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Isomers of C<sub>70</sub> DimerT. Heine,<sup>\*,†,‡</sup> F. Zerbetto,<sup>‡</sup> G. Seifert,<sup>§</sup> and P. W. Fowler<sup>||</sup>

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Calculated binding energies and spectroscopic properties of C<sub>70</sub> dimers are presented. The two most stable isomers of the set of conceivable [2 + 2] cycloaddition products are isoenergetic, and both are compatible with NMR, infrared, and Raman data on the product recently synthesized by Lebedkin et al.

## Introduction

Since the synthesis of (C<sub>60</sub>)<sub>2</sub> through [2 + 2] cycloaddition, several attempts to produce its C<sub>70</sub> counterpart have been made (see, e.g., refs 1 and 2 and references therein). Recently, Soldatov et al.<sup>3</sup> showed that C<sub>70</sub> forms dimers at 200–300 °C and pressures above 1 GPa. At 2 GPa linear chains are formed which were studied using X-ray diffraction.<sup>4</sup> Lebedkin et al.<sup>1</sup> have isolated a fraction produced at 1 GPa<sup>3</sup> which is thought to consist of a single isomer. This isomer has been characterized using <sup>13</sup>C NMR, infrared, Raman, and fluorescence absorption spectra. The experimental <sup>13</sup>C NMR spectrum (Table 1 and Figure 2 of ref 1) shows the expected two signals in the sp<sup>3</sup> region, although the intensity of the peaks is weaker than expected and the peaks are relatively broad.

Model calculations of several isomers on the PM3 level were performed by the authors of ref 1. They find five energetically reasonable isomers, in agreement with previous calculations,<sup>5</sup> but the PM3 energies show little difference between isomers.

Two of the five isomers, which are isoenergetic, have a symmetry compatible in number of peaks and intensities with the recorded <sup>13</sup>C NMR spectrum. These isomers have a cyclobutane intercage bridge connecting equivalent bonds in the caps of the cages of the C<sub>70</sub> molecules (see **ab**<sup>cis</sup> and **ab**<sup>trans</sup> in Figure 1) and differ only in the orientation of the monomers across the bridge. The dimers are of C<sub>2v</sub> (cis) and C<sub>2h</sub> (trans) symmetry, respectively. Calculated intercage bond lengths were equal in both isomers. In the PM3 calculations of Lebedkin et al., three other dimeric isomers are found to be slightly more stable, in contradiction to the predictions of previous MNDO calculations<sup>5</sup> which had picked out the two **ab** isomers as the most stable. Lebedkin et al. interpret their data as evidence for isolation of a single isomer, basing this on the <sup>13</sup>C NMR spectrum and on X-ray analysis of the linear polymer synthesized at 2 GPa.<sup>1,3,4</sup>

In the present article, all possible C<sub>70</sub> dimers with [2 + 2] bridges between hexagon–hexagon bonds are studied. Dimer-

TABLE 1: Calculated Dimerization Energies for the Five [2 + 2] Isomers of (C<sub>70</sub>)<sub>2</sub><sup>a</sup>

isomer	alternative notation <sup>1</sup>	G	dimerization energy			
			DFTB	MNDO	AM1	PM3
<b>ab</b> <sup>trans</sup>	(1,2)/(2,1)	C <sub>2h</sub>	32.2	213.1	144.9	158.6
<b>ab</b> <sup>cis</sup>	(1,2)/(1,2)	C <sub>2v</sub>	32.2	213.1	144.9	159.0
<b>abc</b>	(1,2)/(3,3a)	C <sub>1</sub>	22.3	208.5	143.2	159.1
<b>c</b> <sub>1</sub>	(3,3a)/(3,3a)	C <sub>2h</sub>	12.4	204.1	142.1	159.4
<b>c</b> <sub>2</sub>	(3,3a)/(3a,3)	C <sub>2v</sub>	12.4	203.9	142.0	159.4

<sup>a</sup> All energies are quoted in kJ mol<sup>−1</sup>, relative to the energy of the free C<sub>70</sub> molecule.

ization energies, <sup>13</sup>C NMR patterns, and vibrational frequencies are calculated and compared with experiment and related calculations.<sup>1</sup> Our investigations are compatible with a mixture of two almost isoenergetic isomers in the experimental dimeric fraction.

