column B which indicated the presence of four main components, the largest one 68% of the total. The mixture was separated by flash distillation followed by preparative phase chromatography. The largest component was isolated in a yield of 3.0 g (8.8%) of product, bp 33°; reported for 2-bromo-2-hydrohexafluoropropane, bp 33.5°.[17] Analysis of the product by glpc, ^{1}H nmr, and ^{19}F nmr showed the absence of any impurities. Also, the ir spectrum of an authentic sample[18] was identical with that of the isolated material.

2-Chloro-2-hydrohexafluoropropane. A 128-ml Hastelloy C, high-pressure bomb was charged with 20.0 g (0.12 mol) of 1,1,1,-3,3,3-hexafluoro-2-propanol followed by slow addition of 41.5 g (0.20 mol) of phosphorus pentachloride. The bomb was sealed and heated to *ca.* 140° for 12 hr and then to *ca.* 290° for 20 hr by means of a small cylindrical heating mantle. The bomb was cooled to *ca.* 100° and vented through a Dry Ice–isopropyl alcohol trap. The volatiles collected in the trap were analyzed by glpc on column B and showed three main peaks. The mixture was separated by preparative phase glpc, the largest component being 2-chloro-2-hydrohexafluoropropane. The yield was 3.0 g (13.5%); reported for 2-chloro-2-hydrohexafluoropropane, bp 16°.[17] Analysis by glpc, ^{1}H nmr, and ^{19}F nmr showed the material was completely pure. Also, the ir spectrum of an authentic sample[19] was identical with that of the product.

2-Hydroheptafluoropropane. This carbon acid was prepared by the method described by Hauptshien (for the *n*-propyl isomer).[20] The yield was 6 g (35%). Analysis by ^{19}F nmr was consistent with reported spectra.[6]

2-Hydro-2-iodohexafluoropropane. The preparation was carried out by the general method of Knunyants.[17,19] The crude product was purified by preparative glpc on column B; reported for 2-hydro-2-iodohexafluoropropane, bp 58°, n^{20}D 1.3520.[21]

2-Hydro-2-methoxyhexafluoropropane. The method of Gilbert[21] was used, and purification was carried out by fractional distillation; reported for 2-hydro-2-methoxyhexafluoropropane, bp 50.5°.[21]

Tritiated Deuteriobromoform. This carbon acid was prepared from bromal[22] by the method described by Hine[5b] for the preparation of deuteriobromoform. In this case a mixture of 10 g of deuterium oxide and 0.01 g of tritium oxide in deuterium oxide (1 mcurie/g, obtained from New England Nuclear Corp.) was used.

Tris(trifluoromethyl)methane was obtained from Du Pont Chemical Co.[19]

Kinetic Methods. Procedures used for the preparation and analyses of kinetic samples have been described,[3] and discussed in the text.

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(17) B. L. Dyatkin, E. R. Mochalina, L. T. Lantseva, and I. L. Knunyants, *Chem. Abstr.*, 63, 14691*a* (1965).

(18) The authors thank Drs. R. E. A. Dear and J. J. Murray of Allied Chemical Co. for a generous authentic sample of 2-bromo-2-hydrohexafluoropropane.

(19) The authors thank Drs. C. B. Krespan and D. C. England of Du Pont Chemical Co. for generous samples of 2-chloro-2-hydrohexafluoropropane, 2-hydrohexafluoroisobutyric acid, and tris(trifluoromethyl)methane.

(20) M. Hauptshien, A. J. Saggiomo, and C. S. Stokes, *J. Amer. Chem. Soc.*, 78, 680 (1956).

(21) E. E. Gilbert, *Chem. Abstr.*, 68, 12474z (1968).

(22) "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 87.

Interaction between *p*-Dimethoxybenzene and Norbornylene in Two Rigid Model Compounds[1]

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Abstract: Nonconjugated *p*-dimethoxybenzene (D) and norbornylene (N) have been incorporated in the same molecule at separations of 2.4 and 4 Å in two rigid model molecules, 3′,6′-dimethoxybenzonorbornadiene (**1**) and 5,8-dimethoxy-*endo*,*exo*-1,4:9,10-dimethano-1,4,6,7,9,10-hexahydroanthracene (**2**), respectively. The interaction between the D and N π chromophores in the two model compounds was studied spectroscopically and photochemically. The uv absorption indicated that the increase in D–N separation takes the chromophores from a rather strong mutual perturbation in **1** to weak interaction in **2**. The fluorescence quantum yields of **1** and **2** were the same and equal to those of their dihydro analogs. This, together with the results of experiments in which the four compounds were used as sensitizers in the cis–trans isomerization of piperylene, showed that the $S_1 \rightsquigarrow T_1$ intersystem crossing within D in **1** or **2** is not affected by the presence of N in close proximity. Model compounds **1** and **2** were found to undergo clean photoisomerizations either under direct D excitation or on intermolecular triplet sensitization with formation of photoproducts in which the norbornylene unsaturation is changed to an alicyclic group. Differences in photochemical quantum yields and structure of respective photoproducts suggest two different mechanisms.

