

The observed values for several perfluoroalkylmethylenes are $D \sim 0.72$ and $E \sim 0.021 \text{ cm.}^{-1}$ indicating an angle of $150\text{--}160^\circ$ at the divalent carbon atom.¹¹ Comparison should be made with the corresponding linear structure which would have $D \sim 0.75 \text{ cm.}^{-1}$,¹² in fair agreement with Z^3 dependence.

An interaction between the unpaired electrons, similar in magnitude to those observed in the alkyl nitrenes, was determined for methylsulfonylnitrene which has $D = 1.581 \text{ cm.}^{-1}$, $E = 0.0036 \text{ cm.}^{-1}$. In contrast, the values for phenylnitrene ($D = 0.99 \text{ cm.}^{-1}$, $E < 0.002 \text{ cm.}^{-1}$) indicate significant delocalization of one unpaired electron into the aromatic system.

Acknowledgments.—We are grateful to Mr. R. M. R. Cramer and Mrs. B. I. Feuer for their assistance.

(11) From work with L. Barash, to be published.

(12) J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963). We employ the calculated change in D with change in angle to correct the observed value.

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Preparation of Biaxially Oriented Polycapramide by the Solid State Polycondensation of a Single Crystal of ϵ -Aminocaproic Acid¹

Sir:

The possibility of preparing oriented polymer chains by polymerization in single monomer crystals was first demonstrated by the conversion of trioxane to polyoxymethylene.² Later it was shown that the polymer chains are oriented not only in the direction of the fiber axis but also in the plane perpendicular to it.³ The relationship of the orientation of the polymer crystallites to the crystallographic directions of the parent monomer has been fully clarified.⁴

More recently, it has been shown that the heating of a single crystal of phthalanilic acid at temperatures 50° below its melting point leads to highly oriented crystallites of N-phenylphthalimide.⁵ This example of topotaxy is remarkable in view of the fact that the water split off in the reaction has to diffuse out of the crystal. We have now shown that an analogous phenomenon is possible in a polycondensation. Single crystals of ϵ -aminocaproic acid (m.p. $204\text{--}205^\circ$) heated *in vacuo* for 16 hr. at 173° yielded highly oriented polycapramide as indicated by the X-ray diffraction photograph (rotation around b -axis of monomer) on Fig. 1. Weissenberg photographs proved that biaxial orientation was involved. The monomer crystal belongs to space group $P2_1/c$, $a = 8.56 \text{ \AA.}$, $b = 5.90 \text{ \AA.}$, $c = 15.13 \text{ \AA.}$, and $\beta = 103.13^\circ$,⁶ while the polymer has space group

(1) Abstracted from the Ph.D. thesis to be submitted by N. Morosoff to the Graduate School of the Polytechnic Institute of Brooklyn in June, 1965. This work was supported by grants from the National Science Foundation and the U. S. Atomic Energy Commission.

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(3) J. Lando, N. Morosoff, H. Morawetz, and B. Post, *ibid.*, **60**, S24 (1962); S. Okamura, K. Hayashi, and M. Nishii, *ibid.*, **60**, S26 (1962).

(4) G. Carazzolo, S. Leghissa, and M. Mammi, *Makromol. Chem.*, **60**, 171 (1963).

(5) H. Morawetz, S. Z. Jakabhazy, J. B. Lando, and B. Post, *Proc. Natl. Acad. Sci. U. S.*, **49**, 789 (1963). The paper refers to the reaction product erroneously as N-phenylphthalimide.

(6) F. Günther, *Kolloid-Z.*, **108**, 192 (1944); P. De Wolfe, ASTM Powder Diffraction File Card 7-682.



Figure 1.

$P2_1$, $a = 9.56 \text{ \AA.}$, $b = 17.2 \text{ \AA.}$, $c = 8.01 \text{ \AA.}$, and $\beta = 67.5^\circ$, with the polymer chains parallel to b .⁷ Weissenberg photographs of partially converted monomer crystals showed that the following crystallographic planes of monomer and polymer are parallel to each other: $11\bar{2}_{\text{mon}} \parallel 200_{\text{pol}}$; $112_{\text{mon}} \parallel 202_{\text{pol}}$; $004_{\text{mon}} \parallel 002_{\text{pol}}$.

