High-Resolution Optical Spectroscopy and Laser Isotope Enrichment of Matrix-Isolated *s*-Tetrazine in Argon

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Abstract: It is shown that *s*-tetrazine can be deposited in an argon matrix with sufficient homogeneity that the spectral transitions due to carbon-13 and nitrogen-15 containing molecules (in natural abundance) can be clearly discerned with spectral line widths in the range of ca. 0.7 cm^{-1}. The *s*-tetrazine molecules can be photolyzed with high efficiency to produce N_2 and 2HCN, and by means of a tunable laser these photolyses can be readily carried out with high isotopic selectivity. Absorption, fluorescence, and excitation spectra for the various isotopic species are presented. The modes 6a′ and 6a″ are 702 and 737 cm^{-1} in argon compared with 703 and 736 cm^{-1} in the vapor. The HCN is formed exclusively as dimers that have spectra quite similar to those of HCN dimers formed in HCN argon mixtures at higher temperatures indicating that substantial motion occurs in the site on photolysis. A main result is that isotope separation is demonstrated for a photolabile system under matrix isolated conditions. Not only does this scheme overcome the need for specialized host lattices but renders trivial the chemical separation of photoproducts from the host, and therefore marks a more practical method of solid-state isotope separation than hitherto demonstrated.

The separation or enrichment of rare isotopes by means of laser-induced photochemical processes in solids has only recently been accomplished.[1-4] The principal advantage of this method of isotope enrichment or separation over other photochemical techniques is that in the low-temperature solid the spectral congestion due to overlapping of vibronic states is absent. Thus molecules whose photochemical processes are useful in principle for isotope separation schemes can be used in practice regardless of the molecular complexity. On the other hand, in gases selective isotopic excitations in the optical regime are not expected to be possible for molecules of sufficient complexity that their vapor spectra are highly congested or diffuse.

In order to achieve the sharp optical spectra required for isotopically selective excitations it is necessary to have a sample that is sufficiently homogeneous that the spectral line widths do not exceed the isotope shifts. In previous work this was accomplished by using mixed-crystal systems where the photochemically active guest molecules were held in a substitutional solid solution with the host molecules. Although such mixed crystals have sharp spectra, the choice of host lattices is usually limited to organic molecules having some structural features in common with the guest. Another disadvantage of organic mixed crystal systems is that when photochemical reactions of the guest have occurred, the products or the enriched guest ensemble cannot always be easily separated from the host molecules.

These considerations have led us to investigate the feasibility of isotope separations by laser-induced photolysis of organic molecules in inert gas matrices. It is apparent that for such matrix-isolated systems the main drawbacks encountered with conventional mixed crystals are absent. The problem that remains is that concerning inhomogeneous line broadening. From the literature of matrix isolation spectroscopy it has not been apparent whether sufficiently sharp spectra could be readily obtained for moderately complex organic molecules.

We will report here on high-resolution spectra of a photochemically unstable species, *s*-tetrazine, in a rare gas matrix, argon, at low temperature, 4.2 K.[5] This system had been studied previously[1,2,4] in various mixed-crystal systems resulting in very successful isotope enrichments. Using these mixed crystals it was also demonstrated[6] that low-temperature spectroscopy could be used for the analysis of isotopic compositions with a sensitivity similar to that in mass spectrometry. In the inert gas matrix inhomogeneous bandwidths of ca. 0.7 cm^{-1} were obtained. This line width is comparable with those in the sharpest spectra obtained at 10^{-5} mole fraction of *s*-tetrazine in mixed organic crystals. Isotopic structure assigned to carbon-13 and nitrogen-15 is clearly resolved in the optical spectra of the matrix isolated tetrazine. Selective excitations of $C_2N_4H_2$, $^{13}C^{12}CN_4H_2$, and $C_2{}^{15}N^{14}N_3H_2$ were achieved with selectivities of about 50. In the following, results of laser-induced isotope enrichments and photochemical studies are presented.

