Rod-Like Organic Molecules. Energy-Transfer Studies Using Single-Photon Counting[1,2]

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The synthesis of rod-like molecules was devised wherein the rods were composed of bicyclo[2.2.2]octane units bonded bridgehead to bridgehead. Various end chromophores were placed at the terminal bridgehead sites of [1]-rods and [2]-rods, these being constituted of one and two bicyclooctyl moieties, respectively. Donor moieties employed were α-naphthyl and β-naphthyl. Energy acceptors used were acetyl, benzoyl, and cyclohexanecarbonyl. Control compounds having only the donor or acceptor substituent present were also synthesized. In the bichromophoric rods it was found that excitation of the donor chromophores led to emission by both the donor and the acceptor moieties, with the ratio depending on the system. Single-photon counting was employed to obtain the rates of intramolecular energy transfer and decay exhibited by the bridgehead groups. Two further systems were synthesized and studied. The first had two β-naphthyl groups at the ends of a [1]-rod and the second had an α-naphthyl group at one end and a cis-propenyl moiety at the other end of a [1]-rod molecule. Rate studies revealed intramolecular singlet-energy transfer from the naphthyl moieties to acetyl, cyclohexanecarbonyl, and benzoyl groups, with shortening of the naphthyl moiety S_1 lifetime. Benzoyl was more efficient in draining energy from the donor than were acetyl and cyclohexanecarbonyl. Also transmission from β-naphthyl moieties was more rapid than that from α-naphthyl groups. Rod length was another controlling factor with energy transfer diminishing in rate with increasing distance between chromophores. However, the dependence on distance was greater than the usually anticipated inverse sixth power, and this is discussed in terms of an especially efficient overlap–delocalization mechanism in the case of the [1]-rods. No diminution of lifetime was observed when the two β-naphthyl moieties were placed at opposite ends of a [1]-rod. In the case of the α-naphthyl-cis-propenyl-[1]-rod, neither stereoisomerization nor diminution of naphthyl S_1 lifetime was effected. The donor–acceptor systems were treated kinetically as $A \rightleftharpoons B \rightarrow C$ processes.

Introduction

Three different research areas have been of considerable interest to us. One is the use of single-photon counting in obtaining rates of excited-state phenomena.[3] The second is energy utilization and dissipation in excited-state chemistry,[4] this being central to an understanding of photochemical reactions. The third is the chemistry of "organic rods" consisting of bicyclo[2.2.2]octane moieties attached bridgehead to bridgehead to form "[n]-rods".

The present research combines our interest in these three directions. We report the preparation of [1]- and [2]-rods with chromophoric groups at the termini and the kinetics of energy transfer from one end of the rod to the other. The fixed geometry of these systems promised to allow systematic study of "molecular light pipes" capable of absorbing light at one end of a variable-length rod and emitting light at the other.

In our earlier studies[5] we investigated energy transfer between an α-naphthyl group and a benzoyl moiety at the bridgehead positions of a single bicyclo[2.2.2]octane unit, relying on non-time-resolved emission spectroscopy. Such an approach has been used in many flexible,[6] partially flexible,[7] and relatively rigid[8] bichromophoric systems investigated hitherto.

(1) (a) This paper is no. 124 of our photochemical series; for paper 123, see: Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.*, in press.

(2) For a preliminary report of some of these results, see: Zimmerman, H. E. *Pure and Appl. Chem.* **1977**, *49*, 389–398.

(3) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 439–449.

(4) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718–3725.

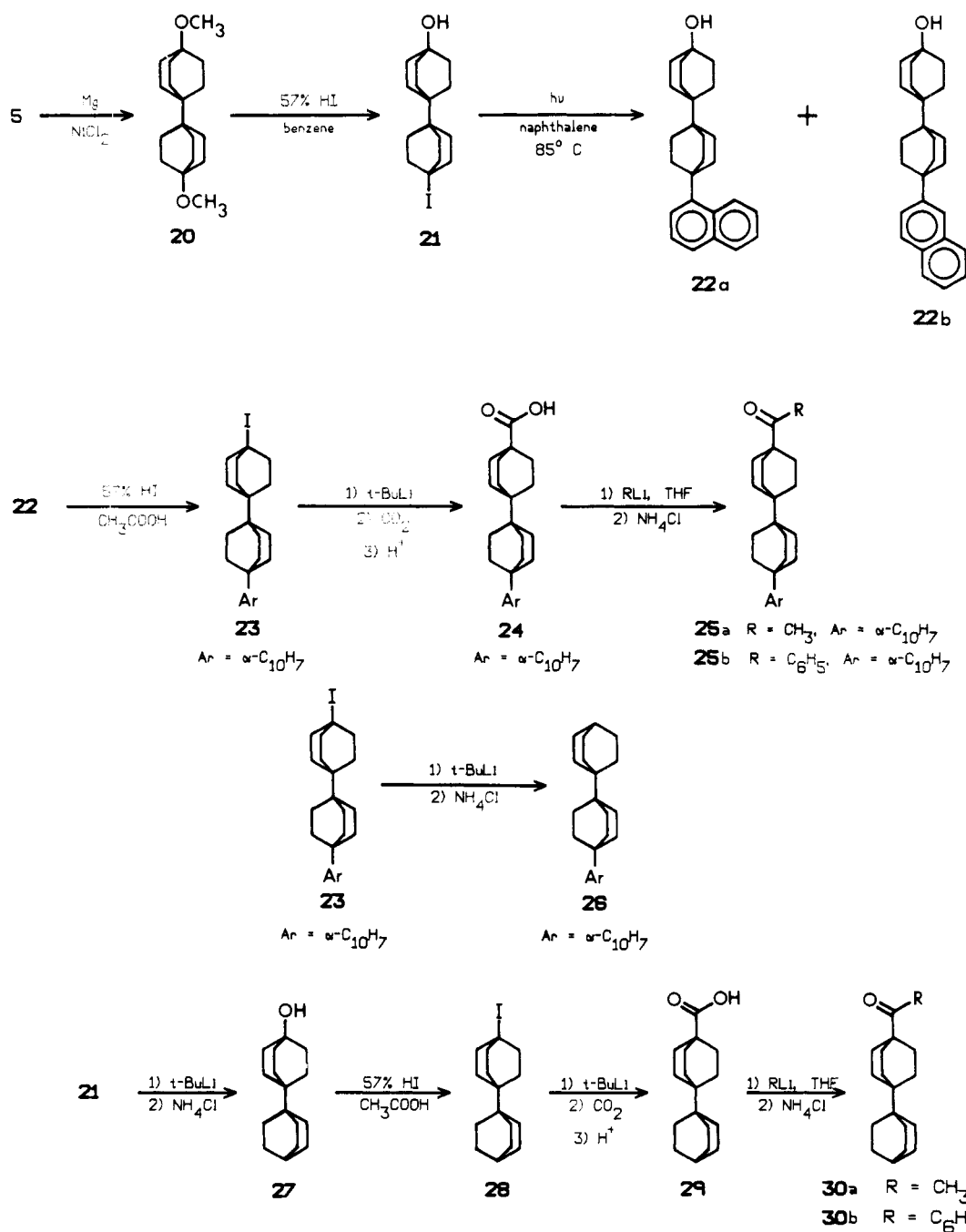(5) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638–3645.

(6) (a) Schepp, O.; Levy, M. *J. Am. Chem. Soc.* **1962**, *84*, 172. (b) Breen, D. E.; Keller, R. A. *Ibid.* **1968**, *90*, 1935. (c) Thiery, C. *Mol. Photochem.* **1970**, *2*, 1.

(7) (a) Latt, S.; Cheung, H. T.; Blout, E. R. *J. Am. Chem. Soc.* **1965**, *97*, 995–1003. (b) Keller, R. A.; Dolby, L. J. *Ibid.* **1967**, *89*, 2768; **1969**, *91*, 1293. (c) Rauh, R.; Evans, T. R.; Leermakers, P. A. *Ibid.* **1968**, *90*, 6897; **1969**, *91*, 1860. (d) Stryer, L.; Haughland, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 719–726.

(8) (a) Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1940. (b) DeMember, J. R.; Filipescu, N. *Ibid.* **1968**, *90*, 6425. (c) Lamola, A. A. *Ibid.* **1969**, *91*, 4786. (d) Filipescu, N.; DeMemeber, J. R.; Minn, F. L. *Ibid.* **1969**, *91*, 4169. (e) Tyer, N. W., Jr.; Becker, R. S. *Ibid.* **1970**, *92*, 1295. (f) Amrein, W.; Shaffner, K. *Helv. Chim. Acta* **1975**, *58*, 397–415. (g) H. Kuhn et al. (*Mol. Crystals* **1967**, *2*, 199–230) in an elegant study use multiple layers of fatty acid salts to separate chromophores with distances ranging from 50 Å upwards.

Chart I. Synthesis of [1]-Rods

Results

Synthetic Efforts. Synthesis of Organic Rods. Our syntheses of [1]-rods utilized 1,4-dichlorobicyclo[2.2.2]-octane[9] which was obtained in 100-g quantities by the method of Kauer.[9] These syntheses are outlined in Chart I. Especially challenging was the attachment of the second chromophore in the naphthyl-iodo-[1]-rods 6 and 7. This was accomplished by reaction of these bridgehead iodo compounds with 2 equiv[10] of *tert*-butyllithium, affording the corresponding bridgehead lithium derivatives. It appears that the necessity for the second equivalent of lithium reagent derives from the reaction of *tert*-butyl iodide, formed in the reaction, with butyllithium to form isobutylene with consumption of 1 equiv of lithium reagent. The bridgehead lithium reagents derived from iodo-[1]-rods 6 and 7 were used with a variety of reagents to introduce the desired second chromophore, as shown in Chart I. A final point is that the Wittig reaction was uniquely suited for generating the cis isomer of the propenyl derivative 12, as would be expected.[11]

(9) (a) Kauer, J. C. French Patent 1 345 138 (1963); *Chem. Abstr.* **1965**, *62*, 14529e. (b) Kauer, J. C. *Prepr. Div. Pet. Chem., Am. Chem. Soc.* **1970**, *15*, B14–B18. (c) The iodo alcohol 4 was mentioned, but not characterized, in ref 9b.

(10) Lansbury, P. T.; Sidler, J. D. *J. Chem. Soc., Chem. Commun.* **1965**, 373.

(11) (a) Schlosser, M.; Christmann, K. F. *Justus Liebigs Ann. Chem.* **1967**, *708*, 1. See also: (b) Rencroft, J.; Sammes, P. G. *Q. Rev., Chem. Soc.* **1971**, *25*, 135–169.

Chart II. Synthesis of [2]-Rods

The [2]-rod syntheses (Chart II) required a practical route to a [2]-rod substrate with functional end groups. Initially it was observed that reaction of 1-iodo-4-methoxybicyclo[2.2.2]octane (5) with magnesium in ether led to ca. 40% yields of 4,4'-dimethoxy-1,1'-bibicyclo[2.2.2]octyl (20). Markedly increased yields of 65–70% resulted when either nickelous chloride or silver iodide was present in molar quantities. Another interesting feature of the [2]-rod syntheses was utilization of a two-phase, benzene–hydriodic acid conversion of [2]-rod dimethyl ether 20 to iodo-hydroxy-[2]-rod 21 in 74% yield. This better than statistical yield seems likely to derive from the greater solubility of the dihydroxy-[2]-rod 31 intermediate in the hydriodic acid phase compared with the iodo-hydroxy-[2]-rod product 21.

The conversion of the iodo-hydroxy-[2]-rod 21 to bridgehead naphthyl substituted product using boron trifluoride led primarily to β-naphthyl-iodo-[2]-rod 23b. Irradiation of iodo-hydroxy-[2]-rod 21 in molten naph-

Table I. Selected Fluorescence Quantum Yields[a]

compd	Φ_f	compd	Φ_f
naphthalene	0.19[b]	α-naphthyl-benzoyl-[2]-rod 25b	0.027
α-naphthyl-[2]-rod 26	0.23	α-naphthyl-acetyl-[1]-rod 9a	0.0061
α-naphthyl-acetyl-[2]-rod 25a	0.18	α-methylnaphthalene	0.21

[a] Naphthyl emission contributions only; acetyl emission of 9a not included. [b] Note ref 12.

thalene at 85 °C proved synthetically useful to obtain α-naphthyl product and led to a 2:1 ratio of α-naphthyl-hydroxy-[2]-rod 22a to β-naphthyl-hydroxy-[2]-rod 22b.

Fluorescence Behavior. It was of interest to inspect the emission behavior of the rod compounds as a preliminary to the study of the rates of energy transfer and decay.

Fluorescence quantum yields were obtained for a selected group of the rod compounds. These were measured

Table II. Fluorescence Maxima for
Mono- and Bichromophoric Systems

compd	emission[a,b] max (1), nm	max (2), nm	ratio of intensities[c]
α-naphthyl-[2]-rod 26	330 ± 5		
α-naphthyl-[1]-rod 13	335 ± 5		
β-naphthyl-[1]-rod 14	331 ± 5		
1-acetyl-[1]-rod 18	400 ± 5		
1-cyclohexanecarbonyl-[1]-rod 19	397 ± 5		
α-naphthyl-acetyl-[2]-rod 25a	330 ± 5		*d*
α-naphthyl-acetyl-[1]-rod 9a	330 ± 5	405 ± 5[e]	5:1
β-naphthyl-acetyl-[1]-rod 11a	329 ± 5	397 ± 5	1:1
α-naphthyl-cyclohexane-carbonyl-[1]-rod 9b	336 ± 5	392 ± 5	1:1
β-naphthyl-cyclohexane-carbonyl-[1]-rod 11b	340 ± 5	390 ± 5	1:3

a The emission maxima reported for 1-methylnaph-
thalene are 325 and 338 nm: Berlman, I. B. "Handbook
of Fluorescent Spectra of Aromatic Molecules"; Academic
Press: New York, 1965. *b* The emission maxima
reported for a series of alkyl ketones were 405 ± 3 nm.
See: O'Sullivan, M.; Testa, A. C. *J. Am. Chem. Soc.*
1970, *92*, 5842. *c* Ratio of naphthyl to carbonyl emis-
sion. *d* Only one emission band was observed. *e* This
was a shoulder in the emission.

with naphthalene, $\Phi_f = 0.19$,[12] as a standard. Table I
summarizes these measurements.

The literature value for α-methylnaphthalene of 0.21 is
seen to be close to the measured quantum yield for the
α-naphthyl-[2]-rod **26** which is also a 1-alkyl-substituted
naphthalene. Thus, this value provides an indication of
efficiency of emission in the absence of chromophores at
the other end of the rod.

Interestingly, the presence of the acetyl and benzoyl
groups at the other ends of the rods is seen to diminish
the fluorescence quantum yields. The effect is small for
an acetyl group in a [2]-rod (note **25a**). The effect is larger
for benzoyl substitution in the [2]-rod. For the [1]-rod
derivatives acetyl dramatically lowers the fluorescence
efficiency and benzoyl leads to a very weakly emitting
compound for which an accurate measurement was diffi-
cult. These effects are not due to bimolecular energy
transfer since it was determined that the results were
concentration independent.

One added exciting result was encountered in fluores-
cence behavior of the α-naphthyl-acetyl-[1]-rod. Here a
fluorescence maximum in addition to the usual 335-nm
naphthyl peak was observed. This was seen at 405 nm;
it was approximately 20% as intense as the naphthyl peak
and at a wavelength characteristic of acetyl emission. A
similar double emission was observed in the cases of β-
naphthyl-acetyl-[1]-rod **11a**, α-naphthyl-cyclohexane-
carbonyl-[1]-rod **9b**, and β-naphthyl-cyclohexane-
carbonyl-[1]-rod **11b**. For the first two of these, the
fluorescence peaks were of similar magnitude, while for the
last the carbonyl fluorescence was stronger (3:1). In con-
trast to the double emission encountered for the [1]-rods,
as noted above, only naphthyl-like emission at 335 nm was
observed in the fluorescence spectra of the [2]-rods. A
summary of these observations is given in Table II.

One possible problem in determining excited-state
lifetimes arises if the rate of Brownian rotation is of the

same order as the rate of excited-state decay. An error
then arises due to partial depolarization, and the observed
rate of decay includes a function of the rate of molecular
rotation.[3,13] In the present study it was found (note Ex-
perimental Section, Table IX) that the molecules of in-
terest show small polarizations at room temperature, where
rate studies were of interest, and thus depolarization is
essentially complete and not a complicating factor. As
expected, at 77 K these molecules do exhibit polarization
(note Table IX).

**Single-Photon Counting Determination of Rates of
Excitation Transfer and Decay.** The information in
hand thus far suggested that excitation of the naphthyl
moiety in the rod compounds led to varying amounts of
energy transfer to the chromophore—be it acetyl, cyclo-
hexanecarbonyl, or benzoyl—at the other end of the rod,
with decay of the two chromophores to ground state. This
decay is both radiative and radiationless.

Thus, we can discuss the processes of interest by using
the kinetic picture in eq 1. Here D is the α- or β-naphthyl

$$\tag{1}$$
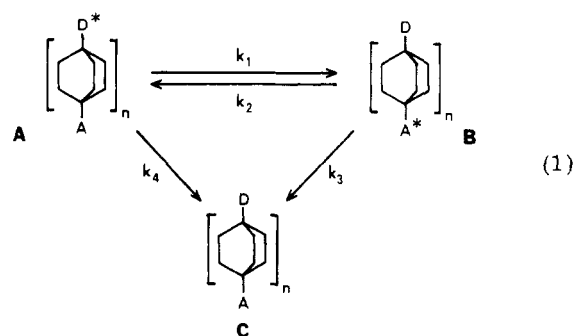
donor moiety, A is the acetyl, benzoyl, or cyclohexane-
carbonyl acceptor moiety and the asterisk indicates elec-
tronic excitation. Since A is generated essentially in-
stantaneously by absorption of light by naphthyl, we do
not need to consider processes leading to A other than
those in eq 1.

Single-photon counting using techniques of the type
described by us earlier,[3] however employing improved data
collection and processing,[14] permitted monitoring con-
centrations of A and B as a function of time. Thus A could
be followed by monitoring single-photon emission at ca.
330 nm while B could be observed at 400 nm and above.
As before, it was made certain that the processes observed
were concentration independent and therefore intramo-
lecular. Also the concentrations were adjusted to keep the
pseudounimolecular rate of diffusion below the rate
studied in each case.

In each case reiterative deconvolution was employed
with efforts to fit the data to both single and double ex-
ponential decay functions. Thus, the kinetics of the system
were observed in two ways: by obtaining the rate of decay
of the naphthyl moiety and also by obtaining that of the
carbonyl group when this emission was observable.

Table III summarizes empirical rate constants. In the
case of the [2]-rods and benzoyl-[1]-rods, the observed
decay nicely fit a single negative exponential and the rate
constant was obtained directly. However, in the acyl-
[1]-rod runs the data required a double exponential fit.
Theory suggested a decay of the form of eq 2a and 2b,

$$[A] = L_1 e^{-m_1 t} + L_2 e^{-m_2 t} \tag{2a}$$

$$[B] = L_3 (e^{-m_2 t} - e^{-m_1 t}) \tag{2b}$$

where A and B are defined above in eq 1 and L_3 is a

(12) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker:
New York, 1973; p 4, 5.

(13) Shinitsky, M. *J. Chem. Phys.* 1972, *56*, 5979–5981.
(14) Zimmerman, H. E.; Blood, J. C., to be published.