The study of intramolecular interaction between nonconjugated chromophores offers distinct advantages and gives additional information which is not available from binary mixed solutions.[2] Using inflexible model compounds one may gain insight in the behavior of chromophores (or molecules) in close proximity and one may ultimately understand in detail the configuration and properties of molecular ground and excited

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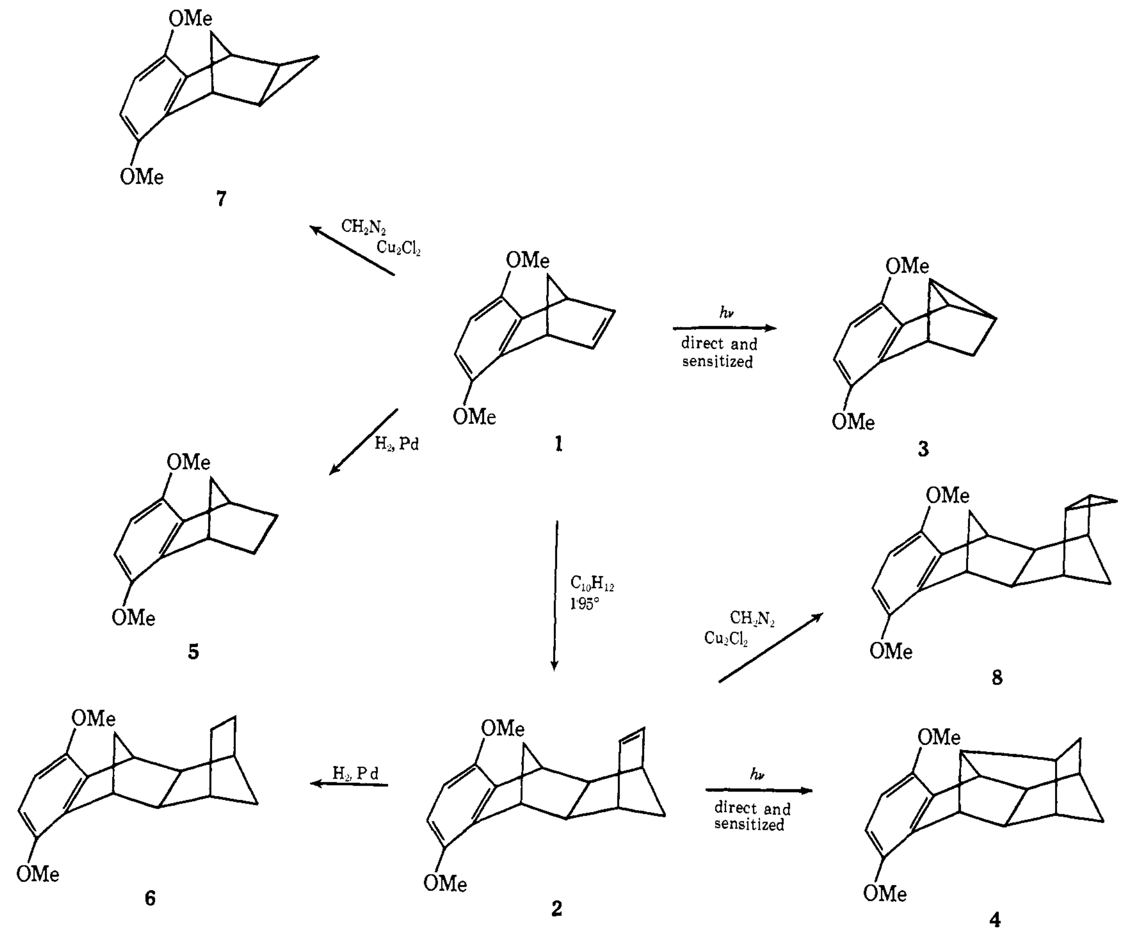
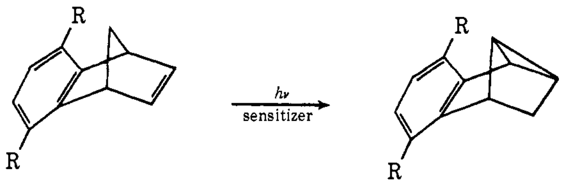
(1) Taken in part from the dissertation of D. S. C. Chang submitted to the Graduate School of The George Washington University in partial fulfillment of the Ph.D. degree, 1970.

(2) (a) O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, 84, 172 (1962); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, 85, 2670 (1963); (c) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, 87, 995 (1965); (d) R. A. Keller and L. J. Dolby, *ibid.*, 89, 2768 (1967); (e) *ibid.*, 91, 1293 (1969); (f) R. D. Rauh, T. R. Evans, and P. A. Leermakers, *ibid.*, 90, 6897 (1968); (g) D. E. Breen and R. A. Keller, *ibid.*, 90, 1935 (1968); (h) D. R. Roberts and E. H. White, *ibid.*, 92, 4861 (1970); (i) D. F. Roswell, V. Paul, and E. H. White, *ibid.*, 92, 4855 (1970); (j) A. A. Lamola, *ibid.*, 92, 5045 (1970); (k) R. P. Hangland, J. Yguerabide, and L. Stryer, *Proc. Nat. Acad. Sci. U. S.*, 63, 23 (1969); (l) H. Morrison, *J. Amer. Chem. Soc.*, 87, 932 (1965); (m) H. Morrison and R. Peiffer, *ibid.*, 90, 3428 (1968); (n) H. Kristinsson and G. S. Hammond, *ibid.*, 89, 5968 (1967); (o) P. A. Leermakers, J. Montiller, and R. D. Rauh, *Mol. Photochem.*, 1, 57 (1969).

Scheme I





9, R = H
10, R = $OCOCH_3$

11, R = H
12, R = $OCOCH_3$

states.[3,4] Both photochemistry[2k–o,3d] and emission spectroscopy[2a–j,3] have been previously used to evaluate the interaction between the two chromophores of model compounds.[4]

In the present paper we describe a quantitative assessment of processes taking place on photoexcitation of two related inflexible model compounds, 3′,6′-dimethoxybenzonorbornadiene (**1**) and 5,8-dimethoxy-*endo*,*exo*-1,4:9,10-methano-1,4,6,7,9,10-hexahydroanthracene (**2**, see Scheme I). Both compounds contain the same two π chromophores, *p*-dimethoxybenzene (D) and norbornylene (N), in apparently nonconjugated relative juxtaposition. The absorption and emission spectra of **1** and **2** are compared with those of their dihydro analogs, **5** and **6**, respectively. On excitation at wavelengths associated with D absorption in fluid solution both **1** and **2** underwent photoisomerizations involving the N chromophore. However, the **1** → **3** and the **2** → **4** photorearrangements had markedly disparate quantum yields and the two respective products **3** and **4** exhibit essential structural differences.

