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Comparative Theoretical and Experimental Analysis of Hydrocarbon σ-Radical Cations

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Abstract—The structures of σ-radical cations formed by ionization of adamantane, twistane, noradamantane, cubane, 2,4-dehydroadamantane, and protoadamantane were optimized at the B3LYP, B3LYP-D, M06-2X, B3PW91, and MP2 levels of theory using 6-31G(*d*), 6-311+G(*d*,*p*), 6-311+G(3*df*,2*p*), cc-PVDZ, and cc-PVTZ basis sets. On the whole, single-configuration approximations consistently describe the structure and transformations of the examined σ-radical cations. The best correlations (r = 0.97–0.98) between the calculated adiabatic ionization potentials and experimental oxidation (anodic) potentials of hydrocarbons were obtained in terms of B3PW91 approximation.

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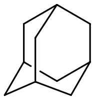
Radical cations are formed as intermediates in a number of important natural processes. They are responsible for repair of damaged DNA [1], antioxidant properties of carotenoids [2], photosynthesis [3, 4], and visual process [5]; radical cations are also formed in chemical reactions occurring in atmosphere [6]. Radical cations are generated during important preparative oxidative transformations, and their study is necessary for understanding fundamental reaction mechanisms [7, 8]. Detection and structural analysis of hydrocarbon radical cations are limited by the existing physical methods. Recording of their electronic spectra is possible when characteristic absorption bands are intrinsic to radical cations [9]. Magnetic resonance methods are more informative, but their application is limited by short lifetime of radical cation intermediates [10]. Unfortunately, most available methods are almost inapplicable to extremely unstable hydrocarbon σ-radical cations, and only a few examples of such studies have been reported [11].

On the other hand, modern computational procedures make it possible to predict the structure and behavior of hydrocarbon σ-radical cations, though the results of theoretical calculations sometimes do not agree with the experimental data because of dynamic effects. For example, DFT quantum-chemical calculations predicted an energy minimum for methane radical cation having C_{2v} symmetry [12], whereas analysis of the ESR spectrum recorded in neon matrix at 4 K indicated equivalence of all four protons [13].

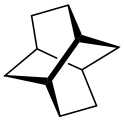
We previously studied the structure and transformations of radical cations derived from adamantane and its alkyl derivatives [14], cubane [15], protoadamantane [16], homoadamantane [17], propellanes [18], and rotanes [19] in terms of the density functional theory (DFT) with the use of popular B3LYP functional. Although in some cases good correlations between the calculated (B3LYP) and experimental data were observed, in particular for diamondoids [20], the problem related to applicability of various theoretical approaches to hydrocarbon σ-radical cations and improvement of their quality remains important. Among other factors, the reason is that standard DFT approximations tend to localize charge and spin density in radical cations [21].

Furthermore, during the past 5 years, appropriateness of DFT methods (especially of B3LYP) for the calculation of even simple hydrocarbon molecules has been put in doubt [22]. We showed that B3PW91 ensured the best results among traditional DFT functionals in the calculation of heats of formation of hydrocarbons [23]. The model structures proposed by us were subsequently used to estimate the efficiency of a new family of highly parameterized M05–M06 functionals [24]. In addition, the quality of calculations on hydrocarbon molecules can be considerably improved by inclusion of dispersion components into traditional DFT functionals (e.g., B3LYP-D [25]).

Despite some advances achieved by the use of new DFT approaches (M06, B3LYP-D) for the estimation of energy of stable molecules, their applicability to reactive intermediates, in particular for the determination of structure and energy of radical cations, is an open question. In the present study we used as model structures six different saturated cage-like hydrocarbons: adamantane (**I**), twistane (**II**), noradamantane (**III**), cubane (**IV**), 2,4-dehydroadamantane (**V**), and protoadamantane (**VI**). As DFT calculation procedures, we tested traditional B3LYP functional, B3PW91 (which showed good results previously [23]), M06-2X [24], dispersion-corrected B3LYP-D functional [25], and MP2 classical *ab initio* method; in addition, orbital basis sets were varied over a wide range (see below). The calculated adiabatic ionization potentials I_a of hydrocarbons **I**–**VI** were compared with the experimentally measured anodic oxidation potentials $E_{1/2}$. As shown previously, the I_a and $E_{1/2}$ quantities correlate well with each other for a large number of organic molecules [26].



