

Possible spectroscopic manifestation of the angular group induced bond alteration (AGIBA) effect in toluene

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Received 20 March 2007; accepted 29 March 2007

ABSTRACT: The most obvious consequence of the concept of aromaticity is the common confidence that in aromatic compounds, bond lengths do not alternate and are between typical to the single and double ones. However, in 1994, performing crystal structure investigations of substituted pyridines and their salts, Krygowski and co-workers have discovered a very surprising angular group induced bond alteration (AGIBA) effect: It appears that some angular substituents, like methoxy or nitrozo groups, can induce bond alternation in aromatic rings. Crystal studies do not allow one to operate with liquids that are more common in organic chemistry. This paper presents the first possible evidence of spectroscopic manifestations of the AGIBA effect. Raman spectra of the liquid toluene are analyzed. It is found that instead of being single, the line corresponding to the ring breathing vibrations is clearly split by 1.0–1.4 cm⁻¹, thus indicating the presence of two (*cis*- and *trans*-) AGIBA isomers. The energy difference between these isomers estimated in temperature dependent Raman studies is found equal to 6.68 kJ mol⁻¹. The low-wavenumber line therefore corresponds to the *cis*-AGIBA isomer and the high-wavenumber line to the *trans*-AGIBA isomer stabilized by the AGIBA effect. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: AGIBA effect; Raman spectra; toluene; vibrational line profile analysis

INTRODUCTION

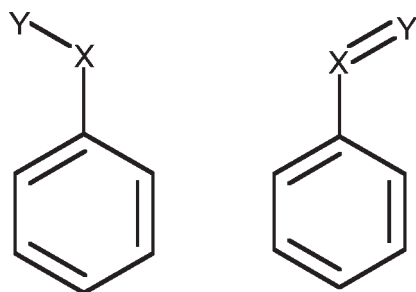
During more than one and a half century aromaticity serves as one of the most important concepts in organic chemistry. The most obvious consequence of this concept is the common confidence that in aromatic compounds, bond lengths do not alternate and are between typical to the single and double ones. However, in 1994, performing crystal structure investigations of substituted pyridines and their salts, Krygowski and co-workers¹ have discovered a very surprising effect that, to certain extent, turns us back to the Kekulé structures. It appears that some substituents can induce bond alternation in aromatic rings, provided the attached groups are angular, like the methoxy, hydroxy, or nitrozo group. The single bonded —X—Y groups cause a lengthening of the *trans* bond and a shortening of the *cis* bond, whereas the double bonded —X=Y groups act in the opposite way, elongating the *cis* bond and shortening the *trans* bond of the benzene ring; changes in bond lengths are of about 0.01 Å (Scheme 1). Supporting quantum chemistry computations

prove the existence of this angular group induced bond alteration (AGIBA) effect.

According to recent reviews,^{2,3} numerous examples demonstrating reality of the AGIBA effect have been accumulated since the time of its discovery. Until now, the only experimental approach to studying the AGIBA effect is the crystal structure (mainly X-ray) investigation of monocrystals. Though being a straightforward method of molecular structure analysis, such an approach does not allow one to operate with liquids that are more common in organic chemistry. Due to this fact, numerous prospective liquid candidates for showing up an AGIBA isomerism remain outside the scope of structural studies. For example, as follows from quantum chemistry estimates,⁴ methoxy substituted benzenes could be such candidates, since some of their conformations might be stabilized by AGIBA with the differences in total energy of *cis*- and *trans*-AGIBA isomers $\Delta E \approx 12$ kJ mol⁻¹. Moreover, effects of intermolecular interactions leading to supra-molecular organization in liquids, that are actively pursued in the past decade,^{5,6} may favor stabilization of AGIBA conformers in the liquid state.

In spite of the fact that simpler methods enabling one to monitor the molecular structure of a substance have not been employed in AGIBA studies yet, some of them, especially, vibrational spectroscopy could appear very

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Scheme 1

useful and might broaden the number of substances prospective for manifestations of the AGIBA phenomenon. However, possible relevance of vibrational spectroscopy to AGIBA studies has never been considered, whereas the following issues could favor such application. The mentioned differences in total energy of *cis*- and *trans*-AGIBA isomers should cause changes in the energy of vibrations of a limited number of bonds of the R—X—Y molecule studied (mainly R—X, X—Y and ring stretching and R—X—Y and ring bending vibrational modes, other modes remaining unchanged). Furthermore, one should not foresee any variations in translational and rotational energy of AGIBA isomers. This means that differences in total energy of *cis*- and *trans*-AGIBA isomers are purely vibrational in nature, being well 'localized', and one could expect spectroscopic manifestations of such differences as vibrational line splitting within the range of several wavenumbers. From this point of view, vibrational spectroscopy could be a suitable tool for recognizing AGIBA effects.

