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PHOTOPHYSICS OF N,N-DIMETHYLDIHYDROPHENAZINE AND BENZOANNELATED--ETC(U)
FEB 80 G B SCHUSTER, S P SCHMIDT, B G DIXON N00014-76-C-0745
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Absorption and fluorescence spectra, fluorescence lifetimes, and fluorescence quantum yields for 5,10-dimethyl-5,10-dihydrophenazine (DMP), 9,14-dimethyl-9,14-dihydrodibenzo[a,c]phenazine (DMAC), 9,14-dimethyl-9,14-dihydrophenanthro[4,5-abc]phenazine (DMPP) and 6,13-dimethyl-6,13-dihydrobibenzo[b,i]phenazine (DMBI) have been measured in benzene solution at room temperature. The excited state behavior of DMP, DMAC, and DMPP is similar. The long natural radiative lifetimes and large separation between absorption and emission maxima suggest that the first transition is symmetry forbidden. DMBI is unique in the series with a (cont.)

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comparatively short natural radiative lifetime and a relatively small separation between absorption and emission maxima. These results, in conjunction with PPP calculations, reveal a different hierarchy of electronic states for DMBI, such that the first transition is strongly allowed.

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Photophysics of N,N-Dimethyldihydrophenazine and Benzoannelated Analogues. Structurally Dependent Excited State Hierarchy,

by

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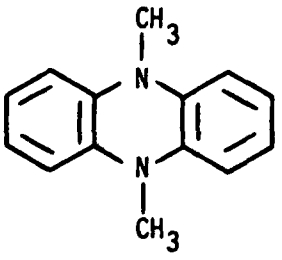
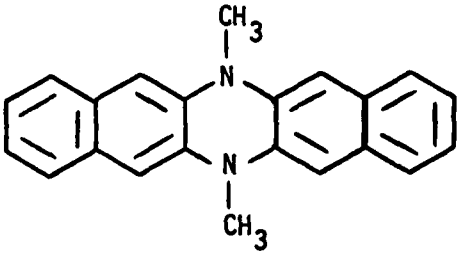
16

Introduction

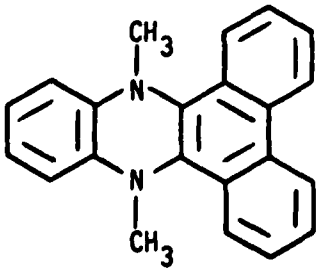
N,N-dihydrophenazines have attracted interest largely because of their relative ease of oxidation.[2] In this regard the electrochemical oxidation,[3] photochemical oxidation,[4] and photoionization[5] of 5,10-dimethyl-5,10-dihydrophenazine (DMP)' have been studied. Our initial interest in dihydrophenazines as wellwas stimulated by their ease of oxidation and hence by their candidacy as potential catalytic activators of peroxide chemiluminescence by the chemically initiated electron-exchange pathway.[6] Indeed, the dihydrophenazines we have investigated, DMP, 9,14-dimethyl-9,14-dihydrodibenzo[a,c]phenazine (DMAC) 9,14-dimethyl-9,14-dihydrophenanthro[4,5-abc]phenazine (DMPP) and 6,13-dimethyl-6,13-dihydrodibenzo[b,i]phenazine (DMBI), have proven to be among the most effective activators of dimethyldioxetanone[7] and 1-phenylperoxyacetate[8] chemiluminescence we have found.



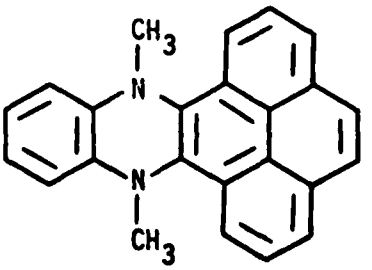
DMP



DMBI



DMAC



DMPP

In connection with our chemiluminescence studies, the excited state behavior of these dihydrophenazines also became of interest to us. Detailed spectroscopic studies of a series of N,N-disubstituted dihydrophenazines have been reported by Huber and coworkers.[9] Their work examined the effect of N-methyl versus N-phenyl substitution on absorption and emission behavior of the parent 5,10-dihydrophenazine system. In this work we examine the absorption and emission behavior of DMP and the three benzoannelated analogues DMAC, DMPP, and DMBI. Emphasis is placed on characterization of excited states and the effect of benzoannelation on the energetics and hierarchy of the excited states.

