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LETTERS TO THE EDITOR

Synthesis of 9,10-Anthracenedione Diethyldithiocarbamates

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Dithiocarbamates are valuable synthetic materials widely used in agriculture as insecticides, herbicides, pesticides, and fungicides [1], in the industry as slimicides in water-cooled engines and paper production [2], vulcanization accelerators [5], in analytical chemistry for determining cations [3], in polymer chemistry as agents for the controlled radical polymerization of [4]. Some dithiocarbamates show antitumor [6, 7], anti-HIV [8], antioxidant [9], antibiotic [10], and anti-histamine [11] activity. Functionalization of dithiocarbamates with biophoric fragments was proved especially useful when creating combinatorial libraries for rapid screening [12] and drug design [13].

9,10-Anthracenedione derivatives are used as dyes, pharmaceuticals, analytical reagents, indicators, phosphors, catalysts [14]. In recent years, they have been widely studied as biologically active compounds with antitumor, antiviral, antidiabetic, antibacterial, and antifungal action [15]. Of special interest is the creation of new 9,10-anthracenedione derivatives as they can be promising objects for multi-purpose use.

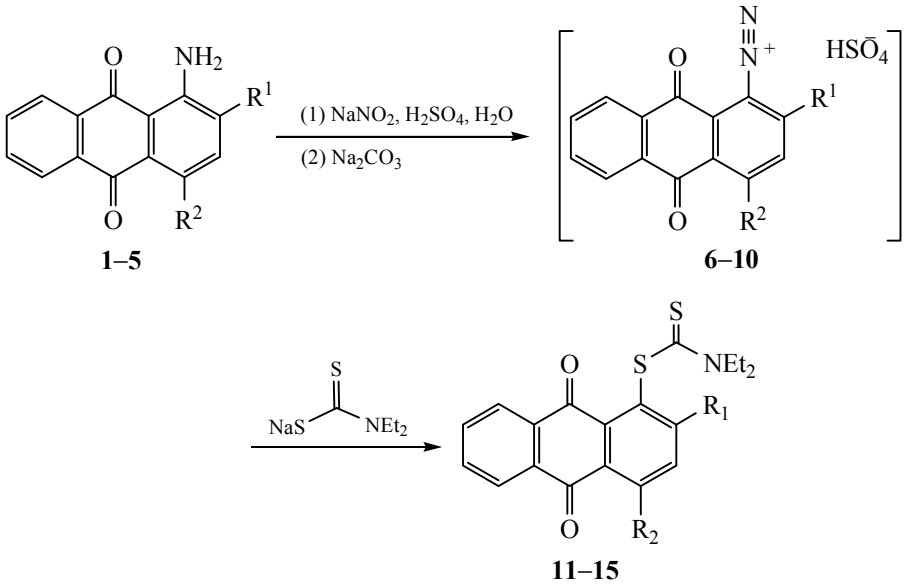
General method for the synthesis of dithiocarbamates is reacting a primary or secondary amines with carbon disulfide in the presence of alkali [16], triethylamine [17] or without a base [18]. The approach comprising the reaction of amines with carbon disulfide and an alkyl halides/acrylates has been reported in [19]. These methods allow obtaining alkyl dithiocarbamates, but not aryl dithiocarbamates. In general, *S*-aryl dithiocarbamates can be prepared under metal-catalysis conditions [20], while in [21–23] the synthesis has been performed by reacting alkali metal dithiocarbamates with aryl and diaryl diazonium salts in the absence of any catalyst. Given the limited number of such publications, it was worthwhile to expand the synthetic potential of diazonium salts derived from amino-9,10-anthracenediones for obtaining new derivatives of dithiocarbamic acids.

At the beginning, 1-aminoanthracenediones **1**–**5** were converted to the corresponding diazonium sulfates **6**–**10** by the method reported in [24]. Neutralization of aqueous solutions with sodium carbonate followed by treating with a 3-fold excess of sodium diethyldithiocarbamate at 5–10°C led to the formation of *S*-(9,10-anthracen-1-yl)dithiocarbamates **11**–**15** with 59–72% yield (Scheme 1).

