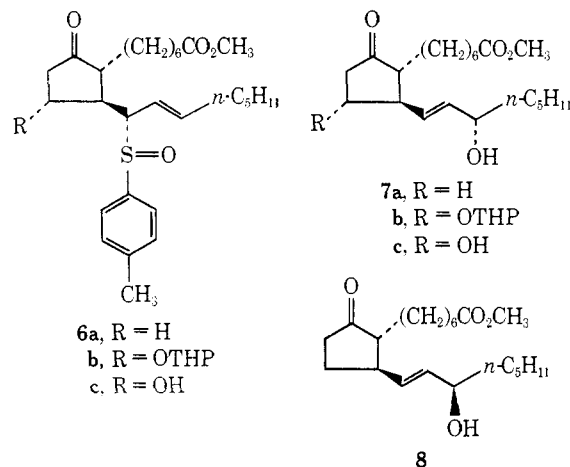


(ϵ 6100); nmr (CDCl_3) δ 2.38 (s, 3, aromatic methyl), 7.1–7.5 (m, 4, aromatic protons); mass spectrum (70 eV) m/e 458 ($M^+ - O$), which was converted to *dl*-11-desoxy-PGE₁ methyl ester (*dl*-7a),⁸ using excess trimethylphosphite in methanol. The two-step sequence (4a \rightarrow 6a \rightarrow 7a) proceeds with complete stereospecificity. None of the 15 β -hydroxy epimer (*dl*-8) could be detected (direct tlc and glpc comparisons to authentic material⁸).



When the initial reaction (*n*-BuLi-*p*-toluenesulfonyl chloride⁹) was carried out with the 11-substituted ketol (*dl*-4b),¹⁰ however, little or none of the desired sulfoxide (*dl*-6b) could be isolated. Rather, PGA-type products or PGA-type derived products resulted from the strongly basic media. Since it is necessary to avoid strong base for the preparation of PGE₁, the usual method of preformation of the alkoxide anion in obtaining sulfenates had to be circumvented. We found that treatment of *dl*-4a in ether containing *ca.* 3 equiv of triethylamine with *p*-toluenesulfonyl chloride (1.4 equiv) at room temperature gave *dl*-6a (87%),¹¹ which was converted to *dl*-7a (92%)¹¹ using excess trimethylphosphite in methanol at room temperature. This same reaction sequence carried out on the 11-protected ketol (*dl*-4b) (triethylamine, 3 equiv; *p*-toluenesulfonyl chloride, 1.5 equiv) gave sulfoxide (*dl*-6b) (81%);¹¹ oil;⁷ ir (film) 1730, 1035 (SO), 970 (*trans*-CH=CH) cm^{-1} ; uv (MeOH) 249 nm (ϵ 6400); nmr (CDCl_3) δ 2.38 (s, 3, aromatic methyl) 7.15–7.6 (m, 4, aromatic protons); mass spectrum (70 eV) m/e 434 ($M^+ - \text{tolylSOH}$), which upon treatment with trimethylphosphite in methanol, afforded the ketol (*dl*-7b) (88%).¹¹ Acid hydrolysis (65% acetic acid) of (*dl*-7b) gave *dl*-PGE₁ methyl ester (*dl*-7c) (90%),¹¹ identical with an authentic sample^{3,8} by tlc, glpc, and nmr).^{12,13}

(7) Satisfactory combustion analysis was obtained.

(8) Previously synthesized: F. S. Alvarez, D. Wren, and A. Prince, *J. Amer. Chem. Soc.*, **94**, 7823 (1972).

(9) These are the usual conditions for the formation of a sulfoxide from an allylic alcohol, *i.e.*, prior alkoxide formation. See, for example, ref 4a and D. A. Evans, *et al.*, ref 5.

(10) Prepared *via* conjugate addition of cuprate (1) to enone (*dl*-3c), followed by mild acid (20% acetic acid) hydrolysis of the more labile ether at C-15 (45%, based on *dl*-3c, unpublished).

(11) Isolated yield.

(12) The two-step conversion applied directly to the unprotected 11-hydroxy ketol (*dl*-4c), gave *dl*-PGE₁ methyl ester (an excess, 3.5 equiv, of *p*-toluenesulfonyl chloride was used—not optimum stoichiometry). Selective sulfenate formation of the allylic hydroxyl group probably occurred.

We are continuing our synthetic investigations by utilizing this nearly stereospecific total synthesis for the preparation of prostaglandin analogs and to determine the generality of the sequence.^{13a}

Acknowledgment. We are indebted to Mr. B. Amos, Mr. V. Hayashida, Mrs. L. Kurz, Dr. M. Maddox, Mrs. J. Nelson, Mrs. A. Nitzan, Mr. J. Smith, and Mrs. Diane Wong for their assistance with analytical measurements and to Dr. G. F. Cooper for helpful discussions.

