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Subject: Informal Quarterly Status Report on
EXPLORATORY POLYMER SYNTHESIS
Under NASA GRANT NGL-15-004-001
Supplement 7 (~~Cont. of Nsg339~~)

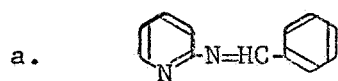
Period Covered: 1 May 1969 to 31 July 1969

By: G. F. D'Alelio, Principal Investigator

CASE FILE
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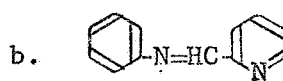
EXPLORATORY POLYMER SYNTHESIS

I. The entire research effort for the period 1 May 1969 to 31 July 1969 was devoted to the project concerned with polymers of enhanced conductivity and a study of the parameters which contribute to conductivity. Polymers were not synthesized during the period and all the research was directed to the study of prototype or model molecules to assure the accuracy of the specific chemistry when it is applied to the polymeric Schiff bases having pyridine rings in the backbone chain, the structures of which were given in the Status Report for the period 1 February 1969 to 30 April 1969, in which the successful syntheses of the following prototype monomers were reported:



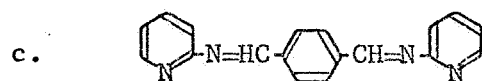
(I)

b.p. 102°C/0.2 mm Hg



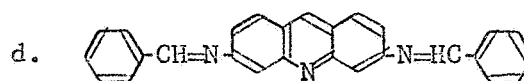
(II)

m.p. 36-37°C



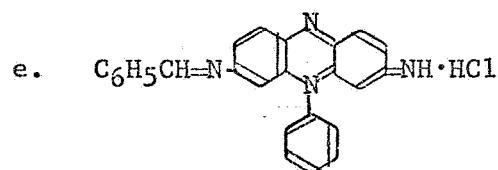
(III)

m.p. 207°C



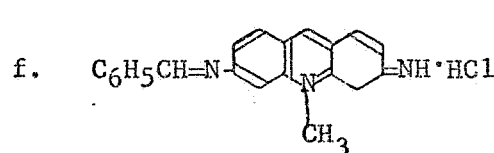
(IV)

m.p. 208-209°C



(V)

m.p. > 300°C



(VI)

m.p. > 300°C.

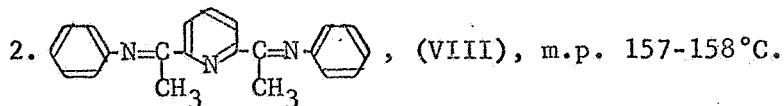
Accordingly, this status report for the second quarter deals solely with the syntheses and reactions of monomers.

II. Pyridine-Type Monomers.

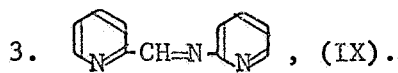
A. Syntheses.

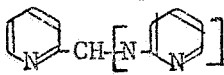


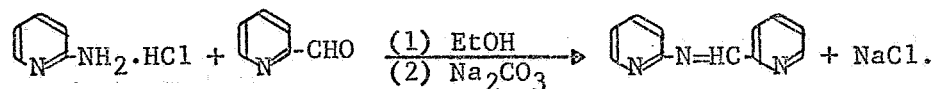
This compound was prepared by the continuous azeotropic method from 2-pyridine carboxaldehyde and p-phenylenediamine in benzene. Its structure was confirmed by elemental analysis, infrared spectrum and NMR.



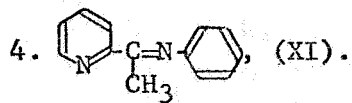
This compound was prepared by the continuous azeotropic method from aniline and 2,6-diacetyl in benzene. Its structure was confirmed by elemental analyses, infrared spectrum and NMR.



Studies are still continuing in attempts to synthesize the monomer. It was established previously that the main product obtained was the bis-compound,  ₂, (X). An attempt was made to pyrolyze the bis-compound with the expectation of obtaining 2-aminopyridine and the desired Schiff base. This experiment was unsuccessful. An attempt is being made to prepare the monomer according to the equation

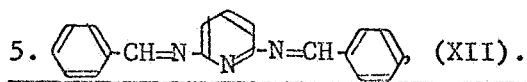


The experiment has been completed. The isolation and purification of the products appear to be difficult and are in progress; the reaction does not appear to be satisfactory.

