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SYNTHESIS OF NEW BRANCHED HYDRAZONES AS POTENTIAL HOLE-TRANSPORTING MATERIALS

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A new class of branched hydrazones has been prepared by the reaction of N-2,3-epoxypropylated N-phenylhydrazones containing photoconductive groups with 2,5-dimercapto-1,3,4-thiadiazole in the presence of the catalyst triethylamine.

Keywords: hydrazones, epoxypropyl derivatives, dithioles, 1,3,4-thiadiazoles triethylamine.

In previous works [1-4] we have reported on novel classes of branched molecules, consisting of conjugated π-electron systems, which hold promise as hole-transporting materials (HTM) for various electro-optical applications. The general synthesis route of such organic photoconductors involves the addition of two molecules of oxiranes containing photoconductive groups to various binding agents, for example 2-phenylindole, aniline derivatives, and dihydroxy compounds. Furthermore, we described the synthesis of well-defined branched hydrazones obtained in the reaction of 9-ethyl-9H-3-carbazolecarbaldehyde N-2,3-epoxypropyl-N-phenylhydrazone (**1a**) and 4-(diethylamino)benzaldehyde N-2,3-epoxypropyl-N-phenylhydrazone (**1b**) with benzenediols [5]. These HTM are low-molecular glasses and can be used for preparation of electrophotographic layers [6].

Herein we report on the synthesis of a novel series of branched hydrazones analogues to the former described ones but having a 1,3,4-thiadiazole ring in the linking fragment. We felt that the 2,5-dimercapto-1,3,4-thiadiazole function offers a two-fold advantage. First is the higher reactivity of the thiol group in nucleophilic oxirane ring opening as well as the commercial availability of the starting agent. Second, some derivatives of 2,5-dimercapto-1,3,4-thiadiazole are used as levelling additives for copper plating electrolytes, giving smooth surfaces [7]. The qualitative surface for the electrophotographic layer could be very important.

Nucleophilic opening of the oxirane ring in hydrazone **1a** according to the known method [5], i.e., by refluxing **1a** with 2,5-dimercapto-1,3,4-thiadiazole (molar ratio 2:1) in 2-butanone in the presence of triethylamine (TEA), gave 2,5-bis[6-(9-ethyl-9H-carbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2a**) with 74% yield. Further investigation showed that the reaction could be carried out in mild conditions (at room temperature), thus giving a somewhat higher yield and a purer product. Based on the developed method, by the interaction of **1b**, 4-(diphenylamino)benzaldehyde N-2,3-epoxypropyl-N-phenylhydrazone (**1c**) and 4-(4,4'-dimethyldiphenylamino)benzaldehyde N-2,3-epoxypropyl-N-phenylhydrazone (**1d**) with 2,5-dimercapto-1,3,4-thiadiazole, the following branched hydrazones in 66-84% yields were synthesized: 2,5-bis[6-(4-diethylaminobenzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole

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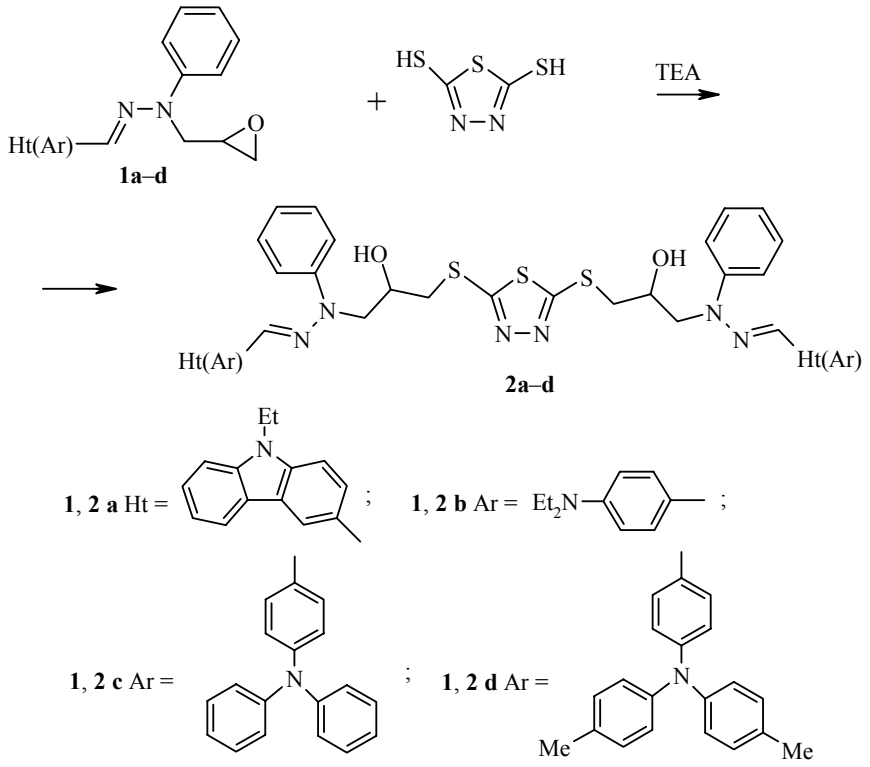
(**2b**), 2,5-bis[6-(4-diphenylamino)benzylidene-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2c**), and 2,5-bis[6-(4,4'-dimethyldiphenylamino)benzylidene-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2d**).



