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# THE DIANION OF [2.2.2]PARACYCLOPHENE; A 20 T-PERIMETER SPECIES?

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A new synthesis of [2.2.2]paracyclophene (1) is presented. On reduction, (1) forms a stable dianion which is neither diatropic nor paratropic. The apparent high symmetry of the dianion and the observed NMR chemical shifts are best explained by a rapid interconversion of a series of  $C_p$ -conformers.

[2.2.2]Paracyclophene<sup>1</sup> (<u>1</u>), originally prepared by Cram and Dewhirst,<sup>2</sup> formally contains an 18  $\pi$ -perimeter in the macrocyclic ring system, and photocyclisation of this cyclophene under carefully controlled conditions gives a diatropic bridged [18]annulene.<sup>3</sup> However, as mulecular models show, the compound (<u>1</u>) is far from planar; a recent crystal structure determination has shown that two of the benzene rings are tilted <u>ca.</u> 50° from the average plane of the three double bonds and that the third benzene ring is essentially perpendicular to that plane.<sup>4</sup> Thus, in the crystal, the symmetry of (<u>1</u>) approaches <u>C</u><sub>2</sub> rather than <u>D</u><sub>3h</sub>.



Figure 1 Averaged torsion angles in [2.2.2]paracyclophene from molecular mechanics calculations (Allinger's MMP2 force field). The numbers in brackets are from the crystal structure determination (ref.4).

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One of the interesting repeating units found in linear polymers and in macrocycles is paraphenylenevinylene ( ) which is contained three times in [2.2.2]paracyclophene (1), four times in [2.2.2.2]paracyclophene (2), and six times in [2.2.2.2.2]paracyclophene (3). Recently, novel charged linear, as well as cyclic,  $\pi$ -systems with paraphenylenevinylene units have been prepared and found to possess interesting electronic properties. Thus, the linear polymer can be doped to give a good electrical conductor<sup>5</sup> and the dianions of (2) and (3) are highly diatropic.<sup>6</sup> Cyclophene (2) can even be reduced to a paratropic tetraanion. The vinylogue of the title compound, [4.2.2]paracyclophene (4), on reduction forms a diatropic dianion with a 22  $\pi$ -perimeter.<sup>6</sup>



The formal cyclic conjugation in (<u>1</u>) and its non-planar structure make it a particularly interesting test compound for the evaluation of the ability of strained molecules to form  $\pi$ -perimeter macrocycles when "doped" i.e. reduced.

In this paper we report a new and convenient synthesis of [2.2.2] paracyclophene, its electrochemical reduction and the formation of a stable dianion  $(1^{2^{-}})$ . For the discussion of steric effects we rely on the crystal structure determination<sup>4</sup> as well as on molecular mechanics calculations (Allinger's MMP2 force field).

Our synthesis of the cyclophene (<u>1</u>) is shown in Scheme <u>1</u>. A <u>Z</u>-selective double Wittig reaction gave the known<sup>7</sup> dialdehyde (<u>5</u>) which smoothly underwent intramolecular reductive coupling upon exposure to low-valent titanium.<sup>8</sup> The total yield for the two steps was <u>ca.</u> 25 %, the physical and spectroscopic properties of the final product being identical to those in the literature.<sup>2,3</sup> The sample used to generate the dianion was purified by chromatography and sublimation.



#### Scheme 1

The cyclic voltammogram (mercury drop, DMF, tetraethyl ammonium perchlorate) of (<u>1</u>) showed three irreversible peaks corresponding to the stepwise reduction of one, two, and three double bonds in the bridges at -2.20, -2.37, and -2.65 V vs. SCE, respectively. Under identical conditions (<u>2</u>) is reversibly reduced to the diamion at -1.73 V and <u>Z</u>-stilbene irreversibly reduced at -2.18 V.<sup>9</sup> Obviously, (<u>1</u>) is as difficult to reduce as <u>Z</u>-stilbene and the presence of the three separate peaks shows that (<u>1</u>) has a larger delocalised  $\pi$ -system than the products of the subsequent electrochemical reductions.

