Calculated Versus "Experimental" Force Fields: The Influence in the Structure Determination of Benzene by NMR Spectroscopy in Liquid Crystal Solvents

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Calculated *Versus* "Experimental" Force Fields: The Influence in the Structure Determination of Benzene by NMR Spectroscopy in Liquid Crystal Solvents

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Very accurate bond distances can be derived from dipolar couplings, D_{ij}, obtained by analysis of the NMR spectra of samples dissolved in anisotropic solvents (LXNMR). To do this, however, the couplings must be corrected for the averaging produced by vibrational motion. The vibrational corrections require a knowledge of the force field, which may be obtained by fitting experimental vibrational frequencies or, much more easily, from quantum-mechanical computations. In the present study, the reliability of the methods used to calculate the force field and the effects on the accuracy of the vibrational corrections to the D_{ij} is tested on benzene for which a very accurate structural study is available.

Keywords: [13]C satellite spectra; liquid crystals; NMR; vibrational corrections

1. INTRODUCTION

The NMR spectroscopy of molecules dissolved in liquid crystalline solvents (LXNMR) may lead to very accurate determinations of bond lengths and angles in "rigid" molecules, i.e., molecules displaying only small amplitude vibrational motions. An accuracy of 10^{-2} Å for distances is possible [1] but, under ideal conditions i.e., "in an inert solvent with small linewidth and high S/N ratio, distance ratios with a precision corresponding to 10^{-4} Å in a bond length" [2] can be

achieved. In order to have larger data set and, more important, information on molecule skeleton, the dipolar couplings between protons and "dilute spin" nuclei, in particular ^{13}C, should be determined and, in principle, this can be obtained by recording and analyzing the spectra of isotopical enriched samples or satellites spectra.

As dipolar couplings are averaged over molecule internal motions, neglecting vibrational corrections will introduce significant errors in the structure determination; it is well known that $^{1}D_{HC}$ and $^{2}D_{HH}$ couplings can be affected by up to 10% of their values and that the contribution of vibrational corrections is not easily predictable [1].

According to the procedure proposed by Diehl *et al.* [3], the molecular force field is all that is needed to take in account the contribution of vibrational corrections. Vibrational frequencies and normal cartesian displacements, which explicitly appear in the equations, are then easily obtained from the eigenvalues and eigenvectors of the force field matrix. The requirement to have an experimentally-derived force field has restricted the calculation of the effects of vibrational motion on dipolar couplings, and it has been suggested that an alternative is to calculate the force field by *semi empirical* molecular orbital [4,5] or density functional [6,7] methods. The quality of the calculated vibrational frequencies is strongly correlated with the level of approximation used (*ab-initio* rather than *semi-empirical* and again *Hartree-Fock* or *DFT* etc.) and with the extension of the *basis-set*. There are many works [8–10] dealing with this problem and some scaling factors, empirically determined *a posteriori* in order to obtain better fits of experimental *versus* calculated frequencies, were successfully proposed. On the other hand the scaling of force field is an independent, more complicated problem to solve. Attempts in this direction can be found in literature [11,12] but the reliability of such scaling factors is hard to assess given the larger number of force constants involved and lack of unambiguous values.

The main aim of this work is the investigation of the influence of the level of approximation chosen for calculation of the force field on the accuracy of the structural determination, i.e. which is the best computational method to perform a calculation of vibrational contributions to dipolar couplings? With this purpose we selected benzene, which has been object of very accurate investigations [2,13–15], as a test case. In fact, due to the high symmetry, D_{6h} point group, only two independent parameters, r_{HC} and S_{yy} (see Fig. 1), are needed to fit the 3 D_{HH} plus 4 D_{HC} dipolar couplings available from spectral analysis. In this way, no independent geometrical assumptions are needed (other than the required fixed distance to avoid the "scaling" effect with the order parameters). Moreover, since the number of data is
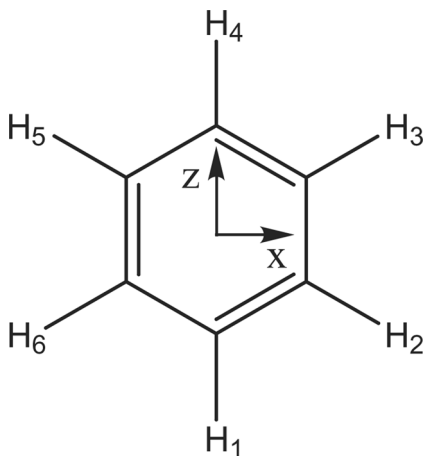
FIGURE 1 Structure, atomic labelling and axes for benzene.

