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Conformational Mobility of 6,7,7-Trisubstituted Methyl Bicyclo-[3.1.1]heptane-*exo*-6-carboxylates

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Abstract—Temperature dependences of the ^{1}H NMR spectra of a series of 6,6,7-trisubstituted methyl bicyclo-[3.1.1]heptane-*exo*-6-carboxylates were studied. The effects of the nature, position, and orientation of substituents on the barrier to inversion of the methoxycarbonyl group about the C^6–C_{sp^2} bond ($\Delta G^{\neq}$ = 36–70 kJ/mol) are discussed with account taken of the X-ray diffraction data.

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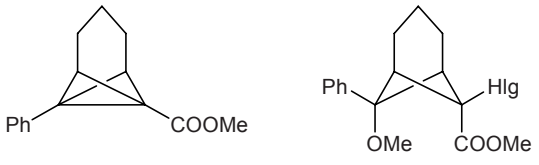
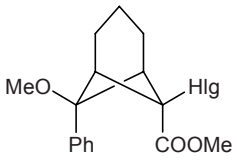
While studying reactions of methyl 7-phenyltricyclo[4.1.0.0^{2,7}]heptane-1-carboxylate (**I**) with *N*-halosuccinimides in methanol [1, 2], we synthesized tetrasubstituted norpinanes **II**–**IV** which were isolated as individual substances and characterized by ^{1}H and ^{13}C NMR spectra. The structure and configuration of compounds **IIa**, **IIIa**, **IIIb**, and **IVb** was unambiguously determined by X-ray analysis [2, 3].



I

IIa–IVa



IIb–IVb

II, Hlg = I; **III**, Hlg = Br; **IV**, Hlg = Cl.

In the present study we focused on conformational mobility of compounds **II**–**IV**. The reason was that we revealed some differences in the spectral patterns of both diastereoisomeric compounds **IIa**–**IVa** and **IIb**–**IVb** and norpinanes **IIa**–**IVa** having different halogen atoms. In the ^{1}H and ^{13}C NMR spectra of **IIb**–**IVb**, protons on C^1 and C^5 and the corresponding carbon atoms were magnetically equivalent, while the C^1H and C^5H fragments in their isomers **IIa**–**IVa** were not. The difference in the chemical shifts increased in going from chloro derivative **IVa** to iodine analog **IIa**. The ^{1}H NMR spectrum of **IVa** contained one broadened singlet at δ 3.49 ppm ($W_{1/2}$ = 24 Hz), whereas in the spectra of **IIIa** and **IIa** the 1-H and 5-H protons appeared as separate less broadened singlets at a distance of 36 and 39 Hz, respectively. Even more distinct differences were observed in the ^{13}C NMR spectra. The chemical shifts of C^1 and C^5 in **IIa** differed by 2.42 ppm, and the peak intensities of their signals were comparable with that of the methoxy carbon atom at δ_C 52.66 ppm; in addition, a difference of 0.12 ppm was observed for C^2 and C^4. The corresponding differences in the spectrum of **IIIa** were 2.44 (C^1/C^5) and 0.11 ppm (C^2/C^4), but the peak intensities were considerably lower. The C^1 and C^5 signals in the spectrum of **IVa** were even less intense, and the C^2 and C^4 nuclei gave rise to a single signal.

The observed spectral patterns led us to presume that nonequivalence of the C^1H and C^5H fragments in molecules **IIa**–**IVa** originates from the presence of irregular CO_2Me group whose rotation about the C^6–C_{sp^2} bond is restricted. If the plane of the methoxycarbonyl group is arranged orthogonally with respect to the norpinane $C^3C^6C^7$ plane, all substituted bicyclo[3.3.1]-heptane-*exo*-6-carboxylates **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**,