(13) Although the above transformations were carried out with *dl* materials, the same results are realized using individual enantiomeric allylic alcohols, *i.e.*, (15*R*)-4a² and (15*R*)-4c² give (15*S*)-7a and (15*S*)-7c, respectively.

(13a) NOTE ADDED IN PROOF. Subsequent investigations (W. K. and K. G. U.) have shown that the 1,4-conjugate addition of 1 to 3b is not as stereoselective as previously reported;² 15-epi-4a:4a, 2.5:97.5; 15-epi-4c:4c, 14:86. Independently synthesized 15-epi-4a and 15-epi-4c were found to be surprisingly nonpolar; rf: 4a (0.47), 15-epi-4a (0.86), 7a (0.56), 7c (0.46), 4c (0.11), 15-epi-4c (0.41), hexane:ethyl acetate, 55:45.

(14) Syntex Postdoctoral Fellow, 1972–1973.

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Tribophosphorescence from Nonphotophosphorescent Crystals

Sir:

Recent studies have shown that triboluminescence (TL), the emission of light caused by the application of mechanical stress to crystals, can originate from both spin forbidden^{1,2} and spin allowed³ transitions of molecules in a crystal in contrast with the previously observed ambient gas discharge processes.^{4,5} In all of the tribophosphorescent or tribofluorescent crystals for which the excited state origins of the TL have been identified, the corresponding intense photoluminescence spectra were similar to the TL spectra and could be measured at the same temperature as that at which the TL was measured. In this paper we report the first examples of room temperature triboluminescence from crystals which are not photoluminescent at that temperature. (No photophosphorescence could be detected using an Aminco-Keirs spectrophosphorimeter or the apparatus described below.) The TL spectra differ markedly from the corresponding photoluminescence spectra. We also report the first example of simultaneous tribofluorescence and phosphorescence.

The TL spectra of phthalic anhydride and acenaphthene were obtained by grinding 0.5-g samples in glass vials with metal, wood, glass, or Teflon rods. Weak TL excited by the thermal shock of immersing a sample in liquid nitrogen could also be visually observed. The ratio of the intensity of a tribolumines-

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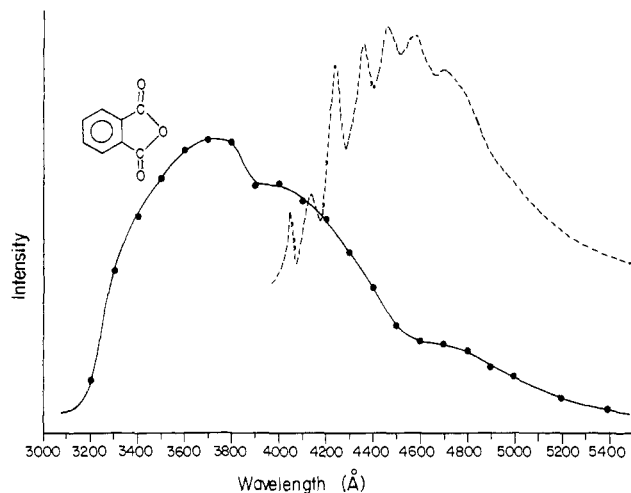


Figure 1. Phthalic anhydride triboluminescence (—, room temperature) and photoluminescence (---, 77°K, obtained with a phosphorimeter). The two spectra are on the same wavelength scale but different intensity scales.

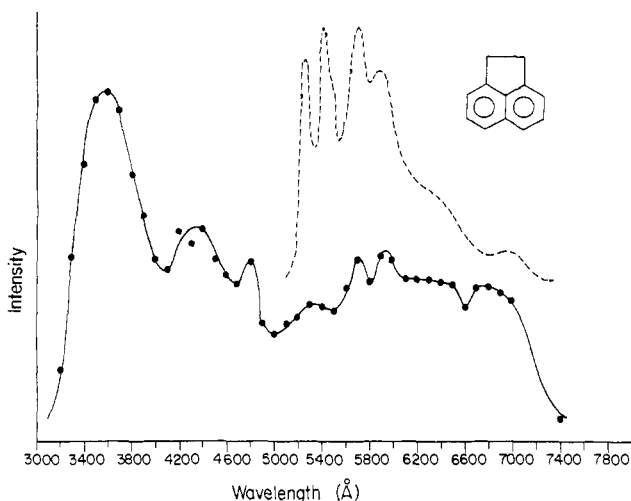


Figure 2. Acenaphthene triboluminescence (—, room temperature) and photoluminescence (---, 77°K, obtained with a phosphorimeter). The two spectra are on the same wavelength scale but different intensity scales.

cence 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 using a 1/4 meter Jarrell-Ash monochromator and an EMI 9558 photomultiplier cooled to -20° and were not corrected for the response characteristics of the instrument.