These data indicate that the polymer chains grow parallel to the intersection of the 004 plane with the 110 or $1\bar{1}0$ plane of the monomer. The polymerization involves a contraction of 17% in the direction of the chain axis and an 18% reduction of volume; it is remarkable that this may be accomplished with retention of chain orientation.

(7) D. R. Holmes, C. W. Bunn, and D. J. Smith, *J. Polymer Sci.*, **17**, 159 (1955).

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The Photochemical Reduction of Rare Earth Ions in Fused Halides¹

Sir:

The reduction by X-rays² and γ -rays^{3,4} of rare earth ions incorporated in crystalline halide hosts to lower oxidation states is well known. Recent studies at these laboratories⁵ have shown that only the locally uncompensated rare earth ions are capable of being photoreduced, and, in addition, the divalent rare earths so produced are readily reoxidized by thermal and optical processes. The instability of the divalent state is due to interstitial halogen atoms which remain in the crystal after irradiation and which eventually recapture their electrons.

Irradiations of molten halides containing rare earths, which would eliminate most of the inherent difficulties associated with the solid-state irradiations, were therefore carried out. In preliminary studies, molten solutions of dried and brominated BaBr_2 with 0.2 mole %

(1) The research reported in this paper was sponsored by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contract No. AF33(657)-11221.

(2) W. Hayes and J. W. Twidell, *J. Chem. Phys.*, **35**, 1521 (1961).

(3) J. R. O'Conner and H. A. Bostick, *J. Appl. Phys.*, **33**, 1868 (1962).

(4) Z. Kiss and R. Duncan, *Proc. I.R.E. (Inst. Radio Engrs.)*, **50**, 1531 (1962).

(5) F. K. Fong, *J. Chem. Phys.*, **41**, 245 (1964).

Tm^{3+} were irradiated with (1) γ -rays, (2) the output of a low pressure mercury lamp, or (3) with a low pressure hydrogen discharge produced within the quartz reaction tube itself. The oxidized anionic species were swept out or trapped out of the reaction tube. Upon cooling the molten bromides, each of the three radiation treatments showed significant quantities of divalent thulium. A typical spectrum of Tm^{2+} in $BaBr_2$ taken at $77^\circ K$. is shown in Fig. 1.

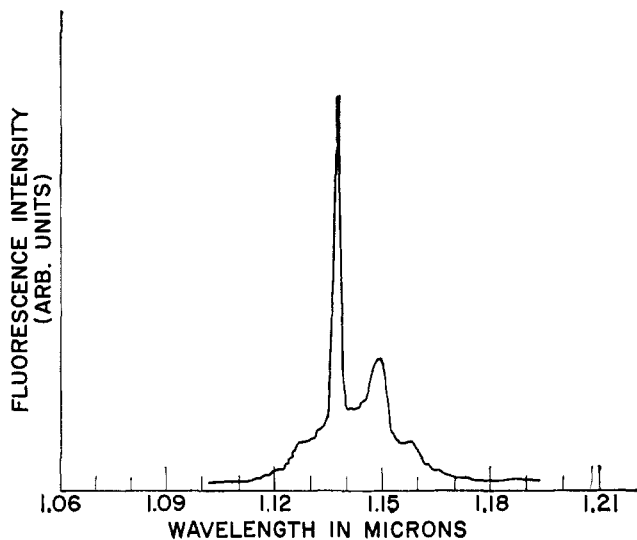


Fig. 1.—Fluorescence of γ -ray reduced (in the fused state) Tm^{2+} in $BaBr_2$ ($T = 77^\circ K$).

In the case of the γ -ray treatment, a dosage of less than 10^4 rads was used. Generally, dosages of up to 10^7 rads were found to be necessary for similar reduction in the solid.⁵ The light from the quartz mercury vapor lamp was focused on the surface of the melt from outside the furnace and the reaction tube. Illumination was carried out for about 1 hr. The low pressure hydrogen discharge was obtained by placing a Tesla coil on the reaction tube with about 0.1 mm. pressure of hydrogen flowing through the tube. The discharge was maintained for about 30 min.

