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Importance of π-Stacking in Photoreactivity of Aryl Benzobisoxazole and Aryl Benzobisthiazole Compounds

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ABSTRACT: Aryl benzobisoxazole and aryl benzobisthiazole compounds in the solid state and in solution have completely different photoreactivity. In the solid state, intermolecular π-stacking interactions between these molecules lead to excimer formation. The excimer undergoes a photoinduced electron transfer to generate an ion radical pair. In the presence of oxygen, the anion radical transfers an electron to molecular oxygen to form superoxide. The cation radical undergoes bond cleavage followed by hydrogen abstraction and other reactions to form benzobisoxazoles (or benzobisthiazoles), benzonitriles, and benzamides. In solution, aryl benzobisoxazole and aryl benzobisthiazole molecules cannot readily π-stack, and therefore photoinduced electron transfer and its subsequent reactions do not occur. The compounds in solution are stable even after prolonged irradiation, suggesting that intermolecular π-stacking plays a very important role in photoreactivity for these molecules. Reversible redox reagents, such as ferrocene compounds, are found to retard the subsequent reactions from the photoinduced electron-transfer reaction and hence improve the photostability of poly{(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene}.

Introduction

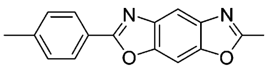
Solid-state morphology of molecular and polymeric materials, in particular the formation of π-stacks, is a topic of tremendous growing interest in biological, organic, and polymer chemistry.[1] Understanding the effect of π-stacking on the photophysical and photochemical properties of conjugated polymers and oligomers is of theoretical as well as practical importance.

The planarity and rigidity of aryl benzobisoxazole and aryl benzobisthiazole compounds and polymers enable the molecules to form π-stacks readily. In a previous publication, we reported dramatically, and sometimes totally, different photophysical properties of these molecules in the solid state where they easily form π-stacks and in solution where the molecules do not readily π-stack.[2] The findings, which were attributed to strong π-stacking interaction in the solid state, are summarized below.

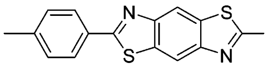
(a) Large excitation and emission energy differences were observed for planar *p*-phenylenebenzobisoxazole and *p*-phenylenebenzobisthiazole model compounds and polymers in solid state, but the same model compounds in solution and those with side groups which hindered the overall structural planarity showed significantly smaller Stokes shifts.

(b) Only one emitting component was observed when a benzobisoxazole model compound in solution was excited. The same compound in the solid state showed two emitting species.

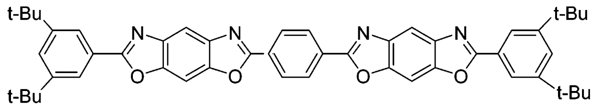
(c) Fluorescence quenching by oxygen of 2,2′-(1,4-phenylene)bis[6-(3,5-bis(1,1-dimethylethyl)phenyl]benzo[1,2-*d*;5,4-*d*′]bisoxazole (**1**), a compound with side groups interrupting its planarity, followed the normal Stern−Volmer quenching plot. The data for 2,6-bisphenylbenzo[1,2-*d*:5,4-*d*′]bisoxazole (**2**), which is planar,[3] did not follow a linear Stern−Volmer quenching relationship. At high pressure, quadratic fluorescence quenching by molecular oxygen was observed. The greater tendency for **2** to π-stack at high pressure due to its planar configuration contributed to the observed difference.



p-phenylenebenzobisoxazole



p-phenylenebenzobisthiazole



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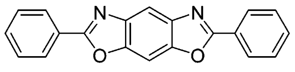

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We report in this article that completely different chemical reactions resulted when *p*-phenylenebenzobisoxazole and *p*-phenylenebenzobisthiazole compounds were photolyzed in the solid state, where the molecules could stack, and in dilute solution, where π-stacking did not happen. A photoinduced electron-transfer mechanism is used to account for this dramatic difference. Photodecomposition of the cation radical is retarded by adding a reversible electron-transfer reagent to the system.

Results and Discussion

Photolysis of Aryl Benzobisoxazole and Aryl Benzobisthiazole Compounds in Solution. Aryl benzobisoxazole and aryl benzobisthiazole compounds have very low solubility in common organic solvents. The very low solubility of these compounds imposes

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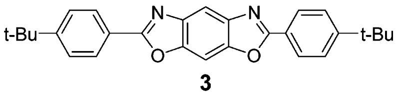
difficulties in following the disappearance of starting materials and characterization and quantitation of reaction products. Compound **1**, 2,6-(4-*tert*-butyldiphenyl)benzo[1,2-*d*:5,4-*d*′]bisoxazole (**3**), and 2,6-(4-*tert*-butyldiphenyl)benzo[1,2-*d*:4,5-*d*′]bisthiazole (**4**), which have *tert*-butyl groups to enhance their solubility, were synthesized to allow the study of photolysis of aryl benzobisoxazoles in solution.



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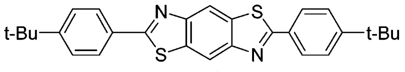

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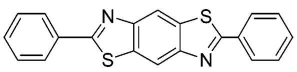
A 3.2×10^{-4} M solution of **3** or **4** in cyclohexane was photolyzed under atmospheric conditions. After photolysis for 150 h, starting material was 100% recovered as measured by weight. The solubility of **1** in cyclohexane was so low that LC peak area integration and MS were used to analyze the disappearance of starting material and possible formation of photochemical products. After photolysis for 150 h, LC peak area integration showed solution concentration did not change, and MS detected only **1** in the sample.

A methylene chloride solution (3.2×10^{-4} M) of **2** was photolyzed for 100 h under atmospheric conditions. GC-MS of the exposed solution showed **2** (96%) and chlorinated **2** (4%), which most likely was the product from methylene chloride photodecomposition. Similar results were observed with 2,6-bisphenylbenzo[1,2-*d*:4,5-*d*′]-bisothiazole (**5**). When experiments were repeated with glass flasks, chlorinated **2** and **5** were not detected. The results suggested that aryl benzobisoxazole and aryl benzobisthiazole compounds in solution are photolytically stable, which is consistent with the report by Güsten and co-workers that **2** and substituted **2** in ethanol or dioxane were stable laser dyes.[9]



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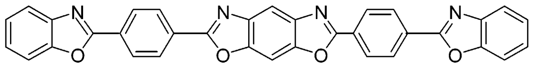
Photolysis of Aryl Benzobisoxazole and Aryl Benzobisthiazole Compounds in the Solid State. For **1**, **2**, and **5**, which have reasonable solubility in chloroform, thin layers of about 0.3 μm thick were cast from chloroform solutions on the inside wall of 100 mL serum vials. The vials were either capped with air inside or purged with nitrogen before capping and then irradiated.2,6-Bis[4-(2-benzoxazoly)phenyl]benzo[1,2-*d*:5,4-*d*′]-bisoxazole (**6**), 2,2′-(1,4-phenylene)bis(6-phenylbenzo-[1,2-*d*:5,4-*d*″]bisoxazole (**7**), and 2,6-bis[4-(2-benzothiazoyl)phenyl]benzo(1,2-*d*:4,5-*d*″)bisthiazole (**8**) are totally insoluble in nonacidic organic solvents. Thin films were cast from TFA solutions in serum vials or deposited on a microscope slide by sublimation.

