^{13}C Chemical Shift Tensors in Organic Single Crystals [and Discussion]

W. S. Veeman and D. J. Greenslade

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^{13}C chemical shift tensors in organic single crystals

By W. S. Veeman
Department of Physical Chemistry, University of Nijmegen,
Toernooiveld, 6525 ED Nijmegen, The Netherlands

It is described how ^{13}C chemical shift tensors can be determined from proton enhanced ^{13}C n.m.r. experiments on single crystals.

^{13}C chemical shift tensors of aromatic ring carbons, carbonyl carbons, carboxyl carbons and methyl carbons are discussed and compared for groups of related molecules.

Introduction

In a nuclear magnetic resonance experiment the resonance frequency of a nuclear spin $\boldsymbol{S}$ is not only determined by the gyromagnetic ratio γ but also by the interaction of the nuclear spin with the surrounding electrons. In diamagnetic materials with no net electron spin or orbital angular momentum, this chemical shift is a second-order effect proportional to the external magnetic field $\boldsymbol{H}_0$ and can be represented by the Hamiltonian:

$$\mathscr{H}_{\text{c.s.}} = \gamma \boldsymbol{H}_0 \cdot \boldsymbol{\sigma} \cdot \boldsymbol{S}, \tag{1}$$

where $\boldsymbol{\sigma}$ is a dimensionless, effectively symmetric (Haeberlen 1976), second-rank tensor, representing the anisotropic shift of the resonance frequency in bulk matter with respect to that of a bare nucleus.

In solutions the molecular rotations average out the anisotropic part of this chemical shift tensor, leaving the isotropic part:

$$\sigma_i = \tfrac{1}{3}\,\mathrm{tr}\,(\boldsymbol{\sigma}) = \tfrac{1}{3}(\sigma_{11}+\sigma_{22}+\sigma_{33}), \tag{2}$$

where σ_{11}, σ_{22} and σ_{33} are the principal elements of the chemical shift tensor. In solids there usually is not enough isotropic molecular rotation to average out the chemical shift tensor. Therefore the resonance frequency of a certain spin in a solid depends on the direction of the external field relative to the sample. This is the experimental manifestation of the fact that the electron cloud surrounding the nucleus usually does not have spherical symmetry. Thus the complete chemical shift tensor gives information about the local symmetry of the electron cloud around the nucleus and therefore presents a much more detailed picture of the chemical bonding of a certain atom than the isotropic chemical shift measured in solution.

The chemical shift tensor is completely defined by three principal elements σ_{11}, σ_{22}, σ_{33} and the direction of three principal axes. Although the principal elements can be determined from powder spectra, the direction of the principal axes can usually only be found from experiments on single crystals. In this review only ^{13}C n.m.r. studies of single crystals are discussed.

In solids the chemical shift interaction is not the only anisotropic interaction that determines the spectrum. The dipolar interaction (Abragam 1961) between spins usually affects the resonance frequency more than the chemical shift interaction. This dipolar interaction in most cases causes such a severe line broadening in conventional n.m.r. that effects of the chemical shift interaction are obscured. The proton enhanced ^{13}C n.m.r. technique of Pines *et al.* (1973) can be applied to systems with ^{13}C and ^{1}H spins. It removes line broadening due to ^{13}C–^{1}H dipolar interaction and enhances the intrinsic low n.m.r. sensitivity of ^{13}C spins, while leaving the ^{13}C chemical shift tensor unperturbed; line broadening due to ^{13}C–^{13}C dipolar interactions can be neglected thanks to the large average distance between the low abundance (*ca.* 1 %) ^{13}C spins. Therefore this technique is very much suited for the study of chemical shift tensors in organic single crystals.

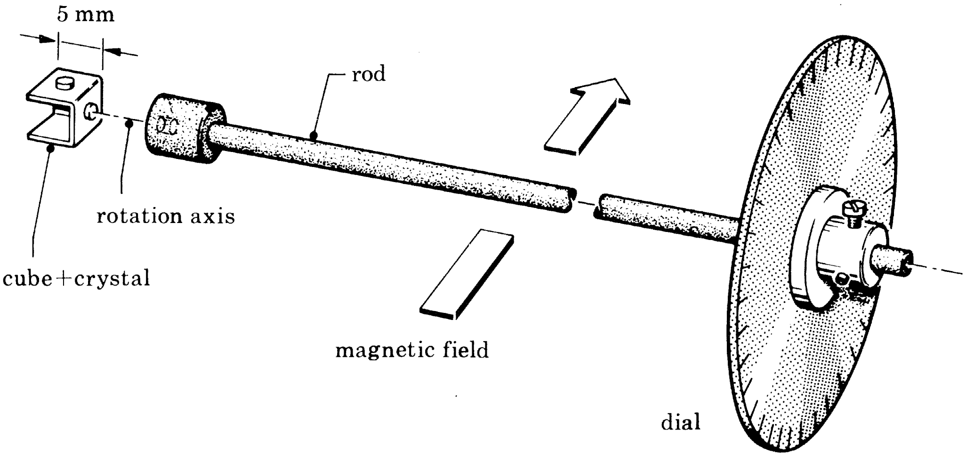

FIGURE 1. Goniometer assembly; the crystal is mounted in a hollow cube made of epoxy resin of which two sides are missing. The cube fits to the rotation axis with three orthogonal planes.

