Steric Effects in Singlet and Triplet Electronic Energy Transfer to Azo Compounds[1,2]

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Abstract: Rate constants have been determined for the solution-phase quenching of singlet and triplet excited states of a variety of sensitizers (aromatic hydrocarbons, aryl and alkyl ketones, α-diketones) by a series of azo compounds with varying steric properties. Both singlet and triplet quenching are attributed to electronic energy transfer by the collisional, electron-exchange mechanism. Steric hindrance to exothermic triplet energy transfer is significant, with azo-*n*-butane a better acceptor than azo-*tert*-butane by a factor of 3.6–10.7. Steric hindrance to singlet energy transfer is less pronounced (comparable steric factors are 1.7–2.9), apparently because diffusion rather than energy transfer is rate limiting in solution. For a given donor–acceptor pair, singlet energy transfer is two to three times faster than triplet energy transfer. The triplet energy level of the azobutanes is estimated to be 53 ± 1 kcal/mol.

Bimolecular electronic energy transfer reactions may

$$D^* + A \longrightarrow D + A^*$$

proceed by at least three different mechanisms:[4,5] (1) long-range resonance energy transfer, which acts over distances up to about 50 Å by dipole–dipole interactions; (2) short-range collisional energy transfer, which requires electron-exchange interactions between the donor and acceptor molecular orbitals; (3) radiative energy transfer, involving donor emission and reabsorption of the photon by the acceptor. For triplet electronic energy transfer, the individual transitions of both the donor and the acceptor are spin-forbidden, and only the collisional electron-exchange mechanism is operative. Singlet electronic energy transfers have been demonstrated to proceed by all of the mechanisms above.

Given the necessity of a collision for electron-exchange energy transfer, steric hindrance might be expected whenever the donor and/or acceptor chromophores are surrounded by bulky groups. In fact, steric hindrance to energy transfer has only infrequently been observed.[6,7,11] Studies which have specifically sought steric hindrance to energy transfer have produced both positive[2,11] and negative[12,13] results. We have undertaken a systematic study of rates of electronic energy transfer from a variety of sensitizers to a series of azo compounds with varying steric properties. Azo compounds were chosen as the main substrates for this study because (1) they have low triplet and singlet energy levels and therefore can efficiently quench a large number of sensitizers;[14-16] (2) the azo chromophore is small and highly localized, and thus can be effectively blocked by steric interactions; (3) azo compounds are readily synthesized with various alkyl groups located on either side of the chromophore; (4) the photochemical behavior of azo compounds has been rather thoroughly studied;[14,15] and (5) singlet energy transfer to azo compounds has been shown to proceed by the electron-exchange mechanism.[16]

Experimental Section

Materials. All the azo compounds were prepared by the method of Stowell,[17] distilled, and determined to be >95% pure by gas chromatographic analysis. Azo-1-adamantane was recrystallized from ethanol, mp 285–286° (lit. 286–294°).[18] Azobis(isobutyronitrile) was recrystallized three times from methanol. Sensitizers and other compounds were obtained from commercial sources and were distilled or recrystallized at least twice. Benzene solvent was either Baker Instra-Analyzed GC-Spectrophotometric Quality or was purified by photolysis with chloranil.[19] Both were found equally satisfactory, as determined by the lifetime of triplet triphenylene in the degassed solvent ($k_0 = 1.0 \times 10^4$ sec^{-1}). Acetonitrile was Matheson Coleman and Bell Spectrograde or was purified by distillation from potassium permanganate followed by slow fractional distillation.[20]

Flash Photolysis Studies. The apparatus was essentially a Xenon Model 710 flash photolysis unit. The photolyzing system consisted of a Xenon Model A high energy micropulser, typically used at 9 kV (250 J), with a Xenon Model C trigger, and a pair of Xenon FP-8 20-cm flashtubes in a Xenon FH-1290 housing. A typical flash had a duration of about 50 μsec, with a 20 μsec width at half-height. The analyzing system consisted of a Bausch and Lomb SP-200 superpressure 200-W mercury light source, normally filtered to pass only light of λ >400 nm, powered by a PEK Model 705A 200-W stabilized dc power supply. After passage through the sample cell, the analyzing beam was focused onto the entrance slit of a Bausch and Lomb Model 33-86-07 0.25-m high-intensity monochromator, set at a wavelength near λ_{max} for the sensitizer triplet state, and the intensity was detected by an RCA 1P28 phototube powered by a Heath Model EU-42A power supply, typically at 800 V. Scattered light from the photolyzing flash was minimized by baffles at either end of the sample cell. The recording of the data was on a Tektronix Model 564 storage oscilloscope with a 10K Ω input load added and the trace was photographed with a Tektronix Model C-12 camera using Polaroid Type 46-L film. The transparency was projected and traced for ease and accuracy of measurement. Samples for analysis were contained in cylindrical Pyrex cells 20 cm long × 13 mm i.d. with fused optical windows. These were attached via a side arm to a 100-ml round-bottom flask where the sample was contained during degassing by five or more freeze–pump–thaw cycles to an ultimate pressure of 10^{-5} Torr or less. Data from a particular sample were taken only on the first flash, and only after the scattered light from the photolyzing flash was negligible.