Thin film samples of **1**, **2**, and **5** after photolysis in the presence of oxygen were analyzed by LC. Table 1 shows the concentration of starting **1**, **2**, and **5** that remained after photolysis in nitrogen or in air as monitored by LC peak area. Reduction in starting material peak area and the appearance of early-eluting, lower molecular weight photoreaction products were observed as compared to control samples. Gaseous compounds in the vial headspace were analyzed by GC-MS. A large amount of CO_2 was found in the serum vial headspace of samples **1**, **2**, and **5** photolyzed in air.



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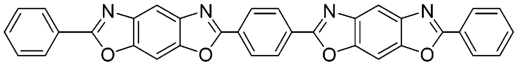

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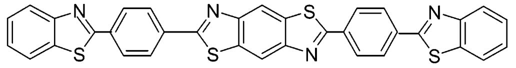

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GC-MS was also used to analyze photolyzed thin-film samples of **2** and **5**. GC-MS of photolyzed **2** showed benzoic acid (0.1%), benzamide (1.0%), phthalimide (0.1%), **9** (0.2%), and **2** (98.5%). Reconstructed total ion chromatograms from the GC-MS analyses of an unexposed sample of **2** compared to a sample exposed in air for 150 h are shown in Figure 1a,b. The mass spectra of the products were compared with and were identical to those of the control compounds. The photolyzed sample of **5** contained 2-phenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (**10**) (0.2%) and **5** (99.8%). When exposure time was increased from 150 to 430 h, the concentration of **10** and **5** was 0.5% and 99.5%, respectively. Formation of **10** from photolysis of **5** was also confirmed with the same procedure as for products from photolysis of **2**. LC analysis showed a lower concentration of remaining **2** and **5** than the concentration of **2** and **5** from the peak areas of the total ion chromatograph. Results based on reduction of LC peak area are the more accurate reaction conversions. The large amount of CO_2 found in the serum vial headspace might be the reason for **2** and **5** not appearing in GC-MS analysis. Products from photolysis of solid state **2** and **5** are shown in Scheme 1.

Analysis and confirmation of photolysis products of **6**, **7**, and **8** were performed with (a) controls, (b) chemical ionization to confirm M^+, (c) single ion profiles for thermal separation of products, and (d) extraction and analysis by GC-MS of lower molecular weight products. Confirmation of photoreactivity of **6** is illustrated in detail.

Parts a and b of Figure 2 are the EI-MS of unexposed **6** and the EI-MS of **6** after it was exposed in air for 150 h. M^+ and M^{2+} were confirmed by chemical ionization. Figure 3 is the single ion profiles for thermal separation of products off the direct exposure probe. Species with specified m/z were detected as they came off of the probe. Lower molecular weight products were extracted with chloroform, and the chloroform solution was analyzed by GC-MS. Figure 4 shows the total ion chromatogram for such an extract. The mass spectra of the three eluted

Table 1

sample	exposure time (h)	peak area	%
1 unexposed to light	0	546 000	100
1 exposed under nitrogen	150	547 000	100
1 exposed in air	150	497 000	91
2 unexposed to light	0	435 000	100
2 exposed under nitrogen	150	434 000	100
2 exposed in air	150	396 000	91
5 unexposed to light	0	591 000	100
5 exposed under nitrogen	430	592 000	100
5 exposed in air	150	579 000	98
5 exposed in air	430	549 000	93

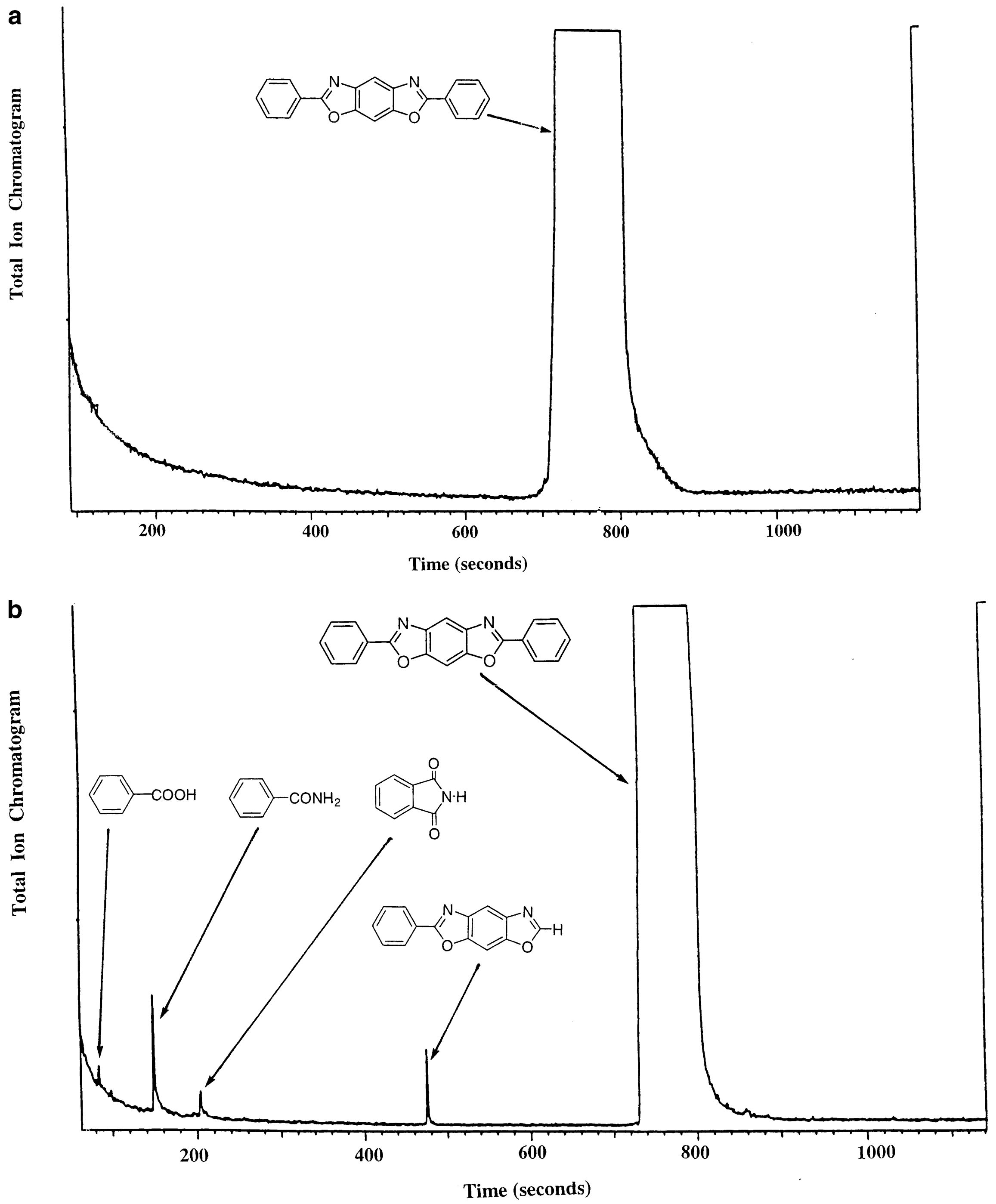
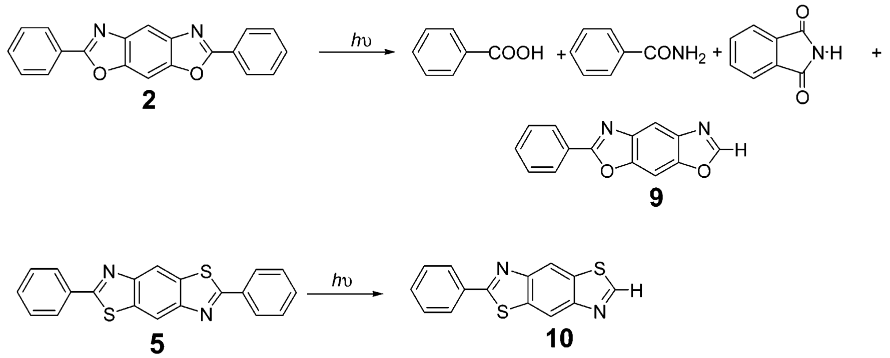


