

Homophenalenyl Cations, New Representatives of Homoaromatic Systems*

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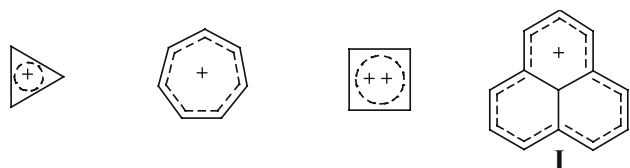
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Abstract—3b,4-*exo*,4a,5-Tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalen-5-yl cation and its *endo*-epimer were proved by NMR method to belong to a new kind of homoaromatic systems: homophenalenyl carbocations.

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The homoaromaticity concept introduced by Winstein [2] is widely spread and treated in textbooks. The most distinctly the homoaromaticity is revealed in positively charged systems, but the number of these systems is limited, and their aromatic “basis” in most cases is a cyclopropenyl or tropylium cation, or cyclobutadiene dication [3].



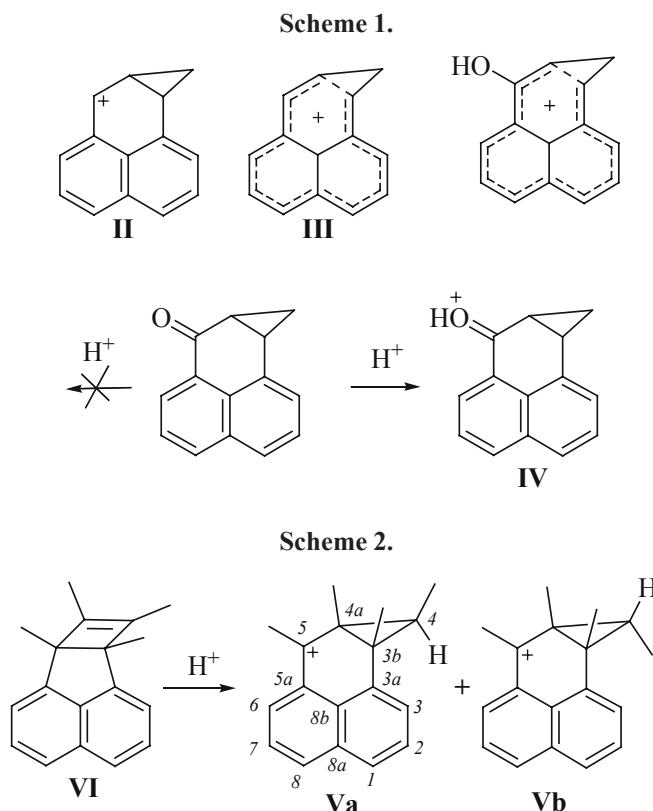
Phenalenyl cation (**I**) is a unique 12π -electron system possessing aromaticity [4, 5]. Based on molecular orbital perturbation theory Haddon suggested that carbocations of **II** type had homoaromatic character [6] [Scheme 1, structure **III**]. The π -system of this structure is isoelectronic to the phenalenyl cation. However the generation of unsubstituted cation **III** failed, and in hydroxy-substituted cation **IV** no homoaromaticity was observed [7].

In [8] long-lived carbocations **Va** and **Vb** were described, close structural analogs of cation **II**. We aimed in this study to establish whether these cations possessed a homoaromatic character.

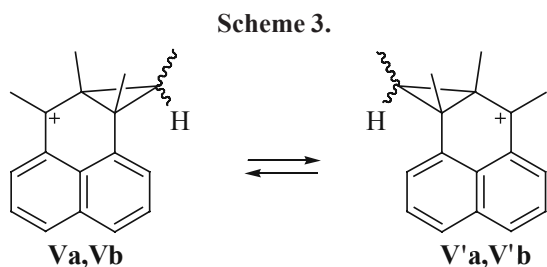
Cations **Va** and **Vb** formed as a mixture with **Vb** prevailing as a result of a complex rearrangement on

the protonation of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobuta[*a*]acenaphthylene (**VI**) [8–10] (Scheme 2).

They are quite stable up to room temperature but suffer a degraded “pendulum” rearrangement (Scheme 3) [8, 11], therefore their study by NMR method requires



* For preliminary communication, see [1].



