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Noncovalent interactions in crowded olefinic radical cations

Aim. To study the effect of electronic (α - and β -hyperconjugations) and steric (noncovalent interactions) factors on the structures of olefinic radical cations.

Results and discussion. The effect of intramolecular dispersion interactions on the structures of crowded alkenes in the neutral and ionized forms has been studied at the density functional theory (DFT) level with and without dispersion corrections included, as well as at the MP2 theory level with medium size basis sets. The results obtained are compared to the available experimental data. An excellent agreement has been found between the experimental and MP2/DFT-computed geometries of sesquihomoadamantene, adamantylidene adamantane, *bis*-2,2,5,5-tetramethylcyclopentylidene, *bis*- D_3 -homocub-4-ylidene, and *bis*- C_5 -homocub-8-ylidene in the neutral and ionized forms. The experimental ionization potentials are better reproduced with the DFT-methods.

Experimental part. The structure and composition of compounds were proved by the methods of ¹H and ¹³C NMR-spectroscopy, and GC-MS-analysis. Elemental analysis was performed for the compounds obtained.

Conclusions. The twisting of the olefinic moieties in the sesquihomoadamantene and adamantylidene adamantane radical cations is determined by the balance between the σ - π -hyperconjugation and residual one-electron π -bonding and is close to that of the prototypical ethylene radical cation (29°). The twisting reaches 55° for the *bis*-2,2,5,5-tetramethylcyclopentylidene radical cation due to substantial steric repulsions between methyl groups. At the same time, the ionized states of *bis*- D_3 -homocub-4-ylidene and *bis*- C_5 -homocub-8-ylidene retain their planarity due to β -CC-hyperconjugation and intramolecular dispersion attractions.

Key words: hyperconjugation; ionization potentials; noncovalent interactions; olefins; radical cations

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Нековалентні взаємодії в просторово-утруднених олефінових катіон-радикалах

Мета роботи. Дослідити вплив електронних (α - і β -гіперкон'югація) та стеричних (нековалентні взаємодії) факторів на структуру олефінових катіон-радикалів.

Результати та їх обговорення. Вплив внутрішньомолекулярних дисперсійних взаємодій на будову просторово-утруднених алкенів у нейтральній та іонізованій формах досліджено на рівні теорії функціоналу густини (ТФГ) з урахуванням та без урахування дисперсійних корекцій, а також на рівні теорії MP2 з базисними наборами середнього розміру. Отримані результати порівняно з наявними експериментальними даними. Знайдено добре узгодження між експериментальними та оптимізованими (MP2/ТФГ) структурами сесквігомоадамантену, адамантиліденадамантану, *bis*-2,2,5,5-тетраметилциклопентилідену, *bis*- D_3 -гомокуб-4-ілідену та *bis*- C_5 -гомокуб-8-ілідену в нейтральних та іонізованих формах. Експериментальні потенціали іонізації краще відтворюються при розрахунку методами ТФГ.

Експериментальна частина. Структуру та склад сполук було доведено методами ¹H та ¹³C ЯМР-спектроскопії, а також ГХ-МС-аналізом. Проведено елементний аналіз одержаних сполук.

Висновки. Скручування олефінового фрагменту в сесквігомоадамантановому та адамантиліденадамантановому катіон-радикалах визначається балансом між σ - π -гіперкон'югацією і залишковим π -зв'язуванням та близьке до такого ж у катіон-радикалі етилену, що був обраний як прототип (29°). Скручування досягає 55° для *bis*-2,2,5,5-тетраметилциклопентиліденового катіон-радикалу через суттєве стеричне відштовхування між метильними групами. В той же час іонізовані стани *bis*- D_3 -гомокуб-4-ілідену та *bis*- C_5 -гомокуб-8-ілідену зберігають свою планарність завдяки β -СС-гіперкон'югації та внутрішньомолекулярному дисперсійному притягуванню.

Ключові слова: гіперкон'югація; потенціали іонізації; нековалентні взаємодії; олефіни; катіон-радикали

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Нековалентные взаимодействия в пространственно-затрудненных олефиновых катион-радикалах

Цель работы. Исследовать влияние электронных (α - и β -гиперконъюгация) и стерических (нековалентные взаимодействия) факторов на структуру олефиновых катион-радикалов.

Результаты и их обсуждение. Влияние внутримолекулярных дисперсионных взаимодействий на строение пространственно-затрудненных алкенов в нейтральной и ионизированной формах исследовано на уровне теории функционала плотности (ТФП) с учетом и без учета дисперсионных взаимодействий, а также на уровне теории MP2 с базисными наборами среднего размера. Полученные результаты сравнены с имеющимися экспериментальными данными. Найдено хорошее согласование между экспериментальными и оптимизированными (MP2/ТФП) структурами сесквигомоадамантена, адамантилиденадамантана, бис-2,2,5,5-тетраметилциклопентилидена, бис- D_3 -гомокуб-4-илидена и бис- C_5 -гомокуб-8-илидена в нейтральных и ионизированных формах. Экспериментальные потенциалы ионизации лучше воспроизводятся при расчете методами ТФП.

