The Structure of Acrolein in a Liquid Crystal Phase

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Abstract: The ^{1}H NMR spectrum of a sample of acrolein dissolved in the nematic liquid crystal phase I52 has been analysed to yield 18 dipolar couplings between all the magnetic nuclei in the molecule; moreover, the ^{13}C and ^{13}C{^{1}H} NMR spectra of a sample of acrolein in $CDCl_3$ were recorded and analysed to determine the indirect J_{ij} couplings. The data were used to obtain the relative positions of the carbon and hydrogen atoms, assuming that these are independent of the conformations generated by rotation around the C–C bond through an angle ϕ, and to obtain a probability distribution $P(\phi)$. It has been found that in the liquid phase, the distribution is a maximum at the *trans* form whereas the abundance of the *cis* form is significantly smaller compared with that found by microwave spectroscopy or high level quantum mechanical calculations. Such calculations produced also a suitable force field needed to develop suitable strategies for vibrational correction procedure in the case of flexible molecules.

Keywords: conformation analysis · liquid crystals · NMR spectroscopy

Introduction

The structure of acrolein has been studied experimentally by microwave spectroscopy[1] and theoretically by molecular orbital calculations up to the MP2 level.[2] These give the structure of an isolated molecule and are in good agreement with regard to both bond lengths and angles; additionally it was determined that the molecule exists in predominantly a planar, *trans* form, but with a second minimum energy structure, the planar *cis*, as shown in Figure 1.

There have also been studies of the relative amounts of the *cis* and *trans* conformers present in solutions of acrolein in various solvents. Thus, the UV absorption spectrum of acrolein dissolved in water[3] and in ethanol[4] shows bands which were attributed to the *trans* conformer, with no evidence of bands from the *cis* form. On the contrary, UV spectroscopic studies on a vapour phase sample[5] revealed absorption bands which were attributed to a certain amount of *cis* structure, along with the expected signals of *trans*-acrolein. A study of ultrasonic relaxation of acrolein in the pure liquid phase[6] concluded that the *cis* form is present, and is 8.6 kJ mol^{-1} higher in energy than *trans*, which corresponds to 3.1 % at 300 K. The barrier to interconversion of the two conformers was found to be 29.4 kJ mol^{-1}.

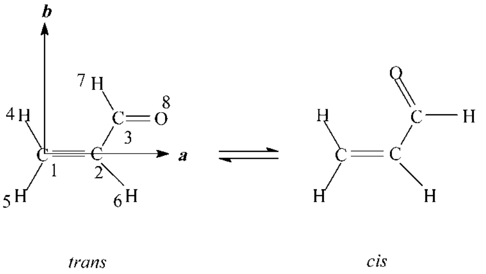

Figure 1. Structures of the *trans* and *cis* forms of acrolein with reference *abc* axes.

We address here the question as to whether acrolein has the same structure and conformer distribution in a liquid phase as in the vapour phase. To solve this we have recorded and analysed the proton NMR spectrum for acrolein dissolved in a liquid crystal solvent. The spectra can be analysed to produce partially averaged dipolar couplings D_{ij}(obs) [see Eq. (1)], which are related to D_{ij}(equil), the coupling for the molecule in a fixed equilibrium structure and D_{ij}(vib), a correction for small-amplitude vibrational motion:

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$$D_{ij}(\mathrm{obs}) = D_{ij}(\mathrm{equil}) + D_{ij}(\mathrm{vib}) \qquad (1)$$

The value of D_{ij}(equil) is related to orientational order parameters S_{ab}, which are defined with respect to *abc* axes fixed in the molecule, and geometrical parameters r_{ij} and θ_{ija}, which are angles between r_{ij} and *a* axis:

$$\begin{aligned} D_{ij}(\mathrm{equil}) &= -(K_{ij}/r_{ij}^3)[S_{aa}(3\cos^2\theta_{ija}-1) \\ &+ (S_{bb}-S_{cc})(\cos^2\theta_{ijb}-\cos^2\theta_{ijc}) + 4S_{ab}\cos\theta_{ija}\cos\theta_{ijb} \\ &+ 4S_{ac}\cos\theta_{ija}\cos\theta_{ijc} + 4S_{bc}\cos\theta_{ijb}\cos\theta_{ijc}] \end{aligned} \qquad (2)$$

and Equation (3):

$$K_{ij} = \frac{\mu_0 \hbar \gamma_i \gamma_j}{16\pi^2} \qquad (3)$$

where μ_0 is the magnetic constant, and γ_i and γ_j are magnetogyric ratios.

This method to determine the structure of a molecule has now a 40-year history,[7] but its application still has problems, which are well illustrated by the example of acrolein. The first problem is that the couplings between the four protons in acrolein yield six dipolar couplings; this is not sufficient to obtain the three unknown, non-zero order parameters and the six relative proton coordinates necessary if acrolein were to exist in a single, rigid conformation. Thus, Courtieu et al.,[8] who obtained and analysed the proton spectrum of acrolein dissolved in a nematic liquid crystal solvent, had to assume that the proton geometry is that determined by microwave spectroscopy, and that the orientational order is independent of the conformation adopted by the molecule.

Another approach is to dissolve the molecule in a liquid crystal solvent in which the solute is very weakly ordered and to record only the couplings between isotopically dilute nuclei, such as ^{13}C, and directly bonded protons. This is a powerful method for macromolecules since there are many such couplings within large molecules, but there are only four for acrolein, and again this is insufficient to provide any structural information. The answer for small molecules is to obtain both H–H and all C–H dipolar couplings. For acrolein this produces 12 more values of D_{ij} for a total of 18 couplings and thus makes it possible to investigate both the structure and the conformational distribution. But, including ^{13}C–^{1}H couplings into the analysis introduces a further complication in that these couplings can be strongly affected by vibrational averaging. It is possible to calculate the effect of vibrational averaging D_{ij}(vib) in Equation (1), if both the vibrational frequencies and Cartesian coordinate displacements have been obtained from an analysis of a vibrational spectrum. There have been several studies of the vibrational spectrum of acrolein, and various force fields have been derived, but there are no published Cartesian displacements.

An alternative is to calculate the required Cartesian displacements by molecular orbital or density functional methods. This purely theoretical method of obtaining values of D_{ij}(vib) has been compared with that using experimental vibrational frequencies and Cartesian displacements in order to obtain values of D_{ij}(equil) for benzene dissolved in a liquid crystal solvent.[9] This found that the Hartree–Fock method MP2/6-31G*, and the density functional approach B3LYP both produce good approximations to D_{ij}(vib) for benzene; the former method will be used here for acrolein in both *trans* and *cis* forms.

