SOME PYRAZOLID-3-ONE DERIVATIVES

V. Dipyrazolidonylarylenes*

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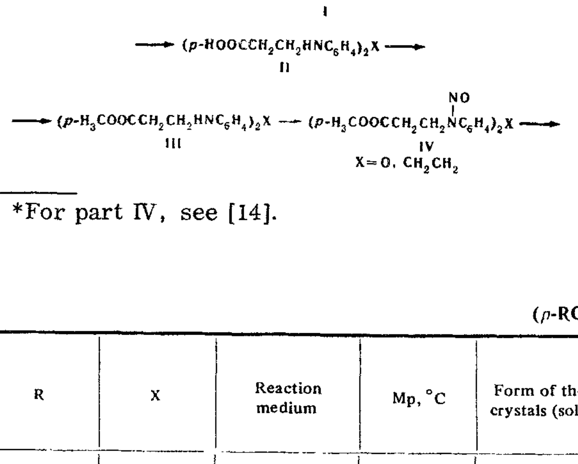
In order to study their photographic properties, starting from the corresponding aromatic diamines the first representatives of a number of dipyrazolidonylarylenes have been synthesized: di[4-(pyrazolid-3-on-1-yl)phenyl] oxide and 1,2-di[4-(pyrazolid-3-on-1-yl)phenyl]ethane.

After Kendall's discovery [1] of the photographic properties of 1-phenylprazolid-3-one, many substances of this class became known. Attempts were made to elucidate the relationship between the structure and photographic properties of these substances [2, 3] and the mechanism of their action was studied [4]. It was shown that the reaction center in the molecule of a 1-arylpyrazolidone in the development process is the pyrazolidone ring [4, 5].

The object of the present work was the synthesis of substances the molecules of which would contain two pyrazolidone rings. These substances could be of interest in the development of light-sensitive cinematographic materials.

The synthesis of the first representatives of this class that we have effected [6] started from di(4-aminophenyl) oxide and 1, 2-di(4-aminophenyl)ethane.

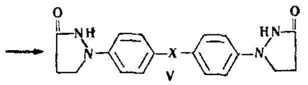


$$(p\text{-}H_2NC_6H_4)_2X \longrightarrow \underset{\text{I}}{(p\text{-}NCCH_2CH_2HNC_6H_4)_2X} \longrightarrow$$

$$\longrightarrow \underset{\text{II}}{(p\text{-}HOOCCH_2CH_2HNC_6H_4)_2X} \longrightarrow$$

$$\longrightarrow \underset{\text{III}}{(p\text{-}H_3COOCCH_2CH_2HNC_6H_4)_2X} \longrightarrow \underset{\text{IV}}{(p\text{-}H_3COOCCH_2CH_2\overset{\text{NO}}{\overset{|}{N}}C_6H_4)_2X} \longrightarrow$$

$X = O,\ CH_2CH_2$



V

As can be seen from the scheme, the first stage of the process is the dicyanoethylation of the aromatic diamines. According to the literature [7] such reactions take place under fairly severe conditions (in a tube, atmosphere of nitrogen, in the presence of copper acetate, 9–15 hr, 90° C). It was found, however, that the dicyanoethylation products are readily formed when the appropriate diamine and an excess of acrylonitrile in glacial acetic acid is heated in the water bath, in analogy with a published process [8].

Fedotova et al. [7] concluded that these substances were unreactive and, in particular, that they do not undergo saponification on being boiled with alkali. According to our results, on being boiled with a 40% solution of caustic soda the dicyanoethylated derivatives of p-phenylenediamine and compounds of type I are readily converted into the disodium salts of the corresponding diacids, which crystallize out when the reaction mixture is cooled and can then be converted into the diacids or diesters. We have tested this method of saponifying cyanoethylated amines and isolating the amphoteric amino acids on a number of other compounds and have found it to be very convenient.