I



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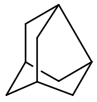

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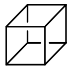

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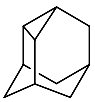
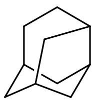


V



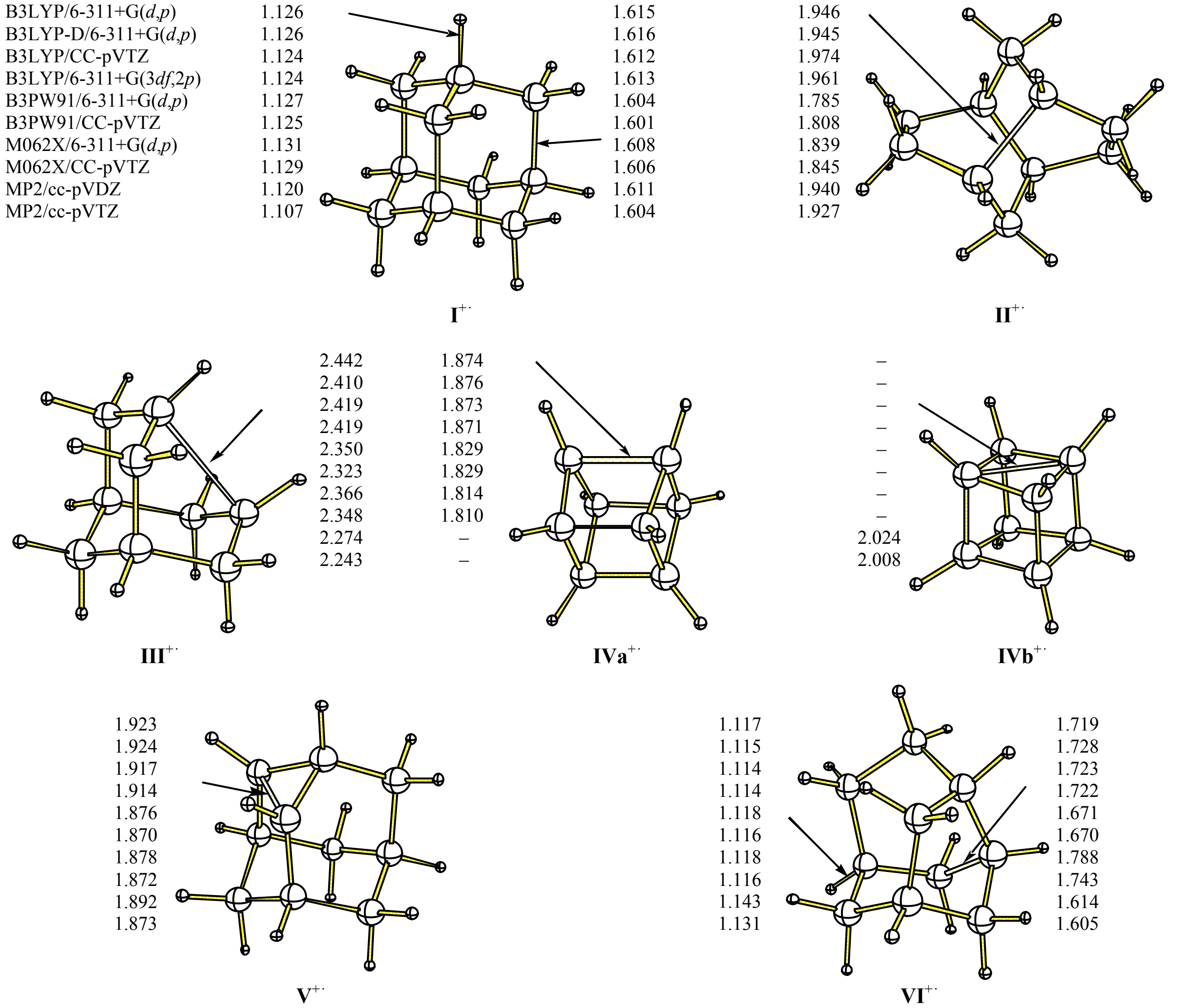
VI

Figure shows optimized structures of radical cations derived from model hydrocarbons **I**–**VI**; key bond lengths therein are also given. Ionization of adamantane (**I**) gives rise to C_{3v}-symmetric radical cation ($\mathbf{I}^{+\cdot}$) with three extended C–C bonds and extended tertiary C–H bond. Twistane is converted into stable C_2 minimum ($\mathbf{II}^{+\cdot}$) with one extended C–C bond. Even stronger extension of C–C bond is observed in radical cation $\mathbf{III}^{+\cdot}$ derived from strained noradamantane. The results of *ab initio* and DFT calculations for radical cations $\mathbf{I}^{+\cdot}$–$\mathbf{III}^{+\cdot}$ were qualitatively similar, whereas calculations of cubane radical cation predicted two different structures $\mathbf{IVa}^{+\cdot}$ and $\mathbf{IVb}^{+\cdot}$. DFT calculations gave C_{2v} minimum having one extended C–C bond ($\mathbf{IVa}^{+\cdot}$), whereas MP2 calculations led to structure $\mathbf{IVb}^{+\cdot}$ in which all eight skeletal carbon atoms participated in charge and spin delocalization. All calculation procedures consistently indicated extension of the C^2–C^4 bond in radical cation $\mathbf{V}^{+\cdot}$; analogous variation of geometric parameters was observed by us previously for the radical cation derived from highly strained 1,3-dehydroadamantane [27]. The structure of protoadamantane radical cation with extended C^6–H bond was obtained at all the examined levels of theory and was analogous to that found previously [17] by B3LYP/6-31G(*d*) calculations.

Thus different results of DFT and *ab initio* calculations were obtained only for highly strained cubane radical cation, which tends to strong Jahn–Teller distortion. Both DFT and MP2 calculations consistently described both primary (**I**) and secondary (**II**) Jahn–Teller distortions for adamantane (**I**) and twistane (**II**). Ionization of hydrocarbons **III**, **V**, and **VI** is not accompanied by change of their symmetry.