The internal rotation about the C2–C3 bond produces one more complication for acrolein. Can the molecule be approximated as existing in a two-site equilibrium, as depicted in Figure 1? This would lead to an averaging of the dipolar couplings according to:

$$D_{ij} = P_{\mathrm{trans}} D_{ij}(\mathit{trans}) + (1-P_{\mathrm{trans}}) D_{ij}(\mathit{cis}) \qquad (4)$$

where D_{ij}(*cis*) and D_{ij}(*trans*) are given by Equation (2) but with order parameters S_{ab}(*cis*) and S_{ab}(*trans*) in each case. Alternatively, and more realistically, there may be a continuous distribution of structures with values of ϕ, the angle of rotation about the C2–C3 bond, in the range 0 to 180°, in which case the averaging is given by Equation (5):

$$D_{ij} = \int P_{\mathrm{LC}}(\phi) D_{ij}(\phi) d\phi \qquad (5)$$

$D_{ij}(\phi)$ is again obtained from Equation (1), but with the order parameters $S_{ab}(\phi)$ which vary continuously with the bond rotation angle. In both the discrete [Eq. (4)] and continuous [Eq. (5)] cases the question of how to allow for small-amplitude vibrational motion in the presence of a bond rotation must also be considered.

By using a liquid crystal solvent to investigate the structure of a dissolved solute does raise the question of whether the structure and conformational distribution are affected by the nature of the solvent. There is evidence for structural deformations due to solvent effects,[10] and in the case of acrolein the magnitude of these effects will be assessed by comparison with the structures determined by microwave spectroscopy and molecular orbital calculations.

The conformer distribution, but not the structure, can also be obtained in principle from the magnitude of scalar spin–spin coupling constants J_{ij}, and again, as reported here, this method is enhanced by measuring both the HH and the CH couplings.

Experimental Section

A small amount of acrolein (purchased from Sigma-Aldrich) was distilled and then dissolved (10% by weight) into the nematic liquid crystal solvent I52 (purchased from Merck, Darmstadt), see Figure 2.

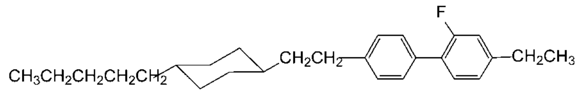


Figure 2. Structure of the nematic liquid crystal solvent I52.

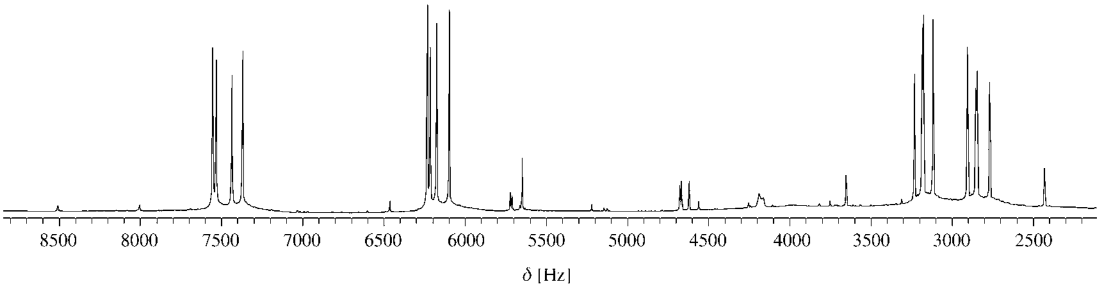


Figure 3. 300 MHz ^{1}H NMR spectrum of acrolein in the nematic I52 at 300 K.

The anisotropic spectrum was recorded on a Bruker AC300 spectrometer at a field strength of 7.04 T. The free induction decay (FID) was stored in 64k of computer memory with a sweep width of 12500 Hz for an Hz/point of 0.19 Hz and a total of 4000 scans in order to obtain such a good S/N ratio to recognize all but the smallest satellites lines. The proton spectrum obtained after Fourier transformation is shown in Figure 3.

The spectrum depends on chemical shifts, dipolar and scalar couplings J_{ij}, and the latter were obtained by analysing the ^{1}H, ^{13}C and selectively proton decoupled ^{13}C{^{1}H} spectra of a sample dissolved in $CDCl_3$. It proved difficult to assign some of the lines in these spectra, thus preventing the determination of the magnitude and signs of some of the couplings. This is a general problem when analysing ^{13}C satellite spectra, and for acrolein it was solved by first calculating the magnitudes and signs of all the couplings for the *trans* form. This was achieved by using the routine in the computer package Gaussian03,[11] with wavefunctions obtained by the B3LYP/6-31G* method. Note that the signs of the couplings are the most important information obtained by the calculations, and with these were it was possible to assign all the lines in the spectrum. This enabled all the lines in the spectrum to be correctly assigned. The spectra were analysed to give the correct magnitudes and signs of all the scalar couplings, as shown in Table 1. In the case of acrolein the calculated magnitudes of the values of J_{ij} are in good agreement with those obtained by analysis of the spectrum, thus validating this combination of theory and experiment, but it remains to be demonstrated that this will be the case for other molecules. These values of the J_{ij} were kept fixed in the analysis of the spectrum in the liquid crystal solvent, which was achieved using the program ARCANA.[12] In Table 1 the experimental spectral parameters are also reported. For the more abundant isotopomers all the calculated lines (25) were assigned; the assigned to calculated line ratio for the satellite spectra was: 50/80 for C1, 48/80 for C2 and 31/80 for C3.

Table 1. Values of the dipolar couplings D_{ij}, chemical shifts ν_i and scalar couplings J_{ij} in Hz.[a]

i,j	J_{ij}(G03)/Hz	J_{ij}(exptl)/Hz	D_{ij}(exptl)/Hz
4,5	0.6	0.7±0.2	115.8±0.5
4,6	14.8	17.4±0.1	−20.3±0.4
4,7	0.1	0.1±0.1	−1418.4±0.1
5,6	9.3	10.0±0.2	−986.8±0.1
5,7	−0.7	−0.1±0.1	−239.0±0.3
6,7	5.8	8.0±0.2	87.1±0.3
R/Hz	–	0.13	0.21
1,4	149.2	156.7±0.2	892.8±0.2
1,5	154.8	162.8±0.2	−2189.4±0.1
1,6	1.3	0.0±0.2	−131.9±0.2
1,7	1.7	0.9±0.2	−170.0±0.1
R/Hz	–	0.26	0.40
2,4	−2.6	−3.3±0.1	−124.7±0.5
2,5	−0.1	−0.6±0.1	−503.4±0.3
2,6	154.4	163.1±0.1	863.3±0.2
2,7	27.2	26.4±0.1	−2.5±0.4
R/Hz	–	0.05	0.91
3,4	9.8	10.1±0.1	−233.6±0.5
3,5	14.6	16.0±0.1	−108.0±0.9
3,6	2.5	2.1±0.1	−9.0±0.8
3,7	159.9	173.4±0.1	739.1±0.5
R/Hz	–	0.08	0.99
ν_i/Hz			
ν_1–ν_3	124.9		
ν_2–ν_3	19.0		
ν_4–ν_3	−1047.3		

[a] Values obtained from the analyses of the 300 MHz ^{1}H and ^{13}C proton satellite spectra of acrolein dissolved in I52, and ^{1}H, ^{13}C and selectively ^{13}C{^{1}H}-decoupled spectra in $CDCl_3$ at 300 K. J_{ij} calculated by Gaussian03 (G03) for *trans*-acrolein are also reported (see text for details).

