

Photochemistry of Hydrazo Aromatic Molecules. I. A Spectroscopic Study of the Polarized Phosphorescence of Some Hydrazo Compounds^{1a}

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Abstract: The two lowest transitions (¹L_b and ¹L_a) in 2,2'-hydrazonaphthalene and hydrazobenzenes have been assigned with help of spectral data and P-P-P SCF MO-CI calculations of the parent molecules, 2-naphthylamine and aniline. The phosphorescence spectra of 2-naphthylamine and 2,2'-hydrazonaphthalene are negatively polarized, indicating some out-of-plane component in the emission. In-plane components also contribute significantly to the triplet-singlet transition probability. On the other hand, phosphorescence of hydrazobenzenes is either zero or positive in degree of polarization (more than 67% in-plane). Here, two-center, spin-orbit coupling terms appear to be significant, arising from nonparallel I^N and p_z^C orbital orientations. 4,4'-Dichlorohydrazobenzene shows an internal heavy-atom effect, which introduces an additional in-plane component into the phosphorescence. The phosphorescence spectrum of 4-ethoxyhydrazobenzene is nearly depolarized across the emission band with respect to excitation at 320 nm (L_b). The cause of the depolarization is unknown at the present time.

The benzidine rearrangement describes a class of acid-catalyzed and thermal reactions which have been investigated extensively.⁴ Attempts to observe photorearrangements of hydrazo aromatic compounds were recently initiated in our laboratories. Recently, also, Hashimoto, *et al.*,⁵ reported the formation of traces of semidines, as well as the commonly formed azobenzene and aniline, when hydrazobenzene was irradiated in *n*-hexane with 2538-Å light. In an effort to characterize the photochemically reactive states of hydrazo compounds, studies of the polarized phosphorescence of pertinent compounds have been carried out. It is hoped that the spectroscopic results will enhance understanding of the photochemical reactivity of hydrazo compounds.

Hydrazo compounds have not been investigated systematically by phosphorescence spectroscopy. Also, there is considerable lack of agreement in the literature on the spectroscopic properties of hydrazobenzenes, possibly because of the susceptibility of hydrazobenzenes to oxidation. Careful absorption spectra of hydrazobenzene have been reported recently by Tosi.⁶ In contrast to the situation with hydrazo compounds, azo compounds have been studied extensively.⁷

Experimental Section

Materials. The hydrazo compounds were prepared by the reduction of chromatographically purified azo compounds. For hydrazobenzene and 4-ethoxyhydrazobenzene, 0.5 g of the azo compound was dissolved in 95% ethanol. To the helium-flushed

solution was added 1 g of potassium azodicarboxylate. Water was added dropwise to the helium-agitated suspension, and when the solution became colorless an excess of water was added to precipitate the hydrazo compound. The cooled slurry was filtered under helium, and after washing, was stored in a vacuum desiccator. For 2,2'-hydrazonaphthalene and 4,4'-dichlorohydrazobenzene, a suspension of the azo compound in acetone was reduced with zinc dust and a small amount of saturated ammonium chloride solution. The colorless solution was filtered under helium into helium-flushed dilute ammonium hydroxide, and the precipitated hydrazo compound was treated and stored as described above. Commercially available 2-naphthylamine was crystallized several times from aqueous ethanol. Ethyl ether, isopentane, and other solvents were Matheson Coleman and Bell spectroquality. Absolute ethanol was redistilled.

Phosphorescence Emission, Lifetimes, and Polarization Measurements. A typical sample was prepared by dissolving a weighed amount of hydrazo compound in 50 ml of helium-flushed EPA (ethyl ether:isopentane:ethanol, 5:5:2). The solution was cooled in an ice bath while helium was bubbled through it and then capped with a rubber septum. A sample of the solution was transferred by syringe to the quartz phosphorescence cell and frozen with liquid nitrogen, giving a colorless EPA glass. Excitation and emission spectra were recorded twice, to ensure reproducibility, on an Aminco-Bowman spectrophotofluorometer equipped with a phosphoroscope and polarizers. The lifetimes were measured on an X-Y recorder equipped with a time-base scan operation.

