bital calculations with no or minor modifications. The results of the simulations have been thoroughly analyzed to obtain intimate descriptions of the liquids' structures. Ammonia, hydrogen fluoride, and methanol are all found to contain winding hydrogen-bonded chains with an average of two hydrogen bonds for each monomer. For ammonia, this is a significant departure from the structure of the solid. Liquid water has a more complex network with many interconnecting rings and an average of 3.5 hydrogen bonds per monomer. The combined quantum and statistical mechanics approach to modeling fluids is a powerful tool that will be most useful in studying solvent effects in organic chemistry and biochemistry.

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Structures and Isotopic Fractionation Factors of Complexes, $A_1HA_2^-$ [1]

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Abstract: The isotopic fractionation factors of homo- and heteroconjugate complexes[2] are shown to reach a minimum just below 0.3 for substances in which the linear motion of the bridging hydrogen is governed by a double minimum potential function, with the lowest allowed vibrational level in the neighborhood of the central maximum. Both biphenolates and bicarboxylates generate such fractionation factors. The electronic spectra of the nitro-substituted biphenolates require that these substances be mixtures of degenerate tautomers, and, therefore, that their lowest allowed vibrational levels should fall somewhat below the central maxima in their potential functions. Crystallographic and other evidence indicates that the bridging proton in the bicarboxylates oscillates about the O···O center, so their lowest allowed vibrational levels appear to fall above the central maximum, but the fractionation factors appear to exclude single minimum potential functions. Many properties of these substances are fairly well modeled with simple, quartic-quadratic potential functions. A heteroconjugate complex is predicted and observed to have a somewhat higher fractionation factor; however, the fractionation factor should not be too elevated if the complex is not too unsymmetric. The fractionation factors of strongly unsymmetrical heteroconjugates should approach those of the uncomplexed acids (about unity). The potentials of heteroconjugates can be modeled with quartic-cubic-quadratic functions.

The structure of bicarboxylate ions and related substances, $A_1A_2H^-$,[2] has been the subject of a large number of investigations.[3-6] These investigations have attempted to distinguish compounds in which the hydrogen oscillates about a central position from those which are mixtures of degenerate or near-degenerate tautomers. In the latter case the lifetime of the individual tautomers is also of interest. In all cases the ultimate objective is to approximate the potential functions governing the motions of the bridging hydrogens. In the present paper we show that a uniquely low isotopic fractionation factor

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(defined by eq 1 and 2)[7]

$$XH + D(L_2O) \rightleftharpoons XD + H(L_2O) \qquad (1)^8$$

$$\phi_{XL} = [(XD)/(XH)](H/D)_{L_2O} \qquad (2)^8$$

is predicted if the linear motion of the bridging hydrogen is governed by a double minimum potential function in which the lowest allowed vibrational level is close to the top of the central maximum. Both biphenolates and bicarboxylates are shown to generate such fractionation factors. The electronic spectra of nitro-substituted biphenolates are shown to require that these substances be mixtures of degenerate tautomers, but a variety of evidence taken from the literature indicates that the bridging hydrogen oscillates about the central position in at least some of the bicarboxylates. Thus, in both groups of homoconjugates, the linear motions of the bridging hydrogens are governed by double minimum potential functions. In the biphenolates (or at least those with nitro substituents) the lowest allowed vibrational level is below the top of the central maximum, while in the bicarboxylates it is above. Heteroconjugates which are not too unsymmetric are shown to be similar.

Experimental Section

Materials. Sulfolane (tetrahydrothiophene 1,1-dioxide) was purchased from Aldrich Chemical Co. and purified by two vacuum distillations from calcium hydride, bp 107-108 °C (0.3 Torr).

Acetonitrile was purchased from Aldrich Chemical Co. with a minimum purity of 99% specified. It was further purified by "procedure I" of Coetzee.[9] Its residual water content was $1.5-4.0 \times 10^{-3}$ M, and it had a specific conductance of $2.0 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$.

Deuterium oxide was purchased from Aldrich Chemical Co. and from Merck and Co., Inc., with a specification of 99.8 atom % D. It was not further purified.

Bis(triphenylphosphine)iminium chloride was purchased from the Alfa Division of Ventron Corp. This material shows a water band in its IR spectrum, and appears to be a hydrate, although it is not labeled as such. Before use it was recrystallized once from water and once from a mixture of acetone and ether, and then dried under vacuum at 184 °C for several days, to remove most of the water. This material had mp 274-275 °C (previously reported 273-274 °C[10]).

p-Nitrophenol, 3,5-dinitrobenzoic acid, pentachlorophenol, benzoic acid, and triphenylmethanol were all purchased from Aldrich Chemical Co., recrystallized from water or mixtures of water with methanol or ethanol, and dried under vacuum at 55 °C. All had sharp melting points consistent with accepted values.

Dr. M. K. Chantooni, Jr., kindly gave us a sample of 3,5-dinitrophenol, which was recrystallized from an ethanol-water mixture before use.[11]

Trifluoroacetic acid and acetic acid were purchased from Aldrich Chemical Co. and further purified by distillation from phosphorus pentoxide in an atmosphere of dry nitrogen. They had the expected boiling points, and neutralization equivalents in agreement with theory.

Trifluoroethanol was purchased from Aldrich Chemical Co., "Gold Label 99+% pure". It was dried over 3A molecular sieves and distilled in an atmosphere of nitrogen before use.

Triphenylmethanol-*O-d* was prepared from 1.3 g (5 mmol) of triphenylmethanol dissolved in 20 mL of dry ether in a separatory funnel. This ether solution was shaken with five successive 2-mL (100 mmol) portions of D_2O. The ether solution was separated and the ether was stripped off under reduced pressure. The residual solid was dried under vacuum at 60 °C. The triphenylmethanol-*O-h* content of the product prepared in this way was determined by the method described below. It ranged from 0.9 to 2.0%.

4-Nitrophenol-*O-d* was prepared by shaking an ether solution of 4-nitrophenol several times with D_2O, separating the ether layer, and then removing the ether under vacuum. The product was recrystallized from an acetonitrile-D_2O mixture.

Tetraethylammonium salts of 4-nitrophenolate, 3,5-dinitrophenolate, 3,5-dinitrobenzoate, and pentachlorophenolate were prepared from tetraethylammonium hydroxide (purchased as a 20% solution in water, from Aldrich Chemical Co.) and the acids by the method of Coetzee and Padmanabhan.[12] Tetramethylammonium trifluoroacetate was prepared in the same way, except that a 20% solution of tetramethylammonium hydroxide in methanol (purchased from the Aldrich Chemical Co.) was used in place of the aqueous tetraethylammonium hydroxide. All the salts except the trifluoroacetate were recrystallized from ethyl acetate-ether mixtures. The trifluoroacetate was recrystallized from 1-butanol. These compounds all had appropriate electronic and/or IR spectra, and, in particular, showed little or no absorbtion in the OH region, 3000-3500 cm^{-1}, when they were dry. All, however, were hygroscopic to one extent or another, particularly tetraethylammonium 4-nitrophenolate, and all were handled in a drybox.

