

Full verification of these assignments of structure can be obtained by examining those proton-proton couplings extractable from the various n.m.r. spectra. In the spectrum of I and of II only one of the bridgehead protons is split into an observable doublet ($J \sim 4$ c.p.s.). In adduct IV neither bridgehead proton is coupled significantly to the hydrogens at the ring junction. On the other hand, in compound III both are coupled to those at the junction ($J \sim 4$ c.p.s.). Anet has demonstrated that significant coupling occurs between the bridgehead protons and those at the ring junction in 7-oxanorbornene derivatives only when the latter protons are in the *exo* position.^{10b} Thus, once more, we can conclude that the stereochemistry of the hydrogens at the ring junction is in I, *endo,exo*, in II, *exo,endo*, in III, *exo,exo*, and in IV, *endo,endo*. One final confirming point, in accord with the literature^{10a} the coupling constant (6 c.p.s.) between the protons on the ring junction in II (*exo,endo*) is smaller than that in the *exo,exo* isomer III (11 c.p.s.).

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The Chemiluminescence of Tetrakis(dimethylamino)ethylene¹

Sir:

The phenomenon of chemiluminescence has recently become the subject of increased study.² Among those

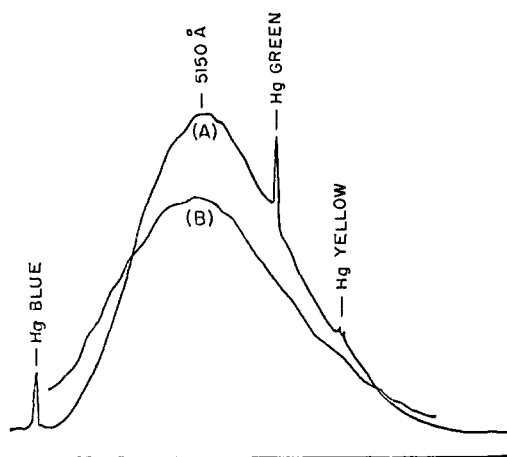


Figure 1. Fluorescent (A) and oxyluminescent (B) spectra of TDE.

systems which chemiluminesce, tetrakis(dimethylamino)ethylene (TDE) is of special interest because of the bright, prolonged, blue-green oxyluminescence

(1) This study by E. I. du Pont de Nemours and Co. was carried out in part under a U. S. Naval Ordnance Test Station Contract supported by A.R.P.A.

(2) E.g., (a) "A Symposium on Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins Press, Baltimore, Md., 1961,

induced simply by exposing the compound to air.³ The chemistry of TDE including its intermediate oxidation states and possible dissociation to a carbene has been discussed in recent publications.⁴ In this communication we report on the centrosymmetric structure of TDE and on its chemiluminescent reaction, including identification of TDE as the light-emitting species, the quantum efficiency, and the need for protonic activation.

The Raman and infrared spectra⁵ provide strong evidence for a centrosymmetric ground-state structure for TDE. The C=C stretching frequency at 1630 cm^{-1} is absent from the infrared spectrum but appears as a strong, highly polarized Raman line. That TDE in the ground state exists as the simple centrosymmetric structure without tendency to dissociate into the corresponding carbene is further confirmed by its proton magnetic resonance.⁶ This consists of a single sharp resonance at -2.55 p.p.m. (tetramethylsilane internal reference), showing all protons to be equivalent.

The fluorescence and oxyluminescence spectra⁷ of TDE at ambient temperatures are essentially equivalent. The spectra (Figure 1) are continuous without fine-line structure and with the maxima at 5150 Å. The known oxidation products^{3b} of TDE do not fluoresce under these conditions. It thus appears that an electronically activated TDE molecule (TDE*) is the emitting species.⁸ This conclusion is confirmed by further observations that at low temperatures both the fluorescence and oxyluminescence spectra of TDE change from blue-green to blue.⁹ TDE* could originate during the

part III, p. 173; (b) E. H. White, O. Zafriou, H. H. Kägi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964); (c) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); (d) E. H. White and M. J. C. Harding, *ibid.*, **86**, 5687 (1964); (e) J. Sonnenberg and D. M. White, *ibid.*, **86**, 5685 (1964); (f) E. A. Chandross, *Tetrahedron Letters*, 761 (1963); (g) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964); (h) D. M. Hercules, *Science*, **145**, 808 (1964); (i) A. U. Khan and M. Kasha, *J. Chem. Phys.*, **39**, 2105 (1963); **40**, 605 (1964); (j) R. F. Vassiliev and A. A. Vichutinskii, *Nature*, **194**, 1276 (1962); (k) R. F. Vassiliev, *ibid.*, **196**, 668 (1962); (l) J. Stauff, H. Schmidkunz, and G. Hartmann, *ibid.*, **198**, 281 (1963).