It is well known that vibrational spectra are successfully applicable to studies of effects of similar magnitude. As follows from our works, resolution of modern infrared and, especially, Raman methods enables one to easily recognize line splitting in liquids arising by the presence of isotopomers ($\sim 3 \text{ cm}^{-1}$),⁷ or caused by very weak intermolecular interactions (noncoincidence effects) (0.4 cm^{-1}).⁸

Therefore the aim of this paper is the search of possible spectroscopic manifestations of the AGIBA effect in the case of the liquid toluene. As a result, it is shown by means of Raman scattering that in this substance, two AGIBA isomers can exist.

EXPERIMENTAL

Toluene (Carlo Erba) was of >99.5% purity. The ring breathing ν_1 (A_1) vibration of this substance was studied at five temperatures from 282 to 350 K. Raman spectra were excited by means of an Ar^+ laser (INNOVA 400, Coherent Radiation Labs, Inc., 10 W all line power) and collected at polarized (VV) and depolarized (VH) scattering geometries on an U1000 Jobin–Yvon–ISA

double monochromator, as described in References 8 and 9.

In order to reach our goal, the following method of vibrational line profile analysis¹⁰ has been applied. According to the theory,^{11,12} VV and VH spectra consist of the so-called isotropic and anisotropic components:

$$I_{VV}(\nu) = I_{\text{iso}}(\nu) + \frac{4}{3}I_{\text{VH}}(\nu) \quad (1)$$

$$I_{\text{VH}}(\nu) = I_{\text{aniso}}(\nu) \quad (2)$$

In turn, isotropic and anisotropic components can be presented in the following form:

$$I_{\text{iso}}(\nu) = \int_0^{\infty} G_V(t) \exp(2\pi i c \nu t) dt \quad (3)$$

$$I_{\text{aniso}}(\nu) = \int_0^{\infty} G_V(t) G_{2R}(t) \exp(2\pi i c \nu t) dt \quad (4)$$

where c is the speed of light, t is the time, $G_V(t)$ is the time-correlation function of vibrational relaxation, $G_{2R}(t)$ is the time-correlation function of rotational relaxation, and the subscript 2 at $G_{2R}(t)$ means that rotation is described by the Legendre polynomial of the 2nd order. The method proposed in Reference 10 is based on employing a model time-correlation function written in the form:

$$G_i(t) = \exp\left\{-\frac{[t^2 + \tau_1^2]^{1/2} - \tau_1}{\tau_2}\right\} \quad (5)$$

that makes it possible to perform the Fourier transform of Eqns (3) and (4) analytically obtaining the vibrational line profile as:

$$I_i(\nu) = 2nc \exp\left(\frac{\tau_1}{\tau_2}\right) \left(\frac{\tau_1^2}{\tau_2}\right) \frac{K_1(x)}{x} \quad (6)$$

where τ_1 and τ_2 are certain characteristic times different for $I_{\text{iso}}(\nu)$ and $I_{\text{aniso}}(\nu)$, $x = \tau_1 [4\pi^2 c^2 (\nu - \nu_0)^2 + 1/\tau_2^2]^{1/2}$, ν_0 is the peak wavenumber, $n = 2$ if $\nu_0 = 0$ and $n = 1$ if $\nu_0 \neq 0$, and $K_1(x)$ is the modified Bessel function of the second kind.

This method has been successfully employed in numerous applications,^{13,14} especially in studies of overlap lines since, unlike other methods that are empirical in nature, its theoretical basis is obvious. Its only limitation lies in the fact that vibrational line profiles at issue are considered symmetric. However, as far as our knowledge goes, there are only two proven examples of asymmetric line profiles, ν of CO chemisorbed on the Pt surface¹⁵ and ν_2 of $\text{C}_5\text{O}_5^{2-}$ (croconate) ion,¹⁶ therefore such limitation seems quite soft.

