

leads, electronic components, stray field, etc.; (2) field fringing within the cell. The first contribution amounts to about 0.04 pF, as determined by physically removing the cell. The remaining 0.02-pF error is attributed to fringing and was determined by comparing the observed dielectric permittivity of Eastman white label toluene ($\epsilon = 2.394$), chlorobenzene ($\epsilon = 5.592$), ethyl acetate ($\epsilon = 5.982$), and 1,1-dichloroethane ($\epsilon = 10.36$) at 25° to the literature values 2.379, 5.621, 6.02, and 10.36, respectively. The typical value of C_0 was 12.5 to 15 pF. We therefore believe the reported permittivities to be accurate to within about 1%.

Summary

It is well known that electrooptical devices utilizing nematic liquid crystals require materials having either a large positive or negative dielectric anisotropy. We have demonstrated how the sign and magnitude of the anisotropy can be estimated easily from the group dipole moments associated with the terminal substituents and the central linkage in several phenyl benzoates and Schiff bases. We have further demonstrated how group dipole moment considerations quickly permit the best terminal location for a substituent. We have also emphasized how the isotropic portion of the effective dipole moment must be retained to understand properly the magnitudes of the observed dielectric permittivities.

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Structural Effects on Photophysical Processes in Saturated Amines. III¹

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Abstract: The vapor-phase absorption spectrum of 1-azabicyclo[3.3.3]undecane (ABCU) is reported between 35 and 49 kcm^{-1} . In this region, four distinct electronic transitions are identified and assigned as Rydberg $\leftarrow n$ on the basis of the quantum defect values. The (adiabatic) ionization potential of ABCU is reported, as are the oscillator strengths of the transitions. The vapor-phase fluorescence spectra of ABCU and an analogous cage amine, 1-azabicyclo[2.2.2]octane (ABCO), are presented. Partial vibrational analyses are performed for these spectra and comparisons are made with the respective $S_1 \leftarrow S_0$ transitions. Zero-pressure lifetime and quantum yield data are also reported, and these values are used to determine the respective radiative rate constants (k_R). For ABCO, the measured k_R value correlates very well with the value calculated from the Strickler-Berg relation. On the other hand, for ABCU, the agreement between the measured and calculated k_R values is rather poor, with the calculated value being about 0.6 that of the measured value. This discrepancy is discussed in terms of possible excited-state vibronic interactions affecting the transition moment. The measured k_R values are: 1.1×10^6 and $2.75 \times 10^6 \text{ sec}^{-1}$ for ABCU and ABCO, respectively. The zero-pressure quantum yield values reported are 1.0 for both amines.

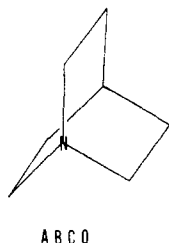
The spectroscopic and photophysical properties of saturated amines have received remarkably little attention. Indeed, it is only recently that fluorescence from these compounds was reported.³⁻⁶ This paper is one of a series dealing with the photophysical and spectroscopic investigations of saturated tertiary amines, and concerns, in particular, certain cage amines. The alkyl groups represented by the cage portion of such molecules can impose structural constraints

upon the nitrogen atom. These effects may lead to rather striking characteristics in the electronic structure and the consequent excited state behavior.

In the saturated tertiary amines, where the chromophore is simply the nonbonding electron pair on the nitrogen atom, it is presumed that in the absence of steric and structural interference by the three alkyl groups, the configurationally relaxed excited singlet states are planar. This as-

signment is made largely in analogy with ammonia, in which case the upper electronic states have been spectroscopically demonstrated to be planar.^{7,8}

The ground states of the saturated amines are expected, of course, to involve tetrahedral bonding about the N atom in the absence of overriding steric interference. An example is provided by the symmetrical cage amine, 1-azabicyclo[2.2.2]octane (ABCO). The electronic absorption spec-



tra of ABCO show extensive vibronic structure which has been interpreted in terms of a strongly coupled upper state vibration (ν_{12})^{9,10} in which the nitrogen atom oscillates along the axis perpendicular to the plane of the three α -C atoms (*i.e.*, the C_3 axis of the molecule).

In ABCO, the effect of the three ethylene bridges on the ground state bonding geometry of the nitrogen atom appears to be minimal. The C-N-C bond angle has been assumed to be 109° .^{11,12} From X-ray diffraction studies of quinuclidinyl benzilate hydrobromide, the C-N-C bond angle was determined as 107.8 – 112.0° .¹³ Furthermore, lack of unusual bonding characteristics in ABCO is confirmed by its "normal" ionization potential (IP) value. The IP of ABCO is close to that measured for triethylamine.¹⁴

In the homologous cage amine, 1-azabicyclo[3.3.3]undecane (ABCU), the rather interesting situation is encoun-



tered in which the three trimethylene bridges appear to constrain the nitrogen to a more planar configuration (with respect to the three α -C atoms), as compared with ABCO.¹⁸ X-Ray diffraction studies of ABCU·HCl reveal that the C-N-C bond angles range from 115.0 to 115.9° .^{21,22} Thus in this cage amine, the bridgehead nitrogen atom is considerably flattened, being only 0.326 \AA out of the plane defined by the three α -C atoms.^{21,22} Some of the rather unusual chemical and spectroscopic properties of ABCU have been published.^{21,23}

Results and Discussion

This paper reports the results of spectroscopic and photophysical studies of ABCU and these results will be incorporated with the analogous data for ABCO in an attempt to assign the $S_n \leftarrow S_0$ transitions in ABCU. One of the most striking aspects of ABCU's electronic absorption spectrum is the considerable lowering of the transition energies. The 0-0 band of the lowest transition, for example, lies at 2783 \AA ($35,930 \text{ cm}^{-1}$). This is contrasted with the 0-0 band of ABCO's $S_1 \leftarrow S_0$ transition which is at 2559 \AA ($39,080 \text{ cm}^{-1}$). This lowering in the transition energy of ABCU can be viewed as a consequence of the destabilization of the nonbonding orbital on the nitrogen atom (*i.e.*, ionization potential lowering, *vide infra*).

