Communication: Molecular gears

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The ^{1}H nuclear magnetic resonance spectrum of hexamethylbenzene orientationally ordered in the nematic liquid crystal ZLI-1132 is analysed using covariance matrix adaptation evolution strategy. The spectrum contains over 350 000 lines with many overlapping transitions, from which four independent direct dipolar couplings are obtained. The rotations of the six methyl groups appear to be correlated due to mutual steric hindrance. Adjacent methyl groups show counter-rotating or geared motion. Hexamethylbenzene thus behaves as a molecular hexagonal gear. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4962221]

Hexamethylbenzene (hmb) is an interesting molecule not only because of its aesthetically pleasing appearance (Figure 1). The presence of six methyl groups, each of which undergoes some sort of rotational motion, raises questions about steric hindrance. Do the six methyl groups undergo their rotational motions completely independent of each other or are their rotations correlated in some way or another? In the case of correlated motion, two possible modes can be envisaged. First, all methyl groups rotate in the same direction, a process we call co-rotating or anti-gearing. Second, the methyls act as cogwheels with adjacent methyl groups rotating in opposite directions, a mode we call counter-rotating or gearing. In the latter case the six methyl groups together form a hexagonal gear, which is an interesting concept physically. Previous magnetic resonance studies investigated tunneling states in solid hmb[1,2] and claim that the six methyl groups are not independent but are coupled to one another rather strongly.[1] However, in these low-temperature solid-state studies, packing effects might be important. In the present paper we shall address this question for hmb as solute in the liquid phase.

First, let us consider toluene, a benzene ring with a single methyl group attached to it. This methyl group occupies a position of highest potential energy with one CH bond in the molecular plane, and one CH bond above and one below the plane.[3] However, the configuration with one CH bond above (in a plane perpendicular to the benzene ring) and two CH bonds below the plane lies only 14.0 ± 0.3 cal/mol lower.[3–5] Clearly, a methyl rotation over π leads to an identical situation energetically.

For hmb there is some debate about the configuration with lowest energy.[6] Since the possible low-energy configurations are close together energetically in any case, the choice of

starting point is not crucial. We assume a low-energy structure to be represented by Figure 1, and with adjacent methyl groups arranged so that methyl-methyl interactions are minimized. Again, rotating all methyl groups by π leads to an identical situation energetically. Since the dihedral angles that define the orientation of the methyl groups will turn out to be important, the zeros of α_1 to α_6 and their directions of increasing angle are specified in Figure 1.

The experimental technique that we employ to study hmb is ^{1}H Nuclear Magnetic Resonance (NMR) which is an invaluable tool for the study of solutes in orientationally ordered solvents such as nematic phases. Such spectra are usually dominated by a multitude of splittings arising from direct dipolar couplings between each pair of protons and may get extremely complicated for solutes containing many protons. Analysing such spectra has a long history. The spectra of solutes with 8 protons or less can usually be solved with conventional techniques.[7,8] Later attempts were made to develop automated procedures.[9] More recently, for solutes with more than 8 protons, the use of novel strategies such as genetic algorithms (GAs) and evolutionary strategies (ESs) has proved extremely effective. For a summary we refer to a recent review article.[10] One powerful feature of the evolutionary approach is that both transition frequencies and intensities are utilized in the fit. Hence, overlapping transitions are generally fitted without difficulty. Clearly, spectral overlap is an important property of ^{1}H NMR spectra arising from solutes that contain a large number of protons.

Evolutionary strategies have now been successfully applied to the spectra of solutes that occur in a single conformation. More challenging are applications to solutes such as the *n*-alkanes that undergo conformational change that is fast on the NMR time scale. Notable examples are *n*-butane (C_4H_{10})[11,12] with two conformations not related by symmetry whose spectrum contains approximately 2000 transitions with intensity >0.3% of the strongest one,