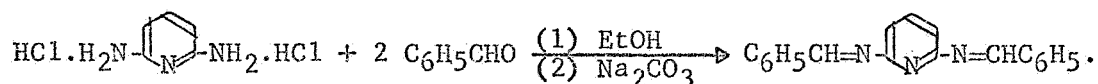


The reaction of 2-acetylpyridine and aniline in benzene using the azeotropic method has been performed. Isolation and purification are in progress;

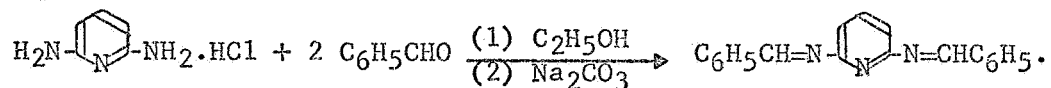
the reaction does not appear to be satisfactory.



The synthesis of this monomer from benzaldehyde and 2,6-diaminopyridine was shown in the first quarterly report to be unsuccessful. Instead of the desired Schiff base, a polymeric polyimine was obtained. An attempt was made, therefore, to react the dihydrochloride of 2,6-diaminopyridine with benzaldehyde in ethanol to obtain the desired product as a reference compound, according to the equation



This required the preparation of 2,6-diaminopyridine dihydrochloride. It appears that the dihydrochloride is either unstable or not isolatable because the reaction of excess gaseous anhydrous HCl with 2,6-diaminopyridine as a dilute solution either in ether or ethyl acetate yielded only the monohydrochloride. This monohydrochloride has been reacted with benzaldehyde according to the equation:



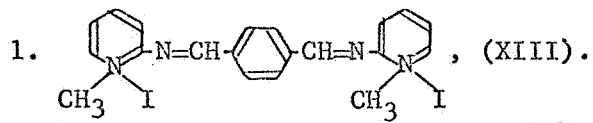
The product isolated melts in the range of 85-89°C and its infrared spectrum shows a peak at 3380 cm^{-1} , indicative of free -NH structures. The reaction appears to be a mixture of substances which were not resolved readily either by thin layer or column chromatography. The experiment is being continued.

III. Derivatives of Pyridine-Type Monomers.

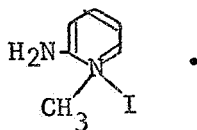
A. Quaternary Derivatives.

The synthesis of one quaternarized Schiff base was reported in the first quarterly letter report; its structure was confirmed by NMR. Anomalous and inconsistent analytical data received after the report have required further.

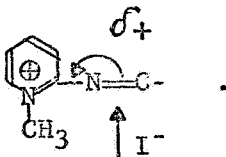
research on this compound and its synthesis. The syntheses of a number of other quaternarized pyridine-type monomers were also undertaken.



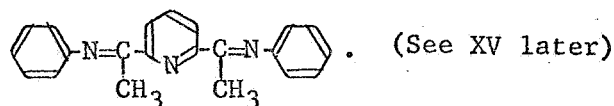
This compound was originally attempted by the reaction of (III) with 2 moles of methyl iodide in DMAC. The crude sample which was precipitated by benzene was evaluated in deuterated DMSO and the integration corresponded exactly to that required for (XIII). The remainder of the sample was purified twice by dissolving it in DMAC and precipitating it with benzene and dried at room temperature at 0.5 mm Hg pressure, and submitted for analysis. The elemental analysis corresponded exactly to a compound of the structure



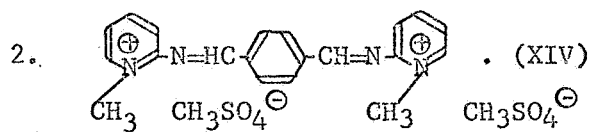
Its infrared spectrum showed strong bands for the presence of -NH_2 and the quaternary structure. Anomalous reactions were also encountered in other attempted quaternarizations performed in DMAC. This observation was shown to be specifically true of those Schiff bases in which the amino nitrogen atoms are in the ortho position to the pyridine nitrogen, that is, the 2- or 2- and 6- positions. The probable explanation is that the positive quaternarized nitrogen withdraws electrons from the -C=N- Schiff base linkage, leaving a partially positive charge which is then attacked by the negative iodine atom:



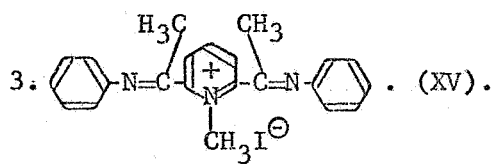
It appears also that DMAC participates in the reaction in some fashion which, at present, is not understood. That DMAC participates was also encountered in the quaternarization of



