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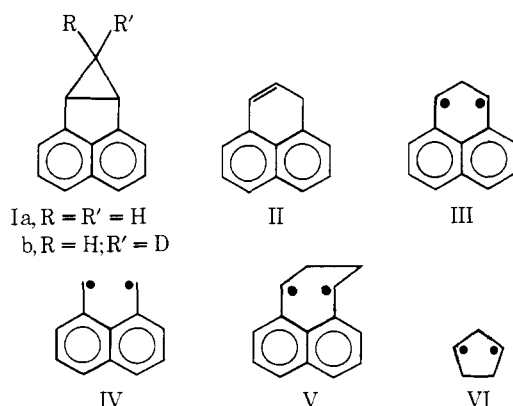
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**π,π -Biradicaloid Hydrocarbons:
Spectral Characterization of Singlet and Triplet
1,3-Perinaphthadiyl and Observation of
Thermal and Photochemical 2,3-Hydrogen Shifts¹**

Sir:

Although biradicaloid geometries² are likely to play a fundamental role in molecular photochemical processes,^{3,4} very little is known from direct observations about molecules at such geometries and, in particular, about the reactivity and physical properties of their excited states. We now wish to report the preparation and spectral characterization of the lowest singlet and triplet states of a trimethylene biradical constrained to a π,π geometry by interaction with the peri positions of naphthalene, as well as the kinetics of a thermal 2,3-hydrogen shift and the observation of a photochemical 2,3-hydrogen shift in the biradical.

When **I**⁵ is irradiated at 77 K in a rigid glass ($\lambda \approx 260$ nm, $\sim 10^{-3}$ M solution in degassed 3-methylpentane, 2-methyltetrahydrofuran, 1-pentanol, or EPA), its UV absorption, emission, and excitation spectra are gradually replaced by those of a new species stable for many hours (Figure 1). Simultaneously, the characteristic lines of a triplet appear in the ESR spectrum ($D/hc = 0.026 \pm 0.001$ cm⁻¹, $E/hc < 0.002$ cm⁻¹). Each member of the two $\Delta m = 1$ pairs of observed lines of the species produced from **Ia**, as well as the $\Delta m = 2$ line, is



split into a triplet. The coupling constant is approximately the same for both pairs, $a_H = 26 \pm 2$ G. The lines of the species produced from **Ib** are similarly split into very poorly resolved doublets. Temperature variation of the ESR intensity (93–123 K, 1-pentanol) is strong, and standard analysis shows that the triplet state lies 640 ± 40 cal above the ground state. The

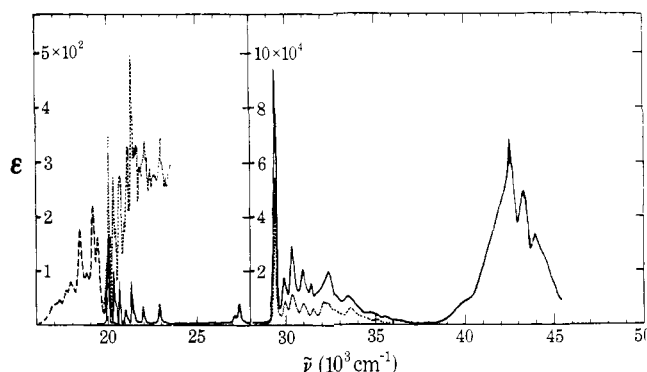


Figure 1. Absorption (—), fluorescence (---), and fluorescence excitation (···) spectra of **II** (3-MP, 77 K). The excitation spectrum is on two unrelated scales.

