J. Am. Chem. Soc. **1995,** *117,* 4367−4373

Intramolecular Energy Transfer from Upper Triplet States in Rigidly-Linked Bichromophoric Molecules

Yijin Ren, Zhijun Wang, Hong Zhu, Stephen J. Weininger,* and W. Grant McGimpsey*

Contribution from the Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received November 2, 1994[⊗]

Abstract: Intramolecular triplet energy transfer has been studied in bichromophoric molecules that incorporate an anthracene donor and ketone or alkene acceptors connected by two rigid, bicyclic saturated hydrocarbon units. Two-laser excitation of the anthracene group results in production of the T_2 state which subsequently undergoes energy transfer to the acceptors ($k \approx 10^{10}$ s^{-1}), as indicated by depletion of the T−T absorption. In **1**, decay of the acceptor (ketone) triplet state involves a competition between ring opening and back energy transfer to the anthracene T_1 state. In **2**−**4**, rotation of the alkene triplets to perpendicular geometries relieves ring strain in the bicyclic connecting units, thus providing a barrier to back energy transfer. A fraction of the twisted triplets relaxes to the ground state without irreversible chemistry.

Introduction

Intramolecular energy transfer, particularly within molecules in which the chromophores are connected by a rigid hydrocarbon framework, is a subject of continuing activity and interest. A recent example is the elegant investigation by Morrison and co-workers of singlet and triplet energy migration in androstane derivatives.[1] Previously, Closs et al. measured the rate of triplet energy transfer in cyclohexanes and decalins,[2] while Paddon-Row, Verhoeven, and co-workers reported on singlet energy transfer in rigid bicyclic systems.[3] All these studies point to the conclusion that singlet and triplet energy transfers within such molecules proceed by way of a through-bond mechanism, and are therefore similar to intramolecular charge transfer in analogous compounds.[4]

A closely related topic is back energy transfer within rigid, bichromophoric molecules. Paddon-Row and Verhoeven noted that the singlet state of the acceptor carbonyl group in their molecules underwent rapid intersystem crossing to the triplet manifold and that the triplet energy was then transferred back to the original aromatic donor.[3] An extensive study of such a sequence was carried out by Amrein and Schaffner, who showed that with the appropriate donor and acceptor groups the process was rapid and efficient.[5]

Our work builds upon this base but has some interesting differences. In none of the literature cited did energy transfer take place from upper excited states. We use the T_2 state of anthracene as a triplet energy donor, taking advantage of its relatively long lifetime.[6]

Furthermore, the chromophores used thus far have invariably been rigid, so that changes in acceptor or donor energy as a function of the conformation of the excited chromophore have not come into play. Recent work of Goodman[7] and Caldwell[8] has made apparent the often substantial energy difference between the spectroscopic and relaxed triplet states of the same molecule, a difference that can have important photophysical and photochemical consequences.[9] Except for the usual carbonyl group, all our acceptors are substituted alkenes. We have found that rotation around the carbon−carbon double bond plays a significant role in determining the deexcitation pathways following energy transfer from T_2, including back energy transfer from the alkene to anthracene T_1.

Recently we reported the results of a two-laser investigation of the triplet state reactivity of anthracene in solution in the presence of a variety of electron and/or energy acceptors.[10] Our study indicated that excitation of the T_1 state of anthracene to an upper triplet level (T_2) caused permanent depletion of the T_1 concentration (bleaching). In the presence of acrylonitrile and benzonitrile, T_1 excitation led to efficient two-laser-induced triplet depletion. With acrylonitrile, several possible upper triplet deactivation channels could have led to depletion: (i) energy transfer from the anthracene T_2 state to acrylonitrile; (ii) [4 + 2] cycloaddition of acrylonitrile to the 9 and 10 positions of the anthracene (supported by observation of the cycloadduct; energy transfer could have been the initiating step in cycloaddition); (iii) electron transfer (we consider this to be an inefficient process since it is endergonic by several kilocalories per mole). While cycloaddition was not observed for benzonitrile, energy transfer is energetically feasible from T_2 to benzonitrile.

In order to allow a clearer determination of the importance of energy transfer from the anthracene T_2 state, we have synthesized several molecules (**1**−**4**) that incorporate both anthracene and various energy acceptors into one bichromophoric molecule (Chart 1). Their behavior is contrasted with

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) Morrison, H.; Wu, Z.-Z. *J. Am. Chem. Soc.* **1992,** *114,* 4119−4128. Wu, Z.-Z.; Nash, J.; Morrison, H. *J. Am. Chem. Soc.* **1992,** *114,* 6640−6648.

(2) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988,** *110,* 2652−2653.

(3) Kroon, J.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1990,** *112,* 4868−4873.

(4) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989,** *111,* 3751−3753.

(5) Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1975,** *58,* 397−413.

(6) Bohne, C.; Kennedy, S. R.; Boch, R.; Negri, F.; Orlandi, G.; Siebrand, W.; Scaiano, J. C. *J. Phys. Chem.* **1991,** *95,* 10300−10306.

(7) Lavilla, J. A.; Goodman, J. L. *Chem. Phys. Lett.* **1987,** *141,* 149−153.

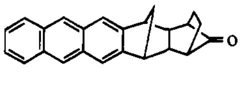
(8) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989,** *111,* 457−464.

(9) Schuster, D. I.; Dunn, D. A.; Heibel, G. E.; Brown, P. B.; Rao, J. M.; Woning, J.; Bonneau, R. *J. Am. Chem. Soc.* **1991,** *113,* 6245−6255.

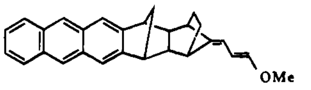
(10) Wang, Z.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem.* **1993,** *97,* 374−378.

0002-7863/95/1517-4367$09.00/0

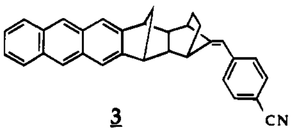
Chart 1



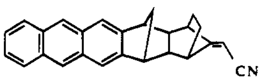
1



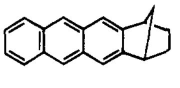
2



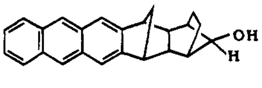
3



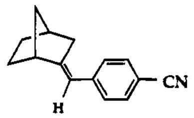
4



5



6



7

that of the model compounds **5** and **6** which each contain only the anthracene chromophore. Compound **7** was synthesized as an analog for the acceptor moiety in **3**. Phosphorescence measurements yielded its triplet energy. In **2**, **6**, and **7** more than one isomeric form of the compound exists.

