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STUDIES OF THE SOLID STATE REACTIVITY AND PROPERTIES OF DIACETYLENE POLYMERS AND ACETYLENES[1]

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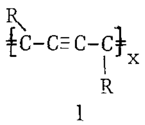
Abstract. The physical considerations which motivate our interest in fully crystalline polymers derived from acetylenic and diacetylenic monomers are presented. The interaction of the polymer derived from 1,6-di-N-carbazolyl-2,4-hexadiyne (DCH) with antimony pentahalides (SbX_5, X=F, Cl) has been studied as a function of polymerization method. It was found that thermally polymerized DCH takes up SbX_5, and the chemical, spectral, crystallographic, and electrical properties of the resultant material are reported. The reactivity in the solid state of the simple hydrogen bonded acetylenes propiolamide and the oxime and semicarbazone of propiolaldehyde using heat and ^{60}Co gamma radiation as stimuli has been studied. While the above acetylenes are unreactive to gamma radiation in comparison to diacetylenes and metal propiolates, their reactivity was enhanced when they were crystallized from chlorinated solvents. Propiolaldehyde semicarbazone is monoclinic, space group P2/n, $\underline{a}$ = 10.582(3), $\underline{b}$ = 3.801(1), $\underline{c}$ = 14.065(4)Å; β = 109.02(3)°; Z = 4. Solved by direct methods, the structure reveals stacks along $\underline{b}$ and important acetylenic carbon-carbon contacts at less than 3.80Å. Several possible considerations relevant to structure-reactivity relationships and mechanistic aspects of reaction initiation are discussed.

INTRODUCTION

Theoretical considerations allow the description of conjugated organic polymers (prototype examples are the polydiacetylenes[3] (PDA, 1),

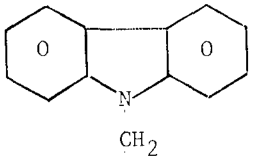

$$[\overset{R}{C}-C{\equiv}C-\underset{R}{C}]_x$$

1

where R is a generalized substituent, and polyacetylene, $(CH)_x$)) as one dimensional semiconductors with wide bands.[4,5] On this basis, it is expected that suitable experimental samples of such polymers should have high carrier mobilities and third order susceptibility coefficients, $(\chi^{(3)})$.[5]

Experimentally, the PDA polymer PTS (1, $R=CH_2OSO_2pC_6H_4CH_3$) as single crystals was reported to have a value of $\chi^{(3)}(3\omega)$ along the conjugated backbone comparable to that of GaAs at 3ω below the absorption edge,[7] and a large value of $\chi^{(3)}(\omega)$ at 1.9μm was also observed for PTS polymer crystals.[8] Langmuir-Blodgett multilayers of the PDA from $CH_3-(CH_2)_{16}-C{\equiv}C-C{\equiv}C-(CH_2)_8-CO_2H$ on a silver grating give a structure which allows coupling of an incident laser photon to a planar guided wave mode in the PDA waveguide or a surface plasmon mode at the silver-PDA interface.[9] Values of $\chi^{(3)}(\omega)$ comparable to those reported[7,8] for PTS polymer have been observed[10] in these PDA structures. Our activities directed toward processing these and other PDAs into supramolecular structures of interest as nonlinear optical elements continue.[11]

With respect to the electronic properties of PDA, electron mobilities greater than $10^3 cm^2V^{-1}sec^{-1}$ in the chain direction have been deduced from pulse photoconductivity studies in PTS polymer[12] and from electron injection[13] and electroreflectance[14] studies of DCH polymer (1, $R=CH_2$-N-carbazolyl,2).



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Consequently, the extremely low dc conductivities of PDA crystals[3,15] manifest an insignificant carrier concentration, and electronic applications would require significant numbers of carriers which would have to be created by charge transfer processes.

