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Singlet Oxygen Production from Excited Singlet and Triplet States of Anthracene Derivatives in Acetonitrile

A. F. Olea[†] and F. Wilkinson^{*,‡}

Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Casilla 233, Santiago, Chile, and Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, U.K.

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The efficiencies of singlet oxygen production from the singlet and triplet states of a series of anthracene derivatives in acetonitrile are reported. For anthracene and for all of the anthracene meso derivatives studied, the efficiency of singlet oxygen production from triplet states quenched by oxygen, f_{Δ}^T , is found to be unity, with the exception of 9-methoxyanthracene, where the value drops to one-third. The efficiencies of singlet oxygen production from excited singlet states quenched by oxygen, f_{Δ}^S , in acetonitrile as solvent, are lower than in cyclohexane and vary from zero to one-half. In addition, the fractions of singlet states quenched by oxygen which yield triplet states, with or without singlet oxygen production, $f_T^{O_2}$, for anthracene and 9-methyl-, 9-phenyl-, and 9,10-dichloroanthracene were measured and the values were found to vary from 0.57 to 0.83. Kinetic considerations allow the determination of estimates of this fraction for the other derivatives. For anthracene derivatives, when dissolved in cyclohexane, all the values obtained for $f_T^{O_2}$ are unity whereas when dissolved in acetonitrile, $f_T^{O_2}$ values were found to be lower than unity except in the case of 9,10-dicyanoanthracene, which is unity in both solvents.

Introduction

Over the past decade, there has been an increased interest in the study of interactions between molecular oxygen and the excited states of organic molecules.^{1–10} It is well-known that singlet oxygen is produced with varying efficiency as a consequence of quenching of both excited singlet and triplet states as depicted in Scheme 1. However, the yield of singlet oxygen and the quenching rate constants vary considerably depending on the structure of the organic molecule, on the nature of the excited state being quenched, and on the solvent.^{1–16}

The lowest excited singlet states of oxygen are the $O_2(^1\Delta_g)$ and the $O_2(^1\Sigma_g^+)$ states which lie 94 and 157 kJ mol⁻¹, respectively, above the $O_2(^3\Sigma_g^-)$ ground state. For triplet sensitizers with energies in excess of 157 kJ mol⁻¹, both the $O_2(^1\Sigma_g^+)$ and the $O_2(^1\Delta_g)$ states may be formed as a result of quenching by oxygen. In fact recently, Bodesheim et al.¹⁷ have measured the relative efficiencies of production of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ for a variety of sensitizers in carbon tetrachloride as solvent where exceptionally emission from $O_2(^1\Sigma_g^+)$ can be detected. The proportion of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ produced depends on the energy of the triplet state being quenched; for example, in the case of the triplet state of 9-bromoanthracene in carbon tetrachloride, the relative yields of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ produced are 42% and 48%, respectively, with the final 10% of quenching collisions yielding the ground state of the oxygen molecule directly.¹⁷ Even in carbon tetrachloride, the lifetime of $O_2(^1\Sigma_g^+)$ is very short (130 ns), and by detecting the emission from both $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$, Schmidt and Bodesheim¹⁸ were able to show that in carbon tetrachloride $O_2(^1\Sigma_g^+)$ decays to give $O_2(^1\Delta_g)$ with unit efficiency. In acetonitrile, the solvent used in this work, all indications are

that any $O_2(^1\Sigma_g^+)$ formed will decay very rapidly to give $O_2(^1\Delta_g)$. In Scheme 1, therefore, we have used 1O_2 to represent $O_2(^1\Delta_g)$ only, and it is this species which is detected in the experiments which are reported here. Any $O_2(^1\Sigma_g^+)$ formed which does not decay to give $O_2(^1\Delta_g)$ would be incorporated in Scheme 1 into step 9, with those which do being included in step 8, which represents the production of $O_2(^1\Delta_g)$ from oxygen quenching of the triplet state by any route.

There have been many symbols used for the fractions of singlet and triplet states quenched by oxygen which yield singlet oxygen $O_2(^1\Delta_g)$, defined in Scheme 1¹⁰ as f_{Δ}^S and f_{Δ}^T , respectively. It is hoped that those working in this area using the various other symbols, for example α and ϵ ,¹⁹ δ and S_{Δ} (see for example ref 20), α_S and α_T ,²¹ and even (a.d) and b²² will start using f_{Δ}^S and f_{Δ}^T , respectively, in the future.

We have recently shown that for a series of anthracene derivatives in cyclohexane the efficiency of singlet oxygen production from the triplet state, f_{Δ}^T , is unity within experimental error in every case.¹⁵ This contrasts with the results we obtained for substituted naphthalenes,^{11,16} where f_{Δ}^T values are sensitive to the oxidation potential of the naphthalene derivative. The difference in behavior between substituted anthracenes and naphthalenes was ascribed to the fact that the energy of the charge transfer state of the encounter complex between oxygen and the hydrocarbon produced following electron transfer from the hydrocarbon to O_2 is higher than the lowest excited triplet state in the case of all the anthracene derivatives in cyclohexane as solvent¹⁵ but is lower in the case of many naphthalene derivatives.¹⁶ Although all anthracene derivatives in cyclohexane have $f_{\Delta}^T = 1$, we have shown that the efficiency of singlet oxygen production from the first excited singlet state f_{Δ}^S varies from close to zero, in the case of anthracene, to unity for 9,10-dicyanoanthracene. In addition, we have demonstrated that the magnitude of f_{Δ}^S is determined by competition between the two processes which form different triplet encounter complexes, namely $^3(T_2-^3\Sigma)$ and $^3(T_1-^1\Delta)$, from the initially formed complex,

[†] Universidad de Chile.

[‡] Loughborough University of Technology.

* Author to whom correspondence should be addressed.