The esterification of the diacids II, the nitrosation of the diesters III, and the reduction of the dinitrosoamines IV took place without complications. The

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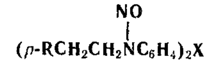
*For part IV, see [14].



$$(p\text{-}RCH_2CH_2\overset{\text{NO}}{\overset{|}{N}}C_6H_4)_2X$$

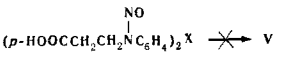
R	X	Reaction medium	Mp, °C	Form of the crystals (solvent)	Empirical formula	Found, %	Calculated, %	UV spectra		Yield, %
								λ_{max}, nm	lg ε	
CN	O	20% HCl	83,5—84	Prisms (methanol)	$C_{18}H_{16}N_6O_3$	22.93 23.19	23.06	221; 285	4.33; 4.22	66.2*
COOH	O	20% HCl	145,5—146	Plates (methanol)	$C_{18}H_{18}N_4O_7$	13.83 13.81	13.92	223; 285	4.32; 4.23	69.5
CN	CH_2CH_2	10% HCl	130—131	Plates (methanol)	$C_{20}H_{20}N_6O_2$**	22.24 22.38	22.32	215; 279	4.23; 4.06	82.5
COOH	CH_2CH_2	20% HCl	159(decomp.)	Prisms (ethanol)	$C_{20}H_{22}N_4O_6$	13.75 13.68	13.52	217; 278	4.33; 4.18	84.8
$COOCH_3$	CH_2CH_2	CH_3COOH	137—138	Needles (CH_3COOH)	$C_{22}H_{26}N_4O_6$	12.63 12.42	12.66	215; 278	4.31; 4.17	60.2

*Extracted from the reaction mixture with chloroform.

**Found, %: C 63.89, 63.92; H 5.50, 5.55. Calculated, %: C 63.81; H 5.35.

final products V consisted of substances sparingly soluble in the usual organic solvents and with well-marked reducing properties. The UV spectra of these substances are similar and, as compared with the spectrum of 1-phenyl-pyrazolid-3-one, have a marked bathochromic shift and a higher absorption coefficient. The molecular weight of V (X = 0), determined by mass spectroscopy (338), confirmed the structure of the substance.

Attempts to obtain compound V by the reduction of the N-nitroso derivatives of the diacids VI, as we proposed previously [9] for the 1-carboxyphenylpyrazolid-3-ones, proved unsuccessful.

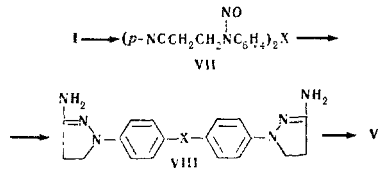


$$(p\text{-}HOOCCH_2CH_2\overset{NO}{\overset{|}{N}}C_6H_4)_2X \not\longrightarrow V$$

VI

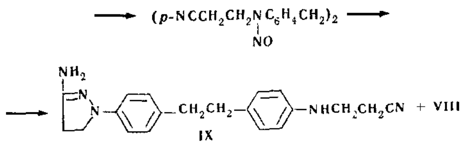
X = O, CH_2CH_2

The total yield of V could be raised approximately twofold with a simultaneous shortening of the process by nitrosating the nitriles I with subsequent reduction and hydrolysis [10].



Intermediate products formed in this process are the di(aminopyrazolidinyl)-arylenes (VIII), which, in some cases, may have independent value as development activators [11].

In the reduction of the nitrosoamine (VII) (X = CH_2CH_2), in addition to the main compound VIII (X = CH_2CH_2), a small amount of a substance $C_{20}H_{35}N_5$ was isolated which is apparently the result of the reduction of one NO group and the splitting out of the second, and has the structure IX.



It must be mentioned that attempts to obtain the simplest representative of the class of dipyrazolidonyl-arylenes from p-phenylenediamine by similar methods were unsuccessful. In all cases the reduction of the corresponding nitrosoamines took place with the cleavage of the N—N bond. This undesirable process frequently competes with the reduction reaction [12].

The authors express their deep gratitude to V. I. Zaretskii for the mass spectrometric determination of the molecular weight.

EXPERIMENTAL

Di[4-(N-β-cyanoethylamino)phenyl]oxide (I, X = 0). A mixture of 15.6 g of di(4-aminophenyl) oxide, 40 ml of acrylonitrile, and 20 ml of glacial acetic acid was heated in the water bath for 7 hr and was left overnight at room temperature. The precipitate that had deposited was filtered off, washed with water and methanol, and dried. Yield 9.0 g (37.6%). Colorless plates with mp 120.5–121° C (from methanol). λ_{max} 257, 306 nm; log ε 4.43, 3.64. (The spectra of all the substances were taken in ethanolic solution at a concentration of 5×10^{-5} mole/l.) Found, %: N 18.64, 18.54. Calculated for $C_{18}H_{18}N_4O$, %: N 18.29.

