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Strongly UV Absorbing Bifunctional Azoalkanes

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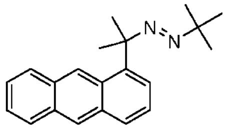
ABSTRACT



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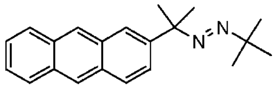

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Two new anthracene-containing azoalkanes (1 and 2) absorb UV light 600 times more strongly than simple azoalkanes. Intramolecular energy transfer from excited singlet anthracene to the azo group is nearly complete, but despite the close proximity of the two chromophores, 1 and 2 continue to exhibit anthracene fluorescence. Thermolysis of these compounds in the presence of monomers affords fluorescent labeled polymers. Compounds 1 and 2 are the first azoalkanes to undergo induced decomposition in solution.

Azoalkanes are widely used thermal free radical initiators,[1,2] yet few applications take advantage of their photochemical lability because of their low extinction coefficients in the near UV.[3] We reasoned that covalent attachment of an azoalkane moiety to a strongly absorbing chromophore might lead to a useful initiator if energy transfer from the chromophore to the azo group were even moderately efficient. Anthracene (AN) was selected as the donor because its extinction coefficient in the near UV is >600 times greater than that of azo-*tert*-butane (ATB). Although anthracene inhibits the polymerization of vinyl monomers, the fact that highly purified 1- and 2-vinylanthracenes can be polymerized[4] suggested that AN-containing azoalkanes would serve as initiators. We describe herein the radical chemistry of unsymmetrical azo compounds **1** and **2** and show that these "chromophore-labeled initiators"[5] are capable of introducing a strongly fluorescent AN group into polystyrene (PS) and poly(methyl methacrylate) (PMMA). Since the AN is linked to the polymer by C−C bonds alone, it will not be removed by hydrolysis, unlike ester-linked fluorescent polymers.[5,6] Fluorescent probes are useful for investigating the physical properties of polymers[7] and energy transfer in polymers,[8] and AN derivatives have been employed in the fields of molecular recognition and sensing,[9] in solid-phase synthesis,[10] and in studies of polymer chain dynamics.[11−15]

Besides examining the potential of **1** and **2** to serve as radical initiators, we wanted to study the efficiency of intramolecular energy transfer, which is a topic of long-standing interest to organic photochemists.[16] Our earlier observation that triplet energy transfer was often surprisingly slow in bichromorphic azoalkanes[17] piqued our curiosity

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about the analogous singlet process. Even when acyclic azoalkanes are promoted to their excited triplet state, loss of nitrogen is usually inefficient.[18] We found many years ago that ATB was a rapid quencher of AN fluorescence and that irradiation of AN caused decomposition of added ATB with a much higher nitrogen quantum yield (Φ_{N_2})[18] than the triplet sensitized reaction. It therefore seemed possible that **1** and **2** would be good photochemical free radical sources.

Synthesis and Nitrogen Yields. Reaction of 2-cyanoanthracene[19,20] with methyllithium and cerium chloride proceeded normally with no loss of the functional groups seen in 2-cyanonaphthalene.[21] Treatment of the resulting amine with *tert*-butylsulfamyl chloride[22] followed by hypochlorite oxidation[23] afforded **2** as a solid that melted and evolved nitrogen sharply at 131 °C.

The more hindered 1-isomer proved to be accessible by initial conversion of 1-acetylanthracene[24] to the tertiary alcohol. Treatment with hydrazoic acid yielded the desired azide plus the dehydration product, 1-isopropenylanthracene. Lithium aluminum hydride reduction of the azide afforded the amine, which was transformed to the unsymmetrical azo compound **1** by a similar method as **2**.

Irradiation of **1** and **2** at 313 nm in benzene afforded N_2 in 85−90% yield, whereas thermolysis at 105−110 °C gave 89−93% nitrogen. The fact that these yields fall short of 100% is attributed to decomposition by ambient light prior to sealing the tubes.

