

Stereochemical Nonrigidity of Homophenalenyl Cations*

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Abstract—A strong temperature dependence was observed of chemical shifts in the ^{13}C NMR spectra of 3b,4-*exo*-4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalen-5-yl cation and its *endo*-epimer revealing their stereochemical nonrigidity.

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The sensitivity to the temperature of chemical shifts in ^{13}C NMR spectra of organic compounds, among them also of carbocations, whose molecules lack atoms of high polarizability, is known to be insignificant (several ppb/ K^{**} [2, 3]) in the absence of fast reversible nondegenerate rearrangements.

It was formerly established that a strong temperature dependence of chemical shifts in the carbon spectra of cyclobutenyl ions (up to 77 ppb/K [4]) was caused by stereochemical nonrigidity inherent to these homoaromatic [5] carbocations.

Inasmuch as 3b,4-*exo*-4a,5-tetramethyl-3b,4,4a,5-tetrahydro-4*H*-cyclopropa[*a*]phenalen-5-yl cation (**Ia**) and its *endo*-epimer **Ib** are also homoaromatic ions [6], it is interesting to establish whether the stereochemical nonrigidity is also characteristic of these cations. To this end we registered a series of their ^{13}C NMR spectra in

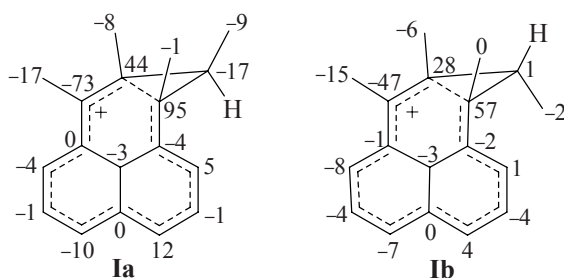
the range 169–325 K. The chemical shifts of carbon atoms were found to depend on the temperature. This dependence in the measured temperature range is close to linear, its coefficients (in ppb/K) for carbon atoms are given in Scheme 1. In calculating the coefficients we used as a reference independent of temperature the signal of C^{8a} atom of cation **Ia**.*** The choice of this signal is based on the low sensitivity of the chemical shift of C^{8a} atom to the variation of the nonrigidity coordinate (see below).

The value of the coefficient of temperature dependence of CD_2Cl_2 signal (–12 ppb/K) observed at the use as reference of the signal of C^{8a} atom is identical to an independently obtained value for CH_2Cl_2 [3] (–12 ppb/K with accounting for the temperature dependence of TMS signal [8]).

The most sensitive to the temperature are the chemical shifts of atoms C^{3b} , C^{4a} , and C^5 (Fig. 1); therewith the significant difference in values and in signs of coefficients (Scheme 1) exclude the possibility of the observed temperature dependence of the chemical shifts to originate from the change in the macroscopic characteristics of the sample and/or from the position of the reference.

It was established in [4] that a strong temperature dependence of chemical shifts in NMR spectra of homocyclopropenyl cations **II** was caused by stereo-

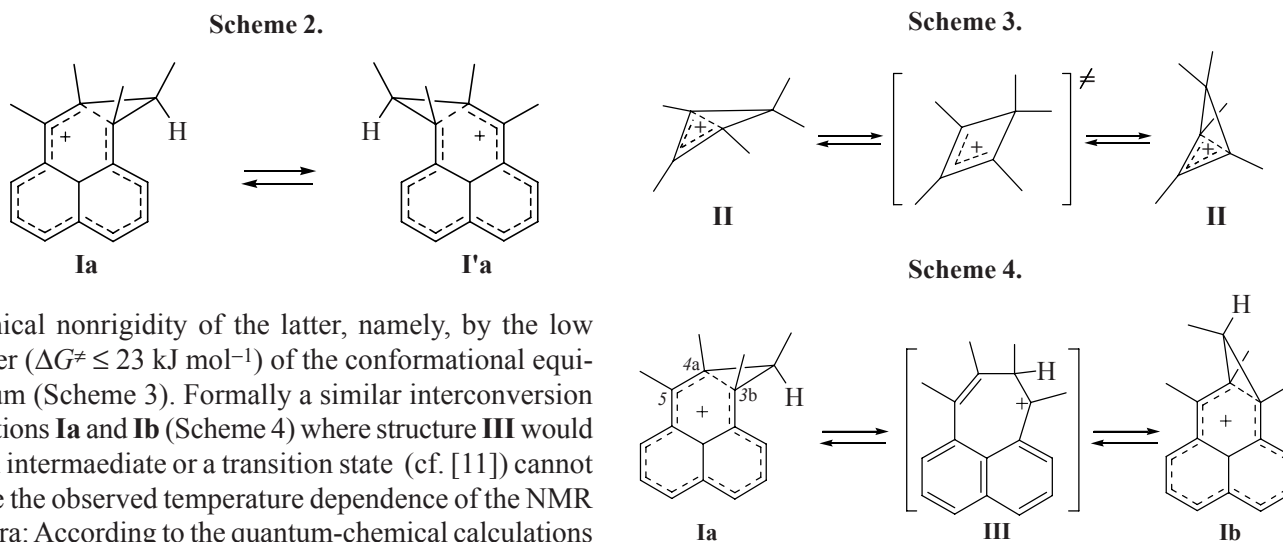
Scheme 1.