Compounds **1**−**4** incorporate two rigid bicyclic saturated hydrocarbon units similar to those described by Paddon-Row.[11] In these rigid molecules cycloaddition is no longer a feasible T_2 deactivation route, while the proximity of the acceptor moieties to the anthracene chromophore enhances the efficiency of excited state interactions. The benzonitrile analog **3** actually contains a *p*-cyanostyryl group, which differs from benzonitrile in its triplet energy (22 kcal/mol lower). This makes energy transfer from anthracene exergonic rather than thermoneutral (as is the case with benzonitrile).

In the present study, anthracene T_1 depletion caused by two-laser irradiation of **1**−**4** has been quantified and is used as a transient probe for investigating the efficiency of both the initial energy transfer step and the subsequent decay pathways of the acceptor triplet. We consider this approach to be particularly useful since the extent of repopulation of the anthracene T_1 state, a measure of the efficiency of back energy transfer relative to other acceptor decay processes, can be determined directly.

Results and Discussion

One- and two-laser studies were carried out in both MeCN and CH. Figure 1 illustrates the one- and two-laser behavior of **4** in MeCN. The inset gives the transient absorption spectrum obtained following one-laser excitation. The transient behavior of each of the compounds **1**−**6** under one-laser conditions was very similar to that of anthracene in the absence of any added substrates; i.e., an intense T−T absorption with λ_{max} between 425 and 435 nm was observed, indicating that there is little interaction between the anthracene T_1 state and the acceptor groups.

In addition to triplet state formation, excitation in polar solvents also leads to photoionization as evidenced by the production of the anthracene cation radical, $\lambda_{max} = 720$ nm.[12] Interestingly, the intensity of the cation radical absorption was consistently higher for **1**−**6** than for anthracene itself. A detailed study of this photoionization phenomenon as well as the effect of the various acceptor groups on the fluorescence quantum yields is in progress.

Excitation of the triplet state with a 456 nm dye laser led to permanent depletion (square symbols in Figure 1) of the T−T absorption for compounds **1**−**4** but not for compounds **5** or **6**, nor for anthracene itself. Table 1 shows the extent of triplet depletion observed, expressed as a percentage of the T−T absorption before the second laser fires. Since the depletion was greatest for **4** in CH, the percent depletion for each of the other compounds is expressed relative to this value.

Since our probe in these experiments is the absorption of the T_1 state, depletion is indicative of a deactivation process or processes that occur from T_2 *other than* internal conversion back to T_1. Table 2 lists the known T_2 and T_1 energies of anthracene, its T_2 lifetime, the spectroscopic triplet energies of molecules corresponding to the acceptor moieties in **1**−**4**, and the relaxed triplet energies and lifetimes of thoae acceptors that are known to undergo triplet relaxation by rotation to perpendicular conformations (**2**−**4**).

These data support the conclusion that *triplet depletion is caused by triplet−triplet energy transfer between the anthracene T_2 state and the acceptor, followed by relaxation of the acceptor triplet. Furthermore, since back energy transfer to the anthracene T_1 state would lead to no depletion, deactivation of the acceptor triplet must occur by an irreversible chemical or photophysical process to account for the observed depletion.*

For example, the lack of triplet depletion in **5** and **6** can be attributed to the fact that neither molecule incorporates a suitable energy acceptor, while **1**−**4** all possess acceptors with triplet energies that lie between the T_1 and T_2 energies of anthracene and thus are capable of acting as exclusive T_2 quenchers. Below we give further evidence for intramolecular energy transfer from T_2 and discuss the relative importance of back energy transfer [T_1 (acceptor) → T_1 (anthracene)] and other competitive acceptor triplet deactivation processes.

It should be pointed out that the participation of higher excited triplet states (e.g., T_3) in energy transfer cannot be ruled out. However, given that the lifetimes of such states must be considerably shorter than that of T_2 (8 ps), we believe that the majority of energy transfer must occur via T_2.

(a) Photoprocesses in 1 (7-Norbornanone Acceptor). From the triplet energies in Table 2 it is clear that the acceptor in **1** (a 7-norbornanone) is capable of quenching only the anthracene T_2 state. In order to confirm that energy transfer is in fact occurring, up to 0.5 M 1,3-cyclohexadiene (CHD) was added to separate solutions of anthracene and **1**. CHD is a known triplet quencher with $E_T \approx 54$ kcal/mol,[13] i.e., between the anthracene T_2 and T_1 energies, but lower than the T_1 energy of the ketone. Therefore, CHD is a possible quencher of both anthracene T_2 and the ketone T_1. In the case of anthracene, no triplet depletion was observed after the dye laser pulse. This is not surprising since the T_2 lifetime is quite short (8 ps)[6] making bimolecular interaction with CHD at this concentration unlikely. However, enhanced triplet depletion *was* observed for **1** (see Table 1). Since it is unlikely that the anthracene T_2 state is longer lived in **1** than in anthracene itself, enhanced

---

[11] Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258−3269.

[12] Vauthy, E.; Haselbach, E.; Suppan, P. *Helv. Chim. Acta* **1987**, *70*, 347−353.