The interchain forces in PDA crystals are of the Van der Waals type. Since solids such as graphites and the metal dichalcogenides, whose interlayer forces are Van der Waals, have their structures "intercalated" by assorted charge transfer reagents, it is noteworthy that such "doping" of PDA crystals typically does not occur, in contrast to the partially crystalline $(CH)_x$.[5] Exposure of PDA thin films and multilayers to halogen vapors reveals color changes and conductivities of the order of $10^{-7}(\text{ohm-cm})^{-1}$, but the crystallographic and spectral consequences of the halogen-PDA interaction were not disclosed.[15,16]

With this background and our own experience with PTS polymer, the observation[17] that treatment of DCH polymer crystals with SbF_5 in pentane led to a dark colored material with a room temperature conductivity of $10^{-3}(\text{ohm-cm})^{-1}$ captured our attention. We elected to study the interaction of DCH polymer with a variety of acceptors on the possibility that there could be a fundamental difference between DCH and other PDA. The chemical, spectral, structural, and electrical properties of these materials are the first topic of this report.

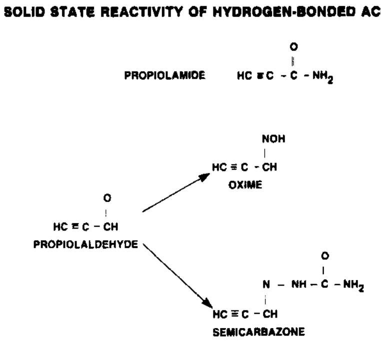
Experimental studies of existing forms of $(CH)_x$ and polymers of substituted acetylenes have led to new conductive materials with potential application in lightweight batteries and suggestions of solitons in the electronic structure.[5] However, such materials are at best partially crystalline, and the need for fully crystalline polyacetylenes has been recognized.[18,19]

Solid state polymerization of acetylenes which are not solids at room temperature may be investigated if the liquid or gaseous compound can be isolated as a solid inclusion complex. Cyclotriphosphazene complexes of acetylene and phenylacetylene upon exposure to ^{60}Co-gamma radiation did not lead to the relevant polymers.[20]

Relatively few studies of the solid state reactivity of acetylenes crystalline at room temperatures have been reported to date.[21-25] The general strategy of the use of nonbonded interactions to orient the triple bonds for polymerization has been studied for the case of metal carboxylates.[22,23] A diacetylene has been successfully used to orient a monoacetylene for polymerization.[25]

In this work we report our initial studies of the solid state reactivity of these crystalline hydrogen bonded acetylenes of relatively simple molecular structure (see Scheme 1): propiolamide[24] and the oxime and semicarbazone of propiolaldehyde. We find that these compounds are relatively unreactive and discuss this by means of a qualitative model. The crystal and molecular structure of the semicarbazone has been determined and the salient intermolecular features are summarized below.

SCHEME 1



EXPERIMENTAL SECTION

General

Experiments with SbF_5 and $SbCl_5$ were carried out in a Labconco dry box under argon. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Electronic spectroscopy in the solid state was performed on a Varian Cary 17 recording spectrophotometer. Infrared spectra were obtained on a Nicolet Fourier FTIR transform instrument between 4000 and $200cm^{-1}$ of samples dispersed in CsI. X-ray powder diffraction was recorded using CuK_α radiation and single crystal analysis using a precision Weissenberg camera and optical goniometer. Electrical measurements were performed on small crystals at room temperature on teflon cradles with 4-.001" Cu lead and silver paint.

Preparation and Polymerization of 1,6-Di-N-Carbazolyl-2,4-Hexadiyne (DCH)

The synthesis and polymerization (both thermal and by ^{60}Co gamma radiation) of DCH monomer were accomplished as previously described.[26] The x-ray powder diffraction of polymer samples may be indexed to the unit cell of the reported structure (*vide infra*) and exhibits the following reflections (d spacings (Å), s=strong reflection): 11.90(s), 11.01, 8.06(s), 5.92(s), 4.26(s), 3.45, 3.24, 2.98(s), 2.86, 2.72, 2.59, 2.51(s), 2.24, 2.22, 2.15, 1.996, 1.92. The polymer FTIR spectrum exhibits the following absorption: 3055(s), 2924, 1926, 1900, 1634, 1611, 1493(s), 1467(s), 1336, 1270, 1231, 1165, 1139, 1099, 1060, 955, 850, 810, 750(s), 719(s), 640, 560, 528, 459, 420, 333, and $228cm^{-1}$.