Results and Discussion

Assuming only the *trans* conformer is present, and neglecting vibrational corrections: We have first interpreted the measured dipolar couplings by assuming that the molecule exists only as the *trans* form, and that vibrational effects can be neglected. There are 18 independent, experimental values of D_{ij}, and these were fitted to calculated values by varying the order parameters S_{aa}, $S_{bb}-S_{cc}$ and S_{ab} and the *a* and *b* coordinates of nuclei 3–7, but keeping r_{12} fixed at 1.340 Å, the value found by microwave spectroscopy.[1] The least squares error, *R*, is defined as

$$R = \sqrt{\frac{\sum_{1}^{N} (\Delta D_{ij})^2}{N}} \tag{6}$$

with

$$\Delta D_{ij} = D_{ij}(\text{equil}) + D_{ij}(\text{vib}) - D_{ij}(\text{obs}) \tag{7}$$

D_{ij}(vib) is set to zero for the present calculations; the value of *R* was found to be 1.8 Hz. This might be considered an acceptable total error, but there are large values of ΔD_{ij} on some of the couplings, and the values obtained for the bond lengths and angles are significantly different from those obtained by the microwave investigation, as shown in Table 2. Clearly, this "geometry filter" and the large values of some ΔD_{ij} reveal that the model of assuming only a *trans* structure and neglecting vibrational corrections is wrong.

Table 2. Geometry derived from the dipolar couplings, and $\Delta D_{ij} = D_{ij}$(equil)$-D_{ij}$(obs) under the assumption that only the *trans* conformer is present and without vibrational corrections. The microwave geometry of the *trans* form is reported for comparison.

Parameters	NMR (*trans*)	Microwave (*trans*)
$r_{1,2}$/Å	1.340[a]	1.340 ± 0.004
$r_{1,4}$/Å	1.09 ± 0.02	1.080 ± 0.003
$r_{1,5}$/Å	1.10 ± 0.02	1.090 ± 0.004
$r_{2,3}$/Å	1.43 ± 0.03	1.468 ± 0.004
$r_{2,6}$/Å	1.09 ± 0.02	1.084 ± 0.005
$r_{3,7}$/Å	1.15 ± 0.03	1.113 ± 0.006
$\sphericalangle_{3,2,1}$/°	120.5 ± 1.0	120.4 ± 0.5
$\sphericalangle_{4,1,2}$/°	120.8 ± 0.8	119.7 ± 0.3
$\sphericalangle_{5,1,2}$/°	121.1 ± 0.9	122.9 ± 0.5
$\sphericalangle_{6,2,1}$/°	122.4 ± 0.6	122.4 ± 0.4
$\sphericalangle_{7,3,2}$/°	116.9 ± 1.0	114.7 ± 0.5
R/Hz	1.8	–
i,j	ΔD_{ij}/Hz	
1,4	0.0	
1,5	−0.1	
1,6	0.7	
1,7	−0.7	
2,4	−1.2	
2,5	−0.6	
2,6	0.1	
2,7	0.4	
3,4	2.5	
3,5	−3.7	
3,6	−1.4	
3,7	0.4	
4,5	0.0	
4,6	−2.0	
4,7	−0.6	
5,6	0.5	
5,7	5.1	
6,7	−1.4	

[a] Kept fixed in the optimization process.

Assuming that only the *trans* conformer is present, but including vibrational corrections: Both harmonic and anharmonic terms can contribute to D_{ij}(vib), but only the former larger term will be considered for acrolein. The magnitude of D_{ij}(vib) is therefore given by[13] Equation (8):

$$D_{ij}(\mathrm{vib}) = -K_{ij} \sum_{\alpha\beta} S_{\alpha\beta} \Phi^{h}_{\alpha\beta,ij} \tag{8}$$

with Equation (9):

$$\begin{aligned}\Phi^{h}_{\alpha\beta,ij} = {} & [C^{ij}_{\alpha\beta} - 5 \sum_{\gamma} \cos\theta_{\gamma}(C^{ij}_{\alpha\gamma}\cos\theta_{\beta} + C^{ij}_{\beta\gamma}\cos\theta_{\alpha}) \\ & + \frac{5}{2}\cos\theta_{\alpha}\cos\theta_{\beta} \sum_{\gamma\delta} C^{ij}_{\gamma\delta}(7\cos\theta_{\gamma}\cos\theta_{\delta} - \delta_{\gamma\delta})] \cdot r_{ij}^{-5}\end{aligned} \tag{9}$$

and

$$C^{ij}_{\alpha\beta} = \sum_{v=1}^{3N} (u^{(v)}_{i\alpha} - u^{(v)}_{j\alpha})(u^{(v)}_{i\beta} - u^{(v)}_{j\beta}) \frac{A}{\omega_{v}} \coth\left(\frac{B\omega_{v}}{T}\right) \tag{10}$$

$$A = \frac{h}{8\pi^{2}c} \tag{11}$$

$$B = \frac{ch}{2k_{B}} \tag{12}$$

The calculations of D_{ij}(vib) requires $u^{(v)}_{i\alpha}$, the Cartesian displacements of the *i*th nucleus in the *v*th normal mode and ω_{v} the vibrational frequencies. The vibrational frequencies of acrolein (in the more stable *trans* form) have been obtained,[14,15] but not the values for the $u^{(v)}_{i\alpha}$. We have therefore calculated values of ω_{v} and $u^{(v)}_{i\alpha}$ by the molecular orbital method MP2/6-31G* as implemented in the Gaussian98W computer program.[16] The calculated and observed vibrational frequencies are compared in Table 3. The agreement is sufficiently close to estimate that the values of D_{ij}(vib) calculated with the theoretical values of $u^{(v)}_{i\alpha}$ will be no more than about 10% in error. This is acceptable when D_{ij}(vib)/D_{ij}(obs) is 10% which is the case for most of the couplings in acrolein. Note, however, that the calculations of D_{ij}(vib) can be susceptible to a larger error when D_{ij}(obs) is small. The molecular orbital calculation fully optimized the geometry of the *trans* form, which is compared with that obtained from the microwave study in Table 3. The bond lengths and angles are in good agreement even though the calculation

Table 3. Comparison between the geometries obtained from a calculation using the MP2 method with a 6-31G* basis set, with full geometry optimisation on the *trans* form, and that for the same conformer derived from rotational spectroscopy.[1] The calculated and experimental vibrational frequencies are also shown.

Parameters	MP2/6-31 G* (*trans*)	Microwave (*trans*)
$r_{1,2}$/Å	1.342	1.340 ± 0.004
$r_{1,4}$/Å	1.087	1.080 ± 0.003
$r_{1,5}$/Å	1.084	1.090 ± 0.004
$r_{2,3}$/Å	1.473	1.468 ± 0.004
$r_{2,6}$/Å	1.087	1.084 ± 0.005
$r_{3,7}$/Å	1.111	1.113 ± 0.006
$\sphericalangle_{3,2,1}$/°	120.6	120.4 ± 0.5
$\sphericalangle_{4,1,2}$/°	121.0	119.7 ± 0.3
$\sphericalangle_{5,1,2}$/°	122.2	122.9 ± 0.5
$\sphericalangle_{6,2,1}$/°	122.4	122.4 ± 0.4
$\sphericalangle_{7,3,2}$/°	115.1	114.7 ± 0.5
	Vibrational frequencies/cm^{-1}	
ν_{k}	Exptl (*trans*)	MP2/6-31 G* (*trans*)
1	157.0	165.0
2	327.0	299.9
3	564.0	565.4
4	593.0	689.2
5	912.0	967.8
6	959.0	980.5
7	980.0	1023.7
8	993.0	1033.9
9	1158.0	1092.4
10	1275.0	1340.0
11	1360.0	1461.5
12	1420.0	1476.0
13	1625.0	1700.4
14	1724.0	1767.5
15	2800.0	3011.2
16	3000.0	3220.5
17	3000.0	3240.8
18	3103.0	3322.5

refers to the equilibrium structure, whilst microwave gives the "least squares" structure which is uncorrected for vibrational motion. Blom et al.[1] argue that this structure should be close to the equilibrium structure.