Figure 1. (a) Total ion chromatograph of an unexposed sample of **2**. (b) Total ion chromatograph of a sample of **2** photolyzed for 150 h in air.

compounds were identical to those of independently synthesized **11**, **12**, and **13**. Because of their lack of solubility in chloroform and their low volatility, 4-(6-phenylbenzo[1,2-*d*:5,4-*d*′]bisoxazol-2-yl)benzonitrile (**14**) and 4-(6-phenylbenzo[1,2-*d*:5,4-*d*′]bisoxazol-2-yl)benzoamide (**15**) were detected by EI-MS as shown by single ion profiles of thermally separated products, but they did not show up in GC-MS analysis of the chloroform extract.

The same methodology was used to analyze the photolytic products from **7**, **8**, and **1**. In the sample of **7**, the compounds **9**, **16**, and 2-(4-(benzo[1,2-*d*:5,4-*d*′]bisoxazol-2-yl)phenyl)-6-phenylbenzo[1,2-*d*:5,4-*d*′]bisoxazole (**17**) were found. For **8**, the compounds **18**, 2-(4-(2-benzothiazolyl)phenyl)benzo[1,2-*d*:4,5-*d*′]bisthiazole (**19**), 4-(6-(4-(2-benzothiazolyl)phenyl)benzo[1,2-*d*:4,5-*d*′]bisthiazol-2-yl)benzonitrile (**20**), and an unidentified compound with *m*/*z* of 294 were detected after photolysis. Sublimed **6**, **7**, and **8** produced the same products as samples cast from TFA solution. 3,5-Bis(1,1-dimethylethyl)benzamide, 4-(6-(3,5-bis(1,1-dimethylethyl)phenyl)benzo[1,2-*d*:5,4-*d*′]bisoxazole (**21**), and 4-(6-(3,5-bis-(1,1-dimethylethyl)phenyl)benzo[1,2-*d*:5,4-*d*′]bisoxazol-2-yl)benzamide (**22**) were identified from photolyzed **1**. Figures 5 and 6 are the EI-MS of **7** and **8** photolyzed in air. Products from photolysis of solid state **6**, **7**, **8**, and **1** are shown in Scheme 2. The headspace of the serum vials as analyzed by GC-MS contained a large amount of CO_2.

Scheme 1



When films of **1**−**8** were photolyzed in a nitrogen atmosphere, only unreacted starting materials were found by GC-MS or DEP-MS. None of the above-mentioned products were detected. It has been reported that physically damaged poly{(benzo[1,2-*d*:5;4-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene} (PBO) filaments exposed to oxygen and light tend to lose a portion of their tensile strength. Physical damage to the filament permits oxygen to enter the otherwise oxygen impermeable filament.[8]

The above results demonstrated the surprising but completely different photoreactivity of aryl benzobisoxazole and aryl benzobisthiazole compounds in solution and in solid state. These compounds in solution are very photolytically stable whereas in the solid state and in the presence of oxygen, they are photolytically labile. Although different photochemistry for organic compounds in solid state and in solution has been a subject of intense activity in the past 30 years,[1] the totally different photoreactivity of aryl benzobisoxazole and aryl benzobisthiazole compounds in solid state and in solution is one of the most dramatic.

Cyclic Voltammetric Study of the Redox Properties of PBO Polymer. The electrochemical reduction of PBO and poly{(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-1,4-phenylene} (PBT) polymers is reversible whereas oxidation is not reversible.[10,11] Integration of the reduction peak current and calculation of the amount of material on the electrode led to an n value of 0.9 electrons per repeating unit, indicating the formation of a poly(anion radical). The formation of this reduced material was accompanied by a color change from yellow to black. The reduction peak and the color change could be cycled repeatedly without apparent loss of film mechanical integrity. The electrochemical oxidation of PBO and PBT was totally irreversible—one scan through the oxidative process was sufficient to deactivate the film electrochemically and destroy its mechanical integrity. Integration of the oxidation current yielded an n value of 0.7 electrons per repeating unit. A poly(cation radical) was formed which readily decomposed.

ESR Spectroscopy of PBO and PBT. Strong ESR signals were observed for PBO, PBT, and their model compounds.[12] Oxygen was not required for the generation of the radicals.[2] This observation was also reported by DePra and co-workers.[11] A PBO fiber sample, which had been sealed in a vacuum for 40 days, showed strong ESR signals. Formation of superoxide from the photolysis of PBO, PBT, and their model compounds in the presence of oxygen was detected by ESR spectroscopy using 5,5-dimethyl-1-pyrroline *N*-oxide as a radical trap as reported in ref 2.

Photoinduced Electron Transfer of Excimers Generated from π-Stacking. We previously reported that intermolecular π-stacking interactions occurred between the planar aryl benzobisoxazole and aryl benzobisthiazole compounds, leading to excimer formation in solid state. In contrast, no excimer formation was detected for these compounds in solution. Intermolecular π-stacking led to the disparity between photophysical properties for aryl benzobisoxazole and aryl benzobisthiazole compounds in solid state and in solution as described in the Introduction section. These compounds in the solid state underwent photoinduced electron transfer, and in the presence of molecular oxygen, the radical ion pair led to the generation of superoxide, as shown in Scheme 3.[13,14] Superoxide was trapped, and the product was identified by ESR. The unstable cation radical decomposes to generate a free radical and a cation. Hydrogen abstraction by the free radical produces benzobisoxazoles and benzobisthiazoles. Oxygen, superoxide, and moisture may react with the cation radical to generate nitriles and amides.

Scheme 3 is also consistent with the fact that strong ESR signals were detected for PBO and PBT fibers that had been sealed in a vacuum for 40 days. Oxygen is not required for the generation of the ion radicals. In the absence of oxygen, the ion radical pair undergoes back electron transfer. In solution, the planar molecules do not π-stack, photoinduced electron transfer cannot occur, and the molecules are photolytically stable.