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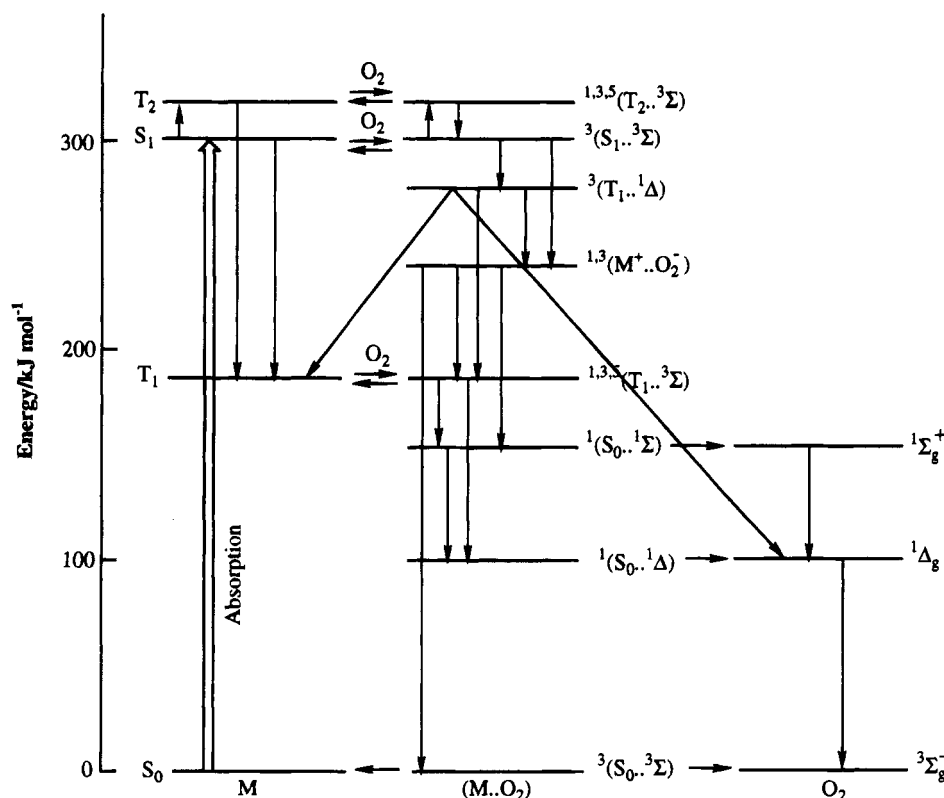
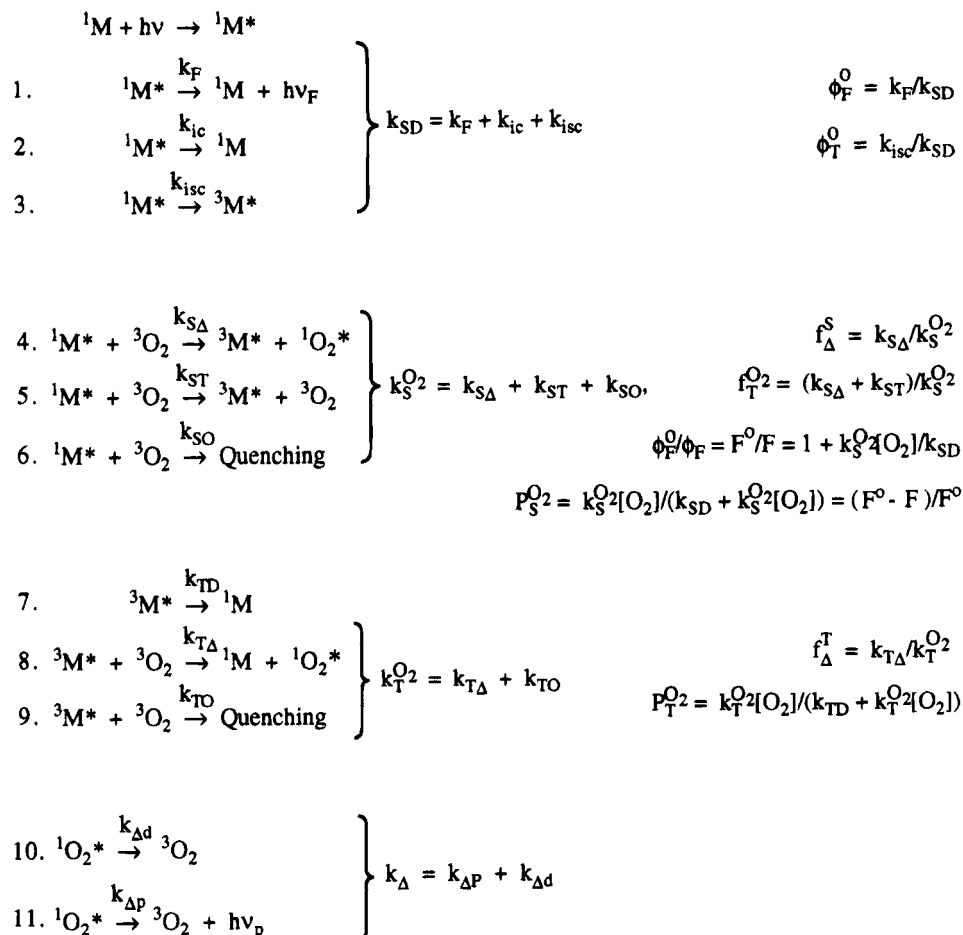


Figure 1. Energy level diagram for a typical meso-substituted anthracene, M, molecular oxygen, O₂, and their contact complex (M·O₂).

SCHEME 1



${}^3(S_1 \rightarrow {}^3\Sigma)$, as illustrated in Figure 1, which shows the various possibilities, with the value of f_{Δ}^S depending on the fractional

production and dissociation of this latter complex, ${}^3(T_1 \rightarrow {}^1\Delta)$, to form singlet oxygen, a process which yields at the same time

