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# *Physical and Inorganic Chemistry*

## Intramolecular Electronic Energy Transfer in Some Indole Alkaloids and Related Donor–Acceptor Systems[1]

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*Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457.* *Received May 4, 1968*

**Abstract:** Spectral and triplet counting methods have demonstrated that intramolecular singlet–singlet transfer occurs with 100% efficiency between nonconjugated, chemically different chromophores in four indole alkaloids: reserpine, deserpidine, rescinnamine, and 17-(α-naphthyl)yohimbol. As Forster's resonance mechanism does not predict such high efficiency for the donor–acceptor separations and restricted orientations involved, exchange modes of singlet–singlet transfer are assumed to operate as well. A low-temperature emission spectroscopic examination of Blout's compound has been carried out, illustrating the absence of triplet–triplet energy transfer at a distance of 20 Å.

Current interest in the intramolecular transfer of electronic excitation between isolated chromophores has still not led to a precise understanding of the mechanisms involved, especially in the case of intermediate and small donor–acceptor separations.[3,4] Forster[5] and Dexter[6] have been largely responsible for theoretical treatments of resonance and exchange modes of electronic energy transfer, the two primary types of processess assumed to be operating in both intra- and intermolecular cases. In addition, there exists a fair amount of experimental data on intramolecular electronic energy transfer between nonconjugated, chemically different chromophores,[7–12] some of which at least appear to be theoretically uninterpretable.

Schnepp and Levy[7] reported singlet excitation transfer from naphthalene to anthracene moieties in a series of three compounds, where the two chromophores were separated by a "bridge" of one to three methylene groups. Transfer efficiency (30 ± 13%) was invariant with methylene chain lengths, and resonance interaction was discussed as a possible mechanism. Our colleagues and we[8] have documented both singlet–singlet and triplet–triplet excitation transfer between isolated chromophores in compounds analogous to those of Schnepp and Levy, but where anthracene was replaced by benzophenone. Triplet–triplet transfer from benzophenone to naphthalene chromophores was 100% efficient, while singlet–singlet transfer (from naphthalene to benzophenone) was 98, 80, and 94% efficient for compounds of one, two, and three methylene bridges, respectively. In both sets of compounds, various conformers (due to the flexibility of the "bridge") caused possible face-to-face approach of the chromophores. Although an exchange mechanism was suggested for triplet–triplet transfer, no rationale for the decreased singlet–singlet transfer efficiency could be given with certainty.

Blout[9] studied singlet–singlet excitation transfer in XII, where the separation of anthracene (acceptor) and naphthalene (donor) constituents is 20 Å, a distance which should rule out the possibility of exchange inter-

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[1] Abstracted in part from the M.A. Thesis of R. D. Rauh, Wesleyan University, 1968.

[2] Alfred P. Sloan Fellow.

[3] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

[4] A. A. Lamola in "Energy Transfer and Organic Photochemistry. Technique of Organic Chemistry," Vol. XIV, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1969.

[5] T. Forster, *Discussions Faraday Soc.*, 27, 1 (1959).

[6] D. L. Dexter, *J. Chem. Phys.*, 21, 836 (1953).

[7] O. Schnepp and M. Levy, *J. Am. Chem. Soc.*, 84, 172 (1962).

[8] P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *ibid.*, 85, 2670 (1963); 87, 2322 (1965).

[9] S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, 87, 995 (1965).

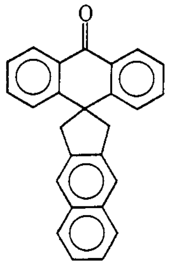
[10] R. A. Keller and L. J. Dolby, *ibid.*, 89, 2786 (1967).

[11] D. E. Breen and R. A. Keller, *ibid.*, 90, 1935 (1968).

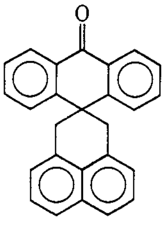
[12] R. A. Keller, *ibid.*, 90, 1940 (1968).

actions. Transfer efficiency was about 20% higher than calculated by the Forster treatment. Restrictions of orientation of the two chromophores was indicated as a possible explanation.

Recently Keller[12] has documented 100% singlet–singlet and triplet–triplet transfer between chromophores in compounds I and II. The lowest singlet and triplet states of the ketone portion are positioned energetically between those of naphthalene, so that it serves as both singlet acceptor and triplet donor in both compounds. Due to the perpendicularity of the donor and acceptor transition moments in I and II, such efficiency can be due only to electronic exchange, or to resonance *via* distorted orientations of the donor and acceptor.