Effect of Reversible Redox Reagents on PBO Photochemistry. According to Scheme 3, a reversible redox reagent, which is able to transfer an electron to the unstable cation radical to make a neutral molecule and then pick up an electron from superoxide, should be an efficient inhibitor of the photochemical reaction. Chemical or anodic oxidation of ferrocene involves a one-electron-transfer process to form ferricenium, which is reversibly reduced back to ferrocene.[15] Ferrocene compounds such as 1,1′-ferrocene−dimethanol and ferrocenecarboxylic acid were infiltrated into PBO fiber by soaking the “wet” fiber in a 1 wt % aqueous solution of the ferrocene compounds. Upon drying, the ferrocene compounds were imbedded in the filaments. The amount of iron in the fiber was typically 7000 ppm, which indicated 3 wt % of ferrocene dimethanol. PBO fibers containing ferrocene compounds showed much better tensile strength retention upon photolysis in the presence of oxygen than PBO fiber without this redox reagent.[8] The results suggest that ferrocene inhibits the photoreaction of PBO by back electron transfer, as shown in Scheme 4.

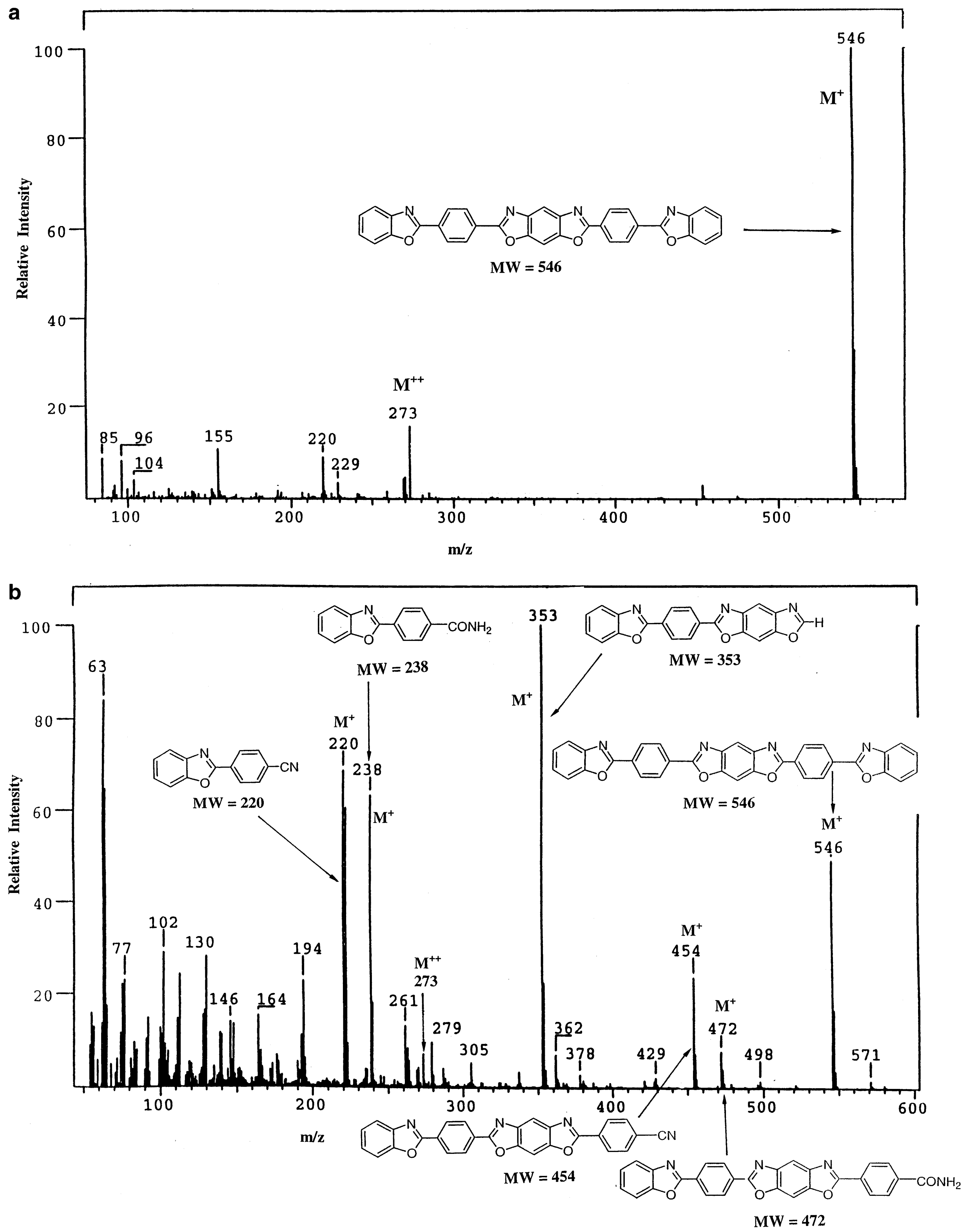


Figure 2. (a) EI-MS of unexposed **6**. (b) EI-MS of **6** photolyzed in air.

Effect of Singlet Oxygen on Benzobisoxazole Compounds. Singlet oxygen was suggested to be a reactive intermediate in the photoinduced degradation of many polymers, including polyacetylene,[16] poly(2,5-bis(5,6-dihydrocholestanoxy)-1,4-phenylenevinylene) in both solution and solid film,[17] and poly(3-alkylthiophenes).[18] The effect of singlet oxygen on aryl benzobisoxazole compounds was studied.

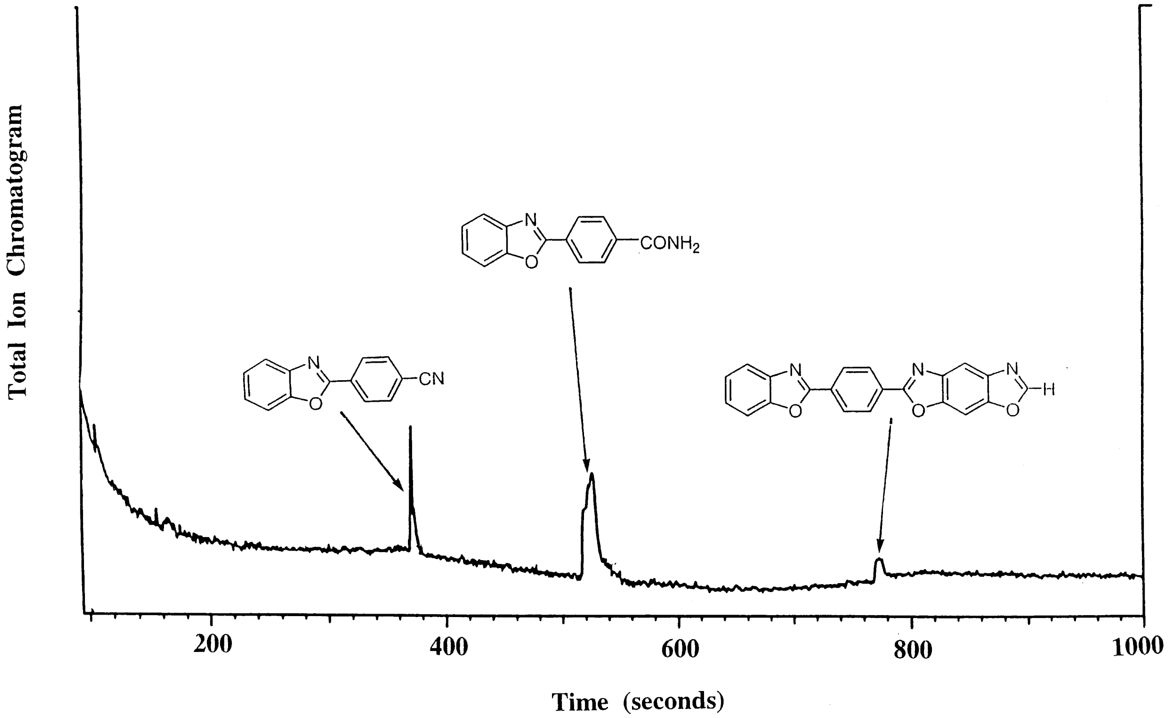


Figure 3. Single ion profiles for thermal separation of products from photolyzed **6**.

