Triboluminescence Spectroscopy of Aromatic Compounds

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Abstract: The triboluminescence spectra of crystals of a variety of molecules containing aromatic groups are reported and assigned. The spectra are compared to the corresponding photoluminescence spectra of the crystals. Five general categories of triboluminescence are identified: fluorescence of the aromatic crystals, phosphorescence of the aromatic crystals, phosphorescence from metal centers in complexes, luminescence from charge transfer complexes, and fluorescence from the second positive group of molecular nitrogen. In general, the triboluminescence spectra are similar to the crystal photoluminescence spectra taken at the same temperature. However, in some cases significant differences are found. The TL spectra frequently contain features which are absent in the photoluminescent spectra, such as new emission bands or large changes in the relative intensities of bands. Some crystals which are triboluminescent are not photoluminescent. Similarities and differences between the photoluminescence and triboluminescence spectra are discussed.

Triboluminescence (TL), the emission of light caused by the application of mechanical stress to crystals, was first reported by Francis Bacon in the early 17th century.[2] The phenomenon was named by Wiedemann[3] and takes its root from the Greek "tribein", to rub. Although both current research and studies of historical interest have been directed toward the elucidation of the mechanisms of the triboexcitation and the excited-state origins of the triboluminescence, neither the mechanisms nor the origins have been fully determined.

The investigations reported in this paper are centered on the spectroscopy of triboluminescence and the excited state origins of the luminescence. Although over 356 substances are known to be triboluminescent[4] and many more remain to be tested, the excited state origins of the TL of only nine were known from qualitative or semiquantitative spectroscopic studies. Quantitative studies have been made on zinc sulfide doped with luminescent impurities,[5] uranyl nitrate,[6] sucrose and other saccharides,[7] sodium fluoride,[5] and lithium fluoride.[8] Qualitative assignments of triboluminescence based on the visual similarity of the colors of the TL and photoluminescences and on indirect evidence have been made for europium,[9] terbium,[9] and manganese[10] coordination complexes, and *cis*-4-octene.[11] With the exception of the preliminary communications of the results of this work, no spectroscopic studies have been made on aromatic molecular crystals.

The potential relationships between the mechanical and electrical properties of crystals and TL have been investigated. The mechanical properties which have been most studied include the fracture of crystals accompanying TL,[5,8,12-16] the plastic and elastic deformations of crystals accompanying TL,[5,14-16] the physical size of the crystals and its effects on TL,[17,18] and the effects of crystal phase changes.[19,20] Electrical properties of triboluminescent crystals including pyroelectric[21] and piezoelectric[22] effects have also attracted attention. A variety of excitation methods including thermal shock,[23] the motion of mercury across surfaces,[24] and crystallization[12,22,25] have been studied in addition to the more common mechanical methods of excitation such as crushing or grinding the crystals. The effects of temperature[21,26,27] and x rays[16,27] on TL have also been studied. No general principles have yet emerged.

In this paper, we report the results of our spectroscopic studies of the triboluminescence of aromatic molecular crystals. Five general categories of TL are identified and the similarities and differences between TL spectra and the photoluminescence spectra are discussed.

Experimental Section

Compounds. Coumarin was purchased from Matheson, Coleman, and Bell and sublimed twice before use. Phenanthrene was commer-

cially obtained. Acenaphthene, resorcinol, *m*-aminophenol, aniline hydrochloride, phthalic anhydride, and *p*-anisidine were obtained from commercial sources and recrystallized before use. The *N*-acetylanthranilic acid,[28] 9-anthrylethanol,[29] triethylammonium tetrakis(dibenzoyl methide)europium(III),[9] and the bis(triphenylphosphine oxide)manganese halides[30] were prepared according to literature methods. Phenanthrene/TCPA was a gift from Dr. T. T. Lin and C. T. Yu.

Hexaphenylcarbodiphosphorane. Under nitrogen, methylidebis-(triphenylphosphonium) bromide (12.4 g, 0.02 mol) is rapidly added to a stirred suspension of powdered potassium (1.0 g, 0.025 g-atom) in 150 mL of boiling diglyme. The mixture becomes yellow orange and gas evolution occurs. After stirring the hot mixture for 45 min, it is filtered, hot, under nitrogen to remove KBr. About 60 mL of diglyme is removed from the yellow solution under vacuum and the remainder is slowly allowed to cool. If allowed to cool slowly with no disturbances, large diamond-shaped crystals appear after 24-48 h. The crystals are much smaller if crystallization times are shortened. When crystals are formed in <1 h from diglyme, they usually appear as needles which are nontriboluminescent. Both forms have a mp of 216-218 °C (lit. 208-210 °C) 7.4 g, 70%.[31]

Instruments. The triboluminescence spectra were taken at 5-nm intervals on the instrument previously described.[32] The samples were ground in glass vials with a stainless steel grinding implement. It was necessary to correct the resorcinol TL spectrum for absorption by the glass vial. All other TL spectra were relatively unaffected by glass absorption. The reported photoluminescence spectra were obtained on the same instrument with the exception of those with peak maxima at wavelengths shorter than 400 nm. The latter spectra were taken on a Spex Fluorolog spectrofluorimeter. All photoluminescence spectra were obtained at room temperature unless otherwise noted. No corrections for the response characteristics of the instruments were made unless noted. Infrared spectra were taken on Perkin-Elmer 337 and 257 spectrometers.