On careful reduction of  $(\underline{1})$  with lithium in dry degassed tetrahydrofuran a stable dianion is formed. The chemical structure proof of  $(\underline{1}^{2-}/2L_{1}^{+})$  rests upon quenching and reoxidation experiments; reaction with oxygen regenerates the starting compound as the only identifiable product, reaction with methanol or dimethyl sulphate affords a dihydro and dimethyldihydro derivative, respectively. The dianion is characterised by its very simple <sup>1</sup>H and <sup>13</sup>C NMR spectra (see Table 1). The <sup>1</sup>H NMR spectrum of  $(\underline{1}^{2-})$  shows only two signals (2:1) at  $\delta$  5.83 (aromatic) and 5.13 (olefinic) which remain sharp down to -100°C. The <sup>13</sup>C NMR spectrum exhibits three sharp signals (2 aromatic, 1 olefinic). For comparison, Table 1 also lists the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of (<u>2</u>) and its corresponding anions. It is obvious from these data that, on reduction, (<u>2</u>) transforms into a <u>diatropic</u> dianion and a <u>paratropic</u> tetraanion.<sup>6</sup>

| Cyclophene    | Nuclei | Chemical shifts (ô) |                        |                    |                |
|---------------|--------|---------------------|------------------------|--------------------|----------------|
|               |        | neutral<br>compound | dianion                | <b>(∆</b> δ)       | tetraanion     |
| ( <u>1</u> )  | H(1)   | 6.84                | 5.13                   | (1.71)             |                |
|               | H(3)   | 6.74                | 5.83                   | (0.91)             |                |
|               | C(1)   | 132.9               | 106.8                  | (26.1)             |                |
|               | C(2)   | 136.2               | 127.9                  | (8.3)              |                |
|               | C(3)   | 129.4               | 124.2                  | (5.2)              |                |
| ( <u>2</u> )* | H(1)   | 6.45                | 9.56                   | (-3.11)            | 2.09           |
|               | H(3)   | 7.32                | 9 <b>.</b> 26<br>-7.07 | (-1.94)<br>(14.39) | 12.74<br>4.48  |
|               | C(1)   | 129.9               | 108.8                  | (21.1)             | 95.9           |
|               | C(2)   | 136.2               | 119.8                  | (16.4)             | 133.3          |
|               | C(3)   | 129.3               | 123.9<br>116.6         | (5.4)<br>(12.8)    | 122.4<br>121.6 |

Table 1. <sup>1</sup>H and <sup>13</sup>C NMR data of cyclophenes (<u>1</u>), (<u>2</u>) and their anions.

\* dianion of (2) is diatropic, tetraanion of (2) is paratropic.

In contrast  $(\underline{1}^{2})$  is neither diatropic nor paratropic, as no ring current induced shifts are observed. The upfield shift of the aromatic and olefinic protons, 0.91 and 1.71 ppm, respectively, is best explained as a charge effect. The total upfield shift for the twelve aromatic and six olefinic protons amounts to 21.2 ppm. The total shift per charge is then 10.6 ppm which is a normal value.<sup>10</sup>

The simple <sup>1</sup>H and <sup>13</sup>C NMR spectrum of  $(\underline{1}^{2^{-}})$  can be rationalised either as being due to a highly symmetrical species  $(\underline{D}_{\underline{2h}})$  with the benzene rings perpendicular to the plane of the three bridging double bonds or, better, by assuming a rapid interconversion of less symmetrical conformers  $(\underline{C}_{\underline{2}})$  as depicted in Scheme 2. Such a process would then exchange the magnetic sites of all the aromatic as well as the olefinic protons. It is known that rotation or flipping of the benzene rings is fast in neutral [2.2.2]-paracyclophenes<sup>8</sup> as well as in [2.2.2.2]paracyclophenes at ambient temperature, and even in  $(\underline{2}^{2^{-}})$  at elevated temperatures.<sup>6</sup>

