

CNDO/S Calculations of Magnetic Circular Dichroism of Some Mono-Substituted Benzenes Using the Complete Angular Momentum Operator

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Magnetic Circular Dichroism (MCD) B term calculations are performed using the CNDO/S method on mono-substituted benzene derivatives. The influence of geometry, origin dependency, extent of Configuration Interaction (CI) and the choice of the basis set is investigated numerically.

For the lowest-lying singlet transitions in these molecules excellent agreement with experiment is obtained.

Key words: Benzenes, mono-substituted, magnetic circular dichroism of \sim -
Magnetic circular dichroism of mono-substituted benzenes

1. Introduction

For the interpretation of magnetic circular dichroism (MCD) spectra of low-symmetric organic molecules (absence of three-fold or higher symmetry) one needs some method of theoretical calculation of the relevant quantities. In MCD there are three such quantities, commonly called *A*, *B* and *C* terms [1-3]. The low symmetry precludes the occurrence of *A* and *C* terms. The first aim of our calculations is to obtain reliable values for the *B* terms that can be compared with *B* terms resulting from the evaluation of experimental spectra.

Several attempts [4-9] have been published recently to test numerical model calculations by comparison with experimental data. Most of them used the Pariser, Parr, Pople (PPP) model. Only in the calculations on the transitions of formaldehyde [8], some adenines [8a] and benzene [9] were the all-valence electrons models CNDO/2 and CNDO/S [10] used.

The PPP model is suited for π -electronic structures only. If one wants to investigate $n-\pi^*$ transitions, molecules containing ring systems with hetero-atoms and the participation of the σ -electronic structure, one needs at least an all-valence electrons model.

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The CNDO/S model presented by Jaffé *et al.* [10] seems well suited for this purpose. The results of this model, with a configuration interaction (CI) calculation included, in the computation of electronic transition energies and oscillator strengths are encouraging [11].

The interaction of the magnetic field with the molecular states calls for the calculation of the matrix elements of the angular momentum operator. Some authors [4-7] use the approach of Linderberg [12], others [8, 9] evaluate the matrix elements exactly for the one-centre contributions using the formula of Pao and Santry [13]. Good results are obtained in the calculation of natural optical activity [14, 15], where all two-centre terms in the evaluation of the matrix elements of the angular momentum operator are also included.

In view of the above we adopted the CNDO/S model for our calculations and computed the complete matrix for the angular momentum operator with the inclusion of all one- and two-centre terms, as is described below.

To test the capabilities of our model we selected a number of mono-substituted benzene derivatives. As a great deal of work has been done on these molecules in the past, we are able to compare our results with those of other authors.

Shieh *et al.* [16, 17] introduced and confirmed the rule that for a given type of substituted benzene, other than 1, 2, 3-, 1, 2, 5-, and hexa-benzene, the ortho-para and meta directing substituents will give rise to opposite signs in the MCD of the transition deriving from the benzene $^1A_{1g} \rightarrow ^1B_{2u}$ transition.

Our model should be able to reproduce these trends. We therefore selected the substituents from strongly electron-donating (ortho/para directing) to strongly electron-withdrawing (meta directing) [18].

Experimental data, that one wants to compare with calculated values, are obtained from the MCD spectra by integration over the band corresponding to the electronic transition [19].

From a theoretical point of view [2] such an integrated B -term may only be compared with the results of model calculation if the assumptions of the Born-Oppenheimer and Franck-Condon approximations are valid. From the work of Shieh *et al.* [17] it becomes clear that there may be some vibronically induced intensity in the MCD spectra of the mono-substituted benzenes.

To account for this one has to augment the model to include vibronic interaction in one way or another. This is demonstrated by the calculations of Douglas *et al.* [20, 21] and Rosenfield *et al.* [9] on the symmetry-forbidden $^1A_{1g} \rightarrow ^1B_{2u}$ transition in benzene, where all intensity is of vibronic origin, and by the work of Dekkers and Westra [22] on azulene.

