Table II. Reactions of Primary Ions at 13.0 eV

Reaction	ΔH, kcal/mol[a]	Rate constant × 10^{11} cm^3 molecule^{-1} sec^{-1} [c]
$CH_3N_2^+ + CH_3N{=}NCH_3 \longrightarrow CH_2{=}NH_2^+ + CH_3NC + H_2 + N_2$	−54	2.5 ± 1.0
$\longrightarrow CH_3NH_3^+ + CH_3NC + N_2$	−87	6.6 ± 1.2
$\longrightarrow C_2H_4N^+ + HCN + N_2 + 2H_2$		4.9 ± 1.8
$\longrightarrow CH_2{=}NHCH_3^+ + HCN + N_2 + H_2$	−71	8.5 ± 3.2
$\longrightarrow (CH_3)_2NH_2^+ + HCN + N_2$	−98	13.0 ± 3.0
$\longrightarrow CH_3NH{=}NCH_3^+ + CH_2N_2$	≤0[b]	12.2 ± 1.4
$\longrightarrow (CH_3)_2N{=}NCH_3^+ + N_2$	−75	3.0 ± 1.0
$CH_3N{=}NCH_3^+ + CH_3N{=}NCH_3 \longrightarrow (CH_3)_2N{=}NCH_3^+ + CH_3 + N_2$	−62	0.38 ± 0.06[d]

[a] Neutral products are assumed. [b] Required because $PA(CH_2N_2) < PA(CH_3N{=}NCH_3)$; see text. [c] Rate constants refer to an ion kinetic energy of ~0.15 eV, attributable to the oscillatory motion of ions in the trapping field. [d] Determined from pressure data at 9.2 eV; see text.

have utilized a photodissociatiom method to determine the limit $\Delta H_f(CH_2N_2) \geq 51$ kcal/mol, which they believe is close to the true heat of formation. Even considering the many uncertainties involved in all of the measurements, it does not appear possible to resolve the discrepancy of ~20 kcal/mol between these results and those discussed above.

(F) Kinetics of Reaction. Rate constants, summarized in Table II, were calculated from the data of Figure 2 for the seven indicated reactions. The rate for *m/e* 73 production from *m/e* 43 was determined from data at pressures low enough to avoid significant contributions from *m/e* 58 (reaction 2). The rate constant for reaction 2 is the slowest of any observed in the azomethane system, $3.8 \pm 0.6 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. While the rate constants of the individual $CH_3N_2^+$ reactions are rather low for ion–molecule reactions in general, the total rate constant for the disappearance of *m/e* 43 is 5.1×10^{-10} cm^3 molecule^{-1} sec^{-1}. Rate constants for processes other than those listed in Table II could not be determined due to the complexity of the reaction scheme.

Acknowledgments. We are indebted to Dr. D. Holtz for his critical evaluation of the manuscript. This work was supported by the United States Atomic Energy Commission under Grant No. AT (04-3)767-8.

Complex Equilibria Involving 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane. I. The Proton Magnetic Resonance Spectrum and Types of Complexation

Nancy K. Wilson

Contribution from the National Institute of Environmental Health Sciences, Research Triangle Park, North Carolina 27709. *Received April 1, 1971*

Abstract: The proton magnetic resonance spectrum of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (the pesticide *p,p'*-DDT) was obtained as a function of the concentration of several complexing agents and of temperature. Equilibrium constants and values of the standard free energy, $\Delta G°$, standard enthalpy, $\Delta H°$, and standard entropy change, $\Delta S°$, on complex formation were calculated. Two types of complexes were observed, one association involving primarily the benzhydryltrichloromethyl grouping of DDT with a polar complexing agent, and the other interaction of the DDT aromatic π-electron system with π electrons in the complexing molecule.

The extensive occurrence of the compound 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, also known as the para isomer of the pesticide DDT,[1] in the global environment makes the interactions of this compound very interesting. Their elucidation may well be an extremely important task. Considerable attention has been given to the interaction of DDT with biological systems.[2] Fewer studies have been undertaken to determine the types of interactions involved and their energies.

