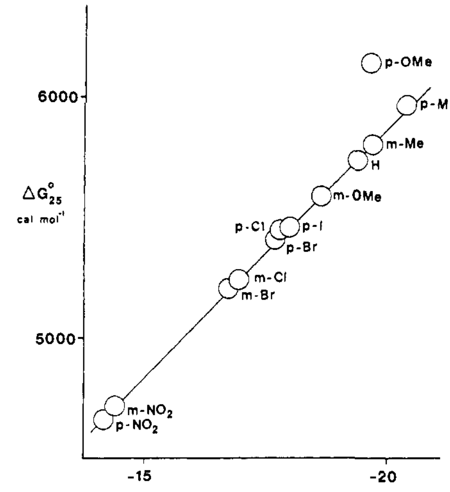

Figure 1. Linear relationship between the standard free energies and entropies of ionization of meta- and para-substituted benzoic acids.

at the 95% confidence level by the method of Clarke and Glew.[9] It should perhaps be emphasized that these are estimates of the precision of the results and they should not be interpreted as measures of the absolute error.

The consistently high precision of these results leads us to believe that they are the best set of data now available for the assessment of substituent effects on the ionization of benzoic acids. Certainly they appear to be free of most of the inconsistencies of the older data which were drawn from different sources of widely varying precision. As Figure 1 shows, providing the *p*-methoxy substituent is omitted from the correlation, a plot of the free energies of ionization against the corresponding entropy values is highly linear ($r = 0.9999$). Similar linearity, again with the *p*-methoxy substituent deviating significantly, is found for plots of $\Delta H°$ against $\Delta S°$ ($r = 0.9992$) and for $\Delta G°$ against $\Delta H°$ ($r = 0.9984$). Thus the ionization of benzoic acids can now be placed in category c above. It is also interesting to note that the least-squares slope of the plot of $\Delta G°$ against $\Delta S°$ is $-205°$K, which is very close to the value of $-218°$K predicted by classic electrostatic theory.[10]

It is possible that the deviation of the *p*-methoxy substituent has its origin in the cross-conjugation effects[11] arising when the $+$M *p*-methoxy substituent is located para to the carboxyl reaction center.

Acknowledgment. We thank the Australian Research Grants Committee for financial support.

(10) E. J. King, "Acid–Base Equilibria," Pergamon Press, Oxford, 1965, p 210.

(11) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

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Pyridinyl Hetero Diradicals. Intramolecular Interaction between Two Different Pyridinyl Radicals

Sir:

Pyridinyl diradicals[1] associate intramolecularly to form molecular complexes which are regarded as radical dimers.[2] In a previous paper,[3] we reported the intramolecular electronic interaction in the pyridinyl cation radicals in which the pyridinyl radical and pyridinium cation were connected with tri- or tetramethylene groups. The intramolecularly associated cation radicals were considered to be dimer radicals.[4] While numerous studies of the radical dimers and dimer radicals have been carried out, only few spectroscopic studies of the electronic interaction between two kinds of radicals have been reported.[5,6]

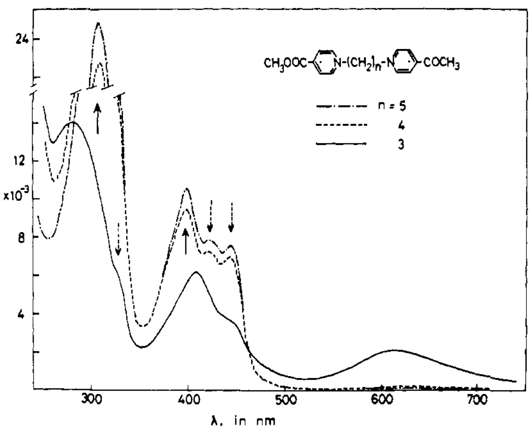
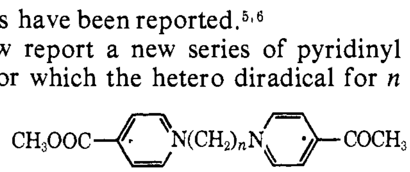


Figure 1. The absorption spectra of the hetero diradicals **3**, **4**, and **5** in MTHF at room temperature (27–28°): ←— and ←--- show absorption bands due to 4-carbomethoxy- and 4-acetylpyridinyl moieties, respectively. Concentration of the diradical was determined by electron-transfer reaction to methylviologen (E.M. Kosower and J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964)).