1,2-Di[4-(N-β-cyanoethylamino)phenyl]ethane (I, X = CH_2CH_2). This was obtained similarly from 31.9 g of 1,2-di(4-aminophenyl) ethane and 80 ml of acrylonitrile in 45 ml of glacial acetic acid. Yield 29.4 g (61.5%). Colorless leaflets with mp 195–196.5° C (from glacial acetic acid.) λ_{max} 253, 299 nm; log ε 3.99, 3.16. Found, %: N 17.45, 17.38. Calculated for $C_{20}H_{22}N_4$, %: N 17.59.

Di[4-(N-β-cyanoethylamino)phenyl]methane (I, X = CH_2). This was obtained similarly from 11.7 g of di(4-aminophenyl)methane and 30 ml of acrylonitrile in 20 ml of glacial acetic acid. After the end of the reaction, the solution was evaporated in vacuum. Yield 6.1 g (33.8%). Colorless leaflets with mp 122.5–123° C (from aqueous ethanol.) λ_{max} 256, 298 nm; log ε 4.49, 3.64. Found, %: C 74.66, 74.93; H 6.73, 6.66; N 18.69, 18.76. Calculated for $C_{19}H_{20}N_4$, %: C 74.97; H 6.62; N 18.40.

Di[4-(N-β-carboxyethylamino)phenyl]oxide (II, X = 0). To 220 ml of a 40% solution of caustic soda was added 21.0 g of I (X = 0), the resulting mixture was boiled for 5 hr, and the white precipitate of disodium salt was filtered off and dissolved with gentle heating in 140 ml of water; the solution was filtered from insoluble impurities and it was treated with 100 ml of conc HCl with ice cooling. The precipitate that deposited was washed with ice water and dried in the air. Yield 9.1 g (38.5%). Colorless plates with mp 141–142.5° C (from water). λ_{max} 257, 307 nm; log ε 4.39, 3.59. Found, %: C 62.69, 62.53; H 5.79, 5.67; N 8.11, 8.23. Calculated for $C_{18}H_{20}N_2O_5$, %: C 62.77; H 5.85; N 8.13.

1,2-Di[4-(N-β-carboxyethylamino)phenyl]ethane (II, X = CH_2CH_2). 15.9 g of I (X = CH_2CH_2) was dissolved with stirring in 120 ml of 20% HCl, the insoluble impurities were separated off, and the solution was boiled for 4 hr and was evaporated slightly in the vacuum of a water pump. The precipitate that deposited on cooling was filtered off and dissolved in the minimum amount of water, and this solution was gradually added to an equal volume of a saturated aqueous solution of 8.2 g of sodium acetate. The precipitate formed was filtered off, washed with water, and dried in the air.

Yield 12.8 g (71.8%). Colorless plates with mp 180–181.5° C (from methanol). λ_{max} 252, 300 nm; log ε 4.41, 3.64. Found, %: N 7.72, 7.58. Calculated for $C_{20}H_{24}N_2O_4$, %: N 7.86.

N,N'-Di(β-carboxyethyl)-p-phenylediamine. Ten grams of N,N'-di(β-cyanoethyl)-β-phenylenediamine [12] was added to 400 ml of 25% caustic potash and the mixture was boiled for 10 hr, and then, with cooling, it was acidified with concentrated HCl and was saturated with sodium acetate. After some time a precipitate separated out, which was filtered off, washed with ice water, and dried at ~100° C. Yield 9.6 g (81.7%). Needles with mp 150–151° C (from ethanol). Found, %: C 56.87, 57.19; H 6.56, 6.67; N 11.42, 11.48. Calculated for $C_{12}H_{16}N_2O_4$, %: C 57.15; H 6.35; N 11.11.

1,2-Di[4-(N-β-methoxycarbonylethylamino)phenyl]ethane (III, X = = CH_2CH_2). A current of dry hydrogen chloride was passed into a suspension of 19.6 g of compound II (X = CH_2CH_2) in 200 ml of methanol. A solution was gradually formed, from which a white precipitate of the hydrochloride of the diester began to deposit. This was filtered off, the filtrate was diluted with 500 ml of water, and 5.6 g of a light yellow substance was precipitated with 30% sodium carbonate solution. Decomposition of the aqueous solution of the hydrochloride of the diester with saturated aqueous sodium acetate solution gave another 10.7 g of diester. The total yield was 16.3 g (77.5%). Light yellow needles with mp 154–155° C (from ethanol). Found, %: N 7.40, 7.36. Calculated for $C_{22}H_{28}N_2O_4$, %: N 7.28. Dihydrochloride. Colorless plates with mp 186–188° C (decomp., from ethanol). Found, %: N 5.95, 6.17. Calculated for $C_{22}H_{28}N_2O_4 \cdot 2HCl$, %: N 6.12.

