Tetrakis(bicyclo[2.2.2]octeno)cyclooctatetraene Dication: a Stable COT Dication with a Tub Structure

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One-electron oxidation of the radical cation of tetrakis(bicyclo[2.2.2]octeno)cyclooctatetraene with SbF_5 gives the corresponding dication, a tub-shaped eight-membered ring, which rapidly inverts with an energy barrier of 10.8 ± 0.7 kcal mol^{-1}.

In comparison with other Hückel aromatic systems, which have been extensively studied, surprisingly little is known about the $6\pi/8C$ system, the cyclooctatetraene (COT) dication. So far there has been only one report, which describes the observation of di- and tetra-substituted COT dications under stable-ion conditions at low temperature.[1] Previously we found that annelation with rigid σ-frameworks such as bicyclo[2.2.2]octene (BCO) is quite effective in stabilizing both the open- and closed-shell cationic π-systems.[2] We now report the successful preparation of a COT dication fully annelated with BCO frameworks, which is stable in CH_2Cl_2 solution at room temperature.

The cyclic voltammetry (CV) of tetrakis(bicyclo[2.2.2]octeno)cyclooctatetraene **1**[3] in CH_2Cl_2 at room temperature showed two oxidation steps, of which only the first step was reversible.[2c] In contrast, the CV in CH_2Cl_2–CF_3CO_2H–$(CF_3CO)_2O$ (20 : 1 : 1)[4] conducted in a vacuum-sealed cell at −78 °C exhibited two well-defined reversible oxidation waves at $E_{1/2}$ +0.39 and +1.14 V *vs* Ag/Ag$^+$ as shown in Fig. 1. This is the first electrochemical detection of both the radical cation and dication of a COT derivative as stable species, and suggests that even the dication could be observed under appropriate conditions.

Previously COT **1** was oxidized to a stable radical cation salt by the use of $NO^+SbCl_6^-$.[2c] When a green solution of $\mathbf{1}^{\cdot+}SbCl_6^-$ in CH_2Cl_2 (or CD_2Cl_2) was treated with a large excess (*ca.* 50 equiv.) of a stronger oxidant, SbF_5, at −78 °C in a vacuum-sealed tube, a red solution immediately resulted, which was stable at room temperature and exhibited only three ^{13}C NMR signals at δ 177.9, 41.0, and 23.9. By comparison of the NMR data with those of **1** and dianion $\mathbf{1}^{2-}$ shown in Table 1, the newly formed red species is assigned as dication $\mathbf{1}^{2+}$. According to the Spiesecke–Schneider relationship,[5] an average of 40-ppm downfield shift of the ^{13}C signal for the COT ring carbon is in good agreement with the consecutive decrease of 1/4 unit charge per carbon in the sequence, $\mathbf{1}^{2-}$, **1**, and $\mathbf{1}^{2+}$. Deshielding of the bridgehead proton of $\mathbf{1}^{2+}$ as compared with **1** ($\Delta\delta_H$ 1.86) is comparable to that reported for the methyl proton in the 1,3,5,7-tetramethyl COT dication ($\Delta\delta_H$ 1.87) recorded at low temperature,[1] suggesting that both of these dications are subjected to ring current effects to a similar extent.

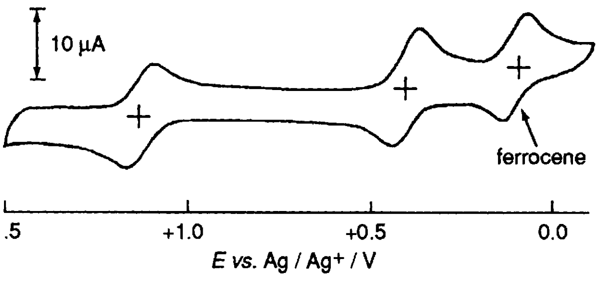
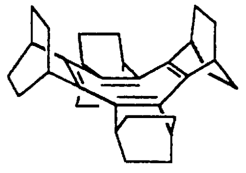


Fig. 1 The cyclic voltammogram of **1** in CH_2Cl_2–CF_3CO_2H–$(CF_3CO)_2O$ (20 : 1 : 1) containing Bu_4NBF_4 (0.1 mol dm^{-3}); scan rate, 0.1 V s^{-1}

All these findings appeared to be in accord with the structure **A** having a planar COT ring. However, upon lowering the temperature down to −80 °C, the original single peak for the methylene carbon in the bicyclic framework at δ 23.9 was found to split into two peaks of equal intensity at δ 24.8 and 20.4. This is ascribed to the presence of lower-energy structure with two non-identical ethano-bridges, *i.e.* the tub-shaped dication **B**, which undergoes rapid ring inversion at room temperature. The energy barrier for this process ($\Delta G^‡$) was estimated to be 10.8 ± 0.7 kcal mol^{-1} from the coalescence temperature of −35 ± 15 °C. In order to rationalize these results, semi-empirical MO calculations were conducted by the use of PM3 method for the structure **A** with the COT ring enforced to a planar geometry, the structure **A′** with a non-planar COT ring obtained by energy minimization of the structure **A**, and the structure **B** with a tub COT ring. The energy-minimized structures thus obtained are shown in Fig. 2 together with the values of heat of formation (ΔH_f). The ΔH_f for the tub structure **B** was found to be lower than those