The Raman spectrum of toluene in the region studied is quite complicated. Except of the line corresponding to the ring breathing ν_1 (A_1) vibrations it comprises several low

intensity lines corresponding to $2\nu_{16a}$ (A_1) and $4\nu_{16b}$ (A_1) vibrations. Its detailed analysis and assignment is presented in Reference 17. For the sake of clarity, here we confined ourselves with analysis of much stronger isotropic Raman spectra, since in the region of the ring breathing vibrations, these are more intensive than anisotropic ones by 80 times.¹⁷

RESULTS AND DISCUSSION

Analysis of our fits of the Raman spectra of the liquid toluene¹⁷ signifies that, in spite of the excellent convergence of the fitting procedure, the characteristic shape of the graph of residuals provides a symptom of possible presence of an extra vibrational line that almost coincides with the line corresponding to the ring breathing ν_1 (A_1) vibration (Fig. 1a). Therefore the starting point of this study has been a belief that in the liquid toluene, two AGIBA isomers can exist, each having its own ν_1 (A_1) line, and the AGIBA effect can contribute to stabilizing the *trans*-conformation. In the absence of the AGIBA effect, *cis*- and *trans*-AGIBA conformations are indistinguishable (Scheme 2a). π -electron structure drawn by means of the Kekulé structure causes dramatic changes in the symmetry of the benzene ring. In

particular, the vertical C_2 axis that lies in the ring plane disappears. This makes the *cis*- and *trans*-AGIBA conformations discernible (Scheme 2b).

In accord with our belief, it has been found in the course of computations that the quality of fits significantly increases (residuals between experimental data and fits decrease and become better statistically averaged showing no signature of an extra line) if two lines characterizing the ring breathing vibrations are introduced (Table 1, Fig. 1b, c). Thus isotropic Raman spectrum of the liquid toluene demonstrates that instead of being single, the line corresponding to the ring breathing vibration at 785 cm^{-1} is better represented by two components split by $1.0\text{--}1.4\text{ cm}^{-1}$. It is noticeable that no significant variations in line widths occur if an extra line is launched. The widths of both possible AGIBA components are closely compared to the width of the ν_1 (A_1) line obtained in Reference 17, being typical for polarized fundamentals, and the width of the nearest neighboring $4\nu_{16b}$ (A_1) line remains practically unchanged (Table 1).

On heating, the lines in question behave as follows. The integrated intensity of the high-wavenumber line decreases, while the integrated intensity of the low-wavenumber line increases suggesting that thermal equilibration between possible AGIBA isomers occurs.

