

A Crown Ether Tetrathiafulvalene Cage

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A novel macrocyclic cage compound incorporating two polyether units as well as a tetrathiafulvalene unit has been prepared and characterised.

Very recently the syntheses of two different cage compounds or cryptands, both incorporating a tetrathiafulvalene (TTF) unit, have been reported.^{1,2} Although the π -donor properties of these examples have not been studied in detail, compounds of this type may show interesting electroactive and cation binding properties. With such molecules there exists the possibility of preparing donor-acceptor charge-transfer complexes containing attractive crown ether cation binding sites.

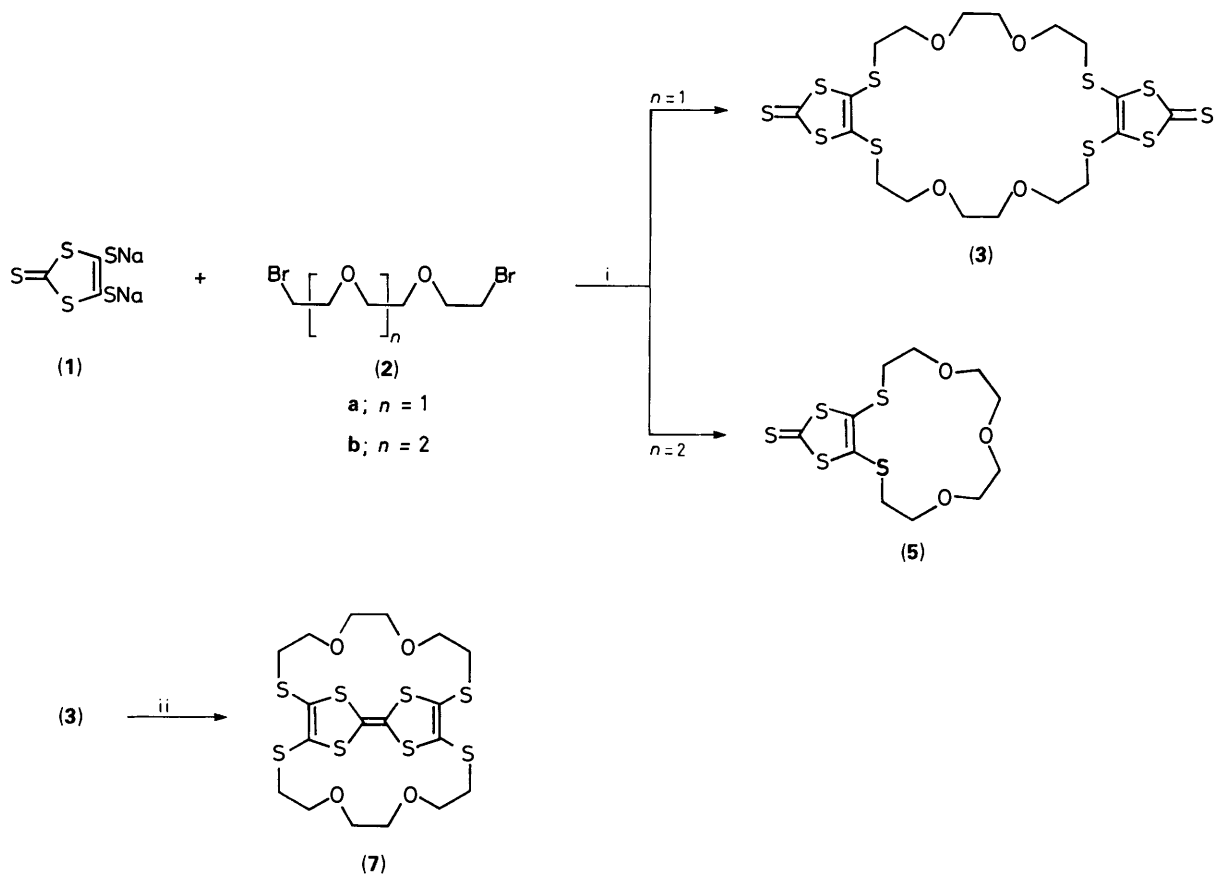
Cyclic polyethers or crown ethers have extensively been used³ for the construction of macrocyclic ligands and host molecules. The combination of the 4,5-dithio-1,3-dithiole-2-thione unit with polyethers was therefore of interest to us particularly in the light of two recent examples.^{1,2} Although Otsubo and Ogura⁴ have reported the preparation of some crown tetrathiafulvalene macrocycles their 4,5-dithio-1,3-dithiole-2-thione derivatives were obtained in low yields.

We now report an improved procedure for the preparation of these types of macrocyclic precursors and the successful intramolecular coupling of one of the precursors to give the first example of a macrocyclic crown ether cage incorporating a tetrathiafulvalene unit.

