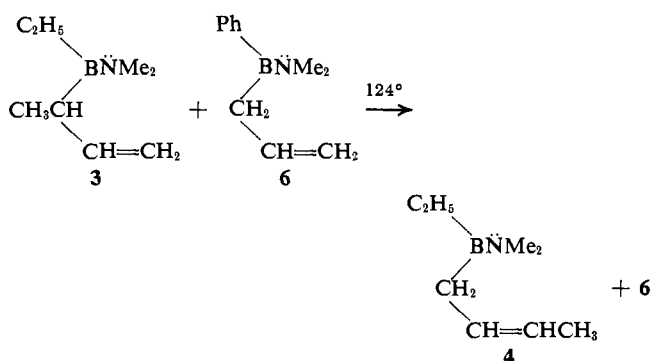2-en-1-yl(dimethylamino)phenylborane (8)[10] rules out alternative intermolecular mechanisms and unequivocally establishes the intramolecularity of the 1,3-aminoboryl shift.[11]

$$
\begin{array}{ccc}
\underset{\underset{\underset{\text{CH=CH}_2}{|}}{\overset{\text{C}_2\text{H}_5}{\underset{}{\overset{|}{\text{CH}_3\text{CH}}}}}{\text{BNMe}_2} & + & \underset{\underset{\underset{\text{CH=CH}_2}{|}}{\overset{\text{Ph}}{\underset{}{\text{CH}_2}}}}{\text{BNMe}_2} \\
\mathbf{3} & & \mathbf{6}
\end{array}
\xrightarrow{124°}
$$

$$
\underset{\underset{\underset{\text{CH=CHCH}_3}{|}}{\underset{\text{CH}_2}{|}}}{\overset{\text{C}_2\text{H}_5}{\underset{}{\text{BNMe}_2}}} \quad + \; \mathbf{6}
$$
$$
\mathbf{4}
$$

Considering the substantial negative $\Delta S^{\ddagger}$ and an E_a well below reasonable estimates of the allylic B–C bond energy,[12-14] a concerted reorganization mechanism such as one involving a four-electron, five-orbital transition state (Figure 1) is suggested.

Mikhailov has reported[1] that the so-called "permanent allylic rearrangement" of allylboranes to symmetrical structures with equivalent α- and γ-carbons in the allylic moiety is inhibited by amines and THF. The **3** → **4** isomerization can be similarly, but not dramatically, retarded. At 101°, the rearrangement of **3** is 3.5 times slower in pyridine than in methylcyclohexane. With lower concentrations of pyridine in methylcyclohexane quenching was negligible. Further inhibition of the isomerization with stronger Lewis bases (e.g., diazabicyclo[2.2.2]octane) was not possible. Dioxane was even less effective as a quencher; less than a 10% rate reduction was noted in dioxane relative to methylcyclohexane.

Unlike allyldialkylboranes, however, the α-methylallyl(amino)borane **3** is subject to Lewis acid catalysis. Addition of 10% by weight of anhydrous ZnCl₂ caused complete isomerization of **3** in 24 hr at 101° (ca. tenfold acceleration), but with some accompanying decomposition. Anhydrous MgCl₂ increased the rate at 101° twofold. Similar catalysis has been observed only for the allylboronate **5**,[7] leading to the conclusion that Lewis-acid catalysis depends on reducing the electron-donor substituent's stabilizing influence.

Finally, considerable thermal stability is clearly conferred upon terminal-olefin allylborane isomers by π-electron-donor substitution at boron. Quantitatively, the activation energy for a 1,3 shift of boron is apparently increased in **3** relative to **1** by ca. the π energy of the N⇌B bond. Thus, for allyldialkylboranes **1**, activation energies of ca. 10 kcal/mol were found by nmr.[1] The N⇌B rotational barrier for sec-butyl(dimethylamino)phenylborane (**9**), a close saturated analog

Figure 1. Concerted mechanism for the 1,3-aminoboryl shift.

of **3**, has been determined as 15 kcal/mol.[15] The agreement between the sum of these values and the experimental E_a of 25 kcal/mol is quite satisfactory.

