ESR Studies of Triplet States in Plastics: Effect of Temperature on the Spectra

Colin Thomson

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ESR Studies of Triplet States in Plastics: Effect of Temperature on the Spectra*

COLIN THOMSON†

Department of Chemistry, University of California, Los Angeles, California

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The use of polymethylmethacrylate (Lucite) as a host medium for the study of aromatic triplet states by ESR has been explored. The zero-field splitting parameter D* and the lifetime of the triplet state have been measured for a variety of aromatic molecules, and the effect of temperature on these parameters studied in the cases of coronene, triphenylene, and naphthalene.

INTRODUCTION

ELECTRON spin resonance (ESR) has been extensively used in the study of the triplet states of aromatic molecules since the triplet state of naphthalene was detected in 1958 by Hutchison and Mangum.[1,2] The degeneracy of the molecular Zeeman levels is lifted even in zero magnetic field as a result of dipolar spin–spin interaction between the unpaired electrons. The Hamiltonian for this interaction is[3]

$$\mathcal{K}_s = g^2\beta^2 \sum_{\mu<\nu} \{ (\hat{S}_\mu \cdot \hat{S}_\nu / r_{\mu\nu}{}^3) - [3(\hat{S}_\mu \cdot \mathbf{r}_{\mu\nu})(\hat{S}_\nu \cdot \mathbf{r}_{\mu\nu})/r_{\mu\nu}{}^5] \}$$

(1)

In this expression $\hat{S}_\mu$ and $\hat{S}_\nu$ are the spin angular momentum operators of electrons μ and ν, and $\mathbf{r}_{\mu\nu}$ is the distance between them; g is the spectroscopic splitting factor, β is the Bohr magneton and the summation is over all the electrons. This Hamiltonian can be written in an equivalent form

$$\mathcal{K}_s' = D\hat{S}_z{}^2 + E(\hat{S}_x{}^2 - \hat{S}_y{}^2),$$

(2)

which gives the same zero-field energy levels and spin states as Eq. (1).[4] The zero-field splitting parameters D and E can be obtained from the ESR spectrum if

the molecule can be studied in a single crystal where it has a well-defined orientation, and these parameters can be calculated theoretically by evaluating the expectation value of Eq. (1), in which case

$$D(\text{cm}^{-1}) = -3g^2\beta^2/4hc \langle \Psi \mid (3z_{12}{}^2 - r_{12}{}^2)/r_{12}{}^5 \mid \Psi \rangle$$

(3)

and

$$E(\text{cm}^{-1}) = -3g^2\beta^2/4hc \langle \Psi \mid 3(x_{12}{}^2 - y_{12}{}^2)/r_{12}{}^5 \mid \Psi \rangle.$$

(4)

In these expressions Ψ is the antisymmetric spatial part of the lowest triplet state wavefunction and the other symbols have their usual meaning. An external magnetic field H_0 further separates the levels, and transitions between them may be induced by microwave radiation of the appropriate frequency. The spectra which are obtained when transitions occur between neighboring sublevels of the triplet ($\Delta m = 1$) are highly anisotropic, and are most easily observed in single crystals. Several aromatic molecules have been studied in this way[1,2,5–7] and accurate values of D and E have been obtained from the spectra. Unfortunately, this technique is of limited use because suitable host crystals are difficult to find for many molecules whose triplet states are of interest to the chemist.

One can, however, study the triplet state of such molecules in rigid glassy solvents, in which the molecules are randomly oriented, by observing the transition

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[1] C. A. Hutchison, Jr., and B. W. Mangum, J. Chem. Phys. 29, 952 (1958).

[2] C. A. Hutchison, Jr., and B. W. Mangum, J. Chem. Phys. 34, 908 (1961).

[3] M. Gouterman and W. Moffitt, J. Chem. Phys. 30, 1107 (1959).

[4] A. D. McLachlan, Mol. Phys. 6, 441 (1963).

[5] R. W. Brandon, R. E. Gerkin, and C. A. Hutchison, Jr., J. Chem. Phys. 37, 447 (1962).

[6] A. W. Hornig and J. S. Hyde, Mol. Phys. 6, 33 (1963).

[7] J. S. Vincent and A. H. Maki, J. Chem. Phys. 39, 3088 (1963).

