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ABSORPTION SPECTRA AND PHOTOCHEMICAL REARRANGEMENT OF OCTATETRAENE AND DECAPENTAENE RADICAL CATIONS IN SOLID ARGON

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Abstract—Parent radical cations of octatetraene and decapentaene have been prepared and trapped in solid argon using matrix photoionization methods with both cyclic and acyclic precursors. Visible absorption spectra are assigned to the all-*trans* cation isomer and several structures with increasing numbers of *cis* configurations. Irradiation into these bands with argon and krypton ion laser lines caused reversible rearrangements among several of the configurations for octatetraene and decapentaene cations. The cold matrix provides an excellent medium for studying molecular cation rearrangements where one structure can absorb light and other structures formed can be relaxed by the matrix before dissociation

INTRODUCTION

The absorption spectroscopy of molecular cations has received considerable attention during the past decade,[1] and matrix-isolation studies have become a valuable part of the field of cation spectroscopy.[2-5] With the exception of a few studies,[6-10] most of the effort has been directed toward producing and characterizing molecular cations instead of examining photochemical rearrangements of the cations. The matrix-isolation technique is especially well suited for studying the photochemistry of cations. With this technique, radical cations of precursor molecules can be produced by matrix photoionization methods and isolated in a cold, inert medium before reaction or rearrangement can occur. Once isolated, the parent cation can be characterized by absorption spectroscopy and then subjected to selective irradiations to promote stepwise photochemical isomerization or dissociation. The cold matrix is particularly effective for quenching internal energy, which allows rearrangement to be favored over dissociation photoprocesses.

One of the first cation rearrangements studied in solid argon involved the closed-shell $C_7H_7^+$ benzyl **1** and tropylium **2** cations.[8] These cations absorb strongly in different spectral regions, **1** at 353 nm and **2** at 263 nm. Consequently, one structural isomer can be excited by irradiating in its characteristic absorption band, which activates the dynamic equilibrium involving structural rearrangement. The cold matrix deactivates the structural isomer not absorbing radiation and preserves it for spectroscopic study. This process can be reversed by irradiating the other structural isomer.

Substituted styrene cations (—CH_3, —Cl and —Br) have been prepared in solid argon and observed to undergo rearrangement from the less stable α-substituted to the more stable β-substituted forms.[10] In these cases irradiation in red absorption bands was not sufficiently energetic to promote the $\alpha \rightarrow \beta$ rearrangement, but irradiation in near UV bands did affect this rearrangement.

A still different type of rearrangement was characterized in the dichlorobenzene cation system. The *p*-dichlorobenzene cation isomer gives rise to a sharp structured band system beginning at 520.6 nm, which was also observed in matrix photoionization experiments with *o*- and *m*-dichlorobenzene precursors; these isomer cations absorb, respectively, at 483 and 542.8 nm.[11] In addition irradiation in the *m*- and *o*-dichlorobenzene cation absorption bands produced growth in the *p*-cation absorption. A "chloronium ion walk" mechanism has been proposed to explain the observation of the more stable *p*-dichlorobenzene isomer in the *m*- and *o*-dichlorobenzene experiments. The chloronium ion hole excited state can be reached directly by argon resonance radiation or by photoexcitation of the ground state *o*- and *m*-dichlorobenzene cations, and in this excited state, the chloronium ion can walk around the aromatic ring to give the more stable *p*-dichlorobenzene cation isomer.