Экспериментальная часть. Структура и состав соединений были подтверждены методами ^1H и ^{13}C ЯМР-спектроскопии, а также ГХ-МС-анализом. Проведен элементный анализ полученных соединений.

Выводы. Скручивание олефинового фрагмента в сесквигомоадамантеновом и адамантилиденадамантановом катион-радикалах определяется балансом между σ - π -гиперконъюгацией и остаточным π -связыванием и близко к таковому в катион-радикале этилена, взятого в качестве прототипа (29°). Скручивание достигает 55° для бис-2,2,5,5-тетраметилциклопентилиденового катион-радикала из-за существенного стерического отталкивания между метильными группами. В то же время ионизированные состояния бис- D_3 -гомокуб-4-илидена и бис- C_5 -гомокуб-8-илидена сохраняют свою планарность благодаря β -CC-гиперконъюгации и внутримолекулярному дисперсионному притяжению.

Ключевые слова: гиперконъюгация; потенциалы ионизации; нековалентные взаимодействия; олефины; катион-радикалы

Single-electron oxidation of neutral molecules leads to positively charged radical ions that are key intermediates in many fundamental chemical and biological processes [1–3]. The ionization of olefines leads to significant geometrical distortions, and radical cations thus obtained usually are quite unstable. The simplest representative is ethylene where electron removal from the bonding highest occupied molecular orbital (HOMO) results not only in the elongation of electron-depleted C=C-bond, but is also accompanied by the twisting of the CH_2 -groups. This is due to σ - π -hyperconjugation [4], (α -hyperconjugation, two-way hyperconjugation) [5], which is maximized for the perpendicular arrangement (Fig. 1A), while the residual one-electron π -bonding stabilizes the planar form. Theory is not very successful in a balanced description between these two stabilization modes predicting a torsion angle for $\text{C}_2\text{H}_4^{+\bullet}$ in the range of 13 to 33° , depending on the approximation level employed [6, 7]; the most trusted experimental estimate is ca. 29° [8]. Theory shows, however, that substituted ethylene radical cations do not necessarily deplanarize since the stabilization may be achieved through hyperconjugation with the participation of the σ -bonds of the neighboring groups (β -hyperconjugation, Fig. 1B). As a result, our computed [9] (MP2/cc-pVQZ) CCCC

torsion angle for the tetramethylethylene radical cation (Fig. 1C) is only 11° due to an effective participation of the CH-bonds of the methyl groups in β -CH-hyperconjugation. As β -CC-hyperconjugation [10] generally is more efficient, the tetraethylethylene radical cation is almost planar (the twisting is only 1.7° , Fig. 1D). Such structural trends agree well with the density functional theory (DFT) computations at the B3LYP and M06-2X levels of the theory.

The experimental verifications of the above theoretical findings are difficult since alkene radical cations readily undergo deprotonation from the allylic positions. In this regard, the sterically hindered cage alkenes (Fig. 2), e. g. sesquihomoadamantene **1** [11] and adamantylidene adamantane **2** [12], with allylic CH-bonds orthogonal to the olefinic p -orbitals are suitable models for structural studies [11].

Attempts to isolate and characterize radical cation **2** $^{+\bullet}$ failed due to its short lifetime (less than 5 seconds) [13]. In contrast, radical cation **1** $^{+\bullet}$ characterized through X-ray crystallography is quite stable [11, 13]. The high stability of **1** $^{+\bullet}$ primarily is due to the steric crowding caused by the CH_2 -groups that surround the C=C bond [13]. Still, the cage is flexible enough to provide a torsion angle of 29° for effective α -hyperconjugation. Even more significant devia-

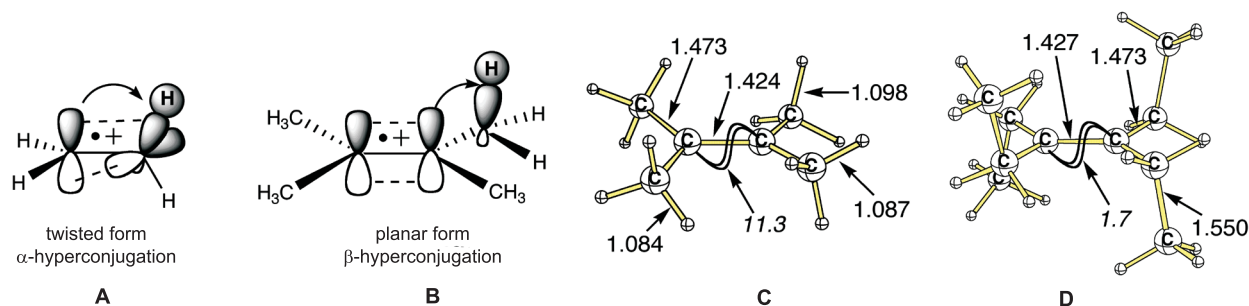


Fig. 1. Hyperconjugations in ethylene **A** and tetramethylethylene **B** radical cations, as well as the MP2/cc-pVQZ optimized structures of tetramethyl- **C** and tetraethylethylene **D** radical cations (intermolecular distances in Å, torsion angles (*italics*) in degrees)