The kinetic analysis followed the method of Herkstroeter and Hammond[19] to separate first- and second-order components of the observed decay, performed by a Wang Model 700 programming calculator.[21] The first-order component of the decay constant was plotted against quencher concentration to obtain a linear Stern–Volmer-type plot, the slope of which was k_Q, the bimolecular rate constant for quenching. At least five different quencher concentrations were employed to obtain such a plot. In general, reproducibility was ±10% for different samples of equivalent composition. As a check upon our procedures, we measured the rate constant for quenching of triphenylene triplets by *trans*-stilbene to be 6×10^9 M^{-1} sec^{-1} (lit. 7×10^9 M^{-1} sec^{-1}).[19]

Quenching of Benzophenone Photoreduction. Determinations of the quenching of the benzophenone–benzhydrol photoreaction in

Table I. Rate Constants for Triplet Quenching by Azo Compounds ($k_Q \times 10^{-8}, M^{-1}\ sec^{-1}$)[a]

	Triplet donor (E_T in kcal/mol)[b]								
Quencher	Acetone[c,d] (78)	Acetophenone[c] (73.5)	Benzophenone[c,e] (68.5)	Triphenylene[f] (66.6)	Naphthalene[f] (60.9)	1,4-Dibromonaphthalene[d,g] (59)	Biacetyl[g] (54.9)	Benzil[g] (53.7)	Fluorene[f] (53.3)
Azo-*n*-butane	31	50	35 (46)	32	23	30	22[c]	1.4[f]	1.8
Azoisobutane	29		15 (25)	30	22		15 (20)[j]	1.1	0.9
Azo-*sec*-butane	23		(31)	20	10		20	0.5	0.9
Azo-*tert*-butane	5.6	15	7.9 (14)	3.0	6.4	4.8	4.4 (3.3)[k]	0.12	<0.03
Azo-1-adamantane			7.6 (22)	6.0	8.5		12	0.36	0.28
Azoisopropane	30		28[h]				14[h]	1.5[h]	
Azobenzene				70	50		50	37	35
Azobis(isobutyronitrile)	4.6					1.3			
2,3-Diazabicyclo[2.2.1]-2-heptene (1)			38[i]	34					
2,3-Diazabicyclo[2.2.2]-2-octene (2)			38[i]				20[l]	2.6[l]	

[a] In benzene solvent at room temperature unless otherwise noted. [b] E_T values from ref 4, pp 92–93. [c] By phosphorescence lifetime quenching. [d] In acetonitrile solvent. [e] Values in parentheses determined by photoreduction quenching. [f] By flash photolysis. [g] By phosphorescence intensity quenching. [h] Isooctane solvent, unpublished results of C. Steel quoted in ref 14. [i] Acetonitrile solvent, ref 28. [j] Hexane solvent, ref 29. [k] Reference 15. [l] Isooctane solvent, ref 28.

benzene solvent were modeled after the procedure of Moore and Ketchum.[22] The actinometry was performed in a standard merry-go-round apparatus.[23] Degassed and sealed samples were prepared with 0.1 *M* benzophenone and 0.1 *M* benzhydrol in purified benzene with various predetermined quencher concentrations. Irradiation at 366 nm was continued to about 20% conversion. The temperature was maintained below 30° during the irradiation. The photolyzed solutions were diluted 25:1 and analyzed spectrophotometrically at 350 nm for benzophenone concentration. Since typical quencher concentrations were of the order of 10^{-5} *M* (before dilution), quencher absorption did not interfere with this analysis. Stern–Volmer plots of Φ_0/Φ vs. quencher concentration gave slopes proportional to k_Q. For quenching by *trans*-stilbene, k_Q was taken to be $6 \times 10^9\ M^{-1}\ sec^{-1}$,[24] and all other quenching rate constants were determined relative to this value.

