Monatshefte für Chemie 125, 549–551 (1994)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Short Communication

A Novel Reaction of 11,11,12,12-Tetracyanoanthraquinodimethane: The Formation of 10-Dicyanomethylene-anthrone Hydrazone

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Summary. A novel reaction of 11,11,12,12-tetracyanoanthraquinodimethane – its transformation into 10-dicyanomethylene-anthrone hydrazone by reaction with hydrazine – is reported. This hydrazone seems to be a convenient starting material in the synthesis of anthracene derivatives and compounds incorporating anthracenic fragments, but is itself as a conjugated donor acceptor system a material with interesting physical properties.

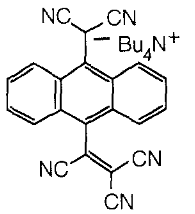
Keywords. 11,11,12,12-Tetracyanoanthraquinodimethane; 10-Dicyanomethylene-anthrone hydrazone; Solvatochromic shift; Non-linear optical properties; Donor–acceptor system.

Eine neue Reaktion von 11,11,12,12-Tetracyanoanthrachinodimethan: die Bildung von 10-Dicyanomethylen-anthronhydrazon (Kurze Mitt.)

Zusammenfassung. Eine neue Reaktion von 11,11,12,12-Tetracyanoanthrachinodimethan – seine Umsetzung zum 10-Dicyanomethylen-anthronhydrazon durch Reaktion mit Hydrazin – wird beschrieben. Dieses Hydrazon könnte als Ausgangsmaterial für die Synthese von Anthracenderivaten dienen, zeigt aber auch selbst als konjugiertes Donor-Akzeptorsystem interessante physikalische Eigenschaften.

11,11,12,12-Tetracyanoanthraquinodimethane (**1**) attracted considerable attention during the last decade owing to its interesting electrochemical properties [1–3] and nontrivial structural features [4, 5]. However, the chemical properties of **1** have not been studied in detail. The only transformation reported so far has been the reaction of **1** with the malonodinitrile anion in dimethylformamide to yield tetrabutylammonium anthracene-9-tricyanovinyl-10-dicyanomethide (**2**) in only 13% yield [2].

Following our investigations of hypericin derivatization [6], it was now found that **1** readily reacted with hydrazine to form 10-dicyanomethylene-anthrone hydrazone (**3**) in nearly quantitative yield. The structure of **3** was evident from its NMR-, M-, and UV-spectra. It was interesting to note, that **1** remained unchanged



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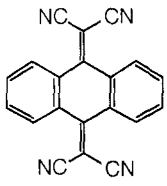

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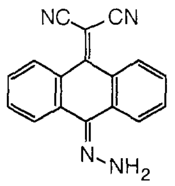

3

in reactions with hydroxylamine or *n*-propylamine, and that the parent compound, 7,7,8,8-tetracyanoquinodimethane underwent reduction upon reaction with hydrazine to form 1,4-bis-(dicyanomethyl)-benzene [7]. According to force field calculations using the PCMODEL program [8], the high steric strain of **1** (compare for its X-ray structural analysis [4, 5]) was relieved on formation of **3**. This was also evident from the smaller torsional angles of about 30° at the hydrazone fragment of the "butterfly" shaped molecule, as compared to about 41° at the dicyanovinyl fragments in **1** and **2**. Thus, this to our knowledge hitherto unknown hydrazinolysis of a dicyanovinyl derivative constituted a thermodynamically governed equilibration reaction.

