDZ	51.6	67.2	61.6	57.9	58.9	49.4	66.3
6-311G(d,p)	46.3	63.7	57.8	56.5	47.2	i43.2	–
6-311++G(d,p)	36.6	58.0	54.4	51.7	39.1	–	–
cc-pVTZ	52.7	64.7	60.2	59.1	49.3	–	–
aug-cc-pVTZ	36.3	58.0	52.0	62.1	62.1	–	–

[a] All the frequencies are unscaled

[b] In the case of the MP2 method, the frequency of the out-of-plane bending mode becomes imaginary with many basis sets

[c] 6-31+G(d,p) on C8 and 6-31G(d,p) on all other atoms

[d] 6-31++G(d,p) on H2 and H7, 6-31+G(d,p) on C2, C7, and C8, and 6-31G(d,p) on all other atoms

[e] aug-cc-pVDZ on C8 and cc-pVDZ on all other atoms

[f] aug-cc-pVDZ on H2, H7, C2, C7, and C8, and cc-pVDZ on all other atoms

computational method to obtain accurate geometric properties of heptafulvenes. The best HF results are obtained with the aug-cc-pVDZ basis set, but with smaller as well as with larger basis sets the MUE can become greater than 1.5%. These large MUEs of the HF method are explained predominantly by the well-known underestimation of double bond lengths by HF. In contrast, the single bond lengths are actually predicted in quite good agreement with experimental data. Comparing only the MUEs of single bond lengths, the HF method gives the best results of all computationally less expensive methods. All DFT methods perform significantly better than HF and roughly comparable to MP2. Only slight differences can be noted between different basis sets. For most of the basis sets, the MUEs of DFT or MP2 levels of theory are approximately 1.0%. However, some basis sets in combination with the B1B95 and M05-2X functionals, as well as the MP2 method, lead to MUEs slightly below 1.0%. Basis sets of triple-split or triple-ζ quality do not give any advantage over smaller split-valence or double-ζ basis sets. Most often (HF, B1B95, M05-2X), the results obtained with the larger basis sets are slightly inferior. In summary, of all the computationally less expensive methods, the DFT method using the M05-2X functional gives the most accurate carbon–carbon bond lengths.

When dynamic electron correlation is included more accurately (CCSD) or when non-dynamic electron correlation is included (CASSCF), the error of carbon–carbon bond lengths can be further improved. In the CASSCF-derived minima, the MUEs are approximately 10% less than those of the M05-2X geometries.

3.3 Intracyclic bond angles

In calculating the MUEs of intracyclic bond angles of all the computationally less expensive methods, the simple HF method and MP2 lead to the best results. Both give MUEs of approximately 0.5%. The DFT methods are slightly inferior to HF or MP2. B3LYP, B1B95 and M05 lead to MUEs in average greater than 0.6%. However, the M05-2X functional gives bond angles almost as good as those obtained by MP2. Surprisingly, for all the methods except HF, the smallest basis sets STO-3G and 3-21G give intracyclic bond angles closest to the values determined experimentally. The computationally more expensive coupled cluster method (CCSD) gives improved bond angles, with MUEs of approximately 0.4%, which is 20% closer to experiment than HF or MP2. With the multi-configurational CASSCF approach, even MUEs smaller than 0.4% are obtained.

Thus, when the MUEs of both bond lengths and bond angles are considered, the DFT approach, using the M05-2X functional, emerges as the best choice for a computationally less expensive method. More efficient inclusion of dynamic electron correlation or the inclusion of non-dynamic correlation gives improved results, at the price of higher computational cost. In this respect, it must be noted that the geometric improvements obtained with more advanced methods are only moderate. The best results are obtained with the CASSCF approach. The MUEs of the bond lengths, however, are only 10% smaller, and those of the bond angles are only 20%, smaller compared to M05-2X results.

The geometric parameters obtained with the basis sets *combi1–combi4* are approximately comparable to the results obtained with their respective parent basis sets, 6-31G(d,p) or cc-pVDZ. Hence, such combined sets can be applied without introducing additional errors, and might be useful for computations of weak interactions of specific positions of the heptafulvene system [55]. However, a significant improvement in the geometric parameters is not observed upon the inclusion of diffuse functions on C8. We take this as an indication that resonance structure **1a** is only of minor importance for the overall description of **1**.

3.4 Analysis of harmonic vibrational frequencies

All the stationary points obtained in the geometric optimizations, with the exception of CCSD, were used to calculate the harmonic vibrational frequencies. These revealed the character of the stationary points as minima or saddle points of the PES. Geometries with only positive eigenvalues of the Hessian matrix are minima, and those with n negative (imaginary) frequency vibrational modes are nth-order saddle points. In this investigation, either minima or geometries with one imaginary frequency vibrational mode were obtained. These first-order saddle points are transition states, meaning that at the respective levels of theory, heptafulvene has a boat form as the minimum energy conformation. In these cases, the planar C_{2v} conformer represents the transition structure, separating the two isomeric C_s boat conformations. The wave number of the lowest frequency vibrational mode, the out-of-plane bending mode, which is of B1 symmetry, is the most important. The frequency of this vibrational mode becomes imaginary when a transition state is obtained by calculation. Furthermore, the wave number of this mode is known from the microwave analysis (70 ± 11 cm^{-1}), so that a comparison with the experimental value can serve as a measure for the accuracy of the respective level of theory. The calculated wave numbers of the out-of-plane bending mode are summarized in Table 3.

The harmonic frequencies in Table 3 are not scaled, in order to account for anharmonicity [56]. Accordingly, this comparison is meant to show trends rather than exact values. However, most often the scaling of harmonic frequencies with common scale factors reduces their wave numbers [56]. In this respect, it is unlikely that scaling the presented frequencies would change any of the following conclusions, because most of the calculated wave numbers are too small, even without scaling. By almost all the computational methods, the wave number of the out-of-plane bending mode is calculated to be smaller than the value determined experimentally (70 cm^{-1}). Only a few results, obtained with the B3LYP functional, are above this value. However, the possible error of the experimental value was estimated to be 11 cm^{-1}, hence all frequencies larger than 59 cm^{-1} are within the experimental error. Such results were obtained with the CASSCF approach or the B3LYP, B1B95 and M05 functionals in combination with certain basis sets. For example, with these methods, the 6-31G(d,p) and the cc-pVDZ basis sets predict the out-of-plane vibrational mode, in accordance with the experiment. The HF method and the M05-2X functional incorporating a large fraction of HF exchange significantly underestimate the out-of-plane bending frequency. In general, the inclusion of diffuse functions in the basis set reduces the wave number of the out-of-plane bending mode. The wave numbers obtained with triple-ζ or triple-split-valence basis sets are smaller than those obtained with the corresponding double-ζ or split-valence basis sets. Accordingly, the best agreement with experimental results is obtained with CASSCF or DFT methods, using the B3LYP, B1B95 and M05 functionals combined with double-ζ or split-valence basis sets without diffuse functions.

