Photophysics and Photostereomutation of Aryl Methyl Sulfoxides[1]

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The effect of a methanesulfinyl group on the photophysics of several aromatic chromophores is reported. The spectroscopic singlet and triplet energies are affected only modestly, compared to that parent arenes, but the fluorescence yields fall by at least 1 order of magnitude. Fluorescence lifetimes are short. Fluorescence enhancements are observed on cooling the sulfoxides from room temperature to 77 K. High quantum yields of stereomutation are reduced as the temperature drops. There is not a consistent effect on triplet or phosphorescence yields. It is proposed that these results are consistent with a nonradiative pathway for deactivation of the singlet that results in stereomutation. A modest activation energy of a few kcal/mol is estimated for the photochemical racemization of 1-methanesulfinylpyrene.

Introduction

The photochemistry of aryl alkyl sulfoxides is dominated by α-cleavage reactions.[2−4] Aryl sulfoxides are generally studied because the unconjugated sulfinyl group is transparent in most of the region of the UV spectrum that is useful to organic chemists. As a result, the excited state involved in the chemistry is at least largely centered on the arene. However, data on the degree of perturbation of the arene excited state by the sulfinyl group have been limited by the low inherent emission of the previously investigated chromophores.[5]

Outside of photochemistry, one of the most important and synthetically attractive features of sulfoxides is their stereochemical stability; the directing effect of the polar group makes the sulfinyl group a useful chiral auxiliary for synthesis.[6−11] However, under photochemical conditions, stereomutation of the sulfur center is observed. This leads to racemization in the absence of other stereogenic centers, but diastereomeric interactions can also be used to make a desired sulfoxide, such as in the early case of the (*SR*) sulfoxides of penicillin derivatives.[12,13]

In principle, photochemical stereomutation can derive from a reversible α-cleavage event, but authors through the years have long suspected that there is a direct inversion pathway that does not involve formation of any radicals. To date, the most convincing of these reports involve molecules with demonstrably low α-cleavage photoproduct yields that nonetheless have high quantum yields for racemization.[2,14,15]

We report here a study of the emission and racemization properties of a series of aryl methyl sulfoxides in which the parent arene is a well characterized emissive chromophore. The methyl group was chosen to minimize α-cleavage reactions.[2,16] The aryl groups were chosen for their photophysical properties[17,18] in order to attempt to relate the substitution-induced changes in those properties to the sulfinyl group and its stereomutation. Substitutional perturbations can be subtle—such as with alkyl groups—but certain substitutions have dramatic influences on excited-state dynamics.[19,20] For example, phenyl and vinyl group substitution results in a significant red shift and enhanced extinction coefficients due to the extension of the chromophore. In rigid planar arenes, the sum of the fluorescence quantum yield (Φ_F) and triplet yield (Φ_T) is generally close to unity at room temperature.[21] But when a heavy atom (e.g., bromine) is introduced, all intersystem crossing processes are facilitated, usually resulting in a dramatic drop in Φ_F, τ_F, and τ_P. Carbonyl groups also often lead to enhanced intersystem crossing, also due to enhanced spin−orbit cou-

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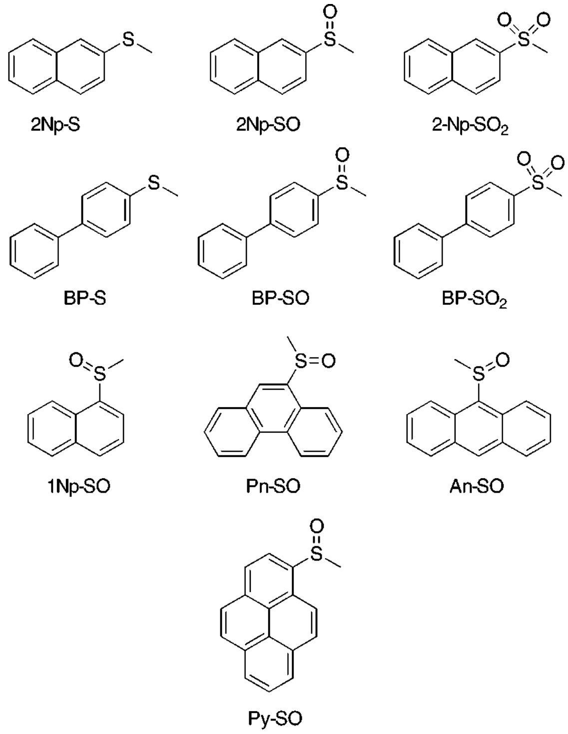
Chart 1



pling. In this paper, we report the photophysics of a series of methanesulfinyl-substituted arenes and those of a control pair of corresponding sulfides and sulfones. We show that there is an efficient nonradiative decay path out of the excited singlet manifold for the sulfoxide that is unavailable to the parent arenes, sulfides, and sulfones. We suggest that it is intimately tied to the racemization process.

