(12)

AD A093805

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 14971.6-C
2. GOVT ACCESSION NO.: AD-A093805
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): Triboluminescence
5. TYPE OF REPORT & PERIOD COVERED: Final Report, 10 Aug 77 — 30 Sep 80
6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s):
William C. Kaska
Jeffrey I. Zink

8. CONTRACT OR GRANT NUMBER(s): DAAG29-77-G-0195

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
University of California
Los Angeles, CA 90024

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

11. CONTROLLING OFFICE NAME AND ADDRESS:
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE: Dec 80
13. NUMBER OF PAGES: 25

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report):

Approved for public release; distribution unlimited.

DTIC ELECTE JAN 13 1981 S E

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

NA

18. SUPPLEMENTARY NOTES:

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number):

triboluminescence	fracture	chemical properties
light (visible radiation)	pressure	synthesis
excitation	impact tests	phosphoranes
luminescence	spectroscopy	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

Triboluminescence is the emission of light caused by the application of mechanical energy to solids. Although the phenomenon has been known since the seventeenth century, neither the excited state origins of the luminescence nor the mechanism by which it is excited were understood until our recent investigations. Our efforts have focussed on the fundamental requirements for triboluminescence. As a result of our research, we have uncovered and studied the fracture

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DDC FILE COPY

81 1 12 033

PII Redacted

20. ABSTRACT CONTINUED

requirement, the pressure requirement, and the structure requirement for triboluminescence activity. These three areas are discussed individually. ~~In~~ addition, we have derived a quantitative theory for the dynamics of triboluminescence. The theo~~ry is~~ based on the dynamics of the creation and interaction of mobile fractures in a crystal. In addition to explaining the time dependence of the luminescence, the theory ~~also~~ treats the effects of size and impact velocity on the luminescence intensity. The instrument which was designed to measure these effects also enabled us to quantitively compare the relative intensities of various crystals. We have continued to study triboluminescence spectroscopy, particularly in conjunction with the above studies. High pressure spectroscopy has also played an important role in investigating the pressure requirements for triboluminescence. The spectroscopic aspects are mentioned briefly in the appropriate discussions. Finally, the synthesis and chemistry of triboluminescent materials, which have continued to be a cornerstone in the above investigations, ~~have~~ led to the discovery of the polymorphic hexaphenylcarbodiphosphorane crystals and to other interesting materials which are described.

Final Report

"Triboluminescence"

Professor William C. Kaska, UCSB

Professor Jeffrey I. Zink, UCLA

ARO Grant DAA629-77-G-0195

I. Resume of Work Completed Under ARO Grant DAA629-77-G-0195

Triboluminescence is the emission of light caused by the application of mechanical energy to solids.[1,2] Although the phenomenon has been known since the seventeenth century, neither the excited state origins of the luminescence nor the mechanism by which it is excited were understood until our recent investigations.[1,3-8] During the first grant period, the spectroscopy of triboluminescence was explored in detail in our laboratories.[1] Five general origins of the luminescence were defined,[1] the most common being emission from the molecules comprising the crystal and emission from adsorbed nitrogen.

Our efforts during the past grant period have focussed on the fundamental requirements for triboluminescence. As a result of our research, we have uncovered and studied the fracture requirement,[7] the pressure requirement,[8] and the structure requirement for triboluminescence activity.[4,5] These three areas are discussed individually below. In addition, we have derived a quantitative theory for the dynamics of triboluminescence.[7] The theory is based on the dynamics of the creation and interaction of mobile fractures in a crystal. In addition to explaining the time dependence of the luminescence, the theory also treats the effects of size and impact velocity on the luminescence intensity. The instrument which was designed to measure these effects also enabled us to quantitively compare the relative intensities of various crystals.[7] We have continued to study triboluminescence spectroscopy, particularly in conjunction with the above studies. High pressure spectroscopy has also played an important role in investigating the pressure requirements for triboluminescence.[8] The spectroscopic aspects are mentioned briefly in the appropriate discussions. Finally, the synthesis and chemistry of triboluminescent materials, which have continued to be a cornerstone in the above investigations, have led to the discovery of the polymorphic hexaphenylcarbodiphosphorane crystals[4] and to other interesting materials which are described below.

