

Unusually strong temperature dependence of ^{13}C chemical shifts and degenerate conformational exchange in cyclobutenyl carbocations

Georgii E. Salnikov,* Alexander M. Genaev and Victor I. Mamatyuk

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 3832 34 4752; e-mail: sge@nmr.nioch.nsc.ru

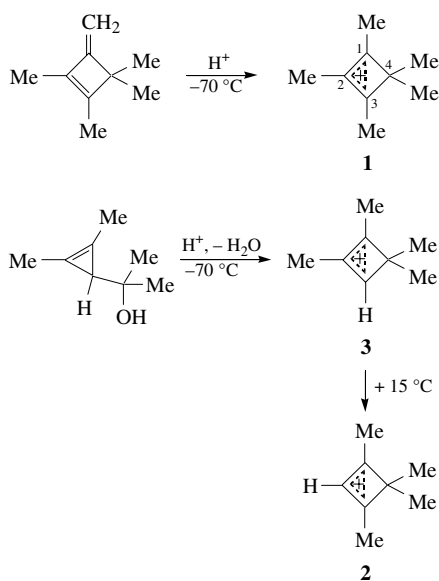
10.1070/MC2003v013n02ABEH001702

The unusually strong temperature dependence of ^{13}C chemical shifts is observed in methyl-substituted cyclobutenyl carbocations because of a very low inversion barrier of a four-membered ring.

The temperature sensitivity of ^{13}C chemical shifts of rigid organic molecules with no atoms of high polarizability, including carbocations, with the absence of fast chemical exchange is usually moderate (around 10^{-3} ppm K^{-1}).^{1,2} In studies of the ^{13}C – ^{13}C coupling constants of several non-classical carbocations, we found that polymethylated derivatives of the cyclobutenyl cation exhibit an unusually strong temperature dependence of ^{13}C chemical shifts (up to 0.077 ppm K^{-1}). The aim of this work was to study the nature of this strong temperature dependence.

The 1,2,3,4,4-pentamethylcyclobutenyl **1** and 1,2,4,4-tetramethylcyclobutenyl **3** cations were obtained by FSO_3H extraction from CD_2Cl_2 solutions of the precursors at -70°C .^{3,4} 1,3,4,4-Tetramethylcyclobutenyl cation **2** was obtained by keeping a solution of **3** at $+15^\circ\text{C}$ for 60 min⁴ (Scheme 1).

The ^{13}C NMR chemical shifts of the ions and their temperature dependence coefficients are shown in Table 1. As the position of the signal of an internal standard (CD_2Cl_2) may

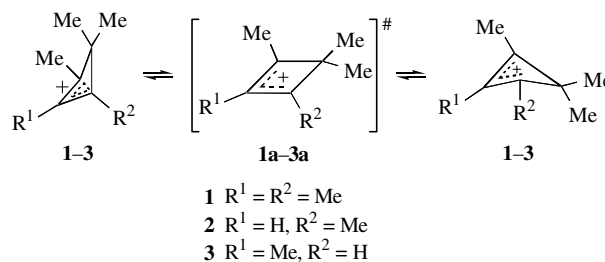


Scheme 1

Table 1 ^{13}C chemical shifts (ppm)^a of ions **1–3** and temperature coefficients (ppm K^{-1})^{b,c}

Ion and temperature range $^\circ\text{C}$	Atom							
	C^1	C^2	C^3	C^4	1-Me	2-Me	3-Me	4-Me
1 (-79 to 35°C)	183.7	180.2	183.7	66.9	13.4	10.5	13.4	22.8
	0.048	–0.008	0.048	—	0.001	–0.004	0.001	0.001
2 (-99 to 20°C)	207.4	162.9	207.4	67.4	17.2	—	17.2	22.5
	0.071	–0.012	0.071	—	0.011	—	0.011	0.006
3 (-99 to 20°C)	162.5	192.6	143.6	69.3	12.6	13.1	—	24.5 ^d
	0.016	–0.003	0.007	—	–0.005	–0.007	—	–0.003

^aIn FSO_3H at -30°C (CD_2Cl_2 , δ 53.6 ppm). ^bShown under the corresponding chemical shifts. ^cObtained by linear approximation of the experimental chemical shifts measured in the given temperature range with steps of 10°C . ^d31 and 17 ppm under slow exchange conditions at -142°C .



