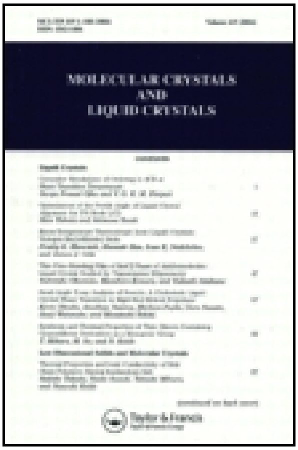

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On the Mechanism of Photodimerization of 9-Cyanoanthracene Monocrystal†

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Abstract—A study of photodimerization of 9-cyanoanthracene single crystals has been performed by following the growth of 4-sided photoetched pits as a function of time, light intensity, and temperature. Growth along the [001] diagonal direction of the pits on the (010) plane is linear in both time and light intensity with an activation energy of 0.75 eV. This suggests that one photon absorption occurs to form the cis-oriented excimer, followed by a rate controlling, thermally activated, re-orientation to the trans-oriented excimer on the perimeter of the etch pit, followed by rapid formation of the trans-photodimer.

1. Introduction

The clearest examples of topochemically controlled reactions involve the correspondence of the geometric structure of a photodimer to the crystal structure of the corresponding monomer.⁽¹⁾ Exceptions to this behavior have, however, been recently reported,⁽²⁾ and the photodimerization of 9-cyanoanthracene (CNA) represents a clear case of a lattice which would lead to a predicted cis-dimer formation, but a product which in fact is exclusively trans-dimer.⁽³⁾

Since 1960 reports have steadily shown that a 9-substituted anthracene that photodimerizes in solution⁽⁴⁻⁹⁾ or as a microcrystalline powder⁽¹⁰⁾ forms the head-to-tail or *trans* structure photodimer rather than the head-to-head or *cis* structure at room temperature. No case of a photodimer from a symmetric 9,10 disubstituted

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anthracene has been reported, though excimers may form.(11) Steric effects probably predominate; however, asymmetric 9,10 disubstituted anthracenes have been reported to form photodimers.(12) Mixed photodimers from symmetric 9,10-disubstituted anthracenes also have been prepared in solution where neither monomer alone forms a photodimer.(13)

The CNA crystal is orthorhombic with space group $P2_12_12_1$ with 4 molecules/unit cell. The molecules are stacked *cis* with anthracenic planes parallel and nearly side by side(14) (Fig. 1).

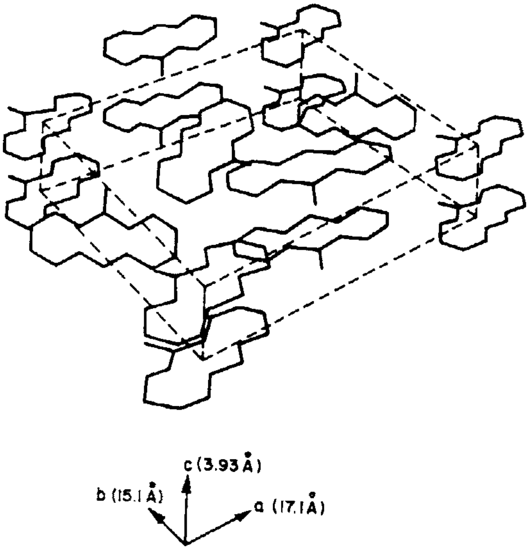

Figure 1. Unit cell of 9-cyanoanthracene.

Craig and Sarti-Fantoni(3) argued that the theory of topochemical preformation of dimer structures would only apply to regions of perfectly ordered crystallinity, and that CNA is a case where reaction occurs at defects, or surfaces, or in zones disordered by dimerization. Where topochemical control does in fact occur, excitation transfer to these sites must be slow, or molecules in a disturbed configuration have higher excitation energies, and thus the photochemistry occurs in regions of perfect crystalline order. Cohen *et al.*(15) have substantiated that photodimerization occurred preferentially at dislocations emerging at *bc* and *ac* faces of CNA monocrystals. According to these workers, the photodimer nuclei appeared in isolation and in pronounced alignments within the monomer host. Irradiated matched cleavage halves produced nearly identical patterns of photoetched pits demonstrating that photoreactions occurred preferentially at dislocations. They identified the following kinds of dislocations present for CNA: (010)[100], (010)[001], (100)[010] and (211) with a component of slip in [100] with (211) particularly favorable for dimerization since the molecules are stacked *trans* along the dislocation. They observed photoetched pits on the surface having amorphous as well as definite geometrical outlines.