Experimental Section

Materials. DMP, prepared by the method of Gilman and Dietrich,[10] was purified by chromatography on neutral alumina, sublimation, and recrystallization from benzene-hexane. DMAC was prepared and purified as described by Smith and Levy.[11] The preparation and purification of DMPP and DMBI have been detailed elsewhere.[7] Benzene (Burdick and Jackson Laboratories, distilled in glass) was shaken with sulfuric acid, saturated sodium bicarbonate, and water, dried over calcium chloride, passed through basic alumina, and distilled under nitrogen.

Apparatus. Absorption spectra were recorded on a Cary 14 instrument. Emission spectra were obtained with a Farrand Mark IV spectrofluorometer. Fluorescence lifetimes of DMAC, DMPP, and DMBI were measured at ambient temperature by excitation with a neodymium YAG laser system (353 nm) and recorded with a Hamamatsu streak camera. The lifetime of DMP was measured in argon purged benzene with a nanosecond nitrogen laser system. Excitation was at 337 nm. The fluorescence quantum yields were determined relative to 9,10-diphenylanthracene (ϕ_f=1.0) (DMP, DMBI)or 9,10-bis(phenylethynyl)anthracene (ϕ_f=0.96) (DMAC, DMPP). Correction was made for the relative response of the photomultiplier tube.

Calculation

Spectral calculations were performed on DMBI by the PPP method. Results are summarized in Table I. The results of the CNDO/2 CI spectral calculation performed on DMP by Huber and coworkers[9] are given for comparison. The assumed geometry is one with the molecule bent along the N-N axis (C_{2V}).

Results and Discussion

The lower energy optical transitions of the absorption spectra of the dihydrophenazines in benzene at room temperature are shown in Figure 1. All are broad and structureless. Benzoannelation of DMP affords a red shift of the maximum of the first band relative to the parent compound. The first maximum of DMAC lies 15 nm to the red of the first maximum of DMP and the maxima of DMPP and DMBI are located 50 nm to the red of the DMP maximum. The DMAC and DMPP bands exhibit very long tails to the red (>100 nm), while the DMBI band does not.

The fluorescence spectra of the four dihydrophenazines in benzene solution are also shown in Figure 1. Direct comparison of these spectra is striking. The emissions of DMAC and DMPP are shaped much like that of DMP, but the maxima are shifted approximately 100 nm to the red relative to the parent compound. The emission of DMBI, clearly the exceptional spectrum of the series, shows more structure than the other emission spectra and, most significantly, the maximum is actually blue shifted by approximately 40 nm relative to that of DMP. The substantial crossover between emission and absorption bands of DMBI is also unique in this series.

The measured fluorescence lifetimes and fluorescence quantum yields, along with the natural radiative lifetimes and oscillator strengths of the four dihydrophenazines are listed in Table II. All parameters of DMAC and DMPP are similar. While the fluorescence efficiency of DMP is relatively high its fluorescence lifetime is comparatively long. Thus the natural radiative lifetime

and oscillator strength of DMP are similar to those of DMAC and DMPP. Again DMBI is unique in the series, its natural radiative lifetime being two orders of magnitude shorter than the lifetimes of the other dihydrophenazines.

In their study of the excited state behavior of DMP, Huber and coworkers concluded that the first absorption maximum does not correspond to an $S_0 \rightarrow S_1$ transition, but rather $S_0 \rightarrow S_2$. This conclusion was based on the large discrepancy between the oscillator strength calculated from emission data and the experimentally determined oscillator strength of the first absorption band (Table II), and on the large separation of fluorescence and absorption maxima. Calculations (Table I) support this contention.

In progressing through the series of phenazines to DMAC and DMPP, similar behavior is evident. Like DMP, DMAC and DMPP display large separation of absorption and emission maxima. Like DMP, the oscillator strengths calculated for the fluorescence transitions are tens of times smaller than those determined for the first absorption band (Table II). Apparently then, the first absorption bands of DMAC and DMPP do not correspond to $S_0 \rightarrow S_1$ transitions. Rather, these transitions are probably located in the very long tails of these absorptions

The spectral characteristics of the final member of the series, DMBI, differ markedly from those of the other three. Separation between emission and first absorption maxima is relatively small. The emission data summarized in Table I demonstrate the uniqueness within this series, of the emitting state of DMBI. The natural radiative lifetime is quite short, indicating a high transition probability between the emitting and the ground states, as is borne out by the large oscillator strength. This oscillator strength also compares favorably with that determined for the first broad absorption band. These findings suggest that for DMBI, unlike the other dihydrophenazines, this absorption corresponds to the $S_0 \rightarrow S_1$ transition. Thus the ordering of excited singlet states of DMBI appear to differ from that of the other dihydrophenazines.