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TABLE I. Zero-field splitting parameter D^* and linewidth of the triplet state ESR signal in Lucite at 77°K, compared with D^* in glassy solvents, in single crystals, and theoretical calculations.

| Molecule | D^* (cm^{-1}) | | | | Linewidth[b] ΔH_{PP} (G) | |
	Lucite (± 0.0004)	Glasses	Single crystals	D^* (cm^{-1})[a] Calculated	Lucite	Glasses
Naphthalene	0.1063	0.1049[o]	0.1036[g]	0.1029	14.1	11.2
Phenanthrene	0.1336	0.1335[c]	0.1269[g]	0.0867 (0.1000)	17.5	12.2
Triphenylene	0.1360	0.1353[e]	···	0.0697 (0.0810)	18.0	7.9
Coronene	0.0983	0.0971[e]	···	0.0522[d] (0.0608)	9.5	7.0
1,12-Benzperylene	0.0718	···	···	···	12.8	···
Biphenyl	0.1111	0.1130[c]	···	···	17.6	12.6
Fluorene	0.1088	0.1096[c]	···	···	18.7	13.7
Acenaphthene	0.1029	···	···	···	28.1	···
Fluoranthene	0.0817	0.076[e]	···	···	23.2	···
1-Chloronaphthalene	0.1056	···	···	···	17.5	···
1-Methylphenanthrene	0.1288	···	···	···	18.7	···
1-Bromophenanthrene	0.1327	···	···	···	16.0	···
Quinoxaline	0.1074	···	0.1055[f]	0.1082[f]	18.4	···
Carbazole	0.1063	0.1044	···	···	16.2	11.1
Triphenylamine	0.0801	···	···	···	27.4	···

[a] Reference 25. Values in parentheses refer to Hoffmann orbitals: others refer to Hückel orbitals.
[b] Linewidth from peak to peak on derivative.
[c] Reference 13. Solvent was EPA.
[d] In Ref. 24, Chiu presents similar results, but by assigning a large mixing coefficient to an excited configuration he obtained $D = 0.096$ for coronene.
[e] Reference 15. Solvent was a mixture of heptane and isopropanol.
[f] Reference 7.
[g] Reference 5.

corresponding to $\Delta m = 2$. Van der Waals and de Groot[8,9] showed that although this transition has a lower probability than that of the $\Delta m = 1$ transition, it is comparatively isotropic and can readily be observed at half-field. At 9000 Mc/sec, this corresponds to a resonance field of $\sim$1500 G. These authors[8,9] showed that the position of the maximum (H_m) on the low-field side of the derivative spectrum is related to the root-mean-square zero-field splitting parameter D^* by the relation

$$D^* = \sqrt{3}[\tfrac{1}{4}(h\nu)^2 - (g\beta H_m)^2]^{\frac{1}{2}} \qquad (5)$$

where

$$D^* = (D^2 + 3E^2)^{\frac{1}{2}} \qquad (6)$$

and ν is the microwave frequency. This relationship has been used in the present work to determine D^* for a variety of aromatic molecules in Lucite. Observation of the $\Delta m = 2$ transition does not enable one to

determine D and E separately unless the rf field is parallel to the static magnetic field[10] (except for molecules with threefold or higher symmetry where $E = 0$) and in this work we have used the usual arrangement with the rf field perpendicular to the static field. The $\Delta m = 1$ transitions can be observed in glasses but the intensity of the absorption is one or two orders of magnitude less than that of the $\Delta m = 2$ transitions.[11] This reduction in intensity for randomly oriented molecules arises because resonance occurs only for those molecules which have a molecular axis parallel to H_0. However, in our samples these transitions were difficult to observe, and in this paper we shall discuss only the resonance lines arising from $\Delta m = 2$ transitions.[8,9,12-15]

[8] J. H. van der Waals and M. S. de Groot, Mol. Phys. **2**, 333 (1959).
[9] M. S. de Groot and J. H. van der Waals, Mol. Phys. **3**, 190 (1960).
[10] P. Kottis and R. Lefebvre, J. Chem. Phys. **39**, 393 (1963).
[11] W. A. Yager, E. Wasserman, and R. M. R. Cramer, J. Chem. Phys. **37**, 1148 (1962).
[12] M. S. de Groot and J. H. van der Waals, Mol. Phys. **6**, 545 (1963).
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Several authors have studied triplet states in rigid glasses at 77°K using ESR techniques[8,9,12-15] but such work is limited to temperatures below 100°K because the temperature range over which most glasses are stable is quite narrow. In plastics, however, one can study the triplet state over a wide temperature range because the plastics are thermally stable and usually remain rigid up to 300°K or more. The phosphorescence spectra of many aromatic molecules have been studied in various plastics recently by Melhuish,[16,17] Oster,[18] and Forster[19] and we have used plastic samples to study the ESR spectra of the triplet state of the molecules listed in Table I. Solutions of the molecules in polymethylmethacrylate (Lucite) were irradiated at 77°K, and the zero-field splitting parameter D^* was obtained from the ESR spectrum of the triplet state (Table I). We have also examined the spectra of the triplet state excited at room temperature in suitable cases. The use of plastics as host media for the aromatic molecule enables one to study D^* and the triplet state lifetime as a function of the temperature from 77° to 300°K, and this information cannot be obtained using the usual glassy solvents.