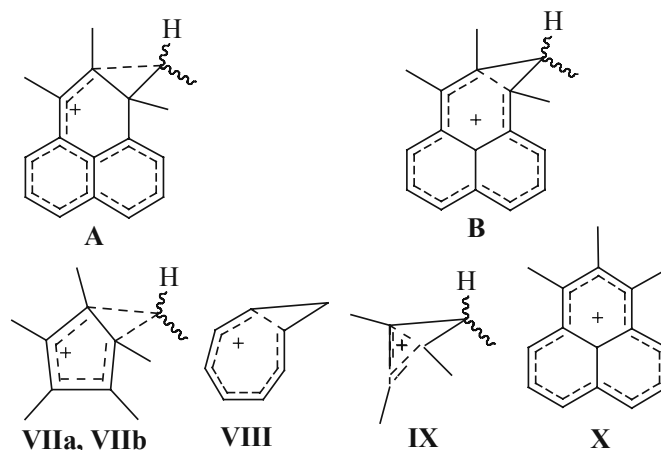
low temperature when the broadening of signals due to this rearrangement is insignificant.

The assignments of signals in the ^{13}C and ^1H NMR spectra of these ions are presented on Fig. 1 (cf. [8]).

It is well known that carbocations are efficiently stabilized by a cyclopropane fragment located in the α -position with respect to the carbocation center. Therewith depending on the alternative of the cyclopropane bonds delocalization structures of various type might form [12, 13]. A priori for cations **Va** and **Vb** a cyclopropylcarbinyl structure of **A** type is presumable whose analogs are bicyclo[3.1.0]hexenyl cations **VIIa** and **VIIb** [14], and a homoaromatic (**B**) one whose analogs are homotropylium **VIII** and homocyclopropenyl **IX** cations. Aromatic "basis" of **B** structure is cation **X**.

One of the characteristic features of homoaromatic structures is the abnormally long "bridging" carbon-carbon bond [15]. Bond lengths $\text{C}^{3b}\text{--C}^{4a}$ in cations **Va** and **Vb** calculated by DFT (PBE/3z) method (1.677 and 1.668 Å respectively) significantly exceed the common length of a C–C bond indicating the homoaromatic character of these cations. The lengths of the analogous bonds in nonhomoaromatic cations **VIIa**, **VIIb**, and **IV** are 1.497, 1.503, and 1.564 Å respectively.

To prove experimentally the homoaromatic nature of **Va** and **Vb** cations we performed an analysis of the data of NMR spectroscopy (Fig. 2). The great difference in the chemical shifts of protons *exo*- H^4 of ion **Va** and *endo*- H^4 of ion **Vb** stands out. The chemical shifts of *exo*- and *endo*-protons in the corresponding neutral precursors **XIa** and **XIb** are virtually identical [8] therefore the anisotropy of the magnetic susceptibility of the naphthalene fragment does not contribute to the observed difference in the chemical shifts (2.03 ppm). This difference also cannot be completely understood based on the unlike orientation of the bonds C--exo-H^4 and C--endo-H^4 with respect to the carbocation center C^5 : This difference is essentially less in cations of **VII** type [17] with the similar orientation of the mentioned bonds with respect to the carbocation center (Fig. 2). It is presumable that in ions **Va** and **Vb** exists a ring current involving all



the phenalenyl system as is inherent to homoaromatic cations. This assumption is in agreement with the fact that the chemical shift values of atoms C^{8b} (δ 124.1 ppm for cation **Va** and 125.8 ppm for **Vb**) are very close to that in aromatic 1,2,3-trimethylphenalenyl cation (**X**)

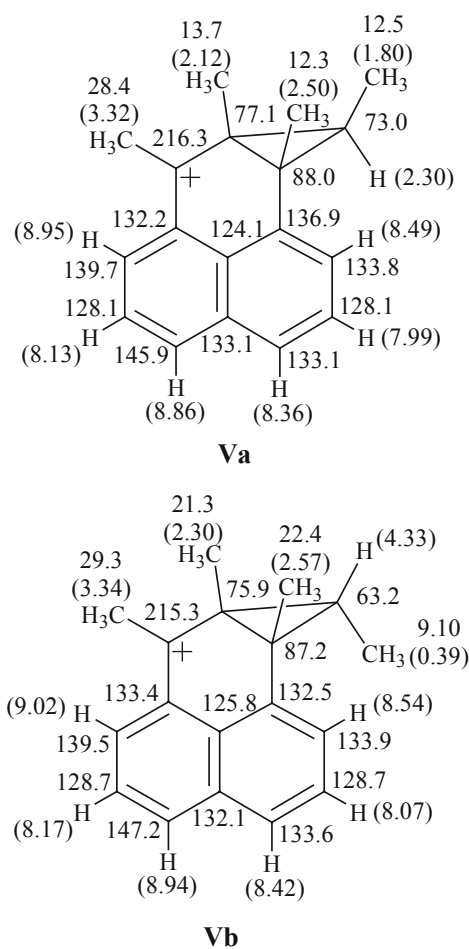


Fig. 1. Chemical shifts in ^{13}C and ^1H (in parentheses) NMR spectra of cations **Va** and **Vb** (1M in $\text{HSO}_3\text{F--CD}_2\text{Cl}_2$, 2:1, v/v) at 216 K.

