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Laser Photodissociation Spectrum of Gas-Phase 1,3,5-Hexatriene Radical Cation

Sir:

Photodissociation spectroscopy of gas-phase ions[1] is a convenient and widely applicable approach to obtaining optical spectroscopic information about such ions. Spectra of a number of ions have been published[1-6] with an optical resolution of the order of 10–20 nm, and the spectra have been found to be highly informative in regard to both the structures of the ions and the properties of their excited electronic states. It has been recognized that spectra of higher resolution showing resolved vibrational or rotational structure would greatly increase the amount and usefulness of the information obtained about an ionic species, and following this path, at least two groups of researchers have used tunable laser techniques to obtain high-resolution spectra.[3,6] The results of these efforts have been disappointing in that, although spectra of good quality were obtained, there was no apparent resolved vibrational structure in the ions studied. The present communication describes the laser photodissociation of the first cation to display prominent resolved vibrational structure, the *trans*-1,3,5-hexatriene cation; the partial analysis of this spectrum so far achieved confirms the expectation that this approach yields high quality information about the vibrational frequencies and vibronic transitions of the ion.

The spectrum at 1 nm (or $\sim$0.003 eV) resolution is shown in Figure 1, and was obtained using conventional steady-state ICR photodissociation methods (11 eV ionizing energy, $\sim 5 \times 10^{-8}$ Torr pressure), with a Coherent Radiation Model 490 CW tunable dye laser pumped by a Model CR-12 argon-ion laser as light source. Dyes used were sodium fluorescein (530–570 nm), rhodamine 6-G (570–645 nm), and rhodamine B (635–670 nm). Because of temporal and spatial variations of laser output for tuning over a wide range, the spectrum was pieced together from segments of varying width, as indicated by the different symbols in Figure 1; except for the interface at 570 nm, where the dyes overlap at only one wavelength, all segment-matching was based on overlap at several wavelengths. Each data series was taken at constant light intensity, removing the uncertainty associated with correcting steady-state ICR photodissociation data for varying light intensity.[7] Ir analysis[8] showed the sample to be a roughly 4:1 mixture of trans and cis isomers. Wavelength was calibrated against a Schoeffel monochromator, and is believed accurate within 1 nm. The laser bandwidth is given as less than 0.1 nm by the manufacturer.

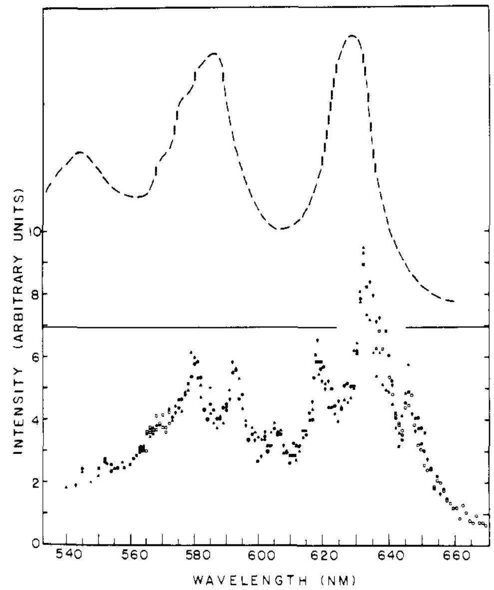

Figure 1. Laser photodissociation spectrum (lower curve) and photoelectron spectrum[9] (upper curve) of 1,3,5-hexatriene radical cation. The photoelectron spectrum is adjusted to put the energy zero at the ion ground state, and plotted in wavelength units. (The photoelectronbaseline is the line at $\sim$7 intensity units.)

Plotted for comparison in Figure 1 is the photoelectron spectrum of *trans*-1,3,5-hexatriene for this energy region,[9] with the zero of energy shifted to the position of the ion ground state. The electronic transition in question here is a $\pi \rightarrow \pi^*$ transition of the cation which promotes an electron from the second-highest occupied π orbital into the highest occupied orbital;[10] therefore the excited state involved is a single-electron excitation from the neutral molecule, and as such is expected to be observed in both photoelectron and photodissociation spectra.[2] As has been discussed,[11] the connection between the photoelectron and photodissociation spectra for such a state is direct, and the two curves in Figure 1 should agree except to the extent that the Franck-Condon factors for photoelectron (initial neutral molecule) and photodissociation (initial ion ground state) differ.

The photodissociation spectrum clearly shows the same vibrational progression at about 1200 cm^{-1} as the photoelectron spectrum; in addition, the higher resolution clearly reveals another clear progression at 350 ± 10 cm^{-1}. The series of three peaks at 632.5, 617, and 605 nm is most probably a typical short vibrational progression corresponding to a 350 cm^{-1} normal mode, and the 0–0 transition is assigned at 632.5 nm; a hot band corresponding to the $1 \rightarrow 0$ transition of the low-energy 350 cm^{-1} vibration is expected to have significant intensity at 646.0 nm, and definitely must account for some or all of the peak at this position. The position of the 0–0 transition for the cis isomer is not certain (assuming it to retain its structural identity) and could be taken to account for some of the intensity at 646.0 nm; however, photoelectron data[8] suggest that it should be of the order of 5 nm to the red of trans, and indeed the photodissociation spectrum does give some indication of a shoulder on the low-energy side of the 632.5-nm peak.