Working with a molecular system similar to **1**, Edman recently reported that benzonorbornadiene (**9**) and its 3′,6′-diacetoxy derivative **10** undergo photoisomerization to 2,3-benzotricyclo[2.2.1.0^{5,7}]heptanes **11** and **12**, respectively, on excitation *via* a triplet sensitizer but failed to rearrange on direct excitation.[5] This behavior was attributed to absence of intersystem crossing in compounds **9** and **10**, the implication being that the photorearrangement was state specific (triplet).

From previous studies, we were aware that, unlike *o*-phenylene in **9**, *p*-dimethoxybenzene exhibits easily detectable phosphorescence which testifies for the occurrence of efficient intersystem crossing in this

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[3] (a) R. A. Keller, *J. Amer. Chem. Soc.*, 90, 1940 (1968); (b) N. Filipescu and J. M. Menter, *J. Chem. Soc. B*, 616 (1969); (c) J. M. Menter and N. Filipescu, *ibid.*, 464 (1970); (d) N. Filipescu and J. R. Bunting, *ibid.*, 1498, 1750 (1970); (e) N. Filipescu, J. R. DeMember, and F. L. Minn, *J. Amer. Chem. Soc.*, **91**, 4169 (1969).

[4] For a recent review see N. Filipescu, *J. Luminescence*, **1**, **2**, 489 (1970).

[5] (a) J. R. Edman, *J. Amer. Chem. Soc.*, **88**, 3454 (1966); (b) *ibid.*, **91**, 7103 (1969).

chromophore.[6] This observation was valid for the norbornane-fused D as well.[7] Consequently, it was of interest to investigate the **1** → **3** photorearrangement on *direct* excitation and to compare the results with the intermolecularly sensitized reaction. The similar photoisomerization of **2**, involving the same D and N chromophores but in a relative spatial disposition corresponding to weak interaction, adds a new dimension to the overall picture. Delocalization of excitation energy in **1** is expected to extend over both π systems since their proximity allows some transannular conjugation (strong interaction). By contrast, the **2** → **4** photoreaction must involve distinct transfer of electronic excitation energy from D to N.

The quantum yields of the inter- and intramolecularly-sensitized photorearrangements of **1** and **2** in fluid and frozen solutions together with the fluorescence and phosphorescence quantum efficiencies and lifetimes are used in this study to analyze the radiationless processes leading to either emission or isomerization and to evaluate the D–N interaction in the two model compounds.

Results

Synthesis of Model Compounds. Rigid molecule **1** was prepared from the cyclopentadiene–benzoquinone Diels–Alder adduct by tautomerization to the hydroquinone anion with hydroxide and methylation with dimethyl sulfate.[8] Catalytic hydrogenation of **1** under mild conditions removed the norbornane unsaturation to yield dihydro analog **5**. Reaction of **1** with diazomethane in the presence of cuprous chloride added methylene in the usual manner to give cyclopropane derivative **7**. In addition to routine analytical data confirming their structure, the nmr spectra of **5** and **7** showed preservation of symmetry and appropriate kind and number of protons.

Model compound **2** was prepared from **1** by Diels–Alder addition of a cyclopentadiene unit generated *in situ* from dicyclopentadiene in a sealed tube at 195°. Although the exo,endo configuration shown for **2** conforms to the kinetically preferential endo orientation of 1,4-added cyclopentadiene in Diels–Alder adducts,[9] we had to prove the structure by removing the other three isomeric possibilities. This was accomplished with the aid of the ir and uv absorption spectra and the established configuration of photoproduct of **2**. Compound **2** shows a sharp band in the ir at 3030 cm^{-1}. This peak has been associated with a high-energy stretch mode of a bridge C–H bond in which the hydrogen is forced into close nonbonding proximity with neighboring atoms.[10] Since the exo,exo and endo,endo isomers lack transannular proximity to the bridge hydrogens, they can be ruled out. An additional reason for discarding the endo,endo possibility is the fact that the uv absorption of **2** is essentially the same as that of compounds **5** and **6**; the mutual perturbation caused by the very close proximity of the norbornylene and *p*-dimethoxybenzene π systems required by the endo,endo configuration would certainly be reflected in the uv absorption spectrum. Probably the most potent indirect evidence for the exo,endo stereochemistry of **2** is the structure of photoproduct **4**, generated in rigid matrix where skeletal rearrangements are most improbable (see below) which also removes the only other alternative left, the endo,exo configuration.

Catalytic hydrogenation of **2** and reaction with diazomethane yielded **6** and **8**, respectively. As for **5** and **7**, the nmr spectra of **6** and **8** showed one clearly defined singlet for the six methoxy hydrogens indicating retention of symmetry, absence of vinyl protons, and expected splittings and intensities for the hydrogen atoms attached to the σ frame.

