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Triboluminescence–Structure Relationships in Polymorphs of Hexaphenylcarbodiphosphorane and Anthranilic Acid, Molecular Crystals, and Salts

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Abstract: In two polymorphic systems, hexaphenylcarbodisphophorane and anthranilic acid, one phase is triboluminescent whereas the other phases are not. The crystal structures of the heretofor unknown phases are reported. The triboluminescence spectra of the active phases and the photoluminescence spectra of all phases are compared and assigned. Triboluminescence activity is correlated with polar crystal structures. This correlation also applies to condensed polycyclic aromatic hydrocarbons, uranyl salts, saccharides, and aromatic organic molecular crystals which exhibit tribofluorescence or tribophosphorescence from the molecules comprising the crystal and/or nitrogen emission triboluminescence. Spectroscopic and crystallographic details are presented. In the case of saccharin, the presence of trace dopants governs the triboluminescence. A general mechanism based on electrical charging of newly created surfaces is discussed.

Introduction

Recent spectroscopic investigations of triboluminescence (TL), the emission of light caused by the application of mechanical force on a solid, have identified a variety of excited state origins of the luminescence.[1] However neither the crystal properties required for TL activity nor the mechanisms by which mechanical force can populate the emitting excited states are fully understood.[1,2] During studies of the spectroscopic and mechanical properties of triboluminescent organic systems, two polymorphic systems, hexaphenylcarbodiphosphorane (PPC) and anthranilic acid were discovered which are TL active in one phase but TL inactive in the other phases. The existence of both triboluminescent and nontriboluminescent phases opened the possibility of investigating the solid-state structural requirements for TL activity from the same molecule and the same excited state.

Two crystalline phases of hexaphenylcarbodiphosphorane $[(Ph_3P)_2C]$ can be isolated.[3] The crystal and molecular structure of the form which is triboluminescent, phase II (monoclinic $C2$, $a = 15.362$ Å, $b = 9.483$ Å, $c = 20.054$ Å, $\beta = 95.1°$), is known.[4] Its TL spectrum is also known.[5] However the existence of nontriboluminescent polymorph (phase 1) was unknown prior to the preliminary communication of its structure.[3]

Three crystalline phases of anthranilic acid are known.[6] The complete structure of phase I, orthorhombic $P2_1cn$ (standard setting $Pna2_1$), $a = 12.868$ Å, $b = 10.772$ Å, and $c = 9.325$ Å, and the space group of phase II (orthorhomic Pbca) have been reported.[7] Phase III is known only to be monoclinic. Only phase I is TL active. The phase transition I $\rightarrow$ II has been observed by differential thermal analysis at 81 °C.[8] The reverse of this phase transition as well as transitions involving form III have not been unambiguously observed.

For an investigation of the possible structural relationships of triboluminescence, the crystal structure and spectroscopic properties of the phases were determined. We report here the structure of the hitherto undetermined phases hexaphenylcarbodiphosphorane I, anthranilic acid II and III and examine the relations between the structures and the TL properties of these two systems. In addition, we report a correlation between TL activity and unit-cell symmetry groups in four families of crystals whose TL spectra are assigned and whose crystallographic space groups are known. In both the polymorphic crystals and the four families of crystals, TL activity is related to the unit-cell polarity. The relevance of piezoelectric charging, the electrical charging produced by applying strain to a noncentrosymmetric crystal, to the excitation mechanism is discussed.

Results

Hexaphenylcarbodiphosphorane. The electronic excited-state differences between the PPC polymorphs are quite apparent from the photoluminescence spectra (Figure 1). The PPC I emission maximum at 540 nm has been assigned as phosphorescence on the basis of its lifetime of 0.11 ms at 77 K.[9] Molecular orbital calculations indicate a (n, π^*) excited state configuration.[10] The TL spectrum of PPC II has been previously reported[5] and is superimposable on the photoluminescence of phase II crystals. On this basis the TL is assigned to the same excited electronic state. The photoluminescence spectrum of PPC I is similar to that of phase II but with the emission maximum shifted to 575 nm.

The molecular structure of PPC I determined at −160 °C is shown in Figure 2. The P—C—P bond angle in this molecule is 131.7 (3)° with an average C=P bond length of 1.635 (5) Å. The PPC II unit cell contains two structurally independent molecules A and B with P—C—P bond angles of 143.8 and 130.1°, respectively.[4] The phenyl rings in PPC I are less eclipsed than in PPC II with torsion angles, defined as C—P—P—C, of 25.0–27.5° in phase I and 5.5–8.3°[4] in phase II. The closest intramolecular phenyl-phenyl interaction is 3.819 Å between phenyl rings on opposite phosphorous atoms of PPC I. Atomic fractional coordinates, temperature factors, bond lengths, and bond angles of phase I are given in Tables I–III.

The nonpolarity of the PPC I unit cell caused by the presence of three perpendicular twofold screw axes is apparent in the unit-cell projection along the a axis (Figure 3). There are no significantly close intermolecular phenyl–phenyl interactions in either of the two phases. Triboluminescent crystals of PPC II lose their TL and apparently convert to form I over a period of 2–3 years. Calculations of the molecular packing energies of PPC I and II using the method of Williams[11] indicate that phase I is about 1 kcal/mole lower in energy.