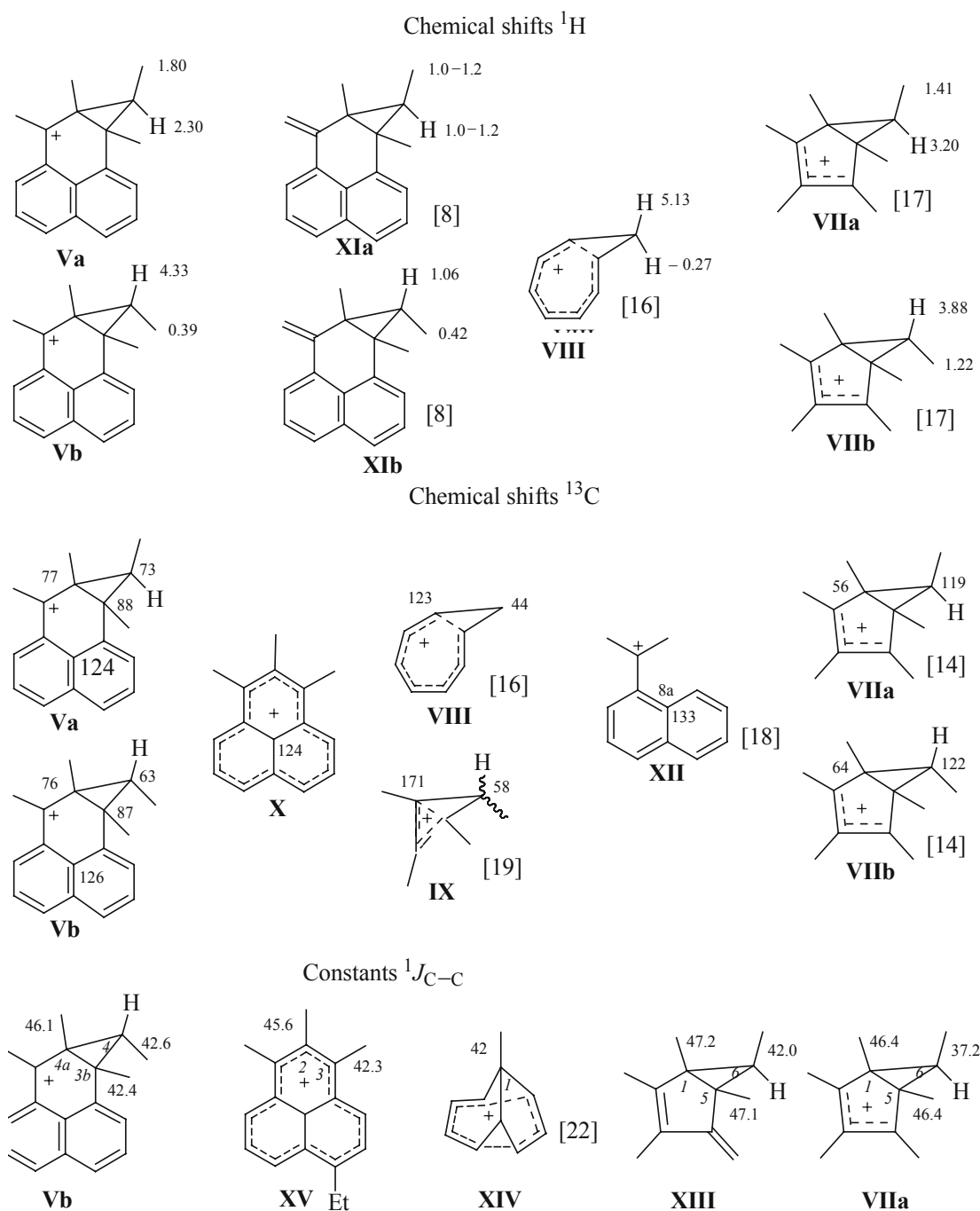


Fig. 2. Some parameters of NMR spectra of cations and their precursors.

