AN INVESTIGATION OF THE STRUCTURAL CHARACTERISTICS AND CHEMICAL CONVERSIONS OF CARBAZOLE AND SOME OF ITS DERIVATIVES

XXIII. Synthesis and Investigation of Dihydroxyphthaloyl Derivatives of Carbazole*

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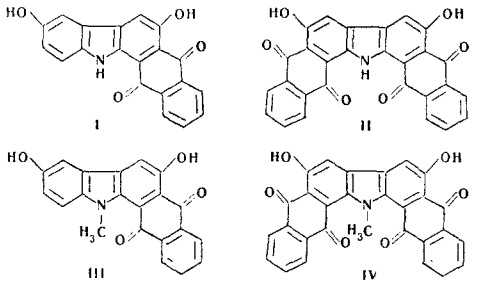
Mono- and diphthaloyl derivatives were synthesized from 3,6-dihydroxy-9-methylcarbazole and from 3,6-dihydroxycarbazole, compounds which are potential complex-forming substances.

The products of the condensation of carbazole with phthalic anhydride are described in the literature as thermostable vat dyes [1]. The 3-aminophthaloylcarbazoles, as potential vat dyes, have also been studied [2–4].

This paper describes the synthesis and properties of the phthaloyl derivatives of 3,6-dihydroxycarbazole and of 3,6-dihydroxy-9-methylcarbazole (I–IV), compounds which are similar to known mordant dyes.



I II III IV

The initial substances, 3,6-dihydroxycarbazole and 3,6-dihydroxy-9-methylcarbazole, were obtained by the alkali fusion of the corresponding sulfonic acids.

The compounds thus obtained were identified by recording their IR spectra in a UR-10 spectrophotometer after dispersion in paraffin oil. These spectra were compared with those of the compounds alizarin and quinizarin, which exhibit a similar distribution of carbonyl and hydroxyl groups. The spectrographs showed that frequencies for carbonyl groups in compounds I–IV were shifted with respect to the frequencies of quinones [5] and lie around 1667 cm^{-1}. The substances drawn for comparison exhibited the same shift. This warrants the supposition that the molecules are associated, and that the observed broad diffuse absorption bands in the 3670–3200 cm^{-1} region may be explained by the presence of hydrogen bonds.

EXPERIMENTAL

3,6-Dihydroxy-1,2-phthaloylcarbazole (I). To a melt of $AlCl_3$-NaCl-KCl-NaF in the weight ratio 12-1-0.7-0.3 g, 1.99 g (0.01 mole) of 3,6-dihydroxycarbazole and 1.5 g (0.01 mole) of phthalic anhydride were added. The mass was stirred for 45 min at 90–100° and again during an equal period at 150°. After acidifying with 20% HCl, the precipitate was filtered off, washed, and boiled in 15% H_2SO_4. After successive washings with hot water, cold water, and warm ether, 2.8 g of I were obtained. Yield 85.5%. Found, %: N 3.91, 3.87. Calculated for $C_{20}H_{11}NO_4$, %: N 4.26. Carbonyl-group frequencies: 1707, 1668 cm^{-1}.

3,6-Dihydroxy-1,2-phthaloyl-9-methylcarbazole (III) was obtained by combining the initial substances in equimolar ratio, as in the synthesis of compound I. Yield 79.5%. Found, %: N 4.31, 4.32. Calculated for $C_{21}H_{13}NO_4$, %: N 4.11. Carbonyl-group frequencies: 1707, 1667 cm^{-1}.

3-6,Dihydroxy-1,2,7,8-diphthaloyl carbazole (II) was obtained by the above procedure, combining 0.01 mole of 3,6-dihydroxycarbazole and 0.02 mole of phthalic anhydride. Yield 88.5%. Found, %: N 3.15, 3.18. Calculated for $C_{28}N_{13}NO_6$, %: N 3.06. Carbonyl-group frequencies: 1707, 1668 cm^{-1}.

3,6-Dihydroxy-1,2,7,8-diphthaloyl-9-methylcarbazole (IV) was obtained by the same method used in the synthesis of II. Yield 79%. Found, %: N 2.94, 2.85. Calculated for $C_{29}H_{17}NO_6$, %: N 2.95. Carbonyl-group frequencies: 1710, 1667 cm^{-1}.

All the hydroxycarbazoles are fine-crystalline substances of various shades of cinnamon color, mp > 490°. They dissolve in 15% alkali and in concentrated H_2SO_4, giving rise to the violet color characteristic of carbazole derivatives. They dissolve readily in dimethylformamide, tetrahydrofuran, ethylene chlorohydrin, quinoline, and pyridine; less readily in ethanol and acetone. They are practically insoluble in benzene, chloroform, ether, and carbon tetrachloride.

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*For part XXII, see [6].