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Rodlike Molecules and Singlet Energy Transfer[1,2]

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In continuing our investigations on rodlike molecules composed of bicyclo[2.2.2]octane units, we studied the effect of interposing a single aromatic ring in the rod. Thus, two [3]-rods were synthesized with the two outer units being bicyclooctyls, the central unit being benzenoid, and with one terminal unit bearing an α-naphthyl moiety and the other terminus bearing an acetyl or benzoyl group. Excitation of the α-naphthyl group led to fluorescence emission by both the naphthyl and the acetyl units. However, compared to the [1]- and [2]-rods previously studied, transmission of singlet excitation proved to be less efficient as determined by the fluorescence emission and also by the singlet lifetimes obtained from single photon counting measurement. Transmission to the benzoyl group proved more rapid than to the acetyl moiety. In assessing the factors controlling energy transmission, Δ-density determinations were employed to describe the distribution of electronic excitation in such systems. It was observed that despite most of the energy being located in the terminal chromophores, some is distributed in the bicyclooctyl units. The extent of this distribution provides a guide to the facility of through-bond energy transfer. Evidence is presented that energy transfer in the short rods is mainly through-bond while in the longer rods Förster through-space transfer is involved.

Introduction

Our interest in the transmission of electronic excitation as well as electron transfer through saturated rodlike moieties goes back very close to three decades.[3] Throughout, these studies have employed bicyclo[2.2.2]octyl moieties fused bridgehead to bridgehead as separators between two chromophores at the terminal bridgehead sites.[3−5] The rod compounds most commonly had a naphthyl group bonded to the bridgehead carbon at one end of a [1]- or [2]-rod and a keto group (e.g., as in acetyl, benzoyl, cyclohexanecarbonyl) at the other terminus. In our original publication,[3] evidence was adduced for singlet energy transfer from a naphthyl group at one end to the acetyl group at the other while triplet energy transfer was found to occur in the reverse direction. The directionality of transfer is controlled by the excited-state energetics. Thus naphthyl S1 energy > benzoyl S1 and acetyl S1,[6] while for the triplet the converse is true. In these papers we described the molecular rods as "light pipes" since emission could be observed from the acceptor moiety. Additionally, the rates of singlet energy transfer were obtained by use of a single photon counting technique and dissection of the emission rate constant data. We have not been alone in studying energy transfer through saturated moieties. For example, there is the elegant work by Michl with Staffane rods.[7] In some instances, irregularly shaped separators have also been termed rods (vide infra). Finally, more recently we have extended our synthesis to prepare [3]-rod and [4]-rod compounds.[5] It was of interest to ascertain the effect of interposing an aromatic ring. This study involves four aspects: (a) The synthesis of [3]-rods with the interposed aromatic ring, (b) measurement of energy transfer by use of single photon counting, (c) a new theoretical tool for prediction of through-bond energy transfer, and (d) correlation of through-bond and through-space contributions with rod length.

Results

Synthesis. The synthesis of [3]-rods is outlined in Schemes 1 and 2. In these syntheses the inverse addition of bicyclic iodides to *tert*-butyllithium was important, since the role of the second equivalent of the lithium compound was to destroy *tert*-butyl iodide formed and thus *tert*-butyllithium needed to be in excess throughout to avoid consumption of bridgehead lithium reactant. One example is the conversions of the 4-benzoyl-1-iodobicyclo[2.2.2]octane ketal **12** and its acetyl counterpart **13** to the bridgehead lithium derivatives which required inverse addition. In another difficult step the conversion

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[1] This is Paper 192 of our photochemical series and Paper 258 of our general series.

[2] For Paper 257, see: Zimmerman, H. E.; Alabugin, I. V.; Smolenskaya, V. N. *Tetrahedron* Symposium-in-Print, **2000**, *56*, 6821−6831.

[3] Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638−3645.

[4] (a) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933−3951. (b) Zimmerman, H. E.; Penn, J. H.; Carpenter, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2128−2132.

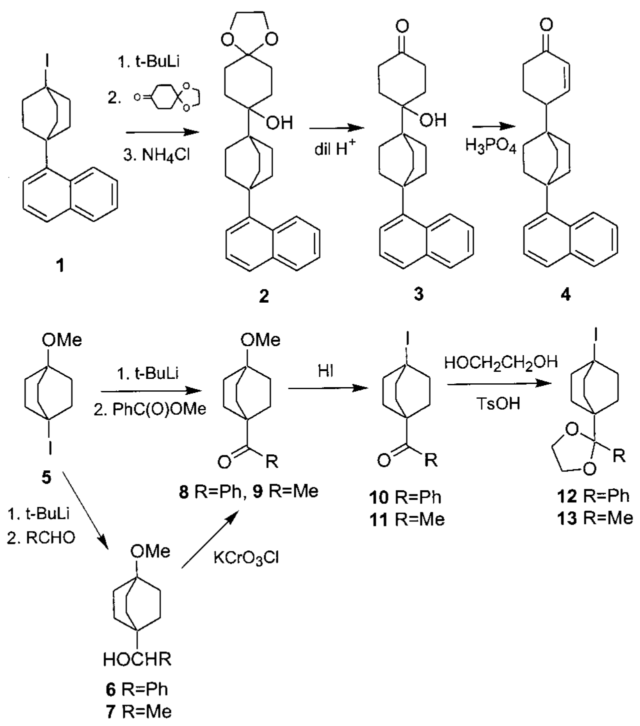
[5] Zimmerman, H. E.; King, R. K.; Meinhardt, M. B. *J. Org. Chem.* **1992**, *57*, 5484−5492.

