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Letters to the Editor

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Dye Sensitization of Photographic Emulsions and the Triplet State

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April 20, 1947

CURRENT research has established the existence of a triplet state associated with unsaturation electrons in organic molecules.¹ The triplet state concept will be shown below to furnish a plausible explanation of dye sensitization of photographic emulsions.

The position of the "long wave-length" limit of absorption of a silver bromide crystal would ordinarily be taken as an indication of the energy of the lowest electronic excited state of the crystal. Actually, considerably less energy than would be involved in the absorption of light by silver bromide can, through the agency of an adsorbed sensitizing dye, produce a photographic latent image. Experiment seems to indicate that there is no destruction of adsorbed sensitizing dye, as would take place if the dye gave up an electron to the crystal.² The most reasonable alternate explanation for the phenomenon of dye sensitization is that there exists another energy level in the crystal, but one that cannot be reached by the action of light.³ In this connection it is interesting to remember that a very stringent selection rule is the one requiring conservation of multiplicity.

A variation solution of the quantum mechanics of the silver bromide crystal requires that, in the first excited electronic state, the probability distribution of an electron be huge with respect to the size of a single-lattice element. This spread-out probability is said to fit the observed phenomenon of photo-conductivity. But a more refined calculation in which exchange integrals are considered explicitly might predict the existence of a new, lower lying, excited electron state (which is in reality a band): a triplet state. In the modified variation solution, the coefficients of atomic orbitals should become large as the orbitals are chosen nearer and nearer to the hypothetical point of ejection, the orbital proper to the atom which absorbed the excitation being represented maximally. An electron in such an excited state would not be identified with the whole crystal from the standpoint of space, but might be from the standpoint of time. The spin parallelism existing in the new low lying excited state ought to prevent

the excited electron from re-pairing, a metastability existing just as with the triplet state of organic molecules.

With the aid of the concept of a triplet state in a silver halide crystal, one can propose a mechanism for dye sensitization. The surface adsorbed sensitizing dye can undergo internal conversion to the triplet state after absorption of light raises it first to the excited singlet state. The ordinarily metastable triplet state of the dye may be very short lived, for the dye returns to its ground singlet state, simultaneously transferring its energy to the silver bromide crystal in a spin conservative process. An electron is thereby ejected from a lattice bromide ion situated adjacent to the dye molecule. The ultimate result of such an excitation of the silver bromide crystal ought to be the trapping of the electron in a sensitivity speck or in a growing latent image silver speck.⁴ If no such "trapping centers" exist nearby, re-pairing of electrons occurs, accompanied, of course, either by the heating of the crystal or the emission of light.

¹ G. N. Lewis and M. Kasha, J. Am. Chem. Soc. **66**, 2100 (1944).

² See for example the discussion by G. Kornfeld, J. Phys. Chem. **42**, 795 (1938).

³ The most recent exposition of this viewpoint is by N. F. Mott, J. Phys. Radium **7**, 249 (1946).

⁴ The Gurney and Mott theory of the latent image is accepted here without caution.

An X-Ray Examination of Cyclooctatetraene¹

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May 5, 1947

CYCLOOCTATETRAENE is an unusual compound which was reported for the first time by Willstätter² and co-workers in 1911. During the last war it was prepared in Germany by the catalytic polymerization of acetylene,³ and more recently it has been produced in this country using similar processes. An extensive x-ray investigation of this compound was undertaken in order to determine the stereochemistry of the molecule in the solid state. The work proceeded to a state where all the details of the structure cannot be given, but because of the unusual interest in this material, we are presenting the data obtained to date.

Cyclooctatetraene (C.O.T.) is a golden yellow liquid of density 0.938 which freezes, at -7 degrees C, to almost colorless needle-shaped crystals. Special low temperature cameras were constructed to obtain suitable powder and single crystal x-ray diagrams using nickel filtered copper radiation. The d -values, observed and computed, and relative intensities of the powder diagram are given in Table I. The density, $1.04 \pm .02$, of the solid was obtained by applying an experimentally derived correction to the liquid density.

The preliminary x-ray examination was done using the Debye-Scherrer techniques. The diagram was remarkably simple in appearance and resembled the line system given by cubic materials. Indeed, all of the Debye-Scherrer lines (Table I) can be reasonably indexed using a cubic unit cell of side $a = 10.85 \text{ \AA}$. The crystals are, however, birefringent, and a cubic structure is therefore unacceptable.

A tetragonal unit cell was then considered, and all of the Debye-Scherrer lines were indexable on the basis of a primitive tetragonal unit cell with $a=7.8\text{\AA}$, $c=10.7\text{\AA}$. The pseudo-cubic character of this cell is evident; $c \approx a(2)^{1/2}$.

