

+53° (c 0.8, H₂O) [lit.³ mp 210–215° dec; [α]^{21D} +45°]. A sample of Gougerotin kindly provided by Iwaski showed [α]^{27D} +53°. The uv data found for synthetic and natural Gougerotin were identical [uv in 0.1 N HCl) λ_{max} 275 nm (ε 13,600), λ_{min} 239 (3000); (in water) λ_{max} 267 and 235 (9400, 9300), λ_{min} 252, 227 (8500, 9200); in 0.1 N NaOH) λ_{max} 267 (9800), λ_{min} 252 (8900)]. The ir spectra of natural and synthetic Gougerotin were identical as were also their paper electrophoretic mobilities (−3.3 cm).

For biochemical and biological comparison, the natural and synthetic samples were chromatographed¹⁴ (Whatman No. 1 paper, descending, *n*-BuOH–HOAc–H₂O, 4:1:2). The band was excised, extracted with water, and concentrated to a powder. The samples were then compared for their capacity to interfere with the formation of *N*-acetylphenylalanyl puromycin from *N*-acetylphenylalanyl RNA and puromycin in a ribosomal system derived from *E. coli*.^{15a} Both samples inhibited this reaction by 58 ± 3% at 4 × 10^{−5} M.^{15b} The growth inhibitory potency of synthetic Gougerotin against *E. coli* B was found to be the same as that exhibited by the natural antibiotic (50% inhibition at 4 × 10^{−5} M).^{15c}

On the basis of the physicochemical and biological comparisons, it is concluded that the synthetic compound 7 is identical with Gougerotin. Since we have previously reported⁸ the preparation of a C substance from D-galactose, the synthesis of Gougerotin presently described constitutes a total synthesis of this nucleoside antibiotic. The syntheses of analogs of Gougerotin and the determination of their biological activities are in progress and will be reported elsewhere.

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(14) The natural Gougerotin sample was found to contain a faster migrating, fluorescent impurity which was removed by this process.

(15) (a) See C. Coutsogeorgopoulos, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **31**, 3603 (1972), for details of this system. (b) Personal communication from Dr. C. Coutsogeorgopoulos, Roswell Park Memorial Institute. (c) Personal communication from Dr. Alex Bloch, Roswell Park Memorial Institute, Buffalo, N. Y.

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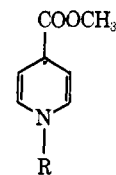
Associated Triplet States of Pyridinyl Radicals

Sir:

Pyridinyl radicals **1** associate intermolecularly to form diamagnetic dimer **2**, in which the self-association of the radicals has been interpreted in terms of charge-transfer complex formation.¹ Kosower and Waits² have found that a small amount of triplet dimer **3** is in equilibrium with the singlet dimer **2**. A triplet state has also been recognized for a two-spin system of 1,1'-

(1) M. Itoh and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 3959 (1967).

(2) E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 438.



1a, R = CH₃

b, R = CH₂CH₃

2, Py·Py· singlet dimer

3, Py·Py· triplet dimer

(Py = 1)

ethylenebis(4-carbomethoxy-pyridinyl) diradical in 2-methyltetrahydrofuran (MTHF) glass.³

We now report the observation of two triplet states in the self-association of pyridinyl radicals in MTHF glass. The results relate to the formation of associated triplet state from the singlet dimer by light irradiation and the complex formation of the radical with sodium iodide.

The epr spectrum of pure 4-carbomethoxy-1-methyl- (or ethyl)pyridinyl (**1a** or **1b**) in MTHF glass (α solution) measured in a dark room showed three pairs of shoulders on both sides of a strong $g = 2$ signal (at 3295 G) due to monoradicals. The spectrum is shown in Figure 1a. This is the indication of the existence of a triplet state which was previously suggested by Kosower and Waits.² Appearance of the $\Delta M = 2$ transition in the epr spectrum at 1645 G clearly proves the triplet. The intensities of the three pairs of lines decrease proportionally with decreasing concentration and disappear at around 3 × 10^{−3} mol/l. The zero-field parameters⁴ estimated roughly are $D = 0.0098$ cm^{−1} and $E = 0.0011$ cm^{−1}, with $D + 3E = 141$ G and $2D = 202$ G. The values are similar for both radicals **1a** and **1b**. The D value is consistent with a spin-spin dipolar interaction for an average separation of 6.5 Å, using the relation $D = -(3/2)g^2\beta^2r^{-3}$.⁵

Irradiation of the α solution at 77°K with visible light added a new triplet signal (B_T signal) to the epr spectrum, as seen in Figure 1b. The intensity of the signal at 1645 G increased, while the signal intensity in the $g = 2$ region did not vary after the irradiation. The B_T signal lived for over 10 hr at 77°K after the light was shut off. Moreover, the phenomenon is completely reproducible for a cycle of warming, cooling, and irradiation.

The B_T signal is observed with rather better resolution and substantially higher intensity when the radical solution is saturated with sodium iodide. The epr spectrum of this solution (β solution = α solution + NaI) at 77°K does not have any shoulders due to the A_T form at around the $g = 2$ signal. Irradiation of the solution with light added a triplet spectrum consisting of two pairs of lines at the same position as those which appeared in Figure 1b. The spectra are shown in Figure 2. The zero-field parameters for the B_T signal are $D = 0.0175 \pm 0.0005$ cm^{−1} and $E \approx 0$, with $2D = 373 \pm 5$ G, an average of the similar values for both radicals **1a** and **1b**. It is suggested from the 0 E value that the association of radicals (B_T form) has more

(3) E. M. Kosower and Y. Ikegami, *J. Amer. Chem. Soc.*, **89**, 461 (1967).

(4) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(5) N. Hirota, *J. Amer. Chem. Soc.*, **89**, 32 (1967).