

NMR and computational studies of the chemical reduction of [2.2]paracyclophane: formation of dianionic *p*-xylylenyl oligomers†

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Received (in Cambridge, UK) 26th September 2003, Accepted 6th November 2003

First published as an Advance Article on the web 26th November 2003

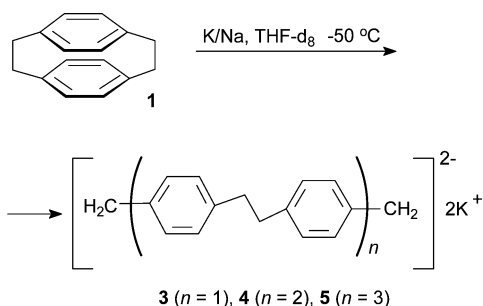
Reaction of [2.2]paracyclophane with K/Na alloy in THF gives a *p*-xylylenyl dianion together with its dimer and trimer which are relatively stable at low temperatures; at ambient temperatures further polymerization takes place.

Since the discovery of [2.2]paracyclophane (**1**) in 1949¹ this molecule has been intensively studied.² Synthetic methods suggest promising materials,³ unique polymers,⁴ and catalysts with planar chirality⁵ can be developed, whereas the theoretical challenge of understanding the structural features of the two adjacent coplanar benzene rings is still under discussion.⁶

Much less attention has been paid to charged [2.2]paracyclophanes. After several characterizations of the extremely unstable blue anion-radical (**2**) by ESR and optical spectroscopy,⁷ Pearson examined a further reduction but was hampered by "the extremely low solubility of the paracyclophanes and other experimental problems".⁸ Furthermore, on the theoretical side, we are unaware of any computational study of negatively charged [2.2]paracyclophanes.

We report here the results of both NMR and computational studies of the reaction of **1** with K/Na alloy in THF. Treatment of **1** with K/Na alloy in THF-*d*₈ at -50 °C† yields an intense red-colored solution of three dianions **3–5** (Scheme 1) containing an admixture of 1,2-di-*p*-tolylethane (**6**).[§] Dianions **3–5** were stable at -50 °C. Monomer **3** and dimer **4** were completely characterized by their ¹H and ¹³C NMR spectra. The possible reduction pathways from **1** to **3–5** were explored with the aid of quantum chemical calculations performed on the reduced [2.2]paracyclophane species **2**, **3**, **7** and **8** (Scheme 2).[¶]

The reduction of **1** in gas-phase is an unfavourable process, as suggested by the negative value of its electron affinity (-0.49 eV) computed at the UB3LYP/6-311++G(d,p)//UHF/6-311G* level of theory. Nevertheless, radical anion **2** has been characterised by ESR at -70 °C in THF and DME solutions, in which it may be stabilized by the donating solvent.^{7,8} The route from **2** to **3** involves a further reduction and ring opening which may occur by two possible mechanisms (Scheme 2). If the second reduction occurs first, the

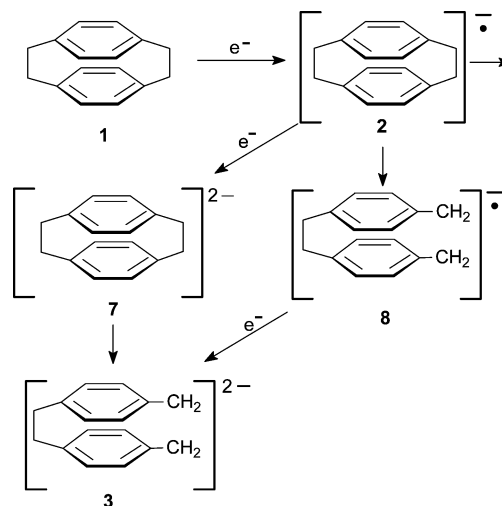


Scheme 1 Synthesis of dianions **3–5**.

closed dianionic species **7** would be the intermediate. Otherwise, a structural rearrangement of **2** can yield an open-shell radical anion (**8**), which is then reduced to **3**. Our gas-phase calculations indicate that both the processes involving ring opening are exothermic by 23 (**2**→**8**) and 52 (**7**→**3**) kcal mol⁻¹. The pathway **2**→**8**→**3** is slightly favored with respect to **2**→**7**→**3** (by 0.26 kcal mol⁻¹). The formation of oligomers (*e.g.* **4** and **5**) corresponds better to the intermediacy of **8** being in equilibrium with the dianion **3**.

The most characteristic signals in the ¹H NMR spectra of **3** are two doublets at $\delta = 5.30$ and 5.70 which are assigned to the negatively charged phenyls (Fig. 1a). In the ¹³C NMR spectra of **3** the strong alternations of the chemical shifts of the two aromatic CH-resonances, $\delta = 109.7$ and 130.6 , as well as of the two quaternary carbons, $\delta = 105.3$ and 150.6 , are remarkable. The spectral assignments for **3** were confirmed after performing a series of GIAO-B3LYP/6-311++G(d,p)//HF/6-311G* chemical shift computations (see Fig. 2).

In the ¹H and ¹³C NMR spectra of **4** the terminal charged aromatic rings give signals very similar to those of **3** ($\delta_{\text{H}} = 5.33$,



Scheme 2 Reduction of [2.2]paracyclophane **1**.

