Hindered Rotation of the Silyl Group in Liquid-Phase NMR Spectra of 9-Silyltriptycene Derivatives: A Comparison with the Methyl Analogues

Tomasz Ratajczyk, Igor Czerski,[†] and Sławomir Szymański*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, Poland

Received: June 17, 2008; Revised Manuscript Received: July 18, 2008

Three 9-silyltriptycene derivatives, 1,4-dichloro- (DCST), 1,4-dibromo- (DBST), and 1,4-dimethyl-9-silyltriptycene (DMST) were synthesized, and temperature-variable ^{1}H NMR spectra thereof were measured. Below 220 K for DMST, and below 250 K for DCST and DBST, rotation of the silyl group becomes practically frozen on the NMR time scale. Iterative line shape analysis of the silyl proton spectra reveals that the familiar Alexander−Binsch line shape equation, employing only one rate constant for the observed rate process, is adequate in these cases. This is at a striking variance with the behavior of the methyl group in the analogous compounds, investigated by us recently, where fingerprints of the damped quantum rotation effect, a phenomenon once predicted by us, are clearly visible in the experimental spectra of the methyl protons. In the damped rotation approach, the relevant dynamics are described in terms of two quantum rate processes characterized by two coherence-damping constants, and the Alexander−Binsch model is obtained as a limiting case where these two constants become equal. The possible reasons of the differences between the dynamics of the silyl and methyl groups in the same molecular environment are discussed.

Introduction

The compounds studied presently, 1,4-dichloro- (DCST), 1,4-dibromo- (DBST), and 1,4-dimethyl-9-silyltriptycene (DMST), see Figure 1, are close analogues of the appropriate peri-substituted 9-methyltriptycene derivatives investigated by us recently.[1−4] In the latter compounds, the methyl group suffers extreme hindrance of its torsional motion such that its stochastic dynamics can be frozen on the NMR time scale at relatively high temperatures, usually above 170 K. The temperature-variable spectra of the methyl protons provided evidence of a nonclassical character of the hindered rotation of the methyl group, in accord with the predictions of the damped quantum rotation (DQR) model.[5−7] In the DQR approach, the dynamics of a rotator of symmetry C_3 are described in terms of two quantum rate (i.e., coherence-damping) processes described by two quantum rate constants, k_t and k_K, and the standard Alexander−Binsch (AB) model[8,9] of classical random jumps between the three equivalent orientations appears there as the limiting case of $k_t = k_K$. The subscripts *t* and *K*, designating "tunneling" and "Kramers", refer to two specific, long-lived coherences each of which engages both spin and space coordinates of the three rotating particles, correlated by the Pauli principle. To a rough approximation, these long-lived coherences are Boltzmann averages of coherences between pairs of the three sublevels of the subsequent torsional levels, transforming as the symmetry species A, E_a, and E_b of C_3. Specifically, the Kramers coherence includes the perfectly degenerate Kramers sublevels E_a and E_b, and the tunneling coherence includes one of the Kramers sublevels and that of symmetry A, shifted in energy from the Kramers pair by a "tunneling" quantum.[5]

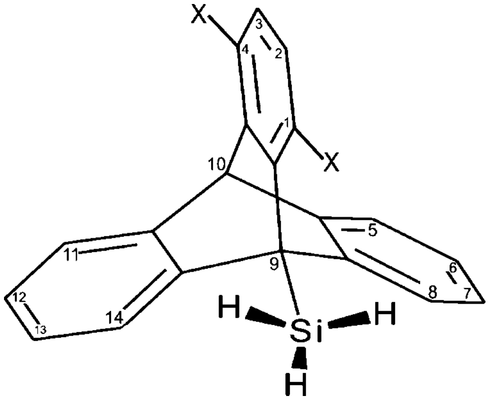

Figure 1. The 9-silyltriptycene derivatives investigated: DBST, X = Br; DCST, X = Cl; DMST, X = Me.