* For preliminary communication, see [1].

** ppb/K is one billionth part per one degree K.

*** The measurement of chemical shifts from one of the signals of compound under study is used in the investigation of their temperature dependence [4, 7].



chemical nonrigidity of the latter, namely, by the low barrier ($\Delta G^\ddagger \leq 23 \text{ kJ mol}^{-1}$) of the conformational equilibrium (Scheme 3). Formally a similar interconversion of cations **Ia** and **Ib** (Scheme 4) where structure **III** would be an intermediate or a transition state (cf. [11]) cannot cause the observed temperature dependence of the NMR spectra: According to the quantum-chemical calculations structure **III** is not a stationary point on the potential energy surface (PES), the interconversion of cations **Ia** and **Ib** occurs by another mechanism [12], and the energy barrier to this process is fairly high ($\sim 90 \text{ kJ mol}^{-1}$) [9]. Consequently the observed temperature dependence of the ^{13}C NMR spectra of cations **Ia** and **Ib** (Fig. 1) is due to other reasons.

Quantum-chemical calculations with variation of the interatomic distance $\text{C}^{3b}\text{--C}^{4a}$ and optimization of the

other geometric parameters show that PES section along this coordinate appears as a very wide well (Fig. 2) meaning that cations **Ia** and **Ib** are stereochemically nonrigid. For the occurrence of a temperature dependence of the chemical shifts in the NMR spectra of stereochemically nonrigid molecules two conditions should be fulfilled: Firstly, the wide potential well should be asymmetric, and, secondly, in moving along the nonrigidity