The phosphorescence emission and excitation polarization spectra were measured at 77° K by using Glan-Thompson exciting and analyzing polarizers. The instrumental depolarizing effects (angle between the excitation and emission beams equal to 90°) were corrected according to the procedure of Azumi and McGlynn,⁸ as described previously.⁹

The slowest recorder scan rate attainable was employed in the polarization measurements. The degree of polarization was calculated using the formula

$$P = \frac{I_{EE} - I_{EB}(I_{BE}/I_{BB})}{I_{EE} + I_{EB}(I_{BE}/I_{BB})}$$

where I_{EE} , I_{EB} , I_{BE} , and I_{BB} represent the intensity for four different combinations of orientations of the prism polarizers. The subscripts E and B refer to the electric vector in the vertical and horizontal plane, respectively, and the first subscript refers to the exciting polarizer. Thus, for each run, there are four different excitation and emission spectra. The intensity at each wavelength was punched into cards as input to calculate the polarized excitation and emission spectra on an IBM 7040 computer.

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(2) Supported by the National Science Foundation, Grant No. GB-8055.

(3) Supported by the Robert A. Welch Foundation, Grant No. D-028.

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Table I. Approximate 0-0 Bands^a and Mean Lifetimes (τ)^b

Compound	¹ E	³ E	(¹ E - ³ E) ^c	τ
Aniline ^{d-f}	~33150	26800	~6350	4.5 ^g
Benzene ^d	37800	29510	8290	7.0
4,4'-Dichlorohydrazobenzene	29400 ^h	25950	3400	0.4
N,N-Dimethylaniline ^f		26500		2.6 ⁱ
4-Ethoxyhydrazobenzene	28950	25600	3350	2.3
Hydrazobenzene	29850	26300	3550	2.4
2,2'-Hydrazonaphthalene	25950	20850	5100	2.0
Naphthalene ^{d,j}	31750	21420	10330	2.6
2-Naphthol ^k	~30120	21100	~9020	1.3
2-Naphthylamine	27000 ^h	21550	5450	1.3

^a In cm⁻¹. ^b In sec. ^c Frequencies were read from the polarized excitation and emission spectra wherever possible. ^d D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). ^e I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, 12 C. ^f See ref 16. ^g 7.5 sec (natural). ^h When the polarized spectra were not easily used, the long wavelength end of the absorption spectrum was taken as the 0-0 band. ⁱ 2.8 sec (natural): ref 24. ^j See ref 14. ^k 54 C of the reference in footnote e. Also see ref 15.

Table II. Transition Energies, Oscillator Strengths (f), and Wave Functions (CI) for 2-Naphthylamine Calculated by the P-P-P SCF MO-CI Procedure

$\pi \rightarrow \pi^*$	eV	nm	f	ψ	Δq_N^b
¹ L _b	4.04	307 (337) ^a	0.04	0.6L _b + 0.5L _a - 0.2B _a + 0.6B _b	0.06e
³ L _b	3.41	364 (?)		0.8L _b + 0.2L _a - 0.2B _a - 0.4B _b	0.06
¹ L _a	4.45	279 (282)	0.20	0.8L _a - 0.4L _b - 0.2B _a - 0.3B _b	0.01
³ L _a	1.89	656 (506)		0.9L _a - 0.2L _b - 0.2B _a - 0.1B _b	0.02
¹ B _a	6.31	196 (?)	0.31	0.7B _a + 0.0L _b + 0.2L _a + 0.1B _b	0.01
¹ B _b	5.62	221 (237)	1.73	0.7B _b - 0.7L _b - 0.0L _a - 0.1B _a	0.08

^a Experimental values in parentheses. ^b The charge transfer from -NH₂ to ring upon excitation.

Absorption Spectra. All spectra were recorded at room temperature on a Beckman Model DK-2A spectrophotometer.