The room-temperature TL spectrum of phthalic anhydride is shown in Figure 1 (solid line). Above it is the 77°K photophosphorescence spectrum of the solid recorded on the same wavelength scale using a phosphorimeter (broken line). The low energy shoulder in the TL spectrum at *ca.* 4100 Å corresponds to the photophosphorescence origin at *ca.* 4100 Å recorded at the lower temperature. The shoulder at *ca.* 4600 Å in the TL spectrum corresponds to the vibronic bands of greatest intensity in the 77°K photophosphorescence spectrum. The photophosphorescence exhibits a 570-cm^{-1} vibrational progression which cannot be detected

at our current TL resolution. The intense feature at 3700–3800 Å in the TL spectrum is absent in the photoluminescence spectrum at both 77 and 300°K (*vide infra*).

The room-temperature TL and the 77°K photophosphorescence spectra of crystalline acenaphthene are shown in Figure 2. The origin of the photophosphorescence progression at 5260 Å corresponds to the weak feature in the TL spectrum at 5300 Å. The strong TL peaks centered between 5700 and 5900 Å correspond to the cluster of vibronic bands between 5680 and 5870 Å in the photophosphorescence spectrum which have been assigned⁶ to several totally symmetric C=C stretching vibrations. In the TL vibrational series (at room temperature), the 5300-Å bands are much weaker in relation to the 5700-Å bands than they are to the corresponding bands in the 77°K phosphorescence spectrum. A similar suppression of high energy bands had been previously observed in the photophosphorescence spectra of acenaphthene as the temperature was raised from 4 to 77°K.⁶

The high energy maximum in the acenaphthene TL spectrum corresponds to the previously reported fluorescence.⁷ The broad TL envelope extending far to the red of the fluorescence maximum is even more pronounced than the similar low energy spectral features we have previously reported in the tribofluorescence of coumarin.⁸ The envelope is absent in the photoluminescence spectrum. It is probably attributable to either or both of the previously proposed dynamic pressure-induced TL mechanisms: excimer formation or vibronic intensity change.³ The monomer-excimer intensity ratio is known to be quite pressure sensitive.⁸ An alternative possibility is emission from pressure-induced traps. The former two effects are expected to be more pronounced in the short-lived tribofluorescence than in the tribophosphorescence.³ The TL of acenaphthene is the first example of simultaneous tribofluorescence and tribophosphorescence.

The high energy maximum at 3700–3800 Å in the TL spectrum of phthalic anhydride is absent in the photoluminescence spectrum at 300 and 77°K. It may represent an extreme example of a pressure-induced emission which is red shifted from a fluorescence at high energy. (We have been unable to measure weak photoluminescences below 3700 Å because of exciting light interferences. To our knowledge, no fluorescence of phthalic anhydride has been reported.) The maximum could also be a pressure-induced charge transfer emitting state.⁹ However, speculation about the origin of this band is probably premature.

It is clear from these studies that TL is more than ordinary gas discharge or crystal emissions which are excited in a new way. Instead, the TL spectra can contain new features which are excited by the mechanical stress but which are absent in the photoluminescence spectra. The possible roles of impurities and traps in the TL excitation process and their contributions to the novel TL spectra are unknown. Our discovery of room temperature tribo-excited phosphorescence of crystals from which photophosphorescence cannot be readily detected raises the possibility of using TL as a direct

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method of determining triplet energies of molecules which do not photophosphoresce. We are currently exploring the potential of this direct application of triboluminescence.

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(*N*-Methylsalicylaldiminato)(*N*-methylsalicylaldiminium)nickel(0). A Novel Example of a π -Coordinated Azomethine Group ($>C=NH-$)

Sir:

Salicylaldimine is known as one of the useful ligands which affords a rich family of transition metal complexes.¹ Without exception, to our knowledge, the Schiff base is incorporated in metal complexes as a chelating anion. We found a novel class of nickel(0) complexes in which the Schiff base was disproportionated into the anion and the protonated species. Here we report the crystal and molecular structure of the *N*-methyl derivative.

Two moles of *N*-methylsalicylaldimine were added to a toluene solution of Ni(cod)₂ (cod = 1,5-C₈H₁₂) at room temperature. On standing, the red reaction mixture gave a good yield (90%) of wine red air-sensitive well-developed crystals Ni(CH₃N=CHC₆H₄OH)₂·C₆H₅CH₃ (**1**),² mp 145–150°. Similarly, *N*- α -phenethylsalicylaldimine gave an analogous complex, mp 145°. The structure of **1** was studied by a single-crystal three-dimensional X-ray analysis.

