

PRNC-107 PUERTO RICO NUCLEAR CENTER Study of Radiation Damage in Organic Crystals Progress Summary Report No. 4 Amador Cobas and Zvi Weisz October 1967 OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT(40-II1833 FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break--- STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS Amador Cobas and Zvi Weisz - Principal Investigators Progress Summary Report I, Work performed at Puerto Rico Nuclear Center Rio Piedras, P. R., under U. S. Atomic Energy Commission Contract AT(H0-1)-1633 (Project 14) October 1987 ---Page Break--- TABLE OF CONTENTS Introduction I. Background Section II. Experimental Section III. Results and Analysis Section IV. Discussion Figures 1 through 9 Bibliography ---Page Break--- DESCRIPTION This project is concerned with the effects of radiation on organic crystals. It is felt that such studies on well-defined crystalline structures can provide a firm foundation for later study of more complex materials including those of direct biological interest. We have chosen anthracene as the initial material for study because this substance has been studied more than any other organic material. The effect of irradiation on anthracene has been studied previously by Komanteur using photocontactivity methods and by others using optical methods. Since these studies were made, experimental and theoretical developments such as charge injecting electrodes to organic crystals, space-charge-limited currents, and non-linear optics, enabled a much better understanding of molecular crystals. We felt that it would be valuable to reopen and expand the previous studies of irradiation effects by including these recently developed techniques. The study we made on the effects of neutron, gamma, and x-ray irradiation on anthracene using space-charge-limited current methods was described previously. In this progress report, the effects of gamma irradiation in anthracene studied by non-linear optical methods are described. Below is a summary of

the results obtained by space-charge limited currents method. ---Page Break--- By irradiating anthracene crystals with gamma or x-rays hole traps are introduced in the crystal. The presence of these traps can be detected by space-charge limited current method using a solution of foline solution in a Kallmann - Pope cell as a hole injecting electrode. From the changes in the steady state space-charge limited current - voltage characteristic curve for crystals before and after irradiation the following results were obtained. 1) The radiation introduces a permanent damage in the crystal in the form of hole traps. 2) The density of these traps varies linearly with the absorbed radiation dose. 3) These traps lie at energy levels distributed uniformly, the largest activation energy being 0.9 eV. 4) For every hole trap formed, about 5 keV energy is absorbed, the lifetime of the carriers was obtained by measuring the transient space-charge limited current. Combining this measurement with the results of the steady state measurements the capture cross-section of these traps for holes was estimated to be of molecular size. ---Page Break--- SECTION T.

BACKGROUND The dynamic properties of optical excitons in molecular crystals have been of particular interest in recent years. Kepler's observation of delayed fluorescence whose intensity depended on the square of the intensity of the exciting light, first showed the existence of an intrinsic bimolecular interaction between long-lived mobile excitation in anthracene crystal. The work of Hirota and Hutchison unambiguously related the delayed fluorescence, the phosphorescence decay, and the decay of spin resonance signal to the triplet state of phenanthrene in a host biphenyl crystal. On the theoretical side, Jortner et al. have investigated problems associated with triplet excitons in anthracene crystal and have concluded that the motion is describable in terms of a diffusion model dominated by excitation hopping between molecular sites. These experimental and

theoretical results are typical of the efforts directed toward an understanding of the properties of excitons. The fluorescence arising from the bimolecular triplet annihilation has been used as the

observable for obtaining information about properties of molecular crystals which are not intrinsically dependent upon the properties of excitons. Avakian and coworkers have utilized the sensitivity inherent in the detection of steady state fluorescence to obtain the weak singlet to triplet (f+) absorption spectrum in a matter of molecular crystals. Weise et al. have used the long life of triplet excitons in crystalline anthracene to observe the decay of delayed fluorescence from which the efficiency of the radiationless transition from singlet to triplet (i+ %) could be deduced. We report here a third type of application of triplet-triplet annihilation which yields information concerning radiation damage in molecular crystals. The sensitivity of detection of the fluorescence, the crucial dependence of triplet lifetime upon weak perturbations, and the mobility of triplet excitons in mechanically good crystals are properties which have been combined in the present investigation to observe the effects of gamma-ray damage. 2e0N TT, Bosna, Anthracene crystals suitable for scintillation work were obtained from the Harsha Chemical Company. Each crystal was about 1 cm cube; the density of striations was such that crystal transparency just allowed book print to be read through 1 cm of crystal. A masked crystal holder was constructed so that a given crystal could be reproducibly mounted and remounted between successive irradiation doses. One surface of the crystal was illuminated by a collimated light beam from a 900 W Xe DC arc lamp. Before impinging on the crystal, the light beam was passed through a 1 cm thickness of 2 parts saturated CuSO4 to 7 parts H2O (v/v) and as a heat filter, followed by one each of Corning's sharp cut off filters C8 3-67 and C8 3-68. The light in the 600-20 nm (85+