Bis(triphenylphosphine)iminium 4-nitrophenolate was prepared from the chloride, by metathesis, in quantitative yield, using the method of Martinsen and Songstad.[10] It was recrystallized twice from water and once from an acetone-ether mixture. It is not hygroscopic in the solid state, mp 180-181 °C.

Anal. Calcd for $C_{42}H_{34}O_3N_2P_2$: C, 74.55; H, 5.06; N, 4.14; P, 9.15. Found: C, 74.44; H, 4.96; N, 4.44; P, 9.29.

Tetraethylammonium hydrogen bis(4-nitrophenolate) was prepared from equimolar quantities of 4-nitrophenol and tetraethylammonium 4-nitrophenolate, dissolved in hot, anhydrous (distilled from CaH_2) *tert*-butyl alcohol. The bis(4-nitrophenolate) separated as yellow needles when the solution was allowed to cool slowly. It had an appropriate IR spectrum (Figure 2). It was not appreciably hygroscopic in the solid state and showed no water band around 3500 cm^{-1} in its IR spectrum.

Anal. Calcd for $C_{20}H_{29}O_6N_3$: C, 58.93; H, 7.18; N, 10.32. Found: C, 59.15; H, 7.21; N, 10.34.

Tetraethylammonium hydrogen bis(3,5-dinitrobenzoate) was prepared in the same way as the bis(4-nitrophenolate). It had major peaks in its IR spectrum (KBr disk) at 3100, 1740, 1630, 1540, and 1350 cm^{-1}, and Evans "window bands" [13] at 700 and 810 cm^{-1}, as well as the expected broad "continuum" [4,5] underlying the fingerprint region, with a maximum intensity around 800 cm^{-1}. It had no water band around 3500 cm^{-1} and was not appreciably hygroscopic in the solid state.

Anal. Calcd for $C_{22}H_{27}O_{12}N_5$: C, 47.72; H, 4.92; N, 12.66. Found: C, 47.65; H, 5.00; N, 12.66.

This compound was also prepared by adding a 0.5-equiv quantity of aqueous 20% tetraethylammonium hydroxide to a near-saturated solution of 3,5-dinitrobenzoic acid in methanol. A heavy, white precipitate formed. After recrystallization from anhydrous *tert*-butyl alcohol it was identical with the material prepared from the acid and the salt, as judged by its IR spectrum.

Tetraethylammonium hydrogen bis(pentachlorophenolate) was prepared by dissolving equimolar quantities of the phenol and its tetraethylammonium salt in acetonitrile, then removing the solvent under vacuum. The residual white solid was used without further purification. This material was somewhat hygroscopic and showed a weak band around 3500 cm^{-1} in its IR spectrum (KBr disk). Otherwise the spectrum had the expected "continuum" [4,5] with a maximum around 750 cm^{-1} and strong bands at 2980, 1490, 1440, 1360, 1215, 1170, and 1130 cm^{-1}, as well as prominent "window bands" [13] at 1585 and 460 cm^{-1}.

Anal. Calcd for $C_{20}H_{21}ONCl_{10}$: C, 36.27; H, 3.20; N, 2.12; Cl, 53.58. Found: C, 36.06; H, 3.27; N, 2.07; Cl, 53.59.

The small amount of water detected in the IR spectrum may be responsible for the small discrepancy between the calculated and observed carbon content, but this is within the anticipated uncertainty in the determination. Solutions of this compound discolored badly on standing for several days, so freshly prepared material was always used in these experiments.

Tetramethylammonium hydrogen bis(trifluoroacetate) was prepared by dissolving 1.87 g (0.01 mol) of tetramethylammonium trifluoroacetate and 0.93 mL (0.012 mol) of trifluoroacetic acid in 20 mL of purified acetonitrile. (The salt is not completely soluble until the acid is added.) The acetonitrile and the excess trifluoroacetic acid were removed under vacuum, and the residual white solid was used without further purification. Neutralization equivalent: calcd for $C_8H_{13}O_4NF_6$, 301; found, 302 ± 1. The hydrogenic "continuum" [4,5] in the IR had a maximum around 850 cm^{-1}. Other prominent bands occur at 3040, 1790, 1500, 1190, 1150, 955, 795, 705, 425, and 385 cm^{-1}. Prominent window bands[13] occur at 1475, 820, and 715 cm^{-1}.

Anal. Calcd for $C_8H_{13}O_4NF_6$: C, 31.88; H, 4.35; N, 4.65; F, 37.86. Found: C, 31.91; H, 4.32; N, 4.55; F, 37.69.

Bis(triphenylphosphine)iminium hydrogen bis(4-nitrophenolate) was prepared in the same way as tetraethylammonium hydrogen bis(4-nitrophenolate) except that the bis(triphenylphosphine)iminium salt was used as a starting material in place of the tetraethylammonium salt. The IR spectrum was very similar to that of the tetraethylammonium salt except that the bands identifiable with the tetraethylammonium ion[14] were replaced by those of the bis(triphenylphosphine)iminium ion.[10]

Anal. Calcd for $C_{48}H_{38}O_6N_3P_2$: C, 70.67; H, 4.82; N, 5.15; P, 7.59. Found: C, 70.60; H, 4.79; N, 4.85; P, 7.74.

Tetraethylammonium hydrogen bis(4-nitrophenolate)-*O-d* was prepared in the same way as the undeuterated compounds, but using 4-nitrophenol-*O-d*. It was recrystallized from *tert*-butyl alcohol-*O-d* (Aldrich Chemical Co., 98% deuterated). The hydrogen and deuterium compounds had identical IR spectra.