Quenching of Phosphorescence Intensity. Luminescence spectra were recorded on an Aminco-Bowman Model 4-8202 spectrophotofluorometer with ratio recording. Samples were degassed through three freeze-pump-thaw cycles to 10^{-2} Torr or less and sealed in 13 × 100 mm Pyrex test tubes which had been previously matched in absorbance at the appropriate wavelengths. Samples contained 0.05 *M* biacetyl or benzil in purified benzene with various predetermined concentrations of the quencher. Biacetyl phosphorescence was excited at 420 nm and monitored at 525 nm, and benzil phosphorescence was excited at 432 nm and monitored at 563 nm.[25] Stern–Volmer plots were linear with slopes proportional to k_Q. For biacetyl quenching, the rate constant for azo-*n*-butane quenching was determined to be $2.2 \times 10^9\ M^{-1}\ sec^{-1}$, by phosphorescence lifetime quenching, and all other biacetyl quenching rate constants were related to this value. For benzil quenching, the rate constant for azo-*n*-butane quenching was determined by flash photolysis to be $1.4 \times 10^8\ M^{-1}\ sec^{-1}$, and all other benzil quenching rate constants were related to this value.

Quenching of the phosphorescence intensity of 1,4-dibromonaphthalene was determined using a Hitachi-Perkin-Elmer MPF-3L fluorescence spectrophotometer. Samples were prepared in acetonitrile solution and degassed by bubbling with nitrogen. Phosphorescence was excited at 324 nm and monitored at 510 nm. Absolute rate constants were obtained from Stern–Volmer slopes using a measured triplet lifetime for 1,4-dibromonaphthalene.

Quenching of Phosphorescence Lifetimes. The time-correlated single photon counting technique was used to determine phosphorescence lifetimes. The sample was excited with an air spark lamp (flash rate = 6-8 × $10^3\ sec^{-1}$). Emission was monitored perpendicular to the incident light, using a Jarrel-Ash 0.25-m monochromator and an Amperex 56 AVP phototube cooled to −70°. Data were usually collected in 256 channels (Tracor-Northern Econ II Series multichannel analyzer) at 31.1 nsec/channel. Samples were nitrogen bubbled for 3 min at −20° for acetonitrile solutions and for 3 min at 8-10° for benzene solutions. Rate constants for quenching were determined from at least five lifetime decay determinations using the following relationship

$$\tau^{-1} = \tau_0^{-1} + k_Q[Q]$$

where τ = triplet lifetime in presence of quencher, Q, and τ_0 = triplet lifetime in absence of quencher. Least-squares analysis was used to determine the best fit of the data. Results from two k_Q determinations were usually the same within ±10%.

Table II. Rate Constants for Singlet Quenching by Azo Compounds ($k_Q \times 10^{-8}, M^{-1}\ sec^{-1}$)

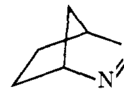
	Quencher	
Singlet donor	Azo-*n*-butane	Azo-*tert*-butane
Acetone[a]	70	41
Adamantanone[b]	29	14
7,7-Dimethylnorbornanone[c]	52	18
Triphenylene[d]	112	56

[a] Acetonitrile solvent, singlet lifetime 2.1 nsec, ref 26. [b] Acetonitrile solvent, singlet lifetime 8.0 nsec, ref 26. [c] Acetonitrile solvent, singlet lifetime 5.0 nsec, ref 27. [d] Benzene solvent, results obtained by fluorescence lifetime quenching.

Quenching of Fluorescence Intensities. An Hitachi-Perkin-Elmer MPF-3L fluorescence spectrophotometer was used to determine emission intensities in the absence and presence of quencher. Stern–Volmer analysis of the data from at least five quencher concentrations yielded values of $k_Q\tau$. Correction for quencher absorption was made when necessary. Least-squares analysis was used to determine the best fit of the data. Results from two k_Q determinations were usually the same within ±10%.

Results

Rate constants for triplet quenching by eight acyclic azo compounds and two bicyclic azo compounds, **1** and **2**, are compiled in Table I.