Results

The majority of the sulfoxides in our previous work had benzene ring(s) for their aromatic moiety.[5] These compounds showed no luminescence at room temperature. Furthermore, weak or no phosphorescence was observed for all of these benzene-based sulfoxides, and fluorescence at 77 K was observed in only three cases.

The compounds used in this study are shown in Chart 1. They are based on larger aromatic chromophores that are more luminescent than benzene, and indeed the sulfoxides exhibit luminescence as reported below. In addition to the racemic samples, three optically resolved sulfoxides (2Np-SO, Py-SO, and An-SO) were prepared with complete optical resolution within the limits of HPLC detection.

Singlet and Triplet Energies. The fluorescence spectra of most of the sulfoxides were very similar in appearance to those of the corresponding unsubstituted arenes. The spectroscopic singlet energies of the sulfoxides, shown in Table 1, are within 4 kcal/mol of those of the parents. At 77 K, greater structure was observed in the spectra, but no significant spectral shifts were evident.

For comparison in this and other sections, analogous data were collected for the corresponding sulfides and sulfones 2Np-S, 2Np-SO_2, Bp-S, and Bp-SO_2. These control compounds were used to determine whether various effects were based simply on the sulfur atom (e.g., heavy atom effects or symmetry-breaking) or were dependent on the oxidation state of the substituent. The singlet energies of the sulfides are lower than the others, but all are within several kcal/mol of the parents.

Table 1. Spectroscopic Solution Singlet and Frozen Matrix Triplet Energies

compd	E_S[a] (kcal/ mol)	E_T[b] (kcal/ mol)
1Np-SO	89	60
2Np-S	85	58
2Np-SO	91	61
2Np-SO_2	88	59
naphthalene[d]	92	61
Bp-S	90	61
Bp-SO	98	69
Bp-SO_2	96	64
biphenyl[d]	94	66
Pn-SO	85	69
phenanthrene[d]	83	62
An-SO	73	*c*
anthracene[d]	76	43
Py-SO	78	*c*
pyrene[d]	77	49

[a] In acetonitrile at room temperature. [b] In 1:1 methanol/ethanol glass at 77 K. [c] Very little or no phosphorescence was observed. [d] Reference 21.

Table 2. Fluorescence and Phosphorescence Quantum Yields

compd	Φ_F (rt)	Φ_F (77 K solid)	Φ_{Ph} (77 K solid)
1Np-SO	0.011	0.031	0.21
2Np-S	0.12	0.027	0.60
2Np-SO	0.015	0.044	0.22
2Np-SO_2	0.36	*a*	*b*
naphthalene[c]	0.21	0.45	0.0039
Bp-S	0.18	0.08	0.59
Bp-SO	0.005	~0	0.53
Bp-SO_2	0.26	0.04	0.41
biphenyl[c]	0.15	0.14	0.24
Pn-SO	0.013	0.066	0.41
phenanthrene[c]	0.13	0.20	0.16
An-SO	0.09	0.19	~0
anthracene[c]	0.27	0.34	0.0003
Py-SO	0.008	0.11	~0
pyrene[c]	0.72	0.92	0.0022

[a] Signal was too weak. [b] See ref 22. [c] Reference 21.

The spectroscopic triplet energies were obtained from the phosphorescence spectra at 77 K in 1:1 ethanol/methanol using the method described in our previous work (Table 1).[5] Relative to the parent arenes, small blue shifts were observed for all sulfoxides that showed phosphorescence. The triplet energies of the control sulfides and sulfones are also similar, with those of the sulfides again the lowest for any given aromatic nucleus. This trend was observed previously.[5]

The sulfoxides with significant phosphorescence in the polar glass were also examined in methylcyclohexane at 77 K. Unlike the phenyl sulfoxides,[5] no significant solvent effect was observed.

Quantum Yields. The fluorescence and phosphorescence yields were measured at room temperature and at 77 K by integration of the emission spectra and are listed in Table 2. At room temperature, the sulfoxides have considerably smaller Φ_F values than the parent arenes, ranging from 0.005 to 0.090 (Table 2). At 77 K, Φ_F values are larger, but still smaller than those of the arenes. In contrast, the Φ_F values for the sulfides and sulfones are much more similar to those of the parents, sometimes exceeding them.