Above 2000 \AA , four distinct electronic transitions are observed. The 0-0 band energies along with the respective os-

cillator strengths are listed in Table I. These transitions, corresponding to the $S_1 \leftarrow S_0$ through $S_4 \leftarrow S_0$ transitions, are depicted, respectively, in Figures 1-4. Each transition is characterized by a prominent 0-0 band; moreover, there is a similar Franck-Condon envelope for all of these transitions. The most intense vibronic member observed in these spectra is the 0-0 band, and the intensities of subsequent progression members decline sharply.

Justification for the assignment of the 0-0 band of the $S_1 \leftarrow S_0$ transition of ABCU is provided by the coincidence of the 0-0 band observed in the $S_1 \rightarrow S_0$ transition (*vide infra*). The respective 0-0 bands of the other higher-lying transitions are identified by the close similarity of each of the $S_n \leftarrow S_0$ transitions (see Figures 1-4).

In each of the transitions, progressions in 190, 564, and 1040 cm^{-1} can be readily identified. The first member of the 1040-cm^{-1} progression is the origin of additional progressions. A partial vibrational analysis is indicated for the $S_1 \leftarrow S_0$ transition in Figure 1. It can be seen that in each of the four transitions shown, there is a rather strongly excited hot band corresponding to a frequency of 179 cm^{-1} , which probably correlates with the 190-cm^{-1} upper state frequency. The relative intensity of the $S_1 \leftarrow S_0$ hot band, about 35% (relative to the 0-0 band), is readily accounted for in terms of the appropriate Boltzmann factor at *ca.* 300°K . Because of the importance of a (relatively) low-frequency vibrational mode in the $S_n \leftarrow S_0$ transitions, it can be anticipated that many sequences would be present in the ABCU spectra. This is probably the reason for the broadness of the major vibronic components in the spectra ($>ca.$ 80 cm^{-1} full width at half mean height).

The shape of the Franck-Condon envelopes which characterizes the ABCU transitions suggests that the upper state geometry of the amine is similar to that of the ground state. *I.e.*, there does not seem to be a significant displacement between the upper and lower state surfaces with respect to the coordinates represented in the optical transitions. In the absence of a normal coordinate analysis for ABCU, it is not possible to determine which molecular motions correspond to those oscillators which are strongly excited in the electronic absorption spectra. In analogy with ABCO, however, it might be suggested that one such motion is the oscillation of the N atom along the (N-C-H) axis of the molecule.⁹

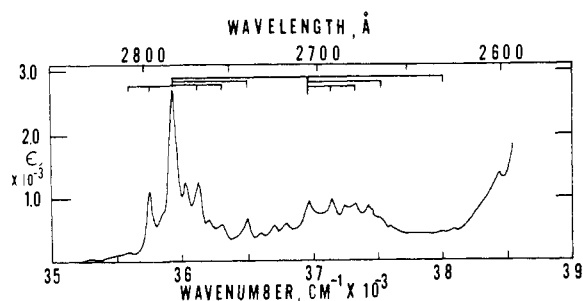
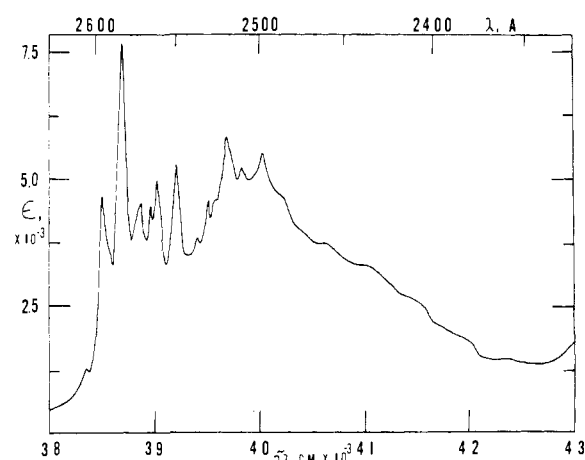
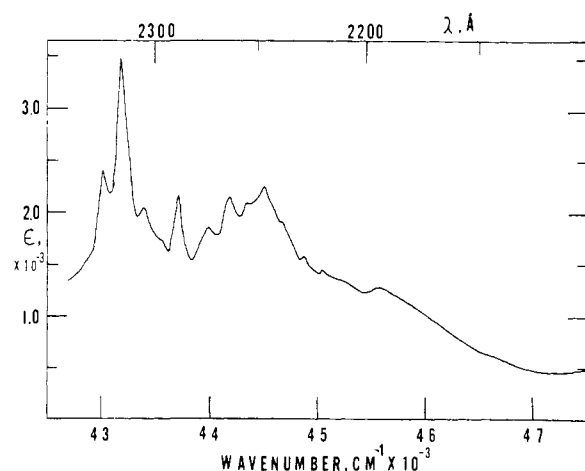
The absorption spectra shown in Figures 1-4 with their dominant 0-0 bands, and relatively narrow transition widths (*ca.* 2 – 3 kcm^{-1}), can be contrasted with the $S_2 \leftarrow S_0$ transition for ABCO (Figure 5). This much broader transition (*ca.* 6 – 7 kcm^{-1}) reveals a Franck-Condon envelope which is characteristic of a rather large displacement between the upper and lower state surfaces *vis-à-vis* a particular coordinate. The nature of the electronic absorption spectra in ABCU and ABCO is consistent with what is known about the ground state geometries (especially the C-N-C bond angles) of these two amines and what is presumed to be the equilibrium geometry for the amines in their excited state(s) (*vide supra*). Thus, ABCU, with a C-N-C bond angle of *ca.* 115° , is configurationally more similar to the geometry of the (relaxed) upper states than is ABCO, where the (ground state) C-N-C bond angle is about 109° .¹³