One of the most interesting rearrangements observed in argon matrices involved alkylbenzene cations. This 1,3-hydride shift was first characterized for toluene cation **3**, which exhibited broad 420 and 275 nm absorptions.[9] Irradiation in the broad 420 nm absorption produced a strong sharp 431.0 nm and a weak sharp 541.0 nm band, which are characteristic of conjugated hexatriene cations, and provided the 5-methylene-1,3-cyclohexadiene cation **4** identification for the photoproduct.[9] Cation **4** is immediately recognized as the McLafferty rearrangement product extensively studied by mass spectrometry. Support for the **4** identification was provided from its formation by rearrangement of the C_7H_8 isomer cycloheptatriene and norbornadiene cations and dissociation of butylbenzene cation in the original study[9] and from X-irradiation of 5-methylenebicyclo[2.2.0]hex-2-ene in solid argon in a recent investigation.[12] Other alkylbenzene cation precursors gave rise to substituted **4** products on visible photolysis; however, near-UV photolysis affected H_2 or CH_4 elimination to give substituted styrene cations.[13] In the case of t-butylbenzene cation, photo-elimination of CH_4 first gave the α-methylstyrene cation, which rearranged to the β-methylstyrene cation on further photolysis.

Photochemical rearrangements among C_6H_8 radical cations including electrocyclic ring opening of cyclohexadiene cations and eventual rearrangement to the all-*trans* isomer were first studied in glassy matrices[6] and subsequently in solid argon.[14,15] Similar electrocyclic ring opening was observed for the 1,3-cycloheptatriene cation and analogous rearrangements were found among 1,3,5-heptatriene cation isomers.[14] The bicyclic norbornene cation precursor also produced these heptatriene cation conformers upon irradiation.[14]

The above rearrangements among conjugated triene cation isomers and ring openings to give the all-*trans* triene cation conformers were extended to the octatetraene and decapentaene systems. Upon photoionization, cyclooctatriene was found to give a mixture of octatetraene cation isomers,[16] a result parallel to that observed in Freon glasses.[17] Several octatetraene cation isomers produced by matrix photoionization were interconverted by selective filtered mercury arc photolysis.[16] The decapentaene cation was first observed following rearrangement of the tricyclodecadiene precursor, dicyclopentadiene cation.[18] Biyclo[6.2.0]deca-2,4,6-triene and decapentaene precursors were employed to confirm this identification of the all-*trans*-decapentaene cation as the final photochemical rearrangement product. Since several of the octatetraene and decapentaene cation isomers absorb lines available in argon and krypton ion lasers, it was decided to reinvestigate the photochemical rearrangements among octatetraene and decapentaene cation isomers using laser photolysis.

EXPERIMENTAL

The matrix-isolation apparatus, vacuum UV photoionization, and mercury arc photolysis procedures have been described in earlier reports.[19-21] Briefly an organic precursor and an electron trapping molecule (CH_2Cl_2) were codeposited with excess argon on a 15 K sapphire plate with concurrent ionizing radiation from a windowless argon resonance lamp. Spectra were recorded on a Cary 17 spectrophotometer; band measurements are accurate to ±0.2 nm. The samples were then subjected to photolysis with radiation from a high pressure mercury arc passing through Corning glass filters or selected lines from argon and krypton ion lasers, and more spectra were recorded. After reflection from two mirrors, the laser beam covered a 1 cm^2 sample area.

The *endo*-dicyclopentadiene sample was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A. and all-*trans*-decapentaene was synthesized using the method described by Christensen and co-workers.[22] Bicyclo[2.2.2]octa-2,5-diene was prepared as recently described,[16] and *trans,trans*-1,3,5,7-octatetraene, kindly supplied by Granville, was stored at −80°. The identity of the conjugated polyenes was verified from structured matrix UV absorption spectra.[23] The precursors were degassed, and samples were prepared by diluting organic vapor with CH_2Cl_2 vapor and excess argon to give final sample concentrations of $Ar/CH_2Cl_2/C_8H_{10} = 1200/1/1$ and $Ar/CH_2Cl_2/C_{10}H_{12} = 400/1/1$. These gas samples were condensed at approximately 1 mmol h^{-1} to form the subject matrix samples.

RESULTS

Matrix photoionization experiments were performed with C_8H_{10} and $C_{10}H_{12}$ precursors to prepare parent radical cation subjects for study of photochemical rearrangements among cation structural isomers.

