This article was downloaded by: [Case Western Reserve University] On: 26 November 2014, At: 22:29 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

THE SYNTHESIS AND STRUCTURE CHARACTERISTICS OF TWO NOVEL AZO-QUINONE DERIVATIVES

Li Hai-ying ^a & Lei Liang-cai ^a

^a Petrochemical Department , Fushun Petroleum Institute , Fushun, 113001, China Published online: 09 Nov 2006.

To cite this article: Li Hai-ying & Lei Liang-cai (2001) THE SYNTHESIS AND STRUCTURE CHARACTERISTICS OF TWO NOVEL AZO-QUINONE DERIVATIVES, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:1, 155-158, DOI: <u>10.1081/SCC-100000193</u>

To link to this article: http://dx.doi.org/10.1081/SCC-100000193

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

SYNTHETIC COMMUNICATIONS, 31(1), 155–158 (2001)

THE SYNTHESIS AND STRUCTURE CHARACTERISTICS OF TWO NOVEL AZO-QUINONE DERIVATIVES

Li Hai-ying* and Lei Liang-cai

Petrochemical Department, Fushun Petroleum Institute, Fushun 113001, China

ABSTRACT

The synthesis of novel LB film materials 2-(4-hexadecyloxyphenylazo)anthraquinone and 2-(4-dodecyloxyphenylazo) anthraquinone is described. These materials were obtained from 2-amino-anthraquinone by azo-coupling with phenol and follwed by Williamson etherification of phenolic hydroxyl group with alkyl bromide. The structures were confirmed by NMR, MS, FT-IR techniques and elemental analysis.

The Langmuir-Blodgett (LB) method is effective for preparing organic ultrathin films with a fine-layered structure and specific properties (1). Thickness of the ultra-thin films can be controlled on a molecular scale by designing the size of the molecule. Some interesting phenomena are observed by attaching different functional groups. The stability of ordered LB films depends on molecule-molecule interaction, substrate-molecule interaction, and their relative strength (2). One can stabilize the structures of the highly organized films through molecular-level designing of the substrate surfaces.

155

www.dekker.com

^{*}To whom correspondence should be addressed.

ORDER		REPRINTS
-------	--	----------

HAI-YING AND LIANG-CAI



Scheme 1.

The highly organized LB films have attracted much attention during the past two decades because of their prospective application in constructing molecular electronic devices (3–5). In this study, we synthesized two novel compounds with a long alkyl chain, an electro-chromic quinone and a photo-chromic azo region in a conjugated system. We expect that aromatic interactions between π system and hydrophobic interactions between alkyl chains will effectively improve the ordered film structure and its stability. Furthermore, the azo functional group can interconvert between the anti- and syn-form and give rise to electrochemical redox reaction. The quinone functional group can undergo reversible red-oxidation. In other words, the individual chemical states can be achieved and interconvert by control of electrochemical and photochemical parameters. LB film from molecules with an azo-quinone group has the potential of information storage and readout process.

These two azo-quinone derivatives, 2-(4-hexadecyloxyphenylazo)anthraquinone and 2-(4-dodecyloxyphenylazo)anthraquinone, can be prepared from 2-aminoanthraquinone by azo-coupling with phenol, followed by Williamson etherification of phenolic hydroxyl group with alkyl bromide.

EXPERIMENTAL

All commercially available reagents were purchased. NMR spectra were recorded in $CDCI_3$ solution using TMS as internal standard on an ARX-400 instrument (Bruke Co. Ltd.). IR spectra were obtained in a JASCO-FTIR-430

Copyright @ Marcel Dekker, Inc. All rights reserved.

Marcel Dekker, Inc.

270 Madison Avenue, New York, New York 10016

ORDER		REPRINTS
-------	--	----------

TWO NOVEL AZO-QUINONE DERIVATIVES

spectrometer with potassium bromide plates. MS data were measured with a VG ZAB-HS instrument and the ultimate analysis data was given from a CARLO ERDA 1106 instrument (Italy). Melting point was recorded in a WRS-1 digital melting point apparatus (China).