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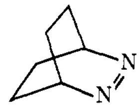

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Rate constants for singlet quenching by azo-*n*-butane and azo-*tert*-butane are compiled in Table II. Singlet quenching rates were determined from Stern–Volmer slopes, $k_Q\tau_0$, and reported singlet lifetimes in the same sol-

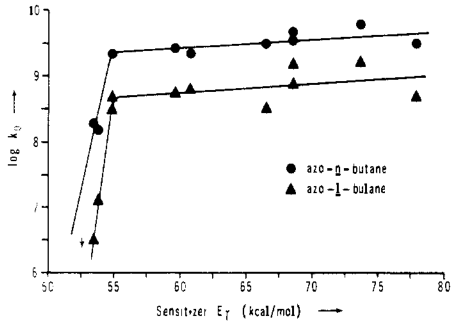

Figure 1. Triplet quenching rate constants as a function of sensitizer triplet energy (data from Table I).

vent.[26,27] Both Tables I and II include relevant rate constants previously reported in the literature.[11,14,15,28,29]

Benzene fluorescence in cyclohexane was quenched by acetone and di-*tert*-butyl ketone. Stern–Volmer slopes yielded values of 212 and 132 M^{-1}, respectively.

Discussion

The Triplet Energy of Azoalkanes. The triplet energy level of azoalkanes has been difficult to ascertain experimentally, since neither direct nor sensitized phosphorescence has been observed from azoalkanes.[14] Calculations for the parent compound, *trans*-diimide, have variously placed the lowest triplet energy level between 40 and 74 kcal/mol.[30-33] The triplet energies of the bicyclic azo compounds, **1** and **2**, have been located at 60 ± 1[34] and 54.5 ± 1 kcal/mol,[28] respectively, by triplet energy transfer studies. The triplet energy levels of azoisobutane[29] and azoisopropane[14] have been estimated as 53 and 54 kcal/mol, respectively, also by triplet energy transfer studies. The most definitive evidence to date is the result of electron impact studies on azomethane, which have located an absorption with maximum at 63 kcal/mol attributable to the lowest triplet state of azomethane.[35] For azo-*tert*-butane, a similar maximum at 61 kcal/mol was observed.[36] Corresponding to these maxima (0,0) triplet energies of approximately 55 and 52 kcal/mol may be estimated from the absorption onset in the spectra of azomethane and azo-*tert*-butane, respectively.

The data of Table I also allow a determination of the triplet energy level of the azoalkanes. Figure 1 is a plot of log k_Q for azo-*n*-butane and for azo-*tert*-butane vs. the triplet energy of the sensitizer. For azo-*n*-butane the plot displays the expected features:[37] with high-energy sensitizers, the quenching rate is relatively constant, near the diffusion-controlled limit;[38] a sharp drop in rate is observed as the sensitizer triplet energy approaches that of the acceptor triplet energy. A typical correlation would locate the triplet energy of the acceptor at the point where the rate has dropped about two orders of magnitude. On this basis, we place the triplet energy of all of the azobutanes at 53 ± 1 kcal/mol.

Because the quenching rates for azo-*n*-butane do follow the expected pattern for triplet energy transfer and because our determination of the triplet energy level of azoalkanes is in agreement with other determinations, we conclude that the triplet quenching observed is indeed triplet energy transfer to the azoalkanes.

Steric Hindrance to Triplet Energy Transfer. Triplet energy transfer must occur by the collisional electron-exchange mechanism in solution[4] and therefore would be expected to be less efficient whenever approach between donor and acceptor chromophores is sterically hindered. There have been few reports of steric hindrance to energy transfer, although steric effects have been specifically sought. Steric hindrance to triplet energy transfer was postulated to be the cause of unusual photoisomerization behavior of the stilbenes when sensitized by 2,4,6-triisopropylbenzophenone. A steric factor of 15 was estimated for triplet energy transfer to *cis*- and *trans*-stilbene.[6] Triplet energy transfer to racemic *trans*-1,2-diphenylcyclopropane from optically active 3-methyl-1-indanone yields, in addition to the cis isomer, a 3% asymmetric induction in the trans isomer. The calculated selectivity in energy transfer rates to the two trans enantiomers is 1.06.[9] The quenching of alkylbenzene phosphorescence by *cis*-piperylene is dependent upon the steric properties of the alkyl groups. Comparison of toluene (unhindered sensitizer) with 1,4-di-*tert*-butylbenzene (hindered sensitizer) gives the largest steric factor of 2.2.[41] On the other hand, it has been concluded that steric effects are minimal in the case of triplet energy transfer from the hindered sensitizers α,α-dimethylvalerophenone or β,β-dimethyl-α-ketobutyrophenone to 2,5-dimethyl-2,4-hexadiene or to 2-chloronaphthalene, based upon the viscosity dependence of the Stern–Volmer quenching parameters, which is the same dependence as observed for the unhindered sensitizer valerophenone. The authors did note, however, that the quenching of α,α-dimethylvalerophenone by 2,5-dimethyl-2,4-hexadiene (hindered quencher) as compared to 2-chloronaphthalene or 1,3-pentadiene (unhindered quenchers) does show a steric factor of 1.3–1.5.[12]