Photorearrangement of 1 and 2. Both direct photolysis of **1** at $\lambda > 240$ nm and sensitization with benzophenone or acetophenone yielded only one photoproduct (8,11-dimethoxytetracyclo[5.4.$0^{2,4}$.$0^{3,6}$]undeca-1,8,10-triene), 3′,6′-dimethoxy-5,6-benzotricyclo[2.2.1.$0^{3,7}$]hept-5-ene (**3**). Elemental analysis and molecular weight determination indicated that **3** was an isomer of **1**. Since the uv absorption of **3** was virtually indistinguishable from that of **5**, it was clear that the *p*-dimethoxybenzene chromophore remained intact. The nmr spectrum of the photoproduct showed molecular asymmetry; the two methoxy groups were no longer in equivalent chemical surroundings and their respective nmr signal, singlet in **1**, became a doublet in **3**. This was confirmed by the signals of the two aromatic protons which split one another in **3**. The signal from the vinyl protons of **1** was absent in **3** while the number of aliphatic hydrogens increased by two. Actually the 0–3.5 ppm region in the spectrum of **3** resembled closely[5] that of **12**.

Direct irradiation of model compound **2** or sensitization with acetophenone resulted in photoisomerization to 11,12-*o*-[3′,6′-dimethoxybenzeno]pentacyclo[6.4.0.$0^{2,10}$.$0^{3,7}$.$0^{5,9}$]dodec-11-ene (**4**). As for **3**, the uv absorption of **4** indicated that the aromatic chromophore was not affected. The absence of an absorption band around 3030 cm^{-1} in the ir spectrum of **4** suggested that the transannular crowding of the bridge hydrogen was removed in the reaction. The fact that the photoproduct remained unchanged upon prolonged heating with hydrogen in the presence of palladium at 150° and 200 psi showed that the compound contained no cyclopropane or cyclobutane rings. The nmr spectrum of **4** revealed molecular asymmetry (the signal of the two unequivalent methoxy groups was narrowly split into a doublet) and absence of vinyl protons. Within the limitations caused by significant overlap, the aliphatic portion of the nmr spectrum of **4** was also consistent with the assigned structure. The configuration of photoproduct **4** is supported not only by the analytical data presented but also by the fact that the transannular photocyclization of the type shown for the **2** → **4** reaction is not without some precedent.[11]

The photoisomerization quantum yields of **1** and **2** were determined (i) in dioxane at room temperature, (ii) in frozen dioxane solution at 0°, (iii) in rigid glass (EPA, ether–isopentane–ethanol, 2:5:5 by volume) at

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(6) J. R. DeMember and N. Filipescu, *J. Amer. Chem. Soc.*, **90**, 6425 (1968).

(7) N. Filipescu, J. R. DeMember, and G. R. Howard, *J. Chim. Phys.*, 67, 84 (1970).

(8) Compound **1** was prepared previously by J. Meinwald and G. A. Wiley, *J. Org. Chem.*, 23, 3667 (1958), from the same adduct *via* diacetoxylation, hydrolysis, and methylation.

(9) A. Wasserman, "Diels–Alder Reactions," Elsevier, New York, N. Y., 1965, Chapter 2.

(10) L. DeVries and P. R. Rayson, *J. Org. Chem.*, **26**, 621 (1961).

(11) (a) H. D. Scharf, *Tetrahedron*, 23, 3057 (1967); (b) W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5475 (1967); (c) A. M. Parsons and D. J. Moore, *J. Chem. Soc. C*, 2026 (1966).

Table I. Photochemical Quantum Yields

Model compd	Dioxane 298°K direct excitation	Frozen dioxane 273°K	EPA glass 77°K	Sensitized reaction $C_6H_5COCH_3$	$(C_6H_5)_2CO$
1	0.027	~0.02[a]	0	0.08	$<10^{-4}$
2	0.480	~0.40[a]	$\sim10^{-4}$	0.16	0

[a] These values are somewhat underestimated because of substantial scatter in frozen polycrystalline dioxane.

77°K, and in dioxane at 298°K by sensitization with (iv) acetophenone and (v) benzophenone. The values obtained in a merry-go-round system with the *cis–trans*-piperylene actinometer are listed in Table I.

The quantum yield for the photolysis of **1** in dioxane at room temperature was found to be 0.027. Under the same conditions, the **2** → **4** photorearrangement exhibited a quantum yield almost 20 times larger, namely 0.48. Acetophenone sensitized both photoreactions; however, the **2** → **4** reaction had a quantum yield twice that measured for the **1** → **3** isomerization. In contrast, benzophenone sensitized only the **1** → **3** reaction but not the **2** → **4**. In frozen dioxane at 0°, both reactions proceeded with approximately the same quantum yields as those obtained in fluid solution under direct excitation. On the other hand, extended irradiation of **1** in frozen EPA glass at 77°K did not yield any photoproduct **3**. All attempts to detect it by gas chromatography were negative. Uner the same conditions (EPA, 77°K), the photoproduct **4** of irradiated solutions of **2** was detectable, though only in small amounts.

The intersystem crossing efficiencies of model compounds **1**, **2**, and **5** were determined in experiments in which they were used as sensitizers for the isomerization of *cis*- and *trans*-piperylene.[12] However, in the calculation of meaningful Φ_{isc} values, we had to consider that both the sensitizer and the piperylene acceptor undergo photoisomerization and that photoproducts **3** and **4** are themselves suitable sensitizers for the cis–trans isomerization of piperylene (see Discussion).

Spectroscopy. The uv absorption spectra of model compounds **1** and **2** and those of their dihydro analogs **5** and **6** were nearly identical consisting of one band between 250 and 312 nm with only one shoulder displaced about 5 nm to the red with respect to λ_{max}.[13] The entire near-ultraviolet absorption band of compound **1**, while retaining the same general features as those of **2**, **5**, and **6**, was simply red shifted by about 20 nm. This undoubtedly is the result of extended transannular delocalization of characteristic $\pi \rightarrow \pi^*$ transitions in D over the nearby norbornylene. It is interesting that although the energy of the antibonding π orbitals is lowered in **1** by the proximity of N to D, the vibrational structure and extinction coefficient remain the same. This seems to indicate that there is little coupling between vibrational modes in the rigid frame and $\pi \rightarrow \pi^*$ transitions in D and that the selection rules for the transition are hardly affected by the additional delocalization.

