

Table III. Rate Constants and Activation Energies for Electron-Transfer Reactions. Sodium Naphthalenide + Naphthalene

System	Characterization	Temp, °C	$k \times 10^{-8} M^{-1} \text{sec}^{-1}$	E_a^a , kcal	Log A^a
Li, THF	Loose ion pair	-30	2.6	3.6	11.7
Na, DME	Loose ion pair	-30	3.4	3.6	11.8
Na, DME, THF	Loose ion pair	-55	1.7	3.3	11.5
Na, DME, THF	Free ion	24	12	2.5	10.9
Na, THF	Loose ion pair	-70	1.5	3.1	11.2
Na, THF	Equil mixture	-10	0.47
Na, THF	Tight ion pair	57	0.27	4.6	10.5
Na, THF, DEE	Loose ion pair	-105	0.35	2.9	11.3
Na, DEE	Tight ion pair	10	0.09	5.1	10.9
Na, DMTHF	Tight ion pair	15	0.03	5.1	10.3
K, THF	Tight ion pair (?)	24	0.32	4.2	10.6
K, DME	Equil mixture	24	0.99
Cs, THF	Tight ion pair	0	0.38	5.1	11.8

^a Determined from the equation $k = A \exp(-E_a/RT)$.

vation energies and the preexponential factors determined for the electron-transfer reactions studied in the present investigations are summarized in Table III. The rates for loose ion pairs at 25° are of the order $10^9 M^{-1} \text{sec}^{-1}$ and the rates for tight ion pairs range from 10^8 to $5 \times 10^6 M^{-1} \text{sec}^{-1}$. The activation energies are 2.9–3.6 kcal for loose ion pairs and 4–6 kcal for tight ion pairs. The preexponential factors are $\sim 10^{10}$ – $10^{12} M^{-1} \text{sec}^{-1}$ for most systems irrespective of the type of ion pair. Neither abnormally high activation energies nor high preexponential factors as reported in the previous work⁵ were obtained in the

present systems. The slower rates in the tight-ion-pair systems seem to be primarily due to the higher activation energies. These energies would be required to remove some solvent molecules from the solvation sphere and to reorganize the solvation sphere to form a transition state, in which the positive ions are shared between two organic molecules, and the environment with respect to two organic molecules is symmetric.

Acknowledgment. The financial support from the National Science Foundation (GP-5040) is appreciated.

Hyperfine Splittings from Naturally Occurring Sulfur-33 in Electron Paramagnetic Resonance Spectra

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Abstract: The cation radicals of 1,4-dithiin, 1,4-benzodithiin, phenoxathiin, thianthrene, and some substituted thianthrenes have been reinvestigated in the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ system. Improved resolution has enabled the proton splitting constants to be analyzed in greater detail than previously possible. Naturally occurring sulfur-33 hyperfine splittings have also been detected in all cases. The theory of the ^{33}S splittings has been considered using the Karplus-Fraenkel formulation. Using spin densities calculated from the McLachlan molecular orbital method, it is found that an equation of the form $a^{\text{S}} = Q_{\text{S}}^{\text{S}(\text{C}_2\text{P})} \rho_{\text{S}}^{\pi}$ holds to a good approximation, where $Q_{\text{S}}^{\text{S}(\text{C}_2\text{P})} = +33.4 \pm 0.7 \text{ G}$.

The low natural abundance of sulfur-33 (0.74%) has made measurements of the hyperfine splitting from this nucleus in esr spectra difficult to detect without resorting to enriching procedures.¹ In fact, only recently has it been found possible to measure these hyperfine splittings in organic radicals² with a natural abundance of ^{33}S . The cation radicals of a number of sulfur compounds have been previously studied in 98% sulfuric acid,^{3–5} but in some cases only a partial analysis of the

proton hyperfine interactions has been possible owing to incomplete resolution.