and **IVb** should exists as couples of enantiomers in which the C^1H and C^5H fragments should become diastereotopic. Generally speaking, it is obvious that orthogonal orientation of the CO_2Me group is optimal for all 6,7,7-trisubstituted bicyclo[3.3.1]heptane-*exo*-6-carboxylates, both **IIa**–**IVa** and **IIb**–**IVb**, but the rate of rotation of that group about the C^6–C_{sp^2} bond should depend on the nature of substituents on C^6 and C^7. Just orthogonal orientation of the CO_2Me group was determined by X-ray analysis [3] of single crystals of compounds **IIb**, **IIIa**, **IIIb**, and **IVa**, and it was reasonable to presume that the same configuration should be retained in solution. Therefore, the observed nonequivalence of the C^1H and C^5H fragments in the NMR spectra of **IIa**–**IVa** may be regarded as quite expected, whereas equivalence of the same fragments in the spectra of **IIb**–**IVb** may be attributed to higher rate of rotation of the CO_2Me group. If so, it might be expected that the C^1H and C^5H fragments in norpinanes **IIb**–**IVb** should become nonequivalent at reduced temperature. In fact, this assumption has been confirmed (Fig. 1). Moreover, the ^1H NMR spectrum of iodo derivative **IIb** at 190 K contained two separate signals not only from 1-H and 5-H but also from *exo*-2-H and *exo*-4-H. These findings suggest that at least in norpinane **IIb** molecule restricted rotation is inherent not only to the methoxycarbonyl group but also to another irregular substituent, methoxy group on C^7, which appears spatially close to *exo*-2-H and *exo*-4-H.

Taking into account the above stated, we examined temperature dependences of the ^1H NMR spectra of norpinanes **IIa**, **IIIa**, **IIIb**, and **IVb**, as well as of three other related compounds, trisubstituted norpinane **Vb** and tetrasubstituted derivatives **VIa** and **VIIb**, which were reported previously [4, 5]. All tetrasubstituted derivatives **IIb**, **IIIa**, **IIIb**, **IVb**, **VIa**, and **VIIb** showed nonequivalence of 1-H and 5-H at a definite temperature, and norpinanes **IIb** and **IIIb** also displayed different signals from the *exo*-2-H and *exo*-4-H protons. For all compounds we determined the coalescence temperatures T_c and calculated the rate constants k_c and Gibbs energies of activation $\Delta G_c^{\neq}$ of conformational transitions related to rotation of the methoxycarbonyl and methoxy groups (Table 1). Neither 1-H/5-H nor *exo*-2-H/*exo*-4-H signal splitting was observed in the ^1H NMR spectra of trisubstituted norpinane **Vb** down to a temperature of 184 K, which may be rationalized in terms of low heights of the conformational barriers for this compound.

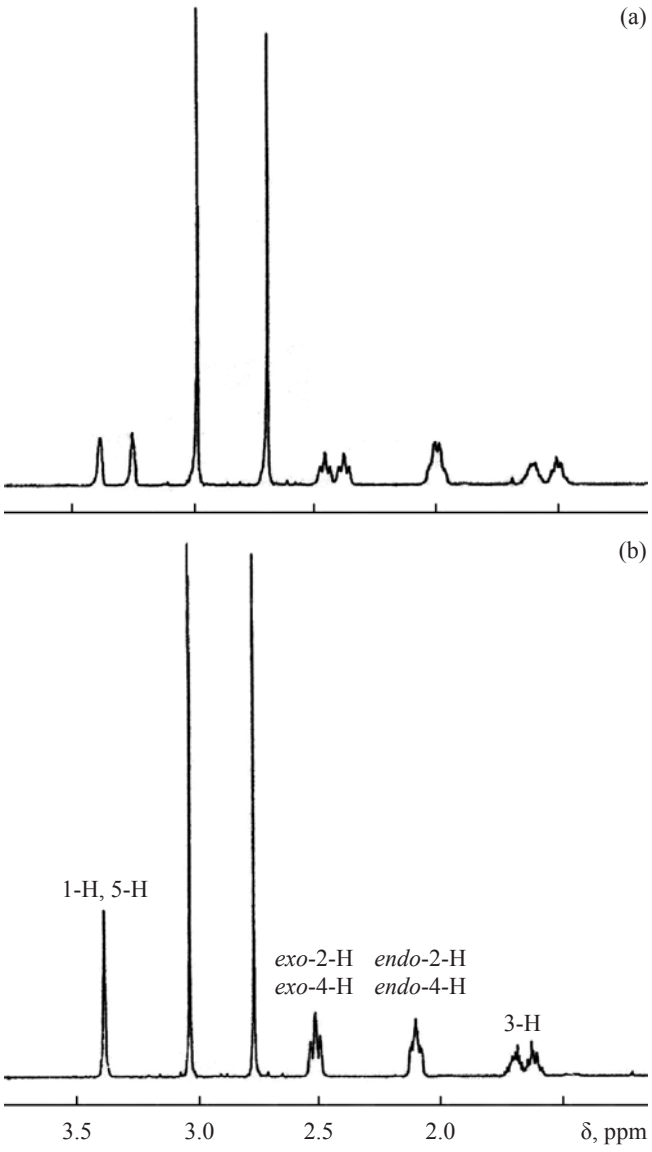
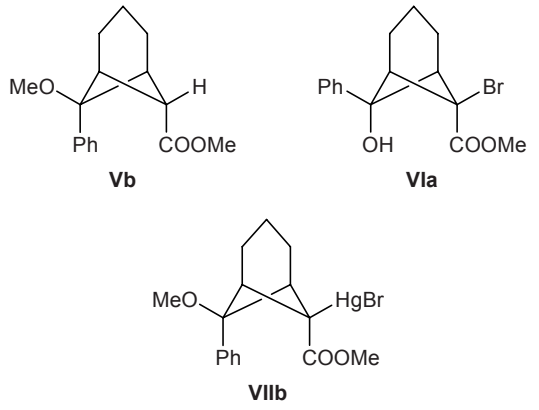