EXPERIMENTAL

^{13}C chemical shift tensors of single crystals can be determined with a high-power proton–carbon double-resonance spectrometer, suitable for the proton enhanced ^{13}C n.m.r. technique (Pines *et al.* 1973), in which the single crystal can be rotated with respect to the external magnetic field. Several of these goniometer designs have been published (Pausak *et al.* 1973; Kempf *et al.* 1974; Pines *et al.* 1974), the main requirement being that the crystal can be rotated around three, preferably orthogonal, axes. Our solution to this problem for an electromagnet (van Dongen Torman 1978) is sketched in figure 1. In many cases one wants to study the chemical shift tensors at a particular temperature or at variable temperatures. It should therefore be possible to cool or heat the sample, for instance with a flow of nitrogen gas of which the temperature can be controlled and kept stable for a sufficiently long time.

DETERMINATION OF CHEMICAL SHIFT TENSORS

Since chemical shifts are small (*ca.* millionths) we may apply first-order perturbation theory to calculate the effect of the chemical shift Hamiltonian (1). For the shift of the energy levels we find

$$\langle m|\gamma \boldsymbol{H}_0\cdot\boldsymbol{\sigma}\cdot\boldsymbol{S}|m\rangle = m\gamma\sigma_{\mathrm{L}}H_0, \tag{3}$$

where σ_{L} represents the component of $\boldsymbol{\sigma}$ parallel to $\boldsymbol{H}_0$. When the chemical shift tensor in some axis system x, y, z is represented by

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}, \tag{4}$$

then σ_L can be written as (Weil *et al.* 1973)

$$\sigma_L = \boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n}^{-1} = \sigma_{xx}\sin^2\theta\cos^2\phi + \sigma_{yy}\sin^2\theta\sin^2\phi + \sigma_{zz}\cos^2\theta + \sigma_{yx}\sin^2\theta\sin 2\phi + \sigma_{zx}\sin 2\theta\cos\phi + \sigma_{zy}\sin 2\theta\sin\phi, \qquad (5)$$

where $\boldsymbol{n}$ is the unit vector along $\boldsymbol{H}_0$, defined by polar angles θ and ϕ in the axis system x, y, z.

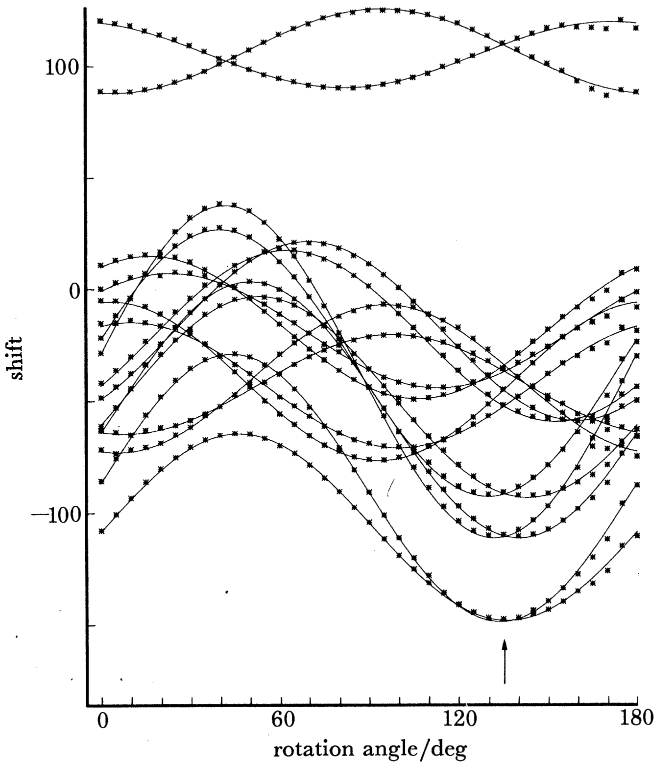

FIGURE 2. Rotational plot of acetophenone for rotation about an arbitrary axis. Shifts are in millionths from liquid benzene.

To find the six components of the chemical shielding tensor it is sufficient to measure the shift σ_L in six well defined independent directions and to solve the resulting six equations (5). If the spectra contain more than one line, because of the presence of chemically and/or magnetically inequivalent (Haeberlen 1976) nuclei, it is difficult to determine unambiguously from the spectra in the six directions which lines arise from the same nucleus. For this reason, a common procedure is to rotate the crystal around three axes and measure the shifts as a function of the rotation angle ρ. Such a rotation pattern for acetophenone (van Dongen Torman *et al.* 1978) is shown in figure 2. The analysis of such patterns have been described for tensor interactions in e.s.r. (Poole 1972) and n.m.r. (Weil *et al.* 1973).

Here I give the procedure used by van Dongen Torman (1978) and will use acetophenone as an example. In this case the sample rotation axis is always perpendicular to $\boldsymbol{H}_0$. We can define an axis system x_i, y_i, z_i, fixed to the sample, such that z_i is parallel to the rotation axis and x_i is chosen parallel to $\boldsymbol{H}_0$ at $\rho_i = 0$, i.e. where the rotation is started. The shift of a particular line k as a function of the rotation angle ρ_i can then be obtained from (5) by inserting $\theta = 90°$ and $\phi = \rho_i$:

$$\sigma_L^{ki}(\rho_i) = \tfrac{1}{2}(\sigma_{xx}^{ki} + \sigma_{yy}^{ki}) + \tfrac{1}{2}(\sigma_{xx}^{ki} - \sigma_{yy}^{ki})\cos 2\rho_i + \sigma_{xy}^{ki}\sin 2\rho_i. \qquad (6)$$

For each rotation axis i we can determine the components σ^{ki}_{xx}, σ^{ki}_{yy} and σ^{ki}_{xy} in the axis system x_i, y_i, z_i for all peaks k by fitting (6) to the measured shift by a least-squares procedure. To relate the rotation patterns of different rotation planes i we make use of the fact that when $\boldsymbol{H}_0$ is parallel to the line of intersection of two planes i and j, the peak positions of all lines in plane i are equal to those of plane j.