TABLE I. Interplanar spacings and relative intensities of cyclooctatetraene from Debye-Scherrer powder diagrams.

d -A (obs.)	d -A (comp.)*	Intensity	$h\ k\ l$
5.34	5.33	m	0 0 2
4.88	4.88	s	1 1 1
3.87	3.89	m	0 2 0-2 0 0
3.49	3.49	m	1 2 0
3.30	3.30	m	2 1 1
3.14	3.14	m	2 0 2-0 2 2
2.98	2.98	m	1 1 3
2.91	2.91	$m-w$	1 2 2
2.65	2.66	$m-w$	0 0 4
2.48	2.48	w	2 1 3
2.39	2.39	$m-w$	3 1 1-1 3 1
2.19	2.19	$m-w$	2 0 4-0 2 4
2.16	2.15	w	3 2 0
2.13	2.12	w	2 3 1
2.02	2.02	m	1 3 3-3 1 3
1.95	1.95	w	0 4 0-4 0 0
1.82	1.82	w	4 0 2-0 4 2
1.67	1.66	w	4 2 2-2 4 2

* In those cases where two sets of indices are given the computed spacing is an average.

At this stage it appeared desirable to employ single-crystal x-ray measurements. A study of the intensities of observed reflections showed that the tetragonal unit cell was untenable. This led to the choice of an orthorhombic pseudo-tetragonal cell where $a \approx b \approx 7.8\text{\AA}$ and $C=10.7\text{\AA}$. This revised cell permitted satisfactory indexing of all Debye-Scherrer lines (Table I) as well as of the single crystal reflections.

The lattice constants were then determined more exactly by a least-squares solution of those Debye-Scherrer lines which could be uniquely indexed. This gave $a=7.76\text{\AA}$, $b=7.80\text{\AA}$, $c=10.66\text{\AA}$. These values were used to calculate the spacings for the powder reflections (Table I). The agreement is good.

Systematic extinctions of the (hkl) reflections for ($k+1$) odd, of the (hol) reflections for h odd, and the (okl) reflections for k odd were found. Two orthorhombic space groups require these extinctions; Aba and $Abam$.

For four molecules per cell, the x-ray density is 1.06 which may be compared to the measured value of 1.04.

Inasmuch as the space group choice is limited to Aba or $Abam$, the molecular centers must be located at special locations in the unit cell. In either case, the centers of the molecules are located at the points of a face centered orthorhombic lattice, and the molecule must possess at least a twofold axis of symmetry. If the space groups were Aba or $Abam$, in addition, the molecule would have to have a plane of symmetry. We now feel that this latter space group is the less likely of the two.

¹ This work represents part of a dissertation to be presented by H. S. Kaufman to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Willstätter and Waser, Ber. 44, 3423 (1911); Willstätter and Heideberger, Ber. 46, 517 (1913).

³ Report by Dr. Walter Reppe on Cyclopolyolefines (Ludwigshafen on Rhine, April 28, 1944).

A New Refinement Technique for X-Ray Structure Analysis

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May 5, 1947

THE standard technique of Fourier refinement, which has been used with such success in many simple structure analyses, is unfortunately reaching a state in which, despite technical improvements,¹⁻³ the time taken for a structure analysis is increasing to a prohibitive extent. Thus, in recent determinations (on geranylamine hydrochloride⁴ and penicillin⁵), times of the order of 3 years have been needed for completion.

At the root of this decline is the fact that, in order for the Fourier process to converge, a set of parameters must be found by trial and error, which are a reasonable approximation to the correct ones. Roughly speaking, the region of convergence of the Fourier method is the same as that of its differential variant.³

Patterson-Harker syntheses cannot be considered the complete solution to the problem of approximate structure determination since, in a wide range of cases, no useful information is obtainable from this technique; and this is especially true in complex organic structures. Similarly, molecular transforms are very difficult to apply in any but the simplest space groups.

It can be stated that the desirable features of any systematic form of structure determination are the following:

- (1) Starting from any arbitrary position, it should be possible to locate the position of a molecule considered as a rigid unit.
- (2) Having found the position of the molecule considered rigid, it should be possible to determine the individual atomic positions.
- (3) If necessary, the method should be applicable to density distributions. This is particularly true for macromolecules since here, although the general shape may be known, the details may be completely obscure.

A solution to these problems is to be found *via* the method of "steepest" descents which, although in some ways a generalization of the least-squares refinement,⁶ is unlike the latter in that it can be applied to systems of any degree of complexity. In addition, it is possible to locate the position of a molecule considered either as a rigid whole or as a set of rigid parts, or to refine a density distribution given at lattice points over the unit cell.

Full details of the method in all its forms, will be published at a later date, but it is proposed to explain here the general philosophy of the attack and to give the equations for the simplest case.

In essence, the scheme is merely a procedure for minimizing either:

$$R_1 = \sum_{hkl} \|F_{\text{obs}} - F_{\text{calc}}\|$$

or

$$R_2 = \sum_{hkl} (F_{\text{obs}}^2 - F_{\text{calc}}^2)^2.$$

Now $R_n = \text{const.}$ represents a surface in the $3N$ dimensional space defined by the atomic parameters x_{rj} ($r=1 \dots N$; $j=1, 2, 3$). The method of minimization is to proceed in the direction of the normal to any given surface until the value of R_n no longer decreases. Having arrived at this