Methods. Equilibrium constants for isotopic redistribution with triphenylmethanol in acetonitrile were generally determined by weighing out a salt of the target substance and triphenylmethanol-*O-d* and making them up to a known volume in a volumetric flask. (In one set of measurements the deuterated bisphenolate and undeuterated triphenylmethanol were used, and produced about the same results.) The concentration of undeuterated triphenylmethanol was then determined from the absorbance of the solution at the maximum of the O-H stretching band, λ_{max}, 2857 nm. After appropriate (small) corrections for adventitious water,[15] residual undeuterated triphenylmethanol, and dissociated homo- or heteroconjugate anion, each of the four relevant equilibrium concentrations could be calculated by difference. These measurements were made in cells of 1.0-mm path length, so that the initial concentration of the target substance could be in the range 0.1-0.2 M, to minimize the dissociation of the homo- and heteroconjugate anions. The initial triphenylmethanol-*O-d* concentration was 0.05-0.3 M. The shape of the triphenylmethanol O-H stretching band, its λ_{max}, and its Beer's law coefficient ϵ_{max}, were shown to be invariant with concentration in acetonitrile as a solvent, up to saturation (~0.3 M).[16]

The most important source of uncertainty in these measurements was in the placement of the base line for the 2857-nm band. In general the bisphenolates have a weak absorbtion in this region (the tail end of the "continuum" absorption), contributing, perhaps, 0.05 absorbance units at 2857 nm in a typical case. (The absorbances being measured were between 0.2 and 0.9 absorbance units in typical cases.) Corrections were made by assuming that the base line and the triphenylmethanol spectrum would match at 2720 nm (as they did in triphenylmethanol solutions without other solutes) and applying, at 2857 nm, the same correction required to create a match at 2720 nm.[17] Absorbances at λ_{max} are thought to be uncertain by 0.01-0.02, largely because of this problem.

Isotopic redistribution between solid triphenylmethanol and triphenylmethanol in acetonitrile solution was achieved by adding more of the solid, finely divided, partially deuterated alcohol than would dissolve to the solvent, and stirring the resulting mixture at 25 °C for at least 12 h. Absorbance at 2857 nm was then constant. From that absorbance the undeuterated triphenylmethanol concentration was determined. The total concentration of triphenylmethanol-*O-L* was determined by weight after removing the solvent. A sample of the undissolved solid was recovered, dried, and weighed. Then its undeuterated triphenylmethanol content was determined from the intensity of its absorption, in solution in a known volume of acetonitrile, at 2857 nm. Thus all four concentrations required for a determination of the equilibrium constant for isotopic redistribution were available.

Solid triphenylmethanol could not be equilibrated with partially deuterated water because no measurable exchange took place, even after weeks of contact. The process was, therefore, facilitated by adding a minimal quantity of toluene to the mixture. Most of the triphenylmethanol remained solid. The exchange was followed by periodically withdrawing small solid samples, drying and weighing them, and determining their absorbance at 2857 nm. When a constant specific absorbance was reached (in about 45 days), the L_2O was removed and its hydrogen content was determined from its spectrum in the 900-1300-nm range by the method of Kreevoy and Straub.[18] The other two required concentrations were determined by difference.

Electronic spectra of homo- and heteroconjugate salts, and related substances, were obtained in sulfolane solution. A drop of solution was placed between sapphire plates, and the plates were pressed together to make a film ~10 μm thick. The electronic spectrum was determined, and then the intensity of absorption at 2890 cm⁻¹, in the IR, which is due to the C-H stretching bands of the sulfolane, was measured. The actual film thickness was determined by comparing the absorbance of the film with that of sulfolane in a cell of known path length.

Over the range 200-3000 nm (50 000-3333 cm⁻¹) spectra were recorded on a Beckman DK-2 spectrophotometer. This instrument was equipped with a jacketed cell compartment, through which water at 25.0 ± 0.1 °C was passed from a constant-temperature bath. Air temperature was maintained at 25 ± 1 °C by means of thermostatically controlled air-conditioning. These measures maintained a temperature of 25.0 ± 0.2 °C in the spectrophotometer cells in which measurements were being made. IR spectra were recorded on Beckman IR-12 or Perkin-Elmer 283 spectrophotometers, without temperature control. IR-tran 2 and KRS-5 windows were used for liquid samples and solutions; NMR spectra were recorded on a Varian XL-100 spectrophotometer, with the field locked on tetramethylsilane, which was also used as an internal standard for chemical shifts. The probe temperature was 25 ± 1 °C.

Results

Electronic Spectra. The electronic spectra, in the region of the intramolecular charge transfer band, $\pi \rightarrow \pi^*$,[19] of 4-nitrophenol, its anion, their homoconjugate, and several related heteroconjugate complexes, all in sulfolane solution, are shown in Figure 1. Using the thin-film technique the spectra of the complexes were obtained on solutions in which very little uncomplexed 4-nitrophenol or 4-nitrophenolate was expected. The homoconjugate would be expected to have a formation constant $>10^3$, as it does in acetonitrile.[11,20] The spectra of the other complexes were obtained in solutions containing an excess of the UV-inactive constituent. The spectra of complexed and uncomplexed 4-nitrophenol and 4-nitrophenolate are significantly different, and the uncomplexed species are not evident.

The homoconjugate clearly shows two overlapping bands, one of which is similar in position to the chloride complex of 4-nitrophenol, and the other to the 2,2,2-trifluoroethanol complex of 4-nitrophenolate. Since benzoic acid is stronger than 4-nitrophenol,[24,25] the heteroconjugate shows a more intense phenol band and a less intense phenolate band than the homoconjugate. In neither case, however, are the bands appreciably shifted. These observations indicate that the complexes are mixtures of tautomers, degenerate in the case of homoconjugate, in which the proton is covalently bonded to one of the oxygens and hydrogen bonded to the other. Similar, though less extensive, observations were made on derivatives of 3,5-dinitrophenol, with similar results.

Isotopic Fractionation Factors. Values of $\phi_{A_1A_2H^-}$ were given by the products, $K_3K_4K_5$, defined in the equations

$$A_1A_2H^-(soln) + (C_6H_5)_3COD(soln) \overset{K_3}{\rightleftharpoons} A_1A_2D^-(soln) + (C_6H_5)_3COH(soln) \quad (3)$$

$$(C_6H_5)_3COD(s) + (C_6H_5)_3COH(soln) \overset{K_4}{\rightleftharpoons} (C_6H_5)_3COH(s) + (C_6H_5)_3COD(soln) \quad (4)$$

$$(C_6H_5)_3COH(s) + D(L_2O) \overset{K_5}{\rightleftharpoons} (C_6H_5)_3COD(s) + H(L_2O) \quad (5)$$

All of these measurements depend on determinations of the concentration of triphenylmethanol from its absorption at 2857 nm. This absorbance was independently measured on 18 different solutions, containing 0.018-0.16 M triphenylmethanol, giving absorbances between 0.2 and 1.8. Five of these solutions contained equimolar amounts of triphenylmethanol-*O-d* and four contained a twofold excess of triphenylmethanol-*O-d*. The