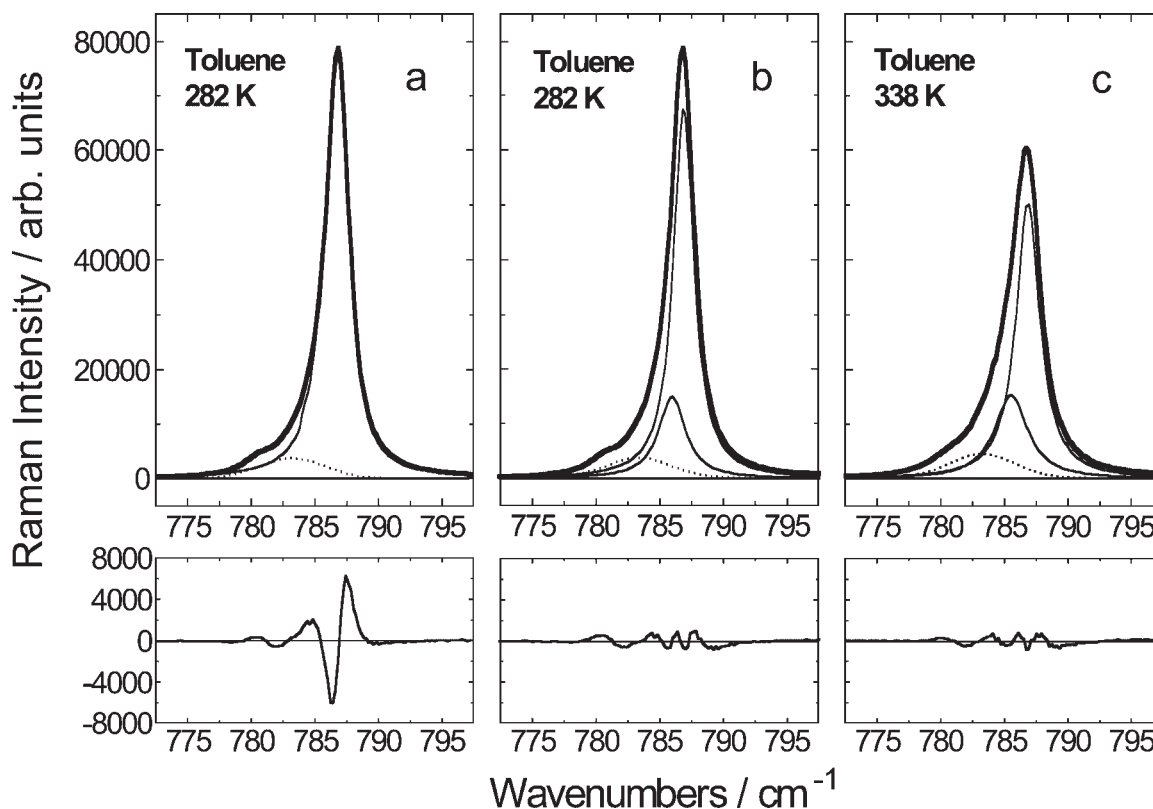
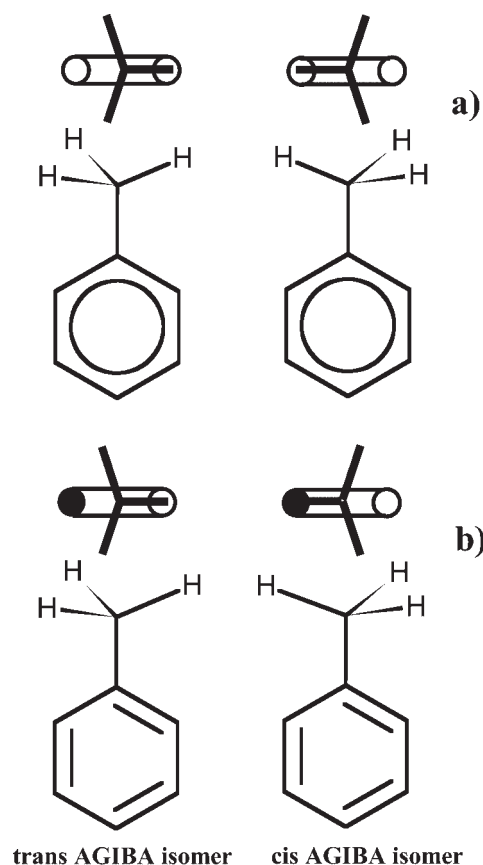


Figure 1. Isotropic Raman spectra of the liquid toluene in the region of the ν_1 (A_1) ring breathing vibration at 282 and 338 K and their fits without (a) and with accounting for the AGIBA effect (b, c). Upper panels demonstrate experimental data and their fits, lower panels – residuals. Thick solid lines represent experimental data, thin solid lines correspond to AGIBA isomers and dot line – to the $4\nu_{16b}$ (A_1) vibration



Scheme 2

Interestingly, the integrated intensity of the $4\nu_{16b}$ (A_1) line increases significantly, thus demonstrating the growth of the thermal population of the ν_{16b} energy level.

In order to understand the nature of split lines, the temperature dependences of Raman spectra may be of great help. Specifically, quantitative Raman intensity measurements at different temperatures enable one to determine the thermodynamics of the chemical equilibrium in a system studied.¹⁸ The integrated intensities of Raman lines I_i and I_j corresponding to species i and j involved in the conformation equilibrium described as:



are related to the concentration of these species c_i and c_j , $I_k \propto c_k$, and to the concentration equilibrium constant K_c ,

$$K_c = \frac{c_j}{c_i} = \frac{I_j}{I_i} \quad (8)$$

and the enthalpy of the reaction (7) can be determined from a Van't Hoff-like plot,

$$R \ln K_c = -\left(\frac{\Delta H^0}{T}\right) + \text{constant} \quad (9)$$

Denoting the high-wavenumber line as corresponding to the species i and the low-wavenumber line as corresponding to the species j we determine the difference of enthalpy of two conformation isomers in toluene as $-6.7 \pm 0.8 \text{ kJ mol}^{-1}$ (Fig. 2). This means that the species i is more stable than the species j and therefore the high-wavenumber line corresponds to the more stable component of the liquid system.

