



Pergamon

Tetrahedron Letters 41 (2000) 4519–4522

TETRAHEDRON  
LETTERS

# Ionization of corannulene and 1,6-dimethylcorannulene: photoelectron spectra, electrochemistry, charge transfer bands and ab initio computations

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Received 11 April 2000; accepted 20 April 2000

## Abstract

The ionization energies of corannulene and 1,6-dimethylcorannulene are measured by PES, voltammetry and UV charge transfer bands and are compared to values predicted by ab initio calculations via  $\Delta$ SCF and Koopmans' theorem. © 2000 Published by Elsevier Science Ltd.

*Keywords:* corannulene; fullerene fragments; photoelectron spectroscopy; ionization energies; electrochemistry.

Corannulene (**1**),<sup>1–4</sup> representing one third of C<sub>60</sub>, is the smallest sub-unit of fullerenes to have a curved surface. The distance from the plane of the rim carbons to the plane of the hub carbons in corannulene is 0.87 Å.<sup>5</sup> The same motif in C<sub>60</sub> has a depth of 1.49 Å.<sup>6</sup> The bonds of corannulene (1.42 Å hub, 1.44 Å flank, 1.39 Å rim and 1.38 Å spoke) are also localized towards a 5-radialene structure like C<sub>60</sub> (1.46 Å and 1.39 Å). How this similarity in bonding and structure relates to physical properties is an active question. Ionization energies (IE) are one gauge of the physical properties. Herein, we report the He(I) photoelectron spectra (PES), electrochemistry, UV charge transfer bands, and ab initio computations of **1** and 1,6-dimethylcorannulene (**2**) (Fig. 1).

Compound **1** is known to undergo facile reduction to the tetraanion, and C<sub>60</sub> has been reduced to the hexaanion. Thus, **1** and C<sub>60</sub> behave as electron deficient  $\pi$  systems. Although the reductions (electron affinity) of **1**<sup>7–9</sup> and C<sub>60</sub><sup>10,11</sup> are well known, the oxidations<sup>12</sup> (IE) are not. To address the IE question, the He(I) PE spectra were recorded on a Perkin–Elmer PS18 spectrometer at 75°C for **1** and 200°C for **2**. The calibration was performed with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the <sup>2</sup>P<sub>3/2</sub> Ar line was obtained.

The PES of **1** (Fig. 2) and **2** are interpreted as follows: The first peak of **1** (7.89–8.3 eV) we assign to four ionic states 2E<sub>2</sub>, 2E<sub>1</sub>. The second peak (10.0–10.3 eV) we assign to three ionic states

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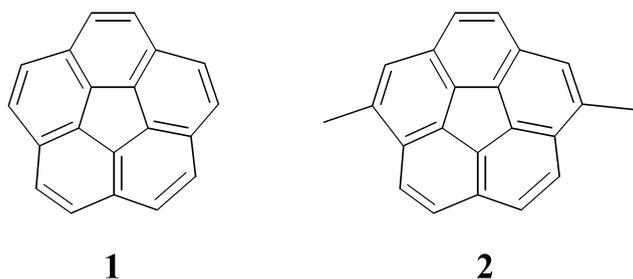


Figure 1. Corannulene (**1**) and 1,6-dimethylcorannulene (**2**)

$2E_2$  and  $2A_1$ . In the case of **2**, the first peak (7.7–8.2) corresponds to four transitions  $2 \times 2A'$ ,  $2 \times 2A''$ , the second peak (9.6–10.2 eV) corresponds to three transitions  $2 \times 2A'$  and  $2A''$ . Due to the high recording temperature (200°C) the quality of the spectrum of **2** is not as good as that of **1**.<sup>13</sup>