Table 3. Singlet Oxygen Yields (Triplet Yields) at Room Temperature

compd	hexane	CH_3CN
1Np-SO	0.41	0.42
2Np-SO	0.12	0.18
naphthalene[a]	0.75	0.80
Bp-SO	0.12	0.12
biphenyl[a]	0.84	
Pn-SO	0.22	0.24
phenanthrene	0.73	0.85
Py-SO	0.50	0.35
pyrene[a]	0.37	0.38

[a] Reference 21, quoting "non polar" and "polar" solvent entries of triplet yields (Φ_T).

Strong phosphorescence was observed at 77 K for 1NP-SO, 2NP-SO, Bp-SO, and Pn-SO. The phosphorescence yields for both 1Np-SO and 2Np-SO are 50 times greater than that for naphthalene. Phosphorescence enhancement of a factor of 2 compared to the parent was observed for Bp-SO and Pn-SO. No phosphorescence was observed for An-SO and Py-SO. Although in no sulfoxide case is the sum of Φ_F and Φ_P at 77 K particularly close to 1.0, those sulfoxides with greater fluorescence were also those with little or no phosphorescence. The control sulfides and sulfones all have modest Φ_F and large Φ_P at 77 K.[22]

The quantum yields of triplet formation (Φ_T) at room temperature were obtained indirectly by measurement of the quantum yield of β-carotene triplet formation and detection of singlet oxygen $O_2(^1\Delta_g)$ using a flash photolysis setup that has been described.[16] Briefly, samples containing a sulfoxide and either β-carotene or O_2 were excited at 355 nm using the third harmonic of a Nd:YAG laser, and the initial intensity of the triplet−triplet absorption of β-carotene or the magnitude of the singlet oxygen emission was compared against known standards.[16] The so-obtained values are listed in Table 3. Because of the comparative inconvenience of the β-carotene method, the singlet oxygen method was preferred. Its validity as a surrogate was examined by comparison in the Py-SO in hexane case. Values of Φ_T were similar: 0.58 by β-carotene and 0.50 by singlet oxygen. All of the data reported in Table 3 are from the singlet oxygen method. We do not offer any specific interpretation of the solvent effects, which are not especially dramatic.

The triplet yields were lower than those of the parent compounds by a factor of 2 or more, except Py-SO, where the values were similar. Since both Φ_F and Φ_T are lower for the sulfoxides than for the parents and their sum is considerably less than 1.0, it was concluded that there an important nonradiative decay pathway was available to the sulfoxides at room temperature. The greater fluorescence at 77 K suggested that it might be weakly activated.

Lifetimes. The fluorescence lifetimes were obtained by time-correlated single photon counting at room temperature and at 77 K and are listed in Table 4. The room temperature fluorescence lifetimes of most sulfoxides were considerably shorter than those of the unsubstituted parents, consistent with the smaller quantum yields. Reliable lifetimes could not be obtained for 1Np-SO, 2NP-SO, and Bp-SO. The low quantum yields inherently make obtaining the lifetimes more difficult and considerably more subject to artifact. Only very slowly accumulating lifetimes that were approximately the same as those of the sulfides were observed, despite further attempts at purification. These data were rejected on the basis that they were obtained under very difficult conditions, their inconsistency with reasonable expectation that they be short, and the known propensity for sulfoxides to deoxygenate, even if only as a minor product.[23,24]

Table 4. Emission Lifetimes at Room Temperature in Solution and 77 K in Frozen Organic Glass

compd	τ_F, ns (rt)	τ_F, ns (77 K)	τ_{Ph}, s (77 K)
1Np-SO	*c*	*c*	>1[a]
2Np-S	13	*b*	>1[a]
2Np-SO	*c*	*c*	>1[a]
$2Np-SO_2$	11	*a*	>1[a]
naphthalene[e]	105	273	2.6
Bp-S	1.9	*b*	>1[a]
Bp-SO	*c*	*c*	0.79
$Bp-SO_2$	2.7	*b*	>1[a]
biphenyl[e]	16		4.6
Pn-SO	2	37	>1[a]
phenanthrene[e]	61	63	3.6
An-SO	1	*b*	*d*
anthracene[e]	5.8	605	0.04
Py-SO	1.3	82	*d*
pyrene	338	515[e]	0.58[e]

[a] The lifetime is longer than the upper limit of the instrument, approximately 1 s. [b] Signal was too weak to measure the lifetime. [c] Only artifactual lifetime obtained. See text. [d] No phosphorescence was observed. [e] Reference 21.