EXPERIMENTAL

Solutions of the aromatic molecule in Lucite were prepared according to the method of Melhuish.[16,17] The appropriate weight of the molecule was dissolved in 10 ml of freshly distilled methylmethacrylate monomer, and the initiator (a solution of 1 mg of benzoyl peroxide in 1 ml of monomer) was added. The volume of the sample (after allowing for the volume contraction during polymerization) was 10 ml. The concentrations used depended on the solubility of the molecule in the monomer, and were usually between $10^{-3}M$ and $10^{-2}M$. The solution was degassed at $-80°C$ using a water pump, sealed off, and heated in an oven at 55°C for 48 h. It was then heated for 24 h at a temperature of $\sim85°C$. The latter step was necessary, since samples which were not treated in this way gave a much weaker phosphorescence than those so treated. Rigorous degassing was not necessary, probably because some of the residual oxygen is scavenged during the polymerization process, and the samples which were not thoroughly degassed gave approximately the same phosphorescence and ESR signal intensity as those which were, although the former were not as stable over a period of several weeks.

After polymerization, the samples were cut to the desired size and polished. The fact that they can be easily machined and polished so that their surface is flat renders them suitable for experiments in which the

TABLE II. D^* of aromatic molecules in Lucite as a function of temperature.

Molecule	T (°K)	D^* (cm^{-1})
Coronene[a]	305	0.0943±0.0004
	221	0.0957±0.0003
	199	0.0959±0.0003
	177	0.0967±0.0004
	147	0.0973±0.0002
	77	0.0983±0.0004
Triphenylene[a]	305	0.1271±0.0004
	77	0.1360±0.0004
Naphthalene	305	0.1020±0.0004
	77	0.1063±0.0004

[a] $D^*=D$.

triplet state is excited using polarized radiation. The polarization of the phosphorescence has been studied in this way for some of the molecules discussed in this paper,[20] but attempts to observe the ESR spectrum of molecules excited with polarized radiation were not very successful, because of the decrease in light intensity which results when one uses a polarizer. A very weak ESR spectrum of the coronene triplet was observed but the line shape and intensity did not depend appreciably on the orientation of the polarized light.

The ESR measurements were carried out with a spectrometer consisting of the basic Varian V4500 components (including 100 kc/sec modulation) with the exception of the microwave bridge. This was replaced by a Varian V153C klystron and a three-port Raytheon circulator. A standard Varian 6-in. magnetic provided the magnetic field. Measurements at temperatures between 77° and 300°K were performed with the sample in the Varian variable-temperature Dewar insert, the sample being cooled by a flow of cold nitrogen gas through the Dewar. The temperature of the sample was altered by varying the gas flow rate, but it proved difficult to control the temperature to better than ±2°C at temperatures below 150°K. A copper–constantan thermocouple at the top of the sample and just outside the cavity was used to measure the temperature. Ultraviolet radiation from a G. E. AH-6 1000 W air-cooled mercury lamp was focused on the sample through the radiation slits in the cavity by means of a quartz lens. A quartz cell containing water was used to filter out infrared radiation.

Most samples gave an intense phosphorescence on irradiation at 77°K. On irradiation at room temperature, the phosphorescence was much less intense.

RESULTS

The results of these experiments are summarized in Tables I and II and Figs. 1 and 2 and are discussed in the following sections.

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[18] G. Oster, N. Geacintov, and A. V. Khan, Nature **196**, 1089 (1962).
[19] C. F. Forster and E. F. Rickard, Nature **197**, 1199 (1963).
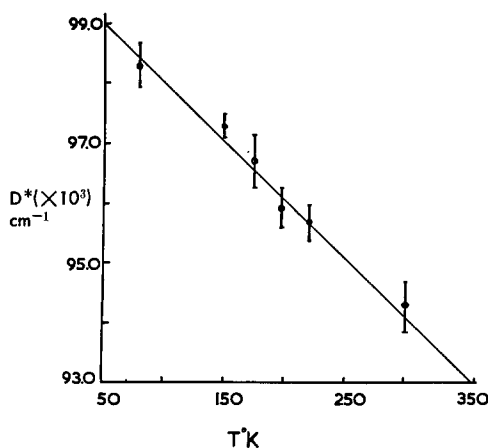[20] M. A. El-Sayed (private communication).

