that the solvent markedly affects both the shape of the curve and the magnitude of the effect. Heretofore, the solvent has not been regarded as an important factor in the annihilation process. However, these results imply that the solvent plays a more significant role than has been previously supposed.

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Wurster's Blue Cation as an Anthracene Triplet Quencher in Fluid Solution and the Effect of Magnetic Field on This Interaction[1]

Sir:

Hoytink[2] has suggested that ion radicals might be effective triplet quenchers in fluid solution. To date, however, the only experimental support for the idea has come from some solid-state studies which showed that radicals do quench triplet excitons effectively.[3] Aside from its interest to investigators working with triplet reactions, and to theories of the influence of paramagnetic molecules on singlet–triplet transitions,[4] the question is important to those concerned with electrogenerated chemiluminescence (ECL), because any triplets generated in an ECL experiment are certainly generated in a region cooccupied by ion radicals. Thus, if triplets are intermediates in the emission scheme for ECL from some systems, and if the radicals are effective as quenchers, there is no doubt that radical quenching is intimately linked to the efficiency of ECL emission. We report here a confirmation that Wurster's blue cation is an effective quencher of anthracene triplets in methylene chloride, and we describe a study of the effect of a magnetic field on the rate of that process.

The experimental work rests on the measurement of the intensities and the lifetimes of delayed fluorescence arising from methylene chloride solutions of anthracene and Wurster's blue perchlorate. All measurements were carried out using the instrument described in the preceding communication.[5] Experimentally the problem is difficult because the radicals are not stable at room temperature at the low concentrations used for the period required for the measurements. The solutions in methylene chloride are not entirely stable, but they do decay slowly enough to permit some useful measurements.

That Wurster's blue cation is an effective quencher of anthracene triplets is shown by the shortened lifetimes in the presence of the radical. As an example, a methylene chloride solution containing initially 1.8×10^{-7} *M* Wurster's blue perchlorate and 8×10^{-5} *M* anthracene showed a delayed fluorescence lifetime of 1.4 msec, thus a triplet lifetime of 2.8 msec. This figure is much shorter than the 6.4-msec triplet lifetime recorded for a solution containing the same anthracene concentration without Wurster's blue cation. The radical decay makes accurate measurement of the quenching rate constant virtually impossible. Nevertheless, one can calculate a lower limit to the quenching rate from the lifetime data by using the initial radical concentration as an upper limit. The triplet lifetime in the presence of quencher concentration [Q] is given by[6]

$$1/\tau = 1/\tau_0 + k_q[Q]$$

where τ is the lifetime in the presence of the quencher, τ_0 is the lifetime measured in the absence of quencher, and k_q is the quenching rate constant. Using the triplet lifetimes mentioned above together with a maximum radical concentration of 1.8×10^{-7} *M*, one calculates a lower limit quenching rate constant of 2×10^9 l./(mole sec). This value is comparable to the quenching rate constant calculated from triplet–triplet energy-transfer data in solvents of similar viscosity. Thus, one must conclude that Wurster's blue cation is a very effective quencher of anthracene triplets, a fact which lends strong support to Hoytink's hypothesis regarding radicals in general.

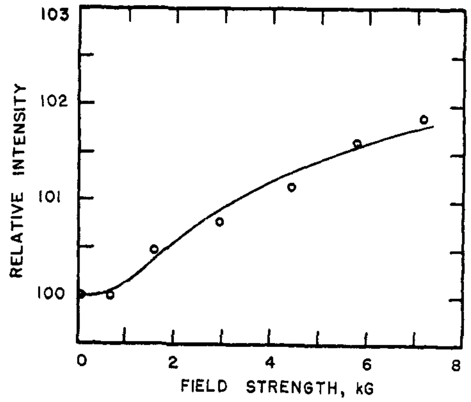

Figure 1. Magnetic field effect on delayed fluorescence from a methylene chloride solution 1.8×10^{-7} *M* in Wurster's blue perchlorate and 8×10^{-5} *M* in anthracene.

The results of a study of magnetic field effects on delayed fluorescence from the solution discussed above are shown in Figure 1. One notes there that the field enhances delayed fluorescence. When one compares these results to those obtained with methylene chloride solutions containing only anthracene (Figure 2), one concludes that the magnetic field inhibits radical quenching of anthracene triplets. Moreover, the longer lifetimes which result from this situation more than compensate for the field effect on the annihilation rate; thus there is a positive change in the intensity as the field is applied. These qualitative conclusions about the direction of the field effect are similar to those reached by Ern and Merrifield[3b] in their solid-state studies.

It is worth noting here that the existence of the field effect on the quenching rate probably indicates that the rate is not entirely diffusion controlled. This observation enables one to place a tentative upper limit on

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[1] This research was supported by the Robert A. Welch Foundation and the National Science Foundation (GP 6688X).

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[3] (a) S. Z. Weisz, P. Richardson, A. Cobas, and R. C. Jarnagin, *Mol. Cryst.*, **3**, 168 (1967); (b) V. Ern and R. E. Merrifield, *Phys. Rev. Letters*, **21**, 609 (1968).

[4] (a) G. J. Hoytink, *Mol. Phys.*, **3**, 67 (1960); (b) J. N. Murrell, *ibid.*, **3**, 319 (1960).

[5] L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **91**, 6495 (1969).

[6] C. A. Parker, "Photoluminescence of Solutions," Elsevier Publishing Co., Amsterdam, 1968.