Fig. 1. ^1H NMR spectra (600 MHz, CD_2Cl_2) of methyl *endo*-6-iodo-*syn*-7-methoxy-*anti*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (**IIb**) at (a) 190 and (b) 300 K.



We believe that the barrier to rotation of the methoxycarbonyl group in the examined compounds is

Table 1. Activation barriers $\Delta G_c^{\neq}$ to conformational transitions of norpinanes **IIa**, **IIIa**, **IIIb**, **IVa**, **IVb**, **VIa**, and **VIIb**

Compound no.	Solvent	T_c, °C (K)	$\Delta\nu_c$, Hz	k_c, s^{-1}	$\Delta G_c^{\neq}$, kJ/mol
IIb	CD_2Cl_2	–23 (250)	78.0	173.2	50.0±1
		–34 (239)	48.0	106.6	48.7±1
IIIa	DMSO-d_6	47 (320)	12.0	26.6	69.8±1
IIIb	CD_2Cl_2	–44 (229)	49.2	109.2	46.5±1
		–54 (219)	32.0	71.0	45.3±1
IVa	CD_2Cl_2 + DMSO-d_6	17 (290)	16.0	35.5	62.2±1
VIa	CD_2Cl_2	–94 (179)	48.0	106.6	36.0±1
VIIb	CD_2Cl_2	–80 (193)	93.2	206.9	37.9±1

determined mainly by the following two factors. The first factor is interaction between the CO_2Me group and the other substituent at the same carbon atom, and the second is transannular donor–acceptor (dipole–dipole) interaction between the CO_2Me group and the opposite methoxy group on C^7 (in molecules **IIa**–**IVa** and **VIa**). According to the X-ray diffraction data [3], the benzene ring in molecules **IIb**, **IIIa**, **IIIb**, and **IVa** is oriented orthogonally to the $C^3C^6C^7$ plane, and this orientation is likely to remain unchanged in going to solution. Therefore, the effect of the benzene ring on the rotation of the CO_2Me group should not change to an appreciable extent both in the series **IIa**–**IVa**, **VIa** and in the series **IIb**–**Vb**, **VIIb**.

Increase of $\Delta G^{\neq}$ in the series **Vb** < **IIIb** < **IIb**, as well as in going from chloride **IVa** to bromide **IIIa**, correlates well with the steric volume of the substituent in the geminal position with respect to the methoxycarbonyl group. As the van der Waals radius of that substituent increases, its repulsion from the trimethylene bridge becomes stronger; as a result, the C^6 and C^7 atoms tend to arrange closer to each other, and the folding angle $C^1C^6C^5C^7$ in the cyclobutane fragment decreases, which leads in turn to increase in the energy barrier to rotation of the CO_2Me group.* The different $\Delta G^{\neq}$ values for diastereoisomers **IIIa** and **IIIb** may be attributed to donor–acceptor interaction between the methoxy and methoxycarbonyl groups in **IIIa**. Analogous interaction, though less effective, is responsible for the high $\Delta G^{\neq}$ value for compound **IVa**.

Appreciable difference in the $\Delta G^{\neq}$ values for methoxy derivative **IIIa** and hydroxy analog **VIa** seems to be somewhat surprising. The van der Waals radii of methoxy and hydroxy groups are fairly similar (1.52 and 1.53 Å, respectively [7]), and the main difference between them is that hydroxy group is capable of forming hydrogen bonds. According to the X-ray diffraction data, molecules **VIa** in crystal give rise to dimers formed via intermolecular hydrogen bonds between the hydroxy proton of one molecule and ester carbonyl oxygen atom of the other (short intermolecular contacts C=O···H 2.143 Å; sum of the corresponding van der Waals radii 2.45 Å [8]; Fig. 2, Table 2).

