mechanisms of intramolecular electron spin transmission through the σ-bonded skeleton.

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References and Notes

(1) A part of our systematic investigation on NMR contact shift studies for the σ-bonded molecules.

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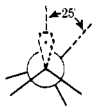

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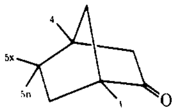

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Stable Hydrogen-Bonded Adducts of Unstable Polyhalogenated *gem*-Diols

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Abstract: Stable adducts involving the *gem*-diols of hydrated hexachloroacetone, pentachloroacetone, 1,3-difluorotetrachloroacetone, and chloral have been formed with several classes of organic acceptors. Although some of the hydrates themselves are stable, e.g., chloral hydrate, others are not, e.g., hexachloroacetone hydrate; however, all of the adducts formed with organic acceptors are quite stable, several being crystalline solids. The stability exhibited by these adducts is believed to originate from the formation of two strong hydrogen bonds. Spectral evidence supporting the formation of a *gem*-diol from the halogenated ketones and its hydrogen bonding to an organic acceptor comes from the disappearance of water absorption in the near ir when a halogenated ketone is added to a "wet" organic acceptor, the absence of the ir carbonyl absorption of the halogenated ketone in the adducts, and the large shifts observed in the ir and Raman absorptions of oxygen functionalities of the organic acceptors upon adduct formation. Possible adduct structures, inferred from the spectral data, are also presented. The Raman spectrum of hexachloroacetone hydrate, an unstable crystalline material previously thought to be a monohydrate, has been obtained and has been shown to be a tetrahydrate by quantitative gas chromatography.

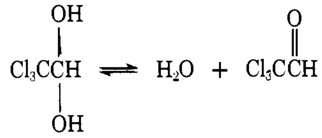
Highly halogenated ketones and aldehydes are expected to form stable hydrates due to the electronegativity of the groups attached to the carbonyl carbon. Thus, stable hydrates are formed from halogenated ethanals and highly fluorinated acetones.[1] These *gem*-diols have been very useful as solvents for polymers and biological membranes[2] due to their ability to form strong hydrogen bonds. Although halogenated ethanal hydrates and hydrates of fluoro ketones are stable *gem*-diols, forming spontaneously when the carbonyl compounds are exposed to moist air, hexachloroacetone can be shaken with

Table I. Physical Constants of Hydrogen-Bonded Adducts

Acceptors	Hydrate	Mp, °C	Δν, cm^{-1}	Method
Cyclohexanone	HCA	49.5-50.5	−41	Raman-ir
	PCA	Liquid	−5	Ir
	Chloral	Liquid	−12	Ir
	1,3-DFTCA	Liquid	−16	Ir
DMSO	HCA	57-60	−50	Raman-ir
	PCA	62-64	−58	Raman-ir
	Chloral	22.5-23.5	−42	Ir
	1,3-DFTCA	Liquid	−45	Ir
DMA	HCA	Liquid	−20	Ir
	PCA	Liquid	−19	Ir
	Chloral	Liquid	−23	Ir
	1,3-DFTCA	Liquid	−41	Ir
DMF	HCA	31.5/34	−15	Ir
Cyclopentanone	HCA	Liquid	−20	Ir
HMPA	HCA	60	−63	Ir
	PCA	Liquid	−54	Ir
	1,3-DFTCA	47-55	−72	Raman-ir
Dioxane	HCA	63-65	−19	Raman

water, without loss of strong carbonyl absorption.

The reversible hydration of carbonyl compounds is a well-known and studied reaction.[3] Thus, while the dissociation constant, K_d, for chloral hydrate (defined by eq 1) has been



$$\mathrm{Cl_3C\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}H} \rightleftharpoons \mathrm{H_2O} + \mathrm{Cl_3C\overset{\displaystyle O}{\overset{\|}{C}}H} \qquad (1)$$

$$K_d = [\text{chloral}]/[\text{chloral hydrate}]$$

determined to be 3.6×10^{-5} at 25 °C,[4] and chloral hydrate is a stable crystal at that temperature, the corresponding K_d for acetone is around 500,[4] and acetone is only hydrated to the extent of 0.2% in dilute aqueous solution at 25 °C. A variety of carbonyl hydration equilibria have been studied by various physical techniques and found to be in excellent agreement with the Taft linear free energy equation using the somewhat dangerous approximation of additivity of steric effect due to two substituents on the same carbon. The observed Taft correlation is shown in eq 2. In this equation, 2.70 is log K_d for

$$\log K_d = 2.70 - 2.6\Sigma\sigma^* - 1.3\,\Sigma E_s \qquad (2)$$

acetone, and −2.6 and −1.3 represent the Taft parameters ρ^* and s, respectively. Applications of eq 2 to the case of chloral leads one to predict $K_d = 4.0 \times 10^{-5}$, in excellent agreement with that found. If one applies the Taft correlation to the case of hexachloracetone (HCA), a prediction of $K_d = 1.9 \times 10^{-6}$ is obtained. That is to say the hydrate of HCA is predicted to be 21 times as stable as chloral hydrate. This prediction is somewhat surprising since chloral reacts vigorously with water while HCA is apparently inert. Although the hydrate of hexachloroacetone has been reported in the late 19th century[5] and is listed in handbooks as having a melting point of 15 °C,[6] we were unable to isolate a monohydrate of HCA but instead prepared a tetrahydrate with an incongruent melting point of 40 °C, which reverts to ketone and water on standing at 25 °C.