The lowering of the transition energies in ABCU relative to ABCO can also be understood in terms of the larger C-N-C bond angle in the former amine. That is, the more "planar" bonding configuration of the N atom in ABCU results in a larger contribution of atomic p character to the nonbonding orbital, with a consequential destabilization of this orbital.

Table I. Transition Energies and Strengths for ABCU and ABCO Vapor^a

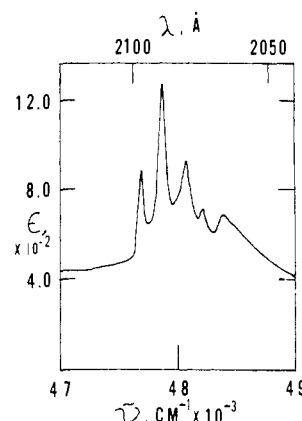
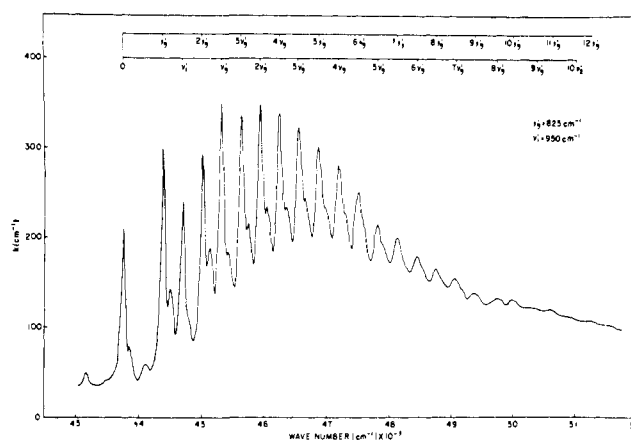
Transition	ABCU	f^b	ABCO ^c	f^b
$S_1 \leftarrow S_0$	35,932 ^d (2783 Å)	7.7×10^{-3}	39,080 (2559 Å)	3×10^{-3}
$S_2 \leftarrow S_0$	38,700 (2584 Å)	6.4×10^{-2}	43,750 (2286 Å)	6×10^{-2}
$S_3 \leftarrow S_0$	43,197 (2315 Å)	2×10^{-2}	53,020 (1886 Å)	
$S_4 \leftarrow S_0$	47,874 (2088 Å)	2×10^{-3}		

^a Vapor phase, 300°K. ^b Oscillator strength, $f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu}$. ^c Taken from ref 9. ^d In cm^{-1} .

**Figure 1.** The $S_1 \leftarrow S_0$ transition of ABCU vapor at 24°.**Figure 2.** the $S_2 \leftarrow S_0$ transition of ABCU vapor at 24°.**Figure 3.** The $S_3 \leftarrow S_0$ transition of ABCU vapor at 24°.

Electronic Transition Assignment

In view of the fact that ABCO's three electronic transitions have been assigned as Rydberg transitions,⁹ it seems logical to consider the upper states in ABCU, also, as Rydberg in nature. In Figure 6, the transition energies of both ABCO and ABCU are represented in a term diagram in which the ionization potentials of the two amines are

**Figure 4.** The $S_4 \leftarrow S_0$ transition of ABCU vapor at 24°.**Figure 5.** The $S_2 \leftarrow S_0$ transition of ABCO vapor at 27° (from ref 9).

used to set the relative energy axes. The transition energies are taken from the 0-0 band values. The IP for ABCO is from ref 9, and the IP of ABCU was determined from its photoelectron spectrum.²⁴ It can be seen in this diagram, that the $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions in ABCO correlate well with the $S_2 \leftarrow S_0$ and $S_4 \leftarrow S_0$ transitions, respectively, in ABCU. For each of the transitions shown for the amines in Figure 6, the respective quantum defects, δ , are calculated from the Rydberg equation

$$\bar{\nu}_n = \text{IP} - \frac{R}{(n - \delta)^2}$$

where $\bar{\nu}_n$ is the observed transition energy; IP is the ionization potential (in cm^{-1}); R is the Rydberg constant ($109,737 \text{ cm}^{-1}$); n is the principal quantum number; and δ is the quantum defect. δ , also called the Rydberg correction, accounts for the penetration of the excited Rydberg orbital into the molecular core. Thus, δ is larger for the more penetrating Rydberg orbitals such as ns types. Moreover, the value of δ can be used to infer the nature of the Rydberg orbital which is implicated in a certain transition, *i.e.*, wheth-