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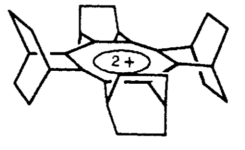
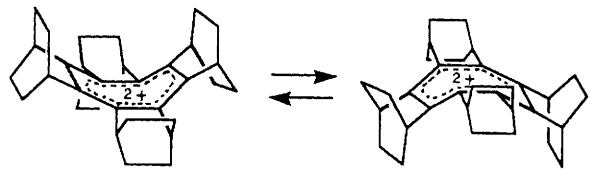


A

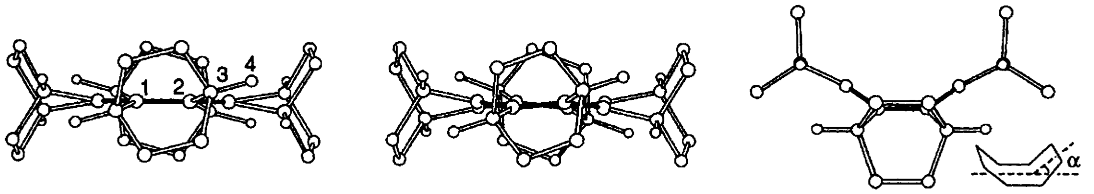


B **B**

Table 1 NMR data for $\mathbf{1}^{2-}$, **1**, and $\mathbf{1}^{2+}$

Compound	Solvent	T/°C	δ_C C(sp^2)	δ_C CH	δ_C CH$_2$	δ_H CH	δ_H CH$_2$
$\mathbf{1}^{2-a}$	[$^2H_8$]THF	25	97.8	35.8	30.6	3.65	1.87, 1.41
$\mathbf{1}^{b}$	[$^2H_8$]THF	25	140.0	33.4	26.6, 25.8	2.33	1.56, 1.38
$\mathbf{1}^{2+c}$	CD_2Cl_2	25	177.9	41.0	23.9	4.19	2.40, 1.65
$\mathbf{1}^{2+c}$	CD_2Cl_2	−80	176.6	39.5	24.8, 20.4	4.09	2.6–1.5

[a] Ref. 3. No spectral change was observed when the temperature was lowered to −60 °C. [b] Ref. 3. No spectral change was observed when the temperature was raised to 150 °C in [$^2H_5$]nitrobenzene. [c] The chemical shifts were read using the CD_2Cl_2 signal (δ 53.1) as a reference.



A $\Delta H_f = 478.7$ **A′** $\Delta H_f = 470.3$ **B** $\Delta H_f = 448.0$

Fig. 2 The PM3 calculated structures (side views) for dication 1^{2+}; with a COT ring enforced to be planar (the dihedral angle 1–2–3–4 = 16.2°) (**A**); with a COT ring energy-minimized starting from the structure **A** (the central ring has a shallow crown shape with a bond angle of 133.6° and a dihedral angle of 27.1°) (**A′**); with a tub-shaped COT ring (bent angle α = 34.5°) (**B**). Methylene hydrogens are omitted for clarity. ΔH_f/kcal mol^{-1}.

for the structures A and A′ by 30.7 and 22.3 kcal mol^{-1} respectively, supporting the experimental observation that the tub form is the most stable. From the observed $\Delta G^‡$ value, conceivably the transition-state for the ring inversion would involve a structure more stable than A′, and/or the ion-pairing effect would be exerting more stabilization to the transition-state structure which has an apparently more planar COT ring.

The electronic spectrum of 1^{2+} in dichloromethane measured in a vacuum-sealed cell exhibited an absorption at much longer wavelength [λ_{max} 532 (log ε 3.8)] than those of other planar 6π aromatic systems that are fully annelated with BCO frameworks (*e.g.* benzene, 260 nm;[2b] tropylium ion, 308 nm[2a] both in acetonitrile). This bathochromic shift also reflects the non-planar structure of the COT ring in 1^{2+} from the following reasoning. As the COT ring of the dication undergoes the transformation from planar to tub structures, the HOMO–LUMO gap gradually decreases due to both the splitting of the originally degenerate LUMOs of the dication and the concomitant rising of the HOMO. In fact, the CNDO/S calculations for unsubstituted COT dication predicted a 0.80 eV decrease in transition energy (the HOMO–LUMO gap) upon going from the planar structure to the tub structure with the bent angle (α) of 34.5° which corresponds to the calculated value for the structure **B**.

It seems that the aromatic stability in the planar COT dication is delicately balanced with destabilization caused by the angle strain.[6] Apparently, the annelation with rigid bicyclic systems in the present dication 1^{2+} induces considerable angle strain as well as the non-bonded interaction between bridgehead hydrogens, in the planar form **A**. Nevertheless, a gain of aromatic stabilization has made the planar (or nearly planar) structure stable enough, so that the ring inversion can occur quite readily in contrast to the case of neutral COT **1**, in which no such inversion was observed on the NMR timescale even by heating at 150 °C (indicating a lower limit of the inversion barrier of 24 kcal mol^{-1}).[3]

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