Structure and composition of the obtained *S*-anthracenyl dithiocarbamates **11**–**15** were unequivocally confirmed by NMR spectroscopy and elemental analysis data. In particular, the ^{1}H NMR spectra of **11**–**15** showed the signals of methyl and methylene groups of diethylamino substituent in the ranges of 1.16–1.37 and 3.84–3.96 ppm, respectively. The ^{13}C NMR spectra contained the signals of C=S moiety of dithiocarbamate fragment at 191–192 ppm.

General procedure for the synthesis of *S*-anthracenyldithiocarbamates 11–15. A solution of 1.15 g (6.72 mmol) of sodium diethyldithiocarbamate in 15 mL of water was added with stirring and cooling (5–10°C) to a mixture of freshly prepared and neutralized with 10% sodium carbonate solution (pH = 7) diazonium salt **6**–**10** prepared from 2.24 mmol of the appropriate aminoanthracenedione **1**–**5** and 0.201 g (2.91 mmol) of sodium nitrite in 20 mL of concentrated sulfuric acid. The reaction

Scheme 1.



1–5 **6–10** **11–15**

$R^1 = R^2 = H$ (**1, 6, 11**); $R^1 = H$, $R^2 = NHMe$ (**2, 7, 12**); $R^1 = H$, $R^2 = 4\text{-HN-}C_6H_4Me$ (**3, 8, 13**); $R^1 = Br$, $R^2 = 4\text{-HN-}C_6H_4Me$ (**4, 9, 14**); $R^1 = Cl$, $R^2 = 4\text{-HN-}C_6H_4Me$ (**5, 10, 15**).

mixture was stirred for 30 min. The resulting precipitate was filtered off, washed with water (2 × 40 mL), and dried in air.

9,10-Dioxo-9,10-dihydroanthracen-1-yldiethylcarbamodithioate (11). Yield 90%, mp >100°C (decomp.). IR spectrum, ν, cm^{-1}: 1674, 1631 (C=O). ^1H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3, J = 6.8 Hz), 1.35 t (3H, CH_3, J = 7.2 Hz), 3.84–3.95 m (4H, CH_2), 7.88–8.24 m (7H, CH_{Ar}). ^{13}C NMR spectrum, δ_C, ppm: 11.68 (CH_3), 13.76 (CH_3), 48.97 (CH_2), 49.61 (CH_2), 126.89, 127.29, 128.05, 132.44, 133.17, 133.87, 134.28, 134.67, 135.01, 135.19, 135.62, 141.55 (C_{Ar}), 182.46, 182.67 (C=O), 192.43 (C=S). Found, %: C 64.31; H 4.74; N 4.12; S 18.12. $C_{19}H_{17}NO_2S_2$. Calculated, %: C 64.20; H 4.82; N 3.94; S 18.04.

4-(Methylamino)-9,10-dioxo-9,10-dihydroanthracen-1-yldiethylcarbamodithioate (12). Yield 72%, mp >110°C (decomp.). IR spectrum, ν, cm^{-1}: 1680, 1645 (C=O). ^1H NMR spectrum, δ, ppm: 1.01 s (3H, CH_3), 1.17 t (3H, CH_3, J = 6.8 Hz), 1.37 t (3H, CH_3, J = 7.2 Hz), 3.85–3.96 m (4H, CH_2), 7.90–8.26 m (6H, CH_{Ar}), 12.99 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.67 (CH_3), 13.92 (CH_3), 48.37 (CH_2), 49.87 (CH_2), 126.77, 126.95, 132.86, 133.67, 133.83, 134.38, 134.78, 136.08, 144.96 (C_{arom}), 182.05, 182.34 (C=O), 191.56 (C=S). Found, %: C 62.74; H 5.08; N 7.45; S 16.51. $C_{20}H_{20}N_2O_2S_2$. Calculated, %: C 62.47; H 5.24; N 7.29; S 16.68.