(124 ppm) and are in stronger field than, e.g., in dimethyl- α -naphthyl cation **XII** [18] where atom C^{8a} has a similar chemical surrounding but is not affected by the ring current characteristic of the phenalenyl aromatic system. It is also indicative that the chemical shifts of C^4 atoms of cations **Va** (δ 73.0 ppm) and **Vb** (63.2 ppm) are close to the values characteristic of homoaromatic cations (like cyclobutenyl [19, 20] and homotropylium [16] ones) and

strongly differ from the chemical shifts of the corresponding atoms of bicyclo[3.1.0]hexenyl ions [14]. The fact that chemical shifts of atoms C^{3b} and C^{4a} of cations **Va** and **Vb** are considerably less than the chemical shifts of the corresponding atoms in other homoaromatic ions **VIII** and **IX** may be ascribed to the lesser fraction of the positive charge on these atoms due to the delocalization along the total homophenalenyl ring.

Exclusively important information on the structure of organic compounds and the nature of carbon-carbon bonds is contained in coupling constants ^{13}C - ^{13}C through one bond ($^1J_{\text{CC}}$) [21]. Presumably, measuring the “bridging” constants C^{3b} - C^{4a} in cations **Va** and **Vb** and their comparison with analogous constants in homoaromatic cations would confirm the homoaromatic character of cations under study. Regrettably, these data are lacking in the literature, and we also failed to measure the “bridging” constant because of insufficient intensity of the ^{13}C signals of quaternary atoms and their additional broadening from the strong temperature dependence. Nonetheless, the data we obtained on the other coupling constants $^1J_{\text{CC}}$ (in ion **Vb**)* make it possible to formulate some important conclusions.

The attention is engaged by the fact that although $^1J_{\text{CC}}$ (C^1 -Me and C^5 -Me) in carbocation **VIIa** and in uncharged compound **XIII** are very close the constant $^1J_{\text{CC}}$ (C^6 -Me) in this cation is considerably less than the corresponding constant in the neutral analog. This decrease in the constant is evidently caused by the partial positive charge on C^6 atom due to its involvement into the charge delocalization [21, p. 236]. Yet the constant $^1J_{\text{CC}}$ (C^4 -Me) in carbocation **Vb** and the constant $^1J_{\text{CC}}$ (C^1 -Me) in methylbishomotropylium cation (**XIV**) [22] have virtually the same value as the constant $^1J_{\text{CC}}$ (C^6 -Me) in neutral model **XIII**. This fact shows that the delocalization along the “cyclopropylcarvinyl” type (structure **A**) which should result in appearance of a partial positive charge on C^4 atom and in decreased constant $^1J_{\text{CC}}$ does not operate in cation **Vb**.

The constants $^1J_{\text{CC}}$ of ring atoms and the linked thereto methyl groups in the neutral aromatic compounds usually are in the range 44–47 Hz [22]. In this interval gets also the value $^1J_{\text{CC}}$ (C^2 -Me) in aromatic phenalenyl cation **XV** (45.6 Hz) where C^2 atom practically lacks a positive charge (δ 142 ppm), and the constant $^1J_{\text{CC}}$ (C^3 -Me) is smaller (42.3 Hz) due to the presence of a partial positive charge on the C^3 atom (δ 165 ppm). The values of constants $^1J_{\text{CC}}$ (C^{4a} -Me and C^{3b} -Me) in **Vb** cation (46.1 and 42.4 Hz respectively) are very close to the corresponding values in cation **XV**. These findings show that ion **Vb** has an aromatic basis isoelectronic to the phenalenyl cation.

One of criteria estimating whether the structure belongs to a series of homoaromatic compounds is a NICS value [3, 23]. The negative value obtained by taking with the opposite sign the magnetic shielding in the center of the ring [NICS(0)], and even better, at 1 Å distance over this center [NICS(1)] indicates the existence of the ring current and aromaticity. In Fig. 3 are given NICS(1) values for some cations under consideration (homotropylium and homocyclopropenyl cations are excluded from the discussion for their large negative NICS values are not informative since they do not originate from the ring current but from the σ -orbitals of the skeleton [3]). In the case of cations **Va**, **Vb**, **VIIa**, **VIIb**, and **IV** from two possible points for calculating NICS(1) of the ring in question the point more remote from the cyclopropane fragment was chosen to minimize the effect of the σ -skeleton of the latter. The NICS values of cations **Va** and **Vb** indicate that not only in the