We chose to study steric effects on triplet quenching by azoalkanes because approach to this chromophore can be effectively hindered by bulky substituents at both ends of the azo group. Table I shows that the rate constants for quenching of nine triplet sensitizers by the series of four azobutanes decrease in the order *n*-butyl > isobutyl > *sec*-butyl > *tert*-butyl. The largest decrease in k_Q usually occurs between azo-*sec*-butane and azo-*tert*-butane. We propose that these data demonstrate a steric effect on triplet energy transfer. Support for this hypothesis can be found by inspection of molecular models of the *trans*-azobutanes. Access to the n or π electrons of the azo group is only slightly changed between azo-*n*-butane and azoisobutane. Some steric hindrance is introduced in azo-*sec*-butane, where two alkyl groups are attached to the α carbon, but the largest difference occurs when a third alkyl group is added (azo-*tert*-butane). Access to the π electrons in azo-*tert*-butane is substantially blocked except for a fraction of the rotamers of the methyl groups. The n electrons remain somewhat more approachable, but the greatest change in their steric environment also occurs between azo-*sec*-butane and azo-*tert*-butane. These observations on models are consistent with the ordering and magnitude of the decreases in k_Q reported in Table I for the series of azobutanes.

An alternative explanation based on inductive substituent effects should also be considered, since the azo group becomes more electron-rich as electron-releasing alkyl groups are substituted on the α-carbon. However, an interpretation of the data in Table I based on this premise is not consistent with the observation that azo-*tert*-butane and azobis(isobutyronitrile) (AIBN), which are sterically similar but electronically very different, show similar quenching rate constants. In fact, AIBN is a somewhat poorer triplet quencher than azo-*tert*-butane for the two cases in which data were obtained. This suggests that the diminished quenching efficiency of tertiary azoalkanes is not caused by electron-releasing substituent effects. The lower quenching rate constants for AIBN compared to azo-*tert*-butane could be explained by the electron-withdrawing effect of the cyano substituents. If this electron withdrawal causes the n and π orbitals of the azo group to be less extended into space, a sensitizer would have to approach even closer for an effective energy transfer interaction; hence greater steric hindrance would be expected. To further substantiate the importance of steric factors, the observed trend in k_Q is the same for a variety of sensitizers: aryl and alkyl ketones, aromatic hydrocarbons, and α-diketones. The generality of the trend would seem to favor an interpretation based on steric rather than electronic factors. Furthermore, if inductive factors were significant, a more regular trend would have been expected in proceeding from primary to secondary to tertiary alkyl groups. The sharp change between secondary and tertiary is more characteristic of steric effects, as indicated by our analyses with molecular models.

In addition to the correlation with steric properties in the azobutane series and the correlation with sensitizer triplet energy discussed in the previous section, several other aspects of the data in Table I can be commented on. First of all, azo-1-adamantane is consistently a more efficient quencher than azo-*tert*-butane, on the average about twice as efficient. This finding is contrary to our initial expectations based upon molecular models, which indicate that the azo chromophores of both compounds are very similarly hindered, with somewhat greater steric hindrance in the case of the 1-adamantyl substituent. A possible explanation can be proposed by considering the entropy change during a quenching interaction. The methyl groups of azo-*tert*-butane must "freeze" to allow close approach of sensitizer and azo group. In azo-1-adamantane the alkyl portions are already frozen. Consequently, quenching by azo-*tert*-butane has a more negative entropy of activation and is therefore slower than quenching by azo-1-adamantane. Secondly, all of the acyclic azo compounds used in this study were the more stable trans isomers. The class of cis azo compounds is represented by the bicyclic compounds **1** and **2**. As quenchers for high-energy triplet sensitizers, **1** and **2** are as efficient as azo-*n*-butane, which is consistent with the lack of steric hindrance in the cis configuration. Finally, azobenzene quenches all of the triplet sensitizers used with nearly maximal efficiency. Two other reported rate constants for triplet quenching by azobenzene amplify this point: β-acetonaphthone (E_T = 59.3 kcal/mol; $k_Q = 34 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$) and 3-acetylpyrene ($E_T$ = 45 kcal/mol; $k_Q = 40 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$).[42] Thus azobenzene apparently has a lowest triplet energy less than 45 kcal/mol. Furthermore, azobenzene is not subject to steric hindrance to triplet energy transfer. These effects could be due to the conjugation of the aromatic rings with the azo group which delocalizes the chromophore, resulting not only in a lower triplet energy but also a more extended and accessible chromophore for collisional energy transfer.