[13] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

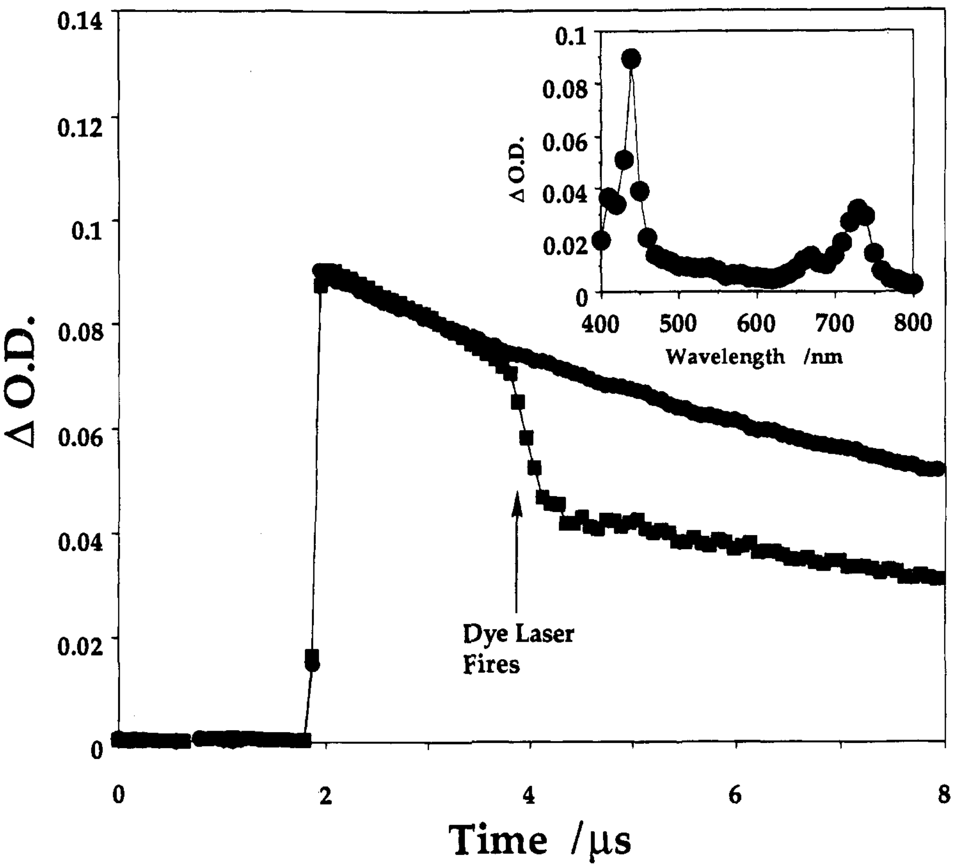


Figure 1. Transient decay kinetics obtained following one- (355 nm; round symbols) and two-laser (355 + 456 nm; square symbols) irradiation of **4** in deoxygenated MeCN. Inset: Transient absorption spectrum obtained 1 μs after 355 nm irradiation in deoxygenated MeCN.

Table 1. Percent Depletion of the T_1 State of the Anthracene Moiety Contained in Compounds 1–6 Induced by Irradiation with a 456 nm Pulsed Dye Laser in the Absence and Presence of 1,3-CHD[a]

compound	cyclohexane	acetonitrile	cyclohexane (1,3-CHD added)
anthracene	0		0
1	12		14
2	37	40	40
3	55	60	55
4	100	83	104
5	0		
6	0		

[a] Normalized to the value for **4** in CH in the absence of 1,3-CHD.

depletion can be taken as an indication of energy transfer quenching of the ketone triplet by CHD. That is, energy is transferred from anthracene T_2 to the ketone, the triplet of which is in turn quenched by CHD before it can undergo back energy transfer to anthracene T_1.

Confirmation of the formation of the ketone triplet now provides an explanation for the observation of triplet depletion in the absence of CHD. Since photoexcited norbornanones are known to undergo irreversible ring opening/rearrangement reactions,[14] we believe that triplet depletion is due to a competition between back energy transfer (from the ketone T_1 to anthracene T_1) and irreversible chemical decay of ketone T_1. In fact, solutions irradiated with several hundred pairs of laser pulses (355 + 456 nm) contained several photoproducts as indicated by TLC. Due to the small quantities generated (micromolar) identification of these products has not yet been possible.

The extent of depletion depends on two effects: (i) the competition between anthracene $T_2 \rightarrow$ ketone energy transfer and $T_2 \rightarrow T_1$ internal conversion and (ii) the competition between back energy transfer and irreversible chemistry. The T_2 lifetime of anthracene in solution has been estimated from Stern–Volmer studies to be $\tau \approx 8$ ps. Thus, in order for depletion to be observable, the forward energy transfer rate constant must be on the order of 10^{10} s^{-1}. Past studies suggest that this is an attainable value; intramolecular triplet energy transfer between rigidly connected anthrone donors and naphthalene acceptors has a rate constant of 1.25×10^{10} s^{-1}.[15]

Given the rigid nature of **1**, we would expect little difference between the forward and reverse energy transfer rate constants. Since depletion is observed, this would suggest that ring opening is also reasonably rapid. In fact, the rate constant for irreversible chemistry in photoexcited 7-norbornanone and related compounds has been estimated at $k > 10^8$ s^{-1}.[16,17] A similar rate constant in **1** is indicated from the relatively small amount of depletion detected. (Ring opening, while rapid, competes inefficiently with back energy transfer.) The photoprocesses of **1** are summarized in Scheme 1.

(b) Photoprocesses in 2–4 (Alkene Acceptors). As with **1**, the spectroscopic T_1 energies of the acceptor chromophores in **2–4** lie between the anthracene T_2 and T_1 energies. Quenching experiments with CHD confirmed the formation of the acceptor triplet in **2** and **4**, but no enhanced depletion was observed for **3** in the presence of CHD. This difference can be understood from a consideration of the possible decay pathways of the alkene triplet states. It is well known that the geometry

---

[14] Thomas, T. F.; Matuszewski, B.; Givens, R. S. *J. Phys. Chem.* **1974**, *78*, 2637–2645.

[15] Maki, A. H.; Weers, J. G.; Hilinski, E. F.; Milton, S. V.; Rentzepis, P. M. *J. Chem. Phys.* **1994**, *80*, 2288–2297.

[16] Thomas, T. F.; Matuszewski, B.; Givens, R. S. *J. Phys. Chem.* **1974**, *76*, 2637–2645.