For our molecules the vibronically induced component on the intensity is very small, so we shall neglect it for the time being.

All models, with the exception of the work of Seamans and Linderberg [7], by virtue of the gauge invariant atomic orbitals, suffer from origin dependency [23, 24] in their results.

Another source of instability in the results is the truncation of the set of wave-functions constituting the configurations in the CI calculation. The inclusion of all singly excited configurations (SCI) in the CNDO/S model, at the moment, is hardly achievable, especially for larger molecules, let alone a complete configuration set. So we hope for satisfactory results at some lower extent of CI. We shall discuss these effects below.

Furthermore we want to pay attention to the influence of molecular geometry on the calculated quantities as well as to the effect of using so-called Löwdin orthogonalized atomic orbitals (LAO's).

2. Method of Calculation

The B term, which completely describes the MCD of an electronic transition ($A \rightarrow J$) in a molecule, where no orbital degeneracy is present, is expressed as [2]

$$B(A \rightarrow J) = \text{Im} \left\{ \sum_{K \neq A} \frac{1}{E_K - E_A} \langle K | \boldsymbol{\mu} | A \rangle \cdot (\langle A | \boldsymbol{m} | J \rangle \times \langle J | \boldsymbol{m} | K \rangle) + \sum_{K \neq J} \frac{1}{E_K - E_J} \langle J | \boldsymbol{\mu} | K \rangle \cdot (\langle A | \boldsymbol{m} | J \rangle \times \langle K | \boldsymbol{m} | A \rangle) \right\} \quad (1)$$

in which \boldsymbol{m} and $\boldsymbol{\mu}$ are the electric and magnetic dipole moment operators respectively, whilst the other symbols have their usual meaning. The summation over K includes all electronic states of the molecule. For our molecules we hope that the summation may be limited to a few terms involving states lying close to J . The calculations of $B(A \rightarrow J)$ were performed using the CNDO/S program obtained from Quantum Chemistry Program Exchange as QCPE 174.1 for the wave-functions and energies of the spectroscopic states. This program also calculates the electronic transition moments to obtain the oscillator strengths for the transitions. These moments, calculated according to the formula given by Ellis *et al.* [25], are needed in the above expression.

We made a small extension to the program to calculate the transition moments between all spectroscopic states. For the magnetic transition moments we augmented the program in such a way that the complete matrix of the angular momentum operator was obtained. The procedure will be described below. As the CNDO eigenvectors in the SCF procedure are obtained in the ZDO approximation, they can be regarded as linear combinations of orthogonalized atomic orbitals, derived from Slater orbitals by the Löwdin transformation [26]. All transition moments needed in Eq. (1) can then be expressed in terms of the Slater orbital coefficients C^X after transformation of the CNDO orthogonal orbital coefficients C^λ according to

$$C^X = S^{-1/2} C^\lambda \quad (2)$$

in which S is the overlap matrix of the Slater type atomic orbitals. This is one way to alter the basis set [27]. By inserting in the program a subroutine which performs the transformation of Eq. (2) we thus obtained two modifications of the model.

To eventually obtain the matrix elements of the magnetic moment operator on the basis of CI wave-functions for the spectroscopic states, we first calculated the matrix

of the angular momentum operator, \mathbf{L} on the basis of atomic orbitals of the molecule. The angular momentum operator is defined as:

$$\mathbf{L} = -i(\mathbf{R} \times \mathbf{p}) = L_x, L_y, L_z \quad (3)$$

Atomic units are used. R_b being the vector that locates centre b in a molecular coordinate system, we may substitute for R : $R = R_b + r'$. Here r' is a local vector referring to centre b . Now if χ_a symbolizes an AO on centre a and χ_b an AO on centre b , the matrix element, for example L_x , becomes [14, 15]:

$$\langle \chi_a | L_x | \chi_b \rangle = -i \left\{ y_b \left\langle \chi_a \left| \frac{\delta}{\delta z'} \right| \chi_b \right\rangle - z_b \left\langle \chi_a \left| \frac{\delta}{\delta y'} \right| \chi_b \right\rangle \right\} + \langle \chi_a | l_x | \chi_b \rangle \quad (4)$$

In this expression l_x is the x -component of the angular momentum operator relative to centre b . Similar expressions hold for the y - and z -components of the operator.