Table III. Rates of Excited-State Decay[a,b]

compd	m_1, s^{-1}	τ_1, ns	m_2, s^{-1}	τ_2, ns
β-naphthyl-[1]-rod 14	$(1.56 \pm 0.01) \times 10^7$	64.2		
α-naphthyl-[1]-rod 13	$(1.54 \pm 0.06) \times 10^7$	65.0		
α-naphthyl-[2]-rod 26	$(1.69 \pm 0.05) \times 10^7$	59.2		
acetyl-[1]-rod 18			$(3.4 \pm 0.2) \times 10^8$	3.0
cyclohexanecarbonyl-[1]-rod 19			$(2.1 \pm 0.05) \times 10^8$	4.7
α-naphthyl-acetyl-[2]-rod 25a	$(2.21 \pm 0.05) \times 10^7$	45.3	c	
α-naphthyl-benzoyl-[2]-rod 25b	$(1.20 \pm 0.02) \times 10^8$	8.32		
α-naphthyl-acetyl-[1]rod 9a	$(1.7 \pm 1.2) \times 10^9$	0.43	$(2.7 \pm 1.1) \times 10^8$	3.0
β-naphthyl-acetyl-[1]-rod 11a	$(4.0 \pm 1.5) \times 10^9$	0.25	$(2.5 \pm 0.3) \times 10^8$	4.0
α-naphthyl-cyclohexanecarbonyl-[1]-rod 9b	$(1.5 \pm 0.4) \times 10^9$	0.67	$(1.7 \pm 0.1) \times 10^8$	5.9
β-naphthyl-cyclohexanecarbonyl-[1]rod 11b	$(3.9 \pm 1.0^d) \times 10^9$	0.26	$(1.7 \pm 0.1) \times 10^8$	5.9
α-naphthyl-benzoyl-[1]-rod 32[e]	$(4.0 \pm 0.8) \times 10^9$	0.25		
β-naphthyl-benzoyl-[1]-rod 11c	$>1 \times 10^{10}$ [f]	<0.1		
α-naphthyl-cis-propenyl-[1]-rod 12	$(1.6 \pm 0.03) \times 10^7$	64.5		
di-β-naphthyl-[1]-rod 15	$(1.6 \pm 0.1) \times 10^7$	64.0		

[a] Rates were determined by the single-photon counting technique. [b] Average values are reported; rates are given with their standard deviations. [c] Acetyl emission was not discernable. [d] One run only for m_1; approximate error limits given. [e] Sample was provided by Dr. R. McKelvey. [f] Rate was beyond the limits of determinability by the single-photon counting technique without an error over 20% with our equipment.

Table IV. Summary of Emission Wavelength Dependence of Preexponential Terms and Rates[a]

compd	wavelength, nm		empirical preexponential term		rate, s^{-1}	
	excitation	emission	W_1	W_2	m_1	m_2
α-naphthyl-acetyl-[1]-rod 9a	270–280	330–335	0.41^b	0.27^b	3.2×10^9 [j]	4.8×10^8 [b,j]
	280	350	0.052	0.023	3.1×10^9 [j]	4.8×10^8 [j]
	270	355	0.027	0.014	7.9×10^8	2.8×10^8
	270	370–405				2.5×10^8 [b]
	270	400–460	-0.072^b	0.057^b	1.7×10^9 [b]	2.7×10^8 [b]
β-naphthyl-acetyl-[1]-rod 11a	265	325	0.20	0.0012	3.5×10^9	9.8×10^7
	265–285	340–360	variant[c]		4.0×10^9 [d]	2.3×10^8 [d]
	275	380				2.9×10^8 [e]
	275	395	−0.096	0.40	4.3×10^9	2.7×10^8
α-naphthyl-cyclohexanecarbonyl-[1]-rod 9b	270–290	325–360	variant[f]		1.6×10^9	1.7×10^8 [g]
	270	385–420	-0.052^h	0.039^h	1.3×10^9 [h]	1.7×10^8 [h]
β-naphthyl-cyclohexanecarbonyl-[1]-rod 11b	275	340	0.16	0.014	3.9×10^9	1.5×10^8
	270	355–415				1.7×10^8 [i]

[a] Rates and amplitudes were determined with the single-photon counting technique: m_1 and m_2 have ca. 10% error limits but W_1 and W_2 are less accurately determined with an uncertainty factor 1.5. [b] Average of four runs. [c] Function of wavelength of emission, see Table XI. [d] Average of seven runs. [e] Average of three runs. [f] Function of wavelength of emission, see Table V. [g] Average of ten runs. [h] Average of two runs. [i] Average of five runs. [j] These values derive from runs with possible lamp flash scattering.

positive constant. We note at this juncture that m_1 and m_2 are operational rate constants which still need interpretation.

Table IV summarizes observed preexponential (W_1 and W_2) and rate values obtained by measurement of time-dependent emission at varying wavelength in the case of acyl-[1]-rods. Additionally, the effect of the monitoring wavelength on the preexponential terms and the rate constants is detailed further for two of the [1]-rod compounds in Tables X and XI.

Interpretative Discussion

Extraction of Rates of Energy Transfer and Decay from the Empirical Rate Data. We begin by again noting that the experimentally observed rate constants, m_1 and m_2, do not correspond directly to the rates of energy transfer and decay (i.e., k_1, k_2, k_3, and k_4) as depicted in eq 1. Similarly, W_1 and W_2 are the experimentally encountered preexponential coefficients while L_1 and L_2 are theoretical quantities.

For a kinetic scheme of the type in eq 1, Evans[15a] has derived the dependence of [A] and [B] as a function of

(15) (a) Evans, R. W. "Integrated forms of certain differential rate expressions in chemical kinetics", M. S. Thesis, University of Wisconsin, 1950. (b) Alberty, R. A.; Miller, W. G. *J. Chem. Phys.* **1957**, *26*, 1231–1237. (c) Our m_1 and m_2 are the negatives of those described by Alberty and Miller in 15b.

time. The operational rate constants m_1 and m_2 are given by eq 3 and 4.

$$m_1 = (1/2)\{(k_1 + k_2 + k_3 + k_4) + [(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2k_4 + k_1k_3 + k_3k_4)]^{1/2}\} \quad (3)$$

$$m_2 = (1/2)\{(k_1 + k_2 + k_3 + k_4) - [(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2k_4 + k_1k_3 + k_3k_4)]^{1/2}\} \quad (4)$$

Thus the experimental rate constants are a combination of the mechanistic rate constants. If the experiment is one which begins with species A (note eq 1) but no B, then in monitoring the concentration of A vs. time, L_1 and L_2 in eq 2 are given by eq 5a and 5b.[15a]

$$L_1 = (k_1 + k_4 - m_2)[A_0]/(m_1 - m_2) \quad (5a)$$

$$L_2 = (k_1 + k_4 - m_1)[A_0]/(m_2 - m_1) \quad (5b)$$

However, if we are monitoring species B, then L_3 is given by eq 6.

$$L_3 = (k_1 + k_4 - m_1)(k_1 + k_4 - m_2)[A_0]/k_2(m_1 - m_2) \quad (6)$$

From eq 3 and 4 one can obtain two useful expressions (eq 7 and 8).

$$m_1 + m_2 = (k_1 + k_2 + k_3 + k_4) \quad (7)$$

$$m_1m_2 = k_2k_4 + k_1k_3 + k_3k_4 \quad (8)$$

Table V. Rate of Energy Transfer and
Decay to Ground State of Acyl-[1]-Rods

compd	k_1, $10^9 s^{-1}$	k_2, $10^8 s^{-1}$	k_3, $10^8 s^{-1}$ [a]	k_4, $10^7 s^{-1}$ [a]
α-naphthyl-acetyl-[1]-rod 9a	1.3	2.9	3.39	1.54
β-naphthyl-acetyl-[1]-rod 11a	2.9	10.0	3.39	1.56
α-naphthyl-cyclohexyl-[1]-rod 9b	1.2	2.9	2.14	1.54
β-naphthyl-cyclohexyl-[1]-rod 11b	3.0	8.2	2.14	1.56

[a] Values taken from model compounds 13, 14, 18, and 19. Error limits for k_1 are ±20%, for k_2 ±50%. This derives from the greater sensitivity of k_2 to measureables compared to k_1.

A third relationship derives from the ratio of the two preexponential terms in eq 2a and as given by eq 5a and 5b. Algebraic manipulation of the ratio affords eq 9.

$$k_1 + k_4 = (L_1 m_1 + L_2 m_2)/(L_1 + L_2) \qquad (9)$$

Thus, one has in 7, 8, and 9 three equations and the four unknowns k_1, k_2, k_3, and k_4. However, eq 9 makes use of L_1 and L_2, and these preexponential terms are subject to a relatively large error.

An alternative approach avoids usage of the preexponential terms. This is done by using the decay rates of model naphthyl and acyl[16] monochromophoric systems to give k_4 and k_3, respectively. Here we need use only eq 7 and 8 to obtain the two remaining unknown rates k_1 and k_2. These results are given in Table V.

Thus far we have considered experiments in which naphthyl emission (i.e., species A) has been monitored. Inspection of eq 2b shows that species B (i.e., the bichromophoric molecule with the acyl moiety excited) also should exhibit a double exponential decay. Furthermore, the two exponential terms have a common preexponential factor L_3 but have opposite signs, with the $e^{-m_1 t}$ term being negative.

Indeed, monitoring of acetyl and cyclohexanecarbonyl emission peaks in the range 400–460 nm did lead to such a double exponential with the theoretically expected negative weighting of one term. The preexponential terms were in the ratio of −1:1 to −2:1 and thus, with a minor error, in agreement with expectation based on eq 2b. More importantly, the rate constants obtained should be the same as those obtained by the naphthyl emission experiments, and they were (note Table IV).

Another point of interest is that as one monitors emission at wavelengths between those expected for naphthyl fluorescence (i.e., 330 nm) and for acetyl and cyclohexanecarbonyl fluorescence (i.e., 405 nm), one should obtain a superposition of fluorescence due to species A and B. Equations 2a and 2b when added in some linear combination continue to afford a double exponential with the same rate constants except for that linear combination in which L_1 and L_3, having opposite signs, cancel. This was precisely the observation as the monitoring wavelength was changed. Thus the large ratio of the observed preexponential terms W_1 and W_2 (note Table IV) decreases with increasing wavelength until the long-wavelength negative

Table VI. Rates for Compounds Exhibiting Single
Negative Exponential Decay Processes

compd	m_1, s^{-1}	k_4, s^{-1} [a]	k_1, s^{-1}
α-naphthyl-acetyl-[2]-rod 25a	2.21×10^7	1.69×10^7	5.2×10^6
α-naphthyl-benzoyl-[2]-rod 25b	1.20×10^8	1.69×10^7	1.03×10^8
α-naphthyl-benzoyl-[1]-rod 32	4.0×10^9	1.54×10^7	3.98×10^9

[a] These values obtained from model compounds 26 and 13.

Table VII. Predicted and Observed Rates
of Energy Transfer

compd	predicted rate, s^{-1}	observed rate, s^{-1}
α-naphthyl-acetyl-[1]-rod 9a	7.0×10^7	1.3×10^9
α-naphthyl-benzoyl-[1]-rod 32	1.39×10^9	4.0×10^9

ratio is obtained. Furthermore, there is an intermediate wavelength where the linear combination has eliminated the $e^{-m_1 t}$ term. There results a deceptively simple single exponential of the form $Ke^{-m_2 t}$. This points to the hazard in obtaining fluorescence decay rates at only one wavelength.

We turn now to benzoyl-[1]- and -[2]-rods. Here, as is seen in Table III, only single negative exponential decays were obtained when naphthyl emission was monitored. If one considers the consequence of k_2 being very small or zero, the expression in eq 2a does become a single negative exponential as a result of m_1 becoming equal to $k_1 + k_4$. Then L_2 in eq 5b becomes zero.

The same conclusions are arrived at for the α-naphthyl-acetyl-[2]-rod 25a, where a single negative exponential decay of naphthyl fluorescence is encountered.

The rate constants for compounds exhibiting single negative exponential decays are summarized in Table VI.

Theoretical Conclusions. The first point we note is that energy transfer in the acetyl- and cyclohexane-carbonyl-[1]-rods is reversible while it is not in the cases of the benzoyl-[1]-rods, benzoyl-[2]-rods, and acetyl-[2]-rods. We attribute the lack of reversibility in the benzoyl examples to a large endothermicity in back transfer from S_1 excited benzoyl (78.7 kcal/mol[17]) to naphthyl (90 kcal/mol[18]) which is 11 kcal/mol endothermic. This contrasts with a ca. 2-kcal/mol endothermicity for back transfer from S_1 acetyl or cyclohexanecarbonyl (88 kcal/mol[19]) to naphthyl (90 kcal/mol). In the case of the acetyl-[2]-rods, the lack of reversibility is attributed to k_2 being diminished by the larger distance between chromophores with k_3 (i.e., decay of S_1 acetyl) remaining relatively undiminished and unchanged. The more rapid transfer to benzoyl compared to acyl derives from the greater overlap between transition dipoles as evidenced by the larger overlap between naphthyl fluorescence and carbonyl absorption.

A second point of interest is the dependence of the rate of energy transfer on distance between the donor and acceptor moieties. Here we focus attention on the [1]- and [2]-rod molecules having α-naphthyl and either acetyl or benzoyl moieties. For dipole–dipole coupled energy transfer an inverse sixth power relationship between rate

(16) (a) Fischer, H. P.; Grob, C. A. *Helv. Chim. Acta* 1964, 47, 564–567. (b) We thank Mr. Christopher Abelt for developing the synthetic route employed by us to obtain this compound; see Chart I and the experimental section.

(17) (a) This is the S_1 energy reported for acetophenone; see: (b) Murov, S. L., ref 12, p 3.
(18) The value of 1-methylnaphthalene is used; see: Murov, S. L., ref 12, p 5.
(19) For the value of acetone, see: Murov, S. L., ref 12, p 3.

of transfer and distance between chromophores is commonly accepted and derives from the Förster relationship;[20] note eq 10.

$$k_{D^*-A} =$$
$$(8.8 \times 10^{-25} K^2 \phi_{fD})/(n^4 \tau_D R^6) \int_0^\infty F_D(\nu)\epsilon_A(\nu)\frac{d\nu}{\nu^4} \quad (10)$$

However, an inverse sixth power relationship with distance is not observed when [1]- and [2]-rods are compared. Thus, as shown in Table VII, if an inverse sixth power relationship is used with the [2]-rod rates, then the rates are too rapid for the [1]-rods by a factor of 19 for acetyl α-naphthyl systems and a factor of 3 for the benzoyl α-naphthyl systems. Only by taking the distance as between terminal bridgehead carbons rather than between chromophore centers could a fit to the inverse sixth power be found. Such a choice is unreasonable. In the [1]-rods the distance between chromophores is only 7.51 Å and is below the distance normally encountered in energy-transfer measurements of rate.

Involvement of a dipole–quadrupole interaction in energy transfer is not helpful since this follows the inverse eighth power of distance between chromophores,[21a] and this is still too weak a function of distance to account for the ratio of rates, especially in the acetyl-α-naphthyl-[1]- and -[2]-rods.

It has been noted by Dexter[21,22] that "exchange effects" lead to another mechanism of energy transfer which can take precedence at short distances or where dipole–dipole interactions are weak. This type of energy transfer follows a negative exponential form as in eq 11, where M and L

$$k_{D^*-A} = Me^{-(2R/L)} \quad (11)$$

are positive constants. Dexter has noted that exchange mechanisms are important in triplet transfer where other modes are inefficient. We now consider the case of singlets.

Such exchange effects seem most likely to occur where the excited states converted into one another have wavefunctions which overlap spatially. Thus, we can write one singlet excited state in proper form, as in eq 12a; this has the excitation heavily localized in moiety A. The singlet wave function written in eq 12b has the excitation heavily localized in moiety D. Here we have selected two bonding

$$\Phi_1^A = (1/\sqrt{2})\{|\psi_1^a(1)\bar{\psi}_3^a(2)\psi_2^d(3)\bar{\psi}_2^d(4)|$$
$$- |\bar{\psi}_1^a(1)\psi_3^a(2)\psi_2^d(3)\bar{\psi}_2^d(4)|\} \quad (12a)$$

$$\Phi_2^D = (1/\sqrt{2})\{|\psi_1^a(1)\bar{\psi}_1^a(2)\psi_2^d(3)\bar{\psi}_4^d(4)|$$
$$- |\psi_1^a(1)\bar{\psi}_1^a(2)\bar{\psi}_2^d(3)\psi_4^d(4)|\} \quad (12b)$$

MO's, ψ_1^a and ψ_2^d, as well as two antibonding MO's, ψ_3^a and ψ_4^d. ψ_1^a and ψ_3^a are heavily localized in moiety A while ψ_2^d and ψ_4^d are heavily localized in moiety D. (The bar indicates assignment of a β spin and absence of a bar an α spin). The matrix interaction element for energetic interaction between these two excited singlets is given in eq 13. The β term is that discussed for rates of radia-

$$\beta = \int \Phi_1^A[e^2/r_{ij}]\Phi_2^D d\tau =$$
$$2\int \psi_3^a(i)\psi_2^d(j)[e^2/r_{ij}]\psi_1^a(i)\psi_4^d(j)d\tau$$
$$- \int \psi_3^a(i)\psi_2^d(j)[e^2/r_{ij}]\psi_4^d(i)\psi_1^a(j)$$
$$= 2G_{3214}^{MO} - G_{3241}^{MO} \quad (13)$$

tionless decay by Frosh and Robinson.[23] The transition probability and rate is proportional to β^2.

For simplicity in considering the value of β we use the ZDO approximation which allows simple evaluation of such MO repulsion integrals where LCAO MO coefficients are known.[24] The MO repulsion integral G_{3214}^{MO} is a sum of terms of the type $C_{3r}C_{1r}C_{2s}C_{4s}\gamma_{rs}$, where r and s refer to pairs of atomic or hybrid orbitals and γ_{rs} is the repulsion energy between two electrons, one in orbital r and one in orbital s. Similarly, G_{3241}^{MO} is a sum of terms of the type $C_{3r}C_{4r}C_{2s}C_{1s}\gamma_{rs}$. Thus if the bonding MO 1 and the antibonding MO 3 are totally localized in chromophore A and the bonding MO 2 and the antibonding MO 4 are totally localized in chromophore D, then the second term, G_{3241}^{MO}, in eq 13 vanishes since C_{3r} will have finite values only if r is an orbital on moiety A, but then C_{4r} is zero since MO 4 is nonzero only on moiety D. Other product terms vanish in the same way. The vanishing term is an exchange integral.

The first integral, G_{3214}^{MO}, in eq 13 is a coulombic term. It will not vanish with localization of excitation since C_{3r} and C_{1r} are both nonzero in one chromophore, as is true of similar products. Looking at this coulombic integral in eq 13 we see that it involves the product of two transition dipoles, $\psi_1^a(i)\psi_3^a(i)$ and $\psi_2^d(j)\psi_4^d(j)$, and the electron-repulsion operator e^2/r_{ij}. This corresponds to the normal interaction between transition dipoles of two excited states.

In the event that the chromophores are close and excitation of one leads to involvement of the other to some extent, and vice versa, then the exchange term G_{3241}^{MO} will not vanish and can dominate as noted by Dexter.[21] Thus, here C_{3r} and C_{4r}, although corresponding to MO's heavily localized on chromophores A and D, respectively, have some finite contribution whether r is on chromophore A or D, since both MO's 3 and 4 are delocalized slightly onto the bicyclooctane moiety[5] and, perhaps, even further (i.e., a through-bond interaction).

The falloff of the exchange integral should be a negative exponential of distance of separation of chromophores, as has been noted by Dexter[21] and mentioned above.

It seems reasonable that the nonconformance to an inverse sixth power relationship between rate of energy transfer and chromophore separation derives from operation of exchange effects in the [1]-rods. Thus at short distances of separation the second (i.e., exchange) integral in eq 13 may dominate and be larger than the first (i.e., the coulomb) integral. This dominance of electron exchange energy transfer at short distances has been noted by Birks.[25-27] Interestingly, one can envisage a situation

(20) (a) Förster, T. "Fluoreszenz Organischer Verbindungen"; Vandenhoek and Ruprecht: Gottingen, 1951; p 85. (b) The formula reported here contains an error as noted by Latt, Cheung, and Blout and independently by Ketskemety; see: (c) Latt, S. A.; Cheung, H. T.; Blout, E. R. *J. Am. Chem. Soc.* **1965**, *97*, 995–1003 (see footnote 15 of this paper); Ketskemety, I. *Z. Naturforsch.* **1962**, *17a*, 666; (d) In eq 11, ϕ_{fD} and τ_D are the quantum yield of fluorescence and the real lifetime, respectively, of the donor in the absence of the acceptor; n is the refractive index of the solvent; R is the distance from center to center between the chromophores, in centimeters; ν is the wave number; $F_D(\nu)$ is the spectral distribution of donor emission, normalized to unity; $\epsilon_A(\nu)$ is the molar extinction coefficient of the acceptor at ν; and K is an orientation factor equal to cos θ_{DA} − (3 cos θ_D)(cos θ_A), where θ_{DA} is the angle between the transition moments of the donor and acceptor, and θ_D and θ_A are the angles they subtend with respect to a vector drawn between the centers of the two chromophores.

(21) (a) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850. (b) In his derivation, Dexter employed a general, simplified description of the wavefunctions involved in the energy-transfer interaction. Use of a more rigorous description of the singlet states (vide infra) yields a factor of two in front of the coulomb term (see eq 13). The use of a more rigorous description of the triplet state results in the disappearance of the coulombic term.

(22) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978–1989.

(23) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187–1203; **1962**, *37*, 1962–1973.

(24) For example, see: Zimmerman, H. E. "Quantum Mechanics for Organic Chemists"; Academic Press: New York, 1975; pp 172–175.

(25) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; p 568.