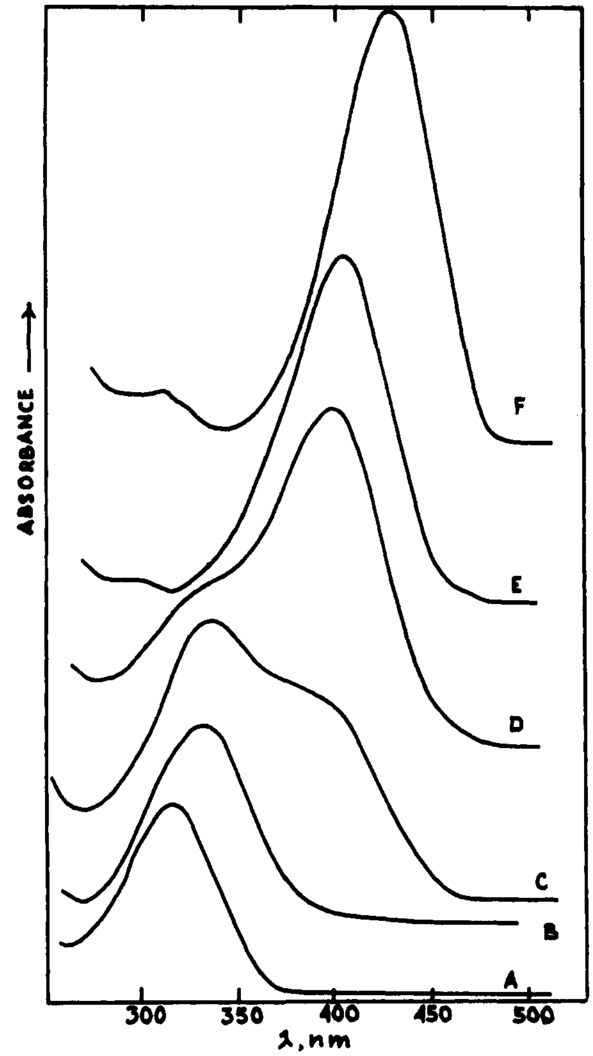

Figure 1. The electronic spectra of 4-nitrophenol, its conjugate base, and a number of their complexes in sulfolane. Curve A is for 0.046 M 4-nitrophenol; path length, 10 μm. Curve B is for 0.046 M 4-nitrophenol in the presence of 0.20 M tetraethylammonium chloride; path length, 9.2 μm. Curve C is for 0.073 M tetraethylammonium 4-nitrophenolate in the presence of 0.073 M benzoic acid; path length, 12 μm. Curve D is for 0.079 M tetraethylammonium bis(4-nitrophenolate); path length, 8.2 μm. Curve E is for 0.042 M tetraethylammonium 4-nitrophenolate in the presence of 0.062 M trifluoroethanol; path length, 9.3 μm. Curve F is for 0.49 M tetraethylammonium 4-nitrophenolate; path length, 12 μm.

Table I. Determination of K_3 for Hydrogen Bis(4-nitrophenolate)

$(A_2H^-)_0$, M	$(C_6H_5)_3COD$, M	A	K_3[f]
0.101[a]	0.103[c]	0.425	0.236
0.100[a]	0.147[c]	0.534	0.278
0.101[a]	0.200[c]	0.617	0.261
0.100[a]	0.304[c]	0.759	0.270
0.207[a]	0.102[d]	0.509	0.201
0.207[a]	0.202[d]	0.812	0.273
0.207[a]	0.312[d]	1.031	0.299
0.104[b]	0.026[e]	0.300	0.284
0.103[b]	0.102[e]	0.439	0.298
0.103[b]	0.166[e]	0.535	0.264
0.108[b]	0.205[e]	0.615	0.287
0.104[b]	0.256[e]	0.673	0.314
0.109[b]	0.304[e]	0.757	0.348

[a] As the tetraethylammonium salt. [b] As the bis(triphenylphosphonium)iminium salt. [c] Containing 5.4% $(C_6H_5)_3COH$; these solutions also contained 2.3×10^{-3} M of H_2O. [d] Containing 1.2% $(C_6H_5)_3COH$; these solutions also contained 2.0×10^{-3} M of H_2O. [e] Containing 0.8% $(C_6H_5)_3COH$; these solutions also contained 3.8×10^{-3} M of H_2O. [f] Appropriate corrections were made for undeuterated triphenylmethanol, adventitious water, and dissociation of the homoconjugate.[1,5] In making the last correction a K_3 value of 1.00 was assumed for the free phenol. These corrections typically lowered the values of K_3 by about 10-15%.

Table II. Isotopic Fractionation Factors in Acetonitrile, at 25 °C, unless Otherwise Specified

ion	K_3[a]	$\phi_{A_1A_2H^-}$[b]
$(4\text{-}NO_2C_6H_4O)_2H^-$ [c]	0.278 ± 0.007	0.31 ± 0.03
$(CF_3CO_2)_2H^-$ [d]	0.378 ± 0.004	0.42 ± 0.05[k]
$[3,5\text{-}(NO_2)_2C_6H_3CO_2]_2H^-$ [e]	0.270 ± 0.004	0.30 ± 0.03
$[3,5\text{-}(NO_2)_2C_6H_3O]_2H^-$ [e]	0.325 ± 0.007	0.36 ± 0.04
$(C_6Cl_5O)_2H^-$ [e]	0.356 ± 0.009	0.40 ± 0.05
$3,5\text{-}(NO_2)_2C_6H_3OH\cdot Cl^-$ [f]	0.427 ± 0.014	0.47 ± 0.06
$[(CH_3)_2SO]_2H^+$ [g]		0.36
$[(CH_3)_2NCHO]_2H^+$ [h]		0.36
$(CH_3)_2NCHOHCl$ [h]		0.37
cis-$C_2H_2(COO)_2H^-$ [i]		0.84
F_2H^- [j]		0.60

