

SYNTHESIS AND PROPERTIES OF [3.3](2,5)FURANO(2,5)THIOPHENOPHANE
AND [3.3](2,5)THIOPHENOPHANE

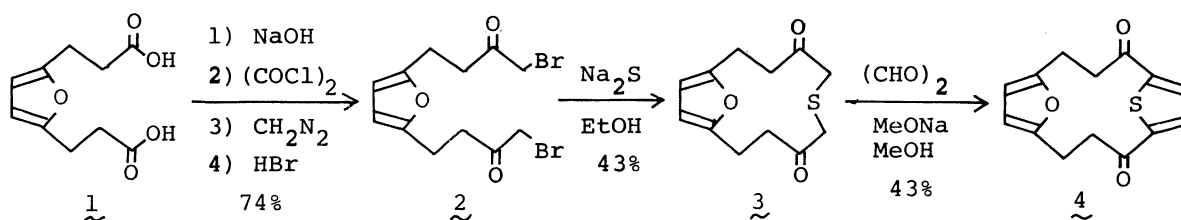
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The title compounds have been synthesized via a route involving cyclization of 4,4'-(2,5-furandiyl)bis(1-bromo-2-butanone) with sodium sulfide followed by condensation with glyoxal to give 1,11-dioxo[3.3](2,5)furano(2,5)thiophenophane, a new intramolecular CT complex. A solution of [3.3](2,5)thiophenophane contains anti and syn conformers in a ratio of ca. 20:1 as shown by a VT-NMR study.

Recently numerous [3.3]cyclophanes have been synthesized as a result of the progress of the synthetic methods¹⁾. However, [3.3]heterophanes have been little studied and only [3.3](2,5)pyrrolophane²⁾ and the tetrakis(ethoxycarbonyl) derivative of [3.3](2,5)thiophenophane³⁾ have been reported. In view of the preferred syn conformation of [3.3]metacyclophane⁴⁾ in contrast to the exclusive or preferred anti conformation of [2.2]metacyclophane, [2.2](2,5)thiophenophane, and [2.2](2,5)-furanophane⁵⁾, it was considered interesting to study the conformational property of [3.3](2,5)thiophenophane. The method we have developed for the synthesis of thiophenophanes involves only simple condensation reactions under mild conditions⁶⁾, and, therefore, was expected to permit the synthesis of rather unstable furan-containing thiophenophanes.

The sodium salt of furan-2,5-dipropionic acid (1) was treated successively with oxalyl chloride, diazomethane, and concentrated hydrobromic acid giving a bis-(bromoacetyl) compound 2 in 74% overall yield⁷⁾. Cyclization of 2 was carried out by simultaneous addition of the solutions of 2 in tetrahydrofuran and sodium sulfide in 70% ethanol to boiling ethanol over 8 h under high dilution conditions in an inert atmosphere. Silica gel chromatography (chloroform) and recrystallization (ethanol) provided a monomeric diketo sulfide 3 in 43% yield. 3: colorless prisms, mp 91.5-92°C; MS M^+ 238; IR(KBr) ν_{CO} 1707 cm^{-1} ; PMR(60 MHz, $CDCl_3$) δ 5.89 (s, furan), 3.44 (s, $COCH_2S$), and 2.86 (A_2B_2m , $-CH_2CH_2-$) ppm.



Conversion of 3 to thiophenophane 4 was effected by the addition of a dilute solution of sodium methoxide in methanol to a solution of 3 and glyoxal hydrate in methanol over 12 h at room temperature. 4: yellow prisms (acetone), mp 128-129°C; IR(KBr) ν_{CO} 1657 cm^{-1} ; PMR(CDCl_3) δ 7.27(s, thiophene), 5.63(s, furan), 2.7-3.5 (complex m) ppm.

