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The Anisotropy of Molecular Magnetic Susceptibility and Its Structural-chemical Aspects

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Experimental data on the anisotropy of the magnetic susceptibilities of molecules and complexes have been summarised and systematised. A tensor additive scheme for the magnetic susceptibilities of the chemical bonds and groups of atoms in diamagnetic compounds has been developed. The application of the additive scheme to the analysis of the effects of the mutual influence of atoms, the problem of aromaticity, conformational structure, solvation, and complex formation has been examined.
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I. INTRODUCTION

For a long time, molecular magnetochemistry, which studies the relationship between the magnetic properties and the structure of molecules, developed chiefly on the basis of a group of methods for determining average magnetic susceptibilities (MS). In the great majority of studies, with the exception of those devoted to the determination of the principal components of the molecular tensors of the MS in crystals, the anisotropies of the MS were not analysed. The intensive study of magnetic anisotropies has become possible as a result of the use in recent years of the molecular Zeeman effect in the gas phase,[1] the effects of linear magnetic birefringence in liquid media and the gas phase,[2-4] and NMR spectroscopy in strong fields.[5] The discussion of these methods in the literature is limited or non-existent, since the emphasis has been on the physics of the phenomena, and not on their application to chemical problems.

Unlike the average MS, the anisotropy is highly sensitive to the effects of intra- and intermolecular electronic interactions, and also to the relative orientation of functional groups. The experimental material which has now accumulated makes it possible to summarise published data on the determination of the anisotropic MS of molecules and the application of this fundamental electronic property to the solution of structural chemical problems.

II. METHODS FOR DETERMINING MAGNETIC SUSCEPTIBILITIES

The magnetic properties of an anisotropic molecule are described completely by nine quantities (k_{XX}, k_{XY}, k_{XZ}...k_{ij}), the set of which is called the MS tensor; from symmetry, $k_{ij} = k_{ji}$. The MS tensor can be represented in matrix form:

$$\begin{vmatrix} k_{XX} & k_{XY} & k_{XZ} \\ k_{YX} & k_{YY} & k_{YZ} \\ k_{ZX} & k_{ZY} & k_{ZZ} \end{vmatrix} \quad (1)$$

After reduction to the principal axes, the tensor becomes "diagonal":

$$\begin{vmatrix} k_{11} & 0 & 0 \\ 0 & k_{22} & 0 \\ 0 & 0 & k_{33} \end{vmatrix} \quad (2)$$

The invariants of a tensor are its trace and anisotropy. The trace is the sum of the diagonal elements, often characterised by the total (Σk_{ii}) or average ($\Sigma k_{ii}/3$) MS; their difference is the anisotropy (γ).[6-9] Methods for finding average MS have been described in detail in many reviews and monographs.[7,8,10-19] The data for approximately 800 compounds have been summarised in Ref.20.

Data on magnetic anisotropies have been analysed to a much smaller extent.

1. Microwave Spectroscopic Effects

The rotational Zeeman effect[1,21] in a gas consists of the splitting of the spectral lines into several components under the influence of a strong magnetic field. It has now become possible to measure and interpret the quadratic Zeeman effect, associated with the anisotropy of the MS. Measurement of the Zeeman effect is practically the only experimental method making it possible to separate the total MS into diamagnetic and polarisation paramagnetic components.[1,22] Since MS anisotropies are determined using the Zeeman effect in the gas phase, they can be regarded as standard. Unfortunately, a number of restrictions are imposed on the materials which can be studied by this method, and this reduces the range of substances which can be examined. These restrictions relate to the thermal stability of the specimens, the number of atoms other than hydrogen in the molecule (not more than 10), and the existence of a permanent electrical dipole moment in the molecule. The last restriction can be removed by studying the weak van der Waals complexes formed by the polar hydrogen halides with the centrosymmetric molecules

under investigation, for example acetylene[23] and cyclopropane.[24] Another approach involves partial deuteriation, used, for example, to determine the anisotropy of the MS of ethane (CH_3-CD_3).[25,26]

The anisotropies of the MS of the simplest molecules can also be determined by double electric resonance in molecular beams.[27,28]

2. The Molecular MS of Single Crystals

To find the principal MS of crystalline substances, it is sufficient to place a single crystal in a magnetic field in such a way that its lines of force coincide with one of the principal axes of the MS. Another approach is based on the tendency for a crystal of low symmetry suspended in a uniform magnetic field to orientate itself always in such a way that the axis corresponding to the MS of greatest absolute magnitude lies in the direction of the lines of force of the magnetic field.[7,8] The total MS tensor of a single crystal can be found by studying it in a non-uniform magnetic field.[8,12] A number of other methods can also be used to determine the principal MS of single crystals.[8]

At present, because of significant experimental difficulties, the tensors of only a limited number of molecules have been determined from data on the MS of crystals. Most of these data for diamagnetic materials have been tabulated;[7,29,30] values have also been obtained for a number of benzoic acids,[31-36] substituted nitrobenzenes,[37,38] and steroids,[39] and data on paramagnetic substances have been summarised;[40] data for lanthanide α,β-diketonates have also been published.[41]

It is assumed that the crystal packing has no influence on the molecular MS tensor, since the average MS of molecules in the liquid and solid phases are similar.[7] This assumption is not wholly correct, however. Rearrangement of the magnetic axes with preservation of their average value is always possible in principle. It would be strictly correct to compare the MS tensors of the same molecules in different states of aggregation. Special studies in this direction have not been carried out, and it has been reported only that these tensors are similar for various compounds, for example benzene and polynuclear hydrocarbons.[5] A correspondence between the results of measurements on crystals and measurements of the Cotton–Mouton effect in solutions has been reported for a number of aromatic compounds.[42,43] For compounds containing highly polar substituents, this question remains open. Thus for *p*-nitroaniline, satisfactory agreement is observed between the results of measurements of the Cotton–Mouton effect and measurements on crystals, whereas this agreement is not observed for *m*- and *p*-dinitrobenzenes.[44]

3. Magnetic Birefringence Effects

Data on magnetic birefringence in a transverse magnetic field can be used to determine the anisotropies of the MS in a gas, pure liquids, and solutions. Three types of magnetic birefringence are distiguished: in colloids[45] (the Majorana effect,[46] discovered in 1901), in diamagnetic molecules (the Cotton–Mouton effect, 1904),[2,3] and in paramagnetic substances, recently observed in solutions of lanthanide salts and complexes.[4,47]

Strange as it may seem, until recently, attempts to detect the paramagnetic effect were either unsuccessful[48] or declaratory in character;[49] in a number of cases the results contradicted one another,[49-51] and the superposition of other magneto-optical effects also took place.[50-57] Thus Elias[54] apparently observed in $Er(NO_3)_3$ the Voigt effect, that is birefringence in the characteristic absorption bands of the substance or in their direct proximity. In view of the tendency for Ce^{3+} salts to undergo hydrolysis,[58] the study of their aqueous solutions[52,53] apparently involved the Majorana effect in colloidal hydroxoaquo-complexes. An anomalously high magnetic birefringence effect was recorded in liquid oxygen.[55-57] Since however liquid oxygen is a liquid crystal[59] (and this state of matter is characterised by extremely large electro- and magneto-optical effects[60]), its high birefringence is due not to its paramagnetic character but to its liquid-crystal structure.