[6] (a) For benzoyl and naphthyl singlet energies there is general agreement.[6b,c] (b) Benzoyl, 79 kcal/mol, Murov, S. L. *Handbook of Photochemistry*, 2nd. ed.; Marcel Dekker: New York, 1993. (c) Naphthyl, 90 kcal/mol, *Idem*. (d) Acetyl, 84 kcal/mol, Dalton, J. C.; Turro, N. J. *Annu. Rev. Phys. Chem.* **1970**, *21* 499−560. (e) Contrast the 102 kcal/mol acetyl value given by Dewar, M. J. C. et al. *J. Comput. Chem.* **1984**, *5*, 480−485. (d) In any case, the more favorable exothermic naphthyl to benzoyl compared with naphthyl to acetyl transfer accounts for the greater rate in the benzoyl example. A greater transition dipole for benzoyl excitation is an added factor; the extinction coefficient for acetophenone is 40 and for acetone is 14 (both n-π*).[6b]

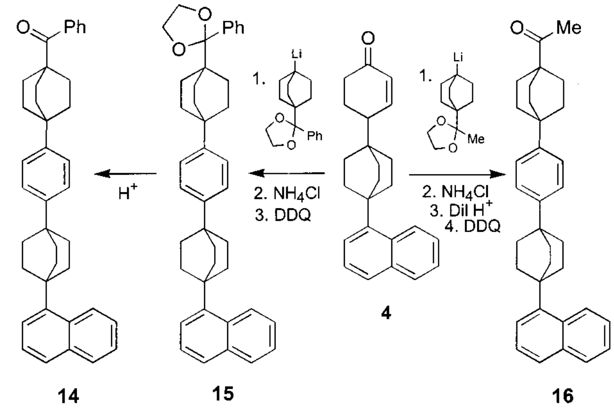
[7] (a) See ref 7b for an excellent review of rod-chemistry; (b) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *1863*, 3−1933.

10.1021/jo0003145 CCC: $19.00

Scheme 1. Synthesis of [3]-Rod Precursors



Scheme 2 The Final Steps in the Acetyl and Benzoyl [3]-Rod Syntheses



of the γ-hydroxyketone **3** to enone **4** required optimization to obtain reasonable yields. Still another reaction which required optimization was the deprotection of ketal **15** where the normal mild conditions used for ketals did not suffice and more strenuous conditions were required. This presumably arises from the conformation of the ketal enforced by considerable steric hindrance. Finally, the known[4] 1-bicyclooctylnaphthalene (**26**) was needed as a reference compound.

Emission and Single Photon Counting Measurement of Lifetimes. Absorption and fluorescence spectra for the 1-naphthyl-[1]-rod **26**, the acetyl-[3]-rod **16**, and the benzoyl-[3]-rod **14** were obtained. In the absorption spectra, the strong maxima at 230 and 280 nm are characteristic of naphthyl compounds. Fluorescence emission strong peaks were seen at 340 nm, again characteristic of naphthyl emission. No acetyl or benzoyl fluorescence emission peaks were observed; these n-π^* bands are anticipated to be weak and, if present, would be obscured by the intense naphthyl absorption and emission. These spectroscopic data are listed in Table 1.

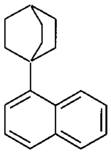
Table 1. Absorption and Emission Data

compound	cbsorption maxima (nm) and extinction coefficients	fluorescence maxima (nm)[a]
naphthyl-[1]-rod **26**	228 (20600) 282 (12400)	325 (340)
benzoyl-[3]-rod **14**	226 (27000) 282 (2600)	325 (340)
acetyl-[3]-rod **16**	226 (24000) 282 (6900)	325 (340)

[a] The 0–0 fluorescence peaks are followed by the fluorescence maxima in parentheses.

The singlet lifetimes were measured using the apparatus described in our earlier publication.[4] The fluorescence emission data were subjected to deconvolution as earlier[8] but with modifications. Thus, a 916A EG&G Ortec multichannel analyzer board with 2048 channels was used with a PC for data collection in the form of counts per channel. Also note the Experimental and Supporting Information Sections. These data were transmitted to a VAX. Deconvolution programming, termed “Photon”, was written in Fortran based on the algorithm described in our earlier study.[8] The results obtained for singlet lifetimes and decay rates are summarized in Table 2.

In Table 2, the 1-naphthyl-[1]-rod **26** is a reference compound and its lifetime is very close to that of typical 1-substituted alkyl naphthalenes. The decay rate of the benzoyl rod compound was more rapid than this reference compound. This difference is due to energy transfer to the carbonyl energy acceptor. Quantitatively, the rate difference gives the rate of energy transfer (i.e., k_{ET}).[4] Quite often it is convenient to think in terms of the reciprocals of the decay rate constants, namely the excited-state lifetimes. Here we note that the 58 ns lifetime of **26** is close to the 67 ns value reported[9] for 1-methylnaphthalene but shorter than the 97 ns reported for naphthalene itself.[9] The lifetimes and rates of decay for the 1-naphthyl-[1]-rod **26** and the acetyl-[3]-rod **16** are virtually within experimental error of one another (i.e., 58 and 55 ns, respectively). In contrast, the benzoyl-[3]-rod **14** has a shorter lifetime (41 ns) and a more rapid rate of decay which is approximately 1.4 times that of the reference compound.[6]



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Computational and Discussion. To understand better the electronic interaction of bridgehead groups with the bicyclooctane units, we carried out ab initio computations of the rods of interest. For this we employed the delta-density matrix approach[10] which gives the distribution of excitation. The method takes the difference between the excited state and ground-state density

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(8) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5094–5095.

(9) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

(10) (a)Zimmerman, H. E.; Alabugin, I. V. *J. Am. Chem. Soc.* **2000**, *121*, 952–953. (b) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* **1978**, 228–230.

Table 2. Single Photon Counting Data[a]

compound	lifetime ($\tau_{1/2}$), ns	decay rate, s^{-1}	no. of runs
naphthyl-[1]-rod **26**	57.9 ± 0.5	$(1.73 \pm 0.02) \times 10^7$	6
acetyl-[3]-rod **16**	55.0 ± 0.8	$(1.82 \pm 0.03) \times 10^7$	7
benzoyl-[3]-rod **14**	40.5 ± 0.4	$(2.47 \pm 0.02) \times 10^7$	5

[a] All runs in cyclohexane; Concentrations: 1-naphthalene-[1]-rod 9.3×10^{-5} M, acetyl-[3]-rod 7.2×10^{-5} M, benzoyl-[3]-rod 7.0 $\times$ 10^{-5} M; Relative std deviations are 0.01, 0.02, and 0.01, respectively.

matrixes obtained for a reactant by ab initio computation. D^*_{rt} and D^o_{rt} terms are the excited and ground-state local electron densities and r and t refer to two Weinhold NHO hybrid orbitals.[11] The S_{rt} terms are overlap integrals which take into account both distance effects and also the orientation of hybrids. The matrix elements, ΔD_{rt}, of the Delta Density Matrix are defined as in eq 1. Each element gives fractional electron density increase or decrease resulting from excitation.

$$\Delta D_{rt} = D^*_{rt}S^*_{rt} - D^o_{rt}S^o_{rt} \tag{1}$$

The diagonal terms afford one-center electron density changes, and each off-diagonal ΔD term gives the change in electron density between a pair of orbitals on excitation. The off-diagonal terms may be thought of as modified bond orders and indications of the excitation energies of the various bonds. For the most part these terms will be negative (i.e., antibonding compared with ground state) indicating concentration of the energy of excitation. A few bonds may be strengthened with lowering of that local energy but most have to be negative as a consequence of the increase in total energy on excitation. Where ΔD elements are zero, there is no excitation. Accordingly, the method is useful in giving the distribution of electronic excitation energy in a molecule. In the present instance of intrarod energy transfer the method then gives an indication of the role of the through-bond component.

