

Structural and Electrochemical Characterization of the Products of the C₆₀-Piperazine Reaction

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Crystal structures of C₆₀N₂(C₂H₄)₂ and C₆₀{N₂(C₂H₄)₂}₂ show that addition occurs with elongation of the C–C bond at the 6:6 ring junction to which the two nitrogen atoms are bonded; electrochemical one-electron reduction potentials of these adducts are shifted by *ca.* 0.1 V to more negative values for each added group.

There have been a number of reports on the addition of amines to C₆₀.^{1–7} With 1,2-diamines, the addition proceeds with apparent loss of two hydrogen atoms to form a variety of products including the single addition product, C₆₀N₂(C₂H₄)₂ **1**, and the double addition product, C₆₀{N₂(C₂H₄)₂}₂, which occurs in several isomeric forms.^{4,6,7} Here we report on X-ray crystallographic and electrochemical studies of C₆₀N₂(C₂H₄)₂ **1**, and of one isomer, **2**, of C₆₀{N₂(C₂H₄)₂}₂.

Samples of **1** and **2** were prepared as described previously^{4,6} and separated by high-pressure liquid chromatography, using 'Bucky-clutcher' column.⁸ The first material to elute was the single addition product **1**, which was followed by six smaller peaks that were also collected separately. The second of these six contained a single isomeric form, the 1,2,51,52 isomer⁹ **2**, of the double addition product C₆₀{N₂(C₂H₄)₂}₂.

The results of X-ray crystallographic studies of **1** and of **2** are shown in Figs. 1 and 2, respectively.† The structure of **1** reveals that the diamine has added across a 6:6 ring junction as expected to produce a local distortion of the fullerene. This distortion is manifest in the displacement of C(1) and C(2) away from their normal positions on the fullerene surface, and an elongation of the C(1)–C(2) bond, the length of which is 1.624(8) Å. In comparison, the length of a normal C–C bond at a 6:6 ring junction of an undistorted fullerene is 1.383(4) Å,¹⁰ and the length of the single bonds within the caged diamine portion of **1** is 1.547(8) Å for C(61)–C(62) and 1.541(8) Å for C(63)–C(64). Similar extreme elongations of fullerene C–C bonds are found in their Diels–Alder adducts¹¹ and in a [2 + 2] cycloadduct.¹² The six C–N distances fall into a narrow range [1.459(8)–1.488(8) Å] and the nitrogen atoms have pyramidal geometry with C–N–C angles in the range 107.4(4)–110.0(4)°. Examination of the rest of the fullerene surface does not show any evidence of distortion that would be expected to occur if the amine hydrogen atoms from piperazine had also added to the molecule.

Two views of the structure of the double addition product **2** are shown in Fig. 2. This particular isomer has C₂ symmetry, with the C₂ axis bisecting the bond between C(23) and C(23'), and hence is chiral. However, each individual crystal is achiral

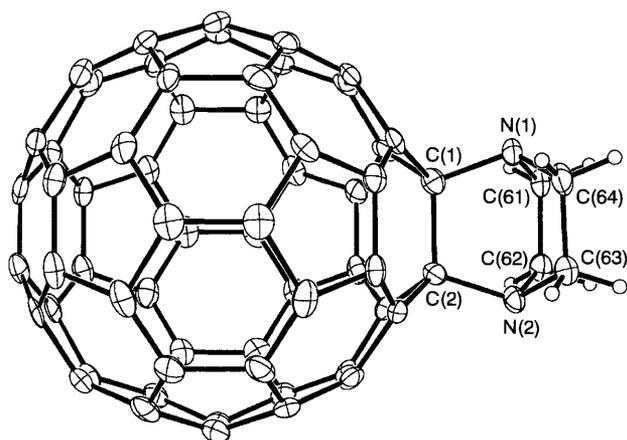


Fig. 1 A perspective view of C₆₀N₂(C₂H₄)₂ **1** with 50% thermal contours for all atoms

and contains a racemic mixture of the double addition product. The introduction of the two diamine functions produces local distortions with extreme C–C bond lengthenings that are similar to those found in **1**.

The electrochemical behaviour of **1** and **2** has been monitored by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a mixture of toluene–acetonitrile (1:4 *v/v*) with tetrabutylammonium perchlorate as the supporting electrolyte and ferrocene–ferrocenium ion as the reference. For both **1** and **2**, four electrochemically reversible reduction waves were observed as shown in Fig. 3. These waves result from the stepwise, one-electron reduction of the two compounds to mono-, di-, tri- and tetra-anions. Adduct formation results in anodic shifts of the reduction processes relative to those observed for C₆₀. The observation that plots of the formal reduction potential *vs.* the charge on the reactant are linear is in agreement with the theory of molecular capacitance.¹³ The sizable cathodic shifts that occur upon adduct formation