The molar constants of the diamagnetic ($_mC$) and paramagnetic ($_mP$) effects are described by expressions including the components of the tensors of the optical polarisability (b_{ij}), the diamagnetic susceptibility (k_{ij}), and the *g*-tensor:[47]

$$_mC = (2\pi N/45kT)\,[\Sigma(b_{ii}-b_{jj})(k_{ii}-k_{jj}) + 6\Sigma b_{ij}k_{ij}], \quad (3)$$

$$_mP = [(2\pi N/45kT(T-\delta)]\,(\mu^2/\Sigma g_{ii}^2)\,[(b_{ii}-b_{jj})(g_{ii}^2-g_{jj}^2) + 6\Sigma b_{ij}g_{ij}^2], \quad (4)$$

where N is Avogadro's number, k the Boltzmann constant, T the absolute temperature, δ the Weiss temperature correction to the Curie law in degrees absolute, and μ the magnetic moment in Bohr magnetons. Eqn. (4) clearly shows why the paramagnetic effect could not be observed in solutions of $FeCl_3$ and $Mn(NO_3)_3$ and in K and Na vapour;[48] the effect should be absent in purely spin systems. For systems with strong spin–orbit coupling, the paramagnetic effect is greater by 2–4 orders of magnitude than the Cotton–Mouton effect.[4,47] The latter can in principle be observed for any system both in the gas and in liquids and dilute solutions.[61-63] Unlike the constants of the electric analogue (the Kerr effect), the Cotton–Mouton constants are independent of the dielectric constant of the medium. This is indicated by $_mC$ data for aromatic compounds; the reliable determination of $_mC$ is possible not only for individual liquids ($_mC_l$) but also for solutions ($_mC_s$).[63,64] Further confirmation is provided by the identical values of the anisotropies of the MS of C_6H_6, alkyl halides, and CH_3CN, found by measuring the Zeeman effect in the gas phase and obtained from combined "solution" (Kerr effect) and "liquid" (Cotton–Mouton effect) data.[64] An exceptional place among other compounds is occupied by nitrobenzene, for which $_mC_l$ is almost twice $_mC_s$. This question is discussed in more detail in Section VI.

4. NMR Spectroscopy

Under the influence of strong magnetic fields (> 90 kG), the signals in high-resolution NMR spectra are split, the splitting being proportional to the magnitude of the anisotropy of the MS of the molecules and the square of the intensity of the applied field. This effect is due to the ordering of magnetically anisotropic molecules in liquids (solutions)[5] or gases,[65] which takes place as a result of the interaction of the quadrupole moment of the nuclei with the external field (the effect of dipole interaction is too small, and does not appear under these conditions). The most convenient object for the study of the NMR of partly oriented molecules is deuterium (^2H), since its quadrupole moment is sufficiently large for the splitting in real magnetic fields to be recorded, and at the same time is not so large that the broadening of the lines which it brings about makes it impossible to observe the splitting.[66] In very strong fields (~140 kG), the effect has also been studied at ^1H nuclei.[67,68]

The number of published studies using this approach is small, although it is undoubtedly promising. At present, this method is the only liquid-phase method which makes it possible to calculate all three components of the molecular MS tensor. Apart from halogenomethanes[69] and hydrogen cyanide,[70] this method has been used to find the anisotropies of the MS of only aromatic molecules[5,68,71-73] and anions.[73,74] It has also been applied to paramagnetic molecules.[67]

An alternative approach to the determination of the paramagnetic anisotropy of complexes is to solve the inverse problem, involving the analysis of the values of the pseudo-contact (dipole) contributions to the isotropic chemical shifts of ^{1}H and (or) ^{13}C due to the presence of the paramagnetic ions Co, Ni, and Ln.[75] Unfortunately, the application and accuracy of this method are restricted by a number of factors.[75,76] Nevertheless, it has been used successfully to determine the anisotropies of various complexes, in particular the bis-adducts of lanthanide dipivaloylmethanates with pyridine.[77] The components found in this way agree with the values previously obtained by direct magnetochemical measurements in single crystals.[41]

III. THE RELATIONSHIP BETWEEN MAGNETIC SUSCEPTIBILITY AND ELECTRIC POLARISABILITY

The electric polarisability and the magnetic susceptibility, which describe the deformability of the electron clouds of particles in magnetic and electric fields, are closely related to one another. This can be seen from the expressions

$$k = -(e^2/6mc^2)\Sigma\bar{r}^2, \quad b = (4/9na_0)\,|\Sigma\bar{r}^2|^2,$$

whose combination establishes the relationship between the MS (k) and the electric polarisability (b)[78]

$$k = -(e^2a_0^{1/2}/4mc^2)\,(nb)^{1/2}. \qquad (5)$$

Here, e is the charge of the electron, m its mass, n the total number of electrons in the system, $\Sigma\bar{r}^2$ the sum of the mean-square radii of the electron orbitals, and a_0 the Bohr radius. Eqn. (5) was obtained by Kirkwood, and is applicable for spherical atoms and monatomic ions. The main criticism of this equation is that the magnitude of the polarisability is determined chiefly by the electrons of the valence level, and not the inter levels, whereas all the electrons are equivalent with respect to precession in a magnetic field.[78] Nevertheless, for monatomic systems, good agreement is obtained between the results of experiment and calculation.[78] Kirkwood's model has also been developed for elliptical molecules and bonds. The magnetic susceptibility k_i oriented along the i axis is a function of the polarisability in two orthogonal directions, b_j and b_k:[79]

$$k_i = [-e^2\,(na_0)^{1/2}/8mc^2]\,[b_j^{1/2} + b_k^{1/2} - (b_j^{1/2} - b_k^{1/2})^2/(b_j^{1/2} + b_k^{1/2})]. \qquad (6)$$

For axially symmetrical systems, the anisotropy of the MS is described by the expression:[80]

$$\gamma = (-e^2/4mc^2)\,(na_0)^{1/2}\,[b_\perp\,(b_\perp^{1/2} - b_\parallel^{1/2})]/(b_\parallel^{1/2} + b_\perp^{1/2}), \qquad (7)$$

where $b_\parallel$ is the polarisability along the axis of cylindrical symmetry, and $b_\perp$ the perpendicular component. Eqn. (5) was subsequently applied to polyatomic molecules, and the difference between the calculated and experimentl MS was assigned *a priori* to the paramagnetic Van Vleck component.[78] Eqn. (6) has been used together with ^{1}H NMR spectroscopic data to estimate the MS and polarisability ellipsoids of the bonds C–C and C–H.[81] Verification of the practical applicability of Eqns. (5)–(7) for the case of the alkyl halides showed, however, that agreement with experiment is not observed at the level of the two invariants and the individual components of the tensor, including that for which the paramagnetic contribution should be small or non-existent.[80]

Analysis of the empirical $\Sigma k_i = f(\Sigma b_i)$ relationships shows that they are for the most part linear, although they are different for compounds of different classes.[82] Thus for a number of organophosphorus compounds containing saturated groups and P–O, P–S, P–Cl, P–H, P–C, P=O, and P=S bonds, the correlation has the form[64]

$$k_i = -0.180\cdot10^{-29} - 1.046(\pm0.037)\,\Sigma b_i\cdot10^{-5}.$$

Correlations with one another should probably be observed not only for the average characteristics of the bonds but also for their anisotropies. This is indicated by the fact that for chloro- and bromohydrocarbons the changes take place in the opposite sense.[80]

IV. THE TENSOR ADDITIVE SCHEME

The efficiency of magnetochemical studies of the structure of molecules depends significantly on the extent to which the additive principle relating molecular properties to the properties of individual atoms, bonds, and fragments is applicable to the anisotropic MS.

This principle is strictly observed for the average MS. This was first noted by Pascal, who pointed out that the difference in the MS of two neighbouring members of the homologue series of n-alkanes is constant. Having analysed the data for a large number of compounds, he concluded that the molar MS averaged over all directions and reduced to one molecule, $\chi_M = N\Sigma k_{ii}/3$, can be described by the relationship $\chi_M = \Sigma n_A\chi_A + \lambda$, where n_A is the number of atoms with MS χ_A in the molecule, and λ a constitutive correction which depends on the nature of the bonds between the atoms.[7,10,12,78] By analogy with the optical polarisabilities (refractions), this relationship can also be expressed in terms of bond characteristics.[78] The additive scheme of scalar MS was subsequently improved many times.[13,83-88] One of its most detailed versions is the system described in Ref.13. The values of the diamagnetic components for different ions are tabulated in Refs.7, 11, and 12. A theoretical validation of Pascal's empirical scheme was given in Ref.89.