## Results and Discussion

In dimers of isolated-pentagon fullerenes, each intracage bond lies at the junction of either two hexagons (h/h) or a hexagon and a pentagon (h/p). [2 + 2] intercage bridges based on h/p bond formations are energetically unfavorable, as might be expected from simple arguments based on Kekulé structures, and are predicted to carry an energy penalty of ~80 kJ mol<sup>−1</sup>.<sup>5</sup> They are not considered further as candidates for possible C<sub>70</sub> dimers in this study.

All 15 h/h isomers were generated and preoptimized by molecular modeling<sup>6</sup> and optimized using the DFTB method<sup>7,8</sup> which has been found to give reliable geometries and energetics in a variety of applications which includes the fullerenes.<sup>9</sup> Only five isomers are predicted to be bound with respect to the monomers, and only these isomers are considered further. All five isomers are linked by [2 + 2] cycloaddition across fullerene bonds in the region of highest curvature, i.e., at atoms a, b, and c (where a–e are the distinct sites counting down from cap to equator<sup>10</sup>). Their binding energies are compared with semi-empirical values in Table 1 and the structures are shown in Figure 1. The two most stable isomers **ab**<sup>cis</sup> and **ab**<sup>trans</sup> (see Figure 1) have intercage linkages at the closest-to-cap positions.

They are practically isoenergetic, with a dimerization energy of 32 kJ mol<sup>−1</sup>, which is similar to the value for the C<sub>60</sub> dimer

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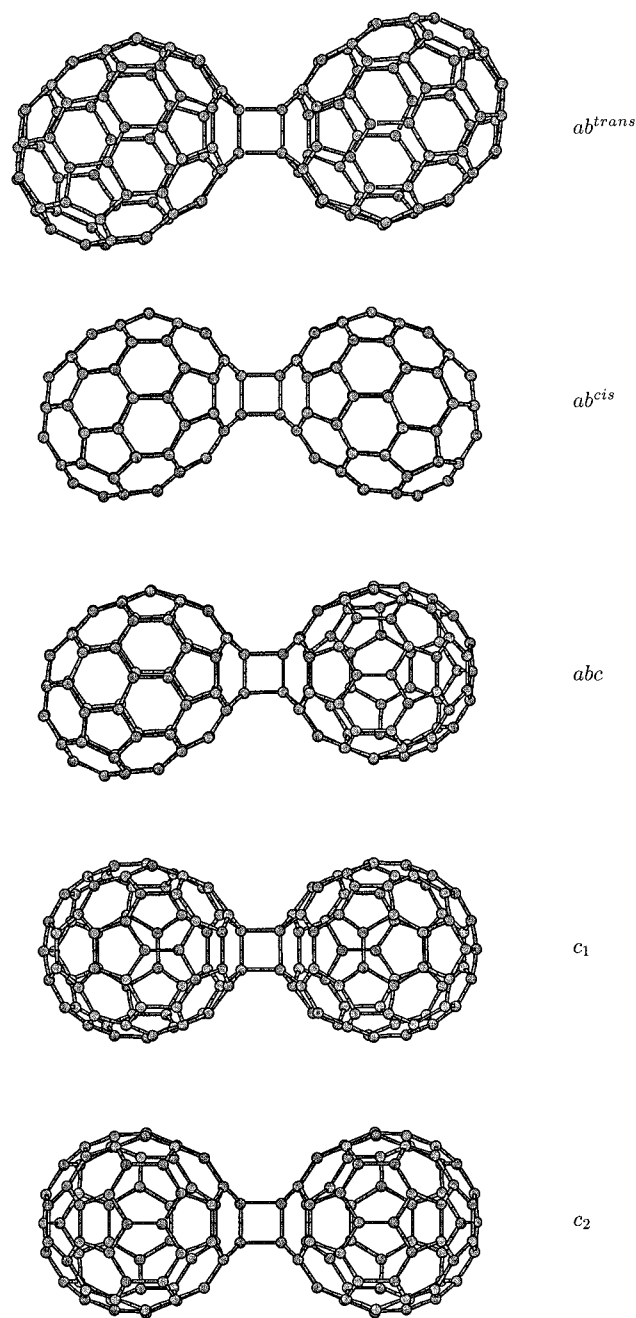


Figure 1. Structures of C<sub>70</sub> dimers.

found in both DFTB and DFT-GGA calculations<sup>11</sup> and several values deduced from experiment.<sup>12–14</sup> Calculations at MNDO geometries<sup>15,16</sup> and one experiment<sup>17</sup> indicate considerably higher values.