The possibility of formation of charge-transfer or other types of molecular complexes involving DDT has been indicated by studies with model systems.[3–5]

Evidence for charge-transfer interaction of DDT with tetracyanoethylene from the ultraviolet–visible spectra has been obtained.[6] The use of nuclear magnetic

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(1) The abbreviation DDT will be used throughout this article for the compound 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane.

(2) See, for example, T. Narahishi and H. G. Hass, *J. Gen. Physiol.*, **51**, 177 (1968); F. Matsumura and M. Hayashi, *Science*, **153**, 757 (1966); R. B. Koch, *J. Neurochem.*, **16**, 269 (1969); R. M. Welch, W. Levin, and A. H. Conney, *Toxicol. Appl. Pharmacol.*, **14**, 358 (1969).

(3) D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).

(4) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 52–55.

(5) R. T. Ross and F. J. Biros, *Biochem. Biophys. Res. Commun.*, **39**, 723 (1970).

resonance spectroscopy to study the behavior of DDT complexes in solution[5,7] enables more precise characterization of the possible molecular association phenomena involved.

Methods Employed

A simple but useful means of obtaining equilibrium data from nmr chemical shifts is based on the fact that for a rapid equilibrium between two species, complexed and noncomplexed, the observed chemical shift is the average of the shifts of the separate complexed and noncomplexed species, weighted according to their populations. Thus for the equilibrium

$$\mathrm{DDT} + \mathrm{E} \rightleftharpoons \mathrm{DDT\cdot E} \tag{1}$$

the observed chemical shift for a given set of DDT protons, for example, the benzhydryl protons, will be

$$\delta = x_C\delta_C + x_D\delta_D \tag{2}$$

where δ is the observed shift, δ_C is the shift of the protons in the complex DDT · E, δ_D is their shift in noncomplexed DDT, and x_C and x_D are the mole fractions of complex and noncomplexed DDT, respectively. For this case, of course, $x_C + x_D = 1$. The equilibrium constant is then

$$K = \frac{\delta - \delta_D}{(\delta_C - \delta)[E]} \tag{3}$$

where [E] is the concentration of complexing agent and can be taken to be equal to its initial concentration if it is kept in considerable excess. Ideal solutions are assumed.

The shift of noncomplexed DDT, δ_D, can be obtained from the shift of a solution of DDT in the same solvent and at the same concentration and temperature in the absence of complexing agent. The complex shift, δ_C, can be obtained by extrapolation of a plot of $1/(\delta - \delta_D)$ *vs.* 1/[E], which is linear for 1:1 stoichiometry, to infinite concentration of complexing agent. This type of analysis of nmr shift data has been used extensively for treatment of hydrogen bond equilibria.[8] Ross and Biros[5] have made preliminary equilibrium measurements on some DDT complexes with aromatic donor molecules this way.

Alternatively, eq 3 can be rewritten as

$$\frac{\delta - \delta_D}{[E]} = -K(\delta - \delta_D) + K(\delta_C - \delta_D) \tag{3a}$$

which gives a linear plot of $(\delta - \delta_D)/[E]$ *vs.* $(\delta - \delta_D)$ for 1:1 stoichiometry, with slope equal to $-K$ and intercept $K(\delta_C - \delta_D)$.[9] Curvature, which indicates the presence of significant amounts of higher order complexes, is most easily seen on this type of plot, making this plot doubly useful as a test of 1:1 stoichiometry when a sufficiently large range of the complex concentration has been covered.[10,11]

In cases where more than one molecule of complexing agent are present in the complex, similar expressions can be written. For equilibrium between 1:1 complexes, 1:2 complexes, and noncomplexed DDT

$$\mathrm{DDT} + \mathrm{E} \rightleftharpoons \mathrm{DDT\cdot E} \qquad K_1$$

$$\mathrm{DDT\cdot E} + \mathrm{E} \rightleftharpoons \mathrm{DDT\cdot E_2} \qquad K_2$$

the observed chemical shift is given by

$$\delta - \delta_D = \frac{K_1[E](\delta_C - \delta_D) + K_1K_2[E]^2(\delta_F - \delta_D)}{1 + K_1[E] + K_1K_2[E]^2} \tag{4}$$