Experimental Section

s-Tetrazine was prepared by a modification[2] of the method of Spencer, Cross, and Wiberg[7] and purified by repeated vacuum distillations. *s*-Tetrazine has a vapor pressure of about 2 Torr at 300 K. The vapor equilibrated over excess solid in a 0.35-L bulb was transferred into a 1.65 L deposition column. High-purity argon (99.995%) was then admitted to the deposition chamber to a total pressure of 600 Torr and thoroughly mixed with the tetrazine. Resulting values of M/R (matrix:tetrazine mole ratio) for these mixtures were typically ca. 1000. Matrices of *s*-tetrazine in argon were deposited by three different techniques: slow uniform deposition at a rate of ca. 0.5 Torr h^{-1}; rapid deposition at 5–10 Torr h^{-1}; and pulsed deposition of 10-μmol aliquots at 2-min intervals. In each case the samples were deposited onto a freshly polished LiF window maintained at 10 K by direct contact with liquid helium. The samples were subsequently cooled slowly to 4.2 K and the $S_1 \leftarrow S_0$ transition photographed at 1-cm^{-1} resolution to verify sample uniformity and determine appropriate exposure times. The matrices were annealed at 40 K for approximately 0.5 h, then slowly cooled to 4.2 K, prior to attempting any high-resolution measurements or selective photochemistry. The singlet-singlet origin and strong vibronic bands were photographed at 0.15-cm^{-1} resolution on a 2-m Ebert mount spectrometer in 15–16 order. The resulting spectra were then traced on a microdensitometer.

A Hänsch-type N_2 pumped (100 kW) dye laser was used as the selective excitation source. The dye laser cavity consisted of a partially reflecting mirror, a flowing dye cell with 6° windows, a 40× beam expander, and a Czerney–Turner mounted echelle grating with 316 grooves per mm blazed for 5000 Å at 63° 26′. The fluorescence was detected by a cooled Ga–As photomultiplier having nearly linear response from 4000 to 8000 Å and <1 nA anode dark current background running at −1.6 kV. The fluorescence was observed either broad band through suitable glass filters to cut out the exciting laser light, or with selectivity through a scanning grating monochromator with adjustable slits and a dispersion of 5 Å/mm. Typical slit widths varied from 200 to 20 μ for fluorescence and single isotopic studies respectively. Maximum instrument spectral resolution was ca. 0.8 cm^{-1}.

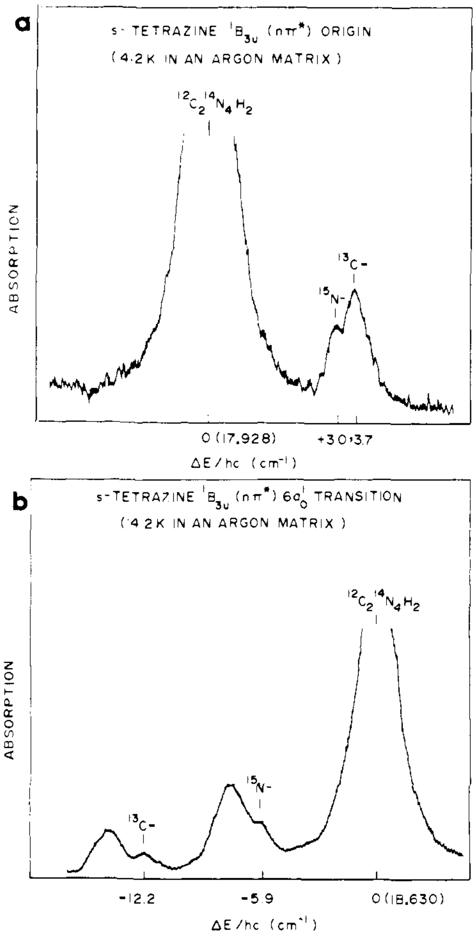

Figure 1. (a) The absorption of the *s*-tetrazine $^1B_{3u} \leftarrow {}^1A_g$ ($n\pi^*$) 0–0 band in an argon matrix at 4.2 K. The spectrum was photographed on a 2-m Ebert mount spectrometer in 15th order. A 450-W Xe lamp was used as the background continuum. (b) The absorption of the *s*-tetrazine $6a_0^1$ transition.

