simplest chemical rule regarding ionization potentials (He first I.P. = 24.58 e.v.; F first I.P. = 17.42 e.v.) leads to the conclusion that HeF_2 is highly unlikely to be bound. This prediction based on this qualitative argument has been stated several times in recent theoretical treatments,[6-8] yet, not unexpectedly, this simple argument is stated with considerably less conviction than would be expressed by a chemist who had no knowledge of xenon chemistry. In fact, a detailed and well-reasoned communication has been published claiming the likely existence of a stable HeF_2.[9] It is for these reasons that the qualitative chemical arguments and their manifestation in terms of simple Hückel-like model theories[6-8,10] are subject to the "strong inference" criticism of Platt[11] and are inadequate to answer decisively the question of the existence of HeF_2. It is also necessary that the electronic wave function for the HeF_2 system be complete enough to provide a description of the free helium atom at the same level of accuracy as that needed to produce a smooth change from a free xenon atom at infinite separation to the observed stable binding. This has been accomplished in our wave function by carrying the ionic state and in–out configuration interaction into the free helium atom as infinite separation is approached.

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Nitroxides. XIV. A Stable Biradical in the Nitroxide Series

Sir:

We wish to report the synthesis of a stable biradical of the nitroxide series which exhibits a particularly evident coupling between the two unpaired spins.

Condensation of 2,2,5,5-tetramethyl-3-pyrrolidone[1] (I) with hydrazine in refluxing diethylene glycol gave the azine III, m.p. 157°. Oxidation of this azine with hydrogen peroxide in the presence of phosphotungstic acid[2,3] gave a mixture, separated by chromatography on alumina, of the monoradical[4] IV, m.p. 147° (from petroleum ether; 29% yield), and the biradical[4] V, mol. wt. 308 (mass spectrometry), large yellow crystals, m.p. 198° (from benzene, 18% yield).

The biradical V can also be obtained from IV by the same oxidation process (23% yield) or by treating a crude solution[5] of II[6] with hydrazine in diethylene glycol (14% yield).
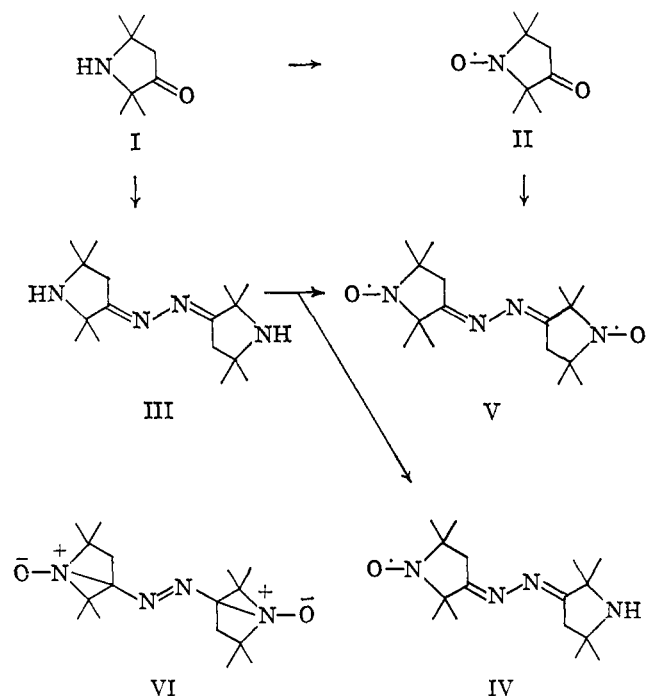
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The ultraviolet [λ_{max} 427.5 mμ (ϵ 17.7), to be compared with the known values (ϵ <10) of analogous nitroxides[4,5,7] and to IV, λ_{max} 427.5 mμ (ϵ 8.9)] and infrared spectra (no absorption in the N–H region, C=N band at 1660 cm.$^{-1}$) confirm the structure: V is composed of two independent nitroxide moieties similar to II. This excludes any structure related to VI. Furthermore, the intensity of e.p.r. absorption of a polycrystalline sample of V is 2.16 times the absorption of a polycrystalline sample of IV containing the same number of molecules.

