sequently, these Aspidosperma alkaloids have the same absolute configuration designated by structure **1** (C_{19}–Hα).

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(13) National Institutes of Health Predoctoral Fellow, 1966–1969.

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Fluorescence Lifetimes of Molecules that Undergo Large Configurational Changes upon Excitation[1]

Sir:

Comparison of measured and calculated lifetimes of molecules can lead to important information regarding the nature of the lowest excited singlet state and the corresponding electronic transition. Measured natural lifetimes (τ_{0m}) are obtained from fluorescence decay (τ_F) and quantum yield (ϕ_F) measurements using the relation $\tau_{0m} = \tau_F/\phi_F$. Calculated natural lifetimes τ_{0c} are estimated using Strickler and Berg's relation.[2]

Agreement between τ_{0m} and τ_{0c} is expected in systems where the approximations used in deriving the Strickler and Berg equation are valid. There it is assumed that $B_{uo \to l} = B_{u \leftarrow lo}$, where $B_{u \leftarrow lo}$ is the sum of the coefficients of induced absorption from the vibrationless lower state (lo) to the upper vibronic states (u) and $B_{uo \to l}$ is the sum of the coefficients of induced emission from the vibrationless upper state (uo) to the lower vibronic states (l). This approximation makes it possible to calculate lifetimes from absorption intensities and from the reciprocal of the mean value of $\bar{\nu}_F^{-3}$ in the fluorescence spectrum. However, $B_{uo \to l}$ is equal to $B_{u \leftarrow lo}$ under certain limited conditions, namely, when the electronic transition moment $M_{lu}(Q)$ is independent of the nuclear coordinates, Q, or if the potential energy surfaces for the upper and lower states are not displaced relative to each other; and when the vibrational wave functions with a given quantum number are the same for the ground and excited states, *i.e.*, potential surfaces of both states have the same shape.

Discrepancies between τ_{0m} and τ_{0c} have been discussed before by Douglas[3] to explain anomalously long lifetimes of small molecules (*e.g.*, SO_2). Birks and Dyson[4] have interpreted anomalously long lifetimes of diphenylpolyenes, *i.e.*, values of α ($\alpha = \tau_{0c}/\tau_{0m}$) less than one, in terms of changes in nuclear configuration as a result of excitation.

Recently, anomalously long lifetimes (10^{-4}–10^{-5} sec) have been observed by Briegleb, *et al.*, for methylpyridinium halides.[5] Large *intermolecular configurational changes* occur during lifetimes of the excited states leading to a configuration unfavorable for the transition. Thus, the transition from the equilibrium excited state is forbidden relative to the transition arising from a ground-state equilibrium configuration.

Here we give an example where the transition becomes more allowed (*i.e.*, $M_{u \to l}(Q') > M_{u \leftarrow l}(Q'')$) owing to *intramolecular configurational changes* in the excited state which give rise to anomalously short lifetimes. Fluorescence lifetimes and quantum yields were measured for β-naphthylamine degassed solutions in cyclohexane and ethanol at room temperature. Lifetimes were calculated using the Strickler and Berg equation, which includes corrections for the refractive index of the solvent and the frequency of emission. The results are summarized in Table I.

Table I. Fluorescence Lifetimes (in nsec) of β-Naphthylamine at Room Temperature

Solvent	τ_F	ϕ_F	τ_{0m}	τ_{0c}	$\alpha = \tau_{0c}/\tau_{0m}$
Cyclohexane	6.9	0.33	21	41	1.95
Ethanol	16.6	0.46	36	56	1.56

The permanent dipole moment of the fluorescent state of β-naphthylamine is 3.5 D larger than the ground-state dipole moment. To explain this large increase in dipole moment, Mataga[6] suggested a structural change of the amino group from the essentially[7] tetrahedral sp^3 configuration of the ground state to a trigonal sp^2 configuration in the equilibrium excited state. In the trigonal configuration larger overlap occurs between the lone-pair orbital on the amino nitrogen and lowest vacant π molecular orbital of the naphthalene ring leading to a stronger mixing of charge-transfer character into the lowest excited state of β-naphthylamine. Due to this larger overlap the charge-transfer transition is more probable in the sp^2 configuration. Therefore, one expects the electronic transition moment $M_{u \to l}(Q')$ to be greater than $M_{u \leftarrow l} \cdot (Q'')$, where Q' and Q'' represent the equilibrium nuclear configuration of the excited and ground states, respectively. This should lead to a value of τ_{0m} smaller than τ_{0c}. The measured natural lifetime is about half the calculated value, as shown in Table I.

The increase in τ_{0m} in going from cyclohexane to ethanol (as a function of polarity of the medium) can be attributed to changes in the refractive index of the medium, changes in the average frequencies of absorption, and particularly large red shifts of the fluorescence spectrum. The latter arises from the relaxation of the solvent cage during the lifetime of the excited state, which has a different dipole moment from that of the ground state. Lifetimes calculated using the Strickler and Berg equation take into account these factors. It appears, however, that greater interaction between the polar solvent molecules and the polar

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(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-2039 and by the National Institutes of Health, National Institute of Neurological Diseases, Blindness and Stroke, Grant No. NB-04145.