Emission also occurs primarily at defects or edges suggesting that light absorbed by the crystal (first excited singlet peak at 442 nm(16)) is transferred as excitons to these defects. Prolonged irradiation produces the photodimer and as the original green emission decreases a blue emission appears. The green emission is due to excimer fluorescence while the blue emission is fluorescence attributed to monomers trapped in the photodimer matrix.(17)

The radiation used in previous work has been limited to the 365 nm line of mercury. Though the absorption coefficient is not exactly known for crystalline CNA,(18) the radiation probably reaches a depth of < 100 Å below the surface of the crystal. A crystal, however, can be converted almost completely to the photodimer on prolonged irradiation since the photoproduct is transparent at 365 nm (light with wavelength < 300 nm must be excluded since the reaction then becomes photoreversible). In view of the previous work, we have extended the study on CNA to include the growth of the photoetched pits with time, light intensity and temperature.

2. Experimental Procedure

Eastman CNA was purified by sublimation and zone refining (100 passes). Single crystals from the melt were grown in a Bridgman oven. Sublimation flakes and needles were obtained in a gradient heated Pyrex tube under 20 torr of argon.

A 900 watt Xenon Schoeffel light source filtered with 6 inches of copper sulfate water solution and an Optics Technology UV 370 filter was used. The light intensity was changed with Optics Technology neutral density filters and measured with an Eppley thermo-

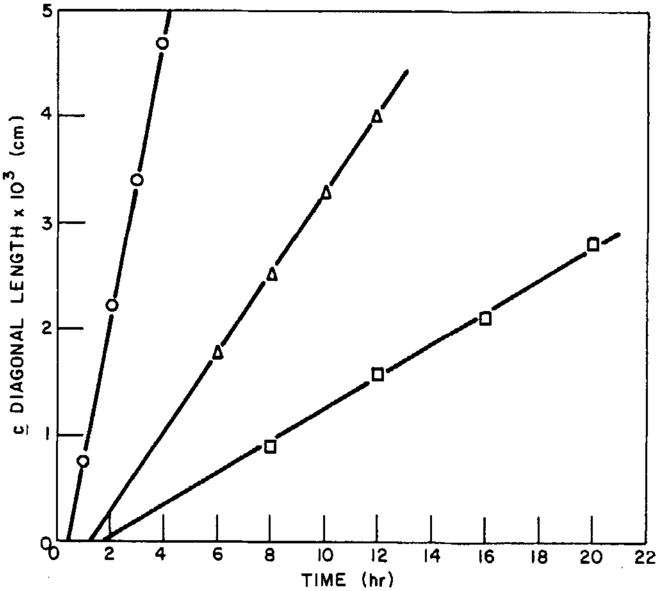

Figure 2. Growth of c diagonal length of photoetched pits with time. Open circles: Relative light intensity, I_R = 1.0; Triangles: I_R = 0.31; Squares: I_R = 0.10; T = 25°.

pile. The maximum intensity with a UV 370 filter was 0.8 mW/cm^2 ($\sim 3 \times 10^{15}$ photons/cm^2 sec). For rate and light intensity measurements, crystals were irradiated under a positive pressure of argon and removed intermittently to microphotograph the photoetched pits. For the temperature dependence of the growth rate of [001] diagonal length, the crystals were sealed in a 1 mm flat-walled quartz cell under an argon atmosphere. The cell was placed in a water-ethylene glycol bath regulated to ± 0.1°. With the crystal in the quartz cell, only 800 × magnification could be used compared to 1400 × used in the room temperature study. In all cases, freshly cleaved surfaces were used.