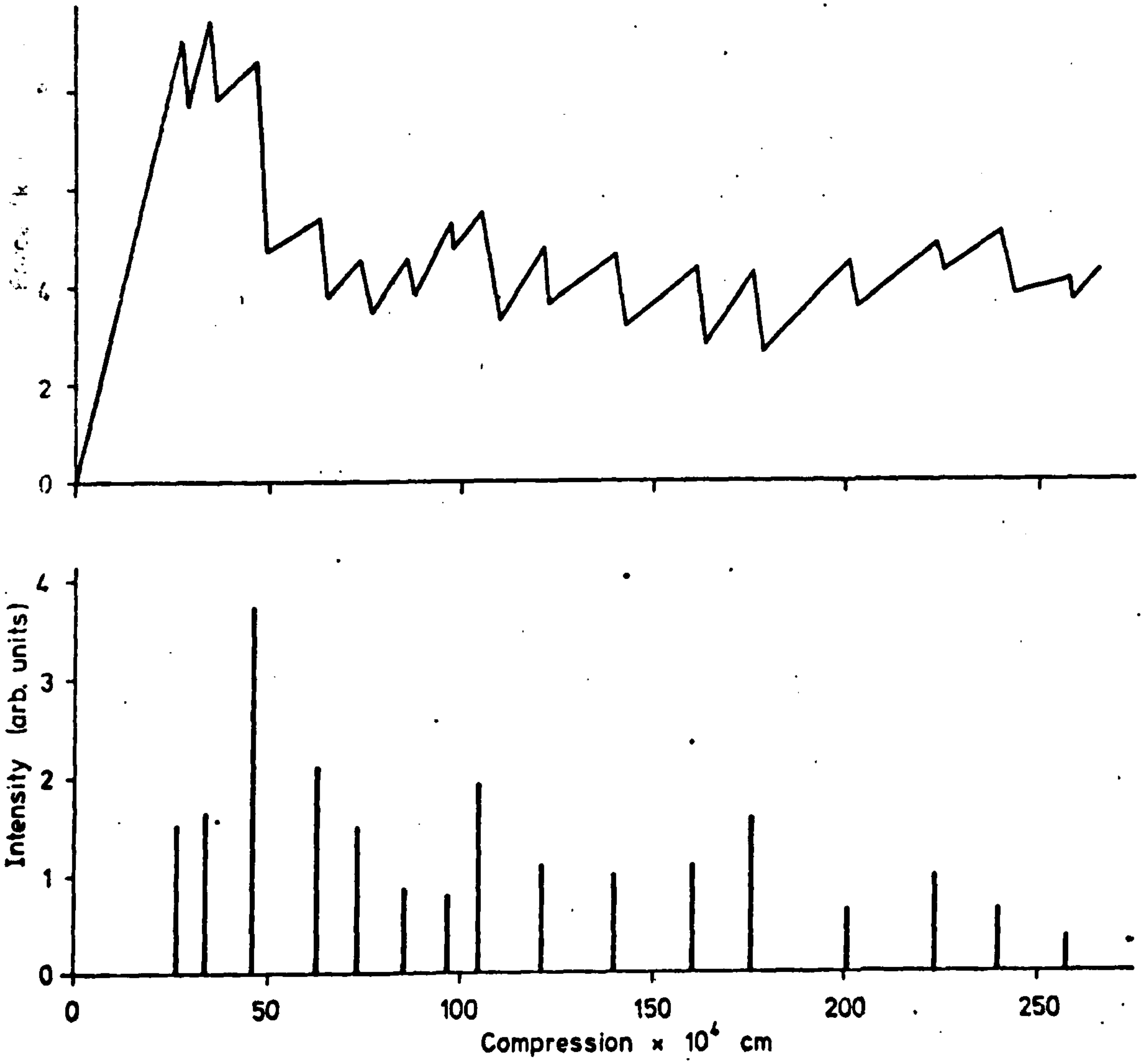
A. Fundamentals

1. Triboluminescence and Crystal Fracture.

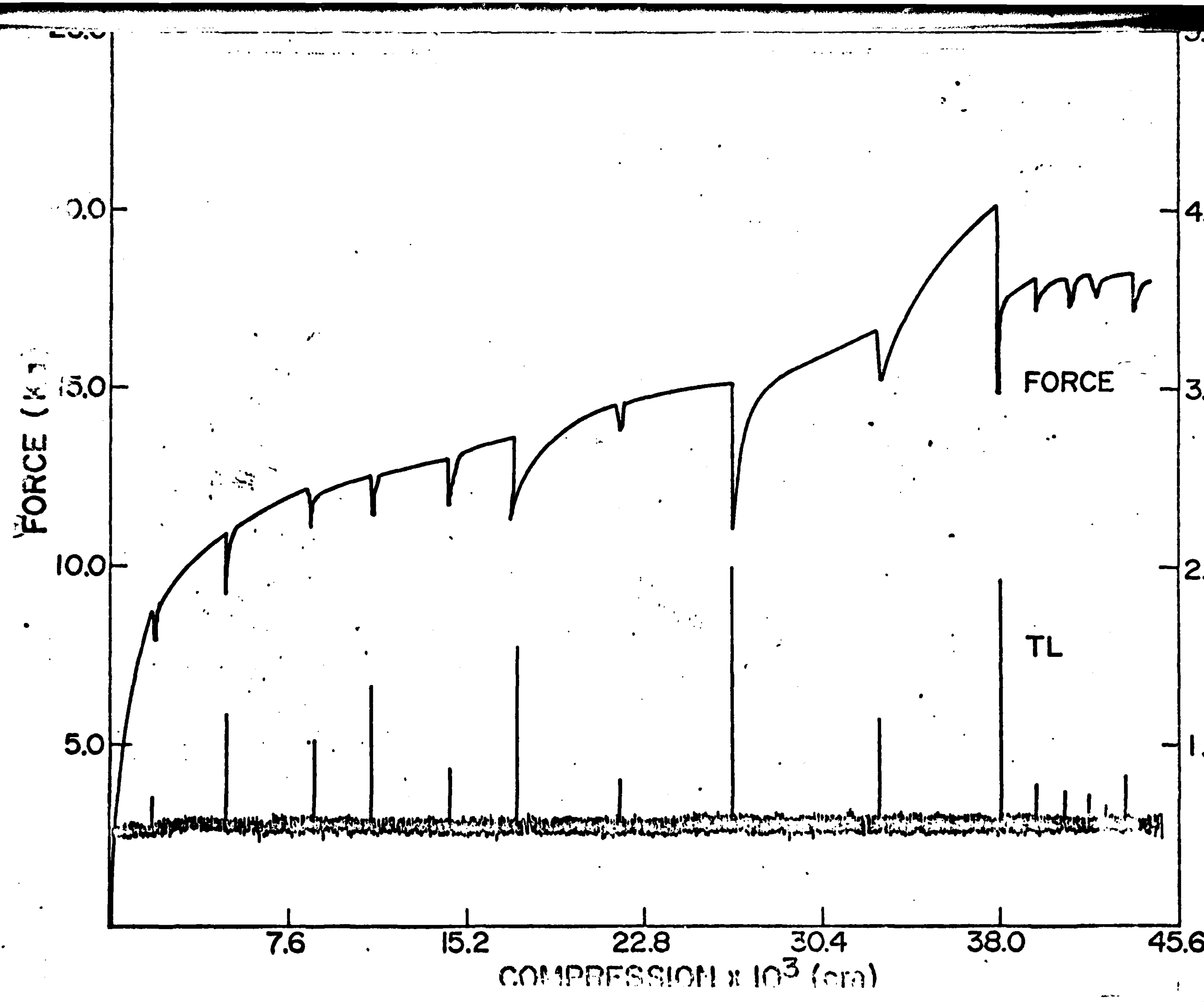
We have discovered that fracture is required for TL in organic molecular crystals[7]. For example, the force versus compression curve and the triboluminescence versus compression curve of a single crystal of tartaric acid is shown in Fig. 1. The triboluminescence appears only during the steps which occur in the force versus compression curve. These steps are caused by the movement of cracks in the crystal and the sudden creation of new surfaces. The surface energy of the crystals increases. The appearance of triboluminescence only when the steps occur shows that the TL in these crystals requires the motion of cracks. This requirement holds for all of the crystals which we have studied to date. The list of substances includes those which exhibit nitrogen emission (sucrose, tartaric acid, citric acid, etc.) and those which exhibit molecular emission from the molecules comprising the crystal (acenaphthene, coumarin, phenanthrene, etc.) A representative example, of the latter that of coumarin, is shown in Fig. 2.

The simultaneous measurements of the triboluminescence versus compression curves and the force versus compression curves of single crystals were carried out using a table model Instron testing machine fitted with a compression cage. The compression of the crystal was measured using a linear variable differential transducer (LVDT) (Model No. 025 MHR, Schaevitz Engineering Company) whose calibration constant was 2530 mV/mm. The load in the crystal was measured by 907.2-kg capacity Lebow load cell (Model No. 3354-2K) in conjunction with a Viatron signal conditioner (Model No. 603). The calibration constant of the load cell was 6.125 mV/kg. The outputs of the load cell and the LVDT were automatically recorded on a Hewlett-Packard Model No. 7004-A x-y recorder. The triboluminescence produced during deformation of the crystal was monitored by an IP 28 photomultiplier tube placed near the crystal. The amplified outputs of the photomultiplier tube and the LVDT were recorded on a second

(3)



0
2
4
8
Intensity (arb. units)
0
1
2
3
4
0
50
100
150
200
250
Compression × 10⁴ cm


FORCE (K
5.0
10.0
15.0
0.0
1.0
2.0
3.0
4.0
FORCE
TL
7.6
15.2
22.8
30.4
38.0
45.6
COMPRESSION x 10^3 (cm)

x-y recorder. The compression of the crystal at any force was determined by subtracting the known machine compression at that force. The triboluminescence versus compression curve of the crystal was determined at the compression rate of 1.69×10^{-3} mm/sec. The time duration of the triboluminescence pulse produced during the motion of a single crack was determined using an IP 28 photomultiplier tube with a response time of 100 nsec connected to the oscilloscope.

2. Pressure At Which TL Occurs.

The pressure at the emitting triboluminescent crystal sites when the TL occurs is unknown for every crystal studied to date. Generally, internal pressures on the order of several kilobars may be attained before fracture of the crystal relieves the strain. Local pressures at the tips of moving cracks may be significantly higher.