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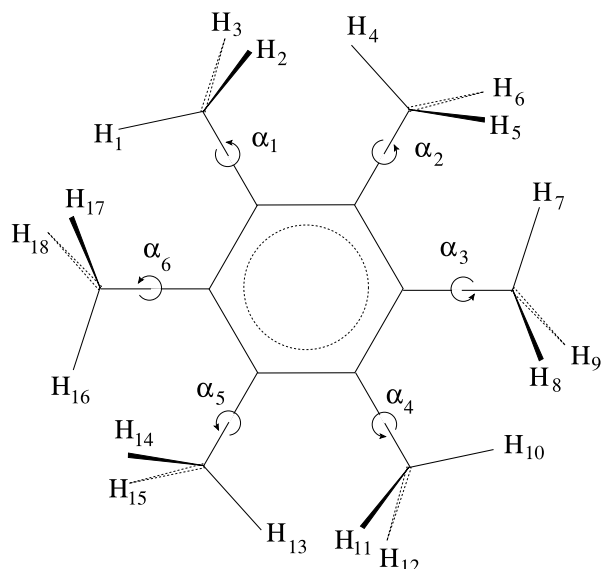c)leo.meerts@science.ru.nl. URL: http://www.leomeerts.nl.

FIG. 1. Hexamethylbenzene. The angles α_i define the methyl rotation and are shown as zero.

n-pentane (C_5H_{12})[13] with five conformations not related by symmetry and about 13 000 transitions, and n-hexane (C_6H_{14}) with ten conformations not related by symmetry and about 150 000 transitions.[14] So far the case of n-hexane with 14 proton spins represents a record in complexity in the study of solutes dissolved in nematic liquid-crystal solvents. A successful study of hmb, $C_{12}H_{18}$, would represent a novel step up in analysing highly complex many-spin ^{1}H NMR spectra.

If accurate direct dipolar couplings between all pairs of spins can be obtained experimentally, in principle much information becomes available about solute geometries in the liquid phase. Although complications such as solute vibrations[15–17] and vibration-reorientation coupling[18] limit the accuracy with which geometrical parameters can be derived,[19] the method is still attractive and has found wide spread use. Neglect of these effects is not expected to invalidate the conclusions of this paper. In that vein, in the present paper we turn our attention to hmb as a solute in the nematic liquid crystal Merck ZLI-1132 (1132 for short), a nematic phase composed of 24% trans-4-n-propyl-(4-cyanophenyl)-cyclohexane, 36% trans-4-n-pentyl-(4-cyanophenyl)-cyclohexane, 25% trans-4-n-heptyl-(4-cyanophenyl)-cyclohexane, and 15% trans-4-n-pentyl-(4-cyanobiphenyl-4)-cyclohexane.[20] Indirect couplings between protons are expected to be unimportant because they are across at least five chemical bonds. The ^{1}H spectrum can therefore be fully described with chemical shifts and direct dipolar couplings alone. Assuming planar geometry for hmb and independent rotation of all methyl groups across a sixfold barrier, thus neglecting interactions between them, the molecule hmb possesses a sixfold symmetry axis (see Figure 1). Hence, its partial orientational order is determined by a single independent Saupe orientation parameter S_{zz}. The entire spectrum scales effectively with this order parameter. Despite the fact that the solute contains as many as 18 protons and shows more than 350 000 transitions (with intensity >1%

that of the strongest one), this feature is expected to be very helpful in the analysis.

An important motivation for studying hmb is because of the possible steric hindrance between the six methyl groups attached to the benzene ring. One can consider various limiting cases. In the simplest case, every methyl group rotates around its axis independently of all the others. This would involve a sixfold barrier. Unfortunately, little experimental evidence is available about details of the barrier.

When the internal rotation of one methyl group interferes with the internal rotation of others, a situation might occur where two adjacent methyl groups rotate in a coordinated fashion. For instance, they could be rotating in identical or in opposite directions. If such a type of coordinated rotational motion would persist longer than the NMR time scale, one would expect that one proton in the methyl group would couple differently to the protons in the adjacent methyl group as do the other two.[21] If this were to be the case, ^{1}H NMR of hmb in a partially oriented phase would be an excellent way to find out. However, if such coordinated motion would be fast on the NMR time scale, only a single coupling between the protons of different methyl groups would be observed. Its magnitude might then contain information about coordinated motion. In this picture hmb possesses again an effective sixfold axis. The concept of coordinated methyl rotational motion has been explored earlier in the case of *ortho*-xylene,[21] but was inconclusive at the time. The last sentence of this paper was as follows: "Such a case probably does not exist with two methyl groups, and may be difficult to find for a molecule for which the NMR spectrum is analysable." As the present study of hmb dissolved in 1132 will show, reliable predictions in the realm of science are difficult to make.