3. Results

Crystals of CNA cleave readily on both (100) and (010) planes. The crystals tend to shred easily into threads and can be bent or twisted about the [001] direction. Gradient sublimation produced *needles elongated in the [001] direction with (100), (010)* as prominent faces although (110) appeared on some crystals. Thin flakes were also obtained with (010) identified as the dominant face.(18)

After moderate irradiation on the (010) surface of CNA at all temperatures, the dominant type of photoetch pits were quadrilaterally shaped with one diagonal parallel to [001] and the second diagonal in the [101] direction. Two opposite sides were in the $[10\bar{5}]$ direction and the other two sides in the [107] direction. Continued irradiation produced general disruption across the surface, i.e., in the areas between the pits. Eventually, cracks or fissure appeared which were generally parallel to [100]. At higher temperatures (~40 °C) some photoetched pits, also 4-sided, but with diagonals in [001] and [100] directions were observed. The sides of the figure were parallel to [102] and $[10\bar{2}]$. Continued irradiation produced pits more amorphous and more circular in shape. Pits with diagonals [001] and [100] with sides parallel to [104] and $[10\bar{4}]$ were observed. Microscopic examination of the back surface of a crystal 2 mm thick irradiated for 4 hours (intensity 0.8 mW/cm^2, UV 370 filter) at 41.5° revealed pits with [001] diagonal length approximately 1/4 times as large as on the irradiated surface. This was ascribed simply to absorption of scattered light. Strong alignment of many photoetched pits along [001] and some evidence of polygonization with pits aligned along [100] were observed. Moderate irradiation on the (100) cleavage surface produced hexagonally shaped pits with sides parallel to [107], $[10\bar{7}]$ and [010]. Most pits could be identified only as having nearly circular outlines.

The length of the [001] diagonal of etch pits on the (010) surface of crystals at 25° was found to increase linearly with time. (Fig. 2) Measurements could not be made with accuracy until the [001] diagonal had a length greater than 0.75×10^{-3} cm. The growth rate of this diagonal varied linearly with light intensity (Fig. 3), and the linear growth with time is shown at several temperatures in Fig. 4. An Arrhenius plot of the rate variation with reciprocal temperature in Fig. 5 yields an activation energy at lower temperatures of 18 kcal/mole (0.75 eV).

At $T > 10°$, there appears to be a period of slow growth that could be associated with a nucleation step. Although this " nucleation

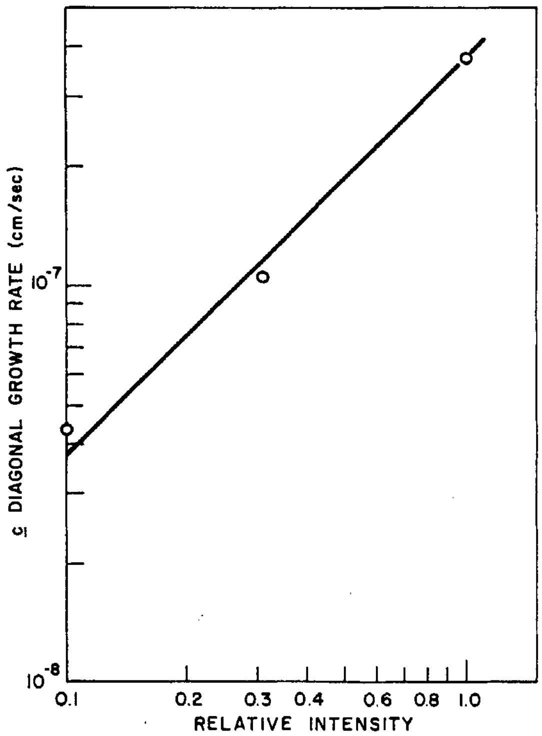

Figure 3. Log c diagonal growth rate of photoetched pit vs log relative light intensity. $T = 25°$.

time " appears to increase with decreasing light intensity, its temperature dependence is irregular, and any speculation regarding its significance is too tentative.