The calculation of D_{ij}(vib) for pure *trans*-acrolein proceeded by using the calculated values of $u_{i\alpha}^{(v)}$, but with the observed values of the frequencies. For benzene, it was found that using calculated rather than observed frequencies has only a small effect on calculated values of D_{ij}(vib) (~ 1 % at the B3LYP level of approximation) and so using either observed or calculated frequencies is probably not important. The results are shown in Table 4. Now the R error is lower than when vibrational corrections were neglected, and the individual residuals are reduced, as shown in Table 4, but there are still unacceptably large values of ΔD_{ij} for some couplings, and there are significant differences between the geometry obtained and that derived by microwave spectroscopy.

Table 4. Geometries, D_{ij}(vib) and $\Delta D_{ij} = D_{ij}(\text{equil}) + D_{ij}(\text{vib}) - D_{ij}(\text{obs})$ obtained from the dipolar couplings with vibrational corrections, and assuming only the *trans* conformer is populated. The geometry of the *trans* form obtained from rotational spectroscopy is reported for comparison.

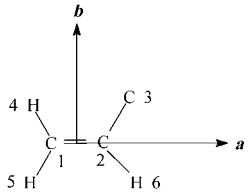
Parameters	NMR (*trans*)	Microwave (*trans*)
$r_{1,2}$/Å	1.340[a]	1.340 ± 0.004
$r_{1,4}$/Å	1.08 ± 0.01	1.080 ± 0.003
$r_{1,5}$/Å	1.07 ± 0.02	1.090 ± 0.004
$r_{2,3}$/Å	1.47 ± 0.03	1.468 ± 0.004
$r_{2,6}$/Å	1.08 ± 0.02	1.084 ± 0.005
$r_{3,7}$/Å	1.12 ± 0.02	1.113 ± 0.006
$\sphericalangle_{3,2,1}$/°	120.2 ± 0.8	120.4 ± 0.5
$\sphericalangle_{4,1,2}$/°	120.5 ± 0.6	119.7 ± 0.3
$\sphericalangle_{5,1,2}$/°	121.4 ± 0.7	122.9 ± 0.5
$\sphericalangle_{6,2,1}$/°	122.6 ± 0.5	122.4 ± 0.4
$\sphericalangle_{7,3,2}$/°	115.2 ± 0.8	114.7 ± 0.5
R/Hz	1.4	–
i,j	D_{ij}(vib)/Hz	ΔD_{ij}/Hz
1,4	−64.6	0.0
1,5	224.9	0.0
1,6	6.4	0.8
1,7	4.1	0.2
2,4	8.7	1.1
2,5	24.0	−0.1
2,6	−42.5	−0.3
2,7	2.4	3.6
3,4	3.4	0.2
3,5	1.8	−1.9
3,6	1.9	−2.9
3,7	−19.3	0.3
4,5	−3.1	−0.4
4,6	3.6	−0.9
4,7	38.1	0.3
5,6	26.3	−0.4
5,7	5.3	0.5
6,7	0.2	2.1

[a] Kept fixed in the optimization process.

Including the rotation about the C2–C3 bond: Can the structures derived by NMR and microwave spectroscopy be brought into closer agreement by allowing for oscillations or rotation about the C2–C3 bond? The NMR spectrum, unlike the microwave spectrum, does not reveal the presence directly of the *cis* conformer, but large amplitude motion about this bond may significantly affect the values of the partially averaged dipolar couplings. To investigate this possibility we have explored two models. The first assumes that there is an equilibrium between two discrete conformers, and the second allows for a continuous distribution of conformers. In both cases it is essential to allow, in some way, for vibrational averaging.

In all cases it is assumed that the bond lengths and angles in the two forms are identical. This is reasonable in view of the changes found by microwave spectroscopy of < 1 %, and that only a small amount (~4 %) of the *cis* isomer was detected in the vapour phase. It is, however, worth noting that the effect in the equilibrium of 4 % of the *cis* isomer does not mean that the dipolar couplings will be affected by this amount since the couplings in each conformation are weighted by different conformationally dependent order parameters.

The fragment (see below) yields 12 values of D_{ij}, and is characterised by eight relative nuclear coordinates. The relationship between those requires values of three local order matrix elements, that is S_{aa}^{ene}, S_{bb}^{ene}–S_{cc}^{ene} and S_{ab}^{ene}, see in Equation (2). The vibrational corrections D_{ij}(vib), were calculated by using the geometry and displacement coordinates calculated by the MP2/6-31G* method, and the experimental vibrational frequencies, as discussed above, for the *trans* form.



Minimising R for the couplings in the ene rigid fragment by varying the order parameters and nuclear coordinates, keeping r_{12} fixed at 1.34 Å produced the data in Table 5, which also compares the values with the least-squares values of the microwave spectrum. Note the large values of D_{36}(vib)/D_{36}(equil) and D_{46}(vib)/D_{46}(equil), both of which are −15 %. This is because the bond order parameters S_{36}^{bond} and S_{46}^{bond} are small [see Eq. (13)]:

$$S_{ij}^{bond} = -D_{ij}(\text{equil})(16\pi^3 r_{ij}^3/\mu_0\gamma_i\gamma_j h) \tag{13}$$

This means that the bond directions $\boldsymbol{r}_{36}$ and $\boldsymbol{r}_{46}$ are on average close to 54.7° with respect to the liquid crystal phase director; at this value the changes in D_{ij}(equil) with respect to angular displacements away from the equilibrium geometry are at a maximum. The value obtained for the bond length r_{23} of 1.505 ± 0.008 Å is significantly longer than the value of 1.468 ± 0.004 Å determined from the rotational spectrum. Fixing r_{23} = 1.468 Å as well as r_{12} = 1.340 Å in the calcula-

Table 5. Geometries obtained from the dipolar couplings between nuclei only in the *ene* fragment, including vibrational corrections (NMR *ene*). The geometry obtained from rotational spectroscopy of the trans form is reported for comparison.