The Raman spectra of the two crystal forms are in general quite similar in the 400–1500-cm^{-1} region. In both cases the most intense scattering peak is observed as a single, sharp line at 1003 cm^{-1} assigned as the C–H bend. However, a striking difference between the Raman spectra of the two phases is observed in the

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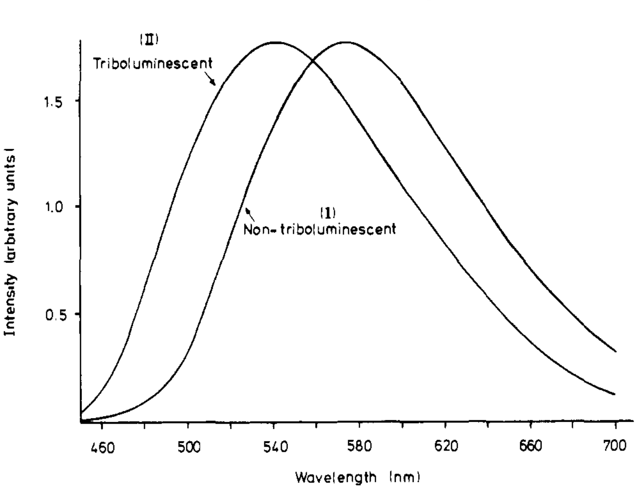

Figure 1. Photoluminescence spectra of nontriboluminescent crystals (phase I) and triboluminescent crystals (phase II) of hexaphenylcarbodiphosphorane.

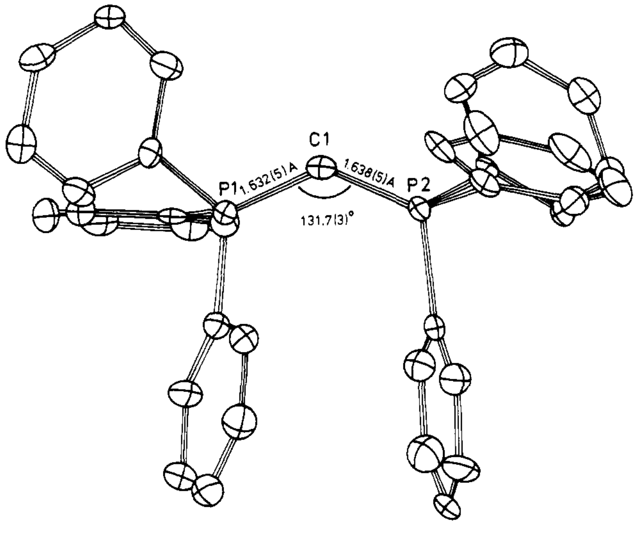

Figure 2. Molecular structure of hexaphenylcarbodiphosphorane in phase I crystals.

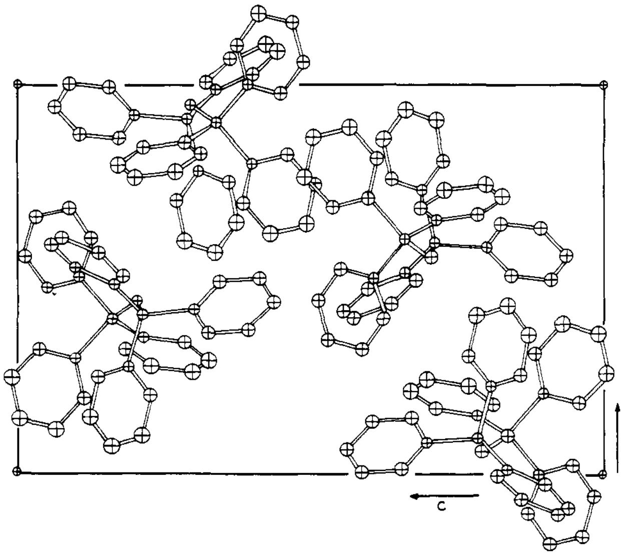

Figure 3. Unit-cell projection along the *a* axis of hexaphenylcarbodiphosphorane (I) demonstrating the nonpolarity caused by three perpendicular twofold screw axes.

P–C–P bending region. In PPC I this bend is observed as a single, sharp line at 661 cm^{-1} with an intensity about the same as that of the 1003-cm^{-1} line. The Raman spectrum of PPC II shows two lines in this region at 661 and 652 cm^{-1}, each about half as intense as the 1003-cm^{-1} line. They are assigned as the P–C–P bends of molecules A and B, respectively.

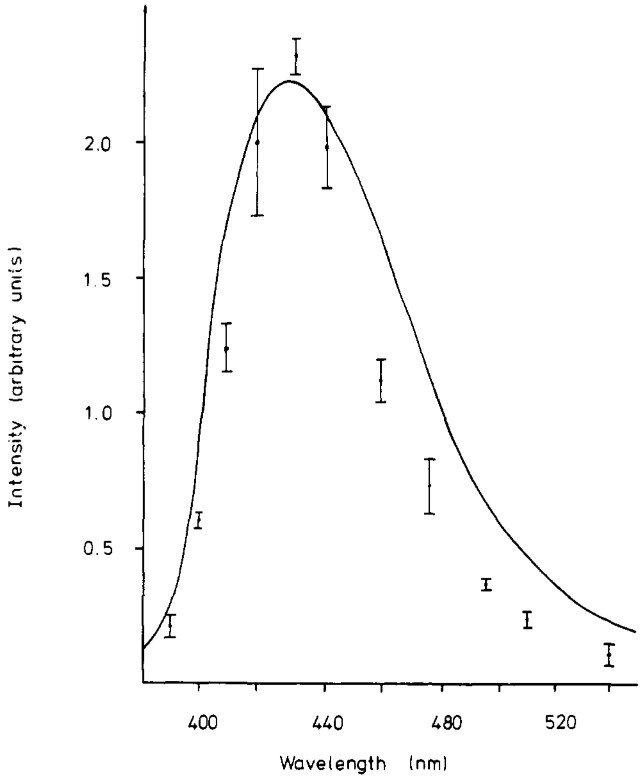

Figure 4. Triboluminescence (bars) and photoluminescence (solid line) spectra of anthranilic acid (I).