Vibrational frequencies were not determined for the CCSD method, because at this level of theory their computation is very costly, as they cannot be calculated analytically with the program packages employed in this study. Therefore, of all the methods in Table 3, the MP2 method represents the method with the greatest level of inclusion of dynamic electron correlation. That is why it is important to note that many of the MP2 results are deceptive. Although the geometric parameters of the C_{2v} geometry are predicted quite well with the MP2 method (Tables 1, 2), grossly diverse wave numbers of the lowest frequency out-of-plane bending mode are observed. Only the STO-3G basis set gives a wave number in accordance with the experimental results. Half of the basis sets result in a negative (imaginary) frequency for the out-of-plane bending, and thus heptafulvene is non-planar at these MP2 levels of theory. For example, using the MP2 method in combination with the popular 6-31G(d,p) (=6-31G**) basis set, we obtained one imaginary frequency vibrational mode for the C_{2v} geometry, which contradicts a recent report of a planar global minimum obtained with the MP2 method, using this basis set [9]. To clarify this discrepancy, the geometric optimization and frequency analysis at this level of theory were repeated under various definitions of accuracy. In most of these calculations, the planar C_{2v} geometry of heptafulvene turned out to be a first-order saddle point and not a minimum at the MP2/6-31G(d,p) level of theory. The highest accuracy obtained was a geometric optimization using the opt=verytight option in the G03 route card, combined with an increase of the SCF convergence criterion of the Gaussian03 suite of programs [29] to 10^{-11}. We also tried to discard the fc approximation and employed the MP2 method with full optimization of the core orbitals (MP2=full). Using tight convergence criteria, this approach reduced the magnitude of the imaginary frequency to $-1.6\ \mathrm{cm}^{-1}$, but did not change the qualitative conclusion that the C_{2v} geometry is a transition state at this level of theory. One might alternatively interpret an imaginary frequency with such a small magnitude as numerical noise, but we stress that although the value of $-1.6\ \mathrm{cm}^{-1}$ is close to zero, it still represents a significant disagreement with the experimental data. However, under tighter SCF convergence criteria (10^{-11}) in conjunction with the MP2=full and opt=verytight options, the C_{2v} geometry was determined as a minimum having the wave number $+1.0\ \mathrm{cm}^{-1}$ for the out-of-plane bending mode. Nevertheless, we interpret this outcome rather as fortuitous. Indeed, the MP2=full option seems to reduce the error of this vibrational mode, so that finally a positive wave number could be obtained. Yet, the magnitude of this wave number reflects an intense disagreement with the experimentally determined value. When the 6-31+G(d,p) basis set is used with the same accuracy, the out-of-plane frequency is only improved to $-144.9\ \mathrm{cm}^{-1}$. Hence, with the latter basis set, **1** is non-planar also when the core orbitals are fully optimized.

3.5 Conformational energies and global minimum

Although the parent heptafulvene has a planar C_{2v} equilibrium structure, several derivatives of heptafulvene are known to crystallize in non-planar conformations. These are boat conformations in which the carbon atoms C1, C4, and C5 are placed above the plane defined by the atoms C2, C3, C6, and C7. For example, both of the heptafulvene units in heptafulvalene (**3**) adopt boat conformations in their crystal structure [3, 57]. Similar boat-like geometries are obtained also for heptafulvene, when nuclear positions are shifted following the lowest frequency vibrational mode (out-of-plane bending). The geometry **1c** in Fig. 1 is an example of such boat conformations, which belong to the point group C_s. In the case of **1**, however, none of these boat forms should be a minimum on the PES. However, the frequency analysis discussed in the previous chapter indicates that the choice of the basis set is crucial for the correct prediction of a planar global minimum of **1** when using electron correlated ab initio methods, such as MP2.

Boat-like geometries of **1** can be obtained by geometric optimization when the dihedral angles d_1 and d_2 are constrained to similar values of opposite sign ($d_1 = -d_2$). The dihedral angles d_1 and d_2 are defined by the carbon atoms C2, C1, C7, and C6 or C3, C2, C1, and C7, respectively (cf. Figs. 1 and 2). In the planar form, both of these dihedrals are 0°. In Figs. 2 and 3, we plot the conformational energy of **1** against the constrained dihedral angle d_1. Each of the two figures presents four curves, which are based on heptafulvene geometries obtained by optimizations at four different levels of theory [HF/6-311++G(d,p), B1B95/6-31++G(d,p), CASSCF(8,8)/6-31G(d,p), and CASSCF(8,8)/6-31+G(2d,p)]. At all these four levels, heptafulvene has a planar minimum. The energies presented in Fig. 2 correspond to SP energy calculations at the CCSD(T)/6-31G(d,p) level of theory, while the energies in Fig. 3 reflect energy calculations at the CCSD(T)/6-31+G(d,p) level of theory. The fundamental difference between the four curves in Fig. 2 and those in Fig. 3 is the geometry of the minimum.

Only with the 6-31G(d,p) basis set used in Fig. 2 is a planar minimum ($d_1 = 0°$) predicted in the CCSD(T) SP calculations. Despite the high level of theory, a slight variation of the basis set in the SP calculations leads to the false prediction of a boat-form minimum of **1**[1]. When the 6-31+G(d,p) basis set is used (Fig. 3), the conformational energy of the planar form is approximately 0.3 kcal mol^{-1} higher than that of a boat form with a dihedral angle d_1 of 20°. This difference between curves in Figs. 2 and 3 is an effect of the different basis sets in combination with a method that includes a large amount of dynamic electron correlation. These significant differences in the minimum geometry are possible due to the high conformational flexibility of **1**. As is demonstrated by the curves in Figs. 2 and 3, we found that heptafulvene has a very flat ground state PES with respect to the lowest frequency out-of-plane bending mode. Especially between dihedral angles (d_1) of 0° and 40°, the conformational energy of **1** changes only marginally (Figs. 2, 3). Therefore, small energy differences, introduced by different basis sets, can lead to great structural differences.

Furthermore, Figs. 2 and 3 underline some of our conclusions drawn from the analysis of geometrical parameters obtained by geometric optimization of **1** (vide infra). As described previously, the HF level of theory generally

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[1] Naturally, the correct dihedral angle d_1 of the respective C_s minima cannot be determined by single point calculations only. However, the exact minimum geometries on all the various levels of theory are not important for these analyses, so that we did not geometrically optimize the folded minima and formally regard the C_s geometry with dihedral angles d_1 and d_2 equal to ±20° as minimum.

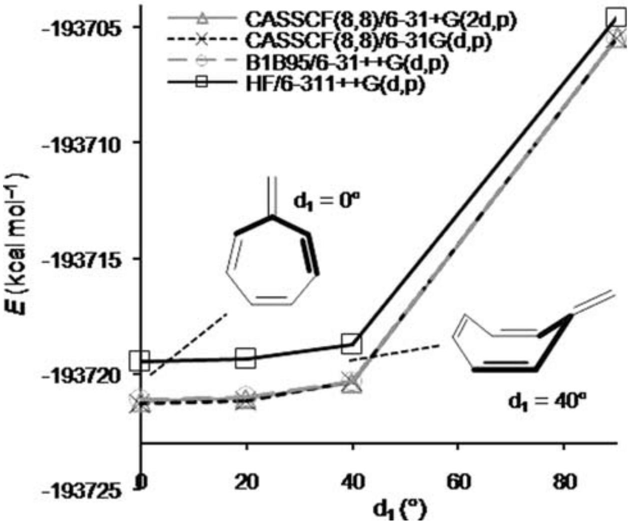

Fig. 2 CCSD(T)/6-31G(d,p) single point energies of different heptafulvene conformations as functions of the dihedral angle d_1, constrained in the previous geometric optimizations at the given levels of theory. The planar geometry ($d_1 = 0°$) is the minimum of all four curves