Crystals of $((CH_3)_3NH)_3Mn_2Cl_7$, which contain chains of face sharing $MnCl_6^{4-}$ octahedra and discrete $MnCl_4^{2-}$ ions in the crystal lattice,[9] triboluminesce brightly in the red region of the visible spectrum. A similar salt, $(CH_3)_4NMnCl_3$,[10] which also contains chains of face sharing octahedra and which is also photoluminescent, is not TL active. In the course of preliminary spectroscopic investigations of the former compound, we found that two different luminescences simultaneously occur, the most intense in the red and the other in the green region of the spectrum. The pressure dependence of the intensities and wavelengths of these luminescences offered a new method of relating the pressure values under which the luminescent centers emit in the TL experiment and in the hydrostatic high pressure photoluminescence experiment. We thus studied the triboluminescence, single crystal polarized luminescence and absorbance, and high pressure spectra of linear chain manganese complexes.

Two observables from the high pressure luminescence spectroscopic study can be used to determine the pressure at triboluminescent sites: the shift of the wavelength of the emission maximum with pressure, and the changes in the relative intensities of the emissions from the two different manganese complexes. The former observable is relatively insensitive to pressure in the present compound while the latter provides the first sensitive quantitive method of determining the pressure.

The shift of the emission maximum is 60 cm^{-1} ± 20 cm^{-1}/kilobar for the six coordinate site and 10 cm^{-1} ± 10 cm^{-1} /kilobar for the four coordinate site. The experimental uncertainty in measuring the TL maximum is on the order of 250 cm^{-1}. Using these values and the experimental-TL data, the pressure at the six coordinate site during its triboluminescence is between zero and six kilobars and that at the four coordinate site is between zero and fifteen kilobars. Although the expected values lie within these calculated ranges, the uncertainties are too large to make them useful.

The change in the relative intensities of the two emission maxima as a function of pressure provides a more sensitive method of calculating the pressure during triboluminescence. The ratio of the intensity of the six coordinate emission to that of the four coordinate emission increases by a factor of one order of magnitude when the pressure is increased from atmospheric pressure to 2 kbar ± 1 kbar. The intensity ratio observed in the triboluminescence spectrum is within experimental error of the intensity ratio observed in the pressure experiment at atmospheric pressure. Thus, the pressure at the emitting sites during triboluminescence is less than 2 ± 1 kbar.

Because the pressure at which TL occurs is an important quantity in the development of the theory of triboluminescence, further studies on different types of crystals are needed in order to determine the generality of the result obtained from the manganese compound. Such studies are proposed in section IID of this proposal.

3. Structural Requirements for Triboluminescence

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 phase. The existence of both triboluminescent and non-triboluminescent 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 $[(PH_3P_2C]$ have been isolated.[4] The crystal and molecular structure of the form which is triboluminescent, phase II (monoclinic C2, a - 15.362, b = 9.483, c - 20.054 Å, β - 95.1), was known.[11] Its TL spectrum is also known.[12] However the existence of a non-triboluminescent polymorph (phase I) was unknown prior to the preliminary communication of its structure.[4]

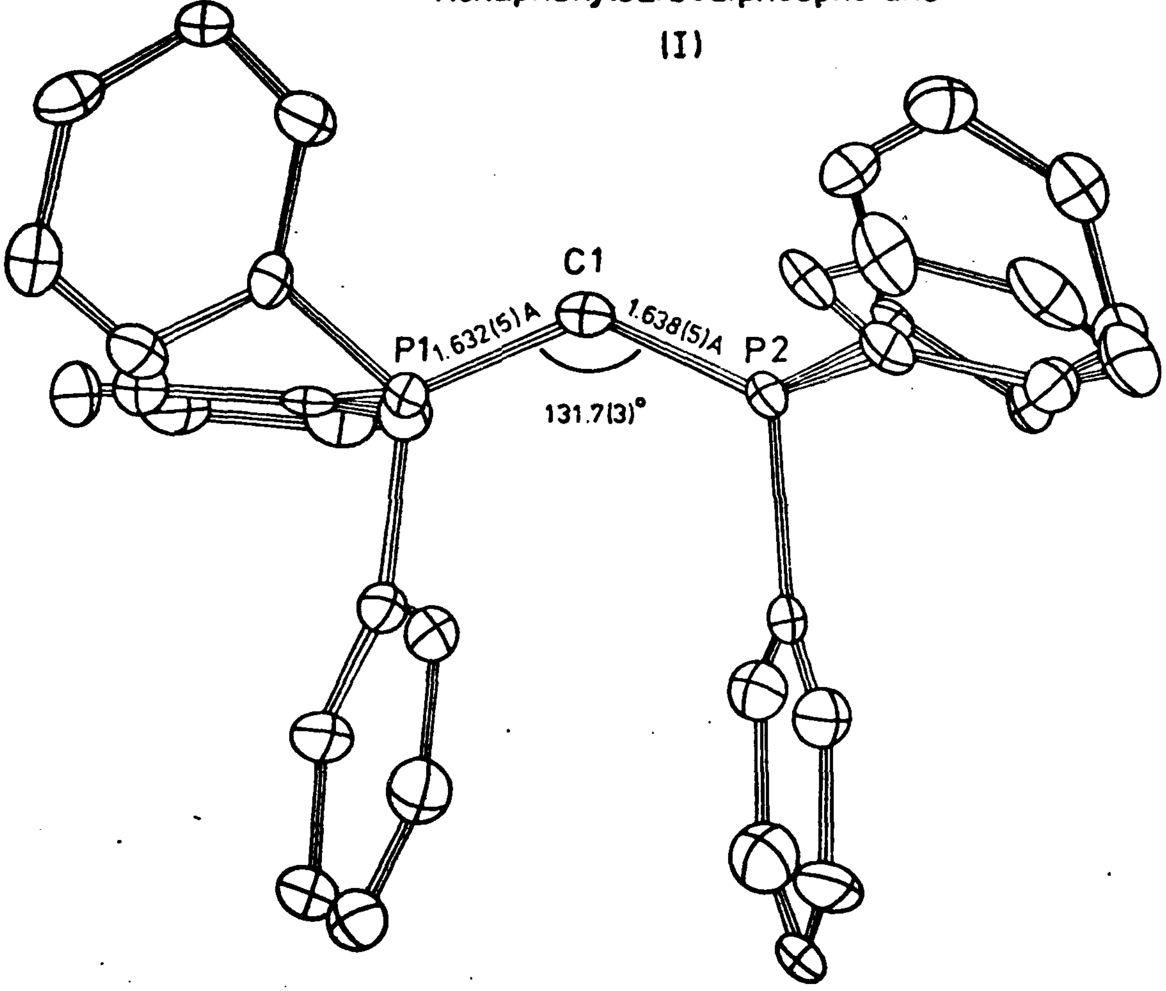
Three crystalline phases of anthranilic acid are known.[13] The complete structure of phase I, orthorhombic $P2_1cn$ (standard setting $Pna2_1$) a = 12.868, b = 10.772, c = 9.325 Å, and the space group of phase II (orthorhombic Pbca) have been reported.[14] Phase III is known only to be monoclinic. Only phase I is TL active. The phase transition I → II has been observed by differential thermal analysis at 81°.[15] The reverse of this phase transition as well as transitions involving form III have not been unambiguously observed.