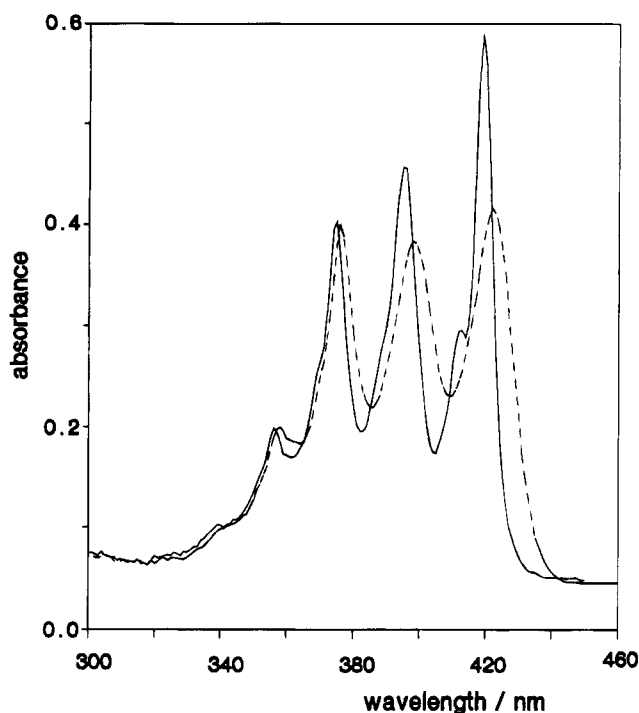


Figure 2. Absorption spectra of 9,10-dicyanoanthracene in cyclohexane (—) and acetonitrile (---).

the molecular triplet state of the anthracene derivative.¹⁵ The two competing processes are summarized as reactions 4 and 5 in Scheme 1.

In this paper, we present results obtained for the same series of substituted anthracenes in the polar solvent acetonitrile. Solvent dielectric effects on oxygen quenching have been attributed to a mixing of the initial and final states via coupling to charge transfer states.²³ Thus, the main aim of this study is to assess, by performing studies using a polar solvent, the influence of more facile charge transfer on the mechanism of singlet oxygen production from both singlet and triplet states.

Experimental Section

Materials. Anthracene and 9,10-diphenylanthracene (Aldrich) were used as received; 9-phenylanthracene and acridine (Aldrich) and 9,10-dichloroanthracene and 9-methylanthracene (Eastman Kodak) were recrystallized from ethanol; 9,10-dibromoanthracene and 9-cyanoanthracene (Aldrich) and 9,10-dicyanoanthracene (Kodak) were recrystallized from benzene; 9-methoxyanthracene was a gift from the late E. J. Brown and was recrystallized from ethanol. Acetonitrile (HPLC grade) was dried by refluxing over powdered lithium aluminum hydride.

Apparatus. Absorption spectra were recorded with a Phillips PU8800 spectrophotometer, and singlet excited state energies were determined from the position of the 0,0 bands, see Figure 2. Fluorescence measurements were carried out using a Perkin Elmer LS4 spectrophotofluorimeter. Transient absorption spectra were obtained using a nanosecond laser flash photolysis system with right angle geometry as described elsewhere.²⁴ Excitation was with 8 ns pulses at 355 nm obtained from a frequency-tripled Lumonics HY200 Q-switched neodymium-YAG laser. Triplet quantum yields of anthracene, 9-methylanthracene, and 9-phenylanthracene were determined using the method of Wilkinson et al.,²⁵ where the fluorescence quenching and the enhanced triplet-triplet absorptions of these hydrocarbons caused by the addition of various amounts of xenon were monitored. Experimental details are given elsewhere.^{15,25}

From the ratio of the triplet absorbances at time $t = 0$ in the presence and absence of oxygen, values of $f_T^{O_2}$ were measured using the following equation, which can easily be derived from the reaction mechanism given in Scheme 1, see also ref 26:

$$f_T^{O_2} = \frac{\phi_T^O \left(\frac{A_T^{O_2}}{A_T^O} - \frac{F}{F^O} \right)}{\left(1 - \frac{F}{F^O} \right)} \quad (1)$$

where $A_T^{O_2}$ and A_T^O are the triplet absorbances in the presence and absence of air, which are directly proportional to $\phi_T^{O_2}$ and ϕ_T^O , respectively.

Emission from singlet oxygen following laser excitation was detected by time-resolved spectroscopy as described previously.¹¹ For ϕ_Δ measurements, air was removed from the solutions by three freeze-pump-thaw cycles and then pure oxygen at pressures up to 3 atm was added to the solutions at room temperature and these were then allowed to equilibrate. The intensity of singlet oxygen phosphorescence P_O at time $t = 0$ was obtained by fitting the singlet oxygen phosphorescence decay curve to a single exponential function. A set of P_O values were obtained for different laser energies, and plots of P_O versus relative laser intensity were linear up to pulse energies of 0.5 mJ/pulse. ϕ_Δ values were determined relative to the slopes obtained for acridine, which was used as a standard, taking its value of ϕ_Δ as 0.82 in acetonitrile.⁸ Since all ϕ_Δ measurements were determined against a standard in the same solvent, no corrections for changes in refractive index or in $k_{\Delta P}$ with solvent were necessary.

According to the kinetic mechanism depicted in Scheme 1, the singlet oxygen quantum yield, ϕ_Δ , the efficiency of singlet oxygen production from the singlet and triplet states, f_Δ^S and f_Δ^T , respectively, the fraction of singlet states quenched by oxygen which yield triplet states, $f_T^{O_2}$, the quantum yield of triplet state production in the absence of oxygen, ϕ_T^O , and the fluorescence intensities in the presence and absence of oxygen, F and F^O , are related through the following equation:¹⁰

$$\phi_\Delta \frac{F^O}{F} = (f_\Delta^S + f_T^{O_2} f_\Delta^T) \left[\frac{F^O}{F} - 1 \right] + \phi_T^O f_\Delta^T \quad (2)$$

when $P_T^{O_2} = 1$, i.e. when $k_T^{O_2}[O_2] \gg k_{TD}$. ϕ_Δ measurements were combined with fluorescence intensity measurements at different oxygen concentrations to evaluate f_Δ^T and $(f_\Delta^S + f_T^{O_2} f_\Delta^T)$, from plots based on eq 2. For each anthracene derivative, six different concentrations of oxygen were used, and for each of these solutions, the relative steady state fluorescence intensity was measured.

Results and Discussion

The photophysical properties of anthracene derivatives in acetonitrile given in Table 1 are very similar to those observed in cyclohexane.¹⁵ The increase in solvent polarity hardly affects the absorption spectra of these compounds, except for the cyano-substituted anthracenes, where a small red shift and a loss of vibrational structure is observed (see Figure 2). Thus, the excited singlet state energies obtained from the 0-0 absorption bands are almost the same in both solvents, the largest difference observed being 2 kJ mol⁻¹ for 9,10-dicyanoanthracene.