Reaction of disodium dithiolate salt (**1**)⁵ with 1,8-dibromo-3,6-dioxaoctane (**2a**) in dry THF gave, after work-up *via* preparative layer chromatography (dichloroethane-chloroform, 60:40), the 2:2 macrocycle (**3**) (R_F 0.4) (25% yield, mp 96–97 °C) as the main product along with a small amount (5%) of the 1:1-macrocyclic (**4**) (R_F 0.5) (m.p. 114–15 °C). In contrast to this, using high dilution and adding (**2b**) slowly, the previously reported⁴ 1:1 macrocycle (**5**) was obtained as the main product in 51% yield along with the formation of a small amount of 2:2 macrocycle (**6**). Otsubo and Ogura⁴ obtained compound (**5**) in 14% yield using (**1**) and tetraethylene glycol 1,11-ditosylate. Thus the dibromides (**2**) appear to be better

electrophiles towards the disodium salt (**1**) and the reaction probably involves a template effect from the sodium ions. A likely reason for improved yields may be the use of the pure disodium salt (**1**).⁵ The yields reported by us have not been optimised although it is likely that a whole range of crowns incorporating (**1**) can be prepared in synthetically useful yields. The structures of the new macrocycles (**3**) and (**4**), and the cage compound (**7**) were confirmed on the basis of spectroscopic and analytical evidence.† Thus, compound (**3**) showed a molecular ion cluster with (M^+) at m/z 624 and an isotopic pattern corresponding to ten sulphur atoms: this confirmed that (**3**) had the depicted 2:2 macrocyclic structure, a result which was further corroborated by elemental analyses and IR and ¹H NMR spectral results.† The macrocycle (**5**) showed analytical and spectroscopic data in good agreement with reported

† All new compounds gave spectroscopic and analytical data in accordance with assigned structures. Data are quoted for compounds (**3**), (**4**), and (**7**). For (**3**): 25% yield; m.p. 96–97 °C; $\delta_H(\text{CDCl}_3)$ 3.76 (t, 8 H, OCH₂), 3.64 (s, 8 H, OCH₂CH₂O), and 3.10 (t, 8 H, SCH₂); $\delta_C(\text{CDCl}_3)$ 211.170 (C=S), 136.798 (SC=), 77.039 (SCH₂), 70.650 (OCH₂), and 36.549 (OCH₂CH₂O); m/z (EI) 624 (M^+); $\nu_{\text{max}}(\text{KBr})$ 1 061 (C=S) and 1 123 cm⁻¹ (CO); $\lambda_{\text{max}}(\text{CHCl}_3)$ 383 (3.23), 321 (2.61), 275 (2.95), and 242 nm (2.92) (Found: C, 34.7 H, 3.9% Calc. for C₁₈H₂₄O₄S₁₀: C, 34.61; H, 3.84%). For (**4**): 5% yield; m.p. 114–115 °C; $\delta_H(\text{CDCl}_3)$ 3.72 (t, 4 H, OCH₂), 3.64 (s, 4 H, OCH₂CH₂O), and 3.08 (t, 4 H, SCH₂); m/z (EI) 312 (M^+); $\nu_{\text{max}}(\text{KBr})$ 1 034 (C=S) and 1 115 cm⁻¹ (CO); $\lambda_{\text{max}}(\text{CHCl}_3)$ 386 (2.90), 277 (2.73), and 243 nm (2.56). For (**7**): 22% yield; m.p. 247 °C (methanol-chloroform, 1:1); $\delta_H(\text{CDCl}_3)$, 2.73 (m, 4 H, SCH₂), 3.37 (m, 8 H, OCH₂CH₂O), 3.49 (m, 4 H, SCH₂), and 3.66 (m, 8 H, OCH₂); $\delta_C(\text{CDCl}_3)$ 34.1 (CH₂), 68.6 (CH₂), 69.6 (CH₂), 121.6 (C=C), and 127.5 (C=C); m/z (EI) 560 (M^+); $\nu_{\text{max}}(\text{KBr})$ 1 132 cm⁻¹ (CO); $\lambda_{\text{max}}(\text{CHCl}_3)$ 338 (3.16), 304 (2.73), and 259 nm (3.15) (Found: C, 38.65 H, 4.3. Calc. for C₁₈H₂₄O₄S₈: C, 38.55 H, 4.31%).



