Figure 1. Second derivative X-band esr spectrum of Co(bzacen)-pyO$_2$, containing 33 atom % $^{17}$O, in CH$_2$Cl$_2$ solution at ca. $- 30°$.

oxygen carrier Co(bzacen)pyO$_2$ has been determined[4] and the M–O–O bond found to be bent, with an angle of 126 $\pm$ 2°. We now wish to report esr measurements on the complex in solution.

Co(bzacen)pyO$_2$ was synthesized with 33 atom % $^{17}$O and 95 atom % $^{17}$O using O$_2$ gas enriched in $^{17}$O (Yeda, Rehovoth, Israel). The second derivative esr spectra in CH$_2$Cl$_2$ are shown in Figures 1 and 2. The spectra are insensitive to the addition of a considerable excess of pyridine. The experimental temperatures were chosen to give maximum resolution. At higher temperatures spin–rotational line broadening obscures the hyperfine structure, as does modulation of the g and hyperfine tensors at lower temperatures. The ratio of unlabeled and singly and doubly $^{17}$O labeled molecules in the complex enriched to 33 atom % of $^{17}$O is 4/9 : 4/9 : 1/9, respectively. The intensities of the satellites from the two $^{17}$O nuclei in the doubly labeled molecules are much less than those from the singly labeled molecules, and therefore only the latter contribute to the observed spectra under our experimental conditions. The outermost $^{17}$O satellites therefore have a separation of $7a_{Co} + 5a_{O_1}$, where $a_{O_1}$ is the unique or larger value of $a_O$, depending on whether the $^{17}$O nuclei are equivalent or not. The value of $|a_{Co}|$ was found, from the spectrum of the isotopically normal complex, to be 12.8 G. The total spread of the spectrum, 198 G, leads to a value of $|21.7|$ for $a_O$, or $a_{O_1}$.

The complex synthesized from 95 atom % $^{17}$O is a superposition of hundreds of lines due to the unlabeled and singly and doubly labeled molecules which are present in the ratios of 0.001 : 0.018 : 0.810. The spectrum was therefore simulated on the computer for a wide range of values of $a_{O_1}$ and $a_{O_2}$. A satisfactory simulation requires the taking into account of the $m_I$ dependent line widths of the esr lines due to modulation of the g and hyperfine tensors by tumbling. To calculate the relative line widths, it is necessary to know the g tensor and the anisotropic $^{17}$O and $^{59}$Co hyperfine tensors. The $^{59}$Co tensor can be taken, on the basis of much previous work, as being effectively isotropic.[5] The $^{17}$O tensors can be confidently estimated from the assumed values of $a_{O_1}$ and $a_{O_2}$, by using the equation $a_O = 41\rho_0$ to estimate the spin densities[6] and taking the anisotropic $^{17}$O splitting for an electron in a 2p orbital, $2\beta(^{17}O)$, to be $-103$ G.[7] This procedure has been shown to be consistent with the known data for the



Figure 2. Experimental and computer simulated second derivative X-band esr spectrum of Co(bzacen)pyO$_2$, containing 95 atom % $^{17}$O, in CH$_2$Cl$_2$ solution at ca. $-30°$.

peroxyl group.[8] The g-tensor was estimated from that for the peroxyl group,[8] but the results are comparatively insensitive to the exact values taken. The esr spectrum of the 95% $^{17}$O enriched complex was simulated for a very wide range of values of $a_{O_1}$, $a_{O_2}$, and $\tau_c$, the rotational correlation time for molecular tumbling. The best fit to the experimental spectrum, shown in Figure 2, was obtained for $|a_{O_1}| = |a_{O_2}| = 21.6$ G, $\tau_c = 10^{-12}$ sec, and natural line width ($m_I$ (independent)) = 16 G. It should be noted that the range over which the values of $|a_O|$ could be allowed to stray from 21.6 g without causing marked differences between the observed and simulated spectrum was no more than $\pm 0.5$ G. For unsymmetrically bonded peroxy groups the values of $|a_O|$ for the unequivalent oxygens fall in the range 16–18 G and 22–24 G.[8,9]

The present esr results are consistent with a complex containing magnetically equivalent oxygen atoms.