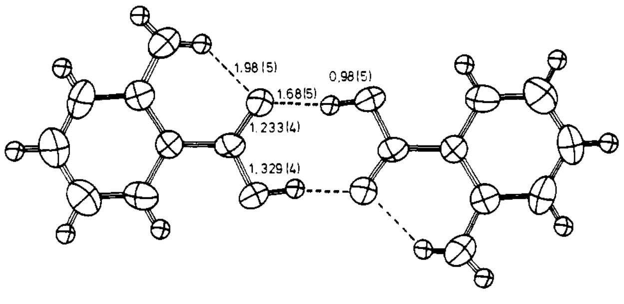

Figure 5. Molecular structure of anthranilic acid (II). The molecular structure of anthranilic acid (III) is the same within experimental error.

Anthranilic Acid. The TL spectrum of anthranilic acid is shown superimposed on the photoluminescence spectrum in Figure 4. The photoluminescence has been assigned to a π–π^* phosphorescence.[12] The TL is assigned to the same electronic excited state on the basis of the similarity of the two spectra. Although the three polymorphs of anthranilic acid all have virtually identical photoluminescence spectra, only phase I is triboluminescent.

The molecular structures of anthranilic acid II and III are identical within the experimental error. In these structures the acid groups form hydrogen bonded dimers (Figure 5) around the unit-cell center of symmetry. Both molecules are coplanar with only 1.680 Å separating the hydroxy hydrogen and the oxygen of the symmetry-related molecule. This oxygen is also intramolecular hydrogen bonded to an amine hydrogen. The planarity of the amine group is indicative of primarily sp hybridization and a large degree of conjugation throughout the molecule. The molecular structure might be better described as a zwitterion composed of an imminium group and a negatively charged oxygen stabilized by two hydrogen bonds. The atomic coordinates, bond lengths, and angles are given in Tables, IV–VII.

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(12) Angelos, B. A. Masters Thesis, UCLA, 1978.

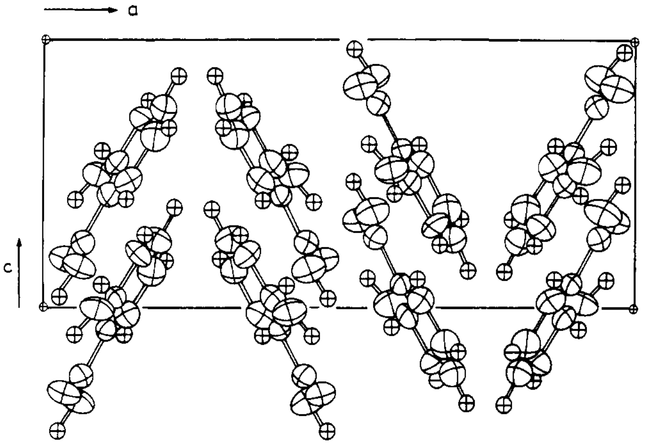

Figure 6. Unit cell of anthranilic acid (II) projected along the *b* axis. Note the similarity to Figure 7.

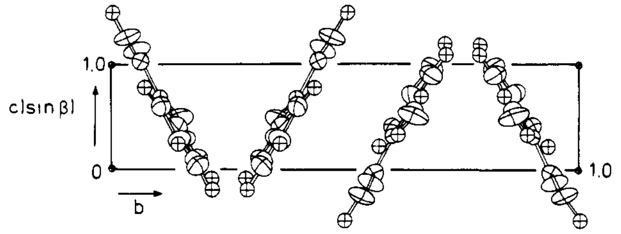

Figure 7. Unit cell of anthranilic acid (III) projected along the *a* axis. Note the similarity to Figure 6.

By contrast, the triboluminescent anthranilic acid I unit cell contains two crystallographically independent molecules,[7] a neutral molecule (A) and a zwitterion (B) consisting of an ammonium and a carboxylate group. These different molecules occupy alternate layers along the crystallographic *a* axis. The molecules within each layer are held together by a system of hydrogen bonds between oxygen and nitrogen atoms, forming a continuous hydrogen-bonded chain.

This system of intermolecular hydrogen bonds is absent in the nontriboluminescent phases II and III. Intramolecular N-H···O bonds exist in all of the forms, but the intermolecular N-H···O bonds that form the chains in phase I are replaced by intermolecular O-H···O bonds forming the centrosymmetric dimers in phases II and III. The hydrogen bonding is reflected in the N-H stretching frequencies. The symmetric and asymmetric NH_2 stretches of anthranilic acid I are at 3240 and 3330 cm^{-1}, respectively, while those of phases II and III are shifted by about 150 cm^{-1} to 3390 and 3500 cm^{-1}. These values are in agreement with the stretching frequencies previously reported for the three phases.[13]

The major difference between phases II and III is a 9.7° twist and subsequent A centering of the phase II lattice. The unit cell chosen for the structure determination of form III is generated by interchanging the *a* and *b* axes of phase II and choosing an appropriate *c* axis such that a primitive cell is defined. The similarity of the lattices is demonstrated in Figures 6 and 7, showing the phase II and III unit cells projected along their respective *b* and *a* axes. No significantly close phenyl–phenyl interactions exist in any of the three forms.