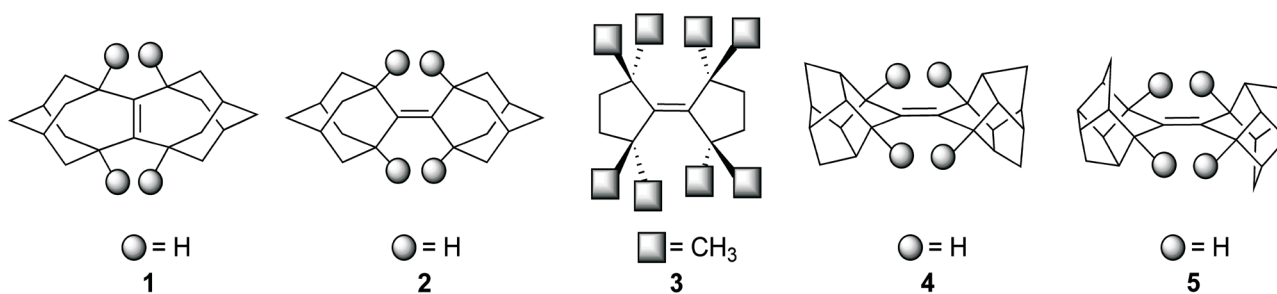


Fig. 2. Sterically congested cage olefins of sesquihomoadamantene **1**, adamantylidene adamantane **2**, bis-2,2,5,5-tetramethylcyclopentylidene **3**, bis-*D*₃-homocub-4-ylidene **4**, and bis-*C*₅-homocub-8-ylidene **5**

tions from planarity were observed for the extremely sterically crowded radical cation of bis-2,2,5,5-tetramethylcyclopentylidene (**3**, Fig. 2). The ESR-spectrum of **3**^{•+} displays “almost perpendicular arrangement of five-membered rings” [14] due to the additional steric repulsion between the methyl groups. Although this hypothesis is only partly confirmed by our computations (*vide infra*), the reasons for the occurrence of planar vs. twisted forms of olefinic radical cations and the role of noncovalent interactions (NCI, primarily London dispersions) still remains open. Herein, we present our study of the neutral and ionized dia-

mondoid olefins **1–2**, highly crowded **3**, as well as homocubane dimers **4** and **5**, as their structures comprise fundamentally different C=C-bond surroundings.

Results and discussion

For comparison, alkenes **1** and **2** in the neutral and ionized states were studied using various DFT levels, as well as the MP2 *ab initio* method (Fig. 3). Previously, we found that DFT reproduced the experimental ionization potentials of large saturated hydrocarbons well [15–19]. Correct descriptions of radical cations derived from **1** and **2** require taking into