Molecular Orbital Computations of Transition Energies and Transition Moments. The Pariser-Parr-Pople SCF MO-CI method^{10,11} within the framework of the restricted Hartree-Fock-Roothaan formulation was used to calculate the transition energies and transition moments in aniline and 2-naphthylamine, these being used as model compounds for interpreting spectral data reported in the present work. A brief outline of the method as applied to flavins has been given previously.⁹

In the evaluation of the Fock matrix elements, according to the Goeppert-Meyer and Sklar (GMS) potential, the values of the ionization potentials were 11.16 eV for carbon and 28.85 for nitrogen; the one-electron core Hamiltonian matrix element β_{rs} was -2.39 eV for a C-C bond and -2.399 for a C-N bond; one-center, electron-repulsion integrals were 11.13 eV for carbon and 16.57 for nitrogen. Two-center, electron-repulsion integrals were evaluated by the Mataga-Nishimoto formula.¹² The configuration interaction (CI) matrices were constructed with 16-30 singly excited configurations. The input geometries for aniline and naphthalene were taken from "Tables of Interatomic Distances."¹³ All computations were performed on an IBM 7040 using FORTRAN IV, and were repeated on a CDC 1604 using FORTRAN 63.

Results and Discussion

Phosphorescence Spectra and Lifetimes. The pertinent phosphorescence data are listed in Table I. The lowest excited singlet and triplet states are assigned to ¹(π, π^*) and ³(π, π^*) because the most likely transitions involve either π electrons or lone-pair electrons in

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conjugation with, and, therefore, part of the π -electron system.

The 0-0 phosphorescence band of 2-naphthylamine is not significantly different from that of either naphthalene¹⁴ or 2-naphthol.¹⁵ However, the phosphorescence lifetimes of 2-naphthylamine and 2-naphthol are identical and shorter than that of naphthalene. The spin-orbit contribution of the 2 substituents to the singlet-triplet transition probability is thus of interest and will be discussed further. The similarities among the spectra of 2,2'-hydrazonaphthalene, 2-naphthylamine, and naphthalene, are sufficient to permit the assignment of bands in the spectra of the first two compounds on the basis of the bands in the naphthalene spectrum. It is particularly noticeable that the 0-0 phosphorescence bands and lifetimes are similar for these three compounds.

The situation is quite different with 2,2'-hydrazobenzene, whose lifetime is considerably shorter than

than of aniline and benzene. It seems that there is an added spin-orbit perturbation introduced by the hydrazo group into the singlet-triplet transition probability, which is not experienced with 2,2'-hydrazonaphthalene. The difference between the two cases probably reflects a difference in the conformational environments of the two hydrazo groups. For example, it is well established that the observed and natural lifetimes of anilines decrease with steric hindrance around the lone-pair orbital of the amino nitrogen,¹⁶ suggesting that the aromatic rings in hydrazobenzene and 2,2'-hydrazonaphthalene may have somewhat different orientations around the respective hydrazo groups.

The data for 4-ethoxyhydrazobenzene are similar to those of hydrazobenzene, whereas the very short lifetime of 4,4'-dichlorohydrazobenzene suggests the existence of an internal spin-orbit coupling contribution of the heavy chlorine substituents.

In general, the singlet-triplet intervals of the hydrazo compounds (3000-5000 cm⁻¹) are considerably smaller than those of the parent hydrocarbons,^{7b} indicating that the ¹L_b states of these compounds possess some (l, a_π) character.

2-Naphthylamine. The spectroscopic data for 2-naphthylamine are recorded in Figures 1 and 2 and in Table II. The absorption spectrum of 2-naphthylamine can be related to that of naphthalene by assigning transitions (first four bands) of 2-naphthylamine ac-

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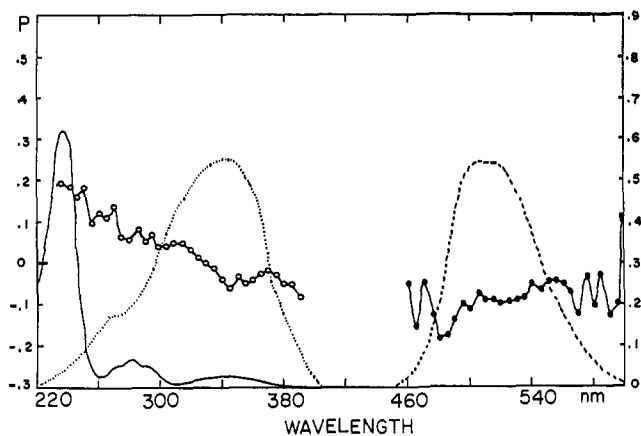