In the Raman spectrum of the liquid toluene, there are no other overtones, hot bands and combination bands around 785 cm^{-1} , except those described in Reference 17.

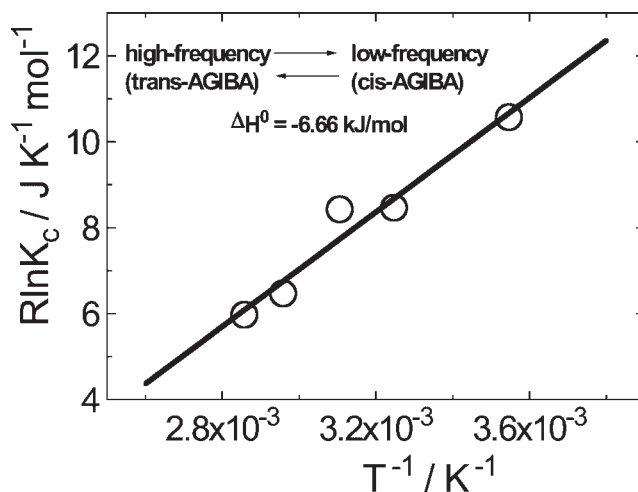


Figure 2. Van't Hoff-like plot for the AGIBA conformation equilibrium in the liquid toluene

Table 1. Computation results for isotropic Raman spectrum of the liquid toluene at 282 K

Parameters of fits	Without AGIBA components	With AGIBA components
$4\nu_{16b}$ (A_1), cm^{-1}	783.2 (6.2)	782.5 (6.0)
ν_1 (A_1), cm^{-1}	786.66 (2.1)	785.83 (2.5)
Best weighted sum of squares	4.4496×10^7	8.8442×10^6
Weighted root mean square error	362.83×10^2	113.71×10^2
Weighted deviation fraction	1.7769×10^{-2}	8.5821×10^{-3}
R^2	0.99912	0.99984

Line widths are given in parentheses.

This means that the results obtained could hardly signify imperfections in our computation procedure, and correctly reflect reality. In order to better understand the nature of the components of the split line and the species that might correspond to them, it is worthwhile to discuss existing data regarding conformational equilibria and dynamics in toluene and other methyl substituted benzenes.

In methylated benzenes, CH₃ groups may be rotated with respect to the benzene frame, having two stationary points corresponding to distinct symmetric configurations. The eclipsed configuration has one of the methyl C—H bonds in the plane of the benzene ring, which is a plane of symmetry. The staggered configuration has one of the methyl C—H bonds in a plane perpendicular to the benzene ring, and this plane is a plane of symmetry. In toluene, a symmetric sixfold potential barrier separates stable conformations. A qualitative picture illustrating this issue is presented in Fig. 3a.

According to a recent review,¹⁹ in the gaseous phase, the energy difference between eclipsed and staggered conformations of toluene determined by various techniques is of about 50–100 J mol⁻¹, so that the CH₃ groups rotate practically freely. Assignment of the lower state is, however, disputable. In the aromatic molecules, the methyl torsional barrier is assumed to originate from the difference in the π -bond order between two ring C—C bonds nearest to the methyl group.²⁰ In this case, the energy of the eclipsed conformation must be greater than that of the staggered one.²¹ On the other hand, supersonic molecular jet spectroscopy²² and quantum mechanics estimates²³ suggest that the staggered configuration has lower energy. Interestingly, splitting of R—X stretching vibrations in eclipsed and staggered conformations is predicted as 0.75 cm⁻¹.²³

It is a well established fact, that on liquefaction, rotational barriers tend to increase.²⁴ Recent NMR and neutron scattering studies entail a certain degree of molecular ordering in the liquid and glassy toluene. This puts constraints to the rotational motion of methyl groups that becomes far from being free and experiences potential barriers of about 3.5 kJ mol⁻¹.^{25–27}

So, one of possible explanations of the data obtained is as follows. We ascribe the lowest energy to the eclipsed conformation. In this case, both AGIBA conformers are considered eclipsed, and the energy of the *trans*-eclipsed AGIBA conformation is lower than the energy of the *cis*-eclipsed AGIBA conformation by $-\Delta H^0 = 6.7$ kJ mol⁻¹ (Fig. 3b). The line corresponding to the *trans*-AGIBA isomer stabilized by the AGIBA effect has higher frequency than the line corresponding to the *cis*-AGIBA isomer.