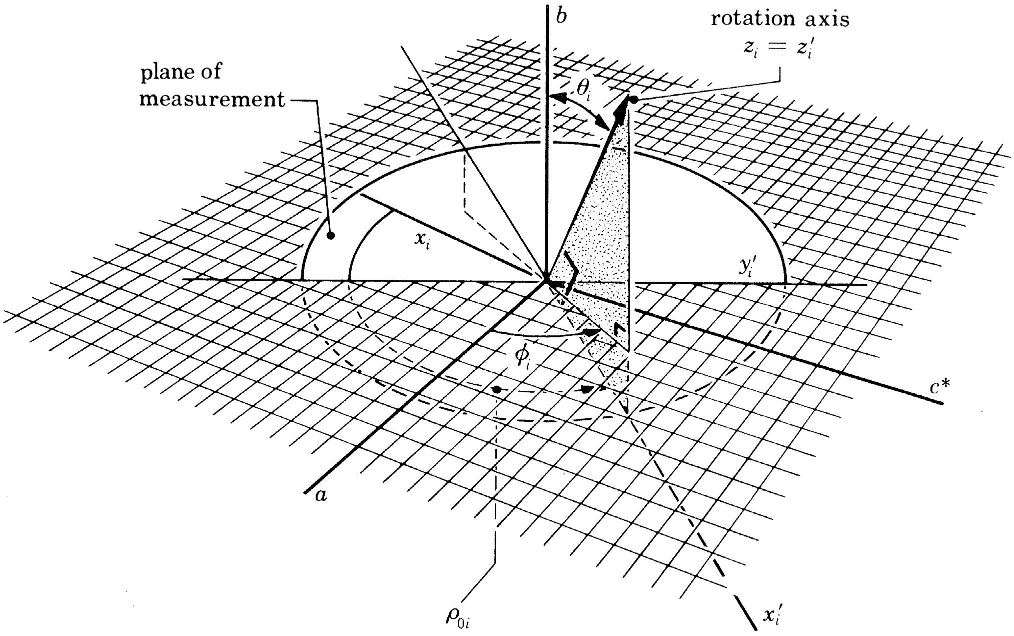

FIGURE 3. Orientation of the rotation axis and the plane of measurement with respect to the crystal axes a, b, c^*.

Although we are ultimately interested in the orientation of the chemical shift principal axes with respect to the molecular axes, it is convenient to calculate the tensor components first with respect to the crystal axes. This has the further advantage that the relation between tensors belonging to symmetry-related molecules takes a particularly simple form. We define an orthogonal crystal axis system a, b, c. For orthorhombic crystals, for instance, the choice of these axes is evident; for monoclinic crystals such as acetophenone the c axis is the c^* axis. As mentioned above, acetophenone is taken as an example and thus we may use the fact that the ac^* plane is a reflexion plane. Other crystals may have other symmetry elements; the following can easily be changed to make use of these other symmetry elements. The transformation from the sample axis system x_i, y_i, z_i, connected to rotation axis i, to the crystal axis system a, b, c^* is performed in two steps. See figure 3 for the location of the axes.

1. With a rotation around the z_i axis we transform to the primed sample axis system x_i', y_i', z_i' of which $z_i' = z_i$ and y_i' parallel to the line of intersection between the x_i, y_i plane (the plane of measurement) and the ac^* plane. Then, automatically, the x_i' axis is in the plane containing both the z_i' axis and the crystallographic b axis. This transformation is described by:

$$R_i = \begin{bmatrix} \cos\rho_{0i} & \sin\rho_{0i} & 0 \\ -\sin\rho_{0i} & \cos\rho_{0i} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad (7)$$

where ρ_{0i} is the angle between x_i and x'_i. To determine ρ_{0i} we make use of the fact that ac^* is a plane of reflexion in the acetophenone crystal. When $\boldsymbol{H}_0$ is parallel to this plane, the number of measured n.m.r. lines is reduced by a factor two because symmetry-related sites become magnetically equivalent. As defined above, the rotational pattern is started with $\boldsymbol{H}_0 // x_i$. When the field is rotated over an angle $(\rho_{0i}+90°)$, $\boldsymbol{H}_0$ is parallel to the ac^* plane where the number of lines is halved (see the arrow in figure 2). Therefore from the rotational plots ρ_{0i} can easily be found, at least when some symmetry is present in the crystal.

2. The transformation from the primed sample axes to the crystal axes is given by Weil *et al.* (1973):

$$U_i = \begin{bmatrix} \cos\theta_i \cos\phi_i & -\sin\phi_i & \sin\theta_i\cos\phi_i \\ \cos\theta_i\sin\phi_i & \cos\phi_i & \sin\theta_i\sin\phi_i \\ -\sin\theta_i & 0 & \cos\theta_i \end{bmatrix}, \tag{8}$$

where θ_i and ϕ_i are the polar angles of the rotation axis i in the crystal axis system a, b, c^*.

In principle, the orientation of the rotation axis i with respect to the crystal axis system can be determined by X-ray spectroscopy. In that case the problem is solved. Using the transformation matrices (7) and (8) we find the chemical shift tensor $\boldsymbol{\sigma}_c^k$ of peak k in the crystal axis system from the measured components of $\boldsymbol{\sigma}^{ki}$:

$$\boldsymbol{\sigma}_c^k = R_i U_i \boldsymbol{\sigma}^{ki} U_i^{-1} R_i^{-1}. \tag{9}$$

If the crystal structure is known, the tensors $\boldsymbol{\sigma}_c^k$ can be transformed to the molecular axes. Diagonalization then yields the principal elements and principal orientations relative to the molecular axes. If the crystal structure is not known, but the unit cell contains two or more molecules related by symmetry, then symmetry elements like n-fold axes and reflexion planes (not an inversion centre) may be determined from the tensors of chemically equivalent but magnetically inequivalent molecules. These tensors are related by the crystal symmetry elements. In this way the chemical shift tensors can be used to help solve crystal structures.