In contrast to the scalar characteristics, the additivity of the MS tensor of molecules is not so obvious, except for aromatic hydrocarbons.[84,86,90] It has been shown that the diamagnetic component of the tensor retains additivity, but definite restrictions are imposed on the polarisation paramagnetic component, which changes with change in the symmetry of the orbitals on going from one molecular system to another.[1] It appears that in systems in which delocalised interactions (conjugation and hyperconjugation effects) predominate, so that the symmetry of a molecular orbital can be identified with the symmetry of the molecular framework, the paramagnetic part of the tensor may not be transferable. On the other hand, in molecules in which the interactions are localised (induction effects), that is in which the symmetry of the molecule is not related to the orbital symmetry, the MS tensor should remain additive, since in this case the molecular property is the sum of the properties of the individual bonds. This should be applicable for any electronic characteristic, including paramagnetism, which is independent of temperature.

Thus the MS tensor of 1,2-dibromoethane can be calculated sufficiently accurately from the MS of ethyl bromide (both compounds are characterised by only inductive interactions), in spite of the fact that these molecules have different symmetries and different positions of the centre of mass.[80] In contrast to this, the tensors of the molecules of benzyl bromide and 1,4-xylylene dibromide are not described by a single set of MS. In both compounds there is a strong interaction between a delocalised π-orbital of the aromatic ring and an antibonding orbital of the C−Br bond: $\pi_{ar}-\sigma^*(C-Br)$. In the case of benzyl bromide, the $\pi_{ar}-\sigma^*(C-Br)$ interaction as a result of the presence of the C−Br bond orientated unsymmetrically with respect to the ring leads to breakdown of the symmetry of the π-orbital as a whole, leading to the appearance of a super-additive contribution of the paramagnetic component in the direction perpendicular to the ring. In 1,4-xylylene dibromide, the CH_2Br groups in the *para*-positions increase the symmetry of the π-orbital of the aromatic ring delocalised over the unoccupied C−Br orbitals, and this "removes" the super-additive contribution of the Van Vleck component.[91]

It is convenient to examine the principles of the additivity of the MS tensors of the bonds and the solution of the inverse problem for a number of simple systems.

For a linear polyatomic molecule, the directions of the principal MS of the molecules and the bonds coincide. For non-linear molecules, the valence angles must be taken into account. For triatomic fragments AB_2 with an angle 2θ between the bonds in the system of principal axes, the following relationships apply:

$$k_1=2k_L\cos^2\theta+2k_T\sin^2\theta,$$
$$k_2=2k_L\sin^2\theta+2k_T\cos^2\theta,\quad k_3=2k_V. \tag{8}$$

Here and subsequently, k_1 is the MS directed along the axis of symmetry of the system, and k_2 and k_3 the MS in the other two orthogonal directions; k_L, k_T, and k_V are the longitudinal, transverse, and vertical MS of the bonds respectively. The solution of Eqn.(8) in the system of principal semi-axes of the MS ellipsoid of the bonds has the form:

$$k_V=k_3/2;\quad \gamma=k_L-k_T=(k_1-k_2)/(4\cos^2\theta-2). \tag{9}$$

similarly, for trigonal pyramidal molecules AB_3 (θ is the angle between A−B and the C_{3v} axis),

$$k_1=3(k_L\cos^2\theta+k_T\sin^2\theta),$$
$$k_2=k_3=1.5(k_L\sin^2\theta+k_T\cos^2\theta+k_V). \tag{10}$$

Assuming cylindrical symmetry of the bond ($k_T = k_V$), the solution of the system of equations (10) takes the form:

$$\gamma=k_L-k_T=(k_1-k_2)/1.5(3\cos^2\theta-1). \tag{11}$$

In the tensor additive scheme there is always a parameter whose value must be introduced arbitrarily or determined independently. This is related to the impossibility of separating the anisotropic molecular characteristics into components, even if the molecules contain bonds of only two types. Thus for example for ethane (and other alkanes), the irreducible combination of the anisotropies of the C−C and C−H bonds has the form:

$$\Gamma(C_2H_6)=\gamma(C-C)-2\gamma(C-H). \tag{12}$$

For mono-substituted methanes, the following relationship is applicable:

$$\Gamma(CH_3X)=\gamma(C-X)-\gamma(C-H)=\gamma(R-X). \tag{13}$$

For substituted benzenes which do not have axial symmetry but which contain a substituent with axial symmetry, the expression analogous to Eqn.(13) is converted into a system of equations including the anisotropy of benzene along the axis of symmetry $\Gamma(C_6H_6)$:

$$\Gamma_1(C_6H_5X)=\Gamma(C_6H_6)-1/2[\gamma(C-X)-\gamma(C-H)],$$
$$\Gamma_2(C_6H_5X)=-\Gamma(C_6H_6)/2+\gamma(C-X)-\gamma(C-H), \tag{14}$$

where Γ_1 and Γ_2 are the anisotropies of C_6H_5X perpendicular to and along the C−X bond respectively. In the more complex case of substituted ethylenes, the C=C bond is characterised by three different MS components, and the anisotropic part of the molecular tensor also includes combinations of the constant difference $\gamma(C-X)-\gamma(C-H)$.[92] This parameter in the calculation of the molecular tensor is reduced if the valence angles of the model systems and the systems being studied are close to one another. For clarity, this can be illustrated for the t-butyl derivative, whose molecular anisotropy is given by the expression

$$\Gamma(t\text{-}C_4H_9X)=\gamma(C-H)-\gamma(C-C)+\gamma(C-X). \tag{15}$$

On substitution of Eqns. (12) and (13) in Eqn.(15) and subsequent summation, γ(C−H) is eliminated:

$$\Gamma(t\text{-}C_4H_9X)=\Gamma(CH_3X)-\Gamma(CH_3X).$$

In contrast to methods involving the use of the Zeeman effect and NMR in strong fields, the method based on the measurement of the Cotton−Mouton effect makes it possible to determine the components of the MS only in the axially symmetrical approximation ($k_\parallel$ and $k_\perp$). The simultaneous examination of ${}_mC$ for several related compounds, for example homologues or molecules containing different numbers of identical functional groups, however, makes it possible to estimate the principal components of the MS for less symmetrical substituents. Thus in the determination of the three components of the MS tensor of the nitro-group it was assumed that γ(C−H) = 0, and a system of equations with three Cotton−Mouton constants for nitrobenzenes and *m*- and *p*-dinitrobenzenes was examined. After substituting the known numerical values of the fundamental constants and the tensors of the electric polarisability and the anisotropy of the MS of the benzene ring with allowance for the geometry of the molecules, expressions were obtained for ${}_mC$ as functions of the anisotropies $\gamma_1 = k_1-k_2$ and $\gamma_2 = k_1-k_3$ (k_1 is directed along the C−NO_2 symmetry axis, and k_3 is normal to the plane of the group):

$${}_mC(NB)=(-2.57\gamma_1+12.40\gamma_2+131.2\cdot10^{-29})/48.08\cdot10^{14},$$
$${}_mC(m\text{-}DNB)=(-15.75\gamma_1+37.8\gamma_2+199\cdot10^{-29})/48.08\cdot10^{14}. \tag{16}$$

Using the known experimental values of ${}_mC$ for NB, *m*-DNB, and *p*-DNB (3.83×10^{-15} emu, 6.00×10^{-15} emu, and 4.70×10^{-15} emu respectively), it can readily be shown that $\gamma_1 = 0.8\times10^{-29}$ cm^3 and $\gamma_2 = 2.7\times10^{-29}$ cm^3.[93] The values of γ_1 and γ_2, and also of k_l for the nitro-group, given in Ref.94, are incorrect, because of an error in writing the system of equations (16). Similarly, the triaxial MS tensor of the carbonyl group was calculated using the values of ${}_mC$ for acetone and cyclohexanone[95] and the tensors of the C=C bond (the corresponding values for *cis*- and *trans*-dichloroethylenes[92]) and the $C_{ar}-O$ bonds (the constants for different substituted anisoles[96]). The tensor characteristics of the bonds of a number of saturated and unsaturated molecules have been found from data on the Zeeman effect by averaging the MS of these bonds by the least-squares method.[1] The assumptions that the anisotropy of the MS of the C−H bond is independent of the hybridisation of the C atom and that k_T and k_V are equal, and also the differences in the valence

angles at the C_{sp^3}, C_{sp^2}, and C_{sp} atoms, made it possible to distinguish γ(C–H). This quantity was found to be negative, as confirmed by the data in Ref.92, although it does not agree with Ref.97.