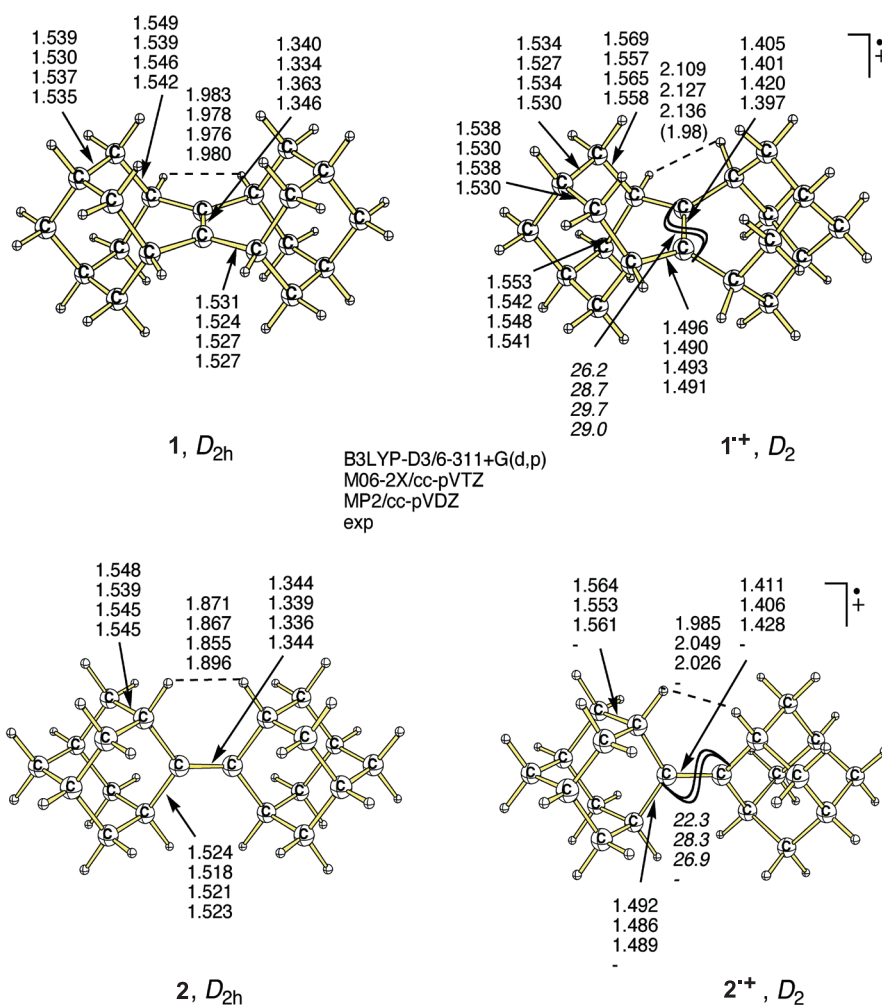


Fig. 3. The optimized structures of neutrals **1** and **2** and their corresponding radical cations **1**^{•+} and **2**^{•+} (bond lengths in Å, torsion angles (*italics*) in degrees)

Table

Computed and experimental adiabatic ionization potentials (eV) of **1** and **2**

#	B3LYP	B3LYP-D3	M06-2X		MP2	Exp.
	6-311+G(d,p)	6-311+G(d,p)	6-311+G(d,p)	cc-pVTZ	cc-pVDZ	
1	7.21	7.21	7.37	7.37	7.50	7.35 [28]
2	7.22	7.22	7.21	7.21	7.60	7.49 [29]
5	7.22	7.22	7.46	7.44	7.60	7.47 [30]

account both electron correlation and noncovalent interactions (NCI) [13, 20] between the groups that surround the C=C bonds. Hydrocarbon **1** provides an opportunity to test the applicability of the recently developed DFT implementations to olefinic radical cations, such as **1**^{•+}, since its X-ray crystal structure is available [13]. We used a popular functional B3LYP with empirical corrections for dispersions (B3LYP-D3 [21]) and M06-2X [22], which was parameterized to account for the medium-range electron correlation. Previously, we used a similar approach to estimate the dispersion contributions in saturated diamondoid dimers [20, 23–25] and graphane clusters [26].

Although there is torsional strain caused by the repulsive [27] intramolecular H•••H contacts of 1.85–2.00 Å across the C=C bond (2.4 Å corresponds to the minimum on the vdW potential [27]), this fragment remains planar in neutral hydrocarbons **1** and **2**. Inclusion of dispersion does not alter this picture, and all methods reproduce the experimental geometries of the neutrals well (Fig. 3). In contrast, the results for radical cations **1**^{•+} and **2**^{•+} are strongly method-dependent. Upon ionization the twisting of the olefinic moiety leads to an insignificant increase of the intramolecular H•••H distances up to 2.1 Å, which is still significantly less than the optimal 2.4 Å. The B3LYP method underestimates the torsional angle even with empirical dispersion corrections included. While MP2 substantially overestimates the length of the central electron-depleted C=C bond, the M06-2X reproduces the experimental interatomic distances and torsion angles of **1**^{•+} exceptionally well.

We also probed the computational reproducibility of the experimental adiabatic potentials [28, 29] of **1** and **2** (Table). Both B3LYP and M06-2X results agree well with the experimental values and accounting for dispersion has almost no effect; again, the M06-2X is slightly more accurate.

The above findings demonstrate that dispersion corrections only insignificantly affect the geometries of radical cations **1**^{•+} and **2**^{•+}. In contrast, due to excessive repulsions between the methyl groups, the olefinic moiety of **3** substantially deplanarizes even in the neutral form **3a** (Fig. 4). The neglect of dispersion reduces significantly the value of the torsion angle (3.4° at B3LYP vs. ca. 7° with B3LYP-D3(BJ)) (Fig. 4). Note that computations with molecular mechanics on **3a** gave an intermediate twisting value of 5.5° [31].

Unexpectedly, we found another highly twisted (ca. 40°) C=C bond rotamer **3b**, which, surprisingly, was only 6–7 kcal·mol⁻¹ less stable than **3a**. Such small differences may be associated with additional destabilization of **3a** due to the presence of very close H•••H-contacts (~1.8 Å); such short contacts are not present in more twisted form **3b**. Ionization reorders the relative stability of conformers due to the partial elimination of the π-bonding that flattens the rotation potential: “planar” **3a**^{•+} becomes less stable than twisted conformer **3b**^{•+}. The computed π-bond twisting in **3b**^{•+} is smaller than “the almost perpendicular arrangement cyclopentane fragments” predicted based on the ESR data [14], but still is exceptionally high (ca. 55° at all levels).

Since α-hyperconjugation affects mostly the structures of highly twisted forms, accounting dispersions has only little influence on the geometry of **3b**^{•+}. Note that for *bis*-2,2,4,4-tetramethylcyclobutylidene, the cyclobutane analog of **5**, where the methyl groups are more distant, the twisting in the radical cation is only 29–30° [32], i. e. essentially the same as in ethylene.