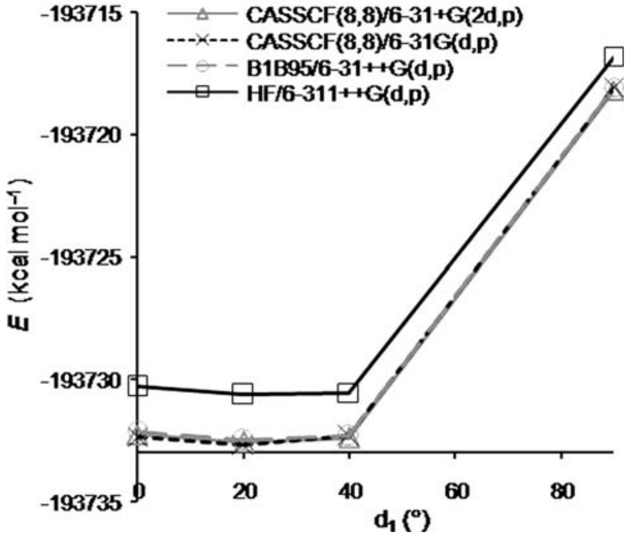

Fig. 3 CCSD(T)/6-31+G(d,p) single point energies of different heptafulvene conformations as functions of the dihedral angle d_1, constrained in the previous geometric optimizations at the given levels of theory. All curves have a boat-form minimum

gives geometries slightly inferior to DFT methods or CASSCF. This is also reflected in the subsequent CCSD(T) energy calculations. The curves representing HF geometries are shifted to slightly higher energies compared to the remaining curves in each figure. However, the differences are small, and the shapes of these HF-derived curves are very similar to the shapes of the other three curves in each of the two figures. Hence, the relative energy differences obtained with post-HF methods can also be predicted quite well based on HF geometries. In both figures, the curves corresponding to the B1B95 and CASSCF geometries are very similar, both in terms of shape and of absolute energies. Accordingly, the good performance of DFT is also underlined in the subsequent high-level energy calculations. These comparisons also allow the conclusion that non-dynamical electron correlation is not highly important for calculations of **1**. Indeed, the geometric parameters of **1** are slightly improved when the geometric optimizations are performed with the CASSCF method instead of less expensive methods (vide infra), yet subsequent CCSD(T) SP energies do not reveal significant energy differences compared to DFT geometries.

A similar trend is observed in the conformational energies obtained with the second-order multireference perturbation theory CASPT2 [58–61], which are presented in Fig. 4. The 6-31G(d,p) basis set yields the correct planar C_{2v} minimum, but after the inclusion of diffuse functions on carbon [6-31+G(d,p)], the C_{2v} geometry becomes a transition structure, separating two isomeric boat-form minima (C_s), convertible by a flip through the molecular plane. Figure 4 also shows that the augmentation with diffuse functions is not the only crucial aspect, but also a suitable incorporation of polarization functions is important, because when the basis set is further increased to include one set of diffuse functions and two sets of d-polarization functions (2d), the C_{2v} minimum is regained.

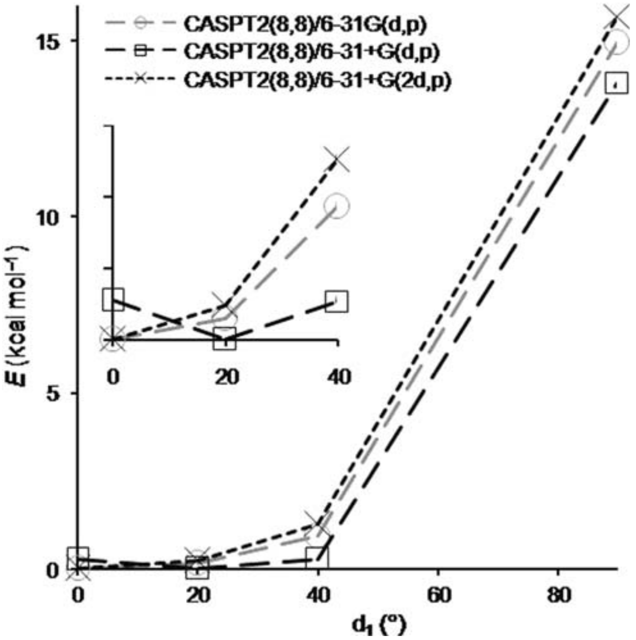

Fig. 4 CASPT2 single point energies of different heptafulvene conformations as functions of the dihedral angle d_1, constrained in the previous geometric optimizations at the CASSCF(8,8)/6-31+G(2d,p) level of theory. Three different basis sets were used for the SP calculations

Table 4 The inability of certain basis sets to predict the correct planar (C_{2v}) minimum, observed in MP2 single point calculations of **1**, optimized at the CASSCF(8,8)/6-31+G(2d,p) level of theory

Type	Basis sets favoring C_{2v} [a]	E_{conf} (C_s)[b]	Basis sets favoring C_s [a]	E_{conf} (C_{2v})[c]
Dunning (correlation consistent)	cc-pVDZ	0.250	–	–
	aug-cc-pVDZ	0.246	–	–
	cc-pVTZ	0.277	–	–
	aug-cc-pVTZ	0.201	–	–
	cc-pVQZ	0.270	–	–
Pople	6-31G(d,p)	0.060	–	–
	6-31G(2d,p)	0.329	–	–
	6-31+G(2d,p)	0.122	6-31+G(d,p)	0.399
	6-31+G(3d,p)	0.223	6-31+G(df,p)	0.418
	6-31+G(2df,p)	0.180	6-31++G(d)	0.435
	6-31++G(2d,p)	0.095	6-31++G(d,p)	0.449
	6-311G(2d,p)	0.262	6-311G(d,p)	0.026
	6-311+G(2d,p)	0.147	6-311+G(d)	0.346
	6-311+G(3d,p)	0.118	6-311+G(d,p)	0.346
	6-311++G(2d,p)	0.140	6-311+G(df,p)	0.399
	6-311++G(2d,2p)	0.153	6-311++G(d)	0.324
	6-311++G(2df,p)	0.174	6-311++G(d,p)	0.368
	6-311++G(3d,p)	0.117	–	–
	6-311++G(3df,3p)	0.219	–	–
Petersson	6-31G(d′)	0.235	–	–
	6-31G(d′,p′)	0.197	–	–
	6-31+G(2d′,p′)	0.214	6-31+G(d′)	0.165
	6-31+G(3d′,p′)	0.236	6-31+G(d′,p′)	0.160
	6-31++G(2d′,p′)	0.194	6-31++G(d′,p′)	0.210
	6-31++G(3d′,p′)	0.213	–	–
Dunning/Huzinaga	D95V(d,p)	0.108	–	–
	D95V(2d,p)	0.437	–	–
	D95V+(2d,p)	0.361	D95V+(d,p)	0.314
	D95V++(2d,p)	0.262	D95V++(d,p)	0.385
	D95(d)	0.070	–	–
	D95(d,p)	0.098	–	–
	D95+(2d,p)	0.392	D95+(d,p)	0.322
	D95++(2d,p)	0.288	D95++(d,p)	0.394
Ahlrichs	–	–	SV	0.227
	–	–	SVP	0.035
	–	–	TZV	1.843
	–	–	TZVP	1.009