Figure 1. Spectra of 2-naphthylamine: —, absorption; ····, phosphorescence excitation ($1.9 \times 10^{-3} M$) with $\lambda_{em} = 508$ nm; phosphorescence emission with $\lambda_{ex} = 342$ nm; ○, polarized phosphorescence excitation; and ●, polarized phosphorescence emission. The polarized spectra refer to the left abscissa where P is degree of polarization. The right abscissa indicates relative intensity or relative absorbance.

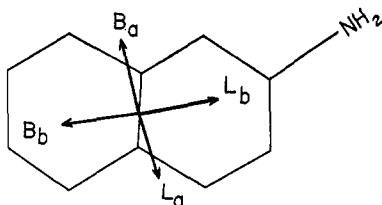


Figure 2. The calculated polarizations of the four lowest transition moments in 2-naphthylamine.

cording to the Platt notation, and the form of the wave functions with reference to naphthalene.

Agreement between the calculated and observed Franck-Condon bands for the singlet-singlet transition energies (Table II) is satisfactory. The calculated oscillator strengths of 2-naphthylamine are also consistent with the relative absorptivities of the spectrum in Figure 1. Configuration interaction among the four lowest excited configurations is very extensive. A similar observation has been made in the case of naphthalene and indole.¹⁷ On the basis of the data in Table II and Figure 2 we assign the absorption and polarized phosphorescence excitation spectra of 2-naphthylamine as L_b (337 nm), L_a (282 nm), and B_b (237 nm).

The polarizations of the four lowest transitions of 2-naphthylamine (Figure 2) are generally similar to those of naphthalene, but slight perturbation by the amino group has caused the directions of the polarizations to be somewhat altered from those in naphthalene. The L_b and B_b species, with direction approximately toward the substituent, thus show some CT character (Table II). Therefore, it is reasonable to label the L_b as partly an analog of an $l \rightarrow a_r$ transition.

With this information on the singlet transitions we can attempt to interpret the polarized phosphorescence spectrum of 2-naphthylamine.

Figure 1 shows that the 0-0 phosphorescence band region is negatively polarized with respect to L_b . Negative polarization is confirmed in the polarized phospho-

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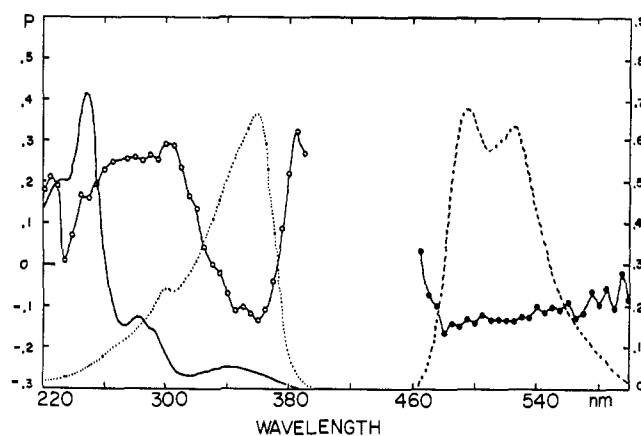


Figure 3. Spectra of 2,2'-hydrazonaphthalene ($1 \times 10^{-3} M$). $\lambda_{em} = 493$ and $\lambda_{ex} = 352$ nm. See caption for Figure 1.

rescence excitation spectrum in the long-wavelength end of the L_b band. The degree of polarization is -0.05 , which indicates that more than 33% of the 0-0 phosphorescence intensity is due to the out-of-plane component. On the other hand, both the L_a and B_b bands show a degree of positive polarization with respect to the emission oscillator at 508 nm. It can be concluded that the 0-0 phosphorescence band, where combining zero point vibrational states are probably totally symmetric, is polarized perpendicular to the molecular plane as a result of the spin-orbit coupling between 3L_a (see Table I) and $^1(\sigma, \pi)^*$ states. However, the in-plane component also contributes to the singlet-triplet transition probability to increase the degree of polarization. The increase in the degree of excitation polarization in the shorter wavelength region suggests a stronger vibronic coupling between 1B_b and $^1(\sigma, \pi)^*$ states than between 1L_a and high-lying, out-of-plane states. Alternatively, the positive polarization in the excitation and emission bands can be regarded as being due to the two-center, spin-orbit contribution of the amino substituent. If the lone-pair orbital is not completely parallel with the carbon p_r orbital at position 2 of the ring, the two-center, spin-orbit coupling matrix element will not be negligible, and its magnitude will be determined by the twisting angle, θ ¹⁸⁻²⁰