Recent work with other methods of producing cation radicals^{2,6} indicated that these compounds might yield further information if the radicals were produced differently. The cation radicals of 1,4-dithiin (1), 1,4-benzodithiin (2), thianthrene (3), phenoxathiin (4), and some substituted thianthrenes were therefore reinvestigated using the aluminum chloride-nitromethane system to produce the radicals.^{6,7}

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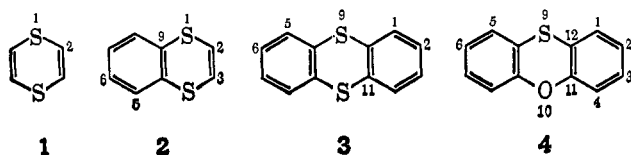
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Molecular-orbital calculations were carried out using the McLachlan perturbation corrections to the Hückel LCAO-MO method.⁸ Values for the sulfur parameters were obtained by comparing the experimental and calculated proton splitting constants.

The Karplus-Fraenkel theory⁹ of hyperfine splittings as developed for ¹³C was also applied to the ³³S splittings in order to estimate the *Q* parameters for this interaction.

Experimental Section

The author is indebted to Dr. H. J. Shine of Texas Technological College for generous samples of substituted thianthrenes and Dr. W. E. Parham for samples of 1,4-dithiin and 1,4-benzodithiin. Other compounds were commercially available samples. The radicals were produced as described previously,^{6,8} and the computer programs were also as used before.¹⁰ The esr spectra were determined on a Varian E-3 spectrometer and also on a modified Varian V-4560 spectrometer using a backward-diode detection system.

Results

1,4-Dithiin (1). This compound was previously studied by Lucken,⁴ and a ring proton splitting constant of 2.80 G was reported. With AlCl₃-CH₃NO₂ a similar spectrum was observed with a splitting constant of 2.82 G and line width of 0.10 G (measured between the extremes of the first derivative curve). A search for carbon-13 splittings was made but none was observed. This suggests that either the magnitude of this interaction is a multiple of 2.80 G, less than 0.05 G, or that the lines are very broad.

Sulfur-33 hyperfine splittings are observed in the wings of the spectrum when more concentrated solutions are used under conditions of over-modulation and high amplification. Only the $\bar{M}_S = \pm 3/2$ groups are completely resolved, some lines of the $\bar{M}_S = \pm 1/2$ groups being lost in the envelope of the main spectrum (cf. Figure 1). The measured intensities of the $\bar{M}_S = \pm 3/2$ satellites correspond to 0.2% of the main spectrum. This compares with a calculated intensity of 0.37% obtained from the natural abundance of sulfur-33. The difference in these intensities is probably caused by the increased line width of the ³³S satellites as compared to the main spectrum. The line width also varies across the spectrum in that the $\bar{M}_S = -3/2$ line was narrower than its $\bar{M}_S = +3/2$ counterpart. This variation was found for all cases of ³³S hyperfine interaction, and a detailed consideration of current line-width theories has suggested that the observation is consistent with a positive ³³S splitting constant.²

1,4-Benzodithiin (2). This compound was also studied in H₂SO₄ by Lucken,⁴ but proton splittings from position 5 were not resolved. In AlCl₃-CH₃NO₂ the better resolution obtained (line width = 0.10 G) enabled all proton splittings to be measured (see Table I). Under high amplification ³³S lines were again

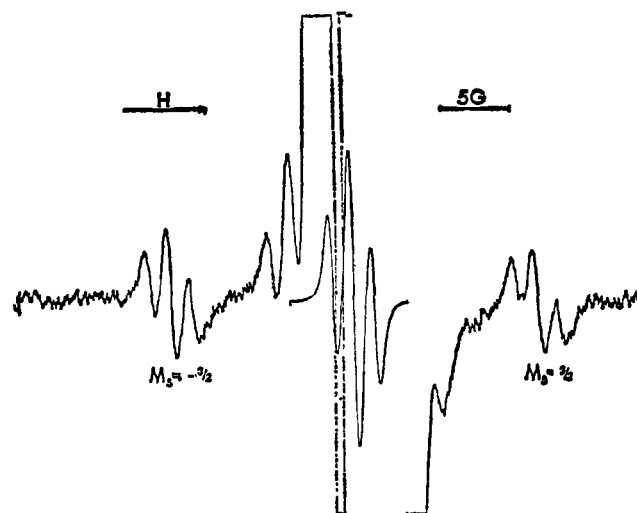


Figure 1. The esr spectrum of 2,7 di-*t*-butylthianthrene. The wings are shown under high amplification and the $\bar{M}_S = \pm 3/2$ groups can be clearly seen. Some of the lines from the $\bar{M}_S = \pm 1/2$ groups are lost in the main spectrum. The main spectrum is shown under low amplification in the center of the figure.

observed in the wings, corresponding to a splitting constant of 9.35 G.