The conclusion can be made that α-hyperconjugation determines the structures of **1**^{•+} and **2**^{•+} as the neighboring C–C bonds undergo only little changes upon ionization. The cage moieties have only little effect on the degree of twisting of the olefinic fragments in the corresponding radical cations **1**^{•+} and **2**^{•+} (ca. 29°, which is close to that for parent ethylene). Even in the almost planar form **3a**^{•+} the β-hyperconjugation is insufficient as the C–CH₃ bond lengths in the neutral (1.54–1.55 Å) and ionized (1.56–1.57 Å) forms are close.

The *D*₃-trishomocubylidene dimer **4** exists in two diastereomeric forms **4a** and **4b** (Fig. 5). Computations at our levels of theory reproduce satisfactorily the experimental X-ray crystal structure geometries of neutral hydrocarbons [33]. Remarkably, the olefinic moiety of **4b** is slightly twisted (3–4°). As the noncovalent CH•••HC contacts across the C=C bond are close to the optimal value of 2.5 Å and are positioned in the attractive part of the vdW potential, such twisting must derive from antibonding interactions in the *D*₂-symmetric helical HOMO-1 of **4b**.

The ionization of **4a** and **4b** is accompanied by only moderate geometric distortions. The *C*₁-radical cation **4a**^{•+}, (the deviation from *C*₂-symmetry is in-

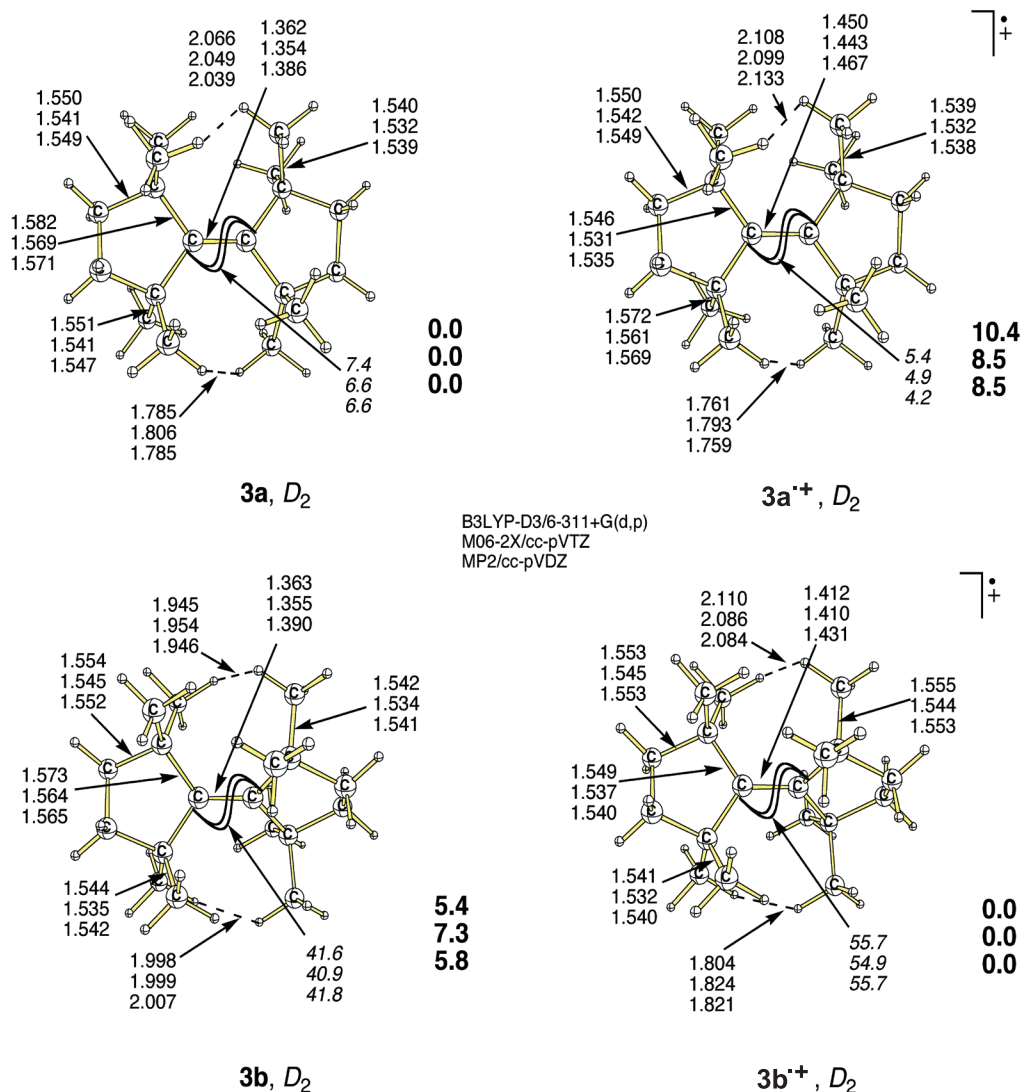


Fig. 4. Structures of neutral and ionized states of *bis*-2,2,5,5-tetramethylcyclopentylidene **3** (bond lengths in Å, torsion angles (*italics*) in degrees, relative ΔH_{298} in kcal·mol⁻¹)