1) Absorption band was efficiently transmitted while the extinction foot at 530 nm was such that transmitted blue and UV light was insufficient to directly excite fluorescing singlets. The blue fluorescence was observed at right angles to the exciting red light after being filtered by a 4.5 cm thickness of saturated CuS, plus one CS 5-58 filter. This combination of filters has a peak transmission at 110 nm while the fluorescence has peaks at 430 nm and 450 nm. The fluorescence signal, Fr, due to steady state red excitation was measured before and after gamma-ray dosage from a Co source. The source intensity was 600 R/min. The measured absorption coefficient of anthracene for the concentration was 0.128 cm<sup>2</sup>/g, so that the calculated energy absorption was 293 erg/cm<sup>3</sup>. There appeared to be no change in Fr measured immediately following irradiation of a crystal or if measured after the crystal had remained at laboratory temperature for several days following irradiation. In addition to the steady illumination experiments, flash experiments were performed in which the temporal response of the blue emission was continuously monitored both during and subsequent to excitation by a high intensity red flash. The arrangements for these portions of the experiment were similar to those given by Weis et al. The filtering for the present experiments consisted of one C8 3-67 and one C6 3-68 between the flash lamp and the crystal. The blue emission was observed with a 1P21 photomultiplier at right angles to the direction of the exciting flash and filtered with the same combination as used in the steady state experiments. The width of the flash intensity at half maximum was 2.2 μs. The peak intensity in the 6000-8000 Å band was about 10<sup>3</sup> ergs/cm<sup>2</sup>. SECTION TITLE, RESULTS AND ANALYSIS. Figure 1 shows the dependence of the blue emission under steady red light excitation as a function of gamma-ray dose. Figure 2 shows a similar graph for the relative fluorescent yield, (Φ<sub>y</sub>) obtained under near...

uv, excitation, Although there was wide fluctuation in \$r roy St was clear that a monotonic decrease of fluorescence efficiency occurs at a dose rate of about 107 R, the result is in general agreement with those of Sharno, who previously had found a linear decrease of fluorescence efficiency for powdered anthracene in the dose range of 105 to 207 R. We adopt the following kinetic scheme to account for the observations: % + Pirea + (singlet triplet absorption); a7(t) % + 2hvrea \*S, (simultaneous double quantum absorption) ty \*tover states st D+H-G+& n®) } sya tye Ty + T+lover

states (self quenching) were 178 + boise ks on xegr8) He = Rett Hay t+ lover states not triplet vy) ---Page Break--- -7- Abe tle) + kggS = OP @ as- é32 (t) + a/err® - ks (2) Eo Pu Ake 85 Ate an unknown generic and sensitivity (3) factor for a given crystal and type of experiment. Under the stationary conditions of steady red {illumination aE a8. 0, for these cases we denote F by the symbol Fs The 900 WD.C. are ie capable of delivering several tenths of a watt per square centimeter of red light which is sufficient to allow measurement of the blue extension but weak enough that kgyS <a = const. andy 12<67, and 4x(t)? < a/ent®, 20 that r, Ate (a PP, " 2 F Assumptions regarding the effect of radiation damage on the crystal parameters are now introduced. If the dose introduces triplet quenching centers without affecting (a), the absorption coefficient © for G%\* Ty, (b) the fluorescence efficiency fp, and (c) the binuclear triplet exciton interaction constant, v5 then the damage effect may be assumed to be of the form ese + a. (5) Graphs of ¥, "V2 vs, D should be of the form FLT? = const. (6° + a) 6) Figure 3 shows a graph of the observed steady state data in excellent agreement with equation (6), ---Page Break--- -8- Assumptions a, b, and c have received direct experimental verification, the observed emission, F,, depends on the rate of absorption of light, not on the quantity of light absorbed; therefore dependence of @ on D will be of