Parameters	NMR *ene*	Microwave (*trans*)	
$r_{1,2}$/Å	1.340[a]	1.340 ± 0.004	
$r_{1,4}$/Å	1.090	1.080 ± 0.003	
$r_{1,5}$/Å	1.086	1.090 ± 0.004	
$\mathrm{r}_{2,6}$/Å	1.094	1.084 ± 0.005	
$\sphericalangle_{4,1,2}$/°	120.5	119.7 ± 0.3	
$\sphericalangle_{5,1,2}$/°	122.0	122.0 ± 0.5	
$\sphericalangle_{6,2,1}$/°	122.5 ± 0.2	122.4 ± 0.4	
R/Hz	≈0.0[b]	–	
$r_{2,3}$/Å	1.505 ± 0.008	1.468 ± 0.004	
$\sphericalangle_{3,2,1}$/°	120.3 ± 0.000	120.4 ± 0.5	
R/Hz	0.55	–	
i,j	D_{ij}(equil)/Hz	D_{ij}(vib)/Hz	ΔD_{ij}/Hz
1,4	955.9	−63.1	0.0
1,5	−2409.7	220.4	0.1
1,6	−138.2	6.4	0.0
2,4	−133.4	8.7	0.0
2,5	−526.9	23.5	0.0
2,6	905.0	−41.7	0.0
3,4	−238.1	3.3	−1.2
3,5	−109.7	1.7	0.0
3,6	−12.3	1.8	−1.5
4,5	118.9	−2.5	0.0
4,6	−23.7	3.5	0.0
5,6	−1012.5	25.7	0.1

[a] Kept fixed in the optimization process. [b] Number of unknowns = number of equations.

tions leads to a significantly worse agreement, as shown by a value of $R=1.1$, and large individual errors such as $\Delta D_{34}=-1.1$, $\Delta D_{35}=-3.3$ and $\Delta D_{36}=-1.5$. It would seem, therefore, that r_{23} is indeed determined to be longer in the liquid crystal phase than for an isolated molecule. However, the difference found may simply reflect the systematic errors in the NMR, microwave spectroscopy and molecular orbital methods.

The geometry obtained for the ene fragment was kept fixed in all subsequent calculations which take into account the averaging of the dipolar couplings by bond rotation. The geometry of the C2-C3-H7-O8 fragment was also assumed to be independent of the bond rotational angle.

Equilibrium between *trans* and *cis* conformers: The variable parameters in this model are the six weighted order parameters:

$$P_{\mathrm{trans}}S_{\mathrm{aa}}^{\mathrm{trans}}$$

$$P_{\mathrm{trans}}(S_{\mathrm{bb}}^{\mathrm{trans}}-S_{\mathrm{cc}}^{\mathrm{trans}})$$

$$P_{\mathrm{trans}}S_{\mathrm{ab}}^{\mathrm{trans}}$$

$$(1-P_{\mathrm{trans}})S_{\mathrm{aa}}^{\mathrm{cis}}$$

$$(1-P_{\mathrm{trans}})(S_{\mathrm{bb}}^{\mathrm{cis}}-S_{\mathrm{cc}}^{\mathrm{cis}})$$

$$(1-P_{\mathrm{trans}})S_{\mathrm{ab}}^{\mathrm{cis}}$$

and the two coordinates which locate H7, and which we take to be r_{37} and θ_{732}. These are varied to bring the calculated values of D_{ij}(equil) into agreement with the 18 values of D_{ij}(obs)−D_{ij}(vib), by using the vibrational frequencies reported for the *trans* form for both conformers, but with Cartesian displacements $u_{i\alpha}^{(v)}$, calculated for each conformer separately by the MP2/6-31G* method. Note that the observed vibrational frequencies for the *cis* form are close to those for the *trans*.[15] The results are given in Table 6, and it is seen that the fit between observed and calculated couplings has improved considerably over the agreement achieved when a single, *trans* isomer was considered (Table 4): the individual values of ΔD_{ij} are all acceptably small, except for $\Delta D_{36}=-1.5$, and the value of R has decreased from 1.4 (see Table 4) to 0.46 Hz. The large value of $\Delta D_{36}/D_{36}$(equil) = 16.7% probably reflects the imprecision in calculating D_{36}(vib) because in this case the bond order parameter S_{36}^{bond}, is small. The improved agreement between observed and calculated dipolar couplings could suggest that some of the *cis* form is present in acrolein dissolved in the liquid crystal solvent.

Table 6. Geometry, order parameters and $\Delta D_{ij} = D_{ij}(\mathrm{equil})+D_{ij}(\mathrm{vib})-D_{ij}(\mathrm{obs})$ obtained from dipolar couplings, with vibrational corrections, and assuming an equilibrium between *trans* and *cis* conformers (NMR *trans/cis*). The geometry of the *ene* fragment is fixed at that in Table 5. The Microwave geometry of the *trans* form is reported for comparison.

Parameters	NMR (*trans/cis*)	Microwave (*trans*)
$r_{3,7}$/Å	1.114 ± 0.001	1.113 ± 0.006
$\sphericalangle_{7,3,2}$/°	114.6 ± 0.1	114.7 ± 0.5
$P_{\mathrm{trans}}S_{\mathrm{aa}}^{\mathrm{trans}}$	0.131 ± 0.001	–
$P_{\mathrm{trans}}(S_{\mathrm{bb}}^{\mathrm{trans}}-S_{\mathrm{cc}}^{\mathrm{trans}})$	0.116 ± 0.003	–
$P_{\mathrm{trans}}S_{\mathrm{ab}}^{\mathrm{trans}}$	0.079 ± 0.001	–
$(1-P_{\mathrm{trans}})S_{\mathrm{aa}}^{\mathrm{cis}}$	0.001 ± 0.001	–
$(1-P_{\mathrm{trans}})(S_{\mathrm{bb}}^{\mathrm{cis}}-S_{\mathrm{cc}}^{\mathrm{cis}})$	−0.002 ± 0.003	–
$(1-P_{\mathrm{trans}})S_{\mathrm{ab}}^{\mathrm{cis}}$	0.001 ± 0.001	–
R/Hz	0.46	–
i,j	ΔD_{ij}/Hz	
1,4	−0.1	
1,5	0.2	
1,6	0.1	
1,7	−0.1	
2,4	0.0	
2,5	−0.1	
2,6	0.2	
2,7	0.1	
3,4	−1.2	
3,5	0.0	
3,6	−1.5	
3,7	0.0	
4,5	0.0	
4,6	0.1	
4,7	0.0	
5,6	0.0	
5,7	0.0	
6,7	0.0	

Unfortunately, the products of P_{trans} and the order parameters cannot be separated, except by assuming values either for P_{trans}, or for at least one of the order parameters. The microwave study gave the value of P_{trans} of 0.96, and by using this gives the order parameters shown in Table 7, and the values of S_{zz}^{trans}, $S_{xx}^{\mathrm{trans}}-S_{yy}^{\mathrm{trans}}$ and S_{zz}^{cis}, $S_{xx}^{\mathrm{cis}}-S_{yy}^{\mathrm{cis}}$ where *xyz* are principal axes for the order tensors (and are at different orientations to *abc* for each conformer); their orientation with respect to the *xyz* axes for the *trans* isomer is shown in Figure 4.

Table 7. Order parameters obtained by dividing weighted order parameters of Table 6 by the values $P_{\mathrm{trans}}=0.96$ or $P_{\mathrm{cis}} = (1-P_{\mathrm{trans}})$ determined by microwave technique.