(3) (a) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950); (b) N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **19b**, 5 (1964).

(4) (a) N. Wiberg and J. W. Buchler, *Angew. Chem.*, **74**, 490 (1962); (b) N. Wiberg and J. W. Buchler, *J. Am. Chem. Soc.*, **85**, 243 (1963); (c) ref. 3b; (d) N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **19b**, 9 (1964); (e) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3000 (1963); (f) N. Wiberg and J. W. Buchler, *ibid.*, **96**, 3223 (1963); (g) N. Wiberg and J. W. Buchler, *ibid.*, **97**, 618 (1964); (h) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964); (i) work of D. M. Lemal, R. A. Lovald, and K. I. Kawano, *ibid.*, **86**, 2518 (1964), indicates the absence of a dissociation equilibrium in other peraminoethylenes.

(5) Reference 3b. This article reports inability to obtain either the ultraviolet or the Raman spectrum (green Hg line) of TDE because of its instability to ultraviolet radiation. TDE was reported to become turbid on storage in a sealed tube in the dark. We have not observed these effects while determining the spectra of pure TDE or on storage of the compound for several years in glass.

(6) References 4a and 3b give the chemical shift as -2.32 p.p.m. (tetramethylsilane external).

(7) The fluorescence spectrum was determined using 3660 Å activation. The oxyluminescence spectrum was obtained from the air-induced light emission of TDE floating on water.

(8) The configuration of TDE* has not been determined because of lack of resolution of vibrational and rotational fine structure in the absorption and emission spectra. The ultraviolet spectrum of TDE vapor possesses a maximum at 2650 Å and a shoulder at 3500 Å. The solution spectrum has two bands near 2400 and 2700 Å. The large Stokes shift from the absorption bands to the center of the fluorescence or chemiluminescence spectrum at 5150 Å (approximately 9000 cm^{-1} from 3500 Å, or approximately 18,000 cm^{-1} from 2700 Å) is several times the C=C stretching frequency.

(9) Private communication from R. G. Bennett, Radiation Physics Laboratory, Engineering Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington 98, Del.

oxidation of TDE by some electronically activated intermediate transferring its energy to an original TDE molecule or by a different process in which a new TDE* is generated.

The fluorescence quantum yield of TDE under 3660 Å. activation was obtained by comparison with fluorescein solutions of known efficiency. Pure TDE and its 1% solution in *n*-decane gave semiquantitative fluorescence quantum yields of 0.03 to 0.05. The over-all oxyluminescence quantum yield is about 3×10^{-4} , corresponding to about three photons emitted for 10,000 molecules of TDE oxidized. This was determined by measuring the total light emitted by 1 ml. of TDE floating on water. The fluorescence and oxyluminescence efficiencies indicate about 1% of the TDE molecules oxidized result in the production of TDE*. This is in contrast to the 50% or more of luminol molecules that are oxidized to excited aminophthalate ions.^{2c}

The oxyluminescence of TDE is profoundly affected by various protonic substances, including water and alcohols. In their absence, there is no significant reaction of TDE with air. The extreme sensitivity of the oxidation to traces of protonic agents can be shown readily by differential thermal calorimetry. Solutions of TDE in *n*-decane containing octyl alcohol as an impurity displayed large heats of reaction and bright oxyluminescence. Similar solutions of TDE in *n*-decane free of protonic agents developed no significant heat or light in the presence of dry air. Addition of a few parts per million of water to such solutions caused immediate oxyluminescence and heat generation.

Protonic agents used to induce oxyluminescence of TDE are consumed in the process. The concentration of agent required for optimum light emission is low and dependent on the agent. This results from the ease with which the oxyluminescence of TDE is quenched. For example, solutions of TDE in lower alcohols are not oxyluminescent. The oxyluminescence is also quenched by tetramethylurea and tetramethyloxamide, two of the oxidation products of TDE.