The geometric parameters of molecule **VIa** differ only slightly from those of **IIIa** [7]. As in molecule **IIIa**, the methoxycarbonyl group in **VIa** is oriented orthogonally to the $C^3C^6C^7$ plane. The phenyl ring on C^7 is also almost orthogonal to the same plane. The C^3 atom deviates by 0.204 Å from the $C^1C^2C^4C^5$ mean-square plane toward the aromatic ring, which corresponds to a dihedral angle of 165.6° between the $C^1C^2C^4C^5$ and $C^2C^3C^4$ planes. The distance between the oxygen atom in the hydroxy group and carbonyl carbon atom is 2.612 Å, which is slightly shorter than the sum of their van der Waals radii (C···O 3.00 Å [8]), and it allows for dipole–dipole interaction between these atoms. However, the dipole–dipole interaction in molecule **VIa** is likely to be weaker than in **IIIa**, taking into account that hydroxy group is a weaker donor than methoxy group. This follows, e.g., from the shorter distance between the carbonyl carbon atom and oxygen atom in the methoxy group (2.594 Å). This factor may be responsible for higher conformational mobility of the CO_2Me group in **VIa** as compared to **IIIa**. No intramolecular hydrogen bond between the hydroxy and methoxycarbonyl groups in compound **VIa** was detected. However, the behavior of molecules

* It is known that the conformational energies of iodine, bromine, and chlorine atoms attached to a six-membered ring are approximately equal [6] and that their van der Waals radii differ considerably: 1.97 (I), 1.86 (Br), 1.73 Å (Cl) [7]. In our case the geminal substituent affects conformational mobility of the methoxycarbonyl group in indirect mode, via variation of geometric parameters of the norpinane skeleton.

VIa in crystal may differ considerably from their behavior in solution. In particular, there are reasons to believe that intermolecular hydrogen bonds should weaken or even disappear completely in going to dilute solution in methylene chloride. In this case, the other possible factor facilitating rotation of the CO_2Me group about the C^6–C_{sp^2} bond in **VIa** is stabilization of the transition state at the maximal-energy point just via intramolecular hydrogen bond. A necessary condition for the formation of the latter is approach of the hydroxy group to the carbonyl oxygen atom, which is possible if the methoxycarbonyl group is oriented in the $C^3C^6C^7$ plane.

Special attention should be given to the temperature dependences of the ^{1}H NMR spectra of norpinanes **IIb** and **IIIb**. Lowering the temperature leads to splitting not only of the 1-H/5-H signal but also of the *exo*-2-H/*exo*-4-H signal (Fig. 3). This means that, apart from restricted rotation of the methoxycarbonyl group, rotation of the methoxy group on C^7 in molecules **IIb** and **IIIb** is also restricted. The 7-MeO group appears spatially close to the *exo*-2-H and *exo*-4-H protons and is oriented in the plane orthogonal to the $C^3C^6C^7$ plane, which is confirmed by the results of X-ray analysis of compounds **IIb** and **IIIb** [2, 3].

One more thing deserves attention. This is the low value of $\Delta G^{\neq}$ for organomercury derivative **VIIb**, which corresponds to a high rate of rotation of the ester group in its molecule. A probable reason is that the BrHg group is characterized by almost zero conformational energy due to high polarizability of the mercury atom [6]. On the other hand, the effective volume of the HgBr group (van der Waals radius 1.63 Å [7]) is obviously smaller than those of halogen atoms but considerably larger than that of hydrogen (1.20 Å). Therefore, unlike trisubstituted norpinane **Vb**, compound **VIIb** does display temperature dependence of the ^{1}H NMR spectrum. However, unlike compounds **IIb** and **IIIb**, the *exo*-2-H/*exo*-4-H signal in the spectrum of **VIIb** does not change down to 184 K, indicating high rate of rotation of the methoxy group about the C^7–O bond.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra of compounds **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**, **IVb**, and **VIa** were recorded on a Bruker DRX-300 spectrometer from solutions in $CDCl_3$. The ^{1}H and ^{13}C NMR spectra of **Vb** and **VIIb** were measured on a Bruker DRX-600 instrument from solutions in DMSO-d_6. Signals in the NMR spectra were assigned using two-dimensional HH-COSY, HC-COSY, and NOESY techniques.