That the K_d of HCA is higher than predicted by eq 2 is not at all unreasonable when one considers the inclusion in that treatment of the summation of steric effects on the same carbon. This approximation holds reasonably well for small groups, but the steric requirements of trichloromethyl are even greater than that for *tert*-butyl (E_s = 2.06 and −1.54, respectively) and the interaction of these two bulky groups can in no way be ignored. Thus, when the carbonyl of HCA is hydrated, the ca. sp^2 carbon is rehybridized to ca. sp^3 forcing the trichloromethyls from a relatively widespread 120° to a steric calamity at 109°. This destabilizing effect on the hydrate of HCA can apparently be overcome by providing hydrogen bonding acceptors to the resulting *gem*-diol.

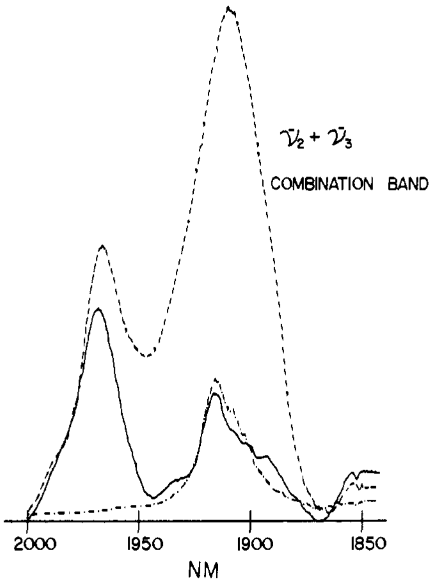


Figure 1. Near infrared absorption spectra of 1% water in cyclohexanone (- - -), hexachloroacetone (-·-), and a 1:1 mixture of the two corrected for path length (—).

This work reports the preparation and isolation of several hydrogen bonded complexes of the *gem*-diols of hexachloroacetone (HCA), pentachloroacetone (PCA), 1,3-difluorotetrachloroacetone (1,3-DFTCA), and, for comparison purposes, chloral to several classes of organic bases. Many of these complexes are, in fact, stable crystalline adducts[7] indicating very strong hydrogen bond formation.

Results

The complexes listed in Table I were prepared by the exothermic reaction of molar mixtures of carbonyl, acceptor, and water. Evidence for the existence of the postulated *gem*-diols contained in the complexes involving the hydrates of the chloro ketones comes from the near ir, ir, and Raman spectra of the adducts.

Near infrared spectra were run on the different organic bases containing 1% v/v water in a 0.5-mm cell vs. the organic base alone in a 0.5-mm reference cell to record the $\nu_2 + \nu_3$ band diagnostic of water[8] at 1915 to 1941 nm (depending upon the base). A 0.5% water solution of the various bases containing an equal volume of the chlorinated ketones was then prepared. The NIR spectra of these solutions were obtained in a 1.0-mm cell vs. a 1.0-mm cell containing a 1:1 mixture of base and chlorinated ketone alone; in all cases no $\nu_2 + \nu_3$ water band could be observed, Figure 1 (spectra run from 1800 to 2000 nm). This result indicated that free water no longer exists in these solutions, but has formed a hydrate of the chlorinated ketone, i.e., a *gem*-diol.

Raman and infrared spectra were obtained for two reasons. First, to examine the carbonyl region of the adducts for absorptions due to the halogenated ketones (these should be absent if a hydrate has truly been formed); and second, to examine the shift in the absorptions of the oxygen functionalities of the organic bases. Hydrogen bonding should lower the frequency of these absorptions.[9] For ketones and amides the absorptions in the 1715-cm^{-1} region and 1650- to 1515-cm^{-1} region were observed, respectively; whereas, the sulfoxide absorbance around 1055 cm^{-1} [10] and the phosphoramide ab-

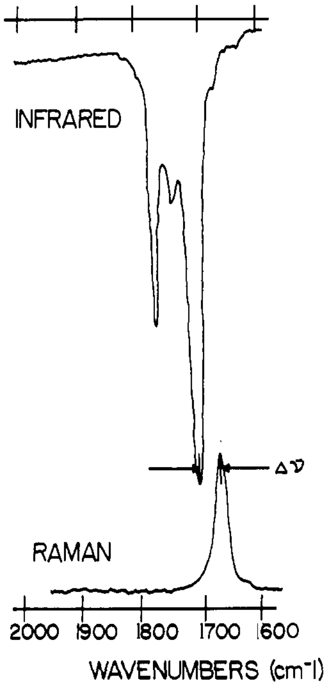


Figure 2. Infrared spectrum of carbonyl region of a mixture of dry hexachloroacetone and cyclohexanone compared with the Raman spectrum of the carbonyl region of the solid hexachloroacetone hydrate cyclohexanone adduct.

sorbance around 1215 cm^{-1} [11] were observed for DMSO and HMPA. For the complex with dioxane, the frequency of the ring stretching mde[12] at 1109 cm^{-1} was observed in the Raman. This 1109-cm^{-1} band has been shown to shift to lower frequency upon complex formation.[13]

Raman spectra were obtained on pure solid adducts of hexachloracetone hydrate with cyclohexanone, DMSO, and dioxane; pentachloroacetone hydrate with DMSO, and 1,3-difluorotetrachloroacetone hydrate with HMPA. In all of these cases no absorbance due to the carbonyl of the halogenated ketone could be observed. Infrared spectra were run on the remaining liquid adducts in Table I and on hexachloroacetone hydrate:HMPA, hexachloroacetone hydrate:DMF, and chloral hydrate:DMSO, which were run as viscous oils. The infrared spectra of these complexes revealed the disappearance of greater than 85% of the original carbonyl absorptions for all of the chlorinated ketones and chloral except for the pentachloroacetone hydrate:cyclohexanone adduct, where about 30% of the original carbonyl absorption of pentachloroacetone remained; this anomaly will be discussed below. These results are again in agreement with the formation of *gem*-diols from the chloro ketones.