[a] The uncertainties cited are the probable errors of the mean values. The general replicability of K_3 is similar to that shown for hydrogen bis(4-nitrophenolate) in Table I. [b] The uncertainties cited are probable errors. They arise mostly from the uncertainty in K_4 and K_5. [c] From Table I. [d] As the tetramethylammonium salt. [e] As the tetraethylammonium salt. [f] As the bis(triphenylphosphonium)iminium salt. [g] In dimethyl sulfoxide solution at room temperature: estimated from information given by J. M. Williams and M. M. Kreevoy, *J. Am. Chem. Soc.*, **89**, 5499 (1967). [h] In dimethylformamide solution: calculated from results given by L. F. Silvester, J. J. Kim, and P. A. Rock, *J. Chem. Phys.*, **56**, 1863 (1972), and G. Sicking, *Ber. Bunsenges. Phys. Chem.*, **76**, 790 (1972). [i] In water. Based on the data of B. M. Lowe and D. G. Smith, *J. Chem. Soc., Faraday Trans. 1*, **70**, 362 (1974); assuming that the fractionation factor of the neutral acid is 1.00. [j] In water. Estimated from information given by A. J. Kresge and Y. Chiang, *J. Phys. Chem.*, **77**, 822 (1973). [k] An earlier value, 0.61, obtained in liquid trifluoroacetic acid as solvent (K-C. Chang, Ph.D. Thesis, University of Minnesota, 1975, p 61) is thought to be higher because of the presence of more complicated species, such as $A_3H_2^-$, etc.

absorbance was a linear function of concentration with a zero intercept, as required by the Beer-Lambert law, without apparent systematic deviation, and with an average deviation from the linear relation of 1%. The extinction coefficient was 110 ± 1. Three measurements each of K_4 and K_5 gave values of 1.00 ± 0.05 and 1.10 ± 0.06, respectively. A value around 1.0 is expected for K_5, which is the isotopic fractionation factor for solid triphenylmethanol, because such values are typical of alcohols[27] and because a value of 1.04 has been reported for tris(4-methoxyphenyl)methanol in aqueous solution.[28] A value near 1.0 is expected for K_4 because the OH stretching frequency in the solid (3480 cm^{-1})[29] is very similar to that in acetonitrile solution. Seven determinations of K_3 were made for tetraethylammonium hydrogen bis(4-nitrophenolate) and six with the bis(triphenylphosphine)iminium salt. The individual concentrations used and the results obtained are shown in Table I. These measurements lead to a mean value of 0.278, with an average deviation from the mean of ±0.025 and a probable error of ±0.007. This gives a value of 0.31 ± 0.03 for $\phi_{A_2H^-}$ with the bulk of the uncertainty due to the uncertainty in K_4 and K_5. The other fractionation factors were measured analogously, though with fewer replications of K_3. The results are summarized in Table II, along with some related values which could be deduced from information in the literature.

The main source of scatter in K_3 is in the location of the base line, which is estimated to be uncertain by 0.01-0.02. Standard methods for the propagation of error[30] indicate that this would lead to uncertainties of 10-20% in the values of K_3, which is consistent with the scatter shown in Table I. In addition to scatter, the average value of K_3 obtained with the tetraethylammonium salt (0.260) is smaller than that obtained with the

Table III. Chemical Shifts of Homo- and Heteroconjugate Ions in Acetonitrile at 25 °C

ion	$\delta_{A_1A_2H^-}$,[a] ppm	δ_{AH},[a] ppm	$\Delta\delta_{A_1A_2H^-}$, ppm
$(4\text{-}NO_2C_6H_4O)_2H^-$ [b]	16.8	8.1	8.7
$(4\text{-}NO_2C_6H_4O)_2H^-$ [c]	16.9	8.1	8.8
$(4\text{-}NO_2C_6H_4O)_2H^-$ [d]	16.9	8.1	8.8
$(CF_3CO_2)_2H^-$ [b]	19.0[f]	11.2	7.8
$[3,5\text{-}(NO_2)_2C_6H_3CO_2]_2H^-$ [c]	17.8	10.1	7.7
$[3,5\text{-}(NO_2)_2C_6H_3O]_2H^-$ [c]	17.1	8.3	8.8
$(C_6Cl_5O)_2H^-$ [c]	13.6	7.8	5.8
$3,5\text{-}(NO_2)_2C_6H_3OH{\cdot}Cl^-$ [d]	12.9	8.1	4.8
F_2H^- [e]	16.3	7.2	9.1
$FH{\cdot}Cl^-$ [e]	10.3	7.2	3.1
$FH{\cdot}Br^-$ [e]	8.8	7.2	1.6

[a] These values have an uncertainty of about 0.1 ppm, as discussed. [b] As the tetramethylammonium salt. [c] As the tetraethylammonium salt. [d] As the bis(triphenylphosphonium)iminium salt. [e] Taken from F. Y. Fujiwara and J. S. Martin, *J. Am. Chem. Soc.*, **96,** 7625 (1974); as the tetrabutylammonium salt, at 34 °C. [f] K-C. Chang, Ph.D. Thesis, University of Minnesota, 1975, p 52, has reported 19.75 in CF_3CO_2H as solvent, and other, somewhat lower, values have been reported for other counterions and/or other solvents.

bis(triphenylphosphine)iminium salt (0.299) and the difference appears to be outside of the experimental uncertainty. With the electrolyte concentrations used it may be expected that the ions will be substantially but not completely dissociated in acetonitrile.[31] This problem, and possible systematic errors, probably makes the K_3 values less reliable than their probable errors would suggest. Their general correctness was tested by obtaining a fractionation factor for benzoic acid in solution in acetonitrile, using the same techniques as those used for the homo- and heteroconjugates. Since the OH absorption band of benzoic acid interferes with the 2857-nm band of triphenylmethanol, a correction for its absorption was made, using an extinction coefficient of 13.4 at 2857 nm. A value of 0.98 ± 0.02 was obtained for K_3, which yields a fractionation factor of 1.08 ± 0.12. This is in good agreement with the value of 1.0 generally attributed to the fractionation factors of monomeric carboxylic acids in solution,[27a] and tends to validate the method. The relative values of K_3 are, of course, more reliable than their absolute values, and K_3 values are more reliable than $\phi_{A_1A_2H^-}$ values. None of these uncertainties jeopardize the conclusion that the lower $\phi_{A_1A_2H^-}$ values in Table II are well below 0.5.

Chemical Shift. In 0.1-0.2 M acetonitrile solutions at 25 °C our homo- and heteroconjugates each show only one, slightly broadened, resonance for OH protons in their NMR spectra. The chemical shift, δ_{obsd}, is the average of the resonance of the bridging proton and those of the small amounts of free phenol and adventitious water. The value for the bridging proton, $\delta_{A_1A_2H^-}$, is given by

$$\delta_{obsd} = (\delta_{A_1A_2H^-}c_{A_1A_2H^-} + \delta_{AH}c_{AH} + 2\delta_{H_2O}c_{H_2O})/(c_{A_1A_2H^-} + c_{AH} + 2c_{H_2O}) \quad (6)$$

where c_i is the concentration of species i. Measurements on dilute solutions of water (0.05-2.0 M) in trideuterioacetonitrile gave a value of 2.30 ppm for δ_{H_2O}. Values for the various δ_{AH} were obtained from measurements on solutions in acetonitrile, in the same concentration range. They are given in Table III. Neither δ_{H_2O} nor the δ_{AH} values were appreciably concentration dependent in these solutions. With δ_{H_2O} and δ_{AH} in hand, c_{H_2O} measured, and c_{HA} calculated from the known homo- or heteroconjugation constant, the $\delta_{A_1A_2H^-}$ values could be calculated from eq 6. They are given in Table III. Some relevant values taken from the literature are also given, for comparison.

