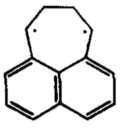
Photochemistry of 1,4-Dihydronaphtho[1,8-*de*][1,2]diazepine. Preparation and Electron Spin Resonance Observation of the Unsubstituted 1,8-Naphthoquinodimethane

Sir:

Previously we have reported[1] on the preparation and characterization of the bridged 1,8-naphthoquinodimethane (1,8-NQM) (**1**) in order to see whether this species had a triplet ground state as predicted by Hückel theory for planar **2**. In fact, a triplet excited state 200 cal/mol above the singlet ground state was found for **1**. Because **2** represents a better and perhaps less biased test of the Hückel prediction,[2] we have attempted to prepare it and wish to report at this time on our results in this area.



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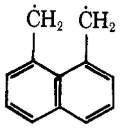
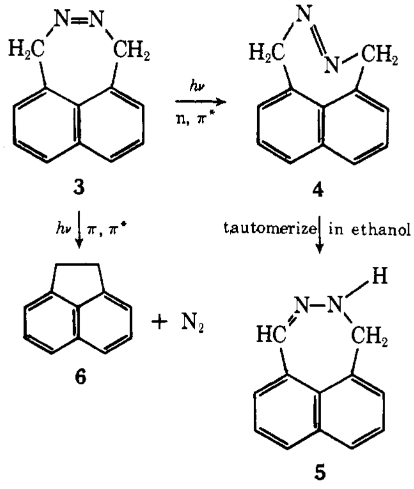


2

Irradiation of a degassed dilute solution of 1,4-dihydronaphtho[1,8-*de*][1,2]diazepine (**3**)[3] in ethanol at room temperature into its n,π* band at 400 nm gave exclusively the tautomer **5**.[4] Since it has recently been demonstrated[5] that **3** undergoes cis, trans isomerization to **4** by n,π* excitation, the strained isomer (**4**) undoubtedly is the precursor of **5**. Irradiation, on the other hand, at >300 nm, where both the π,π* and n,π* states of **3** are populated, afforded acenaphthene (**6**)[6] in addition to **5**.[4] Experiments described below implicate **2** in the conversion of **3** into **6**.[7]



Irradiation of a 4.71 × 10^{-2} M solution of **3** in hexafluorobenzene at 77 K with 300-nm light led to a strong radical resonance in the $g = 2$ region of the ESR spectrum plus resonance lines at 3208.5, 3287.5, 3357.5, 3523.0, 3590.0, and 3675.5 G in a pattern characteristic of a randomly oriented triplet lacking cylindrical symmetry and a cylindrical spin distribution. The D and E values for this triplet and **1** are collected in Table I. In addition to the above lines a very weak resonance was observed at 1703.4 G which corresponds to the $\Delta m_s = \pm 2$ for the triplet. The microwave frequency in the above experiment was 9.189 GHz.[8,9]

Table I. Comparison of the Properties of 1 and 2

Compound	D (cm^{-1})	E (cm^{-1})	Relative thermal stability	ΔE (triplet-singlet) (cal/mol)
1 (in C_6F_6)	0.018	<0.003	More	200
2 (in C_6F_6)	0.0218	0.0021	Less	45

The observed triplet has similar D and E values to those of **1**. In addition, irradiation of **3** leads to **6** under similar, but not identical conditions[10] to those where the triplet is observed by ESR. These facts suggest strongly that the observed triplet belongs to **2**.

2 also is thermally less stable than **1**. Although the triplet of **2** was stable indefinitely at 77 K, raising the temperature even 10° resulted in the rapid decay of the triplet signal, which is in contrast to the behavior of **1**.[1] This also precluded a Curie law study of this triplet in this temperature range.

When the triplet was generated at liquid helium temperature and the signal intensities[11] studied as a function of temperature, the data summarized in Table II were obtained. It can be seen immediately that the experimental intensity ratios are quite different than the ratios predicted by Curie's law (ground state triplet). Thus, **2** must have a singlet ground state. Furthermore, the experimental ratios are close to those predicted[1,12] for a triplet 45 ± 5 cal/mol above the singlet ground state.[13] Again, the simple Hückel theory was able to predict the existence of triplet **2** with remarkable accuracy.