safely larger than unknowns, a physically meaningful minimum is expected in the optimization routine and, what is more, a high quality force field derived from the experimental IR frequencies is available [16,17].

It is also quite interesting to compare how two different experimental approaches to obtain the D_{HC} couplings, isotopical enriched molecules *versus* satellite proton spectra, will influence the accuracy of the geometrical parameters determined. In fact following the latter approach only a limited number of transitions attributed to a given spin system can be safely assigned and, as a consequence, dipolar couplings with lower precision are obtained. On the other hand, since all the D_{HC} couplings can be obtained at once, and at lower cost, this approach is very appealing when there are different chemical sites in the molecule [18,19].

2. THEORY

Dipolar couplings are related to the positions of atoms and order parameters $S_{\alpha\beta}$ by:

$$D_{ij} = -K_{ij} \sum_{\alpha\beta} S_{\alpha\beta} \Phi_{\alpha\beta}^{ij} \tag{1}$$

where

$$\alpha, \beta = x, y, z \tag{2}$$

$$\Phi_{\alpha\beta}^{ij} = \left\langle \frac{r_\alpha^{ij} \cdot r_\beta^{ij}}{r_{ij}^5} \right\rangle_v \tag{3}$$

K_{ij} is related to γ, the magnetogyric ratio and the average is on vibrational motions. A complete decoupling of the molecule internal motions with respect to the overall re-orientational ones has been assumed. Taking into account such coupling [13,14], "solvent induced distortion" effects, observed for benzene too [2], can be eliminated; alternatively proper, "inert" solvents, such as ZLI1132 or ZLI1167, should be chosen. Writing

$$r_{ij} = r_{ij}^e + r_{ij}' \tag{4}$$

with r_{ij}^e the equilibrium distance between nuclei i and j and r_{ij}' the instantaneous excursion of r_{ij} from r_{ij}^e, the tensor Φ can be expanded as

$$\Phi = \Phi^e + \Phi^a + \Phi^h + \cdots \tag{5}$$

where e, a, h stand for equilibrium, anharmonic and harmonic contribution respectively. The anharmonic term Φ^a is usually disregarded while the equilibrium and harmonics contributes are defined according to:

$$\Phi_{\alpha\beta}^e = \frac{c_{r\alpha}c_{r\beta}}{r^3} \tag{6}$$

$$\Phi_{\alpha\beta}^h = \frac{\{C_{\alpha\beta} - 5\sum_\gamma c_{r\gamma}(C_{\alpha\gamma}\,c_{r\beta} + C_{\beta\gamma}\,c_{r\alpha}) + \frac{5}{2}c_{r\alpha}c_{r\beta}\sum_{\gamma\delta} C_{\gamma\delta}(7c_{r\gamma}\,c_{r\delta} - \delta_{\gamma\delta})\}}{r^5} \tag{7}$$

where $c_{r\alpha}$ is the cosine of the angle between r and the α axis; the covariance matrix element, $C_{\alpha\beta}$ is defined as

$$C_{\alpha\beta} = \langle \Delta_\alpha \Delta_\beta \rangle_v \tag{8}$$

Note that the indices i and j have been dropped to simplify notation; they will be reintroduced when explicitly needed.