Results

The triboluminescence of the aromatic molecules studied here has five distinct origins: fluorescence of the aromatic crystals, phosphorescence of the aromatic crystals, phosphorescence from metal centers in complexes, luminescence from charge transfer complexes, and fluorescence from the second positive group of molecular nitrogen. In addition, luminescence from crystal defects and impurities have been identified. In some crystals, combinations of several of the above origins contribute to the TL.

On the basis of our studies to date, the best generalization of the type of TL which can be expected from a crystal is that it will frequently be similar to the crystal photoluminescence at the same temperature. However, some crystals which are triboluminescent are not photoluminescent. In addition, the TL spectra may have features which are absent in the corresponding photoluminescence spectra. Thus, a TL spectrum will

in general be similar to but not identical with the corresponding photoluminescence spectrum of the crystal.

The spectroscopic results are grouped below according to the origin of the most intense TL emission band. The TL spectra are compared to the corresponding photoluminescence spectra and the similarities and differences are noted. The aromatic compounds surveyed here were chosen primarily because of their relatively intense TL, which enabled high quality TL spectra with good signal to noise ratios to be obtained.

Tribofluorescence. The spectra of the crystals which exhibit tribofluorescence may be grouped into two categories: those in which the energies and the intensities of the spectral features are identical in both the triboluminescence and photoluminescence spectra, and those in which the energies of the features are identical in the two type TL and PL spectra, but the intensities are significantly different. All of the compounds in the latter category exhibit significant differences even when the TL and PL spectra are obtained at the same temperature.

The spectra of the compounds for which the TL and PL spectra are superimposable are shown in Figure 1. All of these compounds are substituted phenols. The minor differences observed between the PL and TL spectra are not significant within the accuracy of the TL measurement. The uncertainty in the TL intensity in the resorcinol spectrum is greater than that shown by the error bars which represent one standard deviation of the measured intensities because of the correction for the absorption of the Pyrex vials used in the triboluminescence spectrometer.

The spectra of the compounds for which the intensities of the TL and PL peaks are not identical within experimental error are shown in Figure 2. In Figures 2a and 2b, the TL and room temperature PL spectra of phenanthrene and 9-anthrylethanol are shown. In both cases the peaks in the TL and PL spectra occur at the same wavelength, but the intensities are significantly different. In the TL and PL spectra of phenanthrene, the peaks at 410 nm were normalized to equal intensity. For 9-anthrylethanol, the spectra were normalized at the 445-nm peak. TL was also observed in 9-anthrylmethanol.

A more dramatic change in relative intensities of TL and PL peaks is found in the superposition of the TL spectrum and the room temperature photoluminescence spectrum of solid coumarin shown in Figure 2c. The maximum of the PL peak occurs at 389 nm and has been previously assigned to the $^1(\Pi^*, \Pi)$ fluorescence.[33,34] The maximum of the TL spectrum is the peak at 415 nm. At the 5-nm resolution of the TL spectrum, structure on the fluorescence peak can readily be resolved in contrast to the much less structured photofluorescence peak. The average energy spacing between the peaks between 450 and 360 nm is 1630 cm^{-1}, within experimental error of the 1596-cm^{-1} C=C stretch.[34] However, the band at 395 nm is slightly out of place; if it occurred at 5 nm to higher energy, the bands would be exactly the C=C vibronic progression. In a preliminary report of the TL of coumarin[35] taken at lower resolution, these bands were not resolved. The weaker features observed at wavelengths longer than 450 nm are difficult to assign. The phosphorescence of coumarin occurs in this region. At liquid nitrogen temperature in glasses, five strong vibronic components of the Π^*, Π phosphorescence are found at 457, 471, 493, 510, and 533 nm.[34] A weak component of the C=C vibrational progression of the fluorescence should occur at 480 nm. Features in the TL spectrum corresponding to the four highest energy phosphorescence maxima and to the C=C fluorescence band can be discerned. However, the uncertainties in the very weak portion of the TL spectrum at longer wavelengths than 450 nm make it impossible to discriminate between these choices. At the lower resolution in the preliminary spectrum, these features appeared as a broad band centered
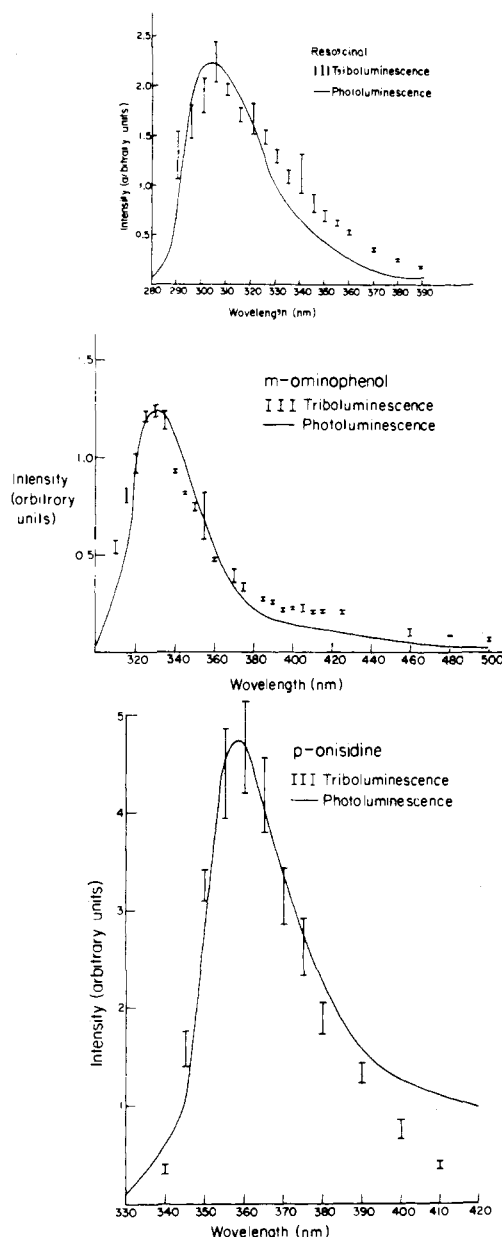