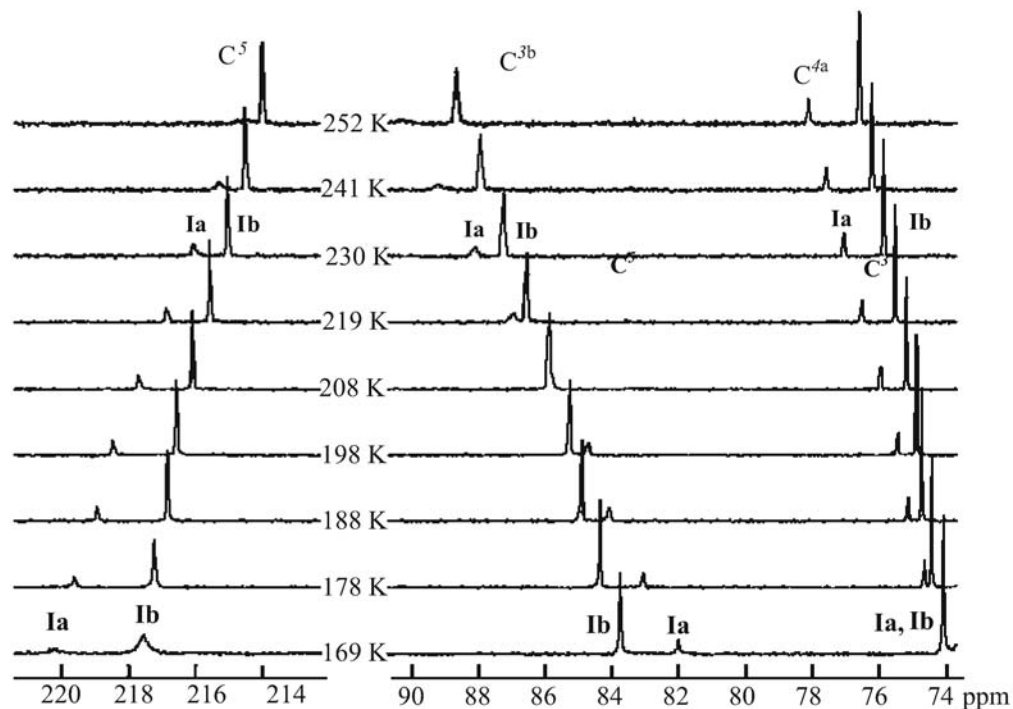


Fig. 1. ^{13}C NMR spectra of cations **Ia** and **Ib** (1 M solution in $\text{HSO}_3\text{F--CD}_2\text{Cl}_2$, 2:1 v/v) in the region of signals of atoms C^{3b} , C^{4a} , and C^5 at temperature variation in the range 169–252 K. At higher temperature signals of atoms C^{3b} and C^5 of cation **Ia** are not observed due to the signals broadening caused by a fast pendulum rearrangement along Scheme 2 [9, 10].

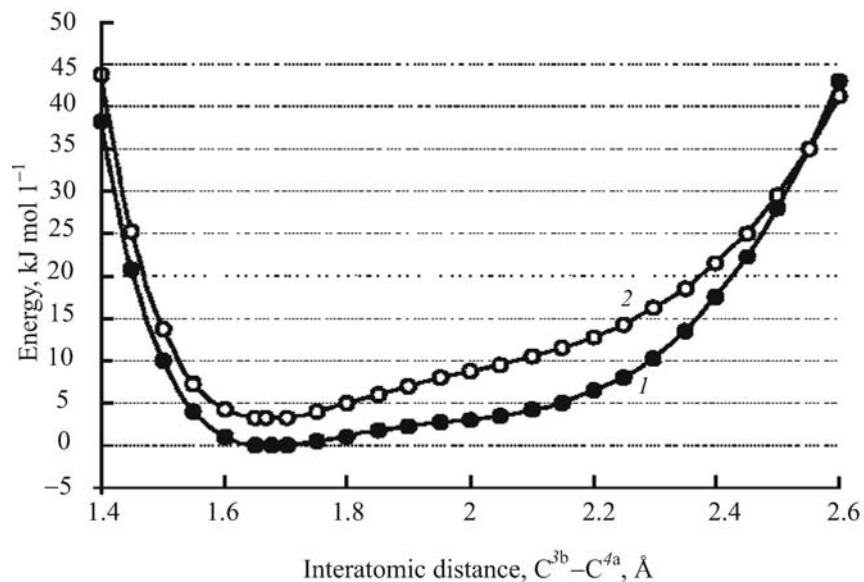


Fig. 2. Calculated (DFT, PBE/3z) PES section along the nonrigidity coordinate. 1, ion **Ia**; 2, ion **Ib**.

coordinate chemical shifts of some atoms should strongly change [4, 13]. Evidently this is the case with cations **Ia** and **Ib** (Figs. 2 and 3).

It is essential that a linear correlation exists between the calculated sensitivity coefficients of chemical shifts to the nonrigidity coordinate and the experimental temperature coefficients (Fig. 4).* This finding indicates

the validity of the choice of the interatomic distance $C^{3b}-C^{4a}$ as the nonrigidity coordinate.

The slope of the correlation plot for cation **Ia** is larger than that of **Ib** (Fig. 4). Inasmuch as the dependence of chemical shifts on the nonrigidity coordinate for both cations is materially identical (Fig. 3), the reason of this difference and of the larger on the average absolute values

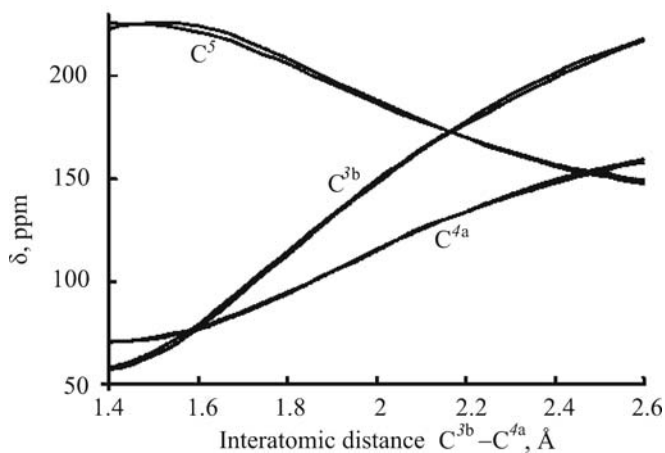


Fig. 3. Calculated (GIAO, PBE/3z; DFT, PBE/3z) dependence of chemical shifts of atoms C^{3b} , C^{4a} , and C^5 in spectra of cations **Ia** and **Ib** on the nonrigidity coordinate.