This reordering of excited states is confirmed by the calculation, Table I. For DMBI the lowest excited state is $^1B_1$; for DMP it is the second excited state which is $^1B_1$. For both molecules the $^1A_1 \rightarrow {}^1B_1$ transition is observed as the first absorption band. For DMP this is a $S_0 \rightarrow S_2$ transition, while for DMBI this transition is $S_0 \rightarrow S_1$.

In sum, we have observed a reordering of electronic states with dibenzo[b,i]annelation of N,N-dimethyldihydrophenazines, a reordering which does not occur with dibenzo[a,c]annelation. The different character of the lowest excited singlet state is reflected experimentally in markedly different radiative lifetimes, and in the separation of emission and absorption maxima.

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References and Notes

(1) Fellow of the Alfred P. Sloan Foundation, 1977-79.

(2) N. Winograd and T. Kuwara, J. Am. Chem. Soc., 93, 4343 (1971).

(3) R. F. Nelson, D. W. Leedy, E. T. Seo, and R. N. Adams, Z. Anal. Chem., 224, 184 (1967).

(4) J. N. Clark-Lewis and K. Moody, Aust. J. Chem., 24, 2593 (1971).

(5) U. Bruhlmann and J. R. Huber, J. Phys. Chem., 91, 386 (1977)

(6) G. B. Schuster, Acc. Chem. Res., 12, 366 (1979). J.-y. Koo and G. B. Schuster, J. Am. Chem. Soc., 100, 4496 (1978)

(7) S. P. Schmidt and G. B. Schuster, J. Am. Chem. Soc., 101, 0000 (1979).

(8) B. G. Dixon and G. B. Schuster, J. Am. Chem. Soc., 101, 3116 (1979).

(9) J. V. Morris, U. Brühlmann, O. Serafimov, and J. R. Huber, Ber. Bunsenges. Phys. Chem., 78, 1348 (1974)

(10) H. Gilman and J. J. Dietrich, J. Am. Chem. Soc., 79, 6178 (1957).

(11) J. G. Smith and E. M. Levi, J. Organometal. Chem., 36, 215 (1972).

Table 1. Calculated and Experimental Optical Transitions of DMBI and DMP (C_{2v}).

DMBI					DMP[b]				
transition	wavelength, nm		oscillator strength		transition	wavelength, nm		oscillator strength	
	calc.	obs.[a]	calc.	obs.		calc.	obs.	calc.	obs.
1 $^1A_1 \rightarrow {}^1B_1$	419	397	0.95	0.15	1 $^1A_1 \rightarrow {}^1A_2$	346	370	0	
2 $^1A_1 \rightarrow {}^1A_2$	385		0		2 $^1A_1 \rightarrow {}^1B_1$	322	337	0.22	0.22
3 $^1A_1 \rightarrow {}^1A_1$	342		0		3 $^1A_1 \rightarrow {}^1A_1$	312	315	0.01	
4 $^1A_1 \rightarrow {}^1A_2$	300		0		4 $^1A_1 \rightarrow {}^1B_2$	278	266	0.16	0.07
5 $^1A_1 \rightarrow {}^1B_2$	288	296	0.17	0.37	5 $^1A_1 \rightarrow {}^1B_1$	245	248	0.83	0.67

[a] In benzene solution at 24°C

[b] Ref 9. Experimental values were determined in 3-methylpentane at 77K.

Table II. Fluorescence Lifetimes, τ_f, Fluorescence Quantum Yields, ϕ_f, Natural Radiative Lifetimes, τ_f°, and Oscillator Strengths, f°, of the dihydrophenazines in Benzene Solution at 24°C.

	τ_f, ns	ϕ_f	τ_f°, ns	f° (calc)[a]	f°[b]
DMP	84 (100)[c]	0.36 (0.48)[c]	230	0.005	.22
DMAC	3.1	0.04	77	0.02	.12
DMPP	4.4	0.03	150	0.01	.24
DMBI	1.8	0.88	2.0	0.6	.15