Interaction of DCH Polymer with Antimony Pentafluoride

To thermally polymerized DCH polymer suspended in perfluorohexane (PCR) was added SbF_5 (7 equiv.). The mixture was kept at room temperature for eighteen hours during which time the polymer crystals slowly sink. The crystals were isolated on a sintered glass filter, washed with perfluorohexane, and vacuum dried.

Anal. Found: C, 72.13; H, 4.27; N, 5.28; Sb, 11.54; F, 6.78. The observed analysis corresponds to $(C_{31.8}H_{22.5}N_{2.0})_2SbF_{3.8}$. An idealized composition would be $(DCH)_2SbF_4$, *i.e.* $(C_{30}H_{20}N_2)_2SbF_4$, whose calculated elemental composition is: C, 71.02; H, 3.97; N, 5.52; Sb, 12.00, F, 7.49.

Interaction of DCH Polymer with Antimony Pentachloride

To thermally polymerized DCH suspended in dichloromethane was added 7 equivalents $SbCl_5$ in dichloromethane. The polymer slowly sank and after 18 hours at room temperature was isolated by suction filtration as above, washed with dichloromethane, and vacuum dried. X-ray powder diffraction revealed this material to be amorphous.

Anal. Found: C, 57.60; H, 2.47; N, 4.74; Sb, 10.27; Cl, 24.71. The observed analysis corresponds to $(C_{28}H_{14.4}N_2)(SbCl_{8.3})$.

Propiolamide. This material was prepared as described in the literature.[27] X-ray powder diffraction of the compound exhibited the following d spacings (Å), (s=strong reflection): 12.54, 11.97(s), 7.39(s), 7.27, 5.99, 5.49, 5.54, 5.13, 5.07, 4.97, 4.64, 4.00, 3.87(s), 3.69(s), 3.50, 3.40, 3.36, 3.27, 3.12, 2.99, 2.85, 2.84, 2.75, 2.65(s), 2.50, 2.45, 2.25, 2.14, 1.72.

The diffraction pattern showed no new lines after exposure to gamma radiation for 15 days. HPLC analysis of a water solution of the irradiated material on a μ-Bondagel column at a flow rate of 1ml./min. revealed two fractions at retention times 2.1 and 3.4 min. with relative areas of 1:10, respectively. The peak of 3.4 min. is the only one observed in our sample of amorphous polypropiolamide (*vide infra*).

Oxime and Semicarbazone of Propiolaldehyde

Propiolaldehyde[28] was converted to its oxime as previously described.[29] The x-ray powder diffraction pattern, before and after exposure to gamma radiation exhibits reflections of the following d spacings (Å) (s=strong reflection): 6.89(s), 5.39, 4.48(s), 3.93, 3.62(s), 3.44(s), 3.27(s), 2.97(s), 2.88(s), 2.78, 2.70(s), 2.51, 2.48, 2.47, 2.38, 2.29, 2.23, 2.21, 2.14, 2.07, 2.03, 2.01, 1.95, 1.94, 1.87, 1.81.

The semicarbazone was prepared by reacting the aldehyde with semicarbazone hydrochloride in water at room temperature, mp 170-172°. Crystals for the structure determination were grown in methanol.