An approach based on the isotropic character of the C–H bonds is widely used in the analysis of tensor electric polarisabilities;[79] it facilitates considerably the calculation of the anisotropic molecular characteristics, since a knowledge of the spatial positions of the C–H bonds in the molecular structures and confirmations is not required. The relative values of the tensor additive MS of bonds, based on the assumption that the C–H bonds are isotropic, are given in Table 1. The values were calculated by the present authors from published data on the molecular ellipsoids or anisotropies of the MS obtained by the above methods. The Table does not include the data from Ref.98, which are erroneous.[43]

Table 1. Tensor additive magnetic susceptibilities of different bonds and groups, calculated assuming that the C–H bonds are isotropic ($k_t(\gamma) \times 10^{29}$, cm^3).

Bond, group	Model compound	$-k_L$ or $-k_1$, (γ)	$-k_T$ ($-k_V$) or $-k_2$ ($-k_3$)	Method	Refs.
C—C	n-alkanes	0.76	0.54	SC	[99]
C–C	aliphatic acids with a long chain	0.83	0.50	CM (l)	[100]
C—C	ethane	0.88	0.48	CM (g)	[61]
C—C	isobutane	0.91	0.46	Z	[101]
C—C	–	0.92*	0.45*	Z*	[1]
C—C	cyclohexane	0.93	0.45	CM (l)	[102]
C—C	ethane	1.21	0.31	Z	[25]
C—C	ethane	1.26	0.29	CM (g)	[103]
C—C	ethane	1.28	0.28	Z	[26]
C=C	trimethyl- and 1,2-dichloroethylenes	0.57	1.23 (3.09)	CM (l)	[92]
C=C	–	0.35*	0.44 (2.50)*	Z*	[1]
C≡C	–	2.83*	2.13*	Z*	[1]
C≡C	acetylene + HCl	2.82	2.14	Z	[23]
C_3	cyclopropane + HCl	2.2	2.2 (3.7)	Z	[24]
C_3	cyclopropane	2.07	2.07 (4.0)	CM (g)	[104]
C_6H_5	benzene	5.6	5.6 (14.5)	CM (g)	[105]
C_6H_5	benzene	5.56	5.56 (14.6)	CM (l)	[43]
C_6H_5	benzene	5.47	5.47 (14.8)	NMR (l)	[5]
C_6H_5	benzene	5.37	5.37 (15.0)	CM (s)	[62]
C_6H_5	benzene	5.27	5.27 (15.2)	SC	[106]
C_6H_5	benzene	5.1	5.1 (15.5)	CM (s)	[43]
C_6H_5	benzene	5.07	5.07 (15.6)	Z	[1]
C_6H_5	benzene	5.07	5.07 (15.6)	CM (s)	[102]
C_6H_5	benzene	4.87	4.87 (16.0)	NMR (s)	[5]
C_{ar}–CH_3	durene	2.31	1.89 (2.12)	SC	[43]
C_{ar}–CH_3	toluene	1.54	2.32	CM (s)	[43]
C_6H_5—C	toluene	5.6	5.2 (16.0)	CM (s)	[43]
C_6H_5—C	benzyl halides	4.9	7.9 (13.9)	CM (s)	[91]
C_{sp}—CH_3	methylacetylene, acetylene	2.80	2.20	Z	[106]
C_{sp}—CH_3	acetonitrile, hydrogen cyanide	2.2	1.7	Z	[106]
C—F	methyl fluoride	1.77	0.41	Z	[106,107]
C—F	methylene fluoride	0.94	0.60 (0.62)	Z	[106]
C—F	fluoroform	(0.2)	—	Z	[107]
C_{ar}–F	fluorobenzene	1.65	0.93	CM (s)	[96]
C_{ar}–F	fluorobenzene	1.73	1.13 (0.64)	Z	[1]
C_{ar}–F	fluorobenzene	1.78	1.16 (0.40)	Z	[108]
C_{ar}–F	fluorobenzene	1.43	1.33 (0.7)	NMR (s)	[71]
C_{ar}–F	fluorobenzene	0.33	1.04 (1.31)	NMR (l)	[71]
C_{sp}—F	fluoroacetylene	1.52	1.36	Z	[106]
C_{sp}—F	fluorine cyanide	1.62	1.62	Z	[107]
C—Cl	methyl chloride	4.06	2.74	Z	[107]
C—Cl	1,2-dichloroethane	4.16	3.06	CM (l)	[80]
C—Cl	isopropyl chloride	4.39	2.95	CM (l)	[80]
C—Cl	t-butyl chloride	4.55	2.88	CM (l)	[80]
C—Cl	methylene chloride	4.59	2.55	CM (l)	[80]
C—Cl	methylene chloride	4.20	2.76 (2.65)	NMR (s)	[69]
C—Cl	chloroform	4.75	2.21	NMR (s)	[69]
C—Cl	chloroform	4.43	2.38	CM (l)	[80]
C_{sp^2}—Cl	1-chlorocyclohexene	3.89	2.96	CM (l)	[92]
C_{sp^2}—Cl	1,2-dichloroethylene	4.16	2.82	CM (l)	[92]
C_{ar}–Cl	chlorobenzene	3.63	3.13 (2.4)	NMR (s)	[71]
C_{ar}–Cl	chlorobenzene	2.35	2.53 (4.15)	NMR (l)	[71]
C_{ar}–Cl	chlorobenzene	3.97	2.06	CM (s)	[43]
C_{ar}–Cl	p-dichlorobenzene	3.88	1.56 (2.10)	SC	[43]
C_{sp}—Cl	chlorine cyanide	3.55	2.95	Z	[109]

Table 1 (continued).

