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Electronic Spectra and Electronic Structures of Aminoanthracenes

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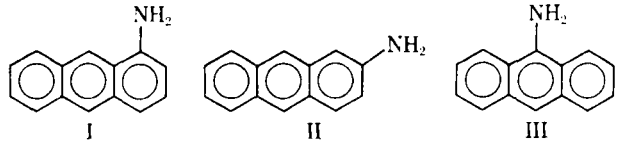
Abstract □ The electronic absorption and fluorescence spectra of the cation derived from 9-aminoanthracene (9-anthrylamine), in water, are anomalous by comparison with those of the 1- and 2-anthrylammonium ions. The similarities of the spectra of the cation of 9-anthrylamine with those of anthrone and its cation lead to the conclusion that the former cation is not the 9-anthrylammonium ion but rather its tautomer, the protonated imine analogous to anthrone. In ethanol and in the solid state, measurable quantities of both the protonated imine and 9-anthrylammonium ions exist.

Keyphrases □ Aminoanthracenes—electronic spectra and electronic structures □ Absorption spectra, electronic, aminoanthracenes—determination □ Fluorescence spectra, electronic aminoanthracenes—determination □ Electronic spectra and electronic structures—determination, aminoanthracenes □ Anthrylamines—electronic spectra and electronic structures

The carcinogenicity of many polycyclic aromatic amines has been recognized since 2-naphthylamine was found to cause bladder cancers in workers in the dye industry (1, 2). Of the arylamines known to have carcinogenic properties, 1-aminoanthracene (I) and, especially, 2-aminoanthracene (2-anthrylamine) (II) are among the most virulent. However, to our knowledge, no carcinogenic properties have been reported for 9-aminoanthracene (III).

Of the functionally substituted aromatic molecules, the derivatives of anthracene have not been particularly well characterized, although many of them have been employed in the dye industry for many years. Recent studies have shown that, in particular, substitution in the 9-position of the anthracene ring often results in molecular species that are quite different in their chemical properties from other aromatic molecules (*e.g.*, benzene and naphthalene) substituted with the same functional groups. On the other hand, substitution in the 1- and 2-positions of the anthracene ring yields derivatives that are similar to the corresponding benzene and naphthalene derivatives. For example, in hydrocarbon solvents, the carboxyl groups of benzoic acid, 1- and 2-naphthoic acids, and 1- and 2-anthroic acids are coplanar and conjugated with the respective aromatic rings, while the carboxyl group of 9-anthroic acid (3) is perpendicular and unconjugated with the anthracene ring as a result of steric interference of the 9-carboxyl group with the peri hydrogen atoms in the 1- and 8-positions of the anthracene ring. Moreover, of the hydroxyanthracenes, 1- and 2-anthrols appear to be well-behaved phenolic molecules (4) while 9-anthrol exists predominately as its keto tautomer, anthrone, and only to a very slight extent as the phenolic 9-anthrol (5, 6).



I II III

Because of interests in the relationships between molecular electronic structure and biological (in this case carcinogenic) activity, the present investigation of the electronic structures of the isomeric aminoanthracenes by electronic absorption and fluorescence spectroscopy was undertaken.

EXPERIMENTAL

Reagents—The 1- and 2-aminoanthracenes[1], anthracene, and 9-aminoanthracene hydrochloride[2] were each recrystallized several times from absolute ethanol.

Analytical reagent grade sulfuric acid[3] was diluted with distilled, deionized water to prepare the solutions used to study the Hammett acidity region. Solutions in the pH range were citrate and phosphate buffers and sodium hydroxide solutions in distilled, deionized water.

Each sulfuric acid or buffer solution in a 10-ml. volumetric flask was injected with 100 μl. of a 1×10^{-2} *M* stock solution of the appropriate aminoacridine in absolute ethanol immediately prior to

[1] Aldrich Chemical Co., Milwaukee, Wis.
[2] K&K Chemical Co., Plainview, N. Y.
[3] Mallinckrodt Chemical Works, St. Louis, Mo.