Discussion

Polymorphic Crystals. One obvious structural characteristic that distinguishes the triboluminescent phases is the presence of two independent molecules per unit cell. Acenaphthene is another example of a triboluminescent crystal with two nonequivalent molecules in the unit cell.[14] However, this property is most likely not a general condition for TL activity. The structures of a large number of triboluminescent crystals are known where only one symmetry-independent molecule exists in the unit cell (e.g., phenanthrene[15]).

Table VIII. Relationships between Symmetry Classes and Piezoelectric Moduli

symmetry class	polarity	types of piezoelectric moduli
triclinic 1	polar	hydrostatic, compression, torsion
$\bar{1}$	nonpolar	none
monoclinic 2	polar	hydrostatic, compression, torsion
m	polar	hydrostatic, compression, torsion
2/*m*	nonpolar	none
orthorhombic 222	nonpolar	torsion only
*mm*2	polar	hydrostatic, compression, torsion
mmm	nonpolar	none

Two general observations of the differences between the polymorphs appear to be particularly relevant to TL. First, the crystals which have polar space groups are triboluminescent while those with nonpolar space groups are not TL active. Second, there is no major difference in phenyl–phenyl interactions between the polymorphs. The correlation between TL activity and space group polarity is not limited to polymorphic systems (vide infra). However, the polymorphic systems provide the most direct opportunity to test such relationships because the same molecule with the same (or slightly perturbed) excited state forms different crystals with different physical properties.

The correlation between crystal polarity and TL suggests that piezoelectricity could play a role in the excitation of TL. The two triboluminescent crystals have polar space groups *C*2 and $P2_1cn$, while the nontriboluminescent crystals have nonpolar $P2_12_12_1$, *P*bca, and $P2_1/a$ space groups. The polar space groups are piezoelectric under compression, torsion, and hydrostatic strain. *Pbca* and $P2_1/a$ are centrosymmetric and therefore nonpiezoelectric, and $P2_12_12_1$ is piezoelectric only under torsional strains. If torsional strains are a minor component of crystal fracture, then the nontriboluminescent phases would also show little or no piezoelectric charging during fracture.

The absence of significant differences between phenyl–phenyl interactions does not support the thermal mechanism of TL excitation.[1,2] This mechanism requires increased intermolecular π-orbital interactions in the crystal under strain. Such interactions, which change the energy difference between the ground and excited states, could allow the excited state to become thermally populated.[16] If this mechanism were significant in the production of TL, the triboluminescent polymorphs should have more and/or larger interactions between the aromatic systems. The most significant phenyl–phenyl interaction is found in the nontriboluminescent phase I of hexaphenylcarbodiphosphorane. It is of interest to note that dimethyltetraphenylcarbodiphosphorane has a very short (3.28 Å) phenyl–phenyl separation, belongs to the *C*2/*c* space group, and is not triboluminescent.[17]

Further Triboluminescence–Structure Correlations. The relationship between crystal polarity and triboluminescence in crystals whose TL spectra exhibit molecular luminescence, simultaneous molecular TL and nitrogen emission, and nitrogen emission only is examined in the following sections. Special attention is given to crystals which are apparent exceptions to the relation. The only previous observation was the suggestion that gas-discharge TL is more frequent in crystals lacking a center of symmetry.[18]

For convenience, the eight symmetry classes of the three most common crystal systems are listed in Table VIII. Of these eight

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Table IX. TL Activities and Space Groups of Condensed Polycyclic Aromatic Hydrocarbon Crystals

sample	TL(obsd)	intensity[a]	space group	symmetry class	ref
phenanthrene	TL	0.37 ± 0.05	$P2_1$	2	*b*
1,2,5,6-dibenzanthracene	TL	(6.7 ± 0.4) × 10^{-3}	$P2_1$	2	12
picene	TL	(3.7 ± 0.2) × 10^{-3}	$Ab2a$	*mm*2	*c*
1,2-benzanthracene	TL		$P2_1$	2	*d*
anthracene	no TL		$P2_1/c$	2*m*	*e*
chrysene	no TL		$C2/c$	2*m*	*f*
naphthalene	no TL		$P2_1/c$	2*m*	*g*
pyrene	no TL		$P2_1/c$	2*m*	*h*
tetracene	no TL		$P\bar{1}$	$\bar{1}$	*i*
triphenylene	no TL		$P2_12_12_1$	222	*j*

[a] Integrated intensity relative to that of acenaphthene. [b] Peters, E. T.; Armington, A. F.; Rubin, B. *J. Appl. Phys.* 1966, 37, 226. [c] Berna, J. D.; Crowfoot, D. *J. Chem. Soc.* 1935, *93*. [d] Friedlander, P. H.; Sayre, D. *Nature (London)* 1956, *178*, 999. [e] Mason, R. *Acta Crystallogr.* 1964, *17*, 547 (1964). [f] Burns, D. M.; Iball, J. *Proc. R. Soc. London, Ser. A 257A*, 491. [g] Cruichshank, D. W. J. *Acta Crystallogr.* 1957, *10*, 504. [h] Camerman, A.; Trotter, J. *Ibid.* 1965, *18*, 636. [i] Campbell, R. B.; Robertson, J. M.; Trotter, J. *Ibid.* 1962, *15*, 289. [j] Ahmed, F. R.; Trotter, J. *Ibid.* 1963, *16*, 503.