FIG. 1. Variation of the zero-field splitting parameter D^* of coronene with temperature.

1. Zero-Field Splitting Parameter D^*

The zero-field splitting parameter D^* was calculated from the observed spectra of a variety of aromatic molecules by means of Eq. (5) and the results are given in Table I. Some of these molecules have been studied previously in glasses and single crystals, and the values of D^* in these matrices are given for comparison. With the exception of biphenyl and fluorene D^* in Lucite is consistently larger than in glasses or single crystals for those molecules where a comparison is possible. Hutchison,[5] however, found that the D and E parameters of phenanthrene in two different host crystals, biphenyl and fluorene, were less sensitive to a change in the host matrix than the results in Table I indicate. It may be that the quite different nature of a plastic and a single-crystal matrix is the reason for the difference which we observe and if this is the case, then interaction with the matrix is not negligible.

It is noteworthy that D^* is relatively insensitive to substituents in the aromatic ring, e.g., compare naphthalene with α-chloronaphthalene and phenanthrene with 1-bromophenanthrene. In the case of naphthalene and quinoxaline, the values of D^* are 0.1063 and 0.1074, respectively. Single-crystal studies on quinoxaline in durene[7] have shown that this increase is a result of an increase in E, whereas D is almost identical to that of naphthalene, but here once again we find that D^* in Lucite is bigger than D^* in single crystals.

The phosphorescence yield increases along the series perylene, 1,12-benzperylene, and coronene, the latter giving the most intense emission we have observed. The ESR signal intensity also increases along the series (perylene, however, gives no appreciable phosphorescence or ESR signal when *pure*) but D^* (1,12-benzperylene) $< D^*$ (coronene).

The D and E parameters of a variety of aromatic hydrocarbons have been calculated theoretically by

several authors recently[3,21-25], using various approximations. Boorstein and Goutermann[25] have extended earlier work[3,21] by including all two-center integrals and have examined the theoretical foundations of the calculations, and Chiu[24] has evaluated many three- and four-center integrals in the cases of benzene, naphthalene, triphenylene, and coronene. The theoretical values of D and E which these authors obtained were not, however (except for benzene, naphthalene, and anthracene) in very good agreement with the experimental values, and it is clear that further theoretical studies are needed in order to explain the discrepancy.

2. Variation of D^* with Temperature

The intensity of both the phosphorescence and the ESR signal decrease as the temperature is increased from 77°K. In the case of the ESR signal, the decrease is fourfold or more between 77°K and room temperature ($\sim$300°K), and this makes it difficult to observe the triplet signal at the higher temperatures unless the signal is strong at 77°K. The spectra of coronene, triphenylene, and naphthalene have a high intensity at 77°K and D^* has been measured at 77° and $\sim$305°K for these molecules (Table II). The signal-to-noise ratios at 305°K were $\sim$20:1, 10:1, and 4:1, respectively. In addition D^* was measured at various intermediate temperatures in the case of coronene (Table II and Fig. 1). The error in D^* is a result of the difficulty with the temperature control mentioned in the second section and in inaccuracies in the measurement of the position of the peak maximum and hence of H_m. Unfortunately, the lack of signal intensity precluded
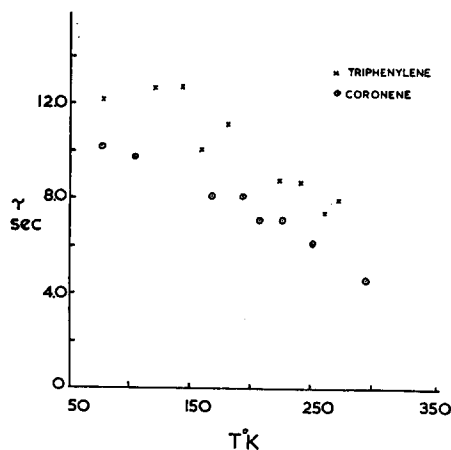

FIG. 2. Variation of the triplet-state lifetime of coronene and triphenylene with temperature.