N,N'-Di(β-methoxycarbonylethyl)-p-phenylenediamine. A mixture of 20 g of N,N'-di(β-cyanoethyl)-p-phenylenediamine and 200 ml of 40% caustic soda was boiled for 5 hr, the precipitate was separated off and dissolved in 750 ml of ethanol, and, with cooling, the solution was saturated with dry hydrogen chloride. The precipitate formed was dissolved in water, precipitated with 20% caustic soda solution, washed on the filter with water and dried in the air. Yield 15.0 g(67.5%) Mp 105–106° C. Found, %: C 59.60, 59.68; H 7.61, 7.42; N 10.10; 10.20. Calculated for $C_{14}H_{20}N_2O_4$, %: C 59.99; H 7.14; N 10.00. Dihydrochloride. Mp 179–181° C (ethanol-ether). Found, %: C 47.58, 47.55; H 6.06, 6.42; Cl 20.07, 20.09. Calculated for $C_{14}H_{20}N_2O_4 \cdot 2HCl$, %: C 47.60; H 6.28; Cl 20.07.

Di[4-(N-nitroso-N-β-methoxycarbonylethylamino)phenyl]oxide (IV, X = 0). With ice cooling, a current of dry hydrogen chloride was passed through a solution of 24 g of compound II (X = 0) in 600 ml of methanol to saturation, about 300 ml of methanol was distilled off in vacuum, and the residue was poured into 1 *l* of ice water containing 50 ml of concentrated HCl. At 2–5° C, a solution of 10 g of sodium nitrite in 50 ml of water was added dropwise, the oily layer that separated out was extracted with chloroform, the solvent was distilled off in vacuum, and the residue was treated with 2–3 ml of methanol, filtered off, washed with a small amount of methanol, and dried. Yield 28.5 g (95% of the initial diacid). Light yellow prisms with mp 83.5–85° C (from methanol). λ_{max} 221.5, 283 nm; log ε 4.34, 4.24. Found, %: C 55.78, 55.70; H 4.93, 4.87; N 13.35, 13.25. Calculated for $C_{20}H_{22}N_4O_7$, %: C 55.80; H 5.15; N 13.01.

N,N'-Di(N-nitroso-β-cyanoethyl)-p-phenylenediamine. Fourteen grams of N,N'-di(β-cyanoethyl)-p-phenylenediamine in 250 ml of glacial acetic acid was nitrosated at 15–17° C by the action of 9.9 g of sodium nitrite in 50 ml of water. The precipitate was filtered off, washed with water, and dried. Yield 16.2 g (91%). Light yellow prisms with mp 144.5–145° C (from methanol). Found, %: C 53.01, 53.03; H 4.55, 4.67; N 30.39, 30.64. Calculated for $C_{12}H_{12}N_6O_2$, %: C 52.95; H 4.40; N 30.88.

N,N'-Di(N-nitroso-β-carboxyethyl)-p-phenylenediamine was obtained similarly from 2.6 g of N,N'-di(β-carboxyethyl)-p-phenylenediamine in dilute HCl (1 : 1). Yield 2.5 g (78.3%). Yellow prisms with mp 155–156° C (from methanol). Found, %: C 46.36, 46.28; H 4.98, 4.77; N 18.13, 18.08. Calculated for $C_{12}H_{14}N_4O_6$, %: C 46.45; H 4.52; N 18.06.

N,N'-Di(N-nitroso-β-methoxycarbonylethyl)-p-phenylenediamine was obtained similarly from 16.5 g of N,N'-di(β-methoxycarbonylethyl)-p-phenylenediamine in dilute HCl (1 : 1). Yield 17.0 g (85.1%). Light yellow crystals with mp 88–88.5° C (from methanol). Found, %: N 16.33, 16.19. Calculated for $C_{14}H_{18}N_4O_6$, %: N 16.56.

Information on the other nitrosoamines is given in the table.

