Multipathway Photodimerization of 2-Methylthianaphthene 1,1-Dioxide. An Example of a Heavy-Atom Effect on Intersystem Crossing in a 1,4 Diradical[1]

Michael J. Hopkinson,[2a,b] William W. Schloman, Jr.,[2a,b] Benjamin F. Plummer,*[2b] E. Wenkert,[2c] and M. Raju[2c]

*Contribution from the Departments of Chemistry, Trinity University,
San Antonio, Texas 78284, and Rice University,
Houston, Texas 77001.* *Received July 20, 1978*

Abstract: The photodimerization of 2-methylthianaphthene 1,1-dioxide (MeTND) at 313 nm produces two photodimers whose structures are shown to be anti head to head (HH) and anti head to tail (HT) about the cyclobutane ring. The major isomer produced is always the HH dimer in oxygen-free solutions. Fluorescence quenching of MeTND by 1,4-diazabicyclo[2.2.2]-octane produces a linear Stern–Volmer relation that yields an estimated singlet lifetime for MeTND of 2×10^{-9} s. The kinetics of the photodimerization of MeTND were studied as a function of concentration of MeTND, solvent, triplet quenchers, and triplet sensitizers. The data suggest that the HH and HT dimers arise from different excited-state precursors. A monomeric excited triplet is the proposed progenitor of the HH dimer while an excimer is proposed to be the precursor of the HT dimer. Heavy-atom perturbation is found to occur on the $S_1 \rightarrow T_1$ transition of MeTND but is not effective for the radiationless $T_1 \rightarrow S_0$ transition. The triplet-sensitized dimerization of MeTND is found to be sensitive to heavy-atom perturbation and this is interpreted as a spin-orbital perturbation on intersystem crossing in the 1,4 diradical.

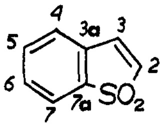
We are engaged in a continuing study of the influence of heavy-atom perturbation on intercombinational processes in susceptible molecules. We surmised that thianaphthene 1,1-dioxide (TND) would meet the criteria for a heavy-atom effect. The influence of spin-orbital perturbations on the intersystem crossing processes $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ in TND and 2-bromothianaphthene 1,1-dioxide (BrTND) was shown to be significant and the mechanism of dimerization of BrTND conformed to a multipathway kinetic analysis.[1] The data were best rationalized by proposing the intervention of monomeric triplet BrTND and an excimer of BrTND. To explore further the mechanistic intricacies of this system, we have studied the photodimerization of 2-methylthianaphthene 1,1-dioxide (MeTND) as a function of solvent, concentration of MeTND, sensitizers, and quenchers. The influence of heavy-atom perturbation is explored and a reaction mechanism consistent with the data is derived.

Results

A. Photoproducts. The photodimerization of MeTND was reported to give a single product in good yield.[3] We have found that irradiation at 313 nm of rigorously degassed solutions of MeTND produces two dimers in about a 9:1 ratio. If oxygen is present, the quantum yield decreases and the two dimers are produced in similar proportions. The two photodimers of MeTND show the typical properties of high melting point and low solubility in ordinary solvents common to this class of structures. The infrared[4] and ^{1}H NMR spectra of the dimers verified the gross structural features. The dimers of MeTND were initially assigned anti head to head (HH) **5** and anti head to tail (HT) **6** geometries by comparison of their physical properties to those of similar dimers previously studied.[1]

The mass spectrum of compound **5** (vide infra) produced a very weak M^+ peak at *m/e* 360 with a base peak at *m/e* 137 and weaker peaks at *m/e* 115, 180, 217, and 253. The presence of an extremely weak peak at *m/e* 296 shows that extrusion of SO_2 is not a favored decomposition pathway for **5**.

The mass spectrum of **6** produced no detectable M^+ peak but produced a significant peak at *m/e* 296 (M − 64), suggesting that SO_2 extrusion occurred readily in this isomer. The differences that occur in fragmentation pathways between **5** and **6** may be partially rationalized by steric arguments.



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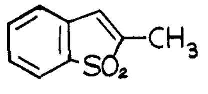

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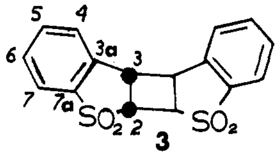

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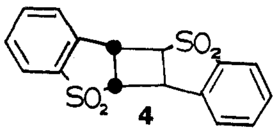

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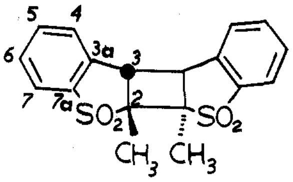

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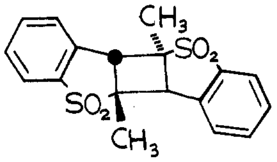

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Assuming that **5** is more crowded than **6**, we anticipate that the cleavage to monomer would occur readily for **5** and thus sulfur dioxide extrusion is not competitive. Since **6** seems to reflect a less crowded environment, as reflected in molecular models, it offers a competitive pathway for SO_2 extrusion to occur.[5]

A recent study of the photodimerization of benzo[*b*]thiophene-3-carboxylic acid 1,1-dioxide[6] verifies that this compound dimerizes to produce a head to head dimer with trans geometry about the cyclobutane ring. This is an interesting parallel to the dimerization of MeTND because it shows a pronounced tendency to form a dimer of the identical stereochemistry.

The best evidence for the stereochemical assignments in the MeTND system is found in a comparison of ^{13}C NMR spectra. The structures of the anti-HH and anti-HT dimers of TND, **3** and **4**, respectively, were chemically proved by Harpp and Heitner[7] and we used these as models for comparison of chemical shift data for MeTND dimers. In Table I are listed the ^{13}C NMR chemical shifts assigned to the individual carbon nuclei. The ^{13}C NMR spectrum of TND (**1**) showed seven signals of which one corresponded to a two-carbon peak. The

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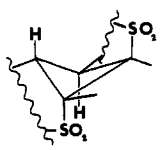
Table I. Carbon-13 Shieldings of Thianaphthene 1,1-Dioxides and Their Photodimers[a,b]

compd	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	Me
TND	130.9	132.7	130.9	125.8	133.8	130.7	120.8	136.2	
2-MeTND	139.9	126.3	131.1	124.8	133.9	129.4	121.1	135.7	8.3
TND dimer (H-H)	56.3	46.1	138.1	130.9	135.4	128.3	122.1	139.9	
2-MeTND dimer (H-H)	61.6	50.1	133.4	131.1	134.8	129.4	122.8	141.3	15.7
2-MeTND dimer (H-T)	59.5	55.3	133.4	132.5	133.0	130.4	120.7	134.8	20.3