Table I. Splitting Constants (in Gauss) for Compounds 1-4

Compound	Position	a_i (this work) ^a	a_i (previous work)
1,4-Dithiin (1)	a_1^S	9.84	
	a_2^H	2.82	2.80 ^b
1,4-Benzodithiin (2)	a_1^S	9.35	
	a_2^H	3.32	3.20 ^b
	a_5^H	0.201	<0.5
	a_6^H	1.056	1.05
Thianthrene (3)	a_3^S	9.15	
	a_1^H	0.135	<0.5 ^b
	a_2^H	1.28	1.30
Phenoxathiin (4)	a_{11}^S	11.91	
	a_1^H	0.561 ^d	0.52 ^c
	a_2^H	0.993	1.04
	a_3^H	2.139	2.08
	a_4^H	0.261	0.26

^a Error in splitting constant equals $\pm 0.5\%$ for $a_i > 1$ G. ^b Reference 4. ^c Reference 14. ^d See Table III for assignment of splitting constants.

Thianthrene (3). The spectra were as described,² and the results are shown in Table I.

Phenoxathiin (4). This compound has been studied by a number¹¹⁻¹⁴ of investigators in sulfuric acid. The analysis of this spectrum¹⁴ has assumed the four pairs of splitting constants to be integral multiples of the smallest. With the increased resolution possible with AlCl₃-CH₃NO₂ (line width 0.075 G), this accidental equivalence breaks down and the corrected splitting constants are shown in Table I. A ³³S splitting constant of 11.91 G is also observed under high amplification.

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Substituted Thianthrenes. For the 2,7-di-*t*-butyl-, 2,7-dimethyl-, 2,7-dichloro-, and 2,7-dibromothianthrenes, the spectra are similar to those in H_2SO_4 ⁵ apart from slightly better resolution in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ (see Table II). For 2,7-dihydroxy- and 2,3,6,7-tetramethoxythianthrene greatly improved spectra were found as compared to those reported in H_2SO_4 .^{5,15}

Table II. Splitting Constants (in Gauss) for Substituted Thianthrenes

Substituted thianthrene	Position	a_i (this work) ^a	a_i (previous work)
2,7-Dibromo-	a_3^{H}	1.39	
	a_3^{S}	8.94	
2,7-Dichloro-	a_3^{H}	1.45	1.49 ^b
	a_3^{S}	8.92	
2,7-Dimethyl-	$a_3^{\text{H}} = a_2^{\text{CH}_3}$	1.64	1.65 ^b
	a_3^{S}	8.73	
2,7-Di- <i>t</i> -butyl-	a_3^{H}	1.52	1.60 ^b
	a_3^{S}	8.72	
2,7-Dihydroxy- ^c	a_1^{H}	0.110	
	a_{OH}^{H}	0.36	
	a_3^{H}	2.05	
	a_4^{H}	~0.0	
	a_3^{S}	8.10	
2,3,6,7-Tetra-methoxy-	a_3^{S}	7.92	

^a Errors estimated as $\pm 0.5\%$ for $a_i > 1$ G. ^b Reference 5. ^c See text for discussion of assignments.

The spectrum of 2,7-dihydroxythianthrene was analyzed in terms of three groups of triplets (see Table II). Further studies in D_2SO_4 ¹⁶ and $\text{D}_2\text{SO}_4\text{-CH}_3\text{NO}_2$ have shown that the OH protons are rapidly exchanged under these conditions, and an assignment of the OH proton splitting constant is therefore possible.

Tetramethoxythianthrene was previously observed as one broad line: the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ system enabled the spectrum to be resolved into approximately 23 equally spaced lines, 0.26 G apart. A more complete analysis of this spectrum was not attempted.

³³S splittings were observed for all the substituted thianthrenes; however, only the $\bar{M}_S = \pm 3/2$ groups were completely resolved, some lines of the $\bar{M}_S = \pm 1/2$ groups usually being lost in the wing lines of the main spectrum (see Figure 1).