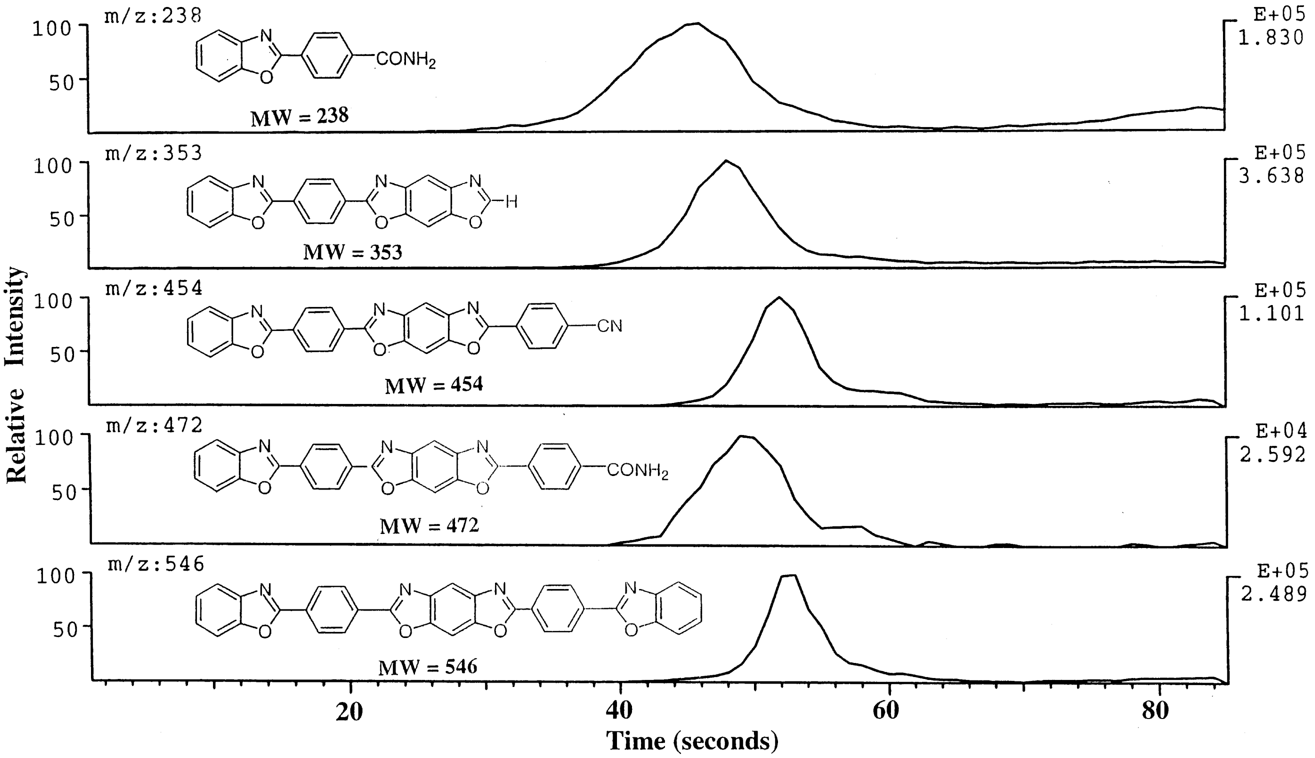


Figure 4. Total ion chromatograph of chloroform-extracted low molecular weight products from photolyzed **6**.

Compound **2** in methylene chloride with methylene blue as the sensitizer was irradiated for 100 h while oxygen was bubbled through the solution. The starting material was 100% recovered. 1,4-Bis(5-phenyloxazole-2-yl)benzene, which is known to react with $^1O_2$, totally decomposed under identical experimental conditions in 20 h.[19] A thin film of **7**, which was deposited on the inside wall of a 100 mL flask, was inert to singlet oxygen produced from hydrogen peroxide and sodium hypochloride.[20] Aryl benzobisoxazole compounds appear to be stable to singlet oxygen.

Experimental Section

Starting Materials and Control Samples. The synthesis and characterization of compounds **1**−**8** have been reported.[2] 2-Phenylbenzo[1,2-*d*:5,4-*d*′]bisoxazole (**9**) was made by stirring 2-phenyl(5-amino-6-benzoxazolol) in formic acid at reflux. The reactant 2-phenyl(5-amino-6-benzoxazolol) was prepared by