All terms on the right-hand side of Eq. (4) can be reduced to overlap integrals by the following relations, that are the only ones pertinent to the problem:

$$\begin{aligned} \frac{\delta}{\delta z'} |1s\rangle &= -\frac{\zeta}{\sqrt{3}} |1p_z\rangle \\ \frac{\delta}{\delta z'} |2s\rangle &= \zeta \left\{ \frac{1}{3} |p_z\rangle - \frac{1}{\sqrt{3}} |2p_z\rangle \right\} \\ \frac{\delta}{\delta x'} |1s\rangle &= -\frac{\zeta}{\sqrt{3}} |1p_x\rangle \\ \frac{\delta}{\delta x'} |2s\rangle &= \zeta \left\{ \frac{1}{3} |1p_x\rangle - \frac{1}{\sqrt{3}} |2p_x\rangle \right\} \\ \frac{\delta}{\delta x'} |2p_z\rangle &= -\frac{\zeta}{\sqrt{5}} |2d_{xz}\rangle \\ \frac{\delta}{\delta z'} |2p_z\rangle &= \zeta \left\{ \left| 1s \right\rangle - \frac{1}{\sqrt{3}} \left| 2s \right\rangle - \frac{2}{\sqrt{15}} \left| 2d_z \right\rangle \right\} \end{aligned} \quad (5)$$

The atomic orbitals in these expressions are Slater orbitals, as defined in Roothaan's paper [28]. The two-centre overlap integrals that now appear are most easily evaluated in a prolate spheroidal coordinate system involving the two centres a and b . Formulae for these overlap integrals can be found in the literature [28, 29].

The one-centre contributions are evaluated according to the formula given by Pao and Santry [13].

The basis set is successively transformed. Via the limited set of wave-functions representing the singly excited configurations, one finally obtains the matrix of the angular momentum operator on the basis of the spectroscopic states resulting from the CI calculation. Insertion of the proper multiplicative factor then gives the matrix for the magnetic dipole moment operator.

The calculated transition moments and energies are inserted in Eq. (1) to give the B term for the transition ($A \rightarrow J$).

3. Results and Discussion

It is stated in the introduction that quantities resulting from calculations on a model are varied by several causes. Some of these are specific for the model, others stem from external sources. To the first kind we reckon the parametrization of the CNDO/S model and the type of integrals used for the electron repulsion in the SCF procedure. The second comprises variation of the origin, slight alterations in the molecular geometry and the extent of CI in the calculation. We did not bother with influences of the first kind and used the parameters given by Jaffé *et al.* [25]. In the CNDO/S model the best results for singlet transitions are obtained with the Mataga-Nishimoto formula [30] for the two-centre electron-repulsion integrals. The influences of the second kind are investigated to some extent. The results are described in detail below. Throughout this work we used experimentally determined molecular geometries, taken from data in the literature. In Table 1 we represent the results for some mono-substituted benzenes. Here we restricted ourselves to those transitions from which the MCD can be determined experimentally. If the calculated B terms are compared in a general way with the experimental data available (see Table 7), we note fair agreement. The rule of Shieh *et al.*, mentioned in the introduction, is followed completely.