For the systems of present interest, the Δ-Density values are given in Figure 1. Computations were carried out for the simple 1,4-dibicyclooctylbenzene **19**, i.e., the basic [3]-rod, the 1-acetyl-4-α-naphthyl-[1]-rod **17**, the 1-benzoyl-4-α-naphthyl-[1]-rod **18**, the 1-benzoyl-4-α-naphthyl-[3]-rod **14**, and the 1-acetyl-4-α-naphthyl-[3]-rod **16**. In the cases of the [1]-rods, 6-31G* was used as a basis in CASSCF with an active space of (6,6). For the [3]-rods, we employed 3-21G* as a practical and reasonable choice. The choice of basis sets and active space was predicated on accessible computation times. However, the adequacy of active space was checked by variation in configurations included, and the choice of basis sets was checked by comparison with earlier computations using more primitive basis sets (e.g., 3-21G with no polarized contributions). In both instances, the Δ-Density values varied only minimally.

What these computations revealed (Figure 1) is that excitation is not localized in the terminal chromophores of the 1,*n*-disubstituted rods nor in the central aromatic ring of the simple [3]-rod **19**. Small but real Δ-Density Matrix elements are found in the bicyclooctyl spacer units. The larger sigma contributions come from bonds which are close to coplanar with the *p*-orbitals of the π-systems. Hence, we find delocalization of excitation, albeit small, throughout the system.[12] Appreciable excitation distribution is seen in all of the different rod compounds—namely the [1]-rods, [2]-rods, and [3]-rods. Thus, the much smaller diminution of lifetime of the naphthyl group in the [3]-rods of the present study cannot be attributed solely to diminished delocalization. The remaining factor is the dependence of transition dipole (i.e., Förster coupling) on distance between the chromophores. In the case of the [1]-rod previously studied[4] the very rapid singlet energy transfer was shown to be too fast to result purely from transition dipole coupling (vide infra). We concluded that both through-bond and through-space electronic transmission occurs with through-bond being dominant at short distances and through-space at long distances.[4a]

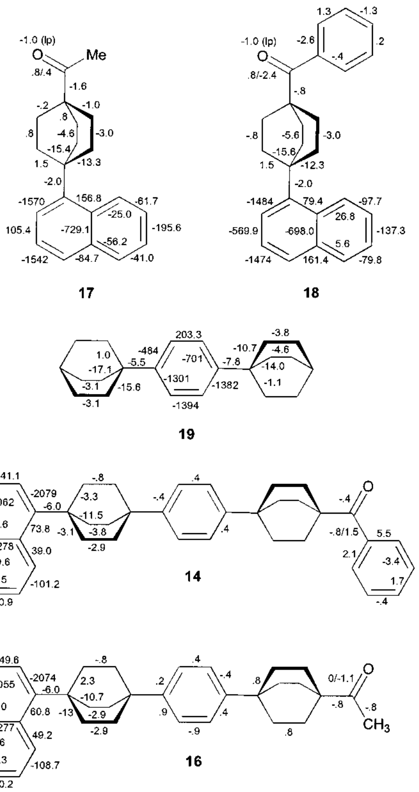

Figure 1. Delta-density values for rod compounds. Where bonds have no values indicated, these are vanishing. "/" gives σ- and π-values in that order. ΔD matrix values are expanded by 10000.

$$k_{ET}(1) = \frac{a}{R(1)^6} + be^{-\beta R(1)} = A1 + B1 \tag{2}$$

$$k_{ET}(2) = \frac{a}{R(2)^6} + be^{-\beta R(2)} = A2 + B2 \tag{3}$$

$$k_{ET}(3) = \frac{a}{R(3)^6} + be^{-\beta R(3)} = A3 + B3 \tag{4}$$

Equations 2, 3, and 4 give the total rate of energy transfer for each of the rods − [1]-rod, [2]-rod or [3]-rod, respectively. These are given as having two components, the Förster through-space portion with an inverse sixth power dependence on chromophore distance, *R*, and the through-bond component, having a negative exponential

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[11] (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218. (b) Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

Table 3. Decay and Energy Transfer Rates for Three Benzoyl Rods

compd	k_{ET}, s^{-1}	through-space (A) k_{ET}, s^{-1}	through-bond (B) k_{ET}, s^{-1}	distance, Å	A:B[b]
[1]-rod[a]	3.98×10^9	7.78×10^8	3.20×10^9	7.14	20:80
[2]-rod[a]	1.03×10^8	5.14×10^7	5.16×10^7	11.23	50:50
[3]-rod	7.4×10^6	6.9×10^6	5.2×10^5	15.70	93:7

[a] From ref 4. [b] Ratio of through-space to through-bond contributions as given in eqs 2, 3, and 4. [c] Values for a, b, and β are 1.03×10^{14}, 4.36×10^{12}, and 1.01 Å^{-1}, respectively.

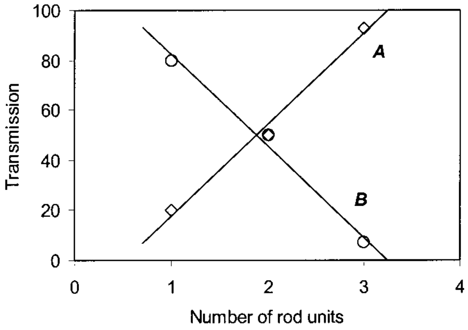

Figure 2. Plot of through-space (A) and through-bond (B) contributions versus number of rod units.

dependence. With three equations of this form and three unknowns—a, b, and β—at most two solutions are possible;[13] note Supporting Information. In this case of the two solutions, only one was physically real. The solution obtained is given in Table 3. Here A gives the weighting of the inverse sixth power Förster contribution while B gives the negative exponential through-bond Dexter transmission.[14] The details of the computations are given in the Supporting Information. Interestingly, a plot of the through-space and through-bond contributions, A and B, against number of rod units is linear; note Figure 2. Furthermore, we see that for the short rod, through-bond energy transmission dominates while for the longer rod through-space is the major contributor. For the [2]-rod, both factors seem to contribute equally.[15]

Conclusion

The energy transfer studies begun nearly three decades ago have been fruitful and have stimulated studies with many different types of systems. The present study reveals that both Förster (through-space) and Dexter exchange (through-bond) transfer participate with the through-bond transfer being dominant in short rods while the Förster transfer becomes dominant for long rods. With both mechanisms being operative, there is no controversy remaining.