All of the sulfoxides have phosphorescence lifetimes close to or greater than 1 s, which is the upper limit of the instrument used here. Such extended lifetimes are typical of aromatic hydrocarbons with $\pi\pi^*$ triplets and indicate that there is not a particularly efficient nonradiative decay pathway out of the triplet states, at least at 77 K.

Racemization. Quantum yields of inversion (Φ_{inv}) were measured with the assistance of a chiral-phase HPLC column. Φ_{inv} is defined as the number of molecules of the new enantiomer formed per photon absorbed. It is thus half the value of the quantum yield of racemization.

Photolysis of the three resolved sulfoxides was done with a Xe arc lamp filtered through monochromator set at 295 nm, illuminating a standard 1 cm cell. The concentration of the samples was about 300 μM; optical densities were well over 1.0. For measurements from 0 to 40 °C, the sample temperature was measured directly by thermocouple and was adjusted by use of a water circulating bath and a hollow brass cell holder. Acetonitrile was the solvent. To obtain a quantum yield in liquid solution at very low temperature, methylcyclohexane solvent was used at −100 °C. Both argon degassed and air-saturated samples were tested and identical values of Φ_{inv} were obtained at any given temperature. No other significant photolysis products were observed, even up to the point of complete racemization. All quantitative data were collected with less than 10% inversion, and they are given in Table 5. Each entry is the average of at least three independent measurements, and the reproducibility error was less than 10%. Some data points were repeated several extra times to ensure the reproducibility of the small differences shown in Table 5.

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Table 5. Φ_{Inv} as a Function of Temperature in Liquid Solution

compd	Φ_{inv} (T, °C)				
2Np-SO	0.27 (39 °C)	0.25 (25 °C)	0.22 (10 °C)	0.20 (0 °C)	0.0030 (−100 °C)
An-SO	0.25 (41 °C)	0.22 (22 °C)	0.21 (10 °C)	0.18 (0 °C)	0.0021 (−100 °C)
Py-SO	0.20 (39 °C)	0.18 (25 °C)	0.15 (10 °C)	0.13 (0 °C)	0.0020 (−100 °C)

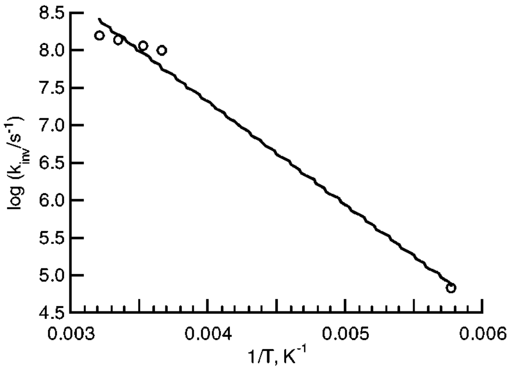

Figure 1. Arrhenius plot for the inversion of 1-methanesulfinylpyrene.

Given the temperature dependence of Φ_{inv} and the fluorescence lifetimes, it was possible to make a crude estimate of an activation barrier for the photochemical inversion process. By use of eqs 1 and 2, in which k_{inv} is the temperature-dependent rate of inversion and k_f and Σk_d are temperature-independent rates of fluorescence and all other nonradiative decay pathways of the singlet, a simple expression for k_{inv} can be written:

$$\tau_f = \frac{1}{k_f + k_{inv} + \sum k_d} \tag{1}$$

An Arrhenius-type plot can then be constructed. For

$$\Phi_{inv} = \frac{k_{inv}}{k_f + k_{inv} + \sum k_d} \tag{2}$$

$$k_{inv} = \frac{\Phi_{inv}}{\tau_f} \tag{3}$$

1-methanesulfinylpyrene, such a graph is shown in Figure 1. For the point at −100 °C, a fluorescence lifetime of 30 ns was estimated from the 77 K and near-room-temperature values, as instrumental limitation forbade direct measurement. This was done by interpolating the rates for total fluorescence decay, i.e., τ_F^{-1}. From the plot, log A is 12.8 ± 0.7 and $E_a = 6 \pm 1$ kcal/mol, where the error limits are two standard deviations of the fit. However, glancing at Figure 1, it is obvious that the low-temperature point—which was arrived at by approximating it as τ_f—dominates the fit and does not extrapolate particularly well from the other four points. Using only the points near room temperature, the log $A = 9.5 \pm 0.2$ and $E_a = 1.9 \pm 0.2$ kcal/mol. If the estimate of τ_F is in substantial error, it stands to reason that the actual value is shorter than the estimated 30 ns because of the lack of rigidity of the solvent, compared to the glass at 77 K. That would bring the low temperature point closer to being in line with the others. The essential interpretation, we argue, is that the activation energy is very low.

