

Short Communication

Structural effects on photophysical processes in saturated amines V: Intermolecular excimer formation

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Excimer formation is a process which has been observed in atoms and in the noble gases for over 50 years [1]. During the past 25 years certain organic molecules, namely some aromatic and heteroaromatic molecules, have been shown to undergo excimer formation in the condensed phases [2]. More recently certain non-aromatic organic molecules, specifically a few saturated tertiary amines, have been shown to form excimers both in the vapor phase [3] and in saturated hydrocarbon solution [4]. These compounds can be considered to be a link between organic molecules and atomic excimers.

For the more complex aromatic molecular excimers, stabilization is presumed to arise from two simple models — charge resonance and exciton resonance interaction. More realistically, excimer stabilization can be considered to arise from the configurational mixing of the appropriate states derived from the respective models. Thus, both the electron density distribution and the transition dipole strengths from the ground state would be expected to take part in the determination of the net excimer stabilization energy. Because these properties vary widely in aromatic molecules, there is no obviously discernible trend in excimer bonding energies with respect to molecular structure within this class of molecules.

In saturated (mono)amines, however, the chromophore is universally the non-bonded electron pair on the nitrogen atom. Moreover, the electronic transitions are presumably based on Rydberg orbitals centered on the nitrogen atom [5]. Therefore it is expected that the transition energies and strengths are related to the electron density on the nitrogen atom. A simple correlation would thus be expected to exist between the spectroscopic properties of a saturated amine and the binding energy of its excimer.

In fact, such a relationship does not appear to exist. For example, although triethylamine and 1-azabicyclo[2.2.2]octane (ABCO) have very similar n-orbital energies and electronic transition energies (they have similar vertical and nearly similar adiabatic ionization potential values) [6], only ABCO shows excimer emission. The binding energy of the ABCO excimer is

substantial (about $8.8 \text{ kcal mol}^{-1}$ *) whereas, although triethylamine has a self-quenching rate constant which is less than the diffusion-controlled value[†], the stability of its excimer (if any) must be of the order of RT . Attempts to observe excimer emission from triethylamine and other simple tertiary monoamines have failed, even at low temperatures and in the neat liquids. Thus we conclude that non-radiative decay must overwhelmingly dominate in the relaxation of any excimer in such amines.

We examined the spectroscopic and photophysical properties of a large variety of saturated amines in order to try to elucidate the structural and spectroscopic criteria for excimer formation in this class of compounds. The general types of compounds which were examined included acyclic monoamines and diamines, monocyclic monoamines and diamines, and bicyclic monoamines and diamines in which the nitrogen atom was situated in either bridgehead or non-bridgehead positions. We found that only one of the amines studied outside the general class of ABCO-type molecules undergoes intermolecular excimer formation, namely 1-azabicyclo[2.2.1]heptane (ABCH)** (Fig. 1). This cage amine shows excimer fluorescence both in *n*-hexane solution and in the vapor phase (Fig. 2). In *n*-hexane solution, the structured monomer emission observed in the vapor phase is replaced by a structureless band in which λ_{max} (255 nm) is at about the same position as the maximum of the Franck-Condon envelope of the vapor spectrum. In both media the excimer band is broad and structureless with λ_{max} at 383 nm. The 0-0 band in the fluorescence spectrum is at 2316 Å and coincides with the 0-0 band observed in the $S_1 \leftarrow S_0$ transition. Some pertinent structural and spectroscopic information for ABCH, ABCO and other homologues are presented in Table 1.



Fig. 1. The structure of the amine ABCH.

An obvious paradox is that, although the ionization potential of ABCH can be presumed to be larger than that of ABCO^{††}, its excimer is more

*This value is obtained from steady state measurements and is somewhat smaller than the binding energy obtained from kinetic measurements (see ref. 4).

†The intermolecular self-quenching rate constant for triethylamine is $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which is about a factor of ten smaller than the diffusion-controlled rate in *n*-hexane.

**ABCH was prepared by the base-catalyzed intramolecular ring closure of 4-iodomethyl piperidine. The latter was obtained from 4-methanol piperidine which was derived from ethyl isonipectoate (Aldrich Chemicals).

††This follows from the presumption that the electronic transition is Rydberg in nature, so that there is a correlation between the electronic transition energy and the ionization potential (see ref. 5).