4. Discussion

The growth of the photoetched pits with time is similar to the behavior of many solid decompositions of the type,

$$A(\text{solid}) \rightarrow B\ (\text{solid}) + C\ (\text{gas}),$$

and also to phase transformations in metals(19) in certain time ranges and excluding new nucleus formation. To account for the linear growth of the photoetched pits with time and light intensity, the

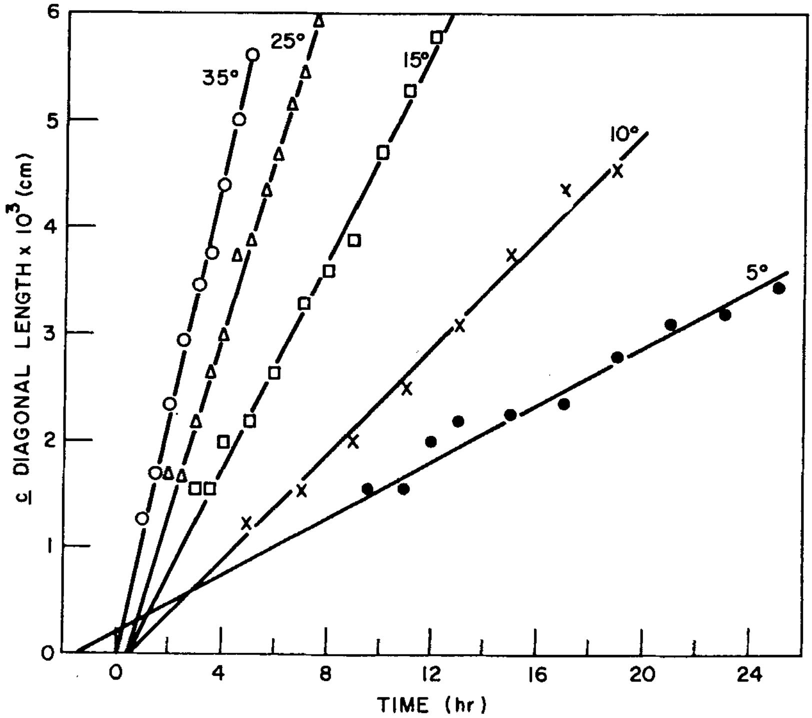

Figure 4. Growth of *c* diagonal length with time at various temperatures.

following mechanism is suggested:

$$\text{Step 1.} \quad n_c \underset{k_d}{\overset{\alpha I}{\rightleftharpoons}} n_c^*$$

$$\text{Step 2.} \quad n_c^* \xrightarrow{k_2} n_t^*$$

$$\text{Step 3.} \quad n_t^* \xrightarrow{k_3} D$$

where the following notation applies:

n_c, the number of cis-oriented monomer pairs on the perimeter of the photoetched pit;

n_c^*, singlet excited cis-oriented pair (excimer);

n_t^*, singlet excited trans-oriented pair (excimer);

D, the number of photochemical dimers formed;

αI, the absorbed light.

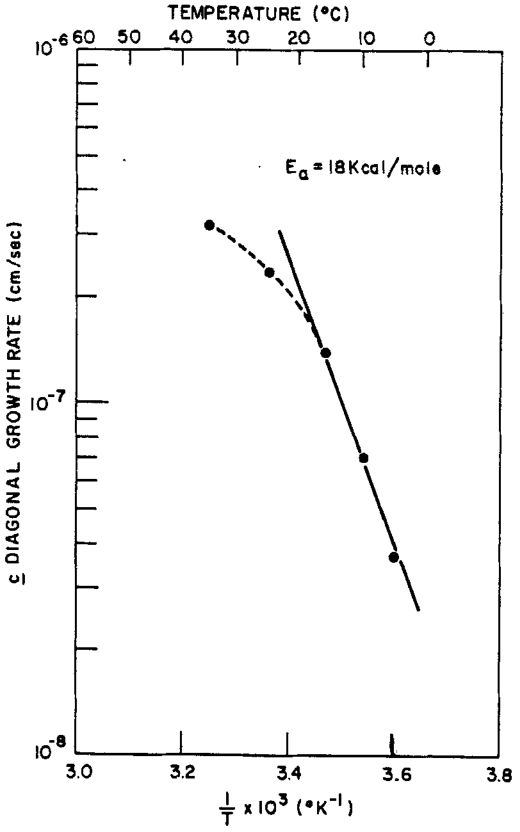

Figure 5. Log c diagonal growth rate vs reciprocal temperature.