I

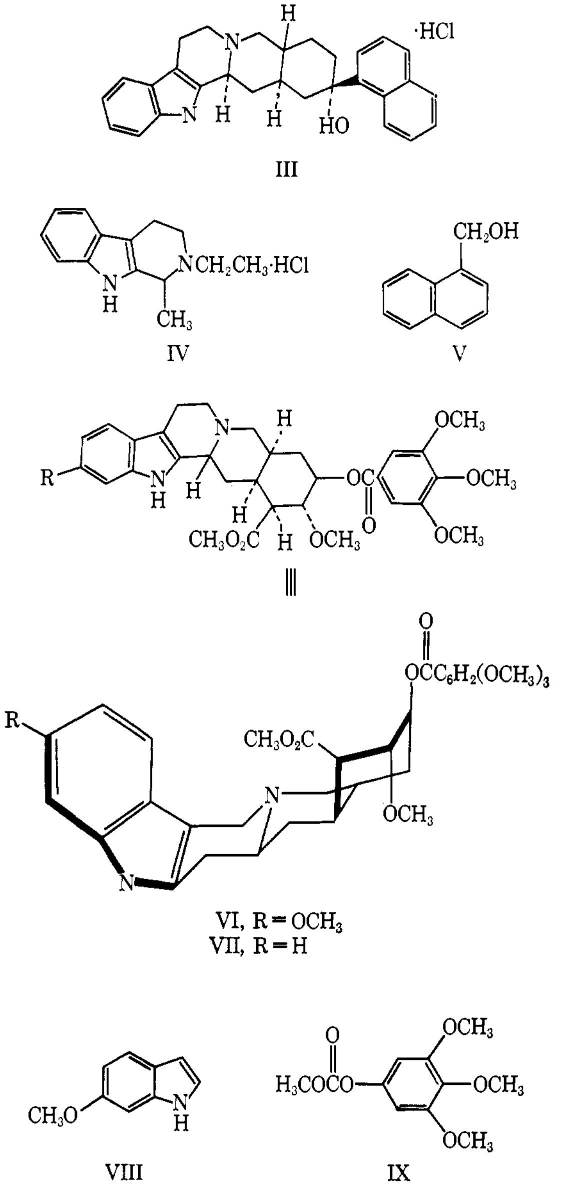


II

It is interesting to note, however, that little is known concerning the factors regulating singlet–singlet excitation transfer in these molecules, so that the relative contributions of exchange and resonance singlet–singlet excitation transfer in most systems with small and intermediate donor–acceptor separations is difficult to determine. Dubois[13,14] has demonstrated that the sensitization of biacetyl fluorescence by a variety of energy-transfer agents proceeds by an exchange mechanism, presumably because of biacetyl's weak $S_0 \rightarrow S_1$ transition, making the resonance process slow and inefficient. Singlet quenching spheres were on the order of 4–6 Å. Therefore, the predominance of resonance excitation transfer, even at relatively small donor and acceptor separations, can be considered to be proportional to the magnitude of the acceptor's transition moment. Collisional separations, or for Terenin and Ermolaev's hard-shell model,[15] quenching spheres of influence for singlet–singlet excitation transfer appear to differ from those for triplet–triplet exchange (see, for instance, our earlier papers[8]). Singlet exchange processes in systems where acceptor $S_0 \rightarrow S_1$ transitions are strong may not have time to occur, and the faster resonance transfer of electronic energy will dominate. In the intramolecular case, the possible orientations of donor and acceptor transition dipoles is also an extremely important factor in the evaluation of resonance-transfer efficiencies, especially in cases where an exchange mechanism is not likely to contribute.

The purpose of this paper is to examine intramolecular singlet–singlet energy transfer between chemically different, nonconjugated chromophores, in four indole alkaloids: reserpine, deserpidine, 17-(α-naphthyl)yohimbol, and rescinnamine. In each case, the indole donor is separated from the acceptor by a saturated, fused-ring network, but some variation in donor–acceptor orientation is allowed. The donor–acceptor separations (5–12 Å) and restricted orientations involved make deviations from the Forster mechanism likely. In addition, triplet–triplet energy transfer in Blout's steroid, where even greater donor–acceptor distances are involved, has been scrutinized with an aim to place an upper limit on distance requirements for the exchange mechanism. (See Chart I for structural formulas.)

**Chart I.** Structures III–XII



III

IV

V

III

VI, R = OCH₃
VII, R = H

VIII

IX

## Experimental Section

**Emission and Absorption Spectra.** Emission spectra were recorded at liquid nitrogen temperature on an Aminco-Bowman spectrophotofluorimeter (SPF) with phosphoroscope and transmission attachments. The SPF was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. Absorption spectra were recorded on a Perkin-Elmer 202 ultraviolet-visible recording spectrophotometer. The solvent used for all emission spectra was a 1:1 mixture of diethyl ether and tetrahydrofuran (THF). All absorption spectra were recorded in this solvent as well as in cyclohexane and ethanol.

**Determination of Intersystem Crossing Efficiency.** Intersystem crossing yields ($\phi_{ic}$) were obtained according to the method of Lamola.[16] Solutions of the compounds to be studied were pre-

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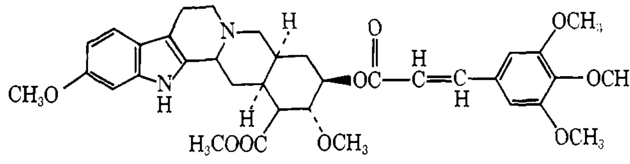
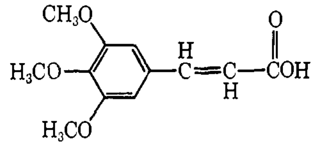
[13] J. T. Dubois and M. Cox, *J. Chem. Phys.*, 38, 2536 (1962).

[14] J. T. Dubois and F. Wilkenson, *ibid.*, 38, 2541 (1962); 39, 377 (1963).

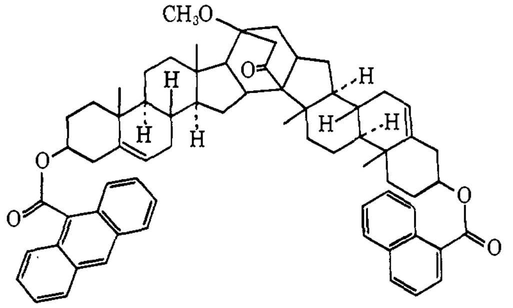
[15] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, 52, 1042 (1956).



X



XI



XII

pared in acetonitrile and the concentrations were adjusted to give an absorbance of 3 at 2537 Å. Each solution was also 0.05 *M* in *cis*-piperylene. Samples of 3 ml were sealed in evacuated, 7-mm quartz tubes by the freeze-pump-thaw method. Irradiation was carried out for 1-1.5 hr at 2537 Å in a Rayonet reactor equipped with a merry-go-round apparatus, as supplied by the Southern New England Ultraviolet Company, Middletown, Conn. At this point, there was no more than 15% conversion of *cis*- to *trans*-piperylene. Benzophenone and naphthalene, whose intersystem crossing yields under these conditions are 1.00 and 0.39,[16] respectively, were used as standards. The ratios of *cis*/*trans* piperylene of each compound under investigation were compared to those of the standards after an equal period of irradiation, and $\phi_{ic}$ values were calculated. Analyses were performed by vapor phase chromatography of the reaction mixtures. A $\beta,\beta'$-oxypropiodinitrile column used at room temperature gave good separation of the two isomers. The "cut out and weigh" method was employed to determine the relative amounts of the two isomers present in each sample.