Although our work has centered on detecting triplet states

Table II. Temperature Dependent Behavior of **2**. Intensity Ratios[a,b]

		Predicted for			
		Ground state[d]	ΔE(triplet-singlet)[e]		
$I(T_1)/I(T_2)$	Exptl[c]	triplet	40 cal/mol	45 cal/mol	50 cal/mol
$I_{12.5}/I_{12.5}$	1	1	1	1	1
$I_{18}/I_{28.5}$	1.25 ± 0.02[f]	1.58	1.31	1.27	1.22
$I_{12.5}/I_{29.0}$	1.29 ± 0.09[g]	2.32	1.45	1.32	1.19

[a] Peak heights were used rather than peak areas since the line widths did not change as a function of temperature. [b] Temperatures were checked before and after each measurement. [c] All intensity changes were reversible. [d] Predicted by Curie's law. [e] Calculated by methods described in ref 1 and 12. [f] Average of two determinations. [g] Average of six determinations.

of **1** and **2**, this does not imply that the final products isolated from these reactions necessarily arise from these triplet states. On the contrary, all the present and previous[1] results are consistent with the singlet states of **1** and **2** isomerizing to the observed products as illustrated below.[14,15]

$$\begin{tikzcd}
 & \text{1,8-NQM (triplet)} \arrow[d, shift left] \arrow[dr, dashed, "?"] & \\
\text{azo precursor} \arrow[r] & \text{1,8-NQM (singlet)} \arrow[u, shift left] \arrow[r] & \text{product}
\end{tikzcd}$$

One of the outstanding questions remaining in this research is the actual shape of the triplet and singlet states of **1** and **2**. A match up of the absorption spectra of **1** and **2** with those calculated by PPP-CI may indicate the geometry of these species. Experiments along these lines are currently being explored.

Acknowledgment. The authors wish to thank the Research Corporation for their generous support of this work. We would also like to thank Drs. G. Closs and S. Buchwalter of the University of Chicago for performing the CIDNP experiments, Dr. D. Devartangian of the University of Georgia for allowing us to use his liquid helium setup, and Dr. J. Wirz for informing us of his work in this area prior to publication.

References and Notes

(1) C. R. Watson, Jr., R. M. Pagni, J. R. Dodd, and J. E. Bloor, *J. Am. Chem. Soc.*, **98**, 2551 (1976), and references cited therein.

(2) **1** was found to be conformationally mobile.[1] Since the diyl carbons are joined together by a $-CH_2CH_2-$ bridge, their motion must of necessity be synchronized. The diyl carbons of **2**, in addition to being unsubstituted, are not forced to rotate in a synchronous manner.

(3) L. A. Carpino, *J. Am. Chem. Soc.*, **85**, 2144 (1963).

(4) Control experiments demonstrated that the isomerization of **3** into **5** is photochemical and not thermal.

(5) M. Gisin and J. Wirz, *Helv. Chim. Acta*, **59**, 2273 (1976).

(6) **5** is not the percursor of **6** for photolysis of **5** under conditions where **3** led to **6** resulted in no reaction. **4** does yield **6** on π,π^* excitation.[5]

(7) Carpino has observed[3] the thermal conversion of **3** into **6**. 1,8-NQM is likely an intermediate in this reaction.

(8) An entirely different triplet was observed in THF-DME at 77 K ($D = 0.0061$ cm^{-1} and $E = 0.000\ 43$ cm^{-1}). We have no conclusive proof as to the identity of this triplet.

(9) Control experiments demonstrated that **5** was not a precursor to the triplet described in the text or in ref 8.

(10) C_6F_6 matrices are not completely transparent and we could not perform preparative irradiations of **3** in this medium at 77 K. Irradiation of **3** in ethanol at 77 K does yield **6**, however.[5]

(11) Power saturation can be a problem at these temperatures. Only those line intensities which did not show any power saturation were used in the Curie law study.

(12) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967).

(13) Direct and benzophenone-sensitized photolysis of **3** in $CDCl_3$ in the probe of an NMR spectrometer afforded acenaphthene (**6**) but no CIDNP was observed in either case. This suggests that **2** has a singlet ground state with a triplet excited state greater in energy by at least a fraction of a calorie per mole. Attempts to observe CIDNP in the direct and benzophenone-sensitized photolysis of the azo precursor to **1** were also negative. S. Buchwalter and G. Closs, unpublished results.