Octatetraene cations

The visible spectrum of an argon/octatetraene/methylene chloride matrix sample subjected to argon resonance photoionization from a 1 mm orifice discharge tube during condensation at 15 K is shown in Fig. 1(a); a broad $CH_2Cl_2^+$ band at 350 nm from photoionization of some electron trapping molecules is not shown.[24] The relative intensities of the structured absorption peaks are similar to those observed in earlier experiments using a 3 mm orifice discharge tube (t origin A = absorbance = 0.15), but the positions of the band maxima are slightly different as listed in Table 1, and there is less evidence of the site splittings in the present experiments. The sample was irradiated by approximately 50 mW of 454.5 nm argon ion laser light directly into the s band at 454.8 nm, and the resulting spectrum, Fig. 1(b), shows a complete destruction of the o, p, q, r and s bands and a 70% increase in the t band system (origin increased to $A = 0.25$). The sample was next irradiated by the 420–470 nm band pass output from the high pressure mercury arc into the strong t band system; the spectrum in Fig. 1(c) shows a 70% decrease in the t band system (origin to $A = 0.08$), and reproduction of the o, p, q, r and s bands with increased absorbances. Irradiation next at 472.7 nm (approx. 50 mW) directly into the q band at 472.4 nm destroyed the o, p, and q bands, increased the r band by 15% and doubled the t band absorbance (origin increased to $A = 0.16$). The sample was again irradiated at 420–470 nm, and the spectrum in Fig. 1(e) shows 75% of the band absorbance of Fig. 1(c). Irradiation next at 488.0 nm (approx. 500 mW) for 5 min into the red side of the 486.8 nm p band destroyed the o and p bands, decreased q, and increased r, s, and t (origin $A = 0.14$).

Another octatetraene experiment was performed; concurrent photoionization and sample condensation for 155 min produced a spectrum similar to Fig. 1(a) with double the absorbance (t origin $A = 0.34$). This time laser lines were employed with decreasing wave-

Table 1. Absorption maxima (nm) following argon matrix photoionization of all-*trans*-octatetraene in solid argon

Absorptions	Identification	Absorptions	Identification
497.5	o	446.3	t (origin)
486.0	p	440.0	t
472.4	q	433.3	t
461.8	r	427.6	t
454.8	s	422.3	t
		417.6	t