The experimental oxidation potentials of compounds **I**–**VI** were measured in the potentiostatic mode in acetonitrile using $LiBF_4$ as supporting electrolyte (see Experimental). The experimental oxidation potentials and adiabatic ionization potentials calculated by different methods are collected in Table 1. Table 2 contains the correlation coefficients found for each calculation procedure with different basis sets.

As might be expected, traditional B3LYP calculations were characterized by the lowest correlation coefficient, and correction for dispersion (B3LYP-D) did not improve the correlation. It should be noted that extension of basis set from 6-311+G(*d*,*p*) to 6-311+G (3*df*,2*p*) also did not improve the quality of calculations. The results of MP2 (*ab initio*) calculations revealed relatively poor correlation coefficients due to contamination of doublet spin states (the observed values of S^2 spin operator ranged from 0.77 to 0.79). Analogous pattern was repeatedly noted for MP2 calculations of molecules with open shells [28]. No considerable improvement of the results was achieved using spin-corrected PMP2 energies. On the average, the use of M06-2X functional somewhat improved the quality of calculations, especially with correlation-dependent cc-PVDZ functional. However, the strongest improvement was achieved using B3PW91 functional;



Structures of radical cations of hydrocarbons **I–VI** optimized at different levels of theory and key bond lengths (Å) therein.

in this case, satisfactory correlations between the theoretical and experimental data were obtained with all basis sets examined in this work. As compared to B3LYP, insignificant dependence of the PW91 calculation results on the basis set used was noted previously [29]. It was also found [29] that PW91 functional is capable of reproducing weak van der Waals interactions. Presumably, these properties of the exchange-correlation constituent of B3PW91 ensure high quality of calculations of hydrocarbon radical cations **I–VI** containing considerably extended σ-bonds.