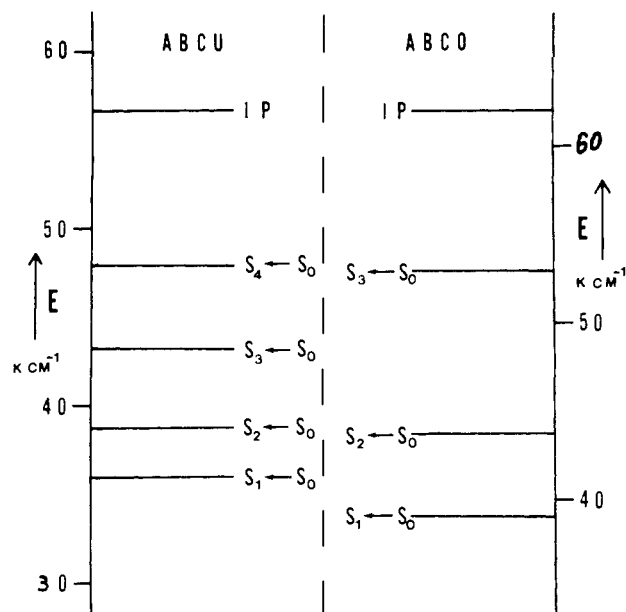


Figure 6. Transition scheme for ABCU and ABCO. Each energy axis is set according to the respective ionization potentials which are used as the common reference point.

er the upper state orbital has atomic s, p, or d, etc., character.²⁵

Table II summarizes the analysis of the absorption spec-

Table II. Transition Assignments for ABCU and ABCO According to the Rydberg Equation

Amine	Transition	n	δ	Rydberg orbital character
ABCU	$S_1 \leftarrow S_0$	3	0.72	3s
	$S_2 \leftarrow S_0$	3	0.53	3p
	$S_3 \leftarrow S_0$	3	0.14	3d
	$S_3 \leftarrow S_1$	4	1.14	4s
	$S_4 \leftarrow S_0$	4	0.47	4p
ABCO	$S_1 \leftarrow S_0$	3	0.82	3s
	$S_2 \leftarrow S_0$	3	0.55	3p
	$S_3 \leftarrow S_0$	4	0.55	4s

tra of ABCU and ABCO in terms of the Rydberg equation. For each value of δ , the respective type of Rydberg orbital is indicated. In both ABCU and ABCO, the constancy of δ for $n = 3$ and $n = 4$ is a good indication that the respective transitions are part of a Rydberg progression involving upper state np orbitals. Without knowing the polarizations of these transitions, it cannot be established whether the Rydberg orbitals involved in these transitions are np_z or np_{xy} types. In ABCO, it has been suggested that the transitions are to 3- and 4 p_z orbitals.⁹

For the $S_3 \leftarrow S_0$ transition of ABCU, two possible assignments are possible. One is that it is an $4s \leftarrow n$ transition, in which case $\delta = 1.14$, which is not unreasonable for an ns -type Rydberg orbital; the other is that it is an $3d \leftarrow n$ transition. In the latter case, δ has a value of 0.14 which is possible for a state involving a 3d orbital. On the basis of the available spectroscopic data, it is not possible to choose between these possible assignments. The lack of constancy in the δ values for the 3s and 4s transitions (0.72 and 1.14, respectively) would seem to cast doubt on the 4s assignment. On the other hand, departures from normally expected δ values are not uncommon for low-lying members of a Rydberg series.

Fluorescence Spectra. The fluorescence spectrum of ABCO will be described first. A structured emission system, which is assigned as the $S_1 \rightarrow S_0$ transition, is observed if ABCO vapor is excited within either the $S_1 \leftarrow S_0$ or the $S_2 \leftarrow S_0$ transition. This fluorescence spectrum is indicated in Figure 7. The spectral region encompassed by the fluorescence was found to be invariant with respect to excitation wavelength; however, the emission was considerably more diffuse when produced by exciting S_2 . This diffuseness gave way to the more resolved spectrum shown in Figure 7 if a small overpressure of some "inert" gas was present. About 40 Torr of thoroughly degassed n -hexane was added to the 2.0 Torr of ABCO vapor in order to ensure complete vibrational relaxation. It was desirable to excite into the $S_2 \leftarrow S_0$ transition because of its stronger absorptivity as compared with the weaker, $S_1 \leftarrow S_0$ transition. The same degree of resolved vibronic structure as observed in Figure 7 was observed if ABCO, alone, was excited at energies low enough within the $S_1 \leftarrow S_0$ manifold. Similar observations were observed for ABCU, and the implications of these phenomena are discussed below.

The fluorescence spectrum of ABCO resembles more closely the $S_2 \leftarrow S_0$ transition than $S_1 \leftarrow S_0$. This is probably because the Franck-Condon envelope of the latter transition is dominated by the much stronger, higher lying transition. The 0-0 band of the fluorescence spectrum at 2560 Å ($39,065 \text{ cm}^{-1}$) coincides with the position of the 0-0 band of the $S_1 \leftarrow S_0$ transition which is at 2559 Å ($39,080 \text{ cm}^{-1}$).⁹ Both the $S_1 \rightarrow S_0$ and the $S_2 \leftarrow S_0$ transitions not only have similar Franck-Condon envelopes but also reach maximum intensity at about 2000 cm^{-1} from the respective 0-0 bands.