Table VIII. Selected Calculated Natural Rates of Fluorescence

compd	k_f, s^{-1}	compd	k_f, s^{-1}
naphthalene	1.9×10^6	α-naphthyl-benzoyl-[2]-rod 25b	3.2×10^6
α-naphthyl-[2]-rod 26	3.9×10^6	α-naphthyl-acetyl-[1]-rod 9a	8.1×10^6
α-naphthyl-acetyl-[2]-rod 25a	4.0×10^6	α-methylnaphthalene	3.1×10^6
			$(3.10 \times 10^6)^a$

^{a} Independent value by Birks, ref 25, p 122.
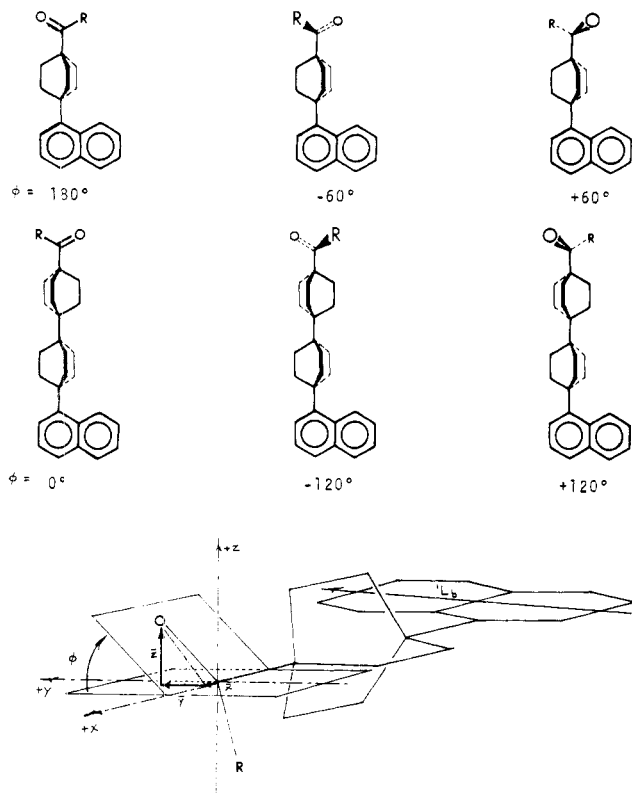
Figure 1. A (upper). Preferred conformations of α-naphthyl-keto-[1]- and -[2]-rods. B (lower). Definition of ϕ and derivation of the direction cosines of acceptor transition moment. Direction cosines in the x, y, and z directions are $\bar{x} = \cos 60°$, $\bar{y} = (\sin 60°)(\cos \phi)$, $\bar{z} = (\sin 60°)(\sin \phi)$.

wherein the positive dipole–dipole integral in eq 13 and the second (exchange) integral cancel at intermediate short distances. Unfortunately, the present study does not offer any [1.5]-rods for testing such an idea.[28]

There is an interesting conformational question which needs discussion. Thus, Figure 1 shows three conformations of the α-naphthyl-[1]- and -[2]-rod compounds. In the [1]-rods the three conformations have dihedral angles between C=O and naphthyl of 60°, -60°, and 180°. In the [2]-rods the molecular models indicate that a staggered conformation between the two bicyclooctyl units is preferred, and the dihedral angles between chromophores become 0°, 120°, and -120°. For each rod the conformations should be approximately equally weighted. The direction cosines for each C–O and L_b naphthyl transition dipole were determined and used to obtain the angles

(26) The electron-exchange mechanism is readily observed in triplet excited state transfer, as the coulomb term vanishes for reasons of spin. For other cases where is has been observed in singlet excited state transfer, see ref 27.

(27) (a) Rauh, Evans, and Leermakers, ref 7c. (b) Bunting, J. R.; Filipescu, N. *J. Chem. Soc. B* 1970, 1750–1755.

(28) (a) Filipescu et al. have observed a bichromophoric molecule in which transfer seems not to be taking place despite an interchromophoric distance of about 9 Å. This may be due to an unfavorable orientation factor and an exchange integral that vanishes for reasons of the molecular symmetry, as discussed by the author: Filipescu, N. *J. Am. Chem. Soc.* 1972, *94*, 4170–4175.
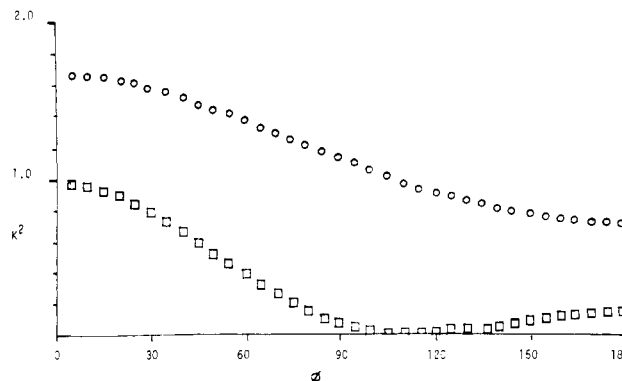
Figure 2. K^2 vs. ϕ, the dihedral angle between planes containing naphthyl and ketone chromophores: (O) β-naphthyl-acetyl-[1]-rod 11a; ($\square$) α-naphthyl-acetyl-[1]-rod 9a. ϕ is chosen as 0 where the naphthyl and carbonyl moieties are syn. The plot of K^2 vs. ϕ for ϕ ranging from 0 to -180° is identical. Values are plotted for the [1]-rods 9a and 11a. Those for [2]-rod 25a are virtually the same as those for 9.

between the C–O and L_b α-naphthyl transition dipoles (note Figure 1B). This was used to obtain the orientation factor K in the Förster relationship of eq 11. K^2 is plotted vs. dihedral angle in Figure 2. The sum of the K^2 factors for the three conformations of the [1]-rod is 0.915 and that for the [2]-rod is 0.978. Thus, conformational questions do not appreciably affect the differences in [1]-rod and [2]-rod transmission for α-naphthyl systems. Similar conclusions apply where L_a transitions are involved and also where β-naphthyl is involved.

Another point concerns the more rapid rate of energy transfer seen for the β-naphthyl systems compared with that for α-naphthyl. This difference is seen for all the compounds studied. We find a large K^2 for all conformations of the β-naphthyl systems compared with that for α-naphthyl. However, it is really K^2/R^6 which relates conformation to energy-transfer rate by dipole–dipole interaction. Nevertheless, it is found that even with inclusion of the $1/R^6$ factor, the β-naphthyl rods are predicted to be more rapid except with conformations below ca. 30° which are not present in the [1]-rod systems.

One further aspect derives from the use of the fluorescence quantum yields in Table I together with the rates of naphthyl decay (i.e., $k_1 + k_4$). Thus from $\phi_f = k_f/k_{d(tot)}$ one can solve for k_f for the compounds in Table I. Here $k_{d(tot)}$ for the naphthalene moiety is $k_1 + k_4$. The values of k_f obtained are given in Table VIII.

It can be seen that these are remarkably closely clustered around 3.6×10^6 s^{-1}, which then must represent the inherent (i.e., natural) rate of L_b fluorescence for an α-alkyl-substituted naphthalene. The high value obtained for the α-naphthyl-acetyl-[1]-rod 9a is probably an experimental artifact rather than a perturbation of the naphthyl transition by the acetyl moiety, since the ultraviolet absorption for this compound was not distinguishable from those of the remaining compounds of the series in the naphthyl region. In principle, the $k_{f(L_b)}$ values could be derived from the experimental integrated extinction coefficient; however, the observed (ca.) 280-nm naphthyl

absorption band seems likely to contain both L_a and L_b overlapping components.

Two further compounds of interest are the di-β-naphthyl-[1]-rod **15** and the *cis*-propenyl-α-naphthyl-[1]-rod **12** whose rates of decay are given in Table III. It is seen that these rates and lifetimes (64.1 ns for **15** and 64.5 ns for **12**) are close to those for a simple naphthalenic model (e.g., 64.2 ns for β-naphthyl-[1]-rod **14** and 65.0 ns for α-naphthyl-[1]-rod **13**). Additionally it is found that irradiation of the *cis*-propenyl molecule in the naphthyl region led to no significant stereoisomerization. Thus, appreciable endothermic energy transfer to the *cis*-propenyl moiety from naphthyl does not occur nor does any type of nonvertical transfer to a twisted propenyl group result.

In the case of the di-β-naphthyl-[1]-rod, energy transfer between the degenerate moieties may occur. However, this transfer must be efficient within experimental error and is not an experimental observable. This becomes apparent from eq 2–6 which show that the rate of disappearance of A is independent of k_1 and k_2 for such a degenerate system with decay of the form $[A] = [A_0]e^{-k_4 t}$ unless there is some new mode of decay introduced in the energy-transfer process. New decay processes would appear as an enhanced k_3 (= k_4) value which is not the case.

Conclusion. The rod chemistry provides a test of mechanisms of energy-transfer dependence on chromophore separation without any molecular flexibility of the type characteristic of many bichromophoric systems. For short distances it is clear that simple dipole–dipole coupling is aided by excitation transmission through the molecule.

Experimental Section

Solvents. Diethyl ether and tetrahydrofuran were each distilled first from lithium aluminum hydride and then from sodium wire immediately before use in organometallic reactions. Pentane and heptane were each purified by treatment with concentrated sulfuric acid until the washings were colorless and then with 10% sulfuric acid saturated with potassium permanganate until the washings remained purple. They were then washed with bicarbonate, dried, and distilled (pentane from lithium aluminum hydride, heptane from calcium hydride). Benzene was treated similarly with concentrated sulfuric acid, then washed with bicarbonate and brine, and dried over magnesium sulfate, and 8% of its bulk was removed by distillation. The rest was dried further over calcium hydride and distilled slowly through a column of metal helices. Ethyl acetate was washed with sodium carbonate and saturated aqueous calcium chloride, dried over potassium carbonate, refluxed, and distilled from phosphorus pentoxide. Pyridine was distilled from potassium hydroxide and stored over molecular sieves.

For UV and emission spectra, and for the emission rate studies, methylcyclohexane and isopentane were prepared in the previously described manner.[4]

Silica gel chromatography was carried out with Grace grade 62 60–200-mesh slurry packed in hexane and 250-mL fractions were collected unless otherwise noted.

Spectra. UV spectra were taken on a Cary 118 or a Cary 15; solvents were 95% ethanol (EtOH) or a 4:1 (v/v) mixture of methylcyclohexane and isopentane (MCIP). IR spectra were taken on a Beckman Acculab 7 or IR4230. NMR spectra were taken on a JEOL JNM-MH-100 (MH) or on a WH-270 (WH)[29] instrument. Mass spectra were taken on a AEK MS902. Analyses were performed by Galbraith, Inc.

Perchlorocyclopentene. This compound was prepared by a modification of the procedure of Newcomer and McBee.[30]

Vacuum distillation afforded perchlorocyclopentene, bp 86–95 °C (0.2 mm), mp 35–37 °C.

Perchlorocyclopent-2-enone. Employment of a modification of the procedure of Newcomer and McBee[30,31] afforded, after distillation, perchlorocyclopent-2-enone as a yellow oil, bp 50–54 °C (0.2 mm) [lit.[32] bp 111–113 °C (17 mm)].

Perchloropentadienoic Acid. This compound was prepared by the procedure of Roedig and Märkel.[32] Recrystallization from hexane gave pure perchloropentadienoic acid, mp 124–125 °C (lit.[32] mp 123 °C).

Perchlorocoumalin. Preparation was by the procedure of Roedig and Märkel[32] with the exception that purification was by distillation [bp 80–82 °C (0.2 mm)] and recrystallization from hexane, giving pure perchlorocoumalin, mp 79.5–80.5 °C (lit.[32] mp 81.5–83.5 °C).

1,2,3,4-Tetrachlorobicyclo[2.2.2]oct-2-ene. This material was prepared by the procedure of Kauer,[9] with some modification. Recrystallization from hexane afforded 1,2,3,4-tetrachlorobicyclo[2.2.2]oct-2-ene as a colorless solid, mp 91.5–93 °C.

1,4-Dichlorobicyclo[2.2.2]octane. This material was prepared by a slight modification of the procedure of Kauer.[9] Recrystallization from hexane give pure 1,4-dichlorobicyclo[2.2.2]octane, mp 230–231 °C (lit.[9] mp 233.5–234.5 °C).

1,4-Bis(β-naphthyl)bicyclo[2.2.2]octane. To a solution of 1.80 g (10.1 mmol) of 1,4-dichlorobicyclo[2.2.2]octane and 6.40 g (50.0 mmol) of naphthalene in refluxing carbon disulfide was added 0.136 g (1.02 mmol) of aluminum chloride in small portions during 2 h. The dark mixture was refluxed for 48 h and then water was added. The aqueous phase was ether and chloroform extracted. The combined extracts were washed with water, 5% sodium bicarbonate solution, and water and dried over MgSO$_4$. The solvent was removed in vacuo to yield a yellow solid which was chromatographed on a 83 × 2.5 cm silica gel column. Elution was with 1.75 L of hexane and 2.75 L of 1% ether in hexane: fractions 3–6, 6.71 g of a mixture of 1,4-dichlorobicyclo[2.2.2]octane and naphthalene; 13–18, 1.12 g (30.5%) of 1,4-bis(β-naphthyl)-bicyclo[2.2.2]octane (pure by NMR), mp 239–241 °C, after recrystallization from hexane.

The spectral data were as follows: IR (KBr) 3.26, 3.39, 3.42, 3.48, 6.13, 6.27, 6.65, 6.87, 7.40, 7.83, 8.05, 8.37, 8.89, 9.80, 10.42, 10.66, 11.23, 11.64, 11.69, 12.27, 13.40 μm; NMR (CDCl$_3$) τ 2.08–2.62 (m, 14 H, arom), 7.88 (s, 12 H, CH$_2$); mass spectrum, m/e (%) 363 (25), 362 (71), 183 (18), 182 (100), 181 (20), 180 (63), 179 (25), 178 (13), 167 (23), 166 (13), 165 (29), 154 (15), 153 (14), 152 (15), 141 (23), 129 (13), 128 (45), 127 (13), 115 (19); high-resolution mass spectrum, calcd for C$_{28}$H$_{26}$ m/e 362.2035, found m/e 362.2040; UV λ_{max} (methylcyclohexane–isopentane, 4:1) 255 nm (sh, ϵ 7417), 263 (9333), 272 (9679), 283 (sh, 6304), 302 (803), 316 (593).

Anal. Calcd for C$_{28}$H$_{26}$: C, 92.77; H, 7.23. Found: C, 92.82; H, 7.14.

1,4-Diiodobicyclo[2.2.2]octane. This compound was prepared by a modification of the procedure of McKinley, Pincock, and Scott.[33] Ethyl iodide was employed as the halogen source, and a 90% yield of the diiodide was typically obtained after recrystallization from hexane, mp 239–240.5 °C (lit.[33] mp 240 °C).

4-Iodo-1-bicyclo[2.2.2]octyl Acetate. A solution of 100 mg (0.276 mmol) of 1,4-diiodobicyclo[2.2.2]octane and 46.2 mg (0.277 mmol) of silver acetate in 20.0 mL of acetic acid was refluxed for 45 min, cooled, and poured onto ice. Ether was added, the layers were separated, and the water was extracted with ether. The combined organics were washed with saturated sodium bicarbonate solution and then water, dried with MgSO$_4$, and concentrated to yield 77.9 mg of white solid. This was chromatographed on a 1 × 45 cm silica gel column, with monitoring by UV absorption. The first peak was eluted with hexane and contained 16.2 mg of starting material. The second peak, eluted with 2% ether in hexane, contained 53.5 mg (76.4% based on consumed starting material) of 4-iodo-1-bicyclo[2.2.2]octyl acetate, mp

(29) (a) We thank Mr. Richard Swafford for obtaining the WH-270 spectra. (b) MH-100 spectra were used to support integration analysis of the Fourier-transform WH spectra.

(30) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* 1949, *71*, 946.

(31) An improved procedure stemming from the literature preparation was given to us by Dr. S. Gelfand of Hooker Laboratories (private communication).

(32) Roedig, A.; Märkel, G. *Justus Liebigs Ann. Chem.* 1960, *636*, 1.

(33) McKinley, J. W.; Pincock, R. E.; Scott, W. B. *J. Am. Chem. Soc.* 1973, *95*, 2030.

127.6–128.4 °C. Recrystallization from methanol and then from heptane gave an analytical sample: mp 128.6–129.2 °C; UV (EtOH) λ_{max} 261 nm (ϵ 810); IR (KBr) 3.38, 3.42, 3.48, 5.73, 7.29, 7.43, 8.02, 9.58, 10.07, 12.41, 15.06 μm; NMR (CDCl₃, WH) τ 7.41–7.47 (m, 6 H, CH₂), 7.86–7.92 (m, 6 H, CH₂), 8.06 (s, 3 H, CH₃COO); mass spectrum (70 eV), m/e (relative abundance) 167 (20.7), 125 (15.7), 107 (32.9), 79 (17.2), 67 (10.7), 43 (100), 41 (16.9), 40 (12.1), 39 (18.1); high-resolution mass spectrum, calcd for $C_{10}H_{15}O_2$ (loss of I) m/e 167.1072, found m/e 167.1064.

Anal. Calcd for $C_{10}H_{15}IO_2$: C, 40.84; H, 5.14. Found: C, 40.85; H, 5.29.

4-Iodo-1-bicyclo[2.2.2]octanol. A solution of 117 g (0.324 mol) of 1,4-diiodobicyclo[2.2.2]octane in 1.6 L of hot glacial acetic acid was treated slowly at reflux with increments of a hot suspension of 54.0 g (0.323 mol) of silver acetate in 900 mL of acetic acid. After the addition was complete, the reaction mixture was stirred at reflux for 1 h, at which point all silver ion had been precipitated. The bulk of the solvent was removed by distillation. Water was added and the suspension was filtered. The precipitate was washed copiously with ether. The solution was ether extracted, the extracts were washed with a saturated solution of sodium bicarbonate until neutral and then dried, and the solvent was concentrated. The crude product was dissolved in a solution of 90.6 g (1.60 mol) of potassium hydroxide in 925 mL of 95% ethanol and refluxed for 2 h until NMR analysis of an aliquot showed complete hydrolysis. The solution was then poured into water, acidified, and ether extracted, and the extracts were dried and concentrated. The resultant solid was chromatographed on a 4 × 60 cm column slurry packed with silica gel in hexane, with UV monitoring. The first band was eluted with hexane and yielded a small quantity of the starting diiodide. The second band, eluted with 50% ether in hexane, contained 57.2 g (70% from the diiodide) of 4-iodo-1-bicyclo[2.2.2]octanol, mp 161 °C. An analytical sample was prepared by recrystallization from ethanol and then from heptane: mp 162–162.2 °C; UV (EtOH) λ_{max} 260.5 nm (ϵ 825); IR (KBr) 3.05, 3.39, 3.43, 3.50, 7.45, 9.21, 12.38 μm; NMR (CDCl₃, WH) τ 7.428–7.487 (m, 6 H, CH₂), 8.214–8.274 (m, 6 H, CH₂), 8.474 (br s, 1 H, OH); mass spectrum (70 eV), m/e (relative abundance) 252 (3.8), 125 (100), 83 (10.4), 81 (14.5), 79 (20.6), 67 (19.7), 55 (61.5), 53 (10.2), 43 (49.2), 41 (26.9), 40 (14.2), 39 (25.9); high-resolution mass spectrum, calcd for $C_8H_{13}IO$ m/e 252.0011, found m/e 252.0001.

Anal. Calcd for $C_8H_{13}IO$: C, 38.12; H, 5.20. Found: C, 38.20; H, 5.40.

4-Iodo-1-bicyclo[2.2.2]octyl Methyl Ether. A solution of 67.8 g (0.269 mol) of 4-iodo-1-bicyclo[2.2.2]octanol and 47 mL of dry methyl iodide in 250 mL of dry dimethoxyethane was treated at room temperature with sodium hydride (18.2 g of a dispersion in mineral oil, 0.427 mol) from which the mineral oil had been washed with hexane. The reaction was monitored by NMR, and upon its completion (ca. 2 h), the excess sodium hydride was carefully quenched by the dropwise addition of water. The solution was then filtered and concentrated, the residue was taken up in water and ether, the water was extracted with ether, and the combined ether layers were washed with diluted hydrochloric acid and then water washed, dried, and concentrated to give a solid, which was recrystallized from hexane to yield 68.8 g (96.1%) of iodo methyl ether, mp 77.4–79.4 °C. An analytical sample, prepared by recrystallization from methanol, had a mp 79.6–79.8 °C; UV (EtOH) λ_{max} 260.3 nm (ϵ 627); IR (KBr) 3.38, 3.42, 3.49, 9.08, 12.41 μm; NMR (CDCl₃) τ 6.876 (s, 3 H, CH₃O), 7.43–7.49 (m, 6 H, CH₂), 8.20–8.26 (m, 6 H, CH₂); mass spectrum (70 eV), m/e (relative abundance) 266 (2.3), 139 (100), 107 (13.0), 91 (10.1), 81 (10.5), 79 (40.1), 67 (17.8), 45 (13.1), 41 (30.6), 39 (25.8); high-resolution mass spectrum, calcd for $C_9H_{15}IO$ m/e 266.0168, found m/e 266.0174.