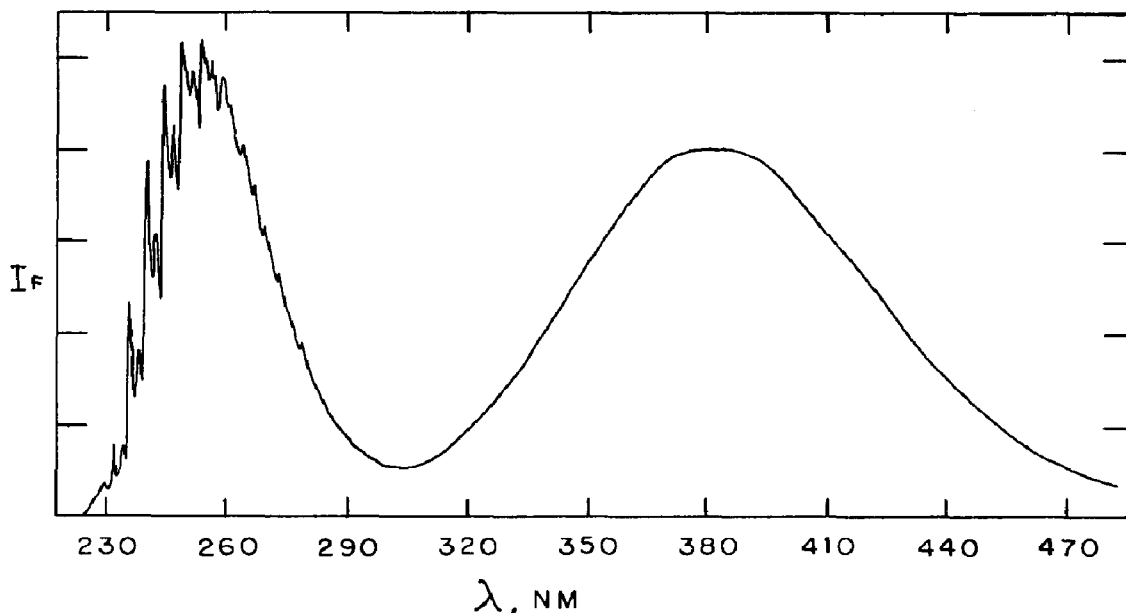


Fig. 2. The uncorrected fluorescence spectrum of ABCH vapor at 23 °C. The partial pressure of ABCH is 12 Torr, and 300 Torr of n-butane are added in order to ensure complete vibrational relaxation of the excimer. λ_{exc} is at 2316 Å which corresponds to the 0-0 band of the $S_1 \leftarrow S_0$ transition.

TABLE 1

Electronic transition energies, oscillator strengths, ionization potential values and excimer binding energies of four 1-azabicyclo[n, l, m] alkanes

Amine	C-N-C angle (°)	$S_1 \leftarrow S_0^a$	$S_2 \leftarrow S_0^a$	$S_3 \leftarrow S_0^a$	Ionization potential (eV)	$\Delta H_{\text{excimer}}^b$ (kcal mol ⁻¹)
[2.2.1]	101 - 103 ^c	2316 [0.010]	2028 [-]	—	(8.4) ^d	12.2 ^e
[2.2.2]	109 ^f	2556 [0.003]	2280 [0.06]	1886	7.72 ^g	8.8 ^h
[3.2.2]	110 - 115 ⁱ	2645 [0.003]	2399 [0.06]	1953	(7.4) ^d	no excimer
[3.3.3]	115 - 116 ^j	2783 [0.0077]	2584 [0.064]	2315	7.02 ^k	no excimer

^a Transition energies in ångströms. The numbers in square brackets are oscillator strengths.

^b Obtained from steady state measurements.

^c Structural data taken from norbornane [7].

^d Based on the term value of the $S_2 \leftarrow S_0$ transition and a quantum defect of 0.55 [5, 8].

^e Measured in n-hexadecane.

^f See refs. 9 and 10.

^g Adiabatic ionization potential from ref. 11; spectroscopic data from ref. 8.

^h Measured in n-hexane.

ⁱ Based on 3-azabicyclo[3.2.2]nonane [12].

^j See ref. 13.

^k Adiabatic ionization potential and spectroscopic data from ref. 14.

strongly bound. It can also be seen that the oscillator strengths of these amines are quite small and cannot, in themselves, account for the large observed binding energies via pure excitation resonance. Although the oscillator strength of the $S_1 \leftarrow S_0$ transition in ABCH is about three times larger than that of the analogous transition in ABCO, it seems unlikely that this property alone can account for the stronger excimerization of ABCH. It has been suggested [4] that one of the key factors affecting excimer stability is the constrained colinearity of the α - β C—C σ bonds with respect to the n orbital. The distinctive structural feature of ABCO-type amines is that they have three such (nearly) colinear bonds. Although there are two such bonds in ABCH, the colinearity is compromised by the presence of the methylene bridge. If this hypothesis is correct, the decreased colinearity of these bonds is expected to decrease the stability of the excimer. The opposite is observed; the binding energy of ABCH is $12.2 \text{ kcal mol}^{-1}$ compared with $8.8 \text{ kcal mol}^{-1}$ for ABCO*.

A possible explanation for the excimer-emitting specificity of ABCO-type molecules and ABCH is that reactive self quenching occurs in the other amines, possibly via α -hydrogen transfer to form an amine intermediate. However, photochemical studies [4] of triethylamine and ABCO do not support such a hypothesis. The two amines appear to have similar degrees of photostability when irradiated by a 500 W mercury lamp in n-hexane solution.

It is quite striking that in 1-azabicyclo[3.2.2]nonane (ABCN), which also has two (distorted) colinear C—C bonds, there is no evidence of excimer emission either in n-hexane solution or in the vapor phase. These observations would suggest either that there is no specific structural feature associated with 1-aza cage amines which controls excimer stability, or that other compensating factors affecting excimerization are present. It is tempting to speculate that the higher transition energy and the somewhat larger oscillator strength of ABCH are connected with the fact that the ABCH excimer is more strongly bound than the ABCO excimer. However, there seems to be no simple correlation between the spectroscopic properties of an amine monomer and the binding energy of its excimer. It is possible that the high stability of the amine excimer gives rise to substantial non-bonded interactions and other involvements associated with the cage atoms in the excimer which render a direct comparison of monomer and excimer properties invalid. Further studies of the kinetics and thermodynamics of the ABCH excimer, and the search for other amine excimers, are in progress.

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*These data are used in order to provide a basis of comparison between the two amines. Photokinetic measurements of the ABCH excimer system are in progress.

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