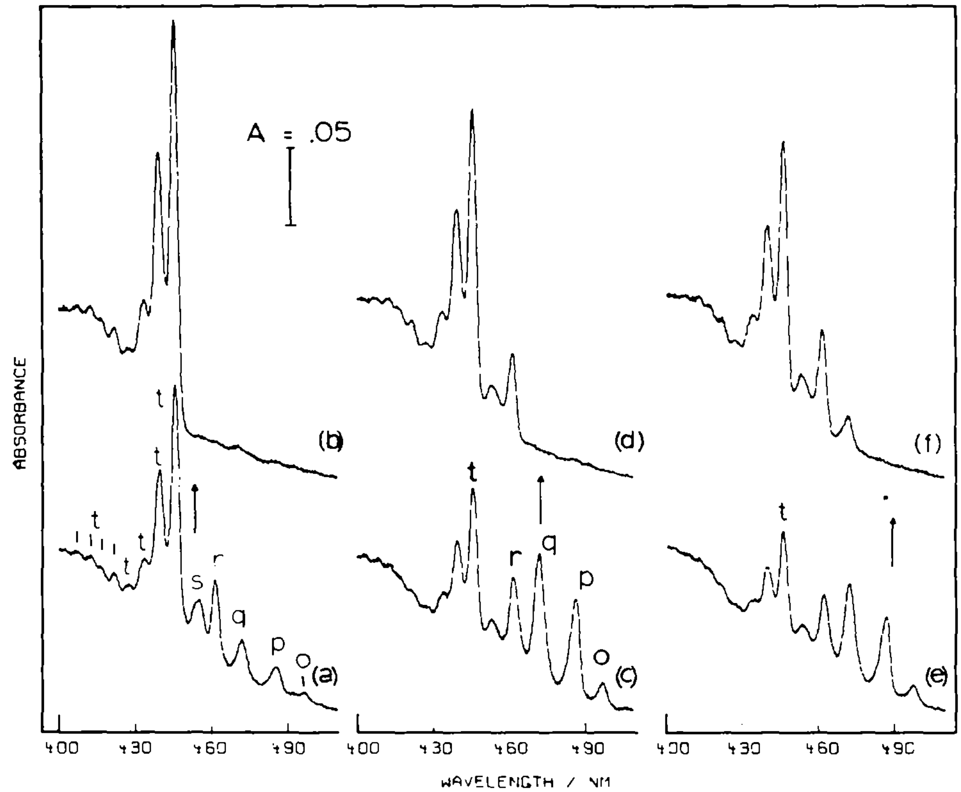


Fig. 1. Visible absorption spectra of argon/octatetraene/CH_2Cl_2 = 1200/1/1 sample: (a) after condensation at 15 K for 80 min with concurrent argon resonance photoionization; (b) after irradiation by 454.5 nm argon ion laser (approximately 50 mW; position indicated by arrow) for 15 min; (c) after mercury arc 420–470 nm band pass (Corning 5113 and 3389 filters) irradiation from high pressure mercury arc for 15 min; (d) after laser irradiation at 472.7 nm (50 mW; position given by arrow) for 10 min; (e) after repeat of 420–470 nm irradiation; and (f) after laser irradiation at 488.0 nm (500 mW; position indicated by arrow) for 5 min.

lengths. Irradiation at 496.5 nm (approx. 150 mW) for 12 min destroyed the o band, decreased p, left q unchanged, increased r by 25%, decreased s and increased t by 20%. Irradiation at 488.0 nm (approx. 500 mW) for 5 min destroyed a weak p band, slightly (~5%) decreased the q, r and s bands and slightly increased the t bands. Irradiation next at 472.7 nm (approx. 50 mW) destroyed q, decreased r, and increased t by 10%. Irradiation at 454.5 nm (approx. 50 mW) destroyed the r and s bands and increased the t band system by 20% (origin to $A = 0.55$) giving a spectrum like Fig. 1(b). A final 420–470 nm mercury arc photolysis produced a spectrum much like that in Fig. 1(c).

Several similar experiments were performed with the structural isomeric bicyclooctadiene precursor. After 5-fold more sample was photoionized during condensation, the visible spectrum in Fig. 2(a) reveals comparable o, p, q and r band absorbances, substantially reduced t band absorbances, and peaks in good agreement (most ±0.2 nm) with those in Table 1. Mercury arc photolysis of this sample in the near-UV increased all peaks, particularly o, p, q, and r, as shown in Fig. 2(b). Further photolysis at 470–650 nm, Fig. 2(c), produced a spectrum similar to Fig. 1(d), but with about twice the absorbance. Final photolysis at 420–470 nm gave a spectrum, Fig. 2(d), with approximately the same product distribution and double the absorbance of the comparable spectrum in Fig. 1(e).

Decapentaene cations

Figure 3(a) illustrates the spectrum following 40 min of 220–1000 nm photolysis of a matrix prepared by argon resonance photoionization of an argon/dicyclopentadiene/methylene chloride sample during condensation for 4 h at 15 K. This spectrum is essentially identical to the analogous spectrum of Fig. 1(d) from an earlier $C_{10}H_{12}$ cation study;[18] the product bands and labels are given in Table 2 for the present laser photolysis experiments. The matrix was sequentially irradiated with approximately 50 mW of yellow and green krypton ion laser light; the former had no effect, but the latter caused photochemical changes that are illustrated in Figs 3(b) and (c). Irradiation at 530.9 nm on the high energy side of band q reduced this band, produced a new shoulder absorption p and increased the strong s and t bands by 10%. Irradiation at 520.8 nm, coincident with the strong s absorption, completely burned out the s absorption at 520.8 nm and left a 519.0 nm shoulder and a sharp, weak 521.6 nm band in this region; the p and q absorptions increased substantially, a weak new o absorption was produced, and the t band system increased 10% with the peak shifted to 513.9 nm. The matrix was subsequently irradiated with approximately 500 mW