Our findings that in the methyltriptycne derivatives the "nonclassicality coefficient" $c = k_t/k_K$ can deviate from its "classical" value 1 by as much as 30%[4] are rather surprising, considering the fact that they involve liquid samples investigated at relatively high temperatures. (For the methyl group in a molecular crystal, *c* can exceed 5, but this involves temperatures below 100 K.[10]) In this context, it seemed natural to ask whether the relevant behavior of the close analogue of the methyl group, the SiH$_3$ group, can be similar to that of the methyl group. To the best of our knowledge, no NMR studies on the hindered rotation of the silyl group have been reported previously. The three silyl derivatives investigated presently, synthesized for the first time, were deliberately chosen as models because of their close similarity to the methyl derivatives mentioned above. It comes out that the dynamics of the investigated silyl groups do not show measurable deviations from the predictions of the jump model. Nevertheless, these observations shed some light on the factors controlling the dynamics of hindered threefold molecular rotors in general.

Experimental Part

1,4-Dichloro- (DCST), 1,4-dibromo- (DBST), and 1,4-dimethyl-9-silyltriptycene (DMST) were synthesized by adapting

---

* To whom correspondence should be addressed. E-mail: sszym@icho.edu.pl.

[†] Present address: Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, Poland.

10.1021/jp8053394 CCC: $40.75

TABLE 1: Chemical Shifts and Coupling Constants of the Silyl Protons in the Compounds Investigated[a]

compd	temp/K	δ_A/ppm	δ_B/ppm	J_{AB}/Hz
DMST[b]	224	4.916(1)	4.460(1)	5.95(1)
DCST[c]	224	5.153(1)	4.575(1)	7.31(1)
DBST[c]	234	5.291(1)	4.567(1)	7.33(1)

[a] Numbers in parentheses are standard errors. [b] In CD_2Cl_2. [c] In toluene-d_8.

the literature procedures.[11,12] The details of these syntheses will be published elsewhere. The structures of the compounds were confirmed by room-temperature ^{1}H NMR spectra.

NMR Measurements. Variable-temperature NMR spectra were measured on a Bruker Avance DRX 500 MHz spectrometer, equipped with a TBI probe with a thermocouple installed in it, and a BVT 3000 temperature control unit. Temperature stability was ca. 0.1 K. The measured samples were degassed and sealed under vacuum of about 1 Torr in NMR tubes of the outer diameter of 5 mm. For DMST, a solution of 4 mg of the compound in 0.7 mL of $CDCl_3$ was used, and for the remaining derivatives, a solution of 4 mg of the compound in 0.7 mL of toluene-d_8. In the NMR measurements, the parameter settings were such as described in ref 3. The temperature was measured with the accuracy generally better than 1 K using the methanol chemical shift thermometer[13] (the dry methanol sample was purchased from Wilmad). Below 330 K, the methanol spectra were recorded for each temperature setting. Above 330 K, the thermocouple readings were recalibrated against the methanol chemical shift data extrapolated linearly from the lower temperatures.

Results and Discussion

The temperature-dependent spectra of the silyl derivatives were measured in the range of 220−300 K for DMST and 260−350 K for DCST and DBST. In accord with the symmetry of the molecules concerned, an A_2B pattern was observed for the silyl protons in the spectra at the lowest temperatures; values of the chemical shifts and the coupling constant are shown in Table 1. For DMST, the low-temperature spectra of the silyl protons show some extra line broadenings, of ca. 1 Hz, which are due to unresolved J-couplings to the C1−CH_3 protons and to the (aromatic) peri protons at C8 and C14. At temperatures where the fine structure due to the interproton J-couplings within the silyl group is not completely obliterated, Carr−Purcell echo spectra[14] were also measured. As an example, a series of such echo spectra for DBST in the slow exchange limit, measured at the same temperature for suitably chosen echo times, is shown in Figure 2. As was shown previously, fits to such series of echo spectra mercilessly reveal deficits of the theoretical model employed in the fits.[3]