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[23] H. F. Hameka, J. Chem. Phys. 31, 315 (1959).
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[25] S. A. Boorstein and M. Gouterman, J. Chem. Phys. 39, 2443 (1963).

any measurements of D^* at room temperature for the other molecules in Table I.

There is a decrease in D^* with increasing temperature in the case of coronene and the plot of D^* vs T is approximately linear with a slope of -2×10^{-5} cm$^{-1} \cdot$ °C^{-1}. The decrease in D^* between 77°K and room temperature is about 5%, and in the case of naphthalene and triphenylene where measurements were carried out only at these two temperatures, the decrease is of the same order of magnitude. There is no reason to believe that this behavior is not a general property of aromatic triplet states, although it could not be determined for the other molecules in Table I. Hutchison[5] measured the dependence of $(D - E)$ on temperature for naphthalene and obtained a value of -1.3×10^{-5} cm$^{-1} \cdot$ deg^{-1}.

The explanation of this effect is not clear. The calculation of D and E involves the evaluation of the expectation values of the dipolar interaction operators $(3z_{12}^2 - r_{12}^2)/r_{12}^5$ and $[3(x_{12}^2 - y_{12}^2)]/r_{12}^5$ with respect to the triplet state wavefunction. Irrespective of the particular approximation used to construct the wavefunction, the calculations reduce to the evaluation of many atomic dipolar interaction integrals of the form

$$\langle a(1)b(2) - a(2)b(1) \mid (3z_{12}^2 - r_{12}^2)/r_{12}^5 \mid c(1)d(2) \rangle \quad (7)$$

and

$$\langle a(1)b(2) - a(2)b(1) \mid 3(x_{12}^2 - y_{12}^2)/r_{12}^5 \mid c(1)d(2) \rangle, \quad (8)$$

where a, b, c, d are atomic orbitals. These integrals may be two-, three-, or four-center integrals and are not easy to calculate exactly. However, it seems likely that one can neglect three- and four-center integrals without introducing serious error since these are always smaller than two-center integrals, but all of the latter should be taken into account in accurate work.[24,25]

The method of calculating D and E used by previous workers and outlined above refers always to the ground vibrational level of the triplet state. One possible explanation of the variation of D^* (and presumably of D and E separately) with temperature is that the higher vibrational levels of the state became appreciably populated at higher temperatures. In qualitative terms, this probably results in an increase in the average distance between the unpaired electrons, and hence a smaller value of D and E. Although the temperature variation of D^* is small, the theoretical calculation of the temperature dependence of D and E would be of considerable interest. However, in view of the difficulty of evaluating D and E accurately for even the lowest vibrational level, calculations of the small variations in D^* which are observed in this work are probably not feasible at present.

The above explanation is by no means the only possible one but it seems to be more likely than a strong dependence of matrix–triplet interactions on

temperature. Much more work is needed in order to understand this effect properly.

3. Linewidth of the ESR Signal

It has not proved possible to measure the temperature-dependence of the linewidth except for naphthalene, triphenylene, and coronene. For the first two molecules the width changes by only 1% to 2% between 77° and 305°K but in the case of coronene the width decreases from 9.6 G at 77°K to 8.4 G at 305°K.

Comparison of the linewidths in Lucite with those measured in glasses shows that there is an increased linewidth in Lucite of $\sim$30% to 40%.

Triphenylene is exceptional in that the linewidth is more than doubled. The width does not appear to be concentration-dependent, although this was only checked over the range $10^{-3}M$ to $10^{-2}M$.

Smaller[13,14] has shown that deuteration of the solvent results in decreased linewidths for aromatic hydrocarbons in EPA and therefore at least some of the width is due to interaction between the triplet state and the nuclear moments of protons in the solvent molecules. A similar explanation in our case could account for some of the increase but the effect we observe is much larger than could be accounted for by this mechanism alone. We cannot, at the moment, do more than suggest one possibility which further experiments might validate. The irradiated plastics contain large concentrations of free radicals which are produced by C–H bond breakage in the polymer. If there is a strong interaction between the radicals and the triplet state at these high concentrations, this could give rise to line broadening. Since the radicals are stable up to room temperature, this sort of interaction could not produce any large temperature-dependence of the linewidth. So far as we know, this sort of interaction has not been discussed previously, and theoretical studies would be very interesting.

The exceptional increase in linewidth noted for triphenylene is not understood at present. The resolved structure observed by van der Waals[9] on the high-field side of the spectrum is broadened beyond detection in our samples.

