Table I. The Fluorescence Lifetime and Quantum Yields of *all-trans*-Retinal as a Function of Excitation Wavelength

λ_{ex}, nm	$\tau_F \pm 0.1$ ns	$\phi_F \pm 0.002$
440	0.61	0.064
420	0.73	0.033
400	0.75	0.025
380	0.69	0.017
360	0.67	0.012
340	0.76	0.015

tron density of the carbonyl oxygen of *all-trans*-retinal from 1.399 in the ground state to 1.414 in the excited state.

Immediately prior to the measurements of fluorescence intensity and lifetime data, *all-trans*-retinal (Sigma Chemical Co.) was purified on silica gel TLC in *n*-hexane–ethyl acetate (30:5, v/v) and then extracted into freshly distilled spectroquality ethanol (U.S. Industries). All procedures were carried out in near darkness.

The fluorescence lifetime measurements were made on an SLM Model 480 phase-modulation fluorometer previously described[8] and fitted with a holder for liquid nitrogen optical Dewar and cell. All measurements were made with a 1-kW Xe arc lamp as a light source at 1-nm excitation band pass. Corrected emission spectra were measured on a Perkin-Elmer MPF3 spectrofluorometer at 77 K. The excitation bandpass was kept constant at 2 nm throughout the measurement. The relative quantum yield of fluorescence was calculated from the relationship

$$\phi_F = \phi_F^r \left(\frac{\int I_F^s(\bar{\nu}) d\bar{\nu}}{\int I_F^r(\bar{\nu}) d\bar{\nu}} \right) (A_\lambda^r / A_\lambda^s)(n_r^2/n_s^2)$$

where ϕ_F^r is the quantum yield of the reference compound, riboflavin tetrabutyrate[9] or 9,10-diphenylanthracene,[10] n_r and n_s are refractive indexes of reference and sample solutions at 77 K, respectively, and I_F and A_λ are fluorescence intensity and absorbance, respectively. The absorbances for reference and sample at each wavelength were kept within 5% in order to minimize errors due to the series approximation to the $(A_\lambda^r / A_\lambda^s)$ term in the above equation and the difference in spectral shape of the excitation spectra of reference and samples at a given wavelength band pass (2 nm). In addition, the absorbances at each λ_{ex} were kept within $\pm 12\%$ in order to minimize errors due to light scattering.

Table I presents the measured fluorescence lifetimes and quantum yields as a function of exciting wavelength. Each lifetime is an average of at least 20 phase shifts and modulation measurements. It can be seen that the lifetimes remain essentially constant across the excitation band covering the absorption maximum and the long wavelength edge region, while the fluorescence quantum yields are wavelength dependent in the same spectral region.

The results in Table I strongly suggest that the fluorescence of *all-trans*-retinal in ethanol at 77 K is largely due to one emitting species, as the phase shift and modulation lifetimes were identical within 200 ps, indicative of a single component decay. Nonetheless, the fluorescence quantum yield depends upon λ_{ex} (Table I and ref 5 and 6) for *all-trans*-retinal in *ethanol* at 77 K. This suggests that a rapid interconversion between free and H-bonded retinal does not occur during the excited-state lifetime (cf. reason b above).

It is also noteworthy that the fluorescence quantum yield of retinal still shows λ_{ex} dependence in the presence of a saturating concentration of KI (85 mM) which enhances fluorescence as a result of $R\text{—}C\text{=}O\cdots K^+$ complex formation.[5] The lifetime also increases with KI by a factor of 2.[11]