[a] In the C_{2v} geometry, the dihedral angle d_1 equals 0° and it was constrained to 20° in the optimization of the C_s geometry

[b] The conformational energy (E_{conf}, kcal mol^{-1}) of the C_s boat form is given, when the planar geometry is of lower energy

[c] E_{conf} (kcal mol^{-1}) of the planar C_{2v} geometry is given, when the folded geometry is of lower energy

3.6 Conformational energies: different basis sets

In order to further analyze the basis set dependency of electron-correlated relative energies, we performed various MP2 SP calculations. In Table 4, we present the results of these MP2 calculations, for which a variety of different basis sets was employed. The table presents separately all the basis sets that give a planar minimum (C_{2v}), and all the basis sets that result in a boat-form minimum (C_s). This classification is based on calculations of the MP2 energies at two geometries of **1**, optimized at the CASSCF(8,8)/6-31+G(2d,p) level of theory, on which **1** has a planar minimum. One of these structures is the planar C_{2v} minimum, and the other one is a C_s boat form that was obtained by constraining the dihedral angles d_1 and d_2 to 20° and −20°, respectively. If the MP2 SP energy of the planar geometry was lower than the energy of the folded form, a planar minimum is assumed and the conformational energy (E_{conf}) of the C_s geometry is given. Otherwise, a boat-form minimum, having an approximate dihedral angle d_1 of 20°, is assumed and the height of the energy barrier of the transition geometry (E_{conf} of the planar form) is presented.

Surprisingly, many basis sets lead to wrong predictions of the minimum. Only in the group of Dunning's correlation consistent plus polarization basis sets (cc-pVnZ) [54], do all the tested basis sets predict the correct minimum. Neither the size of the basis set [n = D (double-ζ), T (triple-ζ), Q (quadruple-ζ)] nor the augmentation with diffuse functions (aug-) falsifies the result on planarity. However, it can be noted that diffuse functions favor boat conformations, as the conformational energies of the C_s structures, obtained with the augmented basis sets (e.g., aug-cc-pVDZ), are smaller than those obtained with the corresponding basis sets without diffuse functions (e.g., cc-pVDZ).

Concerning the split-valence basis sets of Pople et al., we keep in mind that some of these sets result in imaginary frequency vibrational modes, obtained in the frequency analyses of MP2 optimized geometries (Table 3). The SP energies, presented in Table 4, support most of the observations regarding these frequency calculations, but some differences can also be observed. For instance with respect to SP energies, the 6-31G(d,p) set turns out to favor the planar form, although we reported an imaginary frequency of the C_{2v} geometry in Table 3. However, our remarks on the wavenumbers of the out-of-plane bending mode already indicate that an exact evaluation of the 6-31G(d,p) basis set is cumbersome (vide infra). The energies in Table 4 underline this conclusion further. The energy difference $E_{\mathrm{conf}}(C_s)$ between the boat form and the planar form, determined with this basis set, represents the smallest value of $E_{\mathrm{conf}}(C_s)$, obtained with any of the basis sets that favor the C_{2v} geometry. Therefore, we stress once more that the outcome of calculations on **1** using the 6-31G(d,p) appears to be rather fortuitous and depends on small details that can lead to either planarity or non-planarity.

It is especially important to note that the augmentation of Pople-type basis sets with diffuse functions favors boat forms stronger than it is observed for Dunning's correlation consistent basis sets. When diffuse functions are included in Pople's double-ζ basis sets (6-31G), then additionally a sufficient amount of d-polarization functions have to be included in order to obtain the correct planar minimum. For example, the incorporation of only one set of d-functions on carbon and one set of p-functions on hydrogen in the 6-31+G(d,p) basis set does not result in a planar minimum, because the C_s geometry is 0.4 kcal mol^{-1} more stable. In general, at least two sets of d-functions are necessary to obtain the planar minimum with Pople's split-valence double-ζ sets containing diffuse functions [e.g., 6-31+G(2d,p)]. The amount of diffuse functions incorporated does not seem to have a strong influence, in that no remarkable difference could be noted when diffuse functions have been included only on carbon (+) or on carbon and hydrogen (++). Likewise, when Pople-type basis sets of triple-split-valence quality are considered (6-311G), the inclusion of diffuse functions favors heptafulvene boat forms. For example, the barrier height of the planar form is much greater when the 6-311+G(d,p) basis set is used than it is with the 6-311G(d,p) basis set. However, also the latter one predicts a wrong minimum, indicating that the 6-311G(d,p) set is slightly inferior to the 6-31G(d,p) set. Hence, if Pople's triple-split-valence basis sets are used, the inclusion of at least two sets of d-functions is necessary, no matter whether or not diffuse functions are incorporated.

Furthermore, we investigated the basis sets of Petersson et al. [62, 63]. These sets give somewhat better results than the Pople-type basis sets, because they seem to favor the C_{2v} minimum more strongly. When basis sets of Petersson et al. that favor the planar form are compared to corresponding Pople-type basis sets, a greater conformational energy of the folded geometry $E_{\mathrm{conf}}(C_s)$ is observed for Petersson's sets. For example, using the 6-31G(d,p) set, $E_{\mathrm{conf}}(C_s)$ equals to 0.06 kcal mol^{-1}, whereas the greater energy difference of 0.20 kcal mol^{-1} is obtained with the 6-31G(d′,p′) set. Accordingly, the conformational energies of the planar form $E_{\mathrm{conf}}(C_{2v})$ are smaller for Petersson's sets, when corresponding basis sets are compared that favor the boat form [e.g., 6-31+G(d,p) vs. 6-31+G(d′,p′)]. Thus, compared to Pople-type basis sets of similar size, the barrier height between the two isomeric C_s geometries $E_{\mathrm{conf}}(C_{2v})$ is smaller for Petersson's basis sets. However, the augmentation of Petersson's basis sets with diffuse functions (either +or ++) results in comparable effects as described for Pople's basis sets. In this case, at least two sets of d-polarization functions (2d′) have to be incorporated in order to obtain the planar minimum.

The basis sets of Dunning and Huzinaga [64] show a trend similar to that described for the Petersson group of sets. Two sets of d-polarization functions are needed when diffuse functions are used. No obvious difference can be noted when the basis sets of valence double-ζ type (D95V) are compared with the corresponding sets of full double-ζ quality (D95). The basis sets of Ahlrichs et al. appear to be rather unsuitable for calculations on heptafulvenes. None of these basis sets of split-valence (SV) [65] or triple-ζ valence (TZV) [66] type predicts correctly the planar minimum. If the basis set size is increased from SV to TZV, the barrier height of the planar form becomes even greater than for the smaller SV basis sets. The incorporation of polarization functions in the basis sets SVP and TZVP leads to a reduction of the barrier height of the planar form. However, the inclusion of one set of polarization functions is not sufficient to predict the correct boat-form minimum.

It can be concluded that the somewhat deceptive performance of the MP2 method observed in vibrational analysis (vide infra) is reflected also in MP2 SP energy calculations. Caution is necessary in the choice of the basis set. Many basis sets result in fundamentally wrong descriptions of conformational energies of the heptafulvene system. It was found that, in particular, the augmentation with diffuse functions is critical and often worsens the results. A similar conclusion can be drawn from Figs. 2, 3, and 4, which are based on SP calculations, using more advanced electron-correlated methods. These figures show that the inclusion of diffuse functions also affects the results of CCSD(T) and CASPT2 SP calculations significantly.