where δ_F is the shift of the 1:2 complex $\mathrm{DDT\cdot E_2}$. Values of the equilibrium constants K_1 and K_2 and of the complex shifts δ_C and δ_F can be extracted from the data by nonlinear regression analysis[12] of the data set (δ, [E]). The criteria for a good fit using the regression technique were: (a) reasonableness of the values of the constants (*e.g.*, K_1 and K_2 greater than or equal to zero) and (b) a standard error of estimate less than or equal to 0.1 Hz, using a minimum of 12 well-spaced data points for each curve.

The chemical shift of the benzhydryl proton, which has a somewhat broadened single resonance peak, can be easily measured directly from the nmr spectrum. To obtain accurate chemical shifts of the aromatic protons, however, it is necessary to use more sophisticated means to analyze the 24-line pattern of the aromatic proton resonances. Keith, Alford, and Garrison[13] have reported approximate chemical shifts and coupling constants for DDT and related compounds. Sharpless and Bradley[14] have analyzed the aromatic proton spectrum of DDT and several of its analogs and derivatives. With these results as a guide, the analysis of many sets of DDT aromatic proton spectra is a nearly routine task, using the computer programs NMREN/NMRIT,[15] and LAOCN3.[16]

From the temperature dependence of the equilibrium constants calculated from eq 3a or 4, using the appropriate chemical shifts, values for the standard thermodynamic parameters can be obtained. Plots of ln *K* *vs.* $10^3/T$, where *K* is the equilibrium constant and *T* is the absolute temperature, are linear, with a slope of $-\Delta H°/R$, according to the relations

$$\Delta G° = -RT \ln K \tag{5}$$

$$\ln K = -\Delta H°/RT + \Delta S°/R \tag{6}$$

Here $\Delta G°$ is the standard free energy, $\Delta H°$ is the standard enthalpy, and $\Delta S°$ is the standard entropy change on complex formation, and *R* is the gas constant.

Experimental Details

All the chemicals used were commercial reagent grade and were used without further purification. Solutions were 0.1 *M* in DDT. The concentration of the complexing agent ranged from 0.4 *M* up to the maximum limits of solubility. Solvents used were carbon tetrachloride or carbon disulfide. Tetramethylsilane (3%, v/v) was added as an internal reference.

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Table I. Nmr Parameters for DDT at Several Temperatures and Concentrations in Carbon Disulfide Solution

	Chemical shifts, $\tau \times 100$, Hz						Coupling constants, Hz[a]							
	H_1, H_2		H_3, H_4		H_5		J_{12}		J_{13}, J_{24}		J_{14}, J_{23}		J_{34}	
Temp, °C	0.40 *M*	0.050 *M*	0.40 *M*	0.050 *M*	0.40 *M*	0.050 *M*	0.40 *M*	0.050 *M*	0.40 *M*	0.050 *M*	0·40 *M*	0·050 *M*	0.40 *M*	0.050 *M*
27.0	257.87	257.52	277.60	276.73	504.9	504.8	2.42	2.39	0.36	0.24	8.37	8.61	2.43	2.41
−1.7	257.11	256.82	277.27	276.38	504.5	504.8	2.44	2.41	0.17	0.26	8.42	8.42	2.45	2.47
−17.0	257.01	256.40	277.31	276.26	504.7	504.3	2.43	2.46	0.20	0.18	8.41	8.40	2.44	2.44
−34.2	256.89	256.15	277.14	276.16	504.3	504.0	2.44	2.44	0.24	0.13	8.40	8.36	2.41	2.48

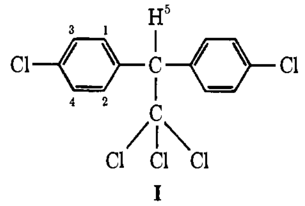
[a] Probable errors are as follows: temperature, ±0.3°; chemical shifts 1 and 2 and 3 and 4, ±0.5 Hz; chemical shift 5, ±0.1 Hz; coupling constants 12 and 34, ±0.14 Hz; coupling 13 and 24 and 14 and 23, ±0.08 Hz.