It is possible that this equivalence reflects a $\pi$-bonded symmetrical structure or that the observed equivalence in solution is the result of a rapid flipping of the O–O group between two bent positions. A dynamic equilibrium would result in line width effects of a kind which we found unnecessary to take into account to give excellent computer simulations of the experimental spectra.

Further work is in progress on this and other synthetic and natural oxygen complexes containing porphyrin ligands in solution. Preliminary results indicate that in all cases so far studied the oxygens are magnetically equivalent.

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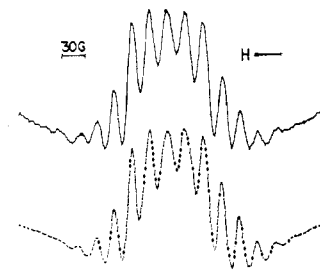
## Triboluminescence of Coumarin. Fluorescence and Dynamic Spectral Features Excited by Mechanical Stress

*Sir:*

The excited state origins of triboluminescence (TL), the emission of light caused by the mechanical deforma-

tion of crystals,[1] have been identified for only two of the many[2] triboluminescent crystals. We have recently found that the triboluminescence spectrum of hexaphenylcarbodiphosphorane is almost identical with the photoluminescence (PL) spectrum of the compound dissolved in a rigid glass.[3] The emission was assigned to the lowest excited triplet state on the basis of its lifetime (0.1 msec). A semiquantitative study of the triboluminescence of tetrakis(dibenzoylmethido)-europium(II) salts[4] identified the luminescence as a metal-centered $^5D_0 \rightarrow {}^7F_2$ transition on the basis of the presence of TL emission intensity only at wavelengths the same as those of the photoluminescence.[5] The lifetime of the TL was about 0.5 msec.[4] The TL of both of the known compounds is a molecular phosphorescence. In this paper the TL of coumarin, the first example of a molecular tribofluorescence, and the dynamic spectral features captured by the short lifetime fluorescence are reported.

The TL spectrum was obtained by grinding 0.5-g samples in a glass vial with metal, wood, glass, or Teflon rods. Weak TL excited by the thermal shock of immersing a sample in liquid nitrogen was visually observed (*vide infra*). The ratio of the intensity of a triboluminescence flash at a given wavelength to the total integrated intensity was measured simultaneously using two detectors. No spectroscopically detectable chemical change occurred as a result of the grinding. The spectra were monitored by an EMI 9558 photomultiplier cooled to $-20°$ and were not corrected for response characteristics of the instrument.

The tribo- and photoluminescence spectra of the solid at room temperature are shown in Figure 1. In methylcyclohexane glass at $77°K$, the PL spectrum is slightly red shifted (40 $cm^{-1}$). This luminescence has been assigned[6,7] to the $^1(\pi,\pi^*)$ fluorescence for which small matrix-dependent shifts were also reported.[6] Because of the correspondence between the TL and PL spectra, the TL of coumarin is assigned to the $^1(\pi,\pi^*)$ fluorescence.

The broad shoulder centered between 4600 and 4700 Å is a reproducible feature of the TL spectrum and is probably a consequence of the pressure exerted on the crystal during the excitation. Similar but more pronounced effects have been found in the tribofluorescence spectra of acenaphthene.[8] The two most plausible mechanisms which could give rise to the new feature are the formation of a pressure-induced intermolecular interaction (such as a pressure-induced excimer), and a pressure-induced change in the vibronic coupling or the Franck–Condon factors between the excited and the ground states. The observed red shift (*ca.* 3200 $cm^{-1}$) of the shoulder in the TL spectrum compared to its parent TL emission maximum is smaller than most of the reported shifts (*ca.* 6000 $cm^{-1}$) of known[9] excimer fluorescences from their parent
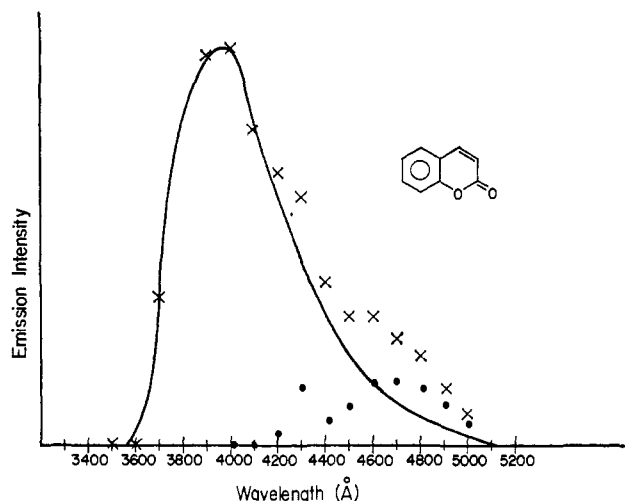
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Figure 1. Luminescence spectra of coumarin normalized to the same intensity at 4000 Å: (——) crystal photoluminescence, room temperature; (XXXX) triboluminescence, room temperature; (●●●●) calculated difference spectrum.