UV-vis absorption spectrum shows only a very slight decrease in intensity when temperature is raised from 77 to 110 K, while the shapes of the fluorescence and fluorescence excitation spectra show no significant change. All of the bands in the optical spectra appear to belong to only one species (fluorescence excitation follows absorption). Thus, they are either all due to light absorption by the singlet ground state, whose fraction in the S_0 - T_1 mixture should only vary between 95 and 86% over this temperature range, or else are all due to a completely unrelated species. The latter alternative is made extremely unlikely by the observation that at higher temperatures both the ESR and the UV signals exhibit a first-order decay in time and that all of the rate constants fall on the same straight line in an Arrhenius plot (119–133 K, annealed 1-pentanol, $\Delta E_{act} = 4.5 \pm 0.6$ kcal/mol, $A = 10^{4.5 \pm 1}$ s⁻¹). Our failure to observe the UV-vis absorption of the T_1 state is understandable, since it comprises only a minor fraction of the mixture and its calculated (PPP⁶) transition energies and intensities lead us to suspect strong overlap with the UV-vis absorption of the S_0 state.

The product of the thermal transformation of the new species is **II**, easily identified by its UV absorption, emission, and excitation spectra. Measurement of its rate of formation by UV absorption yields the same rate constants as above. Also, UV or visible irradiation of the new species produces **II** (77 K). Comparison of quantitative absorption spectra of **I**, of the new species, and of **II** showed that both photochemical steps are quantitative and this permitted us to estimate the extinction coefficients of the new species given in Figure 1 (uncorrected for the fraction present in T_1). Similarly, the thermal reaction is found to be quantitative in the thermal range given. At higher temperatures in 1-pentanol, and already at lower temperatures in less viscous glasses, thermal disappearance of the new species is more complex. The phenalenyl radical is observed in ESR and naphthalene-like absorption in UV spectra. Bimolecular reactions are presumably facile at these lower viscosities, and some return to **I** may be occurring as well.

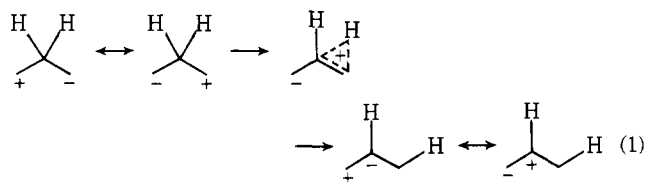
On basis of the combined evidence, we postulate the planar structure **III** for the new species and presume that S_0 - T_1 equilibration is rapid (cf. the related 1,8-naphthoquinodimethanes **IV**⁷ ($D/hc = 0.0218$ cm⁻¹, $E/hc = 0.0021$ cm⁻¹, T_1 45 cal/mol above S_0 , stable at 77 but not at 87 K) and **V**⁸ ($D/hc = 0.018$ cm⁻¹, $E/hc < 0.003$ cm⁻¹, T_1 200 cal/mol above S_0), as well as the related localized 1,3 biradical, **VI**⁹ ($D/hc = 0.084$ cm⁻¹, $E/hc = 0.0020$ cm⁻¹), with poorly resolved hyperfine structure). The larger S_0 - T_1 splitting in **III** is readily assigned to the effect of cyclic hyperconjugation with the methylene group, which raises the energy of the symmetrical nonbonding orbital and leaves that of the antisymmetrical nonbonding orbital essentially intact. Such splitting of the two orbitals should be even larger in **VI** (by about a factor of 1.5

at the HMO level), but the exchange integral, which favors the T state energetically, should also be larger (cf. the larger value of D). The hyperfine coupling constant for the methylene protons is isotropic as expected and of the right order of magnitude (using Hückel spin densities and standard relations,¹⁰ one expects $a \approx (1/2) (3/\sqrt{26} + 3/\sqrt{26})^2 \times 42.6 \times \cos^2 30^\circ = 22$ (G)).

The UV-vis absorption spectrum of III is one of the very few ever recorded for the singlet state of an even conjugated hydrocarbon without a classical valence structure.¹¹ It is strikingly different from the spectra of ordinary alternant hydrocarbons in that it contains a long succession of very weak absorption bands at long wavelengths. It is in fair agreement with our PPP calculation which suggests that there is an additional forbidden transition near 9000 cm^{-1} and that the observed fluorescence is of the $S_2 \rightarrow S_0$ type. Our attempts to locate this predicted transition in the near-IR region failed.

