CF$_3$,[14] and ClSO$_2$NCO[7] (EN), *inter alia*, lead to the formation of M$\overline{\mathrm{C{=}C(R)ENC}}H_2$. In the light of the results presented in this communication, it seems very probable that they proceed *via* the intermediacy of the allene complex which arises by attack of the electrophilic part (E) of EN upon the acetylenic bond. This then rearranges to the cyclic product through the interaction of the nucleophilic atom (N) of EN with the terminal carbon of the coordinated allene.

Acknowledgment. We thank the National Science Foundation for financial support.

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(14) D. W. Lichtenberg and A. Wojcicki, to be submitted for publication.

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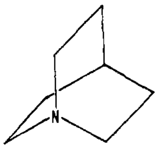
Received July 20, 1972

Excimer Formation in Saturated Amines

Sir:

To date, virtually all studies of excimers (excited dimers) deal with aromatic hydrocarbons and their derivatives.[1] This communication reports part of the results of an investigation of the photophysical properties of saturated amines. Certain tertiary amines exhibit concentration-dependent fluorescence spectra. This phenomenon is shown in Figure 1 for 1-azabicyclo[2.2.2]octane (ABCO, I) in *n*-hexane at 24°.[2] Each spectrum is arbitrarily normalized, and, therefore, the isoemissive point at 3240 Å is only apparent.[4] It is proposed that the broad, structureless band with λ_{max} at 3760 Å, whose net quantum efficiency increases with increasing concentration, is fluorescence from the ABCO excimer. Further support for this hypothesis is provided by results of kinetic studies. The time dependence of the 3760-Å emission band (isolated with a Corning 0-52 filter) shows a gradual buildup to a maximum and subsequent decay. The time delay between the exciting flash and the maximum in emission intensity increases with decreasing ABCO concentration. The observations provide direct evidence for a dynamic (rather than static) mechanism for the production of the species fluorescing with λ_{max} at 3760 Å. Furthermore, the nature of the absorption spectrum in *n*-hexane solution is invariant from 10^{-4} to 10^{-2} *M*. The band with λ_{max} at 2730 Å is fluorescence from the ABCO monomer. The fluorescence maximum for a tertiary amine with a similar degree of alkylation; *e.g.*, triethylamine, appears at 2825 Å in *n*-hexane solution. The corresponding λ_{max} for triethylamine in the vapor phase is 2780 Å.[7,8] The simple trialkylamines all show maximum fluorescence in this region.[7] There is a very large Stokes shift since the simple amines characteristically have maximum absorption in the vicinity of 2000 Å.[8,9] It has been suggested that, in the vapor phase, the lowest lying excited state of the trialkylamines is largely Rydberg in nature,[3,10] although in a condensed medium, this may not be an accurate description.[11]



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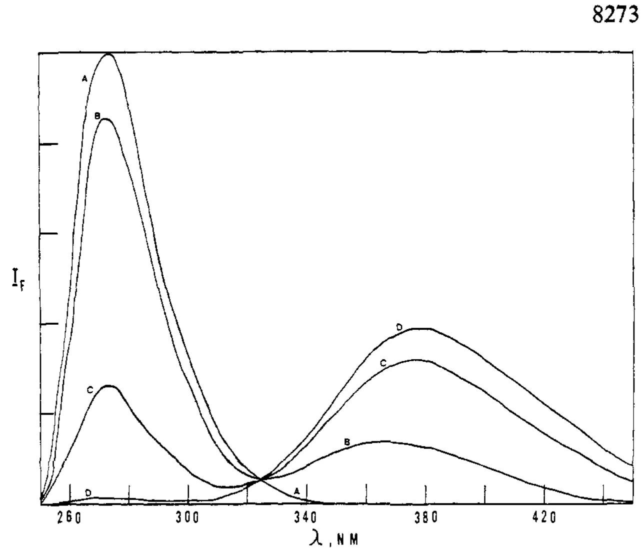

Figure 1. Uncorrected fluorescence spectra of ABCO in *n*-hexane at 24°. Concentrations are: (A) 5.5 × 10^{-5} *M;* (B) 5.5 × 10^{-4} *M;* (C) 5.5 × 10^{-3} *M;* (D) 5.5 × 10^{-2} *M.*