emissions as might be expected for a weak, pressure-induced excimer. In regard to the second mechanism, the 3200-$cm^{-1}$ red shifted shoulder occurs at about the energy of the totally symmetric second overtone of the 1596 $cm^{-1}$ C=C stretch.[7] The point at 4300 Å, red shifted by about 1600 $cm^{-1}$, cannot be definitively assigned at our current 100 Å resolution. However, the shoulder(s) could also be consistent with a stress-induced change in the vibronic intensities. No new low energy features developed in the PL spectrum of the solid taken at $77°K$ after the thermal shock TL had ceased. Thus, the low energy shoulder in the TL spectrum can be associated with the dynamic TL process. The absence of new features in the previously reported tribophosphorescence spectra[3] in comparison with the PL spectra is indicative of mechanical relaxation prior to the longer-lived phosphorescence.

The most commonly proposed triboluminescence excitation mechanism, triboelectrification,[10] has been shown to be responsible for the TL of *cis*-4-octene[11] and of a variety of scintillator compounds.[12] In our previous work, we proposed a molecular deformation mechanism.[3] On the basis of the discovery of the molecular tribofluorescence of coumarin, for which electronic excitation by a specific molecular deformation such as bond bending is less likely, it appears as if a strain mechanism cannot be general for all triboluminescent molecules. However, a macroscopic static electrification excitation mechanism is also incompatible with such observables as the decrease of TL intensity with decrease in the crystal size.[3] A potentially general mechanism, currently under investigation, is excitation *via* a pressure-induced intermolecular charge transfer, which would be proportional to the local pressures in the crystal and which could give rise to electrification as well as luminescence. Because of the short fluorescence lifetimes, tribofluorescent systems

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will provide the most fruitful means of studying the TL excitation mechanisms. In such systems, the TL spectra may contain dynamic features characteristic of the system under stress.

(13) Contribution No. 3291.

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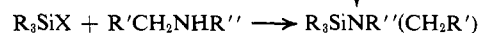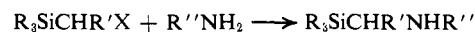## Base-Catalyzed Rearrangement of Aminomethylsilanes to Methylaminosilanes

*Sir:*

Considerable attention has been focused in recent years on the subject of 1,2-anionic rearrangements of organosilicon compounds.[1]

$$R_3SiXYH \underset{\text{base}}{\rightleftharpoons} R_3SiYXH$$
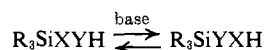
Known examples of this type of reaction are the silylcarbinol–alkoxysilane rearrangement[2] and its reverse[3] (X = C, Y = O), the benzylthiotrimethylsilane-

curred in high yield at room temperature or at 100°, depending on the amine. The reactions could be conveniently carried out in sealed nmr tubes and the relative rates were determined by spectroscopic examination of the solution. The rearrangement products were identified by gas chromatographic and spectral comparison with authentic samples prepared by alternative methods.

$$R_3SiCHR'X + R''NH_2 \longrightarrow R_3SiCHR'NHR''$$
$$\downarrow n\text{-}BuLi$$
$$R_3SiX + R'CH_2NHR'' \longrightarrow R_3SiNR''(CH_2R')$$

Our preliminary rate studies indicate that the reaction obeys pseudo-first order kinetics and the following observations are believed to be significant: (a) aminobenzylsilanes (R' = Ph) rearrange more rapidly than aminomethylsilanes (R' = H); (b) N-methyl compounds rearrange more rapidly than N-benzyl-, N-isopropyl-, or N-cyclohexylamines; (c) silylmethylanilines do not appear to rearrange under any conditions investigated. These facts are in accord with a rearrangement mechanism, analogous to that proposed for the silycarbinol–alkoxysilane rearrangement, in which an initially generated nitrogen anion undergoes a 1,2-migration of silicon from carbon to nitrogen. The resultant carbanion can in turn abstract a proton