Results

The region of the lowest energy singlet-singlet transition [$^1B_{3u} \leftarrow {}^1A_g$ ($n\pi^*$)] of an unphotolyzed matrix of *s*-tetrazine was examined at moderate resolution. Four spectral sites were readily apparent. However, approximately 90% of the observed spectral intensity was due to *s*-tetrazine chromophores in one particular site, or lattice environment, with their origin band at 17 926 cm^{-1}. The bandwidths of the unannealed spectra were 3-5 cm^{-1} regardless of the method used for the deposition. It is important to note that the apparent site intensity distribution was reproducible for a particular deposition procedure but differed considerably as the deposition conditions were varied.

Annealing produced two dramatic changes. There was a considerable decrease in the observed vibronic transition line widths. In many instances the line widths were measured as ca. 0.7 cm^{-1}. In addition, a second set of absorption bands appear to higher energy than the 0-0 and vibronic bands in matrices of $M/R \leq 1000$. These new bands exhibited a significantly different site distribution from the original dilute matrix bands, indicating that they do not correspond to vibronic transition of the *s*-tetrazine monomer in argon. The vibrational spacings between these high-energy bands were the same as observed for the *s*-tetrazine monomer bands. These high-energy bands were strongly reduced in relative intensity in matrices at $M/R \sim 2000$. Thus it seems possible that these new bands arise from a significant amount of aggregation during the annealing process.

Table I. Isotopically Selective Vibronic Spectra of Tetrazine

Assignment	Observed zeropoint energies and vibrational frequencies (vacuum cm^{-1}) $H_2C_2N_4$	^{15}N	^{13}C
	Argon Matrix at 4.2 K		
0–0	17 928	17 931	17 932
6a′	702	693	686
6a″	737	736	730
	Benzene Mixed Crystal at 1.6 K		
0–0	17 234	17 237	17 239
6a′	703	695	684
6a″	727	723	720
	Vapor		
0–0	18 128.0	$\sim$18 131.8	18 131.8
6a′	702.9		
6a″	736.1		

The strongest site 0-0 band of annealed *s*-tetrazine in argon ($M/R = 1000$) at 4.2 K was measured at 17 928 (cf. Figure 1a). Two sharp spectral features associated with this peak at 17 931 and 17 932 cm^{-1} were observed with relative intensities 0.7:1. These two transisitions were assigned to the origin transitions of *s*-tetrazine-$^{15}N_1$ and *s*-tetrazine-$^{13}C_1$ in argon, respectively, by comparisons with the zeropoint isotope shifts observed for naturally abundant *s*-tetrazine in the vapor and in mixed molecular crystals[2] at 1.6 K (see Table I), and by their observed relative intensities in absorption—expect a ratio of 0.64:1.0 from natural abundances.

The high-resolution spectra of annealed samples of *s*-tetrazine in argon at 4.2 K at M/R ratios as low as 300 show weak phonon side-band structure. The phonon side-band centers are removed from the zero-phonon line center by ca. 50 cm^{-1}. We have estimated the ratio of zero-phonon line to side-band intensity at 10^2 indicating very weak excitation phonon coupling. There is no noticeable change in relative phonon side-band strengths over the series of zero-phonon lines $6a_0{}^n$ for $n = 0, 1, \ldots, 5$, spanning a range of ca. 3500 cm^{-1} excess vibrational energy.