Table II. Spectroscopic Data

Model compd[a]	**1**	**2**	**5**	**6**
λ_{max}^{abs}, nm	294	285	284	284
$\epsilon_{\lambda max}$, M^{-1} cm^{-1}	3×10^3	3×10^3	3×10^3	3×10^3
λ_{max}^{fl}, nm	328	314	312	312
λ_{max}^{phos}, nm			407	410
τ_e^{phos}, sec			1.8	1.8
Φ_{fl}	0.2	0.2	0.2	0.2
Φ_{phos}, based on Φ_{fl}	0.0	0.0	0.2	0.15
Φ_{isc}	0.62	0.72	0.65	0.65

[a] λ_{max}^{abs}, $\epsilon_{\lambda max}$, and ϕ_{isc} determined at 298°K; all other quantities refer to rigid matrix experiments at 77°K in EPA.

The emission spectra, quantum yields, and phosphorescence lifetimes of model compounds **1**, **2**, **5**, and **6** were recorded in rigid EPA glass at 77°K. The results are given in Table II. The fluorescence emission of all four compounds was similar, namely, one unstructured, nearly Gaussian peak with a half-width of ~30 nm. The fluorescence λ_{max} of **1** was shifted to higher wavelengths with respect to those of the other three, similar to the respective bathochromic shift in the absorption spectrum. However, the fluorescence quantum yields of the four compounds were equal. Saturated molecules **5** and **6** exhibited nearly identical phosphorescence in broad unstructured bands and with the same decay times. In contrast, the $T_1 \rightarrow S_0$ emission in **1** and **2** was essentially quenched; the extremely weak residual phosphorescence barely detected at the upper limit of instrumental sensitivity after the samples have been exposed to the exciting uv light for some time was undoubtedly originating from very small amounts of formed photoproduct. It can be safely concluded that the transfer of triplet energy from D to N in both **1** and **2** is complete.

Discussion

The near-uv absorption and the fluorescence spectra of model compounds **1** and **2** seem to indicate that the interaction[15] between *p*-dimethoxybenzene and norbornylene olefinic bond changes distinctly from strong coupling in **1** to weak or no coupling in **2**. It is instructive to analyze this interaction in terms of specific energetic states. Apparently Edman considered the transannular interaction of benzene and norbornylene in benzonorbornadiene so strong as to describe the electronic states in terms of a single chromophore.[5] This probably is sufficiently representative of the assumed complete delocalization of excitation energy in molecules such as **1** with two chromophores virtually conjugated by proximity. On the other hand, it is possible to analyze the system retaining the initial identity of the localized chromophores. Even in the case of strong interaction between chromophores, the resultant energy states may be represented in terms of

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(12) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

(13) The absorption spectra of **1**, **2**, **5**, and **6** will not be shown here since that of **5** has been reported previously.[7,14]

(14) A. A. Lamola, *J. Amer. Chem. Soc.*, 91, 4786 (1969).

(15) (a) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963, Chapter 7; (b) Th. Förster in "Modern Quantum Chemistry," Part III, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 93 ff.

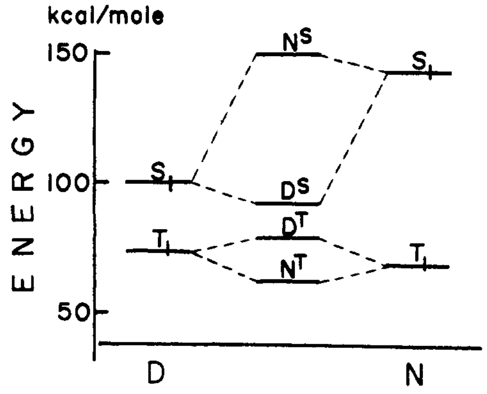


Figure 1. Hypothetical admixture of separate energy states of *p*-dimethoxybenzene (D) and norbornylene (N) in model compound **1**. The amount of mixing, shown for illustrative purpose, is arbitrary.

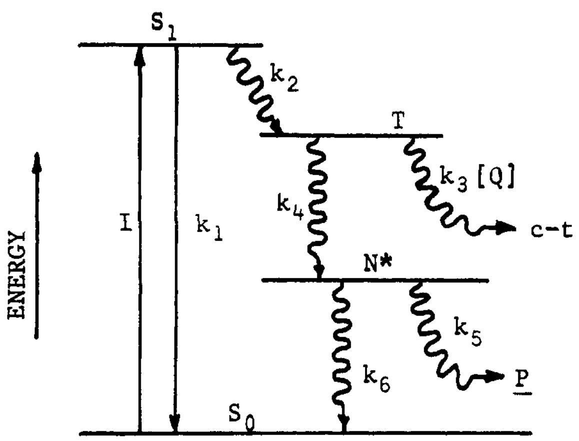


Figure 2. Energy level diagram: S_0 = ground state; S_1 = lowest excited singlet of D in **2**, **3**, or **4** or the D^S state of **1**; T = lowest triplet of D in **2**, **3**, and **4** or the D^T state of **1**; N* = photoreactive state of either **1** or **2**; c–t = cis–trans isomerization of piperylene; [Q] = piperylene (quencher) concentration; P = photoproduct; *k*'s = specific rate constants.

those of the participating chromophores. The mutual perturbation of D and N in compound **1** may be represented in a simplified manner as in Figure 1 in which the singlet levels of the two π systems are shown interacting to form two new energy levels D^S and N^S. The D^S state is associated mainly with the original dimethoxybenzene singlet as indicated by the preservation of general absorption and fluorescence features of **5** in **1**. The N^S energy level, as the initial π,π^* singlet of N, remains rather unimportant in photochemistry, emission, and near-uv (λ >250 nm) absorption.