Anal. Calcd for $C_9H_{15}IO$: C, 40.62; H, 5.68. Found: C, 40.60; H, 5.85.

Alternatively, the following more direct but lower overall yield preparation may be used. A solution of 11.8 g (60.4 mmol) of anhydrous silver fluoroborate in 250 mL of anhydrous methanol was added during 2.25 h to a rapidly stirred suspension of 19.9 g (54.9 mmol) of 1,4-diiodobicyclo[2.2.2]octane in 1 L of refluxing methanol. A yellow precipitate formed and the mixture was stirred for 3 h. After cooling, the mixture was neutralized with solid sodium bicarbonate, filtered, and concentrated in vacuo. Water

was added and the aqueous phase was chloroform extracted. The combined extracts were water washed, dried, and concentrated in vacuo, leaving 17 g of an oily solid which was chromatographed on a 63 × 4 cm silica gel column. Elution was with 4.5 L of hexane, 0.25 L of 1%, 0.5 L of 4%, 2.75 L of 8%, 0.25 L of 25%, and 0.25 L of 50% ether in hexane, and 1.5 L of ether: fractions 5–18, 6.19 g of 1,4-diiodobicyclo[2.2.2]octane; 28–34, 5.35 g of 1-iodo-4-methoxybicyclo[2.2.2]octane; 39–43, 3.03 g of 1,4-dimethoxybicyclo[2.2.2]octane.[34] The 1-iodo-4-methoxybicyclo[2.2.2]octane was sublimed at 50 °C (0.05 mm), giving 5.09 g (51%) of colorless crystals, mp 74–78 °C. An analytical sample was obtained by recrystallization from ether and then hexane at –78 °C, mp 79–79.5 °C. The 1,4-dimethoxybicyclo[2.2.2]octane was distilled under reduced pressure to give 2.56 g (40%), bp 41 °C (0.05 mm). 4-Iodo-1-bicyclo[2.2.2]octyl methyl ether prepared in this manner was identical with material prepared by the reactions described above.

1-Iodo-4-(α-naphthyl)bicyclo[2.2.2]octane and 1-Iodo-4-(β-naphthyl)bicyclo[2.2.2]octane.[35] A mixture of 3.99 g (15.0 mmol) of 1-iodo-4-methoxybicyclo[2.2.2]octane and 7.68 g (60.0 mmol) of naphthalene in 100 mL of hexane (washed with concentrated sulfuric acid and saturated aqueous sodium bicarbonate, dried, and distilled from calcium hydride) was cooled in an ice bath. Boron trifluoride was passed over that mixture for 0.5 h to saturation, causing the formation of a heavy precipitate. Sulfuric acid[36] (18 μL) was added and the mixture was heated at 55 °C for 12 h. After the mixture cooled, water was added and the aqueous phase was neutralized with solid sodium bicarbonate and ether extracted. The combined organic materials were water washed, dried, and concentrated in vacuo to yield 15.1 g of a solid. The products were separated on a 64 × 4 cm silica gel column. Elution was with 4.75 L of hexane: fractions 4–8, 6.90 g of naphthalene and 1,4-diiodobicyclo[2.2.2]octane; 9–20, 3.04 g (56%) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane and 1-iodo-4-(β-naphthyl)bicyclo[2.2.2]octane (57% α and 43% β by NMR).

The α and β isomers were separated by chromatography of 0.28 g of a mixture on a 58 × 3 cm silica gel column with 0.75 L of 0.5% ether in hexane: fraction 5, 0.050 g of the α isomer; 6–7, 0.21 g of a mixture of the isomers; 8, 0.020 g of the β isomer. The pure samples were used as seeds to fractionally crystallize the 3.04-g sample obtained above. Crystallization from hexane using a crystal of the β isomer gave a solid highly enriched in that isomer (by NMR). Concentration of the filtrate and crystallization from ether using a crystal of the α isomer gave a solid highly enriched in that isomer (by NMR). After three of these cycles, the samples enriched in the α isomer were combined and recrystallized from ether with a seed of pure material. This afforded 0.64 g (11.9%) of pure 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane, mp 164–165.5 °C, as colorless prisms. Similarly, the samples enriched in the β isomer were combined and recrystallized from hexane with a seed of pure material. This gave 0.69 g (12.7%) of pure 1-iodo-4-(β-naphthyl)bicyclo[2.2.2]octane, mp 168.5–169 °C, as long colorless needles.

The spectral data for the α isomer were the following: IR (KBr) 3.21, 3.22, 3.33, 3.34, 3.38, 3.39, 3.41, 3.48, 6.26, 6.63, 6.88, 6.94, 7.15, 7.42, 7.61, 7.80, 8.06, 8.55, 8.74, 9.13, 9.30, 9.91, 10.09, 10.42, 10.53, 11.35, 12.17, 12.36, 12.76, 13.47, and 14.73 μm; NMR (CDCl₃) τ 1.48–1.72 (m, 1 H, arom), 2.00–2.80 (m, 6 H, arom), 7.08–7.48 (m, 6 H, CH₂), 7.48–7.88 (m, 6 H, methylene); mass spectrum (70 eV), m/e (relative abundance) 362 (18), 236 (13), 235 (60), 193 (10), 167 (15), 165 (25), 142 (13), 141 (100), 81 (10); high-resolution mass spectrum, calcd for $C_{18}H_{19}I$ m/e 362.0533, found m/e 362.0533.

Anal. Calcd for $C_{18}H_{19}I$: C, 59.68; H, 5.29. Found: C, 59.66; H, 5.36.

The spectral data for the β isomer were the following: IR (KBr) 3.27, 3.29, 3.38, 3.39, 3.42, 3.48, 6.26, 6.65, 6.70, 6.87, 6.90, 7.41, 8.00, 8.85, 9.80, 10.02, 10.12, 10.19, 10.30, 10.39, 10.60, 11.17, 11.22,

(34) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6829.

(35) This selective Friedel–Crafts alkylation was based on the greater reactivity of boron trifluoride toward ethers and alcohols than toward halides. For example, see: Boakman, G. B.; Hellman, H. M. *J. Am. Chem. Soc.* **1948**, *70*, 1772.

(36) Burnell, R. L., Jr.; Elkin, L. M. *J. Am. Chem. Soc.* **1951**, *73*, 502.

11.57, 11.63, 11.92, 12.09, 12.33, 12.39, 13.17, 14.76, 15.11, 15.84 μm; NMR (CDCl$_3$) τ 2.04–2.68 (m, 7 H, arom), 7.20–7.56 (m, 6 H, CH$_2$), 7.76–8.12 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 362 (14), 236 (13), 235 (60), 179 (20), 165 (10), 142 (13), 141 (100); high-resolution mass spectrum, calcd for C$_{18}$H$_{19}$I m/e 362.0533, found m/e 362.0536.

Anal. Calcd for C$_{18}$H$_{19}$I: C, 59.68; H, 5.29. Found: C, 59.59; H, 5.26.

The assignment of isomers was most clearly derived from NMR. The α isomer exhibits a deshielding of the peri hydrogen relative to the remaining aromatic absorptions which is characteristic of α-substituted naphthalenes.[37,38] This effect is absent in the β isomer. In addition, the bicyclo[2.2.2]octyl hydrogens near naphthalene in the α isomer are deshielded with respect to the corresponding hydrogens in the β isomer. This is consistent with these hydrogens being much closer to naphthalene in the α isomer and thus being affected to a greater extent by the aromatic ring current.

1-(α-Naphthyl)bicyclo[2.2.2]octane. To a stirred suspension of 0.043 g (0.12 mmol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane in 1.5 mL each of ether and pentane at −78 °C was added 0.15 mL (0.25 mmol) of 1.68 M *tert*-butyllithium in pentane (Foote Mineral Corp.). The resulting yellow mixture was stirred for 45 min and then 1 mL of methanol was added which discharged the color. After the mixture warmed to room temperature, saturated ammonium chloride was added, the aqueous layer was ether extracted, and the combined organic materials were washed with saturated sodium bicarbonate and water and then dried. Concentration in vacuo gave 0.048 g of a solid which was chromatographed on a 52 × 1 cm silica gel column. Elution in 200-mL fractions was with 400 mL of hexane: fraction 1, 0.010 g (78%) of pure (by NMR) 1-(α-naphthyl)bicyclo[2.2.2]octane; 2, 0.024 g (0.066 mmol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane. Recrystallization from methylcyclohexane afforded colorless solid, mp 113–114.5 °C.

The spectral data were the following: UV λ_{max} (MCIP) 260 nm (sh, ϵ 4263), 269 (6935), 279 (8571), 287 (5703), 292 (5806), 312 (438); IR (KBr) 3.23, 3.28, 3.36, 3.41, 3.49, 6.27, 6.67, 6.88, 7.17, 7.42, 7.53, 9.80, 10.35, 12.50, 12.85 μm; NMR (CDCl$_3$) τ 1.40–1.64 (m, 1 H, arom), 2.00–2.68 (m, 6 H, arom), 7.64–8.00 (m, 6 H, methylene), 8.00–8.40 (m, 7 H, CH$_2$ and CH); mass spectrum (70 eV), m/e (relative abundance) 237 (22), 236 (100), 207 (15), 180 (15), 179 (27), 167 (27), 166 (24), 165 (58), 154 (15), 153 (16), 152 (20), 141 (18), 219 (15), 98 (69), 83 (87), 70 (25), 69 (27), 56 (36), 55 (85); high-resolution mass spectrum, calcd for C$_{18}$H$_{20}$ m/e 236.1565, found m/e 236.1570.

Anal. Calcd for C$_{18}$H$_{20}$: C, 91.47; H, 8.53. Found: C, 91.26; H, 8.35.

1-(β-Naphthyl)bicyclo[2.2.2]octane. To a stirred suspension of 0.225 g (0.622 mmol) of 1-iodo-4-(β-naphthyl)bicyclo[2.2.2]-octane in 6.0 mL each of ether and pentane at −78 °C was added 0.82 mL (1.4 mmol) of 1.68 M *tert*-butyllithium in pentane (Foote Mineral Corp.). The resulting yellow mixture was stirred for 45 min and then 2 mL of methanol was added which immediately discharged the color. After the mixture warmed to room temperature, saturated aqueous ammonium chloride was added and the mixture was ether extracted. The combined extracts were washed with saturated aqueous sodium bicarbonate and water and dried. Removal of solvent in vacuo afforded 0.224 g of a solid which was chromatographed on a 27 × 1 cm silica gel column. Elution with 100 mL of hexane afforded 0.141 g (96%) of pure (by NMR) 1-(β-naphthyl)bicyclo[2.2.2]octane, mp 120.5–122 °C, after recrystallization from hexane.

The spectral data were the following: UV λ_{max} (MCIP) 255 nm (sh, ϵ 2838), 263 (3996), 266 (3978), 273 (4345), 283 (sh, 2926), 302 (349), 316 (253); IR (KBr) 3.26, 3.39, 3.42, 3.48, 6.13, 6.26, 6.65, 6.87, 6.89, 6.97, 7.21, 7.31, 7.40, 7.51, 7.82, 8.01, 8.31, 8.35, 8.84, 9.77, 10.23, 10.31, 10.55, 10.89, 11.23, 11.65, 12.02, 12.18, 12.88,

13.17, 13.34, 15.10 μm; NMR (CDCl$_3$) τ 2.12–2.80 (m, 7 H, arom), 7.96–8.48 (sym m, 13 H CH$_2$ and CH); mass spectrum (70 eV), m/e (relative abundance) 237 (20), 236 (100), 207 (16), 180 (46), 179 (23), 178 (11), 165 (20), 154 (17), 152 (11), 141 (15), 128 (11), 57 (14), 56 (29); high-resolution mass spectrum, calcd for C$_{18}$H$_{20}$ m/e 236.1565, found m/e 236.1568.

Anal. Calcd for C$_{18}$H$_{20}$: C, 91.47; H, 8.53. Found: C, 91.50; H, 8.48.

1-(1-Hydroxyethyl)-4-(α-naphthyl)bicyclo[2.2.2]octane. To a stirred suspension of 0.202 g (0.558 mmol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane in 6.0 mL each of ether and pentane at −78 °C was added 0.70 mL (1.2 mmol) of 1.68 M *tert*-butyllithium in pentane (Foote Mineral Corp.). The resulting yellow mixture was stirred for 45 min and then 0.30 mL (5.3 mmol) of acetaldehyde (freshly distilled from calcium hydride) was added which discharged the color. The cooling bath was removed and after 4 h of further stirring the mixture was quenched with saturated ammonium chloride. The aqueous phase was ether extracted, and the combined organic materials were water washed and dried. Removal of solvent in vacuo gave 0.242 g of an oil which was chromatographed on a 52 × 1 cm Florisil column (Fisher, 60–100 mesh) slurry packed in hexane. Elution was with 250-mL fractions successively of hexane, then 0.5%, 1%, 2%, and 5% ether in hexane, and 750 mL of 10% ether in hexane: fraction 1, 0.020 g of 1-(α-naphthyl)bicyclo[2.2.2]octane; 7, 0.109 g (70%) of 1-(1-hydroxyethyl)-4-(α-naphthyl)bicyclo[2.2.2]octane, pure (by NMR), as an oil which solidified in vacuo. This material was used synthetically without further purification.

The spectral data were the following: IR (KBr) 2.73–3.16, 3.22, 3.27, 3.37, 3.41, 3.48, 6.25, 6.33, 6.62, 6.84, 6.87, 7.15, 7.25, 7.46, 7.57–8.20, 8.51, 8.77, 9.01–9.62, 9.76, 10.01, 10.36, 10.86, 11.35, 11.61, 11.76, 12.44, 12.82, 13.51, 15.30 μm; NMR (CDCl$_3$) τ 1.40–1.68 (m, 1 H, arom), 2.04–2.80 (m, 6 H, arom), 6.52 (q, 1 H, J = 7 Hz, CH), 7.62–8.04 (m, 6 H, CH$_2$), 8.20–8.64 (m, 7 H, methylene and hydroxy), 8.88 (d, 3 H, J = 7 Hz, CH$_3$); mass spectrum (70 eV), m/e (relative abundance) 281 (22), 280 (100), 235 (11), 234 (14), 233 (46), 205 (24), 179 (23), 178 (16), 167 (16), 166 (15), 165 (41), 154 (13), 153 (13), 152 (14), 142 (11), 141 (59), 128 (11), 109 (10), 74 (15), 59 (19), 45 (38), 44 (15), 43 (44), 41 (14), 40 (17); high-resolution mass spectrum, calcd for C$_{20}$H$_{24}$O m/e 280.1827, found m/e 280.1826.

1-Acetyl-4-(α-naphthyl)bicyclo[2.2.2]octane. Chromium trioxide, 0.25 g (2.5 mmol), was added in portions to a solution of 0.40 g (5.1 mmol) of pyridine in 7.0 mL of dichloromethane and the mixture was stirred at room temperature for 20 min.[39] To the mixture was added 0.101 g (0.361 mmol) of 1-(1-hydroxyethyl)-4-(α-naphthyl)bicyclo[2.2.2]octane in 2.0 mL of dichloromethane, causing immediate formation of a black precipitate. After 15 min the dichloromethane solution was removed from the residue and the latter was ether washed. The combined organic materials were thoroughly washed with 5% sodium hydroxide and hydrochloric acid followed by saturated aqueous solutions of sodium bicarbonate and sodium chloride. After the mixture was dried, the solvent was removed in vacuo, giving 0.104 g of a solid which was chromatographed on a 50 × 1 cm silica gel column. Elution was with 250 mL of hexane and 250 mL of 1% and 750 mL of 2% ether in hexane: fractions 4–5 gave 0.094 g (94%) of solid 1-acetyl-4-(α-naphthyl)bicyclo[2.2.2]octane pure (by NMR), mp 80.5–81 °C, after recrystallization from methylcyclohexane.

The spectral data were the following: UV λ_{max} (MCIP) 260 nm (sh, ϵ 4040), 269 (6506), 279 (8080), 287 (5331), 291 (5477), 311 (399); IR (KBr) 3.22, 3.27, 3.37, 3.42, 3.48, 5.90, 6.26, 6.66, 6.89, 7.18, 7.35, 7.42, 7.47, 7.80, 8.10, 8.20, 8.61, 9.30, 9.62, 9.76, 10.07, 10.31, 10.53, 10.75, 11.55, 11.89, 12.49, 12.82, 15.50 μm; NMR (CDCl$_3$) τ 1.48–1.72 (m, 1 H, arom), 2.04–2.72 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 279 (25), 278 (100), 250 (19), 249 (47), 235 (25), 193 (13), 192 (20), 181 (25), 180 (32), 179 (15), 167 (27), 166 (27), 165 (56), 154 (15), 153 (18), 152 (24), 142 (10), 141 (70); high-resolution mass spectrum, calcd for C$_{20}$H$_{22}$O m/e 278.167, found m/e 278.1671.

Anal. Calcd for C$_{20}$H$_{22}$O: C, 86.29; H, 7.97. Found: C, 86.40; H, 7.90.

(37) (a) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 206. (b) Van Bekkum, H.; Nieuwstad, H. J.; Van Barneveld, J.; Klapwijk, P.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1028.

(38) The NMR spectra for the α and β isomers are in excellent agreement with those of 1- and 2-*tert*-butylnaphthalene; see ref 37b.

(39) Ratcliffe, R.; Rodehurst, R. *J. Org. Chem.* **1970**, *35*, 4000.

1-Benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane. This material was available from the previous study of Zimmerman and McKelvey.[5]

1-(1-Hydroxyethyl)-4-(β-naphthyl)bicyclo[2.2.2]octane. To a stirred suspension of 0.257 g (0.708 mmol) of 1-iodo-4-(β-naphthyl)bicyclo[2.2.2]octane in 8.5 mL each of ether and pentane at −78 °C was added 1.6 mL (1.5 mmol) of 0.95 M *tert*-butyllithium in pentane. The resulting pale yellow mixture was stirred for 45 min and then 0.40 mL (7.1 mmol) of freshly distilled acetaldehyde was added, which discharged the color. The cooling bath was removed, and the mixture was stirred for 4.5 h and then quenched with saturated ammonium chloride solution. The aqueous layer was ether extracted, and the combined organic materials were water washed, dried, and concentrated in vacuo, affording 0.30 g of a yellow oil, which was chromatographed on a 85 × 2.7 cm silica gel column. Elution was with 1 L of hexane, 250-mL portions of 1%, 2%, 4%, 8%, and 16%, 500-mL portions of 30% and 60% ether in hexane, and 500 mL of ether: fractions 3–5, 0.031 g of 1-(β-naphthyl)bicyclo[2.2.2]octane; 13–14, 0.125 g (63.6%) of solid 1-(1-hydroxyethyl)-4-(β-naphthyl)bicyclo[2.2.2]octane, pure (by NMR); this afforded 0.080 g (42%) of product, mp 136–137 °C, after recrystallization from ether–hexane.

The spectral data were the following: IR (KBr) 2.77–3.22, 3.27, 3.37, 3.41, 3.43, 3.49, 6.14, 6.27, 6.66, 6.89, 6.98, 7.23, 7.30, 7.36, 7.66, 7.86, 8.05, 8.24, 8.55, 8.92, 9.30, 9.81, 10.20, 10.42, 10.63, 11.29, 12.32, 12.98, 13.51, 15.28, 16.12 μm; NMR (CDCl$_3$) τ 2.12–2.80 (m, 7 H, arom), 6.52 (q, 1 H, J = 7 Hz, CH), 7.80–8.70 (m, 13 H, CH$_2$ and OH), 8.89 (d, 3 H, J = 7 Hz, CH$_3$).

Anal. Calcd for C$_{20}$H$_{24}$O: C, 85.67; H, 8.63. Found: C, 85.52; H, 8.54.

