

Investigations on $C_{70}H_{30}$ obtained by the Birch reduction of C_{70}

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Abstract. Upon Birch reduction, C_{70} forms $C_{70}H_{30}$ as a major product. Besides reporting spectroscopic properties, we discuss the possible structures of $C_{70}H_{30}$ and suggest that the most stable structure is derived by exclusive 1,4-addition to the corannulene units and to the central pentaphenyl belt in C_{70} .

Keywords. Fullerene; Birch reduction; C_{70} ; $C_{70}H_{30}$; MNDO.

Birch reduction of C_{60} has been shown to yield $C_{60}H_{36}$ as a major product (Banks *et al* 1993; Govindaraj 1993). There have been a few theoretical calculations on $C_{60}H_{36}$ and other C_{60} hydrides (Bakowies and Thiel 1992; Rathna and Chandrasekhar 1993a). The likely structure of $C_{60}H_{36}$ appears to be the one involving four benzene rings distributed tetrahedrally in a spheroidal framework. Angle strain, degree of conjugation, the number and magnitude of eclipsing interactions as well as the strain associated with cage distortions seem to be important factors in determining the stabilities of the reduction products of C_{60} . We have been interested in investigating the hydrides of C_{70} for the purpose of understanding the factors that determine their stability in relation to C_{60} hydrides. In this communication, we report the synthesis and spectroscopic properties of $C_{70}H_{30}$ which we have obtained as a major product of Birch reduction of C_{70} . We have also examined the relative stabilities of various possible structures using MNDO (Dewar and Thiel 1977) calculations. Based on the computed energetics as well as the known reactivity pattern in Birch reduction of aromatic rings the most likely structure of $C_{70}H_{30}$ is proposed.

A mixture of fullerenes obtained by contact arc vapourization of graphite (Krätschmer *et al* 1990; Rao *et al* 1992) was subjected to separation and purification by the use of the charcoal-silica gel filtration technique (Govindaraj and Rao 1993). Birch reduction of C_{70} was carried out as follows. To excess Li/liquid NH_3 , a solution containing 30 mg of C_{70} and 5 ml of *tert*-butanol in 200 ml methylcyclohexane was added and stirred vigorously. The temperature of the reaction mixture was maintained at $-33^\circ C$ for 6–7 hours by using a liquid ammonia reflux condenser. The product was quenched with excess of ammonium chloride, washed with water, dried over anhydrous $MgSO_4$ and passed through a silica column to remove possible amine addition products. The new product in TLC essentially showed a single spot (iodine

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active) with an R_f value around 0.34 in 30% CH_2Cl_2 /hexane. After removing the solvent a white solid product was obtained. This product was characterized by mass spectrometry, FTIR, NMR and UV spectroscopy.

The EI mass spectrum of the product obtained after chromatographic purification shows a distribution of peaks (figure 1), but the main line is at $m/z = 870$ corresponding to a hydride of the formula $\text{C}_{70}\text{H}_{30}$. The FTIR spectrum (figure 2) showed characteristic frequencies associated with aliphatic C–H stretching as well as C=C skeletal vibrations. We do not see any features corresponding to NH_2 stretching and bending modes in the FTIR spectrum indicating the absence of ammonia addition products. The ultraviolet absorption spectrum of the hydride (see inset of figure 2) shows a main band at 222 nm, and weaker features at 290 and 300 nm, suggesting the presence of extended conjugation in the hydrocarbon. The ^{13}C NMR spectrum (figure 3) showed distinct bands around 140 ppm and 40 ppm which can be assigned respectively to unsaturated and saturated carbons. The proton NMR spectrum in CDCl_3 showed a broad band in the 2.3 to 4.6 ppm region (see inset of figure 3). This can be assigned to protons which are attached to saturated carbons.

