

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Nuclear Magnetic Resonance Studies of Silver Ions and 1,3,5-Trinitrobenzene Complexes with Heterocyclic Compounds<sup>1</sup>

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A study, using nmr techniques, of the complex forming powers of silver ions and 1,3,5-trinitrobenzene with heterocyclic compounds containing oxygen and sulfur is described. The differences in the results of the oxygen and sulfur complexes are interpreted in terms of the relative role played by the lone pairs in the heteroatoms.

### Introduction

Recently, we have demonstrated<sup>3</sup> the usefulness of the nmr techniques for pointing out localized and delocalized interactions among a number of heterocyclics and hydrocarbons. It has been clearly established that in many of these complexes, the silver ions prefer to interact at localized sites, *i.e.*, either at a part of the molecule with a large double-bond character or with just a single atom. Moreover, we have established that molecules containing sulfur form considerably stronger complexes than the analogous oxygen compounds. In order to understand in more detail the factors involved which make the sulfur complexes form stronger complexes than the oxygen compounds, even though the latter are much stronger electron donors,<sup>4</sup> we have extended these studies to other series of compounds, 1,4-dithiin, 1,4-dioxin, 1,4-benzodithiin, and 1,4-benzodioxin. These compounds provide an opportunity for a systematic study of various possible complexing sites in addition to a study of the relative effects of oxygen and sulfur atoms.

Our purpose was to obtain information concerning equilibrium constants and proton chemical shifts at many different sites in the interacting molecules by studying the changes in the chemical shifts, of all the protons of a donor with respect to one another, upon complex formation. We have, therefore, presented results using two types of acceptors, silver ion and TNB. We thought these acceptors would provide direct evidence of the presence or the absence of localized or delocalized interactions at different particular sites in different types of molecules.

### Experimental Section

The donors 1,4-dithiin, 1,4-dioxin, and 1,4-benzodithiin, and 1,4-benzodioxin were prepared in the laboratory using commercially available products. The method described here requires a large excess of the acceptor compared with the donor. The technique requires solvents capable of dissolving a large amount of the acceptor as well as smaller amounts of organic donors. Acetonitrile (MeCN) will form at least a 10.0 *M* solution of silver nitrate and methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) will dissolve at least 6 mol of *s*-trinitrobenzene (TNB) per kilogram of solvent. We therefore used acetonitrile with all silver nitrate samples and the solvent methylene chloride with all *s*-trinitrobenzene solutions. Unfortunately, the full complexing

of the AgNO<sub>3</sub>-MeCN system was not realized until most of the work had been completed.

Samples of varying concentrations of the acceptors were prepared as described previously.<sup>3</sup> The solutions were made by weight measurements with the acceptor (silver ion or TNB) concentrations being expressed in molal units. The silver nitrate concentrations were varied from 2.0 to 10.0 *m* while TNB concentrations were varied from 0.3 to 2.5 *m*.

The pmr spectra of about 12-15 samples were recorded at a fixed radiofrequency of 100 MHz on a Varian HA-100 instrument with the use of a time-averaging computer and the probe of the instrument was thermostated at 30.0 ± 0.5° during each measurement. The chemical shifts of the various protons of the donors were measured relative to the respective solvent peaks and the necessary corrections for the shift of the MeCN peak with the different concentrations of silver ions were made. The chemical shifts of the various protons of the donors were the average values of about four to six measurements. The chemical shifts were measured to an estimated accuracy of ±0.5 Hz.

### Evaluation of Data

The nmr equation for evaluating the equilibrium constant (*K*) for the 1:1  $\pi$  molecular complex was developed earlier by Hanna and Ashbaugh.<sup>5</sup> When the acceptor species (A) are in large excess over the donor species (D), the equation could be written as

$$\frac{1}{\Delta_o} = \frac{1}{K\Delta_c} \frac{1}{m_A} + \frac{1}{\Delta_c} \quad (1)$$

where  $\Delta_o$  = observed shift of the donor proton(s) in the uncomplexed state and  $\Delta_c$  = shift of the donor proton(s) in the pure complex.

Thus the plots of  $1/\Delta_o$  vs.  $1/m_A$  should be linear for the 1:1 complex and *K* and  $\Delta_c$  may be directly obtained from the gradient and intercept of the line with the ordinate. Only 1:1 complexes are formed in our solutions according to published work<sup>3</sup> and eq 1 has been used to evaluate the data for all our TNB complexes. We believe<sup>3</sup> that the acceptor TNB does not form a complex of significant strength with the solvent CH<sub>2</sub>-Cl<sub>2</sub>.