Definitive analysis of this spectrum will definitely require separate spectra of the cis and trans isomers, which are now being obtained. It may be noted for now, however, that a satisfactory fit to the observed 646–605-nm region is possible on the assumption of equal Franck-Condon factors for all the $n \rightarrow n \pm 1$ transitions of the 350-cm^{-1} vibration, if the effective temperature of the 350-cm^{-1} normal mode is near 1000 K. In the process of obtaining this fit it was found that the assumed shoulder due to the cis isomer has the effect of shifting the apparent position of the 0–0 peak by 1–2 nm to the red, so the true 0–0 position for the trans isomer is somewhat uncertain, and perhaps somewhat shorter than 632.5 nm.[12] The structure of the second series between 592.5 and 560.0 nm is not a reasonable looking progression for a single mode: either the apparent 1200-cm^{-1} mode seen in the photoelectron spectrum is in fact a superposition of nearly degenerate modes, or there is some other more subtle effect leading to the odd looking intensity pattern of these peaks.

Based on the normal-mode analysis of the neutral molecule,[13] the observed ion vibrational progressions are reasonable: only A_g vibrations can be excited in this transition, and since it is a Π-system excitation, only carbon-framework motions are expected to be significantly excited. The ion progression at 350 cm^{-1} corresponds to one of the two framework bending modes ν_{12} (453 cm^{-1} in the neutral) and ν_{13} (347 cm^{-1}), while the progression at $\sim$1200 cm^{-1} is associated with the framework stretching modes ν_5–ν_{10} distributed from 1187 to 1623 cm^{-1} in the neutral. A Huckel-MO analysis[14] of the Π states involved in this optical transition yields additional qualitative insight: The principal bond length changes on excitation should be a lengthening of C_2–C_3 (and C_4–C_5) and a shortening of C_3–C_4. Two modes[13] closely correspond to this motion: ν_5 (1623 cm^{-1}) and ν_9 (1238 cm^{-1}). It is thus reasonable to suspect, as above, the simultaneous excitation of two framework-stretching vibrations in the ion. No similar elementary considerations seem appropriate to the bending motion, and we are unable to choose between the two likely modes.

The photodissociation rate is linear in light intensity; it appears that the heat of dissociation to $C_6H_7^+$ + H is less than the 2.0 eV corresponding to the 0–0 excitation, and that there is no reason to suspect a two-photon process.[15]

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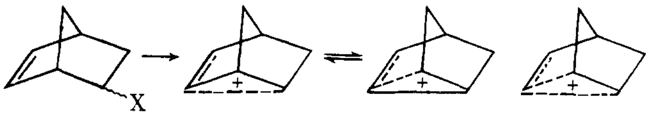
Reactions of 5-Norbornene-2-diazonium Ions and Nortricyclene-3-diazonium Ions

Sir:

The nature of the carbocations intervening in the acetolysis of 5-norbornen-2-yl brosylates (**1**-OBs) has not been established satisfactorily.[1] Both unsymmetrical (**2a**) and symmetrical delocalization (**2c**) have been postulated, based on contradicting reports on the scrambling of labels over positions 2,3 and 1,7.[2-6] Readdition of acetic acid to norbornadiene as a source of scrambling has been maintained by one group[6] but rejected by others.[5]



1 2a 2b 2c

We report here on the decomposition of 5-norbornene-2-diazonium ions (**4**) and nortricyclene-3-diazonium ions (**8**) in aqueous sodium hydroxide. Reactants and reaction conditions are such that carbocations will be generated and trapped irreversibly. The nature of the intermediates was investigated with the aid of optically active precursors as well as by deuterium labels.

Photolysis of tosylhydrazone sodium salts generates diazo compounds[7] which are protonated by ROH to give diazonium ions and products derived therefrom.[8] 5-Norbornen-2-one tosylhydrazone (**3**) and nortricyclanone tosylhydrazone (**7**) afforded product distributions depending but slightly on the concentration of base (Scheme I, Table I). Optically active **3**[9] produced **5** with 40–50% retention of configuration (50–60% racemization) (Table II). Photolysis of **3** in D_2O-DONa introduced deuterium at C-2 of **4**. Mass spectrometric analysis[5,6] of [$^2H_1$]-**5** indicated 27–28% rearrangement of D (i.e., 54–56% equilibration), in agreement with the polarimetric data.

These observations require an asymmetric precursor from which 40–50% of **5** is derived. If the asymmetric precursor was the homoallylic ion **2a**, it should produce **6** with predominant

Scheme I

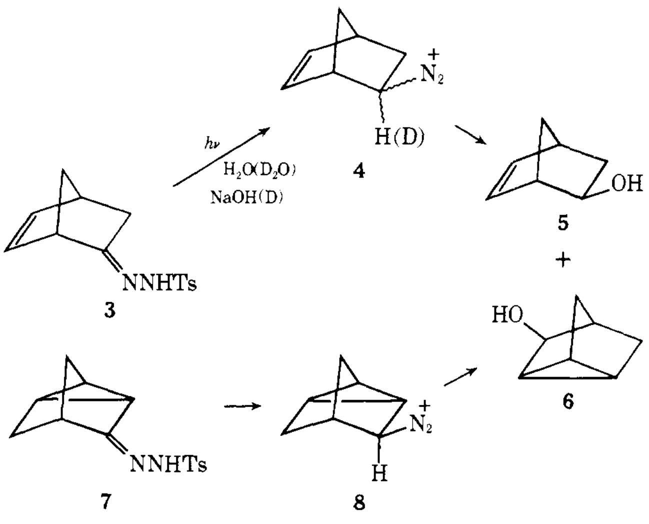


Table I. Product Distributions **5**/**6** Obtained from **4** and **8**

Precursor	**3**	**7**	Scheme III
0.1 N NaOH	9.9/90.1	3.9/96.1	4.0/96.0
0.2 N NaOH	10.3/89.7	3.9/96.1	3.6/96.4
0.5 N NaOH	10.8/89.2	4.4/95.6	
1.0 N NaOH	11.4/88.6	4.5/95.5	