**Materials.** All solvents were of spectroscopic or reagent grade and were used without further purification. Reserpine, deserpidine, and rescinnamine were obtained commercially. A sample of Blout's compound was supplied by Professor E. R. Blout of the Harvard Medical School. The hydrochloride salt of 17-($\alpha$-naphthyl)yohimbol was graciously provided by the Warner-Lambert Research Institute, Morris Plains, N. J., research affiliate of Warner-Chilcott Laboratories.

## Results

**A. Indole Alkaloids.** All four indole alkaloids studied were found to undergo 100% efficient intramolecular singlet-singlet excitation transfer. The energetic dispositions of the lowest singlet and triplet states of the constituent chromophores of each indicate that the indolic portion is the only candidate for singlet or triplet donor in these molecules (Figure 1). Therefore, with completely efficient singlet-singlet transfer, no triplet-triplet transfer may occur. Singlet and triplet energies of the relevant compounds are given in Table I.

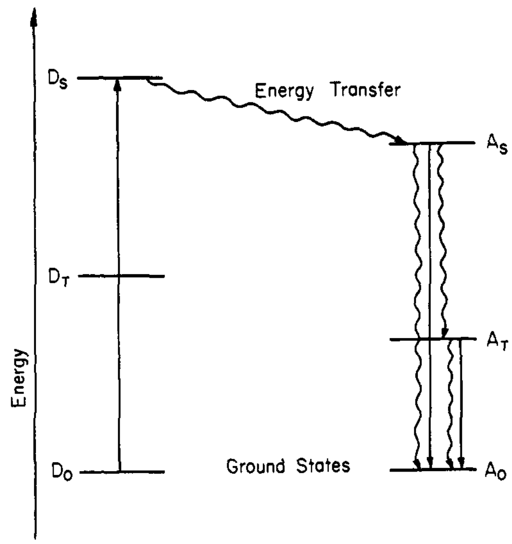


Figure 1. The relative energetic dispositions of donor (D) and acceptor (A) and singlet (S) and triplet (T) states in the compounds studied. Also shown are the radiative (solid arrow) transitions and radiationless (wavy arrow) transitions potentially operating in these cases.

**Absorption Spectra.** The coincidence of absorption spectra of each alkaloid with that of an equimolar (0.001 *M* in each) solution of models of each of its constituent chromophores and with addition spectra composed of spectra of the two models taken separately served to determine the absence of complexes or other independently absorbing species in the alkaloids which might alter energy-transfer results. This result is actually not surprising. The stereochemistry of 17-($\alpha$-naphthyl)yohimbol (III) would make the type of geometry necessary for close face to face interaction unattainable, due to the *trans*-fused ring system and the inability of the naphthalene moiety to explore any conformations except for those arising from rotation about the $C_{17}$ bond.

**Table I.** Energies[a] of the Lowest Singlet and Triplet States of the Bridged Compounds and Donor and Acceptor Models

| Compound | $E_S$, kcal | $E_T$, kcal |
|---|---|---|
| Reserpine (VI) | 91.3 | 67.8 |
| Methyl 3,4,5-trimethoxybenzoate (IX) | 91.3 | 67.0 |
| 6-Methoxyindole (VIII) | 96.0 | 71.5 |
| Deserpidine (VII) | 91.3 | 67.8 |
| Indole | 94.0 | 68.4 |
| 17-($\alpha$-Naphthyl)yohimbol·HCl (III) | 90.6 | 64.5 |
| Indole model (IV) | 98.8 | 74.5 |
| $\alpha$-Naphthyl carbinol (V) | 90.0 | 64.5 |
| Rescinnamine (X) | 84.0 | <69.5 |
| 3,4,5-Trimethoxycinnamic acid (XI) | 84.5 | <69.5 |
| Bout's compound (XII) | 74.4 | 61.5 |
| Methyl 1-naphthoate | 89.4 | 61.5 |
| Methyl 9-anthroate | 74.3 | 45 |

[a] Approximate 0-0 energies. Values of $E_S$ were measured at the point of crossing of excitation and fluorescence spectra. Values of $E_T$ were determined at the onset of phosphorescence where intensity reached 1% of its maximum value.

The *cis* fusion of rings D and E of reserpine (VI) and deserpidine (VII) and the flexibility of the carboxylate group bridging $C_{16}$ and the trimethoxyphenyl constituent make possible a spread of 6 to 10 Å for donor–

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(16) A. A. Lamola, Ph.D. Thesis, California Institute of Technology, 1965; A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

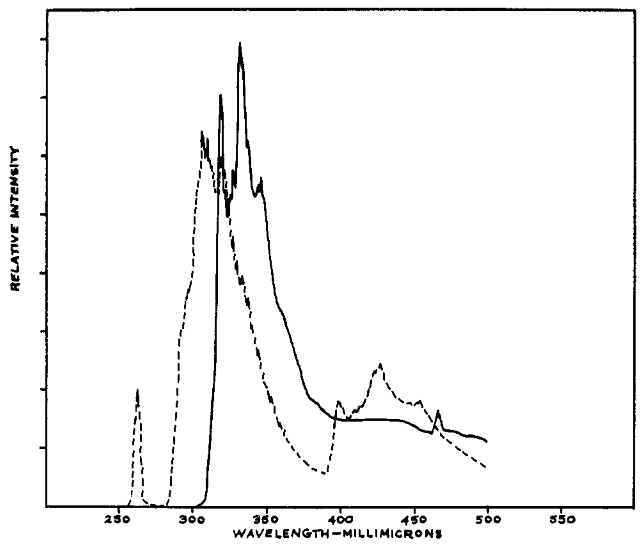

Figure 2. Total emission: indole model (IV), - - - - -; 17-(α-naphthyl)yohimbol (III), ——.