consequence if damage produced impurities are sufficiently strong absorbers of the red light to result in decreased crystal transmission. No optical density in the region was observed in a 0.5 cm thick crystal up to doses of 10<sup>9</sup> R. Therefore, in the dose range of present concern, assumption (a) is valid. The data concerning relative fluorescence yield shown in Figure 2 clearly indicate that no significant change occurs in fp below a dosage of 10<sup>5</sup> R and therefore assumption (b) is valid. The data concerning relative fluorescence yield shown in Figure 2 clearly indicate that no significant change occurs in fp below a dosage of 10<sup>5</sup> R and therefore assumption (b) is valid. It was expected that the bimolecular rate constant, Y, should not be dependent on damage because if one writes  $Y = (k + Pe) n_p \sigma v$ , which k and Fp are respectively the probabilities of forming 1 + 1 or 2 on collision of a pair of triplet excitons of cross section  $\sigma$  and with velocity v, then the probabilities should be dominated by spin and interaction factors determined by molecular parameters while the collision cross section is not expected to become dose dependent until the damage centers are of sufficiently high density to permit cooperative phenomena between centers. The triplet exciton velocity,  $v_{\text{triplet}}$ , should undergo real or apparent alteration due to radiation damage in either of two principal ways; (1) damage introduces shallow triplet traps and thereby imparts a trap modulation character to  $v_{\text{triplet}}$  or (2), damage introduces deep triplet traps but from which annihilation is coherently faster or slower. In order to verify these expectations and thereby confirm assumption (c), measurements of the blue fluorescence produced by a very high intensity, short duration, red flash were performed as a function of gamma-ray dosage. At the time of peak flash intensity I(t) is denoted I\_p. During a flash of microseconds duration, t, the triplets are not contributing a significant amount to the instantaneous singlet population; therefore, equation (2)

becomes s+ Spt m fand the fluorescence given by (3) is denoted by Fy Fat AMgst,2. ) It is to be emphasized that the fluorescence originating from this mechanism is uniformly emitted throughout the crystal volume. During the flash, a triplet population, 1°, 16 built up by direct S,+ 1, absorption and by cross over from the singlets generated by the double quantum process. A simple estimate shows that most of the triplets arise from direct absorption and are therefore approximately given by TOs att) = 10-%calx 102%em?sec~2 x 10°Ssec = 1014øme3(9) since + se oo mml the triplet-triplet mechanisms also cause the resultant fluorescence to be emitted uniformly from the crystal volume. During an interval of time following flash extinction, T1 © T < 6°, the bimolecular term of equation (1) dominates the triplet decay and the fluorescent signal given by (3) is denoted

---Page Break--- -- by  $F_y$  and becomes  $F_y \cdot \frac{1}{2} \frac{A B \rho y^4}{\dots}$  (ao)  $1 + y_e$  Since  $\approx 2 \times 10^6$  Mea eee" 9 enon 2% <<a up to about SOueee. Therefore, comparing (10) with (8) and utilizing (9) gives  $= \frac{1}{2}$  (a) Figure 1 shows the fluorescent behavior in an undamaged crystal from Sin 0 to 500mee and succinctly illustrates the two mechanisms which are operating. Note the almost abrupt change in decay character near 20usee. As previously stated, © does not depend on dosage of less than 108 R, the double quantum absorption coefficient § cannot conceivably depend on dose, therefore a graph of  $F_y/F_p$  should demonstrate the relation of ¥) on dose. Figure 5 shows oscillograms of the triplet generated fluorescence following flash excitation as a function of dose. The peak fluorescence due to double quantum absorption is off scale in these oscillograms but the ratio  $F_y/F_p$  for which  $F_y$  was picked at flash cutoff is shown in Figure 6. Clearly, there was no significant dependence of 1) on dose up to about 104 R and thus assumption (c) is verified for yy to this dosage. This kind of experiment could not be continued to higher dosage because at these dosage levels there had been introduced sufficient

density of triplet quenchers to cause 8 to become comparable to  $w^\circ$  for the flash intensities available. Thus, in this particular flash experiment, determination of the rate of triplet decay by the bimolecular term could not be observed at dosages greater than  $10^4$  R. ---Page Break--- Direct confirmation that equation (5) is the proper representation of dose effect on lifetime is easily obtained from the oscilloscope traces such as those of Figure 5. At longer times following flash extinction,  $t > 7$ , only the A term of equation (2) is of significance; thus  $T = T^\circ \exp(-kt)$  and equation (3) becomes a  $\frac{1}{2}hy$ . Here,  $F(y)$  is the signal for decaying fluorescence at long times. Figure 7 is a log-log plot of the change in triplet decay constant as a function of gamma ray dose, the approach of the slope toward unity is satisfying. Perhaps the slight superlinear behavior is due to the small contributions from second order processes. The data quantum absorption experiments also provide an independent verification of the effect of dosage on the fluorescence efficiency. In the direct excitation of singlets by u.v. light, the absorption depth was at most a few microns. It is conceivable that the damage may have been air-assisted, or that if the damage was of a physical kind (disoriented molecules, etc.), that surface annealing could easily occur. Since the fluorescence emitted due to double quantum absorption uniformly comes from the crystal volume, then the possible complexities are bypassed. The oscillogram of Figure 8 was typical of those obtained for the double quantum generated fluorescence of a highly dosed specimen. Figure 9 is a graph of the peak intensity of this fluorescent response as a function of dose and is of essentially the same nature as Figure 2 for the u.v. excitation. ---Page Break--- -12- the almost complete absence of fluorescence from the triplet-triplet mechanism even at 50 sec. SECTION IV. DISCUSSION Equations (3) and (6) may be written  $F = K(K_0 + P5q^\circ sq\%s's?)$  and  $FL = K(8 + Praca rer)$  (3) which...