REACTIVITY OF DCH POLYMER WITH ANTIMONY PENTAHALIDES

We have studied the interaction of DCH polymer crystals, which we have prepared by both thermal and ^{60}Co gamma radiation polymerization, with SbF_5 and $SbCl_5$. In accord with earlier observations,[30] only crystals polymerized by radiation are suitable for single crystal diffraction study. Table 1 lists two sets of lattice constants determined on such crystals at 20°C along with other sets of lattice constants from the literature.

As noted above, thermally polymerized DCH interacts with SbF_5 to give a material with a composition $[(DCH)_2SbF_4]_x$. This material exhibited an infrared spectrum with all vibrations of pristine DCH polymer with additional absorptions observed at 660, 300, and $280cm^{-1}$. These additional vibrations are consistent with SbF_5 and SbF_6 species,[31] but are not compatible with the vibrations reported for SbF_4^-.[32] The observed composition thus indicates a mixture of Sb species. X-ray diffraction of these solids reveals only the pattern of DCH polymer. The salient feature of the solid state spectrum of these solids is a broad band peaking at 1000-1100nm in the near infrared which is associated with a partially oxidized PDA backbone. All other features of the spectrum have been previously observed[33] in DCH polymer.

The composition $(C_{29}H_{15}N_2)_{0.55}(SbCl_8)_{0.45}$ determined for the material isolated from the interaction of $SbCl_5$ with thermally polymerized DCH suggests, from the loss of hydrogen and the Cl:Sb ratio, that crosslinking and ring chlorination have occurred. An 8:1 Cl:Sb ratio was previously observed[34] on treatment of $(CH)_x$ with $NO^+SbCl_6^-$. Infrared absorption at $336cm^{-1}$ is consistent with either $SbCl_5$ or $SbCl_6$ species,[35] and the remainder of the spectrum is different from that of the DCH/SbF_5 material discussed above. The material had no x-ray diffraction pattern.

The resistivity of pristine DCH polymers exceeds 10^{15}ohm-cm.[36] The DCH polymer/SbX_5 materials discussed above do not exhibit a resistivity less than 10^7ohm-cm, and less resistive materials of this type are not obtained without loss of structural or compositional definition.

The polycrystalline material obtained by thermal polymerization of DCH has a fibrous texture.[30] Accordingly, we exposed single crystals prepared by ^{60}Co gamma radiation

TABLE I

LATTICE CONSTANTS OF DCH POLYMER

a (Å)	12.89[a]	13.03[b]	12.865[c]	12.81[d]	12.77[e]
b	4.90	4.92	4.907	4.89	4.89
c	17.39	17.55	17.403	17.27	17.31
β	108°	108.7°	108.3°	107.85°	108.2°
V (Å^3)	1044.6	1065.7	1043.1	1029.7	1027.3

a. V. Enkelmann, *et al.*, *Chem. Phys. Lett. 52*, 314 (1977).

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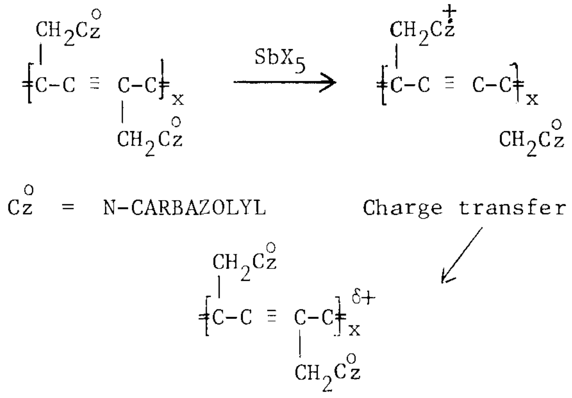
c. P.A. Apgar and K.C. Yee, *Acta Cryst B34*, 957 (1978).

d. Present Work.

e. Present Work.

of DCH to SbX_5 (X=Cl, F). Optical microscopy of the materials resulting from this treatment revealed them to be inhomogeneous. It follows that the Sb species in the thermal DCH polymer occupy defects or vacancies. This conclusion was also reached in a recent study of field-driven introduction of I_3^- or I^- into DCH polymers.[37]