In order to investigate possible structural relationships, the crystal structure and spectroscopic properties of the phases were determined. We will discuss 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.

The molecular structure of PPC I determined at -160° is shown in figure 3. 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. 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° in phase II. The closest intramolecular

Hexaphenylcarbodiphosphorane

(I)



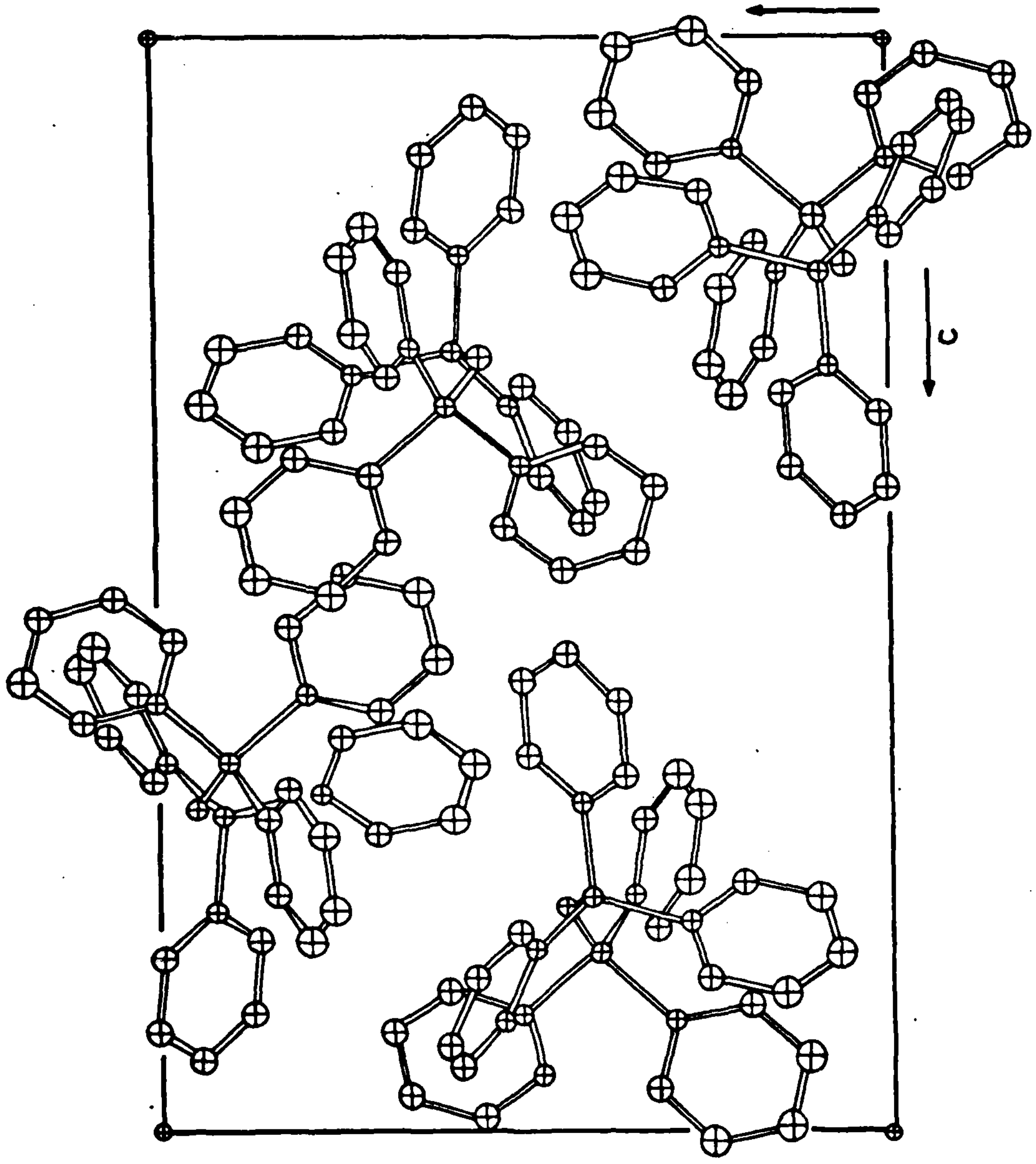
phenyl-phenyl interaction is 3.819 Å between phenyl rings on opposite phosphorous atoms of PPC I.

The non-polarity of the PPC I unit cell caused by the presence of three perpendicular two-fold screw axes is apparent in the unit cell projection along the a axis (figure 4). 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[1] of PPC I and II indicate that phase I is about 1 kcal/mole lower in energy.

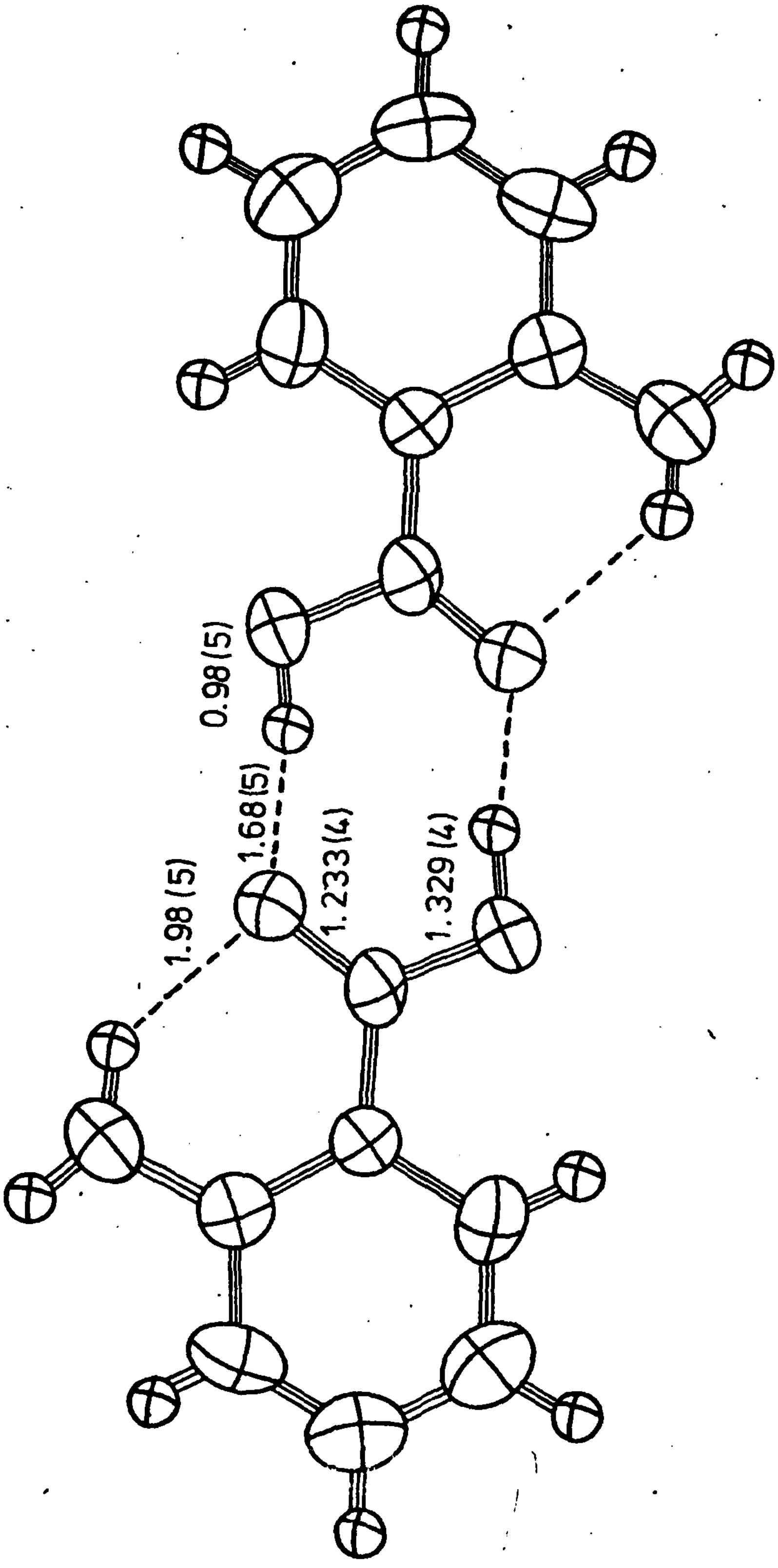
The molecular structures of anthranilic acid II and III are identical within the experimental error. In these structures the acid groups form hydrogen bonded dimers (figure 5) around the unit cell center of symmetry. Both molecules are coplanar with only 1.680 Å separating the hydroxy hydrogen and the 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.