In order to measure the change in frequency of the carbonyl, sulfoxide, and phosphoramide absorbance in the Raman and infrared upon complex formation, spectra were recorded on solutions of 1:1 molar mixtures of dry halogenated ketones and aldehydes with the dry organic bases. The $\Delta\nu$ values given in Table I were calculated from measurements on the adducts and the dry mixtures according to eq 3, Figure 2

$$\Delta\nu = \nu(\text{adduct}) - \nu(\text{halogenated ketone} + \text{base}) \qquad (3)$$

The erythro and threo isomers of 2-(2′,2′,2′-trichloro-1′-hydroxyethyl)cyclohexanone[14] were prepared and isolated as model compounds in comparing the degree of hydrogen bonding to a carbonyl group vs. a trichloromethyl group. Figure 3a indicates that in the threo isomer the trichloromethyl group and the carbonyl group are competing as hydrogen bonding sites for the hydroxyl proton. While this competition still exists in the erythro isomer (Figure 3b), the steric interaction between the trichloromethyl group and the ring is such that hydrogen bonding of the hydroxyl proton to the carbonyl group is disrupted.

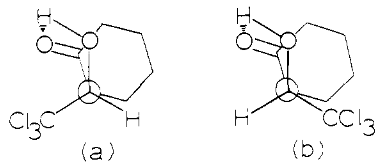


Figure 3. Modified Newman projections of threo (a) and erythro (b) isomers of 2-(2′,2′,2′-trichloro-1′-hydroxyethyl)cyclohexanone showing unfavorable steric interactions resulting from intramolecular hydrogen bonding in the erythro case and favorable steric interactions in the threo.

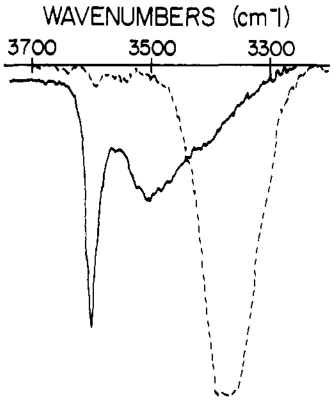


Figure 4. Infrared spectra of O–H stretching region of 0.13 M CCl_4 solutions of *erythro-* (—) and *threo-* (- - -) -2-(2′,2′,2′-trichloro-1′-hydroxyethyl)cyclohexanone.

As shown in Figure 4, the infrared spectra of the threo isomer shows only intramolecular hydrogen bonding up to a concentration of 0.126 M in CCl_4, whereas the erythro isomer exhibits intra (3380 cm^{-1}), inter (3500 cm^{-1}), and free (3605 cm^{-1}) OH absorptions in the infrared. Because of the overlap of these bands in the 3650- to 3300-cm^{-1} region the experimental curves were digitized, converted from percent transmittance into absorbance, and the components resolved using a generalized nonlinear least-squares program.[15] The curves due to inter- and intramolecular hydrogen bonding were assumed to be Gaussian while the free OH was assumed to be Lorentzian. Numerical integrations of these curves are taken as proportional to the concentration of each species. Resolved areas for the erythro isomer were obtained for concentrations varying from 0.0608 to 0.194 M in CCl_4. Figure 5 shows the concentration dependence of the 3380 + 3605-cm^{-1} bands and the 3500-cm^{-1} band thus supporting the band assignments and showing the relative importance of carbonyl hydrogen bonding in a sterically hindered complex.

Having prepared several adducts of hexachloroacetone hydrate, it appeared that a base acting to stabilize the *gem*-diol through hydrogen bonding was indeed necessary. We were therefore quite surprised to see that the monohydrate of HCA had been reported.[5,6] After several attempts to prepare the monohydrate, the only isolable hydrate of HCA was shown to contain 4 mol of water/mol of HCA by quantitative gas chromatography. The tetrahydrate is unstable, slowly reverting to ketone and water at 25 °C. Analogous stable tetrahydrates have been reported for $\alpha,\alpha,\alpha,\alpha'$-tetrachloroacetone,[16a] $\alpha,\alpha,\alpha'\alpha'$-tetrachloroacetone,[16b] and pentachloroacetone.[16c]

Discussion

On addition of water to HCA, PCA, or 1,3-DFTCA vigorous formation of the *gem*-diols does not take place although