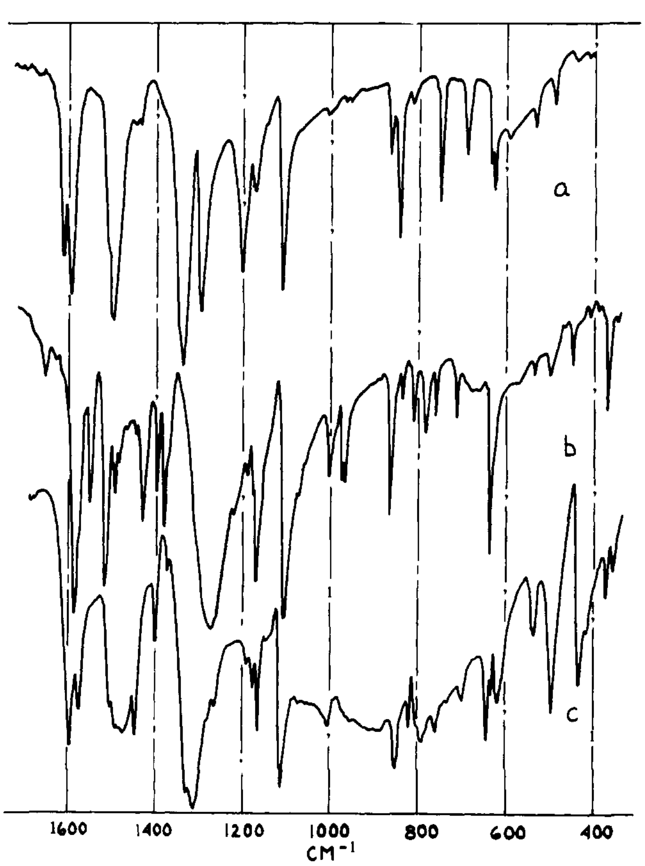

Figure 2. The fingerprint region of the IR spectra of (a) 4-nitrophenol; (b) tetraethylammonium 4-nitrophenolate; (c) tetraethylammonium hydrogen bis(4-nitrophenolate); all solids dispersed in KBr.

Each δ value in Table III is an average of several independent measurements on separately prepared solutions. In the worst case, the average scatter was 0.1 ppm, probably due, mostly, to variability in the amount of adventitious water present. No systematic trends with concentration were noted. In addition to the uncertainties due to scatter, $\Delta\delta_{A_1A_2H^-}$ is also subject to a certain amount of counterion specificity, since, as noted above, these salts are not completely dissociated in acetonitrile in this concentration range. Considering that dissociation is likely to be extensive, counterion effects are not likely to have perturbed the reported values by more than ±0.1 ppm.[32] Values of $\Delta\delta_{A_1A_2H^-}$ are also strongly solvent specific, principally due to the solvent specificity of δ_{HA}, but all the values reported in Table III were determined in acetonitrile. All things considered, an uncertainty of ±0.2 ppm is attributed to the $\Delta\delta_{A_1A_2H^-}$ values.

IR Spectra. Figure 2 shows the fingerprint region of the IR spectrum of 4-nitrophenol, its conjugate base, and its homoconjugate complex. These spectra are all complicated, but, even allowing for the "continuum" absorption and the resulting window bands,[4,5] it is clear that the spectrum of the homoconjugate does not consist of a superposition of the spectra of its progenitors. Nor is the multiplication of bands, predicted by Wood for tautomers separated by a low barrier,[33] apparent. The spectrum is appropriate for a substance with a centralized bridging hydrogen.

Discussion

Most of these diverse and sometimes contradictory appearing results can be semiquantitatively rationalized if the potential function V, governing motion of the bridging hydrogen along the line of the two bridged oxygen atoms, is represented by the power series

$$V = ax^2 + bx^3 + cx^4 \quad (7)$$

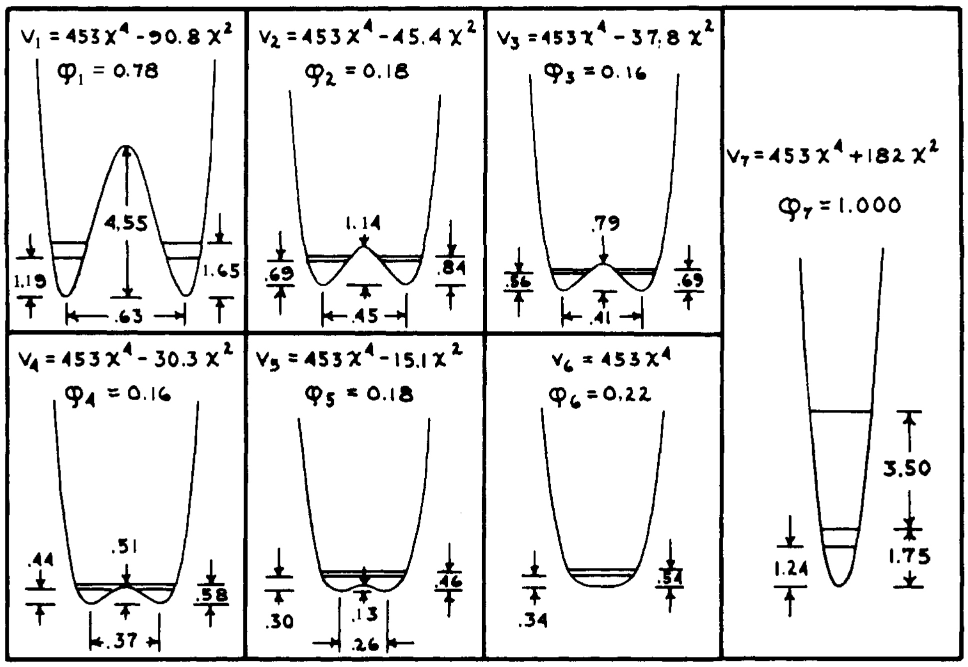

Figure 3. Calculated fractionation factors, ϕ_n, for various one-dimensional quartic-quadratic potential functions V_n, for a protium or deuterium between two identical bases of infinite mass. The lowest allowed energy level for protium is shown to the right of each potential function, and that for deuterium to the left. For V_7 the second allowed level for protium is also shown, and the fundamental frequency. Where a central maximum occurs, its height and its width in ångstroms are shown. The units of the potential functions and all the energy levels and energy-level spacings are 10^3 cm^{-1}. The allowed energy levels were obtained by appropriately scaling dimensionless energy levels given by Laane.[34] Those for V_1 are actually slightly split by tunneling, and the average energy is shown. In the other cases the "tunnel splitting" is at least several hundred cm^{-1} and individual energy levels are shown. The ϕ_n values were obtained from eq 8. V_1 was chosen arbitrarily. V_7 was chosen so as to generate a fundamental vibration frequency of 3500 cm^{-1} and to have curvature at the minimum identical with that at the minima of V_1.