$S_{\mathrm{aa}}^{\mathrm{trans}}$	0.137
$S_{\mathrm{bb}}^{\mathrm{trans}}-S_{\mathrm{cc}}^{\mathrm{trans}}$	0.121
$S_{\mathrm{ab}}^{\mathrm{trans}}$	0.083
$S_{\mathrm{aa}}^{\mathrm{cis}}$	0.025
$S_{\mathrm{bb}}^{\mathrm{cis}}-S_{\mathrm{cc}}^{\mathrm{cis}}$	−0.050
$S_{\mathrm{ab}}^{\mathrm{cis}}$	0.025

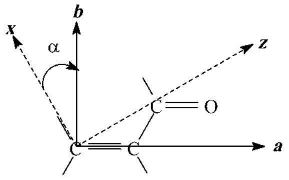


Figure 4. Orientation of *abc* and *xyz* axes for the *trans* isomer. The *y* and *c* axes are parallel and $\alpha=24.2°$.

Note that the small values of $P_{\mathrm{cis}} = (1-P_{\mathrm{trans}})$ leads to imprecise values for the magnitudes of the elements of the order matrix $\mathbf{S}^{\mathrm{cis}}$, but their ratios are more reliably obtained.

The order parameters for the two conformers are well within their limits of 1 to $-{}^{1}\!/_{2}$, but can they be considered reasonable?

To answer this question we have predicted values for these order parameters by the method proposed by Celebre.[17] In his model, the solute is described as a box of length *L*, width *W* and breadth *B*. These dimensions are calculated by taking into account molecular geometries and atomic van der Waals radii. The solute is immersed in a "virtual" nematic solvent consisting of long, axially symmetric particles. *L*, *W* and *B* are along the **S** principal axes *z*, x and *y*. The solute box interacts directly with the nearest neighbour solvent molecules (six $D_{\infty h}$ symmetry prolate particles placed at the sites of a simple cubic lattice) and, through them, with the director of the medium (the introduction of the concept of this "virtual" director of the mesophase allows to bypass the explicit consideration of the solvent–solvent molecular interactions of the infinite solvent molecules forming the bulk of the solvent). Following these guidelines, the solute–solvent interaction potential *U* can be written as:

$$U = -\frac{\varepsilon}{6}\sum_{i=1}^{6}\Lambda_i P_2(\hat{\mathbf{k}}_i\cdot\hat{\mathbf{u}}_i)P_2(\hat{\mathbf{u}}_i\cdot\hat{\mathbf{n}}) \qquad (14)$$

where the positive parameter ε is an energy per unit length, giving the strength of the interaction; Λ_i is the length of the face of the parallelepiped along the *i* direction; $\hat{\mathbf{k}}_i$, $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{n}}$ are unit vectors defining the directions of the *i*th frame axis, the *i*th nearest neighbour itself and the director in the solute reference frame, respectively; P_2 is the second Legendre polynomial.

The parameter $\varepsilon=3.16kT/\text{Å}$ was set to produce the best agreement with the magnitudes of the principal order parameters of *trans* acrolein for the RIS calculations (see Table 8 where also the "simulated" order tensors are given). The agreement between simulated and RIS values of all three order parameters is excellent for the *trans* form, but the simulation produces values for the *cis* conformation which are very different from those derived using the RIS model, and this suggests that the RIS approach fails in predicting a realistic set of order parameters for the *cis* form of acrolein.

Table 8. Principal order parameters of acrolein obtained from NMR data (RIS and AP methods) and simulated by the Celebre model.[17]

	NMR-RIS[a]	NMR-AP[b]	Simulated[c]
S_{xx}^{trans}	−0.044	−0.043	−0.023
S_{yy}^{trans}	−0.129	−0.127	−0.127
S_{zz}^{trans}	0.173	0.170	0.150
S_{xx}^{cis}	−0.024	0.017	0.014
S_{yy}^{cis}	0.002	−0.121	−0.120
S_{zz}^{cis}	0.022	0.104	0.106

[a] Taken from Table 7 but transformed to the principal axes. [b] $k={}^{3}\!/_{2}$ is used. [c] $\varepsilon=3.16\,k\mathrm{T}/\text{Å}$ is used; the box dimensions used are $L=6.70$ Å; $W=5.63$ Å and $B=3.40$ Å (see text for details).

A continuous distribution of conformers: To refine the result obtained so far we now consider a model in which acrolein exists over a range of the bond rotation angle, ϕ. The averaged couplings are now calculated from Equation (5). For this it is necessary to assume a model for the dependence on ϕ of the order parameters $S_{\mathrm{ab}}(\phi)$. This is done by first defining a mean potential $U_{\mathrm{LC}}(\beta,\gamma,\phi)$, which acrolein experiences in the liquid crystal phase, and to express this as

$$U_{\mathrm{LC}}(\beta,\gamma,\phi) = U_{\mathrm{ext}}(\beta,\gamma,\phi) + U_{\mathrm{iso}}(\phi) \qquad (15)$$

where $U_{\mathrm{LC}}(\beta,\gamma,\phi)$ is purely anisotropic, and vanishes in the isotropic phase, whilst $U_{\mathrm{iso}}(\phi)$ contributes in both anisotropic and liquid crystal phases; β and γ are the polar angles that the liquid crystal director makes in molecule-fixed axes. The anisotropic potential for a uniaxial phase, as used in these experiments, can be expanded as the infinite series

$$U_{\mathrm{ext}}(\beta,\gamma,\phi) = -\sum_{\mathrm{L,m}}(-1)^{\mathrm{m}}\varepsilon_{\mathrm{L,m}}(\phi)C_{\mathrm{L,-m}}(\beta,\gamma) \qquad (16)$$

where the $C_{\mathrm{L,m}}(\beta,\gamma)$ are modified spherical harmonics. It is clearly necessary to truncate the infinite series, and when the potential is used to calculate second-rank properties it is a good approximation to include only the rank $L=2$ terms. Note that this approximation improves as the orientational order of the molecules decreases, primarily because of the orthogonality of the $C_{L,m}(\beta,\gamma)$.

$$U_{\mathrm{ext}}(\beta,\gamma,\phi) = -\varepsilon_{2,0}(\phi)C_{2,0}(\beta) - 2\,\mathrm{Re}\,\varepsilon_{2,2}(\phi)C_{2,2}(\beta,\gamma) \quad (17)$$

It is necessary to model the dependence on ϕ of the interaction coefficients $\varepsilon_{2,m}(\phi)$, and we have done this by adopting the Additive Potential method which expresses these coefficients as[18,19] Equation (18)

$$\varepsilon_{2,m}(\phi) = \sum_{j}\sum_{p} \varepsilon_{2,p}(j)D^{2}_{p,m}(\Omega_j) \quad (18)$$

where the $\varepsilon_{2,p}(j)$ are conformationally independent interaction parameters for rigid fragments in the molecule, and $D^{2}_{p,m}(\Omega_j)$ is the second-rank Wigner function which describes the orientation of fragment j in a molecular frame of reference. For acrolein the fragment interaction coefficients used are given in Equation (19):

$$\varepsilon_{2,0}^{C=C} = k\varepsilon_{2,0}^{C=O}$$

$$\varepsilon_{2,0}^{C-C} \quad (19)$$

$\varepsilon_{2,0}^{C-H}$ equal for all C−H bonds

Note that choosing $\varepsilon_{2,0}^{C=C} = k\varepsilon_{2,0}^{C=O}$, where k is a constant, rather than two separate values is dictated by the geometry of the dominant *trans* form in which these bond directions are almost exactly parallel, which means that the contributions of $\varepsilon_{2,0}^{C=C}$ and $\varepsilon_{2,0}^{C=O}$ to the total interaction tensor cannot be separated. This is not true for the *cis* form, and so calculations were done with a range of values of k to ascertain the sensitivity of the results to this parameter.