3.7 Conformational energies: comparison of computational methods

In Fig. 5, the conformational SP energies at the MP2 and CCSD(T) levels of theory are compared to each other. This figure shows that MP2 favors boat conformations too strongly. MP2 not only often falsely predicts boat-form minima, but also the shapes of the conformational energy curves deviate from the shapes of more accurate energy curves, such as CCSD(T). The principal difference is the smaller acceleration of the MP2 curves with increasing dihedral angle d_1. Accordingly, the conformational energies of C_s geometries are in general smaller at the MP2 level. These differences are most obvious in strongly folded geometries ($d_1 = 90°$), when the conformational energies are high. In these conformations, the difference between MP2 and CCSD(T) is greater than 2 kcal mol^{-1} for all of the basis sets employed in Fig. 5.

Figure 6 compares the conformational SP energies of **1** obtained with various computational methods. In addition to the HF, CASSCF, B3LYP, M05-2X, MP2, CASPT2, CCSD, and CCSD(T) methods, which have been described above, it also includes the SP energies obtained at the Brueckner doubles (BD) level of theory. The latter one is a variation of the CC method, using Brueckner orbitals instead of HF orbitals [67]. These, in turn, lead to vanishing single amplitudes at convergence [68, 69]. In the variation BD(T), which was employed in this study, the perturbative contribution of connected triples is included, in analogy to the CCSD(T) method. The use of Brueckner orbitals is especially recommended for problematic cases of artifactual symmetry breaking of the single reference wave function [70, 71]. These aspects will be discussed below.

The comparison in Fig. 6 presents very similar curves for the most advanced computational methods CCSD(T), BD(T), and CASPT2. The conformational energies of the most strongly folded geometry ($d_1 = 90°$) are almost identical with each of these three methods. These curves can be compared to the remaining curves of Fig. 6 in order to evaluate the performance of the other methods. In accordance with the results presented in Fig. 5, it is

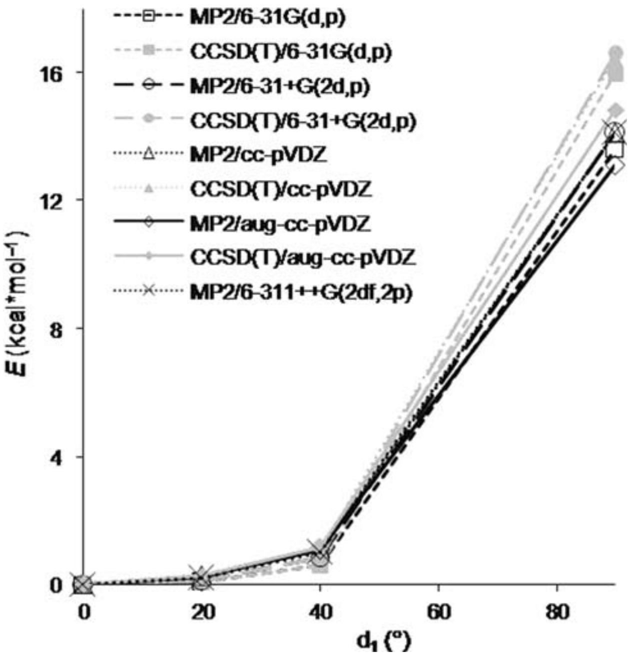

Fig. 5 MP2 and CCSD(T) single point energies of different heptafulvene conformations as functions of the dihedral angle d_1. All the four geometries were obtained at the CASSCF(8,8)/6-31+G(2d,p) level of theory

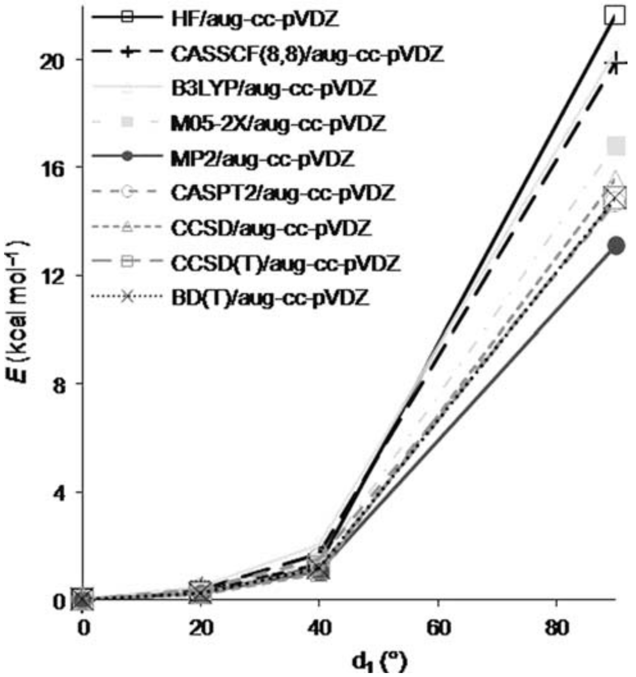

Fig. 6 HF, CASSCF, B3LYP, M05-2X, MP2, CASPT2, CCSD, CCSD(T), and BD(T) single point energies of different heptafulvene conformations as functions of the dihedral angle d_1. As in Fig. 3, the angle d_1 was constrained in the previous geometric optimizations at the CASSCF(8,8)/6-31+G(2d,p) level of theory

apparent that the MP2 conformational energies of boat forms are very small. In contrast to MP2, all the remaining methods overestimate the conformational energies of heptafulvene boat forms, compared to CCSD(T), BD(T) or CASPT2. The best agreement with the three most advanced methods is observed for the CCSD approach, but the energies obtained with the DFT method using the M05-2X functional are also relatively close to the results of the CCSD(T) method. Accordingly, as concerns conformational energies, the MP2 method and DFT with the M05-2X functional are regarded as the best choice for a computationally less expensive method, provided that a suitable basis set is used for MP2. However, the errors of these two methods are systematically different. The relative energies of folded forms are too small with the MP2 method, whereas they are too large with the M05-2X functional. Notwithstanding, the curves in Fig. 4 highlight the improvements that have been achieved with the development of the M05-2X functional, when its performance is compared to the results of the older B3LYP functional. The latter one suffers from the well-known shortcoming of the DFT approach to overestimate resonance energy of conjugated π systems. This, in turn, leads to an erroneously strong preference for the planar conformation, and thus the conformational energies of folded forms are much higher, when the B3LYP functional is used, than they are with the M05-2X functional.

Figure 6 also shows that dynamic electron correlation is important for conformational analyses of **1**. With the exception of B3LYP, all the methods, which include dynamic correlation, give notably smaller conformational energies of folded forms than HF or CASSCF, which do not include dynamic correlation. Accordingly, we note that in comparison to HF the multi-configurational approach CASSCF improves geometries and harmonic vibrational frequencies (Tables 1, 2, 3), but it has only limited effect on relative energies. As with less suitable DFT functionals (e.g., B3LYP), the relative energies of heptafulvene boat conformations are overestimated with computational methods that do not include dynamic electron correlation.

3.8 Adequacy of computational methods: wave function instabilities

The reliability and accuracy of computational results can be limited by various possible complications. Most computational chemistry software, such as the Gaussian03 [29] or MOLPRO [30] program packages used in this study, allows the testing of the suitability of the computational methods for a specific calculation or reports warning messages automatically. Potential problems of computational methods in heptafulvene calculations are discussed in this and the following chapters. In particular, we have sought to find an explanation for the non-planarity of **1**, observed for certain basis sets using correlated methods (vide infra).