1-Acetyl-4-(β-naphthyl)bicyclo[2.2.2]octane. To a solution of 0.40 mL (5.1 mmol) of pyridine in 7.0 mL of dichloromethane was added chromium trioxide (0.25 g, 2.5 mmol) in portions, and the mixture was stirred at room temperature for 15 min. Addition of 0.098 g (0.35 mmol) of 1-(1-hydroxyethyl)-4-(β-naphthyl)bicyclo[2.2.2]octane in 3.0 mL of dichloromethane caused the immediate formation of a black precipitate. After 20 min the dichloromethane was removed and the residue was ether washed. The combined organic materials were thoroughly washed with 5% aqueous solutions of sodium hydroxide, hydrochloric acid, and sodium bicarbonate, followed by a saturated aqueous solution of sodium chloride. After the solution was dried, removal of the solvent in vacuo afforded 0.098 g of a solid which was chromatographed on a 40 × 1 cm silica gel column. Elution was with 200-mL portions of hexane and 1% ether in hexane and 400-mL portions of 2% and 4% ether in hexane: fractions 4–5, 0.079 g (0.28 mmol, 80%) of solid 1-acetyl-4-(β-naphthyl)bicyclo[2.2.2]-octane, pure (by NMR), which afforded 0.056 g (60%) of analytically pure product, mp 134.5–135 °C, after recrystallization from methylcyclohexane.

The spectral data were as follows: UV λ_{max} (MCIP) 255 nm (sh, ϵ 3220), 265 (4420), 274 (4730), 285 (sh, 3220), 303 (390), 317 (260); IR (KBr) 3.27, 3.37, 3.41, 3.49, 5.91, 6.25, 6.65, 6.86, 7.00, 7.36, 7.82, 8.16, 8.41, 8.58, 8.87, 9.50, 9.70, 10.33, 10.66, 10.95, 11.11, 11.24, 11.59, 12.20, 13.18, 15.10 μm; NMR (CDCl$_3$) τ 2.12–2.80 (m, 7 H, arom), 7.87 (s, 3 H, CH$_3$), 7.90–8.29 (m, 12 H, CH$_2$).

Anal. Calcd for C$_{20}$H$_{22}$O: C, 86.29; H, 7.97. Found: C, 86.32; H, 8.02.

Cyclohexyl[4-(α-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol. To a stirred suspension of 0.235 g (0.649 mmol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane in 8.0 mL each of ether and pentane at −78 °C was added 1.40 mL (1.33 mmol) of 0.95 N *tert*-butyllithium in pentane. The resulting yellow mixture was stirred for 40 min, and then 0.75 mL (6.4 mmol) of cyclohexanecarboxaldehyde was added, and the color immediately discharged. After warming to room temperature and being stirred for 3 h, the reaction mixture was quenched with saturated aqueous ammonium chloride. The layer was ether extracted, and the combined organic materials were water washed, dried, and concentrated in vacuo to afford 0.820 g of a colorless oil. This material was chromatographed on an 88 × 2.7 cm silica gel column. Elution was with 250-mL portions of hexane and 0.5% and 1%, 1 L of 2%, 2.25 L of 4%, and 1 L each of 6% and 8% ether in hexane: fractions 4–5, 0.010 g of 1-(α-naphthyl)bicyclo[2.2.2]octane; 8–14, 0.107 g of an unidentified oil; 20–24, 0.183 g (81%) of cyclohexyl[4-(α-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol, identified

by NMR as essentially pure, as a colorless oil which solidifed in vacuo. This material was used without further purification.

The spectral data were as follows: IR (KBr) 2.73–3.17, 3.22, 3.28, 3.42, 3.49, 6.25, 6.33, 6.62, 6.90, 7.15, 7.46, 7.93, 8.62, 9.12, 9.23, 10.33, 10.42, 10.52, 11.22, 12.50, 12.90, 14.92, 16.08 μm; NMR (CDCl$_3$) τ 1.45–1.70 (m, 1 H, arom), 2.05–2.80 (m, 6 H, arom), 6.95 (s, 1 H, OH), 7.52–8.02 (m, 6 H, CH$_2$), 8.02–8.20 (m, 18 H, CH$_2$ and CH); mass spectrum (70 eV), m/e (relative abundance) 349 (24), 348 (83), 247 (57), 179 (36), 167 (31), 165 (51), 141 (100), 95 (31), 93 (28), 83 (36), 81 (30), 71 (29), 69 (33), 57 (41), 53 (71), 45 (36), 43 (47), 41 (60); high-resolution mass spectrum, calcd for C$_{25}$H$_{32}$O m/e 348.2453, found m/e 348.2454.

1-(Cyclohexanecarbonyl)-4-(α-naphthyl)bicyclo[2.2.2]octane. Chromium trioxide (0.300 g, 3.0 mmol) was added in portions to 0.50 mL (6.30 mmol) of pyridine in 7.0 mL of dichloromethane. After the mixture was stirred for 15 min, 0.180 g (0.518 mmol) of cyclohexyl[4-(α-naphthyl)bicyclo[2.2.2]-oct-1-yl]methanol in 2 mL of dichloromethane was added, causing the immediate formation of a black precipitate. After 30 min, the dichloromethane was removed, and the residue was thoroughly rinsed with ether. The combined organic materials were thoroughly washed with 5% aqueous solutions of sodium hydroxide, hydrochloric acid, sodium bicarbonate, and then saturated aqueous sodium chloride and concentrated in vacuo to give 0.169 g of a solid which was chromatographed on a 44 × 1 cm silica gel column. Elution was with 250-mL portions of hexane and 1% and 2% ether in hexane: fractions 2–3, 0.145 g (81%) of 1-(cyclohexanecarbonyl)-4-(α-naphthyl)bicyclo[2.2.2]octane, which afforded 0.067 g (40%) of an analytically pure sample of product, mp 206.5–207.5 °C, after recrystallization from methylcyclohexane.

The spectral data were as follows: UV λ_{max} (MCIP) 262 nm (sh, ϵ 4560), 271 (7050), 281 (8140), 288 (5860), 292 (5950), 312 (510); IR (KBr) 3.22, 3.27, 3.35, 3.41, 3.49, 5.91, 6.25, 6.33, 6.62, 6.74, 6.90, 7.14, 7.30, 7.44, 7.61, 8.00, 8.40, 8.66, 10.34, 10.52, 11.25, 11.70, 11.90, 12.47, 12.86, 14.84 μm; NMR (CDCl$_3$) τ 1.48–1.82 (m, 1 H, arom), 2.10–2.80 (m, 6 H, arom), 7.00–7.32 (m, 1 H, methine), 7.60–7.95 (m, 6 H, methylene), 7.95–8.98 (m, 16 H, methylene); mass spectrum (70 eV), m/e (relative abundance) 347 (24), 346 (93), 263 (11), 236 (20), 235 (100), 179 (25), 167 (12), 165 (17), 149 (13), 142 (12), 141 (80), 83 (33), 81 (12), 57 (27), 55 (33), 43 (27), 41 (40); high-resolution mass spectrum, calcd for C$_{25}$H$_{30}$O m/e 346.2297, found m/e 346.2293.

Anal. Calcd for C$_{25}$H$_{30}$/O: C, 86.66; H, 8.73. Found: C, 86.60; H, 8.59.

Cyclohexyl[4-(β-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol. To a stirred suspension of 0.187 g (0.516 mmol) of 1-iodo-4-(β-naphthyl)bicyclo[2.2.2]octane in 7.0 mL each of ether and pentane at −78 °C was added 1.2 mL (1.1 mmol) of 0.95 N *tert*-butyllithium in pentane. After the pale yellow mixture was stirred for 35 min, 0.58 g (5.2 mmol) of cyclohexanecarboxaldehyde was added, and the color immediately discharged. The mixture was allowed to warm to room temperature, and stirring was continued for 3 h, after which the reaction was quenched with saturated ammonium chloride. The aqueous layer was ether extracted and the combined organic materials were water washed, dried, and concentrated in vacuo to afford 0.729 g of a colorless oil which was chromatographed on a 90 × 2.7 cm silica gel column. Elution was with 250-mL portions of hexane and 0.5%, 1 L of 2%, 2 L of 4%, 1 L of 6%, and 2 L of 8% ether in hexane: fractions 4–5, 0.009 g of 1-(β-naphthyl)bicyclo[2.2.2]octane; 7–14, 0.079 g of an unidentified oil; 21–24, 0.150 g (83%) of solid cyclohexyl[4-(β-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol, pure by NMR. Recrystallization from heptane gave mp 129.7–130.6 °C.

The spectral data were the following: IR (KBr) 2.74–3.15, 3.27, 3.42, 3.49, 6.11, 6.26, 6.67, 6.93, 7.70, 7.88, 8.06, 8.62, 8.89, 9.17, 9.27, 9.35, 9.85, 10.42, 10.64, 11.36, 11.79, 12.24, 12.33, 13.38, 13.89, 15.38 μm; NMR (CDCl$_3$) τ 2.08–2.79 (m, 7 H, arom), 7.01 (s, 1 H, OH), 7.75–9.15 (m, 24 H, CH$_2$ and CH).

Anal. Calcd for C$_{25}$H$_{32}$O: C, 86.16; H, 9.26. Found: C, 86.21; H, 9.42.

1-(Cyclohexanecarbonyl)-4-(β-naphthyl)bicyclo[2.2.2]octane. Chromium trioxide (0.300 g, 3.00 mmol) was added in portions to 0.50 g (6.3 mmol) of pyridine in 7.0 mL of dichloromethane and the resulting burgundy mixture was stirred at room temperature for 25 min. Then 0.120 g (0.345 mmol) of cyclohexyl[4-(β-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol in 3.0 mL of

dichloromethane was added, causing the immediate formation of a black precipitate. After the mixture was stirred for 30 min, the dichloromethane was removed, and the residue was rinsed with ether. The combined organic materials were thoroughly washed with 5% aqueous sodium hydroxide, hydrochloric acid, and sodium bicarbonate, and saturated sodium chloride. Concentration in vacuo afforded 0.125 g of a colorless solid which was chromatographed on a 42 × 1 cm silica gel column. Elution was with 600 mL of hexane and 200 mL of 1% ether in hexane: fraction 4, 0.105 g (88%) of pure (by NMR) 1-(cyclohexane-carbonyl)-4-(β-naphthyl)bicyclo[2.2.2]octane, mp 167.5–169 °C, after recrystallization from methylcyclohexane.

The spectral data were as follows: UV λ_{max} (MCIP) 257 nm (sh, ϵ 3930), 265 (4740), 274 (5050), 285 (sh, 3510), 304 (420), 317 (280); IR (KBr) 3.22, 3.27, 3.42, 3.49, 5.91, 6.26, 6.67, 7.30, 7.57, 8.00, 8.26, 8.49, 8.64, 8.93, 9.83, 10.02, 10.42, 10.63, 11.23, 11.71, 12.22, 13.07, 14,48, 15.36, 15.97 μm; NMR (CDCl$_3$) τ 2.10–2.77 (m, 7 H, arom), 7.00–7.36 (m, 1 H, CH), 7.80–8.20 (sym m, 12 H, CH$_2$), 8.20–8.94 (m, 10 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 347 (32), 346 (100), 263 (17), 236 (52), 235 (85), 193 (12), 180 (14), 179 (43), 167 (13), 165 (15), 142 (33), 141 (90), 107 (10), 83 (32), 81 (12), 79 (11), 55 (33), 41 (25); high-resolution mass spectrum, calcd for C$_{25}$H$_{30}$O m/e 346.2296, found m/e 346.2287.

Anal. Calcd for C$_{25}$H$_{30}$O: C, 86.66; H, 8.73. Found: C, 86.85; H, 8.87.

1-(α-Hydroxybenzyl)-4-(β-naphthyl)bicyclo[2.2.2]octane. To a stirred suspension of 0.229 g (0.632 mmol) of 1-iodo-4-(β-naphthyl)bicyclo[2.2.2]octane in 8.0 mL each of ether and pentane at –78 °C was added 1.4 mL (1.3 mmol) of 0.95 N tert-butyllithium in pentane. After the pale yellow solution was stirred for 45 min, 0.64 mL (6.3 mmol) of benzaldehyde was added, discharging the color. After being stirred for 2.5 h at room temperature, the mixture was quenched with saturated ammonium chloride. The aqueous layer was ether extracted, and the combined organic materials were water washed, dried, and concentrated in vacuo to afford 0.740 g of a yellow oil, which was chromatographed on a 85 × 2.7 cm silica gel column. Elution was with 1.75 L of hexane, 250-mL portions of 0.5%, 1%, 2%, and 4%, and 500-mL portions of 8%, 20%, 40%, and 60% ether in hexane: fractions 4–6, 0.008 g of 1-(β-naphthyl)bicyclo[2.2.2]octane; 13–16, 0.089 g of an unidentified oil; 18–19, 0.128 g (60%) of pure (by NMR) 1-(α-hydroxybenzyl)-4-(β-naphthyl)bicyclo[2.2.2]octane, which afforded 0.080 g (40%) of analytically pure product, mp 154–155 °C, after recrystallization from ether–hexane.

The spectral data were as follows: IR (KBr) 2.76–3.17, 3.29, 3.31, 3.40, 3.44, 3.49, 6.13, 6.28, 6.68, 7.35, 7.69, 7.82, 8.03, 8.86, 9.09, 9.25, 9.61, 9.77, 10.10, 10.41, 11.22, 11.65, 12.21, 12.80, 13.35, 13.90, 14.10 μm; NMR (CDCl$_3$) τ 2.12–2.85 (m, 12 H, arom), 5.69 (s, 1 H, CH), 7.95–8.60 (m, 13 H, CH$_2$ and OH).

Anal. Calcd for C$_{25}$H$_{26}$O: C, 87.68; H, 7.65. Found: C, 87.46; H, 7.47.

1-Benzoyl-4-(β-naphthyl)bicyclo[2.2.2]octane. To 0.35 g (4.4 mmol) of pyridine in 6.0 mL of dichloromethane was added 0.22 g (2.2 mmol) of chromium trioxide and the burgundy mixture was stirred for 15 min. The addition of 0.110 g (0.321 mmol) of 1-(α-hydroxybenzyl)-4-(β-naphthyl)bicyclo[2.2.2]octane in 2.0 mL of dichloromethane caused the immediate formation of a black precipitate. After 20 min, the dichloromethane was removed and the residue was ether washed. The combined organic materials were washed with 5% aqueous solutions of sodium hydroxide, hydrochloric acid, and sodium bicarbonate, and saturated aqueous sodium chloride, dried, and concentrated in vacuo. This afforded 0.121 g of a solid which was chromatographed on a 42 × 2.5 cm silica gel column. Elution was with 250 mL each of hexane and 1% ether in hexane and 1 L each of 2% and 4% ether in hexane: fractions 6–8, 0.082 g (0.242 mmol, 75%) of solid 1-benzoyl-4-(β-naphthyl)bicyclo[2.2.2]octane, which gave 0.060 g (57%) of an analytically pure sample, mp 168–169 °C, after recrystallization from methylcyclohexane.

The spectral data were as follows: UV λ_{max} (MCIP) 265 nm (5480), 274 (5540), 285 (sh, 3760), 303 (530), 350 (tail, 60); IR (KBr) 3.27, 3.40, 3.43, 3.49, 5.97, 6.25, 6.89, 6.94, 7.75, 7.82, 7.93, 8.06, 8.44, 8.88, 9.20, 9.81, 10.67, 11.35, 11.64, 12.30, 12.72, 13.38, 13.70, 14.24, 15.26, 16.00 μm; NMR (CDCl$_3$) τ 2.10–2.85 (m, 12 H arom), 7.68–8.16 (sym m, 12 H, CH$_2$).

Anal. Calcd for C$_{25}$H$_{24}$O: C, 88.20; H, 7.11. Found: C, 88.12; H, 7.30.

[4-(α-Naphthyl)bicyclo[2.2.2]oct-1-yl]methanol. Two flasks connected by glass tubing were flame-dried under nitrogen. The first was charged with 3.5 g (0.12 mol) of paraformaldehyde, and the second with a solution of 1.05 g (0.0029 mol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane in a mixture of 25 mL of pentane and 25 mL of diethyl ether. The solution was cooled to –78 °C and treated with 3.6 mL of 1.68 M tert-butyllithium in pentane (0.0061 mol). After 0.5 h, heat was applied to the paraformaldehyde (ca. 150 °C), and when formaldehyde began to pass into the second flask, its cooling bath was removed. After 5 h, the reaction mixture was quenched with saturated aqueous ammonium chloride. The layers were separated, and the aqueous layer was extracted with ether. The combined organic phase was washed with water and dried and the solvent was removed in vacuo. The residue was then refluxed with 3 mL of ethanol and 0.1 mL of concentrated hydrochloric acid for 4 h. After this cooled, ether was added, followed by saturated aqueous sodium bicarbonate until the solution was no longer acidic. The layers were separated and the aqueous phase was extracted with ether. The combined organic phase was washed with water, a saturated solution of sodium bicarbonate, and water, dried, and concentrated. The residue was chromatographed on a 3 × 76 cm silica gel column, with UV monitoring: after two hexane fractions, fraction 3, 0.25% ether in hexane, 6 mg; 4, 0.25% ether in hexane, 8 mg; 5, 0.5% ether, 58 mg; 6, 1% ether, nil; 7, 2% ether in hexane, nil; 8, 4% ether, nil; 10, 10% ether, 64 mg,; 11, 20% ether, 171 mg; 12, 50% ether, nil; 13, 50% ether, nil; 14, 100% ether, 29 mg of impure [4-(α-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol; 15, ether, 257 mg of impure [4-(α-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol. The impure oils from fractions 14 and 15 were combined and rechromatographed on a 3.5 × 15 cm column slurry packed with Florisil in 25% ether in hexane. Fractions 1–3 gave 266 mg (44.4%) of clear, colorless oil which crystallized on standing: mp 87–89 °C; IR (KBr) 2.86–3.13, 3.22 (m), 3.29 (m), 3.42, 3.51, 6.87 (m), 7.16 (m), 9.43 (ms), 12.48 (ms), 12.87 μm; NMR (CDCl$_3$) τ 1.67–1.53 (m, 1 H, peri-hydrogen of naphthyl), 2.25–2.13 (m, 1 H, arom), 2.45–2.29 (m, 1 H, arom), 2.70–2.51 (m, 4 H, arom), 6.65 (s, 2 H, CH$_2$OH), 7.91–7.67 (m, 6 H, bicyclooctyl CH$_2$), 8.47–8.23 (m, 6 H, bicyclooctyl CH$_2$), 8.61 (s, 1 H, OH); mass spectrum (70 eV), m/e (relative abundance) 266 (100), 235 (17.5), 219 (21.7), 205 (27.7), 191 (10.2), 179 (39.8), 178 (38.6), 165 (69.9), 153 (19.9), 152 (25.9), 141 (46.4), 133 (10.8), 128 (15.1), 91 (13.3), 43 (13.3), 41 (15.1).

Anal. Calcd for C$_{19}$H$_{22}$O: C, 85.67; H, 8.32. Found: C, 82.89; H, 8.40.

4-(α-Naphthyl)bicyclo[2.2.2]octane-1-carboxaldehyde. A solution of 1.08 mL of pyridine in 17 mL of methylene chloride was placed in a flame-dried flask, and 0.67 g (0.0062 mol) of chromium trioxide was added in portions. After this mixture was stirred for 20 min, 0.26 g (0.000 96 mol) of [4-(α-naphthyl)bicyclo[2.2.2]oct-1-yl]methanol was added in 4.0 mL of dichloromethane. A black precipitate formed immediately. After 15 min, the solvent was decanted and the precipitate washed thoroughly with ether. The combined organic phase was washed with 5% hydrochloric acid, saturated sodium bicarbonate, and brine. The solution was dried and concentrated to give a solid which was chromatographed on a 3 × 38 cm silica gel column. Elution, in 25-mL fractions, was monitored by UV absorption to give the following: 1, hexane, nil; 2, 1% ether in hexane, nil; 3, 2% ether, nil; 4, 2% ether, nil; 5, 4% ether, nil; 6, 4% ether, 158 mg of 4-(α-naphthyl)bicyclo[2.2.2]octane-1-carboxaldehyde; 7, 4% ether, 32 mg of the same. The material from fractions 6 and 7 was recrystallized from pentane to give a 75% yield of product that melted at 128–129.5 °C: IR (KBr) 3.40 (m), 3.42 (m), 3.50 (m), 5.80, 12.39 (ms), 12.79 μm; NMR (CDCl$_3$, MH) τ 0.51 (s, 1 H, CHO), 1.75–1.61 (m, 1 H, peri-H of naphthyl), 2.45–2.11 (m, 2 H, arom), 2.71–2.49 (m, 4 H, arom), 7.91–7.63 (m, 6 H, CH$_2$), 8.26–7.97 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 264 (100), 235 (17.6), 192 (10.6), 179 (32.4), 167 (38.8), 166 (34.7), 165 (48.2), 153 (18.8), 152 (21.2), 141 (33.5), 128 (11.2).