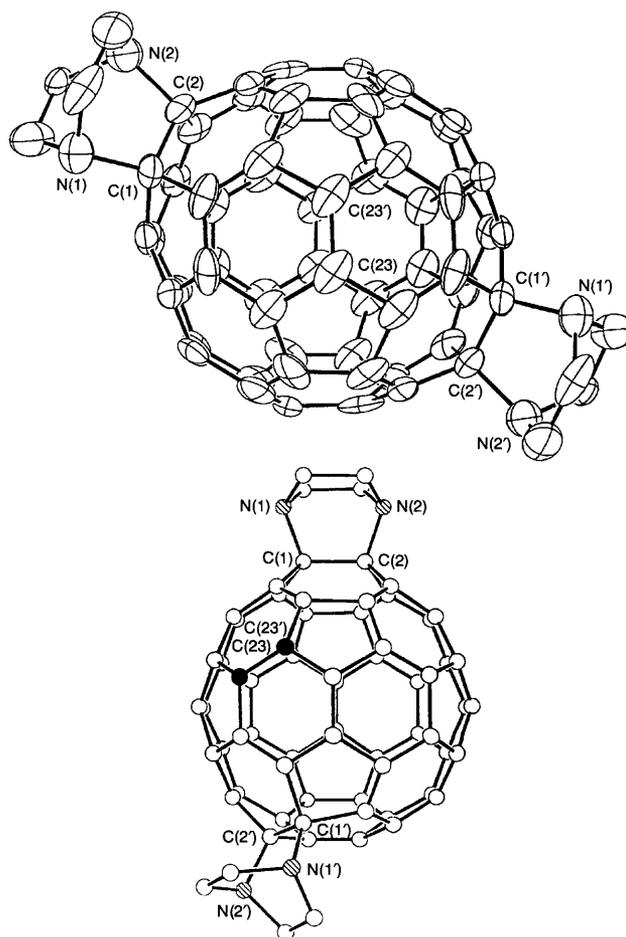


Fig. 2 Two perspective views of 1,2,51,52-C₆₀{N₂(C₂H₄)₂}₂ **2** with 50% thermal contours for all atoms in the top drawing. Owing to the need to accommodate the 2-fold symmetry, the crystallographic numbering of this compound does not conform to the scheme proposed in ref. 9.

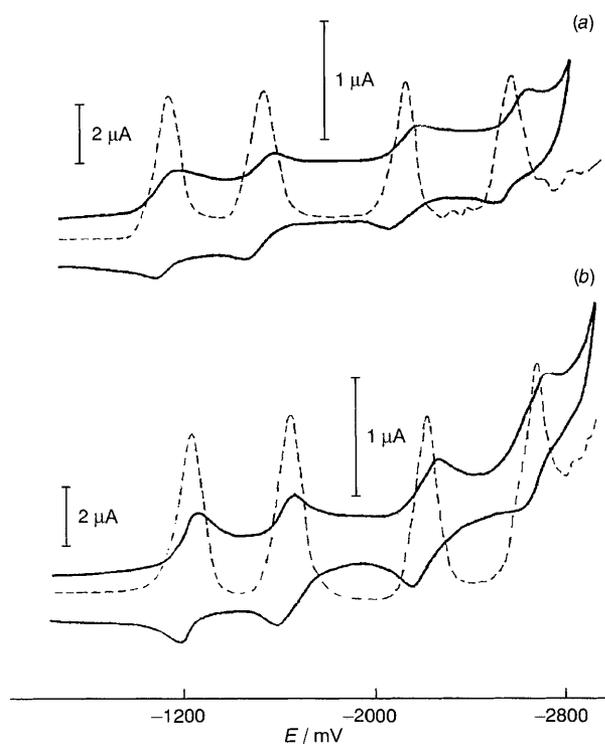


Fig. 3 Cyclic voltammograms (solid lines) and differential pulse voltammograms (broken lines) of (a) $0.15 \text{ mmol dm}^{-3} \text{ C}_{60}\text{N}_2(\text{C}_2\text{H}_4)_2$ and (b) $0.2 \text{ mmol dm}^{-3} 1,2,51,52\text{-C}_{60}\{\text{N}_2(\text{C}_2\text{H}_4)_2\}_2$ in 0.1 mol dm^{-3} tetrabutylammonium perchlorate in a toluene-acetonitrile (1:4) mixture with ferrocene-ferrocinium ion as the voltage reference. Sweep rate, 200 mV s^{-1} (CV) and 20 mV s^{-1} (DPV); pulse amplitude, 50 mV ; pulse width 50 ms ; and pulse period, 200 ms .

probably reflect the removal of two p-orbitals from the conjugated fullerene system and the effects of the proximity of the nitrogen lone pairs to the surface of the fullerene.

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Footnote

† Crystal data for $1.5 \text{ CH}_2\text{Cl}_2 \cdot \text{C}_{65.5}\text{H}_{11}\text{Cl}_3\text{N}_2$, black prisms and needles obtained by diffusion of diethyl ether into a dichloromethane solution of the compound, monoclinic, space group $P2_1/c$ with $a = 12.829(2)$, $b = 9.794(2)$, $c = 27.801(4) \text{ \AA}$, $\beta = 91.52(2)^\circ$ at 130 K with $Z = 4$. Data collection employed $\text{Cu-K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) Ni-filtered radiation. Refinement (based on F) of 3077 reflections with $F > 4.0\sigma(F)$ and 635 parameters yielded a final $R = 0.0601$ and $R_w = 0.0699$; For $2.1.4 \text{ CH}_2\text{Cl}_2 \cdot 0.6 \text{ O}(\text{C}_2\text{H}_5)_2 \cdot \text{C}_{71.8}\text{H}_{24.8}\text{Cl}_{2.8}\text{N}_{4.0}\text{O}_{0.6}$, black plates obtained by diffusion of diethyl ether into a dichloromethane and methanol solution of the compound, orthorhombic, space group $Pbcn$ with $a = 13.475(2)$, $b = 14.711(2)$, $c = 20.481(4) \text{ \AA}$, at 130 K with $Z = 4$. Data collection employed $\text{Cu-K}\alpha$ ($\lambda = 1.54179 \text{ \AA}$) Ni-filtered radiation. Refinement of 2656 reflections and 356 parameters yielded $R_1 = 0.0983$ [based on observed data with $I > 2\sigma(I)$] and $wR2$ (on F^2) = 0.300 for all data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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