Experimental Section

1,4-Dioxaspiro[4.5]decan-8-one (20). (a) Utilization of the method of Crombie et al.[18a] gave **20** as a white solid after recrystallization from hexane (yield 26%), mp 72−73 °C (lit.[18a] mp 72.5−73.5 °C).

(b) The method of Salaün et al.[18b] was employed to give **20** as a white solid after recrystallization from hexane, mp 72−73 °C (lit.[18b] 73 °C). From 7.36 g (36.8 mmol) of cyclohexane-1,4-dione bisethylene ketal, 3.27 g of anhydrous FeCl$_3$, 41 g of SiO$_2$, and 10 mL of 41% aqueous formaldehyde solution mixed for 1 h, ether extracted, and chromatographed with silica gel was obtained 4.94 g (86%) of **20**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.04 (s, 4H), 2.52 (t, 4H, J = 7.2 Hz), 2.02 (t, 4H, J = 7.2 Hz).

1-Iodo-4-(α-naphthyl)bicyclo[2.2.2]octane (1) and 1-Iodo-4-(β-naphthyl)bicyclo[2.2.2]octane (21). A mixture of 8.87 g (35.2 mmol) of 4-iodobicyclo[2.2.2]octan-1-ol[4] **22**, 21.3 g (166.2 mmol) of naphthalene, and 8.8 mL of CH$_3$SO$_3$H was stirred at 110 °C for 3 h. After the mixture was 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. The majority of the naphthalene was removed by sublimation. The remaining mixture was chromatographed on a silica gel column with hexane to give 9.69 g (76%) of a mixture of the isomers **1** and **21** in ratio 1.5:1.0. The crystallization from hexane formed two different kinds of crystals: the α-isomer **1** gave colorless prisms while the β-isomer **21** formed colorless needles. Two of these cycles afforded 5.0 g (39%) of pure 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane **1**, mp 164 °C (lit.[4] 164−165.5 °C); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.38 (dm, 1H, J = 8.4 Hz),7.86 (dd, 1H, J_1 = 7.8, J_2 = 1.8 Hz), 7.70 (dm, 1H, J = 7.8 Hz), 7.46 (m, 2H), 7.41 (t, 1H, J = 7.8 Hz), 7.28 (dd, 1H, J_1 = 7.2, J_2 = 1.2 Hz), 2.71 (m, 6H), 2.35 (m, 6H); and 3.3 g (26%) of pure 1-iodo-4-(β-naphthyl)bicyclo-[2.2.2]octane **24**, mp 167−168 °C (lit.[4] 168.5−169 °C); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.77 (m, 3H), 7.60 (s, 1H), 7.42 (m, 3H), 2.64 (m, 6H), 2.08 (m, 6H).

4-Hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)-cyclohexan-1-one 1,2-ethanediyl Ketal (2). (a) A 0.62 mL (1.054 mmol) portion of 1.7 M solution of *tert*-butyllithium in pentane was added with a syringe to a stirred suspension of 0.2 g (0.552 mmol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane **1** in 9.3 mL of ether at −70 °C. After the pale yellow solution was stirred for 45 min, a solution of 0.083 g (0.53 mmol) of cyclohexane-1,4-dione 1,2-ethanediyl ketal **20** in 2.4 mL of ether was added with a syringe. The yellow color immediately disappeared, and the mixture was allowed to warm to −50 °C for 30 min, kept at this temperature for 1.5 h, and left at room-temperature overnight. A 10 mL portion of saturated aqueous ammonium chloride was added, and the aqueous layer was ether extracted (3 portions of 10 mL) and combined with the ether layer. The precipitate formed was filtered off, connected with the combined organic phase, and chromatographed on a silica gel 5 × 30 cm column eluted subsequently with hexane,

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(12) The ΔD values are meaningful to five significant figures as the density matrix elements arise from multiplication of two four digit numbers. It needs to be recognized that the Δ-density elements derive from products of two MO coefficients, each with an absolute value less than zero. Thus these elements rapidly decrease as the effect of excitation on the wave function decreases. Our contention is that such small elements account for leakage from chromophore to chromophore.

(13) The basis of this conclusion comes from Dr. Olga Holtz of the Mathematics Department, University of Wisconsin, to whom we are indebted.

(14) (a) Note, the work of Dexter[14b] involved triplet energy transfer by an electron exchange mechanism while the singlet counterpart has been treated theoretically with parallel theory by the present author.[4] We also note that despite different terminology, "through-bond mechanisms" correspond to the "exchange processes". (b) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836−850.

(15) The linearity of each contribution with number of spacer units is of real interest. Some precedence is seen in the work of Closs[16a] who used number of coplanar sigma bonds to correlate with through-bond interaction. Further authors[16b−d] have used the same approach with respect to through-bond interactions.[17]

(16) (a) Closs, G. L., Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652−2653. (b) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Cotsaris, E. *Chem. Phys. Lett.* **1988**, *143*, 488−495. (c) Schlicke, B.; Belser, P.; De Cola, L.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207−4214. (d) Kroon, J.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 4868−4873. (e) The studies in refs 16a,c deal with triplet energy transfer while those in refs 16b,d involve singlet energy transfer.

(17) (a) It needs to be noted that the idea that delocalization involves both σ- and π-systems derives heavily from the pioneering observations of Hoffmann;[17b] (b) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397−1412.

(18) (a) Crombie, W. M. L.; Jamieson, S. V.; Tuchinda, P.; Whitaker, A. J. *J. Chem. Soc., Perkin Trans.* **1982**, 1485−1496. (b) Fadel, A.; Yefsah, R.; Salaün, J. *Synthesis* **1987**, 37−40.

ether, and chloroform. The first fraction contained 0.063 g (48%) of 1-(α-naphthyl)bicyclo[2.2.2]octane **26**. The spectral data of **26** were the following: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 8.45 (m, 1H), 7.90−7.50 (m, 2H), 7.50−7.20 (m, 4H), 2.00−2.02 (m, 6H), 2.90−1.60 (m, 7H). The second fraction after evaporation of the solvent afforded 0.074 g (34%) of 4-hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohexan-1-one 1,2-ethanediyl ketal **2**. Crystallization from 50% benzene in hexane gave colorless crystals, mp 245−246 °C. The spectral data were the following: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 8.45 (m, 1H), 7.85 (m, 1H), 7.70 (m, 1H), 7.60−7.30 (m, 4H), 3.95 (s, 4H), 2.20 (m, 6H), 2.05−1.50 (m, 14H), 1.05 (s, 1H); MS *m/e* 392.2362 (calcd for C$_{26}$H$_{32}$O$_3$, 392.2351). Anal. Calcd for C$_{26}$H$_{32}$O$_3$: C, 79.56; H, 8.22. Found: C, 80.11; H, 8.38.