Figure 1. Tribofluorescence and room temperature crystal photoluminescence spectra of substituted phenols: (a) resorcinol; (b) m-aminophenol; (c) p-anisidine.

between 460 and 480 nm. Because the relative intensities of the fluorescence and phosphorescence are very sensitive to the medium and the temperature, small differences between the relative intensities in the TL and photoluminescence cannot be used to infer the mechanisms by which the states are populated.

The TL spectrum of acenaphthene is shown superimposed on the photoluminescence spectra taken at liquid nitrogen temperature in Figure 2d. The most intense photoluminescence peak with a maximum at about 340 nm has been previously assigned as acenaphthene fluorescence.[36] The less intense peaks between 425 and 460 nm are impurity bands which could not be completely removed by recrystallization of the sample. The excitation spectrum obtained by monitoring the peak at 425 nm was different from that obtained by monitoring the acenaphthene fluorescence at 340 nm. Because the TL from acenaphthene is weak, wide slits were required to obtain the spectrum and the resolution is lower than most of the other TL spectra in this study. Consequently, the band which appears at 360 nm in the photoluminescence spectrum was not resolved
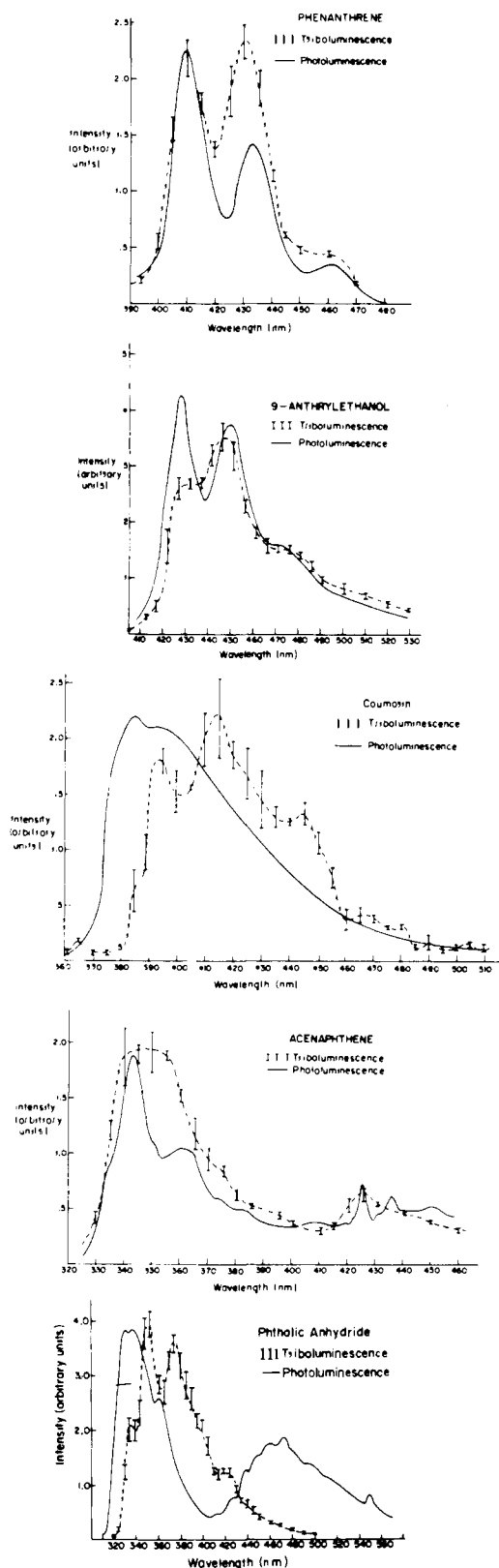
Figure 2. Tribofluorescence and crystal photoluminescence spectra of aromatics demonstrating redistribution of vibronic intensities: (a) TL and room temperature PL of phenanthrene; (b) TL and room temperature PL of 9-anthrylethanol; (c) TL and room temperature PL of coumarin; (d) TL and 77 K PL of acenaphthene; (e) TL and 77 K PL of phthalic anhydride.
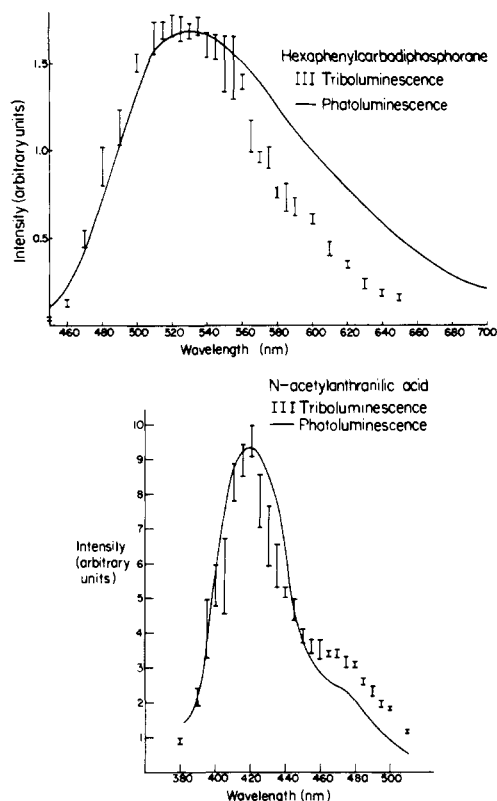
Figure 3. Tribophosphorescence and room temperature crystal photoluminescence spectra of (a) hexaphenylcarbodiphosphorane and (b) N-acetylanthranilic acid.