References and Notes

(1) This work was supported by the R. A. Welch Foundation (D-182) and National Science Foundation (PCM75-05001-A01).
(2) Q. Chae, Ph.D. Dissertation, Texas Tech University, Lubbock, Texas, 1977.
(3) R. S. Becker, K. Inuzuka, J. King, and D. E. Balke, *J. Am. Chem. Soc.*, **93**, 43 (1971).
(4) (a) T. Takemura, P. K. Das, G. Hug, and R. S. Becker, *J. Am. Chem. Soc.*, **98**, 7099 (1976); (b) T. Takemura, P. K. Das, G. Hug, and R. S. Becker, *ibid.*, **100**, 2626 (1978). (c) T. Takemura, G. Hug, P. K. Das, and R. S. Becker, *ibid.*, **100**, 2631 (1978).
(5) P. S. Song, Q. Chae, M. Fujita, and H. Baba, *J. Am. Chem. Soc.*, **98**, 819 (1976).
(6) T. A. Moore and P. S. Song, *Nature (New Biol.)*, **242**, 30 (1973).
(7) R. C. Christensen and B. E. Kohler, *Photochem. Photobiol.*, **19**, 401 (1973).
(8) R. D. Fugate and P. S. Song, *Photochem. Photobiol.*, **24**, 479 (1976).
(9) M. Sun, T. A. Moore, and P. S. Song, *J. Am. Chem. Soc.*, **94**, 1730 (1972).
(10) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966).
(11) To be reported elsewhere.

Robert D. Fugate, Pill-Soon Song*

*Department of Chemistry, Texas Tech University
Lubbock, Texas 79409*
Received November 27, 1978

Quinuclidin-4-yl

Sir:

Long-range orbital interactions in saturated systems can occur either by "through-space" or "through-bond" mechanisms.[1-4] The bridgehead positions in a bicyclooctane structure[5] provide a particularly attractive framework for studies of such interactions. The lone pairs on the two nitrogen atoms of diazabicyclooctane (**1**) provide a four-electron case. Both experimental[6-8] and theoretical[1,3,4] evidence suggest that there is a very strong (~ 1.6 eV) interaction between these two orbitals. Calculations[1,3,4] indicate that direct overlap is small and that the interaction occurs by a "through-bond" coupling of the nitrogens' lone-pair orbitals with the low-lying σ C–C bond orbitals. One-electron systems include bicyclooctyl[9] (**2**) and the quinuclidine radical cation[10] (**3**). The magnitudes of $a^{H\delta}$ in the EPR spectra of **2**[9] and **3**[10] imply that, while there is some "through-bond" coupling to the 4 position, it is not particularly strong.[11] That is, in **2** and **3** the unpaired spin is localized at the formal radical center. Therefore, these radicals are not stabilized[12] and, because they are bridgehead radicals, may even be slightly destabilized. The most important three-electron cases previously studied are **4**, the radical cation of **1**,[6,13-15] and the radical cations derived from structurally related bicyclic diamines[16] and cyclic disulfides.[17,18]

The EPR spectrum of **4** shows two equivalent nitrogens and twelve equivalent hydrogens.[6,13] This was initially interpreted as a fast electron transfer between the nitrogens,[6] which implies a fairly weak interaction between localized orbitals and, presumably, a radical which is, at most, only slightly stabilized. However, it seems much more likely that **4** is very strongly stabilized.[4,7,8,13-15] Hoffmann et al.[4] first suggested "the electron is in fact delocalized over the molecule" and this view is supported by the results of a PES study of **1**,[7,8] by a more
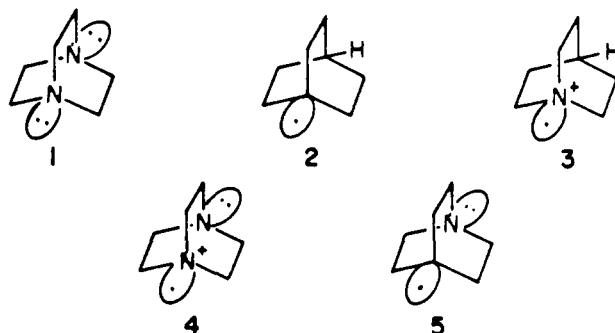
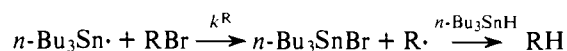Table I. EPR Parameters for Quinuclidin-4-yl and Related Radicals[a]