To determine whether states of triplet multiplicity are responsible for the photoracemization, triplet sensitization experiments were done using 2Np-SO as the substrate and benzophenone (BP) as sensitizer. Using irradiation from broadly emitting 350 nm fluorescent tubes, the great majority of the light was absorbed by BP. A residual absorption of the sulfoxide existed in control experiments without any sensitizer. In a time period that provided complete racemization under these conditions without the sensitizer, no stereomutation was observed when the benzophenone was present.

Triplet quenching experiments were also carried out, using direct irradiation of 2Np-SO. No inhibition of racemization was observed from O_2 in air-saturated solutions. Neither was racemization inhibited by piperylene or isoprene at concentrations up to 25 mM.

Discussion

The study of the racemization of sulfoxides dates back to the 19th century,[25] though serious mechanistic consideration waited for Mislow's pioneering work of the 1960s.[26−29] Sulfoxides without special structural features undergo thermal racemization via pyramidal inversion with activation energies of the order of 40 kcal/mol. Stereomutation can also be induced by a variety of chemical reagents, such as strong acids, acetic anhydride, N_2O_4, and sodium butoxide.[29,30] Among these, perhaps the reaction with HCl has been the most extensively investigated.[29,31,32] It is thought to involve the reversible formation of a chlorosulfonium ion that undergoes degenerate substitution reactions before reverting to the sulfoxide.

Mechanistic study for the *photochemical* racemization of aromatic sulfoxides also dates back to the 1960s, and both α-cleavage and direct inversion have been suggested as mechanisms.[2,29,33−35] Mislow and Hammond carried out most of their work with sensitizers and eventually interpreted their results in terms of exciplex formation.[36,37] The present work reflects instead the case of direct irradiation, where the sulfoxide-modified arene absorbs the light and an excited singlet state of the sulfoxide is unambiguously created.

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Table 6. Sum of Photophysical Parameters[a]

compd	$\Phi_F + \Phi_T$, rt	$\Phi_F + \Phi_T + 2\Phi_{inv}$, rt	$\Phi_F + \Phi_P$, 77 K
1Np-SO	0.43		0.24
2Np-SO	0.20	0.70	0.26
naphthalene	1.01		0.45
Bp-SO	0.13		0.53
biphenyl	0.99		0.38
Pn-SO	0.25		0.48
phenanthrene	0.98		0.36
Py-SO	0.36	0.72	0.11
pyrene	1.10		0.92

[a] Data taken from previous tables.

The data show that sulfinyl substitution on an aromatic chromophore enhances nonradiative decay of the fluorescent state of the arene and, further, that this enhancement is not a simple heavy atom effect of the sulfur. It is specific to the sulfinyl group and does not exist for the sulfide or sulfone. Compared to the parent arene, all of the sulfoxides have low Φ_F values. When measurable, lifetimes are correspondingly shorter. To the extent that singlet oxygen yields can be used as stand-ins for triplet yields, the triplet yields of the sulfoxides at room temperature are modestly lower than those of the parents in most cases. As a result, the sum of Φ_F and Φ_T at room temperature for the sulfoxides is much less than those for the parent arenes. This is summarized in Table 6. Py-SO is the exception for lowered triplet yields, where a slight increase is noted in hexane. The comparable triplet yields of the sulfoxides to the parent arenes in the face of lower fluorescence yields and lifetimes suggests that the nonradiative decay path does not necessarily relate directly to intersystem crossing, but that intersystem crossing is likely faster than in the parent compounds.

For 2Np-SO and Py-SO, data are available for Φ_F, Φ_T, and Φ_{inv} at room temperature. If it is assumed that during the inversion process a given sulfoxide passes through some sort of symmetric intermediate or transition state and that when it does, it has an equal chance of returning to the original enantiomer or inverting, Φ_{inv} is actually representative of half of the "racemization" events. (This is in analogy, for instance, to the photochemical cis−trans isomerization of simple olefins, where the twisted olefin may produce either the E or Z isomer.) Thus, if we sum Φ_F, Φ_T, and $2\Phi_{inv}$, this is approximately the same accounting as summing Φ_F and Φ_T for the simple arenes. The totals for 2Np-SO and Py-SO are 0.70 and 0.72, respectively. These sums are consistent with the interpretation presented here.

