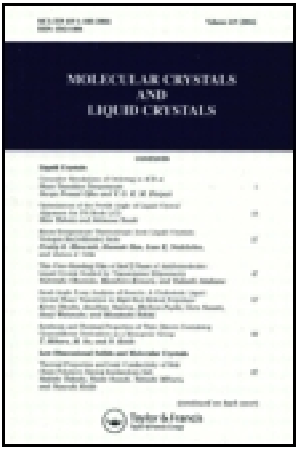

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The Interaction of Vacuum Ultraviolet Light with Crystalline Monoacetylenes: A Progress Report

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THE INTERACTION OF VACUUM ULTRAVIOLET LIGHT WITH CRYSTALLINE MONOACETYLENES: A PROGRESS REPORT

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Abstract With an eye toward a study of crystalline monoacetylene solid state reactivity as an approach to crystallographically ordered polyacetylenes, the crystallographic and absorption and emission spectral characteristics of 10-undecynamide and the cyclohexylurethanes of 5-hexyn-1-ol and 10-undecyn-1-ol have been studied at ambient temperature. Spectral studies at short wavelengths were performed using vacuum ultraviolet radiation from the National Synchrotron Light Source. The compounds investigated are not thermally reactive at temperatures below their melting points and are effectively inert to ^{60}Co gamma radiation at room temperature. The crystal structures of 10-undecynamide and the cyclohexylurethane of 5-hexyn-1-ol have been solved, and both reveal contacts shorter than 3.70 Å between acetylenic carbon atoms. For 10-undecynamide, excitation at all wavelengths between 120 and 300 nm leads to emission at wavelengths greater than 300 nm.

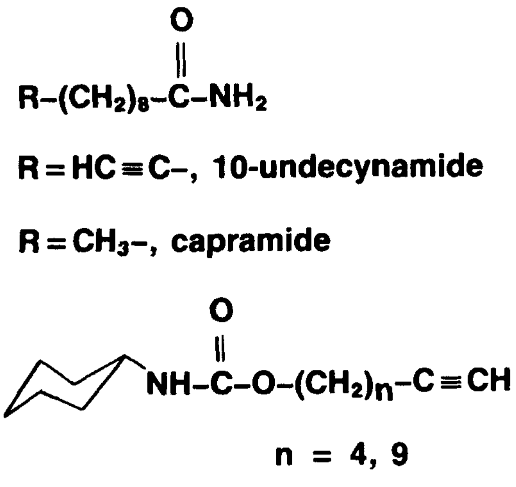
INTRODUCTION

Current interest in the study of crystallographically ordered polyacetylenes and approaches to them largely derives from the reports of interesting electronic, magnetic, and optical phenomena in polyacetylene, $(CH)_x$, a partially crystalline material synthesized by Ziegler-Natta methods which is unstable to ambients. Fully ordered polyacetylenes are also of interest because it is conceivable that their crystal structures could allow significant interchain interactions.

The latter situation is precluded in polydiacetylenes (PDA), the best known class of crystallographically ordered polymers, by the side chains.[1]

Experimentally, the preparation of a crystallographically ordered polyacetylene via a lattice-controlled polymerization has been claimed in only one case.[2] A mixed polyacetylene structure was deduced for the product of a liquid-solid reaction of a PDA with bromine in which crystallographic order is retained.[3] Lattice control of the solid state polymerization of acetylene appears unlikely.[4] Reported examples of solid state reactivity of monosubstituted acetylenes reveal mechanistically divergent situations.[1]

The present experimental program seeks to develop relationships between crystal structure, electronic spectra, photophysical processes, and solid state reactivity in monoacetylenes, $HC\equiv C{-}R$, which are crystalline solids at room temperature. Compounds studied to date in this work include 10-undecynamide, the model compound capramide, and the cyclohexylurethanes of 5-hexyn-1-ol and 10-undecyn-1-ol; their molecular structures are given in Figure 1. The three acetylenes are melt-stable and markedly less reactive to ^{60}Co gamma radiation than analogous diacetylene monomers.[5] The possible use of vacuum ultraviolet light to effect selective photochemistry is clearly of interest.



$R{-}(CH_2)_8{-}C(=O){-}NH_2$

FIGURE 1. Compounds studied.

X-RAY CRYSTALLOGRAPHY

Detailed crystallographic information is clearly central to any discussion of solid state spectra and reactivity. Crystallographic data for the compounds under study are given in Table 1. The lattice constants in Table 1 reveal that 10-undecynamide is isomorphous to the previously studied capramide.[6] Complete structural studies were performed for 10-undecynamide and the cyclohexylurethane of 5-hexyn-1-ol. A view normal to the ac plane of the crystal structure of 10-undecynamide is given in Figure 2, where the distances marked A and B between the terminal acetylene carbons are 3.66 and 3.75 Å, respectively. Contact distances of 3.65 and 3.82 Å were observed between the terminal acetylene carbons of the cyclohexylurethane of 5-hexyn-1-ol. While the contact distances noted in these two structures are significantly shorter than the 4.0–4.2 Å distance commonly taken as an approximate longer limit for topochemical reactivity, it is uncertain at present as to what sort of three-dimensional array would constitute an optimal arrangement for the initiation of solid state reactivity involving terminal acetylenes. This issue has been discussed in detail for diacetylene reactivity.[7]