Scheme 2

significantly vary with temperature,^{2,5,6} the chemical shift of the C^4 nucleus was taken constant (*cf.* ref 5) because it does not change strongly in the test reactions.

According to published data^{7–9} on similar cations, as well as quantum-chemical computations (see below) of cations **1–3**, we can assume that they do not have a flat structure, and the observed equivalence of the 4-Me groups is due to mutual conformational exchange involving fast ring inversion (Scheme 2).

For cation **3** at -142°C , slow exchange conditions have been reached with the 4-Me and 4'-Me NMR signals observed separately; the measured energy barrier of the cycle inversion is $\Delta G^\ddagger = 5.6$ kcal mol^{-1} .

The strong temperature dependence of chemical shifts is usually observed for systems with non-degenerate exchange.⁵ Thus, it is reasonable to suppose that the cyclobutenyl cations are in equilibrium with isomeric cations **1a–3a**, and the observed sensitivity can be easily explained by a change in the equilibrium constant. However, the results of the quantum-chemical computations render this assumption improbable. The Hessian analyses for ions **1a–3a** in the MP2/6-31G* basis always showed the presence of an imaginary vibration frequency related to the bending of a four-membered ring, which characterises the corresponding species as transition states. Moreover, for cation **3** under conditions of slow cycle inversion, no NMR signals were observed, which could be assigned to cation **3a**.

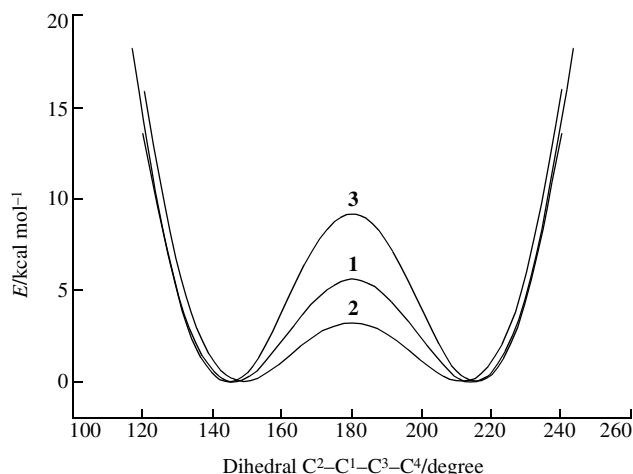


Figure 1 The potential energy surface for the cycle inversion in ions **1–3** computed by the GAMESS¹¹ package (MP2/6-31G* basis).

The most reasonable supposition that, in our opinion, explains the temperature dependence of the chemical shifts in ions **1–3**, is described below (*cf.* ref. 10). The experimentally measured energy barrier between the two non-flat conformations of cation **3** is very low. According to the quantum-chemical data (Figure 1), this barrier should be lower in cations **1** and **2**. The profile of the potential energy surface along the coordinate related to the dihedral angle α C²–C¹–C³–C⁴ contains two shallow minima, which are very far from each other. The energy levels of an oscillator with such a potential are very close,¹² so that even at relatively low temperatures not only the ground state will be significantly populated, but also higher vibrational states, including those situated above the energy barrier. The potential wells of this anharmonic oscillator are highly asymmetric. For high energy levels, greater contributions to the mean chemical shift are made by the structures with near 180° dihedral angles. An increase in the temperature leads to the occupation of higher vibrational states and, as a result, to an increase of the contribution from such structures. This will influence the averaged values of chemical shifts provided that they are essentially different in the flat and the bent conformations. For cations **1–3**, this condition is obviously true. For example, in the case of **1**, the computed chemical shifts (IGLO,¹³ basis II) of C^{1,3} and C² are 137 and 218 ppm, respectively, for a conformation with $\alpha = 130^\circ$, but they are 265 and 159 ppm, respectively, for a conformation with $\alpha = 180^\circ$. At the same time, the chemical shift of C⁴ changes insignificantly (55 and 48 ppm, respectively); therefore, this signal was used as a temperature-independent standard.