Steric Hindrance to Singlet Energy Transfer. Evidence that quenching of triphenylene and ketone singlets by azoalkanes occurs by energy transfer comes from studies of sensitized decomposition of azoalkanes.[15] The observed cage effects and limiting quantum yields are identical with those from direct photolysis, thus providing strong evidence that this sensitization populates the singlet state of the azo compound by singlet energy transfer. Singlet energy transfer to azoalkanes from aromatic hydrocarbons has been determined to occur by the electron exchange mechanism.[16] Energy transfer from ketone singlets would also be expected to occur by the electron exchange mechanism because of the weak transition moment of the n, π^* absorption band of the azoalkanes.[4]

Studies of steric effects on singlet energy transfer have led to the conclusion that they are significant in the vapor phase[11,43] and insignificant in solution.[13] Only in cases of severe steric hindrance have steric effects been noted in solution-phase singlet energy transfer. The quenching of ketone fluorescence by biacetyl (unhindered quencher) or by 2,2,5,5-tetramethylhexane-3,4-dione (hindered quencher) shows a substantial steric factor of 3-5.[13]

Table III. Steric Factors for Energy Transfer[a]

Donor	k_Q(azo-*n*-butane)/ k_Q(azo-*tert*-butane)
Triplet sensitizers	
Acetone	5.5
Acetophenone	3.3
Benzophenone	4.4
Triphenylene	10.7
Naphthalene	3.6
1,4-Dibromonaphthalene	6.3
Biacetyl	5.0
Benzil	11.7
Fluorene	>60
Singlet sensitizers	
Acetone	1.7
Adamantanone	2.1
7,7-Dimethylnorbornanone	2.9
Triphenylene	2.0
Naphthalene (vapor)	9.5[b]

[a] Using k_{et} values calculated from eq 1 results in somewhat larger steric factors. [b] Ref 43.

Table IV. Comparison of Singlet and Triplet Energy Transfer Rates ($k_Q \times 10^{-8}, M^{-1}\ \mathrm{sec}^{-1}$)

	Acceptor	
Donor	Azo-*n*-butane	Azo-*tert*-butane
Acetone singlet	70	41
Acetone triplet	31	5.6
Triphenylene singlet	112	56
Triphenylene triplet	32	3.0

Rate constants for quenching of the fluorescence of three ketones and triphenylene by azo-*n*-butane and azo-*tert*-butane are given in Table II. Although azo-*n*-butane is a better quencher than azo-*tert*-butane in all cases, the magnitude of the steric effect is smaller than for triplet energy transfer (see Table III). Efficient singlet energy transfer to both azobutanes would be expected on the basis of the appreciable overlap of the absorption spectra of the azobutanes with the fluorescence spectra of the sensitizers. We attribute the differences in their quenching efficiencies to steric hindrance to singlet energy transfer.

In the vapor phase, singlet energy transfer to the azobutanes shows substantial steric effects. Absolute rate constants for the quenching of naphthalene fluorescence by azo-*n*-butane, azoisobutane, azo-*sec*-butane, and azo-*tert*-butane, are 30, 19, 13, and 3.2 × $10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, respectively.[43] This corresponds to a steric factor of 9.5 (comparing azo-*n*-butane and azo-*tert*-butane), substantially larger than the steric factors of 1.7 to 2.9 observed for singlet energy transfer in solution.

To further evaluate the phase dependence of steric effects on singlet energy transfer, acetone and di-*tert*-butyl ketone were used as quenchers of benzene fluorescence. In cyclohexane solution, we find acetone to be a more efficient quencher than di-*tert*-butyl ketone by a factor of 1.6. In the vapor phase quenching of benzene fluorescence, these two ketones showed a larger steric factor of 4.1.[11] The interpretation of this phase dependence is discussed below.