The number of possible isomers for $\text{C}_{70}\text{H}_{30}$ is quite large, even if hydride addition is restricted exclusively to the exo face of the cage. By taking into account the electronic structure of C_{70} (Taylor 1992; Rathna and Chandrasekhar 1993b) and the computed stability order of its dihydride derivatives (Karfunkel and Hirsch 1992), several reasonable structures can be proposed. Eleven isomeric forms which retain the five-fold axis of symmetry of the C_{70} cage have been considered in the present study. Bond-length variations as well as computed bond orders in C_{70} indicate that the molecule is best viewed as a combination of two corannulene units held together by a central, equatorial belt of five phenyl rings (figure 4a). There is strong bond alternation within each of the corannulene units, while the pentaphenyl unit is characterised by benzenoid rings with typical 'aromatic' bond lengths connected by

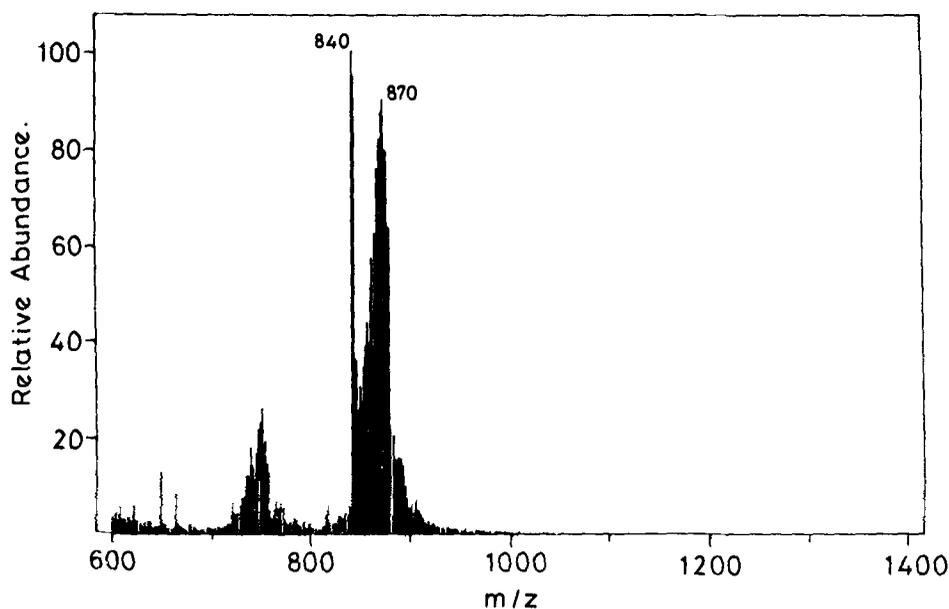


Figure 1. Electron impact mass spectrum of $\text{C}_{70}\text{H}_{30}$.

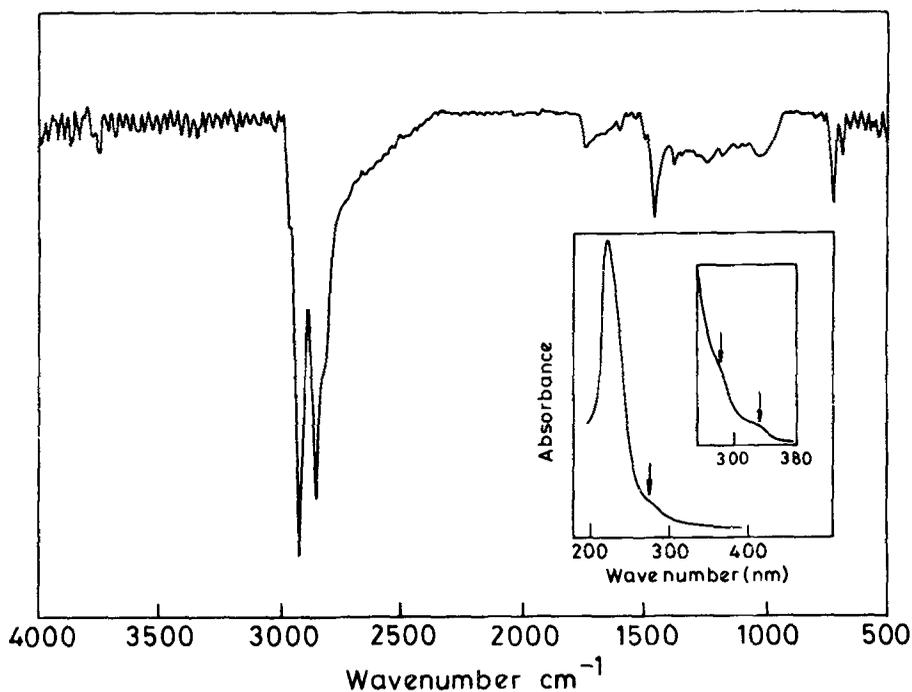


Figure 2. Experimental infrared spectrum (FT) of $C_{70}H_{30}$. Inset shows the ultraviolet absorption spectrum of $C_{70}H_{30}$ in cyclohexane.