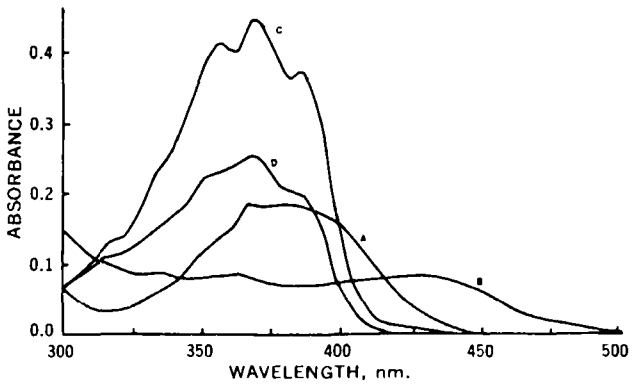


Figure 1—*Electronic absorption spectra of about 1 × 10⁻⁴ M 1-aminoanthracene (A) and 2-aminoanthracene (B) at pH 10.0 and of the respective anthrylammonium ions (C and D) at pH 1.0.*

the taking of spectra to minimize decomposition errors. The spectra of 1×10^{-5} *M* aqueous anthracene were taken in only one solution, pH 10.0.

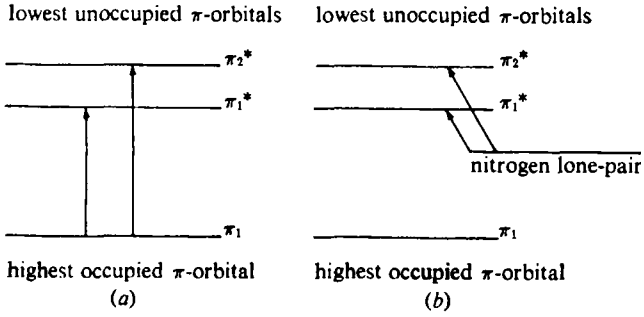
Apparatus—Absorption spectra were taken on a spectrophotometer[4]. Fluorescence spectra were taken on a fluorescence spectrophotometer[5] whose monochromators were calibrated against the xenon line emission spectrum and whose output was corrected for instrumental response by means of a rhodamine-B quantum counter. The pH measurements were made on a pH meter[6] employing a silver-silver chloride-glass combination electrode[7]. IR spectra[8] were taken in silicone fluid.

RESULTS AND DISCUSSION

1- and 2-Aminoanthracenes—The electronic absorption spectra of 1- and 2-aminoanthracenes and their conjugate cations are shown in Fig. 1. The maxima of these and the corresponding fluorescence spectra, along with those of 9-aminoanthracene, its conjugate cation, and anthracene, for comparison, are presented in Table I.

The absorption and fluorescence spectra of the cations of the 1- and 2-isomers are highly structured and similar to those of anthracene itself. The absorption spectra of the neutral 1- and 2-aminoanthracenes, however, each show a diffuse band at ~400 nm. and a partially overlapping vibrational structured band at shorter wavelengths. The fluorescence spectra of the neutral amines are unstructured and lie at wavelengths (~500 nm.) much longer than those of the fluorescence of anthracene (~400 nm.). These spectra are typical of anthracene derivatives and of amino- and ammonium-substituted aromatics and may be explained as follows.

The absorption spectrum of anthracene in the 300–500-nm. region is comprised of two electronic transitions, designated $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ in Platt's system of classification of electronic transitions (7). ^1A designates the ground singlet state, and ^1L_a and ^1L_b are the two lowest electronically excited singlet states. The ^1L_a and ^1L_b



Scheme I—Electronic transitions in anthracene and aminoanthracenes: (a) anthracene and anthrylammonium ions, and (b) anthrylamines

[4] Beckman DB-GT.
[5] Perkin-Elmer MPF-2A.
[6] Orion Model 801.
[7] Beckman.
[8] Beckman model 33 IR spectrophotometer.