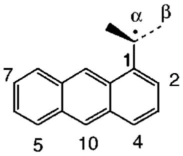
Thermolysis Kinetics. To evaluate the thermal stability of **1** and **2**, we determined the kinetics in our automated gas evolution apparatus.[25,26] Surprisingly, the “first-order” plots for both isomers were curved, falling more slowly as the runs progressed. Because the curvature persisted in several solvents and even in the presence of 1,4-cyclohexadiene, we ran the thermolysis of **1** with added thiophenol, whereupon the first order plots finally became linear (cf. Table 1). Fitting the rate constants for **1** to the Eyring equation gave $\Delta H^{\ddagger} =$ 30.5 kcal/mol and $\Delta S^{\ddagger} = 6.5$ eu, whereas **2** gave $\Delta H^{\ddagger} =$ 29.8 kcal/mol and $\Delta S^{\ddagger} = 7.8$ eu. For comparison of the two isomers, the more meaningful parameter is $\Delta G^{\ddagger}$ (100 °C), which was 28.0 kcal/mol for **1** and 26.9 kcal/mol for **2**.

Thermolysis and Photolysis Products. Thermolysis of **1** in 1-methylnaphthalene with thiophenol at ~96 °C afforded mainly 1-isopropylanthracene. When thiophenol was omitted, the thermolysis mixture became quite complex, revealing minor amounts of 1-isopropylanthracene and 1-isopropenylanthracene plus larger quantities of three compounds whose CI/GC/MS ($M + 1 = 277$) corresponded to recombination of *tert*-butyl radicals with **3**. We assign the last GC peak to the expected α-recombination product, 1-*tert*-heptylanthracene **4**. Reverse-phase HPLC analysis of the product mixture supported the GC/MS results, showing a complex mixture containing several compounds with the characteristic anthracene UV spectrum. A similar product distribution was obtained upon irradiation of **1** at 25 °C, but the amount of disproportionation products was even lower than in the thermolysis.

Table 1. Thermolysis Rates of Azo Compounds **1** and **2** with Added Thiophenol[a]

temp, °C	$10^4\,k$, s^{-1}	R[b]	half-life, min	half-lives[c]
91.94[d]	1.16	0.99953	99.8	2.91
103.09[d]	4.17	0.99956	27.7	3.32
105.12[d]	5.16	0.99955	22.4	3.56
111.16[d]	10.0	0.99847	11.5	3.30
85.88[e]	2.58	0.99962	44.8	3.19
103.09[e]	18.3	0.99942	6.32	5.38

[a] Using 29 mg of azo compound and 40 mg of PhSH in 1 mL of 1-methylnaphthalene solvent. [b] Correlation coefficient. [c] Number of half-lives fitted to first-order line. [d] Compound **1**. [e] Compound **2**.



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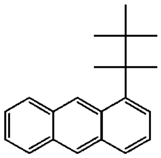
∠βα12 = 15°



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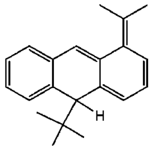

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Despite the temptation to attribute these $M + 1 = 277$ products to simple radical recombination, the curved kinetic plots suggested another mechanism: induced decomposition of **1** by *tert*-butyl radicals. We tested this idea using *tert*-heptyl perpivalate as a *tert*-butyl radical source.[27,28] In separate control experiments, thermolysis of of **1** in C_6D_6 at 63 °C showed no decomposition over the course of 8 h, but under the same conditions, the perester decomposed completely in 6 h. A mixture of **1** with a 4.6-fold molar excess of *tert*-heptyl perpivalate in C_6D_6 was likewise heated at 63 °C, leading to complete disappearance of **1** in 4 h, judging by NMR. The largest GC peak (retention time 16.69 min) corresponded to a previously minor product, showed $M + 1 = 277$ in the CI/GC/MS, and degraded to a complex mixture when subjected to TsOH. The 16.69 min GC peak was accompanied by all of the peaks previously seen in the GC trace, plus others. On the basis of its mass and the observation that HPLC−UV analysis of the perester product mixtures showed hardly any peaks with AN absorption, we assign the new product to a quinoid AN structure such as **5**. In support of this notion, the ^1H NMR spectrum of the thermolyzed mixture exhibited peaks in the olefinic region (5.75−6.26 ppm).

