50 mmol) in tetrahydrofuran (30 ml). Any excess iodine was then decomposed by adding a small amount of aqueous sodium thiosulfate. The diene product was extracted into pentane. Distillation gave 5.42 g of *cis,trans*-5,7-dodecadiene (65%), bp 68–69° (0.8 mm); $n^{22}\text{D}$ 1.4652; $\text{uv}_{\max}$ (hexane) 234 mμ (ε 25,100).

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Received August 19, 1968

Monomer and Excimer Emission of Acetone

Sir:

The fluorescence of acetone has been the subject of many investigations.[1–8] Recently, Borkman and Kearns[1] reported that (a) the fluorescence spectrum and quantum yield of acetone with 313-mμ excitation is independent of solvent and (b) there is an abnormally large displacement between the absorption and emission wavelength maxima.

Fluorescence measurements with 285-mμ excitation obtained in this laboratory indicate that the emission of acetone is concentration dependent and that the fluorescence spectrum reported by Borkman and Kearns[1] for 0.2 *M* acetone in *n*-hexane with 313-mμ excitation is that of the acetone excimer. Our results are directed to points a and b above and indicate that the emission wavelength maximum of acetone at 405 ± 3 mμ with 313-mμ excitation is the result of excimer emission and that the fluorescence wavelength maximum of acetone in dilute solutions of *n*-hexane excited at 285 mμ (ε 13.9) occurs at 345 ± 3 mμ. The larger extinction coefficient of acetone at 285 mμ relative to 313 mμ permits dilute solutions (2.7×10^{-4}–2.2×10^{-2} *M*) to be studied, whereas Borkman and Kearns[1] used 313-mμ excitation and concentrations which were $\geq 10^2$ times larger than those in the present study. The results presented in Figure 1 for acetone in *n*-hexane show two concentration-dependent emitting species. The lack of evidence for dimer formation in the ground state eliminates the possibility of absorbing dimers.

In Figure 2 we have plotted on a wave-number scale the absorption of acetone together with the emission of monomer and excimer. It is quite evident that the large displacement reported by Borkman and Kearns[1] is due to the comparison of monomer absorption with excimer emission.

In contrast to the lack of solvent effect on the emission reported by these workers, the n,π* singlet of acetone is expected and does exhibit absorption and fluorescence shifts with solvent polarity. The results presented in Table I show that the absorption bands exhibit the characteristic blue shift with increasing polarity and hydrogen-bonding ability of the solvents. The fluorescence wavelength maximum of the excimer is independent of the solvent; however, the monomer emission exhibits a red shift upon increasing the dielectric constant of the solvent. Hydrogen-bonding solvents, such as methanol, give rise to wavelength shifts in the n,π* absorption process but have little or no effect on the excited state from which emission occurs, since the hydrogen bond is broken in the n,π* transition.[9] The excited-state dipole moment has been estimated to be 0.86 and 1.84 D, both values being smaller than the ground-state value of 2.84 D.[10,11] Since reorganization with respect to the solvent cage occurs in the excited state prior to emission, the fluorescence shifts to higher wavelengths in solvents of increasing dielectric constants.[9,12]

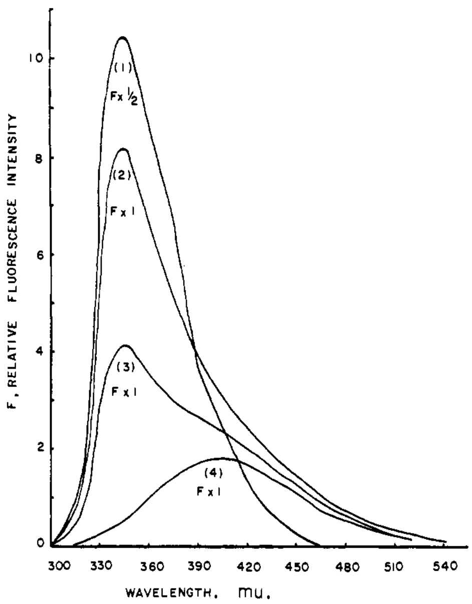

Figure 1. Concentration dependence of monomer and excimer fluorescence of acetone in *n*-hexane solutions at 25° (λ_{exc} 285 mμ): (1) 2.7×10^{-4} *M*, (2) 2.7×10^{-3} *M*, (3) 1.1×10^{-2} *M*, (4) 2.2×10^{-2} *M*.