Bond, group	Model compound	$-k_L$ or $-k_1$, (γ)	$-k_T$ ($-k_V$) or $-k_2$ ($-k_3$)	Method	Refs.
C_{sp}—Cl	chloroacetylene	4.04	3.20	Z	[106]
C—Br	methyl bromide	5.60	4.20	Z	[107]
C—Br	ethyl bromide	5.60	4.20	CM (s)	[80]
C—Br	isopropyl bromide	5.73	4.14	CM (s)	[80]
C—Br	t-butyl bromide	5.83	4.09	CM (s)	[80]
C—Br	methylene bromide	6.46	3.77	CM (s)	[80]
C—Br	methylene bromide	6.08	4.15 (4.0)	NMR (s)	[69]
C—Br	bromoform	6.9	3.1	NMR (s)	[69]
C—Br	bromoform	6.41	3.80	CM (s)	[80]
C_{ar}–Br	bromobenzene	5.4	4.8 (3.9)	NMR (s)	[71]
C_{ar}–Br	bromobenzene	4.1	4.4 (5.7)	NMR (l)	[71]
C_{ar}–Br	bromobenzene	5.64	3.72	CM (s)	[43]
C_{ar}–Br	p-dibromobenzene	5.45	3.24 (3.47)	SC	[43]
C_{sp}—Br	bromoacetylene	5.47	4.50	Z	[106]
C_{sp}—Br	bromine cyanide	5.30	4.47	Z	[106]
C—I	methyl iodide	8.55	6.72	Z	[107]
C—I	methyl iodide	8.40	6.79	CM (s)	[43]
C—I	ethyl iodide	8.42	6.78	CM (s)	[43]
C—I	isopropyl iodide	8.50	6.75	CM (s)	[43]
C—I	t-butyl iodide	8.67	6.66	CM (s)	[43]
C—I	methylene iodide	9.1	6.1 (5.9)	NMR (s)	[69]
C—I	iodoform	10.73	4.05	NMR (s)	[69]
C_{sp}—I	iodine cyanide	8.13	6.63	Z	[106]
C—CN	acetonitrile	3.65	1.98	CM (l)	[93]
C—CN	acetonitrile	3.70	1.96	Z	[1]
C_{ar}–CN	benzonitrile	2.44	2.17	CM (s)	[93]
C_{ar}–CN	benzonitrile, m-dicyanobenzene	1.34	5.05 (0.4)	CM (s)	[93]
C—N	1,3,5-trimethylhexanhydro-1,3,5-triazine	1.15	0.57	CM (l)	[44]
C_{ar}–N	aniline	1.3	0.8 (–0.5)	NMR (s)	[71]
C_{ar}–N	anilines	1.63	1.63 (–1.66)	CM (s)	[44]
C_{ar}–N	N,N-dimethylanilines	1.93	–0.27 (–0.06)	CM (s)	[44]
C_6H_5—N	anilines	6.7	6.7 (13.9)	CM (s)	[44]
C_6H_5—N	N,N-dimethylanilines	7.0	4.8 (15.5)	CM (s)	[44]
C_{ar}–NO_2	nitrobenzene, m-dinitro- and p-dinitrobenzenes	0.53	1.33 (3.23)	CM (s)	[93]
C_{ar}–NO_2	nitrobenzene	–0.1	0.9 (4.3)	NMR (s)	[72]
C_{ar}–NO_2	m-dinitrobenzene	0.9	–0.1 (4.3)	NMR (s)	[72]
C≡N	hydrogen cyanide	2.97	1.77	Z	[1]
C=N	deuterium cyanide	2.70	1.90	NMR (s)	[70]
C—O	dimethyl ether	0.63	0.8 (0.3)	Z	[1]
C—O	dioxan	0.96	0.40	CM (s)	[96]
C_{ar}–O	anisole, p-dimethylanisole	1.07	–0.28 (1.72)	CM (s)	[96]
C_{ar}–O	o,o-dimethylanisole, p-chloro-o,o-dimethylanisole	2.18	0.14 (0.18)	CM (s)	[96]
C=O	formaldehyde	–0.94	0.16 (1.12)	Z	[106]
C=O	–	0.25*	0.09 (2.0)*	Z*	[1]
C=O	acetone, cyclohexanone	–0.25	–0.46 (1.22)	CM (s)	[96]
C_2C=O	acetone, cyclohexanone	0.92	1.13 (1.22)	CM (s)	[96]
C_2O	oxiran	1.25	0.30 (2.35)	Z	[1]
C—S	dimethyl sulphide	1.83	1.13 (1.63)	Z	[1]
C=S	–	–0.84*	1.36 (5.06)*	Z*	[1]
C≡P	–	5.37*	3.97*	Z*	[1]
P—O	1,3,2-dioxaphosphorinanes	(–2.55)	—	CM (l)	[64]
P—F	phosphorus trifluoride	(0.47)	—	Z	[64]
P—Cl	phosphorus trichloride	5.25	1.51	CM (l)	[64]
P=O	phosphorus oxide fluoride	(–0.05)	—	Z	[64]
P=O	phosphorus oxide chloride	1.71	2.15	CM (l)	[64]
P=O	2-oxo-1,3,2-dioxaphosphorinanes	(1.0)	—	CM (l)	[110]
P=S	phosphorus oxide chloride sulphide	6.36	4.22	CM (l)	[110]
P=S	2-thio-1,3,2-dioxaphosphorinanes	(–2.34)	—	CM (l)	[110]

* Calculated from averaged data.[1]

Note: SC = method based on measurements of the MS of single crystals; CM = method based on the use of the Cotton–Mouton effect; Z = method based on the use of the Zeeman effect; NMR = NMR of partly orientated molecules; the state of aggregation of the substance is indicated in brackets: g = gas, l = liquid, s = solution.

The absolute values of the bond and group anisotropies are required in the analysis of intramolecular magnetic parameters such as the chemical shifts or the cones of the magnetic shielding in NMR spectroscopy.

NMR makes it possible to use the values of the chemical shifts (usually of ^{1}H and ^{13}C) to estimate the absolute anisotropies of individual bonds and groups of atoms. This estimation is based on the dependence of the shielding constants of the protons on a number of electronic properties, including the anisotropy of the MS of the fragments adjoining the proton. In existing models, the anisotropic fragment is represented as a point,[111] a one-dimensional dipole[97] or, which is most correct, as a closed contour of finite dimensions with electrons circulating in it.[112,113] It is convenient to carry out specific calculations for a known molecular geometry using the published magnetic iso-shielding map.[113] Here it is also necessary to take into account the contribution of the electrostatic component.[20] To eliminate effects transferred along the chain of atoms, the differences in the chemical shifts of geminal protons or protons in configurational (conformational) isomers are usually examined. It should be emphasised that the approach described is extremely approximate, and includes a number of assumptions, such as the localisation of the centre of the magnetic dipole or the maximum electron density of the substituent; in addition, there arise the questions of the applicability of the models of the dipole and non-dipole approximations used and allowance for intramolecular electronic interactions (induction, conjugation, hyperconjugation, and the field effect). Nevertheless, NMR spectroscopy is apparently the only method which makes it possible, particularly when combined with magneto-optical data, to separate the combinations of the anisotropies of the MS of bonds. This method was used, for example, to determine the anisotropy of the MS of the lone pair of electrons of the phosphorus atom.[110] The tensor additive characteristics of various chemical bonds and groups, found using the above models, are given in Table 2. It is emphasised that the data in Table 2 must be regarded as tentative, since they were obtained by different authors in different approximations. It is also obvious that the values of the anisotropic MS in Tables 1 and 2 cannot be compared without appropriate recalculation.

Table 2. Magnetic anisotropy of bonds and groups from NMR data (10^{29} γ, cm^3).

Bond, group	γ_i (γ_2)	Refs.	Bond, group	γ_i (γ_2)	Refs.
C—H	0	[81]	C—O	0.5	[125]
C—H	0	[114]	C=O	0.8 (1.0)	[126]
C—H	0—0.25	[115]	C=O	1.28 (—0.17)	[126]
C—H	0—0.25	[116]	C=O	—0.83 (—1.0)	[126]
C—H	0.5	[99]	C=O	—0.4 (1.06)	[126]
C—H	0.754	[117]	C=O	2.48 (3.68)	[117]
C—H	1.351	[117]	C=O	2.79 (3.97)	[117]
C—H	—0.7	[92]	C≡N	—5.64	[127]
C—C	0.17	[81]	C—F	—1.0	[128]
C—C	0.25—0.5	[116]	C—Cl	0.5	[125]
C—C	0.32—0.62	[115]	C—Cl	—1.3	[128]
C—C	0.55	[118]	C≡CH	—5.65	[127]
C—C	0.65	[119]	C≡CCl	—6.15	[127]
C—C	0.67	[99]	C≡CBr	—6.13	[127]
C—C	0.73	[114]	C≡Cl	—5.81	[127]
C—C	0.83	[120]	C_6H_6	—3.5	[129]
C—C	1.17	[121]	C_6H_6	—2.5	[130]
C—C	1.126	[117]	C_6H_6	—1.83	[131]
C—C	2.314	[117]	C—NO_2	—7.5 (0.5)	[132]
C=C	—1.2 (—1.21)	[117]	S—O	1.0	[133]
C=C	—1.37	[122]	S—O	2.24	[134]
C=C	—1.8 (2.5)	[92]	Cr(CO)	—4.08	[135]
C≡C	—1.97	[123]	Mo(CO)	—4.69	[135]
C≡C	—2.74	[124]	W(CO)	—5.32	[135]
C—O	0.65	[119]	LPE*	0.27	[110]

*LPE = lone pair of electrons of the phosphorus atom.

The paramagnetic susceptibility of complexes and ions is determined by the number of unpaired electrons and by the symmetry and strength of the ligand field.[9,136] Since the orientational paramagnetism is characteristic of a specific ion, the concept of additivity of the paramagnetic susceptibility tensor for mononuclear systems loses its meaning, and the primary problem becomes its transferability from one type of molecule to another. The transferability of the average characteristic of the tensor in the 4*f* lanthanide elements is well known (their magnetic moments are practically independent of the environment[12]), but it is greatly restricted for transition metal complexes. The individual components of the tensor, and the anisotropy, are more sensitive to the environment of the ion, although judging from paramagnetic birefringence data, satisfactory transferability of the tensor paramagnetic characteristics is also observed in various inner-complex compounds of the lanthanides with different degrees of coordination.[47,137,138] The dependence of the components of the paramagnetic susceptibility tensor on the symmetry of the crystal field has been clearly demonstrated.[139] The quantitative calculations are based on the fundamental theory of Van Vleck.[9] Examples of the calculation of the anisotropies of the lanthanides are given in Refs.76 and 136. One of the corresponding calculation programs is described in Ref.140.

