Solid-State Study of Hydrazonium Tartrate and Deuterated Hydrazonium Tartrate Enantiomers

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A study of the crystallographic, optical, and thermochemical properties of hydrazonium tartrate and deuterated hydrazonium tartrate enantiomers is described. Crystals of the enantiomers are orthorhombic with a tetramolecular cell. The space group is $P2_12_12_1$ with the lattice parameters $a_0 = 7.640 \pm 0.002$ Å, $b_0 = 13.441 \pm 0.003$ Å, and $c_0 = 7.029 \pm 0.002$ Å. No change in lattice parameters is observed on deuteration. Optical second harmonic powder analysis shows the crystals to be phase matchable at 1.06 μm with $d^{2\omega} = 11 \ d^{2\omega} \ \alpha\text{-SiO}_2$. The optical nonlinearity being unaffected by deuterium substitution is attributed to the nonlinear electronic polarizability of the hydrogen bonds. Crystals are transparent from 239 nm to 1.61 μm. Deuteration shifts the long wavelength cutoff to 2.07 μm, without affecting the band edge.

Introduction

Enantiomers by virtue of their molecular dissymmetry crystallize in noncentrosymmetric structures provided that no racemic crystal is formed. Consequently, they will exhibit a nonzero second-order nonlinear susceptibility and are therefore logical candidates for nonlinear optical device applications.

Tartaric acid, $C_4H_6O_6$, a dicarboxylic dihydroxy acid, has two enantiomeric forms and a meso form as a consequence of its two uncompensated asymmetric carbons. These molecular configurations are usually preserved in tartaric acid salts. In this paper we report on the preparation and characterization of the hydrazonium tartrate enantiomers, $N_2H_4 \cdot C_4H_6O_6$, focusing on their crystallographic, optical, and thermochemical properties. We also investigated the deuterium isotope effect and found effects similar to those reported for L(+)-glutamic acid hydrochloride (*1*). The

optical nonlinearity is therefore similarly ascribed to the nonlinear electronic polarizability of the hydrogen bonds.

Experimental

Materials Preparation

The tartaric acid enantiomers (Merck 99.5%) and hydrazine hydrate (Baker 99+%) were used as received. The actual hydrazine content of the hydrate was ascertained at 63.97 wt% by titration with standard acid (HCl). Distilled deionized water was used throughout the work. All solutions were deoxygenated with argon prior to use and all operations in solution were carried out under an argon atmosphere, to prevent the formation of a yellow-green to orange oxidation product.

Hydrazonium tartrate, $N_2H_4 \cdot C_4H_6O_6$, was synthesized by adding hydrazine hydrate to an aqueous solution of the tartaric acid enantiomer according to stoichiometry (*2*). The reac-

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TABLE I

STOICHIOMETRIC ANALYSIS (wt %)

	C	H	N	O
Calcd for L(+) and D(−)	26.38	5.53	15.38	52.71
Found for L(+)	26.18	5.57	15.61	52.67
Found for D(−)	26.28	5.39	15.58	52.84

tion is highly exothermic and the solution was chilled in an ice bath. The crystals precipitate out almost immediately. The product was then washed with water, at 4°C, dried under argon at room temperature, and recrystallized from water.

Table I shows the analyses for the hydrazonium tartrate enantiomers confirming the stoichiometric formula.

All attempts to synthesize the previously reported (2) dihydrazonium tartrates $(N_2H_4)_2 \cdot C_4H_6O_6$ were unsuccessful.

Deuteration was accomplished by first recrystallizing the tartaric acid enantiomers from 99.97% D_2O. The deuterated tartaric acid was then reacted with hydrazine hydrate in D_2O to form the deuterated hydrazonium tartrate. A subsequent recrystallization was performed to increase the D level.