All spectra were obtained on a Varian HA-100 nmr spectrometer, with the Varian temperature controller. Operation was in the internal lock mode, with tetramethylsilane as the lock signal. Temperature measurements were made before and after each spectrum was run. The observed chemical shift of either ethylene glycol or methanol acidified with a trace of hydrochloric acid, was used to determine the probe temperature. The temperature dependence of the chemical shifts of these samples was calibrated with a copper–constantan thermocouple. The temperature could be measured to ±0.5°, and was controlled to ±1°.

To obtain accurate transition frequencies, the spectra were calibrated by direct frequency count from the lock frequency. Most transition frequencies were obtained from the average of three or four spectra.

Results and Discussion

The Nmr Spectrum and Self-Association. Before any study of complex formation by DDT with other molecular species could be interpreted, the question of whether DDT molecules themselves were associated to a significant extent had to be answered. Freezing point lowering measurements, using 0.1 *m* DDT in cyclohexane, gave a molecular weight consistent within 5% with monomeric DDT molecules. The nmr spectrum showed a very slight concentration and temperature dependence, a change of at most 1.6 Hz over the entire range of concentration and temperature. Some of these data are listed in Table I. The system of numbering the protons is shown in I. The two aromatic rings are equivalent.



I

Although self-association may play a part in determining the small temperature and concentration dependence of the nmr parameters, it is probably not extensive. Its effect on the observed chemical shift in DDT-complex systems can be corrected for by using the experimentally determined 0.1 *M* DDT shifts at each temperature for δ_D.

In the typical calculated and observed aromatic region nmr spectra shown in Figure 1, it can be seen that the lower field half of the spectrum, assigned to protons 1 and 2, exhibits an additional splitting of 0.4 Hz. This is due to allylic coupling with the benzhydryl proton, proton 5. Irradiation of proton 5 in a decoupling experiment removes this splitting. The value of the allylic coupling is the same for all the DDT spectra obtained in this study. The allylic coupling is dependent upon the dihedral angle between the C–H bonds of the benzhydryl proton and protons 1 and 2. An estimate of this average dihedral angle can be made[17,18] and is about 12°, which agrees with that measured from space-filling molecular models.

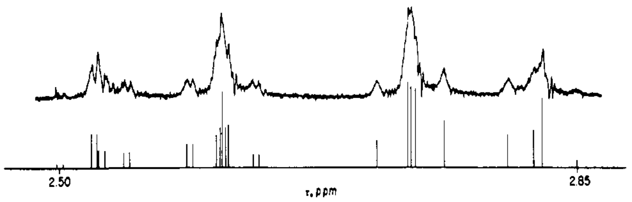


Figure 1. Calculated and observed aromatic proton spectra of 0.4 *M* DDT in carbon disulfide at 27.0°.

Complex Formation. Several characteristics of DDT make it possible for this molecule to be involved in complex formation. In trichloromethylbenzene, the trichloromethyl group has been shown to produce pronounced shifts, relative to benzene, of the aromatic proton resonances toward lower field by 0.80, 0.17, and 0.23 ppm for the ortho, meta, and para protons, respectively.[19] This substantial deshielding results mostly from electron withdrawal from the aromatic ring by the highly electronegative trichloromethyl group. The shifts of the aromatic protons in DDT and a series of related compounds have been shown to be primarily functions of the electronegativity of the functional groups on the α carbon.[14] Thus the trichloromethyl group effects a considerable decrease in electron density on the aromatic rings. The ring chloro substituent has much less effect. Although in chlorobenzene the chlorine is ortho–para directing in electrophilic substitution, its effect on the overall electron density on the aromatic ring is very much smaller than that of a trichloromethyl substituent, as evidenced by the small shifts of the aromatic protons relative to benzene (−0.02, +0.06, and +0.04 ppm for ortho, meta, and para protons, respectively).[20]

Other molecules which are capable of acting as electron donors into the DDT π-electron system can thus complex with the DDT. In the nmr spectrum, this type of complex formation results in a shift of the DDT aromatic protons toward higher field, reflecting the

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(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 316–324.