The temperature-dependent silyl proton spectra were analyzed quantitatively using the methodology described in detail in refs 3 and 4. In the fits, the DQR line shape equation was used. In Liouville space notation, it reads[5,10]

$$Y(\omega) \propto \langle F_+|[-\mathrm{i}(\mathbf{L}+\omega\mathbf{E}) - \frac{k_K}{3}(2\mathbf{E} - \hat{P}\otimes\hat{P} - \hat{P}^{-1}\otimes\hat{P}^{-1}) - \frac{(k_t - k_K)}{2}(\mathbf{E} - \hat{U}\otimes\hat{U})]^{-1}|\rho(0)\rangle \quad (1)$$

where the supervectors $\langle F_+|$ and $|\rho(0)\rangle$ describe the total spin raising operator and the state of the spin system at the start of acquisition of the free induction signal, respectively and $\mathbf{L}$ and $\mathbf{E}$ are the standard spin super-Hamiltonian and unit superoperator, respectively; $\hat{P}$ is the operator of cyclic permutation of the three silyl protons, and $\hat{U} = [2(\hat{P} + \hat{P}^{-1}) - \hat{1}]/3$ is a unitary, self-inverse operator ($\hat{U}^2 = \hat{1}$). As can easily be seen, for $k_t = k_K$ eq 1 is turned into the AB line shape equation describing random jumps of a threefold molecular rotator between its three equivalent, equilibrium orientations.

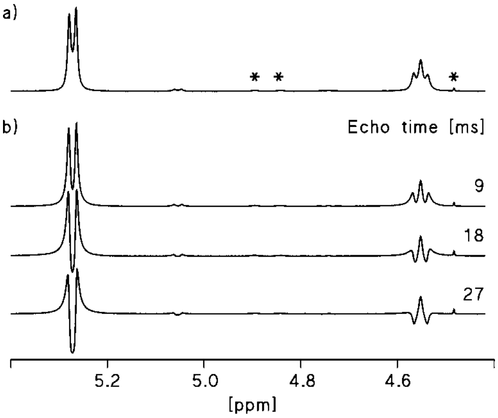

Figure 2. NMR spectra of the silyl protons in DBST at 268.3 K: (a) standard spectrum; (b) series of CP-echo spectra for the indicated echo times. The spectra are normalized to the same maximum amplitude. Impurity signals are marked with ∗.

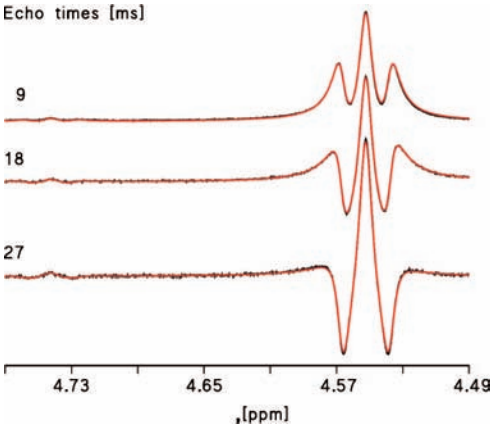

Figure 3. Fit of theoretical echo spectra (red), calculated using the AB equation, to a series of three experimental CP-echo spectra of the silyl protons in DBST, measured at 268.3 K. Only the region of proton B resonances is shown where the line shape is most sensitive to the possible deficits of the model. The calculated spectra are superpositions of contributions from the isotopomers ^{28}Si and ^{30}Si (spin 0, total abundance 95.30%) and ^{29}Si (spin $^1/_2$, abundance 4.70%—see the signal above 4.72 ppm). The $^1J(H_A,^{29}Si)$ and $^1J(H_B,^{29}Si)$ values are 218.0 and 190.3 Hz, respectively.

In the fits to the spectra of DBST with decoalesced resonances of the A and B protons, apart from other relevant line shape parameters[3,4] the two rate parameters, k_K and $c = k_t/k_K$, were adjusted. However, the values of c delivered at convergence, although consistently greater than 1, did not depart from that limiting value by more than 0.05. Accordingly, the "classical" fits (ones with the value of c set to 1) did not reveal discernible misfits, even for series of echo spectra. An example of one such fit to the echo spectra of DBST is shown in Figure 3. The presented example involves the very onset of exchange where the line shapes are most sensitive to the DQR effects. This situation contrasts with our previous observations for the methyl protons in the analogue of DBST, 1,4-dibromo-9-methyltriptycene, DBMT, and in other 9-methytriptycene derivatives investigated by us. For DBMT, fits with the AB equation are