$$\langle 2p_z^C | H_{SO} | 2p_z^N \rangle \sin \theta$$

where $2p_z^N$ is the sp^2 -hybridized, lone-pair orbital, and H_{SO} is the spin-orbit operator which contains a rotation (90°) operator. The magnitude of such a two-center term may be only moderate in 2-naphthylamine, since the lifetime of 2-naphthylamine is only half that of naphthalene, a fact which suggests that the angle θ is not large.

2,2'-Hydrazonaphthalene. The relevant spectra are given in Figure 3. The phosphorescence emission is negatively polarized with respect to L_b . The polarized phosphorescence excitation spectrum indicates that

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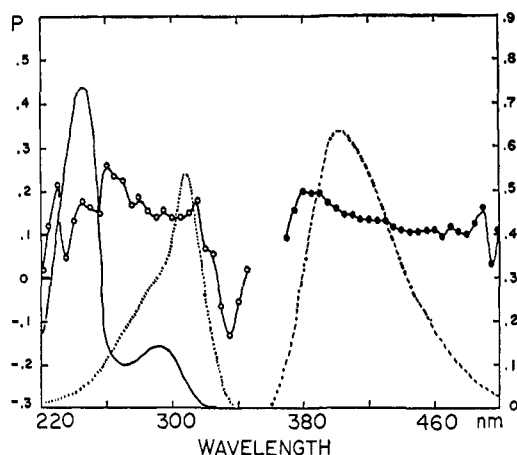


Figure 4. Spectra of hydrazobenzene ($3.6 \times 10^{-3} M$). $\lambda_{em} = 403$ and $\lambda_{ex} = 396$ nm. See caption for Figure 1.

there is also a significant contribution from the in-plane component (L_a and B_b).

The spectra of 2,2'-hydrazonaphthalene differ in several ways from those of 2-naphthylamine. First, the B_b band is red-shifted with a shoulder at 230 nm. Second, the L_a band and the long-wavelength end of the L_b band show a considerable degree of positive polarization with respect to the emission oscillator at 493 nm. Third, the phosphorescence spectrum shows two peaks instead of one broad band. We cannot say whether the positive polarization of the long-wavelength end of the L_b band represents the 0-0 absorption band of L_b or L_a each having CT character. The band is tentatively assigned to the 0-0 L_b (Table I). In so doing the singlet-triplet interval becomes close to that of 2-naphthylamine, as may be expected. It is also possible, however, that the positive polarization of the long-wavelength end of the L_b band represents a new transition arising from weak interactions between either the two rings or the nonplanar, lone-pair orbitals of the NH-NH group. The weak excitation intensity in this region makes the obtaining of phosphorescence emission and polarization spectra for further analysis very difficult. It is apparent, nevertheless, that the Franck-Condon-allowed vibronic bands of L_b are all negatively polarized with respect to the singlet-triplet transition moment.

From the point of view of lone-pair orbital orientation it appears that 2,2'-hydrazonaphthalene can be thought of as two independent naphthylamine molecules, without an appreciable twisting angle θ between the l and p_z orbitals. The positive polarization (practically all in-plane in phosphorescence) across the L_a and B_b excitation bands suggests a contribution from the in-plane singlet-singlet transition moments to the triplet-singlet emission. However, as mentioned in the discussion of the 2-naphthylamine spectra, the twisting angle θ between the lone-pair and the carbon p_z orbitals cannot be large enough to account for all the in-plane component. Higher resolution spectra and a theoretical investigation of multicenter, spin-orbit coupling terms would be helpful in delineating the source of the in-plane components (L_a and B_b) in the phosphorescence emission of 2,2'-hydrazonaphthalene.

