

pass through the origin. In view of the simplicity of the model the small deviation of the best straight line (11.3 for the observed slope and 0.3 for the intercept) from these values of slope and intercept seems quite reasonable.

The large half-intensity width for the Cl-Cl stretching vibration (Fig. 6) is extremely interesting, as has been pointed out by Collin and D'Or.^{2a} For all the complexes studied until now,^{2,3} the weaker complexes had small values for $\Delta\nu^{1/2}$ and this parameter increased as the strength of the interaction increased. We have interpreted³ this fact as an argument against the formation of "contact" charge-transfer complexes²⁰ in these solutions. However, we have perhaps some indication here in the half-intensity width that this extremely weak benzene-Cl₂ complex may actually be an example of a "contact charge-transfer complex."

In conclusion it should be noted that this resonance model provides a basis for the correlation recently found by Bellamy, *et al.*²¹ They found that when the X-H stretching vibrations of a number of compounds were examined in a large number of solvents, the frequency shifts observed could be correlated in the following way. If $\Delta\nu/\nu$ for a particular acceptor molecule, such as H₂O, in a given solvent was plotted against $\Delta\nu/\nu$ for a standard acceptor molecule, such as pyrrole, in the same solvent, then a series of points was obtained, as different solvents were used, which all fell on a straight line. Different acceptor molecules gave a series of lines with different slopes. Now, if we use the diatomic molecule formula for ν , such as was

(20) L. E. Orgel and R. S. Mulliken, *THIS JOURNAL*, **79**, 4839 (1957).

(21) L. J. Bellamy, H. E. Hallam and R. L. Williams, *Trans. Faraday Soc.*, **54**, 1120 (1958).

done in refs. 2 and 3, then

$$\nu^2 = \frac{1}{4\pi^2 C^2} \times \frac{k}{\mu}$$

Taking the derivative of both sides, and dividing the left-hand by ν^2 and the right hand side by $k/4\pi^2 C^2 \mu$, then

$$2(d\nu/\nu) = dk/k \quad (1)$$

Thus as long as $\nu_{\text{gas}} - \nu_{\text{soln}}$ is small enough that second-order effects in equation 1 can be ignored, then the parameter used by BHW²¹ and the "relative change in force constant," $\Delta k/k$, used here differ only by the factor of two.

According to the argument advanced in ref. 3 the relative change in force constant $\Delta k/k$ is directly proportional to the weight of the resonance structure b. This, in turn, will be determined by the donor strength of D and the acceptor strength of the X-Y bond. In the comparison of BHW, the donors are the solvents, and the acceptors are the X-Y bonds. For a given solvent and acceptor, $\Delta\nu/\nu$ (or $\Delta k/k$) is determined by the coefficient of ψ_b , which will differ in general for a different acceptor bond in this solvent because of the difference of the acceptor strength of the two X-H bonds. The difference is constant, however, so that a plot of $\Delta\nu/\nu$ for one acceptor and for a series of donors against this quantity for the other acceptor gives a straight line.

This conclusion was of course already reached by BHW. However, it is further indication of the correlations provided by the simple resonance model proposed above.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

High Resolution Proton Magnetic Resonance Spectrum of Mercury Diethyl: Analysis of an A₃B₂ System

BY P. T. NARASIMHAN AND MAX T. ROGERS

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The high resolution proton magnetic resonance spectrum of mercury diethyl has been studied at both 40 and 60 mc. The spectrum of this compound can be satisfactorily interpreted as an A₃B₂ system. The ratio of the spin coupling constant J to the internal chemical shift δ between CH₃ (A) and CH₂ (B) groups is about 0.73 at 40 mc. and about 0.49 at 60 mc. The presence in the sample of the fairly abundant Hg¹⁹⁹ isotope (with nuclear spin $I = 1/2$) makes possible a direct determination of both the J and δ values for this compound despite the complexity of the spectrum. Theoretical calculations of the line frequencies and relative intensities have been made and the agreement with experiment is satisfactory. Details of the theoretical method for calculating line frequencies and relative intensities of the n.m.r. (nuclear magnetic resonance) spectrum of an A₃B₂ system (with nuclei of nuclear spin $I = 1/2$) are also given.

Introduction

The high resolution proton magnetic resonance spectra of several metal alkyls have been studied in recent years¹⁻³ especially with a view to correlating the electronegativity of the metal atom with the proton chemical shifts. Particular men-

tion may be made of the interesting proton resonance spectrum of lead tetraethyl recorded by Baker³ at 30 mc., and of his ingenious interpretation of the observations. The spectrum consists of a rather broad, intense central line with satellite "ethyl group"-like triplet and quartet lines on either side. These satellite lines were shown by Baker to be the result of unequal spin coupling of the Pb²⁰⁷ isotope ($I = 1/2$, abundance 21.11%) with the CH₂ and CH₃ groups, the dif-

(1) T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, **3**, 104 (1956).

(2) A. L. Allred and E. G. Rochow, *ibid.*, **5**, 269 (1957).