The Franck-Condon maximum of the $^1B_{3u} \leftarrow {}^1A_g$ transition is the $6a_0{}^1$ band. This band is shown resolved in Figure 1b. Unlike the 0-0 band region, the rare (heavier) isotopic species absorb at lower energies in the vibronic bands than the more abundant species. In addition, since the vibrational shifts are generally much larger than the zeropoint shift one can achieve much greater excitation selectivity in vibronic bands. The overall separation of the $6a_0{}^1$ transitions of *s*-tetrazine-$^{15}N_1$ and *s*-tetrazine-$^{13}C_1$ from that of *s*-tetrazine in argon at 4.2 K are 5.9 and 12.2 cm^{-1}, respectively. The absolute line positions and isotope vibrational shifts are included in Table I along with the corresponding data for the benzene mixed crystal and the vapor (isotope separation was recently reported for *s*-tetrazine in the vapor[8]).

Dye laser excitation (excitation bandwidth 0.6 cm^{-1}) of a single isotopic species resulted in fluorescence exclusively from the particular single isotope originally excited. There was no evidence of any isotopic scrambling having occurred during excitation, vibrational relaxation, or subsequent electronic relaxation. Single isotopic species fluorescence, detected at ca. 0.8 cm^{-1} spectral resolution, was used to identify the isotopic $^1B_{3u} \rightarrow {}^1A_g$ origins and vibronic progressions. The fluorescence spectra following selective excitation at the electronic origin (ca. 5576 Å) resulted in a selectivity[9] (α) of 40-50 as shown in Figure 2.

By monitoring fluorescence at a frequency characteristic of a single selected isotopic tetrazine the isotopically selective excitation spectra were obtained. The single isotopic fluorescence excitation spectra of the origin are shown in Figure 3. The vibrational frequencies obtained through this isotopically

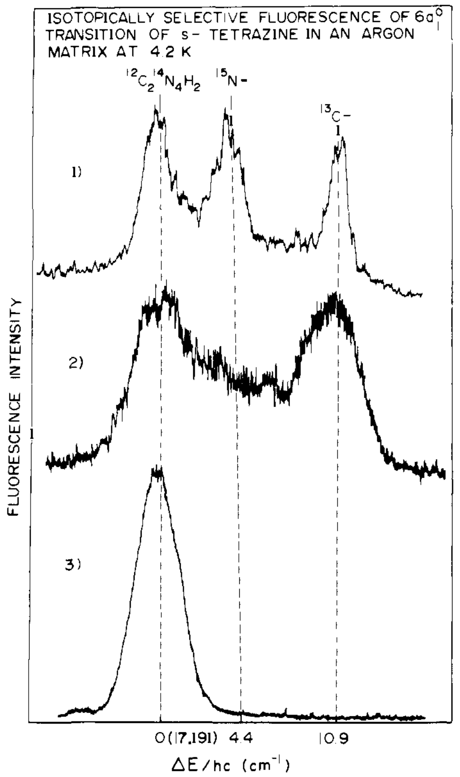

Figure 2. Isotopically selective fluorescence of the $6a_1^0$, transition. A scanning monochromator was swept through the vibronic fluorescence region. A 0.6-cm^{-1} tunable dye laser was used to selectively excite a single isotopic species at the origin: (1) λ_{ex} = 5576.0 Å (^{15}N), (2) λ_{ex} = 5575.4 Å (^{13}C), (3) λ_{ex} = 5576.8 Å (^{12}C).