In many instances, however, the orientation of the rotation axis i cannot be determined by X-ray techniques because the n.m.r. samples are too thick. If in such a case the crystal structure is known and the unit cell contains two or more molecules related by symmetry (chemically equivalent but magnetically inequivalent), then the orientation of the rotation axes i can very often be found by using symmetry arguments. For instance, suppose that in a crystal one of the symmetry operations S relates molecule 1 to molecule 2, then

$$\boldsymbol{\sigma}_c^k(2) = S\boldsymbol{\sigma}_c^k(1)\,S^{-1}, \tag{10}$$

where $\boldsymbol{\sigma}_c^k(2)$ is the chemical shift tensor of carbon k in molecule 2, expressed in the crystal axis system. From the relations

$$\left.\begin{aligned} \boldsymbol{\sigma}_c^k(1) &= R_i U_i \boldsymbol{\sigma}^{ki}(1)\, U_i^{-1} R_i^{-1} \\ \text{and}\qquad S\boldsymbol{\sigma}_c^k(1)\,S^{-1} &= R_i U_i \boldsymbol{\sigma}^{ki}(2)\, U_i^{-1} R_i^{-1}, \end{aligned}\right\} \tag{11}$$

expressions can be found for θ_i and ϕ_i. Often, the symmetry operation S applied to the rotation axis i does not change one of the angles θ_i or ϕ_i (for instance if S represents a reflexion plane as in acetophenone, then ϕ_i does not change). Only one of the angles can then be determined from (11) and one has to use another symmetry operation as well. Once θ_i and ϕ_i are known, we can again proceed by transforming the shifts to the crystal axis system, and, using crystal structure data, to the molecular axis system. Diagonalization in this last axis system yields the principal elements and principal orientations.

Figure 4 shows a pictorial representation of the shielding tensors of acetophenone (van Dongen Torman *et al.* 1978).

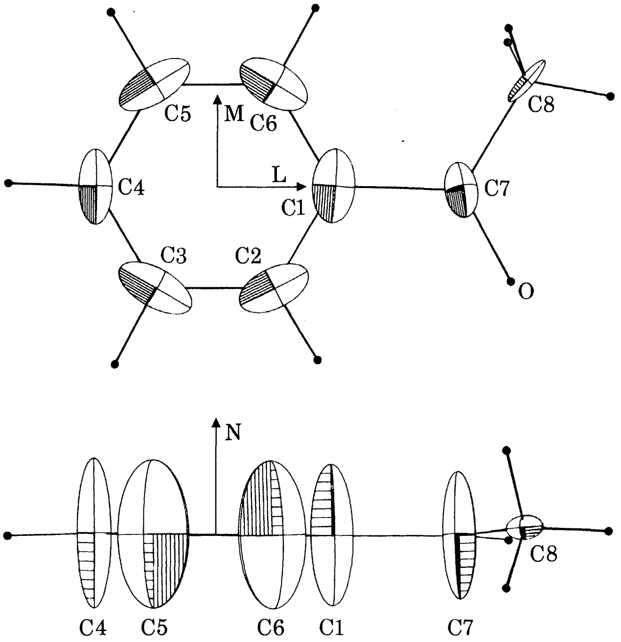

FIGURE 4. Representation of the ^{13}C chemical shielding tensors in acetophenone (van Dongen Torman *et al.* 1978). The length of the ellipsoid axes is proportional to the shielding in that direction relative to a reference that is different for every type of carbon atom and defined by $\sigma_{ref} = \sigma_{11} - \frac{1}{3}(\sigma_{33} - \sigma_{11})$ (Mehring 1976). The size of the ellipsoids is a measure of the anisotropy of the corresponding tensors. The methyl tensor is magnified by two.

^{13}C SHIELDING TENSORS

The number of systems for which the complete ^{13}C chemical shift tensors have been determined from single crystal experiments is rather limited. Many more chemical shieldings have been found from powder experiments; then, of course, the orientation of the principal axes cannot be determined. A survey of all chemical shift data from solid state n.m.r. can be found in Mehring's book (1976). Since then only a few more crystal (van Dongen Torman *et al.* 1977, 1978; Becker *et al.* 1978) and powder studies (Höhener 1978; Linder *et al.* 1979) have been reported. Here I shall limit the discussion to single-crystal studies of some groups of related molecules, methylbenzenes, aromatic carbonyls and carboxylic acids. For these systems a comparison will be made of the chemical shift tensors of aromatic ring, carbonyl, carboxyl and methyl carbons.

Aromatic ring carbons

Table 1 shows the principal elements of the non-substituted carbons in the aromatic rings of *p*-xylene, durene and pentamethylbenzene. Also included are the values for benzene, obtained from powder experiments. For the substituted carbons in these molecules the elements are given in table 2. There are no spectacular differences between corresponding elements of different molecules. Apparently, the principal elements are mainly determined by the local structure around the aromatic carbons. The directions of the principal axes are even more invariant to perturbation of the ring by methyl substitution. In all alkylbenzenes investigated, the most shielded direction, σ_{33}, is perpendicular to the aromatic plane within the accuracy of the experiment. The least shielded directions, σ_{11}, are approximately parallel to the C–H bond and the intermediate shielding direction tangential to the ring. The shielding axes therefore reflect accurately the structure of the isolated molecule, for the alkylbenzenes intermolecular interactions hardly perturb the local symmetry around the ring carbons.