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 not TL active. Second, there is no major difference in phenyl-phenyl interactions between the polymorphs.

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 C2 and $P2_1cn$, while the non-triboluminescent crystals have non-polar $P2_12_12_1$, Pbca, and $P2_1/a$ space groups. The polar space groups are piezoelectric under compression, torsion, and hydrostatic strain. Pbca and $P2_1/a$ are



3


0.98(5)
1.68(5)
1.98(5)
1.233(4)
1.329(4)

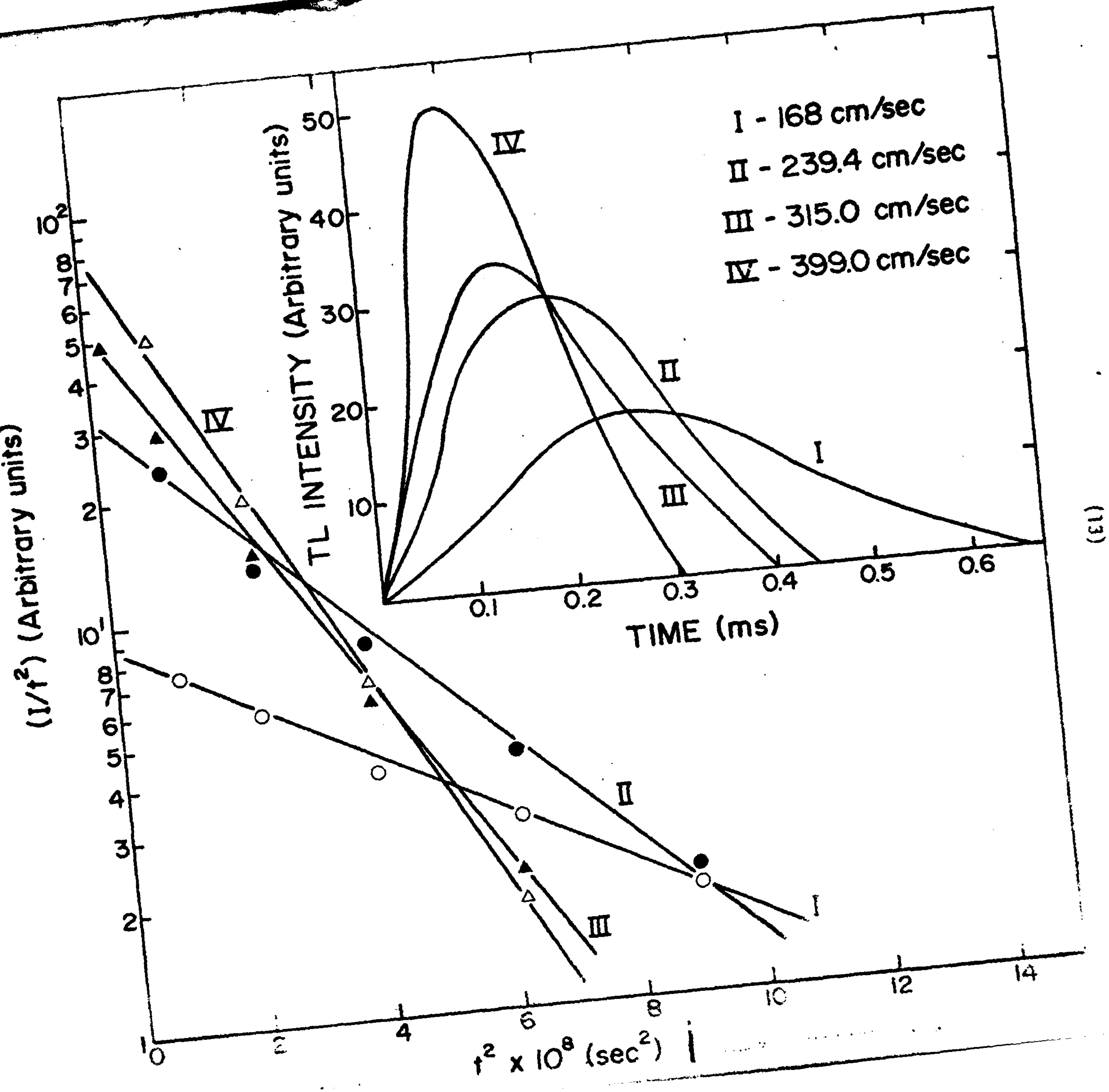
centrosymmetric and therefore non-piezoelectric, and $P2_12_12_1$ is piezoelectric only under torsional strains. If torsional strains are a minor component of crystal fracture, then the non-triboluminescent phases would also show little or no piezoelectric charging during fracture.

B. Dynamic Theory

Fracture is required for triboluminescence in molecular crystals as discussed above. The time duration of the triboluminescence pulse due to the motion of a single crack is in the microsecond range, which is of the order of the time needed for a crack to move through a crystal of the size used in the measurement. However, the time duration of a continuous triboluminescence pulse produced during the fracture of a crystal is of the order of milliseconds and depends on the impact velocity. Thus, the continuous TL signal produced during the impact is a superposition of individual TL pulses produced during the motion of many cracks in the crystal. The theoretical treatment of the time dependence of TL is based on the dynamics of mobile cracks.

The variation of TL intensity (I) with time (t) in single crystals of tartaric acid of uniform size ($1.3 \times 1.3 \times 1.1$ mm^3) is shown in Fig. 6 (top) for different velocities of impact of a piston on the crystals. The crystals were fractured by an air-driven piston whose velocity was monitored by a velocity transducer. The TL intensity was monitored by an IP28 photomultiplier tube (response time 8 μsec) connected to a Tektronix 504 storage oscilloscope. The peak of the TL intensity versus time curve increases and shifts towards shorter time with increasing impact velocity. The time corresponding to the peak of the TL versus time curve for a given impact velocity shifts towards longer values with increasing crystal size.