As described recently<sup>3</sup> the results of molecular complexes between silver ion and organic donors in the solvent MeCN cannot be interpreted by eq 1 due to the specific solvation of the acceptor silver ion. There is conclusive evidence to show<sup>3,6</sup> that when silver nitrate is dissolved in MeCN, most of the silver ions exist predominantly in the 1:2 complex over the concentration ranges studied. In the presence of organic donors, one solvent molecule attached to the acceptor (Ag<sup>+</sup>) is then replaced by one donor molecule to form a 1:1 solvated silver ion-organic complex. This picture of com-

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petition equilibria is similar to the description given earlier by Carter and his coworkers<sup>7</sup> in explaining the importance of solvation in the formation of weak complexes studied by ultraviolet spectroscopy. Thus the equilibrium expression for the formation of the silver ion-organic complex in the solvent MeCN then becomes



where S<sub>2</sub> represent two solvent molecules (S). For eq 2 it is assumed that D is not specifically solvated. If eq 2 is combined with the nmr equation relating to the chemical shifts in rapid equilibrium,<sup>8</sup> we obtain the following equation for the acceptor concentration in molal units

$$\frac{1}{\Delta_0} = \frac{m_S}{K\Delta_c} \frac{1}{m_A} + \frac{1}{\Delta_c} \left(1 - \frac{2}{K}\right) \quad (3)$$

where  $m_S$  = moles of solvent per kilogram of solvent. If any coefficient of eq 3 were greater than 1, then higher order terms would appear and eq 3 would no longer represent a straight line.

However, we obtained good linear plots with positive intercepts using eq 3 from the data on all silver ion-organic complexes reported in this investigation. It may be noted that the shifts of all protons of complexes of silver ion are downfield relative to the protons of uncomplexed donor while for TNB complexes the chemical shifts are upfield. This is expected because almost any conceivable orientation of TNB molecule about the donor or any part of the donor would place the protons of the donors in the shielding region of the diamagnetic anisotropic TNB molecule.<sup>9</sup>

### Results and Discussion

In the discussion which follows all equilibrium constants and chemical shifts of complexes were derived by using molality units in making plots according to either eq 1 or 3. The results are summarized in Tables I and II. We discuss the individual systems separately.

**A. 1,3,5-Trinitrobenzene Complexes.**—It can be seen from Table IA that dioxin and dithiin molecules and their benzo derivatives form the weakest TNB complexes. Even the hydrocarbon styrene, which has no electron-rich components, has been reported<sup>8</sup> to yield a larger equilibrium constant than any of the dioxins and dithiins. This fact indicates that an unfavorable geometry exists for complexing with the large  $\pi$ -delocalized acceptor TNB in these heterocyclic molecules.

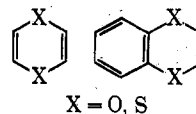
The only major difference in the oxygen and sulfur analogs of the six-membered heterocyclics is in the chemical shifts of the vinyl protons in the hetero ring of the benzo derivatives. The vinyl protons of 1,4-benzodithiin have a change in the shift of about 32 Hz in the complex but the vinyl protons of 1,4-benzodioxin do not show any changes in the shift when the complex is formed. If the benzodithiin complex is such that the nitro groups are interacting with the lone pairs of sulfur atom, then this would surely cause a shift of the vinyl proton resonance. The lack of change in the

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TABLE I  
EQUILIBRIUM CONSTANT ( $K$ ) AND  $\Delta_0$  VALUES FOR TNB  
COMPLEXES WITH HETEROCYCLICS



#### A. Equilibrium Constants

Donor (D)	$K$ , kg of solvent/mol					
	H <sub>2</sub>	H <sub>3</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>
1,4-Dioxin	0.32	0.32	0.32	0.32		
1,4-Dithiin	0.47	0.47	0.47	0.47		
1,4-Benzodioxin	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
1,4-Benzodithiin	0.54	0.54	0.46	0.50	0.50	0.50

#### B. $\Delta_0$ Values

Donor (D)	$\Delta_0$ , Hz					
	H <sub>2</sub>	H <sub>3</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>
1,4-Dioxin	35.3	35.3	35.3	35.3		
1,4-Dithiin	26.8	26.8	26.8	26.8		
1,4-Benzodioxin	<i>a</i>	<i>a</i>	<i>b</i>	61.6	61.6	61.6
1,4-Benzodithiin	32.1	32.1	47.2	42.7	42.7	42.7

<sup>a</sup> Vinyl protons did not change position on complex formation.

<sup>b</sup> Plotted points were too scattered for a straight line.

TABLE II  
EQUILIBRIUM CONSTANT ( $K$ ) AND  $\Delta_0$  VALUES FOR SILVER ION  
COMPLEXES WITH HETEROCYCLICS

#### A. Equilibrium Constants

Donor (D)	$K$					
	H <sub>2</sub>	H <sub>3</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>
1,4-Dioxin	4.4	4.4	4.4	4.4		
1,4-Dithiin	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>		
1,4-Benzodioxin	5.4	5.4	4.4	4.9	4.9	4.9
1,4-Benzodithiin	12.6	12.6	13.9	11.4	11.4	11.4

#### B. $\Delta_0$ Values

Donor (D)	$\Delta_0$ , Hz					
	H <sub>2</sub>	H <sub>3</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>
1,4-Dioxin	16.5	16.5	16.5	16.5		
1,4-Dithiin	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>		
1,4-Benzodioxin	16.2	16.2	7.8	7.1	7.1	7.1
1,4-Benzodithiin	45.5	45.5	31.0	21.6	21.6	24.6

<sup>a</sup> Immediate chemical reaction on mixing components.

chemical shift of the vinyl protons of benzodioxin molecule, on complex formation, may be due to the hetero ring oxygen lone pairs. This argument is consistent with the recent<sup>10</sup> nmr results for benzodioxin and benzodithiin. It has been concluded that there is a large amount of ground-state interaction of the oxygen lone pairs with the benzo electronic system. If the lone pairs are donated to the benzo system, they are not available for interaction with the TNB groups. However, this ground-state contribution to the benzo ring increases the electron richness making this ring a good complexing agent with the TNB ring. The sulfur atom lone pairs of benzodithiin do not contribute nearly so much to the ground state of the benzo ring but these lone pairs are available for interaction with the TNB nitro groups.