Table 1. Chemical shift tensor elements of non-substituted ring carbons in benzene and some polymethylbenzenes

(All shifts are in millionths relative to liquid benzene.)

	temperature/K	σ_{11}	σ_{22}	σ_{33}	σ_i	σ_{solution}	reference
benzene	14	−88	−12	128	9	0	Linder *et al.* (1979)
	223	−60	−60	120	0	0	Pines *et al.* (1972)
p-xylene	100	−98	−9	109	0.6	0.5	van Dongen Torman & Veeman (1978)
		−98	−5	106	1	0.5	
durene	300	−94	6	83	−1.7	−2.5	Pausak *et al.* (1973)
pentamethylbenzene	300	−86	−1.5	81	−2.4	−2.8	Pausak *et al.* (1974)

Table 2. Chemical shift tensor elements of the methyl-substituted ring carbons in some polyalkylbenzenes

(All shifts are in millionths relative to liquid benzene.)

	temperature/K	σ_{11}	σ_{22}	σ_{33}	σ_i	σ_{solution}	reference
p-xylene	100	−104	−33	122	−5	−6	van Dongen Torman & Veeman (1978)
durene	300	−102	−28	111	−5.8	−5	Pausak *et al.* (1973)
		−97	−27	126	−4.3	−5	
pentamethylbenzene	300	−86	−34	109	−3.9	−4.3	Pausak *et al.* (1974)
		−89	−34	109	−4.9	−3.4	
		−87	−31	105	−4.4	−5.8	
		−89	−34	108	−4.8	−3.4	
		−87	−32	108	−3.6	−4.3	
hexamethylbenzene	300	−59	−58	108	−3	−3.6	
	87	−98	−26	110	−4.3	−3.6	
hexaethylbenzene	300	−92	−35	107	−6.6	−8.7	
		−91	−36	108	−6.3	−8.7	
		−92	−35	107	−6.7	−8.7	

When we as usual represent the chemical shift as the sum of a (shielding) diamagnetic part and a (deshielding) paramagnetic part,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\text{d}} + \boldsymbol{\sigma}_{\text{p}},$$

it can be easily seen that the paramagnetic term is at least partly responsible for the fact that the most shielded direction is found perpendicular to the ring. The component of $\boldsymbol{\sigma}_{\text{p}}$ perpendicular to the ring, by symmetry reasons, arises from second-order coupling of the ground state with excited $\sigma\sigma^*$ states. The in-plane shielding components are determined by interaction with $\sigma\pi^*$ and $\pi\sigma^*$ states, which have an appreciably lower excitation energy than $\sigma\sigma^*$ states. Therefore the second-order contribution of the $\sigma\pi^*$ and $\pi\sigma^*$ states to the in-plane components of the paramagnetic shielding is larger than this contribution of $\sigma\sigma^*$ states to the perpendicular component of $\boldsymbol{\sigma}_{\text{p}}$. Because of the negative sign of the paramagnetic shielding, this contributes to the fact that the most shielded direction is perpendicular to the aromatic ring.

From table 1 we see that when the number of CH_3 groups substituted to the ring increases, the shielding perpendicular to the ring of the non-substituted carbons decreases from 128×10^{-6} in benzene to 81×10^{-6} in pentamethylbenzene. The changes of the other elements, σ_{11} and σ_{22}, are either not very significant (σ_{11}) or not very systematic (σ_{22}). The significant change of σ_{33} of the non-substituted carbons upon methyl substitution shows that CH_3 groups not only take part in the π electron bonding of the aromatic ring, but also must change σ electron molecular orbitals of the carbons not directly bonded to the methyl group.

The difference between a non-substituted carbon atom and a methyl-substituted carbon in a methylbenzene is most clearly expressed by the difference in σ_{22}. For non-substituted carbons, σ_{22} is between $+6$ and -9×10^{-6} and for substituted carbons between -27 and -36×10^{-6} (see tables 1 and 2). The effect of further methyl substitution on the principal elements of an already methyl-substituted carbon is not as significant as for unsubstituted carbons. Therefore it is not easy to conclude whether methyl substitution has the larger effect on the carbon to which it is bonded or on the neighbouring, non-substituted carbon.

TABLE 3. ARYL CARBON SHIELDINGS IN ACETOPHENONE AT 100 K
(van Dongen Torman *et al.* 1978)

(All shifts are in millionths relative to liquid benzene.)

carbon†	σ_{11}	σ_{22}	σ_{33}	σ_i	σ_{solution}‡
1	−95	−29	101	−5	−8
2	−99	−28	131	1	0
3	−101	−16	121	1	0
4	−112	−27	125	−5	−3
5	−106	−17	122	0	0
6	−94	−29	121	−1	0

† Carbon 1 is the substituted carbon.
‡ Stothers (1972).

Table 3 shows the effect of $COCH_3$ substitution on the aromatic ring carbons of acetophenone. Figure 4 shows the orientations of the principal axes. For the carbon bonded to the substituent it makes very little difference if the substituent is a $COCH_3$ group like in acetophenone or a CH_3 group like in *p*-xylene or one of the other methylbenzenes. For the non-substituted carbons this difference is somewhat greater.

Tables 1 and 2 also show the value for $\sigma_i = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ and the isotropic value found from solution n.m.r. Usually the values for σ_i and σ_{solution} are quite close, except for the low-temperature values of benzene. Apparently, the low temperature not only stops the benzene rotation around the hexagonal axis but also changes the molecular structure.

Table 1 shows a decrease of the isotropic shielding with an increase of the number of methyl groups. In the literature (see, for example, Stothers 1972) additivity relations have been proposed for these methylbenzenes. However, because the changes in the isotropic values are the sum of larger changes of opposite signs, the value of such additivity relations seems questionable.