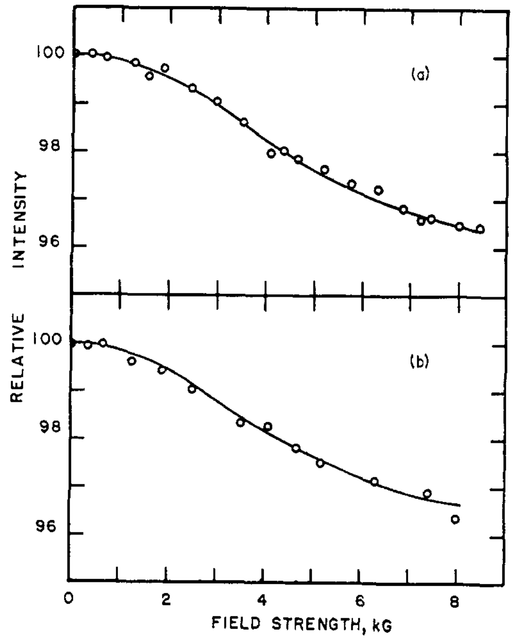

Figure 2. Magnetic field effect on delayed fluorescence from anthracene solutions in methylene chloride: (a) 3×10^{-4} *M;* (b) 8×10^{-5} *M.*

the rate constant by calculating a diffusion-limited constant for methylene chloride at 30°. Using the equation suggested by Osborne and Porter,[7] one obtains a value of 2.6×10^{10} l./(mole sec).

The results of these experiments are very relevant to the interpretation of the magnetic effects reported earlier on ECL emission from energy-deficient systems.[8] They permit one to give a coherent and plausible explanation of those effects in terms of the usually proposed mechanism involving triplet–triplet annihilations and in terms of experimentally confirmed field effects on steps included in that mechanism. One need only emphasize the importance of the radical-quenching steps toward controlling the ECL efficiency. The inhibition of those quenching steps would result in greater ECL efficiencies, hence greater intensities with increasing field. Clearly these experiments do not constitute a demonstration that the proposed mechanism for energy-deficient ECL is operative, but they are consistent with it.

(7) A. D. Osborne and G. Porter, *Proc. Roy. Soc.* (London), **A284,** 9 (1965).

(8) L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.,* **91,** 209 (1969).

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A Polyhedral Gallacarborane

Sir:

Although boron forms a considerable number and variety of electron-delocalized cage structures, including the boranes, carboranes, metalloboranes, and related systems, the remaining elements of group III have not been shown to form characterizable compounds of this type. In this report we describe the synthesis and characterization of the 1-methyl derivative of 1-galla-2,3-dicarba-*closo*-heptaborane(7) (I), for which we propose a structure in which a gallium atom is incorporated into a closed polyhedral system (Figure 1).

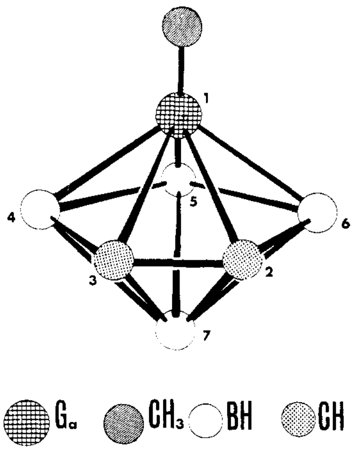

Figure 1. Proposed structure of $CH_3GaC_2B_4H_6$.

The reaction of 3 mmoles of trimethylgallium with 3 mmoles of 2,3-dicarba-*nido*-hexaborane(8) ($C_2B_4H_8$) in the gas phase at 215° produced gray solids, probably including gallium metal, and 50 mg of I (~20% yield based on $C_2B_4H_8$ consumed) plus a small quantity of trimethylboron. Following removal of the latter product by distillation at room temperature, pure I was obtained by sublimation at ~50° *in vacuo.* At room temperature I is a slightly volatile, colorless crystalline solid, mp 33.5–34.5° (sealed tube), which survives at least brief exposure to air. The mass spectrum (Table I) is characteristic of a compact cage structure and contains a sharp cutoff at *m/e* 160, corresponding to the $^{12}C_3{}^{11}B_4{}^{71}Ga{}^1H_9{}^+$ parent ion. The fragmentation pattern is in close agreement with the spectrum calculated for $C_3B_4GaH_9$ based on natural isotope distributions and indicates very little hydrogen abstraction from the parent molecule in the mass spectrometer.

Table I. Partial Mass Spectrum of $CH_3GaC_2B_4H_6$

	Rel intensity	
m/e	Calcd[a]	Found
161	1.6	1.6
160	53.3	53.8
159	53.3	54.3
158	100.0	100.0
157	83.3	81.2
156	30.2	30.5
155	5.0	5.0
154	0.3	0.4

[a] Calculated from isotopic ratios $^{11}B/^{10}B = 4.0$, $^{13}C/^{12}C = 0.011$, and $^{71}Ga/^{69}Ga = 0.667$.

The 32.1-MHz ^{11}B nmr spectrum (Figure 2) contains two partially overlapped doublets at low field and a third doublet at high field, whose relative areas indicate a 2:1:1 distribution of boron atoms with each bonded to a terminal hydrogen. The ^1H nmr spectrum in $CDCl_3$ solution contains resonances at τ 3.43 (area 2) and τ 9.83 (area 3) referenced to external tetramethylsilane, assigned to the cage CH and CH_3 groups, respectively. A quartet centered at τ 10.30 (J = 178 cps) of area 2 is attributed to the equivalent B(4)–H and B(6)–H groups,