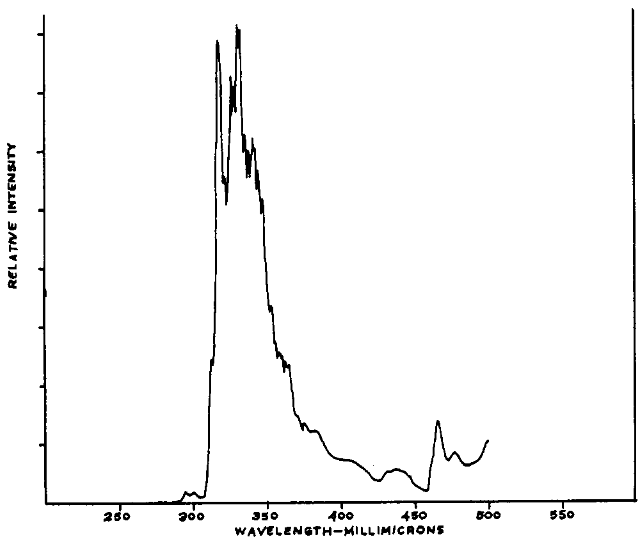

Figure 3. Total emission of α-naphthylcarbinol (V).

acceptor ring separations. Nevertheless, distances of considerably less than 6 Å normally would be required for complex formation, so that even if these alkaloids were present predominantly in their folded forms, independently absorbing and emitting complexes would be expected to be absent. The case of rescinnamine (X) is similar to that of reserpine and deserpidine, except that there is a possibility of a 5 Å donor–acceptor ring separation in the folded form. The stereochemistry of X is similar to that of VI and VII.

**Total Emission Spectra.** The fluorescence spectrum of each compound was compared in shape, frequency and intensity to that of models of the two constituent chromophores. All emission was measured at 77°K in an ether–THF glass. Concentrations were invariably 0.001 *M*. Since, in all cases, both singlet–singlet and triplet–triplet transfer could occur through the same donor, and since none of the donors studied undergo intersystem crossing with high efficiency, lack of donor fluorescence is one criterion for completely efficient singlet–singlet excitation transfer.

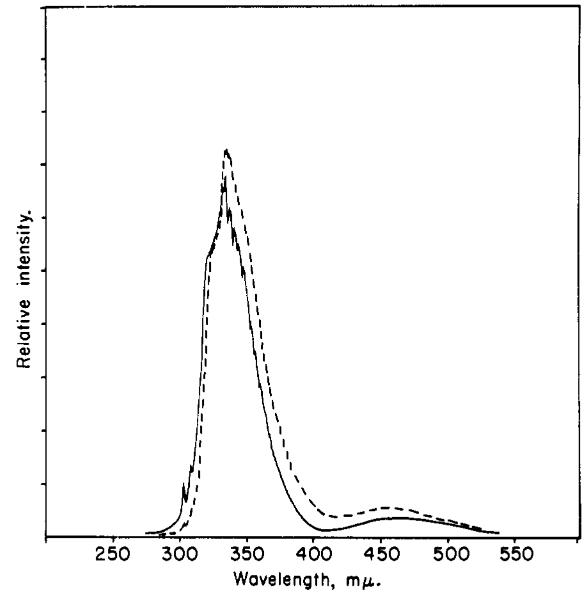

Figure 4. Total emission: methyl trimethoxybenzoate, ——; reserpine (VI), - - - - - -.

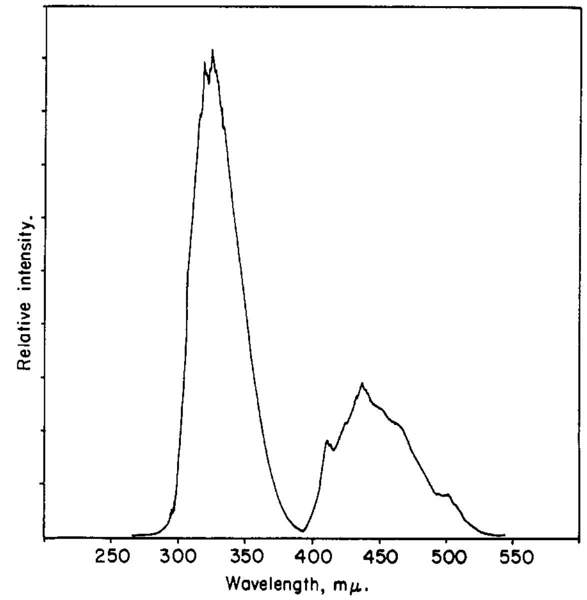

Figure 5. Total emission of 6-methoxyindole (VIII).

Figure 2 gives the total emission spectrum of III (0.001 *M*) compared with that of the indole model (IV). Excitation was at 2537 Å where the indole absorbs 62% of the light. Only emission characteristic of the naphthalene model (V) was found for the alkaloid, as is obvious from comparison of Figures 2 and 3. Figures 4 and 5 show the total emission spectra of reserpine, and models of its indole (VIII) and trimethoxybenzoate (IX) constituents. All reserpine emission is characteristic of the 3,4,5-trimethoxybenzoate acceptor. This result is especially unambiguous since the fluorescent intensity of the indole model is approximately twice that of the benzoate. Identical results were obtained for deserpidine (VII).

