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POLY(DI-1,2-DIAZINEDIYLETHENE-1,2-DIOLS)

RICHARD H. WILEY

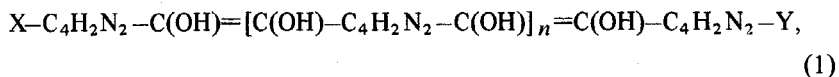
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Palo Alto, California 94306

ABSTRACT

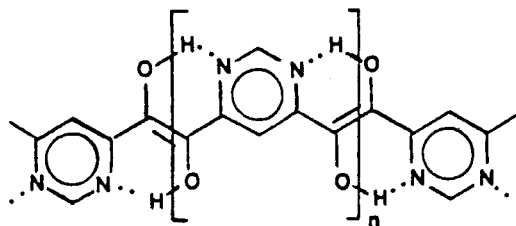
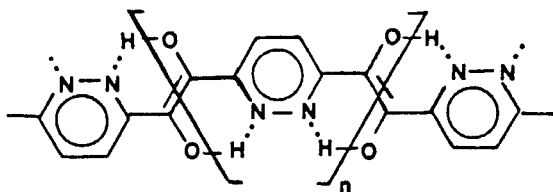
Oligomers of 2 to 9 units having a diazinediylethene-1,2-diol repeating unit have been prepared by a cyanide ion-catalyzed self-condensation of pyridazine-3,6-, pyrazine-2,5-, or pyrimidine-4,6-dialdehyde. These are the first known representatives of a class of conjugated polymeric enediol materials derivable specifically from these three structurally related diazine dialdehydes. The oligomers, isolated as their potassium salts, are soluble in acid and base with an isoelectric point at pH 6.5. In base, they give dark red-brown solutions whose color, attributable to their semidione ion radical form, is rapidly discharged by oxygen (air) or by the addition of ferric ion, which gives an immediate precipitation of the black chelate. Of several possible methods evaluated for the preparation of the free dialdehydes, only that involving ozonization of the distyryldiazines was found to be of preparative value.

INTRODUCTION

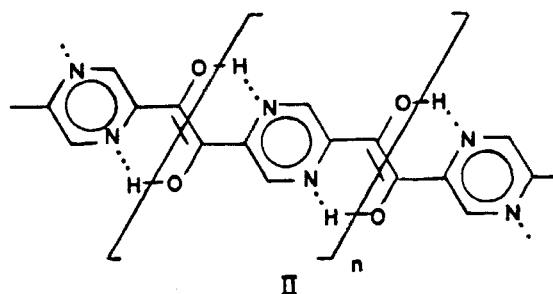
The enediol structure, $-\text{C}(\text{OH})=\text{C}(\text{OH})-$, characteristic of a variety of redox systems [1, 2] and of the enolic forms of the benzoin derivatives derived from azine aldehydes—such as pyridine-2-aldehyde [3], pyridazine-3- [4], pyrazine-2-aldehyde [5], and pyrimidine-4-aldehyde [6]—has not been incorporated in any azine oligomeric or polymeric structure. Such diazinediyl enediols (Formulas 1 and 2):



derived from dialdehydes, in which the formyl groups are not *ortho* to each other and in which each formyl is adjacent to one and only one ring nitrogen, are structurally possible from three dialdehydes only: pyridazine-3,6-, pyrazine-2,5-, and pyrimidine-4,6-dialdehydes. The chelating [7], redox (via semidione [1, 2, 8]), and charge-transfer properties characteristically possible in these polymeric structures have prompted the present study of these monomeric dialdehydes and the oligomeric/polymeric polymers derivable from them. It is to be noted that benzoin polymers from pyridine-2,6-dialdehyde [9, 10], and similarly substituted diazine types with their di-*ortho* (to N) substituted enediol structures, will not have chelating geometry of the type illustrated in Formula 2.



(2)



II

EXPERIMENTAL

2,5-Dimethylpyrazine (Pyrazine Specialties) and 4,6-dimethylpyrimidine (Aldrich) were used as obtained commercially. Analyses (on vacuum-dried samples) were performed by Stanford University Microlab.

