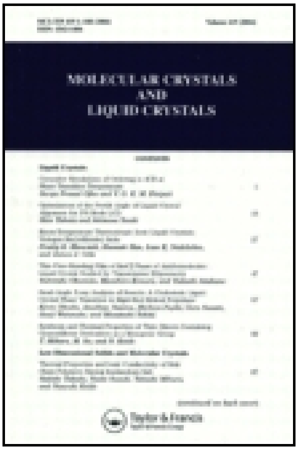


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Formation of Quinhydrone-Type Complexes Composed of Quinone Dimers and Trimers Bearing t-Butyl and n-Dodecyl Substituents

Naoto Hayashi [a], Takahiro Yoshikawa [a], Megumi Kurakawa [a], Takahiro Ohnuma [a], Yuko Sugiyama [a] & Hiroyuki Higuchi [a]

[a] Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama, Japan

To cite this article: Naoto Hayashi, Takahiro Yoshikawa, Megumi Kurakawa, Takahiro Ohnuma, Yuko Sugiyama & Hiroyuki Higuchi (2006): Formation of Quinhydrone-Type Complexes Composed of Quinone Dimers and Trimers Bearing t-Butyl and n-Dodecyl Substituents, Molecular Crystals and Liquid Crystals, 456:1, 133-137

To link to this article: http://dx.doi.org/10.1080/15421400600788617

Mol. Cryst. Liq. Cryst., Vol. 456, pp. 133–137, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600788617

Formation of Quinhydrone-Type Complexes Composed of Quinone Dimers and Trimers Bearing *t*-Butyl and *n*-Dodecyl Substituents

Naoto Hayashi
Takahiro Yoshikawa
Megumi Kurakawa
Takahiro Ohnuma
Yuko Sugiyama
Hiroyuki Higuchi
Department of Chemistry, Faculty of Science, Toyama University,
Gofuku, Toyama, Japan

*Complexation behavior of 5,5′-bis(2-methyl-2-propyl)-2,2′-bi(1,4-benzoquinone) (**1a**), 5,5″-bis(2-methyl-2-propyl)-2,2′;5′,2″-ter(1,4-benzoquinone) (**2**), and 5,5′-didodecyl-2,2′-bi(1,4-benzoquinone) (**1b**) with hydroquinone was investigated. **1a** and **2** yielded no complex due to the bulkiness of t-butyl substituents, while **1b** afforded quinhydrone-type complex, which was revealed to be amorphous by means of X-ray Powder Diffraction (XPD) study.*

Keywords: charge-transfer (CT) interaction; hydrogen bond; quinhydrone

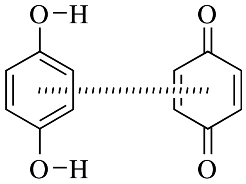
Quinhydrone is a molecular complex composed of equimolar *p*-benzoquinone (quinone) and hydroquinone [1]. In quinhydrone, two intermolecular interactions are essential: face-to-face charge transfer (CT) interaction and OH/O(=C) hydrogen bond [2]. These interactions dictate not only the molecular geometry but also the physical properties of quinhydrone substantially [3,4].

In quinhydrone, hydrogen bond and CT interaction effect in an intermolecular manner. Given a molecule which consists of two or more covalently linked quinone and hydroquinone moieties, it would give quinhydrone-type complex comprised of intermolecular as well

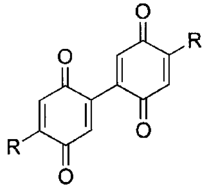
---

Address correspondence to Naoto Hayashi, Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930–8555, Japan. E-mail: nhayashi@sci.toyama-u.ac.jp

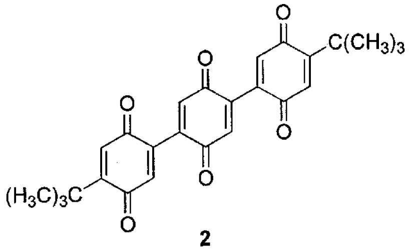
as intramolecular hydrogen bonding. The change in the manner of hydrogen bonding will affect not only on the geometry of molecular assembly but also on properties relating to hydrogen bond. Moreover, it is anticipated that change in electronic character of the molecule would influence properties based on the CT interaction. In the present paper, complexation behavior of quinone dimer **1a-b** [5] and trimer **2** with hydroquinone yielding quinhydrone-type complexes is investigated.