[a] δ_c (ppm) from Me_4Si dissolved in CD_3NO_2. [b] TND dimer (H-T) too insoluble in common solvents to measure.

gated spectrum[8] revealed a 130.9-ppm signal in the form of a doublet of doublets of J = 196 and 3 Hz. Such large one-bond, carbon-hydrogen coupling is characteristic of carbons next to heteroatoms in heteroaromatic compounds,[9] thus indicating the signal to belong to C(2). The 132.7-ppm resonance was split into a broad doublet of J = 178 Hz and could be assigned to C(3) on the basis of its differing from the coupling behavior (J = ca. 168 Hz) of the four benzenoid methines. The shifts of the latter were assigned in analogy with those of indole[10] and benzofuran.[11]



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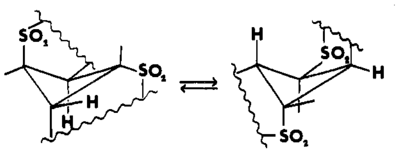

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A similar analysis of MeTND (**2**) and shift comparison with **1** led to the assignments shown in Table I. Since the 139.9-ppm signal was the only nonprotonated carbon center appearing as a quartet in a gated spectrum, it reflected the resonance of the carbon under the methyl group.

The carbon shift assignments (Table I) for the HH dimer of TND and the two photodimers of MeTND, **3**, **5**, and **6**, respectively, proved simple, since the designation of the δ values of the aromatic carbons followed the above routine[12] and the nonaromatic centers represent unique carbon sites.

The progressive deshielding of the cyclobutane methine β to the sulfonyl group from the TND HH dimer (**3**), of known configuration,[7] through the MeTND dimers **5** and **6** is the expected consequence of an increasing number of methyl groups exerting β effects[9] on this site and is consistent with a HH and HT molecular arrangement in the two dimers, respectively.

Two other centers, the sulfonylated aromatic carbon and the methyl group, show a pronounced variance of carbon shifts in the isomers **5** and **6**. Whereas the variation of the aromatic carbon shift is difficult to explain and may be indicative of a difference of the electronic interaction between the sulfonyl group and the benzene ring[13] due to a difference of spatial orientation of these moieties to each other in the two isomers, the dissimilarity of the methyl shifts must have a conformational basis. Conformational analysis of the MeTND isomers reveals the HH dimer (**5**) to prefer conformation **7** and the HT dimer (**6**) to be a rapidly equilibrating mixture of conformers **8** as demanded by its C_i symmetry. Even though the substituent effects operating on the methyl groups vary slightly in the isomers, only the gauche methyl-methyl interaction in **7** yields a strong shielding component, i.e., a γ effect, and thus causes the methyl signals of isomer **5** to be 4.6 ppm upfield of those of isomer **6**.

B. Fluorescence Studies. Solutions of MeTND in cyclohexane show a fluorescence maximum at 355 nm when excited at 313 nm. Fluorescence measurements at concentrations greater than 10^{-5} M show significant self-quenching with no indication of excimer emission at longer wavelengths. Using 2-phenylthianaphthene 1,1-dioxide (PhTND) as a luminescence standard[1,14] the fluorescence quantum yield, ϕ_f, of MeTND was found to be 0.020. The ϕ_f = 0.011 for 2-bromothianaphthene 1,1-dioxide (BrTND)[1] and ϕ_f = 0.74 for PhTND. Thus, both BrTND and MeTND show similar luminescence properties.

The effect of the quenchers cyclooctatetraene (COT), cycloheptatriene (CHT), and 1,4-diazabicyclo[2.2.2]octane (Dabco) on MeTND fluorescence was studied. In each example a Stern-Volmer plot, eq 1, of fluorescence quenching[15] against quencher concentraton gave the expected linear relation with an intercept of unity.

$$\phi_f^0/\phi_f = 1 + k_q\tau[Q] \quad (1)$$

The slopes were found to be 240 ± 7 (COT), 224 ± 6 (CHT), and 19.5 ± 0.6 M^{-1} (Dabco). Using a value of 0.99×10^{10} $M^{-1}\ s^{-1}$ for diffusion-controlled quenching in cyclohexane, calculated from the Debye equation[16]

$$k_q = \frac{8RT}{3000\eta} \quad (2)$$

and the slopes obtained from experimental Stern-Volmer plots, singlet lifetimes of 24 (COT), 23 (CHT), and 2.0 ns (Dabco) were calculated for MeTND. Flash spectroscopy using a pulsed nitrogen laser (bandwidth 8 ns)[17] showed that the lifetime of excited singlet MeTND was less than 3 ns. The apparent longer lifetimes obtained from COT and CHT quenching are attributed to resonance energy transfer quenching.[18] Verification of this was obtained by measuring the Stern-Volmer quenching slope for MeTND by CHT in methanol and ethylene glycol. The slopes were 107 (MeOH) and 196 M^{-1} ($HOCH_2CH_2OH$). Since the viscosities of methanol and ethylene glycol vary by a factor of 50 the majority of the quenching can be attributed to Forster resonance energy transfer.

C. Concentration Dependence of MeTND Photodimerization. The photodimerization of MeTND at 313 nm was studied as a function of substrate concentration in the solvents benzene, dibromomethane, and 1-bromobutane. The data in all solvents conformed to a linear relationship between $1/\phi_{DIM}$ and $1/[MeTND]_{av}$ and the results are summarized in Table II. The correlation coefficient, r, the intercept, i, and the slope of the line, s, are indicated in each table. A general trend was observed in all solvents in that the HH dimer accounted for a smaller proportion of product at highest substrate concentrations (85-90% of the total) as compared to the lowest substrate concentrations (HH accounted for 90-95%). In Figure 1 a plot of the concentration dependence data is illustrative of the various linear correlations observed for all solvents.