A further similarity between the fluorescence and absorption spectra is the relationship between the respective progressions. At least two prominent progressions can be identified in ABCO's fluorescence spectrum. These progressions, having frequencies of 600 ± 2 and $965 \pm 2 \text{ cm}^{-1}$, can be compared with progressions in 625 and 950 cm^{-1} which are observed in all three absorptive electronic transitions.⁹ The 600- and 965-cm^{-1} progressions should correlate with Raman and/or infrared active vibrations in ABCO. Brüesch and Günthard report an infrared active mode of 604 cm^{-1} corresponding to ν_{12} , which is assigned as an a_1 vibration.¹⁰ This vibration, which is also strongly excited in the absorption spectra, corresponds to the "cage-squashing" mode in which the nitrogen atom oscillates along the C_3 axis of the molecule.

The progression in *ca.* 965 cm^{-1} probably correlates with the ground state frequency of $965\text{--}966 \text{ cm}^{-1}$, which is observed to be infrared active. Brüesch and Günthard assign this vibration to ν_{33} which is an e mode and involves changes in the three N-C bond lengths. Certain selection rules apply to degenerate vibrations in vibronic progressions, the consequence of which is that only the overtones are observed in such progressions (in the C_{3v} point group).²⁶ This means that the (1,0) member of the progression should be considerably weaker than the rest of the series. In view of the fact that the (1,0) member of the 956-cm^{-1} progression is rather strongly allowed, it would seem that: (1) this 956-cm^{-1} progression does not correspond to the ν_{33} vibration assigned by Brüesch and Günthard, (2) the ν_{33} mode is not an e type vibration, or (3) the fluorescing species is distorted having lower symmetry than C_{3v} . Possibility (2) can be tested by determining the extent of depolarization of the corresponding Raman band, since totally symmetric vibrations are polarized and nontotally symmetric (*e.g.*, e type) vibrations depolarized.²⁷

The fluorescence spectrum of ABCU, shown in Figure 8, resembles in many ways the corresponding ($S_1 \leftarrow S_0$) ab-

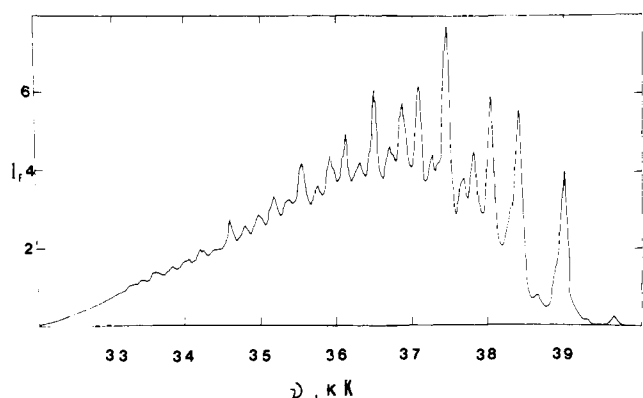


Figure 7. The corrected fluorescence spectrum of ABCO at 24°. Exciting wavelength is 228 nm and 40 Torr of *n*-hexane is added.

sorption spectrum (see Figure 1). There is a prominent 0-0 band located at 35,855 cm^{-1} , and hot bands can be identified both as shoulders and resolved maxima at higher energy. These hot bands correlate with the 190- cm^{-1} frequency observed in the absorption spectra. The fluorescence spectrum contains progressions in three main frequencies: ca. 180, 460, and 1030 cm^{-1} . The respective upper state progressions which would correlate with these frequencies are 190, 564, and 1040 cm^{-1} , respectively (*vide supra*). The 179- cm^{-1} hot band which is present in the absorptive transitions is in good agreement with the 180- cm^{-1} progression identified in the fluorescence spectrum. Also, in analogy with the absorption spectra, the first member of the 1030- cm^{-1} progression is the origin of additional progressions in the other two frequencies. Like the $S_n \leftarrow S_0$ transitions, the $S_1 \rightarrow S_0$ transition is relatively narrow (as compared with the spectra of other amines), extending about 2000 cm^{-1} from the 0-0 band.

The structured emission spectrum illustrated in Figure 8 was obtained using an excitation wavelength of 2584 Å (the 0-0 band of the more strongly allowed $S_2 \leftarrow S_0$ transition) and also by having an overpressure of *n*-hexane vapor (40 Torr) present to ensure vibrational relaxation. The dashed line emission spectrum is observed in the absence of *n*-hexane. Excitation within the S_1 manifold produces the structured spectrum provided that λ_{exc} is not too far below λ_{0-0} . The diffuseness of the spectrum obtained under these conditions indicates that emission takes place from highly vibrationally excited levels within the S_1 manifold. Consequently, there are many sequences present in the spectra. Since the $S_2 - S_1$ gap is about 2780 cm^{-1} , it is this amount of vibrational energy which is produced in the S_1 subsequent to (presumably very rapid) internal conversion from S_2 . Furthermore, the high degree of diffuseness seen in the unrelaxed fluorescence spectrum suggests that this energy is not randomly distributed among the 84 oscillators in ABCU. It would seem that there would be a sufficient number of high-frequency modes which could "absorb" the 2780 cm^{-1} of vibrational energy, in which case the extensive sequence bands superimposed on the progressions would be nearly absent. Perhaps the internal conversion between the S_2 and S_1 manifolds is promoted by certain low-frequency modes which are *also* excited in the subsequent radiative transition (fluorescence).