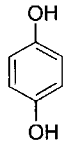
quinhydrone



1



2



hydroquinone

R = $C(CH_3)_3$ (**1a**), *n*-$C_{12}H_{25}$ (**1b**)

When **1a** was mixed with hydroquinone, neither in solution nor in solid were yielded quinhydrone-type complexes. This was confirmed by electronic absorption spectra of the mixture, which was merely superimposition of each component. The lack of complexation should be due to sterically bulky *t*-butyl substituents. Figure 1 illustrates the molecular structure of **1a** optimized by MMFF94 [6] methods, which indicates that *t*-butyl group is large enough to prevent access of hydroquinone to the quinone moiety in a face-to-face manner. The quinone trimer **2** also yielded no quinhydrone-type complex with hydroquinone. Based on the fact that electron acceptor character of **2** is stronger than that of **1a**, this result can be explained in terms of steric hindrance again. Thus, the quinone substituent on the central quinone moiety is also too bulky to form the quinhydrone-type complex, too.

On the other hand, when **1b** was ground with hydroquinone in solid, the mixture immediately turned into deep purple. This change implies

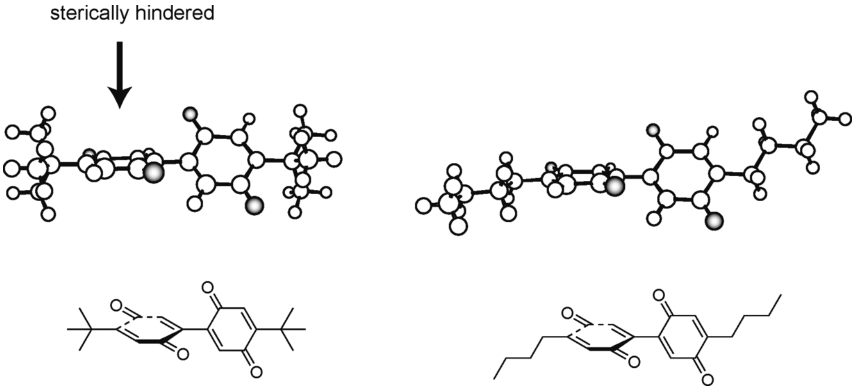


FIGURE 1 Optimized structure of **1a** (left) and 5,5′-di-*n*-butyl-2,2′-bi(1,4-benzoquinone) (right) calculated by MMFF94 methods.

formation of the CT complex of **1b** and hydroquinone, as seen in quinhydrone itself [1]. The formation of quinhydrone-type complex was also supported by IR spectra, where absorption at 1670 cm^{-1}, which is assigned to C=O stretching of **1b** [7], disappeared, and instead new absorption peak emerged at 1633 cm^{-1}. The different behavior between **1a** and **1b** is ascribable to their substituents. As seen in Figure 1, where *n*-butyl derivative is compared to **1a** instead of **1b**, *n*-alkyl substituent would not prevent face-to-face approach of hydroquinone to the quinone moiety. On comparison of IR spectra of **1b**-hydroquinone complexes of various stoichiometric ratios, the C=O stretching absorptions were no longer changed when more than equimolar of hydroquinone was used. This indicates the complexation ratio to be 1:1.

Considering of non-planarity of **1b**, as shown in Figure 1, two models may be proposed to describe the 1:1 complex crystal, where (*a*) one quinone moiety complexes with hydroquinone while the other is free, or (*b*) the molecules arrange in a manner of ···-quinone···hydroquinone···quinone-quinone···hydroquinone···quinone-···, where ··· and - represent CT interaction and covalent bond, respectively [8]. The solid-state structure of the **1b**-hydroquinone complex is, however, not yet elucidated. This is partly because it is amorphous. Figure 2 shows the result of XPD study of hydroquinone, **1b**, and the mixture. The 1:1 molar ratio in spite of amorphous might indicate that strong intermolecular interactions effect within a pair of **1b** and hydroquinone, whereas weak between the pairs. Thus, model (*a*) appears to be more plausible.