Table I—Electronic Absorption (λ_a) (in the 300–500-nm. Region) and Fluorescence (λ_f) Maxima of the 1-, 2-, and 9-Aminoanthracenes and Their Conjugate Cations in Water[a]

	Cation (H_0 − 1.6)		Neutral Amine (pH 10.0)	
	λ_a	λ_f	λ_a	λ_f
1-Aminoanthracene	386	383	378(^1L_a)	530
	369	402	378	
	357	420	363 (^1L_b)	
	342	446	347	
	335		329	
	318			
2-Aminoanthracene	381	387	427(^1L_b)	503
	365	405		
	352	422	362	
	335		343 (^1L_a)	
	327		335	
	320		313	
9-Aminoanthracene	340(sh)	450	400(^1L_a)	519
	301		372	
			353 (^1L_b)	
	Neutral Molecule (pH 10.0)			
Anthracene	λ_a		λ_f	
	377		380	
	358		400	
	341		417	
	326		440	
	312			
	299			

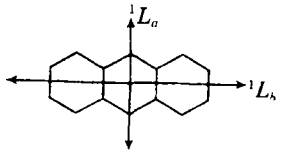
[a] The corresponding spectral features of anthracene in water (pH 10.0) are given for comparison. Spectral maxima are reported in nanometers.

states are derived from the promotion of an electron from the highest occupied π-orbital in the ground state to either of the two lowest unoccupied orbitals (π*) of the anthracene molecule (Scheme I).

In anthracene, the molecular skeleton is fairly rigid, restricting the vibrational freedom of the molecule. The vibrational subtransitions accompanying the electronic transitions occur with essentially no readjustment of the nuclear positions (vibrational motion) during electronic transition. This is a result of the greater rate of the average electronic transition (~10^{15} sec.$^{-1}$) compared with that of the average vibrational transition (~10^{14} sec.$^{-1}$) and represents a statement of the Franck–Condon principle (8, 9). As a result, the vibrational sublevels to which absorption takes place are well defined (quantized) and the vibrational-electronic (vibronic) fine structure of the absorption bands is thus distinct in anthracene. The $^1L_b \leftarrow {}^1A$ transition is polarized along the long axis and the $^1L_a \leftarrow {}^1A$ transition along the short axis of anthracene (Scheme II).

In smaller aromatic molecules (10) (*e.g.*, benzene and naphthalene), the $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions are well resolved, with the $^1L_b \leftarrow {}^1A$ absorption lying at longer wavelengths. In higher aromatics (*e.g.*, tetracene and pentacene), the absorption bands representing the $^1L_a \leftarrow {}^1A$ transitions occur at longer wavelengths than $^1L_b \leftarrow {}^1A$ transitions (10). In anthracene, the absorption bands representing the two transitions overlap to such an extent that they are indistinguishable. However, it is generally believed that the long wavelength side of the $^1L_b \leftarrow {}^1A$ band lies at longer wavelengths than the $^1L_b \leftarrow {}^1A$ band in anthracene.

The introduction of an amino group into the anthracene ring affects the spectra in ways that depend upon the site of substitution in the ring. The amino group has a lone electron pair residing in an orbital on the nitrogen atom, with sp^3 hybrid characteristics. Although this orbital is not perpendicular to the anthracene ring, as are the carbon $2p_z$ orbitals comprising the π-system of the ring, it has a substantial component in that direction; therefore, some in-



Scheme II—Polarizations of the two lowest π → π transitions of anthracene*

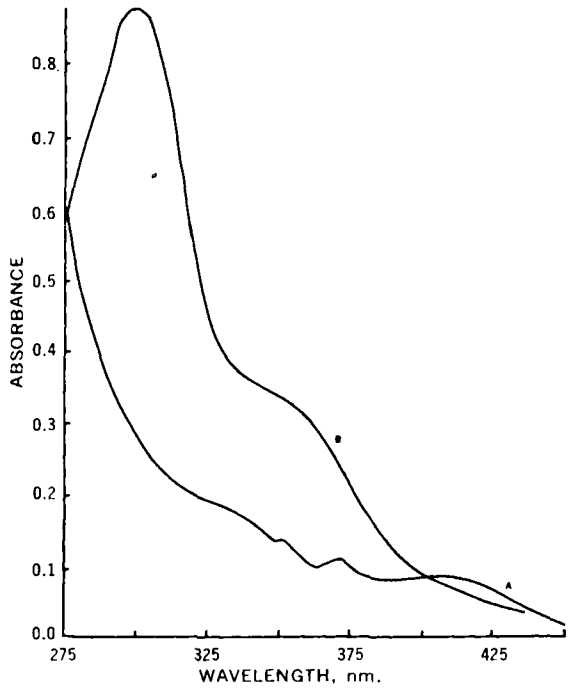


Figure 2—*Electronic absorption spectra of about 1 × 10⁻⁴ M 9-aminoanthracene (A) at pH 10.0 and of the protonated species derived from 9-aminoanthracene (B) at pH 1.0.*