Table I. Solvent Effects on Absorption and Fluorescence Wavelength Maxima of Acetone at 25°

Solvent	Absorption $\lambda_{\max}$, mμ	Fluorescence (λ_{exc} 285 mμ) Monomer $\lambda_{\max}$, mμ	Fluorescence (λ_{exc} 285 mμ) Excimer $\lambda_{\max}$, mμ
n-Hexane	279	345	405
Ethyl ether	276	355	405
Methanol	271	363	405
Acetonitrile	274	366	405

The ratio of fluorescence intensities for monomer to excimer of acetone in *n*-hexane is estimated to be 10. The relative fluorescence yields were determined according to the method of Parker and Rees.[13] The values obtained in hexane for the monomer and excimer are 0.01 and 0.001, respectively, relative to the value of 0.09 for tryptophan.[14] The accuracy of these values is

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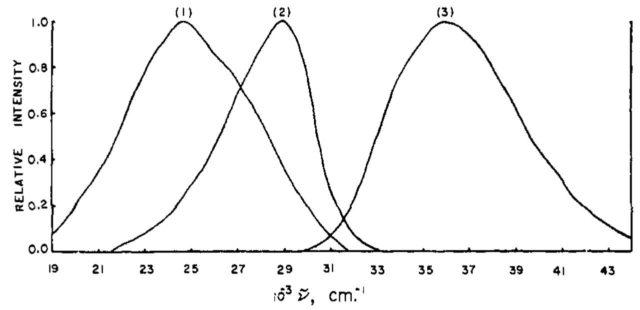

Figure 2. Absorption and emission of acetone in *n*-hexane, normalized to the wavelength maxima, for the excimer fluorescence (1), monomer fluorescence (2), and absorption spectrum (3). Concentrations: (1) 2.2×10^{-2} *M*, (2) 2.7×10^{-4} *M*, and (3) 5.8×10^{-2} *M*.

estimated to be ±25%. Solvents with increasing dielectric constants produce considerable enhancement of monomer fluorescence intensity but have a negligible effect on excimer intensity.[15]

Acetone-d_6 exhibited the same behavior as normal acetone with respect to excimer formation, spectral distribution, and solvent effects. In the deuterated species, however, the fluorescence yield is enhanced for the monomer and excimer. The ratios of the relative intensities of acetone-d_6 to normal acetone were determined to be 2.5 and 1.4 for the monomer and excimer, respectively. Similar results regarding enhancement by deuteration have recently been reported for fluid solutions of deuterated biacetyl.[16]

Kearns and Borkman[2] have reported that energy transfer from acetone to *cis*-pentene-2 is more efficient in neat acetone than in mixed solvent systems. Wagner[17] has shown this effect to be due to dependence of the acetone triplet lifetime on hydrogen abstraction from the solvent. It is also possible that the excimer participates in energy transfer.

The excimer emission of acetone is not unique among aliphatic ketones. We have in fact also observed monomer and excimer emissions from the following aliphatic ketones: diethyl ketone, methyl ethyl ketone, diisopropyl ketone, dicyclohexyl ketone, and di-*t*-butyl ketone. Further studies of ketone excimers are currently in progress.

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Received August 7, 1968

Stereospecific Hydroxyl Proton Spin–Spin Coupling in a Primary Alcohol[1]

Sir:

A number of reports have appeared recently on the use of the hydroxyl proton as a conformational probe,[2] usually including dimethyl sulfoxide as solvent to inhibit proton exchange.[3] In each case, structural conclusions were based on the assumption that angle dependence of the vicinal hydroxyl proton coupling constants, J_{HCOH}, parallels the familiar Karplus relationship for J_{HCCH}.[4] This assumption, though inherently reasonable, has not been demonstrated, a fact which has permitted controversy to develop over conformational equilibria involving the hydroxyl group.[2a] We wish to describe the first case of strongly nonequivalent hydroxyl proton coupling in a primary alcohol,[5] an observation which further supports the proposed angle dependence of J_{HCOH} (see Figure 1).

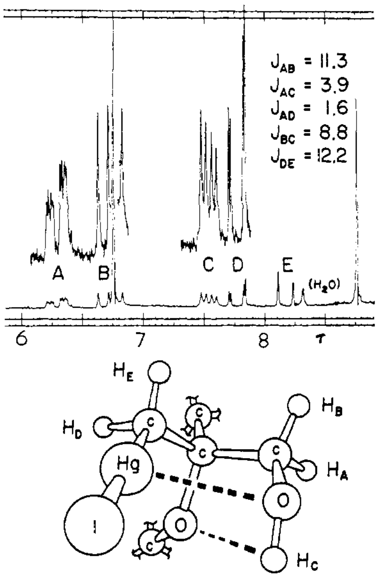

Figure 1. The nmr spectrum (100 MHz, 0.175 *M* in $CDCl_3$) and preferred conformation of 3-iodomercuri-2-methoxy-2-methyl-1-propanol (**1**).

Compound **1**, prepared by methoxymercuration of methallyl alcohol as described previously,[1b] shows a quartet for the hydroxyl proton in acetone, chloroform, or carbon tetrachloride at room temperature. Analysis of the five-spin system represented by protons A–E (Figure 1) over the usable temperature range in $CDCl_3$[6] and straightforward statistical treatment of the resulting data[7] gave limiting values of J_{HCOH} = 11.0 and J'_{HCOH}

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