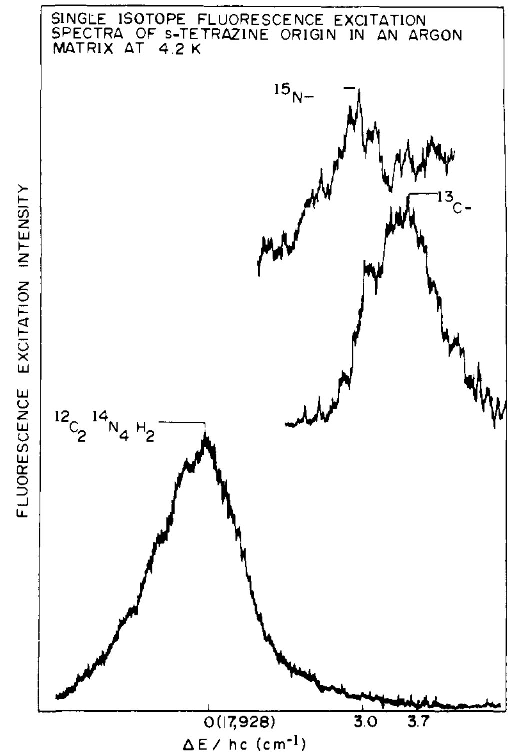

Figure 3. Isotopically selective fluorescence excitation spectra. A scanning monochromator (0.8-cm^{-1} resolution) was tuned to a specific isotope of the $6a_2^0$ transition of *s*-tetrazine. A 0.6-cm^{-1} tunable dye laser was then scanned through the 0-0 absorption region: (1) λ_{em} = 6071.8 Å, (2) λ_{em} = 6068.6 Å, (3) λ_{em} = 6015.2 Å.

selective fluorescence study are presented and assigned in Table I. Broad-band detection of the emission yielded an excitation spectrum that indicated the extent of the spectral overlap of the various isotope transitions. Most of the observed overlapping is the result of inhomogeneous line broadening. Isotopic selectivity of photoprocesses, such as luminescence or a chemical reaction, was readily achieved by choosing the excitation wavelength to correspond to a vibronic region where the desired isotopic species were better resolved than in the 0-0 region.

Laser Isotope Separation. *s*-Tetrazine undergoes a photochemistry with near unit quantum yield[10] and even in the crystal or mixed crystal at 1.6 K the conversion to HCN and N_2 is efficient. The photochemical instability of *s*-tetrazine combined with the chemically stable nature of the ultimate photoproducts makes this a most suitable system for optically induced isotope enrichment. We have performed selective irradiation experiments on a dilute rare gas matrix (M/R ~ 1000 in argon) and achieved enrichment[9] factors in the range 50-500. The starting material was natural *s*-tetrazine in all cases.

The experiments were performed in the manner of the excitation spectra described above except that the wavelength scan was stopped when the transition energy for a particular isotope was reached. The best excitation frequency could be ascertained quite readily either by monitoring the total emission and settling on a particular peak, or by fixing the detector monochromator at a known emission frequency for one of the isotopes and maximizing the fluorescence signal at the detector during a dye laser scan. Finally when the optimum settings of the dye laser are known it is possible to initiate the irradiations of successive matrices with the required excitation wavelength.

The results of the laser-induced isotopic enrichment are shown in Figure 4. The origin region of *s*-tetrazine in argon at 4.2 K (M/R = 1000) is shown in absorption at moderate resolution (ca. 0.8 cm^{-1}). The matrix sample containing 0.5 mg of *s*-tetrazine was irradiated at 17 928.4 cm^{-1} ($C_2N_4H_2$) with a 0.6-cm^{-1} bandwidth dye laser (10-kW peak power, 50 Hz, 6 ns) for 5 min. The sample was probed three times in absorption for isotopic composition. Figure 4a represents the absorption spectrum of an unphotolyzed sample (i.e., natural abundances of nitrogen-15 and carbon-13); and Figure 4c represents the total removal of *s*-tetrazine ($C_2N_4H_2$) from the matrix thereby generating pure $H^{12}C^{14}N$ and $^{14}N_2$.

It is apparent that identical procedures may be used to selectively photolyze *s*-tetrazine-$^{15}N_1$, *s*-tetrazine-$^{13}C_1$, or even less abundant isotopic species such as *s*-tetrazine-$^2H_1$. Following such a selective photolysis, the matrix may be slowly warmed to fractionally distill successively Ar, N_2, HCN, and finally *s*-tetrazine. The species of interest may readily be collected separately in standard vacuum traps.