could be detected at room temperature along with a broad, featureless band centered at 390 nm which was absent at 77 K. Phthalic anhydride is an unusual case because triboluminescence occurs at room temperature even though no photoluminescence can be detected at that temperature.[37] In Figure 2e, the room temperature TL spectrum is shown superimposed on the PL spectrum taken at liquid nitrogen temperature. The intense peak in the PL spectrum at 340 nm is a fluorescence. The phosphorescence maximum, with a lifetime of 800 ms, is centered at 470 nm. The fluorescence contains three resolved peaks at 333, 345, and 363 nm at liquid nitrogen temperature. The fluorescence spectrum was temperature dependent. With decreasing temperature, intensity increased in the high energy region of the spectrum. In the room temperature TL spectrum, well resolved peaks were observed at 335, 355, and 420 nm which are assigned to tribofluorescence. Only tribofluorescence was observed.

Tribophosphorescence. The TL and room temperature photoluminescence spectra of hexaphenylcarbodiphosphorane are superimposed in Figure 3a. The luminescence was assigned as a phosphorescence on the basis of its lifetime of 0.11 ms at 77 K.[23] Hexaphenylcarbodiphosphorane was the first triboluminescent molecular crystal from which the TL was spectroscopically assigned.[23] The room temperature TL and PL spectra of N-acetylanthranilic acid are shown superimposed in Figure 3b. The spectra are normalized at the peak at 420 nm. The greater intensity in the band at 470 nm in the TL spectrum compared to that in the PL spectrum is a reproducible feature of the spectrum. The PL is assigned as a phosphorescence on the basis of its lifetime of 515 ms at 77 K.

Metal-Centered Triboluminescence. The TL and photoluminescence of triethylammonium tetrakis(dibenzoylmethide)europate(III) are shown superimposed in Figure 4a. The line spectrum observed in both the TL and photoluminescence is typical of the europium centered transitions from the $^5D_1$ and $^5D_0$ levels to the lower $^7F_{0...4}$ levels of the ground mul-