Typical plots of the data obtained in acetonitrile in accordance with eq 2 are shown in Figures 3 and 4, and the slopes and intercepts obtained from these plots are collected in Table 2, where our data obtained in cyclohexane¹⁵ are also included for

TABLE 1: Photophysical Parameters of Anthracene Derivatives in Acetonitrile

compd	E_S^a (kJ mol ⁻¹)	E_T (kJ mol ⁻¹)	ΔG_{ct}^b (kJ mol ⁻¹)	ϕ_T^c	τ^d (ns)	$k_S^{O_2} e/10^{10}$ (dm ³ mol ⁻¹ s ⁻¹)
anthracene	318	178	+11	0.70 ± 0.01	4.57	5.0
9-cyano	298	169	+104	0.02 ^f	16.23	0.94
9-methyl	310	173	-5	0.55 ± 0.01	6.97	5.1
9-methoxy	309	~172	~0	0.12 ^g	3.22	4.1
9-phenyl	312	176	+8	0.39 ± 0.01	6.76	3.9
9,10-dibromo	298	168	+47	0.79 ± 0.14 ^h	1.8 ^j	2.9
9,10-dichloro	299	169		0.26 ± 0.05 ^e	8.77	3.4
9,10-dicyano	284	175	+112	0.003 ⁱ	15.15	0.44
9,10-diphenyl	305	171	+22	0.02 ^j	8.39	3.5

^a Determined from the position of the 0-0 band in the absorption spectra. ^b Calculated from eq 3. ^c Determined by enhancement of intersystem crossing by xenon. ^d Measured by photon counting. ^e Calculated from Stern-Volmer constants for oxygen quenching.³³ ^f From ref 35. ^g Determined by comparison of triplet-triplet absorption with 9-methoxyanthracene in cyclohexane. ^h Determined by comparison of triplet-triplet absorption with anthracene in acetonitrile. ⁱ From ref 36. ^j From ref 37.

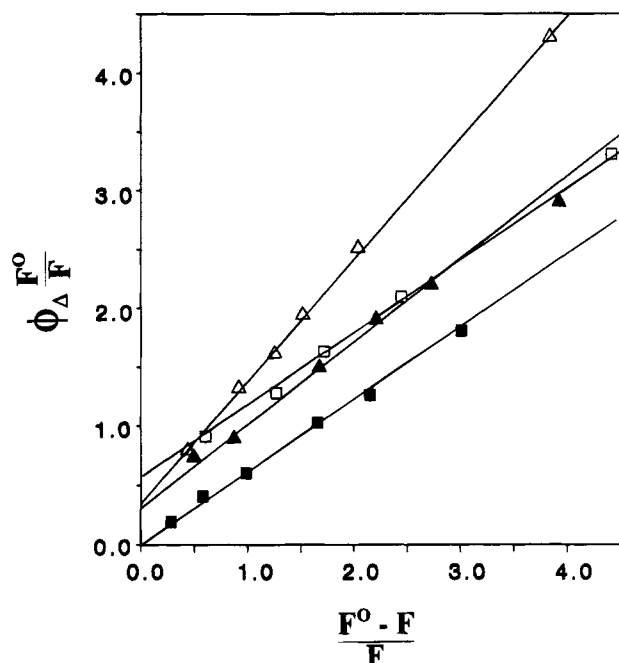


Figure 3. Plots to determine f_S^Δ and f_T^Δ according to eq 2: (Δ) 9,10-dichloroanthracene, (▲) 9-phenylanthracene, (■) 9-methoxyanthracene, (□) 9-methylanthracene.

comparison purposes. The intercepts of these plots which equal $\phi_T^0 f_\Delta^T$ are the same, within experimental error, when acetonitrile and cyclohexane are used as solvents or are slightly smaller with acetonitrile as solvent, with one exception, see later. Combining the intercepts with the triplet quantum yields in acetonitrile given in Table 1 allows values of f_Δ^T to be determined, see Table 3.

The f_Δ^T values in acetonitrile are found to be unity within experimental error for all of the anthracene derivatives studied except for 9-methoxyanthracene. These values are therefore in agreement with the results observed in cyclohexane. Thus the efficiency of singlet oxygen production from the triplet state is not affected by changing the solvent polarity except in the case of 9-methoxyanthracene, for which plots, in accordance with eq 2, give intercepts of 0.25 in cyclohexane and of 0.04 in acetonitrile. This difference is far beyond our experimental error. Since the triplet quantum yield of 9-methoxyanthracene in acetonitrile measured here (0.12) is only one-half the value measured in cyclohexane (0.25), this gives a value for f_Δ^T in the case of 9-methoxyanthracene, the only derivative for which f_Δ^T is not unity, of 0.33 ± 0.2 in acetonitrile. The large error arises because of the small value of the intercept. However, it is apparent that in this case f_Δ^T is considerably less than one.

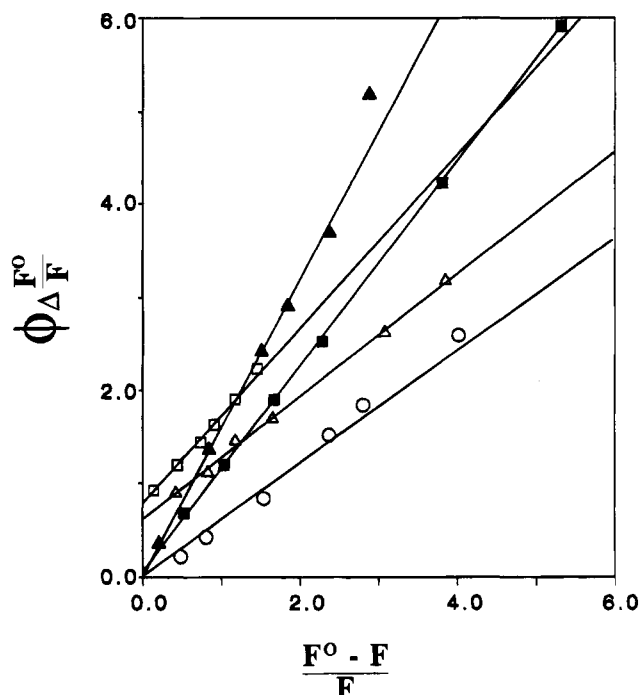


Figure 4. Plots to determine f_S^Δ and f_T^Δ according to eq 2: (Δ) anthracene, (▲) 9,10-dicyanoanthracene, (■) 9-cyanoanthracene, (□) 9,10-dibromoanthracene, (○) 9,10-diphenylanthracene.