The thermal DCH polymer does not take up bromine or iodine from solution. What are the elementary steps that allow it to take up SbX_5? These would involve initial ionization of a carbazole side chain followed by electron transfer from the conjugated backbone to the resultant carbazole cation-radical leaving a partially oxidized backbone, as follows:



This carbazole-assisted ionization process is in accord with the reported solid state ionization energies (I_c) of PDAs[38] and carbazoles,[39] with the former having the lower I_c. Additionally, it is apparent that, on energetic grounds, Br_2, I_2 or SbX_5 can ionize a conjugated chain as found in a PDA or $(CH)_x$, but only SbX_5 can charge transfer with a carbazole group.

SOLID STATE REACTIVITY OF HYDROGEN BONDED ACETYLENES

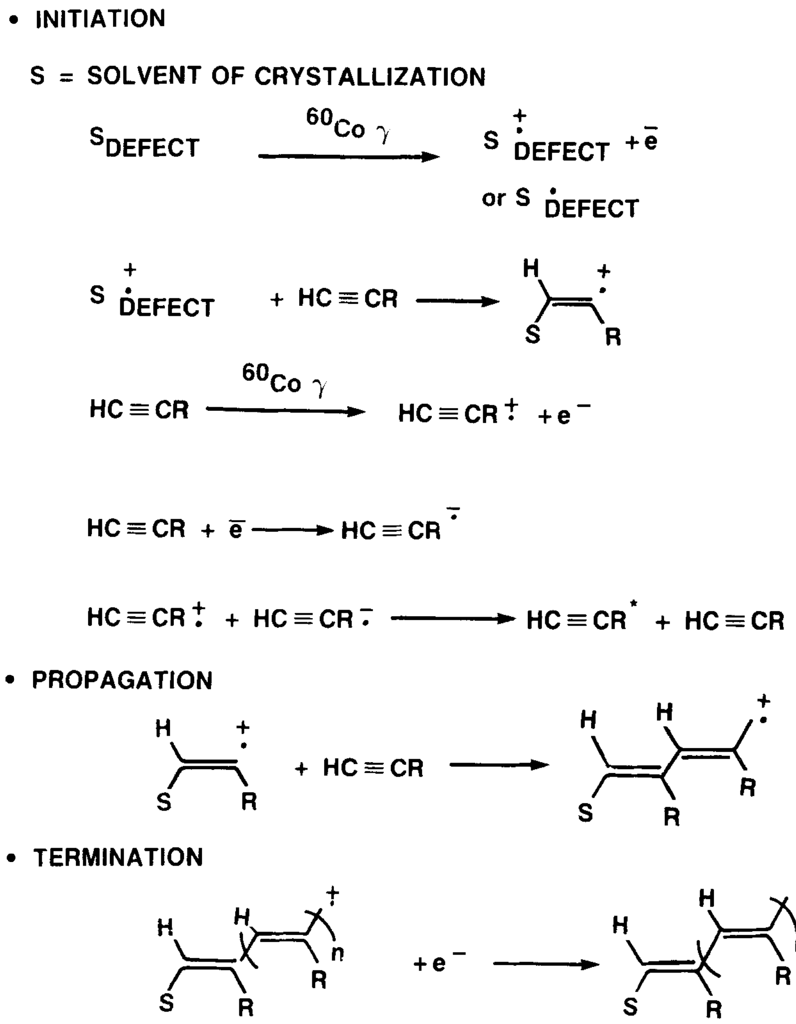
Of the three acetylenes in Scheme 1, propiolamide and the oxime are unreactive below their melting points, 60° and 71°, respectively, in the time frame of a melting point determination. Above their melting points, both decompose. In the case of the amide, a yellow-orange amorphous low molecular weight polypropiolamide is isolated. In the case of the semicarbazone, the compound is thermally reactive, as judged by darkening in color on heating near its decomposition point (172°), but the tendency of the compound to sublime on prolonged heating precludes a quantitative study of its thermal reactivity. Since a study of their thermal reactivity in the solid state below this melting point did not result in facile polymerization, we decided to expose the three compounds to ^{60}Co gamma radiation. They were found to be relatively unreactive, especially, as for the cases of the oxime and semicarbazone, when the experimental samples were vacuum sublimed before irradiation. Experimentally, no changes were detected by infrared spectroscopy and x-ray powder diffraction, and only slight (1-2°) depression of melting point was noted in irradiated samples. Comparatively, these compounds are markedly less reactive to gamma radiation than the zinc[22] and sodium[23] salts of propiolic acid or diacetylenes polymerized by gamma radiation such as DCH or TCDU (1, R=$-(CH_2)_4OCONHC_6H_5$).