Scheme 1. Reagents and conditions: i, THF as solvent, 25 °C. ii, $\text{P}(\text{EtO})_3$, xylene as solvent, reflux 5 h.

values⁴ and yielded the known⁴ TTF derivative (8) (28% yield) with spectral data consistent with reported values.⁴ Treatment of the macrocycle (3)⁶ with an excess of triethyl phosphite in refluxing xylene² gave, after work-up, the new intramolecularly coupled tetrathiafulvalene cage (7) in 22% yield as light amber crystals after recrystallisation from methanol–chloroform (1:1) (m.p. 247 °C). The mass spectrum of (7) showed a molecular ion cluster with (M^+) at m/z 560, with an isotopic pattern confirming the presence of eight sulphur atoms; furthermore, the mass spectrum showed little fragmentation probably reflecting the high stability of this macrocyclic system. Compound (7) gave a characteristic initial red colour¹ on treatment with acid and the UV spectra of compounds (3) and (7) showed a characteristic blue shift in which the bands at 385 and 274 nm in (3) were shifted to 338 and 259 nm respectively in (7). Almost the same relative shift due to the formation of the intramolecular TTF chromophore was seen in the pyridine cage TTF compounds reported in ref. 2; furthermore, the ¹H NMR spectrum of (7) consisted of AA'-XX' systems showing multiplets at δ 2.73 and 3.49 due to the nonequivalence of the SCH_2 protons. Similarly, the remaining protons appeared as complicated multiplets at δ 3.37 and 3.66. The CPK model of this compound reveals that (7) is a very rigid system possessing a bowl-shaped structure with the TTF part at the bottom. From this it can be clearly seen that the various protons of the polyether part are locked in different spatial environments. The presence of three sp^3 and two sp^2 carbon signals in the ¹³C NMR spectrum of (7) showed that this compound is symmetric. The cyclic voltammetry of (7) in 1,1,2-trichloroethane (0.1M Bu_4NClO_4 , Pt working electrode, 120 mV s^{-1}) shows two reversible one-electron oxidation waves at +0.41 and +0.73 V

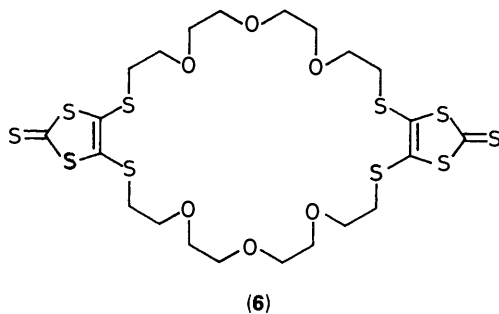
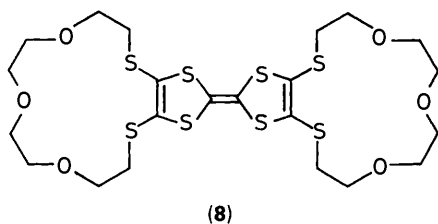
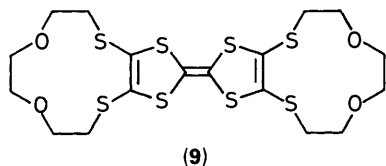
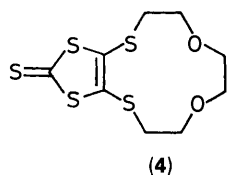
(vs. a silver/silver chloride reference electrode). These oxidation potentials for the TTF derivative (7) suggests that it is relatively more difficult to oxidise than the recently reported² TTF cage compound, but are low enough to indicate good π -electron donor properties compared with the unsubstituted parent TTF molecule.

The surprisingly easy formation of (7) therefore seems to confirm that the intramolecular coupling of 1,3-dithiole-2-thione derivatives yielding tetrathiafulvalene cryptands is indeed a general reaction^{1,2} and, therefore, a whole new series of related macrocyclic structures now appears to be readily accessible.

Experimental

General Procedure for the Reaction of the Disodium Dithiolate Salt (1) with Dibromo Ethers (2a) and (2b).—To a solution of the salt (1) (2.30 g, 9.50 mmol) in dry THF (100 ml) was added, slowly (during 3 h) under nitrogen, a solution of the dibromo ether (2a) or (2b) (9.50 mmol) in dry THF (50 ml). The reaction mixture was stirred overnight. After the completion of the reaction, solvent was distilled off and the residue treated with water and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated and the crude product mixture was purified by preparative layer chromatography (Merck silica gel 60 PF_{254}) using dichloroethane as eluant to give the corresponding 1:1 or 2:2-macrocycles (3), (4), (5), and (6) in 25, 5, 51, and 20% yield respectively.

Synthesis of Cage Compound (7).—To a solution of the macrocycle (3) (0.076 g, 0.12 mmol) in dry xylene (15 ml) was



Scheme 2.

added triethyl phosphite (2.0 ml) and the mixture was refluxed under argon for 5 h. The resulting reddish orange solution was cooled and xylene was distilled off under reduced pressure. Compound (7), which separated as a light amber solid, was filtered off. It was washed with ethanol and recrystallised from chloroform-ethanol by diffusion method to give the cage compound (7) (22%).

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- 6 The macrocycle (3) used for coupling reaction was analytically pure (MS, mp, and TLC) in order to prevent any formation of the intermolecularly coupled isomeric compound (9). However (9) was readily obtained from the monomer (4) using similar coupling methods.

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