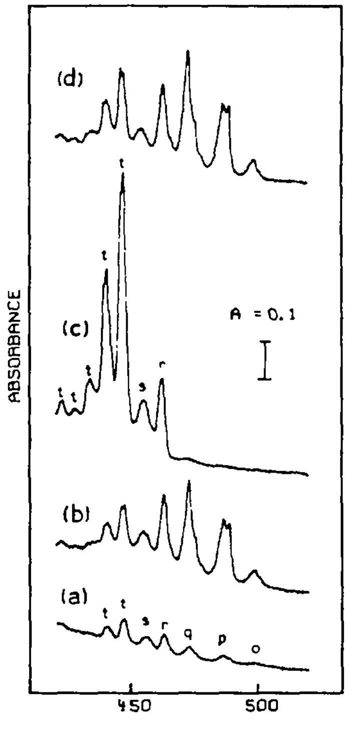


Fig. 2. Visible absorption spectra of argon/bicyclooctadiene/CH_2Cl_2 = 1200/1/1 sample: (a) after condensation at 15 K for 5 h with simultaneous vacuum UV photoionization; (b) after mercury arc photolysis at 310–410 nm for 15 min; (c) after 470–650 nm irradiation; and (d) after 420–470 nm photolysis.

of green and blue argon ion laser lines and the spectroscopic effects are shown in Figs 3(d)–(f). Irradiation at 514.5 nm into the strong 513.9 nm band burned a hole at this position, left a weaker series of t bands beginning at 512.4 nm, produced sharp, new q, r, and s absorptions, and decreased the a and b bands. Irradiation at 476.5 nm reduced the t band series by 25%, produced a sharp new shoulder t series beginning at 515.1 nm, reduced the s and q bands, increased the r band, and decreased the c band relative to the d band. Irradiation at 488.0 nm slightly increased the a, b and c bands, reduced the q, r and s bands and restored the t bands to their original positions and absorbances.

This experiment was repeated three times using different argon and krypton ion laser lines and irradiation sequences. In all of these studies, 514.5 nm irradiation burned a hole to the baseline, left blue-shifted t bands, and increased the r and q bands. Irradiation at 457.9 nm decreased the d, q, and s bands, increased the c band, and substantially increased the t bands.

Decapentaene itself was studied in a series of similar experiments. The initial spectrum after sample photoionization, Fig. 4(a), shows the very strong sharp t bands that were produced only after secondary photolysis in the above dicyclopentadiene experiments and also shows much weaker s, p and o bands. Mercury arc photolysis at 520–1000 nm destroyed the weak o and p bands and increased the s and t bands by 10%, as shown in Fig. 4(b). Photolysis at 504–518 nm through a dielectric filter decreased the s and t bands by 10% and restored the p band, Fig. 4(c). The 514.5 nm laser line had a markedly greater effect on a similar sample, which was demonstrated in Figs 3(c) and (d). Finally, photolysis at 290–1000 nm throughout all of the product absorptions increased only the r and t bands, as shown in Fig. 4(d).

DISCUSSION

The new product absorptions will be identified, and the photochemical rearrangements using visible laser lines will be discussed.

Identification

The basis for identification of the strong, sharp t band systems as all-*trans*-octatetraene cation and all-*trans*-decapentaene cation has been outlined in our earlier papers.[16,18] Briefly, the precursors were ionized directly by the 11.6–11.8 eV output from the argon resonance lamp.[20] Most electrons removed by photoionization were dissociatively captured[25] by CH_2Cl_2 to give CH_2Cl and Cl^-, and these electrons were retained by chloride during the subsequent visible photochemistry since the detachment threshold for chloride is approximately 340 nm.[26] These product band yields decreased substantially in experiments without CH_2Cl_2 added, which supports their assignment to cations. Without CH_2Cl_2 added, electron trapping during the photoionization process is less efficient, which of course, decreases the effective cation yield, and photodetachment from less stable parent anion traps during visible photolysis makes photoneutralization competitive with cation rearrangement. Hence, the CH_2Cl_2 electron trap is an important part of these experiments.