The most striking feature of 4 is the yellow color which is not observed for 3 and open chain 2,5-diacetylthiophenes such as 2,5-divalerylthiophene 7, and for the solutions of 2,5-dimethylfuran and 2,5-diacetylthiophene even in high concentrations. The UV spectrum of 4 shown in Fig. 1 indicates the presence of a broad band at about 360 nm (ϵ ca. 2500) extending to

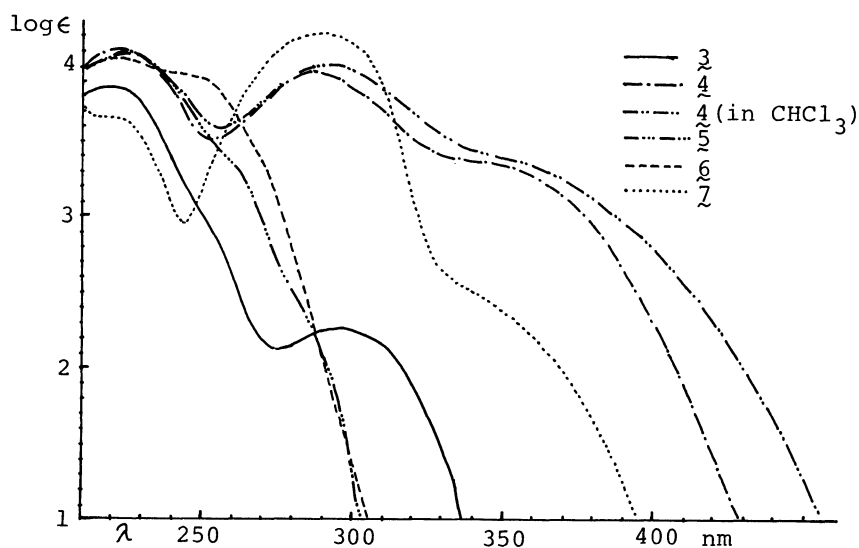
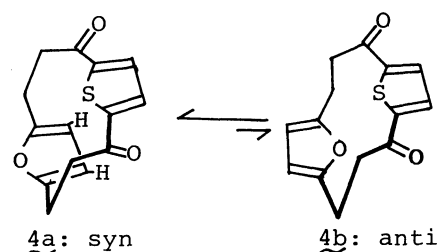
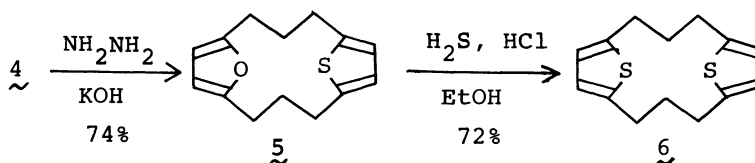


Fig. 1. The electronic spectra of 2-6 in cyclohexane.

the visible region. This band is different in character from the shoulder of 7 ($n-\pi^*$) as shown by the solvent effect. Namely, while the shoulder of 7 was subject to a small hypsochromic shift upon change of the solvent from cyclohexane to chloroform⁸⁾, the longest wave band of 4 revealed a bathochromic shift as shown in Fig. 1. Therefore, this band must arise from the intramolecular charge transfer interaction between the electron-rich furan and the electron-poor 2,5-diacetylthiophene moiety. Since in this new CT heterophane having a weak donor-acceptor pair⁹⁾ the bridging carbonyl groups are involved in the interaction⁸⁾, the conformation must be such that the carbonyl groups and the thiophene ring are nearly coplanar. The high-field shifted furan protons in 4 compared to those in 2 and 3 (0.3 ppm at room temperature and 0.5 ppm at -100°C) indicate the presence of the diamagnetic ring current effect of the thiophene ring. Molecular model examination (Dreiding) suggests that the half-overlapping syn conformation 4a where the furan protons are situated above the thiophene ring is preferred¹⁰⁾. The syn conformation may also be favored by the CT interaction¹²⁾.



The Wolff-Kishner reduction of 4 afforded [3.3](2,5)furano(2,5)thiophenophane



5, easily isolated by steam-distillation, in 74% yield. 5: colorless prisms (MeOH), mp 58-58.5°C; PMR(CDCl₃) δ 6.53(s, thiophene), 5.65(s, furan), 2.2-3.1(m, 8H), and 1.4-2.2(m, 4H) ppm.

When hydrogen sulfide and hydrogen chloride gases were introduced into a solution of 5 in ethanol at 0°C, [3.3](2,5)thiophenophane 6 was obtained as a white precipitate in 72% yield. 6: colorless prisms (chloroform), mp 181-182°C, sublimed at 130°C/0.1 Torr, PMR(CDCl₃) δ 6.45(s, thiophene), 2.5-3.3(m, 8H), and 1.8-2.5(m, 4H) ppm. Whenever pure crystals of 6 were dissolved in several different solvents by application of heat, the singlet peak for the thiophene protons (δ 6.45 in CDCl₃) was accompanied by a small singlet peak at the higher field (δ 6.11 in CDCl₃) in an almost constant ratio (~20:1).