Table X. TL Activities and Space Groups of Uranyl Salts

sample	TL(obsd)	intensity[a]	space group	symmetry class	ref
uranyl nitrate·$6H_2O$	TL	0.19 ± 0.03	$A2_1ma$	*mm*2	*b*
uranyl disalicylate·$2H_2O$	TL	0.12 ± 0.01	$P1$	1	*c*
uranyl acetate·$2H_2O$	TL	0.013 ± 0.001	$Pna2_1$	*mm*2	*d*
uranyl dihydrogen phosphate·$3H_2O$	no TL		$P2_1/c$	2/*m*	*e*
uranyl hydrogen phosphate·$4H_2O$	no TL		$P4/mmm$	4/*bmm*	*f*
uranyl oxalate·$3H_2O$	no TL		$P2_1/c$	2/*m*	*g*
uranyl sulfate·$3H_2O$	no TL		$Pbnm$	*mmm*	*h*
potassium uranylacetate	no TL		$I422$	422	*i*
sodium uranylacetate	no TL		$P2_13$	23	*j*

[a] Integrated intensity relative to that of the acenaphthene. [b] Hall, D. H.; Rae, A. D.; Waters, J. N. *Acta Crystallogr.* 1965, *19*, 389. [c] Manojlovic, L. M. *Bull. Inst. Nucl. Sci.* 1958, *8*, *105*. [d] Armirthalingam, V.; Chandran, D. V.; Padmanabhan, V. M. *Acta Crystallogr.* 1959, *12*, 821. [e] Schrever, J. M.; Baes, F. *J. Am. Chem. Soc.* 1954, *76*, 354. [f] Ross, V. *Am. Mineral.* 1965, *40*, 917. [g] Jenkins, I. L.; Moore, F. H.; Waterman, M. J. *J. Inorg. Nucl. Chem.* 1965, *27*, 77. [h] Traill, R. J. *Am. Mineral* 1952, *37*, 394. [i] Donnay, J. D. M.; Ondik, H. M. *Crystal Data Determinative Tables* 1972, *1*, 122. [j] Zachariasen, W. H.; Plettinger, H. A. *Acta Crystallogr.* 1959, *12*, 526.

symmetry classes, four are polar and four are nonpolar.[19] As shown in the Table VIII, the polar space groups exhibit piezoelectric charging under hydrostatic pressure, compression, and torsion. The nonpolar symmetry class 222 is a special case. The nonpolarity is required by the three perpendicular twofold axes. Because a twofold axis can be destroyed by torsional strains, the nonpolar class 222 will become piezoelectric under torsion.

Condensed Polycyclic Aromatic Hydrocarbons. The TL properties, relative intensities, crystallographic space groups, and symmetry classes of ten polycyclic aromatic hydrocarbons are given in Table IX. The four triboluminescent crystals all belong to polar space groups and the nontriboluminescent crystals are all of nonpolar space groups, supporting the proposed TL–structure relation.

Dibenzanthracene exists as both monoclinic and orthorhombic polymorphs.[20] The polarity requirement predicts that the monoclinic $P2_1$ form should be TL active while the orthorhombic *Pbca* polymorph should be inactive. The monoclinic polymorph is triboluminescent as shown in Table IX. Efforts to obtain the orthorhombic phase were unsuccessful and the absence of TL in this polymorph could be confirmed.

Uranyl Salts. The TL properties, relative intensities, space groups, and symmetry classes of nine uranyl salts are given in Table X. The four TL-active crystals all belong to polar space groups, and the inactive crystals belong to nonpolar space groups.

The TL spectra of all salts except the salicylate salt show the intense green $^3\Pi_u \rightarrow {}^1\Sigma_g{}^+$ phosphorescence of the uranyl ion.[21-24] The TL spectrum of the latter salt is dominated by salicylate ion fluorescence.[23] In all cases the TL spectra also show weaker lines characteristic of nitrogen emission. In the case of the nitrate salt, the intensity of the nitrogen emission is less than 1/50th of that of the uranyl phosphorescence.

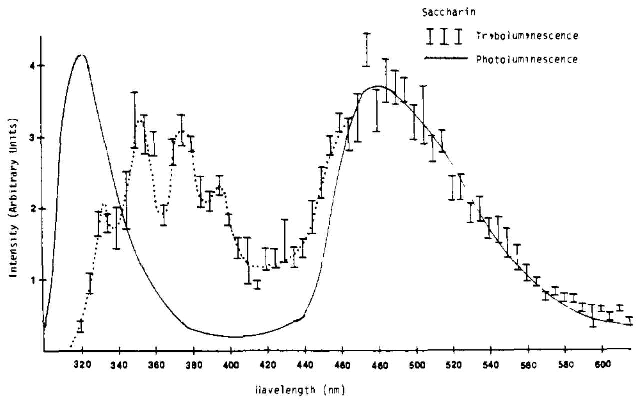

Figure 8. Triboluminescence (I) and photoluminescence (solid line) spectra of commercial saccharin.