	5[b]	2[c]	3[d]	4[e]
a^N	1.80[f]		25.1	16.96 (2N)
$a^{H\beta}$ (6 H)	7.00[f]	6.64	9.39	7.34
$a^{H\gamma}$ (6 H)	g	0.89	2.36	7.34
$a^{H\delta}$ (1 H)		2.69	14.3	
g	2.00294[h]	i	i	i

[a] Hyperfine couplings are in gauss. [b] This work. In cyclopropane at −80 °C, $\Delta H_{pp} = 1.0 \pm 0.1$ G. [c] Reference 9. In cyclopropane at −74 °C. [d] Reference 10. In CF_3SO_3H at −50 to 0 °C. [e] Reference 6. In CH_3CN at 23 °C. [f] ±0.15 G. [g] Not resolved. [h] ±0.0003. [i] Not reported.

recent EPR study of **4** at low temperatures,[13] by the results of a study of the gas-phase basicity of **1**,[14] and by a study of **4** by resonance Raman spectroscopy.[15]

The quinuclidin-4-yl radical (**5**) provides another model for distinguishing a localized from a delocalized spin in a three-electron case, i.e., for distinguishing between a nonstabilized and a highly stabilized radical. In this communication we report chemical and EPR studies which reveal that radical stabilization and/or long-range electron delocalization is comparatively unimportant for **5**. This result stands in surprising contrast to the aforementioned conclusions regarding the large degree of stabilization of **4** and also contrasts with the well-known stabilization of carbon-centered radicals by α hetero-atoms.[21]

Chemical Studies. Relative rates of radical generation from appropriate molecular precursors have long been used to assess the ordering of radicals in terms of their stabilization energies. Competitive reduction[22] of 1-bromobicyclooctane and 4-bromoquinuclidine[23] with a deficiency of tri-*n*-butyltin hydride at 45 °C revealed that **5** was formed only *three times faster* than **2**, i.e., $k^5/k^2 = 3.0$:

$$n\text{-Bu}_3\text{Sn}\cdot + \text{RBr} \xrightarrow{k^R} n\text{-Bu}_3\text{SnBr} + \text{R}\cdot \xrightarrow{n\text{-Bu}_3\text{SnH}} \text{RH}$$

Comparison with literature data[25] indicates that **2** is formed at about one third of the rate for the nonrigid, tertiary, methylcyclohexyl radical. That is, **5** is formed from its bromide at about the same rate as an "ordinary" tertiary alkyl radical (such as *tert*-butyl, for which $k^{Me_3C} = 8.5 \times 10^7$ s^{-1} at 25 °C).[26] We must therefore conclude that **5** is not a stabilized[12] radical and that there is little or no long-range orbital interaction. The fact that $k^5/k^2 \neq 1$ may reflect either the inductive effect of the nitrogen[27] or a more flexible geometry at the radical center for **5** in comparison with **2**.

The foregoing conclusions are supported by the results of a study of the free-radical chlorination of quinuclidine.[28] Products chlorinated at positions 2 and 4 were formed in the statistically corrected ratio of 1.8:1.[28,29] The bridgehead position is *less* active than the C-2 position adjacent to nitrogen despite the fact that in quinuclidin-2-yl conjugative electron delocalization is precluded because the C-2 semioccupied orbital and the N lone-pair orbital are almost orthogonal.

We have also measured the reduction potentials[31] for 1-bromocyclooctane (−2.79 V) and for 4-bromoquinuclidine (−2.71 V). For the electrochemical reduction of halides the radical mechanism is generally considered the most satisfactory.[32] The similarity between these two reduction potentials militates against significant stabilization of **5** relative to **2**. Of course, since the reductions are irreversible these potentials are not truly thermodynamic quantities.[33] However, kinetic effects will be minimized because related compounds undergoing similar electrode processes are being compared.[34]

