Tetrahedron Letters, Vol.30, No.2, pp 159-162, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

CHANGING THE SIZE OF A CAVITY VIA AN ELECTRON-TRANSFER: SYNTHESIS AND REDUCTION OF 1,5,22,26-TETRAOXA-[5,5]-(2,8)-DIBENZO[a,e]CYLOOCTATETRAENOPHANE [1)]

Willi Heinz, Hans-Joachim Räder and Klaus Müllen*
Department of Organic Chemistry, University of Mainz,
J.J.Becher-Weg 18-22, D-6500 Mainz FRG

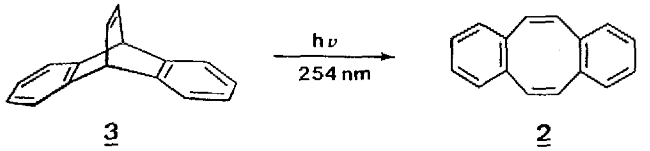
Abstract: The synthesis and electron transfer reactions of the title compound, the first macrocycle incorporating two cyclooctatetraene units, are described.

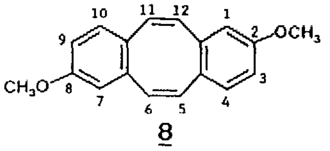
Our studies of electron-transfer-induced conformational changes in cyclooctatetraene (COT) derivatives[2-4] suggested to include systems containing two COT units with a face-to-face arrangement. It should be possible in such cage-type structures to reversibly change the cavity-size via redox processes. Herein we report on the synthesis and the redox behaviour of the dibenzo[a,e]cyclooctatetraenophane 1, which, to our knowledge, constitutes the first example of a macrocycle incorporating two COT-subunits.

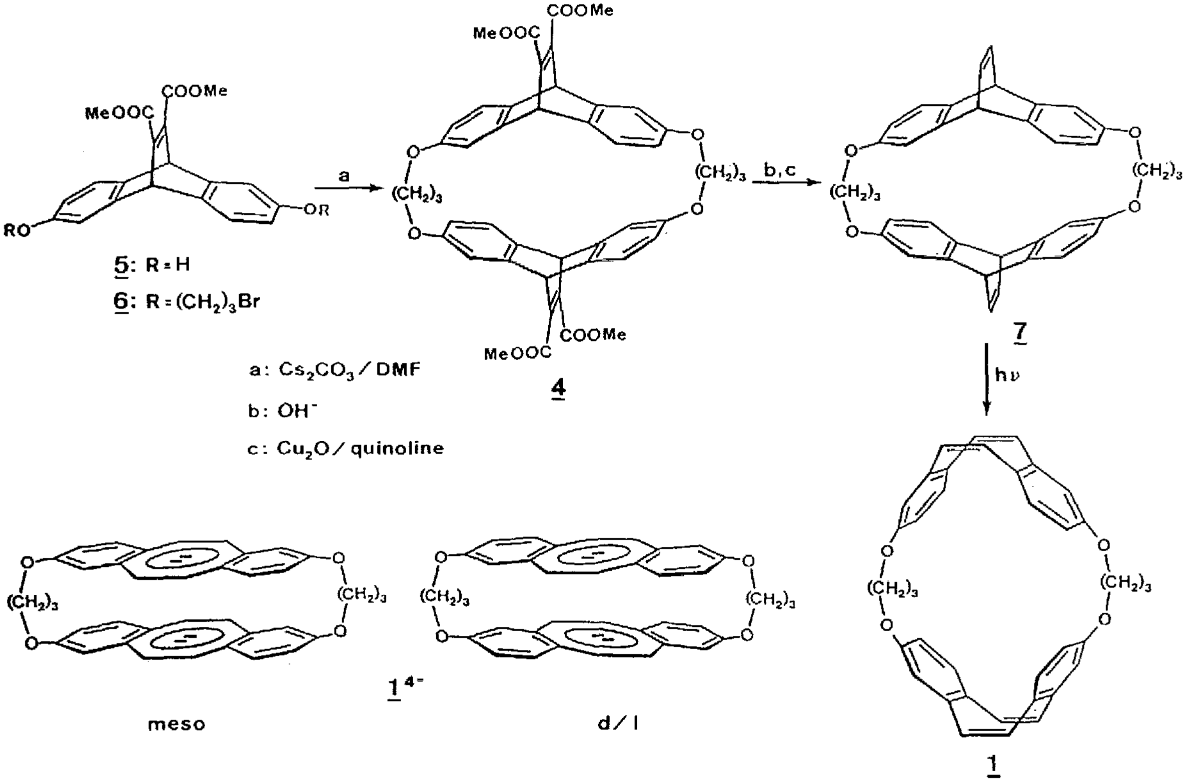
Only a few attempts toward the synthesis of cyclophanes containing COT rings have been reported in the literature.[5] While cyclooctatetraenes can be prepared by irradiation of barrelenes with UV-light (254 nm)[6], attempted ring expansion of benzenoid [2_n]cyclophanes by cycloaddition of dicyanoethylene and subsequent irradiation failed to produce the corresponding phanes with two COT layers.[7] It was crucial for our approach that the conformational and electronic properties of COT remain essentially unaffected in the symmetrically annelated dibenzo compound 2.[8,9] Dibenzo[a,e]COT derivatives can be readily prepared by Diels-Alder addition of acetylene derivatives to anthracenes and subsequent photolysis of the resultant dibenzobarrelenes (3).[10,11]