Saccharin. Saccharin provides a clear example of the importance of trace impurities on TL activity. The intense triboluminescence of saccharin and the existence of impurity effects are known.[28] Crystals of commerically obtained saccharin studied here which were extensively recrystallized from acetone were

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(19) Henry, N. F. M., Lonsdale, K., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I, p 42.

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Table XI. TL Activities and Space Groups of Saccharide Crystals

sample	TL (obsd)	space group	symmetry class	ref
cellobiose	TL	$P2_1$	2	*a*
glucose·H_2O	TL	$P2_1$	2	*b*
lactose·H_2O	TL	$P2_1$	2	*c*
maltose·H_2O	TL	$P2_1$	2	*d*
rhamnose·H_2O	TL	$P2_1$	2	*e*
ribose	TL	$P2_1$	2	*f*
sucrose	TL	$P2_1$	2	*g*
glucose	TL	$P2_12_12_1$	222	*h*
sorbose	TL	$P2_12_12_1$	222	*i*
arabinose	no TL	$P2_12_12_1$	222	*j*
fructose	no TL	$P2_12_12_1$	222	*k*
fucose	no TL	$P2_12_12_1$	222	*i*
galactose	no TL	$P2_12_12_1$	222	*l*
mannose	no TL	$P2_12_12_1$	222	*m*

[a] Brown, C. J. *J. Chem. Soc. A* 1966, 927. [b] Killean, R. C. G.; Ferrier, W. G.; Young, D. W. *Acta Crystallogr.* 1962, *15*, 911. [c] Seifert, H.; Labrot, G. *Naturwissenschaften* 1961, *48*, 691. [d] French, D. *Acta Crystallogr.* 1954, *7*, 136. [e] McGeachin, H. McD.; Beevers, C. A. *Ibid.* 1957, *10*, 227. [f] Furberg, S.; Hordvik, A.; Taugbol, K. *Acta Chem. Scand. 10*, 135. [g] Brown, G. M.; Levy, H. A. *Science (Washington)* 1954, *141*, 921. [h] McDonald, T. R. R.; Beevers, C. A. *Acta Crystallogr.* 1952, *5*, 654; Ferrier, W. G. *Ibid.* 1960, *13*, 678. [i] Cox, E. G.; Goodwin, T. H.; Wagstaff, A. I. *J. Chem. Soc.* 1935, 978. [j] Hordvik, A. *Acta Chem. Scand.* 1961, *15*, 16. [k] Hengstenberg, J.; Mark, H. *Z. Kristallogr., Kristallgeom., Kristallph Kristallchem.* 1930, *72*, 301. [l] Sheldrick, B. *J. Chem. Soc.* 1961, 3157. [m] Marwick, T. C. *Proc. R. Soc. London, Ser. A.* 1931, *A131*, 621.

highly TL active.[29] The space group, $P2_1/c$, is nonpolar[30] and should not be TL active according to the correlation. The space group of the crystals studied here was reinvestigated and verified. The TL spectrum of these crystals is shown superimposed on the photoluminescence spectrum in Figure 8. The TL and PL spectra contain a broad feature at about 480 nm. The TL spectrum also contains the emission lines from nitrogen between 320 and 400 nm which are absent in the PL spectrum. The PL spectrum exhibits an emission at 320 nm which is absent in the TL spectrum.

After saccharin is purified according to the procedure given in the Experimental Section, the crystals are neither triboluminescent nor photoluminescent. Further examination revealed that the 320-nm emission from the unpurified crystals is the luminescence of *p*-sulfamoylbenzoic acid. The 480-nm emission in impure saccharin originates from *p*-toluenesulfonamide. The latter compound alone emits with a maximum at 435 nm at room temperature. When the emission of impure saccharin is obtained in a Me-THF glass at 77 °C, its spectrum is the superposition of the spectra of the two impurities. The observed red shift in saccharin crystals at room temperature is probably caused by lattice effects.

The results given above prove that not only TL activity but also the emitting lumiphore can be governed by trace impurities. Despite the nonpolar crystal lattice, the presence of these impurities can apparently generate local sites of different symmetry where TL is excited. A perturbation of the lattice by the impurities is required in order to create TL activity. The effect of the impurities is not merely the introduction of a lumiphore, as proven by the nitrogen emission in the TL active crystal and its absence in the TL-inactive purified form. The luminescence of the impurity itself in addition to the nitrogen emission suggests the possibility that deliberate doping of organic molecular crystals could produce new types of TL-active crystals with emission wavelengths which can be deliberately chosen by the proper choice of a luminescent dopant.

Saccharides. The TL properties, relative space groups and symmetry classes of ten mono- and oligosaccharides are given in Table XI. All of the saccharides examined crystallize into one of two space groups. The monoclinic $P2_1$ crystals are expected to produce TL while the orthorhombic $P2_12_12_1$ crystals should be inactive. A good but not perfect correlation is observed in Table XI.