(3) E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).

ference in these coupling constants acting very much like a chemical shift between CH_2 and CH_3 to produce the characteristic "ethyl group" appearance; the spin coupling constant $J_{\text{CH}_3-\text{CH}_2}$ (called J_1 hereafter) could be obtained from the line separation within either multiplet. Since this pattern appears on either side of the main peak, corresponding to the two possible values of the magnetic spin quantum number of Pb^{207} , the values of the spin coupling constants $J_{\text{CH}_2-\text{Pb}}$ (42 c.p.s.) and $J_{\text{CH}_3-\text{Pb}}$ (124 c.p.s.) could be obtained from the separation between the quartets and triplets, respectively. Since the chemical shift $\delta_{\text{CH}_2-\text{CH}_3}$ is less than 1 c.p.s. at 30 mc. for lead tetraethyl, the satellite lines appear to be placed almost symmetrically about the main peak.

The spectrum of mercury diethyl should show some similarity to that of lead tetraethyl since a mercury isotope, Hg^{199} , of nuclear spin $I = 1/2$ and abundance 16.86% exists. We have therefore made an intensive study of the spectrum of this substance in order to obtain the various spin coupling constants J and the chemical shift δ . To confirm our interpretation of the spectrum a calculation of the frequencies and relative intensities of the lines in an A_3B_2 type spectrum (for nuclear spin quantum numbers $I = 1/2$) has been made. Details of this calculation are presented along with a comparison of the spectra calculated and observed at 40 and 60 mc. The only previous report of an exact solution of the A_3B_2 spin system is that by Anderson^{4,5} who obtained a solution for the ratio $J/\delta = 0.136$ only; he gives no details of the method so his report was not of use for the present problem. Perturbation theory methods^{4,6} even to second and third order, are not satisfactory for large values of J/δ , particularly in the intensity calculations.

Experimental

Mercury diethyl was synthesized⁷ from the ethyl Grignard reagent and mercuric bromide, and was purified by distillation. A liquid sample contained in a 5 mm. o.d. Pyrex tube was degassed and the tube was sealed off. The spectrum was observed with a Varian V4300B spectrometer and (at 60 mc.) V-4311 R.F. unit. The usual spinning technique and sideband modulation were employed.

Results

The proton resonance spectrum obtained at 60 mcs. is shown in Fig. 1. The frequencies and intensities of the 40 mcs. peaks are listed in Table V. The spectra show certain similarities to that of lead tetraethyl in that satellite "ethyl group"-like lines appear on either side of a central peak. The triplet and quartet lines presumably result from the unequal coupling of the Hg^{199} nucleus with the CH_2 and CH_3 protons and, as for lead tetraethyl, the coupling constant $J_{\text{CH}_2-\text{Hg}}$ appears to be larger than $J_{\text{CH}_3-\text{Hg}}$.

However, a closer inspection of the satellite lines (see Fig. 1) shows a lack of symmetry with respect to the center of the spectrum and in particular it will be noted that while the satellite lines appearing on the lower field side show the triplet and quartet

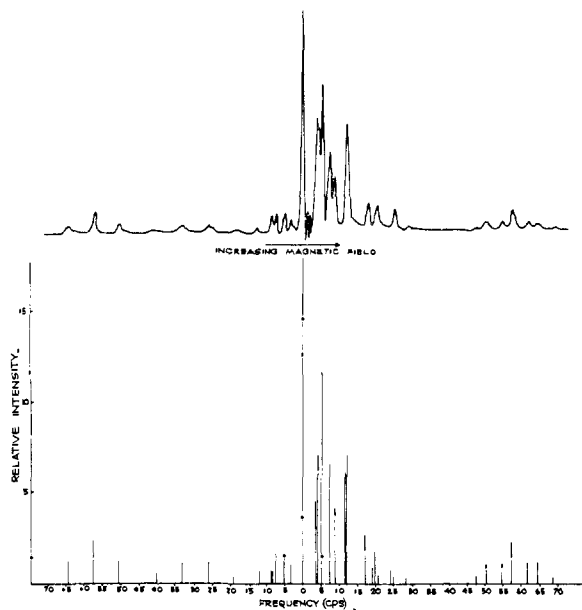


Fig. 1.—Experimental and theoretical proton resonance spectra of mercury diethyl (60 mc.).

lines well separated from one another, those appearing on the higher field side seem to overlap. Also, the main part of the resonance spectrum consists of a complex multiplet pattern with some indication that the methyl group proton resonance falls at a lower field than the methylene group resonance. Since the two ethyl groups in diethyl mercury are known to be chemically equivalent, the spectrum may be interpreted as an A_3B_2 system (in the notation of Bernstein, Pople and Schneider⁸) if one neglects all interactions between the two ethyl groups. In this event the complex central part of the resonance spectrum could be caused by the comparable magnitudes of J_1 and δ , the spin coupling constant and the chemical shift, respectively, between CH_3 and CH_2 group protons. However, the complexity of this part of the spectrum did not seem to offer much hope for the direct determination of the J_1 and δ values for the CH_3-CH_2 group protons in this compound. Fortunately the lack of symmetry of the satellite spectrum mentioned earlier gave us a clue to the determination of both the J_1 and δ values, and as we shall see presently the values thus obtained can be justified by the agreement between the experimental spectrum and the theoretically calculated spectrum at both 40 and 60 mc.