(14) Although we do not know whether the triplet state or singlet state of **1** and **2** yields the observed products, the use of known photochemical data and group additive relations suggest that the conversion of **1** and **2** into the lowest triplet states of the products is endothermic.

(15) Our diyls behave quite differently than the bridged trimethylene methane observed by Berson and co-workers. See J. A. Berson, C. D. Duncan, G. C. O'Connell, and M. Platz, *J. Am. Chem. Soc.*, **98**, 2358 (1976), and earlier papers in the series. Our results and those of Berson suggest that the chemical behavior of diyls will be quite varied and will depend on whether the singlet or triplet is the ground state in addition to the energy gap between the two states.

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Selenation of *Escherichia coli* Mixed Transfer Ribonucleic Acids[1]

Sir:

It has been recently demonstrated that when *E. coli* is grown in a medium containing ^{75}Se as selenite or selenosulfate, part of the Se is metabolized to form 4-selenouridine in tRNA.[2,3] Wise and Townsend[4] observed that synthetic 4-selenouridine is very labile, and predicted that, if proper modifications are made in the current isolation procedures, one should be able to isolate selenopyrimidine nucleosides from certain tRNA species. Presumably, due to the lability of 4-selenouridine and the toxicity of Se to *E. coli*, it has been difficult to isolate selenated tRNA in quantity, and the identification of 4-selenouridine in the *E. coli* tRNA hydrolysate is based on the cochromatography of ^{75}Se radioactivity with authentic 4-selenouridine. In order to prepare selenated tRNA in quantity for biological studies, we decided to try to transform the 4-thiouridine in tRNA to 4-selenouridine.

We observed previously that 4-thiouridine in tRNA can be labeled with ^{35}S by the following sequence of reactions:

$$\text{tRNA(-SH)} \xrightarrow[\text{step 1}]{\text{CNBr}} \text{tRNA(-SCN)} \xrightarrow[\text{step 2}]{-^{35}\text{SH}} \text{tRNA(-}^{35}\text{SH)}$$

Study of the mechanism of reduction of 1-methyl-4-thiocyanatouracil by bisulfide revealed that the reaction proceeds to the extent of 70% by scission of the ring C–S bond and 30% by scission of the exocyclic C–S bond.[5] This finding led us to explore the possibility of transforming 4-thiouridine to selenouridine in tRNA following the same sequence of reactions, using -SeH instead of -SH in step 2. The feasibility of this reaction was first studied with the model compound 1-methyl-4-thiocyanatouracil synthesized by the method of Pal and Schmidt.[6] Conversion of 1-methyl-4-thiocyanatouracil to 1-methyl-4-selenouracil by NaHSe was followed spectrophotometrically in a cuvette purged with nitrogen. The cuvette was fitted with a rubber septum and air was replaced with nitrogen by syringe techniques.[7] The solution of NaHSe was introduced into the cuvette by a microliter syringe.

After NaHSe treatment, the 307.5-nm peak undergoes a bathochromic and hyperchromic shift. The pair of maximum and minimum 307.5- and 272-nm peaks is changed into 363 and 300 nm, respectively (Figure 1). This agrees with the spectrum of authentic 4-selenouridine (365 and 302 nm, respectively (Figure 2). 4-Selenouridine and 1-methyl-4-selenouracil are expected to have similar spectra. (Synthetic 4-selenouridine was a gift from Professor Leroy B. Townsend, University of Utah.)

Encouraged by these results we applied the sequence of reactions to *E. coli* mixed tRNA. One milliliter of aqueous (oxygen free) tRNA ($A_{260} = 61, A_{340} = 1.15$) was treated with 25 μL of 0.5 M phosphate buffer, pH 8, followed by 10 μL of

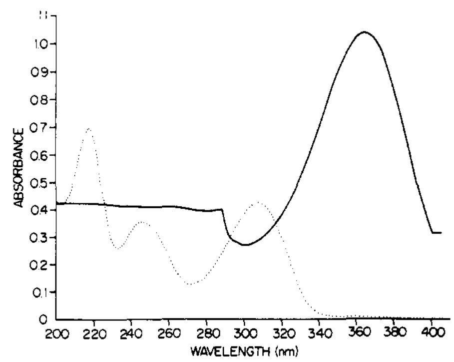

Figure 1. Ultraviolet absorption spectrum of 1-methyl-4-thiocyanatouracil before (···) and after treatment with NaHSe (—).