**EPR Spectroscopy.** Radical **5** was generated from the bromide using photochemically produced $Me_3Si\cdot$, $Me_3Sn\cdot$, and

n-Bu$_3$Sn· radicals. Its EPR parameters at −80 °C in cyclopropane are compared with those of analogous radicals in Table 1. Most notable is the small magnitude of a^N compared with the values reported for **3**[10] and **4**.[6,13] It is clear that in **5** *the spin is not delocalized to the N atom*. The s spin density at this atom (calculated[36] from the observed a^N value) is only 0.28%. For comparison, INDO calculations[38] on **2** and **3** yield s spin densities at C-4 of +0.37 and −0.1%, respectively. The fact that spin in **5** is localized is further confirmed by the small magnitude of $a^{H\gamma}$ (cf. **2**, Table I).

Conclusion. The quinuclidin-4-yl radical (**5**) is not stabilized by long-range electron delocalization (whether "through-space" or "through-bond"). Our results suggest that **4** represents a special case in which electron delocalization, and hence stabilization, arises from the degeneracy of the interacting orbitals.

References and Notes

(1) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.
(2) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.
(3) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.
(4) Hoffmann, R.; Imamura, A.; Hehre, W. *J. J. Am. Chem. Soc.* **1968**, *90*, 1499.
(5) And, of course, in related, rigid, bicyclic species.
(6) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013.
(7) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Tetrahedon Lett.* **1969**, 4025. The results of this study were interpreted in terms of a large splitting between the nitrogens' lone-pair orbitals in 1. See also ref. 8.
(8) Heilbronner, E.; Muszkat, K. A. *J. Am. Chem. Soc.* **1970**, *92*, 3818.
(9) Krusic, P. J.; Rettig, T. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 995.
(10) Danen, W. C.; Rickard, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 2303.
(11) For a review of long-range proton hyperfine couplings in EPR spectroscopy, see King, F. W. *Chem. Rev.* **1976**, *76*, 157. For recent work on bridgehead bicyclic radicals, see e.g., the following. Kawamura, T.; Yonezawa, T. *J. Chem. Soc., Chem. Commun.* **1976**, 948. Wood, D. E.; Bailey, W. F.; Wiberg, K. B.; Pratt, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 268. Kawamura, T.; Matsunaga, M.; Yonezawa, T. *ibid.* **1978**, *100*, 92.
(12) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.
(13) Eastland, G. W.; Symons, M. C. R. *Chem. Phys. Lett.* **1977**, *45*, 422. These authors favor a direct "through-space" interaction for 3 and 4 rather than a "through-bond" electron delocalization.
(14) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1604.
(15) Ernstbrunner, E. E.; Girling, R. B.; Grossman, W. E. L.; Hester, R. E. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 501.
(16) Alder, R. W., Goode, N. C.; King, T. J.; Mellor, J. M.; Miller, B. M. *J. Chem. Soc., Chem. Commun.* **1976**, 173. Alder, R. W.; Gill, R.; Goode, N. C. *Ibid.* **1976**, 973. Alder, R. W.; Sessions, R. B.; Mellor, J. M.; Rawlins, M. F. *Ibid.* **1977**, 747. Alder, R. W.; Sessions, R. B. *Int. Symp. Phys. Org. Chem., 4th, 1978*, **Sept 4-8, 1978**, Abstr. A19. Nelsen, S. F.; Haselbach, E.; Gschwind, R.; Klemm, U.; Lanyova, S. *J. Am. Chem. Soc.* **1978**, *100*, 4367.
(17) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3055. Asmus, K. D.; Bahnemann, D.; Fischer, Ch. H.; Veltwisch, D. *Int. Symp. Phys. Org. Chem., 4th, 1978*, **Sept 4-8, 1978**, Abstr. A16.
(18) For the sake of completeness we add that two-electron systems include bicyclooct-1,4-diyl[19] and quinuclidine.[20]
(19) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.
(20) Bierhi. G.; Heilbronner, E. *Helv. Chim. Acta.* **1974**, *57*, 546.
(21) We are indebted to Dr. P. J. Wagner for reminding us that α-aminoalkyl radicals, $R_1R_2NCR_3R_4$, are significantly stabilized by conjugative electron delocalization with the lone pair on nitrogen:
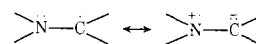
Such stabilization has long been recognized for α-oxyalkyls, but it is probably even greater for the α-aminoalkyls. For example, the relative reactivities per secondary H toward phenyl radicals at 60 °C are ~1:4:16 for propane, Et_2O, and Et_3N, and ~1:1.4:3.3 for cyclohexane, 1,4-dioxane, and piperazine. See G. A. Russell In "Free Radicals", Kochi, J. K, Ed.; Wiley: New York, 1973; Vol. 1, Chapter 7, Tables 16 and 18.
(22) Degassed benzene solutions containing 0.35–0.75 M of total organic bromide were reduced for 1–2 h at [tin hydride]/[total bromide] ratios of 0.53–0.70. The reaction was photoinitiated.
(23) Prepared according to literature procedures.[24] Independent experiments showed that quinuclidine was the quantitative product of reaction.
(24) Grob. C. A.; Brenneisen, P. *Helv. Chim. Acta* **1958**, *41*, 1184.
(25) Fort, R. C., Jr.; Hiti, J. *J. Org. Chem.* **1977**, *42*, 3968. These experiments were carried out at 80 °C.
(26) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(27) See, e.g., Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047.
(28) Bakker, B. H.; Speckamp, W. N. *Tetrahedron Lett.* **1975**, 4065.
(29) For comparison, this ratio is 0.75:1 for bicyclooctane.[30]