Carbonyl carbons

Table 4 shows the principal elements of the carbonyl carbons of benzophenone and acetophenone and figure 5 the directions of their principal axes. In both cases the most shielded direction is perpendicular to the sp^2 plane of the carbonyl carbon. Although the principal elements are quite similar, the directions of the in-plane principal axes are different. In a single crystal the benzophenone molecule has approximately C_2 symmetry and therefore by symmetry one of the principal axes should be nearly parallel to the C=O axis and this has been confirmed by experiment (Kempf *et al.* 1972). For the acetophenone molecule the symmetry is lower and one of the principal axes is no longer confined to be parallel to the C=O axis. For comparison, table 4 also shows the principal elements of thiobenzophenone obtained from a powder spectrum (Kempf *et al.* 1974). Although the principal axes for the C–S carbon in thiobenzophenone have not been determined, Kempf *et al.* conclude, by relating the components of σ_p to the $n\pi^*$ excitation energies in benzophenone and thiobenzophenone, that in thiobenzophenone the least shielded directions, σ_{11}, is parallel to the C–S bond. In benzophenone, σ_{22} is parallel to C=O. This makes thiobenzophenone an interesting candidate for a single-crystal study.

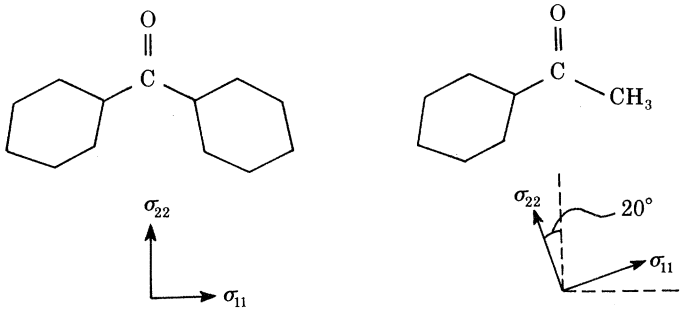

FIGURE 5. The principal axes of the carbonyl carbon in benzophenone (Kempf *et al.* 1972) and acetophenone (van Dongen Torman *et al.* 1978). For both molecules the most shielded orientation, σ_{33}, is perpendicular to the carbon sp^2 plane.

TABLE 4. CHEMICAL SHIFT TENSOR ELEMENTS OF C=O AND C=S CARBONS

(All shifts are in millionths relative to liquid benzene.)

	σ_{11}	σ_{22}	σ_{33}	σ_i	σ_{solution}	reference
benzophenone	−143	−100	30	−71	−66.5	Kempf *et al.* (1974)
acetophenone	−150	−103	45	−69	−67	van Dongen Torman *et al.* (1978)
thiobenzophenone	−255	−146	80	−107	−96	Kempf *et al.* (1974)

Carboxyl carbons

The chemical shift tensors of carboxyl carbons are among the most investigated (Mehring 1976). Here I shall compare the results for acetic acid, benzoic acid and oxalic acid. Table 5 shows the principal elements and figure 6 the directions of the principal axes. For these carboxyl compounds, intermolecular hydrogen bonding plays an important role. In solid benzoic acid, the molecules form dimers because of this hydrogen bonding. All atoms are approximately in one plane and the two halves of the dimer are related by a centre of symmetry. The principal axes of the carboxyl carbon are therefore along symmetry axes of the dimer, showing that the two oxygen atoms of the carboxyl groups are equivalent. In acetic acid, the hydrogen bonding is different from in benzoic acid. Here the molecules form infinite chains (Jönsson 1971) (see figure 7). In this case the two oxygens are not equivalent, as clearly shown by the orientation of the principal axes (figure 6). There is nevertheless not a great difference in the principal elements of benzoic and acetic acids.

In oxalic acid dihydrate and anhydrous oxalic acid, σ_{22} is shifted towards increased shielding. For oxalic acid dihydrate, the directions of the principal axes have been determined. The σ_{33} orientation is abnormal: it is tilted off the perpendicular to the COO plane by *ca.* 20° by a rotation around σ_{22} (Griffin *et al.* 1975). For this compound the oxygens are involved in hydrogen bonding with the water molecules in the lattice and not, as in acetic acid and benzoic acid, between the oxalate molecules. This may cause the difference in the orientation of the principal axes. This illustrates, however, how sensitive the principal axis orientations of carboxyl carbons are to intermolecular interactions, in contrast to aromatic ring carbons. The latter are found in the interior of the molecule and therefore less susceptible to intermolecular interactions.