Anal. Calcd for C$_{19}$H$_{20}$O: C, 86.32; H, 7.63. Found: C, 86.19; H, 7.48.

1-(α-Naphthyl)-4-(1-propenyl)bicyclo[2.2.2]octane. A flame-dried flask under nitrogen was charged with 0.179 g of a

50% mineral oil dispersion of sodium hydride (0.00373 mol) which was then washed three times with dry hexane and dried under a nitrogen stream. Then 4.5 mL of dimethyl sulfoxide was added and the stirred mixture heated to 70 °C. After 0.5 h, hydrogen evolution had ceased, and the solution was cooled to room temperature and treated with 1.40 g (0.00334 mol) of ethyltriphenylphosphonium iodide[40] dissolved in 5 mL of dimethyl sulfoxide. After another 0.5 h, the solution of ylide was treated with a solution of 0.210 g (0.00091 mol) of 4-(α-naphthyl)bicyclo[2.2.2]octane-1-carboxaldehyde in 8 mL of dimethyl sulfoxide and heated to 55 °C. The reaction was monitored by thin-layer chromatography. Upon completion, the red solution was cooled and poured into 100 mL of water, causing immediate decoloration. The mixture was extracted with ether and the extracts were washed with water, dried, and evaporated. The residue was chromatographed on a 3.5 × 27 cm silica gel column. Elution with hexane afforded the following: fraction 1, 11 mg; 2, nil; 250 mL, 15 mg of solid, nearly all trans isomer of product; 4, 104 mg of oil, mixed isomers; 5, 19 mg of oily solid, mixed isomers; 6, 125 mL, 10 mg of oily solid, 3:1 cis–trans isomers of product. Fractions 3–6 were 148 mg (59%) of 1-(α-naphthyl)-4-(1-propenyl)bicyclo[2.2.2]octane as mixed isomers. Gas chromatographic analysis[41] showed the contents to be 62% cis and 32% trans product and 6% impurities. This material was chromatographed on a 20 × 20 cm thick-layer plate coated with a mixture of 40 g of silica gel and a solution of 20 g of silver nitrate in 72 mL of water and subsequently dried. Elution with 5% ether in hexane was continued until the first band had proceeded two-thirds up the plate. The three bands were scraped off and extracted to give the following: band 1, 0.049 g (90%) of pure 1-(α-naphthyl)-4-*trans*-(1-propenyl)bicyclo[2.2.2]octane; band 2, 0.85 g of a yellow solid composed of 89% *cis*- and 7% *trans*-1-(α-naphthyl)-4-(1-propenyl)bicyclo[2.2.2]octane; band 3, 0.044 g of yellow solid, impure 1-(α-naphthyl)-4-*cis*-(1-propenyl)bicyclo[2.2.2]octane.

The material from band 1 was recrystallized from hexane three times to give 0.018 g (7%) of an analytical sample of the trans isomer: mp 115.5–117 °C; UV (EtOH) λ_{max} 252 nm (sh, ε 2192), 262 (sh, 4290), 271 (6720), 281 (8203), 288 (5469), 292 (5469), 302 (sh, 939), 312 (407); IR (KBr) 3.38 (w), 3.42 (mw), 3.50 (mw), 10.34 (m), 12.64 (ms), 12.99 (s) μm; NMR (CDCl₃) τ 1.73–1.51 (m, 1 H, peri-H of naphthyl), 2.47–2.14 (m, 2 H, arom), 2.75–2.51 (m, 4 H, arom), 4.60 (s, 2 H, vinyls), 7.99–7.69 (m, 6 H, CH₂), 8.49–8.19 (m, 9 H, CH₂ and CH₃); mass spectrum (70 eV), m/e (relative abundance) 276 (100), 180 (64.4), 165 (63.0), 154 (11.6), 153 (12.3), 152 (12.3), 141 (11.0); high-resolution mass spectrum, calcd for C₂₁H₂₄ m/e 276.1878, found m/e 276.1899.

Anal. Calcd for C₂₁H₂₄: C, 91.25; H, 8.75. Found: C, 91.18; H, 8.83.

The contents of bands 2 and 3 was combined and chromatographed, with UV monitoring, on a 40 × 3 cm column of silica gel impregnated with silver nitrate (30% w/w) in hexane. Elution increased from 1 to 10% ether in hexane in the first six fractions, continuing at 10% ether until fraction 30, proceeding in 40-mL fractions at 20% ether to fraction 70, and continuing at 40% ether in later fractions. The trans isomer of product ceased by fraction 35. Fractions 35–70 contained pure cis product and later fractions contained impure cis material. The contents of fractions 35–70 was filtered through silica gel, the solvent was evaporated, and the residue was recrystallized from a methanol–water mixture to give 0.029 g (11.6%) of an analytical sample of 1-(α-naphthyl)-4-*cis*-(1-propenyl)bicyclo[2.2.2]octane: mp 55.7–57 °C; UV λ_{max} 251 nm (sh, ε 2177), 261 (4291), 269 (6944), 280 (8595), 286 (5692), 291 (5830), 300 (sh, 926), 311 (400); IR (KBr) 3.41 (m), 3.49 (m), 12.45 (ms), 12.84, 14.25 (m) μm; NMR (CDCl₃, MH) τ 1.54–1.36 (m, 1 H, peri-H of naphthyl), 2.62–2.00 (m, 6 H, naphthyl), 4.65 (s, 2 H, vinyls), 7.92–7.60 (m, 6 H, CH₂), 8.25–8.01 (m, 9 H, CH₂ and CH₃); mass spectrum (70 eV), m/e (relative abundance) 276 (84.7), 179 (83.3), 165 (100), 154 (20.8), 153 (22.2), 152 (25.0), 141 (22.2), 55 (12.0), 41 (18.6); high-resolution mass spectrum, calcd for C₂₁H₂₄ m/e 276.1878, found m/e 276.1880.

Anal. Calcd for C₂₁H₂₄: C, 91.25; H, 8.75. Found: C, 91.19; H, 8.67.

1-Hydroxybicyclo[2.2.2]octane.[42] To 40 mL of 1:1 diethyl ether–pentane (freshly distilled from sodium wire) was added 1.13 g (4.48 mmol) of 1-hydroxy-4-iodobicyclo[2.2.2]octane. The system was placed under nitrogen and cooled in a dry ice–acetone bath. After 15 min, 20 mL of 0.70 N (14 mmol) *tert*-butyllithium in pentane was added via syringe. After 30 min, 6.0 mL of methanol was added. After 15 min, the dry ice–acetone bath was removed and the system was allowed to warm to room temperature. Saturated aqueous ammonium chloride was added and the system was ether extracted. The organic layer was water washed, dried, and concentrated in vacuo to give 674 mg of a white solid. The product was chromatographed on a 62 × 1.9 cm silica gel column. Elution in 200-mL fractions was with 200 mL each of 2%, 4%, 10%, 25%, 40% diethyl ether in hexane and 400 mL of diethyl ether: fraction 5, 353 mg (62.4%) of 1-hydroxybicyclo[2.2.2]octane, mp 139–140 °C; fractions 6 and 7, 228 mg of an unidentified solid, mp 149–150 °C.

The spectral data were as follows: IR (KBr) 2.91–3.20, 3.40, 3.43, 3.50, 6.87, 7.41, 9.05, 10.75, 10.99 μm; NMR (CDCl₃) τ 8.38 (s, 12 H, CH₂), 8.60 (s, 1 H, OH); mass spectrum (70 eV), m/e (relative abundance) 126 (14), 97 (42), 70 (100), 55 (16), 43 (12), 41 (14); high-resolution mass spectrum, calcd for C₈H₁₄O m/e 126.1045, found m/e 126.1047.

1-Iodobicyclo[2.2.2]octane.[43] A solution of 18.3 g (0.146 mol) of 1-bicyclo[2.2.2]octanol in 350 mL of acetic acid was treated at reflux with 170 mL of 57% hydriodic acid. After 1 h, the mixture was poured onto ice, ether extracted, neutralized with potassium hydroxide, and extracted further. The extracts were washed with aqueous saturated sodium bicarbonate, sodium thiosulfate, and water, dried over magnesium sulfate, filtered, and concentrated to give 30.6 g (0.130 mol, 89%) of a clear oil, pure 1-iodobicyclo[2.2.2]octane[43] by NMR.

The spectral data were as follows: IR (KBr) 3.39, 3.41, 3.48, 6.87, 7.64, 7.94, 10.31, 12.35, 15.50 μm; NMR (CDCl₃) τ 7.45–7.61 (m, 6 H, CH₂), 8.19–8.33 (m, 7 H, CH₂ and CH); mass spectrum (70 eV), m/e (relative abundance) 236 (21), 128 (18), 127 (10), 109 (52), 91 (10), 81 (37), 80 (10), 79 (32), 69 (18), 68 (23), 67 (50), 65 (11), 55 (100), 54 (11), 53 (27), 51 (11), 43 (49), 40 (11), 39 (22), 36 (19); high-resolution mass spectrum, calcd for C₈H₁₃I m/e 236.0061, found m/e 236.0063.

1-(1-Hydroxyethyl)bicyclo[2.2.2]octane. To 20 mL of a 1:1 mixture of diethyl ether–pentane (freshly distilled from sodium wire) was added 7.64 g (32.4 mmol) of 1-iodobicyclo[2.2.2]octane. Then under nitrogen with cooling with dry ice–acetone, 100 mL of 0.70 N (70 mmol) *tert*-butyllithium in pentane was added via syringe. After 35 min, 8.6 mL (150 mmol) of acetaldehyde (freshly distilled from calcium hydride) was added. After 30 min, the mixture was allowed to warm to room temperature, saturated aqueous ammonium chloride was added, and the aqueous layer was ether extracted. The organic layers were water washed, dried, and concentrated in vacuo to give 7.0 g of a brown oil. The oil was chromatographed on a 80 × 2.5 cm silica gel column (200-mL fractions). Elution was with 1 L of hexane and 1.25 L of 2% ether, and then 750 mL of 2% and 1 L of 40% ether gave 3.98 g (80%) of a clear oil, 1-(1-hydroxyethyl)bicyclo[2.2.2]octane, pure by NMR. This material was used directly without further purification.

The spectral data were as follows: IR (neat) 2.79–3.09, 3.41, 3.48, 6.85, 7.25, 9.22, 10.87 μm; NMR (CDCl₃) τ 6.56, 6.63, 6.70, 6.76 (q, 1 H, J = 7 Hz, CH), 8.50–8.76 (m, 16 H, CH₂, CH, and CH₃), 8.93, 8.99 (d, 1 H, J = 7 Hz, hydroxyl); mass spectrum (70 eV), m/e (relative abundance) 139 (13), 136 (48), 110 (47), 109 (100), 107 (15), 95 (13), 82 (22), 81 (39), 79 (16), 71 (11), 69 (13), 68 (10), 67 (82), 57 (59), 55 (29), 45 (20), 44 (10), 43 (55), 41 (33), 39 (15), 36 (12); high-resolution mass spectrum, calcd for C₁₀H₁₈O m/e 154.1358, found m/e 154.1354.

1-Acetylbicyclo[2.2.2]octane.[16] To the complex formed from 31.1 mL (386 mmol) of pyridine and 18.2 g (182 mmol) of CrO₃

(40) Krubiner, A. N.; Oliveto, E. P. *J. Org. Chem.* **1966**, *31*, 24.

(41) Analysis was done on a 2 m × 0.125 in. column packed with 5 QF-1 on Chromosorb P at 185 °C. The cis isomer has the longer retention time.

(42) (a) Doering, W. V. E.; Levits, M.; Sayigh, A.; Sprecher, M.; Whelan, W. P., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 1008. (b) Grob, C. A.; Ohta, M.; Renk, E.; Weiss, *Helv. Chim. Acta* **1958**, *41*, 1191–7.

(43) Lansbury, P. T.; Pattison, V. A.; Sidler, J. D.; Bieber, J. B. *J. Am. Chem. Soc.* **1966**, *88*, 78–84.

in 125 mL of methylene chloride was added 3.98 g (25.9 mmol) of 1-(1-hydroxyethyl)bicyclo[2.2.2]octane in 125 mL of methylene chloride. A black precipitate formed immediately. After 20 min, solvent was removed and the remaining solid was washed alternately with ether and a 5% solution of sodium hydroxide. The organic layer was washed with 5% hydrochloric acid, saturated sodium bicarbonate, and saturated brine. The organic layer was dried and concentrated in vacuo to give 3.60 g (91%) of 1-acetylbicyclo[2.2.2]octane, a yellow oil. This material was distilled to give 3.0 g (76%) of colorless oil, bp 81.5–83.5 °C (6 mm), pure by NMR. Purification by gas chromatography on a 10-ft Carbowax 20M column at 140 °C gave material used for rate studies.

The spectral data were as follows: UV (MCIP) λ_{max} 284 nm (ϵ 23.2); IR (neat) 3.41, 3.48, 5.85, 6.85, 7.33, 8.13 μm; NMR (CDCl$_3$, MH) τ 7.98 (s, 3 H, methyl), 8.38 (s, 13 H, methylene and methine); mass spectrum (70 eV), m/e (relative abundance) 152 (30), 109 (100), 81 (20), 79 (11), 67 (79), 57 (57), 55 (22), 43 (53), 41 (31), 39 (16); high-resolution mass spectrum, calcd for C$_{10}$H$_{16}$O m/e 152.1201, found m/e 152.1200.

Anal. Calcd for C$_{10}$H$_{16}$O: C, 78.90; H, 10.59. Found: C, 79.04; H, 10.63.

1-Bicyclo[2.2.2]octyl Cyclohexyl Ketone. A solution of 2.1862 g (9.26 mmol) of 1-iodobicyclo[2.2.2]octane in 100 mL of dry diethyl ether was treated at –78 °C with 14.7 mL of 1.26 M (18.5 mmol) tert-butyllithium in pentane. After being stirred at –78 °C for 0.5 h, the suspension was transferred dropwise under nitrogen via cannula into a stirred sample of cyclohexanecarbonyl chloride,[44] freshly prepared from 7.74 g (60.5 mmol) of the acid.[41] After warming to room temperature, the mixture was treated with a solution of 8.4 g of potassium hydroxide in 20 mL of water and refluxed for 1 h to remove excess acid chloride. The basic water layer was then ether extracted, and the combined organic phase was washed with water, dried, and concentrated. The residue was chromatographed on a 2.5 × 80 cm silica gel column. After 1.9 L of hexane and 800 mL of 1% ether in hexane, fractions 11–13, 200 mL each of 1% ether, gave a total of 1.88 g (92%) of solid 1-bicyclo[2.2.2]octyl cyclohexyl ketone, mp 65–70 °C.

An analytical sample used in the rate studies was obtained by repeated recrystallization from methanol: mp 75.2–76.2 °C; UV (MCIP) λ_{max} 297.5 nm (ϵ 22.7); IR (KBr) 3.40, 3.43, 3.50, 5.92, 6.90 (m), 7.29 (mw), 8.51 (mw), 10.96 (mw), 11.26 (mw) μm; NMR (CDCl$_3$) τ 7.04–7.34 (m, 1 H, CH—C=O), 8.42 (br s overlapping τ 8.14–8.90 (m), 23 H, CH$_2$ and bridgehead CH); mass spectrum (70 eV), m/e (relative abundance) 221 (0.3), 220 (2.5), 165 (0.3), 137 (12.6), 109 (100), 67 (18.7), 55 (8.4), 44 (4.2), 41 (8.4), 40 (16.0); high-resolution mass spectrum, calcd for C$_{15}$H$_{24}$O m/e 220.1827, found m/e 220.1828.

Anal. Calcd for C$_{15}$H$_{24}$O: C, 81.75; H, 10.99. Found: C, 81.57; H, 11.10.

4,4'-Dimethoxy-1,1'-bibicyclo[2.2.2]octyl. A flask containing 12.5 g (0.515 mol) of magnesium turnings was flame-dried and charged with 41.2 g (0.318 mol) of anhydrous nickel chloride. 4-Iodo-1-bicyclo[2.2.2]octyl methyl ether (68.8 g, 0.259 mol) and 250 mL of anhydrous diethyl ether were added, and the mixture was refluxed with stirring for 12 h, during which the mixture turned black. The ether was distilled under nitrogen, and the residual solid was treated with water and washed with ethanol and then extensively with ether until only a fine gray-black powder of nickel remained. The water was removed and extracted with ether. The organic phases were concentrated and the residue was crystallized from hexane to give 17.4 g (48.4%), mp 166.8–168.7 °C. An analytical sample was prepared by repetitive recrystallization from 95% ethanol: mp 168.1–168.5 °C; IR (KBr) 3.40, 3.49, 3.55, 6.83, 7.41, 8.35, 8.65, 9.08, 9.72 μm; NMR (CDCl$_3$, WH) τ 6.86 (s, 6 H, CH$_3$O), 8.43–8.46 (m, 12 H, CH$_2$), 8.50–8.54 (m, 12 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 278 (21.3), 84 (54.5), 40 (12.5), 32 (100); high-resolution mass spectrum, calcd for C$_{18}$H$_{30}$O$_2$ m/e 278.2246, found m/e 278.2245.

Anal. Calcd for C$_{18}$H$_{30}$O$_2$: C, 77.65; H, 11.49. Found: C, 77.85; H, 11.16.

4'-Iodo-1,1'-bibicyclo[2.2.2]octyl-4-ol. A solution of 3.00 g (10.8 mmol) of 4,4'-dimethoxy-1,1'-bibicyclo[2.2.2]octyl in 240 mL

of benzene was treated with 60 mL of 57% hydriodic acid and the reaction mixture was vigorously stirred at reflux, forming an emulsion. After 1 h, the mixture was poured onto ice and sodium bicarbonate was added until the solution was basic. The aqueous layer was carefully acidified with hydrochloric acid until just acid to litmus and then ether extracted. The organic phase was washed with 10% sodium thiosulfate and water, dried, filtered, and concentrated. The material from two such runs (ca. 10 g) was chromatographed on a 2.5 × 62 cm silica gel column. Elution was with 1.3 L of hexane followed by fraction 3, 800 mL of 50% ether, 0.52 g (6.5%) of 4'-iodo-1,1'-bibicyclo[2.2.2]oct-4-yl methyl ether; fraction 4, 4 L of 50% ether, 6.53 g (84%) of 4'-iodo-1,1'-bibicyclo[2.2.2]octyl-4-ol. Recrystallization of fraction 4 gave 5.72 g (73.6%) of pure material, mp 195.3–195.8 °C. An analytical sample was prepared by recrystallization from ethanol: mp 196.6–197.7 °C; UV (EtOH) λ_{max} 260.0 nm (ϵ 990); IR (KBr) 2.90–3.12, 3.39, 3.43, 3.50, 6.88, 7.42, 8.12, 9.26, 9.92, 11.44, 12.32, 15.13 μm; NMR (CDCl$_3$, WH) τ 7.58–7.64 (m, 6 H, CH$_2$), 8.42–8.51 (m, 12 H, CH$_2$), 8.55–8.60 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 360 (very small), 233 (21.8), 232 (44.0), 168.5 (75.7), 166.5 (96.9), 122 (63.7), 110 (85.0), 109 (77.0), 65 (90.1), 45 (100), 44 (79.7), 43 (72.5), 41 (66.5), 36 (70.8); high-resolution mass spectrum, calcd for C$_{16}$H$_{25}$IO m/e 360.0950, found m/e 360.0938.

Anal. Calcd for C$_{16}$H$_{25}$IO: C, 53.34; H, 6.99. Found: C, 53.19; H, 7.10.

4'-(α-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl-4-ol and 4'-(β-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl-4-ol. A solution of 2.00 g (5.55 mmol) of 4'-iodo-1,1'-bibicyclo[2.2.2]octyl-4-ol in 120 g of naphthalene was irradiated for 3 h under nitrogen through a Vycor filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The reaction vessel and the lamp cooling water were maintained at 85–90 °C. At the end of the irradiation, the naphthalene solution was removed. The solidified naphthalene solution and washings were taken up in ether and washed with saturated sodium bicarbonate until neutral, then with 10% sodium thiosulfate to remove iodine, and finally with water. The solution was dried and concentrated. The majority of the naphthalene was removed by sublimation. The remaining material (11.8 g) was chromatographed on a 2.5 × 84 cm silica gel column, with UV monitoring: fraction 1, 400 mL of hexane, nil; 2, 2050 mL of hexane, the majority of the naphthalene; 3, 3 L of hexane, followed by 0.50 L of 1% ether in hexane and then 0.50 L of 5% ether in hexane, 0.28 g of unidentified material; 4, 0.30 L of 5% ether, nil; 5, 50% ether, a trace of unidentified oil; 6, 0.15 L of 50% ether, nil; 7, 0.50 L of 50% ether, 0.70 g of a mixture of α and β 4'-naphthyl-1,1'-bicyclo[2.2.2]octyl-4-ols; 9, 1.30 L of ether, 0.83 g of a mixture of the same. Thus a total yield of 1.52 g (76.0%) of 4'-naphthyl-1,1'-bibicyclo[2.2.2]octyl-4-ols was obtained.