A problem with the wave functions of mono-determinantal methods is the occurrence of wave function instabilities. Such instabilities can be detected when a different HF solution of lower energy can be obtained after a constraint on the HF variation employed is lifted [72]. The instabilities can be external or internal and they are connected to the occurrence of symmetry-broken HF solutions, especially common in compounds with multiple bonds [73]. External instabilities of RHF wave functions, also called triplet or RHF → UHF instabilities, appear when an UHF wave function exists that is of lower energy than the obtained RHF one. Many conjugated π systems are known to exhibit such instability [72, 74]. Internal HF instabilities, often called singlet instabilities, appear when a wave function can be found that is of lower energy than the one initially found, in a self-consistent way. In this case, the originally obtained wave function is not a minimum of the Schrödinger equation and provides only a stationary solution with symmetry-adapted MOs. These kinds of instabilities are related to the ‘symmetry dilemma’ described by Löwdin [75, 76]. They can occur when the MOs of the lower energy wave function belong to a lower symmetry point group than the nuclear coordinates. Accordingly, the reoptimized wave function is of lower energy, but does not have the right symmetry properties [77, 78]. Internal instabilities can be related to the existence of nonadiabatic coupling [77], but frequently they are purely artifactual and thus physically meaningless [78–81].

We note that HF instabilities are often indicated by pronounced biradical character, but a previous investigation has already shown that **1** does not belong to this class of compounds [17]. Nevertheless, we detected internal instabilities in all the calculations of **1** with the HF method. Accordingly, caution is necessary in the interpretation of the results of both HF and post-HF calculations. In general, HF instabilities are quite common for polyene-like compounds. Despite these instabilities, it has been recommended that such compounds should still be geometrically optimized with the restricted variation of the HF method, if they are closed shell in nature [72, 82]. It was found that such instabilities rather indicate that one should take the RHF results with caution than turn away from the RHF method altogether [toward unrestricted (U)HF]. Often the RHF results are still in quite good agreement with experiment, even if instabilities have been detected [83]. Similarly, it has been recommended to use post-HF methods, such as the CCSD based on an RHF wave function in cases of symmetry breaking, and not to switch to an UHF-based approach [84]. Often, the correlation energy of the symmetric solution overcompensates for the higher RHF energy, so that the effects of the HF symmetry breaking are diminished at a higher level of electron correlation [78, 79]. Further, it has been reported that DFT methods tend to avoid artifactual spatial symmetry breaking [85] unless large fractions of HF exchange are included [86]. Accordingly, we confirm that instabilities of **1** cannot be detected for any of the DFT wave functions.

Nevertheless, in general, HF instabilities can be an indication for the importance of non-dynamic electron correlation. Thus, a possible inadequacy of a mono-determinantal ansatz should be considered, not only for the HF calculations but also for post-HF methods. For the CCSD approach, several tests are known to determine the importance of non-dynamical electron correlation and the suitability of the single reference CC method for a given problem. The so-called T_1 diagnostic bases on the norm of the single substitution (t_1) amplitudes [87]. Originally, it was suggested that single reference-based correlation methods, such as CCSD, are unreliable if T_1 is greater than 0.02. We note that cases of symmetry breaking have infrequently been described for which CCSD(T) was not an improvement over CCSD [88]. Usually, however, wave functions that include a perturbational estimate of connected triples [CCSD(T)] are more robust than without this (T)-correction. Therefore, the CCSD(T) level of theory has been shown to perform well for T_1 values up to 0.06–0.08 [89]. More recently, the T_1 diagnostic has been criticized as having undesired properties for large systems and the D_1 diagnostic was suggested, which is also based on the t_1 amplitudes [90, 91]. The critical value that D_1 should not exceed is 0.05 for the CCSD method. The results of the T_1 and D_1 diagnostics are presented in Table 5. Typical values for T_1 in heptafulvene calculations are as low as 0.012 and the values for the D_1 diagnostic are usually between 0.034 and 0.039. These values are well below the suggested critical values, thus underlining the reliability of the CC ansatz [CCSD and CCSD(T)] for the analysis of heptafulvene. It is important to note that, except the small STO-3G basis set, all the different sets give quite comparable values for the T_1 and D_1 diagnostics, respectively. For example, the 6-31G(d,p) set and the 6-31+G(d,p) set have very similar T_1 values, as well as D_1 values, although the 6-31G(d,p) set predicts the C_{2v} minimum and the 6-31+G(d,p) set favors a C_s minimum (vide infra). Therefore, the basis set dependencies of the conformational energies do not seem to result from wave function instability and concomitant inadequacy of a single reference-based wave function.

Another important aspect with respect to reliability of post-HF methods concerns the BD calculations (Fig. 4). The BD(T) level of theory is often more robust against artifactual symmetry breaking than the CCSD(T) method [70, 71]. In this respect, we note that with the aug-cc-pVDZ basis set the SP conformational energies of **1** are almost identical on the BD(T) and CCSD(T) levels of theory. This similarity indicates that spatial symmetry breaking of the single reference wave function is not problematic for heptafulvene conformational energies at the CCSD(T) level. Otherwise, a noticeable difference between these two curves should have been observable.

Table 5 CCSD single point calculations of **1** in different geometries for the determination of T_1 and D_1 diagnostic values

Conf.	d_1 (°)	Basis set	T_1	D_1
C_{2v} [a]	0	STO-3G	0.0041	0.0189
C_{2v} [a]	0	6-31G(d,p)	0.0119	0.0371
C_{2v} [a]	0	6-31+G(d,p)	0.0121	0.0389
C_{2v} [a]	0	cc-pVDZ	0.0117	0.0353
C_{2v} [a]	0	aug-cc-pVDZ	0.0117	0.0342
C_{2v} [a]	0	6-311G(d,p)	0.0120	0.0371
C_{2v} [b]	0	6-31G(d,p)	0.0119	0.0372
C_{2v} [b]	0	6-31+G(d,p)	0.0120	0.0387
C_s [b]	40	6-31G(d,p)	0.0117	0.0358
C_s [b]	40	6-31+G(d,p)	0.0118	0.0368
C_s [b]	90	6-31G(d,p)	0.0115	0.0346
C_s [b]	90	6-31+G(d,p)	0.0116	0.0349

[a] Geometric optimization at the same level of theory given for the SP calculations

[b] Geometric optimization at the CASSCF(8,8)/6-31+G(2d,p) level of theory

We concluded that the existence of HF instabilities is less of a problem in heptafulvene calculations. In fact, the geometric parameters and vibrational frequencies obtained with HF are slightly inferior compared to other methods, but they do not appear to be qualitatively incorrect. The structural differences between HF geometries and those minima, which have been obtained, e.g., with DFT methods, are only numerical. In principle, both these methods predict the same type of geometry with the same symmetry properties. As all of the DFT methods result in stable wave functions, the HF instabilities have to be regarded as artifactual. Various diagnostics for the CC approach indicate that CC wave functions of **1** that are based on unstable RHF solutions represent an adequate description. Accordingly, HF instabilities do not explain the irregularities of the SP energies of **1** obtained with certain basis sets combined with correlated methods (vide infra).