We anticipated that the tetraester 4 recently reported by Dougherty et al.[12] would serve as a suitable precursor of 1. According to the authors, a mixture of meso-/dl-diastereomers of 4 was synthesized by coupling equimolar amounts of 5 and 6 under high dilution conditions (22%) (only the meso-form is shown). We submitted the macrocyclic ester to saponification (2N NaOH/MeOH;

reflux; 6 h, 97 %) without separation of the isomers. Decarboxylation of the resulting tetraacids in quinoline (Cu_2O, 200°C,30 min.) produced the diastereomeric dibenzobarrelenophanes of type 7 in 68 % yield. For the final step of our sequence, the isomerization of 7 to 1, THF-solutions (10^{-3} M) of 7 were directly irradiated with a low pressure Hg-lamp (125 W) in a photochemical reactor. TLC- and ^{1}H-NMR control of the reaction indicated that while one barrelene unit was rapidly converted, the isomerization of the second unit proceeded more slowly. After five days of irradiation, HPLC-separation of the complex reaction mixture yielded a main fraction (16 %) which was identified by NMR- and mass spectroscopy as the desired dibenzocyclooctatetraenophane (see Table) 1, a microcrystalline white solid only sparingly soluble in halogenated and ethereal solvents and insoluble in alcohols.[13] In order to compare the spectroscopic and redox-chemical properties of 1 to those of a monomeric reference compound, we synthesized 2,8-dimethoxydibenzo[a,e]COT (8) via an analogous route from 2,6-dimethoxyanthracene.







a: Cs_2CO_3/DMF
b: OH^-
c: Cu_2O/quinoline

Table: $^{1}H(\delta_H)$-NMR chemical shifts of neutral and charged COT systems

	1,7	3,9	4,10	5,11	6,12	$O-CH_2(O-CH_3)$	$C-CH_2-C$
δ_H (1)$^{a)}$	6.38	6.59	6.81	6.49	6.63	3.93	2.10
δ_H ($1^{4-}/4K^+$)$^{a)}$	6.75$^{b)}$	5.99$^{b)}$	7.67$^{b)}$	6.39$^{b)}$	6.58$^{b)}$	4.03$^{b)}$	2.10-1.60
	7.01$^{c)}$	5.87$^{c)}$	7.49$^{c)}$	6.50$^{c)}$	6.58$^{c)}$	4.20,3.83$^{c)}$	
δ_H (8)$^{a)}$	6.55	6.69	6.90	6.59	6.65	3.69	
δ_H ($8^{2-}/2K^+$)$^{a)}$	7.18	5.99	7.74	6.91	7.01	3.73	

a) 400 MHz, THF-d_8, 20°C; b) dl-form; c) meso-form.

Quite surprisingly, the ^{1}H-NMR spectra of 1 fail to indicate the presence of two diastereomers which contrasts to the situation prevailing in the precursors 4 and 7. We ascribe this finding to a dynamic process which causes a rapid interconversion of the meso- and dl-forms of 1. Model studies demonstrate that such an isomerization can be achieved by the flattening of one dibenzo[a,e]COT subunit accompanied by a 180°-rotation about the phenolic C-O-bonds.

Reduction of the title compound was carried out in a sealed NMR tube by contacting 3 mg of 1 in 0.5 ml THF-d_8 with a highly active potassium mirror. Spectroscopic monitoring of the reaction revealed that after a period of 10-12 h the starting material was completely consumed and that two independent diamagnetic species had been formed. The ^{1}H-NMR resonances of the new species remained unaffected upon prolonged contact (three days). This finding suggests that the two sets of NMR signals must be attributed to a pair of diastereomeric tetraanions of 1 (see Table). Further evidence for the presence of tetraanionic species was obtained from quenching experiments: addition of dimethyl sulphate to the reduction solution yielded a product whose mass spectrum (m/e = 612) clearly points toward a tetramethyl adduct of 1. In contrast to the neutral compound, the internal rotation of the dibenzo-COT units in $1^{4-}/4K^+$ is slow on the NMR-time scale. This can be explained by the increased steric hindrance caused by the solvation shells of the ion pairs.