Hmb was from Aldrich. A sample of approximately 10 mol per cent was made up in 1132 and a small quantity of 1,3,5-trichlorobenzene (tcb) was added as an orientational reference. The sample tube was placed into a Bruker 400 MHz Inverse spectrometer magnet at room temperature ($\approx$298 K). ^{1}H NMR spectra were accumulated by adding 1742 scans. A spectral width of about 14 kHz was measured and line widths of typically 6 Hz were obtained.

Spectral analysis was performed using an Evolutionary Algorithm (EA) as described in Refs. 10 and 22. The agreement between experimental and fitted spectrum is generally excellent, and the earlier hard labour of analysing experimental spectra has been reduced to virtually a routine activity. As part of our analysis procedure, a smoothing algorithm is applied in order to remove or strongly reduce the strong sloping background which arises from the liquid-crystal solvent. The liquid crystal 1132 in addition gives rise to two strong broad peaks. These peaks were artificially removed before starting the EA fitting procedure.

The NMR spectral analysis algorithm LEQUOR[23] is a key ingredient of our EA fitting approach. With 18 protons there are $2^{18} = 262\,144$ proton spin energy levels with the largest Hamiltonian matrix to be diagonalized $48\,620 \times 48\,620$. With the composite spin approach, with each methyl group treated as spin I = 3/2 or 1/2, the largest matrix (for all methyl groups of spin I = 3/2) reduces to 580×580, thus considerably alleviating the computational effort.

The direct dipolar couplings that are obtained experimentally from the studies of solutes in orientationally ordered nematic phases can be expressed as follows:

$$D_{i,j} = -\frac{h\gamma_i\gamma_j}{4\pi^2}\left\langle\frac{1}{r_{ij}^3}\right\rangle S_{ij}, \tag{1}$$

where the degree of orientation S_{ij} is the mean value of $\langle\frac{3}{2}\cos^2\theta_{ij} - \frac{1}{2}\rangle$, θ_{ij} is the angle between the magnetic field direction and the line connecting the two nuclei i and j which are separated by r_{ij}, and γ_i is the magnetogyric ratio of nucleus i. The $D_{i,j}$ can be sensitive probes of the rotational potential V of the methyl groups. In our current description, solute vibrational motions other than methyl rotations and vibration-reorientation interactions are neglected.

The potential which includes the rotational coupling between two adjacent methyl groups can be expressed as a Fourier series similar to that given in Ref. 24,

$$V = \frac{V_3}{2}(2 - \cos 3\alpha_1 - \cos 3\alpha_2) - V_{12}\cos 3\alpha_1\cos 3\alpha_2$$
$$- V_{12}'\sin 3\alpha_1\sin 3\alpha_2$$
$$+ \frac{V_6}{2}(2 - \cos 6\alpha_1 - \cos 6\alpha_2) + \cdots. \tag{2}$$

The angles α are defined in Figure 1. With the substitutions

$$\alpha_+ = \frac{1}{2}(\alpha_1 + \alpha_2),$$
$$\alpha_- = \frac{1}{2}(\alpha_1 - \alpha_2),$$
$$V_a = \frac{1}{2}(V_{12} - V_{12}'),$$
$$V_g = \frac{1}{2}(V_{12} + V_{12}'), \tag{3}$$

and realizing that $V_3 = 0$ in hmb because of symmetry, we obtain

$$V = -V_a\cos 6\alpha_+ - V_g\cos 6\alpha_-$$
$$+ V_6(1 - \cos 6\alpha_+\cos 6\alpha_-) + \cdots. \tag{4}$$

From a given potential $V(\alpha_+, \alpha_-)$ the direct dipolar couplings can now be calculated classically,

$$D_{i,j} = \frac{\int D_{i,j}(\alpha_+, \alpha_-)\exp\frac{-V(\alpha_+,\alpha_-)}{k_BT}d\alpha_+d\alpha_-}{\int \exp\frac{-V(\alpha_+,\alpha_-)}{k_BT}d\alpha_+d\alpha_-}. \tag{5}$$