Determination of the Coupling Constants and Chemical Shifts from the Satellite Spectrum.—The effect of the nuclear spin coupling of the Hg^{199} isotope on the proton resonance spectrum of the ethyl group of mercury diethyl can be adequately treated by means of first-order perturbation theory.⁹ Thus denoting the resonance frequency of the CH_3 group protons by ν_A and that of CH_2 group by ν_B we may expect the following four lines in the proton resonance spectrum of the $\text{Hg}^{199}(\text{C}_2\text{H}_5)_2$

(4) W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

(5) Narasimhan and Rogers, unpublished results.

(6) J. T. Arnold, *Phys. Rev.*, **102**, 136 (1956).

(7) We are indebted to Mr. Terry Haas for carrying out this synthesis.

(8) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Canad. J. Chem.*, **35**, 65 (1957).

(9) H. S. Gutowsky, D. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

system due to the Hg^{199} -H spin interactions (Table I). J_2 and J_3 are the Hg^{199} -H spin-spin coupling constants for the CH_3 and CH_2 group protons, respectively. As before $\delta = \nu_A - \nu_B$, the internal chemical shift between the CH_3 and CH_2 group protons. The $\text{H}(\text{CH}_3)$ - $\text{H}(\text{CH}_2)$ proton spin inter-

TABLE I

	Frequency	Relative intensity
CH_3 group	$\nu_A' = \nu_A + \frac{1}{2}J_2$	3.0
	$\nu_A'' = \nu_A - \frac{1}{2}J_2$	3.0
CH_2 group	$\nu_B' = \nu_A - \delta + \frac{1}{2}J_3$	2.0
	$\nu_B'' = \nu_A - \delta - \frac{1}{2}J_3$	2.0

action is represented by the quantity J_1 . This interaction would serve to split the CH_3 group lines into triplets and those of the CH_2 group into quartets if the magnitude of $|J_2 - J_3|$ is large¹⁰ compared to J_1 . Such a first-order perturbation treatment for the CH_3 - CH_2 interaction in the $\text{Hg}^{199}(\text{C}_2\text{H}_5)_2$ case seems to be adequate as seen from the experimental spectrum. Thus, including the CH_3 - CH_2 proton spin interaction, the $\text{Hg}^{199}(\text{C}_2\text{H}_5)_2$ spectrum may be expected theoretically to consist of the lines listed in Table II.

TABLE II

	Frequency	Relative intensity
CH_3 group	$\nu_1 = \nu_A + \frac{1}{2}J_2 + J_1$	3.0
	$\nu_2 = \nu_A + \frac{1}{2}J_2$	6.0
	$\nu_3 = \nu_A + \frac{1}{2}J_2 - J_1$	3.0
	$\nu_4 = \nu_A - \frac{1}{2}J_2 + J_1$	3.0
	$\nu_5 = \nu_A - \frac{1}{2}J_2$	6.0
	$\nu_6 = \nu_A - \frac{1}{2}J_2 - J_1$	3.0
CH_2 group	$\nu_7 = \nu_A - \delta + \frac{1}{2}J_3 + \frac{3}{2}J_1$	1.0
	$\nu_8 = \nu_A - \delta + \frac{1}{2}J_3 + \frac{1}{2}J_1$	3.0
	$\nu_9 = \nu_A - \delta + \frac{1}{2}J_3 - \frac{1}{2}J_1$	3.0
	$\nu_{10} = \nu_A - \delta + \frac{1}{2}J_3 - \frac{3}{2}J_1$	1.0
	$\nu_{11} = \nu_A - \delta - \frac{1}{2}J_3 + \frac{3}{2}J_1$	1.0
	$\nu_{12} = \nu_A - \delta - \frac{1}{2}J_3 + \frac{1}{2}J_1$	3.0
	$\nu_{13} = \nu_A - \delta - \frac{1}{2}J_3 - \frac{1}{2}J_1$	3.0
	$\nu_{14} = \nu_A - \delta - \frac{1}{2}J_3 - \frac{3}{2}J_1$	1.0

The satellite spectrum should then consist of fourteen lines, seven on either side of the central multiplet group which is due to $\text{Hg}^{200}(\text{C}_2\text{H}_5)_2$ and $\text{Hg}^{201}(\text{C}_2\text{H}_5)_2$. But the experimental spectrum recorded at 40 mc. shows eleven satellite lines—seven lines on the low field side, as expected, but only four lines on the high field side. It was noticed, however, that although the four lines on the high field side have the frequency separation characteristic of a CH_2 group, they do not exhibit the simple 1:3:3:1 intensity ratio. Actually, the ratio of the line intensities experimentally measured from the 40 mc. spectrum is 1:6:9:4 owing to the superposition of the CH_3 multiplets on the CH_2 spectrum. In order to confirm this fact, we obtained the proton resonance spectrum at 60 mc. which clearly shows the separated triplet and quartet lines, although it will be noticed that they do fall in the same region. The separation (experimentally measured in cycles per second) between lines 2 and 5 (see Fig. 2) is equal to J_2 , while that between the centers of the B and B' quartets is

(10) More correctly the quantity $|\delta + \frac{1}{2}J_2 - \frac{1}{2}J_3|$ or $|\delta - \frac{1}{2}J_2 + \frac{1}{2}J_3|$ should be $\gg J_1$. J_2 and J_3 may be shown to have opposite signs from a simple consideration of these conditions.

equal to J_3 ; thus J_2 and J_3 can be determined directly from the experimental spectrum. J_1 is obtained easily from the separation within either of the multiplet groups of the satellite spectrum. The quantity marked Δ in Fig. 2 is the separation between the centers of the triplet and quartet groups on the low field side. It will be seen readily that $\delta_{\text{CH}_3-\text{CH}_2} = \frac{1}{2}J_2 - (\Delta + \frac{1}{2}J_3)$. Thus the satellite spectrum also yields directly the values of J_1 and δ for the ethyl group protons. The consistency of these values can be tested by noting the constancy of the J_1 value at both 40 and 60 mc. and also from the ratio of the δ values obtained at these two frequencies. Table III gives a summary of the spin-spin coupling constants and chemical shifts derived from an analysis of the satellite lines in the observed spectra of mercury diethyl.

