

EFFICIENT TRIBOLUMINESCENCE IN N-ISOPROPYLCARBAZOLE

R. NOWAK, A. KRAJEWSKA and M. SAMOĆ

Institute of Organic and Physical Chemistry, Technical University of Wrocław, 50-370 Wrocław, Poland

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An efficient triboluminescence in N-isopropylcarbazole was found, placing the compound among the most intensively triboluminescent solids. Room-temperature triboluminescence and photoluminescence spectra were measured and found to be essentially identical. The triboluminescence in polar molecular crystals is suggested to be related rather to the pyroelectricity than to piezoelectricity.

Understanding of the phenomenon of triboluminescence (TL) has recently been advanced by a series of papers [1-5], providing results of measurements of TL spectra of several new compounds and suggesting possible mechanisms of TL. It is generally agreed that, at least in molecular solids, a crystal fracture leading to a creation of fresh surfaces is a precondition for TL to be observed. In non-centrosymmetric crystals the propagation of cracks is believed to give rise to so-called piezoelectrification of new surfaces and electrical breakdowns. Excited states of atmospheric nitrogen and/or the solid, produced by the electrical discharges, give rise to TL. Depending on properties of the solid, the TL spectrum may consist of either nitrogen emission or the luminescence of the sample or both.

This note reports on a very efficient TL found in N-isopropylcarbazole (NIPC). Crystals of NIPC grown in this laboratory for other purposes were accidentally found to exhibit surprisingly strong emission of blue light when gently crushed, cleaved or rapidly cooled by immersing in liquid N₂. This emission could be easily seen even by daylight. The discovery of a new strongly triboluminescent solid stimulated our efforts to measure its TL spectrum and compare its TL efficiency with those of other molecular crystals.

Fig. 1 shows a comparison of photoluminescence and TL spectra of NIPC. Both spectra were obtained using the same arrangement consisting of a prism monochromator and an FEU-79 photomultiplier, and were not corrected for the spectral sensitivity of the

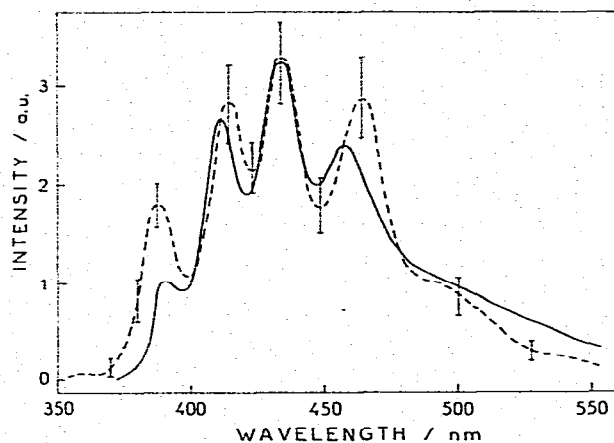


Fig. 1. Comparison between the photoluminescence (solid line) and triboluminescence (dashed line) spectra of NIPC.

system. TL was excited by abrading a sample (surface area $\approx 30 \text{ mm}^2$) by a rotating abrasive disc mounted on a spring-loaded support. The spread of TL intensities obtained in this manner amounted to $\approx 20\%$. There are only minor differences between tribo- and photoluminescence spectra of NIPC, probably due to e.g. different degree of re-absorption in both experiments.

The total intensity of TL in NIPC was found to be substantially higher than those of other known triboluminescent solids (cf. table 1). Strangely, we were not able to detect TL in phenanthrene, reported elsewhere to be strongly triboluminescent (see e.g. ref. [4]). This

Table 1
Comparison of TL intensity of NIPC with other molecular crystals

Crystal	Space group	Total TL intensity (arbitrary units)	
		this work	Chandra and Zink [4]
N-isopropylcarbazol	Ic2a [7]	5.4	—
acenaphthene	Pca2 ₁ [7]	1.0	1.0
resorcinol	Pna2 ₁ [7]	3.2×10^{-1}	5.8×10^{-1}
<i>m</i> -aminophenol	P2 ₁ am [7]	1.0×10^{-1}	3.7×10^{-1}
<i>m</i> -nitroaniline	Pbc2 ₁ [6]	5.6×10^{-2}	—
<i>m</i> -dinitrobenzene	Pbn2 ₁ [7]	1.7×10^{-2}	—
phenanthrene	P2 ₁ [7]	$<1 \times 10^{-3}$	3.7×10^{-1}

may be due to differences in sample purities (all compounds used in this study were carefully purified using various techniques including multiple sublimation and zone refining), or in the methods of excitation.

The question arises as to the possible origin of the triboluminescence in NIPC and other molecular crystals. In most papers hitherto published, TL has been assumed to be due to piezoelectricity of the crystals investigated, although no correlation between the intensity of TL and the values of piezoelectric moduli has been reported. In our opinion, an alternative mechanism should be taken into account in many cases. A majority of strongly triboluminescent crystals belong to the pyroelectric classes of symmetry. Fracture of such crystals should result in formation of fresh surfaces which exhibit large uncompensated charges related to the spontaneous polarization. It can be easily calculated that the resulting electric field should be of the order of 10^7 – 10^8 V m⁻¹, i.e. of at least the same order of magnitude as that due to the piezoelectrification, and sufficiently large to produce an electric breakdown. If the pyroelectricity is the main source of the

electrification, the efficiency of the process should be correlated with the value of spontaneous polarization, and not — as in the case of the pyroelectric luminescence recently reported by Patel and Hanson [8] — with the pyroelectric coefficient (i.e. the temperature derivative of the polarization).

Processes occurring during the breakdown (impact ionization of molecules of the solid under investigation and the ambient gas by accelerated ions and/or electrons, reabsorption of the nitrogen emission, etc.) are less clear and one cannot predict which of them will control the formation of excited states. The efficiency of TL will also depend on the quantum yield of the luminescence of the compound.

It seems that in the case of NIPC, the high efficiency of TL is due to a coincidence of an efficient charging of fresh surfaces (NIPC is both piezo- and pyro-electric as will be reported elsewhere) and a relatively high quantum efficiency of fluorescence which has been estimated by Klöpffer [9] to be $\approx 40\%$ of that of anthracene.

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