Irradiation of **2** at room temperature in C_6D_6 without thiophenol and thermolysis of **2** in C_6D_6 at 110 °C showed

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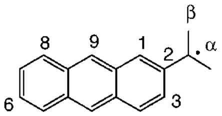
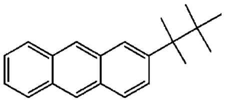
four products by GC, the first two of which were 2-isopropylanthracene and 2-isopropenylanthracene. Next came two compounds with identical EI mass spectra ($m/e = 276$), corresponding to recombination of the 2-anthracenyl-2-propyl radical **6** with a *tert*-butyl radical. On the basis of product isolation and NMR spectroscopy, we assign the last GC peak to 2-*tert*-heptylanthracene **7**.



6

∠βα21 = 0°



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Absorption and Fluorescence Spectroscopy. The excitation and fluorescence spectra of **2** and the absorption spectrum of ATB are shown in Figure 1. The absorption maxima of **2** coincide with its excitation maxima (376, 356, 340, 324 nm) and with those of AN. However, the emission maxima are slightly red-shifted relative to those of AN. UV absorbances and fluorescence intensities are shown in Table 2. On the basis of the integrated area of the emission, the fluorescence efficiency of **1** and **2** is 12 and 7 times less than that of AN, respectively, implying that singlet energy was mostly transferred from AN to the azo moiety. We therefore determined the nitrogen quantum yield of **2**, anticipating that singlet energy transfer would lead to deazatation. Using a benzophenone–DBH actinometer at 313 nm,[29] we obtained $\Phi = 0.74$.

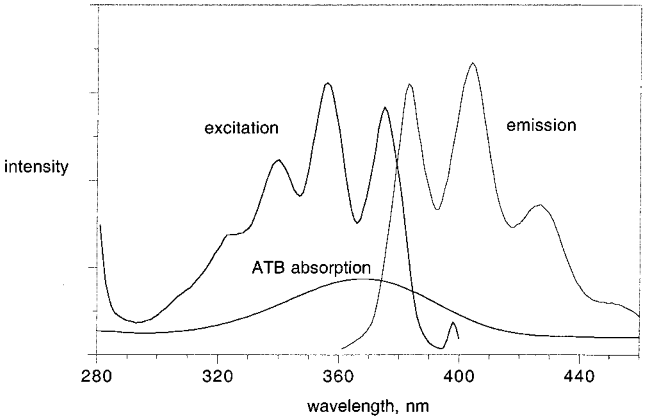

Figure 1. Excitation spectrum of the 398-nm emission of **2**, emission spectrum of **2**, and absorption spectrum of azo-*tert*-butane. Spectral intensities are adjusted to facilitate comparison.

ATB is a very rapid bimolecular quencher of AN fluorescence. Although the quenching rate constant was determined years ago[18] as 2.0×10^{10} M^{-1} s^{-1}, we repeated this experiment using more dilute AN solutions in toluene and more concentrated solutions of ATB. With excitation at 325 nm where ATB has ϵ of only 4, we found a linear Stern–Volmer plot with $k_q = 1.5 \times 10^{10}$ M^{-1} s^{-1}.

Table 2. Fluorescence and Absorbance for AN, **1**, **2**, and Functionalized Polymers

compound	solvent	intensity^a	UV absorbance	corrected intensity^b
anthracene^{c,d}	hexane	(1.0)	0.12^e	(1.0)
1^{c,d}	hexane	0.032	0.043^e	0.082
2^{c,d}	hexane	0.16	0.14^e	0.14
anthracene^{f,g}	toluene	(1.0)	0.21 (360 nm)	
PS from **1**^{f,h}	toluene	0.21	0.032 (366 nm)	
PS from **2**^{f,i}	toluene	0.61	0.12 (360 nm)	
anthracene^{f,j}	toluene	(1.0)	0.46 (360 nm)	
PMMA from **1**^{f,k}	toluene	0.044	0.031 (366 nm)	

[a] Using 325 nm excitation; emission spectrum integrated from 350 to 550 nm. [b] Corrected for varying absorbance at 325 nm. [c] Degassed and sealed. [d] At 6.29×10^{-5} M. [e] At 325 nm. [f] Nitrogen purged for 1 min. [g] Reference solution for PS fluorescence. [h] At .02 mg/10 mL. [i] At 5.11 mg/10 mL. [j] Reference solution for PMMA fluorescence. [k] At 5.33 mg/10 mL.