V. EFFECTS OF THE MUTUAL INFLUENCE OF ATOMS AND THE MAGNETIC SUSCEPTIBILITY TENSOR

1. Magnetic Properties and the Nature of the Chemical Bond

The dependence of the anisotropy of the MS of a chemical bond on its nature (symmetry, multiplicity, and the hybridisation of the atoms forming it) and on the effect of neighbouring substituents has not been studied systematically. Sufficient experimental material (see Table 1) has now been accumulated, however, to make possible a number of simple generalisations.

1) Most bonds with cylindrical symmetry, whether single (C—C, C—F, C—Cl, C—Br, C—I, C—N, C—O, C—S, P—Cl, P—O, N—H) or multiple (C≡C, C≡N, C≡P, P=S), show maximum diamagnetism in the longitudinal direction, that is negative anisotropy.

2) For substituents which do not have axial symmetry, a decrease in the diamagnetism in the plane of the fragment and an increase in the vertical component along the axes of the *p* electrons (P=O, C=S, C=C, C—NO_2) are observed, as in aromatic systems.

3) The absolute magnitude of the anisotropies of the MS of bonds between atoms which have similar electronic structures (C—O and C—S; C=O and C=S; C=N and C=P; C—F, C—Cl, C—Br, and C—I) increases with increase in the atomic number of the element.

The influence of the nature of atoms in the same period of the periodic system does not show clearly defined regularities.

4) The magnetic anisotropy of a bond is not constant, and depends on the nature of the surrounding substituents. Thus its absolute magnitude increases with increase in the electronegativity (methyl and methylene halides and haloforms) and size of neighbouring groups of atoms (halogen derivatives).

The influence of the effects of the immediate environment, in particular the change in the double-bond character, can be clearly seen in the series of C—O bonds on going from aliphatic to aromatic ethers and carbonyl derivatives. In dioxan, as in 2,6-dimethylanisole, where as a consequence of the orthogonality of the methoxy-group there is no conjugation of the phenyl group with the p pair of electrons of the O atom, the MS tensor of the $C_{ar}-O$ bond retains axial symmetry, its components are diamagnetic, and $k_L < k_T$. In anisole, in which as a consequence of $\pi_{ar}-p_o$ conjugation the $C_{sp^2}-O$ bond acquires some multiplicity, the diamagnetism is preserved for k_L, decreases for k_T, and increases for k_V. The existence of paramagnetism in the plane of the C=O double bond is therefore quite regular.

2. Magnetic Susceptibility as a Criterion of Aromaticity

The problem of aromaticity has been examined in a large number of papers on magnetochemistry, dealing with the effects of the mutual influence of atoms. Among the various indices of aromaticity which have been used, the criterion based on the MS obviously has the strongest physical foundation, since the MS tensor is determined directly by the degree of delocalisation of the π-electrons in cyclic systems. Magnetochemical studies of aromaticity have been based on the assumption that any interaction can be described quantitatively by the deviation from additivity of those properties in which this interaction is revealed. For the electric polarisability, deviations from additivity are observed not only for aromatic molecules but also for other conjugated molecules, whereas for MS, super-additive contributions for both the average values ($\Lambda = \chi_{expt}-\chi_{add}$)[141-143] and the anisotropies,[144] and also the vertical components of the tensor,[145] are characteristic mainly of aromatic compounds.

The sharp increase in the diamagnetic properties in aromatic systems compared with all other compounds has been effectively explained using the ring current model.[7,78] From the ratios of the areas of the circulation of the π-electrons (S), expressed in terms of the anisotropy of the MS

$$\sum_p S = -\gamma\,(4\pi mc^2)/e^2$$

and in terms of the geometric dimensions of the ring $\Sigma S = \pi\Sigma\bar{r}_r^2$, it is possible to determine the effective radius of circulation ($\bar{r}^2$) (for a given number of circulating π-electrons p) or the effective number of electrons involved in the circulation.[146] This method has been used to estimate the parameters $\overline{S}$ and $\bar{r}$ for a series of aromatic hydrocarbons and simple heterocyclic compounds.[147] A study of the magneto-optical properties of a number of aromatic hydrocarbons and their corresponding quinone derivatives showed that the aromatic hydrocarbons have a higher MS anisotropy than their quinones, that is the production of the quinone structure leads to a decrease in the mobility of the π-electrons: Γ(benzene)/Γ(1,4-benzoquinone) = 1.37; Γ(naphthalene)/Γ(1,4-naphthoquinone) = 1.16; Γ(anthracene)/Γ(9,10-anthraquinone) = 1.19; and Γ(phenanthrene)/Γ(9-10-phenanthraquinone) = 1.23.[148] The Cotton—Mouton effect was used for a simple estimate of the aromaticity. Thus for 1,4-dithiin, the agreement between the experimental value of ${}_mC$ and the value calculated from the additivity principle indicates that there is no electron delocalisation.[149]

The ring current model has been heavily criticised. An extreme view is that because of the additivity of the MS of aromatic hydrocarbons, the agreement between the conclusions reached from this model and the real properties of molecules is accidental.[90,150,151] This conclusion cannot be fully accepted, however, since it has not been proved that "ring currents" should not obey the rule of additivity, particularly secondary additivity. In a calculation of molecular MS, Musher[150] was forced to introduce different tensor characteristics for the C atoms involved in the formation of C—H bonds on the one hand, and the C—C bonds shared by the two condensed rings on the other. It is not excluded that this differentiation of the magnetic anisotropies includes in implicit form the differences in the change in the number of π-electrons and the areas of their circulation on going from mono- to polynuclear systems. A more correct approach is that in which the MS of an aromatic fragment is represented by two terms: a localised term (k_l) which is due to the induced currents in the individual atoms and bonds and which is calculated using an additive scheme, and a delocalised term (k_d). The latter consists of two components with opposite signs: a diamagnetic component created by the ring currents of a single aromatic π-orbital, and a paramagnetic component produced as a result of a decrease in the delocalisation.[22] For example, it follows from Ref.145 (Table 3) that in benzene the localised component describes the MS completely in the plane of the ring and to the extent of 60% in the perpendicular direction. A similar picture is observed in heterocyclic and polynuclear systems.[152-154] Thus a quantitative measure of the aromaticity (A) of any substance relative to benzene should be provided by the ratios of the perpendicular components corresponding to the anisotropies of the delocalised MS or the exaltations of the average MS for benzene and the molecule being studied (M):

$$A = [k_{\perp d}(C_6H_6)/k_{\perp d}(M)] \approx [\gamma_d(C_6H_6)/\gamma_d(M)] \approx [\overline{\Lambda}(C_6H_6)/\overline{\Lambda}(M)],$$

where $k_{\perp d} = k_{\perp expt}-k_{\perp add}$, $\gamma_d = \gamma_{expt}-\gamma_{add}$, $\Lambda = \Lambda_{expt}-\Lambda_{add}$.

The replacement of a CH group in benzene by N leads to a considerable decrease in the electron delocalisation and hence in the aromaticity in the series benzene > pyridine ≃ pyridazine ≃ pyrazine > pyrimidine > *S*-triazine.[153] The degrees of delocalisation in pyrrole, pyrazole, and imidazole, and also their N-methyl derivatives, are similar to one another.[154] These conclusions show qualitative agreement with results obtained in a study of the Zeeman effect in isoxazole and oxazole,[152] their thio-analogues,[155] and furan;[145] the degree of delocalisation of the electrons in furan is much less than that in benzene; in oxazole and isoxazole, a further decrease in the delocalisation is observed, and the level of aromaticity of thiophene is approximately the same as that of pyrrole. An interesting feature is that cyclopentadiene also shows excess delocalisation, although to a smaller extent than in furan; this arises as a result of the hyperconjugation of the methylene group with the π-electrons of the double bonds; in fulvene, the delocalisation of the electron cloud is even smaller[145] (Table 3).