(15) (a) T. Totani, H. Watanabe, and M. Kubo, Proc. Colloq. AMPERE (At. Mol. Etud. Radio Elec.), 13, 366 (1964); (b) H. Watanabe, T. Totani, K. Tori, and T. Nakagawa, ibid., 13, 374 (1964).

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Multiconfigurational Aspects of the Metastable Triplet State of Cyclopentanone[1]

Sir:

We have recently described some anomalies[2] in the paramagnetism of triplet cyclopentanone and have suggested[2b] their possible connection with the ring scission which copiously occurs via this state.[3] Tacit in our discussion was the assumption that the paramagnetism we had observed arose from a single electronic configuration. In this communication we develop magnetic and optical evidence that triplet cyclopentanone consists, in fact, of several distinct electron-nuclear configurations which interconvert, even at liquid helium temperatures, at rates exceeding 10^3 sec⁻¹. Convergence both of photochemical and spectroscopic interest on such features imparts urgency to our results, and we report them briefly here.

Neat cyclopentanone samples prepared for our previous work exhibited not only the usual triad[4] of zero-field resonances clearly identifiable[2a] with cyclopentanone but also two additional weaker triads (Figure 1(a)) whose PMDR spectra[5] were quite different from the phosphorescence[6,7] of cyclopentanone. Not understanding their origin, we made no mention of them. Since that time we have performed experiments in which

(10) K. G. Hancock and J. D. Kramer, J. Amer. Chem. Soc., 95, 3425 (1973); 5% of **8** was easily detectable in a control experiment.

(11) Alternative crossover experiments involving labeling of the amino function are vitiated by transamination reactions which occur at these temperatures.

(12) In the absence of precise thermochemical data, a rough estimate for the allylic carbon–boron bond energy would be ca. 68 kcal/mol, based on the well-established resonance energy of the allylic radical[13] and the B–C bond energy in trialkylboranes.[14]

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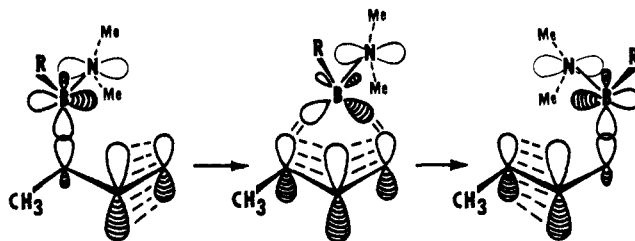(14) E. L. Muetterties, Ed., "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967.

(1) Work supported by the National Science Foundation and the U. S. Army Research Office (Durham).

(2) (a) A. L. Shain, W.-T. Chiang, and M. Sharnoff, Chem. Phys. Lett., 16, 206 (1972); (b) A. L. Shain and M. Sharnoff, ibid., 16, 503 (1972).

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(6) S. R. La Paglia and B. C. Roquitte, J. Phys. Chem., 66, 1739 (1962).