significant) is slightly twisted (13–14°). Two pairs of β -C–C bonds contribute substantially to the stabilization of **4a⁺** as it is seen from their elongations up to 1.58–1.60 Å. Reoptimization with C_2 -symmetry constraints leads to a minimum that is twisted less (3–5°), but structurally and energetically close to the C_1 -form. Significant deviations are obtained for **4a⁺** at DFT and MP2, as the latter predicts an almost planar olefinic moiety. These findings, as well as the pronounced elongation of the neighboring β -C–C-bonds of the cage (up to 1.59 Å) suggest that β -CC-hyperconjugation makes a significant contribution to the structure **4a⁺**. The same applies to the structure of **4b⁺**, which retains the D_2 -symmetry of a neutral hydrocarbon and is characterized by only minor twisting upon ionization. Thus, hydrocarbons **4a** and **4b** display stabilization of the planar ionized states through participation of the neighboring C–C-bonds as in the prototypical case of tetraethylethylene (**D**, Fig. 1). Dispersion interactions thereby play a stabilizing role since

the H•••H interactions over the C=C bonds are attractive.

The previously unknown C_5 -trishomocubane dimer **5** was obtained through a titanium(III)-promoted McMurry dimerization [34, 35] of C_5 -trishomocubane-8-one **6** [36, 37]. As the nature of the titanium salt and of the reducing agent affects the outcome of dimerizations to sterically hindered alkenes [33, 38], we chose the most effective TiCl₄–Zn system in THF for coupling (Fig. 6).

All four possible diastereomers **5a–d** were formed in the approximate statistical ratio (GC) with a preparative total yield of 80–90%. The mixture was subjected to fractional crystallization from hexane resulting in the isolation of the most symmetric C_1 -diastereomer **5a**, which structure was confirmed by the X-ray diffraction single crystal analysis (Fig. 6). The key geometric characteristics of **5a** are in agreement with the computed data (Fig. 7). Neutral **5a** is characterized by close to the optimal H•••H contacts around

