Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst. 1992, Vol. 219, pp. 75–78
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Printed in the United States of America

THE NOVEL DEPENDENCE OF THE HOST-GUEST INCLUSION PROPERTIES ON THE NUMBER OF THE THIOPHENE RINGS IN A NEW HOST SERIES BASED ON LINEARLY CONDENSED POLYTHIOPHENES

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(Received July 12, 1991)

Abstract A new host series for crystalline inclusion complexes, which were designed on the basis of linearly condensed polythiophenes as a rigid backbone, were prepared. The host:guest (DMSO) composition and the conformation of the host molecule in the inclusion crystals exhibited a novel dependence on the number of the condensed thiophene rings.

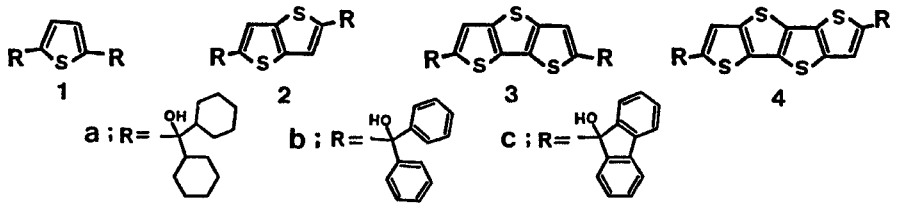
Keywords: Inclusion Compound, Host-Guest, Even-Odd Effects, Polythiophene, Conformation

INTRODUCTION

Rigid backbones and bulky groups are considered to be important requirments in designing host molecules for crystalline inclusion complexes.[1] We have prepared a new host series **1a,b,c–4c** for host-guest inclusion complexes. The rigid plate-like structure of condensed polythiophenes is expected to provide a range of inclusion capacities and cavities in the crystals depending on the length of the plate. We demonstrate here a novel correlation between the number of the thiophene rings and the conformation of the host molecule, which is associated with the host:guest stoichiometric ratio as well.

INCLUSION PROPERTIES

The host compounds, being prepared from the precursor thiophenes,[2] showed broad inclusion properties upon crystallization from various solvents. The results are listed in Table 1, in which the host-guest stoichiometric ratios were determined by means of NMR integration, HPLC analysis, and microanalysis.



Compound **2c** is especially an efficient host. It is interesting to note that the host compounds with an even number of thiophene rings have a tendency to give the host:guest stoichiometry of 1:2, whereas those with odd numbers of thiophene rings tend to give the 1:1 stoichiometry. A typical example is seen in the crystals including DMSO as the guest: the crystalline complexes with the composition of (**1c**)(DMSO), (**2c**)$(DMSO)_2$, (**3c**)(DMSO), and (**4c**)$(DMSO)_2$ were obtained.

TABLE I Formation of crystalline inclusion compounds of host **1a**-**4c** and their host:guest ratios. Numbers specify molecular ratios to the host compounds.

Guest	**1a**	**1b**	**1c**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**4c**
ethanol	0	0	0	2	0	2	2	0	1	
acetone	0	1	0	0	2	2	1	1	1	
DMSO	1	1	1		2	2		1	1	2
DMF	1	1	2	2	2	2	2	1	2	
dioxane	1	2	1	2	1	2	1		1	2
benzene	1	0	0	0	0	4/3	1	2	0	

MOLECULAR AND CRYSTAL STRUCTURE

The host-guest compositions observed for DMSO are associated with the crystal and molecular structures of the inclusion compounds; X-ray crystal structure analyses were carried out on four inclusion compounds with DMSO as the guest. The crystal data are summarized in Table 2.

The most remarkable features are in the conformation of the bulky substituents on the thiophene ring. Two C-OH bonds in the host molecule take a gauche conformation close to the eclipsed one about the C-S bonds of the terminal thiophene rings (e. g., Figure 1). This

means, in (**1c**)(DMSO) and (**3c**)(DMSO) two C-OH groups on the both ends of the rigid backbone are directed to the same side of the backbone, whereas, in the host having the even number of the thiophene rings (**2c**)$(DMSO)_2$ and (**4c**)$(DMSO)_2$, the C-OH groups are directed to the opposite sides of the backbone. Consequently, two fluorenyl groups are arranged on the same side for (**1c**)(DMSO) and (**3c**)(DMSO) and on the opposite sides for the (**2c**)$(DMSO)_2$ and (**4c**)$(DMSO)_2$.

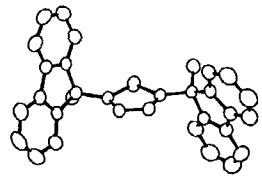
All the guest DMSO molecules are hydrogen-bonded to the OH groups in the host molecules. In (**1c**)(DMSO) and (**3c**)(DMSO) a host molecule holds a guest DMSO molecule by its two OH groups that are aligned on the same side. On the other hand, in (**2c**)$(DMSO)_2$ and (**4c**)$(DMSO)_2$ two OH groups are directed to the opposite sides so that a DMSO molecule is hydrogen-bonded with two host molecules to give the 1:2 stoichiometric ratio.

The present results provide an interesting example in which the direction of hydrogen bonding in the crystal is controlled according to the preferential gauche conformation of the C-OH and C-S bonds, hence depending on the number of the thiophene rings.

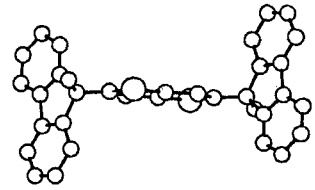
TABLE II Crystal data of the inclusion complexes.

	1c.DMSO	2c.2DMSO	3c.DMSO	4c.2DMSO
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_{1/n}$	$P2_{1/n}$
a(Å)	14.469(5)	12.618(1)	17.942(3)	10.880(1)
b	21.208(5)	13.161(2)	14.831(1)	17.390(2)
c	8.741(4)	11.615(3)	11.487(1)	10.457(3)
α(°)	90.92(2)	115.41(2)	90.00	90.00
β	99.13(3)	97.04(2)	102.42(1)	109.50(1)
γ	94.56(2)	103.41(1)	90.00	90.00
V(Å^3)	2639(2)	1639.7(6)	2984.8(7)	1864.9(6)
Z	4	2	4	2
R factor	0.069	0.10	0.12	0.047

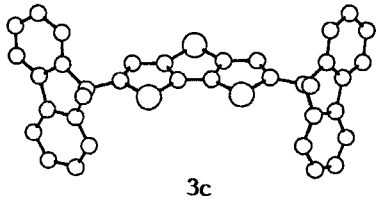
FIGURE 1 Conformations of the host molecules in the DMSO inclusion complexes.



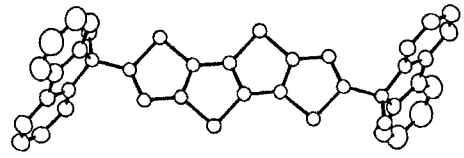
1c



2c



3c



4c

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