D. Quenching of Photodimerization. The excited triplet state of TND was shown to be the single precursor of both dimers.[19] A Stern-Volmer plot, eq 1, for the quenching of TND dimerization by COT was shown to be essentially linear to 75% total quenching.[1] Quenching of BrTND dimerization by COT[1] gave curved Stern-Volmer plots which were shown to be

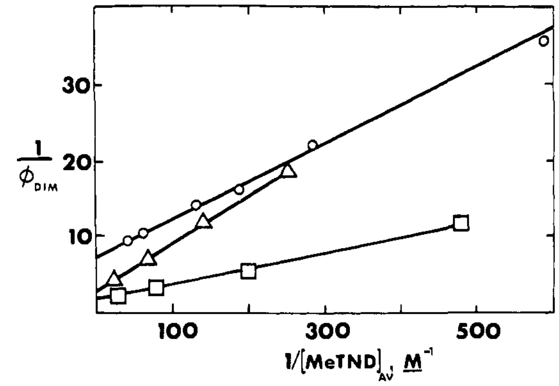

Figure 1. Concentration dependence of quantum yield of MeTND dimer formation in benzene (○), dibromomethane (△), and 1-bromobutane (□).

Table II. Concentration Dependence of Quantum Yield of MeTND Dimer Formation in Various Solvents[a]

ϕ_{DIM}	[MeTND]$_{av}$, M	
	Benzene	
0.110	0.0233	
0.0871	0.0166	
0.0699	0.007 51	
0.0615	0.005 26	
0.0455	0.003 51	
0.0282	0.001 70	
r = 0.998	i = 7.47 ± 0.35	s = 0.0483 ± 0.0012
	Dibromomethane	
0.192	0.0383	
0.139	0.0176	
0.0835	0.008 37	
0.0500	0.004 02	
r = 0.998	i = 3.59 ± 0.33	s = 0.0666 ± 0.0023
	1-Bromobutane	
0.378	0.0361	
0.273	0.0132	
0.158	0.005 13	
0.0930	0.002 06	
r = 0.995	i = 2.42 ± 0.31	s = 0.0174 ± 0.0012

[a] $\phi_{DIM} = \phi_{(MeTND)}/2$.

consistent with the single dimer arising from both excited triplet monomer and excited singlet excimer.

Investigation of COT quenching of MeTND dimerization in the solvents benzene, dibromomethane, and 1-bromobutane gave data that produced a curved Stern-Volmer relationship in every case. The data in Table III include the quenching of total product and separately the quenching behavior of the HH isomer and HT isomer for each solvent. In Figure 2 a plot of the benzene *S-V* data is a representative sample of the plots obtained for all solvents. A GC analysis of the HT/HH dimer ratio at each COT concentration allows a Stern-Volmer relationship to be plotted for each dimer. Figure 3 is a typical plot obtained in benzene. It shows that quenching of the formation of the HT isomer conforms to an approximate linear relationship with a very shallow slope. The behavior of the photodimerization of MeTND in the other solvents was similar. The lifetime of the precursor for the HT dimer was found to be on the order of 10^{-9} s (Table V) suggesting that this dimer arises from an excited singlet state, possibly a singlet excimer.

The curved Stern-Volmer plot for the HH isomer suggests that it arises from both an excited singlet and an excited triplet state, with only the triplet precursor being efficiently quenched by COT. Assuming the equation

$$\phi_{DIM,HH} = {}^{T}\phi_{HH} + {}^{S}\phi_{HH} \qquad (3)$$

to hold true, the data can be made linear by taking an asymptotic limit for the curve, calculating what quantum yield of singlet derived dimer, ${}^{S}\phi$, this implies, and then subtracting ${}^{S}\phi$ from ϕ_{DIM} to give ${}^{T}\phi$, the quantum yield of triplet-derived

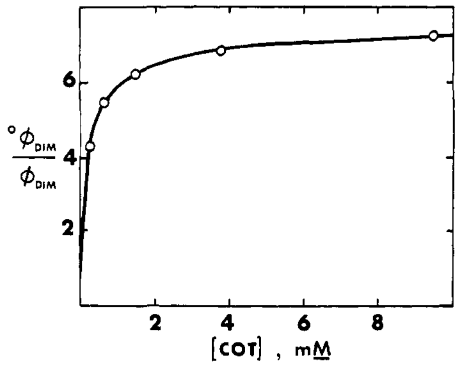

Figure 2. Relative quantum yields for the dimerization of benzene solutions of MeTND in the presence of COT.

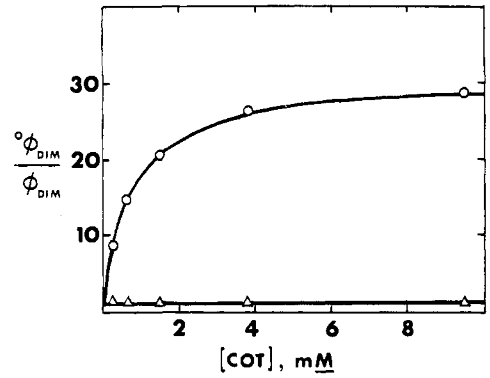

Figure 3. The Stern-Volmer behavior of benzene solutions of MeTND photodimerizing in the presence of COT: (○), HH dimer; (△), HT dimer behavior.

Table III. Relative Quantum Yields for the Dimerization of Solutions of MeTND in the Presence of COT

$\frac{\phi^0_{DIM}}{\phi_{DIM}}$	$\frac{\phi^0_{HH}}{\phi_{HH}}$	$\frac{\phi^0_{HT}}{\phi_{HT}}$	$\frac{{}^{T}\phi^0_{HH}}{{}^{T}\phi_{HH}}$	[COT], mM
		Benzene		
4.29	8.6	1.01	11.6	0.242
5.44	14.8	1.07	27.6	0.605
6.22	20.5	1.13	60.0	1.51
6.84	26.1	1.19	169	3.78
7.27	28.5	1.25	409	9.45
[MeTND]$_{av}$ = 0.0176 M				
		Dibromomethane		
3.50	4.65	1.09	5.0	0.158
5.71	10.6	1.11	12.7	0.394
7.80	20.6	1.18	31.0	0.986
9.52	38.5	1.23	107	2.46
11.7	48.1	1.50	247	6.16
[MeTND]$_{av}$ = 0.0183 M				
		1-Bromobutane		
4.04	5.56	0.993	6.50	0.140
5.47	9.43	0.957	12.9	0.350
7.22	14.2	1.11	24.4	0.875
8.56	24.9	1.02	103	2.19
8.79	28.6	1.00	233	5.47
[MeTND]$_{av}$ = 0.0163 M				