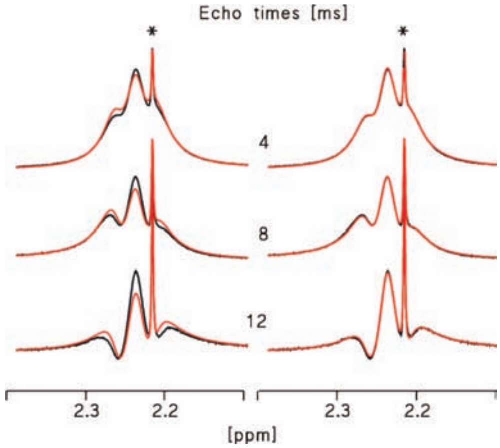

Figure 4. Fits of theoretical echo spectra (red), calculated using the AB (left panel) and DQR equations (right panel), to a series of three experimental CP-echo spectra of the methyl protons in DBMT, measured at 176.2 K (ref 4). Only the region of proton B resonances is shown; in the region of proton A, the misfits of the AB model are less substantial. The values of J obtained from the AB and DQR fits are 11.97 and 12.51 Hz, respectively (see text); from the DQR fit, the value of $c = 1.29$ was obtained. The impurity signal marked with * was included in the fits, with assumed Lorentzian shape.

evidently flawed, whereas those with adjustable c are virtually perfect (see Figure 4).[4] For the latter compound, in the (relatively narrow) temperature range where both rate parameters, k_t and c, can be extracted from the spectra, the values of c remain different from 1, although they show a systematic decrease with increasing temperature, from 1.29 at 176 K to 1.22 at 181 K. (For two of the methyltriptycene derivatives, a partial reversal of such initially decreasing trend was observed.[4]) Such extent of deviations from 1 is strong enough for the inadequacy of the AB model to be manifested also in the fits to individual standard spectra.[1,2,4] For the values of c below ca. 1.10, the flaws of such "individual" fits can be almost perfectly compensated by a severe underestimation of the relevant J-coupling values.[3] In the case of DBST, the values of J-coupling obtained from the fits are identical within the standard error, regardless of whether the AB or DQR model is used. Moreover, at variance with the temperature behavior of J in the 9-methyltriptycenes, the values of J extracted from the spectra of DBST over the range of 254−276 K show no systematic changes with temperature. For the methyl derivatives, the changes of J with temperature, of the amplitude generally not exceeding 1 Hz, originate from a temperature-dependent contribution of Heisenberg's exchange coupling.[4,15−17] Therefore, unlike for the methyl group in the 9-methyltriptycenes, both the coherent and stochastic dynamics of the silyl group in DBST are fully explicable in terms of the standard NMR picture of hindered rotation.

The above conclusion extends also to the silyl group in DCST where, again, the relevant dynamical behavior strikingly contrasts with that of the methyl group in the analogue, 1,4-dichloro-9-methyltriptycene, DCMT.[4] It is also valid for DMST, although in this case the presence of unresolved couplings to the methyl and peri protons (see above) precluded successful use of the echo technique for a definite confirmation of the validity of the AB model in the slow exchange region. The behavior of the methyl group at C9 in 1,4,9-trimethyltriptycene, TMT, the analogue of DMST, was not investigated by us. In an earlier study by Nakamura et al.,[18] decoalescence of the 9-methyl protons in TMT could not be reached even below 173 K.