teraction between the lone-pair and the π-system is to be expected even in the ground electronic state (conjugation or resonance interaction). Upon excitation, however, an electron may be transferred completely from the nitrogen lone-pair into a vacant π^*-orbital of the aromatic ring (intramolecular charge-transfer transition). This process results in greater conjugation of the amino group with the aromatic ring and produces rehybridization of the amino nitrogen atom to an sp^2-type configuration (coplanar with the ring) during the electronic transition [*i.e.*, the Franck-Condon principle is violated (11)].

In the perturbation model of aromatic substitution (12), the lone-pair orbital is at higher energy than the highest occupied π-orbital of the ring in the ground state. This occurs because the lone-pair electrons are not as stabilized as the π-electrons by the π-bonding interaction. Because the lone-pair orbital is higher in energy than the highest occupied π-orbital, the lowest energy transitions of the amino derivatives occur at lower energies (or longer wavelengths) than the lowest energy $\pi \rightarrow \pi^*$ transitions of anthracene itself. The promotion of an electron from the lone electron pair of the amino group is said to mix charge transfer into the $\pi \rightarrow \pi^*$ transitions of the parent hydrocarbon (in the terminology of the perturbation model). The rehybridization of the amino group during the absorption process results in the loss of vibrational structure in those transitions having a great deal of charge-transfer character. Because of the transition polarizations and orbital properties (charge densities) associated with the ^1L_a and ^1L_b excited states (the two lowest excited states), substitution in the 1- and 9-positions (α-positions) of the anthracene ring by an amino group introduces considerable charge-transfer character and vibrational blurring into the $^1L_a \leftarrow {}^1A$ transition of anthracene and practically none into the $^1L_b \leftarrow {}^1A$ transition. This is a result of the colinearity between the $^1L_a \leftarrow {}^1A$ transition, the direction of transfer of charge into the ring from an amino substituent in an α-position, and the perpendicularity between the $^1L_b \leftarrow {}^1A$ transition moment direction and that of charge transfer from an α-amino group. On the other hand, β-substitution (in the 2-position of anthracene) of an amino group results in a large angle between the $^1L_a \leftarrow {}^1A$ transition moment vector and the vector associated with the direction of charge transfer from a β-amino group to the anthracene ring but a much smaller angle between the latter and the $^1L_b \leftarrow {}^1A$ transition moment vector. Consequently, the $^1L_b \leftarrow {}^1A$ transition has the greatest degree of charge transfer, exhibits vibrational blurring, and lies at the longest wavelengths in 2-aminoanthracene while the $^1L_a \leftarrow {}^1A$ transition is only slightly affected.

Protonation of the nitrogen atoms of the anthrylamines removes the lone-pairs from conjugation with the aromatic system, so the spectra of all of the anthrylammonium ions are very close in appearance to that of anthracene, with slight displacements to longer wavelengths because the positive field effect of the ammonium substituent stabilizes the dipolar excited states slightly more than the nearly apolar ground states.

Fluorescence in 1-anthrylamine corresponds to the $^1L_a \rightarrow {}^1A$ transition; in 2-anthrylamine, it arises from the $^1L_b \rightarrow {}^1A$ transition because the ^1L_a and ^1L_b states are the lowest excited singlet states in the 1- and 2-isomers, respectively. During fluorescence, charge is transferred back from the anthracene ring to the amino group and is accompanied by rehybridization of the amino group from an sp^2 to an sp^3 situation. Consequently, the fluorescence bands of 1- and 2-aminoanthracenes are diffuse. That the fluorescence bands of the 1- and 2-aminoanthracenes appear at a much longer wavelength than the corresponding absorption bands is the result of a high energy of solvent cage reorientation, subsequent to excitation, which is reflected in the fluorescence but not in the absorption spectrum, and a small energy of solvent cage reorientation subsequent to emission, which is reflected in the absorption but not in the fluorescence spectrum (13). This is generally observed in intramolecular charge-transfer transitions of molecules which are more polar in the excited state than in the ground state.