1,2-Di[4-(3-amino-2-pyrazolin-1-yl)phenyl]ethane (VIII, X = CH_2CH_2). With stirring and cooling, 17 g of zinc dust was added in small portions to a suspension of 16.5 g of VII (X = CH_2CH_2) in 200 ml of glacial acetic acid (the temperature of the mixture did not exceed 25° C). The excess of zinc was filtered off and, with cooling, the filtrate was added to 800 ml of 20% caustic soda. The precipitate formed was washed with water and with methanol, dried at ~100° C, and crystallized from dimethylformamide. Yield 8.7 g (57%). Colorless plates with mp 254–255° C. λ_{max} 278 nm; log ε 4.44. Found, %: C 68.84, 68.75; H 6.95, 7.05; N 24.18, 24.01. Calculated for $C_{20}H_{24}N_6$, %: C 68.94; H 6.94; N 24.12. **Dipicrate.** Dark yellow prisms with mp 135–136° C (from ethanol). Found, %: N 20.91, 21.09. Calculated for $C_{20}H_{24}N_6 \cdot 2C_6H_3N_3O_7$, %: N 20.84.

The mother solution after the crystallization of the substance from dimethylformamide was evaporated to dryness in vacuum and the residue was dissolved in boiling 50% acetic acid. On cooling, 1.2 g (8.2%) of a substance separated out which was probably 1-[4-(3-amino-2-pyrazolin-1-yl)phenyl]-2-[4-(β-cyanoethylamino)phenyl]ethane (IX). Colorless prisms, decomposing on heating above 200° C. Found, %: C 72.35, 72.06; H 6.99, 7.13; N 21.09, 21.12. Calculated for $C_{20}H_{23}N_5$, %: C 72.04; H 6.95; N 21.00.

Di[4-(3-Amino-2-pyrazolin-1-yl)phenyl]oxide (VIII, X = 0). This was obtained similarly from 7.52 g of VII (X = 0). Colorless leaflets with mp 272–273° C (decomp.; from dimethylformamide). Yield 1.7 g (25.4%). Found, %: C 64.01, 64.13; H 5.81, 5.88; N 24.68, 24.82. Calculated for $C_{18}H_{20}N_6O$, %; C 64.25; H 5.99; N 24.98.

Di[4-(pyrazolid-3-on-1-yl)phenyl] oxide (V, X = 0). A) To 110 ml of glacial acetic acid was added 20.9 g of IV (X = 0) and the mixture was heated to 40° C until dissolution was complete, and was then cooled to 17–20° C and 20 g of zinc dust was added in portions at this temperature, after which the mixture was stirred for 15 min and poured into 110 ml of water and the resulting mixture was heated in the water bath for 3 hr. The solution obtained was treated with activated carbon and filtered into 2 *l* of water. The precipitate that separated out on standing was separated off, washed with water, and dried at ~100° C. Yield 5.8 g (35.4%). Colorless needles with mp 223–225.5° C (from dilute acetic acid). λ_{max} 257 nm, log ε 4.40. Found, %: C 63.65, 63.91; H 5.17, 5.53; N 16.28, 16.57. Calculated for $C_{18}H_{18}N_4O_3$, %: C 63.89; H 5.36; N 16.56.

B) To a solution of 5 ml of concentrated H_2SO_4 in 100 ml of water was added 2.3 g of VIII (X = 0), the mixture was boiled for 2 hr, and after cooling the precipitate was filtered off, washed with water and with methanol, and was dried in the air. This gave 1.1 g (47.5%) of a compound with 222–224° C. A mixture with the substance obtained by method (A) gave no depression of the melting point.

1,2-Di[4-(pyrazolid-3-on-1-yl)phenyl]ethane (V, X = CH_2CH_2). A) This was obtained in a similar manner to V(X = 0) from 2.2 g of IV (X = CH_2CH_2). Yield 0.56 g (25.4%). Pink prisms with mp 235.5–237° C (from dilute dimethylformamide). λ_{max} 252 nm; log ε 4.36. Found, %: C 69.06, 68.81; H 6.45, 6.38; N 16.29, 16.30. Calculated for $C_{20}H_{22}N_4O_2$, %: C 68.55; H 6.32; N 15.99.

b) This was obtained in a similar manner to V (X = 0) from 10 g of VIII (X = CH_2CH_2). Yield 5.1 g (50.8%). Mp 235–236° C. A mixture with the substance obtained by method (A) gave no depression of the melting point.

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