The total emission spectra of rescinnamine (X), and 3,4,5-trimethoxycinnamic acid (XI) are reproduced in Figure 6. Comparing these with the emission spec-

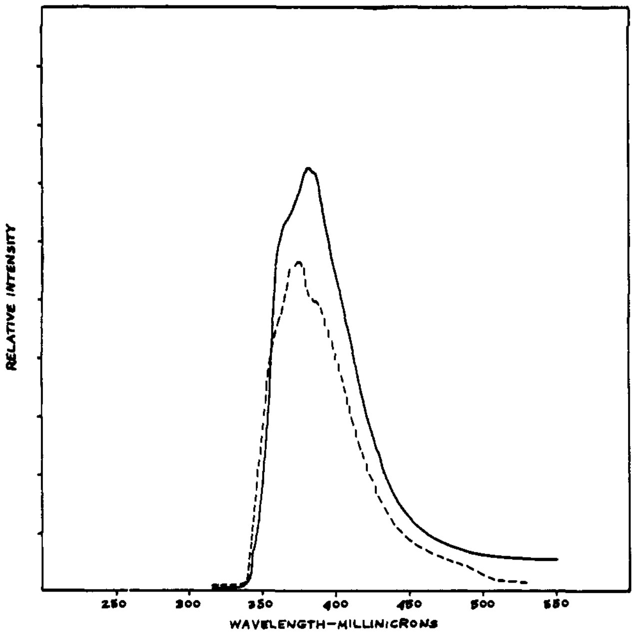

Figure 6. Total emission: rescinnamine (X), ——; trimethoxycinnamic acid (XI), - - - - -.

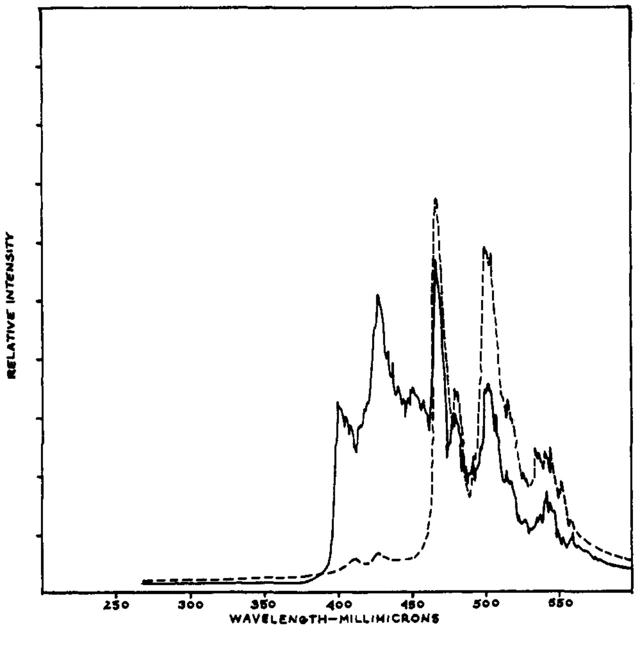

Figure 7. Phosphorescence: 17-($\alpha$-naphthyl)yohimbol (III), - - - - -; equimolar mixture IV and V, ——.

trum of methoxyindole (Figure 5) demonstrates with certainty that all emission is originating from the cinnamate portion of X, even though at the excitation wavelength (3130 Å) the indolic portion absorbs 53% of the light. As with reserpine and diserpidine, the fluorescent intensity of the indolic portion alone is about twice that of the cinnamate portion, so that even very small amounts of donor fluorescence should be detectable.

**Phosphorescence Spectra.** Comparison of the phosphorescence emission spectra of the alkaloids with that of their constituent chromophores serves to verify the results obtained from the fluorescence analysis. If neither fluorescence nor phosphorescence is observed to originate from the donor constituent of each alkaloid, 100% singlet–singlet transfer is further substantiated.

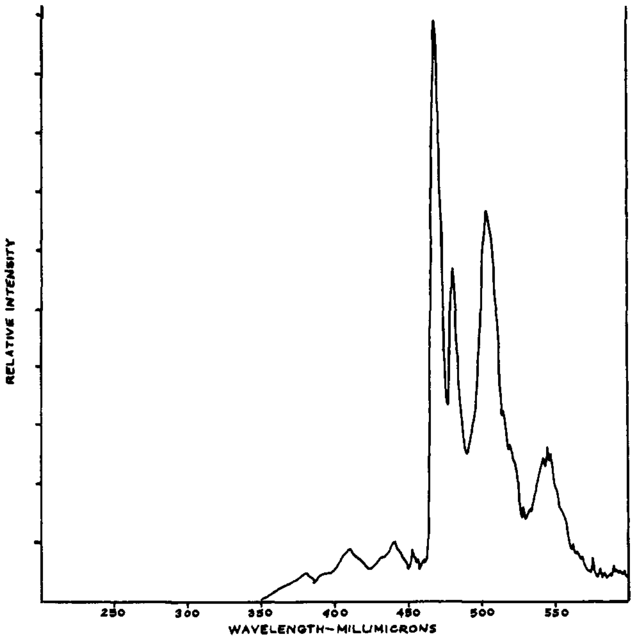

Figure 8. Phosphorescence of $\alpha$-naphthylcarbinol (V).

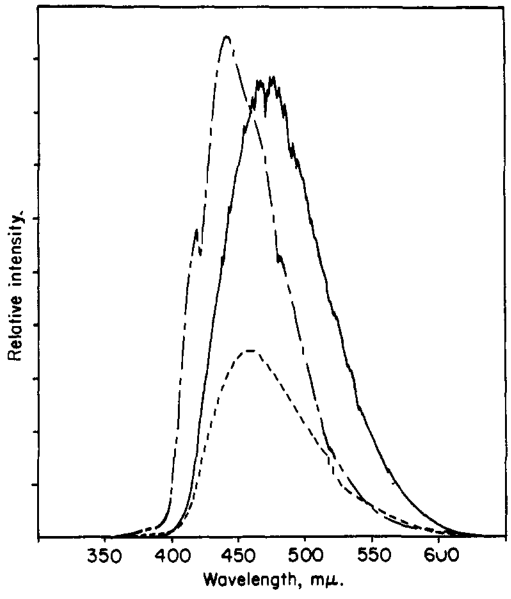

Figure 9. Phosphorescence: 6-methoxyindole (VIII) (attenuated 3×), — — — —; methyl trimethoxybenzoate (IX), ——; reserpine (VI), - - - - -.