There is one rather unusual feature of the ABCU fluorescence spectrum. The second member of the 180- cm^{-1} progression (0-1) (at 35,676 cm^{-1}) is nearly as intense as the 0-0 band. This is in contrast to the analogous vibronic bands (*i.e.*, 1,0) in the absorption spectra. The third member of the 180- cm^{-1} progression (0,2) (at 35,499 cm^{-1}) then shows an abrupt diminution in intensity. These obser-

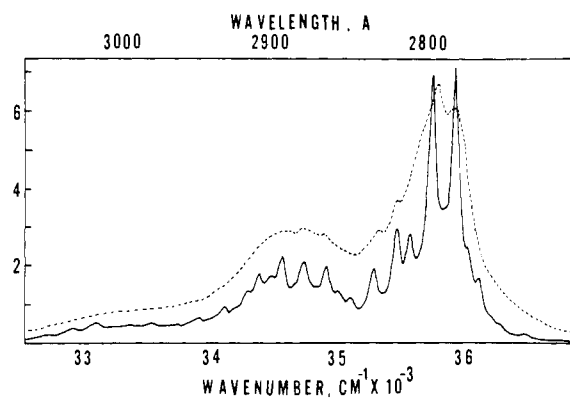


Figure 8. The corrected fluorescence spectrum of ABCU vapor at 24°. The exciting wavelength is 258 nm: solid line, 40 Torr of *n*-hexane added; dashed line, no hexane added.

vations suggest that (1) there is a distortion in the upper state potential energy surface represented by this vibrational mode (180 cm^{-1}), lowering the C_3 symmetry, or (2) the vibrational assignment of the spectra in terms of a 180- cm^{-1} frequency is incorrect. The disparate intensities of the (1, 0) and (0, 1) vibronic bands might also be symptomatic of a vibrationally induced component to the $S_1 \leftrightarrow S_0$ transition moments. Presuming that the electronic transition is allowed, and that the induced moment arises through a totally symmetric perturbing vibration, it is possible to account for an unsymmetrical distribution of respective vibronic components in the $S_1 \leftrightarrow S_0$ spectra.²⁸

Radiative Rate Constants and Excited State Properties

This paper concludes with a discussion of the radiative rate constants, both measured and calculated, of ABCO and ABCU. A summary of the fluorescent lifetimes and quantum yields for these two amines, along with the measured and calculated k_R values, is contained in Table III.

Table III. Fluorescence Lifetimes and Quantum Yields for ABCU and ABCO Vapor Along with the Measured and Calculated Radiative Rate Constants

AMINE	τ_f , nsec	ϕ_f	k_R , sec^{-1}	
			Obsd	Calcd
ABCO	363 ^a	(1.0)	2.75×10^6	2.9×10^6
ABCU	91 ^b	1.0	11×10^6	6.7×10^6

^a Obtained from the intercept of a $1/\tau_f$ vs. pressure plot; λ_{exc} 2559 Å. ^b Pressure = 0.10 Torr; λ_{exc} 2783 Å.

The lifetime of ABCO's excited state (363 nsec) was obtained as the intercept of a $1/\tau_f$ vs. pressure plot²⁹. This Stern-Volmer plot was linear from 0.15 (the lowest pressure studied) to 2.2 Torr, the highest pressure examined (this is the equilibrium vapor pressure at 26°). The exciting wavelength was 2559 Å — the 0-0 band of the $S_1 \leftarrow S_0$ transition, and an interference filter (λ 2786 Å) was used to isolate the fluorescence.

The fluorescence quantum yield of ABCO is close to unity (at low pressures). A precise determination of the fluorescence efficiency is made exceedingly difficult as a result of the weakness of the 0-0 band of the $S_1 \leftarrow S_0$ transition. Using a value for ϕ_f of 1, along with the 0-pressure lifetime of 363 nsec, k_R , the radiative rate constant, is found to be $2.75 \times 10^6 \text{ sec}^{-1}$ (see Table III). This value of k_R is in good agreement with k_R calculated from the "simplified" Strickler-Berg (S-B) relation.³⁰

$$k_R = 2.88 \times 10^{-9} \hat{\nu}_f^2 \int_{S_1 \leftarrow S_0} \epsilon d\nu$$

It was noted above that the $S_1 \leftarrow S_0$ transition is partially obscured by the stronger $S_2 \leftarrow S_0$ transition, and, consequently, the integrated extinction coefficient indicated above may be somewhat underestimated. Thus, the good correlation between the observed and calculated k_R values may, in part, be fortuitous.

At room temperature, the vapor pressure of ABCU is *ca.* 0.10 Torr, and the fluorescent lifetime, measured by exciting the 0-0 band of the $S_1 \leftarrow S_0$ transition, is 91 nsec. Thus, at ambient temperatures, ABCU's excited state is under collision-free conditions. Accordingly, the fluorescence decay is exponential and represents the relaxation of the isolated molecule. The fluorescence quantum yield, also measured by exciting the 0-0 band of $S_1 \leftarrow S_0$ and using toluene vapor as the standard (see Experimental Section), is unity (*ca.* 5% error). k_R measured for ABCU is thus $11 \times 10^6 \text{ sec}^{-1}$.