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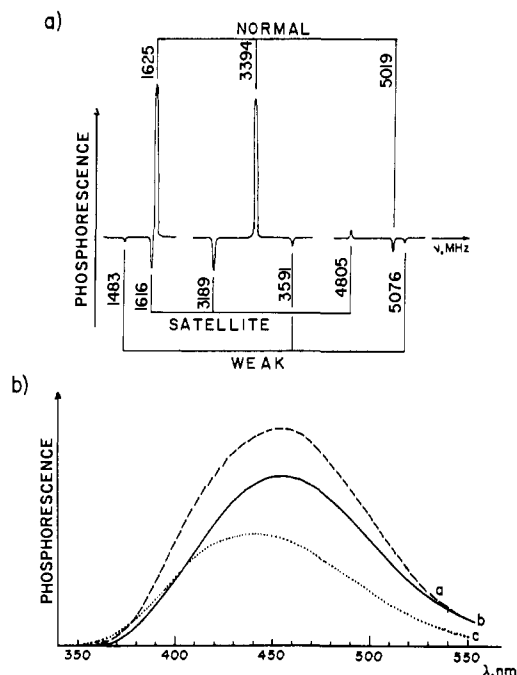
Figure 1. (a) Sketch of the microwave-optical double resonance signals observed in neat cyclopentanone at 1.4°K, showing normal, satellite, and weak triads. The weak triads are shown as being much more intense than they really are. At 77°K the normal and satellite triads are broader and weaker but remain resolved and comparable to each other in intensity. Numbers indicate resonance frequencies in MHz. (b) Emission spectrum of neat cyclopentanone at 4.2°K (curve a); modulated component of phosphorescence obtained by pulsing 1625 or 3394 MHz resonance (curve b) or 1616 or 3189 MHz resonance (curve c). Ordinates in curves a and c have been multiplied by +0.1 and -2.5, respectively, with respect to those of curve b. Microwave and optical signals observed in cyclopentanone-hexane mixed crystals are similar to those shown.

we irradiated our samples simultaneously, at liquid helium temperatures, by two microwave fields.[8,9] The frequency of one of these fields, which was amplitude modulated, was chosen to coincide with one of the resonances of the satellite triad. The resonance was optically monitored in the usual way via the concomitant, synchronous modulation of the phosphorescence.[10-12] We found the amplitude of the phosphorescence modulation to be markedly affected by the presence of the second, *unmodulated* microwave field whenever this additional field became resonant with any line of the normal triad. We interchanged the frequencies of the modulated and unmodulated microwave fields and found the amplitude of phosphorescence modulation again to be affected by the presence of the unmodulated field. Examination of many of the possible combinations of transitions has convinced us that the effect is bidirectional; CW saturation of a resonance in any one of the triads affects the intensities of resonances in the others.

Conceivably, the double resonance effects we have described could be artifacts of interaction between the microwave transmitters which, by impressing modulation upon the field generated by the CW transmitter,

caused both resonances to be directly and coherently modulated. Impressed microwave modulation did occur to a measurable degree in our apparatus, but our calculations show its extent to be 5 orders of magnitude too small to account for the observed enhancements of up to 50% in the modulation of the phosphorescence. The synergy of the AM and CW actions upon our samples thus implies that the spin sublevel populations of the systems in which the triads originate are coupled with each other.

Three sources of coupling appear plausible: (1) magnetic cross-relaxation[13,14] between triplets trapped at different site species; (2) trap-to-trap energy transfer via (triplet) exciton bands of the host;[15,16] and (3) configurational interconversion *within one and the same molecular system*. These mechanisms are to be weighed against the following experimental findings: (a) the double resonance effects are unaffected by a 25-fold variation in the intensity of the uv excitation; (b) normal and satellite triads are also found[17] in mixed crystals of cyclopentanone-hexane (0.01 mol/mol) and show double resonance interaction comparable to that observed in neat cyclopentanone. Finding a excludes mechanism 1; bimolecular cross-relaxation rate constants would be inversely proportional to the cube of the intertrap distance[18] and hence proportional to the uv excitation intensity. The frequencies of our resonances also fail to satisfy the energy conservation requirement of cross-relaxation[13] between traps. Finding b shows that the double resonance effects do not depend upon thermal accessibility of the exciton band(s) of the host, thereby excluding mechanism 2.