Figure 7 shows the phosphorescence emission spectrum of 17-($\alpha$-naphthyl)yohimbol (III), and that of an equimolar mixture of its two constituents (IV, V), while Figure 8 shows that of the acceptor, $\alpha$-naphthyl carbinol (V). Figure 9 give the phosphorescence emission spectrum of reserpine (VI) compared to that of the acceptor model, methyl 3,4,5-trimethoxybenzoate, and that of the donor model, 6-methoxyindole. The deserpidine (VII) case is nearly identical.

The triplet electronic energy of 3,4,5-trimethoxycinnamic acid (XI), the acceptor model for rescinnamine, is very likely dissipated by the radiationless process of twisting around its ethylenic double bond.

Table II. Intersystem Crossing Yields[a] of Indole Alkaloids and Donor and Acceptor Models

| | $\phi_{ic}$(donor) | $\phi_{ic}$(acceptor) | $\phi_{ic}$(alkaloid) |
|---|---|---|---|
| Reserpine | 0.22 | 0.28 | 0.29 |
| Deserpidine | 0.18 | 0.28 | 0.28 |
| 17-($\alpha$-Naphthyl)-yohimbol·HCl | 0.19 | 0.38 | 0.38 |
| Rescinnamine | 0.19 | Unquenchable | Unquenchable |

[a] Average of three values, maximum deviation less than ±10%.

Table III

| | $R_0$, Å | $R_{min}$,[a] Å | $T_{min}$,[b] % | $R_{max}$,[a] Å | $T_{max}$,[b] % | $T_{obsd}$, % |
|---|---|---|---|---|---|---|
| III | 19.5 | 10 | 98.3 | 12 | 94.9 | 100 |
| Reserpine (VI) | 13.3 | 6 | >99 | 10 | 84.8 | 100 |
| Deserpidine (VII) | 13.5 | 6 | >99 | 10 | 86.6 | 100 |
| Rescinnamine (X) | 14.8 | 5 | >99 | 12 | 78 | 100 |
| Blout's compound (XII) | 22[c] | 20[c] | 64[c] | 21[c] | 57[c] | 84[c] |

[a] Distances in the four alkaloids were estimated using Cenco-Petersen molecular models (1 Å = 5 cm). [b] Calculated from eq 1 on the basis of $K^2 = {}^1/_2$, which is only *generally* valid, and not applicable to specific orientations (see text). [c] Data taken from ref 9.

Hence, neither XI nor rescinnamine phosphoresce. Even trace amounts of donor phosphorescence would be evident in this case.

In all four compounds, no donor phosphorescence was found, since all donor excitation was exhausted in singlet–singlet transfer processes and since "reverse" triplet–triplet transfer is energetically improbable.

**Intersystem Crossing Yields.** Values of $\phi_{ic}$ for each alkaloid and for separate models of the donor and acceptor chromophores involved were measured by triplet quenching by *cis*-piperylene, as described in the Experimental Section as well as in previous papers. The results are reported in Table II. The fact that, in all four cases, $\phi_{ic}$(acceptor) = $\phi_{ic}$(alkaloid), demonstrates that only 100% efficient singlet–singlet transfer could be occurring. In the case of rescinnamine, either triplet-state radiationless decay occurs at a much faster rate than energy transfer to *cis*-piperylene, or the triplet energy of rescinnamine and 3,4,5-trimethoxycinnamic acid is too low for quenching by the diene (53 kcal/mol).

**Evaluation of Theoretical Transfer Efficiencies.** The use of Forster's equation[5] for determining $R_0$, the donor–acceptor separation at which energy transfer *via* a resonance mechanism has a 50% chance of occurring, has been reviewed often in the past[9,17] and will not be discussed here. Simply stated in eq 1

$$R_0 = \left(\frac{8.8 \times 10^{-25} K^2 \phi_D J}{n^4}\right)^{1/6} \qquad (1)$$

where $K$ is an orientation factor (see ref 9), $\phi_D$ is the donor fluorescence yield in the absence of energy transfer, $n$ is the refractive index of the solvent, and $J$ is the overlap integral between normalized donor fluorescence and acceptor molar absorbance. The transfer efficiency is then given in eq 2, where $R$ is the actual donor–acceptor separation.

$$T \equiv \text{transfer efficiency} = \frac{(R_0/R)^6}{1 + (R_0/R)^6} \qquad (2)$$

Values of donor–acceptor separations for both fully extended ($R_{max}$) and fully folded ($R_{min}$) forms of the four alkaloids under discussion are given in Table III, along with calculated and observed singlet–singlet transfer efficiencies. It must be noted from these data that, if the energy transfer proceeds solely by a resonance mechanism, only the presence of a predominance of the folded forms of the alkaloids, or peculiarly advantageous donor–acceptor orientations in these compounds, could account for the high efficiencies observed. The second explanation should be ruled out on the grounds that the geometries of the alkaloids and the directions of the transition moments indicate that resonance transfer should be hindered rather than augmented by the geometrical restrictions imposed. Thus, in the evaluation of $R_0$ for all four systems, $K$, Forster's orientation factor, was estimated as $({}^1/_2)^{1/2}$ rather than $({}^2/_3)^{1/2}$, the value for completely random orientations. (It should, however, be noted that, as can be seen in eq 1, $R_0$ varies as the cube root of $K$ and is therefore not a very sensitive function of $K$.)

Alternatively, exchange contributions are possible and will be discussed more fully later.

**B. Blout's Compound.** Blout and coworkers[9] have previously reported the characteristics of singlet–singlet electronic energy transfer in XII. Transfer proceeded from the naphthoate to the anthroate moiety. (The arrangement of the donor and acceptor *triplet* energy levels is analogous to that of the alkaloids, *i.e.*, the chromophore with the highest $S_1$ is also that with the highest $T_1$.) The donor–acceptor separation calculated from $R_0$ for the system and from energy-transfer efficiency was 16.7 Å as opposed to about 20 Å measured on molecular models. Blout hypothesized that this could be due to favorable donor–acceptor orientations in the large bisteroid.