(b) To a mixture of 4.2 mL (7 mmol) of 1.7 M solution of *tert*-butyllithium in pentane and 14 mL of ether stirred at −70 °C was added a solution of 1.22 g (3.37 mmol) of 1-iodo-4-(α-naphthyl)bicyclo[2.2.2]octane **1** in 50 mL of ether (benzophenone ketyl dried) dropwise with a syringe. After the resulting pale yellow solution was stirred for 30 min, a solution of 0.6 g (3.8 mmol) of cyclohexane-1,4-dione 1,2-ethanediyl ketal **20** in 15 mL of ether was added dropwise with a syringe. The mixture was allowed to warm to −50 °C for 30 min, kept at this temperature for 1 h, and then left at room-temperature overnight. A 10 mL portion of saturated aqueous ammonium chloride was added, and the aqueous layer was ether extracted (3 portions of 10 mL) and combined with the organic layer. The precipitate formed was filtered off, connected with the combined organic phase, and chromatographed on a silica gel 5 × 60 cm column eluted subsequently with hexane, ether, and chloroform. The first fraction contained 0.288 g (36%) of 1-(α-naphthyl)bicyclo[2.2.2]octane **26**. The second fraction after evaporation of the solvent afforded 0.814 g (62%) of 4-hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohexan-1-one 1,2-ethanediyl ketal **2**. The compounds obtained were identical those, described by method a.

4-Hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohexan-1-one (3). A suspension of 0.344 g (0.875 mmol) of 4-hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohexan-1-one 1,2-ethanediyl ketal **2** in 10 mL of ether was stirred with 10 mL of 50% aqueous sulfuric acid for 2 h and neutralized with solid sodium bicarbonate until no foaming was observed, and the ether was removed by evaporation. The precipitate formed was filtered off, water washed, and dried on air. It gave 0.306 g (100%) of 4-hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohexan-1-one **3**, which was crystallized from benzene as colorless crystals, mp 223−225 °C. The spectral data were the following: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 8.42 (m, 1H), 7.87 (m, 1H), 7.71 (m, 1H), 7.51−7.35 (m, 4H), 2.78 (dt, 2H), 2.35−2.15 (m, 8H), 2.15−1.70 (m, 10H), 1.35 (s, 1H); MS *m/e* 348.2089 (calcd for C$_{24}$H$_{28}$O$_2$, 348.2089). Anal. Calcd for C$_{24}$H$_{28}$O$_2$: C, 82.72; H, 8.10. Found: C, 82.65; H, 8.19.

4-(4-(α-Naphthyl)bicyclo[2.2.2]octyl)cyclohex-2-enone (4) and 4-(4-(α-Naphthyl)bicyclo[2.2.2]octyl)cyclohex-3-enone (23). A 0.048 g (0.14 mmol) portion of 4-hydroxy-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohexan-1-one **3** was stirred with 2.0 g (20 mmol) of 85% phosphoric acid for 5.5 h at 75 °C. The mixture was treated with 1 mL of water, neutralized with saturated aqueous sodium hydrocarbonate until no foaming was observed, and ether extracted (3 × 10 mL). The organic phase was dried with sodium sulfate. The solvent was evaporated, and the residue was chromatographed on a silica gel 5 × 30 cm column eluted subsequently with hexane, 20% ether in hexane, 50% ether in hexane, and pure ether. Fraction 1 gave 0.0079 g (17%) of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-3-enone **23**. Fraction 2 gave 0.024 g (52%) of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-2-enone **4**. Fraction 3 contained 0.0077 g (16%) of the starting alcohol **3**, identical to the authentic sample. Crystallization of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-3-enone **23** from 20% ether in hexane gave colorless crystals, mp 157 °C. The spectral data were the following: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.45(m, 1H), 7.90 (m, 1H), 7.70 (m, 1H), 7.50−7.30 (m, 4H), 5.50 (m, 1H), 2.90 (m, 2H), 2.6−2.0 (m, 10H), 1.9−1.6 (m, 6H); ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 8.50(m, 1H), 7.75 (m, 1H), 7.60 (m, 1H), 7.40−7.20 (m, 4H), 5.15 (m, 1H), 2.65 (m, 2H), 2.2−1.9 (m, 10H), 1.5−1.35 (m, 6H); MS *m/e* 330.1976 (calcd for C$_{24}$H$_{26}$O, 330.1984). Anal. Calcd for C$_{24}$H$_{26}$O: C, 87.23; H, 7.93. Found: C, 87.46; H, 8.08. Crystallization of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-2-enone **4** from hexane gave colorless crystals, mp 138−140 °C. The spectral data were the following: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 8.43 (m, 1H), 7.87 (m, 1H), 7.71 (m, 1H), 7.50−7.35 (m, 4H), 7.12 (dt, 1H, $J_1 = 10.5$, $J_2 = 1.9$ Hz), 6.07 (dd, 1H, $J_1 = 10.5$, $J_2 = 2.9$ Hz), 2.57 (dt, 1H), 2.37 (ddd, 1H, $J_1 = 16.5$, $J_2 = 14.2$, $J_3 = 5.0$ Hz), 2.23 (m, 6H, $J = 7.7$ Hz), 2.12 (m, 1H), 1.72 (m, 8H); MS *m/e* 330.1995 (calcd for C$_{24}$H$_{26}$O, 330.1984). Anal. Calcd for C$_{24}$H$_{26}$O: C, 87.23; H, 7.93. Found: C, 86.98; H, 8.33.

4-Iodo-1-methoxybicyclo[2.2.2]octane (5). The method of Zimmerman et al.[4] was employed to give **5** as a white solid, mp 78−79 °C (lit.[4] mp 77.4−79.4 °C); ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.14 (s, 3H), 2.54(m, 6H), 1.76 (m, 6H).