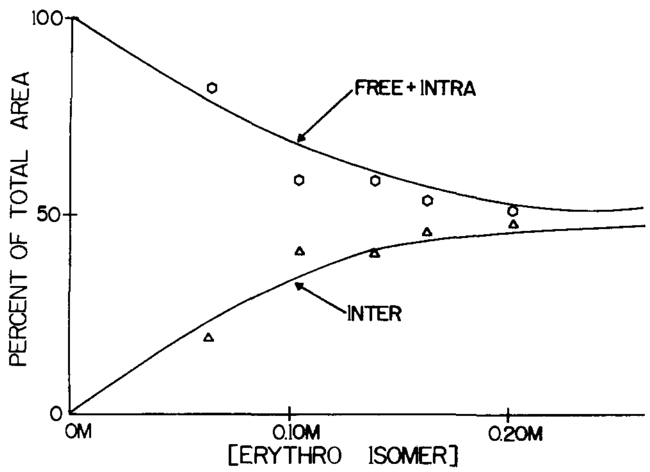


Figure 5. Plot of area percents of free (3605 cm^{-1}) + intramolecularly hydrogen bonded (3380 cm^{-1}) O-H stretching absorptions determined by curve resolution and numerical integration as compared with intermolecular hydrogen bonding (3500 cm^{-1}) as a function of concentration of *erythro*-2-(2′,2′,2′-trichloro-1′-hydroxyethyl)cyclohexanone in CCl$_4$.

Table II. Comparison of Raman Spectra of Hexachloroacetone Hydrate-Dioxane Adduct with Dioxane, HgCl$_2$-Dioxane,[13] and Hexachloroacetone Tetrahydrate (1350-400 cm^{-1})

Dioxane assignments[12a]	Dioxane (liq)	Hexachloroacetone hydrate-dioxane	HgCl$_2$-dioxane	Hexachloroacetone tetrahydrate
$\nu_{25} + \nu_{28}$	1334 vw	1336 vw		
ν_4A_g	1303 w	1306 w	1310 w	
$\nu_{33}B_g$	1216 w	1217 w	1220 w	
		1147 w		1154 vw
ν_5A_g	1127 w	1127 w	1132 w	
				1117 m-s
$\nu_{35}B_g$	1109 w	1090 w	1094 w	
		1052 v-w		1078 v-w
ν_7A_g	1015 w	1020 m-w	1018 m-w	
		1009 m		1009 m
		878 w-m		887 w
ν_6A_g	852 vw		856 w	
		843 m-w		848 w
ν_3A_g	834 m-s	821 m	827 m	
				818 w
		804 w		802 w-m
		663 w		650 w
		615 m-w		615 m-w
$\nu_{38}B_g$	486 w	487 v-w	456 w	
		472 m-w		472 m-w
		442 w		
ν_9A_g	433 vw	431 w		
$\nu_{10}A_g$	422 vw			
		415 s		420 vs

the carbonyl is flanked by electron-withdrawing groups. This lack of reactivity is due to the bulkiness of these substituents, sterically resisting the necessary tetrahedral geometry of the carbonyl carbon in the *gem*-diol. This steric resistance can be overcome by stabilizing the resulting *gem*-diol through hydrogen bonding as evidenced by the disappearance of the $\nu_2 + \nu_3$ water band in the near infrared when a halogenated ketone is added to a "wet" organic base and by the disappearance of the carbonyl absorption of the halo ketone in the infrared and Raman spectra of the adducts. This work has also shown that a number of organic bases are able to supply the required stabilization. That the hydrogen bonds in these compounds are quite strong is evidenced by the exothermicity of the reaction involving their formation, the shift in the infrared and Raman absorptions of the oxygen functionalities of the organic bases, and the isolation of crystalline adducts with sharp melting points.

Although the hydroxyl protons of the *gem*-diol in these complexes have several sites available to them for hydrogen bonding, in the solid adducts, at least, only two arrangements are reasonable. In each complex we have two sites, attempting to attract the hydroxyl proton of the *gem*-diol, a halomethyl group and the oxygen functionality of the base. Spectroscopic studies on 2-haloethanols[17] have shown that the enthalpy of hydrogen bonding to a trihalomethyl group is only about 3 kcal/mol, and that mono- and dihalomethyl form even weaker hydrogen bonds. However, Arnett[18] has found enthalpies of hydrogen bonding of the order of 5-9 kcal/mol in bases similar to those studied here. Thus, one would expect hydrogen bonding to occur preferentially to the oxygen functionality of the organic base. This expectation is realized in the examination of the infrared spectrum of the threo isomer of 2-(2′,2′,2′-trichloro-1′-hydroxyethyl)cyclohexanone. The lone hydroxyl absorbance at 3380 cm^{-1} present in carbon tetrachloride solutions up to concentrations of 0.5 M reveals that only intramolecular hydrogen bonding to the carbonyl group is occurring. In contrast the erythro isomer exhibits three hydroxyl absorption bands due to the steric constraint placed on hydrogen bonding to the carbonyl group by the trichloromethyl-ring interaction. The O-H stretch resulting from "free" O-H (i.e., that not hydrogen bonded to oxygen) of the erythro isomer is quite evident at 3605 cm^{-1}. The hydroxyl absorptions of the adducts are all very broad, extending in a smooth curve from 3600 to 3000 cm^{-1}, being centered at about 3250 cm^{-1}. In no case is a sharp absorption evident near 3600 cm^{-1} indicating again that the amount of free OH or OH hydrogen bonded to the halomethyl group of the diol is indeed very small. Therefore, any proposed conformation of the solid adducts must involve mainly hydrogen bonding to the oxygen functionalities of the organic base.