In practice the integrations are replaced by summations over all α_+ and α_- in which the step size is taken small enough, typically 5 or 10°. The use of symmetry reduces the computational effort. The results of such a classical calculation are not expected to differ significantly from those of a full quantum-mechanical treatment.[21,25]

In order for counter-rotating or geared rotation to be dominant, the barrier V_a to co-rotating or anti-geared motion should be relatively high. In order for co-rotating or anti-gearing to be dominant, the barrier V_g to counter-rotating should be high. A careful glance at Figures 1, 2(c) and 2(d) indicates that, in the case of co-rotating methyl groups, the protons of adjacent methyls occasionally come into close presence during the rotational motion. When the counter-rotating motion is considered, it appears that during their correlated motion protons largely avoid each other's presence. This would suggest that steric hindrance would favour gearing or counter-rotating motion, leading to $V_a \gg V_g$. For the case that the methyl groups (during their rotations) do not show steric hindrance with each other, the V_6 term in the potential would dominate. As we shall see, the present study will allow us to distinguish among the various options.

The ^{1}H NMR spectrum measured for hmb in 1132 at 298 K is shown in Figure 3(a). In this spectrum the customary solvent background and two spurious features arising from the liquid-crystal solvent have not been removed. The solute spectrum is seen to be symmetrical, indicating that all 18 hmb protons have the same chemical shift. Hence, the chemical shift can be found by inspection. Spectral analysis based on evolutionary strategies indicates that the spectrum can be reproduced faithfully with only one chemical shift and
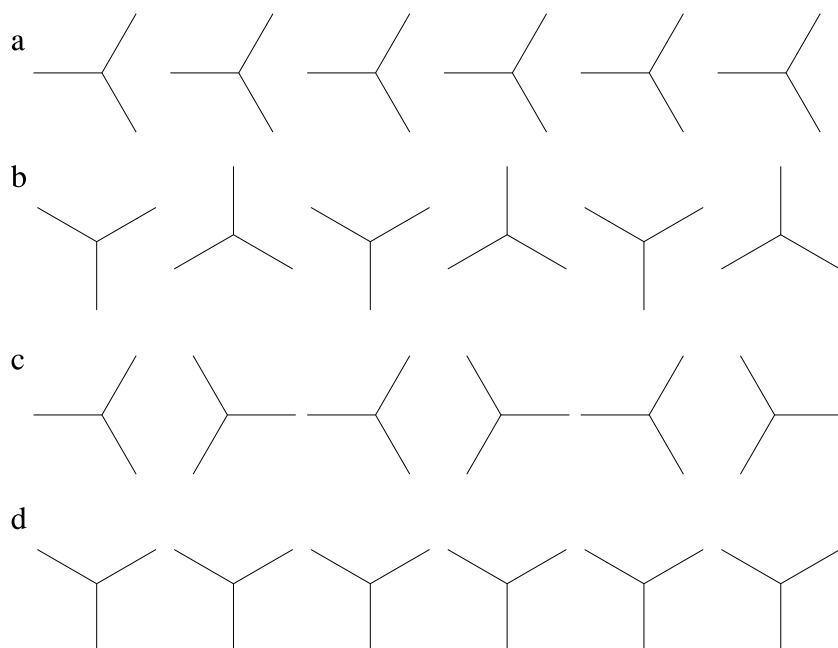