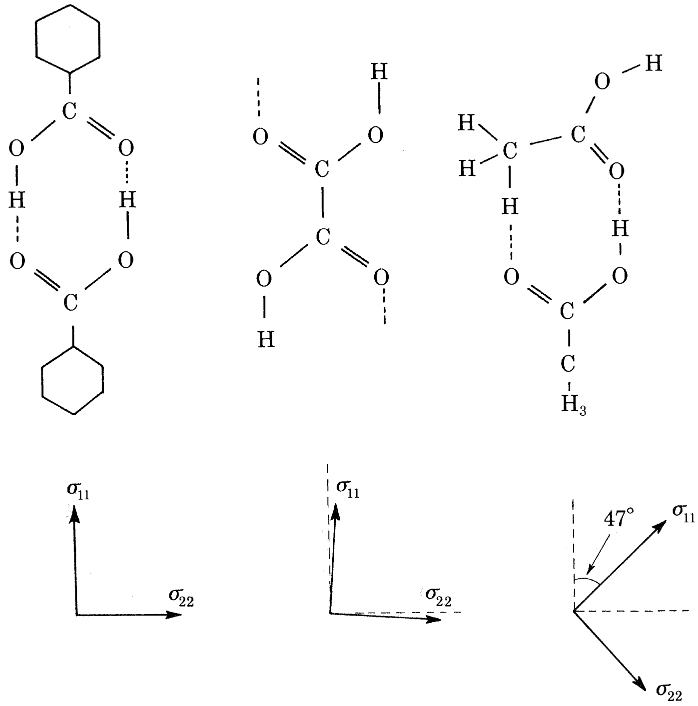

FIGURE 6. The principal axes of the carboxyl carbon in benzoic acid (Kempf *et al.* 1974), oxalic acid dihydrate (Griffin *et al.* 1975) and acetic acid (van Dongen Torman *et al.* 1977). Intermolecular hydrogen bonding is shown for benzoic acid and acetic acid. In oxalic acid dihydrate, hydrogen bonding occurs with H_2O molecules in the lattice. For benzoic and acetic acids the most shielded direction, σ_{33}, is perpendicular to the COO plane; in oxalic acid dihydrate, σ_{33} is tilted by 20°.

TABLE 5. CHEMICAL SHIFT TENSOR ELEMENTS IN SOME CARBOXYL CARBONS

(All shifts are in millionths relative to liquid benzene.)

	σ_{11}	σ_{22}	σ_{33}	σ_i	σ_{solution}	reference
benzoic acid	−102	−59	26	−45	−44	Kempf *et al.* (1974)
acetic acid	−136	−52	24	−55	−49	van Dongen Torman *et al.* (1977)
oxalic acid dihydrate	−120	−3	20	−34	−33	Griffin *et al.* (1975)
anhydrous oxalic acid	−122	6	17	−33	−33	

Table 5 also shows that there is a 6×10^{-6} difference between the isotropic value for acetic acid in the solid and liquid states. This can be attributed to a difference in molecular structure in the two phases. In the liquid state the acetic acid structure is quite complex: open and closed dimers as well as oligomers are assumed to coexist (Haurie *et al.* 1967). In the solid the acetic acid molecules form infinite chains.

Methyl carbons

Table 6 shows the methyl carbon principal elements of *p*-xylene, durene, hexamethylbenzene and acetic acid. In most cases the methyl carbons display almost axially symmetric shielding tensors with the most shielded direction, σ_{33}, along the C–C axis. The anisotropy is small; in hexamethylbenzene it is even close to zero. The approximate axial symmetry is no doubt caused by CH_3 rotation. However, that does not mean that one of the principal axes is automatically along the C–C axis. Acetic acid is a good example. Figure 8 shows the principal axes of the acetic acid methyl group. The σ_{33} axis makes an angle of 19° with the C–C axis. Neutron diffraction studies (Jönsson 1971) have shown that the three C–H bonds are slightly unequal, due to a weak interaction of one of the CH_3 hydrogens with an oxygen atom of a neighbouring molecule (figure 7).

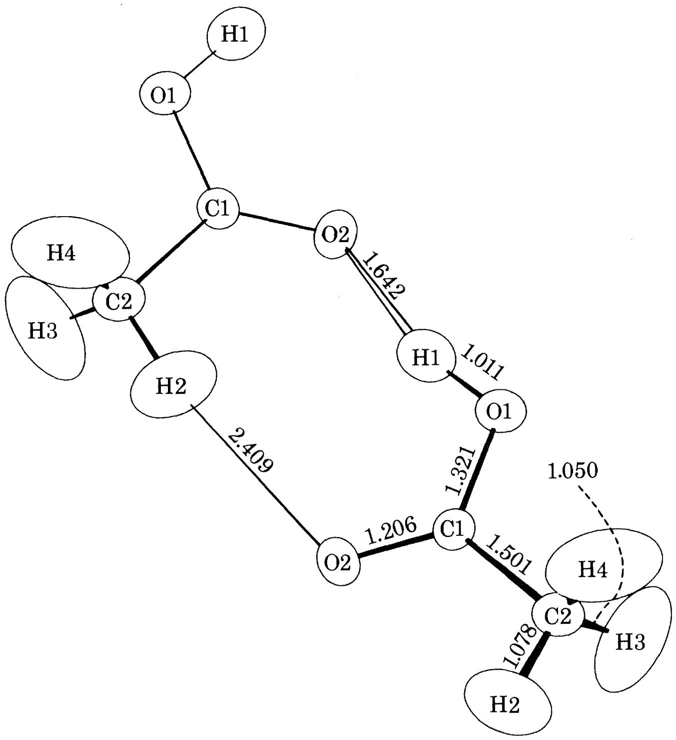

FIGURE 7. In single crystals of acetic acid the molecules form chains.

TABLE 6. METHYL CHEMICAL SHIFT TENSOR ELEMENTS

(All shifts are in millionths relative to liquid benzene.)

	temperature/K	σ_{11}	σ_{22}	σ_{33}	σ_i	σ_{solution}	reference
p-xylene	100	95	106	131	111	108	van Dongen Torman & Veeman (1978)
durene	300	98	105	127	110	109	Pausak *et al.* (1973)
		83	98	105	110	109	
hexamethylbenzene	300	110	112	112	111	111	Pausak *et al.* (1974)
		111	112	113	112	111	
acetic acid	90	89	102	123	105	108	van Dongen Torman *et al.* (1977)

CONCLUSION

Thanks to the development of high-resolution solid state ^{13}C n.m.r. techniques, ^{13}C chemical shift tensors can be determined from single-crystal studies. The principal elements, but especially the principal orientations, are very sensitive to the local structure around the carbon atoms. Much more interesting theoretical and structural information can be obtained from solid state chemical shift data than from solution data.