We must, then, contemplate seriously the possibility that three electronic configurations, each corresponding to a different triad of resonances, can interconvert at temperatures as low as 1.4°K at rates ranging between 5×10^2 sec^{-1} (half the decay constant of triplet cyclopentanone) and 5×10^7 sec^{-1} (an upper limit set by the motional merging[19] of fine structure patterns which becomes inevitable at rates exceeding this). This interconversion, if thermal in origin, would have an activation energy of less than 0.01 kcal/mol. If produced indiscriminately by all phonons, it would become so rapid at 77°K as to motionally merge the three epr triads. That our triads remain well-resolved even at 77°K is persuasive evidence that the interconversion observed at helium temperatures cannot be thermally activated.

Quantum-mechanical tunneling of nuclei through a barrier in the potential energy is a plausible alternative. We have estimated tunneling rates with the help of numbers suggested by optical data available for the first excited singlet of cyclopentanone.[20] Taking a

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(9) J. S. Hyde, J. C. W. Chien, and J. H. Freed, *J. Chem. Phys.*, **48**, 4211 (1968).

(10) M. Sharnoff, *J. Chem. Phys.*, **46**, 3263 (1967).

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(17) The weak triad may very well be present in the mixed crystals, but we have not succeeded in displaying it above the noise in our detection apparatus. Its intensity, even in neat samples, is only several times the instrumental noise.

(18) N. Bloembergen, *Physica (Utrecht)*, **15**, 386 (1949).

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(20) H. E. Howard-Lock and G. W. Kin *J. Mol. Spectrosc.*, **36**, 53 (1970).

rectangular barrier of width 0.5 Å and height 700 cm^{-1}—540 cm^{-1} above the zero-point level of the ν_{25} carbonyl wagging mode—we find a tunneling rate of 5×10^3 sec^{-1} for a particle of mass 16 amu. Thermal hopping over the barrier would become competitive with tunneling at temperatures above 40°K and would attain rates as high as 2×10^7 sec^{-1} at 77°K. The multiplicity of epr triads and the distinct emission spectra (Figure 1) indicate that the potential wells separated by the barrier(s) are not symmetrically disposed with respect to one another.

While these estimates are in encouragingly good accord with our experimental findings, the lack of vibronic structure in the emission spectra suggest that electronic and nuclear motion are strongly coupled in the cyclopentanone triplet. Our picture of nuclei tunneling through a stationary electronic potential barrier must therefore be taken as tentative.

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Structures of the Lythraceae Alkaloids Lythrumine and Acetyllythrumine[1]

Sir:

Five new alkaloids have been isolated from the aerial portions of the Lythraceae plant *Lythrum lanceolatum* obtained near St. Marks, Fla. The structures, absolute configurations, and biosynthesis of two of these alkaloids, lythrumine and monoacetyllythrumine, are reported here. This structural investigation makes it possible to directly correlate the Lythraceae alkaloids of North America with those from Japan and it suggests that the three structural types elaborated by this plant family have a common biosynthesis.

Lythrumine (1), $C_{26}H_{31}NO_4$,[2] mp 214–216°, $[\alpha]^{26}D$ −8.0° (MeOH), shows hydroxyl (3550, 3500 cm^{-1}) and a carbonyl (1700 cm^{-1}), λ max 294 nm (ϵ 6790), in base λ max 296 nm (ϵ 5290).

Monoacetyllythrumine (2), $C_{28}H_{33}NO_5$, mp 184–185°, $[\alpha]^{26}D$ −34°, ν max 3400, 1740, 1705 cm^{-1}, λ max 292.5 nm (ϵ 8030), δ 1.9 (s, 3 H), 3.9 (s, 3 H), 6.8–7.3 (m, 6 H) ppm, yielded the same diacetate (3) obtained from lythrumine as shown by identical ir spectra, melting points, and an undepressed mixture melting point.