FIG. 2. Interesting configurations of hexamethylbenzene. (a) One of the low-energy configurations, having C_{6h} symmetry. (b) A second low-energy configuration, having D_{3d} symmetry. (c) One of the high-energy configurations obtained by rotating all methyls in (a) by 30°. (d) Another high-energy configuration, obtained by rotating all methyls in (b) by 30°.
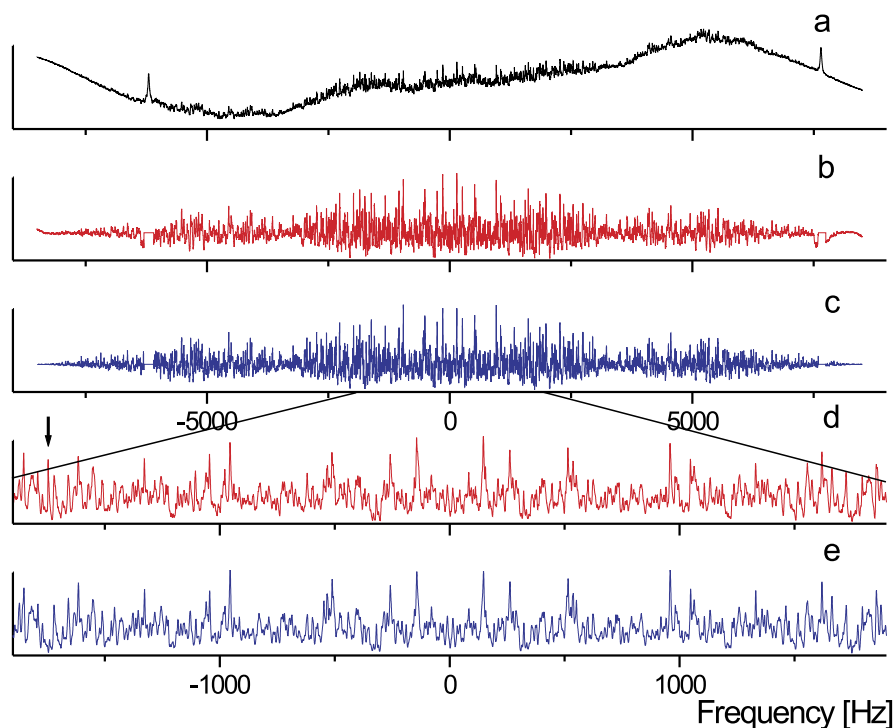
FIG. 3. Experimental and fitted NMR spectra of hmb in 1132 at 298 K. (a) Experimental spectrum (1742 scans). The line broadening applied before Fourier transform is 0.1 Hz. The experimental line full width at half height is of order 6 Hz. The program LEQUOR[23] was used to calculate the simulated NMR spectra. In order to deal with the broad underlying liquid-crystal NMR signal in the experimental spectrum and to improve the dynamics in the spectra, a background signal averaged over 274 Hz is subtracted from both the experimental and calculated spectra depicted in (b) through (e).[10] Here (b) and (d) are the full and zoomed in experimental spectra, while (c) and (e) are the corresponding calculated ones. The blowups (d) and (e) show the excellent fit obtained. The arrow in (d) points to the central line of the tcb triplet.

4 dipolar couplings: one intramethyl coupling and three intermethyl (*ortho, meta, para*) couplings. These couplings (as well as the dipolar coupling from tcb) are given in Table I. Only one attempt was required to obtain this fit, essentially showing that with the use of EA, very complex spectra can be solved routinely. The baseline-smoothed experimental and calculated spectra are shown in Figures 3(b) and 3(c), with expansions in (d) and (e).

Since hmb possesses a sixfold symmetry axis, its partial degree of orientational order is determined by one independent Saupe order parameter S_{zz}. As indirect couplings are too small to influence the spectrum, the entire spectrum scales with this one quantity S_{zz}. Because the dipolar couplings involve a product of S_{zz} and geometrical parameters of hmb, in order to obtain S_{zz} we must make assumptions about the solute geometry.

We assume that the 12 hmb carbons are coplanar with D_{6h} symmetry, and that the methyl groups have local C_{3v} symmetry with constant structure independent of angles α_i. The proton geometry is then completely determined by two parameters, being the distance d of the centre of a methyl HHH plane from the molecular centre and the radius r of the methyl circle joining the 3 H's of a methyl group. For any particular rigid configuration, the angles α that describe the rotation of the methyl groups are also needed. As is obvious from Eq. (1), the dipolar couplings are products of geometric and order parameters, and at least one parameter must be defined. As there is no way to predict the order parameter accurately, we must define one geometric parameter (either d or r) in order to provide a scale for the molecular structure. Here we take values $d = 3.3092$ Å and $r = 1.0383$ Å from data for *p*-xylene[26] and adjust r and S_{zz} only in the fitting.