Photochemistry. The spectra of *s*-tetrazine in an argon matrix are bleached by a few minutes of dye laser irradiation. It was shown previously[1,2] that illuminated mixed crystals of tetrazine ultimately produce only N_2 and HCN. We have performed low-temperature infrared experiments to identify the products of the photolysis in the rare gas matrix. The infrared spectra of *s*-tetrazine and photolyzed *s*-tetrazine in argon at 4.2 K are shown in Figure 5. These spectra were recorded on a Perkin-Elmer 225 infrared spectrometer using CsI windows. The photolyzed spectrum actually represents two experiments, one in which the excitation was a 1000-W Xe arc filtered to pass light of wavelength greater than 455 mm [(selective excitation of T_1 (n, π^*) and S_1 (n, π^*)], and another with a fresh sample such that the wavelength of the photolysis source was less than 455 mm [S_2 (n π^*) and S_3 (π π^*)]. Identical chemical products were obtained for the high- and low-energy irradiation.

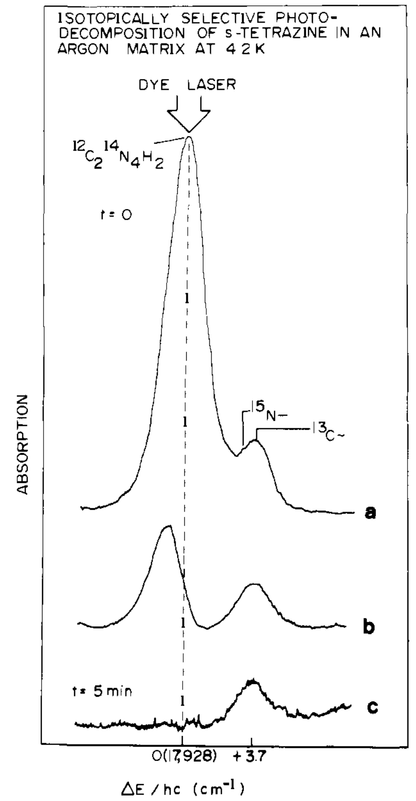

Figure 4. Absorption spectra of the isotopically selective photodecomposition of *s*-tetrazine in an argon matrix at 4.2 K. The photolysis source was a 0.6-cm^{-1} N_2-pumped tunable dye laser tuned to the region of the $^{13}C^{12}CN_4H_2$ absorption. Absorption spectra were recorded photographically on a 3-m Eagle mount spectrometer using a 450-W Xe arc continuum background. The spectral intensity of the $^{12}C^{13}CN_4H_2$ peak was determined to be unchanged owing to *laser* photolysis by comparison to another site well removed from the dye laser line. The electrometer sensitivity was increased to compensate for nonselective photolysis due to the Xe arc used in taking the absorption spectrum.

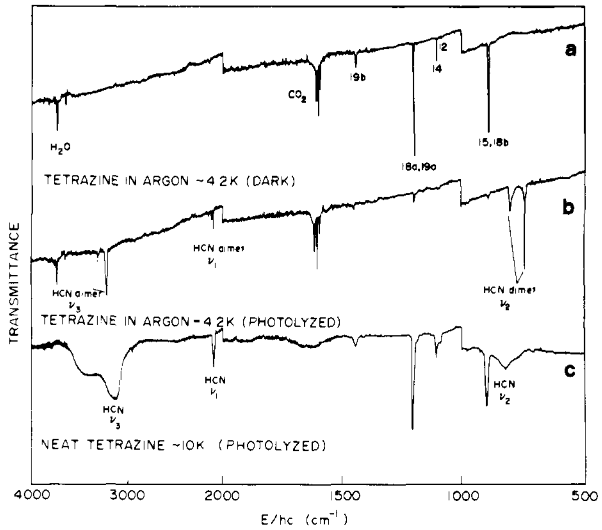

Figure 5. Infrared spectra of *s*-tetrazine in an argon matrix at 4.2 K: (a) unphotolyzed and (b) photolyzed. The photolysis source was a 1000-W Xe lamp filtered to pass either 7500 Å > λ > 4500 Å or only ultraviolet light. The product spectra were identical in both cases. Spectrum (c) shows the results of visible photolysis of a sample of neat *s*-tetrazine. Spectra are for minutes after the photolysis.