3.9 Adequacy of computational methods: near linear dependence

Another potential source of error can be the basis set, which is often the greatest source of inaccuracy [92]. It is important to evaluate possible falsification of results due to the near linear dependence of atomic basis functions. These are numerical problems, also called near singularities of the basis set. They occur when small eigenvalues are present in the overlap matrix, which, in turn, lead to very large MO coefficients in the wave function [92]. Gaussian03 [29] and MOLPRO [30] routinely check for such problems, but the cut-off values are slightly different.

Typically, near linear dependencies are often detected in cases when diffuse functions are included in the basis set or when very large basis sets are used. Problems with near linear dependence can result in unreliable energies. In particular, the relative energies between different conformations of a molecule can be affected drastically [93]. In this respect, it has to be kept in mind that conformational energies result from a subtraction of two very large absolute values. Hence, small proportional inaccuracies of the total electronic energies can result in large proportional errors of the relative energies. In general, those methods that include dynamic electron correlation are affected to a greater extent than HF [92, 93].

Gaussian03 aborts post-HF calculations if any MO coefficient is larger than 1,000 and prints a warning message in less severe cases. In the course of these studies, none of the heptafulvene calculations was aborted due to this problem, but warnings were frequently printed. Table 6 summarizes the largest MO coefficients corresponding to such warning messages, observed in MP2 SP calculations. The energies of these respective calculations are presented in Table 4. In addition to the MO coefficient obtained for the planar form, Table 6 also contains the difference (ΔMO) between the largest MO coefficient of the planar form and that of the boat form with a dihedral angle d_1 of 20°.

The data collected in Table 6 do not reveal any systematic difference between those basis sets that favor the planar form and those that favor a boat-form minimum of **1**. For example, in both groups, basis sets can be found that have small absolute values of the largest MO coefficient and small ΔMO values. Such basis sets favoring the planar minimum are, among others, the cc-pVTZ, the 6-31G(2d,p), the 6-311G(2d,p), and the D95(d,p) set, whereas the 6-311G(d,p) and the SV set favor a boat-form minimum. Similarly, in both groups, basis sets can be found that have relatively large values of the largest MO coefficient and likewise relatively large ΔMO values. These include, e.g., the 6-311++G(2df,p), the 6-31++G(3d′,p′), and the D95V++(2d,p) set, which predict C_{2v} minima, or the 6-311++G(d,p) and the D95++(d,p) set, which predict C_s minima. All of these basis sets are augmented with diffuse functions on both heavy elements and hydrogen. Furthermore, basis sets with relatively great values of the largest MO coefficient and quite small ΔMO values are also represented in both groups. Examples of such basis sets are the 6-31++G(2d,p), the 6-31++G(2d′,p′), and the D95V+(2d,p) set, favoring the planar minimum, and the 6-31++G(d,p), the 6-31++G(d′,p′), and the D95V+(d,p) set, which predict folded minima.

One of the most illustrative comparisons concerns the pair of basis sets 6-31++G(d′,p′) and 6-31++G(2d′,p′). Table 6 shows that these sets give almost equal values of the largest MO coefficients and of ΔMO. Notwithstanding, Table 4 reveals that one of these sets favors the C_{2v} minimum by 0.19 kcal mol^{-1}, while the other one favors the folded geometry by approximately the same energy (0.21 kcal mol^{-1}). Accordingly, we do not find a clear indication that the presence of near linear dependences in the basis sets causes the inconsistency of electron-correlated conformational energies. No systematic difference in the occurrence of large MO coefficients could be detected between the two groups of basis sets.

3.10 Adequacy of computational methods: d-polarization functions

Examples of other unsaturated compounds are known in which the accuracy of calculated out-of-plane vibrational modes is critical, when electron correlated levels of theory are used. In some cases, the error of certain vibrational modes is significantly larger than that of most of the others [94]. In a few of the previously described examples, a strong dependence of these specific vibrational modes on the basis set has been detected [95–97]. The calculated wave numbers can be up to 200 cm^{-1} too low, compared to the observed ones. If these errors cause the frequencies of the respective vibrational mode to become imaginary, unsaturated compounds give anomalous non-planar geometries in calculations with certain basis sets [95]. It was argued that such false non-planar equilibrium structures of benzene are due to a basis set incompleteness error [98]. These inaccuracies reflect the inability of certain basis sets to properly describe two-electron correlation effects. For benzene, especially, the correlation energy between σ and π electrons has been determined as the most important factor, responsible for the erroneous distortions to non-planarity [95].

It was found that Dunning's correlation consistent basis sets perform well in some of such cases [95]. This conclusion is supported by our results, presented in Table 4, which show correct predictions of the planar minimum with all of these basis sets. Some previous studies revealed that the inclusion of f-polarization functions sometimes improves the out-of-plane vibrational frequencies of unsaturated rings [95, 97]. However, f-functions do not seem to be crucial for calculations on heptafulvenes, because the 6-31+G(df,p) basis set does not give a

Table 6 Large MO coefficients observed in MP2 single point calculations of **1**, optimized at the CASSCF(8,8)/6-31+G(2d,p) level of theory

Basis sets favoring C_{2v} [a]	Largest MO coefficient[b]	ΔMO[c]	Basis sets favoring C_s [a]	Largest MO coefficient[b]	ΔMO[c]
cc-pVDZ	–	–	–	–	–
aug-cc-pVDZ	95.6	−93.9	–	–	–
cc-pVTZ	25.4	4.8	–	–	–
aug-cc-pVTZ	135.0	10.0	–	–	–
cc-pVQZ	45.4	−0.3	–	–	–
6-31G(d,p)	–	–	–	–	–
6-31G(2d,p)	10.7	0.6	–	–	–
6-31+G(2d,p)	191.8	71.9	6-31+G(d,p)	189.0	66.6
6-31+G(3d,p)	210.4	70.7	6-31+G(df,p)	189.5	67.1
6-31+G(2df,p)	196.4	75.7	6-31++G(d)	282.2	25.6
6-31++G(2d,p)	291.4	31.9	6-31++G(d,p)	284.3	27.9
6-311G(2d,p)	20.3	2.5	6-311G(d,p)	13.3	2.7
6-311+G(2d,p)	178.6	31.1	6-311+G(d)	183.6	35.5
6-311+G(3d,p)	211.7	29.3	6-311+G(d,p)	183.6	35.7
6-311++G(2d,p)	244.2	109.8	6-311+G(df,p)	185.9	43.5
6-311++G(2d,2p)	245.7	109.8	6-311++G(d)	230.5	97.9
6-311++G(2df,p)	243.1	108.5	6-311++G(d,p)	239.9	107.1
6-311++G(3d,p)	243.0	97.1	–	–	–
6-311++G(3df,3p)	231.2	85.6	–	–	–
6-31G(d′)	–	–	–	–	–
6-31G(d′,p′)	–	–	–	–	–
6-31+G(2d′,p′)	199.6	78.2	6-31+G(d′)	190.8	69.2
6-31+G(3d′,p′)	219.3	65.3	6-31+G(d′,p′)	189.8	68.6
6-31++G(2d′,p′)	295.5	34.2	6-31++G(d′,p′)	287.4	30.3
6-31++G(3d′,p′)	259.1	113.4	–	–	–
D95V(d,p)	12.0	−0.1	–	–	–
D95V(2d,p)	12.8	2.6	–	–	–
D95V+(2d,p)	212.4	−9.7	D95V+(d,p)	211.1	−0.6
D95V++(2d,p)	251.0	124.5	D95V++(d,p)	249.6	114.3
D95(d)	12.5	0.4	–	–	–
D95(d,p)	12.1	0.0	–	–	–
D95+(2d,p)	213.3	−19.0	D95+(d,p)	211.1	−3.8
D95++(2d,p)	251.2	123.7	D95++(d,p)	249.9	115.1
–	–	–	SV	11.6	0.4
–	–	–	SVP	10.6	10.6
–	–	–	TZV	41.8	1.9
–	–	–	TZVP	43.8	5.8

[a] In the C_{2v} geometry, the dihedral angle d_1 equals 0° and it was constrained to 20° in the optimization of the C_s geometry; the energies of these MP2 SP calculations are given in Table 4

[b] The largest MO coefficient obtained for the planar C_{2v} geometry (Gaussian03-warning messages)

[c] The differences (ΔMO; plan − boat) between the largest MO coefficients of the planar forms and those of the C_s boat forms

significant improvement over the 6-31+G(d,p) set. Both sets predict C_s minima.