With this formalism the dipolar coupling can be expressed as

$$D = D^e + d^h + \cdots \tag{9}$$

where clearly:

$$D^l = -K \sum_{\alpha\beta} S_{\alpha\beta}\,\Phi_{\alpha\beta}^l \tag{10}$$

Within this formalism, having neglected the anharmonicity and any other high order contribute, the corrected dipolar couplings are

defined as $D^\alpha = D - d^h \cong D^e$ and the corresponding structure as the r^α structure [1].

With some easy mathematical refinement, the operative equation for the covariance matrix elements needed to calculate the d^h is

$$C_{\alpha\beta}^{ij} = \sum_{v=1}^{3N} (\mathrm{w}_{i\alpha}^v - \mathrm{w}_{j\alpha}^v)(\mathrm{w}_{i\beta}^v - \mathrm{w}_{j\beta}^v) \frac{A}{\omega_v} coth\left(\frac{B\omega_v}{\mathrm{T}}\right) \qquad (11)$$

being T the temperature, $A = h/8\pi^2 \mathrm{c}$ and $B = \mathrm{c}h/2k_\mathrm{B}$ with c, the velocity of the light and k_B the Boltzmann constant. The vibrational frequency, ω_v, and the corresponding normal mode, $\mathrm{w}_{i\alpha}^v$ are obtained as eigenvalue and eigenvector of the Force Field matrix.

3. EXPERIMENTAL

Dipolar couplings from the ^{13}C enriched benzene sample dissolved in ZLI1167 (**I**) are taken from Diehl et al. [2]. Three additional sets of D_{ij} were obtained by spectral analysis of benzene dissolved in ZLI1167 (**IIa**), ZLI1132 (**IIb**) and I35 (**IIc**) (each sample about $\simeq 10\,\mathrm{wt\%}$ in benzene). The nematic phases have been purchased from Merck (Darmstadt); benzene (from Aldrich) was distilled immediately before use. The samples were not degassed. The spectra were recorded at room temperature on an AC300 Bruker spectrometer at 7.04 T. A total of 4000 scans were used to obtain a very good S/N ratio which allows to identify and assign all those lines of the satellite spectra falling in the outer regions externally to the ^{1}H lines whose calculated, un-normalized intensity is about 1 (corresponding approximately to 0.4% of the more intense ^{1}H line). Note that ZLI1167 has a negative diamagnetic anisotropy; for this reason spinning improved linewidth in (**I**) but not in (**IIa**); for this reason (**IIa**) was recorded without spinning. The spectra were recorded without lock.

The spectra have been analyzed using a graphic interactive procedure (dubbed ARCANA) developed during the past years in this laboratory [20] and recently modified to handle satellite spectra. The D_{HH} couplings were obtained from the analysis of the ^{1}H spectra and kept fixed in the analysis of the ^{13}C satellite spectrum. The final D_{ij} are reported in Table 1 together with the RMS, the number of assigned lines and the digital resolution (Hz/point). The J_{HH} and J_{HC} were taken from [2] and kept fixed. Note that in the analysis of the satellite spectra, no transition with calculated un-normalized intensity higher than 1 was left unaccounted for (assigned or buried under a ^{1}H transition).

TABLE 1 Experimental Dipolar Couplings: **I** [13]C Benzene Dissolved in ZLI1167 from Reference [2]; Benzene **IIa** from the ZLI1167 Sample, **IIb** from the ZLI1132 Sample, **IIc** from the I35 Sample. Indirect Couplings for Spectral Analysis of Samples **II** are Taken from Reference [2]. RMS and Number of Assigned Lines Used in the Analysis of the ^{1}H and its [13]C Satellite Spectra, are Reported. The Hz/Point of Each Spectrum is also Given