Comparison of Singlet and Triplet Energy Transfer. The data obtained for acetone and triphenylene quenching allow a direct comparison of singlet and triplet energy transfer processes (see Table IV). Singlet and triplet *quenching* by short range energy transfer differ *experimentally* in two respects: (1) for the same donor and acceptor, rate constants for singlet quenching are two to three times larger than for triplet quenching; (2) triplet quenching is subject to larger steric effects than singlet quenching.

In attempting to understand the reasons for these differences it must be kept in mind that the observed rate constant for quenching is rarely equal to the rate constant for energy transfer. The maximum rate constant for quenching is equal to the rate constant for diffusion in solution. The rate constant for energy transfer may be larger or smaller than the diffusion rate constant. A generalized scheme for energy transfer in solution is shown below:[39]

$$S^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [S^*Q] \xrightarrow{k_{et}} S + Q^*$$

where [S*Q] is an encounter complex in which many collisions can occur. The lifetime of the complex, and thus the number of collisions, depends directly on the viscosity of the solution.

From this model, the observed quenching constant, k_Q, equals

$$k_Q = k_d k_{et}/(k_{et} + k_{-d}) \qquad (1)$$

This model can account for the observed differences cited above between vapor and liquid phase steric effects on singlet quenching. In solution, differences in k_{et} may be hidden by the large number of collisions (10–100) before the nearest neighbors diffuse apart.[44] For very efficient energy transfer processes, rate-limiting diffusion exerts a leveling effect on the observed quenching rate. In the vapor phase, changes in k_{et} are directly reflected in measured k_Q values because a vapor phase encounter can be considered to be a single collision and diffusion is rarely rate limiting.

We can now consider the contrasts between singlet and triplet quenching by energy transfer. The rate constants for quenching of acetone and triphenylene singlets by azo-*n*-butane (7 and 11 × 10^9 M^{-1} sec^{-1}, respectively) are close to the diffusion-controlled values in solution (calculated to be 10 × 10^9 for acetonitrile[40] and for benzene[44]), indicating that nearly every solution encounter results in a quench ($k_{et} \gg k_{-d}$). This contrasts with triplet quenching where k_Q is two to three times smaller than k_d ($k_{et} \sim k_{-d}$). From eq 1 approximate values for k_{et} may be directly calculated to be 2 × 10^{10} sec^{-1} for azo-*n*-butane quenching of acetone or triphenylene triplets.[45]

We can hypothesize at least three reasons why triplet energy transfer is slower than singlet energy transfer. (1) Greater orbital interaction may be required between donor and acceptor for triplet energy transfer to occur, perhaps to induce the forbidden S → T and T → S transitions in triplet energy transfer. Conceivably, both distance of approach and specific orbital overlap may be more critical for triplet energy transfer by the electron-exchange mechanism. (2) Statistical factors having to do with the multiplicity changes involved in triplet–triplet energy transfer may limit the efficiency of the energy transfer process.[46] In this case, even if all other factors (distance, orientation, overlap) were favorable, only one-third or half of these potential transfers would be successful. There does not appear to be a well-defined theoretical rationale for this hypothesis. However, in numerous cases of triplet energy transfer studied, k_Q is usually one-third to half of k_d until high viscosity solvents are employed.[39,46] Our data do not allow a choice to be made between these hypotheses. A third possibility, that singlet energy transfer includes a major contribution from resonance energy transfer, would seem to be ruled out by the finding that singlet energy transfer to azoalkanes predominantly occurs by the electron-exchange mechanism.[16]

The second experimentally observed difference between quenching of acetone and triphenylene singlets and triplets by azoalkanes was that triplet quenching showed a larger steric factor. Much of this is due to the effects of rate-limiting diffusion in singlet energy transfer, as discussed above. However, even after calculating the corresponding values for k_{et} from eq 1[45] for acetone quenching by azo-*n*-butane and azo-*tert*-butane, singlet energy transfer shows a steric factor of three compared to nine for triplet energy transfer. The reason for the greater steric factor on triplet energy transfer may be due to the greater interaction required for triplet energy transfer postulated above or to the inclusion of some resonance energy transfer in singlet energy transfer. The second hypothesis above attributing slower rates of triplet energy transfer to statistical factors would predict that the same steric effect should be found for singlet and triplet quenching.