in the TL spectrum. In a preliminary report of the TL,[37] the intensities of the weaker TL emission bands were exaggerated relative to that of the most intense bands (vide supra). Using the Spex Fluorolog spectrofluorimeter, weak photofluorescence
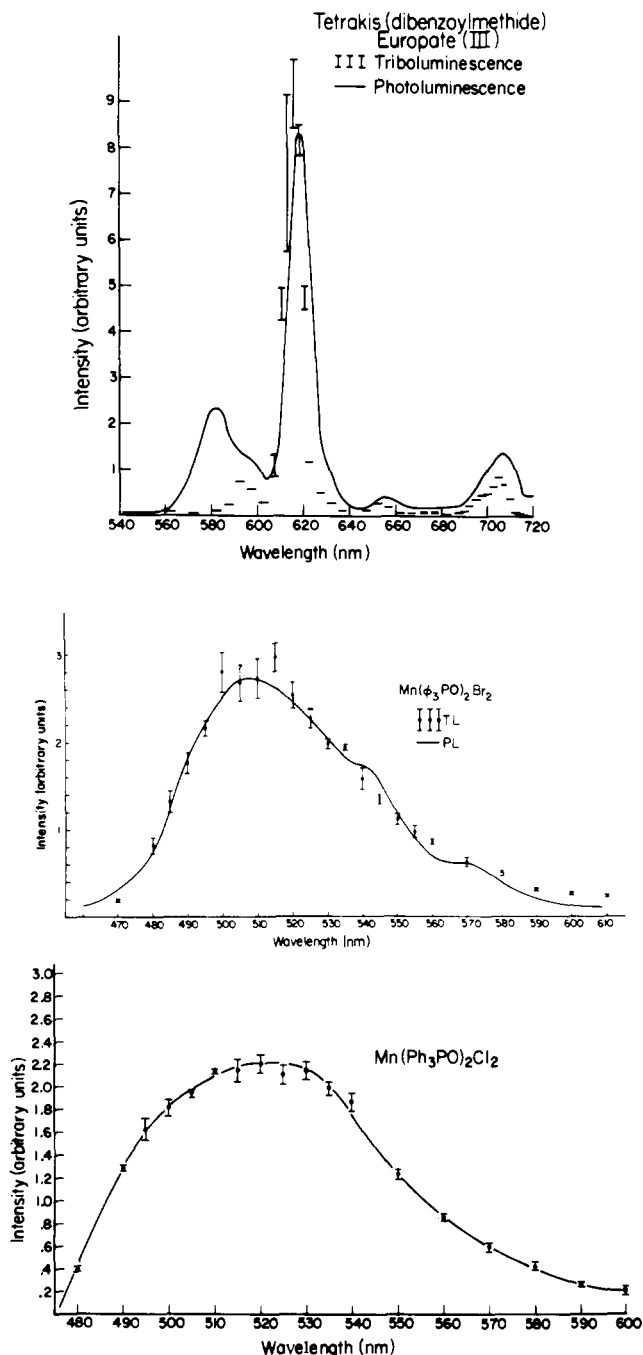
Figure 4. Metal-centered triboluminescence spectra of metal complexes containing aromatic ligands: (a) TL and room temperature crystal PL of tetrakis(dibenzoylmethide)europate(III); (b) TL and room temperature crystal PL of dibromobis(triphenylphosphine oxide)manganese(II); (c) TL of the nonphotoluminescent dichlorobis(triphenylphosphine oxide)-manganese(II).
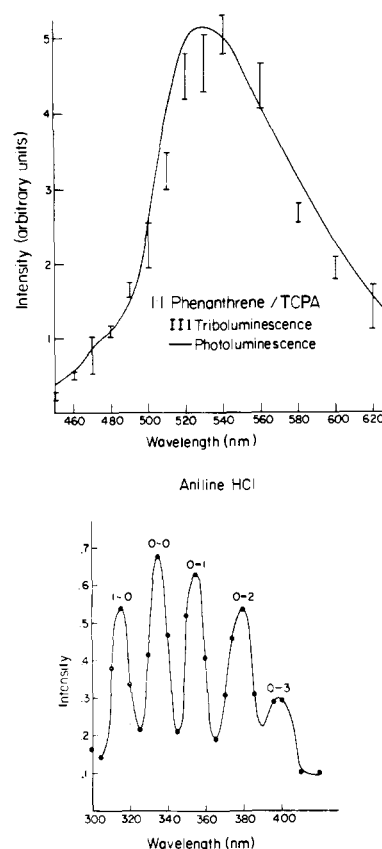

Figure 5. Triboluminescence of novel origin: (a) TL and room temperature charge transfer photophosphorescence of 1:1 phenanthrene/TCPA; (b) TL of aniline hydrochloride showing emission from the second positive group of adsorbed or absorbed molecular nitrogen.

tiplet. (A qualitative study of this compound has been reported.[9])

Both $Mn(Ph_3PO)_2Cl_2$ and $Mn(Ph_3PO)_2Br_2$ are triboluminescent, but only the latter is photoluminescent. The TL spectrum of the latter is shown superimposed on the photoluminescence spectrum in Figure 4b. The TL spectrum of the former is shown in Figure 4c. The luminescences centered at 510 and 520 nm respectively are manganese centered $^4T \rightarrow$ ^6A phosphorescences.[38,39] Because the TL maximum of the nonphotoluminescent $Mn(Ph_3PO)_2Cl_2$ is in the same region as the known photoluminescence maxima in a variety of similar compounds, the TL can reasonably be assigned to the same ^4T $\rightarrow$ ^6A phosphorescence. A complete study of the TL and

pressure dependence of the photoluminescence was reported elsewhere.[32] These two manganese complexes are included in this paper because they simultaneously illustrate TL from a metal center and TL in the absence of measurable photoluminescence.

Charge Transfer Triboluminescence. The TL spectrum of 1:1 phenanthrene/tetrachlorophthalic anhydride (TCPA) is shown superimposed on the charge transfer photoluminescence spectrum in Figure 5a. The emission is identified as a charge transfer phosphorescence with a lifetime of 250 ms at 77 K in the solid state.[40] This TL is the first reported charge transfer luminescence caused by trioexcitation. Other luminescent charge transfer complexes studied were 1:1 anthracene/TCPA, 1:1 fluorene/TCPA, 1:1 chrysene/TCPA, and 2:1 chrysene/ TCPA. TL was not observed in any of these complexes.