Polymerization Experiments. Photolysis of 9-anthryl ketones in the presence of methyl methacrylate yielded AN-tagged PMMA but in low chemical and quantum yield.[30] In contrast, our system produces anthracenyl-2-propyl radicals efficiently upon either photolysis or thermolysis. Compounds **1** and **2** were used to initiate the polymerization of styrene in benzene, yielding fluorescent polystyrene (cf. Table 2). GPC of the PS from **1** gave $M_n = 26300$, $M_w = 41270$, while the PS from **2** showed $M_n = 15240$, $M_w = 28600$. Compound **1** also served to polymerize methyl methacrylate, and like PS, the purified polymer exhibited typical AN absorption and emission spectra. The molecular weight M_n of the PS found by GPC predicts that the AN absorbance should be 3–6 times higher than reported in Table 2, under the reasonable assumption that the extinction coefficient of the AN moiety is unchanged in the polymer. A possible interpretation of this result is that a sizable fraction of the polymer contains quinoid AN end groups, similar in structure to **5**.

The observation that intramolecular singlet energy transfer is incomplete in **1** and **2** is the same as found for intramolecular triplet sensitization of the azo group.[17] However, this result is even more surprising in **1** and **2** because intermolecular singlet energy transfer is very fast and because the chromophores are separated by only two bonds, which is the shortest possible link. The small size of the acceptor chromophore could be responsible for the continued fluorescence of **1** and **2**.[17] The nitrogen quantum yield of **2** (0.74) was higher than the usual 0.5 maximum for acyclic azoalkanes.[2] Since singlet energy transfer is about 90% complete in **1** and **2**, one would expect a maximum quantum yield of ~0.45. The enhanced value found experimentally can be attributed to induced decomposition by *tert*-butyl radicals. The high quantum yield for intramolecular singlet sensitized photolysis of **2** stands in sharp contrast to triplet sensitized irradiation of ATB, whose nitrogen quantum yield is below 0.02.[18]

Turning to the thermolysis results, we note that $\Delta G^{\ddagger}$ (100 °C) of **1** (28.0 kcal/mol) and **2** (26.9 kcal/mol) are not much

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lower than that of *tert*-butylazocumene (28.6 kcal/mol).[31] This result is surprising because azoalkane thermolysis rates generally reflect the stability of the incipient radicals, and the C−H bond dissociation energy (BDE) of 1-methylnaphthalene and 9-methylanthracene lie 2.9 and 6.6 kcal/mol, respectively, below that of toluene.[32] To gain further insight into this discrepancy, we carried out B3LYP calculations on benzylic C−H bond dissociation and the results are summarized in Table 3. While the calculated BDEs of all three compounds are indeed similar, we can detect conformational energy differences that form a consistent picture, despite lying barely outside the error limits of the calculations.

Table 3. B3LYP Calculations on Cumene, Isopropylanthracenes, and Their Radicals

species	energy[a] 25 °C	3° C−H BDE[b] kcal/mol (298 °C)	E_{rel} kcal/mol (298 °C)[c]
H•	−0.498856		
cumene	−350.002478	82.6	0.0
cumyl•	−349.372017		
1-isopropylAN	−657.182854	82.9	2.5
1-isopropylAN•(**3**)	−656.551876		
2-isopropylAN	−657.186782	79.5	(0.0)[d]
2-isopropylAN•(**6**)	−656.561305		

[a] In hartrees. [b] Bond dissociation energy. [c] Strain energy assuming that cumene is unstrained. [d] Assumed same as cumene.