TABLE 2: Experimental Slopes and Intercepts Obtained by Using Eq 2

compd	solvent	slope ($f_S^\Delta + f_T^0 f_\Delta^T$)	intercept ($\phi_T^0 f_\Delta^T$)
anthracene	cyclohexane	0.91 ± 0.05	0.76 ± 0.05
	acetonitrile	0.66 ± 0.02	0.61 ± 0.05
9-cyano	cyclohexane	1.51 ± 0.05	0.13 ± 0.04
	acetonitrile	1.09 ± 0.01	0.09 ± 0.03
9-methyl	cyclohexane	1.12 ± 0.03	0.62 ± 0.05
	acetonitrile	0.63 ± 0.02	0.52 ± 0.05
9-methoxy	cyclohexane	1.27 ± 0.03	0.25 ± 0.07
	acetonitrile	0.58 ± 0.01	0.04 ± 0.03
9-phenyl	cyclohexane	0.97 ± 0.06	0.42 ± 0.07
	acetonitrile	0.65 ± 0.03	0.39 ± 0.06
9,10-dibromo	cyclohexane	1.76 ± 0.19	0.81 ± 0.06
	acetonitrile	1.02 ± 0.04	0.70 ± 0.03
9,10-dichloro	cyclohexane	1.63 ± 0.03	0.36 ± 0.06
	acetonitrile	1.03 ± 0.01	0.35 ± 0.03
9,10-dicyano	cyclohexane	2.08 ± 0.10	0.00 ± 0.13
	acetonitrile	1.53 ± 0.02	0.07 ± 0.03
9,10-diphenyl	cyclohexane	1.22 ± 0.02	0.06 ± 0.04
	acetonitrile	0.64 ± 0.03	0.03 ± 0.06

According to Scheme 1, a f_Δ^T value lower than unity indicates that processes included in reaction 9 are competitive with the energy transfer process represented by reaction 8. It

TABLE 3: Singlet Oxygen Production from Singlet and Triplet States of Anthracene Derivatives in Acetonitrile and Efficiency of Triplet Formation

compd	f_{Δ}^T	f_{Δ}^S	$f_T^{O_2}$	$k_{S^2}^O/k_{O_2}^S(A)^a$
anthracene	0.9 ± 0.1	0.0 ± 0.1	0.83 ± 0.12	0.50
9-cyano	~1	0.25 ± 0.15	0.85 ± 0.15 ^b	0.71
9-methyl	0.95 ± 0.1	0.0 ± 0.1	0.62 ± 0.10	0.44
9-methoxy	0.33 ± 0.2	0.33 ± 0.2	0.87 ± 0.17 ^b	0.66
9-phenyl	1.0 ± 0.16	0.1 ± 0.1	0.57 ± 0.14	0.49
9,10-dibromo	0.9 ± 0.1	0.20 ± 0.2	0.90 ± 0.1 ^b	0.83
9,10-dichloro	1.00 ± 0.20	0.3 ± 0.1	0.70 ± 0.11	0.56
9,10-dicyano	1.0 ± 0.1	0.53 ± 0.1	1.0 ± 0.1 ^b	1.07
9,10-diphenyl	1.0	0.1 ± 0.10	0.60 ± 0.1 ^b	0.49

^a From refs 32 and 33. ^b For derivation of these values, see text.

has been proposed^{11,16,27} that this competition is determined by the degree of coupling between the $^3(T_1 \rightarrow ^3\Sigma)$ state and the charge transfer state. The mixing of initial and final states through the CT states depends on the energy difference between the initial states and the CT states. This difference corresponds to the free energy change required to form free ions from triplet states of organic molecules, and in acetonitrile, this can be calculated from the Rehm–Weller equation²⁸

$$\Delta G_{ct} = F(E_{OX}^D - E_{red}^A) - E_T \quad (3)$$

where F is the Faraday constant, E_{OX}^D is the half-wave oxidation potential of the donor, E_{red}^A is the half-wave reduction potential of the acceptor (-0.78 V versus SCE for O_2^{29}), and E_T is the triplet state energy of the substituted anthracene. Values obtained using this equation which would be expected to be subject to experimental error of ± 20 kJ mol⁻¹ are given in Table 1. Analysis of this data shows that for anthracene and 9-methyl- and 9-phenylanthracene the CT state is close in energy to the triplet state; in fact, in the case of 9-methylanthracene, the calculated value of the CT state is located 5 kJ mol⁻¹ below the triplet state. Unfortunately, only an estimate can be given for ΔG_{ct} in the case of 9-methoxyanthracene since its triplet energy has not been measured. However, considering the electron donating properties of a methoxy group, one can say with certainty that this value will be lower than ΔG_{ct} for anthracene. For example, in the case of substituted naphthalenes, the CT state of 1-methoxynaphthalene is located 16 and 22 kJ mol⁻¹ lower than the CT states of the 1-methylnaphthalene and naphthalene, respectively.¹¹ Recently, we have shown that, for naphthalene derivatives in acetonitrile, f_{Δ}^T values decrease as ΔG_{ct} becomes negative, and in fact, a similar value of $f_{\Delta}^T = 0.3$ is obtained for 2-methoxynaphthalene in acetonitrile.¹¹ The fact that f_{Δ}^T for 9-methoxyanthracene in acetonitrile is much less than one confirms our findings in the case of naphthalene derivatives; thus, when the CT states lies below the local excited triplet state for either naphthalene or anthracene derivatives, the efficiency of singlet oxygen production from the triplet f_{Δ}^T is reduced.