3,6-Dimethylpyridazine. Equimolar quantities of acetylacetone (114 g) and hydrazine hydrate (50 g) were dissolved in 1 L absolute ethanol and refluxed for 30 min. The ethanol was evaporated under vacuum and the residue refluxed in dry benzene (1 L) with 7.5 g of 10% palladium on carbon for 10 h. The residue, after vacuum evaporation of the benzene, was fractionated to give 92 g (85% yield), bp 85-95°C/10 torr, of 3,6-dimethylpyridazine, which crystallizes on cold storage.

3,6-Distyrylpyridazine. A solution of 2 g zinc chloride in 20 g 3,6-dimethylpyridazine and 60 g benzaldehyde, freshly distilled, was heated to gentle reflux for 2 h and then slowly distilled to collect the benzaldehyde/water azeotrope in a Dean-Stark trap. After collection of 6 mL (theory 7.2 mL) water, the reaction mixture was cooled and the precipitated solid product collected, washed with ethanol (or acetone), and dried. Yield, 26 g. Recrystallized from ethanol or methyl ethyl ketone, mp, 226-228°C, reported [12] 230°C.

Analysis. Calculated for $C_{20}H_{16}N_2$: C, 84.51; H, 5.64; N, 9.86%. Found: C, 84.37; H, 5.6; N, 9.8%.

2,5-Distyrylpyrazine was prepared as previously described [16], mp 223°C, reported 230°C. Yield 13%.

Analysis. Calculated for $C_{20}H_{16}N_2$: C, 84.51; H, 5.64%. Found: C, 84.28; H, 5.7%.

4,6-Distyrylpyrimidine was prepared by the technique described for the pyrazine analog [16], mp 162°C, reported [17] 163°C. Yield 14%.

Pyridazine-3,6-dialdehyde. Ozone was passed through a stirred suspension of 2 g distyrylpyridazine in 200 mL methanol cooled to -40°C until the solid dissolved and the blue color of ozone appeared (30-90 min). The following operations were carried out under a blanket of nitrogen. The solution was held at -40°C and to it was slowly added a 23% solution of potassium metabisulfite to the point of a negative starch iodide test. The mixture was warmed to 15°C and filtered to separate a precipitate, which was washed with methanol. The washings were combined with the filtrate and this solution evapor-

ated under vacuum at 30°C to remove the methanol. The residual aqueous solution was purified by extraction with ether, first while acid (pH ~3); then again, after making basic (while cold and with cold 3 N potassium hydroxide). The ether-extracted alkaline solution was extracted 10 times with ethyl acetate, and the ethyl acetate extracts evaporated. There remained a semisolid residue from which, on low temperature vacuum sublimation, there was obtained 0.6 g of slightly yellow, crystalline solid. Alternatively, the semisolid crude residue was recrystallized from ethyl acetate as white crystals, soluble in water and hygroscopic, insoluble in ether, and unstable to heat and air exposure, mp 106-108°C.

Analysis. Calculated for $C_6H_4N_2O_2$ (0.11H₂O): C, 52.94; H, 2.94; N, 20.58%. Found: C, 52.29; H, 3.24; N, 20.23%.

Poly [Di-1,2-(3',6'-pyridazinediyl)ethene-1,2-diol]. The pH of the ether extracted, aqueous solution of the dialdehyde prepared as in the preceding example was adjusted, with cooling, to pH 10-11 and 1 mL of cold 10% potassium cyanide was added, with cooling and stirring to dissipate the considerable heat of reaction. There was an instantaneous formation of a red-brown precipitate which slowly turned black. After 2 h at room temperature, the pH was adjusted to 6.5. The precipitate was collected and dried in vacuum at 55°C to give 0.6 g (0.2-1.9 g in repetitive runs) of a black solid pentamer, soluble in alkali to give a deep maroon solution, soluble in acid, decolorizing on exposure to air to give a yellow solid. Analysis conforms to the pentamer monopotassium salt tetrahydrate (Formula 1, $n = 3$; X = CHO, Y = COOK).

Analysis. Calculated for $C_{30}H_{27}N_{10}O_{15}K$ (4H₂O): C, 44.66; H, 3.34; N, 17.3%. Found: C, 44.44; H, 3.61; N, 17.36%.

This procedure was followed using 0.2 g of the dialdehyde isolated by ethyl acetate extraction and recrystallized as described above. The analysis conformed to a heptamer tripotassium salt tetrahydrate (Formula 1, $n = 5$, X = Y = H).