In a study of the influence of dissociation on the magnetic anisotropy of aromatic molecules by ^2H NMR in a strong field, it was established that Γ for the fluorenyl anion is greater than Γ for fluorene,[73] whereas the values of Γ for anthracene[5] and its carbacation[74] are equal.

Magnetic birefringence has been used to study the influence of the nature of the nitrogen atoms in aniline, N,N-dimethylaniline, and the corresponding anilinium and N,N,N-trimethylanilinium derivatives on the anisotropy of the MS of the phenyl group.[44,156] The anisotropy of the MS of the aromatic ring in the anilines is depressed compared with the MS of benzene, whereas in N,N-dimethylaniline the additivity is preserved; this reflects the difference in the strength of the conjugation of the lone pair of electrons of nitrogen with the

phenyl ring.[44] Protonation of aniline "restores" the magnetic anisotropy to the value characteristic of benzene. Thus the positive charge of the NH_3 group has no influence on the magneto-optical properties of the ring. The anisotropy of the N,N,N-trimethylanilinium cation decreases sharply under the influence of the excess charge.[156] This difference is due chiefly to intermolecular and not intramolecular effects;[157] in the substituent $\dot{N}(CH_3)_3$, the charge is situated chiefly on the N atom and is shielded from the hydrate layer of the solvent by the methyl groups. In the $\dot{N}H_3$ group, the excess charge is delocalised over all the N–H bonds, so that it is compensated to a considerable extent by the surrounding water molecules.

Table 3. Anisotropic magnetic susceptibilities of molecules as a criterion of aromaticity.[145]

Compound	$10^{29} k_{\parallel}$, cm^3		$10^{29} k_{\perp}$, cm^3	
	found	calculated	found	calculated
Benzene	5.80	5.55	15.71	9.87
Fulvene	5.08	5.55	11.23	9.87
Cyclopentadiene	5.53	5.61	11.21	8.39
Furan	5.30	5.20	11.73	7.80
Thiophene	6.76	6.69	15.08	9.43
Pyrrole	5.71	5.73	12.76	7.04
Durene	13.26	13.36	23.90	16.74
Resorcinol	8.17	8.39	17.14	11.81
Benzoquinone	4.15	4.78	10.80	11.05
Phthalimide	9.97	9.93	20.63	13.02
Diphenyl	10.75	10.35	30.53	18.77
Triphenyl	15.37	15.15	45.07	27.84
Dibenzyl	15.08	14.12	33.60	22.43
Stilbene	11.63	12.16	34.82	22.47
Tolane	12.41	12.86	32.94	20.68
Diphenylacetylene	15.35	14.49	34.34	21.76
Naphthalene	8.92	8.52	28.82	15.56
Anthracene	11.50	11.50	41.79	22.11
Anthraquinone	11.68	10.73	36.15	22.44
Fluorene	11.30	11.48	31.40	19.77
Acenaphthene	11.84	11.53	30.81	19.40
Pyrene	15.39	12.33	50.33	23.69

VI. MAGNETIC ANISOTROPY AND PROBLEMS OF STEREOCHEMISTRY

The systematic magnetochemical study of the spatial structure of molecules was begun comparatively recently. It is based chiefly on magneto-optical and resonance methods. Of particular interest are studies based on an analysis of the relationship between magnetic anisotropies and the chemical shifts of the ^1H and ^{13}C nuclei. The extensive information provided by this method, particularly for paramagnetic systems, the relative simplicity of the experimental procedure, and the possibility of theoretical interpretation of the results not only qualitatively but also quantitatively, led in the early nineteen-seventies to the publication of a large number of papers and to the development of an independent field, namely NMR using paramagnetic shift reagents. The method has been described in detail in many monographs, textbooks, and reviews (see for example Refs.75, 76, and 158–161), and therefore will not be discussed in the present work.

1. The Spatial Structure of Molecules and Complexes

Unlike its electric analogue, that is the Kerr effect, the Cotton–Mouton effect has been applied to conformational analysis to only a slight extent, although it should carry information on the spatial structure of molecules.[162] The molar Cotton–Mouton constants, and also the paramagnetic birefringence constants, are macroscopically additive. Moreover, the anisotropic components of ${}_mC$ and ${}_mP$ are also additive at the intramolecular level. The magnetic susceptibility of weakly magnetic substances is practically 1, so that the molecules of a solute are influenced by a magnetic field with practically the same intensity as the external field.[163] It is therefore possible to use magnetic birefringence to study the structure of molecules in the liquid condensed state. The accuracy of the results obtained using the Cotton–Mouton effect in conformation studies is such that the difference between the calculated magneto-optical constants of individual conformers is at least an order of magnitude greater than the uncertainty in their determination from the experimental data.[162]

The possibility of using the Cotton–Mouton effect in conformational analysis was first demonstrated for biphenyl (0°) and its structural analogues 2,2′-bipyridyl (25 °), 9,9′-dianthranyl (62°), 9-phenylanthracene (70°), 1-phenylnaphthalene (66°), and 1,3,5-triphenylbenzene (35°).[164] The dihedral angles φ characterising the deviations from planarity are given in brackets. In 1,3,5-triphenylbenzene and *sym*-triphenyltriazine, the angles φ are 30 ± 10° and 15 ± 15° respectively, and for tri(2-pyridinyl)-S-triazine in CCl_4, the existence of two conformers with different dihedral angles φ = 15 ± 5° has been established.[165] The measured magnetic birefringence in benzophenone and its *p*-chloro-, *p*-bromo-, *p*-methyl-, and *p*-methoxy-derivatives dissolved in CCl_4 was used to estimate the angles φ of the aromatic rings.[95] The angle of non-coplanarity of the nitrogroup in the *ortho*-position relative to the methyl group in trinitrotoluene is 50°,[93] and that in 4-nitrobiphenyl is 23°.[166] The study of individual liquid alkyl halides has confirmed that the *trans*-orientation of the C–Br bonds is preferred in methyl-substituted 1,2-dibromoethanes and cyclohexanes, and the *gauche* orientation of the C–C and C–Hal bonds is preferred in 1,3-dihalogenopropanes.[162] In the series of halogenopropanes and their methyl derivatives with the general formula $C(R^1R^2R^3)C(R^4R^5)Hal$, where Hal = Cl, Br, I, and R = H and (or) CH_3, the asymmetric *gauche* structures predominate in the pure liquids; the conformational energies of these structures are not additive, and are determined by hyperconjugative interactions $\pi[(CH_2)$ or $C(CH_3)_2] - \sigma^*(C-Hal)$.[167]

In the study of compounds containing functional groups with several axes of internal rotation, the simple application of one physical method (except diffraction methods) is insufficient. To solve a many-parameter structural problem, it is usual to employ either a combination of several methods or (and) data obtained by a single method but covering a group of compounds with the same conformation.[168] Studies of the spatial structure and conformational composition of halogen-substituted arylethanes were based on these principles.[169–172] In a complex graphical analysis of the structure of molecules,[168] new methods were proposed for determining conformations using the Cotton–Mouton effect. For this purpose, graphs of the "property–property" type are constructed: ${}_mC(C_6H_5) - {}_mC(p\text{-}X-C_6H_4)$ for a group of compounds with the same conformation,[169] and ${}_mC - {}_mK$ (${}_mK$ is the Kerr constant) for a given compound.[170] Dipole moment and ^1H NMR spectroscopic data show that 2-halogenoethylbenzenes in CCl_4 consist of equilibrium mixtures of the *trans*- and *gauche*-rotamers approximately

equally populated with respect to the ethane bond C—C. In the *gauche* form, according to data obtained using the Kerr effect, the aromatic ring shields the C—H bond. The angle of rotation of the aryl group in the *trans*-conformer was found by analysing the ${}_mC(C_6H_5CH_2CH_2Cl) - {}_mC(p\text{-}Cl-C_6H_4CH_2CH_2Cl)$ relationship.[169] The structures of 1,2-dihalogenoethylbenzenes,[171] 1,1-diphenyl-1,2-dihalogenoethanes,[172] and 1,2,2-tribromo-1-phenylethane[170] were studied similarly.