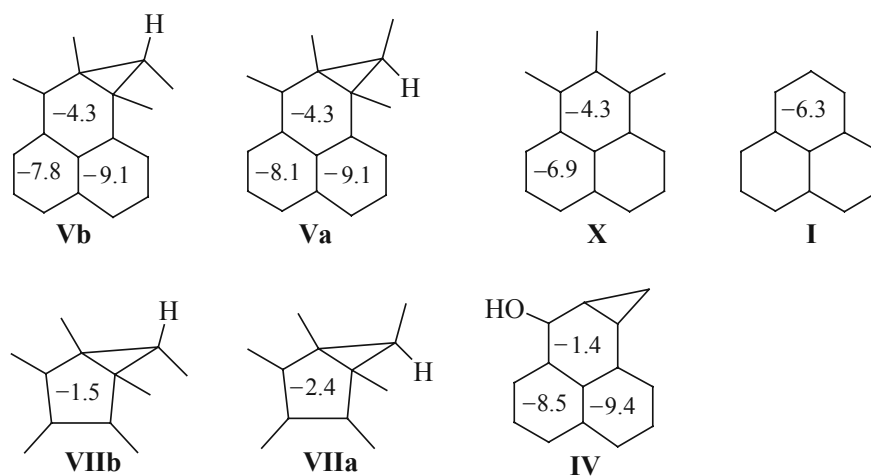


Fig. 3. NICS(1) (ppm) values for cations **I**, **IV**, **Va**, **Vb**, **VIIa**, **VIIb**, and **X** (GIAO/PBE/3z). For cation **I** in [4] was obtained a value -7.8 ppm (GIAO/B3LYP/6-311G**).

* It was impossible to measure J_{CC} constants for ion **Va** due to its small content in the mixture with cation **Vb**.

“naphthalene” rings, but also in the ring fused with the three-membered one ring currents are present confirming the homoaromatic nature of these cations.

Hence the combination of data obtained shows that cations **Va** and **Vb** are a new example of homoaromatic systems: homophenalenyl carbocations.

EXPERIMENTAL

In generation of carbocations were used $\text{CF}_3\text{SO}_3\text{H}$ purchased from Aldrich, distilled CF_3COOH of “pure” grade (bp 72–73°C), twice distilled HSO_3F (bp 158–161°C), CDCl_3 , and CD_2Cl_2 dried with molecular sieves 4A.

The mixture of 3b,4-*exo*,4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalen-5-yl cation (**Va**) and its *endo*-epimer **Vb** in a ratio 1:4 was generated by procedure [8] by adding 0.175 g (0.75 mmol) of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobuta[*a*]acenaphthylene (**VI**) [8, 10] by portions at stirring into a mixture of 0.5 ml of HSO_3F and 0.2 ml of CD_2Cl_2 at –40°C. 1,2,3-Trimethylphenalenyl cation (**X**) [24] formed on dissolving 30 mg of compound **VI** in a mixture of 0.4 ml of CF_3COOH and 0.1 ml of CD_2Cl_2 with subsequent maintaining the solution for 4 days at room temperature (cf. [25]). 1,2,3-Trimethyl-6-ethylphenalenyl cation (**XV**) [25] was generated by adding at stirring a solution of 80 mg of compound **VI** in 0.2 ml of CDCl_3 to 0.2 ml of $\text{CF}_3\text{SO}_3\text{H}$ and maintaining the solution for 24 h at room temperature. 1,2,3,4,5,6-Hexamethylbicyclo[3.1.0]hexenyl cation **VIIa** for the measurement of constants $^1J_{\text{CC}}$ was generated by the protonation of olefin **XIII** in a system $\text{HSO}_3\text{F}-\text{CD}_2\text{Cl}_2$ (cf. [17]).

NMR spectra were registered on spectrometers Bruker AM-400 and DRX-500. The complete assignment of signals in the spectra of compounds **Va** and **Vb** was performed using 2D correlation spectra $^1\text{H}-^1\text{H}$ (COSY) and $^1\text{H}-^{13}\text{C}$ (HETCOR, COLOC). Coupling constants $^{13}\text{C}-^{13}\text{C}$ in compounds **Vb**, **VIIa**, **XIII**, and **XV** were measured by INADEQUATE procedure on the natural abundance of ^{13}C isotope. The temperature in the probes of spectrometers was calibrated by a standard methanol sample (–90...50°C) and by melting point of *n*-pentane (–130°C) and naphthalene (80°C). The intermediate temperatures were found by interpolation.

Quantum-chemical calculations of the geometry and energy of carbocations were performed by DFT method (functional PBE [26]) using the program “Priroda” [27] {basis 3z, (11s6p2d)/(6s3p2d) for C and (5s1p)/(3s1p)}

for H}. The calculation of chemical shifts and NICS were carried out by method GIAO/PBE/3z (program “Priroda”).

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