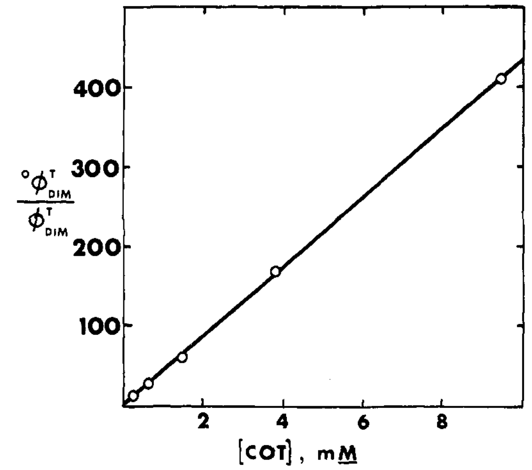

Figure 4. A linear approximation for the Stern-Volmer plot of the quantum yield of photodimerization of HH dimer in benzene with COT quencher.

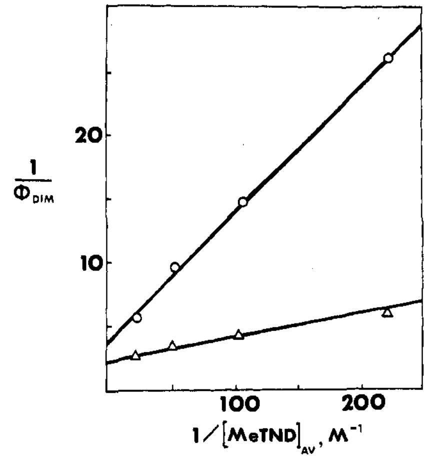

Figure 5. Concentration dependence of quantum yields of photodimerization of MeTND sensitized by benzophenone in benzene (○) and 1-bromobutane (△).

dimer. Variation of the asymptotic limit over a small range maximizes r for the plot of ${}^{T}\phi^{0}_{HH}/{}^{T}\phi_{HH}$ vs. [COT] (Figure 4). Similar treatment of the data in all three solvents leads to a lifetime for the triplet HH precursor of about 10^{-6} s. The asymptotic limits of ${}^{T}\phi_{HH}/{}^{T}\phi_{HH}$ chosen for benzene, dibromomethane, and 1-bromobutane were 30.5, 59.0, and 32, respectively. This suggests that about 3, 1.5, and 3%, respectively, of the HH isomer is singlet derived in each solvent.

E. Sensitized Dimerization of MeTND. The 360-nm irradiation of MeTND and benzophenone in solutions of benzene, dibromomethane, and 1-bromobutane was explored. The quantum yield of sensitized dimerization was studied as a function of MeTND in all solvents. In every case, only the HH dimer could be detected in the sensitized irradiations. The data conformed to a linear relationship between $1/\phi_{DIM}$ and $1/[MeTND]_{av}$ in all solvents. In Table IV are summarized the data from sensitized dimerization. In Figure 5, typical plots of the concentration dependence of sensitized dimerization of MeTND in benzene and 1-bromobutane are shown.

Discussion

A. Proposed Mechanism of the Photodimerization. The very efficient quenching of HH isomer formation by COT implies that the majority of this isomer is formed from a triplet-state precursor. The unquenchable part of HH isomer formation as well as the inefficiently quenched HT isomer appears to be derived from singlet-state precursors, possibly singlet excimers which have previously been invoked in the dimerization of BrTND.[2]

The data from the sensitized dimerizations with benzophenone suggest the presence of some energy-wasting step when the triplet state of MeTND reacts. We assume, as in prior studies, that this involves the partitioning of an intermediate diradical between reactants and products. Using this assumption, the kinetic paths detailed in Scheme I are proposed to account for the experimental observations. E refers to a singlet excimer. D refers to the assumed diradical intermediate and HT and HH refer to head to tail and head to head isomers, respectively.

As the direct irradiation of MeTND solutions produces less than 3% of HT isomer, and the HH isomer formed is almost totally quenchable, then the HH isomer can be approximated as being derived only from the triplet state of MeTND. Using the steady-state approximation and the preceding reaction scheme, the following expression for the quantum yield of dimerization in the absence of quencher can be derived:

Scheme I. Reaction Scheme for MeTND Dimerization

	rate	
$S \xrightarrow{h\nu} {}^{1}S$	Ia	(4)
${}^{1}S \xrightarrow{k_{ic}} S$	$k_{ic}[{}^{1}S]$	(5)
${}^{1}S \xrightarrow{k_f} S + h\nu$	$k_f[{}^{1}S]$	(6)
${}^{1}S + S \xrightarrow{k_e} E(HH)$	$k_e[{}^{1}S][S]$	(7)
${}^{1}S + S \xrightarrow{k_e'} E(HT)$	$k_e'[{}^{1}S][S]$	(8)
$E(HH) \xrightarrow{k_{-e}} 2S$	$k_{-e}[E(HH)]$	(9)
$E(HT) \xrightarrow{k_{-e}'} 2S$	$k_{-e}'[E(HT)]$	(10)
$E(HH) \xrightarrow{k_s} HH\ dimer$	$k_s[E(HH)]$	(11)
$E(HT) \xrightarrow{k_s'} HT\ dimer$	$k_s'[E(HT)]$	(12)
${}^{1}S \xrightarrow{k_{isc}} {}^{3}S$	$k_{isc}[{}^{1}S]$	(13)
${}^{3}S \xrightarrow{k_d} S$	$k_d[{}^{3}S]$	(14)
${}^{3}S + Q \xrightarrow{k_q} S + {}^{3}Q$	$k_q[{}^{3}S][Q]$	(15)
${}^{3}S + S \xrightarrow{k_r} D$	$k_r[{}^{3}S][S]$	(16)
$D \xrightarrow{k_{-r}} 2S$	$k_{-r}[D]$	(17)
$D \xrightarrow{k_T} HH\ dimer$	$k_T[D]$	(18)

$$\frac{1}{\phi_{DIM}} = \frac{1}{\alpha\phi_{isc}} + \frac{k_d}{\alpha\phi_{isc}k_r[S]} \qquad (19)$$

where $\alpha = k_T/(k_T + k_{-r})$ represents the fraction of diradical intermediates going on to product, and ϕ_{isc} is the usual ex-