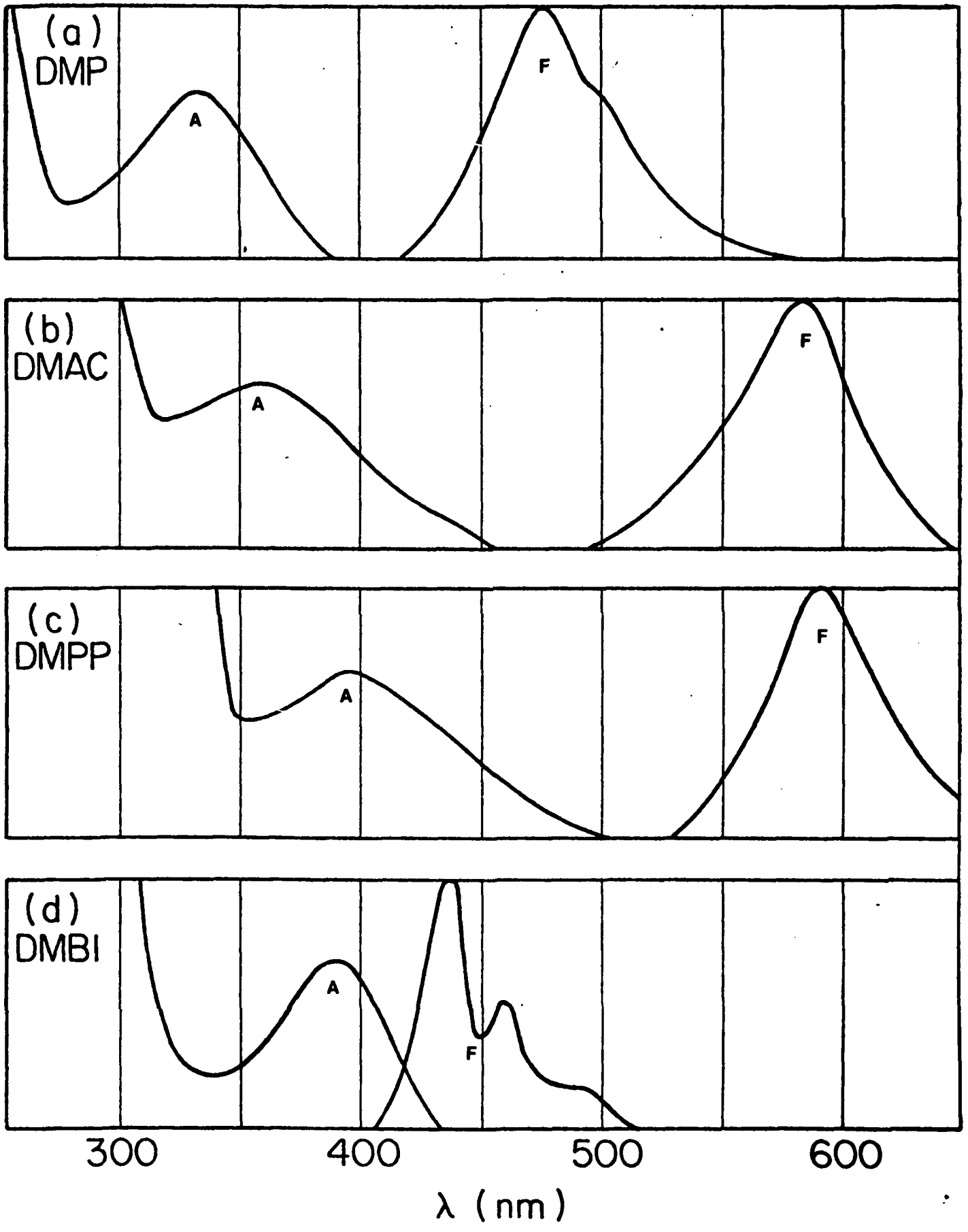
[a]Calculated from emission data according to $f^\circ \sim 1.5/(\tau_f^\circ n^2 \tilde{\nu}^2)$ where n is the index of refraction of the solvent and $\tilde{\nu}$ is the crosspoint of the absorption and emission in wavenumbers.

[b]Determined from first absorption band.

[c]Reference 9. Determined in 3-methylpentane solution at 25°C.

Caption for Figure

Absorption (A) and fluorescence (F) spectra of 5,10-dimethyl-5,10-dihydrophenazine (a), 9,14-dimethyl-9,14-dihydrodibenzo[a,c]phenazine (b), 9,14-dimethyl-9,14-dihydrophenanthro[4,5-abc]phenazine (c), and 6,13-dimethyl-6,13-dihydrodibenzo[b,i]phenazine (d) in benzene at 24°C.


(a)
DMP
A
F
(b)
DMAC
A
F
(c)
DMPP
A
F
(d)
DMBI
A
F
300
400
500
600
λ (nm)

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