	I		**IIa**		**IIb**		**IIc**	
	Hz^{-1}							
$^3D_{HH}$	355.467	± 0.007	348.72	± 0.02	-687.09	± 0.01	-641.81	± 0.02
$^4D_{HH}$	68.927	± 0.009	67.62	± 0.03	-133.23	± 0.02	-123.53	± 0.04
$^5D_{HH}$	44.94	± 0.01	43.99	± 0.03	-86.79	± 0.02	-80.28	± 0.04
$^1D_{HC}$	1011.71	± 0.02	991.8	± 0.1	-1956.2	± 0.1	-1798.1	± 0.1
$^2D_{HC}$	135.99	± 0.01	133.4	± 0.1	-261.9	± 0.1	-243.7	± 0.1
$^3D_{HC}$	34.96	± 0.01	33.9	± 0.1	-67.6	± 0.1	-62.5	± 0.1
$^4D_{HC}$	23.63	± 0.02	23.2	± 0.1	-46.3	± 0.1	-42.7	± 0.1
Ass. lines/76[†]	–		66		66		64	
RMS(^{1}H)/Hz	–		0.37		0.23		0.47	
Ass. lines/400[‡]	–		78		96		79	
RMS(^{13}C)/Hz	–		0.56		0.48		0.54	
Hz/point	–		0.33		0.44		0.78	

[†]Theoretical number of lines for benzene.

[‡]Approximated number of calculated lines.

For **II**a and **II**b 64k fids were recorded, for **IIc** only 32k were used; its higher D_{HH} standard deviations are then a consequence of the higher Hz/point. On the other hand the quality of **IIb** and **I** data is similar.

All the force fields calculated are produced with the Gaussian 03 [21] package run on a PC equipped with a 1.2 GHz AMD Athlon processor and 1 GB of RAM working in the Windows ME (by Microsoft) environment; 30 s, 2 h:20 m, 35 m and 3 h:20 m are needed to optimize geometry and to calculate the force field using *PM3, B3LYP/6-31G*, HF/6-31G** and *MP2/6-31G** respectively.

A graphical friendly program performing structural and conformational analysis by NMR dipolar data developed in our laboratory, AnCon, is used to produce (i) the covariance-matrix elements, $C_{\alpha\beta}^{ij}$, from the proper ".fch" file type produced by Gaussian 03 and (ii) to fit the experimental D_{ij} by varying geometrical and/or orientational parameters. Such calculations, performed on a Compaq Workstation Evo W6000 equipped with two 2.4 GHz Intel Xeon and 2 GB of RAM working under Linux v. 8.1 Professional (by SuSe S.r.l.), needed just a few seconds.

4 RESULTS AND DISCUSSION

Force fields, and the related vibrational frequencies and normal modes, were calculated at four different levels of approximation: namely *PM3, B3LYP/6-31G*, HF/6-31G** and *MP2/6-31G**. Since 3-rd, or higher, row nuclei are absent in the test molecule, significant improvement is not expected from the use of more extended *basis-sets*. Having assumed $r_{CC} = 1.39700$ Å as in [2], in Table 2 the d^h corrections, calculated keeping S_{yy} fixed at the value obtained from the data of the above reference and varying the r_{HC} distance, are reported. Calculated vibrational frequencies were used in the calculations. By comparing columns B–E with A, the best results are those when the *B3LYP/6-31G** force field is used (-80.42 Hz *versus* the "experimentally determined" -82.37 Hz for $^1D_{HC}$). Given such agreement on the d^h it is not surprising that a difference of only $0.6 \cdot 10^{-3}$ Å is found for r_{HC}, which is likely due to the use of different optimization algorithms and/or computer precision. It is important to note the relatively bad performances of *PM3* (column B) with $\cong 55\%$ of relative error on $^3D_{HH}$ and $\cong 10\%$ on $^1D_{HC}$. On the other hand a difference of only $0.3 \cdot 10^{-2}$ Å on r_{HC} is found; from this point of view, at least for this very simple case, the geometric results seem to be not seriously influenced by poorly reproduced harmonic corrections. The *HF* (D) and the *Møeller Plesset* second order perturbation (E) d^h values are respectively lower and higher with respect to (A) but this can be