Table IV. Concentration Dependence of Quantum Yield of Sensitized MeTND Dimer Formation in Various Solvents

ϕ_{DIM}	$[MeTND]_{av}$, M	
	Benzene	
0.150	0.0416	
0.104	0.0198	
0.0685	0.009 41	
0.0365	0.004 49	
[benzophenone] = 0.04 M		
$r = 0.999$	$i = 4.11 \pm 0.36$	$s = 0.104 \pm 0.003$
	Dibromomethane	
0.150	0.0399	
0.102	0.0191	
0.0600	0.009 22	
0.0356	0.004 46	
[benzophenone] = 0.02 M		
$r = 0.998$	$i = 4.28 \pm 0.45$	$s = 0.107 \pm 0.004$
	1-Bromobutane	
0.382	0.0434	
0.298	0.0203	
0.237	0.009 42	
0.164	0.004 55	
[benzophenone] = 0.02 M		
$r = 0.996$	$i = 2.36 \pm 0.12$	$s = 0.0171 \pm 0.0010$

pression

$$\phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{ic} + k_f} \tag{20}$$

From eq 19 and the data presented in Tables II–IV values for $\alpha\phi_{isc}$ and k_d/k_r can be calculated (Table VI).

Benzophenone is known to sensitize the triplet state of molecules such as MeTND and hence eq 19 applies, with the exception that ϕ_{isc} is unity for benzophenone, if we assume that at experimental MeTND concentrations every collision of MeTND and benzophenone molecules allows energy transfer.

To test this assumption the triplet–triplet absorption spectrum of benzophenone was observed by laser flash photolysis.[17] The strong triplet–triplet absorption of benzophenone (0.04 M in benzene or dibromomethane) was completely quenched by the addition of MeTND (0.004 M) showing that energy transfer is indeed 100% efficient. Thus the reciprocal of the intercept of a plot of eq 19 for a sensitized run is a measure of α. The values of α, and hence ϕ_{isc} for direct irradiation, as calculated from data in Table IV are given in Table VI.

In the presence of quencher the quantum yield of dimerization from the excited triplet state is given by the equation

$$\phi_{DIM} = \frac{\alpha\phi_{isc}k_r[S]}{k_d + k_r[S] + k_q[Q]} \tag{21}$$

Combining eq 19 and 21 gives the Stern–Volmer relationship

$$\frac{\phi^0_{DIM}}{\phi_{DIM}} = 1 + \frac{k_q[Q]}{k_d + k_r[S]} \tag{22}$$

The values of k_q (Table V) may then be introduced to obtain values for k_d and k_r (Table VI) since k_d/k_r ratios are known from direct irradiation experiments.

B. External Heavy Atom Effect on 2-Methylthianaphthene 1,1-Dioxide (MeTND). The kinetic data in conjunction with sensitization and quenching results clearly implicates the excited triplet state of MeTND as the primary precursor for the major product, HH dimer. The influence of 1-bromobutane (BuBr) and dibromomethane (DBM) as compared to benzene for MeTND is the most intriguing yet found. We reported that ϕ_{isc} for TND can be increased to unity by heavy-atom perturbation, both externally and internally.[1] MeTND shows contradictory behavior (Table VI) in that $\phi_{isc} = 1$ in BuBr but only 0.6 in DBM. Whereas thianaphthene 1,1-dioxide (TND) and 2-bromothianaphthene 1,1-dioxide (BrTND) showed decreased lifetimes of the excited triplet as evidenced by k_d values ($k_d = 8.8 \times 10^6$ s^{-1} for TND in ethyl bromide and 3.3×10^7 s^{-1} for BrTND in benzene),[1] no significant solvent-sensitive variation for MeTND is found in this study ($k_d \sim 8 \times 10^4$ s^{-1}). The longer lifetime of triplet MeTND is reflected in its greater sensitivity to quenching than either TND or BrTND.

C. The Triplet State. Data from the benzophenone-sensitized dimerization of MeTND in all solvents allows direct evaluation of α as well as the analysis of k_d/k_r ratios because ϕ_{isc} is 1 for benzophenone and the "excimer" mechanism is absent. Thus ϕ_{DIM} now equals ϕ_T where all products are triplet derived.

The data in Table VI illustrate the values determined for α, the fraction of diradicals that proceed on to form product. In comparison, $\alpha = 1$ for the photodimerization of TND[19] and $\alpha = 0.14$ for BrTND.[1] There was no evidence in previous studies to indicate that the diradical would show a large variation in its ability to disproportionate or to form product. The

Table V. Stern–Volmer Derived Values for the Quenching of Photodimerization of MeTND by COT in Different Solvents[a]

solvent	slope, M^{-1} HH	slope, M^{-1} HT	τ, s HH	τ, s HT	r HH	r HT
benzene[b]	$(4.33 \pm 0.07) \times 10^4$	24.8 ± 6	3.6×10^{-6}	2.1×10^{-9}	0.999	0.899
dibromomethane[c]	$(4.07 \pm 0.11) \times 10^4$	71.6 ± 8	5.6×10^{-6}	9.8×10^{-9}	0.998	0.977
1-bromobutane[d,e]	$(4.35 \pm 0.21) \times 10^4$		4.1×10^{-6}		0.996	

[a] The HH data are linearized by approximation (see text). [b] $k_q = 1.2 \times 10^{10}$ M^{-1} s^{-1}. [c] $k_q = 7.3 \times 10^9$ M^{-1} s^{-1}. [d] $k_q = 1.1 \times 10^{10}$ M^{-1} s^{-1}. [e] HT data were unreliable because of small yield of HT dimer.

Table VI. Kinetic Parameters for the Dimerization of MeTND in Various Solvents

	benzene	1-bromobutane	dibromomethane
$\alpha\phi_{isc}$	0.134 ± 0.006	0.413 ± 0.062	0.279 ± 0.028
ϕ_{isc}	0.55 ± 0.07	1	0.603 ± 0.035
α	0.243 ± 0.019	0.413 ± 0.062	0.463 ± 0.047
k_d/k_r, M	$(6.47 \pm 0.46) \times 10^{-3}$	$(7.20 \pm 1.64) \times 10^{-3}$	$(1.86 \pm 0.26) \times 10^{-2}$
k_r, M^{-1} s^{-1}	$(1.2 \pm 0.1) \times 10^7$	$(1.1 \pm 0.1) \times 10^7$	$(5.2 \pm 0.5) \times 10^6$
k_d, s^{-1}	$(7.8 \pm 1.2) \times 10^4$	$(7.6 \pm 3.8) \times 10^4$	$(8.4 \pm 0.18) \times 10^4$
τ, s[a]	1.3×10^{-5}	1.3×10^{-5}	1.2×10^{-5}

[a] Quasi-unimolecular lifetime, $1/k_d$.

