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Raman Study of the Photochemical Ylide Intermediate Produced from a 1,3-diazabicyclo[3.1.0]hex-3-ene

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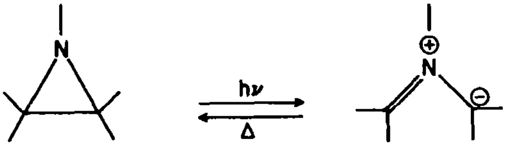
The resonant Raman spectrum of the photochemically produced blue ylide of (A) was obtained in the solid surface. These data are compared with the Raman spectrum of the parent compound. Most of the intense peaks can be understood on the basis of group vibrations of nitrobenzene, benzene, aziridine, and isoimidazole. The symmetric NO_2 stretching (1340 cm^{-1}) is down-shifted in frequency by 24 cm^{-1} in going from the bicyclic azirdine to its ylide. This is rationalized by the drop of the double bond order of the NO_2 through electron resonance.

1 INTRODUCTION

The solid state and low temperature matrix isolation photolysis of aziridines is known to produce highly colored azomethine ylides.[1,2] The stability of these intermediates in the solid state is dependent on both steric and electronic factors. The effect of ring strain due to a second fused ring and strong electron withdrawing group is reflected in the increased solid state lifetime



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of the ylide at room temperature (vide infra). To better understand these effects, the Raman spectra of (A) and its ylide were obtained.

First, the assignment of molecular vibrations of 1,3-diazabicyclo[3.1.0]hex-3-ene will be presented. Then the spectral change in the photochemically produced intermediate will be examined. The frequency shift of the NO_2 symmetric stretching is explained by the resonance contribution to the structure of the dipolar intermediate.

II EXPERIMENTAL SECTION

All bicyclic aziridines shown in Figure 1 were prepared by Heine-Padwa methods.[3,4] Compound (D) was prepared by the procedure described in Ref. 4 using 1,3-diaminopropane instead of ethylene diamine. All compounds in Figure 1 were recrystallized twice from absolute ethanol and dried in a vacuum decicator prior to use. Melting points, determined on a Köfler hot stage, are also given in Figure 1.

A tunable Molectron dye laser DL300 pumped by a UV1000 pulsed nitrogen laser was used in the resonant Raman study of the blue ylides derived from bicyclic aziridines. The Raman scattering of the blue powder produced by continuous photolysis was obtained by front surface excitation. The scattered light was focused onto the entrance slit of a SPEX 0.85 m

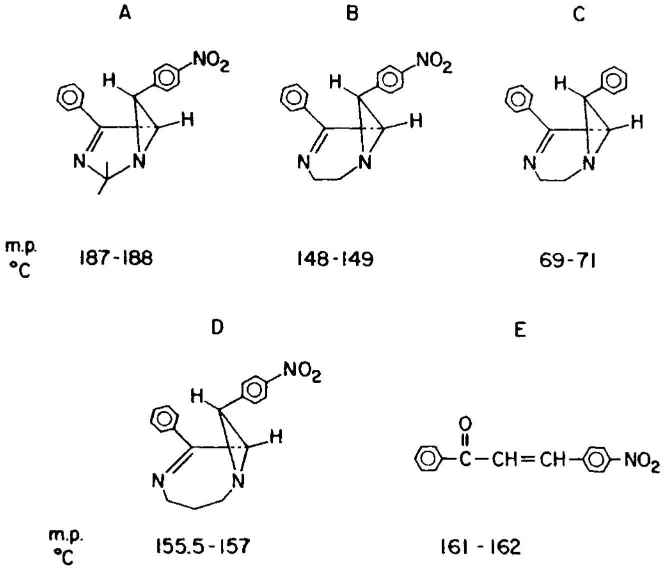


FIGURE 1 Structure of compounds used in this study.

Czerny-Turner double monochromator equipped with RCA C31034 PM tube. The pulsed signal was time resolved by using a Tektronix 547 oscilloscope equipped with a 1S1 plug-in. Laser Raman spectra of the bicyclic aziridines themselves were obtained by using a SPEX Ramalog. A Spectral Physics argon ion laser operated in the stabilized mode was used as the light source. The typical operating power was 400 mw at 5145 Å.

III RESULTS AND DISCUSSIONS

A Raman spectrum of (A)

The Raman spectrum obtained by using 514.5 nm argon ion laser radiation is shown in Figure 2. More than 42 lines were observed. Our approach in attempting to understand this complicated spectrum was to isolate vibrational lines due to nitrobenzene, benzene, aziridine, and the five-membered diaza ring. To understand the contribution due to the diaza ring, we have studied a 1,4-diazabicyclo[4.1.0]hep-4-ene (B) and a 1,5-diazabicyclo-[5.1.0]oct-5-ene (D). This approach is probably oversimplified because after the four components are bonded together, the force constants of the basic

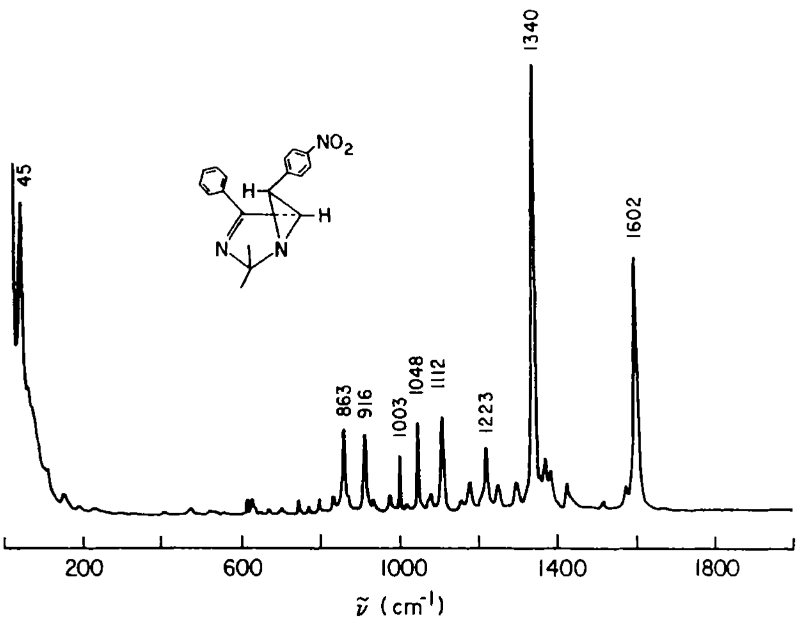


FIGURE 2 Raman spectrum of 1.3-diaza, 2,2-dimethyl, 4-phenyl, 6-exo-*p*-nitrophenyl bicyclo[3.1.0]hex-3-ene.

TABLE I

Vibrational frequencies of (A)

No.	$\tilde{\nu}$(cm^{-1})	Intensity	Assignment	B	C	D	E	F[a]	G[a]
1	45		phonon						
2	156	3							
3	193	1							
4	230	1							
5	410	1							
6	474	1							
7	618	4	benzenic vib.						
8	631	3	benzenic vib.						
9	648	1							
10	671	1							
11	703	2							
12	750	2							
13	774	2							
14	880	3							
15	834	3							
16	863	18	benzenic vib.	yes	yes	yes	yes	yes	yes
17	916	17	C—H out of plane bending in CH_3 groups.	no	no	no	no	no	no
18	938	3							
19	979	3	benzenic vib.						
20	1003	12	benzenic vib.	yes	yes	yes	yes	yes	yes
21	1048	20	five member ring of aziridine vib.	yes	yes	yes	no	no	no
22	1083	3							
23	1112	20	C—N stretch in ϕNO_2	yes	no	yes	yes	yes	no
24	1160	2							
25	1183	5							
26	1223	13	aziridine vib.	yes	yes	yes	no	no	no
27	1257	4							
28	1299	5							
29	1340	100	NO_2 sym. stretch	yes	no	yes	yes	yes	no
30	1372	6	CH_3—C deformation						
31	1387	5							
32	1429	5	CH_2 deformation						
33	1523	2	NO_2 anti-sym. stretch						
34	1578	3							
35	1602	57	benzenic vib.	yes	yes	yes	yes	yes	yes
36	1669	1	C=N stretch						
37	2460	0.4	1112 + 1340						
38	2683	0.5	2 × NO_2 stretch						
39	2946	1	CH stretch in CH_3 group	no	no	no	no	no	no
40	2994	1	CH stretch in CH_3 group	no	no	no	no	no	no
41	3055	1	CH stretch in benzene	yes	yes	yes	yes	yes	yes
42	3072	2	CH stretch in benzene	yes	yes	yes	yes	yes	yes

[a] F and G represent nitrobenzene and benzene, respectively.

components will undoubtedly change, especially since these bicyclic molecules are highly strained. Nevertheless, most of the intense bands of the 1,3-diazabicyclo[3.1.0]hex-3-ene can be accounted for satisfactorily as listed in Table I. Also noted in Table I is the presence or absence of the corresponding vibrational line of related molecules to support the assignment.

The eight lines at 863, 916, 1003, 1048, 1112, 1223, 1340, and 1602 cm^{-1} are intense lines. Three of them at 863, 1003, and 1602 cm^{-1} appear in all the diazabicycloaziridine compounds, the precusor, nitrobenzene, and benzene. These three lines are undoubtedly benzenic vibrations, ν_{10a}, ν_2, and ν_{8a}, respectively. Two most important vibrations, the 1340 and 1112 cm^{-1} vibrations, which will be discussed in more detail in the next section, are undoubtedly due to the presence of NO_2 group since they are absent in compound (C) and benzene. The 1340 cm^{-1} vibration is the symmetric NO_2 stretching, whereas the 1112 cm^{-1} is the phenyl vibration involving C—N stretching.[5] The 916 cm^{-1} vibration is assigned to $C—CH_3$ stretching. It is present in the 1,3-diazabicyclo[3.1.0]hex-3-ene (A) but absent in the rest of the diazabicycloaziridines. The 1223 cm^{-1} vibration, present in all diazabicyclo compounds and in aziridine (ethylenimine) is believed to be the aziridine ring vibration. The only intense vibration which is uncertain is the 1048 cm^{-1} vibration, but it is probably related with aziridine or the second fused ring vibration.

Among the weak lines, the one at 2460 cm^{-1} is clearly due to the combination of the 1112 and 1340 cm^{-1} vibrations, whereas the 2683 cm^{-1} line is the overtone of NO_2 symmetric stretching. The 3055 cm^{-1} line is clearly due to the C—H stretching in the phenyl or the nitrophenyl group. The 2946 and 2994 cm^{-1} vibrations are due to the C—H stretching of the methyl groups and only present in the 1,3-diaza compound, which has two methyl groups. The weak vibrational lines at 1372, 1429, and 1669 cm^{-1} are tentatively assigned[6] to $CH_3—C$ deformation, CH_2 deformation and C=N stretching, respectively.

B Absorption of bicyclic aziridine ylides

Upon exposure to light, the colorless aziridine crystals develop a visible absorption band which has been attributed to the azomethine ylide structure. In the solid state, these photochemical reactions are restricted to the surface (due to the strong absorption of the ylide). In order to obtain the vibrational spectrum of the colored intermediate, one would obviously take advantage of the resonance effect by tuning the laser near the absorption edge of the ylide.

Table II gives the absorption maximum of the ylide in 2-methyltetrahydrofuran matrix at 77 K. All the ylides, except that of compound (C), are blue

TABLE II

Absorption maxima and lifetimes of bicyclic aziridine ylides

Compound	Color	λ max (nm)	Lifetime[a] (hr)
A	Blue	605	12
B	Blue	605	2
C	Pink	545	0.8
D	Blue	610 (broad)	0.07

[a] The time needed for reversion of the ylide in the solid state at room temperature back to its parent compound until no colour is visible.

colored. The stability of the ylide decreases in the order of A > B > C > D, as clearly seen from the lifetimes given in Table II. By decreasing the strain of the fused rings, namely from a five membered fused ring to a six or seven membered ring, the ylide has a shorter lifetime. On the other hand, by introducing an electron withdrawing group in the para position on the phenyl group, the stability of the intermediate is at least doubled as is evident by comparing the lifetime of compounds (B) and (C). This electronic factor will be further discussed by examining the resonant Raman spectra of the ylides.