Single crystals as large as 1 cm³ were grown from H_2O and D_2O solutions via spontaneous nucleation at the stoichiometric pH of 2.8. Both evaporative and temperature-lowering solution growth methods were employed between 20 and 45°C. The D and L forms were observed to possess requisite hemihedrism. Two apparently different growth morphologies were observed. One form crystallized as characteristic orthorhombic sphenoids while the other habit was more of a tetragonal pyramidal modification. X-ray powder diffraction data showed both morphologies to have the same symmetry. Crystals were found to be unusually stable for materials grown from aqueous solution. Natural faces have not clouded after periods of over a year under normal laboratory conditions. All measurements were made on selected clear single crystals. Table II presents the typical cation impurity levels of these crystals, indicating

the tendency of this material to reject heavy metals. This is an important criterion for ultraviolet applications.

Characterization Methods

Solid-state infrared spectra were obtained as Nujol mulls between AgCl plates on a Perkin–Elmer model 283 infrared spectrometer. Single crystal samples ground to ⩾ 36 μm were dried for 4 hr in air at 105°C prior to scanning. Irtran-2 windows were employed for solutions.

Chemical ionization mass spectrometry (CIMS) using D_2O as a chemical ionization reagent was performed as before (1).

The second harmonic generation (SHG) experiments were done with a second harmonic analyzer (3) according to previously described methods (1, 4).

X-ray powder diffraction data were obtained on a Norelco–Philips diffractometer while single crystal data were obtained on an

TABLE II

IMPURITY ANALYSIS OF L(+) HYDRAZONIUM TARTRATE SINGLE CRYSTALS (CONCENTRATION IN ppm)

Element	Undeuterated	$d_8 - 0.97D$	Detection limit
Na[b]	8	8	—
Si[c]	10	8	—
Ca[c]	5	4	—
Fe[a]	n.d.[d]	n.d.	3
Pb[a]	n.d.	n.d.	3

[a] Emission spectrography.
[b] Flame emission.
[c] Atomic absorption.
[d] Not detected.

Enraf-Nonius CAD-4 automated diffracto-meter. Ni-filtered Cu$K\alpha$ radiation was employed for all the X-ray work.

Optical activity in solution was measured with a Rudolph model 51 polarimeter in 100-mm tubes. Measurements are accurate to $0.05°$ arc, and the estimated error in $[\alpha]$ is ± 0.5. The light source was the sodium D line.

Differential thermal analysis (DTA) was described previously (1). In order to maximize the instrument sensitivity samples as large as 35 mg in gold susceptors were employed.

Calorimetric measurements were made with an adiabatic solution calorimeter. Temperature resolution was of the order of $\pm 0.005°C$. Calorimetric values are conservatively estimated to be accurate to $\pm 8\%$.

The optical transmission curves were determined with a Beckman DK-2 UV-VIS Spectrophotometer on 1.47-mm-thick (010) crystals. The crystal plates were polished flat to 5λ and parallel to 40 sec.

Results

Deuterium substitution. The overall deuteration reaction can be written as

$$HOOCCHOHCHOHCOOH \cdot H_2NNH_2 + D_2O$$

$$\rightleftharpoons DOOCCHODCHODCOOD \cdot D_2NND_2 + H_2O.$$
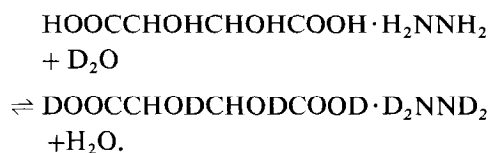
This exchange process was verified by CIMS. Major peaks were observed at m/e equal to 155 and 32 corresponding to eight deuteriums per molecule. Only those hydrogens which are directly bonded to an sp^3 hybridized carbon are not substituted. A deuteration level of $97 \pm 1\%$ was established by infrared absorption spectroscopy on both the D and L crystals. The deuterated hydrazonium tartrate is therefore designated $d_8 - 0.97D$.

X-Ray measurements. Weisenberg photographs of both the undeuterated and $d_8 - 0.97D$ enantiomers revealed no systematic absence among the (hkl), $(0k0)$, $(h0l)$, and $(0kl)$ reflections. On the central lines $(h00)$, $h = 2n$ only; $(0k0)$, $k = 2n$ only; and $(00l)$, $l = 2n$ only, indicating the unique space group $P2_12_12_1$ (D_2^4).

Single crystal data for L(+)- and D(−)-hydrazonium tartrate and the $d_8 - 0.97D$ enantiomers are shown in Table III. One notes that the lattice parameters are virtually identical for both the undeuterated and $d_8 - 0.97D$ salts, and their cell volumes remain constant. The excellent agreement between experimental and calculated densities is indicative of the high deuteration level.