We now report a new series of pyridinyl hetero diradicals for which the hetero diradical for $n = 3$ associates intramolecularly to show charge-transfer interaction (closed form[1,3]) between two different pyridinyl moieties. The previous papers demonstrated that the diradicals (homo) and the cation radicals consist of the open and closed forms in equilibrium, respectively. However, no direct observation of the equilibrium was presented. Now the equilibrium of the open and closed forms of the hetero diradical ($n = 3$) has been directly observed by temperature dependence of the absorption spectra.



$n = 3$, 4, and 5

The pyridinyl hetero diradicals (**3** for $n = 3$, **4** for 4, and **5** for 5) were prepared by reduction of the corresponding diiodides or dibromides in the manner previously described.[1,3] 2-Methyltetrahydrofuran (MTHF) was used as the extractant. The absorption spectra of the MTHF solutions of **3**, **4**, and **5** were determined at room temperature (27–28°), as shown in Figure 1. It is noteworthy that the spectrum of **3** shows a new absorption band at 615 nm, while the

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(1) M. Itoh and E. M. Kosower, *J. Amer. Chem. Soc.*, **89**, 3955 (1967); **90**, 1843 (1968).

(2) See references in ref 1.

(3) M. Itoh, *J. Amer. Chem. Soc.*, **93**, 4750 (1971).

(4) See references in ref 3.

(5) K. Takemoto, S. Nakayama, and K. Suzuki, *Bull. Chem. Soc. Jap.*, **41**, 1974 (1968).

(6) T. Yamazaki and K. Kimura, *ibid.*, **44**, 298 (1971).

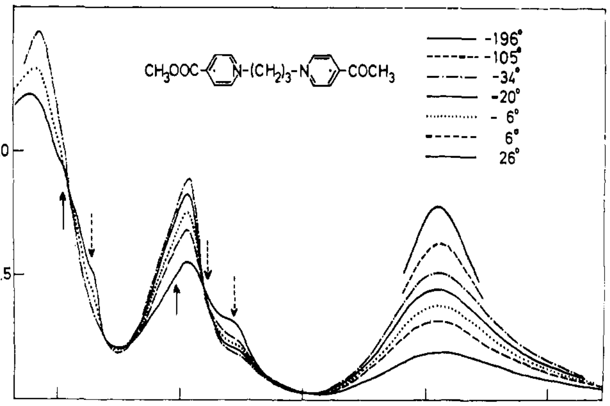

Figure 2. Temperature dependence of the spectrum of **3** in MTHF. Concentration is $0.85 \times 10^{-4} M$: ⟵ and ←--- show absorption bands due to 4-carbomethoxy- and 4-acetylpyridinyl moieties, respectively.

spectrum of **5** is very much similar to the sum of the spectra of 1-methyl-4-carbomethoxy- and 1-methyl-4-acetylpyridinyl radicals.[7] According to the concentration independence of the spectrum of **3** at room temperature (1×10^{-3}–5×10^{-5} *M*), the absorption spectrum of **3** can be ascribed to the intramolecular interaction, and the visible absorption at 615 nm may be a charge-transfer band between two kinds of pyridinyl moieties.