One may suggest other explanations of the results obtained. For example, the split lines may correspond to staggered and eclipsed conformations, both stabilized by interactions with adjacent molecules and separated by a 12-fold potential barrier. Considering the staggered

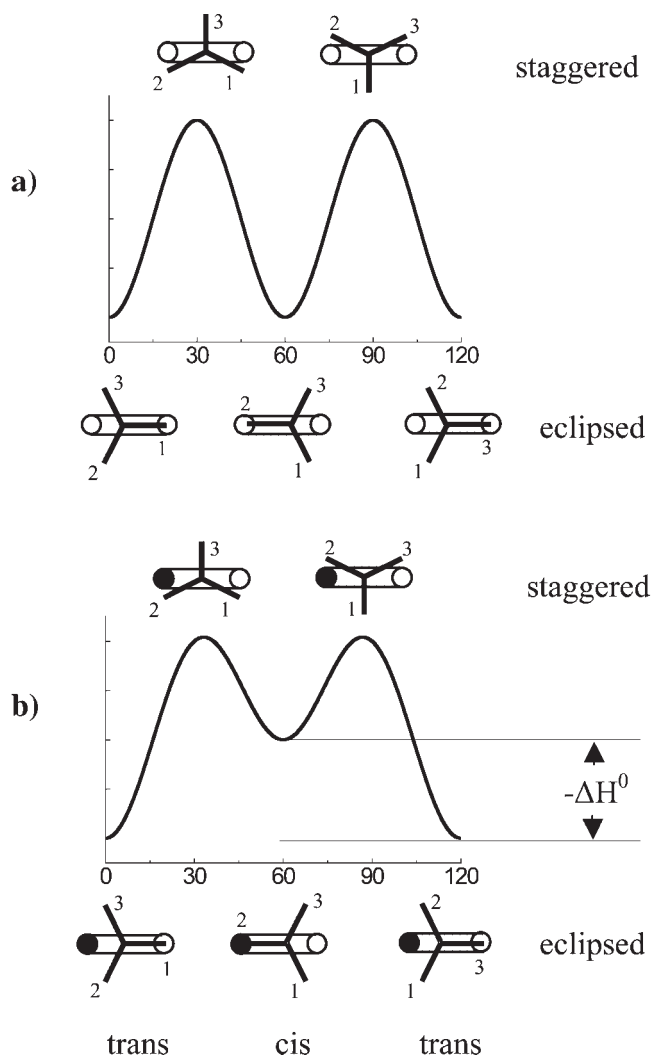


Figure 3. Schematic of a sixfold rotational barrier in a system without (a) and with (b) AGIBA stabilization

conformation as having the lowest energy, it is possible to interpret the data in terms of AGIBA-like stable structures derived from staggered conformations. However, these and other possible explanations seem less probable than that presented above. Further quantum chemistry studies would be of great value for clarifying this intriguing issue.

CONCLUSION

In this paper, we present the first possible spectroscopic evidence of the AGIBA effect in liquids. It is found that Raman spectroscopy may be a powerful tool for recognizing AGIBA effects. In the liquid toluene, instead of being single, the lines corresponding to the ring breathing vibrations are split by ~ 1.2 cm⁻¹. Temperature dependences of intensity reveal that the difference of enthalpy of two conformation isomers in the liquid is

6.7 kJ mol⁻¹. The low-wavenumber line corresponds to the *cis*-AGIBA isomer and the high-wavenumber line to the *trans*-AGIBA isomer stabilized by the AGIBA effect.

It should be noticed that data fits for the liquid toluene-d₈ appear to be unsuccessful. This is probably caused by the fact that the 4ν_{16b} and ν₁ lines in toluene-d₈ are located at 717.2 and 719.04 cm⁻¹ and overlap more closely than in toluene (783.2 and 786.66 cm⁻¹, respectively), therefore facilitating divergence of the fitting procedure. However, using our computational approach to Raman spectra of other methyl substituted benzenes, we have noticed similar splittings in the spectra of xylenes and mesitylene. Treatment of these data is in progress, and results will be published elsewhere.

Acknowledgements

Thanks are due to Prof. I.G. Philis of Ioannina University, Greece, for an illuminative discussion regarding spectroscopic manifestations of staggered and eclipsed conformations.

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