2,3 shifts in 1,3 biradicals have been frequently discussed, e.g., in the thermal rearrangement of cyclopropanes to propenes,¹² and in their photochemical interconversion.¹³ We believe that ours is the first direct observation of a 2,3-hydrogen shift in a 1,3 biradical, and indeed of the whole sequence commonly postulated¹³ in the photochemical process arylcyclopropane $\rightarrow (h\nu)$ 1,3 biradical $\rightarrow (\Delta)$ arylpropene (at 20°C , irradiation of I smoothly produces II).

The expected relative ease of 2,3 shifts in 1,3 biradicals is usually attributed to the partial development of the 1,2 double bond as the transition state is reached. This argument holds only for the S_0 state; such assistance is missing in T_1 state and in the lowest excited singlet state S_1 , in which the reactions are more nearly thermoneutral. Naively, one could expect the reaction to be facile in the "zwitterionic"^{3,14} S_1 state, in which it can be approximately described as a 2,3 shift in a carbonium ion carrying a carbanion substituent (carbon 1) (eq 1). These



qualitative notions and the resulting expectation of an increase in the activation energy for the shift in the order $S_1 < S_0 < T_1$ are supported qualitatively by approximate calculations for the 1,3-trimethylene biradical \rightarrow propene rearrangement which we have performed at the STO-3G SCF + 3×3 CI level, with considerable but not exhaustive geometry optimization.

Accordingly, we would expect the thermal transformation III \rightarrow (Δ) II to involve the S_0 state of III and a nonvanishing activation energy, and the photochemical transformation III $\rightarrow (h\nu)$ II to occur for that fraction of excited molecules which reaches the very low lying S_1 state, with little or no activation energy.

The presently available photochemical results are compatible with these expectations if we postulate that the calculated very weak $S_0 \rightarrow S_1$ transition in the infrared is too weak to be observed against the background of solvent overtones and that a radiationless $S_2 \rightarrow S_1$ process competes with $S_2 \rightarrow S_0$ emission (such emission is plausible in view of the large calculated S_2-S_1 gap). However, the frequency factor of the thermal reaction III \rightarrow II is abnormally low and suggests that the reaction involves either tunneling or a spin-forbidden process such as might result from the presence of a large barrier in the S_0 and a small one in the T_1 surface. We wonder, however, whether the temperature dependence of the reaction rate does not reflect as much the properties of the glass as those of the isolated molecule even for a possibly simple monomolecular

process such as III \rightarrow II. E.g., over the temperature range used (119–133 K), the viscosity of 1-pentanol changes by a factor of 3×10^4 . Similar huge changes also occur for other glasses over the temperature region in which they are transparent and stable. Some curious variations in the frequency factor for the rate of disappearance of trimethylenemethane in glasses were reported recently.¹⁵ Clearly, now that the agreement of the optical and ESR kinetic data for III in 1-pentanol has been demonstrated, it will be necessary to perform ESR studies, which do not require good transparency, in a large number of glasses, and also to explore isotope and substituent effects.

Barriers to ring closure in 1,3 biradicals are of considerable current interest.¹⁵ The absence of competing thermal conversion III \rightarrow I shows that in rigid 1-pentanol the barrier is considerable in the case of III. Since the ring closure requires a larger geometry change than the hydrogen shift, extrapolation to gas phase is not straightforward. Also, the presence of the rigid and conjugating naphthalene unit is undoubtedly unfavorable for ring closure.

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Silacyclobutenes: A Simple Synthesis¹

Sir:

Silacyclobutenes have been largely ignored during the recent surge of interest in the preparation and reactions of strained-ring organosilicon compounds.² This neglect, which seems