Table XII. TL Activities and Space Groups of Spectroscopically Characterized Crystals

sample	TL (obsd)	intensity[a]	space group	symmetry class	ref
acenaphthene	TL	1.00[a]	$Pcm2_1$	*mm*2	*b*
resorcinol	TL	0.58 ± 0.05	$Pna2_1$	*mm*2	*c*
coumarin	TL	0.55 ± 0.04	$Pca2^1$	*mm*2	*d*
n-aminophenol	TL	0.37 ± 0.04	$P2_1am$	*mm*2	*e*
aniline·HCl	TL	0.18 ± 0.01			
tartaric acid	TL	0.14 ± 0.008	$P2_1$	2	*f*
p-anisidine	TL	0.091 ± 0.009	$Pca2_1$	*mm*2	*g*
p-anisidine	TL	0.048 ± 0.004	$P2_1$	*mm*2	*g*
nicotinium salicylate	TL	0.061 ± 0.003	$P2_1$	2	*h*
phthalic hydride	TL	0.05 ± 0.003	$Pna2_1$	*mm*2	35

[a] Integrated intensity relative to that of acenaphthene. [b] Ehrlich, H. W. W. *Acta Crystallogr.* 1957, *10*, 699. [c] Robertson, J. M.; Ubbelohde, A. R. *Proc. R. Soc. London* 1938, *167*, 122. [d] Myasnikova, R. M.; Davydova, T. S.; Simonov, V. I. *Sov. Phys-Crystallogr. (Engl. Trans.)* 1974, *18*, 454. [e] Krc, J.; Hinch, R. *Anal. Chem.* 1956, *28*, 137. [f] Okaya, Y.; Stemple, N. R.; Kay, M. I. *Acta Crystallogr.* 1966, *21*, 237. [g] This work. Zavodnik, V. E.; Poveteva, Z. P.; Zvonkova, Z. V. *Sov. Phys.-Crystallogr. (Engl. Trans.)* 1976, *20*, 514. [h] Kim, H. S.; Jeffrey, G. A. *Acta Crystallogr., Sect. B.* 1971, *B27*, 1123.

The TL activity of sorbose and anhydrous glucose may be exceptions to the correlation. However, in the case of anhydrous glucose, the possible presence of trace amounts of water could provide local sites where the symmetry is changed and TL is produced. Note that hydrated glucose is TL active as expected. (The effect of trace impurities in producing TL activity is proven in the case of saccharin as discussed above.) The TL activity of sorbose could also arise from the same cause. A further complication in measuring TL activity in these crystals is the difficulty in obtaining large crystals. In many of these samples, the common form is a fine powder which cannot be efficiently fractured. Vacuum desiccation of a hydrated sample also often results in a powder. Thus it is difficult to be certain that TL is absent from a given sample. For these reasons, the results reported in Table XI can only be interpreted as being not inconsistent with the structure–TL correlation.

The spectra of the saccharides consist of the emission of molecular nitrogen.[31] Historically, the TL of sucrose was the earliest reported example of the phenomenon.[32] The TL of sugar-containing candies provides an effective demonstration.[33]

Spectroscopically Studied Triboluminescent Molecular Crystals. A compilation of spectroscopically studied TL crystals whose space groups are known is given in Table XII. In all cases they belong to polar space groups.

The space group of *p*-anisidine had been previously reported as $P2_1/n$.[34] The space group was redetermined here. Colorless crystals grown from vacuum sublimination at 30 °C belong to the orthorhombic space group $Pca2_1$, a = 14.26 Å, b 7.56 Å, c = 6.20 Å. These crystals are rapidly oxidized to a brown form if left standing in air. The monoclinic space group previously reported for brown crystals is probably this altered form.

The space group reported for phthalic anhydride is incomplete (Pna*).[35] However, this crystal has been reported to be pie-

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zoelectric.[36] Thus the space group $Pna2_1$ given in Table XII is assumed. Because of the measured piezoelectricity, the TL–polarity correlation is certain.

Mechanistic Implications. The correlation between polar space groups and TL activity in organic molecular crystals suggests that electrical charging is related to the excitation of triboluminescence. In addition, studies of the simultaneous stress–strain and triboluminescence–strain relationships have revealed that TL accompanies fracture in these types of molecular crystals.[37] Together, these observations suggest that the electric fields produced near the tips of mobile cracks excite TL.

An order of magnitude calculation of the electric field supports the feasibility of the mechanism. The piezoelectric constants of organic molecular crystals[38] are generally of the order of 10^{-11} C N^{-1}, and the stress near the tip of a mobile fracture is a minimum of 10^8 N m^{-2}[39] and could be much higher. Thus the charge density of the newly created surface along polar directions will be at least on the order of 10^{-4} C m^{-2}. The electric field between the oppositely charged surfaces, E/ϵ_0, will be at least 10^8 V m^{-1} (where ϵ_0 is the permitivity constant). Electric fields of about this magnitude could cause molecular excitation by several mechanisms including electron impact or perhaps recombination of charge carriers.[40] The calculated field is also sufficiently large to initiate nitrogen discharge. Degassing experiments and studies conducted in nitrogen-free atmospheres have shown that the crystal emissions are usually excited separately from the nitrogen emissions and are not a result of energy transfer from excited states of nitrogen to the crystal.

Exceptions to the correlation between polar space groups and TL activity are expected in certain cases according to an excitation mechanism based on charging of new surfaces. For example, if fracture occurs along an intrinsically charged plane in a crystal comprised of ions, charging of the newly created surface and thus TL activity are expected even though the charging does not originate from piezoelectric charging. As an illustration, fracture along the 111 plane of a crystal having the NaCl lattice would lead to very high surface charging. Thus, the likeliest groups of crystals which are expected to exhibit exceptions to the correlation are ionic crystals. Second, as demonstrated in this paper, impurities and deliberate dopants are expected to provide exceptions to the correlation. In these cases, the impurity could alter the local symmetry and provide a site where charging could occur.