The two isomers were separated by fractional crystallization. Progress was monitored by NMR analysis (either in deuteriobenzene with a WH-270 or in pyridine with an MH-100; in the latter case, the aromatic region is obscured). The use of ethanol favored crystallization of the β isomer, whereas the use of a mixture of heptane and benzene favored crystallization of the α isomer.

Upon obtaining 0.615 g (31%) of an isomerically pure sample of the α-naphthylbibicyclooctylol, mp 291–292.6 °C, an analytical sample was prepared by recrystallization from a mixture of heptane and benzene: mp 296.3–297.6 °C; UV (MCIP) λ_{max} 209.8 nm (sh, ϵ 27 000), 221.3 (sh, 58 400), 225.7 (77 600), 254 (sh, 2140), 263.2 (sh, 4060), 272.0 (6660), 282.2 (8300), 288.8 (5680), 291.5 (5560), 293.6 (5700), 302.5 (sh, 1080), 308 (sh, 491), 313.1 (477); IR (KBr) 2.93 (br), 3.23 (w), 3.29 (w), 3.40, 3.43, 3.50, 6.87 (m), 7.16 (m), 7.41 (m), 9.27, 12.52, 12.94 (vs) μm; NMR (CDCl$_3$, WH) τ 1.55–1.59 (m, 1 H, peri-H of naphthyl), 2.14–2.17 (m, 1 H, arom), 2.30–2.34 (m, 1 H, arom), 2.53–2.64 (m, 4 H, arom), 7.86–7.92 (m, 6 H, CH$_2$ β to α-naphthyl), 8.40–8.45 (br s superimposed on a m, 18 H, CH$_2$), 8.86 (s, 1 H, OH); mass spectrum (70 eV), m/e (relative abundance) 361 (27.0), 360 (100), 180 (60.4), 179 (17.5), 164 (44.9), 141 (25.2), 83 (10.9), 78 (68.2), 69 (18.3), 57 (24.7), 55 (31.3), 45 (44.9), 44 (13.9), 43 (41.1), 41 (24.0); high-resolution mass spectrum, calcd for C$_{26}$H$_{32}$O m/e 360.2453, found m/e 360.2454.

Anal. Calcd for C$_{26}$H$_{32}$O: C, 86.62; H, 8.95. Found: C, 86.46; H, 9.11.

Upon achieving an isomerically pure sample of the β-naphthylbibicyclo[2.2.2]octylol, 0.414 g (21%) of an analytical sample

(44) Rabjohn, N. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. 4, p 339.

was prepared by recrystallization from pyridine, the sample thus obtained being placed under high vacuum for several days to remove residual pyridine: mp 302.1–302.8 °C; UV (MCIP) λ_{max} 251 nm (sh, ϵ 2850), 260 (sh, 4130), 267 (4980), 274.8 (5300), 284 (3720), 304.0 (sh, 465), 310.3 (sh, 273), 318.2 (366); IR (KBr) 2.81 (sh, w), 2.89 (m), 3.27 (mw), 3.39, 3.42, 3.49, 6.82 (m), 7.39 (m), 8.06 (m), 8.85 (m), 9.12, 11.71 (m), 12.24 (m), 13.37 μm; NMR (CDCl$_3$, WH) τ 2.21–2.26 (m) and 2.34 (br s) (4 H, arom), 2.49 (d of d, 6.64 and 1.89 Hz, 1 H, arom), 2.57–2.26 (m, 2 H, arom), 8.11–8.17 (m, 6 H, CH$_2$ β to β-naphthyl), 8.42–8.50 (m, 18 H, CH$_2$), 8.85 (br s, 1 H, OH); mass spectrum (70 eV), m/e (relative abundance) 361 (15.9), 360 (71.9), 181 (11.8), 180 (100), 179 (10.0), 141 (20.6), 83 (12.2), 81 (12.4), 79 (12.1), 73 (15.2), 71 (14.2), 69 (33.8), 60 (17.4), 57 (41.9), 55 (35.2), 45 (31.9), 44 (16.9), 43 (49.7), 41 (34.0); high-resolution mass spectrum, calcd for C$_{26}$H$_{32}$O m/e 360.2453, found m/e 360.2471.

Anal. Calcd for C$_{26}$H$_{32}$O: C, 86.62; H, 8.95. Found: C, 86.52; H, 8.94.

4-Iodo-4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl. A solution of 1.02 g (2.82 mmol) of 4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]-octyl-4-ol in 55 mL of glacial acetic acid was treated with 29 mL of 57% hydriodic acid and maintained at reflux for 4 h. The mixture was poured onto ice and then extracted with carbon tetrachloride. The combined extracts were washed with saturated sodium bicarbonate and 10% sodium thiosulfate, dried, filtered, and concentrated to yield 1.47 g of material which was recrystallized from a mixture of heptane and benzene to give 0.98 g (74%) of 4-iodo-4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl, mp 262.5–266.8 °C, essentially pure.

An analytical sample was prepared by recrystallization from heptane–tetrahydrofuran: mp 266.5–267.3 °C; UV (MCIP) λ_{max} 222.7 nm (ϵ 69 900), 226.9 (108 000), 250.5 (2410), 259.0 (3550), 265.0 (4280), 274.4 (4330), 285 (2720), 304 (sh, 340), 309 (sh, 180), 317.8 (230); IR (KBr) 3.28 (w), 3.39, 3.43, 3.49, 10.07 (m), 10.11 (m), 10.52 (ms), 11.63 (m), 12.20, 13.32 (ms) μm; NMR (CDCl$_3$) δ 7.79–7.66 (m, 4 H, naphthyl), 7.50–7.36 (m, 3 H, naphthyl), 2.45–2.41 (m, 6 H, CH$_2$), 1.88–1.82 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 471 (4.4), 470 (26.4), 344.5 (11.2), 342.5 (25.4), 235 (13.9), 180 (15.2), 141 (53.1), 95 (10.0), 69 (51.3), 57 (30.9), 55 (18.8), 44 (65.4), 43 (41.7), 41 (28.5), 40 (100), 36 (14.3); high-resolution mass spectrum, calcd for C$_{26}$H$_{31}$I m/e 470.1471, found m/e 470.1471.

Anal. Calcd for C$_{26}$H$_{31}$I: C, 66.38; H, 6.64. Found: C, 66.25; H, 6.75.

4'-(α-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl-4-carboxylic Acid. A solution of 519.9 mg (1.105 mmol) of 4-iodo-4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl in 400 mL of ether, dried over lithium aluminum hydride, was cooled to –78 °C and treated under argon with 5.8 mL of a 0.6 M solution of *tert*-butyllithium in pentane. After 0.5 h, about 200 mL of freshly crushed solid carbon dioxide was added, and the mixture was allowed to warm over 2.5 h. The mixture was extracted several times with a 10% solution of sodium hydroxide. The combined alkaline extracts were acidified to a Congo red endpoint with hydrochloric acid and extracted with ether. The combined ether extracts were dried and evaporated to yield 398.2 mg (93%) of essentially pure (by NMR) 4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl-4-carboxylic acid. An analytical sample was prepared by recrystallization from dimethyl sulfoxide, the sample being subsequently rinsed with hexane and placed under vacuum to remove solvent: decomposes on heating around 300 °C; UV (THF) λ_{max} 228 nm (ϵ 62 000), 254 (sh, 2420), 264 (sh, 4440), 272.9 (6960), 283.0 (8540), 288.5 (5980), 294.4 (5800), 294.1 (5930), 302.4 (sh, 1480), 308.6 (sh, 741), 313.3 (691); IR (KBr) 2.93 (br, w), 3.23 (sh, m), 3.39, 3.42 (sh), 3.48, 3.79 (v br, w), 5.86, 7.67 (m), 7.83 (m), 8.03 (m), 10.54 (m), 12.50 (m), 12.84 μm; NMR (CDCl$_3$, WH, integration not possible) τ 1.55–1.58 (m, peri-H), 2.13–2.17 (m, arom), 2.30–2.35 (m, arom), 2.54–2.60 (m, arom), 2.61–2.63 (m, arom), 7.84–7.90 (CH$_2$), 8.17–8.23 (m, CH$_2$), 8.37–8.53 (m, CH$_2$) (the approximate ratio of methylene absorbances is 1:1:2 in order of increasing field); mass spectrum (70 eV), m/e (relative abundance) 389 (22.3), 388 (100), 368 (8.4), 235 (8.0), 180 (63.9), 167 (22.7), 149 (15.8), 97 (11.4), 91 (27.8), 83 (13.1), 78 (57.2), 73 (11.8), 71 (15.2), 69 (10.1), 63 (57.1), 61 (10.1), 60 (12.7), 57 (36.0), 56 (12.7), 55 (16.6), 45 (86.1), 44 (35.0), 43 (33.8), 40 (27.5); high-resolution mass spectrum, calcd for C$_{27}$H$_{32}$O$_2$ m/e 388.2402, found m/e 388.2403.

Methyl 4-[4'-(α-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl]yl Ketone. A solution of 209 mg (0.537 mmol) of 4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl-4-carboxylic acid in 250 mL of dry tetrahydrofuran was treated under argon with 3.0 mL of 1.6 M methyllithium in diethyl ether and refluxed for 23 min. The solution was then forced under argon pressure through a cannula into 125 mL of stirred saturated ammonium chloride. At the end of this addition, the aqueous layer was ether extracted and the ether phase dried, filtered, and concentrated. Recrystallization of the residue from ethanol–benzene afforded 174 mg (84%) of crude methyl 4-[4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl]yl ketone, mp 231.5–234.3 °C. An analytical sample used in the rate studies was prepared by repetitive recrystallization from ethanol–benzene: mp 235.4–236.2 °C; UV (MCIP) λ_{max} 254.3 nm (sh, ϵ 2060), 264 (sh, 4060), 273.3 (6630), 283.5 (8300), 290.1 (5490), 294.9 (5670), 303.5 (sh, 972), 314.3 (425); IR (KBr) 3.23 (w), 3.29 (w), 3.40, 3.43, 3.49, 5.89, 7.36 (m), 7.41 (m), 8.19 (m), 12.50 (m), 12.87 μm; NMR (CDCl$_3$, WH) τ 1.55–1.59 (m, 1 H, peri-hydrogen or naphthyl), 2.14–2.17 (m, 1 H, arom), 2.30–2.34 (m, 1 H, arom), 2.53–2.66 (m, 4 H, arom), 7.85–7.92 (m, 6 H, CH$_2$), 8.29–8.34 (m, 6 H, CH$_2$), 8.48–8.54 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 386 (21.4), 385 (77.3), 180 (53.8), 179 (15.2), 165 (36.9), 141 (25.3), 45 (29.2), 43 (100); high-resolution mass spectrum, calcd for C$_{28}$H$_{34}$O m/e 386.2610, found m/e 386.2610.

Anal. Calcd for C$_{28}$H$_{34}$O: C, 87.00; H, 8.87. Found: C, 86.80; H, 9.07.

4-[4'-(α-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl]yl Phenyl Ketone. A solution of 151 mg (0.388 mmol) of 4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl-4-carboxylic acid in 80 mL of tetrahydrofuran was treated under argon with 2.0 mL of 1.15 M phenyllithium in diethyl ether and refluxed for 1 h. The solution was then transferred under argon via cannula into stirred saturated ammonium chloride. The water layer was ether extracted and the combined ether phase washed with water, dried, filtered, and concentrated to give 178 mg of a brown solid which was chromatographed, with UV monitoring, on a 1 × 40 cm silica gel column: fraction 1, 50 mL of hexane, nil; 2, 125 mL of hexane, 26.5 mg of unidentified material; 3, 85 mL of 5% ether in hexane, nil; 4, 150 mL of 10% ether, 105.1 mg (60%) of pure (by NMR) 4-[4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl]yl phenyl ketone. An analytical sample used for the rate studies, was prepared by recrystallization from benzene–ethanol: mp 212.5–213.6 °C; UV (MCIP) λ_{max} 220.8 nm (sh, ϵ 60 300), 226.2 (85 455), 240 (sh, 8980), 250 (sh, 5140), 265 (sh, 4470), 273.9 (7083), 284.0 (8575), 290.3 (5640), 295.2 (5630), 303.5 (506), and a tail out beyond 340 [330 (ϵ 101), 340 (ϵ 59)]; IR (KBr) 3.23 (w), 3.29 (w), 3.41, 3.49, 6.00, 8.01 (m), 8.11 (m), 12.50, 12.87, 14.22 μm; NMR (CDCl$_3$, WH) τ 1.54–1.58 (m, 1 H, peri-H), 2.13–2.17 (m, 1 H, arom), 2.30–2.35 (m) and 2.37–2.38 (m) (3 H, arom), 2.52–2.64 (m, 7 H, arom), 7.84–7.89 (m, 6 H, CH$_2$), 8.05–8.11 (m, 6 H, CH$_2$), 8.36–8.48 (m, 12 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 448 (100), 180 (56.6), 179 (11.4), 165 (26.3), 141 (24.8), 105 (25.5); high-resolution mass spectrum, calcd for C$_{33}$H$_{36}$O m/e 448.2766, found m/e 448.2765.

Anal. Calcd for C$_{33}$H$_{36}$O: C, 88.35; H, 8.09. Found: C, 88.51; H, 8.20.

4-(α-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl. A solution of 202 mg (0.429 mmol) of 4-iodo-4'-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl in 250 mL of dry ether was treated at –78 °C under argon with 10 mL of 0.60 M *tert*-butyllithium in *n*-pentane and stirred for 0.5 h, after which 10 mL of saturated ammonium chloride was added. The mixture was warmed to room temperature, water was added, the aqueous phase was extracted with ether, and the combined organic phase was dried, filtered, and concentrated. Recrystallization from benzene afforded 130 mg (88%) of 4-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl, mp 247–248 °C. Repeated recrystallization from benzene afforded an analytical sample used in the rate studies: mp 251.8–252.8 °C; UV (MCIP) λ_{max} 254 nm (sh, ϵ 2100), 263.6 (5604), 302.5 (sh, 935), 313.1 (397); IR (KBr) 3.29 (w), 3.41, 3.44, 3.50, 12.64 (mw), 13.21 μm; NMR (CDCl$_3$, WH) τ 1.53–1.57 (m, 1 H, peri-H), 2.14–2.18 (m) and 2.31–2.34 (m) (2 H, arom), 2.53–2.64 (m, 4 H, arom), 7.87–7.92 (m, 6 H, methylene), 8.40–8.50 (m, 13 H, methylenes and terminal methine), 8.57–8.61 (m, 6 H, methylene); mass spectrum (70 eV), m/e (relative abundance) 345 (14.3), 344 (66.5), 180 (61.9), 179 (16.8), 167 (10.5),

165 (54.8), 141 (26.5), 109 (34.6), 86 (56.6), 84 (100), 83 (19.8), 81 (51.4), 71 (19.7), 69 (98.2), 67 (45.1), 57 (56.8), 55 (59.7), 47 (21.0), 45 (28.5), 43 (67.8), 41 (77.3); high-resolution mass spectrum, calcd for $C_{26}H_{32}$ m/e 344.2504, found m/e 344.2505.

Anal. Calcd for $C_{26}H_{32}$: C, 90.64; H, 9.36. Found: C, 90.38; H, 9.60.

1,1'-Bibicyclo[2.2.2]octyl-4-ol. A solution of 0.974 g (2.7 mmol) of 4'-iodo-1,1'-bibicyclo[2.2.2]octyl-4-ol in 300 mL of anhydrous ether was treated at -78 °C under nitrogen with 30 mL of 0.6 M *tert*-butyllithium in pentane. After 1 h, 50 mL of saturated ammonium chloride was added and the mixture allowed to warm to room temperature. Water was added to dissolve the salts, the layers were separated, the water was extracted with ether, and the ether layer was dried, filtered, and concentrated to give a quantitative yield of 1,1'-bibicyclo[2.2.2]octyl-4-ol, mp 254.5-255.5 °C. An analytical sample was prepared by recrystallization from benzene: mp 255-256.5 °C (sealed tube, slight decomposition); IR (KBr) 2.91 (br s), 3.39, 3.42, 3.50, 6.85, 7.43, 9.17 μm; NMR (CDCl$_3$, WH) τ 8.40-8.47 (m, 6 H, CH$_2$), 8.51-8.56 (m, 13 H, CH$_2$ and CH), 8.68-8.75 (m, 6 H, CH$_2$); mass spectrum (40 eV), m/e (relative abundance) 235 (10.9), 234 (100), 216 (10.8), 164 (25.2), 149 (13.1), 135 (16.7), 125 (14.9), 109 (61.1), 81 (19.2), 78 (36.1), 67 (33.9), 57 (24.4), 55 (32.8), 45 (74.2), 43 (44.1), 41 (19.2); high-resolution mass spectrum, calcd for $C_{16}H_{26}O$ m/e 234.1984, found m/e 234.1970.

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.74; H, 11.21.

4-Iodo-1,1'-bibicyclo[2.2.2]octyl. A solution of 777 mg (3.31 mmol) of 1,1'-bibicyclo[2.2.2]octyl-4-ol in 60 mL of acetic acid was treated with 10 mL of 57% hydriodic acid, refluxed for 1 h, and then poured into saturated sodium bicarbonate. Water and ether were added, the layers were separated, and the water was ether extracted. The ether phase was washed with water, saturated sodium bicarbonate until the washings were basic, and then 10% sodium thiosulfate. Drying over magnesium sulfate and concentration gave 1.04 g of solid. This was chromatographed on a 2.5 × 40 cm silica gel column, monitored by UV absorption: fraction 1, hexane, nil; fraction 2, hexane, 799.1 mg (70.1%) of 4-iodo-1,1'-bibicyclo[2.2.2]octyl, mp 146.5-149 °C. An analytical sample was prepared by recrystallization from ethyl acetate: mp 150.8-151.3 °C; UV (EtOH) λ_{max} 261.5 nm (ϵ 1008); IR (KBr) 3.40, 3.43, 3.50, 6.86 (m), 10.28, 11.24 (m), 12.24, 14.93 (m) μm; NMR (CDCl$_3$, WH) τ 7.58-7.64 (m, 6 H, CH$_2$), 8.47-8.57 (m, 13 H, methylenes and CH), 8.73-8.77 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) parent not seen, 217 (92.0), 135 (19.0), 121 (17.8), 109 (100), 107 (11.5), 95 (27.0), 93 (16.5), 91 (21.6), 81 (45.0), 79 (35.2), 77 (13.5), 67 (72.9), 55 (13.2), 41 (22.2); high-resolution mass spectrum, calcd for $C_{16}H_{25}$ (loss of I) m/e 217.1956, found m/e 217.1951.

Anal. Calcd for $C_{16}H_{25}I$: C, 55.82; H, 7.32. Found: C, 55.93; H, 7.49.

1,1'-Bibicyclo[2.2.2]octyl-4-carboxylic Acid. A solution of 743 mg (2.16 mmol) of 4-iodo-1,1'-bibicyclo[2.2.2]octyl in 125 mL of ether was treated at -78 °C under argon with 10 mL of 0.6 M *tert*-butyllithium in *n*-pentane. After 0.5 h, 130 mL of freshly crushed solid carbon dioxide was introduced, and the mixture was allowed to warm to room temperature. The organic solution was then extracted with 10% sodium hydroxide and acidified with hydrochloric acid (Congo red end point), and the aqueous phase was ether extracted. The ethereal extracts were dried, filtered, and concentrated to give 544 mg (96%) of 1,1'-bibicyclo[2.2.2]-octyl-4-carboxylic acid, mp 301.2 °C. An analytical sample was prepared by recrystallization from benzene: mp (sealed tube) 301.2 °C; IR (KBr) 2.91 (m, br d), 3.40, 3.43, 3.50, 3.78 (m, br d), 3.93 (m, br d, sh), 5.91, 7.70, 7.84 μm; NMR (CDCl$_3$, WH) τ 8.25-8.31 (m, 6 H, CH$_2$), 8.50-8.55 (m, 7 H, CH$_2$ and terminal CH), 8.60-8.63 (m, 6 H, CH$_2$), 8.66-8.73 (m, 6 H, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 262 (2.5), 217 (0.1), 162 (trace), 153 (0.1), 149 (0.2), 109 (0.6), 107 (0.4), 44 (18.0), 40 (100); high-resolution mass spectrum, calcd for $C_{17}H_{26}O_2$ m/e 262.1933, found m/e 262.1928.