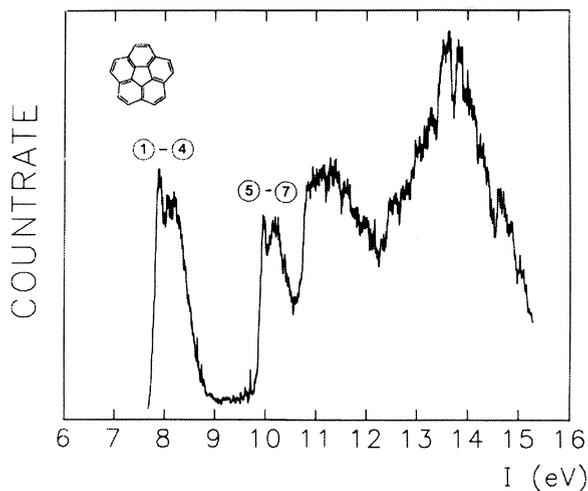


Figure 2. PES spectrum of **1**

To place the IEs in context of solution work, cyclic and OSW voltammetry studies of **1** and **2** were also performed (Table 1). When done in acetonitrile, with tetrabutyl ammonium hexafluorophosphate as the electrolyte and Ag/AgNO<sub>3</sub> as the reference electrode, the reductions of **1** and **2** exhibited two reversible reduction waves and one irreversible oxidation wave. The oxidation of these compounds exhibited a broad shaped wave and rendered the electrode inoperable after one pass. The oxidation remained irreversible using methylene chloride or tetrahydrofuran as the solvent. In order to compare with a previous report,<sup>8</sup> **1** was also studied in acetonitrile with tetrabutyl ammonium perchlorate with an aqueous Ag/AgCl reference electrode. Both reduction waves are consistent with the literature, but the oxidation wave is 0.4 volts more positive than the reported value. Thus, we observe the difference between the oxidation and first reduction wave to be between 3.7 and 3.8 volts, whereas the reported value is 3.3 volts. Using Cavalieri's correlation between anodic oxidation potential and ionization potentials, values of 8.59 and 8.50 eV are obtained for **1** and **2**, half a volt higher than the PES data.<sup>14</sup>

Table 1  
Oxidation and reduction potentials measured by voltammetry

| Compound       | Oxidation (Volts)   | Calculated IE (eV) <sup>d</sup> | Reduction 1 (Volts) | Reduction 2 (Volts) |
|----------------|---------------------|---------------------------------|---------------------|---------------------|
| 1 <sup>a</sup> | + 1.57 irreversible | 8.59                            | - 2.25 reversible   | - 2.80 reversible   |
| 1 <sup>b</sup> | + 1.85 irreversible | 8.44                            | - 1.86 reversible   | - 2.43 reversible   |
| 1 <sup>c</sup> | +1.46 irreversible  | 7.77                            | - 1.88 reversible   | -2.46 reversible    |
| 2 <sup>a</sup> | + 1.52 irreversible | 8.50                            | - 2.29 reversible   | - 2.94 reversible   |

<sup>a</sup> 3 X 10<sup>-3</sup> M in analyte, 0.1M TBAPF<sub>6</sub>, Ag/AgNO<sub>3</sub> reference in acetonitrile, sweep rate 100mV/s

<sup>b</sup> 3 X 10<sup>-3</sup> M in analyte, 0.1M TBAClO<sub>4</sub>, aqueous Ag/AgCl reference in acetonitrile, sweep rate 200 mV/s

<sup>c</sup> from ref. 8: 1 X 10<sup>-3</sup> M, 0.1 M TBAClO<sub>4</sub>, aqueous Ag/AgCl in acetonitrile, sweep rate 200 mV/s

<sup>d</sup> using Cavalieri's correlation (ref. 14).

The ionization energies of C<sub>60</sub> and C<sub>70</sub> have been measured by photon impact to be 7.61 and 7.47,<sup>15</sup> and the anodic potentials of C<sub>60</sub> and C<sub>70</sub> have been measured by CV to be 1.26 and 1.20 volts (versus ferrocene).<sup>11</sup> Using Cavalieri's correlation the IE of C<sub>60</sub> and C<sub>70</sub> are 8.21 and 8.10 eV.

Charge transfer complexes of **1** and **2** and TCNE have been measured as well (Table 2). The charge transfer bands appear at 512 and 541 nm, respectively. The correlation proposed by Kuroda allows for a comparison of the IE and charge transfer bands.<sup>16</sup> IEs calculated from Kuroda's correlation for **1** and **2** are 8.37 and 8.22 eV, respectively.

Table 2  
Charge transfer bands with TCNE

| Compound | CT band with TCNE (nm) <sup>a</sup> | Ionization Energies (eV) |
|----------|-------------------------------------|--------------------------|
| 1        | 512                                 | 8.37                     |
| 2        | 541                                 | 8.22                     |

<sup>a</sup> 6.0 X 10<sup>-3</sup> M in analyte, 1.2 X 10<sup>-2</sup> M in TCNE in CH<sub>2</sub>Cl<sub>2</sub>

Experimental IE values for corannulenes can be compared to ab initio theory.<sup>4,17</sup> Koopmans' theorem and the more accurate  $\Delta(\text{SCF})$  method,<sup>18</sup> at the MP2/cc-pVDZ//MP2/cc-pVDZ level of theory,<sup>19</sup> were used to predict the IEs of **1** and **2** (Table 3). As seen with the electrochemical and charge transfer data, the shift to lower ionization potential upon addition of methyl groups is consistent with an increase in electron density in the corannulene nucleus.

Table 3  
MP2/cc-pVDZ//MP2/cc-pVDZ calculated ionization energies (eV)

| Compound | IE (eV) $\Delta\text{SCF}$ | IE (eV) Koopmans' Theorem |
|----------|----------------------------|---------------------------|
| 1        | 8.77                       | 7.99                      |
| 2        | 8.38                       | 7.66                      |

In conclusion, the oxidations of **1** and **2** have been investigated by PES, voltammetry, charge transfer energies, and ab initio computations. A correction of the literature value of the anodic potential of **1** has been made, and is consistent with values obtained for **2**. The data show relatively high ionization energies for **1** and **2**.

## Acknowledgements

This work was supported by the National Science Foundation (CHE-9628565), the National Institute of Health (NBCR), and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. A grant for computer time was provided by the NRAC program. We thank A. Flatow for recording the PE spectra.

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