Theoretical Basis for Steric Effects on Energy Transfer. The electron-exchange mechanism for electronic energy transfer necessarily requires a very close and specific orbital interaction between donor and acceptor.[47] In simplest terms, the electron exchange must consist of a transfer of an electron from the donor antibonding orbital to the acceptor antibonding orbital while another electron is transferred from the acceptor bonding orbital to the donor bonding orbital; this effectively returns the donor to the ground state and produces an excited state of the acceptor. While it is conceivable that one of these two electron transfers may determine the efficiency of the energy transfer process, our data do not allow such a distinction to be made.

The experimental results can be compared to the theoretical distance dependence of Dexter's formulation of exchange energy transfer[47]

$$k_{et} \propto e^{(-2R/L)} \qquad (2)$$

where L is an effective average Bohr radius for the initial and final electronic states of the donor and acceptor and R is the distance of separation of the donor and acceptor. L has been estimated to be 1 Å.[12,48] For approach to the π face of the azoalkane we can calculate the difference in R when the alkyl group is *n*-butyl or *tert*-butyl. Using van der Waals radii of 2.23 Å for methylene and 3.15 Å for a *tert*-butyl group,[49] the ΔR of 0.92 Å is calculated to result in a k_{et} difference of 6.3, or a k_Q difference of about 4.5, applying eq 1.[45,50] The steric factors for the three aromatic triplet sensitizers bracket the predicted value, and the steric factors for the ketone triplets all fall very close to that value (see Table III).

In summary, we have demonstrated that both singlet and triplet energy transfer to the azobutanes are subject to steric hindrance. The effect is larger for triplet energy transfer. Contrasts between singlet and triplet energy transfer from acetone and triphenylene to the azobutanes have been pointed out and reasons postulated for these differences.

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Microwave Structural and Mechanistic Study of Tricyclo[2.2.0.0^{2,6}]hexane

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Abstract: The microwave spectra of 11 isotopic species of tricyclo[2.2.0.0^{2,6}]hexane have been observed and analyzed. These data are sufficient for a complete structural determination by the r_s method. The internuclear distances are (in Å) C_1–C_2 = 1.513 ± 0.005, C_1–C_4 = 1.584 ± 0.005, C_2–C_3 = 1.523 ± 0.004, C_2–C_6 = 1.533 ± 0.008, C_3–C_4 = 1.549 ± 0.004, C_1–H_7 = 1.079 ± 0.002, C_2–H_8 = 1.081 ± 0.002, C_3–H_9 = 1.099 ± 0.004, C_3–H_{10} = 1.087 ± 0.005, C_4–H_{11} = 1.086 ± 0.002. The dipole moment has been determined by observation and analysis of the second-order Stark effect. The nonzero dipole moment components are μ_b = 0.090 ± 0.01 D and μ_c = 0.203 ± 0.01 D which yield a total dipole moment of 0.222 ± 0.01 D. In addition, the isotopic labeling experiments provide information about the reaction mechanism involved in the reduction of 5,6-dibromobicyclo[2.1.1]hex-2-ene with $LiAlH_4$ to form tricyclo[2.2.0.0^{2,6}]hexane. The reduction is a two-step process in which the initial step is the removal of the bromine exo to the double bond. Following the removal of each bromine, the molecule passes through a nonclassical cationic intermediate species before being reduced by the addition of a hydride ion.

In recent years there have been a number of microwave investigations of small polycyclic hydrocarbon molecules. Among those studied to date are bicyclo[1.1.0]butane,[1] 1-chlorobicyclo[1.1.1]pentane,[2] bicyclo[2.1.0]pentane,[3] tricyclo[3.1.0.0^{2,6}]hex-3-ene (benzvalene),[4a,4b] 4-chlorotricyclo[2.2.1.0^{2,6}]heptane,[5] bicyclo[3.1.0]hexane,[6] and bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene).[7] The list of molecules of this type for which good structural data are available is quite small; however, the importance of experimentally determined structures for these molecules cannot be overemphasized since it is very difficult to predict good structures a priori. One of the goals of these studies is to further our understanding of the different types of bonds in the molecule and to correlate this with reactivity of different atom sites within the molecule.

In this work the microwave spectra of the normal species, five different monodeuterio species, four singly substituted ^{13}C enriched species, and a dideuterio species of tricyclo[2.2.0.0^{2,6}]hexane (hereafter referred to simply as tricyclohexane) have been assigned. The data obtained are suffi-