3.1. Origin Dependency

Shifting the origin creates an extra term in the expression for the B term for the transition $A \rightarrow J$, in which states are coupled to the state J by the dipole velocity operator [23]. For exact wave functions this term vanishes. However, in the case of approximate wave-functions, this term may become large. In benzene (pointgroup D_{6h}), those states which couple by the magnetic moment operator and thus participate in the B term do not couple via the dipole velocity operator by symmetry. So no origin dependency is to be expected there, in accordance with the symmetry rules derived by Seamans and Moscovitz [23]. All molecules studied in this paper are derived from benzene by substitution of one ring proton by a group. This causes lowering of the symmetry, so that origin dependency will occur. If, however, one regards the influence of the substituting groups as merely perturbing the benzene states, one may expect the origin dependency to be small. We kept the origin for our calculations inside the molecule at the centre of charges, following the suggestion of Caldwell and Eyring [24], and calculated B terms several times with the origin moved 1 Å along the axes of the molecular coordinate system. The symmetries of the excited states were determined in accordance with symmetry conventions [31]. As is readily inferred from Table 1 the origin dependency remains small, compared to the uncertainties due to the causes to be discussed presently. If the substituent group is electron-withdrawing (benzotrile and benzaldehyde) the origin dependency is somewhat larger than for the electron-donating groups. This reflects the more drastic reorganization of electrons in the systems with CN and CHO groups.

Table 1. Calculated: Slater Type Orbitals (STO) and Löwdin Atomic Orbitals (LAO), transition wavelengths (λ , nm), oscillator strengths (f), B values ($10^{-5} \times \text{Debye}^2 \times \text{Bohr magneton}/\text{cm}^{-1}$), and origin dependency (%/A)

Substituent	Transition	λ	f	STO			LAO			Orig. Dep.		
				B	x	y	z	B	x	y	x	y
-NH ₂	$^1A' \rightarrow ^1A''$	267.6	0.016	+26.08	-0.16	-0.19		+28.74	-0.31	-0.14		
	$^1A' \rightarrow ^1A'$	218.3	0.187	-98.15	-1.40	+0.09		-84.83	-0.78	-0.46		
-OH	$^1A' \rightarrow ^1A''$	264.9	0.015	+14.81	-0.97	-1.59		+16.46	-0.79	-1.37		
	$^1A' \rightarrow ^1A'$	212.5	0.104	-74.52	-0.97	-2.56		-63.96	-1.95	-1.20		
-F	$^1A_1 \rightarrow ^1B_2$	258.6	0.0016	+1.96		+2.01		+2.17		+1.18		
	$^1A_1 \rightarrow ^1A_1$	206.3	0.0187	-13.66		-0.61		-11.10		+1.63		
-CN	$^1A_1 \rightarrow ^1B_2$	262.4	0.0013	-11.32		-2.54		-11.54		-2.46		
	$^1A_1 \rightarrow ^1A_1$	226.4	0.254	+9.06		+6.65		+28.20		+7.17		
-CHO	$^1A' \rightarrow ^1A''$	263.4	0.0113	-29.86	+0.85	+1.82		-29.09	+1.01	+1.63		
	$^1A' \rightarrow ^1A'$	217.6	0.283	+63.44	-0.58	-7.01		+86.76	+2.25	-5.94		

Geometries from: aniline [34], phenol [35], fluorobenzene [32], benzonitrile [36], benzaldehyde [37].

3.2. Configuration Interaction

The number of mono-excited configurations that participate in the CI calculation may be chosen on several grounds. Computationally the most simple way is to make this number equal to the number of atomic orbitals in the SCF procedure. This number varies of course from one case to another. In Table 2 it is symbolized by N .

We increased the number of configurations, in two successive calculations, to 60 and 100 in order to investigate its influence on the resulting quantities. In general we can say that the B values and oscillator strengths become larger with increasing amounts of CI; the transition wavelengths, however, are much less affected. Better stability is obtained upon division of the calculated B values by the corresponding dipole strength. However, as CNDO/S is a semi-empirical method depending upon optimized parameters, one cannot be certain of the significance of these effects. The parameters in the CNDO/S model are chosen so that only a limited amount of CI will give results that agree with the experiment. The best results are obtained with a truncated CI calculation (TSCI), where the number of configurations is chosen in the way described above. This number (N) for the molecules mentioned in Table 2 is in all cases less than 40.