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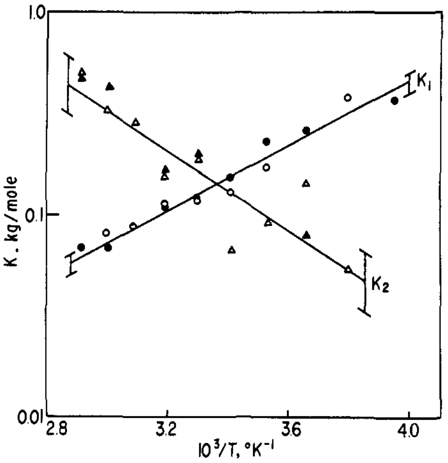

Figure 2. Dependence of the equilibrium constants of the reciprocal of the absolute temperature for DDT–benzene complex formation. The straight lines drawn are the least-squares fits. Brackets show the standard error. The open data points are based on the benzhydryl shift and the shaded data points on the meta shift.

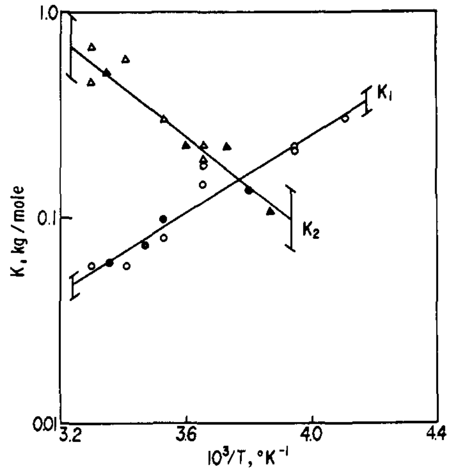

Figure 3. Dependence of the equilibrium constants on the reciprocal of the absolute temperature for DDT–naphthalene complex formation. The straight lines drawn are the least-squares fits. Brackets show the standard error. Open data points are based on the benzhydryl shift and shaded data points on the meta shift.

increased electron density and hence increased shielding of these protons.[19,21] Molecular orbital calculations carried out by Sharpless and Bradley[14] show that the chemical shift of protons 3 and 4, which are ortho to the chlorine substituent on the ring, depends on the π-electron density at those carbons. This chemical shift thus should reflect directly the degree of π-complex involvement of the DDT molecule. The shift of protons 1 and 2 is independent of the π-electron density.

Electron withdrawal by the trichloromethyl group also results in increased polarity of the C–H bond involving the benzhydryl proton. The partial positive charge on the proton might make it possible for it to participate in hydrogen-bond-type association with suitable complexing agents, for example, compounds having lone-pair electrons on an oxygen or nitrogen. Substances having considerable polarity might also be able to complex with the DDT, with the primary interaction being electrostatic attraction between the polar complexing agent and the highly polar H-C-C-Cl grouping. Formation of these types of complex would result in a downfield shift (decreased shielding) of the benzhydryl proton resonance. Some downfield shift of the aromatic protons, especially 1 and 2, might be expected when this type of complex is formed. However, the effect would be greatest on the benzhydryl shift which would logically be used to calculate equilibrium constants for these complexes.

In the case of the complexing agents benzene and naphthalene, it was found that the overall effect of complexation was an upfield shift of the resonances, pointing to electron donation into the DDT aromatic π system by the aromatic donors. Since the data plotted according to eq 3a showed a small curvature, the nonlinear regression technique was used to obtain equilibrium constants for the formation of the 1:1 and higher order complexes. For both benzene and naphthalene, constants for formation of complexes with DDT other than 1:1 and 1:2 were negligibly small. Thus eq 4 was used to fit all the data for these complexing agents. The results obtained using the shifts of the three different sets of protons in the DDT molecule are in agreement within the experimental error. Figures 2 and 3 illustrate some of these results.