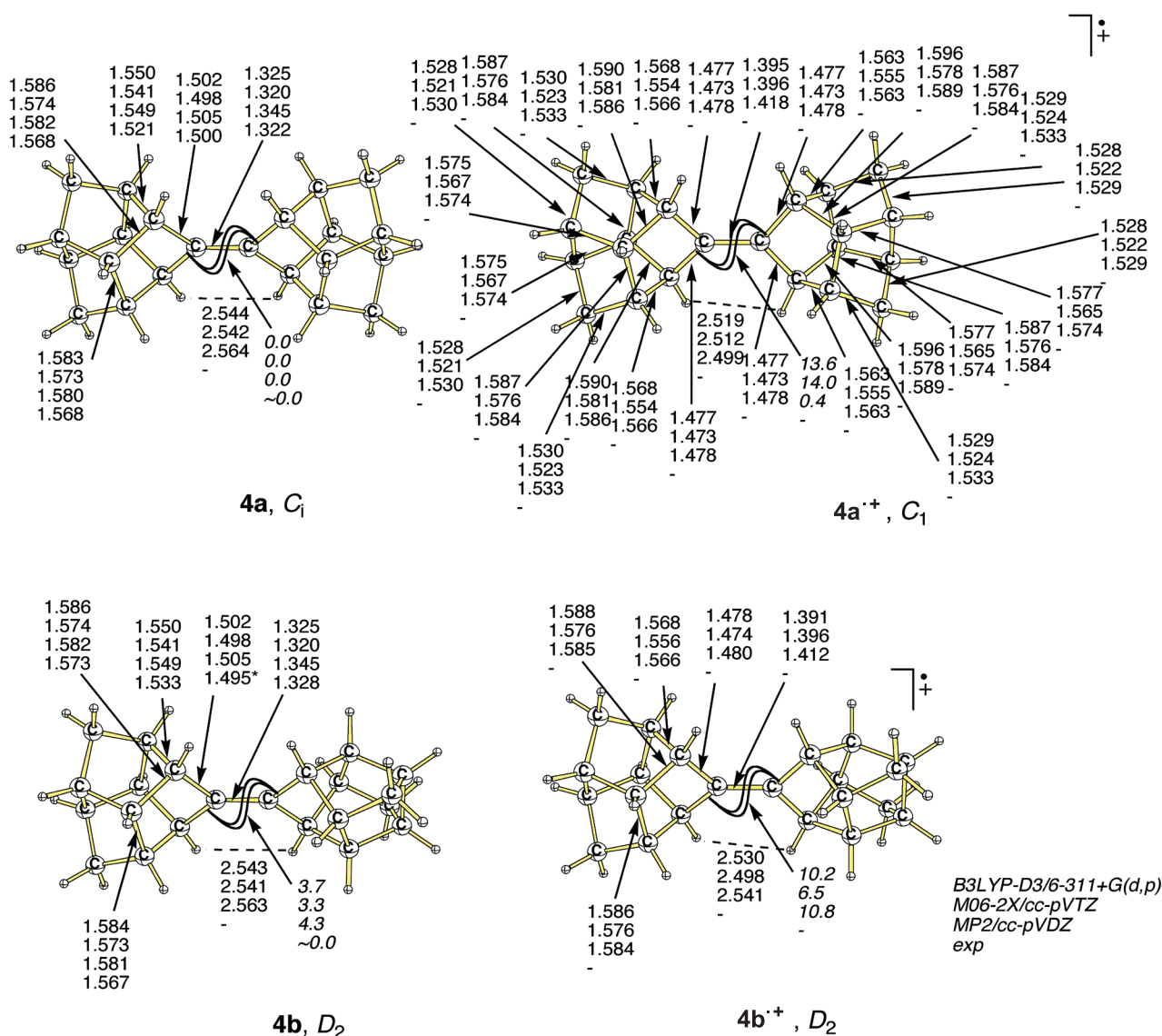


Fig. 5. Structures of the neutral and ionized states of *bis-D*₃-trishomocub-4-ylidene **4** (bond lengths in Å, torsion angles (*italics*) in degrees)

the C=C moiety, which is almost planar (the twisting is less than 2°). As a result, the geometries of **5a** computed with and without dispersion corrections are very close.

The ionization of **5a** gives **5a⁺**, which retains C_i -symmetry (Fig. 7). We conclude that dispersion is stabilizing both in singlet and doublet states of **5a** as the H•••H contacts across the central C=C bond remain constant

(ca. 2.3 Å). The experimental adiabatic ionization potential of **5a** (7.47 eV) [30] is reproduced well with M06-2X, but not at B3LYP or MP2 (Table). As expected, the C=C bond length in **5a⁺** increases relative to the neutral one, however, only little twisting is found at our levels of theory: **5a⁺** remains nearly planar due to the effective β-hyperconjugation with participation of the C–C-bonds of adjacent cyclobutane fragments

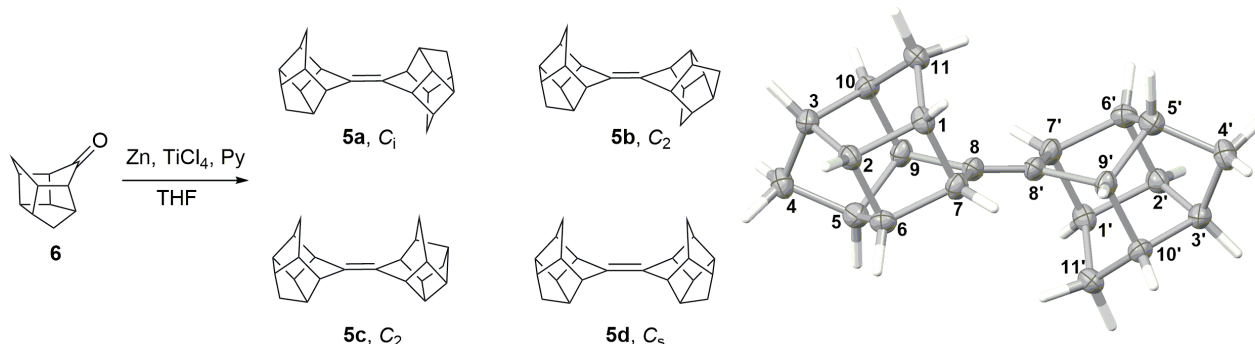


Fig. 6. Preparation of C_7 -trishomocub-4-ylidene **5** and the X-ray crystal structure of the C_i -diastereomer **5a**

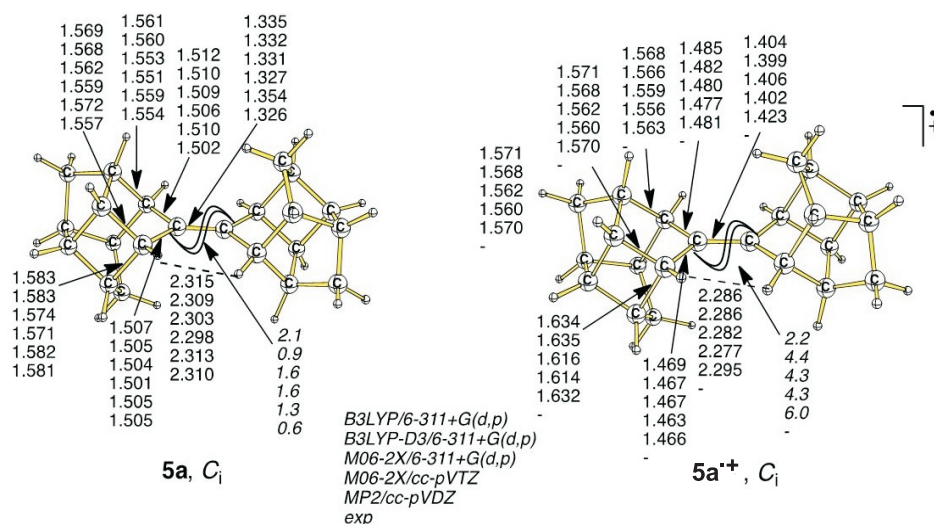


Fig. 7. Structures of the neutral and ionized states of C_7 -trishomocub-4-ylidene (**5a**) (bond lengths in Å, torsion angles (*italics*) in degrees)