essentially single bonds. Therefore, of the 8 types of bonds in the D_{5h} structure of C_{70} , only two sets of bonds have significant double bond character. Using the numbering scheme suggested for C_{70} (Henderson and Cahill 1993), these bonds correspond to $1a-1b$ and $1c-2c$ along with their symmetry equivalent pairs (figure 4b). The other bonds with partial π bond character are the $1d-10d$ and $1d-1e$ type bonds of the central benzenoid rings.

The computed relative stabilities of $C_{70}H_2$ isomers (Karfunkel and Hirsch 1992; Rathna and Chandrasekhar 1993b) conform to the above description of the electronic structure of C_{70} . Thus, the most stable isomers correspond to 1,2-addition to the electron rich $1c-2c$ and $1a-1b$ bonds of the corannulene units. The next stable isomer is obtained by unsymmetrical 1,4-addition ($1d-10d'$) to the benzenoid ring of the equatorial belt. The isomer resulting from unsymmetrical 1,4-hydrogenation of one of the benzene rings of a corannulene unit ($1a-2c$) is computed to be slightly higher in energy. Interestingly, symmetrical 1,4-addition to the central benzenoid ring ($1e-10e$) as well as 1,2-additions to any of the bonds other than those noted above are significantly higher in energy.

Assuming that the above trends are valid for the higher derivatives of C_{70} (plausible for kinetic reasons), 11 combinations of hydride additions to yield $C_{70}H_{30}$ with five-fold symmetry can be envisaged. Two isomers are possible with exclusive 1,2-additions: (1) with additions to all the ten $a-b$ bonds and to five of the $c-c$ bonds; (2) with additions to all $c-c$ bonds and to five of the $a-b$ bonds. In these structures one of the corannulene units is completely saturated and the second is partially hydrogenated, leaving the pentaphenyl unit unaffected. Three high symmetry