Thermodynamic parameters for formation of these complexes are given in Table II. The enthalpy changes for the 1:1 DDT–benzene and DDT–naphthalene complexes are very nearly the same, with a slightly greater binding energy indicated for the naphthalene complex. The greater steric requirements for naphthalene complex formation are evidenced by the more negative entropy parameter. This is reflected in the greater free energy increase for naphthalene complexation. Formation of the 1:2 DDT–naphthalene$_2$ complex appears to be slightly more favorable than formation of the 1:2 benzene complex, although both are endothermic processes. This may be a result of a greater tendency toward self-association on the part of naphthalene.

Table II. Standard Thermodynamic Parameters at 298.16°K for Complex Formation between 1,1,1-Trichloro-2,2,-bis(*p*-chlorophenyl)ethane and Several Complexing Agents

	Benzene-d_6	Naphthalene-d_8	Ethyl acetate
K_1, kg/mol	0.157	0.0624	0.260
$\Delta G_1°$, kcal/mol	1.1 ± 0.2	1.6 ± 0.2	0.8 ± 0.2
$\Delta H_1°$, kcal/mol	−3.6 ± 0.2	−4.2 ± 0.2	−1.2 ± 0.2
$\Delta S_1°$, eu	−16 ± 3	−20 ± 2	−6.8 ± 1.3
K_2, kg/mol	0.148	0.497	
$\Delta G_2°$, kcal/mol	1.1 ± 0.4	0.4 ± 0.3	
$\Delta H_2°$, kcal/mol	4.5 ± 0.3	5.5 ± 0.3	
$\Delta S_2°$, eu	11 ± 6	17 ± 2	

The possibility of generalized solvent effects on the chemical shifts was also investigated. No effect on the DDT spectrum of large variations in the concentration of added cyclohexane and 1,2-dibromoethane was observed. A slight dependence of the aromatic proton shifts on the concentration of added *n*-hexane was observed. Since this was of the order of only 0.4 Hz

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[21] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

Table III. Nmr Parameters for DDT in the Presence of Various Possible Complexing Agents

Added substance[a]	Solvent	Chemical shifts,[b] $\tau \times 100$, Hz: H_1, H_2	H_3, H_4	H_5	Coupling constantz, Hz: J_{12}	J_{13}, J_{24}	J_{14}, J_{23}	J_{34}
None	CS_2	257.84	277.10	504.6	2.40	0.30	8.43	2.38
None	CCl_4	254.52	272.20	505.2	2.42	0.31	8.41	2.43
Benzene-d_6	CCl_4	261.23	277.48	510.6	2.41	0.22	8.32	2.42
Naphthalene-d_8	CS_2	268.46	282.73	515.8	2.40	0.33	8.26	2.37
n-Hexane	CCl_4	254.61	272.59	504.1	2.39	0.29	8.43	2.43
trans-1,4-Hexadiene	CCl_4	254.57	272.61		2.43	0.26	8.48	2.43
cis–trans-1,4-Hexadiene	CCl_4	254.53	272.63		2.41	0.28	8.45	2.43
Ethyl acetate	CCl_4	252.28	273.59	488.4	2.41	0.25	8.40	2.40

[a] Concentration of DDT 0.1 *M*, of added substance 1.0 *M*; all at 27.0°. [b] τ values are shifts in parts per million with TMS as 10.0 and values increasing with increasing field. Probable errors are: chemical shifts 1 and 2 and 3 and 4, ±0.05 Hz; chemical shift 5, ±0.1 Hz; coupling constant 12 and 34, ±0.14 Hz; coupling constants 13 and 24 and 14 and 23, ±0.08 Hz.

over the concentration range 0.4–3.0 *M* *n*-hexane, generalized solvent effects obviously do not account for the much larger concentration dependences observed with the complexing agents studied. (With benzene over this concentration range, the change in chemical shift was greater than 10 Hz.) These concentration dependences are illustrated in Figure 4.