TABLE III

SPIN-SPIN COUPLING CONSTANTS AND PROTON INTERNAL CHEMICAL SHIFT DATA FOR MERCURY DIETHYL

	Frequency	
	40 mc.	60 mc.
J_1 H(CH ₃) - H(CH ₂)	7.0 c.p.s.	7.0 c.p.s.
J_2 Hg ¹⁹⁹ - H(CH ₃)	115.2	115.2
J_3 Hg ¹⁹⁹ - H(CH ₂)	87.6	87.6
Δ	23.4	28.2
$\delta = \nu_A - \nu_B$	-9.6	-14.4

Theoretical Calculation of the Nuclear Magnetic Resonance Spectrum of an A_3B_2 System (Nuclei of Spin $I = \frac{1}{2}$).—The equivalence of the two ethyl groups in diethyl mercury and the assumption of the lack of interactions between these two groups simplifies the problem of the theoretical calculation of the proton n.m.r. spectrum of this compound. Using these simplifications the problem reduces to the computation of the nuclear magnetic energy levels of an A_3B_2 system and finding the allowed transition frequencies and transition probabilities. When the ratio of the spin coupling constant to the chemical shift, that is, J/δ , is quite small simple perturbation theory can be employed to obtain the theoretical spectrum. However, when the ratio is fairly large (as is the case in mercury diethyl) the use of higher order perturbation theory^{4,6} is not feasible and one has to find the energy levels and transition probabilities by direct solution of the secular equations. We wish to deal with this general problem here and arrive at the various expressions that would enable one to calculate the spectrum of an A_3B_2 system. We therefore proceed by writing the Hamiltonian^{4-6,11-14} of the system in a magnetic field as

$$H = H_1 + H_2 + H_3 \quad (1)$$

where

$$H_1 = -1/2\pi \left[\gamma H_A \sum_A I_z(A) \right] = -\nu_A \sum_A I_z(A) \quad (1a)$$

$$H_2 = -1/2\pi \left[\gamma H_B \sum_B I_z(B) \right] = -\nu_B \sum_B I_z(B) \quad (1b)$$

$$H_3 = J_1 \vec{I}(A) \cdot \vec{I}(B) \quad (1c)$$

(11) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **84**, 1246 (1951); **88**, 1070 (1952).

(12) N. F. Ramsey and E. M. Purcell, *ibid.*, **85**, 143 (1952).

(13) N. F. Ramsey, *ibid.*, **91**, 303 (1953).

(14) H. M. McConnell, A. D. McLean and C. A. Rilly, *J. Chem. Phys.*, **23**, 1152 (1955).

and I_z is the z-component (in the direction of the external field) of the spin angular momentum vector \vec{I} , γ is the magnetogyric ratio of the nuclei, and H_A and H_B are the magnetic fields at the nuclei A and B, respectively. The factor $1/2\pi$ has been introduced in order to express the energy levels in units of cycles per second. H_1 and H_2 correspond to the interaction of the A and B group nuclei with the externally applied magnetic field while H_3 corresponds to the spin-spin interaction between the two groups of nuclei. In the case of mercury diethyl the A and B groups would correspond to the CH_3 and CH_2 group protons, respectively.

As zero-order eigenfunctions we may start by using the simple product spin functions of the five nuclei which will be $2^5 = 32$ in number. These spin eigenfunctions will be the correct stationary state functions in the absence of the H_3 term in the Hamiltonian of equation 1. The presence of this spin-spin coupling term however causes some mixing among the product functions and in order to get the stationary state functions we have to use linear combinations of the zero-order spin functions. We may note here that since the total z-component spin angular momentum, that is, $I_z(A) + I_z(B) = \Sigma I_z$, is a good quantum number there is no mixing between states with different values of ΣI_z . The secular equation

$$|H_{mn} - E_n \delta_{mn}| = 0 \quad \text{where } \delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \quad (2)$$

can thus be factorized according to the various allowed values of ΣI_z . In our present case these would be $+5/2, +3/2, +1/2, -1/2, -3/2$ and $-5/2$. The evaluation of the various matrix elements and the solution of the secular equations would then yield the energy levels of the system. The observed resonance frequencies correspond to the transitions among these energy levels subject to well-known selection rules.¹⁴ For the calculation of the transition probabilities one has to first get the correct stationary state functions expressed as linear combinations of the zero-order functions. The coefficients in these expressions may be obtained from the secular equations by substituting the roots and normalizing. The transition probability P_{mn} for a transition between two energy levels due to a perturbing radiofrequency (r.f.) field is given by

$$P_{mn} = 2\pi(\mu_x)_{mn}^2 \rho(\nu) \quad (3)$$

where $\rho(\nu)$ is the energy density of the r.f. field as a function of frequency and $(\mu_x)_{mn}$ is the matrix element of the x-component of the nuclear magnetic moment.

$$(\mu_x)_{mn} = (\psi_m | \mu_x | \psi_n) \quad (4)$$

where ψ_m and ψ_n are the stationary state functions corresponding to states m and n. Assuming the energy density function $\rho(\nu)$ to be independent of frequency we may obtain the relative intensity of a line as $(\mu_x)_{mn}^2$ for the transition.