(the respective bond lengths increase from 1.56 Å in **5a** to 1.63 Å in **5a⁺**, Fig. 7). Thus, the cyclobutane rings participate effectively in hyperconjugation in **5a⁺** removing the excess of the positive charge from the central bond and allowing the effective one-electron π -bonding. As a result, the distortions of the olefinic moiety of **5a⁺** is even less pronounced than that in **4b⁺**. Such a behavior upon ionization makes hydrocarbons **4** and **5** useful for the construction of electronic materials where the structural stiffness of the building blocks upon electron/hole transfer is critical. Derivatives of **4** and **5** may have some advantages over the diamondoid [20, 39, 40] derivatives previously successfully used for the construction of electron emitters and semiconductors [41–45].

Experimental part

The NMR-spectra were recorded with a Bruker Avance II spectrometer; chemical shifts were given in ppm relative to TMS. GC-MS analyses were performed with a HP5890 GC with a HP5971A mass-selective detector. High resolution mass spectra were recorded on a Finnigan MAT 95 instrument.

C_7 -Trishomocub-4-ylidene 5a. Heat under argon a two-neck dry flask (100 mL) equipped with a magnetic stirrer and a reflux condenser with a bubble counter; add 25 mL of freshly distilled dry THF through a septum. Cool the solvent on an external ice bath, and add 1.35 mL (12.3 mmole) of $TiCl_4$. Remove the septum, and add Zn powder (1.62 g, 24.9 mmole) in small portions. After adding Zn reflux the reaction mixture for 1 h, and then cool to ambient temperature. Add pyridine (0.5 mL) first, then the solution of ketone (5.34 mmole) in dry THF (7 mL). Reflux the mixture under argon for 12 h, cool to room temperature, and quench by dropwise addition of 10% water solution of K_2CO_3 (60 mL) with simultaneous cooling. Add dark blue slurry to diethyl ether (150 mL), vigorously stir for 15 min and then filter. Wash the residue with diethyl ether (3 × 50 mL). Separate the layers in the filtra-

te, and extract the aqueous layer with diethyl ether (2 × 50 mL). Wash sequentially the combined organic layers with water (1 × 70 mL), hydrochloric acid (5%, 2 × 50 mL), water (2 × 70 mL), and brine (1 × 50 mL). Dry the organic layer over Na_2SO_4 , remove the solvent in vacuo. Purify the residue (2.0 g, 93%) by column chromatography (hexane) to obtain olefin **5a**. Three sequential crystallizations from hexane gave 0.13 g (6%) of the pure sample.

C_7 -trishomocub-4-ylidene 5a: colorless solid; M. p. 230.5–231.5°C. Anal. Calcd. for $C_{22}H_{24}$, %: C 91.68, H 8.32. Found, %: C 91.61, H 8.39. 1H NMR (200 MHz, $CDCl_3$): 1.06–1.18 (4H, AB, $\tau J = 1.6$ Hz, $^{ABJ} = 12.4$ Hz), 1.29–1.69 (4H, AB, $^{ABJ} = 12$ Hz), 2.12–2.17 (2H, m), 2.27–2.36 (4H, m), 2.55–2.68 (8H, m), 2.95–3.02 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): 30.1 (CH_2), 35.6 (CH_2), 39.1 (CH), 39.8 (CH), 43.4 (CH), 43.6 (CH), 45.2 (CH), 46.8 (CH), 47.0 (CH), 47.3 (CH), 132.9 (C). MS, m/z (I , %): 288 (71) [M] $^+$, 223 (20) [$M-C_5H_5$] $^+$, 222 (68) [$M-C_5H_6$] $^+$, 209 (39) [$M-C_6H_7$] $^+$, 165 (22), 156 (63), 155 (45), 144 (12), 143 (79) [$M-C_{11}H_{13}$] $^+$, 142 (31), 141 (45), 129 (35), 128 (55), 115 (53), 91 (40) [C_7H_7] $^+$, 80 (10), 79 (100) [C_6H_7] $^+$, 78 (24) [C_6H_6] $^+$, 77 (62) [C_6H_5] $^+$, 66 (25) [C_5H_6] $^+$, 65 (24) [C_5H_5] $^+$.

Conclusions

The twisting of the olefinic moieties in the sesquihomoadamantene and adamantylidene adamantane radical cations is determined by the balance between the σ - π -hyperconjugation and residual one-electron π -bonding and is close to that of the prototypical ethylene radical cation (29°). The twisting reaches 55° for the *bis*-2,2,5,5-tetramethylcyclopentylidene radical cation due to substantial steric repulsions between methyl groups. At the same time, the ionized states of *bis*- D_3 -homocub-4-ylidene and *bis*- C_5 -homocub-8-ylidene retain their planarity due to β -CC-hyperconjugation and intramolecular dispersion attractions.

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