The measurements of Φ_{inv}, all done in liquid solution, show that there is a real, but modest dependence on temperature. If the nonradiative decay pathway that is special to the sulfoxides is taken to be the racemization process, the apparently small activation energy is consistent with the simple unimolecular rearrangement that would be required.

The longer τ_F values for the fluorescent sulfoxides at 77 K in the solid glass argue against the substitutionally induced fluorescence lifetime shortening being due simply to symmetry breaking by the sulfinyl substitution. A plausible interpretation of these longer lifetimes is that the rigidity (in addition to the low temperature) of the frozen matrix inhibits isomerization from the fluorescent state.

The phosphorescence yields at 77 K are generally higher for the sulfoxides than the parent compounds. However, given that the same observation is made at 77 K for the sulfides and sulfones, there is no justification to attribute a special effect to the sulfinyl group under the low temperature and rigid conditions of the glass. Considering the results here and in our previous work on phenyl based systems, no particular conclusion about sulfinyl groups facilitating triplet formation at low temperature can be made and an empirical approach must still be taken. It remains our observation, however, that there is no evidence for any long-lived triplets in the room-temperature photochemistry of phenyl based sulfoxides.[2,16,38−40]

Tsurutani and co-workers reported a study of a set of aryl tolyl sulfoxides related to the aryl methyl sulfoxides in Chart 1 while our work was ongoing.[14,15] They showed, as predicted by our previous work[2,16] and related precedent, that photochemistry outside of racemization occurred with low quantum yield. However, for our study we had chosen the methyl substituent over the tolyl to avoid any ambiguity about aryl−aryl exciplex or charge-transfer interactions that might also lead to low emission or racemization yields. They observed low or ~0 fluorescence quantum yields for phenyl, 1-naphthyl, phenanthryl, and pyrenyl tolyl sulfoxides analogous to our aryl methyl sulfoxides and shared our observation that the spectra resembled those of the parent arenes. They also observed inversion quantum yields of about 0.3 at room temperature for all of the compounds, save the pyrene system, which inverted with quantum yields about 1 order of magnitude smaller. Further they found that addition of triplet quenchers did not stop the racemization. On the basis of some CIS/STO-3G calculations, they speculate that racemization occurs as a geometric rearrangement of the molecule in an $n \rightarrow \sigma^*$ state localized at the sulfinyl group.

To the extent that our data sets overlap, the current data are in qualitative agreement with that of Tsurutani. The only significant distinction in our data set comes on Φ_{inv} for our pyrene systems. They find values in the region of 0.02−0.03 at room temperature for pyrenyl tolyl sulfoxide, whereas we find 0.18 for Py-SO. The reason for this difference is not clear. However, this new result makes it apparent that a low $\pi\pi^*$ energy in and of itself is not enough to make inversion inefficient.[15] Beyond the results in their paper, we report triplet yields, triplet sensitization experiments, phosphorescence data, comparisons to the sulfides and sulfones, and the temperature-dependent data.

We can speak in greater detail than previously to the multiplicity issue. The triplet quenching experiments of both Tsurutani and ourselves do not eliminate a near-instantaneous racemization from geometrical relaxation of a triplet state, but the lack of racemization on triplet sensitization makes it considerably less likely that the triplet is involved in any substantive way. Triplet formation *after* racemization cannot be eliminated, but it is at least clear that triplet formation is not sufficient to cause stereomutation and that no long-lived triplet is involved in the process.

We can also address, if not finally resolve, the question of α-cleavage versus direct inversion processes. We have found in other cases[2,39] that triplet sensitization of α-cleavage reactions leads to much greater yields of

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escape products, as might be expected. Thus, since no additional products were observed, if a triplet state is involved in the photoracemization, it must be without α-cleavage. Though these data are certainly most consistent with a singlet based racemization process that involves inversion without radical formation, they do not allow us to be conclusive about eliminating α-cleavage from a purely singlet state process. However, even singlet chemistry usually leads to products other than stereomutated starting material. Such products have been attributed to recombination of sulfinyl and alkyl radicals to form sulfenic esters.[2,39]

As mentioned above, Φ_{inv} is smaller at lower temperature. The differences in the region of 0−40 °C are small, but reproducible. We offer the interpretation that the process is weakly activated, but cannot be particularly specific on what the activated process is. It could be a surface hopping related to the Tsurutani $n \rightarrow \sigma^*$ state hypothesis, for example, or it could be related simply to the geometrical rearrangement that occurs. This remains for further, possibly more extensive theoretical study. However, experimentally, it ought to be generally expected that photochemical racemization will be observed in relatively high quantum yield for nearly any aromatic sulfoxide system.