Table 2. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) of non-hydrogen atoms in the crystalline structure of compound **VIa**

Atom	x	y	z	U_{eq}
Br^1	10615(1)	6000(1)	10627(1)	33(1)
O^1	4283(2)	6111(1)	9324(1)	28(1)
O^2	6943(2)	5236(1)	11486(1)	33(1)
O^3	7095(2)	6323(1)	12082(1)	35(1)
C^1	7035(2)	5674(1)	8587(2)	23(1)
C^2	8232(3)	5741(1)	7505(2)	30(1)
C^3	8691(3)	6476(1)	7238(2)	39(1)
C^4	8316(2)	6981(1)	8326(2)	30(1)
C^5	7071(2)	6698(1)	9240(2)	23(1)
C^6	7917(2)	6044(1)	9956(2)	22(1)
C^7	5520(2)	6233(1)	8406(2)	22(1)
C^8	7235(2)	5813(1)	11231(2)	24(1)
C^9	6504(6)	6144(2)	13345(3)	60(1)
C^{10}	4417(2)	6417(1)	6973(2)	24(1)
C^{11}	4048(3)	7081(1)	6569(2)	33(1)
C^{12}	2957(2)	7239(1)	5270(2)	38(1)
C^{13}	2169(3)	6734(1)	4370(2)	38(1)
C^{14}	2475(3)	6073(1)	4761(2)	37(1)
C^{15}	3610(3)	5914(1)	6053(2)	31(1)

Methyl *endo*-6-iodo-*anti*-7-methoxy-*syn*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (IIa) [2]**.** ^{1}H NMR spectrum, δ, ppm: 0.46–0.66 m (1H, *exo*-3-H), 1.11–1.25 m (1H, *endo*-3-H), 2.11–2.44 m (4H, 2-H, 4-H), 2.86 s (3H, OCH_3), 3.33 s and 3.46 s (1H

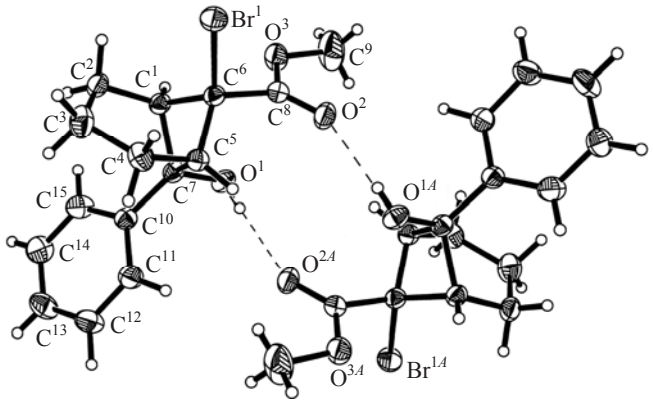


Fig. 2. Structure of methyl *endo*-6-bromo-*anti*-7-hydroxy-*syn*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (**VIa**) according to the X-ray diffraction data; two molecules linked through intermolecular hydrogen bonds are shown.