The rate of formation of the photodimer D is:

$$\mathrm{d}D/\mathrm{d}t = k_3 n_t^*$$

With step 1 at equilibrium and using a steady state approximation for n_t^*:

$$\mathrm{d}D/\mathrm{d}t = k_2 \alpha I n_c / k_{-d} \qquad (1)$$

For a square-shaped pit, in the linear time region, $D = A n_c^2$, where A is a constant which includes the surface densities of D and n_c. Substitution of n_c and integration of Eq. (1) yields:

$$D^{1/2} = k_2 \alpha I t / 2 A^{1/2} k_d \qquad (2)$$

Since $D^{1/2}$ is proportional to the diagonal length, the observed dependence on time and light intensity is consistent with the mechanism.

k_2 is given by the Arrhenius equation:

$$k_2 = k_2^0 \exp(-E_a/kT),$$

where E_a is the activation energy.

Step 1 involves the initial excitation of cis-oriented pairs at the perimeter of the defect, whether through direct absorption of the exciting light or through exciton migration from other points on the surface. It is most likely that n_c^* is a cis-oriented excimer. Birks and Aladekomo(20) postulated that excimer emission from 9-methyl anthracene solution was due to the cis-oriented pair while photodimer formation proceeds from the trans-oriented excimer. (This assignment was reversed in a later article by Barnes and Birks.(21) The assumption in the earlier paper(20) is more likely correct.) Chandross and Ferguson(11) on their studies of excimer fluorescence of trans-oriented 9-substituted anthracene noted that the van der Waal radius of the cyano group is not greater than the 1.7 Å thickness of the anthracene π-electron system, in contrast to the methyl group in 9-methylanthracene. They also observed that upon photolysis of CNA dimer frozen in methylcyclohexane glass which would be expected to produce trans-oriented pairs, only very weak excimer emission (peaking at 5000 Å) was obtained. However, strong monomer fluorescence was found when the glass was softened and refrozen. This contrasts with the strong excimer fluorescence observed in concentrated solutions and in crystals (enhanced at defects(20)). They also found that the short wavelength absorption of sandwich pairs of CNA decreased rapidly in intensity when the sample was exposed to long wavelength light ($>$ 3000 Å); they concluded that formation of the photodimer from the trans-excimer was efficient, more so than for the other trans-oriented pairs studied including 9-methylanthracene. Birks and Aladekomo(20) obtained a rate constant for photodimer formation of 9-methylanthracene in benzene and estimated that 0.4 of the collisions that resulted in trans-oriented pairs resulted in photodimer formation. (On the other hand, Cohen(2) reported faster photodimerization in 9-methylanthracene crystal than in CNA crystal.) Thus, the formation of D from n_t^* would be expected to be a highly efficient reaction. Here, we assume that the photodimer is formed at unit efficiency from the trans-oriented excimer.

After excitation, n_c^* returns to n_c by light emission and radiationless process, or forms n_t^* by rotation, which then yields the photodimer, D. Thus, reaction 2 is the thermally activated step. At higher temperatures, the activation energy drops, due to the increasing thermal instability of the cis-oriented excimer.(22) The dissociation rate constant for the excimer can be written

$$k_d = k'_d + k''_d \exp(-E_d/kT).$$

Thus, when $k'_d \ll k''_d \exp(-E_d/kT)$,

$$D^{1/2} = (k_2^0 \alpha It/2k''_d A^{1/2}) \exp[-(E_a - E_d)/kT]$$

and the activation energy becomes $(E_a - E_d)$. The enthalpy of dissociation of the pyrene excimer with values between 10 and 11 kcal/mole have been found in various solvents.(22) The entropy of dissociation contained in k''_d is also large and for the pyrene excimer, it was found to be 20 cal deg^{-1} mole^{-1}.

There is good evidence that photodimerization in both anthracene and CNA occurs by the interaction of an excited singlet molecule with a ground singlet molecule.(23) The linear intensity dependence of the [001] diagonal length of the photoetched pits demonstrates this for CNA.