and  $cqDiare$  the density of singlet and triplet quenchers introduced by a gamma-ray dose,  $D$ ;  $k^\circ$  and  $8^\circ$  are the singlet and triplet decay constants before dosage, and the other symbols have their usual significance. Defining by  $D \frac{1}{2}$  and  $D' \frac{1}{2}$  the dosages at which  $F$  and  $F_p$  are respectively reduced to  $\frac{1}{2}$ , then equations (Q3) can be combined to give  $P, 2 2. az 22s mes i om)$  From figures 1, 2, 3, and 9,  $D \frac{1}{2} = 5 \times 10^5$  R and  $Dt \frac{3}{2} - 3 \times 10^2$  R so that  $D \frac{1}{2} / p' \frac{1}{2} : 10^3$ . It appears reasonable to take  $Om = "m= 3 \times 10^5$  ea? so that Pog. 2 so. fs. sg 2 pe Ss S Seas xi0. TQ "Tr Te (5) there are two approaches which may now be taken. Experimental values for  $8^\circ$  and  $k^\circ$  vary slightly from crystal to crystal but show that  $\frac{8^\circ}{k^\circ} = 10^{-6}$  is a representative average. No direct measurements for either  $v_g$  or  $v_p$  are available; however, these may be estimated. From the data of Sliver et al. for the interaction of pairs of singlet excitons to yield current carriers,  $v_g$  may be estimated to be  $2 \times 10^3$  ---Page Break--- on see" ( $k = 5 \times 10^7?$  cad eee >; assume  $p = ant \geq 3 \times$

10" ext), the data of Kepler and coworkers indicates that the triplet exciton-exciton interaction to produce fluorescence (self-quenching was assumed to be negligible) has a rate constant of  $2 \times 10^{12} \text{ cm}^{-1}$  and therefore under similar assumptions  $v_p$  is estimated to be  $7 \times 10^3 \text{ cm}^{-1}$ . The near equality of these exciton velocities is difficult to understand and self-quenching and other competing processes surely cause  $P_{ry}$  to be less than unity; however, in one extreme of behavior we take  $v_g/v_p^2 = 1$  and therefore  $F_{y,S} = 2.5 \times 10^3$ . On this basis the net effect of a given gamma-ray dose is to introduce singlet quenchers with an overall quenching efficiency about  $10^3$  greater than that for the triplet quenchers introduced by the same dose. The second extreme approach is based on the reported diffusion lengths of the excitons. Triplet excitons have been shown to have a diffusion length,  $L$ , of about  $10^7$ . Avakian and Merritt<sup>18</sup> found  $L = 10 + 5v$  in the  $ab$  plane ( $8^\circ$  was not specified),

while Kepler and Sritendick obtained  $D = (0.4 - 2) \times 10^9$  and Levine reported  $D = (2.0 + 0.5) \times 10^9$  for the triplet exciton diffusion coefficients and from which lengths,  $l = (D/v)^{1/2}$ , of 150 $\mu$  and 20 $\mu$  respectively may be calculated for  $t = 10$  msec, the diffusion length for singlet excitons,  $L = 2Dt/v$  was approximately 600 Å as deduced by Simpson in polycrystalline samples of anthracene while Erenenko and Medvedev report 2000 excitons. The diffusion length may be given by  $L = v_p/v$  in which  $v$  is the instantaneous velocity and  $p$  the ratio of drift velocity to instantaneous velocity. If it is assumed that the value of  $p$ 's for singlet and triplet exciton motion is unity, i.e., if there is similar anisotropy for the motion of both, then in lean but unaligned crystals the ratio of the velocities should be equal. As per pattern, 108 see  $v_y, v_t$  or the ratio of diffusion lengths  $L_g = v_g/v_t = 1072$ . Introducing the last ratio which depends on the assumption of similar anisotropy of exciton motion into (15) results in  $P/P_{yy} = 0.25$ . On this basis, the net effect of a given gamma-ray dose is to introduce 4 singlet quenchers with an overall efficiency about the same as that of the triplet quenchers introduced by the same dose. The two approaches bracket the ratio of the net efficiencies between about 2 and  $10^3$ . The essential point is that singlets are equally or more efficiently quenched than triplets by a given gamma-ray dose even though the triplet quenching is observable at smaller dosages. If one now combines the 1 to  $10^3$  efficiency ratio with the ratio of volumes sampled by the excitons, then it is seen that the triplets sample a volume  $23 = 18$  times larger than do the singlets and thus it remains necessary to require a  $10^3$  to  $10^6$  greater density of singlets to be produced by a given dose of gamma radiation for the same degree of quenching. A detailed study of the density of each kind of quenching center is in