Further evidence for the conformation of the component molecules of the adducts comes from the Raman spectrum of the hexachloroacetone hydrate-dioxane complex. Comparing the Raman spectra of liquid dioxane, whose bands have been assigned[12] and is known to exist in a chair conformation, with those of the hexachloroacetone hydrate-dioxane it can be seen that the bands shifted in the adduct are those due to skeletal modes of the dioxane ring occur at 1109 and 834 cm^{-1} (Table II). Since the remaining bands of dioxane are unchanged it can be inferred that the dioxane ring has maintained its chair conformation. Strength can be added to this argument by consideration of the x-ray crystal structure[19] and Raman[13] spectra of the crystalline adduct formed between mercuric chloride and dioxane. The x-ray crystal structure for the HgCl$_2$-dioxane adduct shows that the dioxane ring is indeed in the chair conformation. A comparison of the Raman spectra of this adduct with that of hexachloroacetone hydrate-dioxane reveals that for both adducts the bands of the skeletal modes of dioxane at 1109 and 834 cm^{-1} are shifted to lower frequency by roughly the same amount (Table II). From these data it seems that the dioxane ring in the solid hexachloroacetone hydrate-dioxane adduct must also be in the chair conformation, and this being so, the two hydroxyl protons of the *gem*-diol must be involved in hydrogen bonding to two different dioxane molecules. Because of the 1:1 stoichiometry of the dioxane: hydrate in the adduct, hydrogen bonding of the diol to two dioxane molecules produces extended chains of alternating dioxane-*gem*-diol molecules.

A recent ab initio molecular orbital calculation[20] on the *gem*-diol of formaldehyde has been reported. By studying the

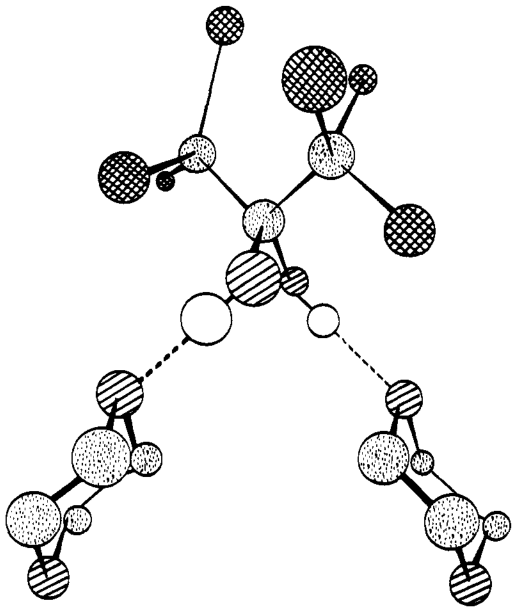


Figure 6. Computer generated perspective drawing of hexachloroacetone hydrate dioxane adduct using structural parameters determined for chloral hydrate[21] and dioxane:[28] carbon ◌, oxygen ⊘, chlorine ●, and hydrogen ○.

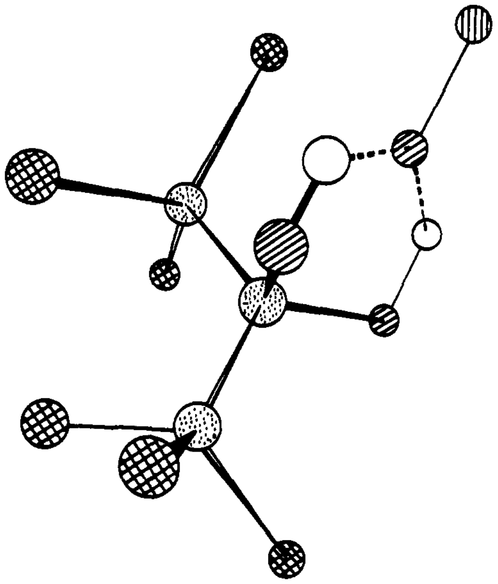
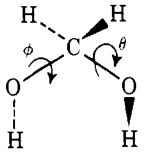


Figure 7. Computer generated perspective drawing of hexachloroacetone hydrate in a hydrogen bonded structure chelated to the oxygen of an acceptor molecule, using structural parameters determined for chloral hydrate:[21] carbon ◌, oxygen ⊘, chlorine ●, hydrogen ○, and general atom ⦶.

energy as a function of the two torsional angles ϕ and θ the only type of rotamer to be expected is one in which ϕ and θ are about 60°. Note, however, that this conformation has the two hydroxyl protons of the *gem*-diol on opposite sides of the O–C–O plane.



The H–O–C–O–H bonds in chloral hydrate[21] have been found to have the arrangement predicted from the methanediol model, and if this arrangement persists in the hexachloroacetone hydrate case the structure shown for the dioxane adduct in Figure 6 may be predicted.