Analysis. Calculated for $C_{40}H_{26}N_{14}O_{12}K_3$ (4H₂O): C, 44.36, H, 3.05; N, 18.11%. Found: C, 44.61; H, 3.31; N, 18.18%. Neutral equivalent 1106.

Poly [Di-1,2-(2',5'-pyrazinediyl)ethene-1,2-diol]. The dialdehyde was prepared as described above by the low-temperature ozonization of 2,5-distyrylpyrazine. From 2 g distyrylpyrazine there was obtained 15 mL of the ether-extracted aqueous solution of the dialdehyde. The pH of this solution was adjusted to 10, and 5 mL of 2% aqueous potassium cyanide was added. There was an immediate precipitation. The reaction mixture was

heated for 5 min on a steam bath. The red-brown precipitate was collected. On drying at 55°C in vacuum, there was obtained 0.3 g of a black solid, soluble in alkali to give a maroon solution, and soluble in acid. Acid base titration established the isoelectric point at pH 6.5. The analysis conformed to that of a potassium salt of a nonamer hydrate (Formula 1, $n = 7$, $X = Y = \text{COOK}$).

Analysis. Calculated for $\text{C}_{54}\text{H}_{33}\text{N}_{18}\text{O}_{20}\text{K}_3$ ($12\text{H}_2\text{O}$): C, 40.80; H, 3.27; N, 15.87%. Found: C, 41.46; H, 3.26; N, 15.78%. Neutral equivalent 1667.

Poly [Di-1,2-(4'6'-pyrimidinediyl)ethene-1,2-diol]. The dialdehyde was prepared as described above. One milliliter of 10% potassium cyanide was added to the ether-extracted alkaline solution from the ozonization reaction. There was an immediate precipitation of a black solid. The reaction mixture was heated for 15 min, collected, and vacuum dried to give 0.3 g of a black solid, soluble in acid and in base, turning colorless on standing in air. The analysis conformed to that of a decarboxylated monopotassium salt, heptamer tetrahydrate (Formula 1, $n = 5$, $X = \text{H}$, $Y = \text{COOK}$).

Analysis. Calculated for $\text{C}_{41}\text{H}_{27}\text{N}_{14}\text{O}_{18}\text{K}$ ($4\text{H}_2\text{O}$): C, 46.85; H, 3.33; N, 18.66%. Found: C, 47.00; H, 3.54; N, 18.71%. Neutral equivalent 1360.

Di[1,2-(6,6'-dicarboxy-3,3'-pyridaziny)] ethene-1,2-diol. Two grams of 3,6-distyrylpyridazine in 200 mL methanol was cooled to -50°C. Ozone was passed in until solution was complete. Two milliliters of dimethyl sulfide was added at -50°C and the solution warmed to room temperature under nitrogen and tested to assure negative starch iodide reaction (Caution). Five milliliters of water was added. The solution was vacuum evaporated at room temperature to remove the methanol, taken up in 10 mL of water, and ether extracted. The cold, extracted aqueous solution was adjusted to pH 9 with cold dilute potassium hydroxide. A solution of 0.1 g potassium cyanide in 2 mL water was added. Heat was evolved and a precipitate formed. The mixture was heated on a steam bath for 10 min. The precipitate was collected, washed, and dried. It was soluble in alkali to give a red solution which turned yellow when blown with air and formed a black solid precipitate on adding ferric chloride solution. The analysis conformed to that of a dimer (Formula 1, $n = 0$, $X = Y = \text{COOH}$).

Analysis. Calculated for $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_6 \cdot \text{H}_2\text{O}$: C, 44.72; H, 3.11; N, 17.4%. Found: C, 44.93; H, 3.19; N, 17.45%.

Pyridazine-3,6-dicarboxylic Acid. The procedure of the preceding experiment was followed using 1 g distyrylpyridazine in 30 mL methanol at -25°C and 1 mL dimethyl sulfide. The product from the potassium cyanide addition precipitated as the monopotassium salt.

Analysis. Calculated for $C_6H_3N_2O_4K$: C, 34.95; H, 1.5; N, 13.6%. Found: C, 35.11; H, 3.72; N, 14.04%.

Recrystallized from dilute hydrochloric acid as the free acid.

Analysis. Calculated for $C_6H_4N_2O_4$ ($0.33H_2O$): C, 41.4; H, 2.68; N, 16.1%. Found: C, 41.32; H, 2.80; N, 16.26%.