A variable temperature NMR study revealed that these two peaks (δ 6.37 and 6.00 in d₈-toluene) coalesced to a singlet at 105°C as shown in Fig. 2. The presence of an exchange process led us to assign, considering the diamagnetic shielding effect of a thiophene ring, the large peak at the

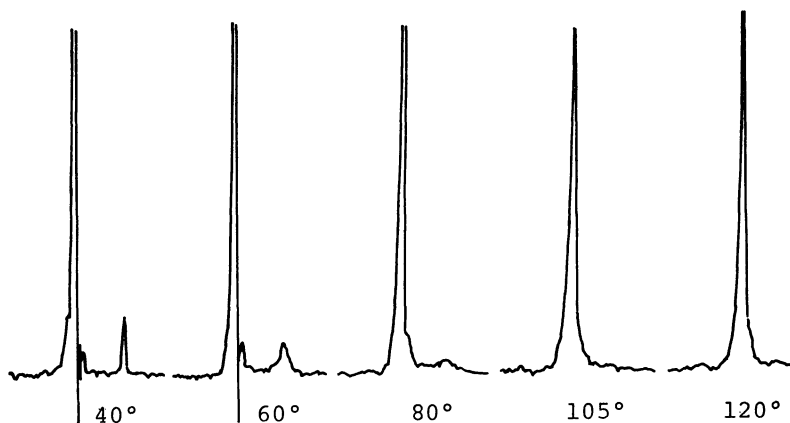
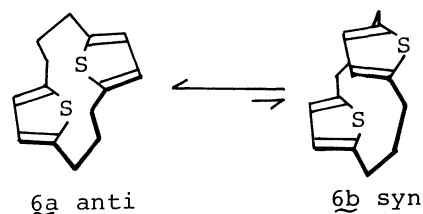


Fig. 2. The thiophene region of the PMR spectra of 6 at different temperatures (d₈-toluene, 60 MHz)

normal position of thiophene protons and the small upfield-shifted peak to an anti (6a) and a syn (6b) isomers, respectively.

The singlet peaks for thiophene and furan protons of 5 did not show such a behavior even when the sample solution was cooled down to -90°C, indicating the free rotation of the furan (and the thiophene) ring(s). These results demonstrate the bulkiness of the sulfur atoms in 6.

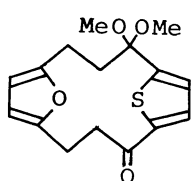


References and Notes

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- 7) All the new compounds gave correct elemental analyses except for bromoketone 2 which was contaminated with the corresponding chloride (ca. 6%) as indicated by the elemental analyses and PMR data.
- 8) Alcohols could not be used as the solvent because 4 readily reacted with methanol just by recrystallization yielding a monoketal 8.



8: colorless needles, mp 153-154.5°C

IR(KBr) ν_{CO} 1648 and ν_{MeO} 2830 cm^{-1}

PMR(CDCl_3) δ 6.96(d, $J=4.2\text{Hz}$), 6.69(d, 4.2Hz),
5.76(d, $J=3.2\text{Hz}$), 5.68(d, 3.2Hz), 3.27 and
3.35(s, OMe), and 2.3-3.1(m, 8H) ppm.

- 9) Among numerous examples of CT cyclophanes there are a few of them which show CT absorption despite the mixtures of the corresponding open-chain electron donor and acceptor do not. See, for example, H. A. Staab and H. Hafner, Chem. Ber., 110, 3358 (1977), H. A. Staab and V. Taglieber, Chem. Ber., 110, 3366 (1977), and M. W. Haenel, A. Flatow, V. Taglieber, and H. A. Staab, Tetrahedron Lett., 1977, 1733.
- 10) Although an S,O-cis rotamer is usually predominant for the 2-carbonyl derivatives of thiophene¹¹⁾, the S,O-cis conformation is unlikely for 4, because the molecular model suggests that the carbonyl groups tend to be out of the plane of the thiophene ring.
- 11) See, for example, S. Caccamese, G. Montaudo, A. Recca, F. Fringuelli, and A. Taticchi, Tetrahedron, 30, 4129 (1974).
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