In summary, the complexation behavior of quinone dimers **1a-b** and trimer **2a** with hydroquinone has been investigated to reveal

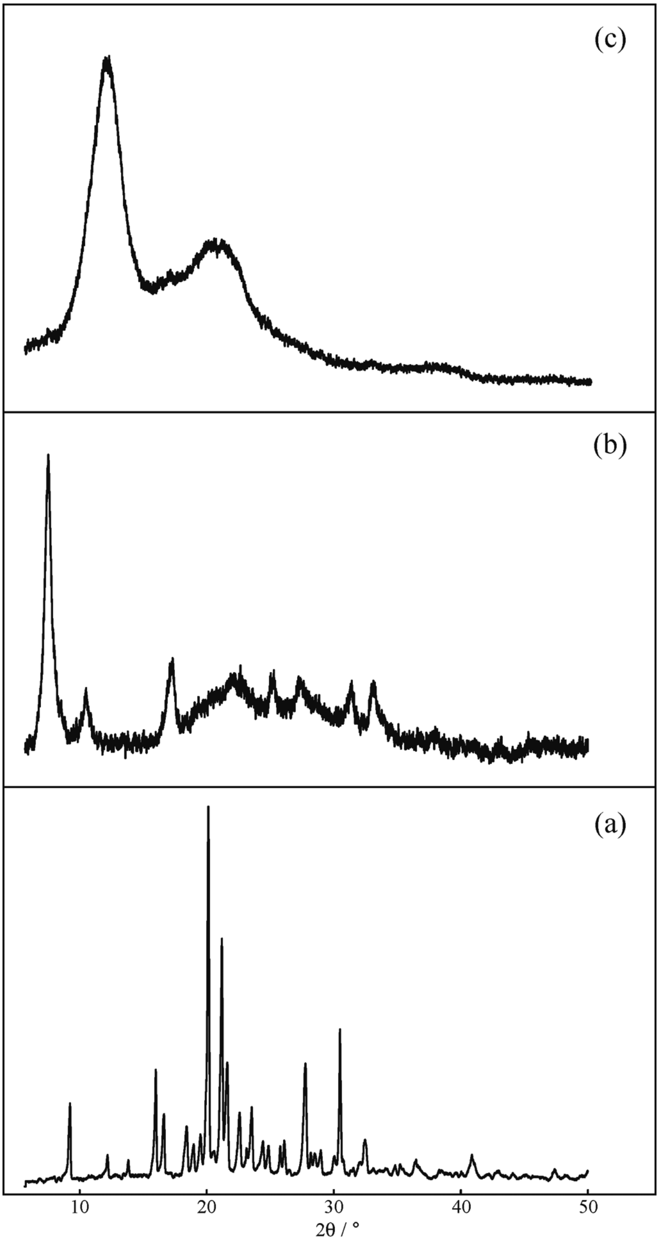


FIGURE 2 XPD charts of hydroquinone (a), **1b** (b) and 1:1 mixture of **1b** and hydroquinone (c).

that sterically bulkiness of the substituent is essential for the complexation. It is found that quinone dimer **1b**, which bears *n*-dodecyl substituent, formed quinhydrone-type complex with hydroquinone, though its solid-state structure is not yet determined because of the complex being amorphous. Study on complexation behavior between quinone dimers and trimers is currently underway.

Financial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (90281104) is gratefully acknowledged.

REFERENCES

[1] Foster, F. (1969). *Organic Charge-Transfer Complexes*, Academic Press: New York, USA.

[2] (a) Eggins, B. R. & Chambers, J. Q. (1970). *J. Electrochem. Soc.*, *117*, 186; (b) Moser, R. E. & Cassidy, H. G. (1965). *J. Am. Chem. Soc.*, *87*, 3463; (c) Parker, V. D. (1969). *Chem. Commun.*, 716.

[3] Shigeta, Y., Kitagawa, Y., Nagao, H., Yoshikawa, Y., Toyada, J., Nakasuji, K., & Yamaguchi, K. (2001). *J. Mol. Liq.*, *90*, 69.

[4] Keyes, T. E., Forster, R. J., Bond, A. M., & Miao, W. (2001). *J. Am. Chem. Soc.*, *123*, 2877.

[5] (a) Erdtman, H., Granath, M., & Schultz, G. (1954). *Acta Chem. Scand.*, *8*, 1442; (b) Lounasmaa, M. (1965). *Acta Chem. Scand.*, *19*, 540; (c) Madkour, T. M. (1997). *Polymer J.*, *29*, 670.

[6] (a) Halgren, T. A. (1996). *J. Comput. Chem.*, *17*, 490; (b) Halgren, T. A. (1996). *J. Comput. Chem.*, *17*, 520; (c) Halgren, T. A. (1996). *J. Comput. Chem.*, *17*, 587; (d) Halgren, T. A. & Nachbar, R. (1996). *J. Comput. Chem.*, *17*, 616.

[7] Czuchajowski, L., Duraj, S., & Kusharska, M. (1976). *J. Mol. Struct.*, *34*, 187.

[8] Patil, A. O., Curtin, D. Y., & Paul, I. C. (1984). *J. Am. Chem. Soc.*, *106*, 4010.