Poly [Di-1,2-(2',5'-pyrazinediyl)ethene-1,2-diol]. The preceding procedure for ozonization, using dimethyl sulfide to decompose the peroxide but run at $-50^\circ C$ throughout, was followed with 2 g 2,5-distyrylpyrazine. The product precipitated from the alkaline solution and was isolated as a yellow solid. The analysis conformed to that of the dipotassium salt of the trimeric dicarboxylic acid tetrahydrate (Formula 1, $n = 1$, $X = Y = COOK$).

Analysis. Calculated for $C_{18}H_{10}N_6O_8K_2$ ($4H_2O$): C, 36.73; H, 3.06; N, 14.28%. Found: C, 36.66; H, 2.91; N, 14.38%.

DISCUSSION

Pyridazine-3,6-dialdehyde and the corresponding 3,6-dicarboxylic acid monopotassium salt were prepared by ozonolysis of 3,6-distyrylpyridazine. 3,6-Distyrylpyridazine was prepared in good yields from dimethylpyridazine (available directly by a simple modification of the previously described [11] reaction of acetonylacetone with hydrazine hydrate) by condensation with benzaldehyde as previously described [12]. Ozonolysis, a process also useful for the preparation of pyrazinealdehyde [13] and pyridinedialdehydes [10], has been adapted, by use of a bisulfite ozonide decomposition step, to the preparation of the much more sensitive dialdehydes. Attempts to prepare the dialdehyde by the nitron [14] reaction gave reaction mixtures from which the dinitrophenylhydrazone of the dialdehyde was isolated, but attempts to isolate the free aldehyde by extraction or chromatographic techniques were unsuccessful, presumably due to the thermal and oxidative lability of the dialdehyde in the reaction mixtures. The hydride reduction of the diester [10], the manganese dioxide [4], and the selenium dioxide [15] oxidations of the dimethyl- or dihydroxymethylpyridazines proved to be cumbersome because of their solubility characteristics and also because of the instability of the dialdehyde. The use (at higher temperatures) of dimethyl sulfide for decomposition of the ozonide [16] gave unisolated aldehydes from which a dimer (azinoin) and a dicarboxytrimer were isolated.

Pyridazine-3,6-dialdehyde was isolated as white crystals, mp $106-108^\circ C$, recrystallized from ethyl acetate, or as a yellow solid, by low-temperature

vacuum sublimation from the ozonolysis (bisulfite decomposition) reaction mixture. The sublimation must be carried out below the temperature of decomposition ($\sim 30\text{--}40^\circ\text{C}$). After isolation the dialdehyde, which is hygroscopic, was stored under nitrogen, cold, and in the dark for a few days. On standing, it slowly turned green and then to a black oily residue. It need not be isolated as both the isolated form and the purified ozonolysis reaction mixture have given the same dinitrophenylhydrazone and both give the polyenediol oligomers. The isolated dialdehyde gave the higher molecular weight polymeric product.

The oligomeric structure (Formulas 1 and 2) was formed from the isolated pyridazine-3,6-dialdehyde (heptamer, $n = 5$), or from the solution of the dialdehyde prior to isolation (pentamer, $n = 3$), by addition of aqueous alcoholic potassium cyanide to an aqueous alcoholic solution of the dialdehyde. The oligomers are red-brown to black solids which precipitate from the reaction mixture under controlled conditions of pH and concentration. The isoelectric point of the oligomers is at pH 6.5 and the oligomers are soluble in either acid or base. The dark red-brown basic solution, presumably the semidione ion radical [2, 8], decolorized rapidly on exposure to air. The color was also discharged immediately with the formation of a black precipitate on addition of ferric ion. As with other ionic polymers, the molecular weight is probably indeterminate. Titration data indicate approximate neutral equivalents (for monopotassium salts) in the 1100 range. Elemental analyses confirm but, it is realized, do not provide conclusive proof of the assigned structures.

Pyrazine-2,5- and pyrimidine-4,6-dialdehydes were prepared from their corresponding distyryl derivatives [17, 18] by the above-described ozonization procedure and converted to their oligomeric diazinediylenediols directly from the ether extracted aqueous solution without isolation to give a nonamer ($n = 7$, pyrazine) and a heptamer ($n = 5$, pyrimidine). Both have properties such as those described for the pyridazine oligomers.

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