Fig. 6 (bottom shows) that the plot of Log (I/t^2) versus t^2 is linear with a


I - 168 cm/sec
II - 239.4 cm/sec
III - 315.0 cm/sec
IV - 399.0 cm/sec
TL INTENSITY (Arbitrary units)
10
20
30
40
50
TIME (ms)
0.1
0.2
0.3
0.4
0.5
0.6
I
II
III
IV
(I/t^2) (Arbitrary units)
10^0
2
3
4
5
6
7
8
10^1
10^2
$t^2 \times 10^8$ (sec^2)
0
2
4
6
8
10
12
14

negative slope and a correlation factor between 0.95 and 1.0, which suggests the relation

$$I = I_0 t^2 \exp(-\lambda t^2) \qquad (1)$$

The physical meaning of the parameters I_0 and λ will be discussed below. The slope λ increases with the velocity v of impact and decreases with the thickness h of the crystal. The time dependence of triboluminescence produced during impact of a piston with the crystal will be described phenomenologically in terms of the number of mobile cracks.

Let dN be the number of cracks produced during the change of strain from ε to $\varepsilon + d\varepsilon$. Then dN may be written as

$$dN = Md\varepsilon, \qquad (2)$$

where M is the correlation factor between the number of cracks and the strain of the crystals.

When a crystal is compressed, its volume will change linearly with the strain and consequently the number of point defects in the crystal will increase with the strain.[16] Because the increase in the number of point defects will increase the probability of nucleation of cracks in a crystal, the correlation factor M will increase with the strain of the crystal. Thus dN may be given by

$$dN = M_0 \varepsilon d\varepsilon \qquad (3)$$

where M_0 is constant.

From the above equation, the total number of cracks may be given by

$$N_T = \tfrac{1}{2} M_0 (\varepsilon^2 - \varepsilon_f^2), \qquad (4)$$

where ε_f is the strain needed to fracture a crystal. Because the total number of cracks will be directly proportional to the volume V of the crystal, the above equation may be written as

$$N_T = bV(\varepsilon^2 - \varepsilon_f^2), \qquad (5)$$

where M_0 is 2bY.

Only a fraction f of the total number of cracks will remain mobile. The number N_m of mobile cracks will be fN_T. As N_T increases, the fraction f will decrease due to the interaction between the cracks. Assuming a first-order rate process for the decrease of f with N_T per unit volume, f may be written as

$$f=\exp - \frac{\lambda N_T}{V} \quad , \tag{6}$$

where λ is a constant related to the interaction between the cracks.

The above discussion suggests the following equation for the strain dependence of the number of mobile cracks:

$$N_m = bV(\varepsilon^2 - \varepsilon_f^2)\exp[-\beta(\varepsilon^2 - \varepsilon_f^2)], \tag{7}$$

where β is equal to λb.

If the triboluminescence emission is excited by the motion of cracks, the number of triboluminescence centers excited in the strain range from ε to ε + dε will be proportional to the probability $N_m(\varepsilon)d\varepsilon$ of the creation of mobile cracks in the strain range. Thus, the number of excited triboluminescence centers during the change of the strain from ε to ε + dε may be written as

$$dn=\eta N_m d\varepsilon$$

or

$$\frac{dn}{d\varepsilon} = \eta bV(\varepsilon^2 - \varepsilon_f^2)\exp[-\beta(\varepsilon^2 - \varepsilon_f^2)], \tag{8}$$

where η is the normalization constant which takes into account the triboluminescence activity of the crystal.

If the strain ε is measured after the fracture of the crystal, that is, after the appearance of triboluminescence, the term $\varepsilon^2 - \varepsilon_f^2$ can be replaced by ε^2 and the above expression may be written as

$$\frac{dn}{d\varepsilon} = \eta bV\varepsilon^2\exp(-\beta\varepsilon^2). \tag{9}$$

The compression rate of the crystal is $dk/dt = k_0\alpha\varepsilon^{-\alpha}$ where k is the compression. If the initial velocity of impact of the piston is v, then $k_0\alpha$ should be equal to v and

$$k= \frac{v}{\alpha}(1 - e^{-\alpha t}). \qquad (10)$$

If the crystals of small dimensions are chosen the compression of the impact instrument becomes important and the real compression of the crystal may be expressed as

$$k= \frac{uv}{\alpha} (1 - e^{-\alpha t}), \qquad (11)$$

where u is a factor which takes account of the compression of the impact instrument. Thus, from Eqs. (9) and (11), the triboluminescence intensity, that is, the rate of excitation of triboluminescence centers may be given by

$$I= \frac{dn}{dt}$$

$$= \frac{\eta bVu^3v^3}{\alpha^2h^3}e^{-\alpha t}(1 - e^{-\alpha t})^2\exp\left(- \frac{\beta u^2v^2}{\alpha^2h^2}(1 - e^{-\alpha t})^2\right), \qquad (12)$$

where h is the thickness of the crystal and $\varepsilon = k/h$.

For high values of the impact velocity, the time duration of triboluminescence is small and thus αt is much smaller than 1. Therefore, Eq. (13) may be written as

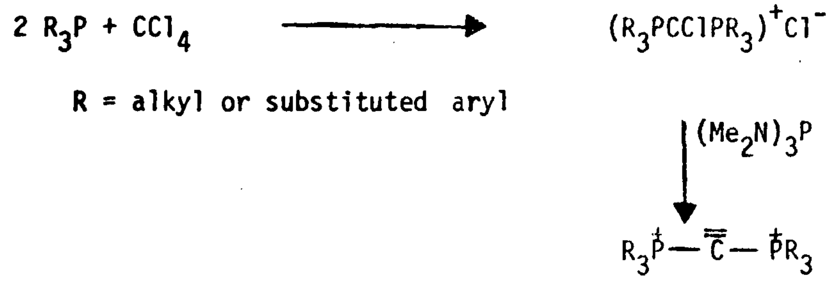
$$I = \frac{\eta bVu^3v^3t^2}{h^3} \exp\left(- \frac{\beta u^2v^2t^2}{h^2} \right). \qquad (13)$$

The similarity between the observed time dependence of triboluminescence empirically expressed by Eq. (1) and the derived expression given by Eq. (13) is consistent with the interpretation of the time dependence of triboluminescence in terms of the number and motion of mobile cracks.

C. Synthesis and Chemistry of Triboluminescent Materials.

Our preparative efforts during the past grant period have been several fold: (1) To synthesize triboluminescent molecules for wavelength tuning and (2) to explore the possibility of making triboluminescent molecules which contain metal atoms. The basic reason for the latter is that metal atoms often have excited states which can be populated by triboluminescent effects. Energy transfer can often be controlled by judicious choice of a metal atom and hence tuning of the triboluminescence can occur.