9,10-Dioxo-4-(*p*-tolylamino)-9,10-dihydroanthracen-1-yldiethylcarbamodithioate (13). Yield 69%, mp >110°C (decomp.). IR spectrum, ν, cm^{-1}: 1674, 1649 (C=O). ^1H NMR spectrum, δ, ppm: 1.17 t (3H, CH_3, J = 6.8 Hz), 1.37 t (3H, CH_3, J = 7.2 Hz), 2.35 s (3H, CH_3), 3.86–3.95 m (4H, CH_2), 7.37 m (2H, CH_{Ar}), 7.56–7.75 m (3H, CH_{Ar}), 7.87–8.07 m (3H, CH_{Ar}), 8.21–8.29 m (2H, CH_{Ar}), 13.07 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.51 (CH_3), 13.73 (CH_3), 47.57 (CH_2), 52.09 (CH_2), 124.39, 126.71, 128.24, 129.86, 130.82, 133.97, 134.39, 135.21, 136.02 (C_{Ar}), 181.78, 182.45 (C=O), 191.63 (C=S). Found, %: C 67.65; H 5.09; N 6.134; S 14.12. $C_{26}H_{24}N_2O_2S_2$. Calculated, %: C 67.80; H 5.25; N 6.08; S 13.92.

2-Bromo-9,10-dioxo-4-(*p*-tolylamino)-9,10-dihydroanthracen-1-yldiethylcarbamodithioate (14). Yield 67%, mp >110°C (decomp.). IR spectrum, ν, cm^{-1}: 1681, 1637 (C=O). ^1H NMR spectrum, δ, ppm: 1.17 t (3H, CH_3, J = 6.8 Hz), 1.37 t (3H, CH_3, J = 7.2 Hz), 2.32 s (3H, CH_3), 3.85–3.96 m (4H, CH_2), 7.26–7.41 m (3H, CH_{Ar}), 7.87–8.05 m (3H, CH_{Ar}), 8.11–8.19 m (3H, CH_{Ar}), 11.27 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.83 (CH_3), 13.84 (CH_3), 21.08 (CH_3), 47.68 (CH_2), 52.19 (CH_2), 112.86, 114.09, 118.86, 124.89, 126.81, 127.19, 129.12, 130.95, 132.62, 134.12, 135.03, 135.53, 136.53, 145.27, 150.51 (C_{Ar}), 182.21, 184.07 (C=O), 191.66 (C=S). Found, %: C 57.97; H 4.27; Br 14.89; N 5.13; S 11.95. $C_{26}H_{23}BrN_2O_2S_2$.

Calculated, %: C 57.88; H 4.30; Br 14.81; N 5.19; S 11.88.

9,10-Dioxo-4-(*p*-tolylamino)-2-chloro-9,10-dihydroanthracen-1-eydiethylcarbamodithioate (15). Yield 59%, mp >110°C (decomp.). IR specrtum, ν, cm^{-1}: 1681, 1637 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.16 t (3H, CH_3, J = 6.8 Hz), 1.38 t (3H, CH_3, J = 7.2 Hz), 2.32 s (3H, CH_3), 3.85–3.96 m (4H, CH_2), 7.56–7.70 m (3H, CH_{Ar}), 7.88–7.96 m (3H, CH_{Ar}), 8.12–8.22 m (3H, CH_{Ar}), 12.14 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.26 (CH_3), 13.66 (CH_3), 21.27 (CH_3), 47.63 (CH_2), 52.25 (CH_2), 112.75, 116.76, 118.16, 124.87, 126.97, 130.88, 132.28, 134.59, 135.39, 135.89, 135.98, 141.09, 150.42 (C_{Ar}), 182.07, 184.56 (C=O), 191.69 (C=S). Found, %: C 63.36; H 4.84; Cl 7.10; N 5.649; S 12.87. $C_{26}H_{23}ClN_2O_2S_2$. Calculated, %: C 63.08; H 4.68; Cl 7.16; N 5.66; S 11.88.

^{1}H and ^{13}C NMR spectra were registered on a Varian Mercury-400 spectrometer in the solutions of DMSO-d_6 (399.96 and 100.61 MHz, respectively), internal reference TMS. IR spectra (KBr) were recorded on a Specord M-80 spectrometer. Purity of compounds obtained was monitored by TLC method (Silufol UV-254 plates, benzene–acetonitrile, 6 : 1).

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