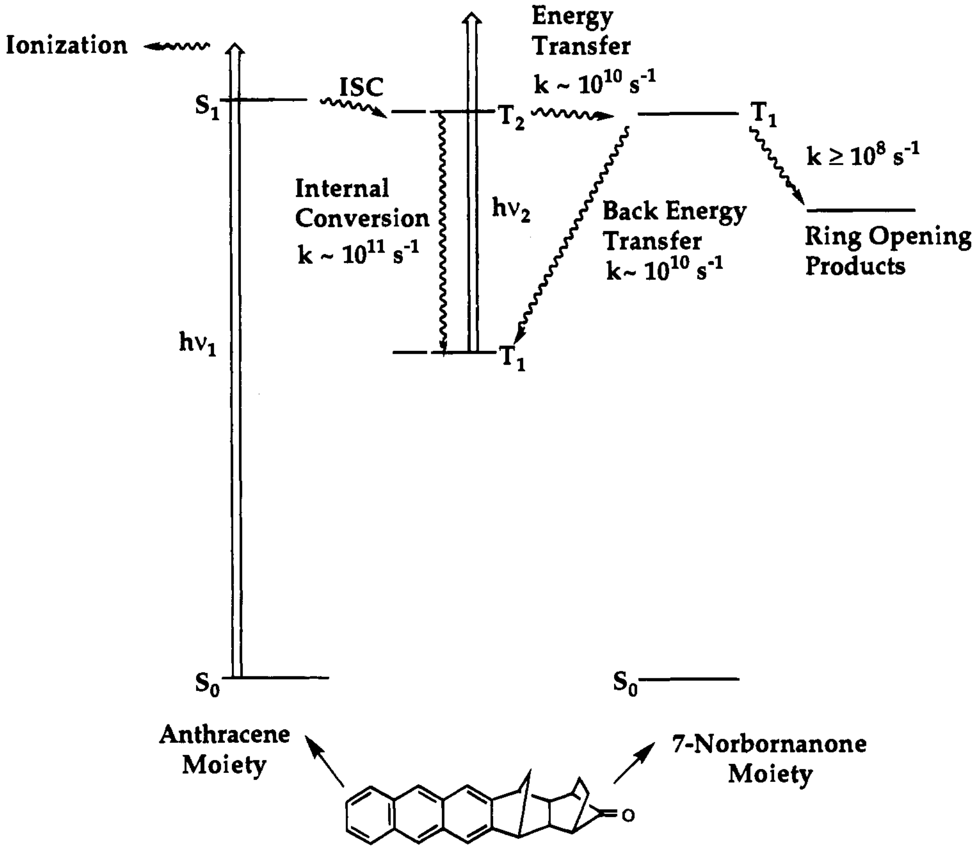
[17] Schuster, G.; Turro, N. J. *Tetrahedron Lett.* **1975**, 2261–2264.

Table 2. Spectroscopic and Relaxed Triplet Energies and Relaxed Triplet Lifetimes of Model Compounds Similar to the Acceptor Chromophores in Compounds 1–4 (References Are for Triplet Lifetimes)

model compound	no. of molecules containing model compound	triplet energy[a] (kcal/mol) spectroscopic	relaxed	triplet lifetime[b] (ns)	ref
anthracene		74 (T_2) 42 (T_1)		0.008 (T_2)	6
2-norbornanone	1	~74	–	<10	14
2,5-dimethyl-2,4-hexadiene	2	57	53	49	7
p-cyanostyrene	3	55	45	22	8
acrylonitrile	4	~71	58	28	7

[a] Spectroscopic triplet energy of *p*-cyanostyrene estimated from the phosphorescence spectrum of **7**. Relaxed energy of *p*-cyanostyrene estimated from the difference between spectroscopic and relaxed energies of styrene. [b] Relaxed triplet lifetimes for 2,5-dimethyl-2,4-hexadiene and acrylonitrile are from the specified reference. The value for 2-norbornanone is estimated from the ring opening rate constant. The value for *p*-cyanostyrene was assumed to be the same as that for styrene.

Scheme 1



of many alkenes changes dramatically following excitation. Initially planar alkene triplet states (spectroscopic) undergo rapid relaxation by rotation around the double bond to give a perpendicular conformation that is essentially a biradical.[8,18] Intersystem crossing by this perpendicular triplet state to the ground state then proceeds rapidly with rate constants in the range 10^7–10^8 s^{-1}. There is also a significant decrease in triplet energy that accompanies relaxation from spectroscopic to perpendicular states. It is this relaxation that allows us to account for the lack of CHD-enhanced triplet depletion in **3**. The spectroscopic energy of the triplet acceptor in **3**, which we have estimated from the phosphorescence spectrum of model compound **7**, is approximately equal to the triplet energy of CHD. However, if the triplet acceptor in **3** undergoes a rotational relaxation similar to that of styrene, we would expect its relaxed triplet energy to be ca. 44 kcal, well below the CHD triplet energy.

In fact, it is this rotational relaxation of alkene triplets which offers the most consistent explanation for the observed depletion and for the differences in the two-laser behavior **1** and **2**–**4**. These differences include the following observations: (i) triplet depletion was more extensive **2**–**4** than in **1**, with the greatest depletion observed for **4**; (ii) no permanent product formation was observed for **2**–**4**, indicating the lack of irreversible chemical decay pathways in these compounds. The lack of photoproduct formation with **2**–**4** indicates that the relaxation of the alkene triplets occurs without ring opening. This is not surprising since the excitation energy that is localized in the norbornane carbonyl group in **1** is significantly delocalized in **2**–**4**.

We suggest that depletion in **2**–**4** occurs as a result of the following sequence of events. Initial energy transfer from anthracene T_2 to the acceptor group forms the planar, spectroscopic acceptor triplet state. At this point back energy transfer may occur, although this process is transparent to our transient probe. However, there exists a strong competitive driving force for relaxation to the perpendicular triplet—alleviation of strain in the norbornane ring. Rotation to the biradical conformation will result in conversion of the "bridgehead" carbon (C–16) from sp^2 to sp^3 geometry. Caldwell has shown convincingly

---

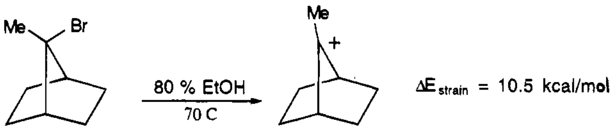
(18) Caldwell, R. A.; Zhou, L. *J. Am. Chem. Soc.* **1994**, *116*, 2271–2275.

that perpendicular, or twisted, triplets behave essentially like 1,2-biradicals.[18,19] 7-Norbornyl radicals assume a pyramidal rather than a planar conformation, presumably because the pyramidal structure suffers less angle strain. It thus seems highly probable that relief of bond angle strain in the norbornyl bridge accelerates the twisting about the acceptor double bond.

Reported rate constants for the decay of the relaxed acceptor triplet states to the ground state for the acceptor moieties in **2**−**4** are in the range 2×10^7 to 5×10^7 s^{-1}.[7,8] Since these values are similar to that estimated for decay of the ketone in **1**, the observed differences in triplet depletion *must* be due to more efficient competition between relaxation to the ground state and back energy transfer; i.e., back energy transfer *must* be less efficient in **2**−**4** than in **1**.