The same type of state mixing would generate two new triplet levels, D^T and N^T. In this case, however, the D^T energy state is higher since the triplet of the original D was higher than that of N. Tracing the path of excitation energy causing the **1** → **3** photoisomerization in **1**, it is apparent that following absorption to the D^S level, intersystem crossing, and competing with fluorescence would take the molecule from D^S *via* D^T to the lowest triplet, N^T, which is presumably the photoreactive state. The hypothetical intramolecular energy transfer step from the absorbing D-like state (D^S) to the reacting N-like state (N^T) in **1** can be treated simply as internal conversion within the triplet manifold from D^T to N^T.

Unlike in **1**, the two chromophores in **2** are separated by about 4 Å. Consequently the degree of interaction between them should decrease substantially. For exchange interactions, which are strongest at close proximity, the π orbital mixing of D and N in **2** should diminish significantly since (i) the π electron density decreases exponentially away from the carbon atoms at the edge of the chromophores and (ii) the atomic 2_p orbitals on norbornylene are nearly perpendicular to those of D, minimizing overlap. In fact, the uv absorption spectrum of **2** in the 250–350-nm region is nearly identical with that of **6** suggesting a very weak, if any perturbation of the D singlet levels by N. Since this implies localization of excitation energy and since N is transparent to light around 300 nm, it is clear that **2** → **4** photorearrangement of the N moiety can be looked upon as involving transfer of excitation energy from D to N.

The lowest triplet level of N in **2** is slightly above 68.5 kcal/mol whereas that of **1** is somewhat below this value since benzophenone sensitized the **1** → **3** but not the **2** → **4** reaction. On sensitization with acetophenone, the **2** → **4** reaction had a quantum yield of only twice that of **1** → **3** isomerization, possibly because of partial transfer, since the lowest triplet of N in **2** is very close to that of the sensitizer.[16] The outcome of the sensitized reactions strongly suggests that the photoreactions proceed *via* the lowest triplet state. Since the quantum yields of the photolyses in frozen dioxane were found to be the same as in fluid solution, the possibility of significant intermolecular D to N triplet energy transfer in the photoreactions at 298°K is ruled out. The fact that both rearrangements are very inefficient in frozen EPA at 77°K indicates that photoproduct formation is a consequence of efficient thermal deactivation of excited N and not that triplet energy transfer from D to N does not take place, since, under the same conditions, D phosphorescence is quenched in both model compounds.

The determination of singlet–triplet intersystem crossing efficiencies in **1** and **2** was important not only because their quantities are relevant to their photorearrangement but also because comparison with $\phi_{\rm isc}$ in **5** and **6** would indicate what influence, if any, the nearby presence of N has on the S–T crossover in D. Since the fluorescence quantum yields of **1**, **2**, **5**, and **6** at 77°K are the same, it is very probable that, in rigid matrix, $\Phi_{\rm isc}$ of D in compounds such as **5** and **6** is not affected by the additional respective unsaturation in **1** and **2**.

In fluid solution, the calculation of $\Phi_{\rm isc}$ must take into account the experimentally observed formation of photoproduct in competition with triplet transfer to piperylene, the detected piperylene quenching of photoisomerization, and the subsequent cis–trans photosensitization by the photoproduct. Figure 2 shows a simplified energy level diagram including the various radiative, radiationless, and photoreactive processes that may occur in the model compound or its photoproduct. Despite the marked difference between the D–N interaction in **1** and in **2**, we made no distinction in the calculation of $\Phi_{\rm isc}$ because intersystem crossing may be simply defined for both model compounds as

(16) H. D. Scharf and F. Korte, *Tetrahedron Lett.*, 821 (1963).

the radiationless transition from the lowest excited singlet, which emits D-like fluorescence, to a lower-lying triplet which may be initially localized in D or may extend over both the D and N chromophores.

In the model-compound–piperylene irradiation experiments, the rate of photoproduct formation is

$$C_s(dR/dt) = I\Phi(1 - \Phi_q)(1 - R) \qquad (1)$$

where C_s is the sensitizer concentration, R the fraction of sensitizer photoisomerized, I the rate of light absorption, Φ the overall quantum yield of photoisomerization when the model compound is irradiated in the absence of piperylene (equal to $\Phi = \Phi_{isc}k_5/(k_5 + k_6)$), Φ_{isc} the intersystem crossing efficiency in the sensitizer ($\Phi_{isc} = k_2/(k_1 + k_2)$), and Φ_q the probability of triplet quenching by piperylene ($\Phi_q = k_3[Q]/(k_3[Q] + k_6)$). All the rate constants refer to the processes shown in Figure 2. Integration of differential eq 1 gives

$$R = 1 - \exp(-kt) \qquad (2)$$

with $k = I\Phi(1 - \Phi_q)/C_s$.