It is noteworthy that both the spectral and temporal properties mentioned above are also observed for ABCO in the vapor phase at 24°. These results are depicted in Figures 2 and 3. The monomer fluorescence is replaced by a highly structured emission system;[12] however, the structureless excimer fluorescence in the vapor system is not observed unless a few centimeters of an inert gas (such as *n*-hexane or cyclohexane) are added to the amine vapor. Presumably this is necessary in order to achieve complete thermal stabilization of the excimer; apparently internal vibrational degrees of freedom are inadequate in dissipating the energy released by a newly formed ABCO

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(1) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley Interscience, London, 1970, Chapter 7.

(2) ABCO was obtained as the hydrochloride from Aldrich Chemical Co. The free base was liberated by combining very concentrated ABCO·HCl and NaOH aqueous solutions. This solid amine was filtered and twice sublimed *in vacuo* through a layer of previously dried sodium hydroxide, mp 159–160° (lit.[3] mp 161.5–162°).

(3) A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49** 1348 (1968).

(4) The conditions of the experiment were such that the optical densities of the solutions varied over a wide range. For ABCO in *n*-hexane, λ_{max} is 2090 Å; ϵ_{max} is 1600 M^{-1} cm^{-1}.[5] Therefore, in order to obtain satisfactory signal-to-noise ratios, the exciting wavelength was changed from 237 (for dilute solutions) to 249 nm (for concentrated solutions). Thus, each spectrum would have to be corrected with respect to the optical density and the intensity of the exciting radiation in order to obtain the true isoemissive point. In all cases the emission spectra were otherwise independent of exciting wavelength. Preliminary thermodynamic experiments reveal that there is a well-defined isoemissive point for both the ABCO and 1-AA (*vide infra*) systems.[6]

(5) A. M. Halpern, E. Maratos, and R. B. Walter, unpublished data.

(6) A. M. Halpern and R. J. Sternfels, to be submitted for publication.

(7) C. G. Freeman, M. J. EcEwan, R. F. C. Clairidge, and L. F. Phillips, *Chem. Phys. Lett.*, **8**, 77 (1971).

(8) A. M. Halpern and R. B. Walter, unpublished results.

(9) E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

(10) Y. Muto, Y. Nakato, and H. Tsubomora, *Chem. Phys. Lett.*, **9**, 597 (1071).

(11) See M. B. Robin and N. A. Kuebler, *J. Mol. Spectrosc.*, **33**, 724 (1970), and references cited therein.

(12) A. M. Halpern and E. Maratos, unpublished results. Details will be reported separately.

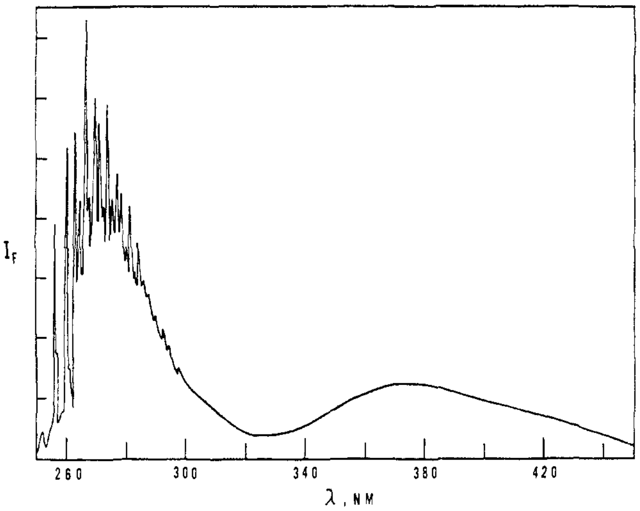


Figure 2. Uncorrected emission spectrum of ABCO vapor at 24° in the presence of 7 cm of n-hexane vapor.

excimer. At 24°, the vapor pressure of ABCO is approximately 2 Torr[13] (1.1×10^{-4} M), and thus the relative amount of excimer formed appears to be similar to that in the solution phase at this concentration. Fluorescence from ABCO vapor in equilibrium with solid ABCO which is kept at 0° (vapor pressure *ca.* 0.3 Torr[13]) was too faint to detect with the fluorimeter used; however, the time dependence of the (total) emission was easily measured[14] and found to follow a single exponential decay. The emission reached maximum intensity instantaneously with respect to the lamp flash.