We obtained a sample of XII in order to study triplet–triplet transfer in this system and thus to determine whether any exchange interactions operate at these distances. Figure 10 shows the phosphorescence emission spectra of XII and that of an equimolar mixture of methyl 1-naphthoate and methyl 9-anthroate. Both spectra were recorded in a 1:1 diethyl ether–THF glass at 77°K. The exciting wavelength was 3000 Å, the naphthoate absorbing 68% of the light. Unfortunately, the instrument was incapable of recording the low-energy triplet emission of the anthroate constituent, so that Figure 11 shows only the naphthoate-like emission from XII. Both curves correlate closely in shape and intensity. The intensity of phosphorescence from XII is actually somewhat greater than expected on the basis that 80% of the naphthoate's excitation energy had already been dissipated through singlet–singlet transfer and that triplet–triplet energy transfer in the reverse direction is energetically unfeasible. This effect

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(17) R. L. Perlman, A. van Zyl, and H. Edelhoch, *J. Am. Chem. Soc.*, 90, 2168 (1968).

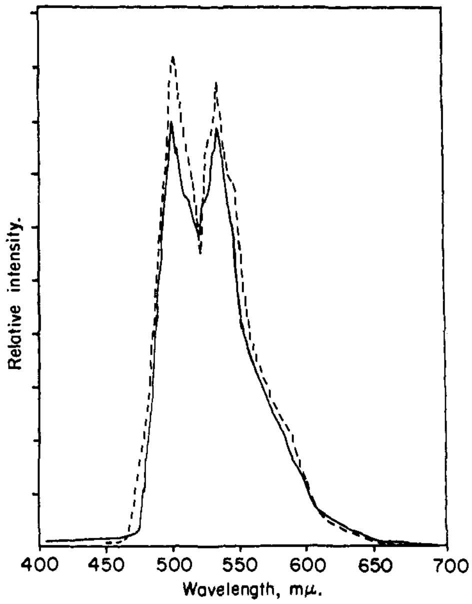
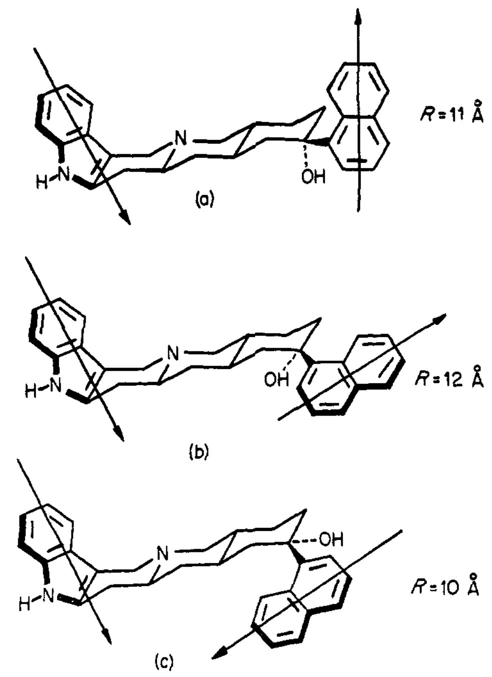


Figure 10. Phosphorescence: Blout's compound (XII), ——; methyl 1-naphthoate, - - - - - (from an equimolar mixture of methyl 1-naphthoate and methyl 9-anthroate; see text).



III ($R_0$ = 19.5 Å)

Figure 11. $R$ measured between centers. Various relative orientations of the transition dipoles and interchromophore distances in III (see text).

cannot be readily explained, but makes doubtful any triplet–triplet transfer in this system, which would almost surely result in an attenuation in naphthoate phosphorescence intensity.

Phosphorescence emission lifetimes were recorded for XII, for the equimolar mixture of donor and acceptor models, and for the donor alone. In all three cases, $\tau_p$ was 0.15 sec, that of the naphthoate donor, a fact which substantiates the conclusion that *no* triplet–triplet transfer processes occur in XII.

## Discussion

As shown in Table III, only 100% singlet–singlet excitation transfer was observed in the indole alkaloids studied, while Blout's compound shows about 84% singlet–singlet excitation transfer and *no* triplet–triplet exchange interactions. The maximum donor–acceptor separations in the four alkaloids vary from 10 Å for reserpine and deserpidine to 12 Å for the yohimbine–naphthalene derivative. The tertiary structures of these compounds are not known, but the folded forms of reserpine, deserpidine, and rescinnamine might be expected to be more sterically hindered than the extended forms. On the other hand, weak $\pi$ interactions could stabilize the folded forms, giving a large representation of these conformers in both fluid solution and in glassy solvents at 77°K.[18]

As was previously mentioned, not only the distance separating the donor and acceptor, but also the possible orientations of the two chromophores is important in determining the extent of resonance excitation transfer in these compounds. Shimada and Goodman[19] report that the $^1L_b(\pi,\pi^*) \leftarrow A_1$ transition in benzenoid carbonyl compounds is polarized perpendicular to the plane of the ring. The relatively high extinction coefficients (2000–2500) of the long-wavelength absorption maxima in the models of the trimethoxybenzoate and cinnamate acceptors in reserpine, deserpidine, and rescinnamine along with their fairly unstructured emission indicate that the $^1L_b(\pi,\pi^*)$ state is the $S_1$ state. In addition, it has long been established that the $S_1$ state of indole and of 6-methoxyindole is $\pi,\pi^*$ and is polarized along the long axis, as in naphthalene.[20] Hence, singlet–singlet transfer in reserpine, deserpidine, and rescinnamine proceeds from the indolic $S_1(\pi,\pi^*)$ state to the $^1L_b(\pi,\pi^*)$ state of the benzoate acceptor; in the case of 17-($\alpha$-naphthyl)yohimbol, transfer proceeds to the lowest $^1(\pi,\pi^*)$ state of naphthalene (polarized along the long axis).