The synthesis of carbodiphosphoranes as an important triboluminescent material led to the discovery of two different crystalline forms of the molecule.[4] A particularly versatile synthetic approach now allows the preparation of almost any aryl substituted carbodiphosphorane

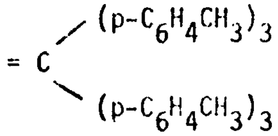


$$2\ R_3P + CCl_4 \longrightarrow (R_3PCClPR_3)^+Cl^-$$

R = alkyl or substituted aryl

$$\xrightarrow{(Me_2N)_3P} R_3\overset{+}{P}-\overset{=}{\bar{C}}-\overset{+}{P}R_3$$

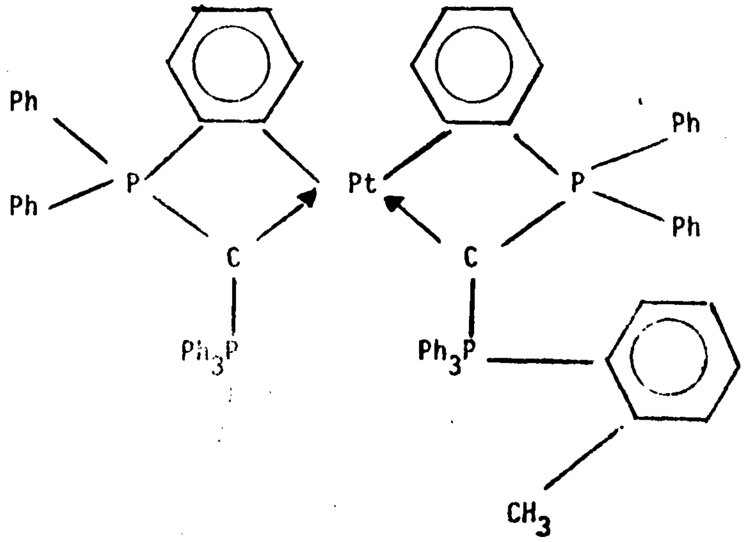
The following substituted carbodisphosphorane has been synthesized and suitable crystals for a structural study are anticipated,



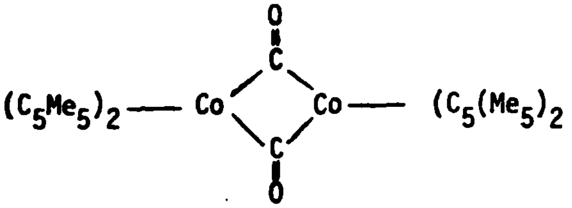
$$=C\begin{matrix}\nearrow (p\text{-}C_6H_4CH_3)_3 \\ \searrow (p\text{-}C_6H_4CH_3)_3\end{matrix}$$

The interaction of metal compounds with carbodiphosphoranes, particularly $Me_3Pt^+\ PF_6^-$ led to the discovery of an interesting series of o-metalation processes,[17]

$Me_3Pt^+PF_6^- + 3\ C(PPh_3)_2 \longrightarrow CH_4\ +$

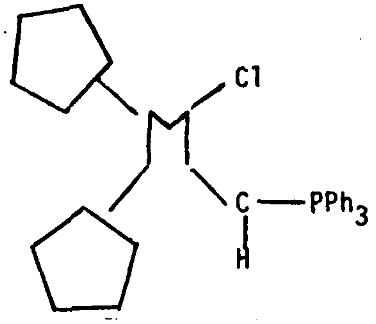


Attempts to synthesize new cobalt carbonyl compounds led to the synthesis of



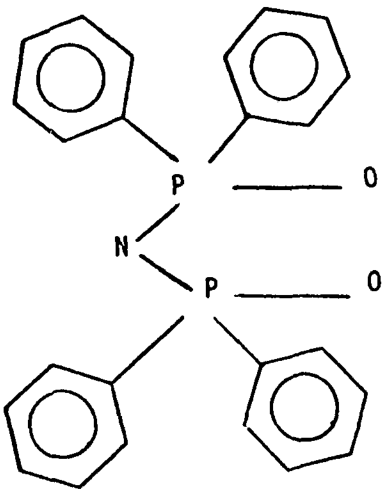
which showed a metal-metal bond to be present in the x-ray molecular structure.[18]

Other studies with $(C_5H_5)_2$ MCl_2,M= Hf, Zr and $\overset{-}{C}H_2 - \overset{+}{P}Ph_3$ led to the discovery of the new carbophosphorane,



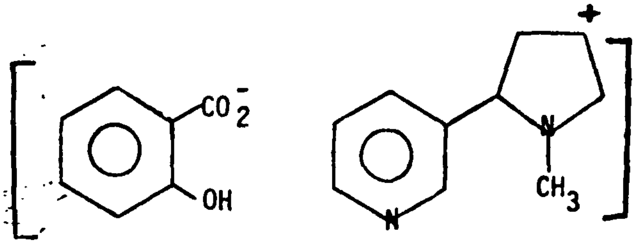
which has been described by its x-ray molecular structure.[19]

In the europium series of triboluminescent materials we synthesized the ligand,



and formed the Eu^{3+} complex. The material is a white solid in contrast to the light organe bezoylacetylacetone complex of Eu^{3+} which is brightly triboluminescent.

The brightly triboluminescent salt of nicotine has been prepared for high pressure and other spectroscopic studies,



Finally, the newly reported indene dimer as a triboluminescent compound has been prepared in good yield according to the literature. However, triboluminescence of the pure material has not been observed as reported by the original authors.

References

1. J.I. Zink, Accounts Chem. Res., 11, 289 (1978).
2. E.N. Harvey, "A History of Luminescence", The American Philosophical Society, Philadelphia, Pa, 1957, Chapter 10.
3. G.E. Hardy, J.C. Baldwin, J.I. Zink, W.C. Kaska, P.H. Liu, and L. Dubois, J. Am. Chem. Soc., 99, 3552 (1977).
4. G.E. Hardy, J.I. Zink, W.C. Kaska, and J.C. Baldwin, J. Am. Chem. Soc., 100, 8001 (1978).
5. R. Angelos, J.I. Zink, and G.E. Hardy, J. Chem. Ed., 56, 413 (1979).
6. G.E. Hardy, B.P. Chandra, J.I. Zink, A.W. Adamson, R.C. Fukuda, and R.T. Walters, J. Am. Chem. Soc., 101, 4554 (1979).
7. B.P. Chandra and J.I. Zink, Phys. Rev. B, in press.
8. J.I. Zink and G. Gliemann, J. Am. Chem. Soc., 102, 0000 (1980).
9. R.E. Caputo, S. Roberts, R.D. Willett, and B.C. Gerstein, Inorg. Chem., 15, 820 (1976).
10. B. Morosin and E.J. Graeber, Acta Cryst., 23, 766 (1967).
11. P.J. Carroll and D.D. Titus, J. Chem. Soc., Dalton Trans., 824 (1977).
12. J.I. Zink and W.C. Kaska, J. Am. Chem. Soc., 95, 7510 (1973).
13. W.C. McCrone, J. Whitney, and I. Corvin, Anal. Chem., 21, 1016 (1949).
14. C.J. Brown, Proc. Roy. Soc. A., 302, 185 (1968).
15. P.R. Arnold and F. Jones, Molec. Cryst. Liq. Cryst., 19, 133 (1972).
16. F. Seifz, Rev. Mod. Phys., 18, 384 (1946).
17. W.C. Kaska and J.C. Baldwin, Inorg. Chem., 18, 873 (1979).
18. J. Organometal. Chem., 165, 373 (1979).
19. J.C. Baldwin, N.L. Keder, C.E. Strouse and W.C. Kaska, submitted for publication.

II. Biographical Notes on Co-Principal Investigator

PII Redacted

JEFFREY I. ZINK, Associate Professor [redacted]. B.S., 1966, University of Wisconsin, Ph.D., 1970, University of Illinois, Assistant Professor, UCLA, 1970-1976, Associate Professor, 1976 to date. Member, American Chemical Society, Phi Kappa Phi, Phi Lambda Upsilon. Awards and Honors: NDEA Title IV Fellowship, 1966-1969; Proctor and Gamble Research Fellowship, 1969-1970; UCLA Faculty Summer Fellowship, 1972; Camille and Henry Dreyfus Teacher-Scholar Award, 1974-1979, Alexander von Humboldt Fellowship, 1979.