3.3. Molecular Geometry

To obtain the data of Table 1 we used the molecular geometries recently determined by means of microwave spectroscopy. The importance of correct molecular geometry is demonstrated by the systematic improvement of calculated B values upon changing the carbon to fluorine distance in fluorobenzene. The values for this bond length, found in earlier literature, vary from 1.28 to 1.35 Å; 1.354 Å being the value recently determined by Nygaard *et al.* [32]. In Table 3 we show the values obtained for the lowest singlet transition of fluorobenzene for different carbon to fluorine distances ranging between the above-mentioned values. Although there is only a variation of 0.07 Å in the bond distance, the corresponding values of the B term change by more than a factor two. The transition wavelengths, however, are much less affected. In all cases, except aniline, the use of experimental geometries gives substantially better results for the calculated spectroscopic properties than the use of standard model geometries [33]. The discrepancy in the aniline data may arise from several causes. The ground-state geometry of aniline, according to Lister *et al.* [34], is slightly pyramidal. The excited state configuration is altered [35]. We therefore repeated the calculation for aniline assuming a planar structure. However, this did not vary the results significantly. The reason might well be the parametrization for nitrogen in the CNDO/S model. For when we used the geometry given by Jaffé *et al.* [11], where the carbon to nitrogen differs markedly (0.05 Å) from that given by Lister *et al.* [34], the results improved.

The calculated B term was 45.7×10^{-5} Debye² × Bohr magneton/cm⁻¹. This suggests the need for adaptation of the nitrogen parameters in the model even more so as the calculated transition wavelength in aniline deviated substantially from its true value, too, contrary to all other molecules. However, more data are needed to safely readjust the parametrization of the CNDO/S model.

Table 2. Influence of the extent of configuration interaction on the spectroscopic properties of the lowest singlet transitions

Substituent	Transition	Number of Configurations								
		60			100					
		λ	f	B	λ	f	B			
-NH ₂	$^1A' \rightarrow ^1A''$	267.6	0.016	28.7	267.7	0.017	26.8	268.2	0.022	39.7
	$^1A' \rightarrow ^1A'$	218.3	0.187	-84.8	219.1	0.205	-89.9	223.1	0.240	-141.4
-OH	$^1A' \rightarrow ^1A''$	264.9	0.015	16.5	265.2	0.015	16.7	265.6	0.021	31.1
	$^1A' \rightarrow ^1A'$	212.5	0.104	-64.0	212.5	0.100	-69.6	226.1	0.127	-104.9
-F	$^1A_1 \rightarrow ^1B_2$	258.6	0.0016	2.2	258.6	0.0015	2.4	258.7	0.0023	4.9
	$^1A_1 \rightarrow ^1A_1$	206.3	0.019	-11.1	206.5	0.027	-14.2	218.1	0.051	-24.7
-CN	$^1A_1 \rightarrow ^1B_2$	262.4	0.0013	-11.5				275.6	0.0055	-10.5
	$^1A_1 \rightarrow ^1A_1$	226.4	0.253	28.2		^a		208.7	0.124	17.1
-CHO	$^1A' \rightarrow ^1A''$	263.4	0.013	-29.1	263.4	0.012	-32.0	263.9	0.013	-34.7
	$^1A' \rightarrow ^1A'$	217.6	0.283	86.8	218.2	0.328	68.3	219.9	0.341	101.3

Units: See Table 1.

^a At 60 configurations incorrect ordering of states resulted for benzonitrile.

Table 3. Influence of the C-F distance in fluorobenzene on the spectroscopic properties of the lowest singlet transition

C-F Distance	λ	B
1.28	262.1	5.44
1.29	261.8	4.87
1.30	261.6	4.34
1.31	261.3	3.85
1.32	261.1	3.39
1.33	260.9	2.96
1.34	260.7	2.57
1.354	260.4	2.02

Units: See Table 1. C-F distance in Å.