157

2-(4-Dodecyloxphenylazo)anthraquinone

Conc. Sulfuric acid (12 mL) was added dropwise to 2-aminoantraquinone (2.3 g) in a 100-mL Erlenmeyer flask. The mixture was stirred for 15 min at room temperature. Then sodium nitrite (0.83 g) in water (5 mL) was added dropwise and the mixture stirred for 45 min. The reaction mixture was poured slowly to a solution of phenol (0.94 g) and sodium hydroxide (9.5 g) in distilled water (50 mL). The mixture was stirred for 1 h, acidified with acetic acid (50%), and the formed precipitate collected by filtration. The filter cake was washed with water and dried in vacuo to give 2-(4-hydroxyphenylazo)anthraquinone (2.7 g). Yield: 82%. 2-(4-Hydroxyphenylazo)-anthraquinone (1.64 g) in THF (10 mL) was added dropwise to the mixture of 1-bromododecane (2.5 g) and sodium hydroxide (0.4 g) and THF (25 mL). The mixture was refluxed until complete reaction. After cooling to room temperature, the mixture was extracted with either $(3 \times 100 \text{ mL})$ and the combined extracts washed with saturated brine. The solvent was evaporated under reduced pressure and the residue was crystallized from the mixture of ether and THF (5:1), obtaining 2-(4-dodecyloxypbenylazo)anthraquinone (1.9 g) as a reddish brown solid. Yield: 76.6%. mp: 88.8°-89.5°C. MS (EI) m/e: 496(M⁺). Anal. calcd: C, 77.38; H, 7.31; N, 5.64. Found: C, 77.39; H, 7.25; N, 5.58. ¹H NMR (CDCI₃) δ : 0.87–0.90 (t, 3H, J=6.8, -CH₃); 1.27–1.37 (m, 16H, -(CH₂)-₈); 1.47–1.51 (m, 2H, -CH₂CH₂CH₂O-); 1.82–1.87 (m, 2H, -CH₂CH₂O-); 4.06–4.09 (t, 2H, J = 6.5, -C H_2 O-); 7.03–7.05 (dd, 2H, J = 7.0 and J = 2.0, $H_{\beta\beta'}$); 7.82–7.84 (m, 2H, $H_{AA'}$); 7.99–8.02 (dd, 2H, J=7.0 and J=2.0, $H_{\alpha\alpha'}$); 8.22–8.25 (dd, 1H, J = 8.2 and J = 2.0, H_3 ; 8.34–8.38 (m, 2H, $H_{BB'}$); 8.44–8.47 (d, 1H, J = 8.3, H_4); 8.75 (d, 1H, J = 1.95, H_1).

2-(4-Hexadecyloxyphenylazo)anthraquinone

Prepared similarly as described above. mp: $93.2^{\circ}-94.4^{\circ}$ C. MS (EI) m/e: 552 (M⁺). Anal. calcd: C, 78.22; H, 8.02; N, 5.07. Found: C, 78.11; H, 8.07; N, 4.99. ¹H NMR (CDCI₃) δ : 0.90–0.86 (t, 3H, J = 6.8, -C H_3); 1.26–1.37 (m, 26H, -(C H_2)-₁₃); 1.80–1.85 (m, 2H, -C H_2 CH₂O-); 4.06–4.09 (t, 2H, J = 6.5, -C H_2 O-); 7.03–7.05 (2H, dd, J = 7.0 and J = 2.0, $H_{\beta\beta'}$); 7.82–7.84 (m, 2H, $H_{AA'}$); 7.99–8.02 (dd, 2H, J = 7.0 and J = 2.0, $H_{\alpha\alpha'}$); 8.22–8.25 (dd, 1H, J = 8.3 and J = 2.0, H_3); 8.34–8.38 (m, 2H, $H_{BB'}$); 8.44–8.47 (d, 1H, J = 8.3, H_4); 8.75 (d, 1H, J = 1.95,



ORDER		REPRINTS
-------	--	----------

HAI-YING AND LIANG-CAI

*H*₁). IR (KBr) cm⁻¹: 2917 (ν_{C-H}), 2855 (ν_{C-H}), 1673 (ν_{C=O}), 1590 (ν_φ), 1472 (δ_{*H*-*C*-*H*), 1300 (ν_{as},-φ-O-C), 1250 (ν_s,-φ-O-C), 1147 (ν_φ-N), 708 (ν_φ-H).}

REFERENCES

- 1. Buchel, M.; Sekkat, Z.; Paul, S.; Weichart, B.; Menzel, H., Knoll, W. Langmuir **1995**, *11*, 4460.
- 2. Miller, C.J.; Cuendet, P.; Gratzel, M. J. Phys. Chem. 1991, 95, 877.
- 3. Schildkraut, J.S.; Penner, T.L.; Willand, C.S.; Ulman, A. Opt. Lett. **1988**, *13*, 134.
- 4. Li, H.; Liu, Z. Synthetic Comm. 1998, 20, 3779.
- 5. Yamada, S.; Nedano, T.; Matsuo, T. Thin Solid Film 1994, 245, 196.

Received April 2, 2000



158

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the <u>U.S. Copyright Office</u> for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on <u>Fair Use in the Classroom</u>.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our <u>Website</u> <u>User Agreement</u> for more details.

Order now!

Reprints of this article can also be ordered at http://www.dekker.com/servlet/product/DOI/101081SCC100000193