From all spectral indications, it would seem that ABCU would be a molecule whose k_R value could be successfully calculated from the S-B relation. The $S_1 \leftarrow S_0$ transition is allowed (with a strong 0-0 band), and the $S_1 \leftarrow S_0$ transition is apparently unencumbered by higher lying states. Notwithstanding this favorable prognosis, there is poor agreement between the observed and calculated k_R values with $k_R(\text{obsd})$ being about 1.7 times greater than $k_R(\text{calcd})$ (see Table III). The simplified S-B relation furnishes a value of $6.7 \times 10^6 \text{ sec}^{-1}$, and the more exact formulation for k_R ³⁰ fails to improve this discrepancy, giving a value of $6.1 \times 10^6 \text{ sec}^{-1}$.

In view of the rather good agreement between $k_R(\text{obsd})$ and that calculated from the S-B relation for ABCU (*vide supra*), it is surprising that this correlation fails in ABCU. In ABCU, it is possible that a portion of the $S_1 \leftarrow S_0$ transition is hidden by the more strongly allowed $S_2 \leftarrow S_0$ transition. If this were the case, then approximately 40% of the total $S_1 \leftarrow S_0$ transition strength would have to underlie the $S_2 \leftarrow S_0$ transition. This situation is unlikely (see Figures 1 and 2).

A possible cause of the discrepancy between $k_R(\text{obsd})$ and $k_R(\text{calcd})$ in ABCU is the presence of a vibronic perturbation on the $S_1 \leftrightarrow S_0$ transition moments.²⁸ This would be consistent (qualitatively) with the anomalies observed in some of the vibronic intensities of the $S_1 \leftrightarrow S_0$ transitions (*vide supra*).

As far as errors in k_R (calcd) are concerned (*i.e.*, in τ_f and ϕ_f), the probable error in τ_f is *ca.* 2% and in ϕ_f *ca.* 5%, unless there is a systematic error in the Burton and Noyes value of ϕ_f for toluene. Agreement between the observed and calculated k_R values would require that ϕ_f for toluene reported in ref 35 be too large by a factor of 1.7. This appears to be unlikely.

Like ABCO, ABCU's excited state undergoes self quenching^{6,29} in solution but the consequences of self quenching are quite different. ABCU does not form excimers in solution, although the excited state is self quenched at the diffusion-controlled rate (in *n*-hexane). In fact, at higher concentrations, Stern-Volmer kinetics are not followed as a result of radiative transfer. This phenomenon arises because of the large overlap between the absorption and emission spectra.³¹ It is possible that the failure of ABCU to form an emissive excimer might be a consequence of strong excited state-ground state interaction (intermolecular).³² This might be analogous to the situation in anthracene where this interaction results in photodimerization, whereas 9-methylanthracene (being somewhat shielded) does excimerize. Photochemical studies of saturated amines such as ABCU will clarify this point.

Experimental Section

Materials. ABCU was provided as ABCU·HCl through the courtesy of Professor N. J. Leonard and Dr. J. C. Coll. The free base, which was liberated by combining very concentrated aqueous solutions of ABCU·HCl and NaOH, was sublimed from a solid mixture of anhydrous BaO. Although attempts were made to exclude oxygen from the amine while it was being stored, the base appeared to be unstable, becoming slightly colored in a period of weeks. It was found that the pigmented component was nonvolatile (at room temperature) enabling the free ABCU to be both retrieved and purified by sublimation. Solutions of ABCU in *n*-hexane (10^{-4} – $10^{-2} M$) were also observed to be unstable over a time period of several weeks. Experiments utilizing ABCU solutions were performed within hours of preparation, and vapor phase studies were always carried out using freshly sublimed samples.³³ The melting point of the free base was 175° (sealed tube).

The vapor pressure of ABCU was determined by allowing the vapor above the solid amine to equilibrate in a calibrated volume (1094 cc). The solid ABCU was kept in a side arm immersed in a constant temperature bath (23°). After equilibration, the reservoir side arm was isolated from the system, and the ABCU vapor was condensed into another side arm, which was subsequently removed. The removed amine was then dissolved in 10.0 ml of diethyl ether and the concentration was determined spectrophotometrically using ϵ (240 nm) of $2935 M^{-1} \text{ cm}^{-1}$.²³ The results of three experiments provided a value of 0.090 ± 0.006 Torr. This was later confirmed by using a capacitance manometer (MKS Instruments).

Absorption spectra were measured using a Cary Model 15 spectrophotometer. The spectral resolution was usually less than 0.8 Å, occasionally being as high as 2 Å at the low-wavelength region (1880–2000 Å). Emission spectra were obtained using a conventional dc fluorimeter described elsewhere.⁴

The fluorescence quantum yield of ABCU was determined by using toluene vapor as a primary standard. Toluene was chosen because its emission spectrum lies in the same region as ABCU's. Moreover the fluorescence quantum yield of toluene has been carefully measured over a wide range of specified conditions, such as excitation wavelength, bandpass, pressure, etc.³⁴ An excitation wavelength of 2658 Å was used for the ABCU quantum yield measurement. Although this was not one of the wavelengths used in ref 35, $\phi_f = 0.30$ was nevertheless used because the fluorescence lifetime of toluene (56 nsec) was invariant with excitation wavelength between 2658 and 2668 Å (the 0-0 band), one of the excitation wavelengths used in ref 34. The value of τ_f (56 nsec) is in excellent agreement with that reported by Breuer and Lee.³⁵

The fluorescence of a 2.8-Torr sample of toluene was compared with the emission from ABCU vapor in equilibrium with the solid at 25° ($p = 0.10$ Torr). The fluorescence spectra of both compounds were uncorrected because of the favorable overlap of the emission spectra. The fluorescence quantum yield of ABCU was calculated in the usual manner.³⁶ The average value of three determinations is $\phi_f(\text{ABCU}) = 1.0 \pm 10\%$.