The photochemical interconversion of bands for each compound, and the observation of the same bands with acyclic precursors and electrocyclic ring

Table 2. Absorption maxima (nm) following matrix photoionization and photolysis of dicyclopentadiene in solid argon

Absorptions	Identification	Absorptions	Identification
545	o	499.7	t
537	p	492.9	t
532.8	q		
525.3	r	482.1	a
520.8	s	476.8	b
513.6	t (origin)	469.7	c
506.7	t	459.6	d

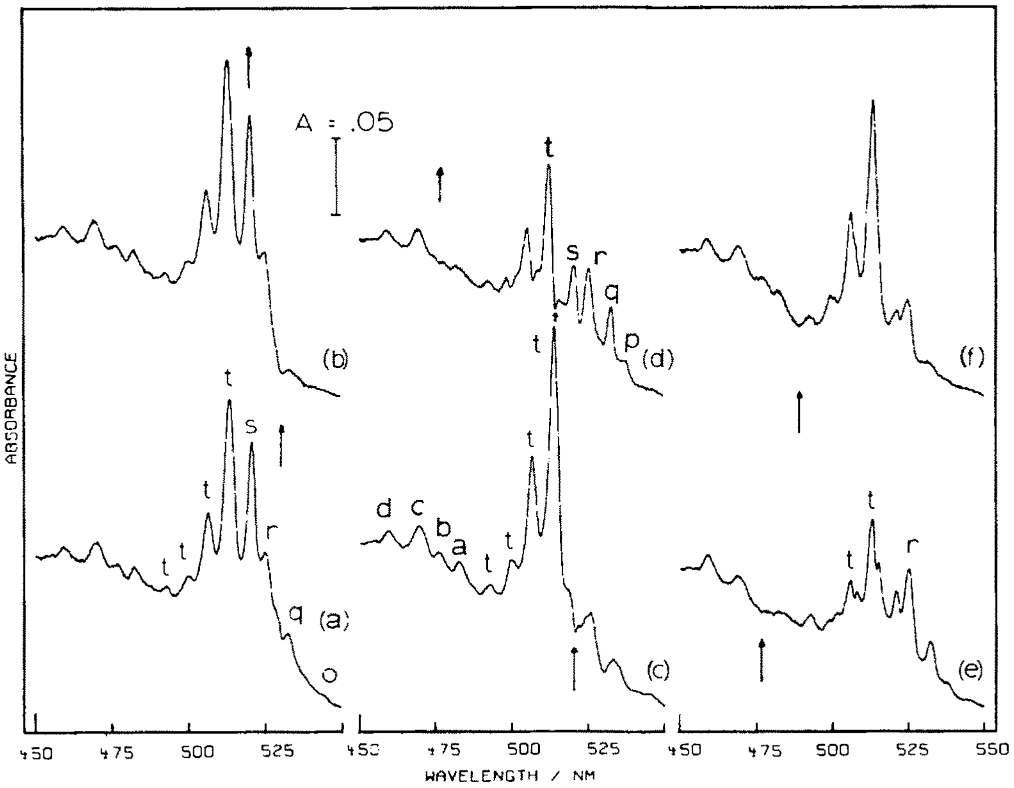


Fig. 3. Visible absorption spectra of argon/dicyclopentadiene/CH_2Cl_2 = 400/1/1 sample: (a) after condensation at 15 K for 4 h during exposure to argon resonance photoionization and 220–1000 nm photolysis for 40 min, (b) after irradiation by 530.9 nm krypton ion laser (50 mW; position indicated by arrow) for 30 min; (c) after irradiation at 520.8 nm for 37 min; (d) after irradiation by 514.5 nm argon ion laser (approximately 500 mW, position marked by arrow) for 20 min, and (f) after irradiation at 488.0 nm for 14 min.

opening[27] of cyclic precursors support the conjugated polyene cation identification. In addition, theory predicts transitions for polyene cations in the visible region,[28] which is substantially lower energy than observed for the neutral precurors.[23] Finally, the markedly increased yield of the t band systems using the all-*trans*-precursors substantiates the identification of the all-*trans*-cations.