The structures of **2a-d** were confirmed by the spectral data. The doublet of the OH group at 5.6-5.2 ppm in the ^{1}H NMR spectra recorded in DMSO-d_6 solutions confirmed the nucleophilic opening of the oxirane ring at the primary carbon atom. Some individual downfield peaks were assigned to characteristic protons of heterocyclic or aromatic moieties: a singlet at 8.25, a doublet at 8.12 (4-H and 2-H of carbazole ring in **2a**, respectively), or a triplet at ca. 7.0 ppm (4-H of phenyl ring in **2a**,**b**). The singlet of a proton of the CH=N fragment appears in the region of 7.6-7.8 ppm while the protons of the flexible aliphatic bridge, between the aromatic thiadiazole fragments, usually give peaks at 4.47-3.20 ppm. In the ^{1}H NMR spectrum of **2d** the most clearly defined ABX systems of the nonequivalent geminal protons of NCH_2 and CH_2S were observed. The resonances of NCH_2 protons appeared as two doublets of doublets at 4.02 (H_A) and at 3.96 ppm (H_B) with J_{AB} = 15.0, J_{BX} = 7.0 and J_{AX} = 5.1 Hz, due to the coupling with CH, while the protons of CH_2S moiety respectively gave two dd in the region of 3.65-3.3 ppm (J_{AB} = 14.3, J_{AX} = 3.7, J_{BX} = 7.3 Hz). In the ^{1}H NMR spectrum of **2a** a double set of signals of the AB part of an ABX system of CH_2S is observed at 3.65-3.25 ppm, indicating that the obtained product is a mixture of diastereomers. Hence, the synthesized branched hydrazones containing two stereogenic centers were usually obtained as mixtures of diastereomers. Only in the case of **2d** was one stereoisomer registered.

In the IR spectra hydroxy groups participating in hydrogen bonding give rise to a broad oscillation band at 3630-3100 cm^{-1}.

The existence of several diastereomers, the possibility of intermolecular hydrogen bonding, and the flexibility of aliphatic linking chains make crystallization in the solid state difficult, so **2a-d** are molecular glasses. Moreover, such compounds usually do not have definite melting points and are often characterized by their glass transition temperatures (T_g) [8]. Furthermore, after some attempts, **2a-d** were crystallized from

toluene. The presence of hydroxy groups make them cross-linkable with, for example, polyisocyanates. Such cross-linked systems enable one to prepare electrophotographic photoreceptors with high solvent resistance and good mechanical properties. The newly synthesized branched hydrazones **2a-d** showed high morphological stability and excellent charge transporting properties, which we reported recently in [9].

EXPERIMENTAL

2,3-Epoxypropyl derivatives of hydrazones **1a-d** were prepared according to our earlier procedure [10]. The ^{1}H NMR spectra were registered on a Bruker AC 250 (250 MHz) and Mercury-VX (400 MHz) spectrometers with TMS as the internal standard. The IR spectra were taken in KBr on a Perkin-Elmer (Spectrum BX II) spectrometer. The course of the reactions and the purity of the products were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates, using 4:1 acetone/*n*-hexane as the eluent. Silica gel (grade 62, 60-200 mesh, 150 Å, Aldrich) was used for column chromatography.

2,5-Bis[6-(9-ethyl-9H-carbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2a**). A. To a solution of compound **1a** (10.0 g, 27.1 mmol) and 2,5-dimercapto-1,3,4-thiadiazole (2.03 g, 13.55 mmol) in 25 ml of 2-butanone was added 1.9 ml (13.5 mmol) of TEA and the mixture was refluxed for 1 h. After evaporation of 2-butanone and TEA, the residue was dissolved in 25 ml of toluene and cooled till -5°C. The crystals formed upon standing (24 h) were filtered off and washed with 2-propanol to give 8.9 g (74.1%) of **2a**; mp 167-170.5°C (toluene). ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 8.25 (2H, s, 4-H Ht); 8.12 (2H, d, *J* = 7.8, 1-H Ht); 7.83 (2H, d, *J* = 7.8, 2-H Ht); 7.81 (2H, s, CH=N); 7.50-7.14 (16H, m, Ht, Ar); 6.99 (2H, t, *J* = 7.0, 4-H Ar); 4.44 (2H, m, CH); 4.27 (4H, q, *J* = 6.8, $C\underline{H}_2CH_3$); 4.06-3.82 (6H, m, OH, NCH_2); 3.60 and 3.55 (2H, m, H_A, double set of signals of AB part of ABX system, CH_2S); 3.36 and 3.31 (2H, m, H_B, double set of signals of AB part of ABX system, CH_2S); 1.37 (6H, t, *J* = 6.8, $CH_2C\underline{H}_3$). IR spectrum, ν, cm^{-1}: 3368 (OH, br); 3048 (CH_{arom}); 2972, 2930 (CH_{aliph}); 806, 747, 730, 694 (CH=CH of carbazole, monosubstituted benzene). Found, %: C 67.39; H 5.38; N 12.72. $C_{50}H_{48}N_8O_2S_3$. Calculated, %: C 67.54; H 5.44; N 12.60.