Lebedkin et al.<sup>1</sup> performed PM3 calculations on the five isomers and find them to be (i) isoenergetic within 1 kJ mol<sup>−1</sup> and (ii) 5 times more strongly bound than in DFTB. MNDO calculations<sup>5</sup> gave the same order of isomers as DFTB but with a smaller spread of energies. To explore these differences between methods, it was decided to check all the MOPAC semiempirical Hamiltonians. PM3, AM1, and MNDO calculations were performed with the MOPAC 93 package,<sup>19</sup> since Gaussian 98<sup>20</sup> calculations failed to converge into the correct local minima when the TIGHT option was chosen, and gave poorly defined relative energies when it was not. With the MOPAC package<sup>19</sup> the values of Table 1 were calculated. The results show that (i) all methods give much higher dimerization

TABLE 2: Inter- and Intracage Bond Lengths (in Å) in the Bridging Square Ring of the C<sub>70</sub> Dimers<sup>a</sup>

isomer	inter		intra	
<b>ab<sup>trans</sup></b>	aa 1.580 (1.547)	bb 1.582 (1.547)	ab 1.591 (1.601)	ab 1.591 (1.601)
<b>ab<sup>cis</sup></b>	aa 1.580 (1.547)	bb 1.582 (1.547)	ab 1.591 (1.601)	ab 1.591 (1.601)
<b>abc</b>	ac 1.583 (1.551)	bc 1.584 (1.551)	ab 1.591 (1.600)	ac 1.573 (1.579)
<b>c<sub>1</sub></b>	cc 1.586 (1.555)	cc 1.586 (1.555)	cc 1.573 (1.578)	cc 1.573 (1.578)
<b>c<sub>2</sub></b>	cc 1.586 (1.554)	cc 1.586 (1.554)	cc 1.573 (1.579)	cc 1.573 (1.579)

<sup>a</sup> Nomenclature is as in ref 10. Values of ref 1 are given in brackets.

energies than DFTB, which corresponds to similar observations on the C<sub>60</sub> dimer, and (ii) MNDO and AM1 give the same order of isomers as DFTB, while PM3 does not separate the isomers in energy.

Analogy to the C<sub>60</sub> dimer shows that the MNDO energy is an overestimate which can be traced to overly short intercage bonds in the MNDO optimal geometry. The MNDO bond lengths of 1.560/1.616 Å<sup>15</sup> for inter/intracage values compared with 1.575/1.581 Å from X-ray data,<sup>18</sup> which confirms that the DFTB method gives a more reliable geometry (1.583/1.590 Å) and, by implication, a more reliable estimate of the dimerization energy. The same applies to the similar AM1 and PM3 Hamiltonians. For a summary of measured and calculated dimerization energies for C<sub>60</sub>, see ref 16.

DFTB bond lengths for the bridging ring are indicative of approximately equivalent single bonds around the ring (Table 2). They are compared with PM3 values (Table 2 of ref 1) which show shorter intercage distances. Calculated vibrational frequencies for the intercage modes in the DFTB model for the five isomers with positive dimerization energy are again very similar. They are in good agreement with the Raman experiment (Figure 6 of ref 1), but do not provide grounds for distinguishing isomers with the observed Raman frequencies of 89, 118, and 129 cm<sup>−1</sup> (see Table 3). Symmetry arguments could distinguish between the two **ab** isomers for the intercage modes, as one isomer is centrosymmetric and one is not, but IR experiments are difficult to perform at the required low frequencies.

Calculations of <sup>13</sup>C NMR chemical shifts for the five isomers were performed with the IGLO-DFTB model.<sup>21</sup> The calculated patterns are compared with the idealized experimental spectrum in Figure 2. The spectra of isomers **ab<sup>trans</sup>** and **ab<sup>cis</sup>** are both compatible with the experimentally observed pattern<sup>1</sup> and show half-intensity signals in the sp<sup>3</sup> region at 67.8 and 67.5 ppm (**ab<sup>trans</sup>**) and 2 times 67.5 ppm (**ab<sup>cis</sup>**), respectively.