The reason for less efficient back energy transfer can be attributed to the effect on the geometry of the system caused by rotational relaxation of the alkene. Back energy transfer cannot occur vertically from the perpendicular acceptor triplet since to do so would require 70 kcal of energy—40 kcal to populate the anthracene T$_1$ state and a further ~30 kcal to produce the perpendicular ground state of the acceptor. This is a process that would require between 20 and 30 kcal of activation (depending on the energy of the acceptor triplet). Thus, back energy transfer must be coupled with rotation around the acceptor double bond. However, a significant barrier to such rotation exists due to the increase in ring strain accompanying reestablishment of the planar configuration.

Since C-16 in these molecules is equivalent to C-7 of a norbornane ring, the properties of 7-norbornyl radicals should be germane to the behavior of the triplets of **2**−**4**. Reactivity studies support the conclusion that 7-norbornyl radicals are pyramidal.[20] To estimate the strain energy difference between the pyramidal configuration characteristic of the perpendicular triplet, and the planar configuration characteristic of both the spectroscopic triplet and the ground state, we turn to studies of polycyclic carbocations. Muller and co-workers have calculated that conversion of 7-bromo-7-methylnorbornane to the 7-methyl-7-norbornyl cation results in a strain energy increase of 10.5 kcal/mol (eq 1).[21] In our systems the corresponding change might be even more endothermic due to the additional strain that arises when two norbornyl rings are fused.



(1)

Thus, rotation of the perpendicular acceptor triplet to the planar configuration in the course of energy transfer to anthracene T$_1$ would involve the reimposition of some considerable quantity of ring strain, which would in turn act as a barrier to that rotation. The net effect of this barrier would be to slow the back energy transfer, thus allowing a greater proportion of acceptor triplets to decay to the ground state. It has already been shown that both inter- and intramolecular triplet energy transfer to biphenyl is slowed by the barrier to rotation from the twisted ground state to the planar triplet state.[22] A rotational barrier in the triplets of **2**−**4** would thus account in part for the greater triplet depletion encountered with these compounds than with **1**. Scheme 2 summarizes our conclusions regarding the photoprocesses occurring in **2**−**4**.

Conclusions

Photoexcitation of the T$_1$ state of the anthracene group in compounds **1**−**4** results in rapid energy transfer from the T$_2$ state to the planar spectroscopic triplet of the acceptor groups. Since the anthracene T$_2$ lifetime has been estimated previously as 8 ps, the energy transfer rate must be $k \approx 10^{10}$ s^{-1}.

In **1**, ring opening in the acceptor ketone triplet competes with back energy transfer to anthracene T$_1$. In **2**−**4**, the alleviation of strain in the norbornane ring as a result of double bond rotation in the acceptor triplets provides a barrier to back energy transfer. Thus, deactivation to the ground state becomes competitive with back energy transfer, and greater triplet depletion is observed than for **1**.

Experimental Section

Acetonitrile (MeCN) and cyclohexane (CH) were spectrophotometric grade and were used as received. 1,3-Cyclohexadiene (CHD) was distilled prior to use. Anthracene was recrystallized from ethanol. Elemental analysis was performed by Quantitative Technologies, Inc., Bound Brook, NJ. Low-resolution mass spectra (LRMS) were obtained with a Hewlett-Packard 5703B mass spectrometer. High-resolution mass spectra (HRMS) were obtained with a Kratos Concept-1S double focusing mass spectrometer using LSIMS.

Laser Flash Photolysis. The laser flash photolysis apparatus in the one- and two-laser experiments has been described in detail elsewhere.[10,23] Briefly, in the one-laser experiments, samples were irradiated by the UV pulses of a frequency-tripled Continuum Nd/YAG laser (355 nm; <50 mJ/pulse; 5 ns duration). In the two-laser experiments, the UV pulse was followed after a short delay (ca. 1.0 μs) by the pulse from a Candela SLL 250 flashlamp-pumped dye laser (456 nm; <150 mJ; 350 ns). Samples were caused to flow continuously through a specially constructed 7 × 7 mm^2 quartz cell, ensuring that a fresh volume of the sample was irradiated by each laser pulse (or pair of pulses in the two-laser experiments). Unless otherwise indicated, all samples were deoxygenated prior to irradiation by passing a stream of dry N$_2$ through the sample for 25 min.

Triplet depletion values (T−T absorbance loss after the dye laser pulse divided by the T−T absorbance at the time that the dye laser fired) were obtained relative to the depletion of **4** in CH. The T−T absorbances for each compound at 456 nm were matched at the time that the dye laser fired. Matching of the samples was accomplished by attenuating the 355 nm laser with neutral density filters. Care was taken to ensure that the percent depletion was a linear function of the dye laser energy.

Synthesis (Scheme 3). 1,4-Dihydro-1,4-methanotetracene (9), 1,2,3,4,-Tetrahydro-1,4-methanotetracene (5), and (1α,4α,4aα,5β,14β,14aα)-1,2,3,4,4a,5,14,14a-Octahydro-1,4:5,14-dimethanopentacen-16-one (1). Compound **9** was synthesized according to the literature procedure.[24] Hydrogenation of **9** over Pd/C gives **5**.[25]

Reaction of **9** with 5,5-dimethoxy-1,2,3,4-cyclopentadiene, dechlorination of the product with Na, and catalytic reduction of the resulting alkene[11] give the dimethyl ketal of **1**: ^{1}H NMR (CDCl$_3$) δ 1.6−1.8 (m, 5 H), 2.14 (s, 2 H), 2.25 (s, 2 H), 2.41 (d, J = 10 Hz, 1 H), 3.13 (s, 3 H, OCH$_3$), 3.26 (s, 3 H, OCH$_3$), 3.35 (s, 2 H), 7.38−7.43 (m, 2 H), 7.61 (s, 2 H), 7.93−7.97 (m, 2 H), 8.28 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 22.0 (2 CH$_2$), 41.0 (2 CH), 43.2 (CH$_2$), 43.7 (2 CH), 45.0 (2 CH), 50.37 (OCH$_3$), 50.41 (OCH$_3$), 116.9 (*C*(OMe)$_2$), 117.0 (2 CH), 124.7 (2 CH), 125.6 (2 CH), 127.8 (2 CH), 131.2 (2 C), 131.3 (2 C), 149.5 (2 C).