Several workers, for example, Kristiansen et al.,⁴ report singlet oxygen yields extrapolated to infinite oxygen concentrations. When singlet oxygen is produced following oxygen quenching only of triplet states³⁰ or only of the singlet states,³¹ a linear extrapolation of the inverse of the singlet oxygen yield versus the inverse of the oxygen concentration can be used to obtain ϕ_{Δ}^{∞} . When oxygen quenching of both singlet and triplet states yields singlet oxygen, the dependence of the singlet oxygen yield on oxygen concentration can be obtained by substituting $(k_{SD} + k_{S^2}^O[O_2])/k_{SD}$ in place of F^O/F into eq 2, which upon

rearrangement gives

$$\phi_{\Delta} = \frac{(f_{\Delta}^S + f_{\Delta}^T f_T^{O_2}) k_{S^2}^O[O_2] + k_{iso} f_{\Delta}^T}{k_{SD} + k_{S^2}^O[O_2]} \quad (4)$$

As $[O_2] \rightarrow \infty$, eq 4 gives $\phi_{\Delta}^{\infty} = f_{\Delta}^S + f_{\Delta}^T f_T^{O_2}$ as the limiting value. However, the value of $(f_{\Delta}^S + f_{\Delta}^T f_T^{O_2})$ can be obtained as the slope of linear plots of the type shown in Figures 3 and 4 at pressures well below those where ϕ_{Δ} reaches its limiting value. A comparison of the slopes of the plots shown in Figures 3 and 4 with those obtained in cyclohexane,¹⁵ see Table 2, shows that the $(f_{\Delta}^S + f_{\Delta}^T f_T^{O_2})$ values are 30–50% lower in acetonitrile. A similar but somewhat larger solvent effect was observed by Kristiansen et al.⁴ for the values of $(f_{\Delta}^S + f_{\Delta}^T f_T^{O_2})$ they measured for several aromatic hydrocarbons, but the magnitude of the change they reported for 9,10-dicyanoanthracene is somewhat smaller than that found here. The smaller slopes of the plots according to eq 2 must be due to decreases in f_{Δ}^S and/or $f_T^{O_2}$ when the solvent polarity increases since we have already shown that f_{Δ}^T does not change upon changing the solvent from cyclohexane to acetonitrile and the value is unity for all of the compounds investigated in both these solvents except in the case of the 9-methoxyanthracene. It is interesting to note that Potashnik et al.²⁶ measured $f_T^{O_2}$, the fraction of singlet states quenched by oxygen that give triplet states, to be 0.95 and 0.9 for oxygen quenching of excited singlet anthracene in toluene and acetonitrile, respectively. These authors also showed that $f_T^{O_2}$ values for acetonitrile solutions of pyrene and phenanthrene were equal to 0.60 and 0.55, respectively. In the case of pyrene, they were able to observe the transient absorption due to the cation radical. In order to measure $f_T^{O_2}$ using eq 1, it is necessary for the triplet lifetimes to be substantial in the presence of sufficient oxygen to partially quench the fluorescence and for ϕ_{Δ}^O values to be greater than ~5%. We have measured $f_T^{O_2}$ in the case of anthracene and 9-phenyl, 9-methyl, and 9,10-dichloroanthracene, i.e. for all cases where this was possible with our equipment. These $f_T^{O_2}$ values, which are all less than unity, are given in the last column of Table 3. The value obtained for anthracene in acetonitrile, $f_T^{O_2} = 0.83 \pm 0.12$, is within experimental error, equal to that reported by Potashnik et al.²⁶

Thus, for four anthracene derivatives, all the three determining factors, f_{Δ}^T , $f_T^{O_2}$, and f_{Δ}^S , can be evaluated separately. As is shown in Table 3, f_{Δ}^S values of 0, 0, 0.1 ± 0.1 , and 0.3 ± 0.1 are obtained for anthracene, 9-methylanthracene, 9-phenylanthracene, and 9,10-dichloroanthracene in acetonitrile, respectively. All of these values are equal to or less than the values obtained for these same compounds in cyclohexane. The values of f_{Δ}^S obtained in cyclohexane are also given in Table 3, and from these measurements, we can say that $f_{\Delta}^S(\text{cyclohexane}) \geq f_{\Delta}^S(\text{acetonitrile})$. Thus, for all those cases where we can measure all the determining parameters, both $f_T^{O_2}$ and f_{Δ}^S are shown to be less in acetonitrile than in cyclohexane.

Although many groups have measured the rate constants for quenching of excited singlet states by oxygen in cyclohexane, including anthracene derivatives,³² only a few measurements have been made with acetonitrile as the solvent.^{3,4} Two groups^{3,4} have measured $k_{S^2}^O$ for 9,10-dicyanoanthracene in acetonitrile and obtained values of 6.4×10^9 and 1.0×10^{10} dm³ mol⁻¹ s⁻¹, respectively. Kikuchi et al.³ have reported that they find that the plots for oxygen quenching of the fluorescence of 9,10-dicyanoanthracene are curved and their value is determined from plots at oxygen concentrations below 2×10^{-3}

mol dm⁻³. Since steps 4, 5, and 6 in Scheme 1 determine $k_S^{O_2}$ and the relative efficiencies of steps 4, 5, and 6 determine $f_\Delta^{O_2}$ and $f_T^{O_2}$, we have measured $k_S^{O_2}$ for all the derivatives we have studied under the conditions of our experiments. The value we obtained for 9,10-dicyanoanthracene in acetonitrile is 4.4×10^9 dm³ mol⁻¹ s⁻¹, based on fluorescence lifetimes measured for air- and oxygen-saturated solutions. In the light of the variation in the values given in the literature and for consistency with our treatment for other anthracene derivatives where no literature values are available, we have used our own values to obtain estimates for $f_T^{O_2}$ as outlined below. It is worth noting that the value we obtained for oxygen quenching of the fluorescence of 9-cyanoanthracene in acetonitrile of 9.4×10^9 dm³ mol⁻¹ s⁻¹ is once again considerably lower than the value of 1.6×10^{10} obtained by Kikuchi et al.³ It is obvious that agreement between literature values is not good, and the reasons for this will be discussed elsewhere.³³