Averaging over the full range 0 to 180°: Since dipolar couplings are a continuous function of ϕ, in principle the continuous dependence on ϕ of vibrational wavefunctions should be known. Since for acrolein, at the best of our knowledge, such dependence has not be studied, in the present work we have used the approximation of calculating the force fields, $\mathbf{F}_{\mathrm{trans}}$ and $\mathbf{F}_{\mathrm{cis}}$ just for the *trans* and *cis* forms, which are both positions of minimum energy. The values of $C^{ij}_{\alpha\beta}$ for $0 \leq \phi \leq 90°$ were derived from the calculated $\mathbf{F}_{\mathrm{trans}}$, and for $91 \leq \phi \leq 180°$ a similar procedure was used by with $\mathbf{F}_{\mathrm{cis}}$ replacing $\mathbf{F}_{\mathrm{trans}}$. In both cases the experimental frequencies of the *trans* form are used instead of the calculated one. No significant difference is observed by using for the *cis* form its own set of experimental vibrational frequencies.[15]

When averaging over small-amplitude vibrations and bond rotational motion it is essential not to include vibrational modes which correspond to torsional oscillations about the bond direction in the calculation of $D_{ij}(\mathrm{vib})$. Thus, for acrolein the vibrational mode with frequency 157.0 cm^{-1} was omitted when calculating $D_{ij}(\mathrm{vib})$ for couplings to H7, but included for the other couplings.

The variation of the energy of the isolated acrolein molecule with the bond rotation angle was calculated by the MP2/6-31G* method at 10° intervals with full geometry optimisation at each step, and the results are shown in Figure 5. The theoretical curve was fitted by a Fourier series, see Equation (20):

$$V(\phi) = V_1\cos\phi + V_2\cos 2\phi + V_3\cos 3\phi + V_4\cos 4\phi \quad (20)$$

with the coefficients given in Table 9, column A.

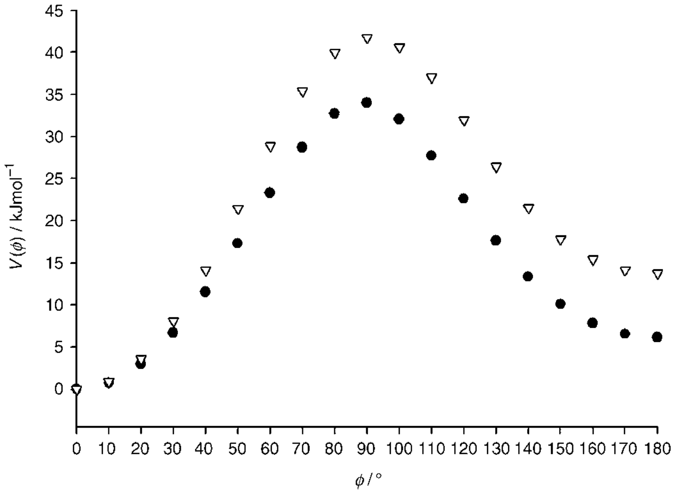


Figure 5. Potential function $V(\phi)$ calculated at the MP2/6-31G* level (●) and derived by fitting the dipolar couplings by the AP method, by using $k=3/2$, and adjusting the coefficients in a Fourier expansion (▽).

This function was equated to $U_{\mathrm{iso}}(\phi)$ in Equation (15) and the calculated dipolar couplings were fitted to those observed by varying the three interaction coefficients given in Equation (19). A value of $k=3/2$ was used, which, as we shall see, is a reasonable value. The values of r_{37} and θ_{237} were also varied, and the results are shown in Table 9, column A. The agreement between observed and calculated couplings is poor, with an unacceptable R value of 11.5 Hz. The calculation was repeated but varying also V_1 and V_2, and now the value of R has decreased to 0.84 Hz, with values of the individual residuals, ΔD_{ij}, shown in Table 9, column B.

The new function $V(\phi)$ is compared with that calculated for the isolated molecule in Figure 5, which shows that the NMR data predict a smaller amount of conformations in the range 90 to 180° ($\approx$0.5%) than does the MP2 calculation (8–10%) and the microwave data ($\approx$4%).

Fitting calculated to observed dipolar couplings by varying Fourier coefficients has the general problem that changing these coefficients affects the whole bond rotation potential and not just the relative amounts of the two conformers. A simpler approach has been developed recently[20] which overcomes this disadvantage of the Fourier method, and

Table 9. Geometries, ε values, Fourier coefficients, probability parameters of Equation (21), and $\Delta D_{ij} = D_{ij}(\text{equil}) + D_{ij}(\text{vib}) - D_{ij}(\text{obs})$ obtained using: i) the potential from MP2/6-31G* fitted as a Fourier series (column A); ii) a potential where V_1 and V_2 were optimized with respect to MP2/6-31G* potential (column B); iii) the probability function of Equation (21) (column C). In all cases vibrational corrections are included and the *ene*-fragment geometry was kept fixed at that in Table 5.

Parameters	A	B	C
$r_{3,7}$/Å	1.057 ± 0.011	1.121 ± 0.003	1.122 ± 0.004
$\measuredangle_{7,3,2}$/°	112.6 ± 0.5	114.5 ± 0.2	114.5 ± 0.2
$\varepsilon_{2,0}^{(C=C)} = (^3/_2)\cdot\varepsilon_{2,0}^{(C=O)}$/kJ mol^{-1}	0.453 ± 0.006	0.430 ± 0.002	0.430 ± 0.002
$\varepsilon_{2,0}^{(C-C)}$/kJ mol^{-1}	0.551 ± 0.004	0.554 ± 0.001	0.554 ± 0.001
$\varepsilon_{2,0}^{(C-H)}$/kJ mol^{-1}	0.053 ± 0.004	0.076 ± 0.002	0.076 ± 0.002
V_1/kJ mol^{-1}	1.93 ± 0.08[a]	5.5 ± 0.4	–
V_2/kJ mol^{-1}	15.17 ± 0.08[a]	15.7 ± 1.7	–
V_3/kJ mol^{-1}	1.27 ± 0.08[a]	1.27 ± 0.08[a]	–
V_4/kJ mol^{-1}	−1.77 ± 0.08[a]	−1.77 ± 0.08[a]	–
A	–	–	5.1 ± 0.3
$h_t = h_c$/°	–	–	12.5 ± 0.8
R/Hz	11.50	0.84	0.85
i,j	ΔD_{ij}/Hz	ΔD_{ij}/Hz	ΔD_{ij}/Hz
1,4	4.6	−0.1	−0.1
1,5	5.1	0.0	0.0
1,6	0.4	0.0	0.0
1,7	−8.0	0.8	0.8
2,4	0.4	0.0	0.0
2,5	−0.1	0.0	0.0
2,6	3.6	−0.1	−0.1
2,7	−11.9	2.6	2.7
3,4	−1.1	−1.2	−1.2
3,5	0.1	0.0	0.0
3,6	−0.5	−1.5	−1.5
3,7	−2.1	0.2	0.2
4,5	6.9	−0.2	0.0
4,6	−0.5	0.0	0.0
4,7	0.0	0.0	0.0
5,6	0.2	0.1	0.1
5,7	−10.7	−0.7	−0.7
6,7	−44.1	−0.9	−0.9