Both cumyl radical and **6** are planar; hence, the 3.1 kcal/mol lower BDE of 2-isopropylanthracene suggests greater resonance stabilization of **6** than cumyl. On the other hand, repulsion between methyl and the 9-hydrogen, which twists the side chain of **3** out of plane by 15°, raises its energy 5.9 kcal/mol above that of **6**. Similar steric repulsion in 1-isopropylanthracene elevates its energy 2.5 kcal/mol above that of the 2-isomer, with the net result that the C−H BDE of 1-isopropylanthracene is 3.4 kcal/mol greater than that of 2-isopropylanthracene. In dissociation of **1** and **2**, the radicals must again differ by 5.9 kcal/mol, but the 1.1 kcal/mol lower $\Delta G^{\ddagger}$ (100 °C) of **2** compared to that of **1** means that the ground-state energy of **1** lies 4.8 kcal/mol above that of **2**, if entropy effects are ignored. Quite reasonably, the steric repulsion that elevates 1-isopropylanthracene above its 2-isomer becomes more severe in **1** versus **2**. Thus ground-state steric repulsion narrows the $\Delta G^{\ddagger}$ (100 °C) gap (1.1 kcal/mol) between **1** and **2** more than expected on the basis of the C−H BDE difference between 1-isopropylanthracene and 2-isopropylanthracene (3.4 kcal/mol).

Although the structure of only three products (isopropyl, 2-propenyl, and *tert*-heptyl anthacenes) was determined with certainty, it is clear from GC/MS and HPLC/UV that there are at least two radical recombination products from **6** and three from **3**. A clue about their possible structures can be obtained from the spin density of radicals **6** and **3**. The values calculated by density functional theory for **6** are 0.643, 0.436, and 0.223 at the α, 1, and 9 positions, respectively, and those of **3** are 0.599, 0.388, 0.358, and 0.152 at the α, 2, 4, and 10 positions, respectively. No other ring position exhibited a spin density over 0.11. Ignoring steric hindrance, these values predict several recombination products for **6** and **3**. Such hindrance does not affect AN itself, where the 9 and 10 positions are attacked preferentially by radicals.[33,34] In addition to the AN recombination products that we see by HPLC/UV and GC/MS, there are others that lack the AN chromophore. These are assumed to be quinoid compounds such as **5** derived from recombination on the ring without rearomatization. The complexity of the products from **1** and **2**, the difficulty of separating the various ANs and quinoid ANs, and their sensitivity to acid rendered a complete analysis impractical.

Four lines of evidence point to induced decomposition of **1** and **2**: the curved first-order plot without thiophenol, the linear plot with thiophenol, the high nitrogen quantum yield of **2**, and the fact that thermolysis of *tert*-heptyl perpivalate in the presence of **1** causes disappearance of the azo compound and yields mostly non-AN products. To our knowledge, there is no previous case of induced decomposition of an azoalkane, except for some early gas phase work.[35] For example, the linear activation plot for thermolysis of allylic azoalkanes[36] argues against induced decomposition. A likely reason why we see this complication in **1** and **2** is that AN is highly prone to radical attack. Thus its methyl affinity is about 16 times greater than that of a simple 1-olefin and is over 1300 times larger than that of benzene.[37] 2-Cyanopropyl and benzyl radicals readily attack AN at the 9-position,[33,34] supporting the notion that the 16.69 min GC peak from the perester and **1** has the structure **5**.

In summary, the new azo compounds **1** and **2** are strong UV absorbers by virtue of their AN chromophore. On irradiation, singlet electronic energy is mostly transferred from the AN ring to the azo group; however, despite the close proximity of these chromophores, energy transfer is incomplete. Compounds **1** and **2** are effective photoinitiators that yield *tert*-butyl radicals plus radicals **3** and **6**. Thermolysis occurs at moderate temperatures, and the rate constants can be rationalized by a combination of steric and radical-stabilization arguments. If the *tert*-butyl radicals are not scavenged, they attack the AN ring, leading to the first case of solution phase induced decomposition of an azo compound. Initiators **1** and **2** convert styrene and methyl methacrylate to end-labeled fluorescent polymers.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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