Molecular-Orbital Calculations. The McLachlan perturbation corrections to the Hückel LCAO-MO method ($\lambda = 1.2$) was used throughout. Only the p-orbital model⁴ for sulfur was considered since good agreement with experiment was found without considering the d orbitals. For compounds 1-3 there will be only two unknown parameters if it is assumed *a priori* that all carbon bonds have the same resonance integral. The two unknowns will be the Coulomb and resonance integrals of sulfur as defined by $\alpha_S = \alpha + h_S\beta$ and $\beta_{CS} = k_{CS}\beta$, where α and β are the Coulomb and resonance integrals of the carbon atom and carbon-carbon bond, respectively. Calculations were carried out for 1,4-dithiin with various values of h_S and k_{CS} . The calculated spin densities were related to the experimental ring proton splitting constants by the McConnell equation, $a_{\text{H}} = \rho_{\text{C}}Q_{\text{CH}}^{\text{H}}$. Recent work involving the

benzene cation radical¹⁷ suggests that Q_{CH}^{H} should be somewhat higher than previously used values for anion radicals which have ranged from 22 to 27. Q_{CH}^{H} was therefore set equal to -28 for this work.

A series of h_S and k_{CS} values were obtained for 1,4-dithiin which correctly predicted the ring proton splitting constants. These parameters were next applied to the thianthrene cation. However, no set could be found which predicted the correct proton splitting constants for both molecules within reasonable limits.

A comparison of the crystal structures^{18,19} of the two neutral compounds revealed that the carbon-carbon bond length in 1,4-dithiin is 1.29 Å, whereas all carbon-carbon bond lengths in thianthrene are close to 1.40 Å. This indicates that the assumption regarding the equality of the resonance integrals of all carbon-carbon bonds is not valid. To take the differences in bond length into account, the value of the carbon-carbon resonance integral in 1,4-dithiin should be increased. The dependence of the resonance integral on bond length has been discussed and summarized by Streitwieser.²⁰ For a bond length of 1.29 Å the resonance integral should be approximately 1.15 times that for a bond length of 1.40 Å. Repeating the calculations with this value, two sets of parameters were found which gave good agreement for both compounds. These were $h_S = 1.20$ and $k_{CS} = 0.65$ or 0.55 (see Table III); the difference between the two k_{CS} values is that the larger value predicts a positive spin density at the one position of thianthrene whereas the lower value predicts a negative spin density at this position. The spin densities at the other positions are unaffected by the choice of k_{CS} . Since the sign of the splitting constant in the one position of thianthrene is not known, a choice of k_{CS} values cannot be made.

The crystal structure of 1,4-benzodithiin is unfortunately not available; therefore, the assumption is made that it is intermediate between those of 1 and 3. That is, the carbon-carbon bond between positions 2 and 3 is assumed shorter than that between positions 9 and 10. The molecular-orbital calculations using this approximation do show reasonable agreement with the experimental proton splitting constants. The approximation, however, is probably an over-simplification in that the 2-3 and 9-10 bonds may be longer and shorter, respectively, than predicted. The somewhat poorer agreement for 1,4-benzodithiin is, therefore, not too surprising.

Phenoxathiin requires the evaluation of two other unknown parameters, namely the h_{O} and k_{CO} values for the oxygen atom. Using the h_S and k_{CS} values above, h_{O} and k_{CO} were varied, and it was found that values of h_{O} in the range 1.70-2.00 and k_{CO} in the range 0.80-0.90 reproduce the proton splitting constants to the same degree of accuracy. In Table III the parameters used were $h_{\text{O}} = 1.70$ and $k_{\text{CO}} = 0.80$. The relative magnitudes of the parameters (*i.e.*, $h_S < h_{\text{O}}$, $k_{CS} < k_{\text{CO}}$) are physically realistic. From electronegativity differences, h_S would be expected to be smaller than h_{O} , and k_{CS} should be less than k_{CO} because of the loss of

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Table III. Summary of Molecular Orbital Calculations