(4-Methoxybicyclo[2.2.2]octyl)phenylcarbinol (6). To a stirred suspension of 0.207 g (0.77 mmol) of 1-iodo-4-methoxybicyclo[2.2.2]octane **(5)** in 5 mL of ether at −70 °C was added 0.90 mL (1.55 mmol) of 1.7 M pentane solution of *tert*-butyllithium with a syringe. The solution was stirred at −70 °C for 45 min, and 0.79 mL (0.824 g, 7.77 mmol) of benzaldehyde (freshly distilled from calcium hydride) was added with a syringe. The mixture was allowed to warm to room temperature for 30 mi and then was poured into 5.0 mL of saturated aqueous ammonium chloride. The aqueous layer was extracted with chloroform (3 × 10 mL). The combined organic phase was water washed, dried with sodium sulfate, and concentrated in vacuo to give an oil, which was chromatographed on a silica gel 5 × 30 cm column and eluted subsequently with hexane and 25% ether in hexane. The obtained material (119 mg) was crystallized from hexane to give 0.060 g of (4-methoxybicyclo[2.2.2]octyl)phenylcarbinol **6**, mp 114−115 °C. The mother solution was chromatographed under the same conditions to give additional 0.030 g of the alcohol **6**. The total yield of (4-methoxybicyclo[2.2.2]octyl)phenylcarbinol **6** was 0.090 g (47%). The spectral data for **6** were the following: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 7.4−7.1 (m, 5H), 4.35 (s, 1H), 3.15 (s, 3H), 1.9−1.4 (m, 13H); MS *m/e* 246.1618 (calcd for C$_{16}$H$_{22}$O$_2$, 246.1620). Anal. Calcd for C$_{16}$H$_{22}$O$_2$: C, 78.00; H, 9.01. Found: C, 78.12; H, 9.18.

4-Benzoyl-1-methoxybicyclo[2.2.2]octane (8). (a) To a stirred suspension of 0.138 g (0.50 mmol) of 4-iodo-1-methoxybicyclo[2.2.2]octane (**5**) in 5.0 mL of ether at −70 °C was added 0.6 mL (1.00 mmol) of 1.7 M pentane solution of *tert*-butyllithium with a syringe. The mixture was stirred at −70 °C for 45 min, and 0.062 mL (0.50 mmol) of methylbenzoate (freshly distilled from calcium hydride) was added. The temperature rose to −50 °C, and the mixture was stirred at this temperature for 3 h, allowed to warm to room temperature, and stirred overnight. Then 10 mL of saturated aqueous ammonium chloride was added, and the aqueous layer was extracted with chloroform (3 × 5 mL). The combined organic phase was water washed, dried with sodium sulfate, and concentrated in vacuo to give an oily mixture, which was chromatographed on a 5 × 30 cm silica gel column eluted subsequently with hexane and 20% ether in hexane. Fraction 2 afforded 0.072 g (59%) of 4-benzoyl-1-methoxybicyclo[2.2.2]octane **8** as a colorless oil, identical that described below.

(b) A mixture of 0.0235 g (0.1 mmol) of (4-methoxybicyclo[2.2.2]octyl)phenylcarbinol **6**, 0.0175 g (0.1 mmol) of potassium chlorochromate, and 3.0 mL of acetic acid was heated on a steam bath until it became green (approximately 5 min). It was then poured into 20 mL of water, neutralized with solid sodium bicarbonate until no foaming was observed, and extracted with chloroform (3 × 10 mL). The chloroform layer after drying with sodium sulfate was concentrated in vacuo to give 0.019 g (82%) of 4-benzoyl-1-methoxybicyclo[2.2.2]octane **8** as a colorless oil.

(c) To a stirred suspension of 0.927 g (3.48 mmol) of 4-iodo-1-methoxybicyclo[2.2.2]octane **5** in 40 mL of ether at −78 °C was added 4.1 mL (6.96 mmol) of 1.7 M *tert*-butyllithium in pentane. The resulting yellow mixture was stirred for 45 min, and then 1.09 mL (1.323 g, 9.40 mmol) of freshly distilled benzoyl chloride was added which discharged the color. The cooling bath was removed, and after 4 h of further stirring the mixture was quenched with saturated solution of ammonium chloride. The aqueous phase was ether extracted, and the combined organic materials were water washed and dried. Removal of solvent in vacuo gave an oil, which was chromatographed on a silica gel column (elution with hexanes−ether, 3:1) to give 0.527 g (62%) of 4-benzoyl-1-methoxybicyclo-[2.2.2]octane **8** as a colorless oil, R_f 0.1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.39 (m, 3H), 3.20 (s, 3H), 2.07 (m, 6H), 1.74 (m, 6H); IR (neat) 1653 cm^{-1}; MS *m/e* 244.1465 (calcd for $C_{16}H_{20}O_2$, 244.1463).

4-Benzoyl-1-iodobicyclo[2.2.2]octane (10). A 400 mg (1.64 mmol) amount of 4-benzoyl-1-methoxybicyclo[2.2.2]octane **8** was treated with 45 mL of 57% HI. The mixture was heated, and methyl iodide and water were distilled out. The distillation head was replaced with a condenser, and reflux was continued overnight. The mixture was poured onto ice, ether extracted, neutralized with solid sodium bicarbonate, and extracted further. The extracts were washed with aqueous saturated sodium bicarbonate, sodium thiosulfate, and water, dried over calcium chloride, and concentrated to give 459 mg of white solid. It was chromatographed on silica gel (elution with hexanes−ether, 9:1) to yield 395 mg (71%) of 4-benzoyl-1-iodobicyclo[2.2.2]octane **10** as a white solid, R_f 0.28; mp 82−84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.43 (m, 3H), 3.19 (s, 3H), 2.07 (m, 6H), 1.74 (m, 6H); IR (film) 1662 cm^{-1}; MS *m/e* 340.2089 (calcd for $C_{15}H_{17}IO$, 340.0320). Anal. Calcd for $C_{15}H_{17}IO$: C, 52.96; H, 5.04. Found: C, 53.21; H, 4.96.