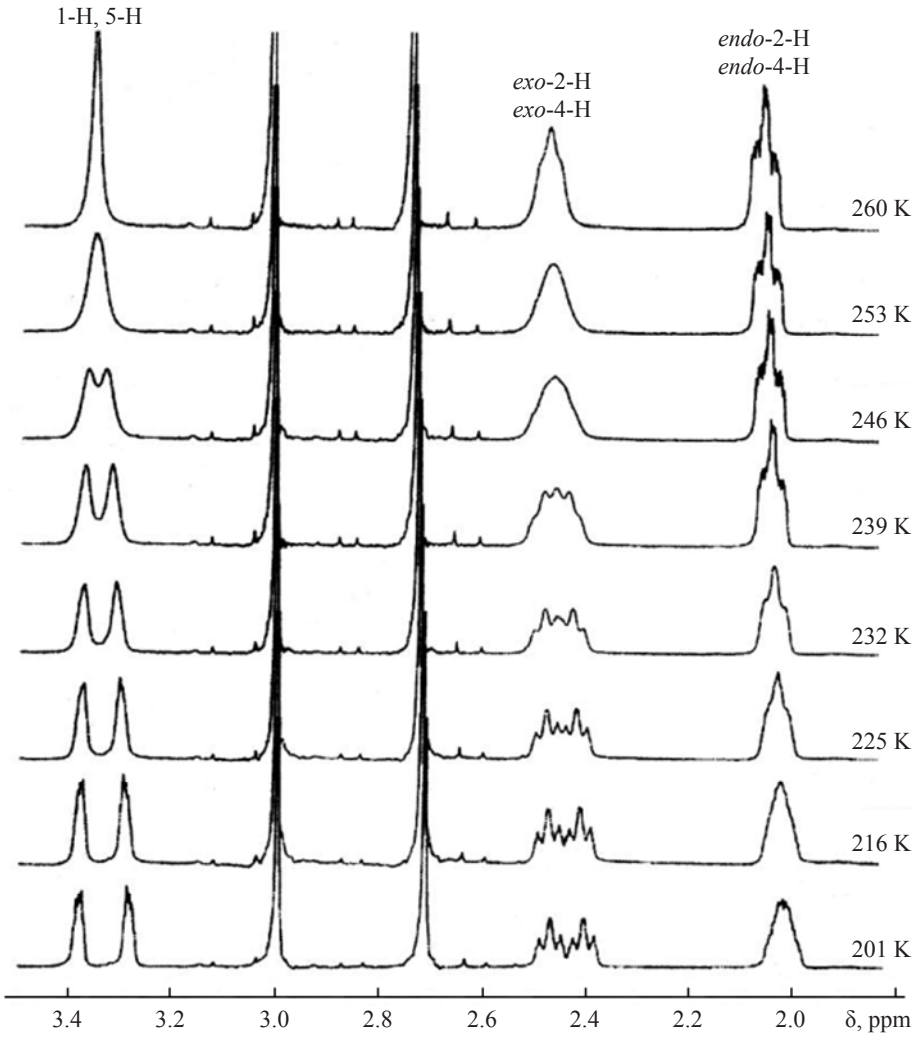


Fig. 3. ^{1}H NMR spectra of methyl *endo*-6-iodo-*syn*-7-methoxy-*anti*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (**IIb**) at different temperatures.

each, 1-H, 5-H, $W_{1/2}$ = 15 Hz), 3.82 s (3H, CO_2CH_3), 7.23–7.30 m (2H, H_{arom}), 7.33–7.45 m (3H, H_{arom}). ^{13}C NMR spectrum,** δ_C, ppm: 11.21 (C^3), 30.72 {125} and 30.84 {125} (C^2, C^4), 47.75 {115} and 50.17 {120} (C^1, C^5), 49.86 (OCH_3), 52.66 {100} ($CO_2\mathbf{C}H_3$), 56.55 (C^6), 83.22 (C^7), 126.71 (2C), 128.04, 128.0 (2C), 137.83 (C_{arom}), 172.84 (C=O).

Methyl *endo*-6-iodo-*syn*-7-methoxy-*anti*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (IIb) [2]**.** ^{1}H NMR spectrum, δ, ppm: 1.60–1.85 m (2H, 3-H), 2.12–2.31 m (2H, *endo*-2-H, *endo*-4-H), 2.51–2.66 m (2H, *exo*-2-H, *exo*-4-H), 2.87 s (3H, OCH_3), 3.13 s (3H, CO_2CH_3), 3.49 s (2H, 1-H, 5-H), 7.23–7.53 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.02 (C^3), 30.05 (C^2, C^4), 48.20 (C^6), 50.35 (C^1, C^5), 51.48 (OCH_3), 52.04 ($CO_2\mathbf{C}H_3$), 77.31 (C^7), 126.72 (2C), 127.72 (2C), 128.22 and 138.01 (C_{arom}), 172.54 (C=O).

Methyl *endo*-6-bromo-*anti*-7-methoxy-*syn*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (IIIa) [1]**.** ^{1}H NMR spectrum, δ, ppm: 0.49–0.70 m (1H, *exo*-3-H), 1.14–1.30 m (1H, *endo*-3-H), 2.08–2.40 m (4H, 2-H, 4-H), 2.86 s (3H, OCH_3), 3.41 s and 3.53 s (1H each, 1-H, 5-H, $W_{1/2}$ = 15 Hz), 3.85 s (3H, CO_2CH_3), 7.22–7.31 m (2H, H_{arom}), 7.34–7.45 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 11.56 (C^3), 26.89 {45} and 27.00 {45} (C^2, C^4), 47.10 {[35} and 49.54 {35} (C^1, C^5), 49.79 (OCH_3), 52.71 {100} ($CO_2\mathbf{C}H_3$), 68.65 (C^6), 84.32 (C^7), 126.95 (2C), 128.12, 128.18 (2C), 137.01 (C_{arom}), 171.20 (C=O).

Methyl *endo*-6-bromo-*syn*-7-methoxy-*anti*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate

** Hereinafter, peak intensities of the C^1, C^5, C^2, and C^4 signals in the ^{13}C NMR spectra of **IIIa** and **IVa** are given in braces (relative to the $CO_2\mathbf{C}H_3$ signal {100}).