The distance of the hydrogen from the midpoint of the bridge is x for the symmetrical functions. For the unsymmetrical functions x is the distance from the central maximum. For homoconjugates b is zero, and a symmetrical, quartic-quadratic potential function, which has been extensively discussed before,[34,35] results. If a is negative, it is a double-minimum function. A nonzero b introduces the asymmetry required by heteroconjugates. A series of quartic-quadratic potential functions are shown in Figure 3 and a series of three-term functions in Figure 4. In the unsymmetrical functions, the location of the central maximum with respect to the two bases is not defined, but it clearly shifts progressively to the high-energy side as the cubic asymmetry is introduced. Such a model represents the two bases which are bridged by the hydrogen as infinite, stationary, point masses, and also has no bearing on the off-line motions of the hydrogen, so that a considerable oversimplification must result. Nevertheless, the main features of the results are reproduced to a remarkable degree, and the remaining results appear to follow plausibly from effects neglected by the model.

The eigenvalues for protium or deuterium atoms governed by such potential functions can be obtained, by approximation methods, to any desired level of accuracy.[34,36] For the potential functions in question, the lowest eigenvalues for H and D are shown in Figures 3 and 4. They are thought to differ from the exact solutions by less than 1 cm^{-1}. Fractionation factors can be estimated from these energy levels, most simply at the one-dimensional zero-point energy level of approximation, as shown in the equation[37]

$$\phi_n = \exp \frac{hc}{kT}(\mathrm{ZPE}_{\mathrm{H},n} - \mathrm{ZPE}_{\mathrm{D},n} - \mathrm{ZPE}_{\mathrm{H,L_2O}} + \mathrm{ZPE}_{\mathrm{D,L_2O}}) \tag{8}$$

Since water is the reference substance for fractionation factors, one member of the series, V_7, has been made to represent the (nearly harmonic) stretching frequency of water. The required zero-point energies (ZPE), expressed in cm^{-1}, are the lowest eigenvalues of the potential functions.[38] The other symbols have their usual significance, and hc/kT is 4.84×10^{-3} cm at 25 °C. For symmetric functions the calculated ϕ_n pass through a deep minimum when their lowest eigenvalues are in the neighborhood of the central maximum, and rise toward unity again for high barriers. There is no sharp differentiation between functions whose lowest eigenvalues are just above the barrier and those which have lowest eigenvalues just below the barrier. Thus the bicarboxylates can be assigned functions like V_4 or V_5, which would lead to a centralized hydrogen, in accord with the neutron diffraction evidence.[39,40] Further evidence for the centralized proton in the bicarboxylates is provided by the identity of the H, D, and T chemical shifts in their NMR spectra.[41] Biphenolates can be assigned functions like V_2 or V_3, as required by their electronic spectra. Their fractionation factors can be as low as those of the bicarboxylates. Figure 4 shows that the calculated fractionation factors do not rise abruptly as asymmetry is introduced. A function like V_9 can be assigned to the chloride complex of 3,5-dinitrophenol. This potential function predicts the proton to be entirely on the left-hand (phenolate) side of the center, but the fractionation factor is still less than twice its value in the related symmetrical function.

Fractionation factors in aqueous solution appear to be much closer to unity than would be the case for analogous substances in aprotic solvents. It may be that water, by interacting with the acceptor groups, weakens and lengthens the AHA$^-$ hydrogen bonds, and possibly lengthens the A-A distance, raising the fractionation factors.

All of the calculated fractionation factors are lower than those observed in the substances to which the relevant functions are assigned by a factor of about 2. However, this is easily understood as a consequence of the neglected bending modes. The four hydrogenic bending modes in liquid water include one internal bending mode, with a frequency of 1640 cm^{-1}, and three librational modes with frequencies of about 430, 550, and

730 cm^{-1},[42] giving an average bending frequency of ~840 cm^{-1}. The homo- and heteroconjugate complexes each have two hydrogenic modes, with frequencies which might be as high as the bending frequency in F_2H^-, 1220 cm^{-1}.[43,44] Deuteration can be expected to reduce the bending frequencies by a factor of ~1.4. (That for F_2D^- has been observed at 880 cm^{-1}.[43]) If one includes in ZPE_{H,L_2O} twice 840 cm^{-1} for the two bending modes associated with a hydrogen in water, and in $ZPE_{H,n}$, twice 1220 cm^{-1} for the bending modes in the complexes, along with their equivalents for the deuterated species, the calculated ϕ_n rise by a factor of 1.7, which accounts for most of the discrepancy between the observed and the calculated values.

The model accounts for the observation of electronic spectra associated with two different kinds of 4-nitrophenolate moieties in bis(4-nitrophenolate)—one similar to that of the acid and the other similar to that of the conjugate base. The lowest allowed vibrational level, but only that level, lies below the central maximum. Two Franck-Condon excitations are available; an electron from the oxygen covalently bound to hydrogen can be excited or one from the other side can be excited. The two excited state wave functions are different both in location and in energy. In the former case λ_{max} is that of hydrogen-bonded 4-nitrophenol, while in the latter case it is that of hydrogen-bonded 4-nitrophenolate. The two electronic bands are separated by ~2800 cm^{-1}. In order for them to be averaged by exchange, the lifetime of a wave packet on one side of the barrier would have to be less than about 2×10^{-15} s.[45] On the other hand, only one set of bands is seen in the IR spectrum. The vibrational bands which coalesce are separated by no more than a few tens of cm^{-1}, so that coalescence would be observed for lifetimes shorter than about 2×10^{-13} s. The latter is plausibly achievable for hydrogen in potential functions like V_2 or V_3. The former is not.[46]