Samples of the amide and semicarbazone which have been crystallized from chlorinated solvents are somewhat more reactive to ^{60}Co than sublimed samples. For example, with samples of the semicarbazone crystallized from carbon tetrachloride, chloroform, or dichloromethane, the monomer is consumed to the extent of 10-15 per cent compared to significantly less than 5 per cent for vacuum sublimed samples exposed to the ^{60}Co source simultaneously for 16 days. Since the x-ray powder pattern for these compounds is not dependent on the history of the sample, we conclude that the chlorinated solvent molecules reside in defects in the crystal. We have verified this hypothesis for the case of the semicarbazone where GC/MS analysis of crystals grown in chloroform reveals solvent in five times the concentration found in vacuum sublimed crystals exposed to chloroform vapor.

We summarize our initial studies of the solid state (un)reactivity of these hydrogen bonded acetylenes toward direct gamma radiation by means of the qualitative model in Scheme 2. While the model at present emphasizes the ionizing aspects of gamma radiation, it should be recalled that such radiation can produce higher lying states resulting from both dipole allowed and forbidden processes. Since, as noted above, the compounds under discussion are more reactive when crystallized from a chlorinated solvent than when solvent free or crystallized from benzene, a key feature of the model is initiation via excitation of a

SCHEME II

MODEL OF RADIATION INDUCED SOLID STATE REACTIVITY



solvent molecule residing in a crystal defect.

Another important feature involves capture of an electron by a neutral acetylene leading to an anion-radical. While such a species can, in principle, propagate, if it is adjacent to a cation-radical, electron transfer will lead to two neutral molecules, one of which might be vibrationally excited, and any reactive species are effectively quenched. This type of quenching process involving electron transfer between adjacent ionized sites may also be applicable to the processes involved in the radiation resistance of aromatic molecules and polymers.[40] It should also be noted that electron capture by a propagating cationic chain can terminate the process. It is equally important to realize that such a terminated chain, e.g., is more easily ionized than monomer, and that if such a chain is not terminated by a solvent fragment, subsequent ionization can lead to further chain propagation in the presence of unreactive monomer, as observed for propiolamide.

The detailed role of the chlorinated solvent in a defect in the initiation process merits further comment. Since the interaction of radiation with matter is directly related to the atomic number of an absorber atom, and chlorine is the heaviest atom in the crystal, the chlorinated molecules may be the easiest to excite. It is also known that the first vertical gas phase ionization potentials of chloroform and dichloromethane are as low or lower than acetylene and electronegatively substituted acetylenes.[41]

Our observation of the role of chlorinated solvents in crystalline defects in the initiation step contrasts with the situation reported for diacetylene and related polymerizations. In at least three cases,[42] solvents such as dioxane and chloroform are present stoichiometrically, and their presence plays a crucial role in the orientation of the monomer for reactivity.