Deketalization of this intermediate with HCOOH in THF[26] produces **1**: IR (KBr) 2970, 1769, 902 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.78−2.05

---

(19) Caldwell, R. A.; Diaz, J. P.; Hrncir, D. C.; Unett, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 8138−8145 and references therein.

(20) Giese, B.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 594−595.

(21) Muller, P.; Milin, D. *Helv. Chim. Acta* **1991**, *74*, 1808−1816.

(22) Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5012−5017.

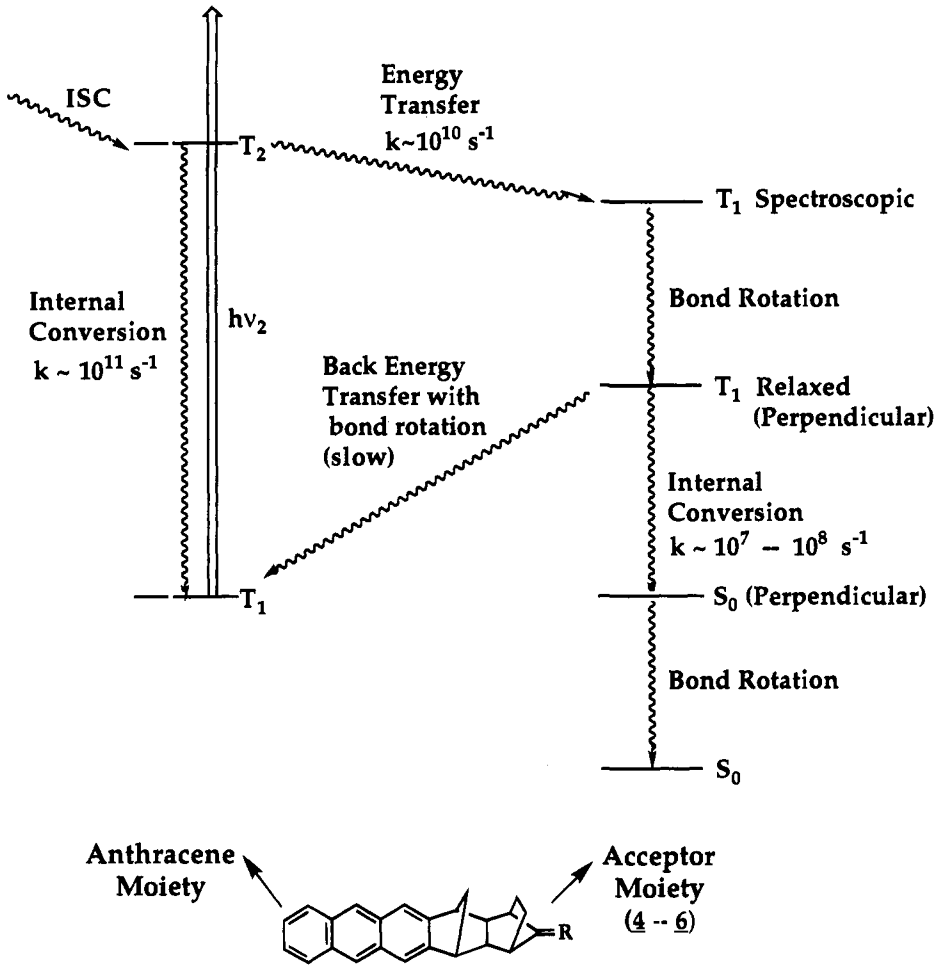
(23) Smith, G. A.; McGimpsey, W. G. *J. Phys. Chem.* **1994**, *98*, 2923−2929.

(24) Patney, H. K.; Paddon-Row, M. N. *Synthesis* **1986**, 326−328.

(25) Hayes, P. C.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 1257−1261.

(26) Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1145−1150.

Scheme 2



(m, 5 H), 2.11 (s, 2 H), 2.26 (s, 2 H), 2.49 (d, $J = 10$ Hz, 1 H), 3.59 (s, 2 H), 7.40−7.45 (m, 2 H), 7.67 (s, 2 H), 7.94−7.97 (m, 2 H), 8.30 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.3 (2 CH_2, C-2, C-3), 29.7 (CH_2, C-15), 39.5 (2 CH, C-1, C-4), 43.1 (2 CH, C-5, C-14), 44.4 (2 CH, C-4a, C-14a), 117.7 (2 CH, C-6, C-13), 124.9 (2 CH, C-7, C-12), 125.8 (2 CH, C-8, C-11), 127.9 (2 CH, C-9, C-10), 131.2 (2 C, C-5a, C-13a), 131.3 (2 C, C-6a, C-12a), 147.9 (2 C, C-7a, C-11a), 211.4 (C═O); HRMS for $C_{24}H_{20}O$, calcd 324.1515, found 324.1506.