Table II. Assignment of Infrared Spectrum of Photoproducts of *s*-Tetrazine in an Argon Matrix at 4.2 K[a]

E/hc, cm^{-1}	Assignment	HCN/argon[b]
3300	ν_3 HCN dimer	3301
3205	ν_3 HCN dimer	3202
2110	ν_1 HCN dimer	2114
2090	ν_1 HCN dimer	2090
790	ν_2 HCN dimer	792
730	ν_2 HCN dimer	732

[a] Bands around 3725 and 1600 cm^{-1} are due to H_2O and CO_2 impurities respectively. In the experiments shown in Figure 5, a dilute matrix was employed to guarantee that intramolecular effects were absent. [b] Reference 11.

The photolysis spectrum is qualitatively similar to but uniquely distinct from the neat *s*-tetrazine spectrum (Figure 5c) which has been previously reported and for which assignments were made. The photolyzed matrix showed HCN as the only infrared-active photoproduct. All the HCN was present as dimers $(HCN)_2$ having spectra similar to those reported previously[11] for concentrated matrices of HCN in argon. Infrared assignments of the photoproducts are given in Table II.

Discussion and Conclusions

The main result of this work is the demonstration that a photochemically unstable system can be deposited in a rare gas matrix with sufficient homogeneity that naturally abundant isotopic molecules can be distinguished optically. The observed line width of ca. 0.7 cm^{-1} was sufficiently narrow that a tunable laser could be used to selectively decompose distinct isotopic species. This result has preparative implications, because the host lattice is both inert and can be readily removed completely from the unphotolyzed tetrazine. Since in the example presented here the ultimate products of the photolysis are HCN and N_2, they can be readily evaporated from the photolyzed film and collected in highly pure form. The unphotolyzed tetrazine, having the required isotopic purity, is also easily separated from N_2, HCN, and Ar simply by distilling the photolysis mixture.

Because the photolysis of tetrazine was carried out in an argon matrix it was possible to use infrared spectroscopy to characterize the reaction product HCN. Since each tetrazine is known to yield two HCN molecules it is hardly surprising that only HCN dimers are observed after the photolysis at 4.2 K. The dimer spectra seen after the tetrazine photolysis are very similar to those obtained when HCN molecules are allowed to diffuse together in argon at 40 K, or are formed by deposition in argon of HCN dimers from the vapor.[11] These results indicate that there is substantial motion of the atoms composing the HCN molecules, away from their locations in the *s*-tetrazine molecule. The stable dimer structure is hydrogen bonded head-to-tail, as in HCN——HCN, so considerable motion of a number of atoms away from their equilibrium positions in tetrazine would be required to occur during or after the photolysis of tetrazine at 4.2 K. Possibly at even lower temperatures this rearrangement could be slowed down sufficiently that the HCN infrared spectrum would provide additional clues regarding the structural changes occurring during the photochemical reaction.

We have also reported here the results of an ultraviolet photolysis in argon and have shown that again HCN and N_2 are the only products at long times after irradiation.

A survey of the literature of optical spectra of matrix isolated species does not evidence that the spectral line widths achieved here are common. We have found that when great care is taken in the deposition and annealing procedures, and in choosing the vapor-phase composition, the line widths obtained are a few tenths of a cm^{-1} and therefore are perfectly suitable for isotopically selective chemistry. The technique of matrix isolation combined with tunable lasers thereby offers a substantial practical improvement over previous solid-state isotope separations because of the ease of separating reactants and products. Obviously it will be possible to study other features of the photolysis in the argon matrix, such as yields and time resolved product spectra. Such experiments are planned.