On the (010) surface, the dominant type of photoetched pit had diagonals in the [101] and [001] suggesting that photodimerization is preferred at a certain type of dislocation. The dislocations (010)[001], (010)[100], (100)[010] and (211) with component [001] had been identified previously by Cohen *et al.*(15) who suggested that photodimerization would largely be favored at dislocations with the (211) slip plane, since the CNA molecules would be stacked in a *trans*-configuration along the dislocation. This has yet to be demonstrated. However, we would expect instantaneous nucleation for photodimerization at such dislocations with preformed trans-pairs.

The alignments of the photoetched pits in CNA along [001] and [100] directions strongly suggests that photodimerization occurred at (100)[001] dislocations, and that the growth direction of the diagonals within the photoetched pit is determined by recrystallization of the photodimer. Lonsdale(24) has observed that for the orientation of anthracene photodimer in anthracene: the [010] axes coincided in direction, the [100] direction was changed by 13°, and the [001] of the dimer was the original [102] of the monomer.

5. Summary

Photodimerization occurs preferentially at dislocations when CNA absorbs light in its first excited singlet band. Growth along the [001] diagonal direction on the (010) plane is linear in time and light intensity, suggesting a one photon mechanism for the formation of a trans-oriented excited singlet pair from an excited singlet *cis*-oriented pair on the perimeter of the nucleus.

9-substituted anthracenes are less efficient in forming photodimers in solution than anthracene; however, in crystals, the situation is reversed. This certainly suggests some kind of topochemical effects are involved and the need for further studies in this area.

REFERENCES

1. Schmidt, G. M. J., in *Reactivity of the Photoexcited Organic Molecule*, Interscience, New York, 1967.
2. Cohen, M. D., *Mol. Cryst. and Liq. Cryst.* **9**, 287 (1969).
3. Craig, D. P. and Sarti-Fantoni, P., *Chem. Commun.*, 742 (1966).
4. Applequist, D. E., Abstract of 131st Meeting of ACS, Miami, April 1957.
5. Applequist, D. E., Friedrich, E. C. and Rogers, M. T., *J. Am. Chem. Soc.* **81**, 457 (1959).
6. Calas, R., Lalande, R. and Mauret, P., *Bull. Soc. Chim. France*, 148 (1960).
7. Greene, F. D., *Bull. Soc. Chim. France*, 1356 (1960).
8. Calas, R., Lalande, R., Faugere, J. and Moulines, M., *Bull. Soc. Chim. France*, 119 (1965).
9. Chapman, O. L. and Lee, K., *J. Org. Chem.* **34**, 4166 (1969).
10. Bouas-Laurent, M., Lapouyade, R. and Faugere, J., *Compt. rend.* **265C**, 506 (1967).
11. Chandross, E. A. and Ferguson, J., *J. Chem. Phys.* **45**, 3554 (1966).
12. Calas, R. and Lalande, R., *Bull. Chim. Soc. France*, 770 (1959).
13. Lapouyade, R., Castellan, A. and Bouas-Laurent, M., *Compt. rend.* **268C**, 217 (1969).
14. Rabaud, H. and Claustre, J., *Acta Cryst.* **12**, 911 (1959).
15. Cohen, M. D., Ludmer, Z., Thomas, J. M. and Williams, J. O. *Chem. Commun.* 1172 (1969).
16. Sarti-Fantoni, P., *Mol. Cryst.* **5**, 303 (1968).
17. Stevens, B., Dickinson, T. and Sharpe, R. R., *Nature* **204**, 876 (1964).
18. Sarti-Fantoni, P. and Teroni, R., *Mol. Cryst. and Liq. Cryst.* **6**, 431 (1970).
19. Galwey, A. K., *Chemistry of Solids*, Chapman and Hall, Ltd., London, 1967.
20. Birks, J. B. and Aladekomo, J. B., *Photochem. Photobiol.* **2**, 415 (1963).
21. Barnes, R. L. and Birks, J. B., *Proc. Roy. Soc.* (*London*) **A291**, 570 (1966).

22. For a general review on excimers, see Th. Förster, *Angew. Chem. Internat. Edit.* **8**, 333 (1969).
23. Bowen, E. J. and Tanner, D. W., *Trans. Farad. Soc.* **51**, 475 (1955).
24. Lonsdale, K., in *Physics of the Solid State*, S. Balakrishna, M. Krishnamurthy and B. R. Rao, Eds., Academic Press, New York, 1969.