4. Lifetime of the Triplet State

The decay time of the triplet state signal at 77°K was determined for the molecules in Table I. The decay curve was exponential except in the first 0.25 sec, the deviation in this region is due to the response time of the recorder, and from a logarithmic plot of intensity vs time one can calculate the lifetime of the triplet states. This was measured as a function of temperature in the case of the triplet states of coronene and triphenylene (Fig. 2). The results are not very reproducible, because it was found that the lifetime was dependent on the previous history of the sample, such

as the length of time the sample had been exposed to oxygen after its preparation, the length of previous irradiation by uv, etc. This effect has been shown to be the result of oxygen diffusion into the sample.[17] Quantitative work on the lifetimes in plastics will necessitate the use of samples in sealed quartz tubes. Oster[18] has shown that the triplet state phosphorescence lifetime of a particular molecule is also dependent on the nature of the host plastic.

The lifetime of the ESR signal of a variety of triplet states has been measured in hydrocarbon glasses[9,14] and also in single crystals.[1,2] Hutchison found that the half-life of the resonance of the triplet state of naphthalene was in good agreement with the lifetime of the phosphorescence and for deuterated samples, the lifetime approaches the radiative lifetime.[14,26] The lifetimes of the ESR signals in plastics are close to those reported previously in glasses and single crystals, and also to the phosphorescence lifetimes,[17] although exact agreement is not expected. There has been some recent work on the lifetime of the phosphorescence in glasses at 77°K and in single crystals at 4°K and 77°K.[27] The decay curves were exponential at 4°K for naphthalene and phenanthrene crystals but were not purely exponential at 77°K, although the decay curves in EPA at 77°K were purely exponential. Our results are in qualitative agreement with the lifetimes reported by these workers at 77°K, and the exponential decay agrees with the results in glasses at 77°K.

A more extensive investigation by Hadley, Rust, and Keller[28] in which the phosphorescence lifetime of naphthalene in durene was measured as a function of temperature from 77° to 325°K, showed that the lifetime remains almost constant up to ~200°K. Although we did not measure the lifetime of the naphthalene triplet as a function of temperature, the coronene and triphenylene lifetimes decrease more or less continuously as the temperature is raised from 77°K. This is probably a reflection of the different efficiencies of the radiationless transitions to the ground state in the different molecules and media.

The temperature dependence of D^* and of the triplet state lifetime are probably related, since the increase in the population of the higher vibrational levels of the triplet at higher temperatures, which we believe is the reason for the decrease in D^*, will also result in an increase in the vibrational overlap integral, and therefore an increase in the rate of radiationless transitions to the ground state.[29]

5. Other Triplet States in Lucite

An attempt was made to observe ESR absorption from the $(n-\pi^*)$ triplet state of pyrazine in Lucite.

This molecule gives a strong phosphorescence in Lucite[17] but no ESR absorption was found in the field range 0 to 7000 G. It is not clear whether the failure to observe the triplet state by ESR is due to its short lifetime (~0.03 sec) or to the fact that D^* is predicted theoretically to be bigger for $(n-\pi^*)$ states than for $(\pi-\pi^*)$ states,[30,31] and may exceed the value of the rf quantum used in these experiments (0.3 cm^{-1}). This would make it difficult to observe a signal in randomly oriented samples. We also failed to detect an ESR signal from the $(n-\pi^*)$ triplet state of nitrobenzene. The $(\pi-\pi^*)$ triplet states of α-chloro- and α-bromo-naphthalene have phosphorescence lifetimes of 0.30 and 0.018 sec, respectively, and give good phosphorescence yields, and examination of these molecules indicates that the lifetime may be a limiting factor in the case of pyrazine. The former gave a weak ESR signal but the latter gave no signal. From these results it seems likely that for triplet lifetimes of less than 0.1 sec, the steady-state concentration becomes too low and no ESR absorption can be detected, and this may be the reason no ESR is seen from the pyrazine triplet. The linewidth of the ESR line of most of these triplets is 10–20 G, which makes it difficult to detect low triplet concentrations.

CONCLUSIONS

The results of these investigations show that the use of plastics as host media for the study of the triplet states of aromatic molecules has several advantages compared with the use of glasses. The temperature dependence of D^* and the triplet-state lifetime can be studied over a wide temperature range. However, much more rigid plastics where the diffusion of oxygen is reduced will have to be used in order to obtain more quantitative information than has been obtained in this work; and furthermore in view of the strong dependence of the lifetime on the nature of the plastics,[18] a more extensive investigation of the dependence of the various parameters on the plastic and of the nature of the triplet–matrix interactions is needed.

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