Triboluminescence from Absorbed Nitrogen. The TL spectrum obtained from crystals of aniline hydrochloride is shown in Figure 5b. The line spectrum is the $^3\Pi_g \rightarrow {}^3\Pi_u$ fluorescence (the second positive group) of molecular nitrogen.[41] Excitation of nitrogen to its $^3\Pi_g$ emitting level requires a minimum energy of 88 000 cm^{-1}. The nitrogen origin of TL is also found in aniline hydrochloride,[42] mono- and disaccharides including sucrose,[7] and cis-4-octene.[11] The nitrogen emission spectrum may also be superimposed on the crystal luminescence as in the case of tetrahedral manganese complexes.[32] However, aniline hydrochloride is the only aromatic crystal from which molecular nitrogen emission has been identified to date.

Discussion

1. General Trends. The excited state origin of the triboluminescence in the aromatic molecular crystals which have been studied to date is most frequently the same as that of the crystal photoluminescence. The major exceptions to this generalization

are those crystals which exhibit luminescence from adsorbed or absorbed molecular nitrogen. In the tetrahedral manganese complexes, crystal luminescence and nitrogen luminescence are observed simultaneously. It is generally not possible to determine whether or not both origins occur simultaneously in aromatic molecular crystals because the molecules often have very large molar absorptivities between 300 and 360 nm where the nitrogen emission intensity is greatest and absorption by the crystal could mask the nitrogen emission. For that reason, we have not yet been able to determine whether or not the two types of luminescence have the same excitation mechanism. In every case in which the two types of luminescence have been observed simultaneously, the nitrogen emission can be eliminated by vacuum degassing the crystal without significantly changing the molecular crystal luminescence.[32] Thus, in those cases at least, nitrogen emission is not required for crystal TL to occur.

Although the TL and photoluminescence can generally be assigned to the same electronic excited state, significant differences are found in the detail of the luminescence spectra. These differences most commonly take the form of enhanced structure and/or intensity changes in the bands in the TL spectra relative to those in the photoluminescence spectra. The most extreme difference occurs in two compounds which are triboluminescent, but have no detectable photoluminescence even at the most sensitive instrumental settings. In one case, $Mn(Ph_3PO)_2Cl_2$, the TL is in exactly the same spectral region as the photoluminescence of a series of closely related tetrahedral manganese complexes and can be confidently assigned to the same excited state.[32] In a second case (phthalic anhydride), the TL but no detectable photoluminescence occurs at room temperature. At liquid nitrogen temperature, a photoluminescence peak is observed at the same energy as that of the TL, but the band envelope and the width are quite different. All of the above differences will be discussed individually below.

The mechanical properties of the crystals giving rise to triboluminescence are qualitatively quite different. In some cases (e.g., phthalic anhydride, acenaphthene), crystals must be vigorously pulverized in order to produce detectable TL. In other cases (e.g., tetrakis(dibenzoylmethide)europate(III), N-acetylanthranilic acid), microcrystals or powders can be gently pressed against the wall of the vial to produce bright TL. The qualitative appearance of the emission from the two types of crystals is also different. In the former case, the TL generally takes the form of discrete flashes, while in the latter cases the TL is almost continuous. Experiments are in progress to quantify the lifetimes of the TL emissions and to determine the efficiency of the conversion of mechanical energy to light energy in these different systems.

2. Differences between TL and PL Spectra. The primary differences between the TL and the PL spectra which have been found to date are (1) more detailed structure in the main peak of the TL spectrum compared to that in the corresponding PL spectrum; (2) changes in the relative intensities of two or more bands compared to those in the PL spectrum. A third difference which is a consequence of the first two is an apparent shift, most frequently to the red, of the band envelope of the TL spectrum relative to the PL spectrum. The appearance of nitrogen emission bands, which also constitutes a major difference between the TL and PL spectrum, is a result of a completely different mechanism and will be treated in the next section.

In the spectra which have been studied to date, both the appearance of detailed structure and the changes in the relative intensities of emission bands appear to be related to changes in the Franck–Condon factors and thus to the changes in the vibronic intensities of the emission caused by the application of mechanical energy or pressure to the crystals in the TL experiment. Large changes in the vibronic intensity distributions in aromatic molecular crystal luminescence spectra caused by hydrostatic pressure are known from high pressure studies.[43] In the TL spectra, the energies of the vibronic bands generally correspond to those in the PL spectra if the latter can be resolved. Individual examples will be discussed in detail below.

Other explanations for changes in the relative intensities of the emission bands include (1) the appearance of new luminescent centers such as crystal defects or traps; (2) changes in the relative quantum yields of fluorescence and phosphorescence; (3) self absorption of anti-stokes vibronic emission bands; and (4) impurity effects. Because the grinding of the crystals required to produce the TL is also conducive to the production of crystal defects, luminescence from traps or specific sites in the crystal is expected to be important. However, in all of the spectra studied to date, the new peaks which appear in the TL are well separated from the other peaks with energy spacings on the order of the skeletal vibrations. Emission from traps is thus probably not the cause of the detailed structure or the changes in the relative intensities of the bands, although it may be responsible for the generally observed increased broadness of the TL spectra relative to the corresponding PL spectra. The possible effects of impurities on the spectra are more difficult to quantify. The fluorescence spectrum of micro-crystalline phenanthrene has been shown to depend on the method of sample purification.[44] Because the TL and PL spectra in the present study were obtained from samples purified in the same manner, the differences between the spectra are probably not a direct result of impurities. However, as mentioned above, one of the effects of pressure in the TL experiment might be to produce traps whose presence and nature could be related to impurities in the sample. Spectral changes caused by the second and third categories have been observed and will be discussed below.