(IIIb) [1]. ^{1}H NMR spectrum, δ, ppm: 1.54–1.64 m (1H, *endo*-3-H), 1.65–1.75 m (1H, *exo*-3-H), 2.11–2.20 m (2H, *endo*-2-H, *endo*-4-H), 2.32–2.42 m (2H, *exo*-2-H, *exo*-4-H), 2.86 s (3H, OCH_3), 3.13 s (3H, CO_2CH_3), 3.53 s (2H, 1-H, 5-H), 7.32–7.43 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.00 (C^3), 27.25 (C^2, C^4), 50.08 (C^1, C^5), 52.11 (OCH_3), 52.83 ($CO_2\mathbf{C}H_3$), 64.79 (C^6), 79.27 (C^7), 128.55 (2C), 129.06, 129.55 (2C), 138.22 (C_{arom}), 170.75 (C=O).

Methyl *endo*-6-chloro-*anti*-7-methoxy-*syn*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (IVa) [2]. ^{1}H NMR spectrum, δ, ppm: 0.50–0.71 m (1H, *exo*-3-H), 1.15–1.31 m (1H, *endo*-3-H), 1.99–2.15 m (2H, *exo*-2-H, *exo*-4-H), 2.22–2.40 m (2H, *endo*-2-H, *endo*-4-H), 2.86 s (3H, OCH_3), 3.49 s (2H, 1-H, 5-H, $W_{1/2}$ = 24 Hz), 3.85 s (3H, CO_2CH_3), 7.24–7.32 m (2H, H_{arom}), 7.33–7.46 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 11.79 (C^3), 24.78 {160} (C^2, C^4), 46.59 {7} and 49.06 {7} (C^1, C^5), 49.71 (OCH_3), 52.72 {100} ($CO_2\mathbf{C}H_3$), 71.19 (C^6), 84.12 (C^7), 127.09 (2C), 128.08, 128.21 (2C), 136.62 (C_{arom}), 170.81 (C=O).

Methyl *endo*-6-chloro-*syn*-7-methoxy-*anti*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (IVb) [2]. ^{1}H NMR spectrum, δ, ppm: 1.62–1.75 m (1H, *endo*-3-H), 1.80–1.93 m (1H, *exo*-3-H), 2.28–2.41 m (4H, 2-H, 4-H), 2.90 s (3H, OCH_3), 3.18 s (3H, CO_2CH_3), 3.55 s (2H, 1-H, 5-H), 7.30–7.49 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.65 (C^3), 24.65 (C^2, C^4), 49.24 (C^1, C^5), 50.96 (OCH_3), 52.15 ($CO_2\mathbf{C}H_3$), 67.51 (C^6), 78.88 (C^7), 127.4 (2C), 128.0 (2C), 128.5, 137.9 (C_{arom}), 170.35 (C=O).

Methyl *syn*-7-methoxy-*anti*-7-phenylbicyclo-[3.1.1]heptane-*exo*-6-carboxylate (Vb) [4]. ^{1}H NMR spectrum, δ, ppm: 1.61–1.76 m (2H, 3-H), 1.91–1.98 m (2H, *endo*-2-H, *endo*-4-H), 2.10–2.16 m (2H, *exo*-2-H, *exo*-4-H), 2.63 s (1H, 6-H), 2.70 s (3H, OCH_3), 3.06 s (3H, CO_2CH_3), 3.21 s (2H, 1-H, 5-H), 7.28 t (1H, H_{arom}, J = 7.2 Hz), 7.34 t (2H, H_{arom}, J = 7.2 Hz), 7.39 d (2H, H_{arom}, J = 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.50 (C^3), 24.15 (C^2, C^4), 38.50 (C^6), 43.15 (C^1, C^5), 50.12 (OCH_3), 50.71 ($CO_2\mathbf{C}H_3$), 79.26 (C^7), 127.56 (3C), 128.15 (2C), 139.75 (C_{arom}), 173.32 (C=O).

Methyl *endo*-6-bromo-*anti*-7-hydroxy-*syn*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (VIa) [5]. ^{1}H NMR spectrum, δ, ppm: 0.52–0.71 m (1H, *exo*-3-H), 1.13–1.30 m (1H, *endo*-3-H), 1.93 s (OH), 2.18–2.39 m (4H, 2-H, 4-H), 3.40 s (2H, 1-H, 5-H), 3.85 s (3H, CO_2CH_3), 7.26–7.35 m (2H, H_{arom}), 7.35–7.46 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 11.31 (C^3), 27.28 (C^2, C^4), 51.27 (C^1, C^5), 52.91 ($CO_2\mathbf{C}H_3$), 68.72 (C^6), 79.41 (C^7), 125.12 (2C), 128.07, 128.91 (2C), 141.78 (C_{arom}), 171.13 (C=O).