(30) Müller, E.; Trense, U. *Tetrahedron Lett.* **1967**, 2045.
(31) Peak potentials, against a standard calomel electrode were determined by triangular-wave, stationary-electrode, cyclic voltametry on PAR Model 170 using a three-electrode system and grid. The working electrode was vitreous carbon. The sample concentration was 10^{-3} M in dry DMF with 0.10 M tetrabutylammonium perchlorate as the supporting electrolyte. Samples were scanned between -2.0 and -3.0 V at 50 mV/s. The reductions were irreversible.
(32) Perrin, C. L. In "Organic Electrochemistry", Zuman, P., and Perrin, C. L., Eds.; Interscience: New York, 1969; p 257 and references therein.
(33) We are indebted to a referee for bringing this point to our attention.
(34) This similarity is indicated by the fact that the same number of electrons are transferred while the degree of reversibility and the character of the limiting currents are also similar (see ref 35).
(35) Zuman, P. "Substituent Effects in Organic Polarography", Plenum Press: New York, 1967.
(36) The isotropic hyperfine coupling arising from an electron in a nitrogen 2s orbital is taken to be 1811 MHz.[37]
(37) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.
(38) Danen, W. C., private communication.
(39) Issued as N.R.C.C. No. 17467.

Shelton Bank,* William K. S. Cleveland

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

D. Griller, K. U. Ingold*

Division of Chemistry
National Research Council of Canada
Ottawa K1A 0R6, Canada[39]
Received October 19, 1978

Organic Photochemistry with 6.7-eV Photons: Bicyclo[4.1.0]hept-3-ene. Internal Transfer and Carryover of Electronic Energy

Sir:

In studies on the solution-phase photochemistry at 185 nm of cyclic monoolefins[1-3] and cyclic diolefins (both conjugated[4] and unconjugated[5]), it was found that the lifetimes of the electronically excited state that was involved were too short to promote bimolecular processes in which an electronically excited molecule was a reactant. Even intramolecular transfer of electronic energy was not observed to influence the photochemistry of a compound such as 4-vinylcyclohexene.[5] In more rigid bichromophoric molecules such as **1**, an internal [2 + 2] addition is a major reaction at 185 nm,[5] but this may not be related to an actual transfer of electronic energy between the double bonds. In this communication, results on the photochemistry of bicyclo[4.1.0]hept-3-ene (**2**, hereafter BCH) at 185 nm are reported. These demonstrate that the incident photon is most probably absorbed by the π bond while the reactions that are observed are mostly those of the cyclopropyl group.