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Tetraaminoethylenes

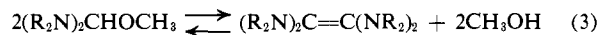
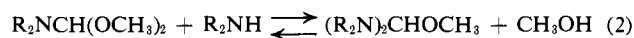
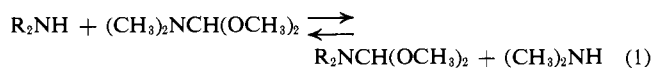
Sir:

A number of previously unavailable and unusually reactive tetrakis(dialkylamino)ethylenes have now been synthesized and their chemistry studied.¹ The new tetraaminoethylenes are obtained by the novel reaction of 1,1-dimethoxytrimethylamine² with appropriate aliphatic secondary amines. Under distillation conditions dimethylamine and methanol are eliminated with the intermediate formation of bis(dialkylamino)me-

(1) Previously known tetraaminoethylenes include tetrakis(dimethylamino)ethylene (13) first reported by R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3649 (1950), and aryl-substituted bis(imidazolidines) (14) reported by H. W. Wanzlick, F. Esser, and H. J. Kleiner, *Chem. Ber.*, **96**, 1208 (1963).

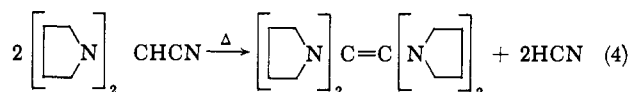
(2) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Chem. Ber.*, **96**, 2671 (1963); M. Brown, U. S. Patent 3,092,637 (June 4, 1963).

thoxymethanes³ which on further heating condense to the corresponding tetrakis(dialkylamino)ethylenes.



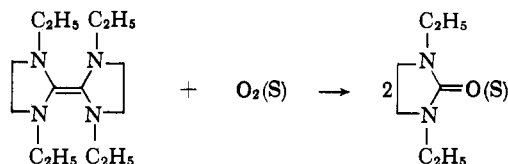
The reaction rates of the various equilibria are influenced by the basicity of the amine, increasing with increasing basicity, and by steric factors. Cyclic secondary amines, such as pyrrolidine and, particularly, *N,N'*-dialkylethylenediamines, are eminently suitable as intermediates to the ethylenes. The nature of the amine and the reaction conditions (temperature, time) dictate the relative proportions of the products.

In the coupling reaction (eq. 3) other stable anions besides methoxyl can serve as leaving groups, as is shown by the evolution of HCN on heating α,α -bis(*N*-pyrrolidinyl)acetonitrile with the formation of tetrakis(*N*-pyrrolidinyl)ethylene.



Several of the new tetraaminoethylenes synthesized by reaction of 1,1-dimethoxytrimethylamine with the appropriate secondary amine are listed in Table I.⁴ The compounds 1-9, with the exception of 7, exhibit the unusual property of emitting visible light on air oxidation.⁵ For example, when a small quantity of 2 is exposed to air, it chemiluminesces brightly, fumes, and is consumed in a short time. Solutions of 2 in inert aliphatic hydrocarbon solvents exhibit strong blue-green oxyluminescence, and exposure to only traces of air is sufficient to cause the luminescence. The fluorescence spectrum of a solution of 2 in cyclohexane under 3660 Å. activation coincides with the air-induced chemiluminescence spectrum of the same solution. The spectra are continuous with the maxima at 5060 Å. The known oxidation products of 2 do not fluoresce under these conditions, which suggests the oxyluminescence arises from electronically excited 2.

The ultimate oxidation product of 2 with air is the imidazolidinone; sulfur reacts similarly to form the corresponding thio analog. With bromine and iodine



the new tetraaminoethylenes give high yields of water-soluble bisquaternary salts analogous to those from tetrakis(dimethylamino)ethylene (13)⁶ and tetraphenyl-

(3) H. Brederick, F. Effenberger, and G. Simchen, *Angew. Chem.*, **74**, 353 (1962); H. Brederick, F. Effenberger, and H. Botsch, *Chem. Ber.*, **97**, 3397 (1964).

(4) Satisfactory elemental analyses were obtained for all new compounds. Spectra characterizations including H^1 n.m.r. were consistent with the proposed structures. All manipulations involving peraminoethylenes were carried out under nitrogen.

(5) The strong oxyluminescence of tetrakis(dimethylamino)ethylene (13) was first observed by Pruett and co-workers, ref. 1. The aryl-substituted bis(imidazolidines) (14) do not oxyluminesce.

(6) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963).