The best examples of the spectral changes caused by changed Franck–Condon factors are found in the spectra of coumarin, phenanthrene, and 9-anthrylethanol. Of these three, the spectrum of coumarin provides the most detailed comparisons (Figure 2c). The room temperature PL spectrum is an almost featureless envelope with its maximum at 384 nm and shoulders at 394, 420, and 438 nm. In contrast, the room temperature TL spectrum consists of four intense, well-resolved bands at 365, 395, 415, and 445 nm with the most intense band at 415 nm. (The TL spectrum was taken at 5-nm intervals.) At about 100 K, the bands in the photoluminescence spectrum become better resolved with clearly defined peaks at 365, 377, 398, and 419 nm and shoulders at about 385, 435, and 445 nm. Within the experimental error of the TL measurements, the peaks in the room temperature TL spectrum have corresponding peaks in the low temperature PL spectrum and some corresponding shoulders in the room temperature PL spectrum. Although the energies of the peaks correspond, the intensities of the peaks are drastically different. A complete vibronic assignment of the peaks has not been reported to our knowledge. However, it is clear that at least several of the peaks correspond to the C=C skeletal vibration at 1596 cm^{-1}.[34] It is thus reasonable to attribute the observed changes in intensity to changes in the Franck–Condon factors caused by the mechanical stress on the crystal in the TL experiment. The net effect appears to be an enhancement of the intensities of the higher order vibronic bands causing an apparent shift of the maximum of the band envelope to the red. This enhancement is consistent with increased distortion of the emitting molecules in the crystal in the TL experiment compared to that in the PL experiment. It is possible that only certain specific vibronic bands corresponding to specific normal modes are enhanced. For example, the highest energy band observed in the TL spectrum at 365 nm is absent in the room temperature PL

spectrum, but is very prominent in the low temperature PL spectrum.

The TL and room temperature PL spectra of phenanthrene and 9-anthrylethanol contain three bands. In the PL spectrum, the highest energy band is the most intense, while in the TL spectrum the middle band is most intense. This increase in intensity in bands to the red of the maximum is consistent with the Franck–Condon explanation proposed above. In many of the other TL spectra, most notably that of N-acetylanthranilic acid, the intensity of the low energy portion of the TL spectrum is greater relative to the high energy portion than it is in the PL spectrum. In terms of the above explanation, the increased intensity is caused by enhanced but unresolved vibronic intensity.

The Franck–Condon enhancement of vibronic bands caused by the mechanical stress is prominent in many tribofluorescence spectra. Fluorescence, with a very short lifetime, can occur from molecules which are affected by the mechanical action at the time they are emitting. It is reasonable to expect that much longer lived emissions would not exhibit such effects because the relaxation of the mechanical action could occur before the molecules emit. However, some types of pressure-induced luminescence features require a time scale on the order of days in order to relax, probably because of the length of time required for the crystal to anneal at room temperature.[45] Thus, at the present time, it is impossible to identify the exact pressure effect which causes the new TL spectral features. Elucidation of these effects will require the discovery and spectroscopic study of more examples of tribophosphorescent crystals.

Although examples of tribophosphorescence are much rarer than tribofluorescence, there is some evidence that spectral features to low energy of the tribofluorescence bands may be weak tribophosphorescences. For example, in the TL spectrum of coumarin, the very weak shoulders which occur between 460 and 510 nm correspond to known phosphorescence maxima. Similarly, low energy peaks between 410 and 490 nm in the TL spectrum of phthalic anhydride may be tribophosphorescence. However, in both cases, the observed intensity is too weak to allow unambiguous assignments to be made.

3. TL from Molecular Nitrogen. The examples of nitrogen emission from molecules containing aromatic rings which have been found to date are aniline hydrochloride[42] and $Mn(Ph_3PO)_2Br_2$.[32] Nitrogen TL is also observed from saccharides[7] and cis-4-octene.[11] As we have previously discussed, nitrogen TL is a high energy process requiring 88 000 cm^{-1} to reach the emitting excited state. We have previously shown that the nitrogen TL does not require an atmosphere of nitrogen surrounding the crystal.[7] However, the details of the role of nitrogen in the process are not completely understood. Other workers have shown that gases other than nitrogen can also triboluminesce. When cis-4-octene was placed under an atmosphere of neon, a red TL characteristic of emission from that gas was observed.[11] It is likely that the gases do not play a direct role in the excitation process, but instead are excited by the crystal in which they are trapped. In the only case in which both nitrogen emission and molecular phosphorescence were simultaneously observed, $Mn(Ph_3PO)_2Br_2$, the nitrogen luminescence was eliminated by vacuum degassing the crystal without affecting the molecular luminescence.[32] In this case, the molecular TL is not caused by energy transfer from excited nitrogen to the phosphorescing manganese sites. It will be difficult to determine how frequently nitrogen emission occurs in aromatic molecular crystals because the crystals have large molar absorptivities in the nitrogen emission region and absorption by the crystal could obscure the nitrogen lines. As was true in the manganese complexes, energy transfer from nitrogen will probably not be important in aromatic systems. We have measured the TL of vacuum sublimed coumarin and