TABLE 2 Experimental Dipolar Couplings for ^{13}C-Benzene Dissolved in ZLI1167 (I); Harmonic Vibrational Contributions, d^h, r_{HC} and RMS obtained using Experimental Force Field (A), PM3 (B), B3LYP/6-31G* (C), HF/6-31G* (D), MP2/6-31G* (E). The Order Parameters $S_{yy} = 0.09133$ Calculated from Data of Reference [2] is Used. Normal Modes and Vibrational Frequencies are Calculated According the Reported Computational Methods

		A	B	C	D	E
	I			d^h/Hz		
$^1D_{HC}$	1011.467	-82.37	-90.60	-80.42	-68.98	-86.57
$^2D_{HC}$	135.993	-2.60	-3.07	-2.45	-2.11	-2.58
$^3D_{HC}$	34.962	-0.24	-0.29	-0.23	-0.20	-0.25
$^4D_{HC}$	23.630	-0.09	-0.11	-0.09	-0.08	-0.09
$^3D_{HH}$	355.467	-5.00	-7.72	-4.67	-3.86	-5.17
$^4D_{HH}$	68.927	-0.50	-0.63	-0.49	-0.42	-0.52
$^5D_{HH}$	44.940	-0.20	-0.23	-0.20	-0.17	-0.21
r_{HC}/Å		1.08026	1.07747	1.08089	1.08464	1.07889
RMS/Hz		0.13	0.45	0.15	0.25	0.30

attributed to the quality of the vibrational frequencies produced by the two approaches. In fact, it is well known that, whereas both overestimate high frequencies, lower frequencies are overestimated by *HF* but underestimated by *MP2*. Such behavior has been recognized and corrected [9] by introducing scaling factors (0.9061 for *HF/6-31G** for low and 0.8953 for high frequencies *versus* 1.0214 and 0.9434 for *MP2* respectively). Since, according to Equation 11, $C_{\alpha\beta}$ depend strongly on lower frequencies, the behaviour of the d^h fits is as expected since *DFT* methods are claimed [10] to produce the best sets of vibrational frequencies.

On the other hand, when IR frequencies are available, a mixed set of experimental frequencies and computational cartesian displacements can be used. To explore this point and to find a *modus operandi* we repeated the calculations by combining normal modes of vibration, calculated by Gaussian 03 at the same four levels as above, with experimental vibrational frequencies. The results are reported in Table 3. Clearly, by using experimental frequencies, the d^h sets improve: all the *ab-initio* methods explored, at least at the 6-31G* *basis-set*, seem to lead to very good results (3.7% on d^h and 0.2% on r_{HC} with *MP2* the worst case); again the best values have been obtained at the *B3LYP/6-31G** level. A technical consideration must be pointed out: it is well known that the *HF* and much more the *MP2* method are very expensive in time (due to its high symmetry and simplicity, benzene represents a noticeable exception) and, in particular *MP2*, in memory allocation (even for little more complicated molecules, *MP2* calculations will require hardware requisites not available in standard PC configurations). On the contrary, the *DFT*

TABLE 3 As in Table 2 But Using the Experimental Vibrational Frequencies from [16]

	I	A	B	C	D	E
				d^h/Hz		
$^1D_{HC}$	1011.467	− 82.37	− 89.28	− 82.43	− 80.71	− 79.62
$^2D_{HC}$	135.927	− 2.60	− 2.79	− 2.51	− 2.51	− 2.33
$^3D_{HC}$	34.962	− 0.24	− 0.26	− 0.24	− 0.24	− 0.23
$^4D_{HC}$	23.630	− 0.09	− 0.11	− 0.09	− 0.09	− 0.08
$^3D_{HH}$	355.467	− 5.00	− 6.66	− 4.59	− 4.90	− 4.01
$^4D_{HH}$	68.927	− 0.50	− 0.56	− 0.50	− 0.49	− 0.47
$^5D_{HH}$	44.940	− 0.20	− 0.24	− 0.20	− 0.20	− 0.19
r_{HC}/Å	–	1.08026	1.07795	1.08025	1.08078	1.08118
RMS/Hz	–	0.13	0.14	0.29	0.09	0.35