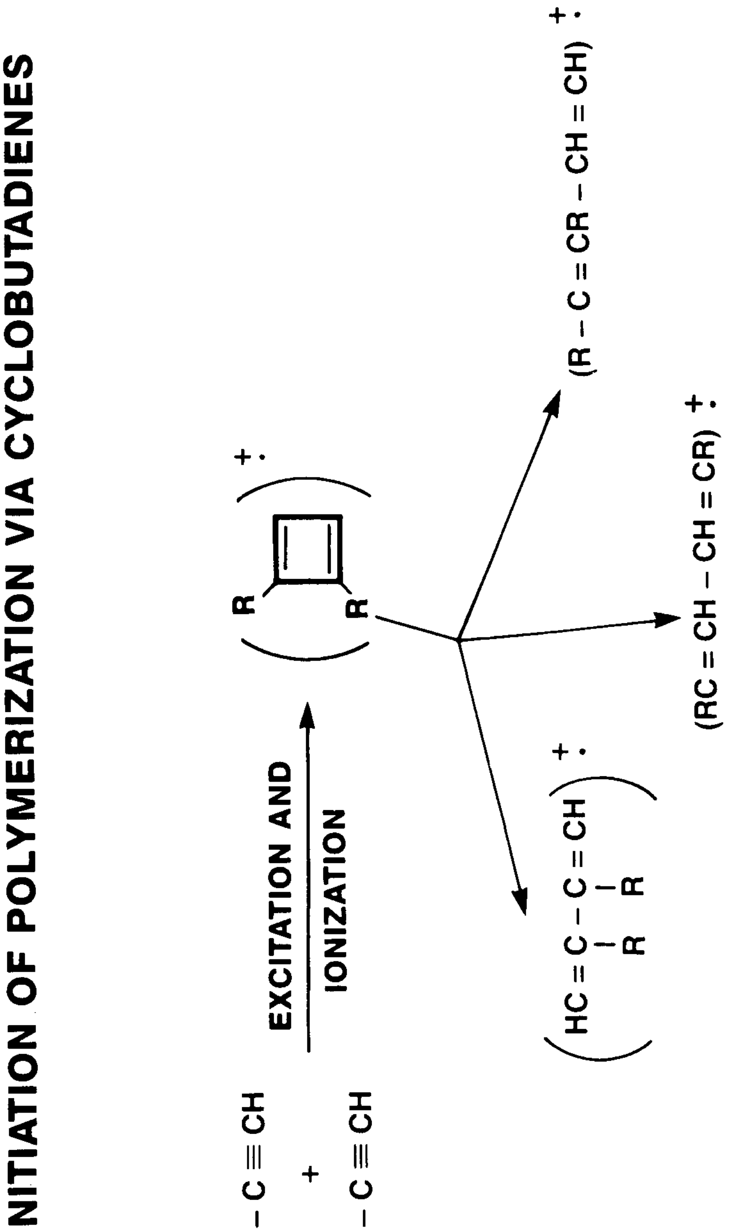
Crystallographic information is required for development of structure-reactivity relationships. A projection of the propiolamide structure revealed an infinite array of C(1)···C(2') acetylenic contacts at 3.82Å and intermolecular NH-oxygen hydrogen bonding.[24] The structure of the semicarbazone, given in the next section, also exhibits significant intermolecular acetylenic contacts. For direct 1,2-addition polymerization of the triple bonds oriented by a nonbonded interaction (hydrogen bond), the contact distances of 3.5-4.0Å must shorten to a covalent bond length of less than 1.5Å, likely requiring a modification of the orientation of the nonbonded interaction.

A priori, in addition to direct 1,2-addition polymerization, it is relevant to consider initiation via photocycloaddition of two acetylenic groups to give a cyclobutadiene, a process not precluded by orbital symmetry considerations. The situation is summarized in Scheme 3. It is important to recognize that the three ring opened cation-radical intermediates in Scheme 3 are constitutionally isomeric to that given above in Scheme 2, and that these intermediates can propagate in the same manner as given above in Scheme 2.