The molecular mechanics calculation on the neutral cyclophene results in a low energy conformation which is almost identical to the X-ray structure (see Figure 1). The gain in delocalisation energy obtained by allowing two of the benzene rings to overlap with the olefinic  $\pi$ -systems in the neutral cyclophene (1), should be considerably larger in the dianion (1<sup>2</sup>) in accordance with experience obtained for structurally related compounds such as stilbene and 1,4-distyrylbenzene.<sup>11</sup>



#### Scheme 2

Scheme for the interconversion of all aromatic protons in [2.2.2]paracyclophene dianion via a series of  $\underline{C}_2$ -conformers in which one of the benzene rings is perpendicular to the delocalised and charged  $\pi$ -system.

## Conclusions

Although [2.2.2]paracyclophene can be converted to a diatropic bridged [18]annulene on irradiation, the steric requirements of the benzene rings prevent cyclic conjugation around the perimeter in the neutral molecule as well as in the dianion. Favourable charge delocalisation in the dianion is realised by the overlap of the  $\pi$ -systems of two of the benzene rings and the three double bonds rather than by simultaneous involvement of all three benzene rings.

#### **EXPERIMENTAL**

## Synthesis of [2.2.2]paracyclophene (1)

TiCl<sub>4</sub> (2.2 ml, 20 mmol) was added with stirring under argon to dry THF (100 ml) at 0<sup>o</sup>C. Zinc powder (2.62 g, 40 mg-atom) was then added carefully in small portions, followed by dry pyridine (<u>ca</u>. 1 ml). The resultant black mixture was refluxed for 1 h before slow dropwise addition of a solution of dialdehyde <u>5</u> (see ref. 7 for the preparative details, 0.68 g, 2 mmol) in THF (75 ml). The addition required several hours. The resultant mixture was held at reflux until TLC indicated complete disappearance of starting material, cooled to 0<sup>o</sup>C and quenched by slow addition of 10 % K<sub>2</sub>CO<sub>3</sub> solution. The grey precipitate was filtered off and both filtrate and filter-cake extracted with dichloromethane. The combined organics were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the yellow residue was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to yield the desired cyclophene as pale yellow crystals. Sublimation of this material yielded colourless crystals (0.30 g, 50 %) <u>m.p.</u> 128-129<sup>o</sup>C (lit.<sup>3</sup> 130-132<sup>o</sup>C). <u>1 H NMR</u> (270 MHz, CDCl<sub>3</sub>) & 6.74 (s, 12H, aromatic) and 6.84 (s, 6H, olefinic). <u>MS:</u> m/e 306 (M<sup>+</sup>, 100 %). <u>Abs. mass</u>: 306.1408, calc. for C<sub>24</sub>H<sub>18</sub> 306.1409.

For the reduction experiments 5 mg of <u>1</u> were placed at the bottom of an NMR tube and dry  $[D_g]$ -tetrahydrofuran (0.5 ml) was distilled in from a storage vessel. After the solution had been degassed by three freeze and pump cycles lithium wire was inserted under vacuum by means of a specially constructed press and deposited in the upper part of the tube. Finally the tube was sealed. The progress of the reduction (initiated by contacting the solution with the metal at  $-78^{\circ}$ C) could be monitored <u>via</u> <sup>1</sup>H NMR spectroscopy. The NMR measurements were performed at 300 (<sup>1</sup>H) and 75.5 MHz (<sup>13</sup>C) on a WM 300 spectrometer (Bruker). For the reoxidation of  $1^{2^{-}}/2\text{Li}^{+}$  the tube was broken and dry oxygen bubbled through the solution. <u>1</u> was identified by its <sup>1</sup>H NMR spectrum. For the quenching experiments an excess of methanol or dimethyl sulphate was added to the dianion solution. The incorporation of two electrophiles in both experiments was proven <u>via</u> the detection of the relevant molecular ions in the mass spectra. The small scale of the experiment did not allow the isolation of the quench products.

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