In reserpine, deserpidine, and rescinnamine examination of molecular models will show that in the fully extended and fully folded forms, donor and acceptor transition moments are mutually perpendicular yielding low net dipole–dipole interactions. Therefore, in these compounds, most resonance excitation transfer must originate from intermediate forms.

Some possible conformations of 17-($\alpha$-naphthyl)-yohimbol are given in Figure 11. Complete coincidence of donor and acceptor transition moments is impossible in this case, but only forms such as that depicted in 11b will cause zero dipole interaction.

In the case of rescinnamine, placement of an isomerizable ethylenic linkage between the carbonyl and trimethoxyphenyl groups increases singlet–triplet splitting in the acceptor portion. Thus the lowest singlet state of trimethoxycinnamic acid is $^1(\pi,\pi^*)$, and the lowest triplet state is the $^3(\pi,\pi^*)$ state, as is borne out by the spectral data. Phosphorescence

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(18) It is evident that placing these compounds in a rigid matrix does not alter the transfer efficiency, since $\phi_{tc}$ data, collected at room temperature, and spectral data, collected at 77°K, agree. Hence it is safe to assume that, statistically, the same distributions of donor–acceptor orientations are present in both media.

(19) R. Shimada and L. Goodman, *J. Chem. Phys.*, 43, 2027 (1965).

(20) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

emission lifetimes of the other benzoate models (~0.5 sec), as well as their phosphorescence emission spectra, indicate that $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states are relatively close in energy, the $^3(\pi,\pi^*)$ state being the lowest triplet in all cases.

The use of the Forster equations for these systems is not entirely justified. The orientation factor, $K^2$, is evaluated on the basis of average donor–acceptor transition dipole orientations. Nevertheless, due to the imposed geometries of reserpine, deserpidine, and rescinnamine, the forms where donor and acceptor are in closest proximity yield small dipole–dipole interactions, as do all forms where the donor and acceptor rings are parallel or nearly parallel. Other mechanisms of energy transfer must be considered in these cases, to explain the high efficiencies observed.

When the donor and acceptor are in close proximity, some singlet–singlet energy transfer would be expected as a result of physical overlap of their $\pi$ clouds. Intermolecular singlet–singlet quenching spheres have been measured for the biacetyl system.[13,14] We conclude from these results that singlet–singlet exchange interactions can occur for donor–acceptor separations on the maximum order of 6–9 Å in the absence of dipole–dipole coupling.[15] Measurements on compounds where resonance excitation transfer is unlikely, such as I and II discussed in Keller's recent paper,[12] substantiate this assumption. In the case of the four alkaloids under consideration here, where transfer is between two $^1(\pi,\pi^*)$ singlets rather than from the donor $^1(\pi,\pi^*)$ to the carbonyl-localized $^1(n,\pi^*)$ level as in the biacetyl or carbazole systems, exchange interactions could be even greater due to the possible spatial interaction of *two* relatively large molecular orbitals. As was shown in the case of Blout's compound, however, such interactions definitly cannot occur at distances of 20 Å, even between the relatively long-lived and probably spatially diffuse triplet state of naphthalene and the ground state of anthracene. Nevertheless, for the donor–acceptor separations in the alkaloids presented here, exchange interactions probably occur when dipole–dipole coupling is weak, especially in the folded and some intermediate forms of reserpine, deserpidine, and rescinnamine.

It should also be noted that, in the case of the three alkaloids with flexible carboxylate bridges, the extended forms should not transfer energy efficiently by either resonance or exchange mechanisms. If these forms did predominate, some residual fluorescence should be observed from the indolic donor, *i.e.*, singlet–singlet energy transfer would not be so efficient. Hence, it is tempting to postulate some special stability of the folded and intermediate forms of these compounds due to weak ground-state interactions, or some special selectivity in excited donor–ground-state acceptor orientations.

This leads to the following mechanism of singlet–singlet energy transfer in the four indole alkaloids discussed. In the case of reserpine, deserpidine, rescinnamine, and 17-($\alpha$-naphthyl)yohimbol, all excitation to the $S_1(\pi,\pi^*)$ level of the indolic donor is transferred to the $S_1(\pi,\pi^*)$ level of the 3,4,5-trimethoxybenzoate, cinnamate, or $\alpha$-naphthyl acceptor. Therefore, donor–acceptor separations should be measured from the indole center to the benzoate or naphthalene center. If the donor–acceptor transition moments are properly aligned, the mode of transfer will be predominately *via* dipole–dipole resonance interactions. If orientation makes this mechanism improbable, the somewhat weaker exchange mechanism will operate, more certainly at smaller intermediate donor–acceptor separations. In the case of rescinnamine, $R$ is nearly the same as for reserpine and deserpidine. Singlet–singlet energy transfer from the indolic donor to the trimethoxycinnamate $^1(\pi,\pi^*)$ state is followed by fluorescence of the latter and, probably, intersystem crossing to the lowest $^3(\pi,\pi^*)$ state of the acceptor whose energy is dissipated at least partially *via trans–cis* isomerization of its ethylenic double bond.

## Conclusions

It is of importance to note that exchange and resonance modes of energy transfer seem to supplement one another in these cases, a condition which explains the high transfer efficiencies observed. In view of these findings, it is obvious that the Forster treatment is not entirely applicable to many analogous systems with donor–acceptor separations much less than those found in Blout's compound. Although there may be some finite probability of donor–acceptor orbital overlap at distances of 20 Å, such probability is so small that the rate of exchange would be nowhere near the rate of triplet decay. The nonexistence of triplet–triplet transfer in XII serves, at least, to determine this upper limit, even for transfer between two relatively diffuse $^3(\pi,\pi^*)$ states, the donor having a triplet lifetime of 0.15 sec. In the alkaloids, however, exchange transfer appears, both from this study and from previous evidence, to have a rate comparable to donor singlet lifetimes for distances less than 9 Å. Although this process is not as efficient as resonance excitation transfer, it serves to increase the general energy-transfer efficiency in that it is operant when dipole–dipole orientations are unfavorable.

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