progress. Comparison between carrier trapping, triplet quenching, and damage produced by the signal appears feasible at dosages far below those amenable to conventional chemical approaches. The present experimental determination of the dependence of  $\gamma$  on dose was insensitive to the  $y$  term. However, the present findings are consistent with those of Kepler who has found that the emission produced by the triplet-triplet mechanism in undoped monocrystalline anthracene was not affected by trapping until temperatures below about 100°K. Thus, these independent results indicate that trap modulated velocity terms in  $y$  are of little consequence at room temperatures. From a practical viewpoint, it appears that an individual single crystal of anthracene may permit the determination of gamma or x-ray dose over a range from 10 to  $10^9$  R, the low end from 20 to  $10^4$  R can be measured through triplet quenching, the range of  $20^3$  to  $10^6$  R by space-charge-limited current technique, the  $10^6$  to  $10^7$  R range by singlet quenching, and the high dosage range of  $10^7$  R and over by direct optical coloration. The lower limit depends on  $8^\circ$ . If instead of a xenon flash or a dc xenon arc, one would use a switched laser, then a change in  $g$  could be measured from 10 R up to about  $5 \times 10^9$  R, and from about  $10^7$  to  $10^8$  R the quenching of double quantum generated singlets could be measured. A range of  $20^8$  -

10<sup>7</sup> R could be continuously covered with one crystal and one excitation source, ---Page Break---  
a TRIPLET GENERATED FLUORESCENCE FIG. 1 Steady Red Unit = 10<sup>3</sup> ap, horizontal: 1 unit >  
swentgens Dose ---Page Break--- Dose RELATIVE YIELD. FIG. 2 Free. Blue Fluorescence under  
steady 3130 & Excitation Vertical: relative yield Horizontal: 1 unit = 10 Roentgens. The present data  
shows reference 9 \$\$\$ 8. 10<sup>g</sup> Dose ---Page Break--- DOSE FIG. 3 Blue Fluorescence under  
Steady Red Excitation test scale Unit. Horizontal: 2 units ---Page Break--- + Figures Time et Fy The  
Fluorescent Response of an Undamaged Crystal to a

Hie Intensity fed Flash Upper: Rw 1K; time const. #1 w sec. Lower: Rye 1K; time const. &2 usec. s.  
Tae 16 Dependence of the Fluorescent Response con Dosage within tho Bimolecular Time Domain  
Upper: © Measurements; Hg © 100 ky time const, 5 psec. Middle: 4.8 x 10<sup>3</sup> Roentgens; Ry = 100  
K; time const. 5 psec. Lower: 1.9 x 10\* Roent gens; Ry = 100 Ky time const. 5 u sec. ---Page  
Break--- DOSE "th FIG. 6 F/Pp va. log Dose RUI8 of Fluorescence Generated by Triplet 'Triplet and  
Vertical Horizontal: ---Page Break--- o FIG. 7 log (4 ~49) va. log Dose Change of Triplet Decay due  
to Buildup Produced quenchers Vertical: i unit = 10 eo Horizontal: un + 30 Roentgens eee ---Page  
Break--- oa factor ie. 10 ysfem 50 Tfen FIG.8 Fw. Mae Tao Dependence of the Double Photon  
Generated Fluorescence on dosage Uppers 0 Roentgens; H+ 1 Ki time const. usec lower 2.5 x 10<sup>o</sup>  
Roentgens; K+ 4 Ki time const. 1 w sec. ---Page Break--- he type -Tay-- 0 DOSE LOG Foggy MB  
10g Dose pesk Effect of Radiation on Fluorescence Generated in Crystal Bulk aence Uniformly.  
Vertical: i unit = 10 arbitrary Horizontal: 1 unit = 10 Roentgens eee ---Page Break--- oe  
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