In the case of 9,10-dichloroanthracene, f_Δ^S drops by 50% on going to the polar solvent. In terms of Scheme 1, when $f_T^{O_2} = 1$, this demonstrates that reaction 6 is negligible, but when $f_T^{O_2} < 1$, the rate constant for reaction 6 is comparable with those for reactions 4 and 5. The occurrence of oxygen quenching of excited singlet states by another channel, reaction 6, is also manifest in the large increase in the rate constants for quenching $k_S^{O_2}$, which often occurs on going from cyclohexane to acetonitrile (see refs 3 and 33). The ratio of the quenching rate constant can be written as

$$\frac{k_S^{O_2}(\text{cyclohexane})}{k_S^{O_2}(\text{acetonitrile})} = \frac{k_S^{O_2}(C)}{k_S^{O_2}(A)} = \frac{k_{S\Delta}^C + k_{ST}^C}{k_{S\Delta}^A + k_{ST}^A + k_{SO}^A}$$

Note that as given in Scheme 1

$$f_T^{O_2}(\text{acetonitrile}) = \frac{k_{S\Delta}^A + k_{ST}^A}{k_{S\Delta}^A + k_{ST}^A + k_{SO}^A}$$

In Table 3, the values of $[k_S^{O_2}(C)/k_S^{O_2}(A)]$ are given, and in the case of the four measured ratios, they are all $< f_T^{O_2}$ (acetonitrile). From this it follows that $(k_{S\Delta}^A + k_{ST}^A) > (k_{S\Delta}^C + k_{ST}^C)$ for all cases measured. In other words, in addition to the extra process, reaction 6, which occurs in acetonitrile, the polar solvent increases the rate constants for steps 4 and 5, i.e. catalyzed intersystem crossing by oxygen with and without energy transfer is enhanced. Despite this increase, the occurrence of reaction 6 leads to a reduction in both f_Δ^S and $f_T^{O_2}$ when compared to the values obtained in cyclohexane. In those cases where $f_T^{O_2}$ cannot be measured, we can assume by analogy to those cases where it can, that $(f_T^{O_2}(A) \geq k_S^{O_2}(C)/k_S^{O_2}(A))$. This inequality allows us to calculate $f_T^{O_2}$ and thus f_Δ^S from the measured slopes and intercepts given in Table 2 as outlined below. It is worth noting that, in addition, by definition (see Scheme 1) $f_T^{O_2} \geq f_\Delta^S$, since $f_T^{O_2} = f_\Delta^S + k_{ST}/k_S^{O_2}$.

In the case of 9,10-dicyanoanthracene, we did not find an increase in efficiency of the oxygen quenching of its singlet state in the more polar solvent. Although it has to be borne in mind that there is disagreement between the two literature values^{3,4} for the rate constant of oxygen quenching of the fluorescence of 9,10-dicyanoanthracene as mentioned earlier, and neither value agrees with the one measured by us. The reasons for these variations need to be investigated further.³³ However, the value that we obtained for $k_S^{O_2}(C)/k_S^{O_2}(A)$ of 1.07 suggests the absence of any quenching by reaction 6, in which

case $f_T^{O_2} = 1$ for 9,10-dicyanoanthracene in acetonitrile as it does in cyclohexane. Since f_Δ^T and $f_T^{O_2}$ are both equal to 1.0, it follows that f_Δ^S has been reduced by ~50% for 9,10-dicyanoanthracene on going to the polar solvent (see Table 3). In the case of 9-cyanoanthracene, $f_T^{O_2}$ could not be measured and only an estimate based on the rate constant ratios of 0.71 is possible. We therefore can assume $f_T^{O_2} \geq 0.7$, and since f_Δ^T is unity and the slope of the plot for 9-cyanoanthracene shown in Figure 4 is 1.09 ± 0.01 , it follows that f_Δ^S lies between 0.1 and 0.4. In Table 3, we therefore give for 9-cyanoanthracene in acetonitrile $f_T^{O_2} = 0.85 \pm 0.15$ and $f_\Delta^S = 0.25 \pm 0.15$. This latter value is again 50% of the value obtained in cyclohexane.

For 9,10-dibromoanthracene in acetonitrile, from the ratio of the fluorescence quenching rate constants, we can say $f_T^{O_2} \geq 0.8$ or $f_T^{O_2} = 0.9 \pm 0.1$ and we have measured $f_\Delta^T = 0.9 \pm 0.1$. It follows, therefore, from the slope of the plot for 9,10-dibromoanthracene shown in Figure 4 that $f_\Delta^S = 0.2 \pm 0.2$. In the case of 9,10-diphenylanthracene in acetonitrile, we assume, from the ratio of the fluorescence quenching rate constants, that $f_T^{O_2} \geq 0.5$, and since $f_\Delta^T = 1$, from the slope of the plot for 9,10-diphenylanthracene shown in Figure 4, it follows that $(f_\Delta^S + f_T^{O_2}) = 0.64 \pm 0.03$, which gives $f_T^{O_2} = 0.6 \pm 0.1$ and $f_\Delta^S = 0.1 \pm 0.1$ for 9,10-diphenylanthracene in acetonitrile. All these data are consistent with f_Δ^S decreasing by ~50% and $f_T^{O_2}$ decreasing by up to 50% on changing from cyclohexane to acetonitrile as the solvent in the case of these anthracene derivatives. Finally, considering 9-methoxyanthracene in acetonitrile, for which $f_\Delta^T = 0.33 \pm 0.2$, the ratio of the singlet state quenching constant in the two solvents suggests $f_T^{O_2} \geq 0.66$ or $f_T^{O_2} = 0.88 \pm 0.17$, and therefore, from the slope of the plot for 9-methoxyanthracene shown in Figure 3, it follows that $f_\Delta^S = 0.3 \pm 0.2$.