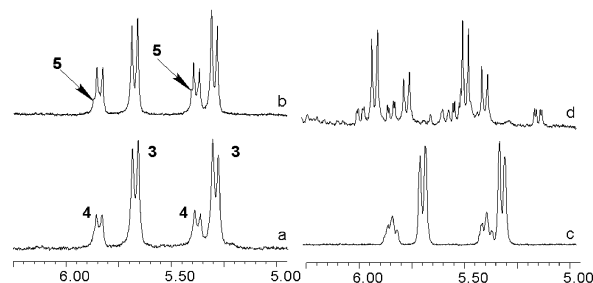


Fig. 1 ¹H NMR spectra (300 MHz, THF-*d*₈) of the reaction mixture obtained by reacting **1** with K/Na at a) -50 °C, b) -30 °C, c) -10 °C, d) 20 °C after 12 h.

† Electronic Supplementary Information (ESI) available: experimental and computational details, and spectral data for the trapping products. See <http://www.rsc.org/suppdata/cc/b3/b311885a/>

5.80; $\delta_C = 107.9, 110.4, 131.5, 152.3$), whereas the protons and carbon atoms of the internal phenyls resonate at normal δ values ($\delta_H = 6.8\text{--}7.2$; $\delta_C = 128.5, 128.8, 139.9, 141.0$). The NMR spectra of the dianion **5** are very similar to those of **4**, so it was impossible to detect its signals reliably in the NMR spectra of the reaction mixture (see however Fig. 1b).

Quenching the reaction mixture obtained after stirring **1** with a large excess of K/Na alloy in absolute THF for 30 minutes at -50°C with trimethylchlorosilane, resulted in 65% of **1** and afforded disilyl derivatives **9–11** in a ratio of 2 : 1 : 1 (Scheme 3). The products were separated by preparative GPC and characterized individually.

When the reaction mixtures from the NMR experiments were warmed to room temperature, further polymerization took place, as is evident from the Figs. 1c,d and 3.

Since the spectral region of 5.0–6.0 ppm is characteristic of the protons of charged terminal aromatic rings, each cross-peak in Fig. 3 corresponds to a certain oligomeric dianion, and the number of cross-peaks gives a good estimation of the number of compounds present in the reaction mixture. Hence, one can conclude from the Fig. 3 that oligomerization of this sample leads to dianionic species

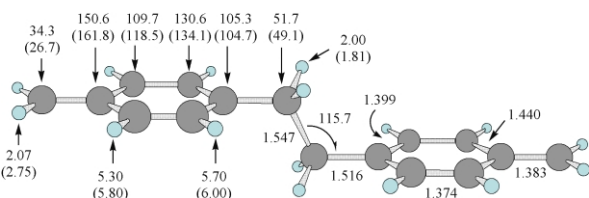
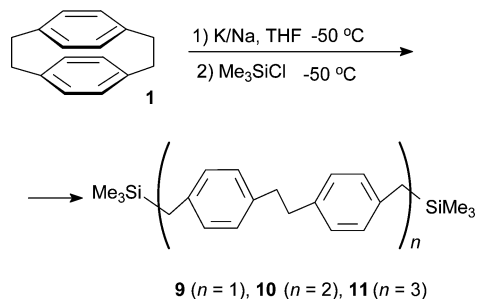


Fig. 2 Experimental and computed (in brackets) chemical shifts for the optimized (C_{2h}) structure of **3**. Relevant bond lengths (\AA) and bond angles ($^\circ$) are also reported.



Scheme 3 Quenching experiment.

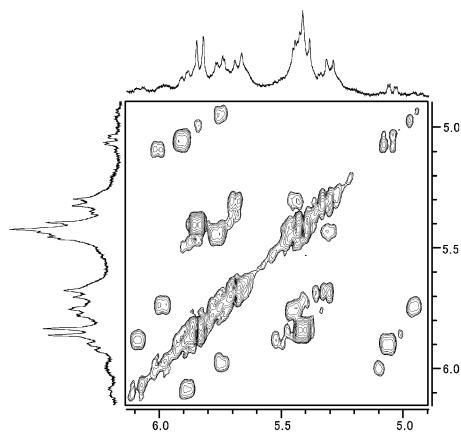


Fig. 3 $^1\text{H}\text{--}^1\text{H}$ COSY NMR spectrum (300 MHz, THF-d_8 , 298 K) of the reaction mixture from Scheme 1 stored for 5 days at ambient temperature. At least 15 cross-peaks attributed to aromatic protons in the terminal anionic units are observed.

with $n = 15\text{--}20$ which corresponds to molecular weights of several thousands. Poly(xylylenes) are useful materials with applications as encapsulants in electronic devices.⁴ They are prepared from **1** according to the Gorham process¹² by vapor deposition polymerization which requires elaborate equipment and temperatures of around 650°C . The results presented here suggest that a “living” polymerization of **1** is possible under mild conditions which might be useful for the development of an alternative route to poly(xylylenes). Further theoretical and experimental studies on the mechanism responsible for the formation of dianionic *p*-xylyl species will follow.

This work was financially supported by the COE Program “Giant molecules and complex systems” of MEXT hosted at Tohoku University.

Notes and references

‡ The reaction of **1** with K/Na can also occur at lower temperatures (-90 to -70°C). Under such conditions broad signals of paramagnetic species are observed together with **3–5**.

§ The solvent must be completely anhydrous and contact with air must be excluded to avoid exclusive formation of **6**; see the ESI† for details. Ishitani⁷ and Pearson⁸ suggested that *p*-xylene is the final product of the reaction of **1** with K/Na in THF, however, we never observed this product in our experiments.

¶ All the calculations were performed with the Gaussian 98 software package.⁹ Geometry optimizations and vibrational frequency calculations were performed at the HF/6-311G* level of theory while chemical shifts were computed using the GIAO method¹⁰ at the single-point B3LYP/6-311++G(d,p) level of theory.¹¹

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