The method of evaluation of the relevant matrix elements has been discussed by several authors.^{8,4,11,14-17} Although the simple product

(15) M. K. Banerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc. (London)*, **A226**, 490 (1954).

(16) D. R. Whitman, Ph.D. Thesis, Yale University, 1957.

(17) E. B. Wilson, *J. Chem. Phys.*, **27**, 60 (1957).

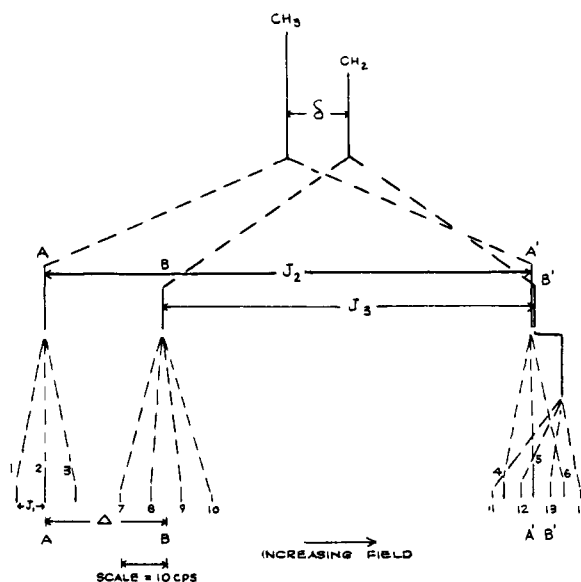


Fig. 2.—The effect of $\text{Hg}^{199}\text{-H}$ and H-H spin coupling on the proton magnetic resonance spectrum of $\text{Hg}^{199}(\text{C}_2\text{H}_5)_2$ (60 mc.). Heights of the lines correspond to relative intensities. The internal chemical shift δ between CH_3 and CH_2 group protons is equal to $1/2 J_2 - (\Delta + 1/2 J_3)$.

spin functions are straightforward to handle, they are often unwieldy when one encounters larger systems. Further, the evaluation of the off-diagonal matrix elements is often tedious when one uses the simple product functions. McConnell, *et al.*,¹⁴ and Wilson¹⁷ have shown that in the cases of equivalent (interchangeable) nuclei, or nuclei arranged in a symmetric framework, it is easier to use spin functions that belong to the irreducible representations of the symmetry group common to these nuclei. Thus the three equivalent protons in the methyl group (A_3) and the two equivalent protons in the methylene group (B_2) may be shown to have the symmetry spin functions given in Table IV. These functions have been derived

TABLE IV

	Zero-order symmetry functions	Designation according to McConnell, <i>et al.</i> ¹⁴	Designation according to Whitman ¹⁶
A_3 group	$\phi_1 = \alpha\alpha\alpha$	${}^4(A_1)_{3/2}$	Q_3
	$\phi_2 = 1/\sqrt{3}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$	${}^4(A_1)_{1/2}$	Q_1
	$\phi_3 = 1/\sqrt{3}(\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha)$	${}^4(A_1)_{-1/2}$	Q_{-1}
	$\phi_4 = \beta\beta\beta$	${}^4(A_1)_{-3/2}$	Q_{-3}
	$\phi_5 = 1/\sqrt{6}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$	${}^2(E')_{1/2}$	D_1
	$\phi_6 = 1/\sqrt{6}(2\beta\beta\alpha - \beta\alpha\beta - \alpha\beta\beta)$	${}^2(E')_{-1/2}$	D_{-1}
	$\phi_7 = 1/\sqrt{2}(\beta\alpha\alpha - \alpha\beta\alpha)$	${}^2(E')_{1/2}$	D_1'
	$\phi_8 = 1/\sqrt{2}(\alpha\beta\beta - \beta\alpha\beta)$	${}^2(E')_{-1/2}$	D_{-1}'
B_2 group	$\phi_9 = \alpha\alpha$	${}^3(A_{1g})_1$	T_1
	$\phi_{10} = 1/\sqrt{2}(\alpha\beta + \beta\alpha)$	${}^3(A_{1g})_0$	T_0
	$\phi_{11} = \beta\beta$	${}^3(A_{1g})_{-1}$	T_{-1}
	$\phi_{12} = 1/\sqrt{2}(\alpha\beta - \beta\alpha)$	${}^1(A_{2u})_0$	S_0

earlier by McConnell, *et al.*,¹⁴ following group theoretical methods and we give them here not only for the sake of completeness but also to follow a notation different from these authors. Our present notation is based on the multiplicity character of the spin functions and is the same as that used by Whitman.¹⁶ As usual α and β denote spin functions