Both optimized structures of radical cations and the character of distortion of geometric parameters upon ionization of hydrocarbons are generally similar for calculations performed at all the examined levels of theory. The only exception is cubane (**IV**) for which DFT and MP2 calculations revealed qualitatively different structures of radical cations (see figure). We can state with certainty that modern quantum-chemical methods based on single-configuration approximation, appropriately describe such complex systems as σ-radical cations. This is confirmed not only by the above correlations but also by the experimental data on the behavior of saturated hydrocarbons **I–VI** in electrochemical oxidation performed at a preparative scale. According to the calculations, radical cations derived from adamantane (**I**) and protoadamantane (**VI**) contain considerably extended tertiary C–H bonds (see figure) at C^1 and C^6, respectively. As a result, anodic oxidation of compounds **I** [30] and **VI** [31] involves loss of proton from the corresponding positions with selective formation of acetamides **VII** and **VIII**

Table 1. Calculated adiabatic ionization potentials (I_a, kcal/mol) and experimental anodic oxidation potentials of hydrocarbons **I**–**VI**

Calculation method	Basis set	**I**	**II**	**III**	**IV**	**V**	**VI**
MP2	6-31G(*d*)	204.2	206.3	208.1	194.2	185.6	218.3
	cc-PVDZ	204.2	206.3	208.1	194.2	190.9	213.2
B3LYP	6-311+G(*d*,*p*)	204.0	198.8	201.9	193.6	186.3	203.4
	6-311+G(*d*,*p*)-D	203.9	198.7	202.1	193.5	186.0	205.8
	6-311+G(3*df*,2*p*)	203.5	198.2	201.1	192.7	186.1	205.5
	cc-PVTZ	203.3	198.0	200.9	192.8	185.9	205.4
M062X	6-311+G(*d*,*p*)	209.8	205.4	209.4	195.9	192.4	212.9
	cc-PVDZ	208.5	204.1	208.7	195.5	191.7	211.2
	cc-PVTZ	209.4	204.8	208.7	195.6	192.2	212.2
B3PW91	6-311+G(*d*,*p*)	203.2	198.7	204.8	193.9	187.6	205.2
	6-311+G(3*df*,2*p*)	202.6	198.0	204.0	193.0	187.2	204.6
	cc-PVTZ	202.4	197.9	203.8	192.9	187.1	204.5
	cc-PVDZ	202.1	197.5	204.4	193.3	186.7	204.0
Oxidation potential (s. c. e.), V		3.0	2.8	3.4	2.4	1.9	3.2

(Scheme 1) in 75 and 70% yield, respectively. When the electrochemical oxidation of **I** and **VI** was carried out in the presence of $LiBF_4$ as supporting electrolyte, the preparative yields of acetamides **VII** and **VIII** even exceeded 90%.

We also found that preparative oxidation of twistane (**II**), noradamantane (**III**), and 2,4-dehydroadamantane (**V**) under analogous conditions leads to complex mixtures of mono- and bis-acetamides (according to the GC-MS data; see Experimental). This result is also very consistent with the theoretical data for the corresponding radical cations: calculations performed at all levels of theory revealed structures with extended C–C bonds. Extension of C–C bond may be accompanied by both its dissociation during the oxidation process and proton abstraction from different secondary carbon atoms, which is observed experimentally.

Table 2. Coefficients of correlations between anodic oxidation potentials and calculated adiabatic ionization potentials of hydrocarbons **I**–**VI**

Calculation method	Basis set	*r*
MP2	6-31G(*d*)	0.89
	cc-PVDZ	0.88
B3LYP	6-311+G(*d*,*p*)	0.93
	6-311+G(*d*,*p*)[a]	0.89
	6-311+G(3*df*,2*p*)	0.87
	cc-PVTZ	0.87
M062X	6-311+G(*d*,*p*)	0.9
	cc-PVDZ	0.92
	cc-PVTZ	0.89
B3PW91	6-311+G(*d*,*p*)	0.98
	6-311+G(3*df*,2*p*)	0.96
	cc-PVTZ	0.97
	cc-PVDZ	0.96