In Table IV the powder data for the undeuterated crystals are given only, since these are identical with those of the $d_8 - 0.97D$ salt. The cell constants and indices calculated for the powder pattern are consistent with those determined from single crystal data.

Nonlinear optical measurements. The results of the second harmonic generation (SHG) experiment are summarized in Table V. The signal level, $d^{2\omega}$, is taken relative to an α-SiO_2

TABLE III

Single Crystal X-Ray Data for L(+)- and D(−)-Hydrazonium Tartrate

	Undeuterated	$d_8 - 0.97D$
Lattice parameters (Å)		
a_0	7.640 ± 0.002	7.638 ± 0.002
b_0	13.441 ± 0.003	13.443 ± 0.003
c_0	7.029 ± 0.002	7.030 ± 0.002
Cell volume (Å³)	721.801	721.821
Point group	222	222
Z	4	4
$\rho_x (g\ cm^{-3})$	1.676	1.749
$\rho_M (g\ cm^{-3})$	1.691 ± 0.005	1.742 ± 0.005

TABLE IV

POWDER DIFFRACTION DATA FOR L(+)- AND D(−)-HYDRAZONIUM TARTRATE

$h\,k\,l$	d_{calcd} (Å)	d_{obsvd} (Å)	Intensity[a]
1 1 0	6.643	6.632	m
{ 0 2 1	4.858	4.848	m
{ 1 1 1	4.828	—	—
1 3 0	3.865	3.867	vs
2 0 0	3.820	3.834	m
0 0 2	3.517	3.520	m–w
1 3 1	3.387	3.389	m
2 0 1	3.357	3.370	s
2 2 0	3.321	3.326	m
1 1 2	3.107	3.110	m–w
{ 1 3 2	2.600	2.600	m
{ 2 0 2	2.588	—	—
2 4 0	2.523	2.522	m
3 1 0	2.502	2.439	s
2 2 2	2.414	2.419	w
2 4 1	2.375	2.374	m–w
0 6 0	2.240	2.243	m
{ 0 2 3	2.213	2.217	m
{ 1 1 3	2.210	—	—
3 3 1	2.112	2.113	—
2 4 2	2.050	2.053	vw
3 5 0	1.849	1.848	m–w
1 7 1	1.800	1.801	m–w
2 6 2	1.693	1.695	vw
4 4 0	1.661	1.661	vw
3 3 3	1.609	1.613	w
2 1 0 0	1.268	1.269	vw

[a] s = strong, m = medium, w = weak.

standard under optimum conditions. The samples were nearly index matched, however birefringence effects were neglected. The

TABLE V

OPTICAL SECOND HARMONIC POWDER ANALYSIS DATA AT 25°C

	Particle size (μm)	$\bar{n}$ (5300 Å)	$d^{2\omega}\alpha$–SiO$_2$ Level
L(+)	212–300	1.560	11.5
D(−)	212–300	1.560	11.3
L(+)-d_8-0.97D	212–300	1.560	11.1
D(−)-d_8-0.97D	212–300	1.560	11.8

birefringence in these crystals is on the order of 0.05. The average index of refraction at 5300 ± 50 Å, measured by the Becke line method, does not change (Table V) to within ±0.002 upon deuteration, indicating little or no change in linear bond polarizabilities. Within our experimental error the signal in the D and L forms can be considered identical since the standard deviation of the measurements is 30%. This behavior in the SHG signal upon deuteration of the hydrazonium tartrates is similar to that described for L(+) glutamic acid hydrochloride (1). It may be interesting to note that we observe both D and L tartaric acids to generate second harmonics of the order of 0.3 α-SiO$_2$, indicating that the enhancement in the optical nonlinearity of the hydrazonium tartrates probably involves the NH—O bonds.

The relative SHG intensity is shown as a function of particle size in Fig. 1. The particle size dependence indicates that the crystals are phase matchable at 1.06 μm with a coherence length of about 20 μm. It was determined that the coherence length remains virtually unchanged upon deuteration.