Conclusions

Sulfinyl substitution on an arene causes a great decline in the fluorescence quantum yield that is not accompanied by a corresponding increase in triplet yield. The loss of fluorescence is not necessarily accompanied by significant photochemistry, unless stereochemistry of the sulfur center is accounted for. In the case of aryl methyl sulfoxides, sulfur inversion quantum yields as high as 0.8 have been observed for phenyl systems,[2] whereas values of approximately 0.2 were observed for larger aromatic systems. This should be expected generally. In the cases examined here, we conclude that racemization is intimately tied to the nonradiative decay of a singlet excited state. This is based on the lack of racemization with triplet sensitization, lack of quenching of racemization with dienes and the much greater impact the sulfinyl substituent has on singlet photophysics than triplet. The process that leads to racemization appears to be only very slightly activated.

Experimental Section

General Instrumentation. All luminescence spectra and lifetimes were recorded with an Edinburgh Instruments FL900 spectrometer or a Spex FluoroMax fluorometer. Reported lifetimes at room temperature are clean single exponentials. At 77 K, data were fit to a distribution of exponentials to account for inhomogeneity, and the quoted lifetime is the center of a single Gaussian band. A transparent Suprasil liquid nitrogen dewar was used to hold samples, which were contained in EPR tubes, at 77 K. At or near room temperature, standard 1 cm cells were used. Analytical chromatography was done either with a Hewlett-Packard 5890 II GC equipped with HP-1 or DB-17 capillary columns and a flame ionization detector or a Hewlett-Packard 1050 series HPLC equipped with a diode array UV/Vis detector. For chiral analyses, a CHIRACEL OB column from Daicel Chemical Industries was used. The eluent was an 80:20 mixture of hexane and 2-propanol. For a representative case, the retention times for the enantiomers of 2Np−SO were 10 and 14 min. UV/Vis measurements were performed with a Shimadzu PC-3101 spectrophotometer. NMR spectra were obtained with a Varian 300 MHz instrument. Flash photolysis data were collected as described previously.[16,41]

Compounds. Two types of sulfoxide samples were prepared. One group is a series of racemic mixtures and the other is single enantiomers. All of the compounds are previously reported and match literature spectra reports where given.[42−54] Starting materials were obtained from Aldrich, Akros, or Fisher and used as received. Solvents were freshly distilled under Ar from an appropriate drying agent. All recrystallizations were done from 95% ethanol.

No direct characterization to determine the stereochemistry of the sulfur centers of the enantiomerically pure sulfoxides was done, as it was unnecessary for this study. However, the reaction of a Grignard reagent with a sulfinic ester is known to result in inversion at the sulfur in general. The menthyl ester of the corresponding (S*S*)-naphthalene sulfinate has been characterized previously[55] and should lead to (*R*)-sulfoxides. This enantiomer came out first on chiral HPLC analysis. The other two resolved sulfoxides also came out earlier than their enantiomers in HPLC and were prepared from analogous precursors; it is assumed that they too are of the same configuration.

Representative Preparation of Racemic 9-Methanesulfinylanthracene (An-SO). Under Ar, 1.82 mmol of 9-bromoanthracene was dissolved in 20 mL of anhydrous ether. The solution was chilled to −20 °C. To this was added 2.2 equivalents of commercial *t*-BuLi in hexane, followed by stirring for 30 min. Then 3.0 mmol methyl disulfide was added to the mixture. After 30 min, the cold bath was removed and the reaction was worked up after stirring overnight. The reaction was quenched with aqueous NH_4Cl. After extractive workup, the 9-methanesulfenylanthracene (9-anthryl methyl sulfide) was isolated in over 70% yield after silica chromatography.

The oxidation from sulfide to sulfoxide was done with one equivalent of hydrogen peroxide (as 30% aqueous) in acetone at room temperature for 10 h. The 9-methanesulfinylanthracene was obtained after extractive workup and purification with silica chromatography (3:1 CH_2Cl_2/hexane). The isolated yield was 50%. After recrystallization, no impurities could be detected by HPLC.