**B. Silver Nitrate Complexes.**—The equilibrium constants and chemical shifts for silver nitrate complexes with the heterocyclics studied in this investigation are given in Table II. It can be seen that all of the compounds have equilibrium constants greater than 4.0. The picture derived from equilibrium constants alone for the benzodioxin and dithiin is some-

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what confused. Part of this confusion is believed to be attributable to the existence of two or more isomeric or trimeric complexes for these compounds as described earlier.<sup>3</sup>

Equilibrium constants of the benzodioxin and benzodithiin indicate that the sulfur analog forms a stronger complex than the oxygen analog. It is further observed that the strength of neither the oxygen complex nor the sulfur analog is affected by the addition of a second benzo group onto the hetero ring as in the case of thianthrene and diphenyldioxane.<sup>3</sup> Values of about 5.0 and 13.0 for oxygen and sulfur analogs, respectively, are obtained for both the benzo and dibenzo derivatives. Again it must be concluded that the silver ion interacts at the heteroatom lone-pair electrons rather than the double bond of the benzodioxin or benzodithiin. The interaction of the silver ion at the lone pair and also the stronger interaction of the silver ion with the sulfur atom lone pair again suggest strong interaction of the oxygen lone pair with the delocalized system.

In both benzodioxin and dithiin the vinyl protons have larger chemical shift changes than the aromatic

protons when the complex forms. This is expected if the silver ion is complexed predominantly in the hetero ring. The resonance of the aromatic protons of the sulfur analogs which are  $\alpha$  to the sulfur atom is changed about 27.0 Hz while the protons  $\beta$  to the sulfur atom are shifted only 21 Hz on complexation. The shift of the aromatic protons of benzodioxin are very small on complexing and show no significant difference between  $\alpha$ - and  $\beta$ -proton shifts. Thus, for both the benzo- and dibenzo-derivative complexes the protons on the sulfur analogs have much higher shifts than the corresponding protons on the oxygen analogs. This may be a reflection of the higher equilibrium constants for the sulfur analogs, which in turn are due to a stronger interaction between the sulfur filled orbitals and silver ion vacant orbitals.

The formation constant of 1,4-dioxin-silver ion complex is about the same as that shown by 1,4-benzodioxin (Table IIA). Also chemical shifts of 1,4-dioxin complex protons are about the same as those of the vinyl protons in complexed 1,4-benzodioxin. Unfortunately, 1,4-dithiin reacts immediately when added to silver nitrate solution.

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## Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. IV. Kinetics of Partial Dissociation of the Cadmium and Zinc Complexes of 1,3-Propylenediaminetetraacetic Acid<sup>1</sup>

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Dynamic nuclear magnetic resonance methods have been used to determine the average lifetimes of the magnetically non-equivalent acetate methylenic protons before interchange in the cadmium and zinc complexes of 1,3-propylenediaminetetraacetic acid (1,3-PDTA). Magnetic nonequivalence is indicated by AB multiplet patterns for the methylenic protons. The lifetimes were determined over a range of temperatures from the extent of collapse of the AB multiplet patterns by matching experimental nmr spectra with theoretical nmr spectra which were calculated as a function of the average lifetime before interchange using the density matrix formulation. It is proposed that these lifetimes are a measure of the rates of partial dissociation of the cadmium and zinc complexes of 1,3-PDTA.

### Introduction

Nuclear magnetic resonance (nmr) studies have revealed through AB splitting patterns that the two protons of a given acetate methylenic group of ethylenediaminetetraacetic acid (EDTA)<sup>2-10</sup> and of several analogs of EDTA<sup>3,6,8-16</sup> are magnetically nonequivalent

on the nmr time scale in a number of metal complexes of these ligands. The nonequivalence has been interpreted as indicating the inertness on this time scale of at least some if not all of the metal-ligand bonds. Day and Reilley<sup>2</sup> proposed, for example, that the cadmium-nitrogen bonds in  $\text{Cd}(\text{EDTA})^{2-}$  are inert on the nmr time scale on the basis of the nonequivalence of the methylenic protons of the complexed EDTA; the two protons of a given methylenic group can interchange environments and thus collapse the AB pattern to a single resonance, only by inversion of the nitrogen atom, which presumably is possible only when the nitrogen atom is not metal coordinated. Inherent in this interpretation is the assumption that, once the metal-nitrogen bond dissociates, inversion occurs at least once before the metal-nitrogen bond re-forms.

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