Lifetime Measurements. Fluorescence lifetime measurements utilized the time-correlated single-photon technique. This approach has been shown to be a highly sensitive and accurate method for determining the direct time dependence of both singlet state³⁷⁻³⁹ and triplet state⁴⁰ emission. The instrument used an H₂ (D₂)-filled (0.5 atm) flashlamp which was gated with an E.G. & G. HY-2 (later HY-6) ceramic hydride reservoir thyatron. The thyatron grid pulse (+360V max, 15 nsec rise time) was produced by a relaxation oscillator which incorporated 24 pnpn diodes (thyristors) in series, each having a forward breakdown potential of *ca.* 15 V.⁴¹ By applying a voltage to the thyatron grid pulser of between 535 and 700 vdc, the pulse repetition frequency could be set between *ca.* 5.6 and *ca.* 20 kHz. Most experiments were done using a lamp frequency of about 12 kHz.

With no external capacitance added, the lamp flash had a full width at half mean height of *ca.* 2.8 nsec and a decay time ($1/e$) of 0.8 nsec. The flash decay was exponential for about three decades of intensity. This decay was interrupted, however, by a shoulder at about 7 nsec following the main flash peak. This feature was sometimes observed as a resolved maximum and is believed to be an artefact produced by the photomultiplier tube.³⁶ The magnitude of this bump could be mitigated by an appropriate adjustment of the accelerating grid and early dynode potentials of the photomul-

tiplier tube.^{37,42}

An Amperex 56DUVP/03 photomultiplier tube, selected for low dark counts, was used. At an applied voltage of 2500 V, and at a discriminator threshold of 150 mV, the total background rate was observed to be *ca.* 30 Hz at 23°. Under conditions of high ambient humidity, however, the background rate of the photomultiplier tube increased by several orders of magnitude. This undesirable situation was corrected, at first, by purging the photomultiplier tube housing with dry nitrogen. This effect was believed to originate from the front end of the tube, rather than the base area. The problem was satisfactorily improved by using the photomultiplier tube with the cathode at ground potential and by capacitively coupling the anode to the rest of the apparatus. A positive high voltage, then, was applied to the last dynode.

Anode pulses from the 56DUVP/03 were processed by an ORTEC constant fraction timing discriminator (Model 453). The discrimination threshold was set between 150 and 200 mV, and the constant fraction was 0.2. The fast NIM logic pulses (STOP pulses) from the 453 were then coupled with an ORTEC time-to-amplitude converter (TAC) (Model 437A).

Start pulses were produced by an antenna which was mounted inside the flash lamp housing and located approximately 3 cm from the spark gap. This antenna consisted essentially of one lead (*ca.* 1.5 cm) of a 50.0- Ω resistor, whose other lead was grounded; the ungrounded part of the resistor was connected to a 50 Ω impedance coaxial cable. A very well-defined, negative-going pulse (*ca.* 700 mV), which was free of ringing, was produced synchronously with the firing of the lamp. The START pulse derived in this manner was found to be free of jitter and entirely satisfactory. This START pulse was suitable for direct processing by the TAC, but for the purpose of pulse uniformity, it was first passed through an E.G. & G. discriminator (Model T100A). No discernible difference was observed in the performance of the lifetime apparatus whether this electronically derived START pulse was used or an optical pulse, produced by a 1P28 photomultiplier tube which viewed the lamp flash, was used. Acquisition times were a few hours or less.

Output pulses from the TAC, amplified by an ORTEC Gated Biased Amplifier (Model 444), were fed into a Nuclear Data multichannel analyzer (Model 1100). The memory contents could be displayed on an oscilloscope or *directly* fed into a Univac 1108 computer⁴³ via a teletype and an acoustical coupler (Anderson-Jacobson ADAC 242). Alternatively, data could be read out on punched (paper) tape and subsequently read into the computer. An X-Y plotter (Time Share Peripherals Model-212) was coupled to the computer through the teletype enabling the computer-processed data to be plotted. Lamp profile as well as fluorescence decay were read into the computer. Then, various theoretical decay functions (usually single-component relaxation) were convoluted with the lamp profile and these respective convoluted functions were plotted and compared with the actual observed data. Allowance as component lifetimes, and fractions of scattered light were read into the computer through an interactive program.^{43,45} In this manner, *i.e.*, by convoluting and comparing, lifetime values were obtained. As the case warranted, a two-component exponential decay function could also be tested and compared with the data using the technique described above.

All fluorescence decay measurements were obtained under conditions of narrow band excitation and broad band emission. The flash lamp arc was focused onto the entrance slit of a Jarrell-Ash 0.25 m Ebert monochromator (band pass 16–32 ÅÅ). The sample cell was mounted close to the exit slit, and the photomultiplier tube was oriented at right angles to the excitation axis. Region-selecting filters were placed between the sample cell and detector.

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