For adducts involving carbonyl, sulfoxide, or phosphoramide moieties, hydrogen bonding with the *gem*-diol may be envisioned to occur either through a chelated structure (Figure 7) or through the extended chain structure proposed for dioxane. That both of these structural models involve two hydrogen bonds to the acceptors is not unreasonable. 1,8-Dihydroxyanthraquinone exists with one of the carbonyl oxygens acting as a receptor for two hydrogen bonds.[22] Also, an ab initio LCAO-MO-SCF calculation has predicted a hydrogen bond energy for the trimer $H_2CO\cdots 2H_2O$ to be 5.88 kcal/mol whereas a hydrogen bond energy of 3.39 kcal/mol has been predicted for $H_2CO\cdots H_2O$.[23] These results indicate that a second hydrogen bond to formaldehyde gives a stabilizing energy that is 73% of the first one. The principle energy difference between the two proposed structural types comes from the rotamer of the diol involved. The energy difference between the rotamer present in the extended chain structure and the rotamer necessary for the chelated structure is calculated to be about 5 kcal/mol.[20] The heats of hydrogen bond formation to *p*-fluorophenol in the pure acceptor have been determined for all of the base partners listed in Table I.[18] As expected, the heat of hydrogen bond formation for DMSO (7.21 ± 0.08 kcal/mol) and HMPA (8.72 ± 0.11 kcal/mol) was found to be substantially higher than that for cyclohexanone (5.66 ± 0.07 kcal/mol) and cyclopentanone (5.50 ± 0.09 kcal/mol) indicating a stronger hydrogen bonding interaction for these compounds. Although two hydrogen bonds are formed to the carbonyl groups of the ketones which amounts to a heat of formation of not more than about 9 kcal/mol, the extended chain structure remains entirely possible due to the rather large energy difference of the diol rotamers.

The two hydrogen bonds present in the adducts of DMSO and HMPA enhance the possibility of a chelated structure since their heats of formation could permit higher energy rotamers of the diol to exist. Adducts of HMPA may require the chelated structure due to the bulkiness of the dimethylamine substituents. In an extended chain structure the three dimethylamine groups on the phosphorus atom would interact sterically with those of neighboring HMPA molecules; this interaction would make the extended chain structure less favorable.

The heats of hydrogen bond formation of *p*-fluorophenol to *N*,*N*-dimethylformamide (6.97 ± 0.11 kcal/mol) and to *N*,*N*-dimethylacetamide (7.44 ± 0.13 kcal/mol) indicate the formation of stronger hydrogen bonds than those to the ketones; however, because of the lack of any bulky substituents on the bases both the extended chain and chelated structures are entirely possible.

An x-ray crystal structure would settle the question of extended chain vs. chelates unambiguously. We have attempted several times to grow crystals of these adducts for this purpose, but every attempt to date has failed because of striations contained in the crystals. The possibility that these striations are a macroscopic reflection of the extended chain structure has neither been proven nor disproven to date.

The anomalous carbonyl frequency shift in the pentachloroacetone hydrate–cyclohexanone adduct can be explained by comparing the two effects that determine the strength of the hydrogen bonds. The formation of any hydrogen bond is determined by the electron-donating ability of the base and, in the case of the adducts, the availability of the *gem*-diol. The equilibrium between *gem*-diol and halogenated acetone greatly favors the acetone, as evidenced by the lack of reactivity of these compounds toward water. However, this equilibrium can be shifted toward the *gem*-diol by trapping it with a base. The efficiency of this trapping depends upon the availability of electron density to the *gem*-diol. Of all the bases studied cyclohexanone forms the weakest hydrogen bonds, so if a base were going to fail as a donor in adduct formation it would be one of the ketones. Likewise, comparing the dichloromethyl group with trichloromethyl and fluorodichloromethyl, it is the weakest electron-withdrawing group, while the steric interaction between trichloromethyl and dichloromethyl substituents on a tetrahedral carbon is still quite large. These factors combine to favor the haloacetone side of the equilibrium between haloacetone and *gem*-diol. Therefore, in the pentachloroacetone hydrate–cyclohexanone case we are attempting to form an adduct from the worst donor and the worst acceptor, the result of this attempt being practically no reaction.

As can be seen in Table I the $\Delta\nu$ found for the pentachloroacetone hydrate adduct with cyclohexanone is anomalously small. However, the carbonyl absorption of cyclohexanone occurs at 1712 cm^{-1} in dry HCA whereas this absorption occurs at 1705 cm^{-1} in dry PCA. This 7-cm^{-1} solvent effect on the carbonyl absorption must be considered in evaluating the effect of hydrate hydrogen bonding. Thus, the actual carbonyl frequency observed in the pentachloroacetone hydrate cyclohexanone adduct is quite consistent with those observed for adducts with 1,3-DFTCA and chloral which do not notably effect the carbonyl frequency of cyclohexanone when dry.

Since hexachloroacetone tetrahydrate is observed to slowly revert to water and hexachloroacetone, the observed K_d must be in excess of 1 which is more than six orders of magnitude higher than that predicted by the Taft equation (eq 2). This difference in equilibrium constant of 10^6 can simply be accounted for by a free-energy difference of ~8 kcal/mol, which in turn can easily be explained by the formation of two fairly strong hydrogen bonds. Thus, the adducts formed can be viewed as stable due to formation of hydrogen bonds in either the extended or chelated form. Measurements of K_d which have been made in dioxane/water solutions should, therefore, be viewed as composites of two equilibria, one involving hydration of the carbonyl and one involving hydrogen bonding to solvent. Such hydrogen bonding must be taken into account when one examines the stability of any *gem*-diol structure, but would be most significant in those cases possessing strongly electron-withdrawing groups. In the crystal, chloral hydrate, for example, hydrogen bonds to two neighbors in a helical chain.[21]