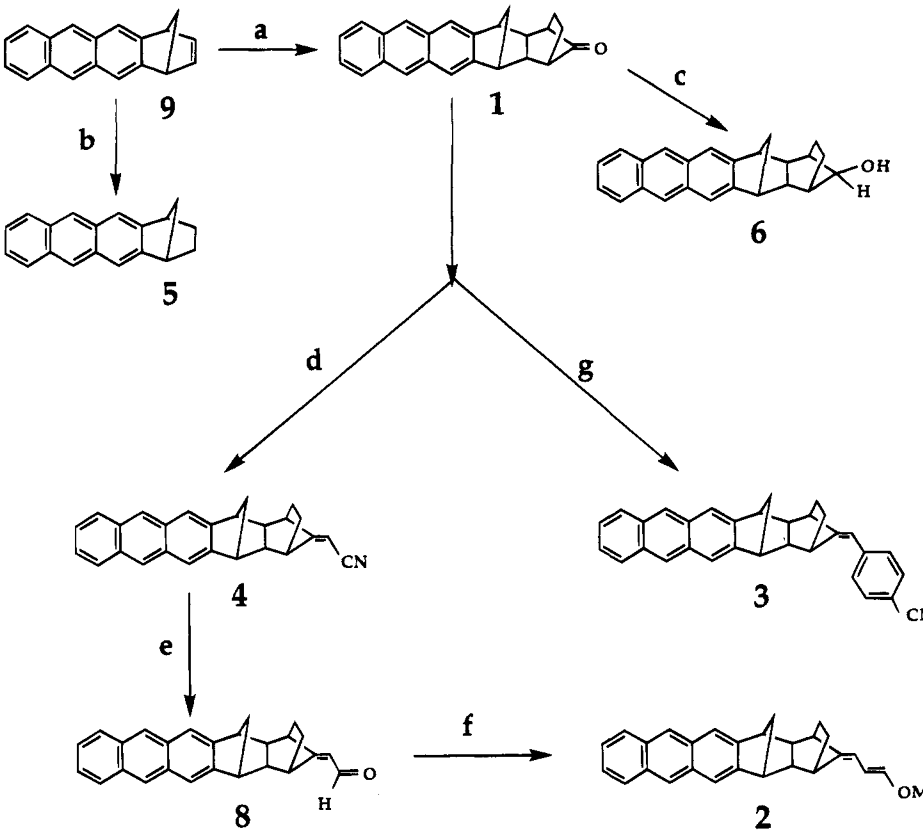
(1α,4α,4aα,5β,14β,14aα)-1,2,3,4,4a,5,14,14a-Octahydro-1,4:5,14-dimethanopentacen-16-ol (6). Reduction of **1** with $NaBH_4$ in MeOH/CH_2Cl_2 (3:1) gives **6** (mixture of stereoisomers): yield 80%; ^{1}H NMR ($CDCl_3$) δ 1.53−2.30 (m, 11 H), 3.39 (s, 2 H), 4.17 (s, C*H*OH, 1 H), 7.37−7.45 (m, 2 H), 7.60 (s, 2 H), 7.93−7.97 (m, 2 H), 8.27 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 29.7 (2 CH_2, two isomers), 42.7 (CH_2), 43.3, 43.9 (2 CH, two isomers), 43.7, 44.3 (2 CH, two isomers), 44.7, 45.7 (2 CH, two isomers), 81.0, 85.1 (CHOH, two isomers), 117.2 (2 CH), 124.6 (2 CH), 125.6 (2 CH), 127.9 (2 CH), 131.23 (2 C), 131.32 (2 C), 149.6 (2 C).

16-(Cyanomethylene)-(1α,4α,4aα,5β,14β,14aα)-1,2,3,4,4a,5,14,-14a-octahydro-1,4:5,14-dimethanopentacene (4). At 0 °C, to a suspension of sodium hydride (50% dispersion in oil, 14 mg, 0.28 mmol) in THF was added dropwise diethyl (cyanomethyl)phosphonate (50 mg, 0.28 mmol) in THF. After reaction had ceased (2 h), ketone **1** (45 mg, 0.14 mmol) in THF was added dropwise. After being stirred at room temperature for 8 h, the mixture was extracted with CH_2Cl_2, and the extract was washed with water. The solvent was removed to give the crude product. It was purified by chromatography (SiO_2, CH_2Cl_2/hexane, 6:4) to give **4** (50 mg, 100%): mp > 300 °C; IR (KBr) 3045, 2965, 2212, 1669, 901 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.65−2.15 (m, 7 H), 1.77 (d, $J = 10$ Hz, H-15), 2.37 (d, $J = 10$ Hz, 1 H H-15), 2.75 (t, $J = 3.8$ Hz, 1 H, H-1 or H-4), 3.12 (t, $J = 3.8$ Hz, 1 H, H-1 or H-4), 3.47 (s, 1 H, H-5 or H-14, 3.51 (s, 1 H, H-5 or H-14), 4.90 (s, 1 H, ═CH), 7.40−7.45 (m, 2 H), 7.62, 7.64 (2s, 2 H, H-6, H-13), 7.92−8.00 (m, 2 H), 8.28, 8.29 (2s, 2 H, H-7, H-12); ^{13}C NMR ($CDCl_3$) δ 22.2 (CH_2) 22.5 (CH_2), 42.4 (CH_2), 43.3 (CH), 44.0 (CH), 44.4 (2 CH), 44.5 (CH), 44.9 (CH), 115.7 (CN), 117.54 (═CH), 117.7 (2 CH), 124.9 (2 CH), 125.7 (2 CH), 127.8 (2 CH), 131.2 (2 C), 131.3 (2 C), 148.3 (2 C), 176.4 (═C); MS *m/z* (relative intensity) 347 (M^+, 4), 110 (27), 91 (100), 65 (26), 63 (48), 57 (43), 55 (34); HRMS for $C_{26}H_{21}N$, calcd 347.1675, found 347.1668.

16-(Formylmethylene)-(1α,4α,4aα,5β,14β,14aα)-1,2,3,4,4a,5,14,-14a-octahydro-1,4:5,14-dimethanopentacene (8). To a solution of **4** (40 mg, 0.12 mmol) in 2 mL of dry CH_2Cl_2 at −78 °C was added a solution of diisobutylaluminum hydride (DIBAL) in CH_2Cl_2 (1 M, 0.19 mL, 0.19 mmol), and the reaction solution was stirred for 8 h after the addition was complete. The mixture was quenched by methanol at −78 °C and warmed to room temperature. H_2SO_4 (5%, 3 mL) was added to the solution which was stirred for 1 h. $NaHCO_3$ was added to the mixture to adjust the pH to 7, followed by saturated aqueous potassium sodium tartrate (1 mL), and the whole was stirred until the two layers were almost clear. The solution was extracted with CH_2Cl_2. The solid residue left upon evaporation of the dried organic layer was purified by chromatography (SiO_2, CH_2Cl_2/hexane, 6:4) to give **8** (30 mg, 85%; 5 mg of starting material was recovered): mp > 300 °C; IR (KBr) 3045, 29.645, 1669, 901 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73−2.25 (m, 8 H), 2.59 (d, $J = 12$ Hz, 1 H), 3.00 (m, 1 H), 3.68 (s, 1 H), 3.70 (s, 1 H), 5.86 (d, $J = 8$ Hz, 1 H, ═CH), 7.57−7.62 (m, 2 H), 7.81 (s, 2 H), 8.10−8.15 (m, 2 H), 8.45 (s, 2 H), 9.91 (d, $J = 8$ Hz, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_2), 22.6 (CH_2), 39.2 (CH), 42.4 (CH_2), 44.06 (CH), 44.13 (2 CH), 45.0 (CH), 45.5 (CH), 115.3 (═CH), 117.5 (2 CH), 124.9 (2 CH), 125.7 (2 CH), 127.9 (2 CH), 131.2 (2 C), 148.4 (2 C), 176.7 (═C), 192.1 (CHO); MS *m/z* (relative intensity) 350 (M^+, 27), 91 (12), 65 (100), 63 (32), 52 (19).