B. TEA (1.9 ml, 13.5 mmol) was slowly added to a solution of compound **1a** (10.0 g, 27.1 mmol) and 2,5-dimercapto-1,3,4-thiadiazole (2.03 g, 13.55 mmol) in 15 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30°C. Then the reaction mixture was stored overnight at room temperature and the product was isolated according to procedure A. The yield of **2a** was 10.1 g (84.1%). A sample of this product with the product obtained according to procedure A did not give a depressed melting point.

2,5-Bis[6-(4-diethylaminobenzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2b**) was prepared and isolated as described for **2a** (procedure B), except that compound **1b** (8.7 g, 27.1 mmol) instead of **1a** was used. The yield of **2b** was 7.6 g (70.4%); mp 114.5-116°C (toluene). ^{1}H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 7.74 (2H, s, CH=N); 7.48-7.14 (12H, m, Ar); 6.80 (2H, t, *J* = 7.1, 4-H Ar); 6.64 (4H, m, *J* = 8.7, Ar); 5.54 (2H, d, *J* = 3.9, OH); 4.20-3.90 (6H, m, NCH_2CH); 3.30 (8H, q, *J* = 6.9, $C\underline{H}_2CH_3$); 3.18 (4H, m, CH_2S); 1.06 (12H, t, *J* = 7.1, $CH_2C\underline{H}_3$). IR spectrum, ν, cm^{-1}: 3324 (OH, br); 3019 (CH_{arom}); 2968, 2927, 2957 (CH_{aliph}); 813, 749, 694 (mono- and *p*-disubstituted benzene). Found, %: C 63.11; H 6.46; N 14.20. $C_{42}H_{52}N_8O_2S_3$. Calculated, %: C 63.28; H 6.58; N 14.06.

2,5-Bis[6-(4-diphenylamino)benzylidene-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2c**) was prepared as described for **2a** (procedure B), except that compound **1c** (11.2 g, 27.1 mmol) instead of **la** was used. The product was isolated by subjecting the reaction mixture to chromatography using propanone/hexane (1:4) as the eluent. After removal of the eluents, the residue was recrystallized from toluene. 8.9 g (66.4%) of **2c** was filtered off and washed with 2-propanol; mp 165-167°C (toluene). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 7.61 (2H, s, CH=N); 7.53 (4H, m, *J* = 8.8, Ar); 7.40-6.97 (34H, m, Ar); 4.47

(2H, m, CH); 4.08-3.90 (6H, m, NCH_2, OH); 3.62 and 3.59 (2H, m, H_A, double set of signals of AB part of ABX system, SCH_2); 3.41-3.32 (2H, m, H_B from SCH_2). IR spectrum, ν, cm^{-1}: 3384 (OH, br); 3060, 3033 (CH_{arom}); 2914 (CH_{aliph}); 827, 752, 695 (mono- and *p*-disubstituted benzene). Found, %: C 70.33; H 5.28; N 11.41. $C_{58}H_{52}N_8O_2S_3$. Calculated, %: C 70.42; H 5.30; N 11.33.

2,5-Bis[6-(4,4'-dimethyldiphenylamino)benzylidene-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]-1,3,4-thiadiazole (**2d**) was prepared as described for **2a** (procedure B), except that compound **1d** (12.1 g, 27.1 mmol) instead of **1a** was used. The target product was isolated according to the procedure described for **2c**. The yield of **2d** was 9.6 g (68.1%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 7.60 (2H, s, CH=N); 7.49 (4H, m, *J* = 8.2, Ar); 7.39-7.29 (8H, m, Ar); 7.08-6.96 (22H, m, Ar); 4.46 (2H, m, CH); 4.03 (2H, d, *J* = 3.8, OH); 4.02 (2H, dd, J_{AB} = 15.0, J_{AX} = 5.1, H_A of NCH_2); 3.96 (2H, dd, J_{BX} = 7.0, H_B of NCH_2); 3.60 (2H, dd, J_{AB} = 14.3, J_{AX} = 3.7, H_A of SCH_2); 3.37 (2H, dd, J_{BX} = 7.3, H_B from SCH_2); 2.29 (12H, s, 4-CH_3). IR spectrum, ν, cm^{-1}: 3355 (OH, br); 3024 (CH_{arom}); 2919, 2858 (CH_{aliph}); 815, 750, 693 (CH=CH of mono- and *p*-disubstituted benzene). Found, %: C 71.17; H 7.69; N 10.81. $C_{62}H_{60}N_8O_2S_3$. Calculated, %: C 71.23; H 7.79; N 10.72.

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