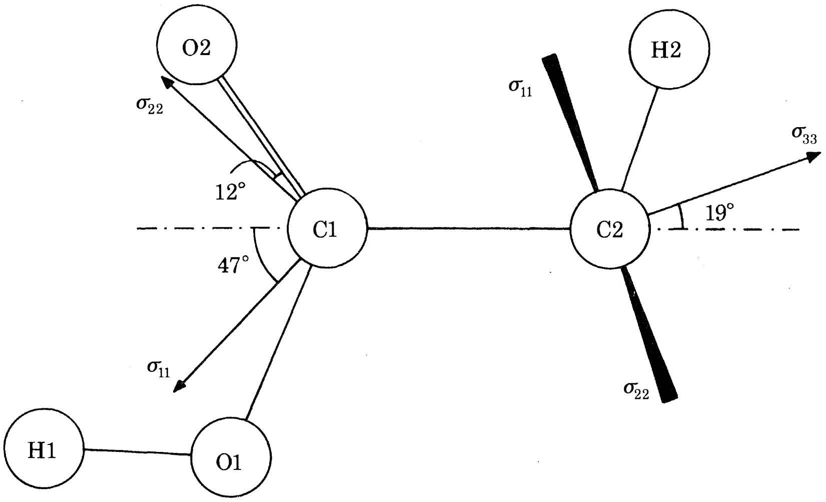

FIGURE 8. Principal orientations of the methyl and carboxyl carbons in acetic acid.

REFERENCES (Veeman)

Abragam, A. 1961 *The principles of nuclear magnetism*. London: Oxford University Press.
Becker, J. D., Suwelack, D. & Mehring, M. 1978 *Solid State Commun.* **25**, 1145–1148.
Van Dongen Torman, J. 1978 Ph.D. thesis, University of Nijmegen.
Van Dongen Torman, J. & Veeman, W. S. 1978 *J. chem. Phys.* **68**, 3233–3235.
Van Dongen Torman, J., Veeman, W. S. & de Boer, E. 1977 *Chem. Phys.* **24**, 45–49.
Van Dongen Torman, J., Veeman, W. S. & de Boer, E. 1978 *J. magn. Reson.* **32**, 49–55.
Griffin, R. G., Pines, A., Pausak, S. & Waugh, J. S. 1975 *J. chem. Phys.* **63**, 1267–1271.
Haeberlen, U. 1976 *Adv. magn. Reson.* (*suppl.*).
Haurie, M. & Novak, A. 1967 *C. r. hebd. Séanc. Acad. Sci., Paris* B **264**, 694.
Höhener, A. 1978 *Chem. Phys. Lett.* **53**, 97.
Jönsson, P. G. 1971 *Acta crytallogr.* B **27**, 893.
Kempf, J., Spiess, H. W., Haeberlen, U. & Zimmermann, H. 1972 *Chem. Phys. Lett.* **17**, 39–42.
Kempf, J., Spiess, H. W., Haeberlen, U. & Zimmermann, H. 1974 *Chem. Phys.* **4**, 269–276.
Linder, M., Höhener, A. & Ernst, R. R. 1979 *J. magn. Reson.* **35**, 379–386.
Mehring, M. 1976 *High resolution NMR spectroscopy in solids*. Berlin, Heidelberg and New York: Springer-Verlag.
Pausak, S., Pines, A. & Waugh, J. S. 1973 *J. chem. Phys.* **59**, 591–595.
Pausak, S., Tegenfeldt, J. & Waugh, J. S. 1974 *J. chem. Phys.* **61**, 1338–1344.
Pines, A., Chang, J. J. & Griffin, R. G. 1974 *J. chem. Phys.* **61**, 1021–1030.
Pines, A., Gibby, M. G. & Waugh, J. S. 1972 *Chem. Phys. Lett.* **15**, 373–376.
Pines, A., Gibby, M. G. & Waugh, J. S. 1973 *J. chem. Phys.* **59**, 569–590.
Poole, C. P. & Farach, H. A. 1972 *The theory of magnetic resonance*. New York: Wiley.
Stothers, J. B. 1972 *Carbon-13 NMR spectroscopy*. New York and London: Academic Press.
Weil, J. A., Buck, T. & Clapp, J. E. 1973 *Adv. magn. Reson.* **6**, 183.

Discussion

D. J. Greenslade (*Department of Chemistry, University of Essex, Colchester, U.K.*). Dr Veeman has noted the analogy between the σ, chemical shift 'tensor' and the g 'tensor' of electron paramagnetic resonance. Abragam & Bleaney (1970) point out that the g factor is not truly a Cartesian tensor: is this so for σ?

Reference

Abragam, A. & Bleaney, B. 1970 *Electron paramagnetic resonance of transition ions*, §15.6. Oxford University Press.

W. S. Veeman. The sentence of the book by Abragam & Bleaney that Dr Greenslade refers to, reads: 'The deeply ingrained habit of calling the $g_{q\alpha}$ and $a_{q\alpha}$ tensors, proceeds from a confusion between the fictitious spin $\sigma/2$ of the Kramers doublet and a real electronic spin and is a serious misnomer in general....' In n.m.r. the nuclear spins are real and therefore I would think the σ tensor indeed is a tensor.

D. J. Greenslade. In the theory of electron paramagnetic relaxation, in solution it is common to use the irreducible tensor form of the g 'tensor'. This implies a neglect of off-diagonal elements in the Hamiltonian. The same may be true of the irreducible tensor form of the chemical shift 'tensor', and this form has been discussed in other papers at this Meeting. It seems that there is need of a careful study of this approach to ensure that it does not introduce gross errors into the analysis of shift 'tensors'.