As the cycle inversion barrier was lowered (Figure 1), the temperature sensitivity of chemical shifts for cations **1–3** increased (Table 1). However, for the systems with an extremely low barrier the inverted temperature dependence may be observed (for example, the temperature sensitivity coefficients reported¹⁰ for the barriers of 3.12 and 0.06 kcal mol^{–1} have opposite signs).

Thus, we suppose that the temperature dependence of the ¹³C chemical shifts of cations **1–3** contains information on the height and, probably, the shape of the barrier of ultrafast conformational exchange, according to Scheme 2, which cannot be frozen in traditional DNMR experiments.

Direct barrier height measurements *via* high-resolution Raman and far-IR vibrational transition frequencies analysis is usually possible only for a gas phase.¹⁴ The proposed approach is applicable to solutions. As a restriction, we can note the condition of the degeneracy of the conformational exchange (otherwise, the temperature dependence originating from the change in the vibrational level occupation and from the displacement of the non-degenerate equilibrium would be hard to separate).

Another restriction is the requirement that some chemical shifts (or other NMR parameters such as coupling constants) of the structures corresponding to an energy minimum and a saddle point must be significantly different.

This work was supported by the Russian Foundation for Basic Research (grant nos. 02-03-32881 and 00-03-40135). We are grateful to Professor V. G. Shubin for valuable discussions.

References

- 1 H.-J. Schneider and W. Frietag, *J. Am. Chem. Soc.*, 1976, **98**, 478.
- 2 V. I. Mamatyuk, *Ph.D. Thesis*, Novosibirsk, 1978 (in Russian).
- 3 V. A. Koptug, I. A. Shlejder, I. S. Isaev, L. V. Vasilieva and A. I. Rezvukhin, *Zh. Org. Khim.*, 1971, **7**, 1089 [*J. Org. Chem. USSR (Engl. Transl.)*, 1971, **7**, 1117].
- 4 I. A. Shlejder, I. S. Isaev and V. A. Koptug, *Zh. Org. Khim.*, 1972, **8**, 1337 [*J. Org. Chem. USSR (Engl. Transl.)*, 1972, **8**, 1357].
- 5 J. B. Lambert, A. R. Vagenas and S. Somani, *J. Am. Chem. Soc.*, 1981, **103**, 6398.
- 6 H.-O. Kalinowski, S. Berger and S. Broun, *¹³C-NMR-Spektroskopie*, Thieme, Stuttgart, New York, 1984, S. 82 (in German).
- 7 G. A. Olah, J. S. Staral, R. J. Spear and G. Liang, *J. Am. Chem. Soc.*, 1975, **97**, 5489.
- 8 G. Maier, R. Emrich, K.-A. Schneider, M. Nixdorf und H. Irgartinger, *Chem. Ber.*, 1985, **118**, 2798.
- doi: 9 C. Krüger, P. J. Roberts and Y.-H. Tsay, *J. Organomet. Chem.*, 1974, **78**, 69.
- doi: 10 M. Garcia-Viloca, R. Gelabert, A. González-Lafont, M. Moreno and J. M. Lluch, *J. Am. Chem. Soc.*, 1998, **120**, 10203.
- 11 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
- 12 N. M. Sergeev, *Spektroskopiya YaMR (NMR Spectroscopy)*, Izd. Mosk. Univ., Moscow, 1981, p. 102 (in Russian).
- 13 W. Kutzelnigg, U. Fleischer and M. Schindler, in *NMR Basic Principles and Progress*, eds. P. Diehl, E. Fluck, H. Günter, R. Kosfeld and J. Seelig, Springer, Berlin, 1991, vol. 23, p. 165.
- 14 J. Laane, *Pure Appl. Chem.*, 1987, **59**, 1307.

Received: 19th December 2002; Com. 02/2028