Experimental Section

Hexaphenylcarbodiphosphorane crystals were grown from diglyme solution.[9] Anthranilic acid was obtained from Matheson, Coleman and Bell and vacuum sublimed at 85 °C. The triboluminescent form of anthranilic acid (phase I) was grown by slow evaporation of an aqueous solution. Nontriboluminescent crystals of anthranilic acid phase II were grown from evaporation of an aniline solution. Nontriboluminescent crystals of phase III of anthranilic acid were grown from the melt. Phenanthrene (99.999% pure) was obtained from Materials Limited. This sample was zone refined more than 100 passes to achieve greater purity. Aniline hydrobromide was made by vigorously stirring a mixture of aniline and 48% hydrobromic acid. The solid product was filtered and recrystallized twice from methanol. All other compounds were purchased from commercial sources and were recrystallized before use.

Saccharin was purified by using a procedure based on that of Frac.[41] Approximately 5 g of saccharin were dissolved in a mixture of 70 mL of concentrated H_2SO_4 and 30 mL of concentrated HNO_3 at 0 °C. The solution was stirred for 30 min and filtered to remove any undissolved solid. A 200-mL sample of cold distilled water was added to precipitate saccharin. The product was filtered and washed with cold water. All samples used in this study were treated at least twice by this procedure.

The infrared absorptions of anthranilic acid in a KBr matrix were measured on a Perkin-Elmer 521 spectrometer. The Raman scattering of hexaphenylcarbodiphosphorane (PPC) was recorded on the solid at room temperature with a Cary 81 Raman spectrometer. The TL intensity measurements were made by using an air driven piston at an impact velocity of 4 m/s as described previously.[37] Triboluminescence spectra measured at room temperature as previously described.[42] Photoluminescence spectra of the solids were recorded at room temperature on a Spex fluorolog spectrofluorometer.

Structure of Hexaphenylcarbodiphosphorane I. Yellow needles of PPC were cleaved to obtain diamond-shaped specimens of approximate dimensions 0.20 × 0.16 × 0.16 mm. X-ray diffraction data were collected at −160 °C under a stream of cold, dry nitrogen on a Syntex $P\bar{1}$ automated diffractometer using monochromatic Mo Kα radiation. Fifteen automatically centered reflections were used to determine the lattice parameters a = 11.184 (4) Å, b = 12.956 (4) Å, c = 19.410 (5) Å, and V = 2812.5 Å^3. Intensity data were collected with θ–2θ scan to a maximum $2\theta = 47°$. Systematic absences indicated the space group $P2_12_12_1$, $Z = 4$. Refinement of the structure was based on 1776 observed reflections of $I > 3\sigma$.

The coordinates of all nonhydrogen atoms were determined by standard Patterson and difference Fourier techniques. The positions and anisotropic temperature factors of the central P–C–P atoms as well as positions of all phenyl atoms (as groups) were refined to an R value of 0.052. All nonhydrogen atoms were further refined anisotropically to a final R value of 0.041. Hydrogen atoms were assigned isotropic temperature factors of 2.0. No corrections were made for crystal absorption (μ = 1.38 cm^{-1}).

Diffraction data collected at room temperature were refined to a final R = 0.059 with essentially the same crystal and molecular structure as that obtained for the crystal at −160 °C. Crystal decomposition in this case resulted in a 30% decrease in standard reflection intensities. Unit-cell parameters measured at room temperature are a = 11.396 (3) Å, b = 13.088 (3) Å, and c = 19.482 (3) Å.

Structure of Anthranilic Acid II. Diffraction data were collected on a brown, diamond-shaped crystal of dimensions 0.35 × 0.35 × 0.05 mm grown from aniline solution. Data collected at room temperature as described above to a maximum $2\theta = 50°$ revealed the orthorhombic space group $Pbca$, a = 15.992 (4) Å, b = 11.624 (5) Å, c = 7.160 (1) Å, V = 1331.0 (7) Å^3, and $Z = 8$. Refinement was based on 469 observed reflections of $I > 3\sigma$.

The positions of all of the nonhydrogen atoms were determined by direct methods (MULTAN 74). Full-matrix, least-squares refinement of atomic coordinates and anisotropic temperature factors of these atoms followed by a difference Fourier map revealed the hydrogen atoms' positions. Further refinements converged to a final R = 0.040.

Structure of Anthranilic Acid III. Data were collected on a brown, irregular shaped specimen (approximately 0.30 × 0.20 × 0.05 mm) cleaved from a larger mass solidified rapidly from the melt phase under a dry-nitrogen atmosphere. Diffractions measured at room temperature as described above to a maximum $2\theta = 53°$ indicated the monoclinic space group $P2_1/a$ (standard setting $P2_1/c$), a = 12.226 (6) Å, b = 15.336 (5) Å, c = 7.560 (3) Å, β = 152.56 (5)°, V = 653.2 (5) Å^3, and $Z = 4$. Refinement based on 447 observed reflections of $I > 3\sigma$ was carried out as described above for phase II to a final R = 0.040.

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Supplementary Material Available: Atomic fractional coordinates, temperature factors, bond lengths, and bond angles of hexaphenylcarbodiphosphorane (Tables I–III) and anthranilic acid (Tables IV–VII) (7 pages). Ordering information is given on any current masthead page.

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