1   2   3

4   5   6
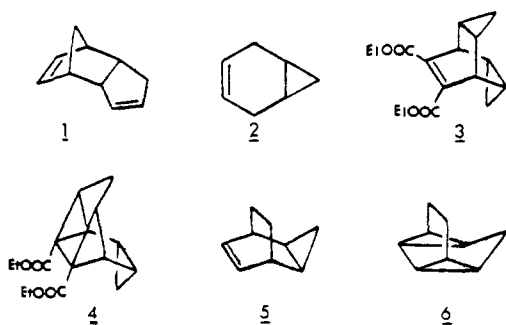
The ring system **2** is incorporated in numerous compounds which were studied by Prinzbach and his co-workers.[6] Typically, they found that **3** on triplet sensitization gave **4** as a major product. This reaction can be duplicated at 185 nm in
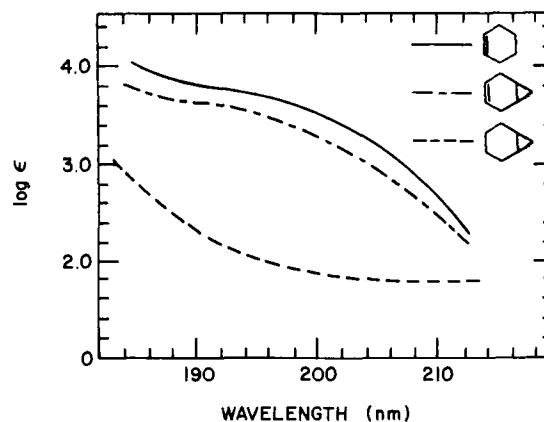
Figure 1. Ultraviolet absorption spectra of bicyclo[4.1.0]hept-2-ene and model compounds. Spectrum of cyclohexene was taken in hexane.[8] the rest in pentane.

Table I. Photolysis of Bicyclo[4.1.0]hept-3-ene in Solution (Solvent, Pentane; Concn, 2×10^{-2} M; Time, 30 Min)

Product					% Conversion w.r.t. starting material
7	8(a+b)	9	10	unknown	
Yield %					
8.3	36.1	16.7	30.6	8.3	16.8

[a] W. Kirmse and K. Pöhlmann, *Chem. Ber.*, **100**, 3564 (1967). [b] Consisted of 1:2 trans:cis. [c] Identified by comparison with authentic material. [d] E. A. Hill, R. J. Theissen, C. E. Cannon, R. Miller, R. B. Guthrie, and A. T. Chen, *J. Org. Chem.*, **41**, 1191 (1976).

the solution-phase irradiation of **5** which gives a nearly quantitative yield of **6**.[7] These observations will be referred to later.

The solution-phase ultraviolet spectrum of a highly purified sample of BCH is shown in Figure 1 along with the spectra of cyclohexene[8] and bicyclo[4.1.0]heptane.[9] The resemblance between the spectra of the first two compounds and the absence of any feature that would be indicative of any mixing between the excited states of the olefin and cyclopropyl groups is noteworthy. Of course, this does not *prove* the absence of such an interaction.

Photolysis of BCH in pentane solution[10] gave five isomeric products in significant yield which together accounted for 92% of the material that disappeared. The identities of the products and relevant kinetic data are given in Table I.[11] The remaining 8% was made up of three products which were not identified. The mass balance was 100% within the experimental uncertainty ($\pm 5\%$) up to 16% conversion, but beyond that point secondary photolysis of the initial products was evident. The rate of disappearance of the reactant was 1.2 (± 0.2) relative to the rate of cis $\rightarrow$ trans isomerization of cyclooctene.[2]

The formation of **7** from BCH is a typical reaction of the cyclohexene ring in solution phase photochemistry at 185 nm.[1,3,12] It can be represented to proceed via a carbene intermediate (eq 1). 1,3,6-Heptatriene and 1,4-cycloheptadiene are