Arrhenius plots of the rate constants $k_K = k_t$ for the silyl groups investigated are shown in Figure 5. The corresponding activation energies and preexponential Arrhenius factors are collected in Table 2, together with the relevant data for the methyl groups in DBMT and DCMT. The latter involve the values of k_K extracted from the DQR fits in which c was adjusted in the slow exchange limit only; for faster exchange the value of c was set equal to the average of the values obtained in the slow exchange region.[4]

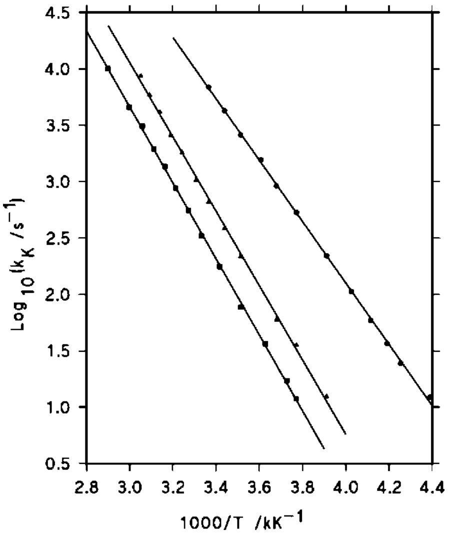

Figure 5. Arrhenius plots of the rate constants $k_K = k_t \approx k_{K0} \exp(-E_a/kT)$ for DBST (squares), DCST (triangles), and DMST (circles).

TABLE 2: Arrhenius Activation Energies and Preexponential Factors k_{K0} for the Experimental Rate Constants $k_K(T)$[a]

compd	temp range/K	$c = k_t/k_K$	$\log_{10}(k_{K0}/s^{-1})$	E_A/kJ mol^{-1}	ref
DMST	228−297	1	13.0(1)	52.1(3)	this work
DCST	256−328	1	13.9(1)	62.9(6)	this work
DBST	265−345	1	13.8(1)	64.4(4)	this work
DBMT[b]	176−234	1.250[c]	13.2(1)	38.7(6)	4
DCMT[b]	173−225	1.185[c]	13.0(2)	37.2(6)	4

[a] Numbers in parentheses are standard errors. [b] For a solution of 3 mg of the compound in 0.7 mL of CS_2/CD_2Cl_2 3:1 v/v. [c] Averages of the values determined in the slow exchange limit.

If the data for the methyl analogues had not been available, the present results would have hardly deserved further comments: it is generally taken for granted that molecular rate processes in condensed phases are classical by their very nature. But now, one should try to rationalize the differences in the observed behavior of the silyl and methyl groups placed in exactly the same molecular environment. Paradoxically, because at least at the very onset of exchange discernible deviations from the jump model do occur for all of the 9-methyltriptycenes investigated by us,[4] the radical absence of such effects for the $-SiH_3$ group even becomes an intriguing question.

In view of the data in Table 2, these differences appear to be concerned with a substantial increase of the torsional barrier on passing from the methyl to the silyl group. Considering the definition of the relevant long-lived coherences, invoked in the Introduction, one might conclude that the convergence of k_K and k_t is due to the concomitant collapse of the tunneling splittings at the subsequent torsional levels, succeeding in a substantial reduction of the differences between the individual components of these coherences (the degenerate Kramers pairs (E_a, E_b) vs the nondegenerate "tunneling" pairs (A,$E_{a,b}$)). However, in view of our previous considerations,[5] the situation does not seem to be so simple. Actually, the considered stochastic behavior depends mainly upon the properties of the highest torsional levels near the barrier top. The tunneling splittings of these crucial levels are not very much sensitive to the barrier height, whereas they are dependent on the relevant moment of inertia. In the rigid rotator approximation, the magnitude of the latter for $-SiH_3$ is only about 1.8 of that of $-CH_3$, which, in view of our earlier considerations to be invoked later on,[7] is not a critical difference. However, the question of whether the rigid approximation can be valid in the discussed temperature range deserves a closer examination. Before discussing this question, the role of the torsional barrier should be reconsidered from a different perspective.

The height of the barrier does appear to be critical, but mostly as a factor controlling the location of the temperature range where the line shape effects are apparent. The higher the temperature, the more and more vibrational degrees of freedom, apart from the torsional coordinate, will be engaged in the observed process. On intuitive grounds (to be substantiated later on) one may expect that under such circumstances any distinctive features of the relevant quantum coherences will be leveled off. This should in particular occur in systems where either the rotator itself or its immediate surrounding are flexible moieties. The silyl group is evidently a less stiff object than the methyl group, especially when swinging of the C9−Si axis is compared with the corresponding mode of the C9−C axis. In combination with the fact that for the silyl groups the relevant temperature range is substantially shifted upward, this would suggest the direction where to seek explanation of the results reported above.