Experimental Section

Instrumentation. Melting points (uncorrected) were determined on a Büchi melting point apparatus. The near-infrared spectra were obtained with a Cary Model 14 spectrophotometer equipped with a special 0 to 0.2 mV slidewire. The infrared spectra were recorded using a Perkin-Elmer 621 model spectrophotometer and cells with either silver chloride or sodium chloride windows. The Raman spectra were recorded either on a Beckman Model 700 spectrophotometer using a Spectra Physics Model 164 laser or on a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Model 53 argon-ion laser using 5145-Å excitation. Spectra of hexachloroacetone hydrate:dioxane and 1,3-difluorotetrachloroacetone hydrate:HMPA were obtained on the Cary 82 at ambient temperature while the Raman of HCA tetrahydrate was obtained at −80 °C using a low-temperature cell described by Miller and Harney.[24] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Materials. Hexachloroacetone (Aldrich) and 1,3-difluoroacetone (Columbia Organics) were dried by distilling from phosphorus pentoxide at reduced pressure. Dimethyl sulfoxide (Matheson Coleman and Bell, spectrograde) was dried by heating at 90 °C over sodium hydroxide and then distilled at reduced pressure.[27] Pentachloroacetone (Aldrich), cyclohexanone (Aldrich), cyclopentanone (Columbia Organics), hexamethylphosphoramide (Aldrich), and *N,N*-dimethylacetamide (Eastman) were dried over calcium hydride and distilled at reduced pressure. Dioxane (Baker) was dried over sodium and distilled. Chloral was prepared by refluxing chloral hydrate over phosphorus pentoxide and then distilling. All of the above compounds were stored under dry nitrogen after distillation. *N,N*-Dimethylformamide (Matheson Coleman and Bell) was used directly.

Preparation of Adducts. All adducts of pentachloroacetone, hexachloroacetone, 1,3-difluorotetrachloroacetone, and chloral with cyclohexanone, DMSO, DMA, HMPA, DMF, cyclopentanone, and dioxane except hexachloroacetone hydrate–HMPA were prepared by adding a molar amount of water to a 1:1 molar solution of the halogenated ketone and organic base. Hexachloroacetone hydrate adducts with DMSO, cyclohexanone, and dioxane are stable at room temperature. A sample preparation follows.

Adduct of 1,1,1,3,3,3-Hexachloropropanediol with Cyclohexanone (Hexachloroacetone Hydrate–Cyclohexanone). Into a 400-ml beaker containing a magnetic stirring bar was placed 76 ml (0.50 mol) of HCA. The HCA was stirred at room temperature while 50 ml (0.508 mol) of cyclohexanone was added from a 50-ml pipet. While stirring this mixture rapidly, 9 ml of distilled water was added. The temperature of the reaction mixture rose to about 48 °C in 4 min. After reaching this maximum temperature the solution began to cool, the stirring was stopped, and white crystals of the adduct began to form about 15 min after the addition of the water. After the solid had cooled to room temperature it was recrystallized from heptane: mp 49.5/50.5 °C. Anal. Calcd for $C_9H_{12}Cl_6O_3$: C, 28.38; H, 3.18; Cl, 55.84. Found: C, 28.30, H, 3.24; Cl, 55.96. Raman spectrum of solid exhibited no absorption due to carbonyl of HCA; carbonyl of ketone occurred at 1671 cm^{-1}.

Pentachloroacetone hydrate–cyclohexanone: ir (neat) 1699 cm^{-1} ($C=O$ of cyclohexanone).

Chloral hydrate–cyclohexanone: ir (neat) 3260 (OH), 1697 cm^{-1} ($C=O$ of ketone).

1,3-Difluorotetrachloroacetone hydrate–cyclohexanone: ir (neat) 3240 (OH), 1697 cm^{-1} ($C=O$ of cyclohexanone).

Hexachloroacetone hydrate–DMSO: ir (neat-viscous oil) 1015 cm^{-1} ($S=O$); Raman (solid) 1010 cm^{-1} ($S=O$); mp 57/60 °C. Anal. Calcd for $C_5H_8Cl_6O_3S$: C, 16.62; H, 2.22; Cl, 59.00; S, 8.86. Found: C, 16.85; H, 2.14; Cl, 58.80; S, 8.71.

Pentachloroacetone hydrate–DMSO: Raman (solid) 1000 cm^{-1} ($S=O$); mp 62/64 °C. Anal. Calcd for $C_5H_9Cl_5O_3S$: C, 18.38; H, 2.92; Cl, 54.36; S, 9.80. Found: C, 18.49; H, 2.76; Cl, 53.46; S, 9.14.

Chloral hydrate–DMSO: ir (neat) 3210 (OH), 1015 cm^{-1} ($S=O$); mp 22.5/23.5 °C.

1,3-Difluorotetrachloroacetone hydrate–DMSO: ir (neat) 1015 cm^{-1} ($S=O$).

Hexachloroacetone hydrate–DMA: ir (neat) 3120 (OH), 1620 cm^{-1} ($C=O$ of amide).

Pentachloroacetone hydrate–DMA: ir (neat) 1621 cm^{-1} ($C=O$ of amide).

Chloral hydrate–DMA: ir (neat) 1622 cm^{-1} ($C=O$ of amide).

Hexachloroacetone hydrate–DMF: ir (neat) 3140 (OH), 1660 cm^{-1} ($C=O$ of amide); mp 31.5/34 °C.