Compound	Position	ρ_1 (calcd) ^a	a_1 (calcd) ^b	a_1 (expt)
1,4-Dithiin	1	0.289 (0.293)		
	2 (S)	0.105 (0.104)	-2.94 (2.90)	2.82
Thianthrene	1	0.0037 (-0.0043)	-0.103 (+0.110)	0.135
	2	0.0421 (0.0419)	-1.17 (-1.17)	1.28
	9 (S)	0.275 (0.281)		
	11	0.0669 (0.0716)		
1,4-Benzodithiin	1 (S)	0.282 (0.290)		
	2	0.1558 (0.1573)	-4.36 (4.40)	3.32
	5	0.0075 (-0.0013)	-0.210 (+0.036)	0.20
	6	0.0227 (0.0196)	-0.635 (-0.532)	1.05
	9	0.0320 (0.0344)		
Phenoxathiin	1	0.0138	-0.39	0.56
	2	0.0363	-1.01	0.99
	3	0.0614	-1.72	2.14
	4	-0.0079	+0.22	0.26
	9 (S)	0.3520		
	10	0.1280		
	11	0.0849		
	12	0.0715		
2,7-Dihydroxythianthrene	1	-0.0156	+0.44	0.110
	2	0.0458		
	3	0.0675	1.89	2.06
	4	0.0002	0.005	~0.0
	9 (S)	0.2402		
	11	0.0923		
	12	0.0599		
	Oxygen	0.0101	-0.20 ^c	0.36
2,7-Dimethylthianthrene	1	-0.006	+0.168	<0.04
	2	0.044	+1.20 ^d	1.64
	3	0.529	-1.48	1.64
	4	0.003	0.074	<0.04
	9 (S)	0.261		
	11	0.064		
	12	0.078		

^a Calculated with $h_s = 1.20$, $k_{CS} = 0.65$, values for $h_s = 1.20$ and $k_{CS} = 0.55$ are given in parentheses. ^b Calculated from $a_{CH^H} = \rho_C Q_{CH^H}$, where $Q_{CH^H} = -28$. ^c Calculated from $a_{OH^H} = \rho_O Q_{OH^H}$, where $Q_{OH^H} = -20$. ^d Calculated from $a_{CH^H} = \rho_C Q_{CH^H}$, where $Q_{CH^H} = +27$.

overlap due to the extension of orbitals in the sulfur atom. The assignment of the proton splitting constants follows directly from the MO calculations and they are in agreement with an assignment made by simply extrapolating the experimental splitting constants from dibenzo-*p*-dioxin¹⁴ and thianthrene.

Molecular-orbital calculations were also carried out for 2,7-dihydroxy- and 2,7-dimethylthianthrenes. The parameters for the hydroxyl and methyl groups were those derived from studies on the cation radicals of hydroquinone²¹ and methyl-substituted hydroquinones.²² Reasonable agreement was found for 2,7-dimethylthianthrene (see Table III), but poor agreement was found for 2,7-dihydroxythianthrene. This was attributed to a too large interaction of the hydroxyl group caused by using the parameters derived for hydroquinone ($h_O = 1.60$, $k_{OC} = 1.37$). The agreement could be improved by lowering the k_{OC} parameters (which is physically realistic), and the results in Table III are those obtained with $h_O = 1.60$ and $k_{OC} = 0.80$. The splitting constants were therefore assigned as shown in the table, bearing in mind that the hydroxyl splitting constant has previously been assigned from the D_2SO_4 studies.

Theory of Sulfur-33 Splittings. Karplus and Fraenkel⁹ have developed a general theory for hyperfine splittings in esr spectroscopy. It was developed specifically for ¹³C but should be generally applicable to

other nuclei, such as ³³S. Using their notation we can relate the splitting constant (a^S) in a C-S-C fragment to the π -electron spin densities with the following expression

$$a^S = (P^S + 2Q_{SC}^S)\rho_S^\pi + Q_{CS}^S \sum_C \rho_C^\pi \quad (1)$$

where P^S includes the spin polarization of the sulfur 1s and lone-pair electrons. Q_{SC}^S is the contribution from the spin polarization of the 2s electrons on the sulfur atom in the S-C bonds. Q_{CS}^S represents the contribution to a^S from the π spin densities on the carbon atoms, and ρ_S^π and ρ_C^π are the π spin densities on the sulfur and carbon atoms, respectively. Letting $(P^S + 2Q_{SC}^S) = Q_{S(C;P)}^S$, eq 1 can be rewritten as