Thus reaction 6 shown in Scheme 1 occurs with enhanced efficiency in acetonitrile compared to cyclohexane, increasing from negligible to about 40% for oxygen quenching of the excited singlet states of several of these anthracene derivatives. In previous work on 9,10-diphenylanthracene in toluene, Darmanyan obtained $f_T^{O_2} = 0.33 \pm 0.2$,³⁴ suggesting that reaction 6 was more efficient than reaction 4 in this case. The data of Drew et al.²² and that of Stevens and Mills¹⁹ in benzene may be said to be not inconsistent with this value of $f_T^{O_2}$. Darmanyan interpreted this process as being due to the formation of sterically hindered conformers.³⁴ Obviously such a process could not account for the occurrence of reaction 6 in several of the meso derivatives studied in this work.

Since for many of these anthracene derivatives $k_S^{O_2}$ (acetonitrile) $> k_S^{O_2}$ (cyclohexane), it follows that the polar solvent causes more rapid decay of the $^3(S_1 \rightarrow ^3\Sigma)$ complex. The simplest explanation would be direct decay of this encounter complex to give the CT state, hence reducing both f_Δ^S and $f_T^{O_2}$, if internal conversion back from the charge transfer state to yield the complex $^3(T_1 \rightarrow ^3\Sigma)$, which can dissociate to yield the molecular triplet, were not 100% efficient. The fact that $f_T^{O_2} < 1$ requires either direct internal conversion from the CT state to the ground state $^3(S_0 \rightarrow ^3\Sigma)$ or enhanced CT assisted internal conversion from the $^3(T_1 \rightarrow ^3\Sigma)$ state. It is interesting to note that enhanced CT assisted internal conversion from $^3(T_1 \rightarrow ^3\Sigma)$ to the ground state cannot be very efficient in the case of most anthracene derivatives where the energy of the $^3(T_1 \rightarrow ^3\Sigma)$ state is greater than that of the CT states since all of these derivatives, except for 9-methoxyanthracene, have $f_\Delta^T \geq 0.9 \pm 0.1$ in acetonitrile, indicating a low probability for this process.

An alternative interpretation would be the suggestion that in

the polar solvent the charge transfer nature of all the M-O₂ states is increased, enhancing internal conversions to and from the charge transfer state and to and from each other. This could explain the decrease in $f_{\text{T}}^{\text{O}_2}$ in the case of the aromatic hydrocarbons studied by Potashnik et al.²⁶ and of all these anthracene derivatives, except for 9,10-dicyanoanthracene. It should be noted that, although the charge transfer state has the highest energy in the case of 9,10-dicyanoanthracene, in the case of this derivative, the charge transfer state lies close in energy to its S₁ state. Apparently there is a considerable intrinsic free energy of activation for charge transfer enhanced oxygen quenching of excited singlet states of aromatic hydrocarbons (see ref 33).

Kanner and Foote⁵ have measured the singlet oxygen production from singlet and triplet states of 9,10-dicyanoanthracene in benzene and acetonitrile by using dimethyliodobenzene to enhance the intersystem crossing in 9,10-dicyanoanthracene. The quantum yield of singlet oxygen at infinite oxygen concentration determined by them is equivalent to the slope of plots made according to eq 2 measured in this work. For acetonitrile these authors found a value for $(f_{\Delta}^{\text{S}} + f_{\Delta}^{\text{T}} f_{\text{T}}^{\text{O}_2})$ of 1.46 ± 0.1 , which agrees well with the value of 1.53 ± 0.02 obtained here, see Table 2. Recently, Scurlock and Ogilby⁹ have claimed that the value obtained by Kanner and Foote⁵ was in error and that the value of 2.0, reported previously by Dobrowolski et al.,³ is a better value since they, Scurlock and Ogilby,⁹ obtain a value for $(f_{\Delta}^{\text{S}} + f_{\Delta}^{\text{T}} f_{\text{T}}^{\text{O}_2})$ of 2.06 ± 0.4 . Our results clearly indicate that in acetonitrile the value of $(f_{\Delta}^{\text{S}} + f_{\Delta}^{\text{T}} f_{\text{T}}^{\text{O}_2})$ for 9,10-dicyanoanthracene is well below the maximum value of 2, confirming the work of Kanner and Foote⁵, who also obtained values for the efficiencies of singlet oxygen production from the singlet and triplet states of 9,10-dicyanoanthracene in benzene and acetonitrile. In benzene, their measured value for f_{Δ}^{T} was 0.70 ± 0.2 , and they assumed the same value in acetonitrile. Using this value for f_{Δ}^{T} and assuming that $f_{\text{T}}^{\text{O}_2} = 1.0$, they obtained 0.76 for f_{Δ}^{S} in acetonitrile. As explained above, we use f_{Δ}^{T} and $f_{\text{T}}^{\text{O}_2}$ equal to unity to calculate 0.53 for f_{Δ}^{S} . Thus the discrepancy arises from the f_{Δ}^{T} values assumed. The difference is substantial, but unfortunately, both methods have large experimental errors due to the uncertainties in extinction coefficients of the triplet states of 9,10-dicyanoanthracene and of acridine used as a standard⁵ and, in the results presented here, due to the uncertainty in the intercept of the plot shown in Figure 4 for 9,10-dicyanoanthracene due to the small value of $\phi_{\text{T}}^{\text{O}}$. For the reasons given above we consider that it is most probable that the singlet oxygen productions from the triplet states of 9,10-dicyanoanthracene and of all the anthracene derivatives, except for 9-methoxyanthracene, are close to unity.

Conclusion

Comparison of the yields of singlet oxygen production in acetonitrile and cyclohexane for a range of anthracene derivatives has shown that an increase in solvent polarity causes a decrease in the quantum yield of singlet oxygen production at infinite oxygen concentration. In acetonitrile, the oxygen quenching of excited singlet states occurs through an additional channel, reaction 6 in Scheme 1, which is negligible in cyclohexane. This additional process brings about an increase in the quenching rate constant and lowers the efficiencies of formation of triplet states resulting from oxygen quenching of singlet states and the efficiencies of singlet oxygen production from singlet excited states quenched by oxygen. In addition, we have shown that the fraction of triplet states quenched by

oxygen which yield singlet oxygen is unity in acetonitrile in all cases studied except for 9-methoxyanthracene, for which a value of 0.33 is obtained. It is suggested that this difference is due to the charge transfer state having a lower energy than the molecular triplet state in this compound.

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