BRIEF COMMUNICATIONS

STRUCTURE OF THE REACTION PRODUCTS FROM CARBAZOLE OR N-METHYLCARBAZOLE AND FORMALDEHYDE

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Formaldehyde reacts with carbazole or N-methylcarbazole in the presence of concentrated hydrochloric acid to give dimers, and also more highly polymerized products (crosslinked or linear respectively with three or more carbazole (or N-methylcarbazole) units per molecule.

According to available results [1–3], reaction of carbazole with formaldehyde in the presence of acids (e.g., heating with glacial acetic acid, conc H_2SO_4, as catalysts) gives dimers. According to [1], this is N, N'-dicarbazolylmethane, but according to [2] it is 3, 3'-dicarbazolylmethane. Reaction of formaldehyde with 3, 6-dibromocarbazole leads to the isolation of 3, 6, 3', 6'-tetrabromo-N, N'-dicarbazolylmethane [3]. Carbazole and formaldehyde are assumed to give a product of similar structure.

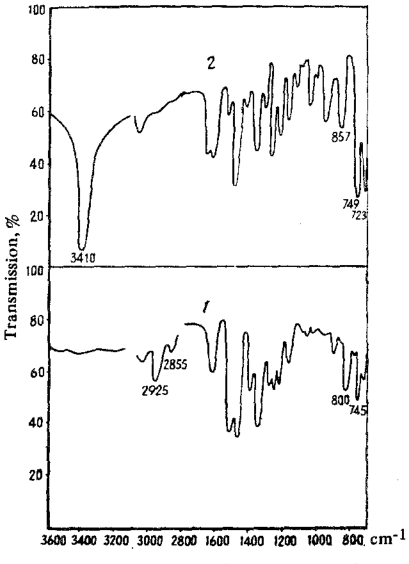


Fig. 1. IR spectra: 1) condensate A; 2) carbazole.

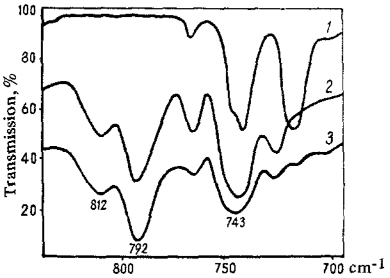
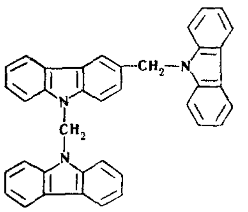


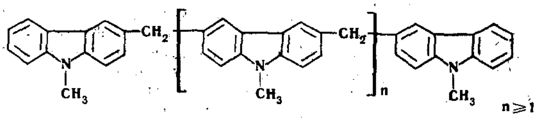
Fig. 2. IR spectra: 1) N-methylcarbazole; 2) di(N-methylcarbazolyl-3)methane; 3) condensate C.

The carbazole molecule contains three positions, 3, 6, 9, of enhanced nucleophilicity [4, 5]. Hence when carbazole reacts with formaldehyde in the presence of an acid catalyst, it is possible to assume not only formation of dimers (of the structure stated above), but also of highly condensed products, e. g., of crosslinked structure (of the thermoreactive phenol-formaldehyde resin type [6]). The N-methylcarbazole molecule has only two centers of enhanced activity towards electrophilic reagents, viz., positions 3 and 6, so that reaction with formaldehyde most probably gives products of linear structure. Reaction of formaldehyde with carbazole in the presence of concentrated hydrochloric acid led to the isolation of condensate A, an amorphous pale sulfur-yellow powder. Analysis of its IR spectrum (Fig. 1) enabled the following conclusions to be drawn regarding its structure. The absence of absorption bands corresponding to valence vibrations of NH bonds (in the 3500–3100 cm^{-1} region) indicates complete blocking of the carbazole NH group by reaction with formaldehyde. The bands at 880 and 800 cm^{-1} are characteristic of a 1, 2, 4-trisubstituted benzene ring [7], here corresponding to condensate A containing carbazole units substituted at position 3(6). Confirmation of this is to be found in a paper [8] comparing the IR spectra of 1-, 2-, 3-, and 4-monomethylcarbazoles. The 2925 and 2855 cm^{-1} bands in the region of valence vibrations of CH bonds correspond to the presence of CH_2 groups in the condensate A. The spectroscopic data adduced the very low solubility of condensate A in organic solvents (nitrobenzene, pyridine, aniline, etc.), and its infusibility (it gradually chars when heated above 360° C), confirms our assumption that the reaction of carbazole with formaldehyde gives crosslinked structures, e.g.,



The product of reaction of carbazole with formaldehyde in glacial acetic acid (conc H_2SO_4 catalyst), condensate B, has similar IR spectra and different physical properties.