MATRICES FOR SCALAR PRODUCTS OF ANGULAR MOMENTA FOR TWO GROUPS A_3 AND B_2
 $Q(A) \cdot T(B)$

$$\begin{array}{c}
 \left. \begin{array}{ccccccc}
 6 & & & & & & \\
 & 0 & 2\sqrt{6} & & & & \\
 & 2\sqrt{6} & 2 & & & & \\
 & & & -6 & 2\sqrt{6} & 0 & \\
 & & & 2\sqrt{6} & 0 & 4\sqrt{2} & \\
 & & & 0 & 4\sqrt{2} & 2 & \\
 1/4 & & & & & & 2 & 4\sqrt{2} \\
 & & & & & & 4\sqrt{2} & 0 & 2\sqrt{6} \\
 & & & & & & 0 & 2\sqrt{6} & -6 \\
 & & & & & & & 0 & 2\sqrt{6} \\
 & & & & & & & 2\sqrt{6} & 0 \\
 & & & & & & & & 6
 \end{array} \right\} \phi_{(A)}\phi_{(B)} = \left. \begin{array}{l}
 Q_3T_1 \\
 Q_3T_0 \\
 Q_1T_1 \\
 Q_3T_{-1} \\
 Q_1T_0 \\
 Q_{-1}T_1 \\
 Q_1T_{-1} \\
 Q_{-1}T_0 \\
 Q_{-3}T_1 \\
 Q_{-1}T_{-1} \\
 Q_{-3}T_0 \\
 Q_{-3}T_{-1}
 \end{array} \right\}
 \end{array}$$

with the z -components of $+1/2$ and $-1/2$. In Table IV the last column gives the notations for the symmetry functions with Q , T , D and S_0 representing quartet, triplet, doublet and singlet states, respectively. It will be noticed that the eight functions of the A_3 group and the four functions of the B_2 group yield the 32 product spin functions for the A_3B_2 system. These can be simply written, for example, as follows: $Q_3T_1, D_{-1}S_0$, etc. Owing to their symmetry properties the Q and D states do not mix nor do the T and S_0 states. Thus the secular equations can be set up separately for $QT, QS_0, DT, DS_0, D'T$ and $D'S_0$ functions. The simplification resulting from this procedure is obvious.

We shall now direct our attention to some details concerning the evaluation of the various matrix elements required in this problem. We note that matrix elements involving H_1 and H_2 may appear only in the diagonal while terms involving H_3 may appear both in the diagonal and off-diagonal elements. It can be shown¹⁶ that

$$(H_1 + H_2)_{mn} = - \left\{ \sum_A m_A \nu_A + \sum_B m_B \nu_B \right\} \quad (5)$$

Thus, for example

$$(Q_3T_1 | H_1 + H_2 | Q_3T_1) = -3/2\nu_A - \nu_B = -5/2\nu_A + \delta \quad (6)$$

These matrix elements thus can be very easily written by inspection. For the evaluation of the matrix elements in H_3 we shall follow the method of generalized angular momentum matrices as outlined by Whitman.¹⁶ According to this method one proceeds to find the matrix elements of H_3 by constructing the relevant matrices for the scalar products of angular momenta of the various "spin-particles." Since, as mentioned before, the Q and D functions do not mix, a group of three interchangeable nuclei each with spin of $1/2$ can be thought of as a single "spin-particle" with spin $3/2$ or $1/2$. The total z -component of the angular momentum of such a group can be shown to be a good quantum number and hence the concept of a "spin-particle" is useful. Now we have

$$(H_3)_{mn} = \left[\begin{array}{c} \vec{I}_{(A)} \cdot \vec{I}_{(B)mn} \\ (I_y(A))_{mn}(I_y(B))_{mn} + (I_z(A))_{mn}(I_z(B))_{mn} \end{array} \right] = (I_x(A))_{mn}(I_x(B))_{mn} + (I_y(A))_{mn}(I_y(B))_{mn} + (I_z(A))_{mn}(I_z(B))_{mn} \quad (7)$$

The matrix elements for the x , y and z components of the angular momentum can be evaluated following the methods of the generalized angular momentum matrices for the various "spin-particles." The method of constructing such matrices is well-

known (see, for example, Schiff¹⁸). In the present case for the A_3B_2 system we need the matrices for scalar products of the angular momentum involving QT and DT functions only since the matrix elements of H_3 involving the S_0 function vanish. Also the D and D' functions can be treated in the same way. Whitman has given the relevant matrix for DT functions and we have worked out the corresponding matrix for QT functions. The spin functions are given on the right. Using these matrices it is a simple matter to write down $(H_3)_{mn}$. Thus, for example

$$(Q_3T_{-1} | H_3 | Q_1T_0) = \sqrt{6}/2J_1$$

where J_1 is the spin-spin coupling constant between A and B . In this manner the secular equations for the various ΣI_z values may be set up. Corresponding to the QT functions we have two 1×1 , two 2×2 and two 3×3 determinants, while for the DT functions we have two 1×1 and two 2×2 determinants. The determinants for the $D'T$ functions are exactly the same as those for DT and hence need not be computed separately. However, the calculated relative intensities of the transitions involving DT functions have to be doubled in order to take into account the $D'T$ functions. The relative intensities of the various transitions may be obtained as mentioned earlier by finding the normalized coefficients in the secular equations and thus the stationary state functions. The product functions QS_0, DS_0 and $D'S_0$ are themselves stationary state functions. The selection rule $\Delta m = \pm 1$ is then used and the matrix elements of I_x between functions for which $\Delta m = \pm 1$ and which are in the same class (QT, DT , etc.) yield the relative intensities. Here again use may be made of the angular momentum matrices corresponding to the x -component.¹⁵