As can be seen from Eq. (5) the direct dipolar couplings depend in principle on details of the potential. However, trial calculations show that the intramethyl ($D_{1,2}$) and intermethyl *meta* ($D_{1,7}$) and *para* ($D_{1,10}$) couplings are essentially independent of details of the potential. When with the above hmb geometry we do a least squares analysis to obtain S_{zz} and r from these three dipolar couplings, we obtain an excellent fit with an RMS difference of about 0.1 Hz (Table I footnote b). The remaining dipolar methyl *ortho* coupling ($D_{1,4}$) is not fitted since it depends strongly on the methyl rotation potential. Hence, only this coupling can be used to extract information about this potential.

First, several trial calculations assuming a classical barrier were performed to test the sensitivity of $D_{1,4}$ to the potential energy parameters V_6, V_g, and V_a. On varying these parameters

TABLE I. Dipolar couplings and fit parameters for hmb in 1132 at 298 K. Only numbers with errors are fit parameters; errors in last digit are in parentheses.

Experimental D_{ij} in Hz				
$D_{1,2}$	$D_{1,4}$	$D_{1,7}$	$D_{1,10}$	D_{tcb}
1629.4(4)	−456.6(2)	−89.4(3)	−57.1(4)	−212.9(4)

Effect of potential parameters				
Calcn.	V_a / cal/mol	V_g / cal/mol	V_6 / cal/mol	$\Delta D_{1,4}$[a] Hz
r & S_{zz}[b]	0	0	0	−70.4
V_6	0	0	100	−70.8
V_a	100	0	0	−60.4
V_g	0	100	0	−70.4
All V_i	100	100	100	−60.1
Vary V_a	850(10)	0	0	0

[a] $D_{1,4}$(calculated) − $D_{1,4}$(experimental).
[b] The fit to $D_{1,2}$, $D_{1,7}$ and $D_{1,10}$ gives $S_{zz} = -0.3180 \pm 0.0001$ and $r = 1.0407 \pm 0.0001$/Å (the value of r from *para*-xylene is 1.0383 Å[26]). RMS difference is 0.1 Hz.

between zero and 3000 cal/mol, these trials show a slight dependence of $D_{1,4}$ on V_6, hardly any dependence on V_g, and a strong dependence on V_a. The other dipolar couplings were affected by less than their experimental error in the calculations reported in Table I.

How to proceed? Clearly a non-zero V_a is needed to bring the calculated $D_{1,4}$ dipolar coupling into correspondence with experiment for reasonable potential parameters. In view of the trial calculations, it is reasonable to take $V_g = 0$.

If in addition we neglect the slight dependence on V_6 by also assuming $V_6 = 0$ (not unreasonable in view of the low value of V_6 derived from the microwave work on toluene), a value for V_a can be estimated. Note that in this picture, the actual height of the barrier for anti-gearing amounts to $2V_a$. Following this approach, $V_a = 850$ cal/mol is obtained. This completely rules out the uncorrelated motion of adjacent methyl groups.

So far we have discussed the problem in terms of two interacting adjacent methyl groups. In order to compare our results with those of *ab initio* calculations, we should consider configurations with all six methyl groups. In Figure 2 we show a few possible low-energy ((a) and (b)) and high-energy ((c) and (d)) configurations. The energy differences between these configurations are obtained by considering all six adjacent pairs of methyl groups. The difference in energy between (a) and (c) (and between (b) and (d)) is $12V_a$, i.e., the barrier to all six methyl groups to undergo simultaneous anti-gearing rotation. The energy difference between (a) and (b) (and between (c) and (d)) is $12V_g$, i.e., the barrier to simultaneous geared rotation of all six methyl groups.

From *ab initio* calculations that assume a planar benzene structure and undistorted methyl groups with C_{3v} symmetry, an energy difference between configurations 2(a) and 2(b) of 0.4 kcal/mol is estimated.[6] This would lead to a small value of $V_g = 33$ cal/mol. Another *ab initio* calculation[27] focuses on gear slipping of one methyl group with respect to its two adjacent methyl neighbours, and a barrier of $4V_a = 2.8$ kcal/mol is obtained. This compares reasonably well with our value of $4V_a = 3.4$ kcal/mol. It is pleasing to note that this estimate is in the realm of what was calculated from theory.[6,27] This lends credence to our assertion that the methyl rotation in hmb is significantly hindered and shows a geared motion with adjacent methyl groups moving in counter-rotating fashion. Our experimental results shed new light on an old problem.

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