* In the plot on Fig.4 for abscissa values were taken derivatives of calculated chemical shifts with respect to the interatomic distance $C^{3b}-C^{4a}$ (Fig. 3) in the points corresponding to the minima on PES [1.677 (**Ia**) and 1.668 E (**Ib**)]. The values of ordinates are given on Scheme 1.

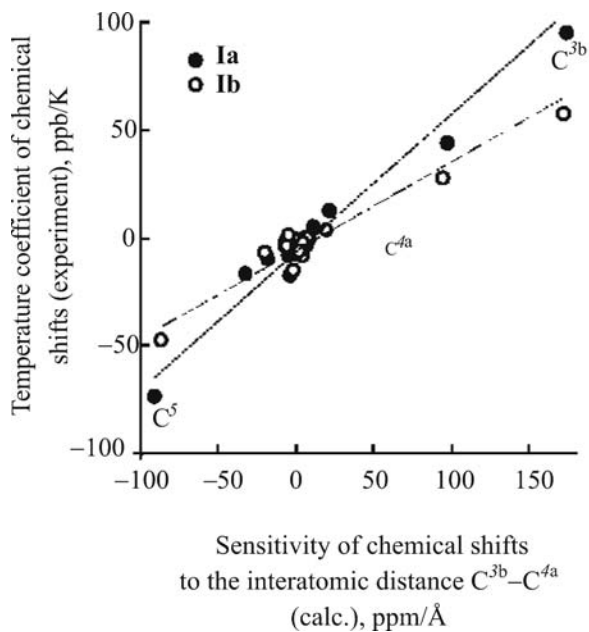


Fig. 4. Correlation "Temperature coefficient of chemical shifts - Sensitivity of chemical shifts to changes in interatomic distance $C^{3b}-C^{4a}$."

of temperature coefficients for the first of cations compared to the values for the second one (Scheme 1) is the different form of PES. As seen from Fig. 2, in both cases the sections of PES along the nonrigidity coordinate (interatomic distance $C^{3b}-C^{4a}$) are wide potential wells. The energy levels of one-dimensional oscillating system with such a potential are strongly convergent [14], therefore even at low temperature not only the zero level but also higher states are populated, and the increase in the temperature results in still greater occupancy of the higher levels. Each level possesses its proper effective (averaged for the given level) geometry that due to the strongly asymmetric potential well in going to the next level moves along the nonrigidity coordinate to the larger interatomic distance $C^{3b}-C^{4a}$ (Fig. 5). In the same direction displaces also the “averaging” by all levels populated at high temperature leading, for instance, in event of atom C^5 to the upfield shift of its signal. The similar consideration of atoms C^{3b} and C^{4a} results in a conclusion that on the contrary their signals would shift downfield, and the stronger shift corresponds to atom C^{3b} . These conclusions are fully consistent with the experimental findings.

The potential well for cation **1a** has flatter bottom (Fig. 2) resulting in population of a larger number of levels at growing temperature and consequently to larger sensitivity of the chemical shifts of this cation to the temperature compared with cation **1b**, as is also observed experimentally.

EXPERIMENTAL

NMR spectra were registered on spectrometers Bruker AM-400 and DRX-500. The temperature in the probes of spectrometers was calibrated by a standard methanol sample ($-90...50^{\circ}\text{C}$) 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 [16]) using the program “Priroda” [17] {basis 3z, (11s6p2d)/[6s3p2d] for C and (5s1p)/[3s1p] for H}. The calculations of chemical shifts were carried out by method GIAO/PBE/3z (program “Priroda”).