**Table I.** Rearrangements of Secondary Aminomethylsilanes Catalyzed by *n*-Butyllithium

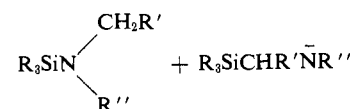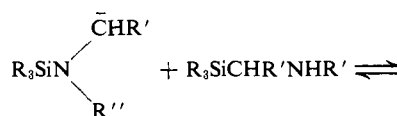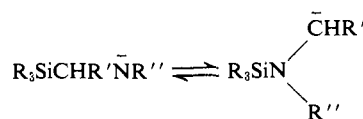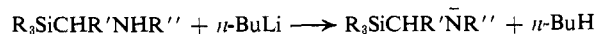| Aminomethylsilane | Equiv of *n*-BuLi | Reaction conditions[a] | | Silylamines[b] |
| | | temp, °C | time, hr | |
|---|---|---|---|---|
| Me₃SiCH₂NHCH₂Ph | 0.10 | 100 | 40 | Me₃SiNMeCH₂Ph (A) |
| Me₃SiCH₂NHC₆H₁₁ | 0.10 | 100 | 0.5 | Me₃SiNMeC₆H₁₁ (A) |
| Ph₃SiCH₂NHCH₂Ph | 0.17 | 25 | 37 | Ph₃SiNMeCH₂Ph (B) |
| Me₃SiCHPhNHMe | 0.10 | 25 | 1 | Me₃SiNMeCH₂Ph |
| Me₃SiCHPhNH-*i*-Pr | 0.10 | 25 | 36.5 | Me₃SiN(CH₂Ph)-*i*-Pr (B) |
| Me₃SiCHPhNHC₆H₁₁ | 0.20 | 25 | 60 | Me₃SiN(CH₂Ph)C₆H₁₁ (B) |
| Me₃SiCHPhNHC₆H₁₁ | 0.20 | 100 | 0.25 | Me₃SiN(CH₂Ph)C₆H₁₁ (B) |
| Me₃SiCHPhNHCH₂Ph | 0.10 | 25 | 24 | Me₃SiN(CH₂Ph)₂ (B) |
| Me₃SiCH₂NHPh | 0.10 | 100 | 40 | No reaction |
| Me₃SiCHPhNHPh | 0.10 | 100 | 40 | No reaction |

*[a]* Rearrangements carried out in benzene solution in nmr tubes sealed under nitrogen. *[b]* Method of alternative synthesis: A, R₃SiCl + R'R''NH + Et₃N; B, R'R''NLi + R₃SiCl.

α-trimethylsilylbenzyl mercaptan rearrangement[4] (X = S, Y = C), the silylhydrazine rearrangement[5] (X = Y = N), and the rearrangement of 1,1-bis(trimethylsilyl)-1,2-diphenylethane[6] (X = Y = C).

We wish to report a new example of this type of reaction, the base-catalyzed rearrangement of secondary aminomethylsilanes to the isomeric aminosilanes (X = C, Y = N).

When benzene solutions of a variety of aminomethyl- and aminobenzylsilanes (Table I), prepared by the method of Speier,[7] were treated with a small amount of *n*-butyllithium (0.1–0.2 equiv) the rearrangement oc-

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from the parent amine to give the product and regenerate the nitrogen anion.

$$R_3SiCHR'NHR'' + n\text{-}BuLi \longrightarrow R_3SiCHR'\bar{N}R'' + n\text{-}BuH$$

$$R_3SiCHR'\bar{N}R'' \rightleftharpoons R_3Si\underset{R''}{\overset{\bar{C}HR'}{N}}$$

$$R_3Si\underset{R''}{\overset{\bar{C}HR'}{N}} + R_3SiCHR'NHR' \rightleftharpoons$$

$$R_3Si\underset{R''}{\overset{CH_2R'}{N}} + R_3SiCHR'\bar{N}R''$$

Thermodynamic calculations using available bond energies suggest that the overall reaction will vary in