Hydrazobenzene. The relevant spectra are given in Figure 4. The long-wavelength band of the absorption

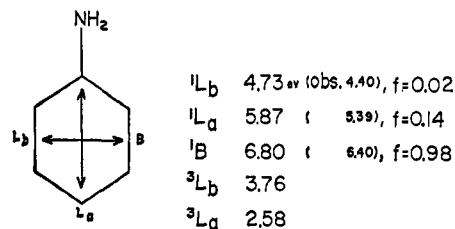


Figure 5. The predicted directions of the three lowest transition moments, energies (in eV), and oscillator strengths (f) for aniline.

spectrum (290 nm) is assigned to L_b (290 nm in aniline) while the short-wavelength band (245 nm) is assigned to L_a (245 nm in aniline). Other bands, such as B species, are not seen. The assignments are also consistent with the direction of polarization of L_b , L_a , and B species (Figure 5). The 0-0 phosphorescence band and its vibronic components are all positively polarized (degree 0.1 or higher with respect to the 306-nm excitation). This implies that the in-plane component predominates in the phosphorescence. The polarized phosphorescence excitation spectrum is also positively polarized, confirming the predominant in-plane orientation of the singlet-triplet transition moment. However, the 0-0 L_b band seems to be perpendicularly polarized with respect to the phosphorescence emission oscillator (Figure 4). The negative polarization of the 0-0 excitation region (L_b) is consistent with the contribution of out-of-plane components in emission.

Vibronic bands across L_b and L_a are positively polarized, which may be interpreted as arising from vibrational modes involving distortion or twisting vibration of hydrazobenzene. The predominant in-plane component in the emission can then be explained in terms of two-center, spin-orbit coupling between l and p_z orbitals. This seems to be reflected in the phosphorescence lifetime of hydrazobenzene. Our results with hydrazobenzene are consistent with the interpretation of the spectra of sterically hindered anilines by Lim and coworkers,¹⁶ in which the L_b and L_a bands are positively polarized with respect to phosphorescence emission.

The angle between the l and p_z orbitals in aniline is reported to be 46° .²¹ The most likely geometry of hydrazobenzene is *trans*, and the twisting angle is probably larger than 46° because of N-H and $C_{2,6}$ -H hydrogen-hydrogen interactions. The twisting angle is apparently larger than that in 2,2'-hydrazonaphthalene.

There is one feature common to the polarized phosphorescence spectra of hydrazobenzene and 2,2'-hydrazonaphthalene. The singlet-singlet transition moments oriented approximately perpendicular to the direction of the amino substituent (L_a in hydrazonaphthalene, and L_b in hydrazobenzene) contribute significantly to the in-plane component of their respective phosphorescence emission. This comparative aspect is, of course, restricted to the two lowest transitions (L_b and L_a), since B bands are too high in energy for hydrazobenzene. By using aniline²² and the phenoxide ion²³ for analogy, and with the help of Figure 5, we have

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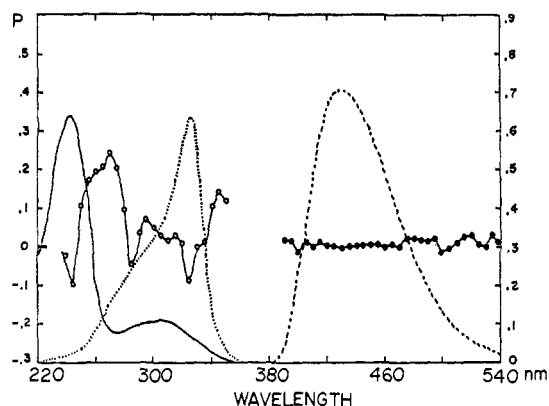


Figure 6. Spectra of 4-ethoxyhydrazobenzene ($4.5 \times 10^{-3} M$). $\lambda_{em} = 427$ and $\lambda_{ex} = 320$ nm. See caption for Figure 1.