We also examined SHG as a function of temperature from −60°C to decomposition. No transitions were observed.

Linear optical measurements. In order to confirm the enantiomeric nature of the hydrazonium tartrates we measured their optical activity in aqueous solution. For the L(+) and D(−) we found $[\alpha]_D^{25} = +21.2$ and $[\alpha]_D^{25} = -21.0$, respectively, and for the $d_8 - 0.97$D enantiomers $[\alpha]_D^{25} = +20.4$ and $[\alpha]_D^{25} = -20.7$. These measurements indicate that the hydrazonium tartrate enantiomers probably form with retention of configuration. The possibility of complete inversion occurring in both cases cannot be excluded.

Conoscopic examination of the crystals indicated that they are biaxial. The significance of this is that symmetry arguments on enantiomeric molecular crystals (5) dictate only three allowable point groups: 1, 2, and 222. The choice of point group 222 is consistent with the X-ray data and the SHG data.

Infrared spectroscopy. The solid-state vibrational spectra for the undeuterated and $d_8 - 0.97$D L(+)-hydrazonium tartrate are
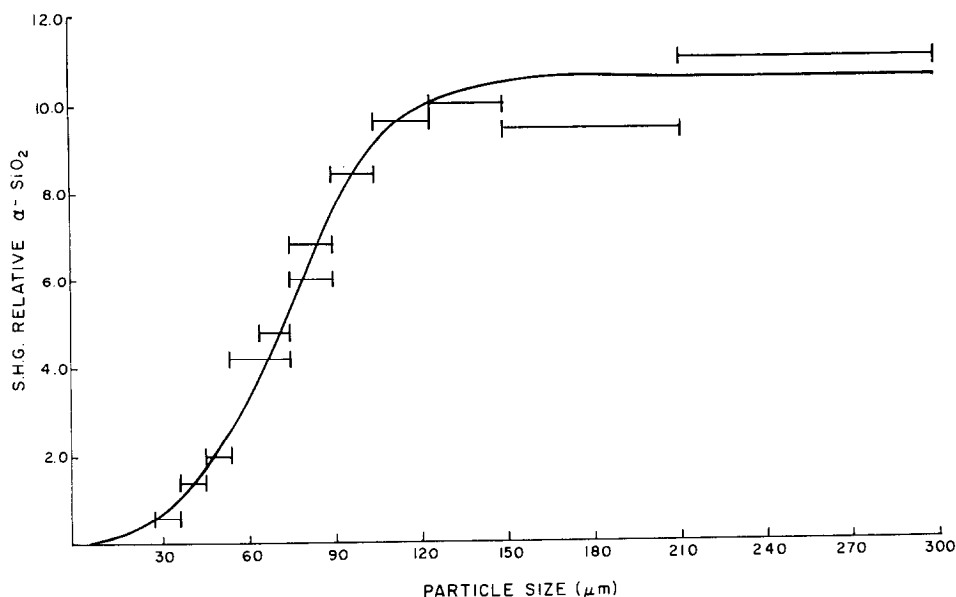
FIG. 1. Second harmonic intensity in L(+)- and D(−)-hydrazonium tartrate as a function of particle size at 25°C.