3.4. The Basis Set

In the calculation of the excited state magnetic moments of coronene and triphenylene, Stephens *et al.* [38] demonstrated the necessity of transforming the basis by the Löwdin procedure to an orthogonal set to obtain the correct sign for the A term of the degenerate transition (cf. the allowed ${}^1A_{1g} \rightarrow {}^1E_{1u}$ transition in benzene at 54 000 cm^{-1}). The molecules studied in this paper exhibit transitions in the 54 000 cm^{-1} region that are derived from the ${}^1A_{1g} \rightarrow {}^1E_{1u}$ transition in benzene, but the degeneracy is lifted to some extent by the perturbing substituents. So two close-lying, nearly degenerate states, are formed. This lifting of the degeneracy is, however, small enough to give the MCD spectrum the appearance of an A term in this spectral region. The sign of the excited state magnetic moment for various poly-substituted benzenes is positive, as is determined by Kaito *et al.* [39]. As the positive moment is also found in toluene [40], we expect the same sign for the mono-substituted benzenes studied in this paper.

Calculated A/D values for these states are presented in Table 4, where we included toluene. both types of basis were used. The correct sign was found only upon application of the Löwdin transformation.

The agreement of the value for toluene with experiment [40] is excellent. The influence of transforming the basis set on the B terms is much less pronounced. As may be inferred

Table 4. Calculated A/D values for the nearly degenerate transition, derived from ${}^1A_1 \rightarrow {}^1E_{1u}$ transition in benzene

Substituent	Calculated A/D Values	
	STO	LAO
-CH ₃	0.003	0.096
-NH ₂	0.038	0.113
-OH	-0.012	0.089
-CN	-0.065	0.021
-F	-0.055	0.056

Units: A/D in Bohr magneton.

from Table 1, only a slight improvement of the results is obtained. This fact is also recognized by Rosenfield *et al.* [9] in their vibronic calculations for the ${}^1B_{2u}$ state of benzene.

4. Separate Contributions to the B Terms

According to Eq. (1) the summation over K includes all electronic states. In Table 5 we separated out for the two lowest transitions the contributions of the four states that for these molecules are derived from the benzene ${}^1B_{2u}$, ${}^1B_{1u}$ and ${}^1E_{1u}$ states, numbered 1 to 4 in the table. These four states are sufficient to describe the B terms almost com-

Table 5. Fractional separate state contributions to the B terms of the two lowest singlet transitions

Contributing State	-NH ₂	-OH	-F	-CN	-CHO
First Singlet Transition					
First	0.005	0.003	0.000	-0.002	-0.005
Second	1.860	2.047	2.413	-1.837	-1.777
Third	0.027	0.021	0.021	-0.068	0.314
Fourth	-0.919	-1.056	-1.432	0.801	0.497
Total	0.973	1.014	1.002	-1.106	-0.971
Second Singlet Transition					
First	-0.641	-0.493	-0.400	0.693	0.594
Second	0.000	0.000	0.000	0.000	0.000
Third	-0.342	-0.495	-0.545	0.359	0.232
Fourth	0.001	0.004	-0.000	0.000	0.111
Total	-0.984	-0.984	-0.945	1.042	0.937

pletely for both transitions. In both cases there are only two states that contribute substantially, except in benzaldehyde. This could have been anticipated on symmetry grounds. The main contribution comes from the second term on the right-hand side of Eq. (1). Here only those states contribute which are coupled by the angular momentum operator. In C_{2v} symmetry there are only two states out of the four that are of the correct species. The C_{2v} molecules fluorobenzene and benzonitrile behave as expected, also aniline and phenol do not deviate greatly from this behaviour. In benzaldehyde, however, the symmetry is distorted to a larger extent, resulting in the different distribution scheme of Table 5. The fact that only four states are needed justifies the procedure to calculate the B terms by insertion of the experimental energies into the denominator of the second term on the right-hand side of Eq. (1).

The results obtained in this way for some of the molecules are shown in the eighth column of Table 6. The agreement with the experimentally determined B terms for the first singlet transitions is now excellent.