The identity of values for the H, D, and T chemical shifts in the NMR spectra of bicarboxylates is anticipated by this model because the lowest energy levels in the potential functions assigned to these substances are above the central maxima. Thus the wave functions would be centralized for all three isotopes, and expected O-L distances would be the same in all three. On the other hand, 1,1,1,5,5,5-hexafluoro-2-hydroxy-2-penten-4-one (the enol form of hexafluoroacetylacetone) shows successively smaller values of δ_H, δ_D, and δ_T for the exchangeable hydrogen. To explain this, the hydrogen, which bridges between the two oxygens,[47] would be assigned a potential function in which the lowest allowed level is below the central maximum. Since the level for deuterium is below that for protium, and the level for tritium would be lower still, the wave functions for the three isotopes would be successively displaced away from the central maximum, which would make the O-L distance successively shorter. Since the very large values of δ_L are associated with very long O-L bonds, shortening them would be expected to reduce δ_L. This explanation is identical with that given by the original authors; we have merely given a mathematical form to V. We can now confirm this explanation by noting that ϕ for the enol form of hexafluoroacetylacetone is ~0.5.[48] This permits us to assign L a potential function between V_1 and V_2. The differences between δ_H, δ_D, and δ_T should be even larger for the biphenolates, and their measurement will now be undertaken.

The model can be related to the O-O distance by noting that the distance between each oxygen and its nearer minimum should approximate an O-H bond length, 0.97 Å.[49] Thus the predicted O-O distance is 1.84 Å plus the interminimum separation: ~2.2 Å for bicarboxylates and ~2.4 Å for biphenolates. The actual values for bicarboxylates are ~2.45 Å,[6] which is not an unreasonable disagreement for such a simplified model. If a similar discrepancy is maintained in the biphenolates, an O-O distance of ~2.6 Å might be anticipated.

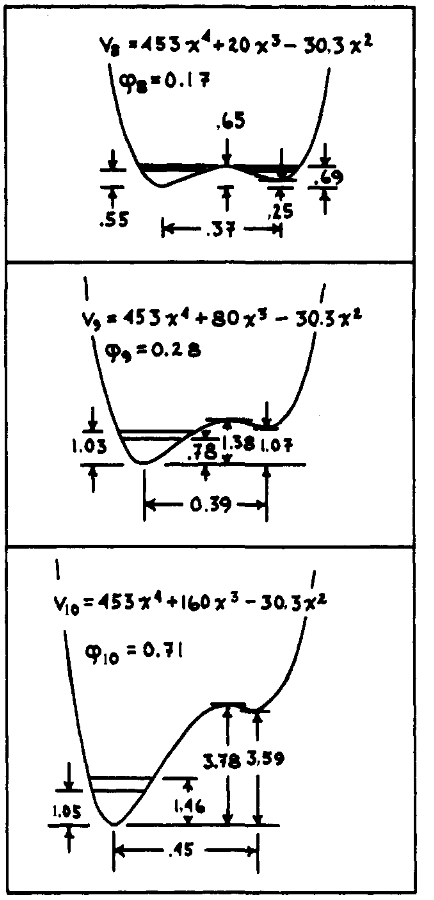

Figure 4. Calculated fractionation factors, ϕ_n, for various quartic-cubic-quadratic potential functions, V_n, for a protium or deuterium between two nonidentical bases of infinite mass. The lowest allowed energy levels for protium and deuterium are shown, along with the energy separation of the two minima, the height of the barrier, and the distance between the two minima. All energies are given in units of 10^3 cm^{-1} and distances in ångstroms. The ϕ_n values were obtained from eq 8, using V_7 as the potential function for the standard substance (mimicking the O-H stretching frequency of water).

Remarkably, considering the large number of bicarboxylate structures which are known, no biphenolate structure has been published.

The root mean square amplitude of oscillation of the hydrogen along the O-O axis is ~0.2 Å in bicarboxylates.[39b,51] This is clearly consistent with the dimensions of V_5.

The model does not anticipate the continuum which constitutes the hydrogenic absorption in the IR spectrum of the bicarboxylates and biphenolates. However, the continuum has been attributed to the polarizability of these structures,[5] which the model does provide for.

It is of some interest to compare the present results with the long-continuing discussion of the structure of purportedly "nonclassical" carbocations. In the context of that discussion the bifluoride ion would be designated nonclassical, the biphenolates and enols of β-dicarbonyl compounds classical, and the bicarboxylates would be hard to classify, since the participants have generally failed to note that a double-minimum potential function could still lead to centralized wave functions, depending on the location of the energy levels with respect to the central maximum. Among the methods which have been used on the homoconjugates only electronic spectroscopy, neutron diffraction, and the comparison of δ_H, δ_D, and δ_T appear to be able to distinguish centralized from noncentralized protons. The NMR technique is unavailable if it is the location and bonding of a carbon atom which is in question; X-ray diffraction could be substituted for neutron diffraction if suitable crystals could be prepared, but this has not yet been achieved; the various forms of electronic spectroscopy seem to have the best prospects. It seems unlikely that the various types of kinetic experiments which have been devised will ever really draw such a fine distinction unambiguously. Examination of Figure 3 also suggests that the choice of names, "classical" and "nonclassical", has given the discussion more impetus than its substance would justify.

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(1) (a) This work was supported by the National Science Foundation through Grants GP-31360X and CHE76-01181 to the University of Minnesota. (b) A preliminary report of this work has appeared as a communication; M. M. Kreevoy, T. M. Liang, and K.-C. Chang, *J. Am. Chem. Soc.*, **99**, 5207 (1977). (c) M. M. Kreevoy was the guest of the Physical Chemistry Laboratory, Oxford, while much of this work was in progress. He wishes to thank Drs. W. J. Albery and R. K. Thomas, of that laboratory, and Dr. J. C. Speakman of the University of Glasgow for stimulating and helpful discussions of this work.

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A Resonance Raman/Iodine Mössbauer Investigation of the Starch–Iodine Structure. Aqueous Solution and Iodine Vapor Preparations

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Abstract: The structure of the blue-black iodine complex of amylose (the linear, helical component of starch), prepared either from iodine and iodide in aqueous solution or from crystalline amylose and iodine vapor, has been studied by resonance Raman and iodine-129 Mössbauer spectroscopy. In both cases it is concluded that the identity of the major chromophore is essentially the same: the pentaiodide (I_5^-) anion. For the material prepared from iodine vapor, the iodide required for I_5^- formation is produced by hydrolysis or alcoholysis of iodine. The other product of this reaction, a hypoiodite, has been assigned in the iodine Mossbauer spectrum.

Historically, scientific interest in the interaction of the various fractions of starch with iodine has stemmed from the striking color changes which accompany complexation.[3] Amylose, the linear starch fraction, which is comprised of

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