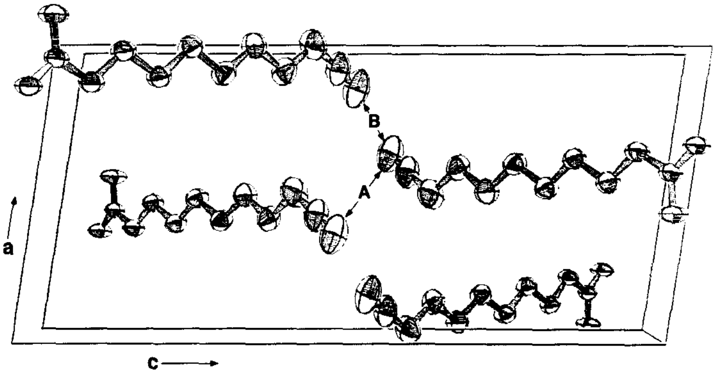


FIGURE 2. View of the crystal structure of 10-undecynamide down the crystallographic b axis. A = 3.66 Å, B = 3.75 Å.

TABLE 1. Crystallographic information

COMPOUND	a, Å	b, Å	c, Å	β	SPACE GROUP	R
10-undecynamide	9.742(2)	5.694(2)	21.276(3)	98.83(2)°	$P2_1/a$	0.049
Capramide	9.830	5.555	21.224	103.45°	$P2_1/a$	0.091
Cyclohexylurethane of 5-hexyn-l-ol	5.109(2)	6.546(2)	40.133(8)	90°	$P2_12_12_1$	0.077
Cyclohexylurethane of 10-undecyn-l-ol	4.90(30)	11.91(9)	37.72(130)	103(1)°	—	—

ELECTRONIC SPECTRA

Preliminary work showed, as expected, that the four compounds under investigation are transparent at wavelengths longer than 230 nm both in solution and the solid state. Solid state spectra were recorded using crystalline thin films, found by x-ray powder diffraction to be the same phase as bulk crystals, grown on silica substrates. Using the facilities of National Synchrotron Light Source (NSLS) Beam Line U9A,[8] spectra were recorded of the thin film samples between 170 and 300 nm. In these initial studies, capramide and 10-undecynamide exhibited the absorption maxima expected[9] for aliphatic amides at 184 and 184.5 nm, respectively. The spectra of both amides indicate additional features on the low energy side of the maximum. The cyclohexylurethane of 5-hexyn-1-ol displayed a maximum at 183 nm; this is apparently the first study of aliphatic urethanes to these short wavelengths.

EMISSION SPECTRA

Preliminary studies in either ethanol solution or in crystalline thin films revealed emission maxima in the 330–380 nm range for the four compounds under investigation. The excitation spectra associated with these emissions were in the 250–300 nm range, wavelengths where no strong absorption is observed. A literature search revealed that amides emit light at comparable wavelengths from a long-lived state.[10]

In experiments using a thin crystalline film of 10-undecynamide on a LiF crystal at NSLS Beam Line U9A, the excitation spectrum (120–300 nm) which leads to emission at wavelengths longer than 300 nm is displayed in Figure 3. In this figure, the relatively small number of counts at wavelengths shorter than ca 125 nm is primarily due to reduced LiF transmission at these wavelengths, and features at higher energy are not precluded. With reference to Figure 3, it is apparent that at least four transitions, of as yet unidentified origins, led to the observed emission. In this context it could be advantageous to regard 10-undecynamide as a trichromophoric molecule in which all of the chromophores, an alkyl acetylene, an alkyl amide, and an alkane chain, can interact. Relevant studies of alkane emissions and their lifetimes in gas, liquid, and solid states have been reported.[8]

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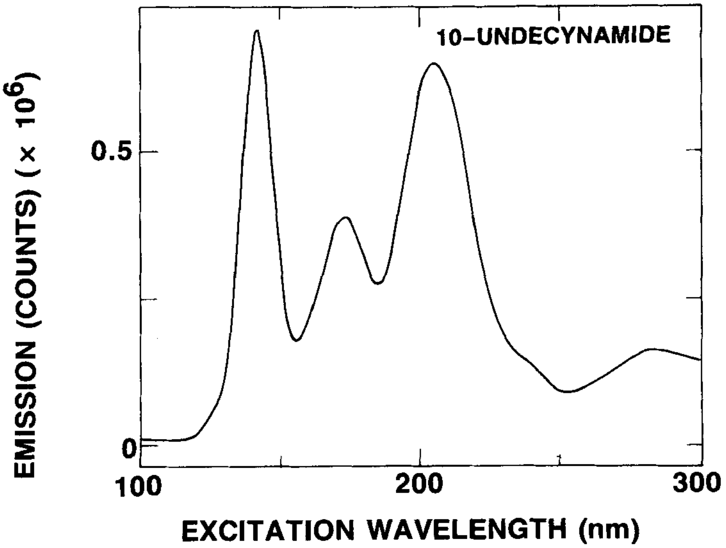

FIGURE 3. 10-undecynamide excitation spectrum for emission at wavelengths longer than 300 nm.

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