vacuum degassed phthalic anhydride with no apparent spectral change compared to that obtained from the nitrogen-saturated crystals. On the basis of the results to date, nitrogen emission, when it occurs, appears to be the result of independent (but perhaps simultaneous) excitation of absorbed or adsorbed gas.

4. TL from Nonphotoluminescent Crystals. One of the most intriguing observations is that TL can occur in crystals from which no photoluminescence can be detected. Two examples have been found to date: $Mn(Ph_3PO)_2Cl_2$ and phthalic anhydride. In the latter case, crystal photoluminescence can be detected at low temperature, but not at room temperature, in contrast to the relatively weak but readily observable TL at room temperature. In the manganese complex, no photoluminescence can be detected down to temperatures of 77 K. In a preliminary communication of the TL of acenaphthene, room temperature TL, but no room temperature photoluminescence, was reported.[37] Using a more sensitive instrument, room temperature photoluminescence has been found. Thus, the observation of TL, but not photoluminescence, may in some cases be more accurately described as an enhancement of the luminescence intensity when excited by mechanical stress relative to the intensity of photoluminescence. This enhancement may be related to the intensity redistribution in the vibronic peaks discussed earlier. In support of this interpretation, the TL spectrum of phthalic anhydride occurs in the same wavelength region as the liquid nitrogen temperature photoluminescence, but differs markedly in detail. (No room temperature photoluminescence was detected.) Thus, the TL may result from enhanced vibronic emission. The vibronic bands are clearly present and markedly enhanced relative to the photoluminescence. It is well known that pressure can change both fluorescence and phosphorescence lifetimes in aromatic hydrocarbons.[46] The luminescence quantum yields can also be changed by pressure.[47] In the case of the manganese complex, no photoluminescence was observed at any temperature and thus no comparisons between the spectra can be made. However, in the series of compounds which we have studied,[32] all of the manganese centered phosphorescence occurs within a 15-nm region centered at 515 nm. Thus, the TL of the nonphotoluminescent complex can reasonably be assigned to manganese phosphorescence and not to a different origin. In both the phthalic anhydride and manganese compounds, emission from traps or defects is likely in the TL experiment as discussed previously. Thus, it is possible that the emitting centers have a larger cross section for excitation by the TL process than by absorption of a photon. Studies are in progress in an attempt to find the solution to the question raised by these observations.

5. Comments on the Mechanisms of TL Excitation. The mechanisms by which TL is excited are not completely understood. The proposed mechanism which may have the most general validity is excitation by electrification. There are at least three possible methods of creating an electrical potential difference in the molecular crystals under consideration here: frictional electrification caused by rubbing two dissimilar materials together, piezoelectrification caused by compressing noncentrosymmetric crystals, and internal electrification at cleavage planes or shear planes in the crystal. In addition to the electrical mechanisms, excitation by pressure-induced compression or molecular distortion must be considered. High pressure studies have demonstrated that the energy separation between ground and excited states can change as a function of pressure[48] and that thermal population of a state which is an excited state at atmospheric pressure can occur at high pressure.[49] Upon release of the pressure, emission could occur. A third mechanism of excitation could be chemical reactions leading to chemiluminescence. Although tribochemistry is known to occur when mercury flows over surfaces,[50] all of the

TL we have observed originates from the original molecules and not from new reaction products. Furthermore, we do not have any spectroscopic evidence that a chemical reaction has taken place as a result of grinding the samples.

The existence of one of the electrical mechanisms is difficult to assess because frequently one or several of them could be operative. For example, the importance of frictional electrification[51] was probed by grinding the triboluminescent crystals with a variety of materials in a variety of vessels. The observed TL was qualitatively unaffected by the type of implement (conducting, nonconducting). TL can be excited in many cases by thermal shock caused by immersing the crystals in liquid nitrogen. TL will also be observed by grinding the crystals under liquids in which they are insoluble. In all of the above cases, frictional electrification *could* occur because dissimilar materials are used. However, if frictional electrification were of primary importance, large differences in TL intensity would be expected as the grinding implement is changed. For these reasons, surface frictional electrification does not appear to be of primary importance. However, internal electrification cannot be eliminated or even tested as easily. Piezoelectrification can be eliminated as a possibility when the crystal is centrosymmetric. The space groups of only eight of the aromatic crystals studied here have been unambiguously determined.[52-60] Of these, only *p*-anisidine is centrosymmetric.[60] In this one example, piezoelectrification cannot be important. On the basis of the results to date, no single mechanism can definitely be chosen.

References and Notes

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