4-Benzoyl-1-iodobicyclo[2.2.2]octane 1,2-Ethanediyl Ketal (12). A solution of 320 mg (0.94 mmol) of 4-benzoyl-1-iodobicyclo[2.2.2]octane **10**, 524 μL (583.5 mg, 9.4 mmol) of ethylene glycol, and 10 mg of *p*-toluenesulfonic acid in 10 mL of benzene was refluxed with a Dean−Stark adapter for 4.5 h. The mixture was washed with saturated solution of sodium bicarbonate, dried, and evaporated to give 332 mg (92%) of **12** as a white solid, pure by NMR. Purification by column chromatography (silica gel, hexanes−ether, 14:1) and recrystallization from hexane gave an analytical sample of 4-benzoyl-1-iodobicyclo[2.2.2]octane 1,2-ethanediyl ketal **12**: R_f 0.32; mp 200−202 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5H), 3.89 (m, 2H), 3.63 (m, 2H), 2.38 (m, 6H), 1.74 (m, 6H); IR (film) 1068 cm^{-1}; MS *m/e* ($M^+ - I$) 257.1529 (calcd for $C_{17}H_{21}O_2$, 257.1542). Anal. Calcd for $C_{17}H_{21}IO_2$: C, 53.14; H, 5.51. Found: C, 53.49; H, 5.58.

4-(1-Hydroxyethyl)-1-methoxybicyclo[2.2.2]octane (7). To a stirred suspension of 2.007 g (7.54 mmol) of 4-iodo-1-methoxybicyclo[2.2.2]octane **5** in 50 mL of ether at −78 °C 8.87 mL (15.08 mmol) of 1.7 M *tert*-butyllithium in pentane was added. After 45 min, 4.2 mL (75.4 mmol) of acetaldehyde (freshly distilled from calcium hydride) was added. Over 1 h the mixture was allowed to warm to room temperature, saturated aqueous ammonium chloride was added, and the aqueous layer was extracted with chloroform. The organic layers were water washed, dried, and concentrated in vacuo to give 2.01 g of yellowish oil. The oil was chromatographed on a silica gel column. Elution with hexanes−ether, 1:1 gave 1.13 g (89%) of 4-(1-hydroxyethyl)-1-methoxybicyclo[2.2.2]-octane **7** as a colorless oil, R_f 0.24; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.43 (q, 1H, J = 6.6 Hz), 3.18 (s, 3H), 1.63 (m, 12H), 1.25 (m, 1H), 1.07 (d, 3H, J = 6.6 Hz); IR (neat) 3446 cm^{-1}; MS *m/e* 184.1450 (calcd for $C_{11}H_{20}O_2$, 184.1463).

4-Acetyl-1-methoxybicyclo[2.2.2]octane (9). To the complex formed from 8.29 mL (105.7 mmol) of pyridine and 5.18 g (51.8 mmol) of CrO_3 in 145 mL of methylene chloride was added 1.25 g (6.78 mmol) of 4-(1-hydroxyethyl)-1-methoxybicyclo[2.2.2]octane **7** in 50 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 5% solution of sodium hydroxide. The organic layer was washed with 5% hydrochloric acid and saturated solution of sodium bicarbonate. Then it was dried and concentrated in vacuo to give the quantitative yield (1.23 g) of 4-acetyl-1-methoxybicyclo[2.2.2]octane **9** as colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.19 (s, 3H), 2.09 (s, 3H), 1.84 (m, 6H), 1.68 (m, 6H); IR (neat) 1689 cm^{-1}; MS *m/e* 182.1300 (calcd for $C_{11}H_{18}O_2$, 182.1307).

4-Acetyl-1-iodobicyclo[2.2.2]octane (11). A 210 mg (1.15 mmol) amount of 4-acetyl-1-methoxybicyclo[2.2.2]octane **9** was treated with 20 mL of 57% HI. The mixture was heated, and methyl iodide and water were distilled out. The distillation head was replaced with a condenser, and reflux was continued overnight. The mixture was poured onto ice, chloroform extracted, neutralized with dry sodium bicarbonate, and extracted further. The extracts were washed with aqueous saturated sodium bicarbonate, sodium thiosulfate, and water, dried over calcium chloride, and concentrated in vacuo to give 263 mg of white solid. It was chromatographed on a silica gel column (hexanes−ether, 5:1) to yield 208 mg (65%) of pure 4-acetyl-1-iodobicyclo[2.2.2]octane **11** as a white solid, R_f 0.21; mp 80−81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (m,6H), 2.06 (s, 3H), 1.84 (m, 6H); IR (film) 1699 cm^{-1}; MS *m/e* 278.0166 (calcd for $C_{10}H_{15}IO$, 278.0164). Anal. Calcd for $C_{10}H_{15}IO$: C, 43.18; H, 5.44. Found: C, 43.06; H, 5.37.

4-Acetyl-1-iodobicyclo[2.2.2]octane 1,2-Ethanediyl Ketal (13). The mixture of 170 mg (0.6 mmol) of 4-acetyl-1-iodobicyclo[2.2.2]octane **11**, 401 μL (446 mg, 7.2 mmol) of ethylene glycol, and 4 mg of *p*-toluenesulfonic acid in 12 mL of benzene was refluxed with a Dean−Stark adapter for 4 h. The mixture was washed with saturated solution of sodium bicarbonate, dried, and evaporated to give 193 mg (quantitative yield) of ketal **13** as a white solid, pure by NMR, mp 117−118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.92 (m, 2H), 3.84 (m, 2H), 2.44 (m, 6H), 1.72 (m, 6H), 1.13 (s, 3H); MS *m/e* 322.0432 (calcd for $C_{12}H_{19}IO_2$, 322.0426). Anal. Calcd for $C_{12}H_{19}IO_2$: C, 44.74; H, 5.94. Found: C, 44.51; H, 5.97.