The intensity of the Tm^{2+} fluorescence obtained from the low pressure hydrogen discharge material indicates a level of reduction much greater than that possible through reduction by solid-state irradiation. The extent of reduction in the solid-state irradiation is limited by the site-selection mechanism mentioned above.^{5,6} In the molten state, the ionization of the anions by radiation and their subsequent removal from the solution should permit the reduction of all the rare earth ions present. The $BaBr_2$ - Tm^{2+} crystals were fused and regrown several times with little or no loss of the divalent state. This is indicative of the stability of the reduced rare earth ions produced by radiation in the fused state to thermal reoxidation. No optical reoxidation experiments were done, but in the absence of known electron traps, such processes are not expected to occur.

Further work on other halide hosts containing various rare earth ions and on the mechanism of the reduction process is in progress and will be described more fully at a later date.

(6) P. M. Heyman and Z. Kiss, private communication.

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1,6-Oxido[10]annulene and 1-Benzoxepin¹

Sir:

We have found that base treatment of 2,3,6,7-tetrabromo-9,10-oxidodecahydronaphthalene (II) gives rise to 1,6-oxido[10]annulene (IV), as well as to 1-benzoxepin (VI).² This synthesis of IV resembles the recently described synthesis of the related 1,6-methano[10]annulene by Vogel and Roth.³

The tetrabromide II was prepared by addition of bromine to 9,10-oxido-1,4,5,8,9,10-hexahydronaphthalene (I)⁴ in chloroform solution, whereby one isomer (m.p. 160 – 162°) was isolated by crystallization in *ca.* 45% yield. Dehydrobromination of this substance with ethanolic potassium hydroxide at 50 – 55° , followed by chromatography on alumina, produced first the oxepin VI (*ca.* 20% yield) and then the annulene IV (*ca.* 50% yield).

1,6-Oxido[10]annulene (IV), $C_{10}H_8O$, formed light-yellow crystals, m.p. 53 – 54° , infrared band (KBr) at 6.51μ . The ultraviolet spectrum [λ_{max}^{EtOH} 255 m μ , 299, and complex band at *ca.* 392 (ϵ 72,000, 6900, and 240)] resembled that of the corresponding 1,6-methano-compound,³ and pointed to the fully conjugated structure IV rather than to the alternative tricyclic formulation III. The n.m.r. spectrum⁵ showed an A_2B_2 pattern in the τ 2.23–2.81 region (centered at τ 2.52), similar to that of naphthalene (τ 2.05–2.71, centered at 2.38).

The annulene IV is a ten π -electron system, and therefore complies with Hückel's rule. Moreover the carbon skeleton is presumably not seriously distorted from a mean plane, and the substance should consequently be aromatic.⁶ That the compound in fact is aromatic is shown by the n.m.r. band positions at low field, demonstrating the existence of a ring current. The annulene is best represented by the expression V, indicating delocalization of the π -electron system.

1,6-Oxido[10]annulene can be made to undergo electrophilic substitution reactions. For instance, nitration with cupric nitrate and acetic anhydride for 5 min. at room temperature produced two isomeric mononitro compounds, $C_{10}H_7NO_3$, each in *ca.* 30% yield. The more strongly absorbed on alumina [m.p. 48 – 49° ; λ_{max}^{EtOH} 242 m μ , 279, and 349 (ϵ 21,500, 26,500, and 7500)] proved to be the β -nitro isomer VII, since the lowest field bands in the n.m.r. spectrum⁵ consisted of a one-proton singlet (H^1) at τ 1.22 as well as a one-proton doublet (H^3) at τ 1.40 ($J = 10$ c.p.s.). The

(1) Part XXXIII in the series "Unsaturated Macrocyclic Compounds." For part XXXII, see A. E. Beezer, C. T. Mortimer, H. D. Springall, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc.*, in press.

(2) The isomeric 3-benzoxepin has been reported previously [K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961); for derivatives of 3-benzoxepin, see K. Dimroth and H. Freyschlag, *Ber.*, **90**, 1623 (1957)].

(3) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964).

(4) This substance is readily available from naphthalene in high yield by a two-step sequence [W. Hückel and H. Schlee, *Ber.*, **88**, 346 (1955); C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960)].

(5) All n.m.r. spectra were determined in deuteriochloroform solution at 60 Mc./sec.

(6) See F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).