Anal. Calcd for $C_{17}H_{23}O_2$: C, 77.82; H, 9.99. Found: C, 78.09; H, 9.83.

4-(1,1'-Bibicyclo[2.2.2]octyl)yl Methyl Ketone. A solution of 198 mg (0.754 mmol) of 1,1'-bibicyclo[2.2.2]octyl-4-carboxylic acid in 50 mL of tetrahydrofuran was treated under argon with

3.0 mL of 1.6 M methyllithium in diethyl ether and then refluxed for 0.5 h. The solution was then cooled and transferred under argon, dropwise, into 50 mL of saturated ammonium chloride. Water was added, and the aqueous layer was ether extracted. The combined ether phase was dried, filtered, and concentrated. The residue was recrystallized from ethyl acetate to give 181 mg (90%) of pure (by NMR) 4-(1,1'-bibicyclo[2.2.2]octyl)yl methyl ketone. An analytical sample was prepared by recrystallization from ethanol-methanol (sealed tube), subliming at 280 °C: UV (MCIP) λ_{max} 285 (ϵ 24.1); IR (KBr) 3.41 (vs), 3.50, 5.90 (ms), 6.87, 7.34 (m), 7.43 (m), 7.99 (m), 8.06 (m), 8.16 (m) μm; NMR (CDCl$_3$, WH) τ 7.95 (s, 3 H, CH$_3$), 8.352-8.409 (m, 6 H, CH$_2$), 8.500-8.549 (m, 7 H, CH$_2$ and CH), 8.598-8.628 and 8.656-8.685 (m and m, 12 H total, CH$_2$); mass spectrum (70 eV), m/e (relative abundance) 261 (13.1), 260 (100), 232 (19.6), 231 (99.8), 218 (20.5), 217 (25.1), 123 (13.2), 109 (68.5), 107 (10.2), 95 (15.9), 93 (24.0), 91 (13.9), 81 (26.7), 79 (21.9), 67 (49.6), 55 (18.6), 43 (76.1), 41 (21.5); high-resolution mass spectrum, calcd for $C_{18}H_{28}O$ m/e 260.2140, found m/e 260.2140.

4-(1,1'-Bibicyclo[2.2.2]octyl)yl Phenyl Ketone. A solution of 85.0 mg (0.324 mmol) of 1,1'-bibicyclo[2.2.2]octyl-4-carboxylic acid in 20 mL of tetrahydrofuran was treated under argon with 5.0 mL of 1.15 M phenyllithium in diethyl ether, refluxed for 1 h, and then transferred into 50 mL of a stirred saturated solution of ammonium chloride. The water layer was ether extracted and the ether layer dried (MgSO$_4$), filtered, and concentrated. The solid obtained was chromatographed on a 1 × 42 cm silica gel column, with UV monitoring: fraction 1, 300 mL of hexane, nil; 2, 70 mL of 5% ether in hexane, nil; 3, 20 mL of 5% ether, a mixture of 4-(1,1'-bibicyclo[2.2.2]octyl)yl phenyl ketone and material tentatively identified as 4-(1,1'-bibicyclo[2.2.2]octyl)-yldiphenylcarbinol; 4, 50 mL of 5% ether, 4-(1,1'-bibicyclo-[2.2.2]octyl)yldiphenylcarbinol. The contents of fraction 3 was rechromatographed on a 1 × 35 cm column. After elution of 60 mL of hexane and then of 90 mL of 1% ether in hexane, a band was eluted in 80 mL of 1% ether containing 51.2 mg (0.159 mmol, 49%) of 4-(1,1'-bibicyclo[2.2.2]octyl)yl phenyl ketone, mp 163.2-167.3 °C. An analytical sample was prepared by recrystallization from heptane and then from ethanol: mp 168.6-168.9 °C; UV (MCIP) λ_{max} 238.6 nm (ϵ 6993), 275 (431), 289 (sh, 240), 320 ± 5 (79), tailing out to 360 nm; IR (KBr) 3.42, 3.50 (ms), 6.00, 6.91 (m), 7.76 (m), 7.96 (ms), 10.373 (w), 11.261 (mw), 12.755 (w), 13.831 (m), 14.164 (ms) μm; NMR (CDCl$_3$, MH) τ 2.46-3.00 (m, 5 H, phenyl), 8.08-8.31 (m, 6 H, methylene), 8.39-8.86 (m, 19 H, methylene and methine); mass spectrum (70 eV), m/e (relative abundance) 323 (18.0), 322 (100), 217 (15.6), 183 (26.5), 149 (12.6), 135 (16.1), 121 (15.0), 111 (32.2), 109 (78.6), 105 (82.6), 95 (21.8), 81 (35.1), 77 (45.4), 67 (57.0), 57 (70.6), 55 (56.7), 45 (20.3), 43 (56.3), 41 (73.5); high-resolution mass spectrum, calcd for $C_{23}H_{30}O$ m/e 322.22966, found m/e 322.2297.

Emission and Rate Studies. Sample Preparation. Solutions of analytically pure samples of compounds **9a**, **9b**, **11a**, **11b**, **11c**, *cis*-**12**, **13**, **14**, **15**, **18**, **19**, **25a**, **25b**, **26**, and **32** in fluorescence-free 4:1 (v/v) mixtures of methylcyclohexane and isopentane, generally having an optical density of 0.8, were degassed in quartz cuvettes by repetitive freezing, evacuation, and thawing of the samples. From 10 to 20 such cycles were executed, after which the cuvettes were sealed. UV absorption spectra were then taken to precisely determine the concentration of substrate in each.

Emission. Emission spectra were obtained with an Aminco-Kiers spectrofluorometer equipped with a Hanovia 901C-1 150-W xenon lamp; no correction was made for the wavelength dependence of the photomultiplier response, which was never less than 90% of its maximum value in the region studied.

The naphthyl models behaved as follows:

Degassed solutions of 1-(α-naphthyl)bicyclo[2.2.2]octane (**13**) fluoresced strongly at room temperature. Excitation at 270 nm resulted in an emission band from 298 to 430 nm. The maximum was at 335 (±5) nm.

Degassed solutions of 1-(β-naphthyl)bicyclo[2.2.2]octane (**14**) fluoresced strongly at room temperature. Excitation at 270 nm gave an emission band from 296 to 413 nm with a maximum at 331 (±5) nm.

Degassed solutions of 4-(α-naphthyl)-1,1'-bibicyclo[2.2.2]octyl (**26**) fluoresced strongly at room temperature. Excitation at 275

nm resulted in an emission band from 304 to 415 nm. The maxima of the fine-structured emission were at 323 and 334 nm.

The ketone models behaved as follows:

Degassed solutions of 1-acetylbicyclo[2.2.2]octane (18) fluoresced moderately at room temperature. Excitation at 285 nm resulted in an unstructured emission from 330 to 550 nm with a maximum at 401 nm.

Degassed solutions of 1-(cyclohexanecarbonyl)bicyclo[2.2.2]-octane (19) fluoresced moderately at room temperature. Excitation at 295 nm resulted in emission from 330 to 540 nm, with a maximum at 393 nm.

The bichromophoric compounds behaved as follows:

Degassed solutions of 1-acetyl-4-(α-naphthyl)bicyclo[2.2.2]-octane (9a) fluoresced with an intensity between that of compound 9b and 13, 14, and 15. The emission band began at 292 nm and reached a maximum at 329 (±5) nm. Unlike compounds 13-15, the curve for 9a began to flatten at 368 nm and continued past 408 nm where it began to fall more rapidly. The band extends to 517 nm. The fluorescence intensity at 400 nm is approximately 20% of the intensity at 330 nm.

Degassed solutions of 1-(cyclohexanecarbonyl)-4-(α-naphthyl)bicyclo[2.2.2]octane (9b) fluoresced at room temperature with an intensity weaker than that of 1-acetyl-4-(α-naphthyl)-bicyclo[2.2.2]octane (9a). Excitation at 270 nm gave an emission band from 295 to 525 nm with maxima of approximately equal intensity at 336 ± 5 and 392 ± 5 nm.

Degassed solutions of 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]-octane fluoresced weakly at room temperature. Excitation at 270 nm gave an emission from approximately 300 to 412 nm with a maximum at 331 (±5) nm.

Degassed solutions of 1-acetyl-4-(β-naphthyl)bicyclo[2.2.2]octane (11a) fluoresced weakly at room temperature. Excitation at 265 nm gave an emission from 295 to 520 nm with maxima of approximately equal intensity at 329 ± 5 and 397 ± 5 nm.

Degassed solutions of 1-(cyclohexanecarbonyl)-4-(β-naphthyl)bicyclo[2.2.2]octane (11b) fluoresced at room temperature with an intensity approximately equal to that of 9b. Excitation at 270 nm gave an emission band from 299 to 520 nm with a single maximum at 390 ± 5 nm and with a shoulder of approximately one-third the maximum intensity at 340 ± 5 nm.

Degassed solutions of 1-benzoyl-4-(β-naphthyl)bicyclo[2.2.2]-octane (11c) fluoresced very weakly at room temperature. Excitation at 265 nm gave an emission band from 295 to 420 nm with a maximum at 327 ± 5 nm.

Degassed solutions of 1-(α-naphthyl)-4-(1-cis-propenyl)bicyclo[2.2.2]octane (cis-12) fluoresced strongly at room temperature. Excitation at 270 nm gave emission from 298 to 425 nm, with a maximum at 334 nm.

Degassed solutions of 1,4-bis(β-naphthyl)bicyclo[2.2.2]octane (15) fluoresced strongly at room temperature. Excitation at 270 nm resulted in an emission which extended from 297 to 413 nm. The maximum emission was at 330 (±5) nm.

Degassed solutions of 4-(α-naphthyl)-4'-acetyl-1,1'-bibicyclo-[2.2.2]octyl (25a) fluoresced strongly at room temperature, though somewhat less than naphthyl dimer 26. Excitation between 260 and 310 nm gave emission from 310 to 440 nm, with maxima at 323 and 335 nm.

Degassed solutions of 4-(α-naphthyl)-4'-benzoyl-1,1'-bicyclo-[2.2.2]octyl (25b) fluoresced moderately at room temperature, less than compounds 26 or 25a but more than compound 9a. Excitation at 270 nm results in emission from 312 to 420 nm, with maxima at 323 and 335 nm.

Polarization of Emission. The polarization of the emission from compounds 9a, 11a, 25a, 25b, and 26 was determined at room temperature and at 77 K. The Aminco-Kiers spectrofluorimeter was equipped with Glan prisms in the excitation and emission beams. Polarization of the emission was determined at various wavelengths by the method of Azumi and McGlynn.[45] The results are tabulated in Table IX. No correction was made for instrumental polarization effects.

Rates. Single-Photon Counting Procedure. The procedure and apparatus have been previously described.[3] Both excitation and emission monochromators were used and were adjusted to

(45) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* 1962, *37*, 2413.

Table IX. Polarization of Emission at 77 and 295 K[a]

compd	wave-length of emission, nm	polariza-tion at 77 K	polariza-tion at 295 K
naphthalene	330	0.12	-0.12
α-naphthyl-[2]-rod 26	334	0.24	0.04
α-naphthyl-acetyl-[2]-rod 25a	332	0.16	0.02
α-naphthyl-benzoyl-[2]-rod 25b	333	0.24	0.02
	400	-0.10	
	472	-0.16	b
	505	-0.15	b
α-naphthyl-acetyl-[1]-rod 9a	333	0.27	0.03
	400	0.31	-0.09
	476	-0.22	b
	508	-0.21	b
β-naphthyl-acetyl-[1]-rod 11a	333	0.15	0.05
	400	c	0.10

[a] Polarization taken as equal to $(I_{ee} - I_{eb})/(I_{ee} + I_{eb})$. Values for I_{ee} and I_{eb} were obtained on an Aminco-Bowman spectrophosphorimeter with polarizing prisms interposed in the excitation and emission light path. [b] These emission bands, due to phosphorescence, were not observed at room temperature. [c] This fluorescence was not observed at low temperature.

maintain the photon count rate at less than 1/20th of the lamp frequency, which varied between 18 and 30 KHz in these determinations. Data collection was continued until the maximum number of counts per channel was 2000-10000. Time calibrations were measured by obtaining the lamp flash (Ludox scattering solution) and then a delayed lamp flash with the use of a standardized delay cable.

Deconvolution of Experimental Curves. Both single and double exponential descriptions of excited state decay were attempted for each experiment involving a bichromophoric compound. Wherever a double exponential deconvolution of the data proved feasible, such a treatment also gave the best fit to the data. For all compounds studied, the kinetics of emission were independent of exciting wavelength or of concentration of the sample. A summary of the data is given in the following format. Compound: range of concentrations; range of excitation (ex) wavelengths (nm); range of emission (em) wavelengths (nm); average first rate (lifetime); average second rate (lifetime).

1-(α-Naphthyl)bicyclo[2.2.2]octane (13): (1.20-3.28) × 10⁻⁴ M; ex 270 nm; em 335-350 nm; (1.54 ± 0.06) × 10⁷ s⁻¹ (65.0 ns).

1-(β-Naphthyl)bicyclo[2.2.2]octane (14): (2.29-2.54) × 10⁻⁴ M; ex 265-275 nm; em 300-460 nm; (1.69 ± 0.05) × 10⁷ s⁻¹ (64.2 ns).

4-(α-Naphthyl)-1,1'-bibicyclo[2.2.2]octyl (26): 1.032 × 10⁻⁴ M; ex 250-315 nm; em 300-460 nm; (1.69 ± 0.05) × 10⁷ s⁻¹ (59.2 ns).

1-Acetylbicyclo[2.2.2]octane (18): 3.34 × 10⁻² M; ex 255-315 nm; em 350-480 nm; (3.39 ± 0.21) × 10⁸ s⁻¹ (2.96 ns).

1-(Cyclohexanecarbonyl)bicyclo[2.2.2]octane (19): (0.846-4.08) × 10⁻² M; ex 265-325 nm; em 360-480 nm; (2.14 ± 0.05) × 10⁸ s⁻¹ (4.68 ns).

1-(α-Naphthyl)-4-acetylbicyclo[2.2.2]octane (9a): (1.098-2.27) × 10⁻⁴ M. The data for this compound is expressly detailed in Table X.

1-(α-Naphthyl)-4-(cyclohexanecarbonyl)bicyclo[2.2.2]octane (9b): (1.71-2.26) × 10⁻⁴ M. The data for this compound is expressly detailed in Table XI.

1-(α-Naphthyl)-4-benzoylbicyclo[2.2.2]octane (32): (1.76-2.24) × 10⁻⁴ M; ex 270-295; em 335; (4.0 ± 0.8) × 10⁹ s⁻¹ (0.25 ns).

1-(β-Naphthyl)-4-acetylbicyclo[2.2.2]octane (11a): (1.22-3.47) × 10⁻⁴ M. The data for this compound is expressly detailed in Table XII.

1-(β-Naphthyl)-4-(cyclohexanecarbonyl)bicyclo[2.2.2]octane (11b): (2.28-2.85) × 10⁻⁴ M; ex 275; em 340; 3.9 × 10⁹ s⁻¹ (0.256 ns); 1.48 × 10⁸ (6.76 ns); ex 270; em 355-415; 1.7 × 10⁸ s⁻¹ (5.9 ns).

1-(β-Naphthyl)-4-benzoylbicyclo[2.2.2]octane (11c): 1.97 × 10⁻⁴ M. Emission from this compound was too weak to permit rate determination either at room temperature or at 77 K.

Table X. Rate Data for α-Naphthyl-acetyl-[1]-rod 9a

excitation	emission	amplitude	rate, s⁻¹	ratio of amplitudes
270	335	0.031	1.87×10^9	1.2:1
		0.0256	4.75×10^8	
270	335	0.035	2.36×10^9	1.3:1
		0.027	4.54×10^8	
280	335	0.046	3.53×10^9	1.6:1
		0.029	5.05×10^8	
270	330	0.081	4.89×10^9	3:1
		0.027	4.80×10^8	
280	350	0.052	3.102×10^9	2.2:1
		0.0234	4.80×10^8	
270	355	0.0269	7.93×10^8	1.9:1
		0.0139	2.84×10^8	
270	370		2.808×10^8	
270	370		2.645×10^8	
270	380		2.375×10^8	
270	390		2.288×10^8	
270	405		2.268×10^8	
270	400	−0.079	1.40×10^9	−1.3:1
		+0.062	2.85×10^8	
270	420	−0.065	1.86×10^9	−1.25:1
		+0.052	2.51×10^8	
270	440	−0.080	1.39×10^9	−1.3:1
		+0.051	2.54×10^8	
270	460	−0.064	1.98×10^9	−1.25:1
		+0.051	2.54×10^8	

Table XI. Rate Data for α-Naphthyl-cyclohexanecarbonyl-[1]-rod 9b

excitation	emission	amplitude	rate, s⁻¹	ratio of amplitudes
270	325	0.0969	2.239×10^9	51:1
		0.001899	1.63×10^8	
270	330	0.0800	1.336×10^9	40:1
		0.00202	1.496×10^8	
270	345	0.109	1.67×10^9	11:1
		0.0097	1.75×10^8	
270	355	0.065	1.72×10^9	4.0:1
		0.016	1.66×10^8	
280	355	0.048	1.60×10^9	3.0:1
		0.0158	1.79×10^8	
290	355	0.028	8.82×10^8	1.8:1
		0.015	1.73×10^8	
270	360	0.0437	1.437×10^9	1.8:1
		0.0247	1.687×10^8	
270	385	−0.0491	1.337×10^9	−1.47:1
		+0.0335	1.61×10^8	
270	420	−0.0544	1.165×10^9	−1.23:1
		+0.04427	1.746×10^8	

1-(α-Naphthyl)-4-(1-*cis*-propenyl)bicyclo[2.2.2]octane (*cis*-12): (1.24–3.22) × 10⁻⁴ M; ex 270; em 335; (1.55 ± 0.03) × 10⁷ s⁻¹ (64.5 ns).

1,4-Bis(β-naphthyl)bicyclo[2.2.2]octane (15): (0.809–1.256) × 10⁻⁴ M; ex 265–275; em 330–335; (1.56 ± 0.09) × 10⁻⁷ s⁻¹ (64.1 ns).

4-(α-Naphthyl)-4'-acetyl-1,1'-bibicyclo[2.2.2]octyl (25a): (0.0869–1.176) × 10⁻⁴ M; ex 240–315; em 290–470; (2.20 ± 0.09) × 10⁷ s⁻¹ (45.5 ns).

Table XII. Rate Data for β-Naphthyl-acetyl-[1]-rod 11a

excitation	emission	amplitude	rate, s⁻¹	ratio of amplitudes
275	340	0.185	3.59×10^9	35:1
		0.00532	2.08×10^8	
275	350	0.187	4.452×10^9	16:1
		0.0115	2.386×10^8	
265	355	0.2337	6.12×10^9	18:1
		0.0128	2.29×10^8	
275	355	0.02139	2.76×10^9	1.6:1
		0.01377	2.37×10^8	
285	355	0.1068	2.76×10^9	7:1
		0.0143	2.37×10^8	
275	360	0.0932	3.08×10^9	5:1
		0.0180	2.30×10^8	
275	365	0.0386	1.666×10^9	1.6:1
		0.0232	2.518×10^8	
275	380		2.91×10^8	
275	395	−0.0956	4.297×10^9	−2.4:1
		+0.0397	2.667×10^8	

4-(α-Naphthyl)-4'-benzoyl-1,1'-bibicyclo[2.2.2]octyl (25b): 9.98 × 10⁻⁵ M; ex 240–315; em 310–450; (1.20 ± 0.03) × 10⁸ s⁻¹ (8.32 ns).

A detailed description of the rate behavior, including the variance of the preexponential coefficients, is given for compounds 9a, 9b, and 11a in Tables X–XII, respectively.

Cis-Trans Photoisomerization of 1-(α-Naphthyl)-4-(1-*cis*-propenyl)bicyclo[2.2.2]octane. Irradiations were performed on the microoptical bench described previously.[46] The runs were analyzed by vapor-phase chromatography (0.64 × 150 cm, 5% QF-1 on Chromosorb P, 180 °C). Irradiation of 0.0046 mmol (1.28 mg) of 1-(α-naphthyl)-4-(1-*cis*-propenyl)bicyclo[2.2.2]octane in 40 mL of *tert*-butyl alcohol for 6.0 h gave no cis–trans isomerization (Φ ≤ 0.007).

(46) (a) Zimmerman, H. E. *Mol. Photochem.* 1971, *3*, 281. (b) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. *J. Ibid.* 1977, *8*, 379.