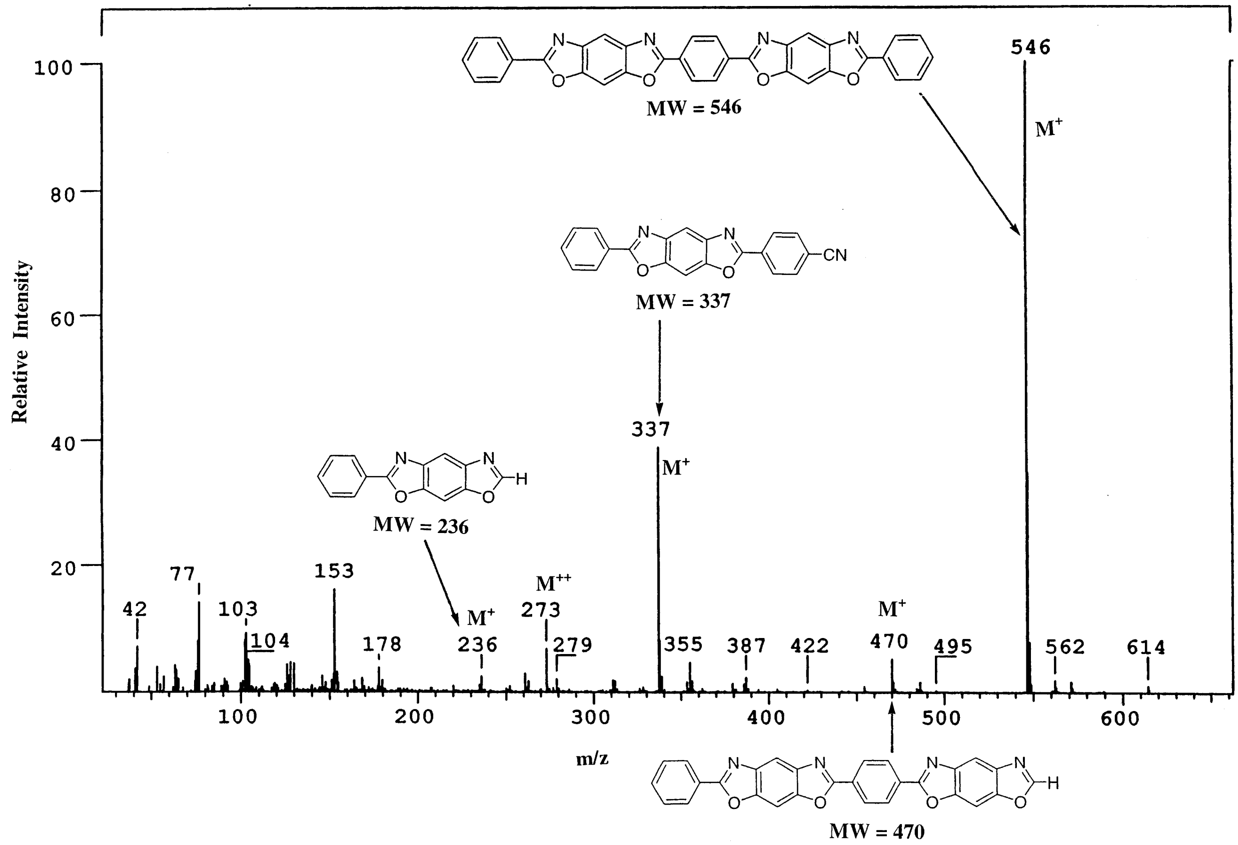


Figure 5. EI-MS of **7** photolyzed in air.

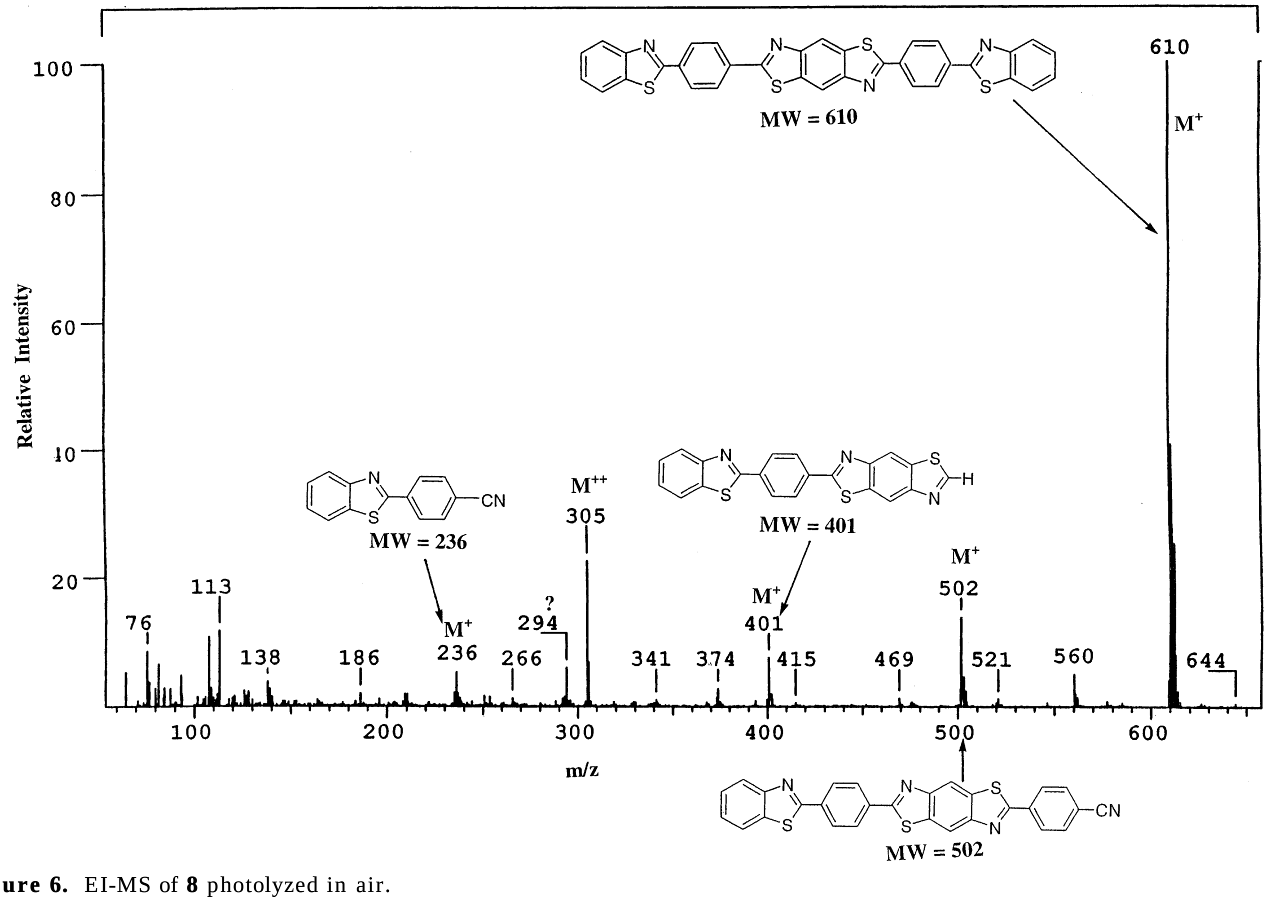
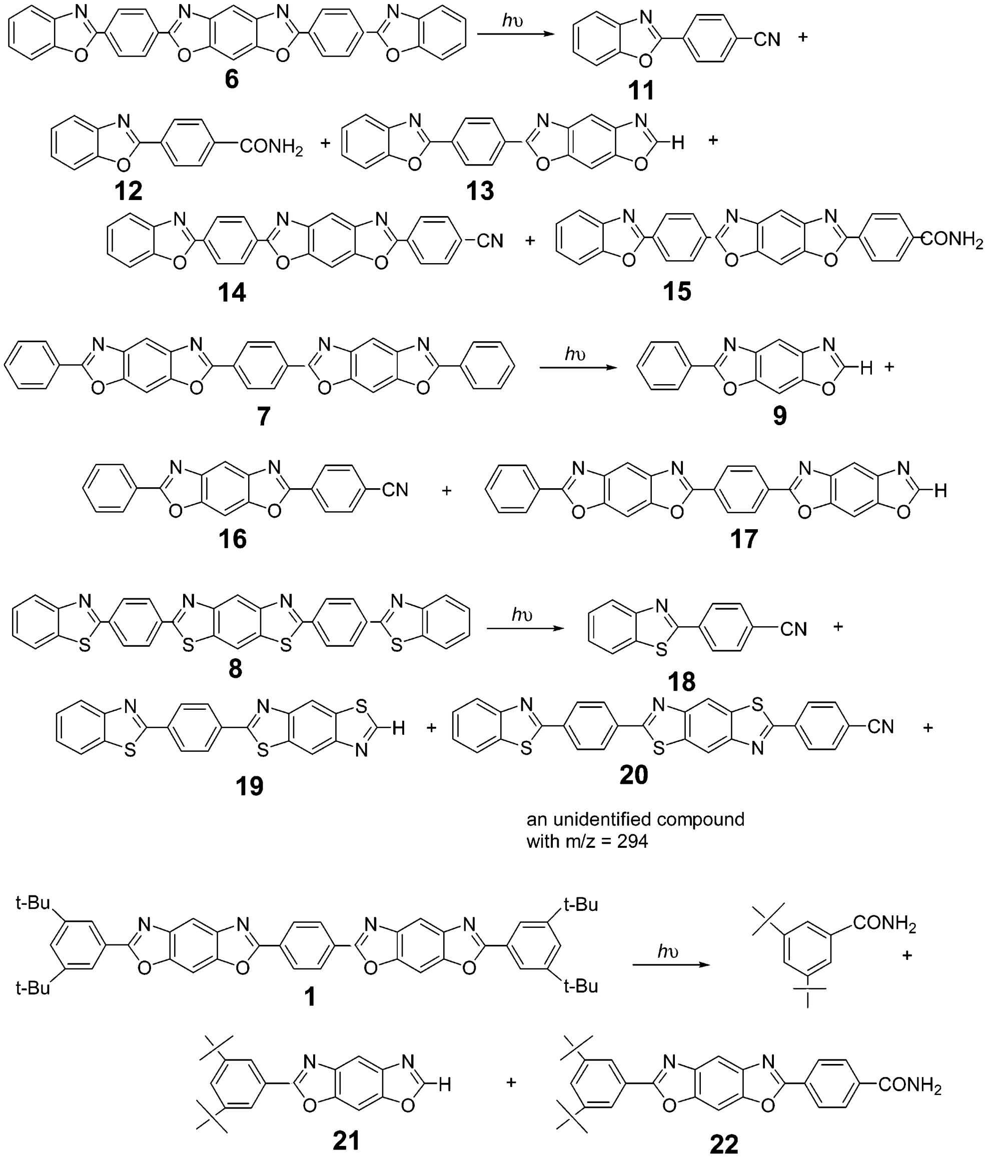