The other sulfides and racemic sulfoxides were prepared in the same manner in very similar yields. The ^1H NMR of Py-SO has not been reported previously:[56] ^1H NMR ($CDCl_3$, 300 MHz) δ 2.92 (s, 3 H), 8.07−8.31 (m, 7 H), 8.40 (d, 1 H, $J = 8.2$ Hz), 8.68 (d, 1 H, $J = 8.2$ Hz).

Representative Preparation of Optically Resolved 1-Methanesulfinylpyrene (Py-SO). 1-Pyrenesulfonyl chlo-

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ride was prepared from pyrene by the method of Colter.[57] A single diastereomer of menthyl 1-pyrenesulfinate was prepared in 30% yield from the sulfonyl chloride by the method of Klunder.[55] Purification was done by sequential silica chromatography and recrystallization.

Menthyl 1-pyrenesulfinate (156 mg, 0.39 mmol) was dissolved in 30 mL dried ether. The solution was chilled to −78 °C. To this solution 0.5 mL (1.5 mmol) of 3 M commercial methylmagnesium bromide was added. The cold bath was allowed to slowly warm and workup the next day provided 30% isolated yield of the sulfoxide after chromatography and recrystallization. Chiral HPLC showed only the first eluting enantiomer and the NMR, IR, and UV spectra matched with racemic Py-SO.

Two other sulfoxides were prepared, 2-methanesulfinylnaphthalene (2Np-SO) and 9-methanesulfinylanthracene (An-SO). The same procedure was used from sulfonyl chloride to chiral sulfoxide for these two compounds.[55,58,59] Similar yields were obtained in each case.

Luminescence Measurements. All the fluorescence measurements at room temperature were done in acetonitrile and all the 77 K measurements were done in either 1:1 ethanol/methanol glass or methylcyclohexane glass. HPLC grade acetonitrile and methanol were used. Ethanol was held at reflux over CaH_2 until required and then distilled under dry Ar for each use. For quantum yields, spectra were integrated against naphthalene in cyclohexane as a standard for room temperature measurements and all sample optical densities were approximately 0.1. At 77 K, benzophenone phosphorescence was used as the standard.[60] All quantum yields represent averages from multiple independent samples. Emission quantum yields above ca. 0.1 were reproducible to within less than 5% from run to run and the smaller ones were reproducible to within 10%. Singlet energies were estimated from normalized emission and excitation spectra.

Inversion Quantum Yields. Photolysis of azoxybenzene to from 2-hydroxyazobenzene was used as an actinometer.[61] A 254 nm light source was used initially, but proved to be too intense to make experiments practical. A 150 W Xe arc lamp filtered through a monochromator set to 295 nm with slits set to ±12 nm linear dispersion was used. Magnetic stirring was also applied. At the exit slit of the monochromator, a hollow brass cell holder that allows for internal circulation is attached for temperature regulation to ±1 °C with a Lauda circulating bath. Photolysis times were 2−10 min for several percent racemization. Progress was quantified by chiral HPLC analysis. All data represent at least three separate measurements. The reproducibility error was <10% of the average. Some points were measured repeatedly and it was ensured that the small differences reported in Table 5 were reproducible.

Samples were prepared as approximately 0.3 mM solutions. The points obtained near room temperature were done with standard 1 cm cells, and nearly 100% of the light was absorbed. In general, samples were Ar-flushed to remove O_2. Control experiments using either freeze−pump−thaw degassing cycles or no degassing at all provided essentially identical results.

For the 173 K data, an EPR temperature controller (ER4111 VT by Bruker) that boils and heats liquid N_2 was used with a homemade L-shaped quartz dewar. Samples were contained in EPR tubes and actinometry was repeated in this sample geometry. The temperature was controlled to within 10 °C.

Quenching and Sensitizing Experiments. Benzophenone was used as a triplet sensitizer after recrystallization. 2Np−SO was the substrate and the ordinary concentration of ~300 μM was used. Irradiation was from “black lights” in a mini-Rayonet reactor. These bulbs have broad emission centered at approximately 350 nm. At this range of irradiation, sufficient sensitizer was used such that benzophenone absorbed virtually all the light when it and the sulfoxide were present, but a small absorption tail allowed absorption by the sulfoxide in its absence. No inversion was observed in the experimental samples after an irradiation time sufficient for complete racemization of control samples that did not contain benzophenone.

In separate experiments, direct irradiation of 2Np-SO was carried out using oxygen, piperylene, and isoprene as triplet quenchers. Photolysis was done with the Xe arc lamp under conditions described previously for quantum yields. Addition of up to 25 mM diene did not affect the rate of racemization, nor did the presence of oxygen (air saturated) in the sample.

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