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solute in the excited state tends to affect the transition probability such that α is smaller in the polar media, its value being greater than one in all the media studied. An increase in τ_{0m} as a function of polarity of the medium was also observed for α-naphthylamine and 5-dimethylaminonaphthalene-1-sulfonamide (DNSA).

The dependence of τ_{0m} on the solvent leads to an interesting temperature dependence. For DNSA in ethanol the radiative lifetime increases from a low value of 20 nsec at 77°K to a higher limiting value of 34.4 nsec at temperatures above 190°K. At low temperatures when the solvent cage reorientation cannot occur during the lifetime of the excited state, emission arises from a Franck–Condon state which has an equilibrium configuration similar to that of the ground state. Under these conditions it is expected that τ_{0m} is smaller and the emission blue shifted compared to results at room temperature, as has been observed for DNSA.

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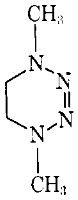
1,4,7,10-Tetramethyl-1,2,3,4,7,8,9,10-octaazacyclododeca-2,8-diene. A Cyclic Bis-2-tetrazene

Sir:

Our interest in 2-tetrazenes[1,2] led us to attempt preparation of the cyclic-2-tetrazene **1**, for comparison of its properties with *trans* analogs, such as tetramethyl-2-tetrazene (**2**). The oxidation of **3**[3] with potassium bromate[4] gave moderate yields (17–29%) of a solid, which was purified by alumina chromatography and crystallization from pentane (dec 123–123.5° with gas evolution).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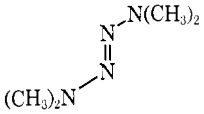
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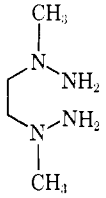
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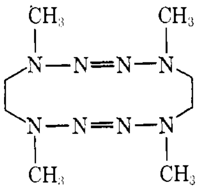
4

Several spectral properties indicated that this material was a 2-tetrazene. The uv spectrum ((heptane) λ_{max} 241 (ϵ 4.4 × 10^3), 258 (6.0 × 10^3), 267 (9.0 × 10^3), 276 (9.3 × 10^3), 300 nm shoulder (1.6 × 10^3)) is qualitatively similar to that of **2**, λ_{max} 250 and 277 nm.[5] The ir spectrum is also consistent with a 2-tetrazene structure (6.80, 7.01, 7.34, 7.70, 7.90, 9.28, 9.63, 10.04 μ) and the analysis[6] fits **1** (Calcd for $C_4H_{10}N_4$: C, 42.07; H, 8.83; N, 49.10. Found: C, 41.97; H, 8.81; N, 49.22); the nmr shows the expected two singlets ($CDCl_3$) at δ 2.83 and 3.67, 3:2 intensity ratio. The mass spectrum showed, however, that the solid was a dimer of **1**; at 70 eV (AEI MS 9 spectrometer, direct inlet), the parent at *m/e* 228 was 40% of the intensity of the base peak at 42, and 6.9 times as intense as the 114 peak. In carbon tetrachloride, observed osmometric molecular weights were 229 (0.091 *M*), 227 (0.046), 225 (0.019).

The data require structure **4** for the isolated oxidation product of **3**. The formation of the twelve-membered ring dimer in preference to a six-membered ring is quite surprising.

The thermal stability of **4** is inconveniently great for accurate measurement of its decomposition rate by our nitrogen evolution apparatus,[1] but five runs at 159 ± 1° in tetralin gave times for half-decomposition in the range 138 ± 12 min (5 × 10^{-3} *M* initial concentration). Curvature was evident in first-order plots, which might be expected from the bistetrazene structure, since concerted cleavage of both nitrogens is not likely. Clearly **4** is somewhat stabler than **2**, which has an extrapolated half-life of 91 min at 159° (vapor phase);[7] the only reported decomposition rate in solution corresponds to a half-life of 206 min at 145° (cumene),[8] at which temperature the vapor phase half-life is about 340 min. Since it is apparent[9] that a *cis*-azo linkage in an azoalkane lowers the activation energy for decomposition by approximately 10 kcal/mol over that for a *trans*-azoalkane (in the absence of strain, which lowers the activation energy even more[10]), the thermal stability of **4** is most consistent with it possessing *trans*-2-tetrazene groups.

The nmr spectrum of **4** is temperature dependent; the methylene absorption is noticeably broadened even at room temperature, and at −45° appears as a double doublet, ν_{ab} = 57, J_{ab} = 11.3 Hz; the methyl absorption remains sharp. The coalescence temperature for the methylene absorption is about +5°, giving an apparent ΔG^* for interconversion of the methylene hydrogens of about 13.5 kcal/mol. This free energy of activation is remarkably high for a twelve-membered ring, and actually is somewhat above values observed for several saturated azamethyl cyclohexyl systems.[11] *trans*-Azo linkages would seem necessary to give sufficient rigidity to the ring system to observe the slow interconversion of the methylene hydrogens. Whether additional rigidity is imparted by significant hindered rotation about the four amino nitrogen–azo nitrogen bonds must remain an open question without further data, but no temperature dependence has proved observable in the nmr spectrum of **2**.[12]

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