$$a^S = Q_{S(C;P)}^S \rho_S^\pi + 2Q_{CS}^S \rho_C^\pi \quad (2)$$

For compounds 1-3, provided that the spin density distributions are known, $Q_{S(C;P)}^S$ and Q_{CS}^S can be evaluated from the experimental ³³S splitting constants and eq 2. Unfortunately only in the case of 1,4-dithiin are the spin densities known without recourse to molecular-orbital calculations. However, in view of the good agreement between the calculated and experimental proton splitting constants (see earlier), some confidence can be placed in the calculated spin densities. Using these spin densities for compounds 1-3, eq 2 can be solved for $Q_{S(C;P)}^S$ and Q_{CS}^S ; the values found were 32.4 ± 0.7 G and 1.8 ± 1.5 G, respectively. In view of the magnitude of Q_{CS}^S , eq 2 can be approximated to

$$a^S = Q_{S(C;P)}^S \rho_S^\pi \quad (3)$$

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Table IV. Predicted and Experimental Sulfur-33 Splitting Constants

Compound	a^S , ^a predicted	a^S , actual
Phenoxathiin	11.76	11.91
2,7-Dihydroxythianthrene	8.02	8.10
2,7-Dimethylthianthrene	8.74	8.73

^a Predicted from eq 3.

Solving this equation for 1-3 gives $Q_S^S(C,P) = 33.4 \pm 0.7$ G. This parameter may be tested by calculating a^S for phenoxathiin, and 2,7-dihydroxy- and 2,7-dimethylthianthrene for which the molecular-orbital calculations are also available. Table IV shows the predicted values from eq 3. Excellent agreement

is found for all three compounds, lending additional weight to the conclusions reached above. Added significance may be attached to these results when it is remembered that the molecular-orbital calculations were fitted to the proton splitting constants only.

Acknowledgments. The author thanks Professor J. R. Bolton of the University of Minnesota and Professor W. F. Forbes of the University of Waterloo, under whose guidance this work was carried out. The author is also indebted to Professor H. J. Shine of Texas Technological College for helpful discussions. This research was supported under Grant No. GP-5847 from the National Science Foundation and a departmental equipment grant (No. GP-6991) from the National Science Foundation.

Calculation of the Carbon-13 and Proton Chemical Shifts in Pyridine

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Abstract: Nmr parameters are given for pyridine in a variety of solvents. Using several sets of π -electron wave functions together with symmetry MO's for the σ electrons, diamagnetic and paramagnetic contributions to the proton and carbon-13 shifts were evaluated. Paramagnetic shifts were calculated by the methods of McConnell, Karplus, and Pople. The diamagnetic term for protons was equated to $-10z$ where z is the charge on carbon. The calculated proton shifts obtained with an SCF treatment nearly reproduced the experimental shifts. However, for the carbon-13 shifts the calculated values are always lower than the experimental ones. An empirical term which when added to the paramagnetic contribution fits the experimental results is $-160z$, where z is the charge on carbon. The best results for carbon-13 shifts were obtained, also with the SCF wave function. Altogether it is found that the paramagnetic contribution to these shifts together with a direct π -charge term nicely account for the shifts.

The analysis of the nmr spectrum of pyridine and related compounds has been the object of intensive investigation. Studies have been made of pyridine,^{1,2} deuteriopyridines,^{1,2} polymethylpyridines,^{3,4} 3-substituted pyridines,⁵⁻⁷ γ -substituted pyridines,⁶⁻⁸ and pyridine derivatives.⁹ Recently the original analysis of pyridine by Schneider, Bernstein, and Pople¹⁻³ has been refined by the use of higher resolution nmr equipment together with iterative computer-based analyses which fit a set of nmr parameters to the experimental data. These analyses are the work of Merry and Goldstein,¹⁰ Castellano, Sun, and Kostelnik,¹¹ and Fraenkel, Adams, and Dean.¹²

Ordinarily the calculation of chemical shifts from first principles presents insurmountable problems.¹³ However, for certain types of compounds, it is possible to simplify the calculations by means of reasonable assumptions such as those described by McConnell¹⁴ and Pople^{15,16} and Karplus.¹⁶

Gil and Murrell have calculated contributions to the proton shifts in pyridine¹⁷ using the anisotropy of nitrogen, the effect of the dipole associated with the lone pair on nitrogen, the perturbation of the ring current by nitrogen, and π -electron densities.

It is the object of this paper to show that shifts can be calculated quite accurately using approximate methods which have been already described in the literature.¹⁴⁻¹⁶ In this work we give nmr parameters for pyridine in different solvents. The various para-

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