Accordingly, the quaternarization was attempted in CH_3NO_2 primarily because it would also tend to neutralize the charge on the quaternarized pyridine nitrogen. The reaction of the Schiff base with 4 moles of CH_3I was performed in CH_3NO_2 for 9 hours at 50°C . The product was isolated by precipitation with benzene or ether and found to be a mixture of 25% mono-quaternary and 75% of diquaternary derivatives complexed with one molecule of CH_3NO_2 to the quaternarized pyridine nitrogen. Thus the mono-quaternary was complexed with one mole of CH_3NO_2 , and the di-quaternary was complexed with 2 moles of CH_3NO_2 . Since it has been established that quaternarization by CH_3I is a slow reaction, the reaction is being repeated for a longer period of time, during which the extent of reaction will be followed by TLC. Since preliminary experiments have also shown that quaternarization with $(\text{CH}_3)_2\text{SO}_4$ is more facile and complete than with CH_3I ; quaternarizations with $(\text{CH}_3)_2\text{SO}_4$ have also been performed.

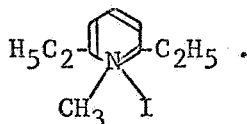


The quaternarization was performed using $(\text{CH}_3)_2\text{SO}_4$ and the corresponding Schiff base (III) in nitromethane. The elemental analysis of the crude product, m.p. $80-85^\circ\text{C}$, isolated by evaporation at reduced pressure of the reaction solution, indicates that the compound has been obtained as a complex with approximately 2 moles of nitromethane. The infrared spectrum appears to confirm the presence of the product desired. Purification of the product is in progress.



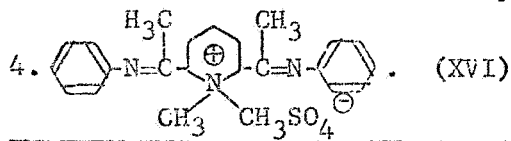
(a) The synthesis of this compound was attempted using CH_3I and the

diketanyl, (VIII), in DMAC. A product melting at 177-179°C was isolated which was not the desired compound, $C_{23}H_{25}N_3I_2$; instead the elemental analyses and infrared spectra established the compound as $C_{10}H_{16}NI$ of the structure,

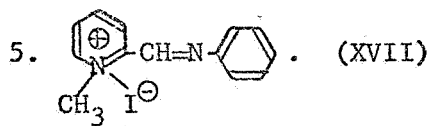


This indicated a reductive-cleavage in which the DMAC probably participated since the same product was not obtained when nitromethane was used as the reaction medium.

(b) The quaternarization was repeated using CH_3I and VIII in CH_3NO_2 at 50°C until TLC showed only one reaction product and that the reaction was complete. The product was isolated by evaporation of the solvent at reduced pressure and dried; the yield of crude product was substantially quantitative, m.p., 90-95°C. Purification is in progress to prepare a sample for analysis.



The quaternarization was performed using $(CH_3)_2SO_4$ and VIII in nitromethane. The m.p. of the isolated product, after reprecipitation, was 171-173°C. Elemental analysis and its infrared spectrum confirmed the synthesis of the compound. Some CH_3NO_2 is complexed with the product. Further studies are in progress.

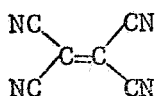


(a) Quaternarization was attempted using CH_3I and the Schiff base (II) in $(C_2H_5)_2O$. Reaction did not occur.

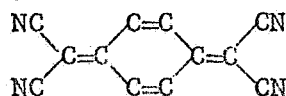
(b) The reaction of CH_3I and (II) in DMAC yielded a compound, m.p. 65-67°C, whose elemental analysis and infrared spectrum confirmed the structure of the desired compound (XVII).

B. Charge-Transfer Complexes.

Exploratory experiments have been performed to establish whether or not the prototype pyridine monomers will form charge transfer complexes with selected acceptors such as TCNE and TNCQ:



TCNE



TCNQ

To the present, experimentation has been performed only with TCNE and Schiff base (III).