However, the e.p.r. spectrum of V in solution is very different from spectra of cognate nitroxides[5,6]: while the monoradical IV displays the classical triplet (intensity ratio 1:1:1, a_N = 14.40 oersteds in dimethylformamide, g = 2.0055) corresponding to the hyperfine interaction of the unpaired electron with one nitrogen nucleus (Figure 1a), the biradical V shows a well-resolved quintet (Figure 1b) associated with the interaction of each unpaired electron with the nitrogen nuclei of the two equivalent nitroxide groups (intensity ratio 1:2:3:2:1, a_N = 7.20 oersteds in dimethylformamide, g = 2.0055). Thus, the important conclusion drawn from the e.p.r. spectrum is that this biradical behaves like a triplet state where the unpaired electrons present an exchange interaction greater than the hyperfine interaction.[8-10] However, coupling of electrons is neither sufficient to displace the absorption of the n → π^* transition in the ultraviolet spectrum nor sufficient to broaden the lines of the e.p.r. spectrum by dipolar interaction.[11] So, in the study of electronic interactions in organic molecules, the biradical V takes place between Chichibabin biradical,[9] where the hyperfine structure characterizes the inde-

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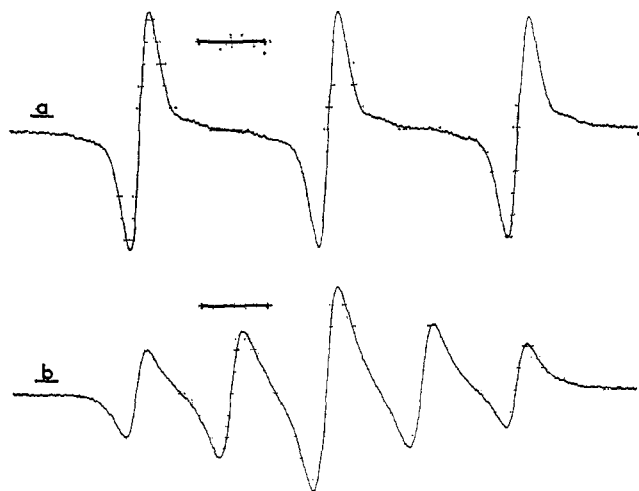(11) S. I. Weissman, *J. Chem. Phys.*, **29**, 1189 (1958).

Figure 1. First derivative e.p.r. spectra of: (a) monoradical (IV) and (b) biradical (V) in dimethylformamide. The scale is 5 oersteds for the two spectra. These spectra were recorded on samples which were not degassed. Degassed samples display essentially the same pattern, except for a narrowing of the individual lines.

Figure 1. Flash photolysis spectra of photodecarboxylation intermediates (see Table I).

pendence of the two moieties,[11a] and bisgalvinoxyl,[12] where no hyperfine structure can be observed in solution. Since structural parameters or solvent effects may change these interactions, further work is now in progress on the synthesis of related biradicals of the general type[12a]
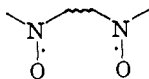
Acknowledgment. We thank Dr. G. Berthier for suggestions on free radicals and Dr. A. Witkowski for interesting discussions concerning dimers.

(11a) NOTE ADDED IN PROOF. We are indebted to a referee for pointing out that Chichibabin biradical is now known to exist in polymeric form in solution, so that interpretation of its spectrum should be ignored at this stage. See R. K. Waring and G. J. Sloan, *J. Chem. Phys.*, 40, 772 (1964).

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(12a) NOTE ADDED IN PROOF. We have now examples of biradicals in which the exchange interaction becomes approximately equal to or significantly less than the hyperfine interaction, according to the distance between the two NO groups. Our results suggest that the interpretations of spectra of biradicals in solution do not necessarily involve explanations such as the so-called "biradical paradox." See H. M. McConnell, *J. Chem. Phys.*, 33, 1868 (1960).