Octatetraene cation photochemistry

The absorption spectra in Fig. 1 produced from all-*trans*-octatetraene and Fig. 2 from bicyclooctadiene demonstrate that the t bands are due to the all-*trans*-cation **5** and that the o, p, q, r and s bands are isomers and conformers with mixtures of *cis* and *trans* configurations. Since the visible transition involves an upper state with some degree of antibonding π character,[6,16] photoexcitation can cause rotations about double as well as single bonds. The mixed *cis* configurations will be difficult to identify from spectra alone, but some clues are provided by the present observations. The destruction of all but t bands with 454.5 nm irradiation (Fig. 1(b)) demonstrates that the all-*trans* configuration is the most photochemically stable, and that the o, p, q, and r band systems have weak absorption at 454.5 nm. The increase of only r and t with 496.5 nm radiation (described but not shown) suggests that r is due to the second most photochemically stable arrangement. It also appears reasonable, even for excited conjugated polyene cations, that rotation about a single bond will be more likely than rotation about a double bond. This suggests *trans,cis*-octatetraene cation **6**, a stable isomer, which can further rearrange to **5**, as the source of the r band; the *cis,cis*-configuration is less likely to be formed in these experiments.

The five *s-cis*-conformers formed by rotations about single bonds in all-*trans*-cation **5** are candidates for the o, p, q and s bands as are possibly rotations of one single bond of the *trans,cis*-cation **6**. Of these the two likely are *s-cis* (2–3) **7** and *s-cis* (4–5) **8**, which involve one rotation and the former has twice the statistical weight of the latter. Photoionization of all-*trans*-C_8H_{10} (Fig. 1(a)) produced equal yields of the q and s bands; however, 420–470 nm irradiation of cation **5** produced a 6-fold greater yield of q and a 5-fold greater yield of p compared to s (Figs 1(a) and (c)) which is reproduced (Fig. 1(e)). We tentatively identify q as **7** and s as **8** since they appear to be produced directly from **5**; the product distribution will also be affected by the dynamics of rearrangement within the matrix cage. The p and o bands remain, and p clearly arises from the more probable configuration. Considering rotamers of **5** that involve two single-bond rotations, the *s-cis* (2–3, 4–5) conformer has twice the probability of *s-cis* (2–3, 6–7); we tentatively associate p with the former and o with the latter rotamer.

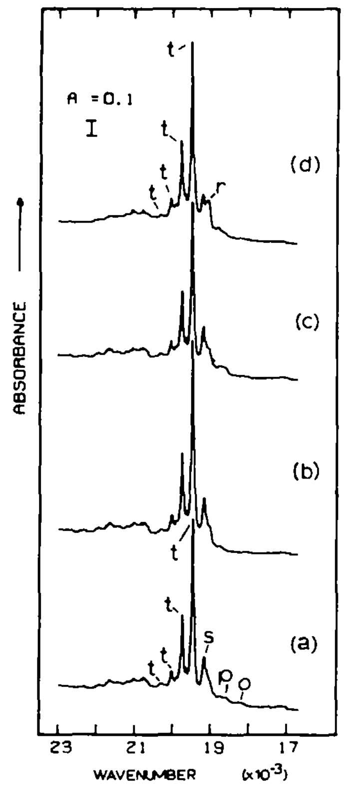
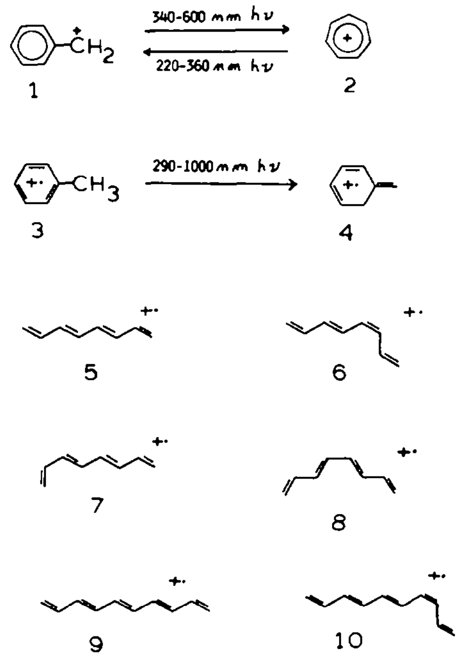