1-(4-Benzoylbicyclo[2.2.2]octyl)-4-(4-(α-naphthyl)-bicyclo[2.2.2]octyl)benzene 1,2-ethanediyl Ketal (15). To a stirred suspension of 0.192 g (0.5 mmol) of 1-benzoyl-4-iodobicyclo[2.2.2]octane 1,2-ethanediyl ketal **12** in 10 mL of absol ether, cooled to −70 °C under nitrogen, a 0.47 mL (0.8 mmol) portion of 1.7 M solution of *tert*-butyllithium in pentane was added dropwise. The resulting slightly yellow solution was allowed to warm to −50 °C and stirred at this temperature for 30 min. Then a solution of 0.111 g (0.34 mmol) of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-2-enone **4** in 25 mL of absol ether was added dropwise with a syringe. The mixture was stirred at −60 to −70 °C for 2 h, allowed to warm to room temperature, and stirred overnight, followed by quenching with 5 mL of aqueous saturated ammonium chloride, extracting with chloroform (3 × 5 mL), drying with sodium sulfate, and concentrating in vacuo. The residue was chromatographed on a 3 × 30 cm silica gel column and eluted subsequently with hexane, 10% ether in hexane, 20% ether in hexane, 50% ether in hexane, and pure ether. Fraction 2 (the richest of the desired material) was concentrated in vacuo to give 90 mg of a white solid. A 10 mg portion of this material was refluxed with 20 mg (0.088 mmol) of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone in 2.0 mL of benzene for 1.25 h, cooled to room temperature, and chromatographed on a 3 × 30 cm silica gel column, eluted subsequently with hexane, 50% ether in hexane, and pure ether. It gave 7.0 mg (0.012 mmol) of 1-(4-benzoylbicyclo[2.2.2]-octyl)-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)benzene 1,2-ethanediyl ketal **15** as a white solid. The yield of **15** counting on initial enone **4** was 32%, mp 301−303 °C. The spectral data were the following: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.9−1.7 (m, 12H), 2.00 (m, 6H), 2.30 (m, 6H), 3.65 (m, 2H), 3.95 (m, 2H), 7.5−7.2 (m, 13H), 7.70 (m, 1H), 7.85 (m, 1H), 8.50 (m, 1H).

1-(4-Benzoylbicyclo[2.2.2]octyl)-4-(4-(α-naphthyl)-bicyclo[2.2.2]octyl)benzene (14). A 7.0 mg (0.012 mmol) portion of 1-(4-benzoylbicyclo[2.2.2]octyl)-4-(4-(α-naphthyl)-bicyclo[2.2.2]octyl)benzene 1,2-ethanediyl ketal **15** was heated with stirring at 100 °C under nitrogen with 1.0 mL of acetic acid and 0.20 mL of concentrated HCl for 30 min. The mixture was then diluted with 5 mL of water, extracted with ethyl acetate (3 × 2 mL), washed with water (2 × 3 mL) and then with aqueous saturated sodium hydrocarbonate (2 × 3 mL), dried over sodium sulfate, and evaporated. The residue was chromatographed on a silica gel column, eluted subsequently with 4:1 hexanes−ether, ether, chloroform. It gave 6 mg of a solid, which was washed with ether (3 × 0.5 mL) and dried. This procedure afforded 5 mg (83%) of 1-(4-benzoylbicyclo[2.2.2]octyl)-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)benzene **14**, mp 301−303 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.44 (d, 1H, J = 8.4 Hz), 7.79 (d, 1H, J = 7.2 Hz), 7.63 (d, 1H, J = 7.2 Hz), 7.55 (d, 2H, J = 6.9 Hz), 7.44−7.25 (m, 7H), 7.24 (s, 4H), 2.24 (m, 6H), 1.98 (m, 12H), 1.83 (m, 6H); IR (film) 1676 cm^{-1}; MS *m/e* 524.3094 (calcd for $C_{39}H_{40}O$, 524.3079).

1-(4-Acetylbicyclo[2.2.2]octyl)-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)benzene (16). To a stirred mixture of 0.18 mL (0.30 mmol) of 1.7 M pentane solution of *tert*-butyllithium and 3 mL of ether at −70 °C was added a solution of 0.115 g (0.36 mmol) of 4-acetyl-1-iodobicyclo[2.2.2]octane 1,2-ethanediyl ketal **13** in 5 mL of ether dropwise with a syringe. The mixture was stirred for 45 min at −70 °C, and 5 mL of ether solution of 0.081 g (0.24 mmol) of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-2-enone (**4**) was added with a syringe. The resulting solution was kept at −70 °C for 1 h, allowed to warm to room temperature for 1 h, poured into 5 mL of aqueous saturated ammonium chloride, extracted with chloroform (3 × 5 mL), dried over sodium sulfate, and concentrated in vacuo. The residue was chromatographed on a 3 × 30 cm silica gel column, eluted subsequently with hexane, 10% ether in hexane, 20% ether in hexane, 50% ether in hexane, and pure ether. Fraction 1 contained 0.039 g (34%) of starting compound **13**. Fraction 2 contained 0.014 g (18%) of starting enone **4**. Fraction 4 gave 0.045 g of a white solid; a portion of 0.033 g of this solid was stirred with 1 mL of 50% sulfuric acid and 3 mL of ether for 4 h, sodium hydrocarbonate neutralized, ether extracted, and dried over sodium sulfate. Concentration of the solution gave 0.016 g of a white solid. A mixture of 0.016 g of this solid, 0.024 g (0.106 mmol) of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone, and 2.0 mL of benzene was refluxed for 15 min, cooled to room temperature, and chromatographed on a 3 × 30 cm silica gel column, eluted with 20% ether in hexane to give 0.012 g of 1-(4-acetylbicyclo[2.2.2]octyl)-4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)benzene **16**. Totally 0.081 g (0.24 mmol) of 4-(4-(α-naphthyl)bicyclo[2.2.2]octyl)cyclohex-2-enone **4** gave 0.012 g (0.026 mmol, 11%) of **16**. Crystallization from 20% ether in hexane gave colorless crystals, mp 288−289 °C; the spectral data were the following: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.50 (m, 1H), 7.9 (m, 1H), 7.7 (m, 1H), 7.5−7.2 (m, 8H), 2.4−2.3 (m, 6H), 2.2−2.0 (m, 9H), 2.0−1.8 (m, 12H); MS *m/e* 462.2921 (calcd for $C_{34}H_{38}O$, 462.2923). Anal. Calcd for $C_{34}H_{38}O$: C, 88.26; H, 8.28. Found: C, 88.24; H, 8.52.

Single Photon Counting Procedure. The single photon counting equipment is that largely described.[4a,8] Nitrogen lamp pressure of 70 psi and 6 kV gave a pulse width of 3 ns. Wavelengths: excitation 270 nm, emission 320 nm. Details of the instrumental settings are given in the Supporting Information.

Computational Methodology. Computations were run using Gaussian98.[19] Initially the ground-state geometry was optimized using RHF/3-21G. This was followed by CASSCF single point computations. The CASSCF active space (n,n) was adjusted to parallel the rod molecule being studied. The first singlet excited state was run using ground-state geometry. S0 and S1 computations produced density matrixes. The DelDen program[20] was used to subtract the ground-state density matrix from the corresponding first excited-state one and to print out the matrix elements.

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Supporting Information Available: Includes single photon counting details, evidence on the adequacy of the basis set selection; details on the solution of the eqs 2−4, a general analysis of the number of solutions anticipated from equations as 2−4, and NMR spectra of key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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