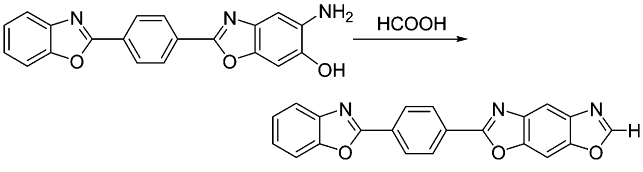
Figure 6. EI-MS of **8** photolyzed in air.

reacting benzoic acid with excess 1,3-diamino-4,6-dihydroxybenzene dihydrogen chloride in poly(phosphoric acid). 4-(2-Benzoxazolyl)benzonitrile (**11**) was made from *o*-aminophenol and 4-cyanobenzoyl chloride.[4] 4-(2-Benzoxazolyl)benzamide

Scheme 2



(**12**) was made from **11** with 3% hydrogen peroxide and 25% KOH.[5] 2-(4-(2-Benzoxazolyl)phenyl)benzo[1,2-*d*:5,4-*d*′]bisoxazole (**13**) was made by refluxing 2-(4-(2-benzoxazolyl)phenyl)-(5-amino-6-benzoxazolol) in formic acid.



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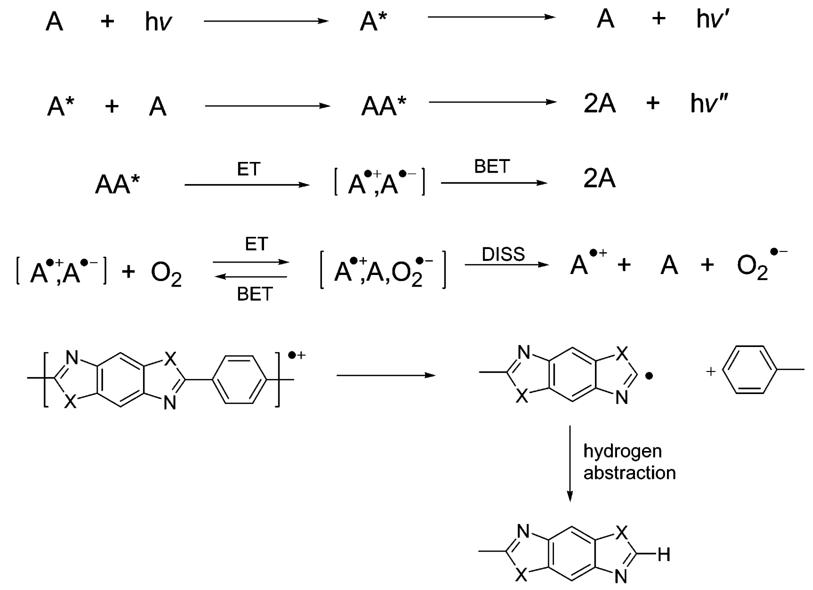
4-(6-Phenylbenzo(1,2-*d*:5,4-*d*′)bisoxazol-2-yl)benzonitrile (**16**) was made from 2-phenyl(5-amino-6-benzoxazolol) and 4-cyanobenzoyl chloride. 4-(2-Benzothiazolyl)benzonitrile (**18**) was synthesized from *o*-aminothiophenol and 4-cyanobenzoyl chloride.[2]

Sample Preparation. The compound of interest (2.00 mg) was dissolved in chloroform or trifluoroacetic acid (TFA) in a 100 mL serum vial with inside surface area of approximately 100 cm^2. A thin layer of the compound was formed on the inside wall by rotating the vial to allow the solvent to evaporate. Coating was visibly uniform. The thickness of the layer was about 0.3 μm.[6] Samples cast from TFA solutions were heated in a vacuum oven to remove TFA. To prepare a sublimed film, a 10 mg sample was placed in a 100 mL, one-necked flask containing a 1 cm × 5 cm microscope slide. The flask was connected to a vacuum pump. The lower portion of the flask was immersed in a sand bath at 350 °C. A thin film of sublimed **6**, **7**, or **8** condensed on the upper portion of the slide. Film thickness ranged from 0.2 to 0.3 μm as measured by a profilometer, Alpha-Step 200 from Tencor Instruments.

Photolysis Procedures. Photolysis was performed with either an apparatus manufactured by Oriel Corp., which was equipped with a 200 W medium-pressure mercury lamp manufactured by Hanovia, or a Suntest CPS (Trademark of Heraeus Co.). The Suntest used a filtered xenon lamp that roughly mimics solar radiation in both intensity and wavelength distribution. The output at the lamp source was 765 W/m^2.

A 250 mL solution of the compound was placed in a quartz or glass flask equipped with a stirring bar and a condenser. The flask was 50 cm away from the Oriel apparatus, and a water filter was placed between the flask and the light source. Light intensity at the sample site was measured with a Newport laser power meter model 820. The light intensity at the site was about 200 W/m^2. For photolysis of compounds in solid state, the serum vial was placed horizontally in the Suntest for radiation. The exposure time was 150 h unless specified. For the sublimed sample, the microscope slide was placed in the capped serum vial during photolysis. All solid-

Scheme 3



Scheme 4

$$(h\text{-}C_5H_5)_2\,Fe + A^{\bullet+} \longrightarrow (h\text{-}C_5H_5)_2\,Fe^{+} + A$$

$$(h\text{-}C_5H_5)_2\,Fe^{+} + O_2^{\bullet-} \longrightarrow (h\text{-}C_5H_5)_2\,Fe + O_2$$

state photolysis experiments were performed with serum glass vials.