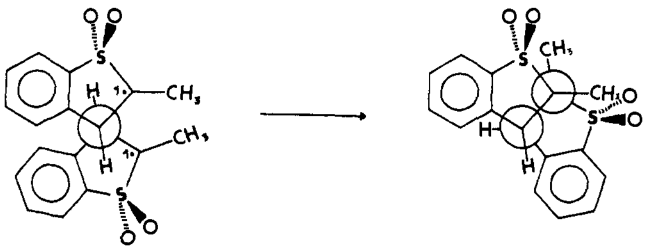

Figure 6. Conformational perspective for the 1,4 diradical.

increase in the value of α for MeTND in heavy-atom solvents as compared to benzene was an unexpected result. The variation of α with solvent does not correlate with bulk solvent properties because data derived from acetonitrile[20] rule out a specific polarity effect. We believe that the higher values for α in heavy atom containing solvents are evidence for a heavy-atom effect on the partitioning of the 1,4-diradical intermediate. One possible explanation for this is that heavy-atom solvents enhance intersystem crossing of the intermediate triplet 1,4 diradical to form singlet ground state products, in conformations that are favorable to ring closure. Any reaction from conformations not favorable to ring closure must lead to monomer. Conformations favorable to ring closure can either rotate to unfavorable conformations or ring close via a singlet diradical to form product. A heavy-atom effect in these favorable conformations would increase the rate of intersystem crossing with respect to the rate of rotation to unfavorable conformations. This would lead to an increase in α. Although this is a rare occurrence, it is not unprecedented. Morrison et al.[21] proposed that a heavy atom effect occurred on the closing of the 1,4-triplet diradical that intervened during the photodimerization of coumarin in CCl_4. Pappas and Zehr[22] studied the photocyclization of methyl *o*-benzyloxyphenylglyoxylate to isomeric benzofuran derivatives and found that the cis/trans product ratio was sensitive to heavy-atom perturbation. They proposed that enhanced intersystem crossing induced by heavy-atom perturbation in the triplet biradical caused a change in the cis/trans product ratio.

The fact that the values for α vary in the order TND > MeTND > BrTND suggests that a steric effect is operating in addition to a spin-orbital perturbation. Since $\alpha = 1$ for TND there exists no chance for a measurable heavy-atom perturbation to occur in the closing of this 1,4 diradical. It is likewise probable that BrTND has a maximized intersystem crossing efficiency in its 1,4 diradical because of the internal heavy atom effect. Thus, α in BrTND is almost totally a function of steric interference to ring closure. The methyl substituent in MeTND would cause some impediment to ring closure, but the magnitude of steric inhibition to ring closure should be less than that of bromine because of the smaller van der Waals size of CH_3 compared to Br. Because MeTND shows a unique heavy-atom effect on the triplet 1,4 diradical we theorize that conformational requirements in this diradical may be such that collision with a heavy-atom perturber is effective.

The illustration in Figure 6 is a rendering of the conformational requirements of the 1,4 diradical for the MeTND system. The steric inhibition to ring closure is seen to arise because of the increased number of eclipsing interactions in the transition state leading to product. This increased energy barrier to ring closure may prolong the lifetime of the diradical so that additional collisions with heavy-atom perturbers become effective in enhancing intersystem crossing.[23]

D. The Excimer Mechanism. The proposed mechanism involves an unquenchable excited state whose participation is required by the discovery of nonlinear Stern-Volmer kinetics. We have found that added oxygen quenches the formation of HH dimer but does not quench HT dimer formation. This leads us to believe that the HT dimer arises solely from an excimer because no HT dimer is formed in the triplet-sensitized runs.

The excited-state lifetime of about 10^{-9} s for the precursor to the HT dimer is derived based upon the assumptions that diffusion-controlled quenching by COT of the proposed excimer occurs and that k_q for COT conforms to the Debye equation. The value of $k_q\tau$ of about 25 M^{-1} for COT quenching of the assumed HT excimer differs by a factor of 10 from the 240 M^{-1} value derived from our fluorescence quenching experiments. The molar concentrations of COT that are effective in quenching the competing triplet processes for HH dimer formation are more dilute by a factor of 10^2 than were required to quench the fluorescence emission of MeTND. As the Dabco quenching and laser data indicate, the $k_q\tau$ value for fluorescence quenching appears to be attributable to physical quenching and Forster transfer by COT whereas the assumed excimer quenching of HT dimer in the photochemical runs does not significantly involve these processes because the COT concentration is too dilute.

The preference for an excimer pathway in the formation of HT dimer rather than through a triplet-state stepwise addition is not readily explained. We note that the dipole-dipole interaction for the HT excited state appears favorable for excimer formation. Also, the conformational fit between bulky groups in the excited state seems best accommodated by an oriented collision rather than a stepwise process.

We suspect that the propensity for HH dimer to form by the triplet 1,4-diradical pathway is due to the steric bulk of the substituents as the MeTND molecules collide and to the greater stability of the radical sites that are formed in the 1,4 diradical. These sites are not only tertiary radicaloid centers, but they are also adjacent to the sulfone function so that the stability of the radicaloid centers is likely enhanced. The production of tertiary radicaloid centers may also explain the formation of only HH photodimers from benzo[*b*]thiophene-3-carboxylic acid 1,1-dioxide[6] and benzo[*b*]thiophene-3-methyl 1-oxide.[24]

What is clear is the fact that subtle energy factors that are essentially unpredictable are causing product distribution to be directed preponderantly toward the HH dimer.

The fact that ϕ_{isc} is less than unity in dibromomethane for the formation of HH dimer may be a result of competitive excimer processes. Under such circumstances ϕ_{isc} is defined as

$$\phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{ic} + k_f + k_e[S]} \qquad (23)$$

The term $k_e[S]$ in the denominator reflects the competitive process of excimer formation. There is evidence that suggests that some solvents may stabilize excimers.[25] It may be that dibromomethane enhances k_e, which could cause a reduction in the corresponding value of ϕ_{isc}. We have carefully investigated the absorption characteristics of dibromomethane to see if there was physical absorption of the light. Our data show that this is not a significant problem in this system. If some trace photochemical impurity is building up in the DBM solvent, this could explain the lower intersystem crossing quantum yield since the impurity might act as a quencher. We have not been able to detect such an occurrence.