Methyl *endo*-6-bromomercurio-*syn*-7-methoxy-*anti*-7-phenylbicyclo[3.1.1]heptane-*exo*-6-carboxylate (VIIb) [4]. ^{1}H NMR spectrum, δ, ppm: 1.72–1.81 m (1H, *endo*-3-H), 1.89–1.99 m (1H, *exo*-3-H), 2.05–2.10 m (2H, *endo*-2-H, *endo*-4-H), 2.12–2.19 m (2H, *exo*-2-H, *exo*-4-H), 2.71 s (3H, OCH_3), 2.99 s (3H, CO_2CH_3), 3.50 s (2H, 1-H, 5-H), 7.27 t (1H, H_{arom}, J = 7.2 Hz), 7.31 t (2H, H_{arom}, J = 7.2 Hz), 7.40 d (2H, H_{arom}, J = 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.30 (C^3), 29.06 (C^2, C^4), 50.87 and 51.21 (OCH_3, $CO_2\mathbf{C}H_3$), 51.19 (C^1, C^5), 68.17 (C^6), 82.19 (C^7), 127.69 (2C), 128.20, 129.39 (2C), 140.29 (C_{arom}), 174.08 (C=O).

Low-temperature NMR studies were performed on a Bruker DRX-600 or DRX-400 instrument using CD_2Cl_2 or DMSO-d_6 as solvent; methanol was used as standard for temperature calibration. The rate constant k_c (Hz) for conformational exchange at the coalescence temperature was calculated by the equation $k_c = \pi\,\Delta\nu/\sqrt{2} = 2.22\,\Delta\nu$, and the Gibbs energy of activations $\Delta G_c^{\neq}$ (kJ/mol) was calculated by the Eyring equation [9]: $\Delta G_c^{\neq} = 19.14\times10^{-3}\,T_c\,[9.97 + \log(T_c/\Delta\nu)]$. The calculated parameters are collected in Table 1. No signal coalescence was observed for compound **Vb** down to 184 K (600 MHz, CD_2Cl_2).

X-Ray analysis of compound VIa. The X-ray diffraction data for a single crystal of **VIa** (placed in a glass capillary using a microscope) were acquired on a Siemens-CCD-SMART diffractometer at 223(2) K (MoK_α irradiation, graphite monochromator, θ–2θ scanning). The crystal system and unit cell parameters were determined using SMART software package [10]. The experimental reflection intensities were processed using SAINT program [11]. The structure was solved by the direct method and successive syntheses of electron density. The positions of non-hydrogen atoms were refined with respect to F^2 by the full-matrix least-squares procedure in anisotropic approximation. Hydrogen atoms were localized from the geometry considerations, and their positions were refined according to riding model with U(H) = 1.2U(C), where U(C) is the equivalent temperature factor of carbon atom to which the given hydrogen atom is attached. All calculations were performed using SHELXTL 5.1 software package [12]. In all cases U_{eq} was defined as 1/3 of the orthogonalized U_{ij} tensor. The coordinates of non-hydrogen atoms and their equivalent isotropic thermal parameters are listed in Table 2. Anisotropic thermal parameters of non-hydrogen atoms, as well as

coordinates and equivalent isotropic thermal parameters of hydrogen atoms, are available from the authors. The structure of molecule **VIa** is shown in Fig. 2. Monoclinic crystals, space group $P2(1)/c$ (no. 14); unit cell parameters: a = 7.3953(9), b = 19.965(3), c = 9.7837(12) Å; β = 102.619; V = 1409.6(3) Å^3; crystal habit 1.00×0.50×0.50 mm; Z = 4; d_{calc} = 1.532 g/cm^3. Intensities of 9119 reflections (3390 independent reflections with R_{int} = 0.0210) were involved in the structure solution and refinement, $F(000)$ = 664, θ_{max} = 28.75°. A correction for absorption (μ = 2.917 mm^{-1}) was introduced using SADABS software [13]. The final divergence factors were R_1 = 0.0284 [F_{hkl}; 3390 reflections with $I > 2\sigma(I)$] and wR_2 = 0.0726 (F^2_{hkl}; for all 9119 reflections used in the final refinement step), number of refined parameters 240, goodness of fit 1.057.

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