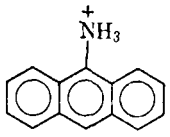
The fluorescences of the 1- and 2-anthrylammonium ions are similar to those of anthracene and, lacking intramolecular charge-transfer properties, are highly structured. On the basis of the present experiments, it cannot be stated with certainty whether the fluorescences of the anthrylammonium ions originate from the ^1L_a or ^1L_b states.

The similarities between the absorption and fluorescence spectra of anthracene and the anthrylammonium ions are typical of the spectroscopic behavior of arylammonium ions. For example, the spectra of the anilinium ion are similar to those of benzene, while the spectra of the 1- and 2-naphthylammonium ions are similar to those of naphthalene (14–16). Moreover, the differences between the absorption and fluorescence spectra of anthracene and the 1- and 2-anthrylamines are comparable to the differences between the absorption and fluorescence spectra of benzene and aniline and between those of naphthalene and the 1- and 2-naphthylamines. Thus, in the electronic structural sense, the 1- and 2-aminoanthracenes and their conjugate cations may be considered to be well-behaved aminoanthracenes and anthrylammonium ions, respectively.

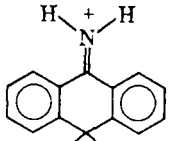
The pKa values for the prototropic equilibria at 25° between the 1- and 2-aminoanthracenes and their respective conjugate cations were determined by spectrophotometric pH titration and are: 1-aminoanthracene, 3.85 ± 0.00; and 2-aminoanthracene, 4.00 ± 0.04. These pKa values are representative of arylamines in general. Moreover, the slightly more acidic pKa of the 1-isomer is consistent with the weaker basicity of α-arylamines relative to β-arylamines. For example, the pKa of 1-naphthylamine is 3.92 and that of 2-naphthylamine is 4.11 (17). This difference is derived from the greater degree of conjugative interaction in α-positions than in β-positions of linearly annellated polyacene rings. The pKa values support the conclusion that the 1- and 2-aminoanthracenes and their conjugate cations are chemically well-behaved arylamines and arylammonium ions, respectively.

9-Aminoanthracene—The electronic absorption spectra of 9-aminoanthracene in alkaline and acidic aqueous solutions are shown in Fig. 2. The principal maxima of these spectra are listed in Table I. The absorption and fluorescence spectra of the neutral molecule (in alkaline solution) are similar to those of 1- and 2-aminoanthracenes. Because the 9-isomer is an α-substituted anthracene, the longest wavelength, diffuse absorption band must arise from the $^1L_a \leftarrow {}^1A$ transition while the shorter wavelength, structured band represents the $^1L_b \leftarrow {}^1A$ transition. The fluorescence of the neutral 9-isomer corresponds to the $^1L_a \rightarrow {}^1A$ emission. The spectra of 9-aminoanthracene indicate that it is a typical derivative of anthracene.

The spectra of 9-aminoanthracene in aqueous acidic media are quite different from those of the 1- and 2-anthrylammonium ions and of anthracene. The absorption spectrum of the cation derived from 9-aminoanthracene shows an intense structureless band at 301 nm. with a less intense structureless shoulder at 340 nm. This spectrum is similar in general appearance to the absorption spectrum of anthrone (6), whose intense band and shoulder lie at 275 and 305



IV



V

nm., respectively, and to that of the conjugate cation of anthrone (6), whose intense band and shoulder should occur at 351 and 375 nm., respectively (anthrone is the keto tautomer of 9-anthrol). The fluorescence of the cation derived from 9-aminoanthracene is structureless and has its maximum at 450 nm. Anthrone does not fluoresce, presumably because its lowest excited singlet state is of the n,π^*-type and favors radiationless deactivation of the lowest excited singlet state (18). However, the cation derived from anthrone demonstrates a structureless fluorescence band with a maximum at 475 nm.