Analogous results were obtained upon reduction with lithium, except that the tetralithio salt of 1^{4-} exhibits dynamic behaviour at room temperature. While the ^{1}H-NMR spectrum of $1^{4-}/4Li^+$ at -30° C is similar to that of the tetrapotassio salt, the spectrum at ambient temperature shows only broad averaged signals for the different nuclei of both diastereomers. This observation can be ascribed to a rotational process similar to that occurring in the neutral compound. Obviously, on going from the tetrapotassio to the tetralithio salt the steric hindrance to the isomerization is decreased due to the favoured formation of solvent separated ion pairs.[14]

NMR spectroscopic studies have shown that the alkali metal reduction of tub-shaped dibenzo[a,e]COT produces a planar, strongly diatropic dianion.[9,15] The flattening of benzo-fused COT compounds upon dianion formation is even observed if the planar structure is highly strained.[3] The examination of molecular models suggests that a charge-induced flattening of the COT units in 1^{4-}/4K^{+} should significantly alter the size of the cyclophane cavity: the centers C-5 and C-5′ (C-6 and C-6′) of the opposite eight-membered rings approach each other from 12 Å (1) to approximately 5-6 Å (1^{4-}).

Experimental evidence for such a conformational change can be deduced from the fact that the ^{1}H-NMR signals undergo substantial upfield shifts (up to 0.4 ppm compared to the reference dianion 8^{2-}/2K^{+}) due to the mutual shielding of the flattened, parallel-oriented subunits.

The failure to detect a dianionic species may be due to the higher solubility of 1^{2-}/2K^{+} in comparison to the neutral compound. (Note that the greatest portion of the starting compound is only suspended in THF.) As a consequence, the further reduction of 1^{2-}/2K^{+} proceeds faster than the dissolution and reduction of 1.

Cyclovoltammetric reduction of 1 [DMF, TBAP (0.1 m), SCE as reference electrode] revealed two well-separated waves at E_{max}= -2.31 and -2.40 V. On the other hand, the peak maxima associated with the first and second electron transfer step in the electrochemical reduction of the monomeric dibenzo[a,e]-COT systems 2[16] and 8 are not resolved under identical conditions. Therefore, in the case of 1 we assign the first wave to dianion and the second wave to tetraanion formation. The spacing of the two reduction waves (90 mV) indicates that there is only a weak Coulombic interaction of approximately 2.5 kcal/mole between the doubly charged subunits of the tetraanion.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References:

1. Nomenclature according to: F.Vögtle,P.Neumann, Tetrahedron 1970, 26, 5847.
2. W. Huber, A. May, K. Müllen, Chem. Ber. 1981, 114, 1318.
3. W. Heinz, P. Langensee, K. Müllen, J. Chem. Soc., Chem. Commun. 1986, 947.
4. W. Heinz, P. Langensee, K. Müllen, Angew. Chem. 1987, 99, 1306; Angew. Chem. Int. Ed. Engl. 1987, 26, 1291.
5. V. Boekelheide, Top. Curr. Chem. 1983, 113, 87.
6. H.E. Zimmerman R.W. Binkley, R.S. Givens, J.L. Grunewald M.A. Sherwin, J. Am. Chem. Soc. 1969, 91, 3316.
7. R. Gray, V. Boekelheide, J. Am. Chem. Soc. 1979, 101, 2129.
8. G.H. Senkler, Jr., D. Gust, P.X. Riccobono, K. Mislow, J. A. Chem. Soc. 1972, 94, 8626.
9. T.J. Katz, M. Yoshida, L.C. Siew, J. Am. Chem. Soc. 1965, 87, 3784.
10. P.W.Rabideau, J.B.Hamilton, L. Friedman, J. Am. Chem. Soc. 1968, 90, 4465.
11. H.P. Figeys, A. Dralants, Tetrahedron 1972, 28, 3301.
12. M.A. Petti, T.J. Shepodd, D.A. Dougherty, Tetrahedron Lett. 1986, 27, 807.
13. 1: mp 301-302°C;^{1}H-NMR: cf. Table; ^{13}C-NMR (100 MHz,$CDCl_3$, 20°C): 158.0 (C-2, C-2′,C-8,C-8′),138.3 (C-6a,C-6a′,C-12a,C-12a′),132.8 (C-6,C-6′,C-12, C-12′),132.4(C-5,C-5′,C-11,C-11′),129.9(C-4,C-4′,C-10,C-10′),129.5(C-4a,C-4a′,C-10a,C-10a′),114.9,111.8(C-3,C-3′,C-9,C-9′;C-1,C-1′,C-7,C-7′), 62.8 (CH_2-O), 29.7 (-CH_2-).
    8: mp 94°C; ^{1}H-NMR: cf. Table;^{13}C-NMR (50 MHz,$CDCl_3$,20°C):158.6(C-2,C-8), 138.6 (C-6a,C-12),133.1 (C-6,C-12),132.5 (C-5,C-11),130.4 (C-4,C-10),129.5 (C-4a,C-10a),113.5,113.4. (C-3,C-9;C-1,C-7),55.2 (CH_3-O).
14. K. Müllen, Chem. Rev. 1984, 84, 603.
15. H.Günther,M.-E.Günther,D.Mondeshka,H.Schmickler,Liebigs Ann.Chem 1978,165.
16. H.Kojima,A.J.Bard,H.N.C.Wong,F.Sondheimer, J.Am.Chem.Soc. 1976, 98, 5560.

(Received in Germany 18 October 1988)