Acknowledgments. It is a pleasure to acknowledge the partial support of this investigation by the National Science Foundation (No. CHE 75-16177) and the Material Research Laboratory at the University of Pennsylvania (No. DMR 76-00678).

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$$\alpha = R^*/R_I$$

where R^* is the isotopic ratio of excited species. The effective *enrichment* may be characterized by the factor $\beta = R_f/R_I$ where R_f is the isotopic ratio of enriched products.

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Carbon-13 Magnetic Resonance. 27. The Dependence of Chemical Shifts on Methyl Rotational Conformations and Dynamics in the Methylated Benzenes and Naphthalenes

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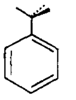
Abstract: The aromatic carbon-13 chemical shifts of the methylated benzenes are analyzed in terms of the conformational states of the methyl rotors and associated steric, dynamic, and electronic effects. Two formal parametric analyses are developed, based on differing models. The resulting parameters enable highly accurate predicted chemical shift values to be calculated. The analysis is then extended to the carbon-13 chemical shifts of the methylnaphthalenes, incorporating additional features characteristic of this system. The results are compared and contrasted with those previously obtained. Extension of the analysis to more complex systems is investigated by considering the chemical shifts of some methylated derivatives of phenanthrene and anthracene.

Substituted benzenes have been the object of ^{13}C NMR studies for more than 15 years.[2] It was observed[2-5] that approximately additive chemical shift effects obtain for the aromatic carbons when various substituents are added to the ring, including methyl groups.

Utilizing least-squares, linear regression techniques, Woolfenden and Grant[6] demonstrated that the ^{13}C chemical shifts of methyl groups in the methylbenzenes are also additive and exhibit conformational dependence. Although an isolated methyl group such as that found in toluene has available two minimum energy orientations of equal probability, **1** and **2**, the aromatic portion of the proton-decoupled, ^{13}C spectrum of toluene does not reveal the six lines which would be expected for either of these forms, even at very low temperatures. This results because the sixfold barrier to internal rotation of the methyl in toluene is only 0.06 kcal/mol.[6] Thus, thermal energies at ambient spectrometer temperatures are sufficient to populate extensively many rotational states beyond the top of the rotational barrier; a methyl group having access to such a continuum of rotational states may appropriately be termed a "free rotor".[6] Hence, at ambient temperatures the aromatic portion of the proton-decoupled ^{13}C spectrum of toluene contains only four lines, the chemical shifts of carbons 2 and 6 and carbons 3 and 5 being averaged.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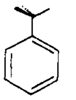
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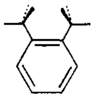
Four symmetrical minimum energy conformations can be proposed for *o*-xylene, **3–6.** However, in this case the various conformers are not of equal energy. The 2-2 orientation)**3**) is the lowest in steric repulsion energy, while conformations **4** and **5** are of equal, but somewhat higher, energy. The steric strain energy of structure **6** is considerably higher than that of **3**, **4**, or **5.** The assertion that **3** is the lowest energy conformer was introduced in the previously published treatment of the methyl shifts[6] and was substantiated by the results of the analysis. It is not expected that conformation **6** will contribute significantly to the rotamer population distribution of *o*-xylene or, in fact, to that of any of the methylbenzenes. In instances (vide post) where such conformations must be considered, appreciable structural distortion will probably result.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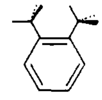
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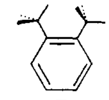
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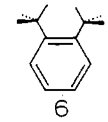
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In the previous treatment[6] it was assumed (1) that conformations **3**, **4**, and **5** were the only ones which required consid-