Summary

We have shown that the photodimerization of MeTND occurs to produce predominantly anti head to head photodimer derived from a triplet-state process. The photodimerization is susceptible to heavy-atom perturbations as we had anticipated. An unusual heavy-atom effect on an intermediate 1,4 biradical is proposed to explain the enhanced quantum yield of triplet-sensitized dimerization of MeTND. The formation of the major product is related to the assumed stability of the biradicaloid system. The minor HT product is derived from an excited state that is concluded to be an excimer. The data reported suggest that future studies on thianaphthene 1,1-dioxides will continue to furnish intriguing results to test photochemical theory.

Experimental Section

Materials. 2-Methylthianaphthene 1,1-dioxide (MeTND) was prepared as described in the literature[26] and purified by recrystallization from absolute ethanol. 2-Phenylthianaphthene 1,1-dioxide was prepared as described in the literature[27] and recrystallized twice from 95% ethanol with activated charcoal decolorization.

Benzophenone (Eastman) was recrystallized from absolute ethanol. Cyclooctatetraene (Chemical Samples Co.) and cycloheptatriene (Aldrich) were distilled under reduced pressure and passed through a short alumina column before use. Benzhydrol (Aldrich), diazabicyclo[2.2.2]octane (Dabco) (Aldrich), and 1,3-cyclohexadiene (Aldrich) were used without further purification.

Benzene and cyclohexane (Eastman Spectrograde) were freshly distilled from CaH_2 before use. Dibromomethane and 1-bromobutane (Aldrich) were freshly distilled before use.

Instrumentation. GLC analyses were performed using a 5 ft × 1/8 in. column of 1.5% OV-101 on Chromosorb G on a Varian 2400 with a Sargent SR recorder equipped with a ball-disk integrator. Ultraviolet measurements were made on a Cary 118 recording spectrophotometer. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrometer. A Varian T-60 NMR spectrometer operating at 60 MHz was used to obtain ^1H NMR spectra at 34 °C. A Finnegan 1015C System/150 computer-controlled ensemble with gas chromatograph was used to generate mass spectra at 70 eV. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Irradiations. General. Preparative irradiations were carried out in a 500-mL capacity photolysis vessel equipped with a nitrogen inlet, reflux condenser, and Pyrex immersion well. The solutions to be irradiated were subjected to a 45-min purge with nitrogen. Irradiations were performed with a Hanovia 450-W mercury-arc lamp. The apparatus was housed in a box designed to keep out stray light.

Direct irradiations for concentration and quenching studies were performed with a Hanovia 450-W mercury-arc lamp and Corex sleeve placed in a quartz immersion well through which cold K_2CrO_4-K_2CO_3 solution was circulated to isolate the light output around 313 nm.[28] This combination was centered in a Rayonet MGR-500 merry-go-round apparatus and housed in a box designed to keep out stray light.

Sensitization studies were carried out with the lamp placed in a Pyrex immersion well through which cold 0.7 M $Cu(NO_3)_2$ solution was circulated. Corning CS-7-60 filters were placed around the immersion well[29] so that a band of light between 360 and 390 nm was transmitted.

Pyrex tubes (15 × 100 mm) equipped with a Teflon tapped vacuum stopcock (Pierce) were charged with 10 mL of the solution to be irradiated. These were then degassed using several freeze-thaw cycles by means of a previously described apparatus.[30] All nonpreparative runs were carried out to low (<20%) conversions of reactants. After irradiation was terminated the amount of unreacted MeTND was determined by quantitative spectrophotometric analysis at 313 nm using previously determined extinction coefficients. Relative dimer yields were obtained from a GLC analysis of the photolysis mixture at 200-290 °C on a 5 ft × 1/8 in. column of 1.5% OV-101 on Chromosorb G.

Actinometry. The actinometers used were either the benzophenone-sensitized dimerization of 1,3-cyclohexadiene,[31] analysis performed as previously described,[1] or the benzophenone-benzhydrol actinometer according to the literature method.[32]

Beer-Lambert Studies of MeTND. Spectrophotometric analyses were made at 313 nm of the absorbance (A) of MeTND solutions of varying concentrations in a variety of solvents. Least-squares analyses of the absorbance data indicate the following (solvent, molar extinction coefficient, A_∞): 1-bromobutane, $(2.18 \pm 0.01) \times 10^3$, 0.002 ± 0.005; dibromomethane, $(2.24 \pm 0.01) \times 10^3$, 0.002 ± 0.003; benzene, $(2.35 \pm 0.01) \times 10^3$, 0.002 ± 0.003.

Preparative Dimerization of MeTND. Irradiation of 500 mL of an 0.089 M solution of MeTND in benzene was carried out until ultraviolet analysis of the reaction mixture indicated that <5% of unreacted starting material remained (total irradiation time 4.5 h). The photolysate mixture was filtered to afford 4.2 g of crystalline residue. Removal of solvent from the filtrate afforded 3.8 g of additional photoproduct. Recrystallization of the photolysis mixture residue from nitromethane afforded 3.7 g of **5**. An additional 0.6 g (total recovery 54%) of pure **5** was obtained as a first crop from the filtrate residue. Dimer **5** was isolated as colorless prisms: mp 318.5-320 °C; NMR (Me_2SO-d_6) δ 1.12 (6 H, s), 4.53 (2 H, s), and 7.83 ppm (8 H, m); IR (KBr) 3070, 2965, 2928, 1472, 1452, 1303, 1193, 1152, 760, 550, 522, and 500 cm^{-1}; mass spectrum *m/e* (rel intensity) 360 (4), 253 (17), 217 (20), 215 (11), 181 (19), 180 (30), and 137 (100). Anal. Calcd for $C_{18}H_{16}O_4S_2$: C, 59.98; H, 4.47; S, 17.79. Found: C, 59.94; H, 4.31; S, 17.97. After early fractions containing >94% of **5** were obtained, recrystallization of the filtrate residue from nitromethane afforded a total recovery of 1.3 g (16%) of pure dimer 6 as colorless prisms: mp 257-259 °C; NMR (Me_2SO-d_6) δ 2.02 (6 H, s), 4.39 (2 H, s), and 7.48 ppm (8 H, m); IR (KBr) 3070, 2980, 2917, 1470, 1450, 1318, 1190, 1149, 1112, 747, 618, and 550 cm^{-1}; mass spectrum *m/e* (rel intensity) 360 (0.25), 296 (26), 181 (13), 180 (22), and 137 (100). Anal. Calcd for $C_{18}H_{16}O_4S_2$: C, 59.98; H, 4.47; S, 17.79. Found: C, 60.18; H, 4.53; S, 17.86.