Distinction between isomers **ab<sup>trans</sup>** and **ab<sup>cis</sup>** is difficult on the basis of the calculated <sup>13</sup>C NMR spectra, as both fit the experimental data with an average error of less than ~1 ppm. On the other hand, the spectra of isomers **abc**, **c<sub>1</sub>**, and **c<sub>2</sub>** differ considerably from the experimental isomer pattern.

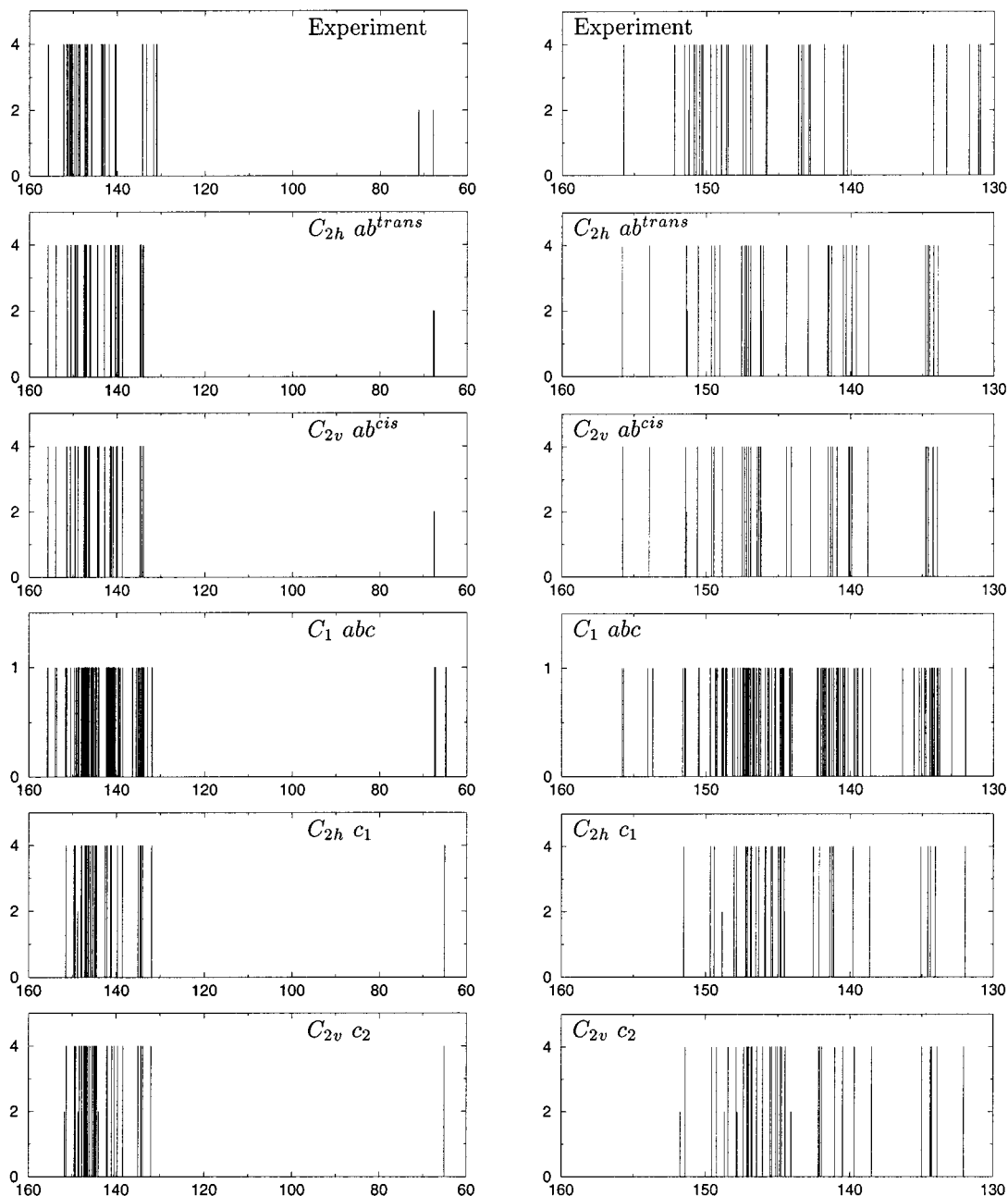
## Conclusion

The spectroscopic evidence is compatible with the presence of either of the energetically favored isoenergetic isomers **ab<sup>trans</sup>** and **ab<sup>cis</sup>**. Given the close similarity of the spectra, the experimental dimer fraction could conceivably consist of a mixture of both isomers, masked by the line width, which, as the calculations indicate, would not need to exceed 1 ppm in the NMR and 1 cm<sup>−1</sup> in the Raman and IR spectra. Since error bars in our present NMR calculations are relatively high, much smaller deviations are possible. The barrier of interconversion between the two isomers is estimated to be less than 62 kJ mol<sup>−1</sup>, corresponding to an interconversion rate of about 10<sup>2</sup> s<sup>−1</sup> at room temperature. This estimate was obtained by considering dissociation via single-bonded (a–b, a–a, and b–b)