The rate of piperylene isomerization is

$$C_p(dx/dt) = I\Phi_q\Phi_{isc}(1 - R)\alpha(1 - x) - I\Phi_q\Phi_{isc}(1 - R)(1 - \alpha)x + I\Phi'_{isc}(\alpha - x)(1 - \exp(-kt)) \qquad (3)$$

where C_p is the piperylene concentration, x the fraction of piperylene isomerized, α the fraction of piperylene isomerized at the photostationary state, and Φ'_{isc} the intersystem crossing efficiency of the photoproduct. With appropriate substitutions and integration, eq 3 becomes

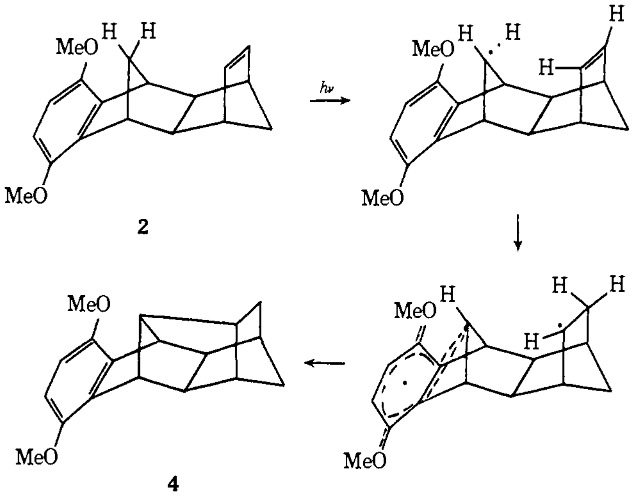
$$\ln[\alpha/(\alpha - x)] = [(\Phi_q\Phi_{isc} - \Phi'_{isc})/\Phi(1 - \Phi_q)]R + I\Phi'_{isc}t/C_p \qquad (4)$$

Equation 4 was used to calculate Φ_{isc} since all other quantities are measurable: α from the relative extent of photoisomerization of *cis*- and *trans*-piperylene irradiated simultaneously, x and R measured directly, Φ'_{isc} from separate experiments with **5** (or **6**) and piperylene, Φ from direct photolysis of **1** or **2** without piperylene, It from the actinometer, and Φ_q from eq 1. The accuracy in the Φ_{isc} values is estimated to be limited by the use of differences in the above expression to no better than 10%.

The intersystem crossing efficiencies of **1** and **2** were found to be 0.62 and 0.72, respectively. These values are close enough to the Φ_{isc} value (0.65) determined for the saturated analog **5** to suggest that even in fluid solution no substantial alteration of the singlet–triplet crossover in D is introduced upon placing a norbornylene chromophore in close proximity as in **1** or **2**.

Both photorearrangements **1** → **3** and **2** → **4** involve displacement of a hydrogen atom on the bridge next to the dimethoxybenzene group. Consequently, one may formulate a mechanism in which the excited D may cause an initial C–H fission followed by H addition to the double bond and cyclization as shown below.

Some evidence against the above mechanism was provided by the photolysis of cyclopropane derivatives **7** and **8** prepared from **1** and **2**, respectively, by reaction with diazomethane in the presence of cuprous chloride (see Scheme I). In spite of irradiation times in excess of 100 times those needed to produce detectable amounts of photoproducts **3** and **4**, **7** and **8** remained unchanged. In both cases the cyclopropane group is located at a site where it has been shown to participate in solvolysis reactions at the bridge positions involved.[17] It seems that except for the initial intersystem crossing step the **1** → **3** photorearrangement takes place in a manner analogous[5] to that described for **9**. On the other hand the **2** → **4** reaction involves a distinct transfer of triplet energy from the absorbing D to the reacting N.



Finally, one may ask how appropriate is the characterization of weak and strong interaction between unsaturated nonconjugated chromophores based only on the electronic absorption spectra. Perhaps one should refer to sets of specific energetic states. For example, examinations of the near-uv absorption spectrum of **2** reflect no mutual perturbation of the constituent D and N chromophores. This implies weak or no interaction. However, it must refer to the ground and lowest excited singlet states only since the triplet energy of D is totally transferred to N. Apparently the excited triplet of D extends far enough in the interchromophoric space in the direction of N to overlap with the ground state of N and yield a relatively high value for the exchange integral. We know a great deal about the ground state of isolated olefinic groups[18] but relatively little about the size and shape of excited aromatic triplets.[19] Besides their relevance to photochemistry, it is hoped that experiments such as those described herein contribute to defining the spatial properties of molecular excited states and their interaction with other nearby molecules or chromophores.

Experimental Section

General. Most of the quantum yields were carried out with a merry-go-round set-up in a Rayonet photochemical reactor employing a bank of low-pressure mercury arcs.[20] In a few cases, an alternate procedure was used which passed the uv light from a 120-W Hg arc *via* a Bausch and Lomb high-intensity monochromator along

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(20) The Southern N. E. Ultraviolet Co., Middletown, Conn.

an optical train through either sample cell or solvent-filled cells. This latter method employed a ferrioxalate actinometer.[21] The sensitized isomerization of piperylene was used not only as an actinometer but also to measure intersystem crossing efficiencies of model compounds. To determine photochemical conversion and to perform product analysis we used an F & M gas chromatograph with a 6 ft × 1/8 in. column packed with Apiezon L on Chromosorb W. Analysis of isomeric piperlyene mixtures was performed with a 20 ft × 0.25 in. column of triscyanoethoxypropane on Chromosorb W. A dual-flame ionization detector was used with both columns. Ir and uv spectra were recorded in double beam with a Beckmann Model IR5A and a Cary Model 15 spectrophotometer, respectively. Nmr spectra were recorded on a Hitachi-Perkin-Elmer H-16 spectrometer. Emission spectra were obtained on an Aminco-Bowman spectrophotofluorometer in frozen EPA at 77°K.

3',6'-Dimethoxybenzonorbornadiene was prepared from cyclopentadiene–benzoquinone adduct, aqueous sodium hydroxide, and dimethyl sulfate as described by Meinwald and Wiley[8] for methylation of 3',6'-dihydroxybenzonorbornadiene.