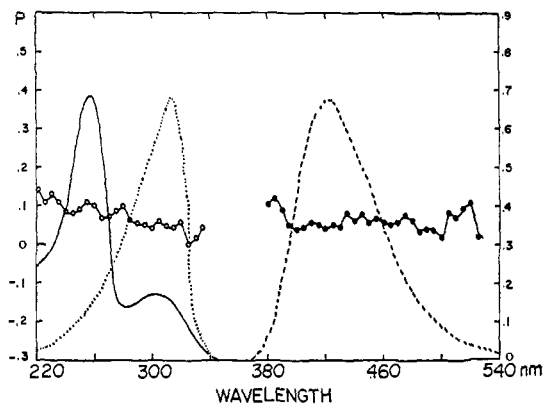


Figure 7. Spectra of 4,4'-dichlorohydrazobenzene ($1.1 \times 10^{-3} M$). $\lambda_{em} = 424$ and $\lambda_{ex} = 310$ nm. See caption for Figure 1.

assigned the phosphorescent state of hydrazobenzene to 3L_a .

4-Ethoxyhydrazobenzene. The relevant spectra are given in Figure 6. The 1L_b and phosphorescence bands are red-shifted, while the L_a band is at about the same position with respect to hydrazobenzene (Figure 4). The general features of the polarized phosphorescence spectra of the two compounds are qualitatively similar; that is, the excitation bands are positively polarized with respect to the emission at 427 nm. On the other hand the degree of phosphorescence polarization is nearly zero (cf. 0.1 for hydrazobenzene), corresponding with about 33% out-of-plane and 67% in-plane components.²⁴ This is because the excitation was set at 320 nm where the degree of excitation polarization is approximately zero. If we rule out the possibility of depolarization due to inter- or intramolecular energy transfer, the near-zero polarization would mean that the phosphorescence possesses coincidentally equal contributions of all three components (x , y , and z). Alternatively, depolarization can be obtained through intramolecular relaxation processes, such as the torsional vibration around the hydrazo bond, a possibility which is not unreasonable because the potential energy curve for torsional vibration about the NH-NH bond is rather shallow.²⁵

4,4'-Dichlorohydrazobenzene. The relevant spectra are given in Figure 7. The lifetime of phosphorescence (Table I) is considerably shorter than that of hydrazobenzene. This is most likely due to the internal heavy-atom effect of chlorine (one-center, spin-orbit coupling), a possibility which is supported by the positive degree of polarization. Both the two-center, spin-orbit coupling (between the I, a_π and the singlet-triplet transitions) and the vibronic spin-orbit coupling (be-

tween the π, π^* and singlet-triplet transitions²⁶) introduce the in-plane character of the phosphorescence emission. It is thus likely that the in-plane component predominates in the singlet-triplet transition moment of 4,4'-dichlorohydrazobenzene.

Conclusions

(1) The spin-allowed singlet transitions in 2,2'-hydrazonaphthalene and hydrazobenzenes can be assigned with the use of data for the parent molecules, 2-naphthylamine and aniline, respectively, and the aid of P-P-P SCF MO-CI calculations. Perturbation by the hydrazo substituent was not large enough to affect at least the two lowest transitions, 1L_b and 1L_a .

(2) The phosphorescence spectra of both 2-naphthylamine and 2,2'-hydrazonaphthalene are negatively polarized with respect to excitation in the L_b region, indicating that phosphorescence emission contains some out-of-plane component. In-plane components also contribute significantly to the emission, particularly by borrowing intensities from the Franck-Condon L_a bands. 2,2'-Hydrazonaphthalene can be regarded as consisting of two independent 2-naphthylamine molecules with only weak interaction.

(3) The phosphorescence of the hydrazobenzenes is either zero or positive in degree of polarization. Two-center, spin-orbit coupling terms appear to be present, arising from either nonplanar C-NH bonds or non-parallel I and p_z orbitals.

(4) An internal, heavy-atom effect is found in 4,4'-dichlorohydrazobenzene, which introduces an in-plane component to the phosphorescence.

(5) The phosphorescence spectrum of 4-ethoxyhydrazobenzene is nearly depolarized across the emission band with respect to excitation at 320 nm (L_b). The cause of this depolarization is not known.

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