**TABLE 3: Calculated Inter cage Vibrational Frequencies ( $\nu$ ) in  $\text{cm}^{-1}$ <sup>a</sup>**

isomer	G	$\nu$					
<b>ab</b> <sup>trans</sup>	$C_{2h}$	18 (20, A <sub>u</sub> )	20 (22, A <sub>u</sub> )	29 (32, B <sub>u</sub> )	82 (87, A <sub>g</sub> )	120 (123, B <sub>g</sub> )	135 (134, A <sub>g</sub> )
<b>ab</b> <sup>cis</sup>	$C_{2v}$	18 (21, A <sub>2</sub> )	20 (22, B <sub>1</sub> )	29 (32, A <sub>1</sub> )	83 (88, A <sub>1</sub> )	120 (123, A <sub>1</sub> )	134 (133, B <sub>2</sub> )
<b>abc</b>	$C_1$	18 (20)	20 (22)	29 (32)	82 (87)	118 (120)	134 (134)
<b>c</b> <sub>1</sub>	$C_{2h}$	18 (20, A <sub>u</sub> )	19 (22, A <sub>u</sub> )	30 (33, B <sub>u</sub> )	80 (85, A <sub>g</sub> )	117 (120, B <sub>g</sub> )	134 (134, B <sub>2</sub> )
<b>c</b> <sub>2</sub>	$C_{2v}$	18 (20, A <sub>2</sub> )	19 (22, B <sub>1</sub> )	30 (33, A <sub>1</sub> )	82 (88, A <sub>1</sub> )	114 (117, A <sub>1</sub> )	134 (134, B <sub>2</sub> )

<sup>a</sup> Values are obtained within the DFTB method. Frequencies in brackets are taken from a PM3 calculation.<sup>1</sup>



**Figure 2.** Schematic  $^{13}\text{C}$  NMR patterns of  $(\text{C}_{70})_2$  isomers. On the left-hand side is shown the full spectrum, on the right an expansion of the  $\text{sp}^2$  region. Shifts are given in ppm, and lines have the idealized intensities proportional to the number of equivalent sites. Note that the idealized experimental spectrum itself is idealized from the version printed in ref 1.

intermediates whose energy was calculated by stretching the contact between the monomers and reoptimization. Higher estimates of this barrier for  $\text{C}_{60}$  were obtained by B3LYP//MNDO calculations.<sup>16</sup> These may suffer from the problems of MNDO geometries for the dimer itself. Since the  $^{13}\text{C}$  NMR spectrum is acquired at 125.76 MHz and 30 °C, it could well be a time average for the two **ab** isomers. This might explain

the broad signals in the range of 152–140 ppm<sup>1</sup> and the low intensities of the  $\text{sp}^3$  signals.

One piece of evidence favoring isomer **ab**<sup>trans</sup> is the repeat unit of the high-pressure linear-chain polymer produced at 2 GPa.<sup>1,4</sup> Polymers of isomers **ab**<sup>trans</sup> and **ab**<sup>cis</sup> would form nonlinear three-dimensional structures which are unfavorable at high pressures. Transformation between isomers, even if it

requires dissociation and re-formation of the dimer, is predicted by the DFTB method to be a much less costly process than Hartree–Fock based methods<sup>1,5</sup> would suggest. The transformation rate between the two **ab** isomers would be about  $5 \times 10^7 \text{ s}^{-1}$  at a temperature of 600 K with an energy barrier of 62 kJ mol<sup>-1</sup>. Thus, the presence of the linear chains containing one dimeric isomer does not rule out the possibility that the dimeric fraction may comprise a mixture of the **ab** isomers.

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**Supporting Information Available:** Tables listing Cartesian coordinates and calculated chemical shifts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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