The novel hydrazone **3** might be envisaged as a convenient starting material in the synthesis of anthracene derivatives and compounds incorporating anthracene fragments. However, beyond this potential use in organic synthesis, it is a molecule with conjugated acceptor and donor groups and therefore is a rather interesting molecule in itself. Thus, in addition to the transition at about 320 nm that was also characteristic of **1**, a charge transfer band at above 400 nm was observed. It displayed a rather large solvatochromic shift of about 73 nm on proceeding from cyclohexane to dimethylsulfoxide solutions, whereas the main band at about 320 nm remained more or less unshifted. This pronounced effect made **3** also a candidate for non linear optical properties. An estimate using the solvatochromic shift method [9] placed its second order polarizability value in a range that was comparable to common materials for non linear optical properties. The hydrazone **3** did not exhibit fluorescence ($\Phi_f < 10^{-4}$), and it was found to be a weak base of $pK_a = 1.5 \pm 0.1$.

10-Dicyanomethylene-anthrone Hydrazone (**3**)

To a stirred suspension of 1.52 g (5 mmol) of **1** [10] in 70 ml methanol, 0.65 g (5 mmol) of hydrazine sulfate and 1.4 ml (10 mmol) of triethylamine were added. The suspension was stirred for 3 h at room temperature and quenched with 350 ml of water. The bright orange colored precipitate thus formed was filtered off and dried. Yield 1.3 g (96%). It was crystallized from methanol/chloroform; m.p.: 240 °C (dec.). ^{1}H-NMR (200 MHz, δ, CDCl$_3$): 8.33–8.22 (m, 2H$_{\text{arom}}$), 8.13–8.00 (m, 2H$_{\text{arom}}$), 7.73–7.43 (m, 4H$_{\text{arom}}$), 6.42 (s, NH$_2$) ppm. IR (KBr): 3385, 3291, 3291, 3210, 2214, 1626, 1576, 1549, 1509, 1462, 1329, 1316, 1287, 1189 cm^{-1}. ^{13}C-NMR (90 MHz, δ, CDCl$_3$): 163 (C10), 137 (C9), 135 (C$_{\text{arom}}$), 132.2 (HC$_{\text{arom}}$), 132.0 (C$_{\text{arom}}$), 131 (HC$_{\text{arom}}$), 129 (C$_{\text{arom}}$), 128 (HC$_{\text{arom}}$), 127.7 (HC$_{\text{arom}}$), 127.6 (HC$_{\text{arom}}$), 126.7 (C$_{\text{arom}}$), 126.4 (HC$_{\text{arom}}$), 125 (HC$_{\text{arom}}$), 124 (HC$_{\text{arom}}$), 114.2 (CN), 114.0 (CN), 79 (=C(CN)$_2$) ppm. UV (cyclohexane): $\lambda_{\max} = 391, 318$ nm. UV (tetrachloromethane): $\lambda_{\max} = 407, 320$ nm. UV (chloroform): $\lambda_{\max} = 412, 325$ nm. UV (ethylacetate): $\lambda_{\max} = 425, 319$ nm. UV (methanol): $\lambda_{\max} = 430$, 320 nm. UV (ethanol): $\lambda_{\max} = 434$ (6 500), 323 (18 300), 220 (30 300) nm (ε). UV (tetrahydrofuran): $\lambda_{\max} = 436, 322$ nm. UV (dimethylformamide): $\lambda_{\max} = 455, 322$ nm. UV (dimethylsulfoxide): $\lambda_{\max} = 464, 326$ nm. Spectrophotometric titration of **3** in 80% ethanol/water as the solvent: $\lambda_3 = 440, 325$ nm, $\lambda_{3\cdot\text{H}^+} = 325$ nm;

$pK_a = 1.5 \pm 0.1$. MS (70 eV, 160 °C): m/e (%) = 270 (100, M^+), 244 (26), 243 (24), 215 (25), 214 (35), 212 (15), 206 (20), 205 (24), 188 (15), 176 (5), 135 (7), 121 (5), 108 (22), 94 (20), 81 (5), 57 (8), 55 (6), 45 (9).

Acknowledgment

A Lise Meitner post doc stipendium of the Fonds zur Förderung der Wissenschaftlichen Forschung to A. V. is acknowledged.

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Received August 2, 1993. Accepted August 26, 1993