approach is very light in terms of hardware and also relatively fast. This point is not important for systems as simple as benzene but becomes very important for more complex molecules. Taking into account that *DFT* methods give by far the best results when IR experimental frequencies are not available, in our opinion this is the approach of choice when "experimental" force fields are not available. Note also the importance of proper vibrational corrections on $^3D_{HH}$. Due to a unlucky combination of a relatively short distance and the interprotonic direction near the *magic angle*, the relative error on d^h (Table 2 and Table 3) and the deviations from the regular hexagonal structure involving the ortho couplings (Table 4) are the largest in all the samples.

Looking at the standard deviations reported in Table 1, it appears clearly that the D_{HC} obtained from the analysis of the satellites spectra (samples **II**) are determined with an accuracy about one order of magnitude lower than the relative D_{HH} (see also the data reported in reference [15]), whereas the standard deviations for (**I**) fall in a very narrow range. Note also that the D_{HH} standard deviations of samples (**II**) are of the same order as the respective values of sample (**I**), their slightly higher values reflecting a lesser care in the sample preparation (see Experimental section) and/or a higher Hz/point value. The effect of the higher standard deviations has been tested by varying the D_{ij} randomly within their standard deviations and observing the values of the difference, Δr_{HC}, between the greater, r_{HC}^{max}, and the smaller, r_{HC}^{min} calculated with different D_{ij} sets. In Table 5 the values of Δr_{HC} obtained after 100 runs are reported. The Δ values of samples **II** are about one order of magnitude greater than of sample **I** but still within the accuracy obtainable by LXNMR; only with standard deviations as high as 1.0 Hz on the D_{HC}, Δ values greater than 10^{-3} are obtained. When possible, i.e. if the satellites spectra due to chemically

TABLE 4 Deviation of Proton Distance Ratios from Hexagon for Samples **II** Using $d^{h\ddagger}$

	IIa		IIb		IIc	
	*	**	*	**	*	**
$\Delta(m/o)^\dagger$	−2.74	−6.52	−2.48	−6.26	20.98	17.23
$\Delta(p/o)^\dagger$	1.10	−2.90	−3.37	−7.36	29.03	25.06
$\Delta(p/m)^\dagger$	3.80	3.63	−0.89	−1.11	8.03	7.80

$^\dagger\Delta(a/b) = \{[(r_a/r_b)_{measured} - (r_a/r_b)_{hexagon}]/(r_a/r_b)_{hexagon}\} * 10^4$ as in [2].

‡From: *, "Experimental"; **, B3LYP Force Field

TABLE 5 Mean Value of r_{HC} and $\Delta r_{HC} = r_{HC}^{max} - r_{HC}^{min}$ from 100 Runs Varying D_{ij} Within Their Standard Deviations (see Table 1) and Optimizing on S_{yy} and r_{HC}

	I	IIa	IIb	IIc
	Experimental FF			
$\bar{r}_{HC}$	1.07973	1.08013	1.07922	1.08979
Δr_{HC}	$6.4 \cdot 10^{-5}$	$4.1 \cdot 10^{-4}$	$1.85 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$
B3LYP/6-31G* calculated FF				
$\bar{r}_{HC}$	1.07972	1.07937	1.07846	1.08903
Δr_{HC}	$6.4 \cdot 10^{-5}$	$4.1 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$

different ^{13}C can be recognized and analyzed, this approach is much more convenient than using ^{13}C enriched samples.

As shown in Table 4 the deviations from the regular hexagon ratio are significant for benzene in I35 (**IIc**) and therefore this solvent cannot be defined as "inert" according to the definition of Diehl *et al.* in reference [2]. Thereafter the differences found for the r_{HC} values of sample (**IIc**) against (**IIa**) and (**IIb**) (Table 5) have no physical meaning since the coupling between internal vibrational and overall re-orientation motions should be dealt as proposed by Lounila and Diehl [14,13] to produce the correct value for **IIc**.

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