That the absorption spectrum of the cation derived from 9-aminoanthracene, in water, lies at much shorter wavelengths than that of anthracene and lacks the characteristic vibrational structure of anthracene or the typical anthrylammonium ions indicates that the extended aromaticity of the anthracene ring in the cation has been disrupted. The similarity between the absorption spectra of the protonated amine and the neutral and protonated ketone, anthrone, strongly suggests that the cation of 9-aminoanthracene in water is not the 9-anthrylammonium ion (IV) but rather a tautomeric protonated imine (V). The similarities between the electronic structures of V and those of anthrone and its cation are obvious, thereby accounting for the similarities between their absorption spectra.

The absorption spectrum of V may be considered to be that of benzene substituted with an electron-withdrawing group. The intense band at 301 nm. corresponds to the $^1L_a \leftarrow {}^1A$ transition in benzene, and the shoulder at 340 nm. corresponds to the $^1L_b \leftarrow {}^1A$ transition in benzene. The ^1L_a and ^1L_b absorption bands of benzene, however, lie at 203 and 255 nm., respectively. The corresponding bands in anthrone, its cation, and V lie at much longer wavelengths because of the charge-transfer character mixed into the lowest excited singlet states of benzene by interaction with the vacant π-orbital of the keto, protonated keto, or protonated imino group. In anthrone, its cation, and V, the lower absorptive transitions entail transfer of an electron from the benzene ring to the electron-acceptor keto, protonated keto, or protonated imino functional group. The greater the electron-withdrawing strength of the electron-acceptor group, the lower are the energies of the long wavelength absorption bands. The order of the wavelengths of the absorption spectra, anthrone < protonated 9-aminoanthracene < protonated anthrone, follows from the greater electron-withdrawing capability of the protonated imine relative to anthrone by virtue of the formal positive charge on the nitrogen atom. The greater electron-withdrawing capability of protonated anthrone relative to the protonated imine is derived from oxygen's electronegativity being greater than that of nitrogen. The latter reasoning also accounts for the longer wavelength of fluorescence of protonated anthrone relative to that of the protonated imine.

The pKa 6.34 of the 9-isomer is anomalously high for an arylamine and supports the chemical distinction of at least one member of the 9-anthrylamine–protonated 9-anthrylamine conjugate pair from the corresponding species derived from 1- and 2-anthrylamines. Moreover, the pKa values of the anthrylamines are such that, except in the stomach, the 1- and 2-isomers are essentially entirely in the neutral form *in vivo*, while the 9-isomer is appreciably protonated at all biological pH's.

The keto–enol tautomerism of anthrone has been shown to favor quantitatively the keto form in water (6). In lower dielectric media, however, the enol form, although never predominant, exists in measurable amounts. Correspondingly, in acidic ethanol solutions a structured absorption band, with vibronic maxima at 386, 366, and 348 nm., appears in the spectrum of protonated 9-aminoanthracene in addition to the diffuse ^1L_a and ^1L_b bands of the protonated imine structure which lie at 294 and 325 nm. in ethanol, respectively. The structured absorption band in acidic ethanol has the appearance and position in the spectrum characteristic of an anthrylammonium ion and is thus assigned to the 9-anthrylammonium ion (IV). IR spectra of the commercial sample of 9-aminoanthracene hydrochloride showed carbon–nitrogen stretching frequencies at 1588 and 1400 cm.$^{-1}$. The latter is characteristic of arylammonium ions, and the former is characteristic of imino groups. In contrast, the IR spectra of the hydrochlorides of the 1- and 2-aminoanthracenes demonstrated only the ammonium-type C–N stretch at 1405 and 1400 cm.$^{-1}$, respectively. Hence, in the solid state, both the arylammonium and protonated imine tautomers of the cation from 9-aminoanthracene are stable. This serves to point out that IR spectra taken in nonaqueous media may be of only limited value in establishing the chemical natures of species present in biological systems. Electronic absorption and fluorescence spectroscopy, however, when applicable, are not subject to restriction to nonaqueous circumstances, often imposed upon IR measurements. Moreover, the electronic spectroscopic methods are more sensitive and less subject to interference by impurities.

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