Fig. 4. Visible absorption spectra of argon/decapentaene/CH_2Cl_2 = 400/1/1 sample: (a) after photoionization during condensation at 15 K for 5 h; (b) after mercury arc photolysis at 520–1000 nm for 15 min; (c) after mercury arc photolysis through 504–518 nm dielectric filter for 2 h; and (d) after 290–1000 nm photolysis for 15 min.

Decapentaene cation photochemistry

The absorption spectra in Fig. 4 produced by photoionization of all-*trans*-decapentaene show that the t bands produced by rearrangement of dicyclopentadiene cations in Fig. 3 are due to the all-*trans*-decapentaene cation **9**. The q, r and s bands produced in higher relative yield in Fig. 3 are clearly due to decapentaene cations with *cis* and/or *s-cis* configurations. In the earlier dicyclopentadiene experiments, the s band system was dominant after 290–1000 nm photolysis, but the t system increased at the expense of s on 220–1000 nm irradiation.[18] This suggests that the s absorption arises from the next most stable isomer *trans,trans,cis*-decapentaene cation **10**, which upon sustained photoexcitation can rearrange to the all-*trans*-cation **9**. The *trans,cis,trans* isomer is, of course, a possibility, but the latter is only half as probable as **10**.

The laser photolysis is particularly graphic in Fig. 3; irradiation in the s band destroyed s and produced a marked increase in the t band system. Irradiation at 514.5 nm, almost coincident with the t origin peak at 513.9 nm, burned a hole to the baseline, produced a weaker 1.5 nm blue-shifted t band system, and increased q, r and s bands. Irradiation at 476.5 nm reduced t and produced a new weaker red t series, and increased the r band relative to the s absorption. The production of r at the expense of t suggests that the r band likely arises from a rotamer of **9**; the q band is conceivably due to another rotamer of **9**. Any attempt to associate the weaker o and p bands with specific rotamers of **9** or **10** would be speculative.



It is also noted that the a, b, c and d bands change relative intensities during the photolysis sequence. These bands were tentatively associated with cyclodecatetraene cation precursors to acyclicdecapentaene cations in the earlier study, based on their appearance in the octatetraene region and photochemical history; the laser photolysis observations tend to support this identification.

CONCLUSIONS

Argon matrix photoionization methods successfully produced and trapped octatetraene and decapentaene cations in solid argon with electron trapping by CH_2Cl_2 doped into the sample. Laser photolysis in bands due to specific isomers and conformers of these conjugated polyene cations caused reversible rearrangements. In the case of all-*trans*-decapentaene cation, laser photolysis created and destroyed absorption due to this one isomer suggesting that the observed band is an inhomogeneous collection of argon matrix packing configurations around the relatively large all-*trans*-decapentaene cation, and the narrow laser photolysis beam selectively rearranged some but not all of these matrix packing arrangements or "sites" giving rise to absorption in the band profile. Visible laser photolysis caused the same rearrangements as the filtered mercury arc, but the more narrowly defined laser source allowed the rearrangements between different isomers and conformers to be done in a more stepwise manner.

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