16-(3-Methoxy-2-propenylidene)-(1α,4α,4aα,5β,14β,14aα)-1,2,3,4,-4a,5,14,14a-octahydro-1,4:5,14-dimethanopentacene (2). To a three-necked flask under N_2 cooled to 0 °C was added (methoxymethyl)-triphenylphosphonium chloride (206 mg, 0.6 mmol) in 5 mL of THF followed by phenyllithium (1.8 M in cyclohexane/ether, 0.25 mL, 0.45

Scheme 3. Synthesis of 1−6[a]



[a] Reagents and conditions: (a) (i) 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene; (ii) Na, EtOH; (iii) H_2, Pd/C; (iv) DDQ; (v) HCOOH. (b) H_2, Pd/C. (c) $NaBH_4$. (d) $(EtO)_2P(O)CH_2CN$, NaH, THF. (e) DIBAL, CH_2Cl_2. (f) $CH_3OCH_2PPh_3Cl$, PhLi, THF. (g) $(EtO)_2P(O)CH_2C_6H_4CN$, NaH, DME.

mmol). Compound **8** (35 mg, 0.1 mmol) in 6 mL of THF was then added dropwise. The mixture was warmed to room temperature and allowed to stir overnight. The reaction was quenched with H_2O and the product extracted with CH_2Cl_2. The product was purified by chromatography (SiO_2, hexane/EtOAc, 20:1) to give **2** (10 mg, 26%, mixture of isomers): ^1H NMR ($CDCl_3$) δ 1.43−1.82 (m, 5 H), 1.97 (s, 2 H), 2.36, (d, J = 10 Hz, 1 H), 2.52 (s, 1 H), 1.90 (s, 1 H), 3.36 (s, 2 H), 3.53, 3.58 (OCH_3, 3 H, two isomers), 4.99−6.46 (m, =CH, 3 H), 7.37−7.42 (m, 2 H), 7.58 (s, 2 H), 7.91−7.96 (m, 2 H), 8.25 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.2, 23.3, 23.4, 23.6 (2 CH_2, two isomers), 39.0, 39.2 (CH, two isomers), 42.20, 42.24 (CH_2, two isomers), 43.86 (CH), 43.90 (CH), 44.2 (CH), 45.9, 46.2 (CH, two isomers), 46.4, 46.8 (CH, two isomers), 56.4, 59.9 (OCH_3, two isomers), 103.2, 104.3 (=CH, two isomers), 104.2, 107.3 (=CH, two isomers), 117.1 (2 CH), 124.6 (2 CH), 125.5 (2 CH), 127.9 (2 CH), 131.2 (2 C), 131.3 (2 C), 146.8, 149.3 (=CH(OMe), two isomers), 149.4 (2 C), 150.3, 152.3 (=C, two isomers); HRMS for $C_{28}H_{26}O$, calcd 378.1985, found 378.1994.

16-[(4-Cyanophenyl)methylene]-(1α,4α,4aα,5β,14β,14aα)-1,2,3,4,4aα,5,14,14a-octahydro-1,4:5,14-dimethanopentacene (3). A mixture of ketone **1** (50 mg, 0.156 mmol) and diethyl (4-cyanobenzyl)phosphonate (76 mg, 0.3 mmol) in 3 mL of dry DME was cooled in ice. NaH((50% suspension in oil, 14.4 mg, 0.3 mmol) was added in several portions. The ice bath was removed, and the reaction mixture was stirred at room temperature for an additional 6 h. The solvent was evaporated, and the residue was extracted with CH_2Cl_2. The extract was washed with water and dried. The light yellow solid residue left upon solvent evaporation was chromatographed (SiO_2, CH_2Cl_2/hexane, 3:7) to give **3** (55 mg, 84%): IR (KBr) 3044, 2955, 2922, 2225, 1604, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59−1.91 (m, 5 H), 2.05 (s, 1 H), 2.38 (d, J = 10.5 Hz, 1 H), 2.69 (s, 1 H), 3.21 (s, 1 H), 3.44 (s, 2 H), 6.01 (s, 1 H, =CH), 7.25−7.29 (m, 2 H), 7.38−7.43 (m, 2 H), 7.51 (AB, J = 8 Hz, 2 H), 7.59 (s, 1 H), 7.62 (s, 1 H), 7.92−7.97 (m, 2 H), 8.26 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.8 (CH_2), 23.1 (CH_2), 39.8 (CH), 42.2 (CH_2), 43.9 (2 CH), 45.5 (CH), 45.9 (CH), 46.1 (CH), 109.2 (C), 111.1 (=CH), 117.3 (2 CH), 119.2 (CN), 124.7 (2 CH), 125.6 (2 CH), 127.8 (2 CH), 128.3 (2 CH), 131.2 (4 C), 132.0 (2 CH), 143.1 (C), 148.9 (2 C), 158.0 (=C); HRMS for $C_{23}H_{25}N$, calcd 423.1987, found 423.1971.

2-[(4-Cyanophenyl)methylene]bicyclo[2.2.1]heptane (7). Compound **7** (Scheme 1) was synthesized by the same procedure as **3**, starting with norcamphor. A viscous oil was obtained (mixture of isomers): ^1H NMR ($CDCl_3$) δ 1.32−1.69 (m, 5 H), 1.95−2.50 (m, 4 H), 2.84, 3.19 (s, 1 H, H-1, two isomers), 6.08, 6.28 (s, 1 H, =CH, two isomers), 7.32 (AB, J = 8 Hz, 2 H), 7.53 (AB, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.0, 28.1 (CH_2, two isomers), 28.4, 29.3 (CH_2, two isomers), 35.6, 37.1 (CH, two isomers), 39.0, 39.8 (CH_2, two isomers), 39.1, 40.8 (CH_2, two isomers), 41.6, 48.1 (CH, two isomers), 108.4, 108.6 (C, two isomers), 116.9, 117.7 (=CH, two isomers), 119.3 (CN), 127.9, 128.2 (2 CH, two isomers), 132.0 (2 CH), 153.7, 155.0 (=C, two isomers).

Acknowledgment. We acknowledge the financial support of U.S. Army Natick Research Development and Engineering Center, Contract DAAK-60-91-K-0002, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Dr. Jeffrey Kiplinger and his staff of Pfizer Central Research, Groton, CT, for the high-resolution mass spectra.

JA9435697