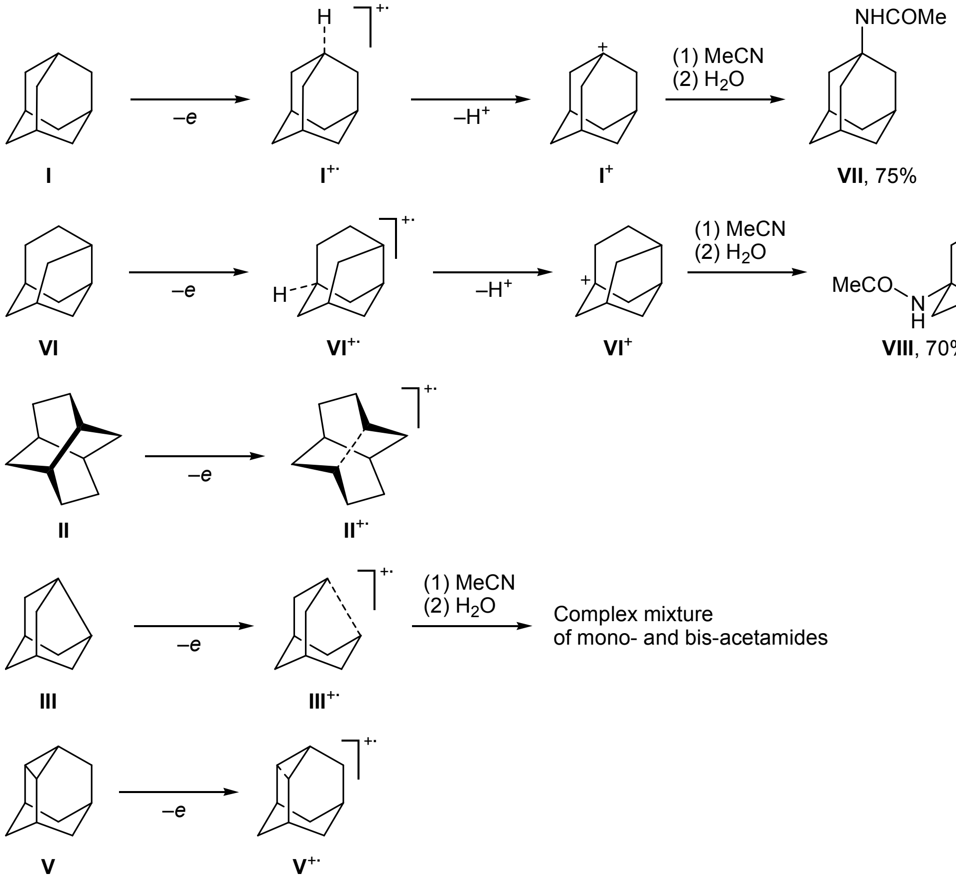
[a] B3LYP-D.

EXPERIMENTAL

Cyclic voltammograms were recorded with the aid of an AFRDE5 analytical instrument (Pine Instrument Company) in the potentiostatic mode at potential sweep rates of 100 and 200 mV/s in acetonitrile using 0.1 M $LiBF_4$ as supporting electrolyte. A platinum disk was used as working electrode, a saturated calomel electrode was used as reference electrode, and a platinum wire served as auxiliary electrode. Working solutions were preliminarily deoxygenated by bubbling dry argon therethrough. The voltammograms were recorded at a disk rotation speed of 1000–3000 rpm.

Adamantane (**I**) was purified by recrystallization of commercial product from hexane–methanol, followed by sublimation. Twistane (**II**) was synthesized according to a 11-step scheme from cyclohexa-1,3-diene and ethyl acrylate [32], noradamantane (**III**) was prepared in 4 steps from protoadamantanone [33],

Scheme 1.



cubane (**IV**) was obtained by an improved procedure from cyclopentanone [34], 2,4-dehydroadamantane (**V**) was synthesized by pyrolysis of spiro[adamantane-2,3′-diazirine] as described in [35], and protoadamantane (**VI**) was prepared in 4 steps [36] from commercially available adamantan-1-ol. Lithium tetrafluoroborate (Aldrich) was used without additional purification. Acetonitrile was distilled twice over calcium hydride in a stream of argon.