The necessary computations have been programmed for calculation of the theoretical A_3B_2 spectrum using the high speed digital computer MISTIC at Michigan State University. The secular determinants and the coefficients are first obtained employing a standard eigenvalue eigenvector program. The data thus obtained are then utilized by a second program that gives directly the n.m.r. transition frequencies and relative intensities.

The Proton N.m.r. Spectrum of Mercury Diethyl.—Using the J and δ values obtained earlier the theoretical spectrum of mercury diethyl was

(18) L. I. Schiff, "Quantum Mechanics," McGraw-Hill Book Co., New York, N. Y., 1949, pp. 140-147.

TABLE V
 OBSERVED AND CALCULATED SPECTRA OF MERCURY DIETHYL AT 40 Mc.^a

Line	Transition ^{b,c}	Frequency (c.p.s.)		Relative intensity ^c	
		Calcd.	Obsd.	Calcd.	Obsd.
1	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-64.6	-64.6	1.22	1.25
2	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-57.6	-57.6	2.44	2.50
3	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-50.6	-50.6	1.22	1.25
4	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-44.7	-44.7	0.41	0.40
5	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-37.7	-37.7	1.23	1.20
6	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-30.7	-30.7	1.23	1.20
7	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	-23.7	23.7	0.41	0.40
8	3/2 → 5/2 (QT)	-13.0	-14.0	.36	.31
9	1/2 → 3/2 (QT)	-11.2	-12.1	.26	.20
10	1/2 → 3/2 (DT)	- 8.7	- 8.9	.50	.50
11	1/2 → 3/2 (QT)	- 7.3	- 7.1	1.12	1.25
12	-1/2 → 1/2 (DT)	- 4.4		0.64	
13	-1/2 → 1/2 (QT)	- 4.3	- 4.4	1.47	2.20
14	(Transitions in QS ₀ and DS ₀)	0		12.00	
15	-3/2 → -1/2 (QT)	+ 0.3	0	2.76	18.05
16	-1/2 → 1/2 (QT)	+ 0.6		3.29	
17	-5/2 → -3/2 (QT)	+ 2.8	+ 2.6	4.75	
18	-3/2 → -1/2 (QT)	+ 3.1		7.52	
19	-1/2 → 1/2 (QT)	+ 3.7	+ 3.6	8.35	40.42
20	-3/2 → -1/2 (DT)	+ 4.2	+ 4.5	4.88	
21	1/2 → 3/2 (QT)	+ 4.5		7.38	
22	3/2 → 5/2 (QT)	+ 5.1	+ 5.1	4.64	
23	1/2 → 3/2 (QT)	+ 7.0	+ 7.2	2.21	
24	-1/2 → 1/2 (DT)	+ 7.2		6.86	15.0
25	1/2 → 3/2 (DT)	+ 7.8		5.50	
26	-1/2 → 1/2 (DT)	+12.0	+12.0	2.47	2.50
27	-1/2 → 1/2 (QT)	+14.9	+15.0	0.65	0.60
28	-3/2 → -1/2 (DT)	+15.9	+16.0	1.12	1.20
29	-1/2 → 1/2 (QT)	+19.3		0.18	...
30	-3/2 → -1/2 (QT)	+19.5	+19.5	.48	0.50
31	-3/2 → -1/2 (QT)	+21.9	+22.2	.23	.25
32	-5/2 → -3/2 (QT)	+24.3	+24.7	.25	.25
33	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+42.9	+42.9	.41	.40
34	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+49.9	+49.9	1.23	2.50
35	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+50.6	+50.6	1.22	
36	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+56.9	+56.9	1.23	3.70
37	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+57.6	+57.6	2.44	
38	CH ₂ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+63.9	+63.9	0.41	1.65
39	CH ₃ group of Hg ¹⁹⁹ (C ₂ H ₅) ₂	+64.6	+64.6	1.22	

^a $|J/\delta| = 0.73$; the CH₂ group is shifted to higher fields than CH₃. ^b ΣI_n values are given. Q, T, D and S₀ refer to quartet, triplet, doublet and singlet functions. See text for details. ^c Transitions with relative intensities less than 0.1 have been omitted.

obtained by treating it as an A₃B₂ system. The spectrum thus calculated for 60 mc. is shown in Fig. 1 along with the corresponding experimental spectrum. The observed and calculated frequencies and intensities for 40 mc. are compared in Table V. It will be seen that the agreement with experiment is satisfactory. The relative intensities of the satellite lines were calculated from the relative natural abundance of Hg¹⁹⁹ by assuming first-order interaction between CH₂ and CH₃ groups in Hg¹⁹⁹(C₂H₅)₂. The agreement with the experimental spectrum for these lines is also seen to be satisfactory. The proton resonance spectrum of the compound could thus be characterized by two quantities, namely, J_1 and δ , and this fact serves to justify our earlier assumption regarding the lack of any interaction between the protons of the two different ethyl groups. The negative sign of the chemical shift between the CH₃ and CH₂ group protons shows that the CH₃ protons are less

shielded than those of the CH₂ group. The internal chemical shift may be used to calculate the electronegativity of the Hg atom in this compound. The Dailey-Shoolery equation¹⁹ gives a value of 1.54 for the electronegativity of mercury. The probable value of the electronegativity of the divalent mercury atom is 1.9 (Pritchard and Skinner).²⁰