It is implied in the foregoing that the classical limit of random jumps between equivalent orientations is in a sense natural for the rotators considered. Actually, the first observations of the DQR effects, involving a CD_3 group in a single molecular crystal at temperatures below 40 K, have revealed a monotonical decrease of c with temperature down to the value of 0.70, that is, *below* 1, with no indications that further increase of the temperature would lead to a reversal of the trend.[19] This would suggest nonexistence of a classical limit in that case. On the other hand, for the protonated methyl and silyl groups investigated above 170 K, the estimated values of c never drop below 1 by more than the experimental error. Moreover, with the two already mentioned exceptions, their temperature trends seem to head consistently for 1 (however, these trends can be monitored only over narrow temperature intervals, generally below 10 K[4]).

Some light on this specific instance of the general, long-debated problem of the quantum to classical transition[20,21] was shed by our recent numerical calculations for a “sizeable” rotator, the benzene ring embedded in a hindering potential and interacting with a thermal bath.[7] In the calculations only one degree of freedom was addressed, that of planar rotation of the ring. For a sixfold molecular rotator there can be as many as nine potentially different quantum rate constants, whereas there are only three possible jump types: direct jumps over one, two, and three maxima of the corresponding sixfold torsional potential.[6] A general inference from those calculations is that, with growing impact of the bath, a specific clustering of these nine quantum rate constants about only three values is observed. The clustering is reflected in an automatic transformation of the quantum stochastic terms in the corresponding DQR line shape equation into the appropriate Alexander−Binsch terms describing the three direct jump processes.[7] For the system−bath interactions of low and moderate strength, the clustering progresses with increasing temperature. A similar scenario is observed in our yet unpublished numerical results for “sizeable” three-, four-, and fivefold rotators. Thus, in the sense of the picture reflected in NMR line shape, the jump model as the classical limit appears to be natural for such sizable rotators, in agreement with common sense expectations.

From a consideration of the formalism underlying the above calculations it follows that the stochastic behavior critically depends on the energy (frequency) gap separating the torsional quanta and the tunneling splittings of the individual torsional levels (the latter are negligibly small for sizable rotators).[7] When the vibrational relaxation rates, controlled by the magnitudes of the system−bath interactions, can become comparable with this gap, the possible deviations from the classical limit will be quenched in the whole temperature range relevant to NMR line shape studies; the jump model reproduced in this way is virtually exact.[7] The underlying microscopic mechanism involves “awakening” of some, otherwise strongly nonsecular, off-diagonal vibrational relaxation matrix elements connecting two sorts of dynamical events in the rotator system: from one side, the dephasing processes of the torsional coherences and, from the other, the rate processes operating in the manifold of the low (or zero)-frequency coherences between the torsional sublevels, where only the latter are directly relevant to NMR experiments. Our yet unpublished calculations show that a brute-force zeroing of these crucial off-diagonal elements precludes exact numerical modeling of the tendency to the classical limit even for sizable rotators.

In the harmonic approximation valid for the lowest torsional states, this critical gap scales as inverse square root of the moment of inertia of the rotator. The relevant moments of inertia of the silyl and methyl groups are far too small for the above inferences to be applicable at hand to such groups. However, when the flexibility factors discussed above are taken into account, the above mechanism of generation of classicality can be extended also to such systems. The substance of those intuition-based considerations becomes apparent if the true, i.e., multidimensional, character of the high-temperature processes considered presently is mapped onto one-dimensional model. Then the effect of swinging of the axis connecting the rotating group to the rest of the molecule can be viewed as an apparent increase of the moment of inertia of the rotator, progressing with temperature. The progress is concerned with growing population of higher levels of the relevant bending vibrations, characterized by growing delocalization of the corresponding state functions. This would ultimately lead to a considerable narrowing of the critical energy gap considered above and, consequently, to an evening out of the rate constants k_K and k_t. The effective moment of inertia of the $-SiH_3$ group, resulting from swinging of the rotation axis, may be sufficiently large already at the onset of the stochastic exchange for the quantum character thereof to be quenched. Efforts to quantify, within our recent DQR formalism,[6,7] the effect of swinging of the rotation axis, using X-ray estimates of the appropriate thermal ellipsoids, are underway.