5,8-Dimethoxy-*endo,exo*-1,4:9,10-dimethano-1,4,6,7,9,10-hexahydroanthracene (2). In a sealed tube were placed 11.3 g of 3',6'-dimethoxybenzonorbornadiene and 5.6 g of dicyclopentadiene. The tube was heated at 195° for 6 hr. The resultant oil crystallized from heptane to give 8.4 g (60%) of an off-white solid. Several recrystallizations from heptane gave colorless needles: mp 128–129°; ν_{KBr} 3030, 2950, 2850, 1490, 1480, 1430, 1350, 1270, 1250, 1175, 1105, 1080, 1060, 990, 910, 900, 850, 820, 795, 785, 755, 730, and 705 cm^{-1}; nmr (CCl_4) δ 6.27 (2 H, $H_{6,7}$, singlet), 5.98 (2 H, $H_{2,3}$, triplet), 3.63 (6 H, OCH_3, singlet), 3.20 (2 H, $H_{9,10}$, triplet), 2.90–2.57 (3 H, $H_{1,4,15a}$, complex), 2.19 (2 H, $H_{13,14}$, broad singlet, and 1.70–0.95 ppm (3 H, $H_{15s,16a,16s}$, complex).

5,8-Dimethoxy-*endo,exo*-1,4:9,10-dimethano-1,2,3,4,6,7,9,10-octahydroanthracene (6). Hydrogenation of 0.3 g of **2** was accomplished in a low-pressure hydrogenation apparatus in 50 ml of methanol over 0.1 g of palladium black. After charging the mixture with hydrogen, the reaction was magnetically stirred for 1 hr at room temperature. The catalyst was filtered, the solvent evaporated, and the residue recrystallized from ethanol as white crystals: mp 123–124°; ν_{KBr} 3080 (bridge (C–H)); nmr (CCl_4) δ 6.31 (2 H, $H_{6,7}$, singlet), 3.68 (6 H, OCH_3, singlet), 3.27 (2 H, $H_{9,10}$, triplet), and 1.2–2.2 ppm (10 H, complex). The compound gave a negative permanganate test for unsaturation.

8,11-Dimethoxytetracyclo[5.4.0^{2,4}.0^{3,6}]undeca-1,8,10-triene (3). **1** (2 g) in 200 ml of ether was irradiated for 2 hr with a 450-W Hanovia medium-pressure Hg arc. After evaporation of the ether, the residue, a dark yellow oil, was chromatographed on a silica gel column with benzene. The resulting yellow solid was recrystallized from ethanol and then from heptane as light yellow crystals: mp 65–66.5°; nmr (CCl_4) δ 6.40 (2 H, $H_{9,10}$, singlet), 3.76 (3 H, OCH_3, singlet), 3.64 ppm (3 H, OCH_3, singlet), complex patterns further upfield.

11,12-*o*-[1',4'-Dimethoxybenzeno]pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{5,9}]-dodec-11-ene (4). **2** (1 g) in ether was irradiated through a Pyrex filter for 20 hr with light from a 450-W Hanovia medium-pressure Hg arc. Evaporation of the ether gave a quantitative yield of off-white crystals which were recrystallized from heptane to give white cubic crystals: mp 88–88.5°; ν_{KBr} 2950, 2875, 2700, 1600, 1490, 1460, 1350, 1320, 1280, 1260, 1190, 1140, 1110, 1090, 1065, 1020, 990, 975, 805, 795, and 710 cm^{-1}; nmr (CCl_4) δ 6.25 (2 H, $H_{2',3'}$, singlet), 3.66 (3 H, OCH_3, singlet), 3.6 ppm (3 H, OCH_3).

***exo*-3,6-Dimethoxytetracyclo[6.3.1.0^{2,7}.0^{9,11}]undeca-2,4,6-triene (7).** An ethereal solution of 0.30–0.35 g of diazomethane was distilled into a cooled, stirring mixture of 0.5 g of **1**, 0.05 g of cuprous chloride, and 30 ml of ether. After the addition was complete, the solution was stirred for another 30 min, filtered, and evaporated to dryness. The residue was recrystallized from ethanol: mp 97–98°; nmr (CCl_4) δ 6.32 (2 H, aromatic H, singlet), 3.69 (6 H, OCH_3, singlet), 3.39 (2 H, benzylic H, complex), and 0.5–1.5 ppm (6 H, aliphatic H, complex).

***exo,endo,exo*-11,14-Dimethoxyhexacyclo[7.6.1.1^{3,7}.0^{4,6}.0^{2,8}.0^{10,15}]-heptadeca-10,12,14-triene (8).** This compound was prepared from **2** the same way as **7** from **1**, white crystals: mp 91.5–92°; nmr δ 6.27 (2 H, aromatic H, singlet), 3.66 (6 H, OCH_3, singlet), 3.39 (2 H, benzylic H, complex), and 0.5–2.7 ppm (12 H, aliphatic H, complex).

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Spin-Density Distribution in Some Heterocyclic Systems

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Abstract: Nmr contact shift measurements have been made on a number of Ni(II) aminotroponeiminates containing heterocyclic substituents. From these measurements the spin-density distributions in the heterocyclic moieties have been evaluated. The spin densities are compared with those previously reported for analogous aromatic fragments and are discussed in terms of the valence bond formalism. Both odd alternant and even alternant systems are considered. In general, the results demonstrate the participation of ionic resonance structures in heterocyclic compounds, and qualitative estimates of the importance of such structures are presented. Competitive π bonding in mixed Ni(II) aminotroponeiminates enables a quantitative measurement of the electron-accepting or -donating properties of a heterocyclic group relative to a phenyl group to be obtained. Results for several such groups expressed in terms of the Hammett σ parameter are presented.

We have previously reported the use of nmr contact-shift measurements on the ligands of paramagnetic transition metal chelates to study conjugation[1] and hyperconjugation.[2] In the present paper this approach is extended to heterocyclic systems. It has long been recognized that pyridine and furan, for example, have chemical properties similar to aromatic molecules

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