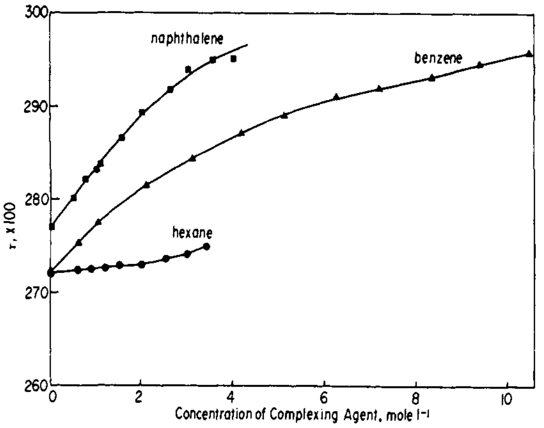

Figure 4. Dependence of the chemical shift of DDT aromatic protons 3 and 4 on the concentration of several possible complexing agents at 27.0°. The curves shown for benzene and naphthalene are the calculated curves from nonlinear regression analysis using eq 4.

Interaction of DDT and nonaromatic π-electron systems is another possibility. The cis and trans isomers of 1,4-hexadiene were used as possible complexing agents. The nmr parameters for the aromatic resonances of DDT in the presence of the trans isomer, and in the presence of the mixed isomers (approximately 80% cis), do not differ significantly from those parameters in the presence of *n*-hexane. The concentration dependences are very small. Thus, involvement of the DDT aromatic rings in complexation with the dienes must be either small or nonexistent. The hexadiene resonances masked that of the DDT benzhydryl proton, so it was not possible to determine the benzhydryl shifts.

Since the benzhydryl proton could possibly participate more directly in some types of complex formation, this was also explored. The high polarity of the benzhydryl C–H bond might result in the benzhydryl proton being able to participate in hydrogen bonding to a suitable lone-pair electron donor. Ethanol and *n*-butyl alcohol were used as representative complexing agents of this type. It was found that the change in the benzhydryl proton chemical shift with concentration of either of these alcohols was only 0.9 Hz toward low field over the concentration range 0.4–1.6 *M* alcohol. This is less than 10% of the change observed with the other complexing agents used in this study, and of the order of magnitude attributable to generalized solvent effects rather than specific complex formation. Hydrogen bonding of the benzhydryl proton does not appear to be an important means of complexation for DDT molecules.

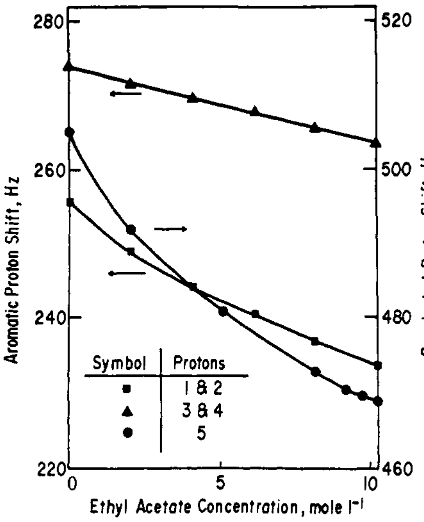

Figure 5. Dependence of the chemical shift of all three sets of DDT protons on the concentration of ethyl acetate at 27.0°.

The second type of complex formation in which the benzhydryl proton might be a major participant is association with a polar complexing agent. Ethyl acetate was used as a representative complexing agent. Figure 5 shows the dependence of the shifts of both sets of aromatic protons and the benzhydryl proton on the ethyl acetate concentration. The shifts moved toward low field (deshielding) upon complex formation. The three sets of protons had shifts which gave good linear fits using eq 3a and values of K_1 in agreement within experimental error. K_1 values obtained from the nonlinear regression program were the same as those obtained from the simple linear fit. The K_2 values from the nonlinear fit were less than 2% of the K_1 values, indicating that the 1:2 ethyl acetate complex is unimportant. Thermodynamic parameters for the ethyl