Crystals of lythrumine hydrobromide were grown by slow evaporation of a methanol solution. Preliminary X-ray photographs displayed $2/m$ Laue symmetry and the systematic absence for hkl (absent if $h + k = 2n + 1$). Diffractometer measured cell constants are $a = 36.62$ (1), $b = 10.294$ (5), $c = 12.618$ (5) Å, and $\beta = 83.40$ (4)°. A calculated density of 1.34 g/cm^3 was interpreted to mean $Z = 8$ or two molecules per asymmetric unit in the monoclinic space group C_2. A total of 3481 reflections were measured and 3115 were judged to be observed after standard corrections for Lorentz and polarization effects.

(1) Lythraceae Alkaloids. XI. For the previous paper in this series see J. P. Ferris, C. B. Boyce, R. C. Briner, U. Weiss, I. H. Qureshi, and N. E. Sharpless, *J. Amer. Chem. Soc.*, **93**, 2963 (1971).

(2) The details of the isolation and purification of these alkaloids will be presented later. Elemental analyses and mass spectra were obtained in agreement with the elemental composition shown.
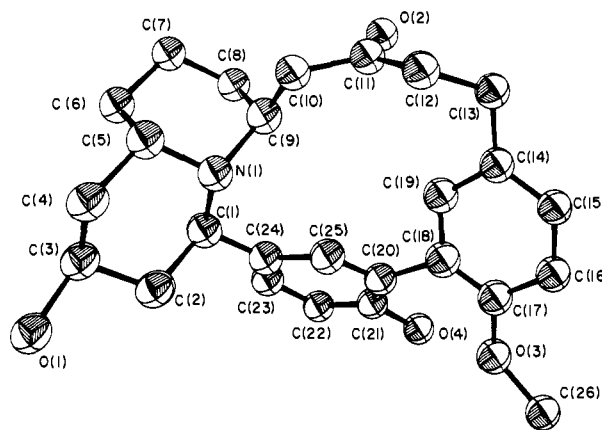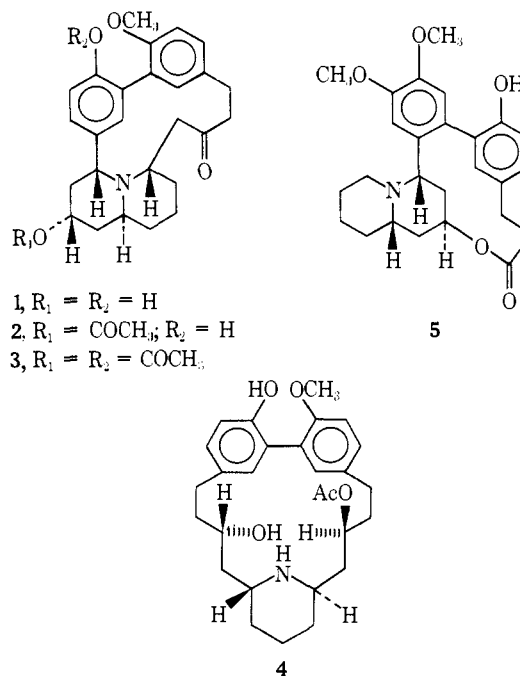

Figure 1.

1, $R_1 = R_2 = H$
2, $R_1 = COCH_3$; $R_2 = H$
3, $R_1 = R_2 = COCH_3$

5

4

A sharpened three-dimensional Patterson synthesis was computed.[3] A satisfactory deconvolution of the Patterson was discovered with three independent bromines rather than the anticipated two. One full bromine was in a general position and two half-bromines were on the twofold axes at $(0,y,0)$ and $(0,y,\frac{1}{2})$. The remaining 62 nonhydrogen atoms were revealed on successive three-dimensional electron density syntheses. Full-matrix least-squares refinements with anisotropic temperature factors for all nonhydrogen atoms lowered the discrepancy index to 0.093.[4] The mirror image was fully refined to a discrepancy index of 0.096 indicating that the correct enantiomer of the molecule had been chosen at the start.[5] Both molecules in the asymmetric unit have the same configuration and conformation and the final X-ray model for one is shown in Fig-

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(4) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965. See paragraph at end of paper regarding supplementary material.

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