Emission from ABCO microcrystals was examined at 25° and found to resemble that of the ABCO excimer fluorescence. Thus, a blue-violet emission was observed with λ_{max} at 3490 Å.

The emission spectrum of the related cage amine 1-azabicyclo[3.3.3]undecane (ABCU)[16] was studied and found to be independent of concentration. This amine showed only monomer fluorescence.[17] From lifetime measurements, however, it was determined that ABCU undergoes self-quenching at the diffusion-controlled rate in n-hexane at 24°. The fluorescence spectra of 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylamine were also found to be concentration independent in the same solvent.[8,18] DABCO's fluorescence lifetime was invariant with concentration between 10^{-4} and 10^{-2} M while triethylamine was found to undergo self-quenching at nearly the diffusion-controlled rate.

Another cage amine, 1-azaadamantane[19] (1-AA, II), was observed to have the same type of concentration-dependent luminescent properties in n-hexane as ABCO. For 1-AA, λ_{max} (monomer) is 2860 Å. Preliminary data imply that the ABCO and 1-AA excimers have similar enthalpies, but the former appears to have a larger $\Delta G°$. Results of further studies relating to thermodynamic and structural properties of saturated amine excimers will be reported separately.

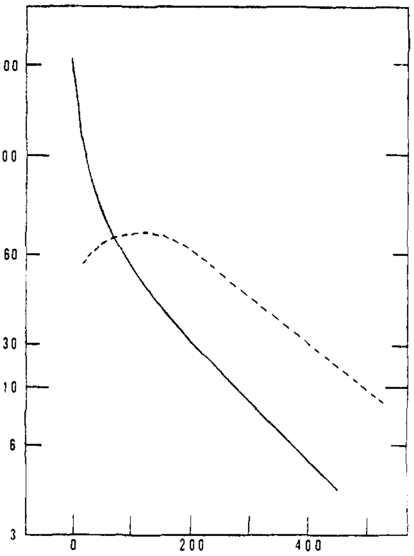
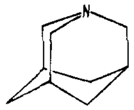


Figure 3. Time dependence of the emission from ABCO vapor at 24°: (——) total emission observed; (- - -) emission isolated with a Corning 0-52 filter. Fluorescence intensity units are arbitrary for each decay curve.



II

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[13] H. C. Brown and S. Sujushi, *J. Amer. Chem. Soc.*, **70**, 2878 (1948).

[14] The time-correlated single-photon technique was employed for all lifetime measurements. The apparatus which is similar to one previously described[15] will be mentioned in detail elsewhere.

[15] A. M. Halpern and W. R. Ware, *J. Chem. Phys.*, **53**, 1969 (1970).

[16] This compound, also called manxine, was provided as ABCU·HCl through the courtesy of Professor N. J. Leonard and Dr. J. C. Coll.

[17] Results of photophysical and spectroscopic studies of ABCU will be reported shortly; however, see N. J. Leonard, J. C. Coll, A. H.-J. Wang, R. J. Missavage, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 4628 (1971).

[18] The fluorescence spectrum and lifetime of DABCO have been reported: A. M. Halpern, *Chem. Phys. Lett.*, **6**, 296 (1970); see also A. M. Halpern and R. M. Danziger, *ibid.*, **16**, 72 (1972).

[19] 1-AA was kindly provided by Professor W. N. Speckamp.

[20] National Science Foundation Undergraduate Research Participant, summer, 1971.

Crystal Structure of the Biscarborane Complex $Co[(B_{10}C_2H_{10})_2]_2^-$

Sir:

The reaction of 2,2′-dilithiobiscarborane with various anhydrous metal salts has produced[1] a series of transition metal biscarborane complexes of general

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[1] D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 3194 (1970); **93**, 873 (1971).