Hexachloroacetone hydrate–cyclopentanone: ir (neat) 3240 (OH), 1725 cm^{-1} ($C=O$ of cyclopentanone).

Hexachloroacetone hydrate–HMPA. This adduct is more difficult to form than the others and requires the addition of a molar quantity of HCA to an equimolar solution of water in hexamethylphosphoramide; mp 50/60 °C. The sample remained stable for only 3 days after recrystallization from heptane. Ir (neat) 1144 cm^{-1} ($P=O$).

Pentachloroacetone hydrate–HMPA: ir (neat) 1147 cm^{-1} ($P=O$); mp 47/55 °C.

Hexachloroacetone hydrate–dioxane: Raman (solid): 1090 cm^{-1} (ring stretching mode of dioxane); mp 63/65 °C. Anal. Calcd for $C_7H_{10}Cl_6O_4$: C, 22.67; H, 2.72; Cl, 57.36. Found: C, 22.37; H, 2.63; Cl, 56.13.

Hexachloroacetone Tetrahydrate. An emulsion of 44 ml of HCA (0.29 mol) and 5 ml of H_2O (0.28 mol) was made by shaking the mixture. The emulsion was allowed to react overnight at 4 °C and was then suction filtered and washed with iced heptane to yield 22.5 g of white crystals (60% of yield of tetrahydrate); mp 39.5–40.5 °C (incongruent). On standing the crystal reverts to HCA (ir 1775 cm^{-1}) and H_2O after several days at room temperature. A quantitative yield of the tetrahydrate was also realized by repeated shaking of a mixture of 4.4 ml of HCA (0.029 mol) and 2.0 ml of H_2O (0.11 mol) at −18 °C for several days. The water content of acetonitrile solutions of the adduct was determined by GLC on an F & M Model 500 (thermal conductivity) equipped with a 6 in. × ⅛ in. stainless steel column packed with Porapak Q. Quantitation was performed by means of a Vidar 6300 digital integrator and standard calibration curves. Raman spectrum of solid at −80 °C: 3557 vw, 3469 vw, 1169 m, 1009 w, 891 vw, 848 vw, 802 w, 650 vw, 615 m, 472 w, 422 s, 382 m, 337 w, 285 m, 269 m.

Preparation of *erythro*- and *threo*-2-(2′,2′,2′-Trichloro-1′-hydroxyethyl)cyclohexanone.[25,14] To a solution of 33.69 g (0.202 mol) of 1-morpholino-1-cyclohexene[26] in 100 ml of dry chloroform contained in a 300-ml round-bottomed flask equipped with a stirring bar, addition funnel, and nitrogen inlet tube was added a solution of 31.45 g (0.213 mol) of chloral in 50 ml of dry chloroform over a 1-h interval. After the addition the solution was permitted to stir in a dry nitrogen atmosphere at room temperature for 2 h. At the end of the stirring period 75 ml of an acetic acid-sodium acetate buffer was added; the resulting mixture was refluxed for 2 h.

At the end of the reflux period the aqueous layer was separated from the organic layer and washed with 25 ml of $HCCl_3$ and the organic layers were combined, washed with 75 ml of saturated sodium bicarbonate, 75 ml of saturated sodium chloride, and 75 ml of water and dried over anhydrous $MgSO_4$. After filtration and removal of the chloroform by rotary evaporation, 31.2 g of an oil was obtained that appeared to be about a 50:50 mixture of both isomers by ^1H NMR. The erythro and threo isomers were obtained in pure form by chromatography on silicic acid (Mallinckrodt, Silicic Acid A. R. 100 mesh, Chromatography Grade) using 20% (by volume) petroleum ether in benzene as eluent. The melting points, ir, and ^1H NMR spectra of the two isomers agreed with those of Kiehlman and Loo.[14]

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Borine Carbonyl. Bonding and Properties in the Single-Determinant Approximation

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Abstract: Using the Hartree–Fock–Roothaan approximation, we investigate the $^1A_1$ ground electronic state of borine carbonyl with two Slater and two contracted Gaussian basis sets. The total energies range from −138.6832 au for a minimal (2s1p/1s) Slater basis to −139.1723 au for a near-Hartree-Fock (9s5p1d/2s1p)/[5s3p1d/2s1p] Gaussian basis. The Hartree–Fock limit energy, which is estimated to be −139.210 ± 0.004 au, is employed to extract the molecular extra correlation energy of −0.21 ± 0.01 au. Reaction energies relative to the decomposition of BH_3CO are also examined in terms of Hartree-Fock and correlation contributions. A variety of one-electron properties are computed and compared with available measurements. Hybridization of the orbitals at boron and other local features of the bonding are discerned from electron density maps.

I. Introduction

Borine carbonyl is an example of what Mulliken[2] has termed a "two-way donor–acceptor complex", namely a loose confederation in which the BH_3 and CO fragments function more or less as both electron donors and acceptors. Although the preparation,[3a] chemical properties,[3a] and molecular structure[3b-7] of this complex were first reported in 1937, only three ab initio theoretical studies[8-10] have appeared on its ground $^1A_1$ electronic state and these were carried out without polarization functions in the basis set. Apart from these studies, the charge distribution has been interpreted semiquantitatively in terms of resonances between valence-bond structures[2,3b,5] and with semiempirical molecular orbital (MO) theory.[11,12] It therefore appears