Quantum Efficiency of MeTND Fluorescence. Fluorescence emission in cyclohexane was measured for a 26 μM solution of PhTND ($\phi_f = 0.74$)[14] and a 59 μM solution of MeTND. Spectra were corrected for instrument response[33] and relative incident light absorption. Comparison of the relative areas under the corrected emission curves indicated $\phi_f = 0.020$ for MeTND.

Fluorescence Quenching of MeTND. Fluorescence emission of cyclohexane solutions of MeTND was measured in the presence of varying amounts of the quenchers cyclooctatetraene (COT), cycloheptatriene (CHT), and 1,4-diazabicyclo[2.2.2]octane (Dabco). Spectra were corrected for instrument response and the area under the corrected curves taken as a direct measure of fluorescence emission.

Acknowledgment. We thank the Robert A. Welch Foundation for support of this study and the National Science Foundation for matching funds to purchase the Cary 118C spectrophotometer. The laser flash spectroscopy data were obtained on equipment funded by the Biotechnology Branch of the Division of Research Resources (NIH RR-0086). One of us (B.P.) thanks the Southern Regional Education Board for a travel grant.

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Investigation of the Zeolite Catalyzed Alkylation of Toluene Using Carbon-13 Nuclear Magnetic Resonance

Michael D. Sefcik

Contribution from Monsanto Company, St. Louis, Missouri 63166.

Received April 10, 1978

Abstract: The role of alkali metal cation exchange in the catalytic synthesis of styrene monomer from methanol and toluene over X-type zeolites has been investigated by ^{13}C NMR. Catalytic materials were examined with respect to both their physical and chemical interactions with various substrates. The replacement of sodium cations by cesium alters the distribution of methanol thermolysis products and enhances the yield of styrene and ethylbenzene via a restricted transition-state selectivity. As identified from the ^{13}C NMR spectra, the predominant reaction of the NaX is the dehydration of methanol to dimethyl ether followed by aromatic substitution on the toluene to yield undesirable ring alkylation byproducts. Cracking competes favorably with dehydration on the CsX, thereby reducing the yield of dimethyl ether. The restricted mobility of aromatic adsorbates on the CsX, as indicated by the NMR line shape, suggests that ring alkylation is hindered by the presence of cesium cations in the adsorption cavity which sterically restrict the formation of transition states which lead to these products.

Introduction

The zeolite catalyzed alkylation of toluene by methanol or formaldehyde to form styrene and ethylbenzene has been studied in several laboratories.[1-7] Both Japanese[1] and Russian[2] workers have reported that X-type zeolites are more active than Y-type and that selectivity of the catalyst for alkylation is dependent on the zeolite cation. Freeman and Unland[4] reported that selectivity in the toluene + methanol reaction to styrene and ethylbenzene increased with alkali-metal cation size and that the borate-promoted, cesium-exchanged X zeolite was the most favorable of those studied.[5]

On the basis of laser Raman[4] and diffuse reflectance[6] measurements, Unland and Freeman and Unland concluded that the reaction selectivity was influenced by the electrostatic fields experienced by the aromatic nucleus. These interactions, primarily through perturbation of the π electrons, increased with loading level in a particular zeolite or with increasing cation size. Infrared studies[7] of the decomposition of methanol and formaldehyde on the Na, K, Rb, and Cs forms of X-type zeolites have shown that methoxide, carbonate, and formate species are formed in varying amounts and types on the different samples. The increased selectivity of these catalysts afforded by incorporation of borate into the zeolite is not understood. The failure of the borate to affect the adsorption of benzene has lead to the suggestion[4] that the borate may act on the methanol decomposition rather than the toluene activation in the toluene–methanol reaction.

The application of rare-spin nuclear magnetic resonance to the investigation of surface interactions of molecules has proven to be useful in elucidating the subtle dynamics of adsorbate-adsorbent interactions.[8-13] Analysis of the ^{13}C NMR line shapes provides information about the rotational freedom of molecules under the influence of surface interactions, while the wide chemical-shift range facilitates the identification of chemical intermediates and products formed during catalytic reactions. We have applied these techniques to the characterization of the dynamic interactions between various substrate molecules and a series of modified X zeolite materials which have been developed as catalysts for the synthesis of styrene monomer. With the results of this investigation we hope to explain the various catalytic properties of these modified molecular sieves, particularly the product distribution and relative yields.

Experimental Section

A. The Nuclear Magnetic Resonance Experiment. The carbon-13 pulsed Fourier transform nuclear magnetic resonance spectra of isotopically enriched compounds adsorbed on the molecular sieve samples were obtained on a modified Bruker spectrometer. The spectrometer operates at 22.6 MHz and is equipped with a time-shared external ^{19}F field-frequency stabilization system, a quadrature ^{13}C detector,[14] and a ^{13}C–^{1}H probe capable of accepting high power, long bursts of radio-frequency power at both the ^{13}C and ^{1}H Larmor frequencies without breakdown or cross talk. The spectrometer is free from base line artifacts.[15,16]

Three types of NMR experiments were performed in this study: scalar-decoupled Fourier transform (FT),[17] dipolar-decoupled Fourier transform,[18] and cross-polarization.[19] Scalar-decoupled FT NMR involves the application of a weak radio-frequency field ($\gamma H_2/2\pi$ = 3 kHz) to eliminate spin–spin coupling between the directly bonded carbons and protons. Scalar-decoupled FT NMR detects only those molecules which are rotating sufficiently fast ($>10^5$ Hz) to average the ^{1}H–^{13}C dipolar interactions to nearly zero. Dipolar-decoupled FT NMR, the second type of experiment performed in this study, requires

0002-7863/79/1501-2164$01.00/0