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Transient Photodecarboxylation Intermediates

Sir:

In the photolysis of aqueous solutions of nitrophenylacetate ions, spectra have been observed which are identified as those of transient photodecarboxylation intermediates. These are probably carbanions which have a strong resonance contribution from their corresponding *aci*-anion structures. The following reaction shown f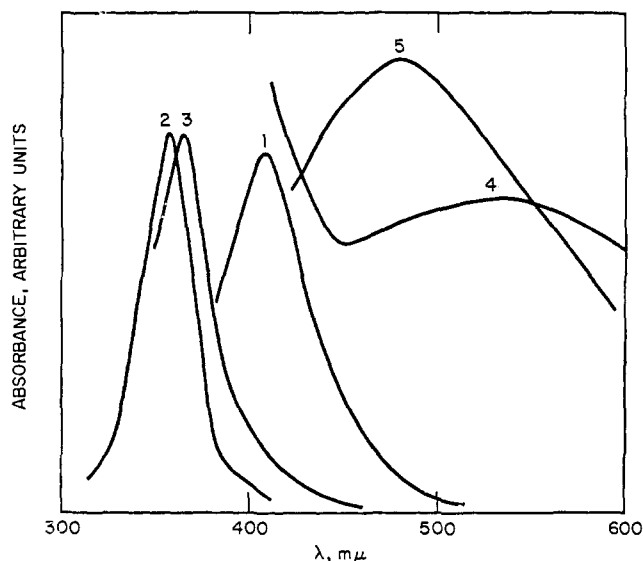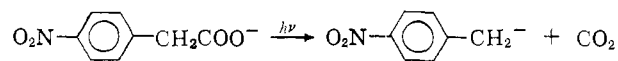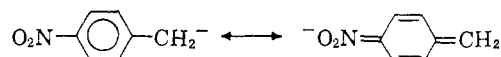or 4-nitrophenylacetate ions is believed to be typical of the photolyses in which a transient intermediate was observed.

$$O_2N-\langle\bigcirc\rangle-CH_2COO^- \xrightarrow{h\nu} O_2N-\langle\bigcirc\rangle-CH_2^- + CO_2$$

Where

$$O_2N-\langle\bigcirc\rangle-CH_2^- \longleftrightarrow {}^-O_2N=\langle\bigcirc\rangle=CH_2$$

The reaction products and the spectra of the photodecarboxylation transients are shown in Table I and Figure 1.

The transient shown from the flash photolysis of 2-nitrophenylacetate ions had an absorption maximum (408 mμ) and a first-order decay constant (1.0 sec.$^{-1}$ in the absence of O_2) identical with those of the *aci*-anion species observed by Wettermark in his photolysis of 2-nitrotoluene.[1] The relative efficiencies for the formation of this species were measured and found to be about three times greater by photodecarboxylation than by the photolytic hydrogen transfer reaction. Nevertheless, the quantum yield of decarboxylation was less than 0.1 at 367 mμ.

No transients with lifetimes longer than 0.5 msec. were found in the photolysis of 3-nitrophenylacetate ions. In contrast to the 2-nitro and 4-nitro compounds, a much weaker contribution to the resonance hybrid would be expected from an *aci*-structure in the 3-nitrobenzyl anion. However, photodecarboxylation occurred readily with a quantum yield of about one-half at 367 mμ.

The intermediate from photolysis of 4-nitrophenylacetate ions had an absorption maximum at 355 mμ in aqueous base. The maximum shifted to 360 mμ with *t*-butyl alcohol added up to 92% by volume. The latter position is in close agreement with the spectrum of the carbanion intermediate found by Miller and Pobiner[2] from the reaction of *t*-butoxide ions on 4-nitrotoluene in *t*-butyl alcohol. Their e.p.r. studies as well as the earlier ones of Russell and Janzen[3] showed that this intermediate was not a free radical,

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