To extend the Dailey-Shoolery equation to atoms of low electronegativity Shoolery²¹ has suggested that the value of the constant in the original equation be changed from 1.71 to 2.10. Use of this modified equation leads to a value of 1.93 for the electronegativity of mercury. The better agreement with the modified Dailey-Shoolery equation seems to illustrate a characteristic feature of the

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(21) J. N. Shoolery, Lecture Notes, Varian Associates Conference, (Nov., 1957).

latter equation when one is concerned with atoms or groups with low electronegativity values.^{21,22}

Acknowledgment.—We wish to thank the staff of the MISTIC computer laboratory of Michigan

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Molecular Complexes and Their Spectra. X. Molecular Complexes between Iodine and N,N-Dimethylaniline Derivatives

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n-Heptane solutions of the iodine complexes with N,N-dimethylaniline or its methyl derivatives have been found to be stable when the iodine concentrations in the solutions are quite low (of the order of $3 \times 10^{-5} M$). All these solutions show strong absorption bands in the near ultraviolet, which are interpreted as the charge transfer absorption bands due to the complexes. The equilibrium constants and the heats of formation of the 1:1 complexes have been determined from the intensity measurements of these bands. While the heats of formation obtained for the iodine complexes with N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine are very large (-8.2 and -8.3 kcal./mole, respectively), those for the iodine complexes with N,N-dimethyl-*o*-toluidine and N,N-dimethyl-2,6-xylylidine (-2.3 and -1.7 kcal./mole, respectively) are much smaller than the former two. From the inspection of the energies and shapes of the molecular orbitals of N,N-dimethylaniline, it has been concluded that the charge transfer in the complex between N,N-dimethylaniline and iodine occurs mainly from the lone pair of electrons of the nitrogen atom. In the *ortho*-methylated N,N-dimethylanilines, the *ortho* methyl group approaches the lone-pair of electrons of nitrogen, owing to the twisting of the dimethylamino group. The decrease in donor strengths of these *ortho*-methylated N,N-dimethylanilines is therefore attributed to the steric effect of the methyl group on the iodine molecule approaching the lone pair of electrons.

Introduction

The donor molecules which form donor-acceptor complexes with iodine may be divided into two groups: hydrocarbon donors such as olefins and aromatic hydrocarbons (π -donors) and compounds which contain heteroatoms such as oxygen or nitrogen atoms with lone-pair electrons (*n*-donors). Generally speaking, the latter group has stronger donating properties than the former, and especially aliphatic amines and aza-aromatic compounds like pyridine² interact very strongly with iodine.

Although the anilines are expected to have considerable donor strengths toward iodine, no study has ever been made on the molecular compounds between the anilines and iodine. As donor molecules, the anilines cannot be classified rigorously as either *n*- or π -donors, because the amino group and the benzene ring form $n\pi$ mixed donor orbitals, as well as a pure π -donor orbital, as a consequence of the resonance between them. (For details, see below.) It is a problem, therefore, to decide whether the anilines behave mainly as *n*-donors or as π -donors in complex formation with iodine; in other words, whether the orbital of the electron which is donated to the iodine molecule is mainly concentrated on the nitrogen lone-pair electron orbital or spreads over the molecule.

When the hydrogen atom at the *ortho* position of N,N-dimethylaniline is substituted by a methyl group, the dimethylamino group is rotated around the nitrogen-carbon bond, due to steric hindrance between the ring and amino methyl groups and, consequently, resonance of the lone-pair on the

nitrogen atom with the benzene π -electrons will be prevented to a large extent. The twisted dimethylamino group plus the ring methyl group will also produce a steric effect toward the iodine molecule approaching the nitrogen atom. It is interesting to see what change will occur in the donor strength of this compound with iodine.

The donating properties of these hindered anilines toward aromatic acceptors such as trinitrobenzene³ and chloranil⁴ have been studied already. It was found that the complexing strength of N,N-dimethylaniline is greatly diminished by the substitution of a methyl or a larger group at the *ortho* position. Somewhat similar studies were made for the donor strengths of hindered biphenyls toward *s*-trinitrobenzene.⁵ It was again concluded that the complexing power is large only when the molecule retains the coplanar structures. These results are quite reasonable from the theoretical viewpoint that the benzene rings of the donor and acceptor in these cases should lie parallel and as close as possible to each other to obtain a large binding energy. The steric requirements for the iodine-aniline complexes may be different from those of the above mentioned π - π complexes. There is evidence that, in many complexes formed between halogens and *n*-donors, the halogen lies in a straight line passing through the *n*-donor, like O—X—X or N—X—X.⁶ Even in the case of benzene-halogen complexes, there are some experimental results which support the structure with the halogen mole-

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