shown in Fig. 2. Absorptions due to Nujol have not been omitted. The assignments for some of the vibrational modes are listed in Table VI. These assignments are based upon stoichiometry, isotope shifts, and geometric considerations. The NH_3^+ deformation at 1600 cm^{-1} indicates that the carboxylate groups are in an ionized state also. Unfortu-
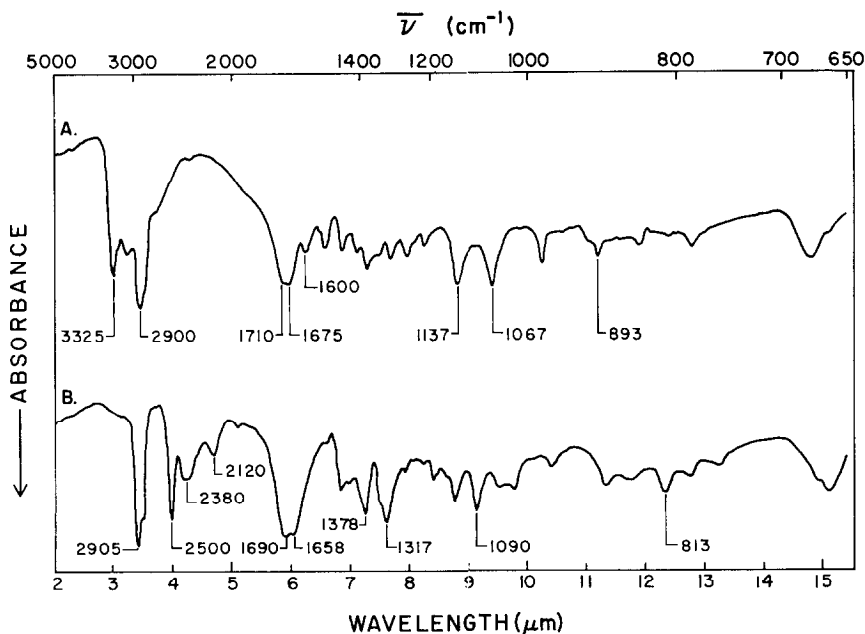

FIG. 2. Solid-state vibrational spectra of (A) L(+) and D(−)-hydrazonium tartrate and (B) L(−) and D(−) d_8 − 0.97D hydrazonium tartrate at 22°C.

TABLE VI

Solid-State Infrared Spectral Data at 22°C

(cm^{-1})	Intensity[a]	Assignment
(A) L(+)-hydrazonium tartrate		
3325	s	OH stretch
3310	s, b	NH$_3{}^+$ sym. and asym. stretch
2900	s	CH stretch
2675	w	NH$_3{}^+$ stretch overtone
1710	s	C=O stretch
1675	s	C=O stretch
1600	m	NH$_3{}^+$ asym. def.
1137	m	C—O stretch
1090	m	C—O stretch
(B) d_8 − 0.97D L(+)-hydrazonium tartrate		
2905	s	CH stretch
2500	s	OD stretch
2380	m, b	ND$_3{}^+$ sym. and asym. stretch
1690	s	C=O stretch
1658	s	C=O stretch
1460	m	ND$_3{}^+$ asym. def.
1139	m	C—O stretch
1067	m	C—O stretch

[a] s = strong, m = medium, w = weak, b = broad.

nately, the ionized carboxylate vibration which normally lies at about 1650 cm^{-1} is hidden by the broad carbonyl stretches at 1710 and 1675 cm^{-1}. Two carbonyl stretches are observed since we are dealing with a dicarboxylic acid salt. The broad OH stretch at 3325 cm^{-1} is attributed to the dihydroxy groups of the tartrate species. One should also note their complementary C–O stretches at 1137 and 1090 cm^{-1} which upon deuteration shift to 1139 and 1067 cm^{-1}, respectively. The small shift exhibited by the latter vibration is pro-

bably a consequence of OH——O and NH——O bonding involving a C–O hydroxy.

Thermal measurements. DTA studies showed that the hydrazonium tartrate enantiomers decompose at 151°C in air with a heating rate of 10°C min^{-1}. The d_8 − 0.97D enantiomers decompose at 153°C. At heating rates of 1°C min^{-1} or slower, the samples first discolored, turning brown, and then finally decomposed at 181°C. However, crystals held in an oven at 150°C in air were observed to discolor in a matter of minutes.

DTA measurements from −160°C to the decomposition point revealed no phase transitions. This is in agreement with our SHG data.

The heat of reaction of hydrazonium tartrate was obtained via a Born–Haber cycle. The results are given in Fig. 3. The values obtained are the integral heats of solution of that solute for that specified concentration.