Analysis of Products from Photochemical Reactions. (a) Liquid Chromatography. Tetrahydrofuran (THF) (20 mL) was added to the vial, which was then placed on a bottle roller until all visible residue was dissolved. A sample (10 μL, 0.1 mg/mL) was analyzed by a liquid chromatography (LC) system consisting of a Perkin-Elmer model 410 gradient pumping system, a Perkin-Elmer ISS-200 autosampler, and a Perkin-Elmer 235 photodiode array UV detector. A Zorbax-SB phenyl column (4.6 × 150 mm, 5 μm) was used for all separations. The mobile phase was 62% THF and 38% water with 0.02 M H_3PO_4 with a flow rate of 1.5 mL/min. The detector wavelength was 270 or 330 nm. LC peak areas were the average of three duplicated injections. The relative precision was 1% or better.

(b) Gas Chromatography−Mass Spectroscopy. Chloroform (10 mL) was added to the vial. A sample (1 μL) of the filtered solution was injected onto a Finnigan SSQ700, SN TS00417, quadrupole gas chromatography−mass spectroscopy (GC-MS) system in the electron impact (EI) mode. The column was a 15 m × 0.25 mm (0.25 μm film) DB-5 with a temperature program of 80−320 °C at 16 °C/min. The MS was scanned from 35 to 650 atomic mass unit at 1 s/scan. Product identification was performed by comparison of GC retention time and MS fragmentation pattern of control compounds.

(c) Direct Exposure Probe (DEP) Mass Spectroscopy. Control samples and photolyzed samples were dissolved in TFA. A drop of the solution was placed on the DEP filament probe. The current of the probe was ramped from 0 to 750 mA at 500 mA/s. MS was run in EI and ammonia chemical ionization modes.

(d) Analysis of Serum Vial Headspace. A serum vial containing a sample photolyzed for 150 h was warmed to 80 °C. A 5 mL aliquot of the headspace was injected onto the GC-MS system in EI mode. The front 2 in. segment of the 25 m × 0.25 mm (0.25 μm film) DB-FFAP (Durabond-Free Fatty-Acid Phase) GC column from J&W Scientific was cooled with liquid nitrogen to cryofocus the volatile organic compounds. The liquid nitrogen cup was removed 2 min after sample injection. The temperature program was 40 °C for 6 min and then 20 °C/min to 200 °C for 1 min. A room air blank from an empty serum vial at 80 °C was analyzed as the control. A computer reconstructed total ion chromatograph showed the level of CO_2 in the headspace over the photolyzed sample was about 30-fold higher than that of air. Acetone and acetonitrile were detected, but CO_2 was the much bigger component in the headspace. Sulfur dioxide was found in photolyzed aryl benzobisthiazole compounds.

Cyclic Voltammetric Study. Cyclic voltammetry was performed with a Bioanalytical System (BAS, West Lafayette, IN) model 110A electrochemical analyzer equipped with the standard voltammetric cell stand. The working electrode was a 3 mm diameter, glassy carbon disk, the reference electrode was Ag/AgCl, and the counter electrode was a platinum wire. A 0.14% solution of PBO polymer was prepared by dissolving a known amount of fiber in methanesulfonic acid (MSA). A 1 μL aliquot of this solution containing 1.4 μg of PBO polymer was applied to the electrode surface and spread around to produce a uniform film of liquid. MSA was removed by rinsing with a large volume of deionized water. Prior to voltammetric analysis, the electrode was placed in a large volume of acetonitrile to remove most of the water. The electrolyte was 0.1 M tetrabutylammonium perchlorate in acetonitrile, and the scan rate was 10 mV/s. The number of electrons per repeat unit was calculated from the Faraday equation since the charge passed, the amount of material on the electrode, and the molecular weight of the repeat unit were known.

Electron Spin Resonance Spectroscopy. Instrument and measurement conditions for electron spin resonance (ESR) spectroscopy were reported in ref 2.

Stabilization of PBO Fiber with Ferrocene Compounds. PBO was synthesized from terephthalic acid and 1,3-diamino-4,6-dihydroxybenzene in poly(phosphoric acid) (PPA). Fiber was spun from the solution, and PPA was leached out as the fiber was coagulated in water. The “wet” fiber was soaked in a 1 wt % aqueous solution of 1,1′-ferrocene−dimethanol (from Aldrich Chemical Co.) for 30 min. The fiber was then air-dried and rinsed with water to remove the ferrocene compound on the fiber surface. The processed fiber contained 7000 ppm of iron as analyzed by neutron activation, which indicated 3 wt % of ferrocene dimethanol.

The fiber was knitted into fabrics which were then deknitted to introduce physical damage for oxygen penetration.[7] The fiber was exposed in the Suntest unit for 200 h. Tensile strength of fiber samples was measured in accordance with ASTM D-2101 on an Instron 4201 universal testing machine. Samples embedded with ferrocene compounds showed severalfold better tensile strength retention over control samples.[8]

Singlet Oxygen on Aryl Benzoxazole Compounds. Compound **2** (0.312 g, 1.0 mmol) and methylene blue (0.94 g, 0.25 mmol) were dissolved in 250 mL of methylene chloride in a 500 mL, three-necked flask equipped with a condenser, a glass tube extended to the bottom of the flask, and a stopper. Oxygen was bubbled through the stirred solution. The experiment was performed under room light. After 100 h, the solution was analyzed by GC with 2-phenylbenzoxazole as the internal standard. Analysis results showed 0.312 g of **2** (100% recovery) in solution.

Compound **6** (3.0 mg) was dissolved in 10 mL of TFA and deposited as a thin film on the inside wall of a 100 mL, round-bottom flask. The thin film was treated with singlet oxygen produced from H_2O_2 and NaClO as follows. Methanol (50 mL) and 10 mL of H_2O_2 (30%) were added to the flask. The solution was stirred. Sodium hypochlorite solution (50 mL, available chlorine 5% minimum) was added dropwise with the stem of the addition funnel extended to the bottom of the flask. When addition was completed, the solid (3.0 mg) was collected and identified as **6** by mass spectroscopy. Electron impact-MS results suggested that **6** was the only component in the recovered solid. Infrared spectra of the recovered solid and **6** were identical.

Conclusion

Aryl benzobisoxazole and aryl benzobisthiazole compounds are rigid-rod molecules that readily π-stack. Their very low or even complete lack of stability in common organic solvents imposes difficulties in studying these compounds. With a combination of liquid chromatography, several mass spectroscopy techniques, and the use of controls, we demonstrated that completely different chemical reactions resulted when aryl benzobisoxazole and aryl benzobisthiazole compounds were photolyzed in the solid state, where the molecules could stack, and in dilute solution, where π-stacking did not happen.

Combining these results with our previously published results, we conclude that intermolecular π-stacking interactions between the planar molecules led to excimer formation in the solid state. A photoinduced electron transfer mechanism is consistent with this dramatically different reactivity, the observed ESR signal, and the anodic instability of these materials. Benzo[1,2-*d*:5,4-*d*′]bisoxazoles and benzo[1,2-*d*:4,5-*d*′]-bisthiazoles were products from heterogeneous dissociation of *p*-phenylenebenzobisoxazole cation radical and *p*-phenylenebenzobisthiazole cation radical followed by hydrogen abstraction. In the absence of oxygen, the ion radical pair underwent back electron transfer, which explains the photostability of these compounds under nitrogen. The subsequent reactions from this photoinduced electron transfer reaction were retarded by reversible redox reagents such as ferrocene compounds.[21]

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