The mutual orientation of the chelate rings in molecular complexes of the lanthanides based on α,β-diketones has been studied by paramagnetic birefringence.[137,138] For the complexes of Pr and Dy with *tris*-3-trifluoroacetylcamphors, which are monomeric in $HCCl_3$ [Ln(Facam)$_3$] and dimeric in CCl_4 [Ln_2(Facam)$_6$], octahedral structures were found.[137] A structure close to octahedral was established for the adducts $Dy_2(Facam)_6.3DMF$ and $Dy(Facam)_3.2DMF$. Paramagnetic birefringence also gives information on the orientation of the molecular or ionic fragments of complexes relative to the direction of the paramagnetic anisotropy of the central ion.[47,173] In the mono-adducts of Er and Tb dipivaloylmethanates with pyridine [Ln(DPM)$_3$Py] in CCl_4, the plane of the aromatic heterocyclic ring is perpendicular to one of the principal axes of the paramagnetic susceptibility tensor.[47]

2. Orientational Effects of Solvation and Complex Formation

Magnetic birefringence and NMR spectroscopy are extremely sensitive to the effects of liquid-phase structure formation. Thus in ^1H NMR, the phenomenon of a chemical shift induced by aromatic solvents is observed; this is produced by the magnetically anisotropic continuum created by preferentially orientated aromatic molecules of the solvent arranged round the polar molecule of the solute.[174–176] New possibilities for studying intramolecular interactions influencing the alignment of molecules in liquids are being opened up by high-resolution NMR spectroscopy in strong magnetic fields.[5] In a study of the influence of the concentration of the substance and the nature of the solvent on the magnitude of the anisotropies of the MS of nitrobenzene and *m*-dinitrobenzene, a sharp decrease in the anisotropy of nitrobenzene was observed on going from the pure liquid ($\Gamma_1 = -34 \times 10^{-29}$ cm^3) to the solutions with extrapolation to infinite dilution ($_\infty\Gamma = -15 \times 10^{-29}$ cm^3).[72] In the case of benzene, a slightly different picture is observed; in $(CD_3)_2CO$, $_\infty\Gamma = -11.1 \times 10^{-29}$ cm^3, but with increase in concentration; $|\Gamma|$ begins to decrease, reaching a constant value of -9.3×10^{-29} cm^3 in a 60% solution of benzene in deuterioacetone. For naphthalene, a concentration dependence of Γ was not observed.[72] The data obtained agree with the results of magneto-optical studies;[43,62] the ratios $C_1/_\infty({}_mC)$ for benzene and nitrobenzene are of the same order of magnitude as the ratios $\Gamma_1/_\infty\Gamma$.

A quantitative approach to the estimation of the effects of liquid-phase ordering, estimated by the Cotton—Mouton method, has been proposed.[177] In the continuum model and the axially symmetrical approximation, the Cotton—Mouton constant of a solvated molecule has the form

$$ {}_mC = (2\pi N/45kT)\{2(b_\parallel - b_\perp)(k_\parallel - k_\perp) + [(b_\parallel - b_\perp)(k'_\parallel - k'_\perp) + (b'_\parallel - b'_\perp)(k_\parallel - k_\perp)]\langle(3\cos^2\theta - 1)\rangle\}, $$

where $\langle(3\cos^2\theta - 1)\rangle$ is the angular correlation factor, and b_i, k_i and b'_i, k'_i the electric and magnetic parameters of the molecules of the solute and the solvent respectively. For an individual liquid, the expression is simplified:

$$ {}_mC_l = (4\pi N/45kT)[(b_\parallel - b_\perp)(k_\parallel - k_\perp)]\{1 + (1/2)\langle\Sigma(3\cos^2\theta_j - 1)\rangle\}. $$

The corresponding solvation contribution obviously has the form:

$$ \Delta_mC = (2\pi N/45kT)(b_\parallel - b_\perp)(k_\parallel - k_\perp)\langle\Sigma(3\cos^2\theta_j - 1)\rangle. $$

Δ_mC is determined experimentally as the difference in the molar constants of the individual liquid and its dilute solutions in an inert solvent with subsequent extrapolation to infinite dilution: $-\Delta_mC = {}_mC_l - {}_\infty({}_mC_s)$. The angular correlation parameters can then be found from the relationship

$$ \Delta_mC_l/_\infty({}_mC_s) = (1/2)\langle\Sigma(3\cos^2\theta_j - 1)\rangle. $$

The numerical values of the ratios $\Delta_mC_l/_\infty({}_mC_s)$ are small, and their signs may be different; negative signs indicate the existence of chiefly ternary mutually perpendicular correlations, and positive signs indicate the existence of parallel correlations. They have been calculated for a large group of aromatic compounds.[63,64] The orientational effects of solvation are revealed most clearly in the magneto-optical anisotropy of nitrobenzene. The Cotton—Mouton constants have been obtained for nitrobenzene in 19 solvents of different character and polarity.[63] The ${}_mC$ values for this compound vary over a very wide range from $(3.3-3.4) \times 10^{-15}$ emu in dioxan, CCl_4, C_6H_6, and $HCCl_3$ to 7.5×10^{-15} emu in benzonitrile; for individual liquid nitrobenzene, ${}_mC = 6.4 \times 10^{-15}$ emu. In this case, the Cotton—Mouton constant is described by the relationship

$$ {}_mC = {}_mC_0 + A\mu\Delta k_\mu + B\mu\Delta b_\mu, $$

where Δk_μ and Δb_μ are the anisotropies of the MS and the polarisability in the direction of the molecular electric dipole moment μ. The theoretical analysis carried out indicated that a decisive role in determining the orientations round the solute molecules is played by interactions of the "solute dipole—solvent dipole" and "solute dipole—solvent quadrupole" type. A similar conclusion was reached in Refs.174—176.

In the study of the phenomena of complex formation and solvation in solutions of paramagnetic compounds, important information can be obtained by examining the effect of paramagnetic birefringence. This effect is extremely marked for complexes consisting of molecules or ions of two kinds, one of which is characterised by high anisotropy of the MS and low anisotropy of the electric polarisability, while the other has the opposite properties. For simple mixing of these species, that is in the absence of complex formation, the paramagnetic birefringence effect is small, and it is increased sharply only by the formation of associates accompanied by preferential mutual orientation of the central ion and the ligands.[173] Magneto-optical titration in CCl_4 has established the formation of an adduct of DMF with dysprosium *tris*-3-trifluoromethylacetylcamphorate with the 3 : 2 composition. The magnetic birefringence constant of this complex (-1300×10^{-15} emu) is approximately four orders of magnitude greater than the corresponding constant of DMF (0.17×10^{-15} emu). In an excess of DMF, the 1 : 2 complex is formed.[138] The formation of mono-adducts of Ln(DPM)$_3$ with pyridine in CCl_4 was confirmed similarly.[47]

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Several new fields of study have developed in molecular magnetochemistry on the basis of the study of the rotational Zeeman effect, the Cotton—Mouton effect, linear birefringence in solutions of paramagnetic substances, and the high-resolution NMR of partly

oriented molecules in strong magnetic fields. The study of the anisotropic properties of molecules gives information of a qualitatively higher level than the study of their average properties. This makes it possible to include in the range of interests of magnetochemistry a number of fundamental problems of the stereochemistry of organic and complex compounds, and intramolecular and intermolecular interactions. Among the most promising fields of application of data on magnetic anisotropy, special mention must be made of the theory of the mutual influence of atoms, and in particular the problem of aromaticity. A second field is the study of the orientational effects of association and complex formation in liquid media, the effects of structure formation appearing in pure liquids, and the structural aspects of solvation, including that in electrolyte solutions. Finally, a third field is the conformational analysis of molecules in condensed liquid media and polar solvents, and also of complex ionised species and compounds of biological importance. The progress of molecular magnetochemistry in these fields obviously depends directly on the further development and improvement of the magnetic susceptibility tensor additive scheme.

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