The generation of cations was performed using double distilled HSO_3F (bp $158-161^{\circ}\text{C}$) and CD_2Cl_2 dried with molecular sieves 4\AA

The mixture of cations **1a** and **1b** in the ratio 1:4 was

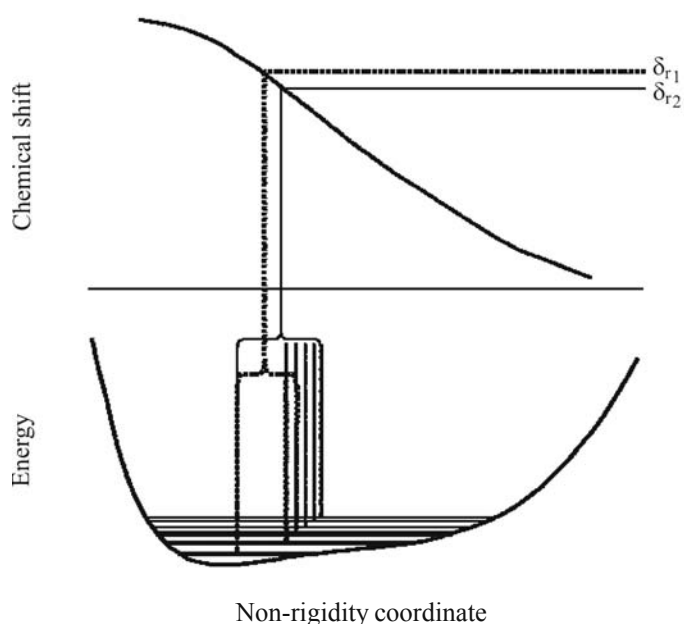


Fig. 5. The effect of rising temperature on the occupancy of vibration levels and the chemical shift displacement. With bold horizontal lines the levels populated at temperature Φ_1 are shown, with thin lines, additional levels populated at higher temperature Φ_2 . The vertical dotted lines show the nonrigidity coordinates for effective geometric structures of each level and for their “averaging” at different temperatures.

generated by adding by portions 0.175 g (0.75 mmol) of 6b,7,8,8a-tetramethyl-6b,8a-dihydrocyclobuta[*a*]ac-naphthylene [9, 15] at stirring to the mixture of 0.5 ml of HSO_3F and 0.2 ml of CD_2Cl_2 at -40°C (cf. [9]).

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REFERENCES

1. Sal'nikov, G.E. and Genaev, A.M., Abstracts of Papers, *Vserossiiskaya nauchnaya konferentsiya Sovremennye problemy organicheskoi khimii* (All-Russian Sci. Conference on Modern Problems of Organic Chemistry), 2007.
2. Schneider, H.-J. and Freitag, W., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 478.
3. Mamatyuk, V.I., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk, 1978.
4. Salnikov, G.E., Genaev, A.M., and Mamatyuk, V.I. *Mendeleev, Commun.*, 2003, p. 48.
5. Williams, R.V., *Chem. Rev.*, 2001, vol. 101, p. 1185.

6. Sal'nikov, G.E., Genaev, A.M., Mamatyuk, V.I., and Shubin, V.G., *Zh. Org. Khim.*, 2008, vol. 44, p. 1011.
7. Lambert, J.B., Vagenas, A.R., and Somani, S., *J. Am. Chem. Soc.*, 1981, vol. 103, p. 6398.
8. Morin, F.G., Solum, M.S., Withers, J.D., Grant, D.M., and Dalling, D.K., *J. Magn. Res.*, 1982, 48, 138.
9. Osadchii, S.A., Mikushova, N.V., and Shubin, V.G., *Zh. Org. Khim.*, 1999, 35, 1813.
10. Bushmelev, V.A., Genaev, A.M., Sal'nikov, G.E., and Shubin, V.G., *Zh. Org. Khim.*, 2007, vol. 43, p. 1659.
11. Osadchii, S.A., Drobysh, V.A., Mikushova, N.V., and Shubin, V.G., *Zh. Org. Khim.*, 1989, vol. 25, p. 1838.
12. Bushmelev, V.A., Genaev, A.M., and Shubin, V.G., *Zh. Org. Khim.*, 2006, vol. 42, p. 236.
13. Forsyth, D.A., Botkin, J.H., Puckace, J.S., Servis, K.L., and Domenick, R.L., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 7270.
14. Sergeev, N.M., *Spektroskopiya YaMR (NMR Spectroscopy)*, Moscow: Izd. MGU, 1981, p. 102.
15. Rybalova, T.V., Gatilov, Yu.V., Kochubei, N.V., Osadchii, S.A., and Shubin, V.G., *Zh. Strukt. Khim.*, 1997, vol. 38, p. 1140.
16. Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett.*, 1996, vol. 77, p. 3865.
17. Laikov, D.N., *Chem. Phys. Lett.*, 1997, vol. 281, p. 151; Laikov, D.N. and Ustynyuk, Yu.A., *Izv. Akad. Nauk, Ser. Khim.*, 2005, p. 804.