Table 6. Comparison of calculated B terms for some semi-empirical MO models with experiment of some monosubstituted benzenes for the two lowest single transitions corresponding to ${}^1A_{1g} \rightarrow {}^1B_{2u}$ and ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transitions in benzene

Substituent	Transition	ME ^a	SL ^b	SL ^c	MM ^d	OH ^e	OH ^f	Exp. ^g
-NH ₂	${}^1A_{1g} \rightarrow {}^1B_{2u}$	+17.2	+33.1	+56.9	+100	+28.7	+34.2	+38.8
	${}^1A_{1g} \rightarrow {}^1B_{1u}$	-63.9	-43.6	-82.0	-220	-84.8	-70.9	
-OH	${}^1A_{1g} \rightarrow {}^1B_{2u}$		+16.9	+30.0	+70	+16.5	+16.2	+16.1
	${}^1A_{1g} \rightarrow {}^1B_{1u}$		-20.7	-40.8	-185	-64.0	-52.8	
-CN	${}^1A_{1g} \rightarrow {}^1B_{2u}$	-31.9	-17.1	-28.6		-11.5	-12.2	-12.0
	${}^1A_{1g} \rightarrow {}^1B_{1u}$	+51.1	+22.4	+41.4		+28.2	+26.6	

Units: See Table 1.

^a Ref. [6]: PPP model with explicitly orthogonalized orbitals, usual perturbation formula and SCI approximation.

^b Ref. [7]: PPP model with gauge invariant orbitals, finite perturbation technique and SCI approximation.

^c Ref. [7]: PPP model with gauge invariant orbitals, finite perturbation technique and time dependent Hartree-Fock approximation.

^d Ref. [5]: PPP model with usual perturbation formula and SCI approximation.

^e This work: CNDO/S model with explicitly orthogonalized orbitals, usual perturbation formula and TSCI approximation.

^f Same as under^e, with use of experimental transition energies.

^g Exp: Experimental values.

5. The Experimental B Terms

In the papers of Seamans and Linderberg [7] and Shieh *et al.* [17] the experimental B terms for the lowest transitions of the molecules considered in this paper are reported. There seems to be some discrepancy in the results, probably due to the methods of extracting the B terms from the experimental data. We redetermined the B terms using the method of moments [19] according to

$$B = - \frac{10^2}{1.0002 \times c \times l \times H} \int \frac{\Delta A}{\nu} d\nu$$

in which c is the concentration of the sample in grammoles per litre; l is the optical path-length of the sample and H is the magnetic field strength in Gauss. We used the MCD spectra (ΔA) versus the frequency (ν , cm^{-1}) obtained on our home-made instrument. The B terms are given in Table 7. Unfortunately, numerical values for the B terms of the second singlet transitions are not reported in the literature. Owing to unfavourable signal-to-noise conditions and overlapping transitions, we could not obtain accurate data for these transitions. From the work of Shieh *et al.* [17] these transitions display a B term that is always oppositely signed to the first and the magnitude of which is larger.

Table 7. Experimental B values from various sources for the first singlet transitions

Substituent	D ^a	SLE ^b	OH ^c
-NH ₂	+58.3	+46.6	+38.8
-OH	+23.4	+16.2	+16.1
-F		+0.9	+0.88
-CN	-18.7	-14.6	-12.0
-CHO		-36.1	-29.8

Units: See Table 1.

^a Duffield, J., cited in Ref. [7].

^b Ref. [17].

^c This work.

6. Concluding Remarks

The merits of the model used in this paper are best demonstrated by comparison with other approaches. In Table 6 we compiled our results with those of other workers. From this table we conclude that the use of the PPP model already gives quite satisfactory results. The more sophisticated CNDO/S model, however, gives almost quantitative results. The need for experimental geometries is stressed. Even the use of a limited CI gives satisfactory results. The problem of origin dependence has been shown to be negligible.

Concluding, we may state that, at least for the molecules studied, the CNDO/S model is very dependable for the description of such complex quantities as the B term. This encourages us to investigate further its possibilities in the handling of $n-\pi^*$ transitions and vibronic mechanisms in transitions.

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