Crystal data: Ni(C₁₆H₁₈N₂O₂)·C₇H₈; M = 421.2; *a* = 13.776 (2), *b* = 12.159 (2), *c* = 12.724 (2) Å; β = 91.97 (2)°; space group *P*2₁/*n*; Z = 4; *D*_x = 1.313 g cm⁻³. The X-ray diffraction data were collected on a computer-controlled Rigaku four-circle diffractometer with a maximum 2 θ value of 45°, and Zr-filtered Mo K α radiation was used. The structure was solved by the heavy atom method and refined by the least-squares method to an *R* value of 0.060 for 1340 nonzero reflections. Anisotropic thermal vibrations were assumed for all the non-hydrogen atoms. The location of the somewhat disordered methyl group of the toluene molecule was not established definitely. Nevertheless all the hydrogen atoms of the complex molecule were revealed from a difference Fourier map.

Figure 1 shows the structure of the complex molecule, two of which form a cyclic dimer as a result of hydrogen bonding between O(2) and O(1) (O(2)–O(1) distance = 2.61 Å). The crystallographic symmetry of the dimer of **1** is *C*_i. In each molecule the hydroxyl proton of one of the Schiff base ligands may be regarded as being transferred to the nitrogen atom of the other. The deprotonated ligand (ligand A) is then described

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(2) Satisfactory elemental analysis was obtained.

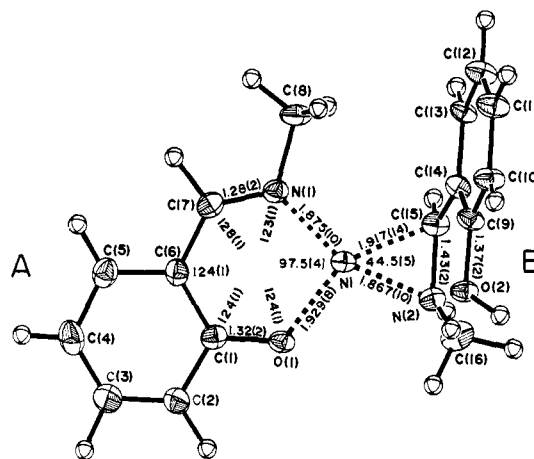


Figure 1. Stereochemistry of and important bond lengths and angles in (*N*-methylsalicylaldiminato)(*N*-methylsalicylaldiminium)nickel(0).

as a *N*-methylsalicylaldiminato anion and the protonated one (ligand B) as a *N*-methylsalicylaldiminium ion. The ligand B bonds to the Ni atom through the N(2)=C(15) group. Thus the Ni atom has a trigonal planar coordination, if the N(2)=C(15) group is taken to be a monodentate ligand. The atoms, Ni, O(1), N(1), N(2), and C(15), are almost coplanar within the mean atomic deviation of 0.03 Å; the dihedral angle between the planes defined by O(1)–N(1) and that by N(2)–Ni–C(15) atoms is only 4.4°. The angle compares with the values in Ni(*t*-BuNC)₂Un, Un:PhN=NPh³ (**2**) (1.2°), (NC)₂C=C=N-*t*-Bu⁴ (**3**) (7.9°), and C₂(CN)₄⁵ (**4**) (23.9°). In ligand A the Ni–N(1) distance of 1.875 (10) Å is shorter than the Ni–O(1) distance, 1.929 (8) Å; these relative lengths are different from those observed in several salicylaldiminato Ni(II) complexes⁶ (Ni–N, 1.92–2.05 Å, Ni–O, 1.84–2.01 Å). In ligand B, the Ni–N, 1.867 (10) Å, and Ni–C distances, 1.917 (14) Å, are longer than the corresponding values, 1.843 (3) and 1.855 (4) Å, found in **3** and may be compared with the values 1.894 (4) Å for Ni–N in **2** and 1.954 (4) Å for Ni–C in **4**. The N(2)=C(15) bond length of 1.43 (2) Å is considerably longer than the N(1)=C(7) distance and rather close to the normal single-bond distance of N–C. A distortion from planarity of the C(16)N(2)H=C(15)–HC(14) fragment is observed as in π -bonded olefin complexes; the H[N(2)]–N(2)–C(16) and the H[C(15)]–C(15)–C(14) planes bend away from the Ni atom. The N(2)=C(15) vector forms angles of 55 and 77°, respectively, with the normals of those planes. The bond angles around the π -coordinated C=N bond indicates a contribution of sp³ hybridization at the C and N atoms. It appears that the presence of intermolecular hydrogen bonds is important to the stability of the solid.

The structure in solution was examined by the ¹H nmr spectrum of a pyridine-*d*₅ solution of **1**: δ (ppm, TMS) 2.65 (3 H, doublet, *J* = 5.4 Hz, =NH(CH₃)),

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