Optical transmission. The ultraviolet transmission curve for a 1.5-mm-thick (010) crystal plate of d_8 − 0.97D L(+)-hydrazonium tartrate is shown in Fig. 4. The band edge at 239 nm is essentially the same for the undeuterated tartrate. This is verification that deuterium substitution has little effect on the linear bond polarizabilities. The sharpness of the cutoff and the fact that both samples exhibit 75% transmission at 257 nm is very desirable for ultraviolet applications. The near-infrared curve for the undeuterated tartrate (Fig. 5) and the deuterated tartrate (Fig. 6) reveal some interesting differences. For the undeuterated tartrate the upper wavelength cutoff corresponding to about 15% transmission is at 1.610 μm with two absorption bands at 1.417 and 1.464 μm. Deuteration extends the cutoff to 2.073 μm while the two bands shift to 1.738
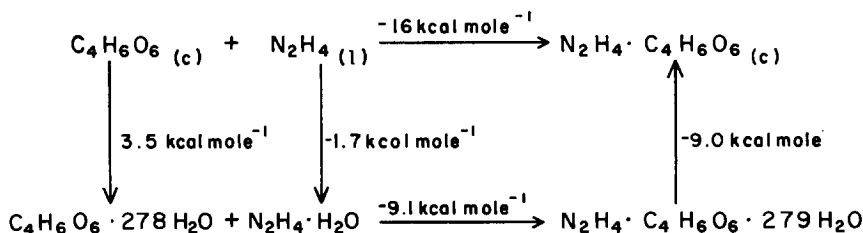

$$C_4H_6O_6 \text{ (c)} + N_2H_4 \text{ (l)} \xrightarrow{-16 \text{ kcal mole}^{-1}} N_2H_4 \cdot C_4H_6O_6 \text{ (c)}$$

3.5 kcal mole^{-1} -1.7 kcal mole^{-1} -9.0 kcal mole

$$C_4H_6O_6 \cdot 278\,H_2O + N_2H_4 \cdot H_2O \xrightarrow{-9.1 \text{ kcal mole}^{-1}} N_2H_4 \cdot C_4H_6O_6 \cdot 279\,H_2O$$

Fig. 3. Born–Haber cycle for L(+)- and D(−)-hydrazonium tartrate at 25°C.

FIG. 4. Ultraviolet transmission curve in a single crystal of $d_8 - 0.97D$ L(+)-hydrazonium tartrate.

Discussion

In a previous study (1) of L(+)-glutamic acid hydrochloride it was shown that deuterium substitution had virtually no effect upon lattice parameters and interatomic bond distances. The macroscopic optical nonlinearity and linearity was found to be unaltered upon deuteration. The optical nonlinearity in L(+)-glutamic acid hydrochloride was ascribed to the nonlinear polarizability of the hydrogen bonds due to their inherent anharmonicity. Since the optical nonlinearity was unaltered upon deuteration affecting only the vibrational character of the bonds, the nonlinear polarization was considered primarily electronic in character. For the hydrazonium tartrate enantiomers we observe this same isotope effect. Our X-ray data clearly shows that the unit cell parameters and more importantly the cell volume are not affected by deuteration. The observed ΔT of 2°C for the decomposition point also indicates an insignificant change in bond energies upon deuteration. Our major assumption is that no major shifts in atomic positions has occurred upon deuteration, so that we may neglect any differences in orientational polarization. This point will be verified by the complete crystal structure work which will be published separately. We therefore ascribe the optical nonlinearity to the nonlinear electronic polarizability of the hydrogen bonds.

and 1.839 μm, respectively. The band at 1.417 μm is attributed to the $2\tilde{v}_2 + \tilde{v}_3$ vibrational modes of the OH groups while the 1.738 μm band is due to the OD groups. The band at 1.464 μm which shifts to 1.839 μm may be due to NH and ND vibrational modes. The large shift in the upper wavelength cutoff resulting from deuterium substitution is certainly a consequence of the replaceable hydrogens. In both samples a maximum of about 10% transmission was observed out to 2.5 μm. No corrections were made for reflection losses.
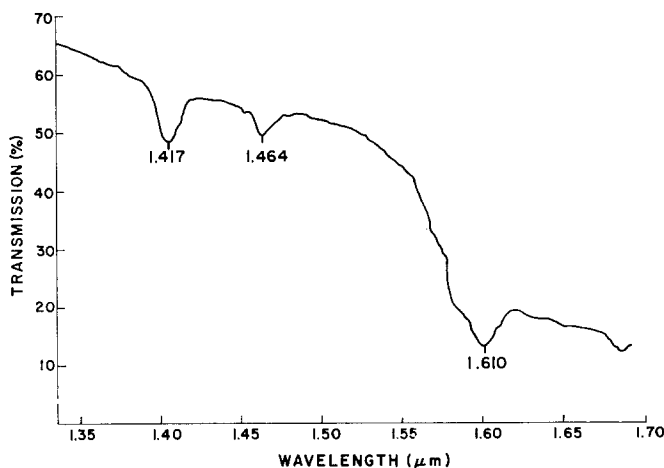