Reaction of N-methylcarbazole with formaldehyde in the presence of conc HCl leads to isolation of di(N-methylcarbazolyl-3)methane (I) and a pale sulfur-yellow amorphous powder, condensate C. The positions of the bands in the two substances (Fig. 2) is practically the same. However, the high intensity of the bands at 812 and 792 cm^{-1} (appearing when a substituent is put at position 3 in N-methylcarbazole) in comparison with the band at 743 cm^{-1} (1, 2-disubstituted benzene ring in the N-methylcarbazole molecule) in the IR spectrum of condensate C is to be noted. These results, the very low solubility of condensate C in organic solvents, as well as its showing plasticity at about 320° C, are in agreement with the hypothesis that reaction of N-methylcarbazole with formaldehyde under conditions of acid catalysts, gives linear condensation products, e.g.,



EXPERIMENTAL

Condensate A. A solution of 3.34 g (0.02 mole) carbazole and 1.52 ml (0.02 mole) 37% CH_2O in 100 ml acetone, was added dropwise to 300 ml conc HCl, at 20° C, which was kept stirred. After 3 hr the products were poured into 500 ml water, the solid filtered off, dried, and exhaustively extracted with benzene. The product was a pale sulfur-yellow powder, yield 1.65 g (46%, calculated on the fragment $C_{12}H_8NCH_2$), condensate A. IR spectrum: 2925, 2855, 1635, 1607, 1492, 1460, 1380, 1328, 1278, 1234, 1212, 1154, 1026, 924, 880, 800, 745, 722 cm^{-1}. IR spectrum of carbazole: 3410, 1632, 1609, 1497, 1454, 1341, 1242, 1211, 1144, 1013, 931, 914, 857, 749, 723 cm^{-1}.

Condensate B. 1–2 Drops conc H_2SO_4 was added to a gently refluxing solution of 3.34 g (0.02 mole) carbazole and 1.52 ml (0.02 mole) 37% CH_2O in 150 ml glacial AcOH, and heating continued for a further 20 min, the products cooled, and condensate B isolated similarly to condensate A.

Reaction of N-methylcarbazole with formaldehyde. A solution of 10 g (0.055 mole) N-methylcarbazole and 1.71 ml (0.0275 mole) 37% CH_2O in 50 ml acetone was dripped into 150 ml conc HCl, and the mixture stirred for 3 hr at 20° C. The products were then poured into 500 ml water, the precipitate filtered off, washed with water, dried, and the unreacted N-methylcarbazole extracted with MeOH (yield 4 g). The solid was then extracted with benzene, and the extract chromatographed (Al_2O_3, benzene), to give compound I, as white minute crystals, mp 223°–224° (ex benzene). Found: C 86.86; 86.75; H 6.09; 6.15; N 7.50; 7.59%; M 370; 389, calculated for $C_{27}H_{22}N_2$: C 86.8; H 5.74; N 7.48%; M 374. IR spectrum: 2925; 2852, 1635, 1602, 1495, 1427, 1361, 1328, 1250, 1154, 1020, 923, 880, 812 and 792, 767, 743, 723 cm^{-1}. The residue remaining after extraction was condensate C, a pale sulfur-yellow powder, very slightly soluble in organic solvents, softening point 315°–320° C. IR spectrum: the positions of the bands fully duplicate the IR spectrum of compound I.

The IR spectra were determined with an IKS-14 spectrophotometer: a) regions 3600–3100 cm^{-1} and 1800–700 cm^{-1} using vaseline mulls (LiF and NaCl prisms); b) region 2800–3100 cm^{-1} tableted with KBr (LiF prism).

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ELECTRONIC STRUCTURES AND DIPOLE MOMENTS OF 4- AND 5-PHENYL-1, 2-DITHIOL-3-THIONES

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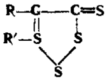
The simple LCAO MO method is used to calculate π-electron configurations of 1, 2-dithiol-3-thione and its 4- and 5-phenyl derivatives. In these compounds the heterocyclic ring has an aromatic character, but the S—S bond is almost excluded from conjugation. The phenyl group in 4-phenyl-1, 2-dithiol-3-thione is an electron acceptor, whereas in the 5 isomer it is an electron donor. The exocyclic sulfur atom has considerable negative charge, while the two endocyclic ones are positively charged. The dipole moments of 4- and 5-phenyl-1, 2-dithiol-3-thione are determined, and the values found are compared with the calculated ones.

In recent years 1, 2-dithiol-3-thione (I) has acquired considerable theoretical and practical interest [1–6].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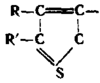
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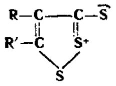
III

X-ray investigation of 4-methyl-1, 2-dithiol-3-thione (Fig. 1) [7] and 1, 2-dithiol-3-thione [8], show the aromatic nature of the ring, the lengths of the C—C and C—S bonds being close to those corresponding bonds in benzene and thiophene [9]. However, the S—S bond in I does not differ in length from the bond between sulfur atoms in the S_8 molecule and saturated