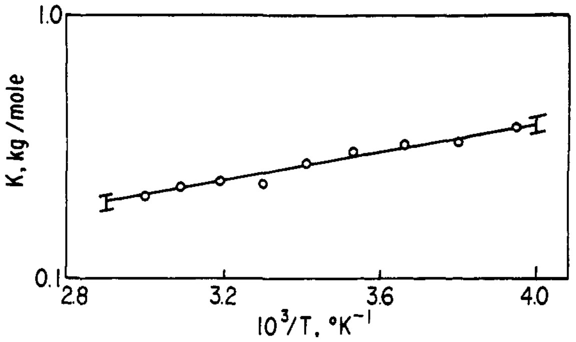

Figure 6. Dependence of the equilibrium constant on the reciprocal of the absolute temperature for DDT–ethyl acetate complex formation. The straight line drawn is the least-squares fit. Brackets show the standard error.

acetate complex, obtained from the plot in Figure 6, are listed in Table II. The enthalpy and entropy changes are both considerably less than those for formation of DDT complexes with the aromatic donors. Weaker binding and a much less specific spatial orientation of the complexing agent are indicated. This type of complex formation appears to depend on both the presence of the polar H—C—C(Cl$_3$) grouping in the DDT molecule and a highly polar complexing agent, such as one for which structures such as R—C(O$^-$)═O$^+$—R can be written. Preliminary measurements on DDT complexes with amides and ureas support these requirements.

A comparison of nmr parameters in the various systems studied is given in Table III. Additional nmr experiments are underway in this laboratory on complexes of DDT with model compounds of biological interest.

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Electron Paramagnetic Resonance Spectra of Copper(II) and Oxovanadium(IV) Complexes Oriented in Nematic Glasses from Liquid Crystal Solvents

John P. Fackler, Jr.,* Joel D. Levy,[1] and James A. Smith

Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106.
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Abstract: The electron paramagnetic resonance (epr) spectra of a series of copper(II) and oxovanadium(IV) complexes oriented in nematic glasses formed from liquid crystals have been measured. Data are presented which show that anisotropic epr parameters obtained by this convenient, easily interpreted technique compare favorably with published values obtained by dilute single crystal procedures. The results are substantially better than data obtained from randomly oriented frozen solutions or powders. The applicability of available theories concerned with the order present in liquid crystal solutions is discussed as it relates to the precision of the epr parameters. As an illustration of the usefulness of the technique, epr parameters are obtained for ten copper(II) and seven oxovanadium(IV) metal–organic complexes. Molecular orbital coefficients are calculated for the copper(II) species.

Single-crystal electron paramagnetic resonance (epr) spectra have been exceedingly valuable in helping to interpret bonding and structural parameters in paramagnetic transition metal compounds.[2] However, this technique suffers especially from two inherent experimental difficulties, the need to grow suitable single crystals and the requirement that the paramagnetic material be magnetically dilute. This latter problem usually is alleviated by doping an ion or molecule into a diamagnetic host, a procedure that requires the availability of suitable host materials.

We show here that liquid crystals can be used to orient metal–organic complexes in magnetic fields in order to produce epr results that compare well with data obtained from oriented, magnetically dilute single-crystal measurements. Furthermore, the information is achieved without the inherent drawbacks of the single-crystal technique and without precise knowledge of the crystal structure of the complex provided the paramagnetic material of interest is soluble in the nematic liquid crystal and substantial orientational ordering of the solute occurs. A preliminary report of this work has been published.[3]

Experimental Section

Liquid Crystals. Butyl *p*(*p*-ethoxyphenoxycarbonyl)phenyl carbonate was obtained from Eastman Organic Chemicals; this compound has a nematic range from approximately 56 to 87°. VL-1047-N is a room temperature nematic of undisclosed structure obtained from Vari-Light Corp., Cincinnati, Ohio; this material has a nematic range from approximately 10 to 47°. *N*-(*p*-Methoxybenzylidene)-*p*-butylaniline, another room temperature

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(1) Abstracted in part from the thesis of J. D. L. submitted in partial fulfillment for the Ph.D. degree in 1970 at Case Western Reserve University.

(2) (a) B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966), and references cited therein; (b) M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, 7, 2548 (1968).

(3) J. P. Fackler and J. A. Smith, *J. Amer. Chem. Soc.*, **92**, 5787 (1970). G. Heppke and F. Schneider, *Ber. Bunsenges. Phys. Chem.*, **75**, 61 (1971), obtained similar results with the nematic *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline.