kcal/mol higher than those of their corresponding amide isomers **8** and **10**, and the increase in PA for increasing the ring size from five to six members is 2.3 kcal/mol. The unusually large stabilizing effect of the extra methylene group in **10** and **11** could be attributed to a hyperconjugative delocalization of the positive charge into the ring unavailable to the piperidinium ion. These PA effects have been interpreted in the usual way in terms of changes in ionic stabilities rather than changes in neutral stabilities. This is usually the only approach available in the absence of information about structural effects on the stabilities of the neutral species. For an alternative approach which is useful if the relative stabilities of the bases are available, see the text.

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(21) The value of $E(4)$ can range from 20 to 30 kcal/mol depending on the resonance energy assigned to pyridine and to **3**. To be complete, the scheme should also include 2 mol of hydrogen. Semiquantitative correspondence of the "aromaticity" of 2-pyridone as measured by thermodynamic and magnetic criteria has been shown: A. K. Burnham, J. Lee, T. G. Schmaltz, P. Beak, and W. H. Flygare, *J. Am. Chem. Soc.*, **99**, 1836 (1977). An extension of such a comparison to protomeric systems and other estimates of aromatic character has been reported: M. J. Cook, A. R. Katritzky, and P. Linda, *Adv. Heterocycl. Chem.*, **17**, 255 (1974).

(22) A value of 7 kcal/mol for the total inductive effect in **6** is reasonable from a model for such an effect in the absence of resonance effects. In the comparison of PAs of quinuclidine and quinuclidi-2-ene, the PA for quinuclidine is 2.7 kcal/mol higher, ref 18.

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(25) The N-methylated and O-methylated cations should have similar ionic sizes, so this difference in solvation energy appears to be the result of preferential specific solvation for the proton bonded to positive oxygen over that for a proton bonded to a positive nitrogen. It is known, for example, that the hydronium ion is better solvated in water than the ammonium ion by some 14 kcal/mol as a result of stronger H bonding due to increased charge density at O vs. N.[14b]

(26) Entropy terms in gas-phase proton-transfer reactions are generally very small and can be neglected for systems considered here.[14] Therefore $\Delta H^\circ_{g,est}$ and $\Delta G^\circ_{g,est}$ from the Ebert equation are the same in the present cases.

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(29) The differences observed in these cases are in accord with the known 4–6 kcal/mol preferences for N-methylation over O-methylation from heats of formation of simple model compounds and from group additivity paramters: J. D. Cox and G. Plicher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970, p 590.

(30) Apparently the charge in **5** is distributed sufficiently equally between N and O that the polarization stabilization by the methyl group is the same at either site.

(31) Thus, the effect of chlorination is to produce an inductive effect making N-methylation relative to the pyridone **1** 7 kcal/mol less favorable than O-methylation relative to **2** and to produce a compensating 5 kcal/mol inductive effect in the ion **25** making N-methylation less favorable than in **5** relative to O-methylation. This small methylation energy difference may result because the inductive stabilization of the polar resonance contributor to **12** and destabilization of the polar contributor to **13** is much less significant for the unmethylated species **18** and **19**. In fact, the close correspondence between ΔG°_g for **1–2** and **20–21** in Table IV could be taken to indicate little or no such inductive effect in the latter pair. The methyl groups in **12** and **13** seem to be sufficiently capable of stabilizing positive charge in the dipolar resonance contributors in the gas phase to produce this net 8 kcal/mol inductive effect. Such an effect is found in other systems: ref 14.

(32) A recent case which provides impressive support for the basicity method in solution has been reported by Bensaude, Dubois and co-workers, who found by temperature-jump spectroscopy that the equilibrium constant for tautomerization of cytosine to the 3(*H*)-aminooxo form is 2.5×10^{-3}, while that predicted by the p*K* method is 1.25×10^{-3}: M. Dreyfus, O. Bensaude, G. Dodin, and J. E. Dubois, *J. Am. Chem. Soc.*, **98**, 6338 (1976).

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Rearrangements among Gas-Phase Ions of C_8H_8 Isomers. A Photodissociation-Spectroscopic Investigation

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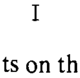
Abstract: Photodissociation spectroscopy is used to explore the structures of the $C_8H_8^{+\cdot}$ and $C_8H_9^+$ ions obtained in gas phase from styrene, cyclooctatetraene, and barrelene. The $C_8H_8^{+\cdot}$ ions do not interconvert on a time scale of seconds, and the parent ions of styrene and barrelene appear to retain the neutral structure, while the structure of the COT parent ion is uncertain. The $C_8H_9^+$ ions obtained by H_3O^+ protonation all have the same spectrum, and are assigned as having the styryl ion structure.

Introduction

The technique of photodissociation spectroscopy is ideally suited to investigating rearrangement processes in many gas-phase ions.[2a] It was recently shown[2b] that the $C_8H_8^{+\cdot}$ parent ions obtained from styrene (I) and from cyclooctatetraene (COT, II) do not interconvert, and that the styrene ions, at least, probably retain the structure of the neutral. The preparation of a sample of bicyclo[2.2.2]octa-2,5,7-triene (barrelene, III)[3] has provided a chance to extend our knowledge of rearrangements on the $C_8H_8^{+\cdot}$ potential surface. In addition, the recent demonstration[4] of rearrangement of protonated hexamethyl(Dewar benzene) to the hexamethylbenzene structure suggests the possibility that rearrangements are facile among protonated hydrocarbon isomers, and it was of interest to elucidate rearrangement processes on the $C_8H_9^+$ surface. Accordingly, photodissociation spectra were obtained for both the parent ions and the protonated parent ions of all three of these C_8H_8 isomers, in order to compare and identify the ion structures.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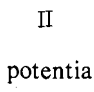
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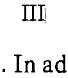

III

Experimental Section

The photodissociation spectra were taken with ICR detection, using a pulsed mode of ICR operation, which has been described.[4] Normally the ions were trapped and irradiated for 5 s before the detection pulse, although some checks were made to be sure that the measured rates were independent of trapping time. In looking at the parent ions, neutral gas pressures of $1\text{-}2 \times 10^{-8}$ Torr (indicated at the ion pump) were used, at an ionizing electron energy near 15 eV. The protonated molecules were observed by introducing 3×10^{-7} Torr of water at electron energies in the 11-15 eV range. H_3O^+ is formed rapidly at this pressure, and protonation of the hydrocarbon is presumably

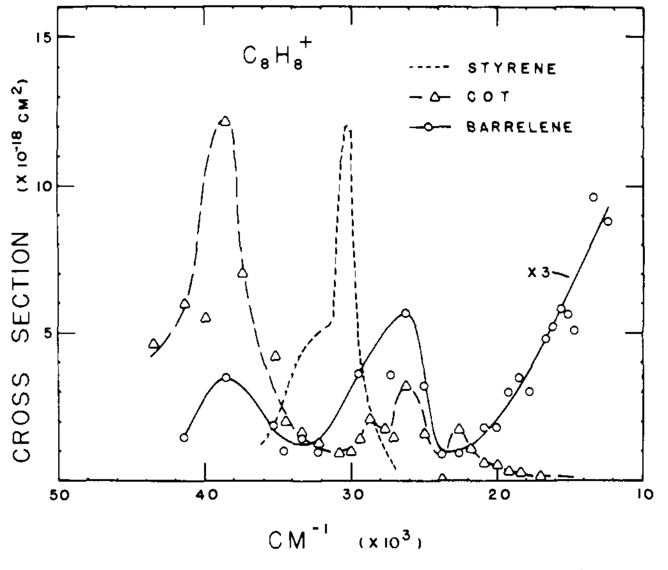


Figure 1. Photodissociation spectra of radical parent ions ($C_8H_8^{+\cdot}$) from styrene, COT, and barrelene. The barrelene curve has been expanded × 3.

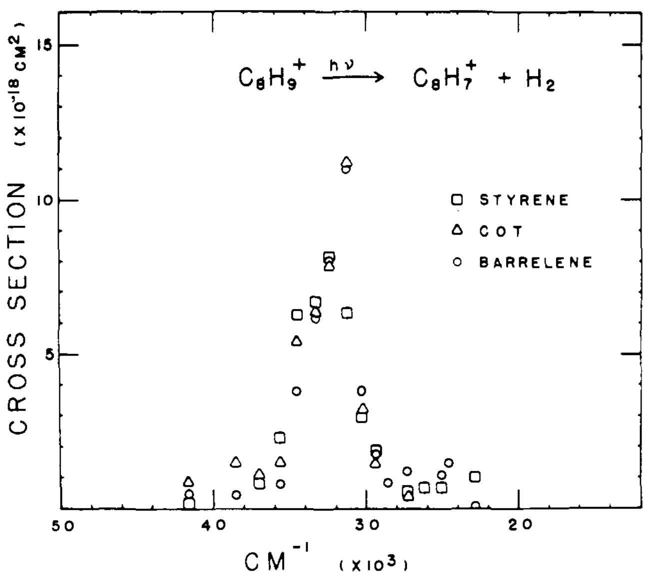


Figure 2. Photodissociation spectra of $C_8H_9^+$ ions obtained by H_3O^+ protonation of styrene, COT, and barrelene.

predominantly by proton transfer from water. The arc lamp, filters, and monochromator used in these experiments have been described.[5]

To check for possible isomerization in the inlet, the barrelene was recovered from the inlet after each run, and at the conclusion of the experiments was found by NMR to contain negligible impurities. COT from Aldrich was used as received.

Results and Discussion

Parent Radical Ions. The spectrum of the parent ion obtained from cyclooctatetraene was reexamined with the pulsed spectrometer and is shown in Figure 1. The spectrum agrees well enough in shape and intensity with that of ref 2b, except that the large peak near 20 000 cm^{-1} has disappeared. It seems clear that the spectrum of ref 2b was a superposition of at least two ion structures, one of which is less abundant in the pulsed-ICR experiment, presumably as a result of the limiting of ion residence times.[6] In ref 2b it was pointed out that the steady-state photodissociation spectrum was in poor agreement with the PES spectrum of the neutral, suggesting possible rearrangement. The pulsed-ICR spectrum reported here is in somewhat better agreement: Batich et al.[7] assign two excited π states of COT parent ion at 9.78 and 11.15 eV based on the PES spectrum and theory. Both states are optically allowed from the ground state of the ion. Taking the adiabatic ion ground state at 8.0 eV, this leads to a predicted optical spectrum with peaks at 1.78 (14 300 cm^{-1}) and 3.15 eV (25 600 cm^{-1}), as well as $\pi \rightarrow \pi^*$ peaks not observable in the PES spectrum. The photodissociation peak near 26 000 cm^{-1} is in good agreement with this expectation; and the strong peak at 39 000 cm^{-1} is presumably a $\pi \rightarrow \pi^*$ excitation. There is, however, no indication of a peak in the red or near IR, which could mean that the optical transition is weak, that the ion does not dissociate from this excited state, or that the ion has rearranged. In summary, the photodissociation spectrum of $C_8H_8^{+\cdot}$ from COT is not inconsistent with the PES spectrum, but the correspondence is not good enough to rule out the possibility that the molecule rearranges following ionization.

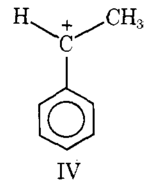
The spectrum obtained for the parent ions in barrelene is shown in Figure 1. The product of photodissociation, as for the other $C_8H_8^{+\cdot}$ species, was the $(M - 26)^{+\cdot}$ ion, corresponding to acetylene loss from the parent. It is clear immediately that the barrelene ions do not rearrange to either a styrene structure or to any structure obtained from COT. A comparison with the PES spectrum[8] suggests that the parent structure may well be retained: the lowest (adiabatic) IP is at 8.23 eV, corresponding to the highest occupied $a_2(\pi)$ orbital. The next IP (vertical) is near 9.65 eV, corresponding to a degenerate $e(\pi)$ orbital, and is broadened or split by a Jahn–Teller interaction into two or more components. The first π–π transition in the ion (allowed in x–y polarization) should therefore give a broad or split peak centered around 1.4 eV (11 600 cm^{-1}), which is in excellent accord with the broad photodissociation feature observed in the red wavelength region in barrelene ions. The two UV peaks presumably arise from $\pi \rightarrow \pi^*$ excitations. Cyclic olefin cations[1] and polyene cations[9] exhibit both near- and far-UV $\pi \rightarrow \pi^*$ transitions, and the peaks observed in barrelene ions are not unreasonable.[10]

Protonated Parent Ions. Spectra of the protonated parent ions of styrene, COT, and barrelene are all shown in Figure 2. The dissociation product was $(P - 1)^+$ corresponding to the reaction

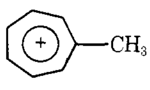
$$C_8H_9^+ \xrightarrow{h\nu} C_8H_7^+ + H_2$$

The small apparent differences in the three spectra are not considered significant; in fact, a further careful comparison between the protonated styrene and COT ions with 7-nm monochromator resolution at several wavelengths near 300 nm gave results identical within experimental error. It seems highly unlikely that ions of differing structures could give photodissociation spectra so similar in position and intensity with the same band shape, and we conclude that protonation of these isomers by H_3O^+ is followed by rapid ($\gg 1$ s^{-1}) rearrangement to a common ion structure. This common structure gives a photodissociation peak at 31 700 ± 500 cm^{-1} with a peak cross section of about 1×10^{-17} cm^2, and a broad feature peaking near 400 nm with cross section about 1×10^{-18} cm^2.

It seems reasonable to limit consideration of the ion structure to the most plausible six-, seven-, and eight-membered ring forms, which are the styryl ion IV, the methyltropylium ion V,



IV



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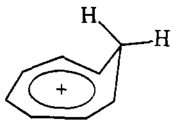

VI

and the homotropylium ion VI. The only guide is a comparison with the solution spectra. While too few cases have been studied for reliable generalization, the solution and gas-phase spectra of several protonated aromatics have been found to be closely similar,[4,11] with the gas-phase photodissociation peaks showing a blue shift of zero to 1000 cm^{-1}, and (in one case[4]) similar cross section.

Assuming methyltropylium ion to be spectroscopically similar to tropylium ion, structure V can be ruled out at once, as the longest wavelength tropylium ion peak is at 36 560 cm^{-1}.[12] The choice between IV and VI is quite clear: VI has solution peaks at[12] 43 010 ($\sigma = 1.3 \times 10^{-16}$ cm^2) and 32 100 cm^{-1} ($\sigma = 1.2 \times 10^{-17}$ cm^2); IV is not known in solution, but by analogy with its alkyl-substituted analogues[12] can be presumed to have peaks at about 31 250 ($\sigma \simeq 4 \times 10^{-17}$ cm^2) and 25 600 cm^{-1} ($\sigma \simeq 4 \times 10^{-18}$ cm^2). Both in peak positions and (to an order of magnitude) in cross sections the photodissociation spectrum matches the spectrum expected for styryl ion, IV, and we conclude that this is the ultimate product of gas-phase H_3O^+ protonation of all three of the C_8H_8 isomers studied.

H_3O^+ is a rather energetic protonating reagent, making available about 30 kcal of excess energy to protonated styrene (thermochemical values for COT and barrelene are not available). Wide traversal of the $C_8H_9^+$ potential surface is thus not very surprising. A detailed study of this question with other protonating agents is in progress; however, protonation of COT by proton transfer from tetrahydrofuran gives an ion apparently identical with that obtained from H_3O^+ protonation.[14] THF is a much milder protonating agent, being 26 kcal more basic than water and only 4 kcal less basic than styrene,[15] so that even with much lower internal energy rearrangement still occurs in the $C_8H_9^+$ ions.

Conclusion

The results of this study are in accord with the limited picture thus far built up of gas-phase hydrocarbon rearrangements: the radical cations formed by electron bombardment of the three C_8H_8 isomers do not rearrange to a common structure, and at least styrene and barrelene ions appear to retain the structure of the parent neutral. The ions formed by H_3O^+ protonation of the isomers, however, undergo complete rearrangement to structure **IV** within the time scale of seconds appropriate to this technique, indicating that IV is the most stable gas-phase $C_8H_9^+$ structure.

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(1) (a) Case Western Reserve University; (b) University of Southern California.

(2) (a) See, for instance, R. C. Dunbar, *Anal. Chem.*, **48**, 723 (1976). (b) E. W. Fu and R. C. Dunbar, *J. Am. Chem. Soc.*, **100**, 2283 (1978); E. W. Fu, Ph.D. Thesis, Case Western Reserve University, 1976.

(3) We are grateful to Professor Leo Paquette for kindly providing the sample.

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(5) E. W. Fu, P. P. Dymerski, and R. C. Dunbar, *J. Am. Chem. Soc.*, **98**, 337 (1976).

(6) One of the important problems with the steady-state operating conditions of ref 2b is the possibility that a nonreactive ion species accumulates in the ion trap to an abundance far greater than its true relative abundance, as apparently occurred with a $C_8H_8^+$ isomer in the COT experiments. Such problems are eliminated or at least greatly reduced in pulsed operation.

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(8) E. Haselbach, E. Heilbronner, and G. Schröder, *Helv. Chim. Acta*, **54**, 153 (1971).

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(10) Attempts to check the homogeneity of the barrelene ion population at 366 and 580 nm were inconclusive, and the possibility of a mixed ion population cannot be ruled out. It can only be said that none of the peaks in this spectrum corresponds to any peak of other known C_8H_8 spectra, except that a small extend of rearrangement to the $COT^{+\cdot}$ structure cannot be ruled out, as is seen from Figure 1.

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A MINDO/3 Study of the Bridged Pyramidal C_8H_9 Cation and Its Congeners

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Abstract: The heats of formation, geometries, and formal atomic charges have been calculated for the bridged bishomo pyramidal C_8H_9 cation together with 13 of its congeners. Minimum energy reaction paths have been determined interconnecting the pyramidal cation with its valence isomers.

Introduction

Some time ago the ingenious suggestion was made that the most stable member of the $C_5H_5^+$ family of cations is the square pyramidal species **1**. Although subsequent calculations[1-4] have considerably refined the original proposal,[5] it has nonetheless given rise to the innovatory principle that stable, pyramidal cations may be created by the formal centrolinear addition of the carbyne cation to cyclic polyenes containing $4n$ π electrons.[6] A pertinent illustration is the bridged bis homologue **3** obtained by formal adjunction of the carbyne cation to the endo side of norbornadiene (**2**), a classic example of a bishomo-conjugated diene.[7]

NMR spectroscopic evidence has been presented in favor of **3**;[8] however, it is not unambiguous as it could well be compatible with rapid equilibration between classical cations such

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