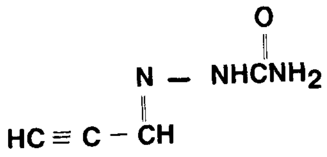
It is also relevant to discuss the observations reported herein *vis-a-vis* Schmidt's topochemical postulate, a structurally-based concept which notes that reaction in the solid state occurs with a minimum of atomic or molecular movement. In the preceding paragraph, it is noted that for the system discussed herein that reaction initiation could proceed either by direct addition oligomerization or via the intermediacy of a cyclobutadiene. While the former possibility is the least motion case, the topochemical postulate, being a structural concept, provides no basis to decide between the two situations. It is also noteworthy that while Schmidt advanced his ideas to emphasize the importance of lattice regularity rather than lattice imperfections for solid state reactivity,[43] we find that the initiation of reaction by ^{60}Co gamma radiation in our systems is strongly influenced by the presence of solvent in lattice defects.

THE CRYSTAL STRUCTURE OF PROPIOLALDEHYDE SEMICARBAZONE

Crystals of the semicarbazone are monoclinic, space group P2/n, with *a* = 10.582(3), *b* = 3.801(1), *c* = 14.065(4)A; β = 109.02(3)^o; Z = 4. The structure was solved using direct methods. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for C, N and O atoms and positional and isotropic thermal parameters for H atoms, using 774 observed reflections for which $F > 3.92\sigma(F)$ and $\Theta_{MoK\alpha} \leq 25.0^o$ led to R = 0.034 and Rw = 0.048. Figure 1 shows a partial packing diagram of the molecule, showing stacks along the crystallographic *b* axis. Dashed lines in the figure indicate important C···C


INITIATION OF POLYMERIZATION VIA CYCLOBUTADIENES
R – C ≡ CH
+
R – C ≡ CH
EXCITATION AND
IONIZATION
R
R
+·
(R – C = CR – CH = CH) +·
(RC = CH – CH = CR) +·
HC = C – C = CH
R R
+·

SCHEME III



$HC\equiv C-CH=N-NHC(=O)NH_2$

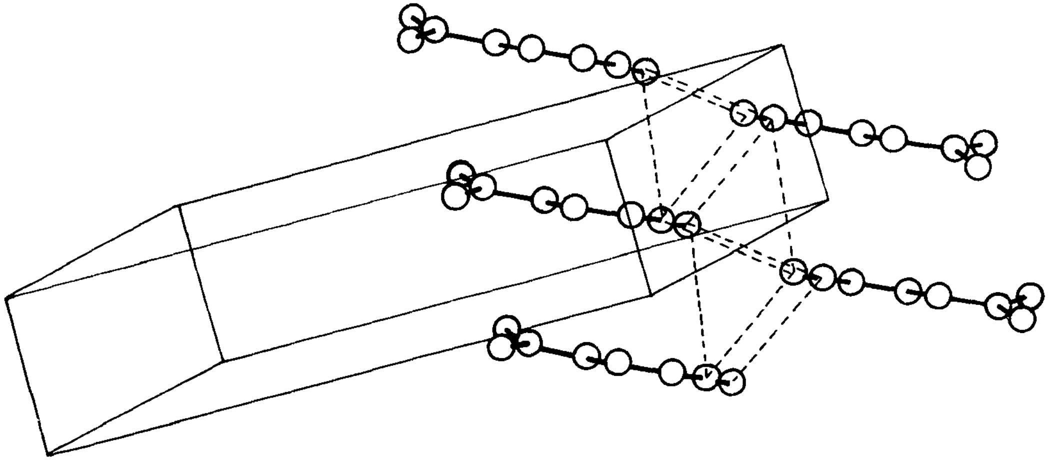


Figure 1. Partial packing diagram of propiolaldehyde semicarbazone showing stacks along the crystallographic b-axis.

contacts <3.80Å; there are three unique contacts of the α-β type at 3.64, 3.66 and 3.77Å, and one of the α-α type at 3.60Å. These are significantly less than the 4.0Å suggested as an upper limit for solid-state reactivity.

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