The spectrum of the MTHF solution of **3** shows remarkable temperature dependence with several isosbestic points, as shown in Figure 2. The intensities of 615- and 408-nm absorption bands increased, while the absorption due to each pyridinyl moiety decreased with decreasing temperature. These temperature dependences of the absorption bands remove a possibility of the equilibrium between singlet and triplet states[8] in the closed form of **3**, and suggest the equilibrium of the open and closed forms, mentioned above. If ϵ_c is assumed to be a molar absorption coefficient of the closed form of **3**, since the molar absorption (ϵ) at 615 nm increased to approach 7800 with decreasing temperature, plots of $\log [\epsilon/(\epsilon_c - \epsilon)]$ against $1/T$ show a straight line in dilute solution, as shown in Figure 3. The enthalpy ($-\Delta H$) and entropy (ΔS) changes from the open to the closed form were evaluated to be 5.6 kcal and -10.5 eu, respectively. Deviation of the plots from the straight line in rather concentrated solution may be due to intermolecular interaction between the diradicals.

An unexpectedly low-spin concentration of **3** (~14%) was observed at room temperature.[9] However, Figure 2 suggests that the open form of **3** in MTHF amounts approximately to 70%. A similar difference between observed spin concentration and the expected one from the absorption spectrum was also observed in **4**. The effective distance for the spin dipolar interaction seems to be greater than that for the observable charge-transfer band between two radical moieties. From these considerations, it seems that the open-form diradical, in which the charge-transfer band is unobserved, is divided into two kinds of conformations. These open forms are a weakly *interacted* conformation of the radical moieties and a *noninteracted* one, which are energetically similar. In the former, the spin dipolar interaction of two moieties results in undetectable broad esr through motional broadening in liquid solution.

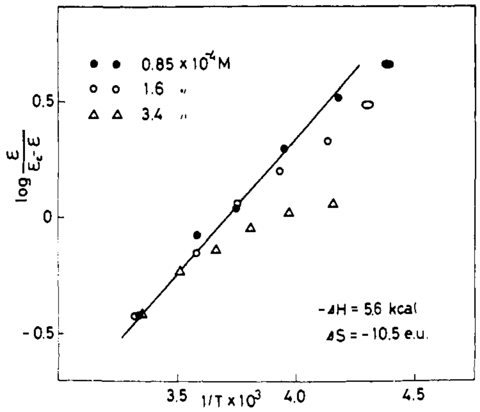

Figure 3. Plots of $\log [\epsilon/(\epsilon_c - \epsilon)]$ against $1/T$ in the hetero diradical **3**. A straight line was obtained by a least-squares fit, where the data at $-48°$ were excluded from the calculation.

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[8] T. Sakata and S. Nagakura, *ibid.*, **42**, 1497 (1969).

[9] Determination of relative spin concentration was done using the same procedure as described in the previous papers (ref 1).

Quenching of Excited States by Stable Free Radicals. The Effect of Di-*tert*-butyl Nitroxide on Stilbene and Naphthalene Triplets

Sir:

Several authors have recently reported the use of stable free radicals as quenchers of reactive intermediates in photochemical reactions.[1,2] Curiosity about the interactions between free radicals and excited species, and a desire to evaluate quenching by free radicals as an adjunct to existing methods for studying photochemical reactions, prompted us to undertake a systematic study of the mechanism by which di-*tert*-butyl nitroxide[3] (DTBN) quenches photoexcited triplets in solution. We have initially chosen to monitor DTBN quenching of sensitized trans → cis isomerization of *trans*-stilbene. This system has been studied extensively and seems to be well understood.[4] We present here our initial results, which indicate that DTBN quenches both benzophenone and stilbene triplets with high efficiency, and that these triplets are quenched significantly more rapidly than naphthalene triplet.

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[2] L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6497 (1969).

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[4] (a) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (b) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966); (c) J. Saltiel, *ibid.*, **89**, 1036 (1967); (d) J. Saltiel, *ibid.*, **90**, 6394 (1968); (e) H. A. Hammond, D. E. de Meyer, and J. L. R. Williams, *ibid.*, **91**, 5180 (1969); (f) R. A. Caldwell and R. P. Gajewski, *ibid.*, **93**, 532 (1971).