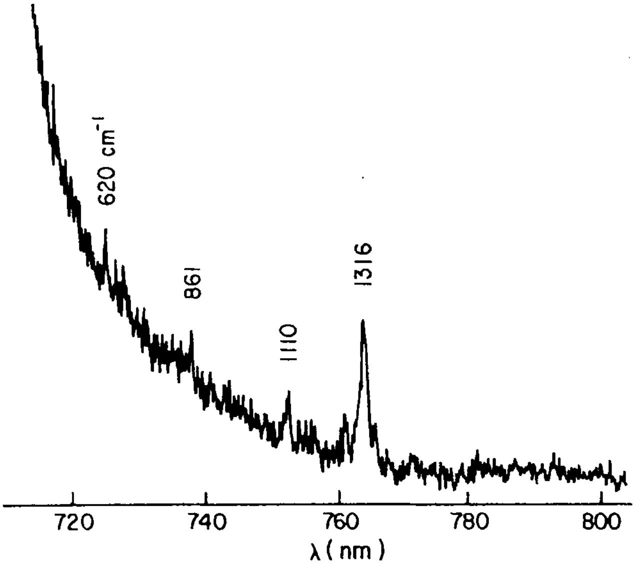
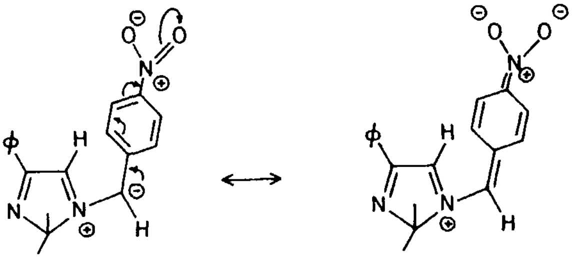


FIGURE 3 Resonant Raman spectrum of the ylide derived from (A) under continuous 4 w low pressure Hg lamp irradiation.

C Resonant Raman of (A)

The resonant Raman spectrum of the photochemical intermediate is shown in Figure 3. The laser wavelength used is 691.5 nm. Only four prominent lines were observed. The main reason that the weak lines cannot be resolved is that too much dye fluorescence is passing through the detection system due to the front surface excitation. In addition, the resonant Raman technique is a powerful method to sort out those vibrations which are related with the chromophore. The 1316, 1110, 861 and 620 cm^{-1} vibrations are all related with the nitrophenyl vibration. The most intense vibration is related with NO_2 symmetric stretching of the nitrobenzene. It is considerably down-shifted in frequency in comparison with the parent compound. The shift in frequency is determined to be 24 ± 2 cm^{-1}. It should be noted that DoMinh and Trozzolo also observed a new 1320 cm^{-1} band in the colored intermediate.[2]

The down-shift in stretching frequency is due to a drop in bond order caused by conjugation of the 1,3-dipolar ylide into the nitrophenyl group.



It is known that the stretching frequency is sensitive to the electronegativity of the substituents at *o*- and *p*-positions. Addition of a dimethylamino group, for example, results in a reduction of the stretching frequency in nitrobenzene.[6] We have also examined the stretching in the ylide of (B). The frequency shift is 22 ± 3 cm^{-1}, which is identical to the shift of the ylide derived from (A).

Finally we wish to mention the interesting biphotonic photochemistry of (A). When (A) is irradiated by long wavelength visible light such as the red light, photochemistry should not take place since (A) does not absorb in this wavelength range. Under the intense red laser pulse, however, (A) can absorb two photons *simultaneously*. At 694 nm the dye laser can deliver a power density as high as 10^6 w/cm^2, and in such a case, we are able to see a blue spot created by the biphotonic process. As a matter of fact, the laser Raman spectrum produced by the 694 nm laser consists of both the lines due to the ylide and its parent molecule.

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