The mass spectra were obtained on a Hewlett–Packard HP 5970B mass-selective detector coupled with an HP 5890 Series II gas chromatograph (HP-1 30-m capillary column, oven temperature programming from 100 to 250°C at a rate of 10 deg/min).

Preparative electrochemical oxidation of hydrocarbons I–VI (*general procedure*). An electrochemical cell (platinum wire helix as cathode, platinum cylinder with an area of 100 cm^2 as anode; the cathodic and anodic spaces were separated by porous glass to reduce diffusion) was charged under argon with 100 ml of acetonitrile, 940 mg of $LiBF_4$, and 1.5 mmol of compound **I**–**VI**. The oxidation was carried out under stirring at a potential exceeding by 50 mV (saturated silver chloride electrode as reference) the corresponding oxidation potential (determined from the data of cyclic voltammograms). The oxidation was complete after passing 0.003 F of electricity ($n = 2$).

The yield of acetamide **VII** was 75%; the product was identical to an authentic sample. The yield of acetamide **VIII** was 70%; the product was identical to an authentic sample. The oxidation of twistane (**II**) gave a mixture of four acetamides with the general formula $C_{12}H_{19}NO$. GC–MS data: 20.6 min (40%), mass spectrum, m/z (I_{rel}, %): 193 (45) $[M]^+$, 150 (15) $[M - CH_3CO]^+$, 134 (100) $[M - CH_3CONH_2]^+$, 119 (7), 108 (66); 21.2 min (10%), mass spectrum, m/z (I_{rel}, %): 193 (14) $[M]^+$, 150 (15) $[M - CH_3CO]^+$, 134 (75) $[M - CH_3CONH_2]^+$, 119 (18), 60 (100); 21.3 min (6%), mass spectrum, m/z (I_{rel}, %): 193 (42) $[M]^+$, 178 (6) $[M - CH_3]^+$, 150 (3) $[M - CH_3CO]^+$, 134 (100) $[M - CH_3CONH_2]^+$, 119 (11); 21.6 min (44%), mass spectrum, m/z (I_{rel}, %): 193 (99) $[M]^+$, 178 (15) $[M - CH_3]^+$, 150 (11) $[M - CH_3CO]^+$, 134 (100) $[M - CH_3CONH_2]^+$, 119 (43), 60 (76). The oxidation of noradamantane (**III**) gave a mixture of two acetamides with the general formula $C_{11}H_{17}NO$. GC–MS data: 19.7 min (25%), mass spectrum, *m*/*z* (I_{rel}, %): 179 (90) $[M]^+$, 164 (96) $[M - CH_3]^+$, 136 (52) $[M - CH_3CO]^+$, 120 (58), 105 (37); 19.9 min (75%), mass spectrum, *m*/*z* (I_{rel}, %): 193 (14) $[M]^+$, 164 (28) $[M - CH_3]^+$, 136 (57) $[M - CH_3CO]^+$, 120 (100). The oxidation of 2,4-dehydroadamantane (**V**) gave a complex mixture of products, among which we identified monoacetamides with the general formula $C_{12}H_{19}NO$: 21.2–21.4 min (38%), mass spectrum, *m*/*z* (I_{rel}, %): 193 (100) $[M]^+$, 178 (24) $[M - CH_3]^+$, 150 (31) $[M - CH_3CO]^+$, 134 (56) $[M - CH_3CONH_2]^+$, 119 (14), 92 (70); and bis-acetamides $C_{14}H_{22}N_2O_2$: 24.1 min (5%), mass spectrum, *m*/*z* (I_{rel}, %): 207 (44) $[M - CH_3CO]^+$, 179 (100), 164 (31) $[M - 2CH_3CO]^+$, 136 (26), 120 (48).

Quantum-chemical calculations were performed using Gaussian09 [37] and Gaussian03 software packages [38] supplemented by the Grimme dispersion corrections.* All optimized structures occupied minima on the potential energy surface, as followed from the calculation of their normal vibration frequencies ($N_{imag} = 0$). The calculated relative electronic energies were neither corrected nor scaled.

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