[a] Kept fixed in the optimization process.

which expresses the probability $P_{\text{iso}}(\phi)$, as a sum of Gaussian functions. For the case of acrolein the Gaussian functions are centred at ϕ equal to 0 and 180°, with widths at half maximum height of h_t and h_c, see Equation (21):

$$P_{\text{iso}}(\phi) = \frac{1}{(2Q_{ct}h_t^2\pi)^{1/2}}\exp[-\frac{\phi^2}{2h_t^2}] + \frac{e^{-A}}{(2Q_{ct}h_c^2\pi)^{1/2}}\exp[-\frac{(\phi-180^o)^2}{2h_c^2}] \tag{21}$$

With Equation (22)

$$Q_{ct} = (1+e^{-2A}) \tag{22}$$

$P_{\text{iso}}(\phi)$ is not in general equal to $P_{\text{LC}}(\phi)$, but for low ordered solutes as is the case for acrolein in I52, the two functions are practically identical. Fitting the dipolar couplings calculated with this probability function by varying A, $\varepsilon_{2,0}^{C=C} = k\varepsilon_{2,0}^{C=O}$, $\varepsilon_{2,0}^{C-C}$, $\varepsilon_{2,0}^{C-H}$, r_{37} and θ_{237} and independent values of h_t and h_c does not produce a stable solution because the latter two variables are strongly correlated. This correlation was removed by making $h_t = h_c$.

Calculations done with values of $k < 3$ produce R values of < 0.9 Hz, and all predict $P_{\text{cis}} < 0.007$. These calculations give always the same $\mathbf{S}_{\text{trans}}$ (Table 8) since, as mentioned above, it depends on the total interaction tensor given by the sum $\varepsilon_{2,0}^{C=C} + \varepsilon_{2,0}^{C=O} = (1+k)\varepsilon_{2,0}^{C=O}$; on the contrary, on changing k the calculations give a different order matrix $\mathbf{S}_{\text{cis}}$, as shown in Figure 6 where the order parameters values calculated at different k are compared with the values simulated by the model of Celebre[17] discussed above. The box dimensions used are $L = 6.70$ Å; W = 5.63 Å and $B = 3.40$ Å: there is excellent agreement between observed and calculated order matrices for $k = ^3/_2$ as reported in Table 8, and there is also good agreement between the NMR, microwave, and MP2 derived values for the C–H bond length, r_{37}, and the CCH bond angle θ_{237}. These calculations suggest that acrolein in this liquid crystal solvent is almost entirely in the *trans* form with a Gaussian distribution of $P(\phi)$ with a width at half height of 12.5 ± 0.8° (Table 9, column C).

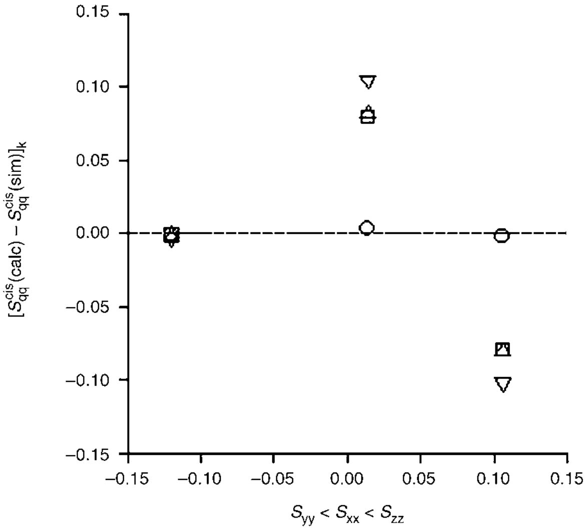


Figure 6. Differences between simulated and AP-calculated $\mathbf{S}_{\text{cis}}$ order parameters for different k values: ○: $^3/_2$, □: 1, △: $^2/_3$, ▽: $^1/_3$.

A estimate of the conformer distribution from scalar couplings: A calculation of $^2J_{HH}$ and $^3J_{HH}$ coupling constants for single *cis*- and *trans*-conformations of acrolein has been carried out by the CS-INDO method.[21] It is claimed that this method, which allows for electron correlation, gives accurate values for the H–H couplings, and it is used here to give an estimate of the relative weights of the *cis* and *trans* conformations of acrolein dissolved in $CDCl_3$. So, in the hypothesis of a two-site equilibrium of the molecule, the theoretical values reported in Table 10, $J_{ij}(\textit{trans})$ and $J_{ij}(\textit{cis})$ have been used, according to the Equation (23):

$$J_{ij} = P_{\text{trans}} J_{ij}(\textit{trans}) + (1-P_{\text{trans}}) J_{ij}(\textit{cis}) \tag{23}$$

Table 10. Observed and theoretically predicted scalar couplings $^{2}J_{HH}$ and $^{3}J_{HH}$ for acrolein dissolved in $CDCl_3$.

	Scalar couplings/Hz Calculated[21]			Evaluated from
	cis-acrolein	*trans*-acrolein	Experiment	Eq. (23), with $P_{trans} = 0.95$
$^{2}J_{4,5}$/Hz	0.91	0.93	0.7 ± 0.2	0.9
$^{3}J_{4,6}$/Hz	17.92	18.01	17.4 ± 0.1	18.0
$^{3}J_{5,6}$/Hz	11.34	9.66	10.0 ± 0.2	9.7
$^{3}J_{6,7}$/Hz	1.57	8.24	8.0 ± 0.2	7.9

to obtain a value of $P_{trans} = 0.95$ optimising the whole agreement ($R = 0.35$) with experimental values. It is difficult to estimate an error on this value of P_{trans} but it indicates that the conformational distribution of acrolein in solution is not strongly influenced by changing from a relatively complex molecule such as I52 to the simpler $CDCl_3$.

Conclusion

The present NMR data for acrolein dissolved in I52 indicate that there is a small, <1%, of the *cis* conformer present at equilibrium at 300 K. This is significantly smaller than the amount of *cis* present in the vapour phase at 295 K, which could be a real effect of the solvent on the equilibrium, but may also reflect, in part, the systematic errors introduced by the approximations necessarily introduced when calculating values of D_{ij}(equil). The geometry of acrolein derived from the dipolar couplings is essentially that of the *trans* form, and is in good, but not perfect agreement with that derived by the microwave study. The differences probably reflect the neglect of vibrational averaging of the microwave data, hence producing a “least squares” and not an equilibrium geometry, together with systematic errors in the method for treating the NMR data. There could certainly be a real solvent effect on the geometry, which in the case of a liquid crystal phase could be correlated with the orientational order.

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