Publications and Manuscripts Submitted for Publication, ARO Grant DAAG29-77-G-0195

(1) "Triboluminescence and Pressure Dependence of the Photoluminescence of Tetrahedral Manganese(II) Complexes", G.E. Hardy and Jeffrey I. Zink, Inorg. Chem., 15, 3061 (1976).

(2) "Triboluminescence Spectroscopy of Aromatic Compounds", Gordon E. Hardy, James C. Baldwin, Jeffrey I. Zink, William C. Kaska, Po-Hsin Liu, and Lawrence Dubois, J. Amer. Chem. Soc., 99, 3552 (1977).

(3) "Triboluminescence", Jeffrey I. Zink, Accounts of Chemical Research, 11, 289 (1978).

(4) "Structure and Triboluminescence of Polymorphs of $(Ph_3P)_2C$", Gordon E. Hardy, Jeffrey I. Zink, W.C. Kaska, and J.C. Baldwin, J. Amer. Chem. Soc., 100, 8001 (1978).

(5) "Triboluminescence Spectroscopy of Common Candies", Rebecca Angelos, Jeffrey I. Zink and Gordon E. Hardy, J. Chem. Ed., 56, 413 (1979).

(6) "Pulsed Infrared Laser Induced Luminescence", G.E. Hardy, B.P. Chandra, Jeffrey I. Zink, Arthur W. Adamson, Robert C. Fukuda, and R.T. Walters, J. Amer. Chem. Soc., 101, 2787 (1979).

(7) "Triboluminescence and the Dynamics of Crystal Fracture", B.P. Chandra and Jeffrey I. Zink, Phys. Rev., in press.

(8) "Triboluminescence and Single Crystal Polarized Absorption and Luminescence of Linear Chain Manganese(II) Compounds", Jeffrey I. Zink and G. Gliemann, Inorg. Chem., in press.

(9) "Mechanical Characteristics and Mechanism of Triboluminescence of Fluorescent Molecular Crystals", B.P. Chandra and Jeffrey I. Zink, J. Chem. Phys. accepted for publication.

Lectures Given Related to Current Grant

Triboluminescence, Picatinney Arsenal, New Jersey, 1977

Triboluminescnece, Xerox Corporation, Rochester, New York, 1977

Triboluminescence, Universität Würzburg, 1979

Informal Conference on Photochemistry and Photophysics, sponsored by ONR, Feb. 18, 1977.

Pacific Conference on Chemistry and Spectroscopy, Oct. 12-14, Anaheim, CA, Session Chairman, 1977

National ACS Meeting, Chicago, Aug. 1977

Southern California Photochemistry Conference, Capra Ranch, June 24-26, 1977.

Southern California Photochemistry Conference, Rancho Oso, June, 1978.

Informal Conference on Photochemistry and Photophysics, Massachusetts Institute of Technology, Sept. 8, 1978.

Biographical Notes on Co-Principal Investigator

PII Redacted

WILLIAM C. KASKA, Professor [redacted]. [redacted] [redacted]. B.S., 1957, Loyola University of Los Angeles, California; Ph.D. 1963, University of Michigan, Ann Arbor, Michigan; Postdoctoral Research Associate, 1964, The Pennsylvania State University; Assistant Professor, University of California, Santa Barbara, 1965-1971; Associate Professor, 1971-1979; Member, The Chemical Society, American Chemical Society.

Publications Under the Current Grant DAAG29-77-G-0195

(1) "The Interaction of Hexaphenylcarbodiphosphorane with Iridium Olefin Cations," W. C. Kaska and R. F. Reichelderfer, J. Organometallic Chem., **78**, C47(1974).

(2) "Improved Isolation Procedure for the Preparation of Iodo(trimethyl)-platinum(IV)," W. C. Kaska and J. C. Baldwin, Inorg. Chem., **14**, 2020 (1975).

(3) "Triboluminescence of Hexaphenylcarbodiphosphorane, Emission from a Molecular Excited State Populated by Mechanical Stress," J. I. Zink and W. C. Kaska, J. Am. Chem. Soc., **95**, 7510(1973).

(4) "The Interaction of Methylenetriphenylphosphorane with Tris(methylvinyl ketone)tungsten," W. C. Kaska, R. F. Reichelderfer and L. Prizant, J. Organometallic Chem., **129** 97(1977).

(5) "Triboluminescence Spectroscopy of Aromatic Compounds," G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P. H. Liu and L. Dubois, J. Am. Chem. Soc., **100** 8001(1978).

(6) "The Interaction of Hexaphenylcarbodiphosphorance with Trimethyl-platinum(IV) Cation," W. C. Kaska and J. C. Baldwin, Inorg. Chem., **18** 873(1979).

(7) "Molecular Structure of Bis(pentamethylcyclopentadienyl)dicarbonylcobalt, W. I. Bailey, Jr., D. M. Collins, F. A. Cotton, J. C. Baldwin and W. C. Kaska, *J. Organometallic Chem.*, **165** 373(1979).

(8) "The Interaction of Zeise's Dimer with Polar Olefins, P. P. Ponti, J. C. Baldwin and W. C. Kaska, *Inorg. Chem.*, **18** 873(1979).

(9) "The Synthesis and X-ray Molecular Structure of Bis($^5\eta$-cyclopentadienylzirconium) and Hafnium methylides," J. C. Baldwin, N. L. Keder, C. E. Strouse and W. C. Kaska, submitted.

(10) "The Interaction of Methylenetriphenylphosphorane with Trimethylplatinum IV Cation," J. C. Baldwin and W. C. Kaska, submitted.

(11) "The Interaction of Rhenium Pentacarbonyl Bromide with Methyllenetriphenylphosphorane," J. C. Baldwin and W. C. Kaska, In Preparation.

(12) "Spectroscopic Properties of Methylplatinum Complexes," J. S. Harrington, J. C. Baldwin and W. C. Kaska, In Preparation.

(13) "The Synthesis of Hexakis (p-tolyl) carbodiphosphorane," W. C. Kaska To be submitted for publication.

(14) "The Coordination Chemistry of Ylides," H. Schmidbaur, M.S. Hussain, and W. C. Kaska, In Preparation.

Lectures Given Related to Present Grant

(1) Sixth International Conference on Organometallic Chemistry, Amherst, Massachusetts, 1973, Organometallic Ylides.

(2) Seventh International Conference on Organometallic Chemistry, Venice, Italy, 1975, Organometallic Ylides.

(3) First Chemical Congress of North American Continent, Mexico City, 1975, Organometallic Ylides.

(4) National ACS Meeting, Miami, Florida, September, 1979.

Personnel

1. UCLA

Gordon E. Hardy	(earned Ph.D., 1979)
Badri P. Chandra	(postdoctoral)
Rebecca Angelos	(earned M.S., 1979)
William Beese	(B.S., 1980)
Lawrence DuBois	(research assistant)

2. UCSB

James C. Baldwin	(earned Ph.D., 1979)
R. F. Reichelderfer	(earned Ph.D., 1975)
L. Prizant	(earned Ph.D., 1976)
P. P. Ponti	(postdoctoral)