Conclusions

Three 9-silyltriptycene derivatives, DCST, DBST, and DMST, were synthesized, and temperature-variable ^1H NMR spectra thereof were measured. Below 220 K for DMST, and below 250 K for DCST and DBST, rotation of the silyl group becomes practically frozen on the NMR time scale. Iterative line shape analysis of the silyl proton spectra reveals that the familiar jump model, employing only one rate constant, is adequate for the observed rate process even at the very onset of exchange. This is at a striking variance with the behavior of the methyl group in the analogous compounds, investigated by us recently, where fingerprints of the DQR effect are clearly visible in the experimental spectra of the methyl protons. The differences between the dynamics of the silyl and methyl groups in the same molecular environment are qualitatively explained in terms of combination of two effects: the higher torsional barrier of the silyl group and its greater flexibility as compared to the methyl group. The higher barrier causes the relevant temperature range to be shifted upward, which in turn makes more room for the flexible modes of the system to come into play and quench the quantum character of the stochastic motion. The probable quench mechanism, previously identified as such for sizable rotators like the benzene ring, is ultimately concerned with a temperature-induced increase of an effective moment of inertia of the silyl group.

Acknowledgment. This work was sponsored by the Public Funds for Sciences in years 2006−2009 as the N20404831/1286 research project.

References and Notes

(1) Bernatowicz, P.; Szymanski, S. *Phys. Rev. Lett.* **2002**, *89*, 023004.
(2) Czerski, I.; Bernatowicz, P.; Jazwinski, J.; Szymanski, S. *J. Chem. Phys.* **2003**, *118*, 715.
(3) Bernatowicz, P.; Czerski, I.; Jazwinski, J.; Szymanski, S. *J. Magn. Reson.* **2004**, *169*, 284.
(4) Czerski, I.; Szymanski, S. *Pol. J. Chem.* **2006**, *80*, 1233.
(5) Szymanski, S. *J. Chem. Phys.* **1999**, *111*, 288.
(6) Ratajczyk, T.; Szymanski, S. *J. Chem. Phys.* **2005**, *123*, 204509.
(7) Ratajczyk, T.; Szymanski, S. *J. Chem. Phys.* **2007**, *127*, 184504.
(8) Alexander, S. *J. Chem. Phys.* **1962**, *37*, 967.
(9) Kleier, D. A.; Binsch, G. *J. Magn. Reson.* **1970**, *3*, 146.
(10) Gutsche, P.; Schmitt, H.; Haeberlen, U.; Ratajczyk, T.; Szymanski, S. *ChemPhysChem* **2006**, *7*, 886.
(11) Rudinger, S.; Beruda, H.; Schmidbaur, H. *Chem. Ber.* **1992**, *125*, 1401.
(12) Schrock, R.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *J. Organomet. Chem.* **1996**, *509*, 85.
(13) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.
(14) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954**, *94*, 630.
(15) Apaydin, F.; Clough, S. *J. Phys. C: Solid State Phys.* **1968**, *2*, 932.
(16) Mottley, C.; Cobb, T. B.; Johnson, C. S. *J. Chem. Phys.* **1971**, *55*, 5823.
(17) Horsewill, A. J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *35*, 359.
(18) Nakamura, M.; Oki, M.; Nakanishi, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2415.
(19) Szymanski, S.; Olejniczak, Z.; Detken, A.; Haeberlen, U. *J. Magn. Reson.* **2001**, *148*, 277.
(20) Joos, E.; Zeh, D. H.; Kiefer, C.; Giulini, D.; Kupsch, J.; Stamatescu, I. O. *Decoherence and the Appearance of a Classical World in Quantum Theory*; Springer: Berlin, 2003.
(21) Breuer, H. P.; Petruccione, F. *The Theory of Open Quantum Systems*; Clarendon: Oxford, 2002.

JP8053394