1. III.n TCNE Complexes.

The reactions of Schiff base (III) with TCNE were performed in DMAC in which both reactants were soluble. The Schiff base (III) has two pyridine rings, each of which would be expected to act as donor to at least one molecule of TCNE. Thus, the equivalent complex should be (III.2 TCNE). In efforts to establish the value of n for (III), a series of reactions were performed in DMAC using a mole ratio of 1 mole of (III) with one, two and four moles of TCNE respectively. The reaction temperature was 50°C for five hours. In all cases, a marked change in ^{the} almost colorless solution containing the monomer and the TCNE occurred within the first few minutes of the reaction; and as the reaction continued, the color darkened to a maximum and did not change further. The color of the solutions at ten minutes of reaction time and the final color for the compositions containing the various moles of TCNE per each mole of (III) were

Monomer	Moles of TCNE	Color at 10 min.	Final Color
III	1	orange	brown
III	2	brown	black
III	4	black	black

At the end of the reaction time, the solutions were divided into two equal portions, A and B, and processed separately.

Portion A. Evaporated Product.

One-half of each solution was concentrated at 40°C under 0.5 mm Hg pressure to obtain solid products. The yield at this stage, based on one-half of the total, for the three complexes were found to be:

<u>Complex</u>	<u>Yield % of Theory</u>
III. 1 TCNE	100.0
III. 2 TCNE	110.0
III. 4 TCNE	110.0

Analysis of the products showed in the 2 TCNE and the 4 TCNE complexes that DMAC had been retained in the complex as follows:

<u>Complex</u>	<u>Moles of DMAC Retained</u>
III. 1 TCNE	0.0
III. 2 TCNE	2.0
III. 4 TCNE	3.0

Portion B. Precipitated Products.

The remaining halves of the solutions of the complexes were precipitated by the addition of benzene and the precipitates isolated by filtration. The precipitates were then redissolved in DMAC precipitated by $(C_2H_5)_2O$, isolated and dried at 50°C in a vacuum oven. Additional quantities of products were obtained by concentration of the mother liquors and purified by redissolution and DMAC followed by precipitation. The total yields of the precipitated complexes for the various ratios of TCNE used were:

<u>Complex</u>	<u>Yield % of Theory</u>
III. 1 TCNE	100.0
III. 2 TCNE	110.00
III. 4 TCNE	110.00

Elemental analysis of the precipitated III. 1 TCNE confirmed the 1:1

complex and that the product did not contain retained DMAC.

Elemental analyses of the precipitated III. 2 TCNE showed the presence of oxygen and that it appeared to complex with approximately one mole of DMAC.

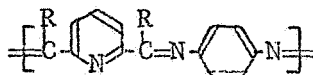
Elemental analyses of the precipitated III. 4 TCNE showed the presence of oxygen and it appeared to be complexed with approximately four moles of DMAC.

The conclusions concerning the retention of DMAC, on the basis of oxygen analyses, are only tentative at this time. Further studies will be performed to establish that the complex has not reacted with oxygen, even though the complexes are very stable. For the present, it appears to be more than fortuitous that the elemental analyses of these complexes are close to the values expected for the complexes with DMAC. The infrared spectra of the various complexes showed strong bands for CN at 2200 cm^{-1} and the spectra of the three complexes were substantially identical except that in the case of the 1:1 complex, the intensity at 2200 cm^{-1} was noticeably less than for the 1:2 or 1:4 complex. In addition, the three complexes did not melt when heated to 360°C . Attempts to purify the complexes further will be performed.

IV. Discussion.

The current research on the prototype monomers, both with regard to their syntheses and reactions has opened up previously unknown areas of chemistry for these substituted pyridines. The type of chemistry encountered is in marked contrast with the chemistry which was expected on the basis of the published chemistry on related pyridines. These anomalous reactions have made rapid progress difficult but the attrition that has come from continued effort has shown that the problems can be solved. Of particular interest is the findings that the chemistry of pyridines having amino- or azomethine linkages ortho to the nitrogen of the pyridine ring is not what would be predicted, complicating not only the synthesis of monomeric or polymeric Schiff base

but also the quaternarizing of both monomers and polymers. The data obtained to date tentatively points to the fact that the pyridine-type Schiff base polymer should be of the structure wherein the carbonyls are attached to the pyridine ring, for example,



to permit successful quaternarization. The finding that quaternarization is best performed in CH_3NO_2 preferably with $(\text{CH}_3)_2\text{SO}_4$ rather than CH_3I is also considered important.

It is also believed that the results obtained to date more than justify, not only the importance, but the necessity of establishing the chemistry on prototype compounds before attempting the chemistry on polymers containing the projected repeating units. Undoubtedly, without such information, the results obtained from the quaternarization of a pyridine-type Schiff base polymer would be uninterpretable.