FIG. 5. Near-infrared transmission curve in a single crystal of L(+)-hydrazonium tartrate.
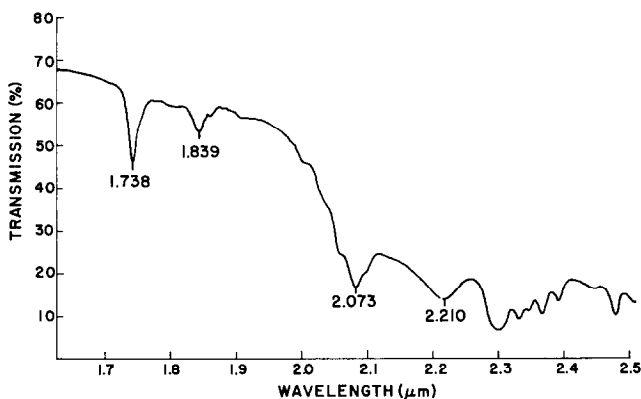
FIG. 6. Near-infrared transmission curve in a single crystal of $d_8 - 0.97D$ L(+)-hydrazonium tartrate.

In Fig. 7 we propose a probable molecular configuration for the hydrazonium tartrate enantiomers as a highly ionic complex. This structure is consistent with the stoichiometric analysis and the vibrational spectroscopic assignments. We have depicted this structure in accordance with probable bond angles and bond lengths obtained from molecular models and energetic considerations.

From the Born–Haber cycle (Fig. 3) we calculated the heat of formation for hydrazonium tartrate as -16 kcal mole^{-1} at 25°C. Accordingly, we estimate the strength of the two NH——O bonds to be of the order of 5 kcal mole^{-1} with a corresponding bond distance of about 3 Å. The heat associated with the formation of these bonds in solution (Fig. 3) was found to be -9.1 kcal mole^{-1}. This results in minimal angle strain and the formation of a six-membered ring. This of course assumes the two NH——O bonds to have the same bond geometry and relative configuration. They are probably in staggered orienta-

tion relative to each other. The remaining energy, ~ 6 kcal, is probably taken up in rather weak secondary hydrogen bonding of the type NH——N, OH——O, and OH——N.

Summary and Conclusions

L(+)- and D(−)-hydrazonium tartrates have been characterized by optical, crystallographic, and thermochemical methods. Preliminary nonlinear optical measurements show the crystals to be promising for possible nonlinear optical device applications. The large nonlinear optical coefficient, long optical transmission range extending well into the ultraviolet, and chemical stability, are some of the desirable properties of these crystals. The deuterium isotope effect has also been investigated. The X-ray data indicate that interatomic bond distances are unaltered upon deuteration while the optical nonlinearity is unaffected also. Consequently, the optical nonlinearity is primarily ascribed to the non-
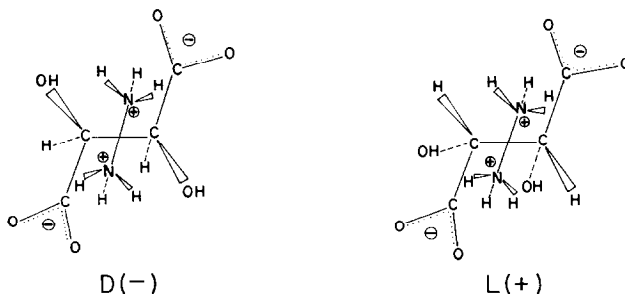

FIG. 7. Proposed molecular configuration for hydrazonium tartrate enantiomers.

linear electronic polarizability of the two NH—O bonds. Secondary contributions might be expected to arise from other hydrogen bonds of the type OH—O, NH—N, and OH—N.

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