For calculations on heptafulvenes, an appropriate inclusion of d-polarization functions seems to be more important. Analyses of ethene showed that accurate values for its b_{2g} out-of-plane frequency are only obtained when the basis set includes at least two sets of d-polarization functions [96]. It was argued that particularly the d-functions with small exponents α_d are important in this case. Such d-functions having sufficiently small exponents are typically not present, when the basis sets include only a single set of d-functions. Investigations of conjugated π ring systems highlighted the fact that it is often important to include d-functions with an exponent close to $\alpha_d = 0.4$, in order to obtain reliable out-of-plane frequencies for unsaturated rings [97]. In Pople-type basis sets, d-functions with such an exponent are present in basis sets that incorporate two sets of d-functions, such as the 6-31G(2d,p), the 6-31G(2df,p) or the 6-311G(2d,p) set, but not basis sets such as the 6-31G(d,p), the 6-31G(3d,p), or the 6-31G(df,p) set. The 6-31G(d,p) and the 6-311G(d,p) set, e.g., have the d-exponents $\alpha_d = 0.8$ and $\alpha_d = 0.6$, respectively [97]. In contrast, the d-exponents of the 6-31G(2d,p) set are 0.4 and 1.6, and if three sets of d-functions (3d) are present, the exponents are 0.2, 0.8, and 3.2.

Our classification of basis sets into two groups that predict either a planar or a boat-form minimum for **1** (Table 4) partly fits into this scheme. In particular, the augmentation with diffuse functions demands an appropriate inclusion of d-polarization functions. For calculations of **1**, not only the basis sets with two sets of d-functions (2d), but also the sets with three sets of d-functions (3d) perform noticeably better than those with only one set [e.g., 6-31+G(d,p)]. Accordingly, we cannot declare that an exponent (α_d) of exactly 0.4 is optimal for heptafulvene calculations, as the smallest exponent of the 3d set is not 0.4 but 0.2. We note, however, that a d-exponent significantly smaller than 0.8 (e.g., 0.2 or 0.4) should be included. We also report that this trend is not only observed for Pople-type basis sets. The families of Dunning/Huzinaga and Petersson basis sets also require at least two sets of d-functions, when diffuse functions are incorporated.

4 Conclusions

In this study, we evaluated the suitability of various computational methods to describe the heptafulvene system. For that purpose, we compared the geometric parameters and the wave numbers of the lowest frequency vibrational mode with experimentally obtained values, and also compared the conformational energies obtained with different methods to each other. All calculations were performed on the parent heptafulvene **1**. However, we expect most of our conclusion to be valid also for derivatives of **1**.

The HF method gave the worst results for the geometric parameters and conformational energies. Furthermore, the wave numbers of the analyzed vibrational modes are in disagreement with experiment. Although we detected internal instabilities of all the HF wave functions, we concluded that the wave function instabilities do not account for the inaccurate HF results. The instabilities are artifactual, because when compared to the results of other computational methods, the errors obtained with HF are best characterized as numerical differences. In principle, the restricted HF method gives the same type of heptafulvene structure, with the same symmetry properties, as all the other analyzed methods. Similarly, the HF instabilities do not seem to limit the reliability of post-HF methods, as indicated by the acceptable values of the T_1 and D_1 diagnostics of the CCSD method.

In the geometric optimizations, the best results were obtained with the multi-configurational CASSCF approach. With this method, MUEs for carbon–carbon bond lengths below 0.9% and MUEs for intracyclic bond angles below 0.4% can be obtained. Geometric optimizations with the CCSD method yield geometries almost as good as those obtained with CASSCF, but CCSD calculations are more expensive. It is a particularly significant disadvantage of the CCSD method that it requires harmonic frequencies to be calculated numerically with the program packages employed herein.

Among the computationally less expensive methods (HF, DFT, MP2), the DFT method using the M05-2X functional gave the best results for most of the analyzed criteria. Compared with experimental results, the geometric parameters obtained with the M05-2X functional have small MUEs. Furthermore, the differences between conformational energies obtained with the M05-2X functional and those of very accurate methods, such as CCSD(T), are also comparably small. Accordingly, for energies and geometric parameters, the M05-2X functional appears to be a good compromise, providing accuracy at low computational cost. Notwithstanding, due to the incorporation of a large amount of HF exchange in the M05-2X functional, significant errors are observed in the wave numbers of the lowest frequency out-of-plane vibrational mode. This frequency is strongly underestimated with the HF method, but DFT methods using other functionals, such as the B3LYP, B1B95 or M05 functionals, give wave numbers that are closer to the experimental results.

In order to obtain accurate conformational energies of **1**, the computational method has to account for dynamic electron correlation; otherwise, the energies of folded geometries are overestimated. The most accurate methods employed herein are the CCSD(T), the BD(T) and the CASPT2 methods. All of these give almost identical conformational energies. However, with the exception of DFT, great caution is necessary when computational methods are used that include dynamic electron correlation. We report that the performance of MP2, CC, or CASPT2 is highly sensitive toward the basis set. For example, on the MP2 level, the planar C_{2v} conformation of **1** is not obtained as a minimum with approximately half of the basis sets analyzed. Only the group of Dunning's correlation consistent plus polarization basis sets consistently predicts the correct minimum. For all the other classes of basis sets analyzed, we noted that false predictions of the minimum are observed often (but not exclusively) when the basis sets are augmented with diffuse functions. Analogously to similar problems infrequently observed for other unsaturated rings, we found that an adequate incorporation of d-polarization functions is most important in electron-correlated calculations of **1**, other than DFT. The basis set has to include d-functions with an appropriate exponent α_d. Most often, the basis sets do not include d-polarization functions with suitable exponents when only one set of d-functions is present. For the basis sets of Pople et al., Petersson et al. and Dunning and Huzinaga, the inclusion of two sets of d-functions (2d) was found to be a good choice.

As regards the properties of heptafulvenes, the reported conformational energies allow the conclusion that **1** has a very flat PES in the vicinity of the planar C_{2v} minimum. Accordingly, **1** is best characterized as a conformationally flexible molecule, which explains the great geometric differences introducible by slight changes of the basis sets. We note that with respect to planarity or non-planarity of **1**, its conformational energies are strongly related to the torsion potential between conjugated double bonds. Hence, the results presented herein might also indicate caution in the computational analysis of other π-conjugated compounds not belonging to the heptafulvene class.

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