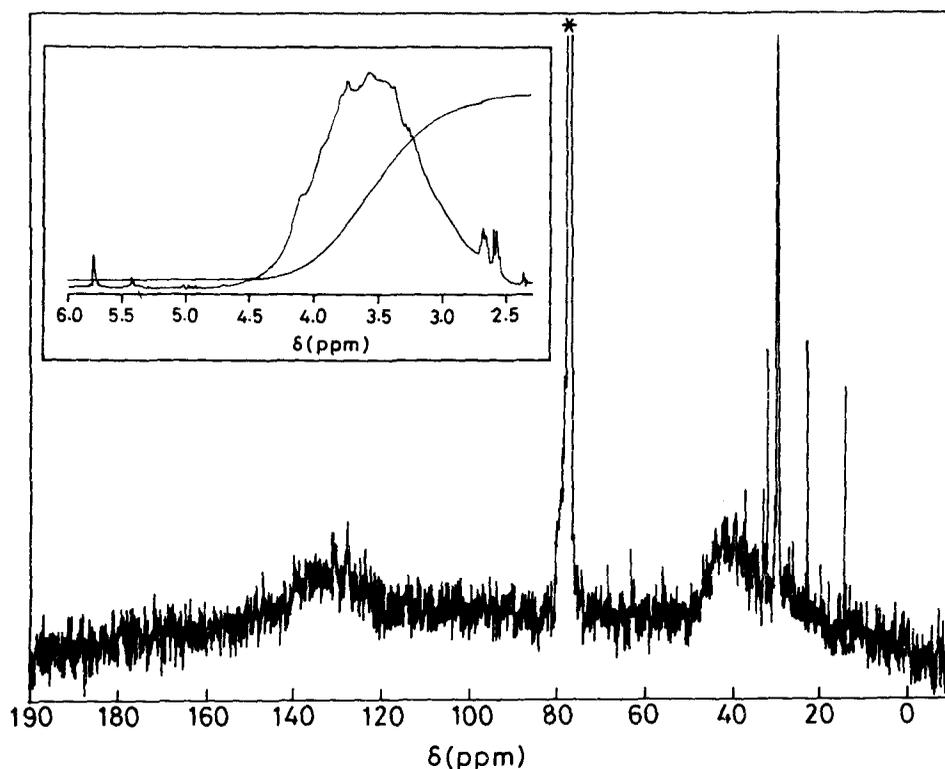


Figure 3. ^{13}C NMR spectrum of $\text{C}_{70}\text{H}_{30}$ in CDCl_3 . Inset shows the proton NMR spectrum of $\text{C}_{70}\text{H}_{30}$ in CDCl_3 . Asterisk indicates signal due to solvent.

structures, 3–5, are possible if exclusively 1,4-additions to the corannulene units as well as to the pentaphenyl rings are considered. In these isomers, the preferred unsymmetrical mode of 1,4-addition to the central phenyl rings is considered, while the additions to the benzene rings of the corannulene units have been chosen in such a way that the central pentagon is fully saturated, ensuring five-fold symmetry. Three additional isomers, 6–8 result by allowing for 1,4-additions to the pentaphenyl belt and 1,2-additions to 10 of the 15 electron rich bonds of the corannulene units. Finally three isomers 9–11 have been considered in which 20 hydrogen atoms have been added to all the *d–d* bonds of the pentaphenyl rings. Further 1,4-addition of 10 hydrogen atoms to one of the corannulene units results in 9. On the other hand, isomers 10 and 11 are derived by 1,2-additions to one set of *a–b* and *c–c* type bonds, respectively.

Geometry optimizations of the various isomers at the MNDO level lead to heats of formation shown in table 1. The computed heats of formation vary over a large range. As noted in an earlier analysis of C_{60} derivatives (Rathna and Chandrasekhar 1993a), the relative stabilities are primarily determined by the extent of angle strain at the various sp^2 and sp^3 hybridized carbon atoms. Deviations from the corresponding ideal angles of 120° and $109^\circ 28'$ lead to significant destabilization of the cage. Analysis of the computed geometries reveals that isomers 3, 4, 5 and 9 have the least angle strain (figure 5). These are indeed computed to be the four most stable structures. The remaining structures suffer from significantly greater strain and are correspondingly higher in energy.

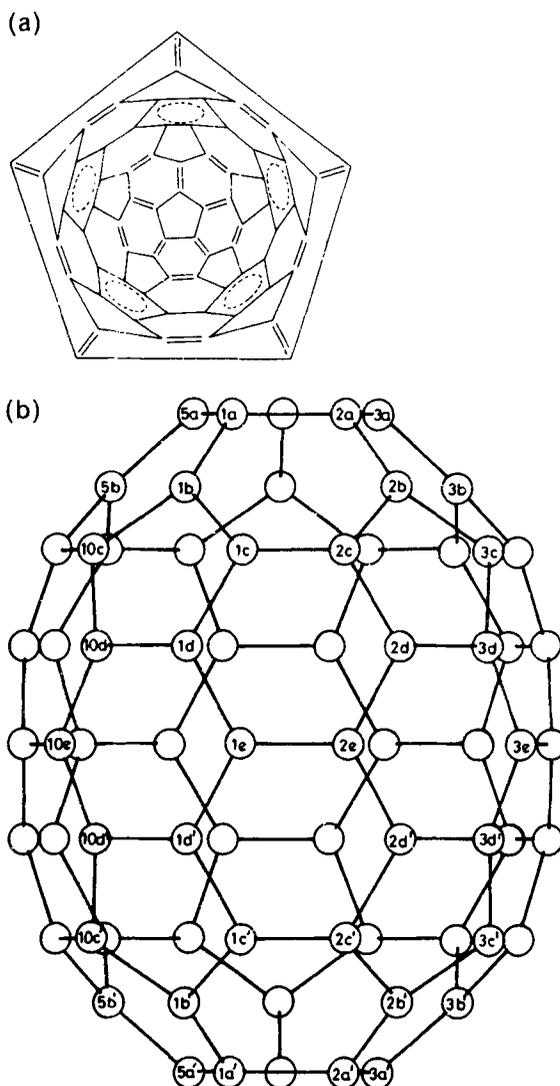


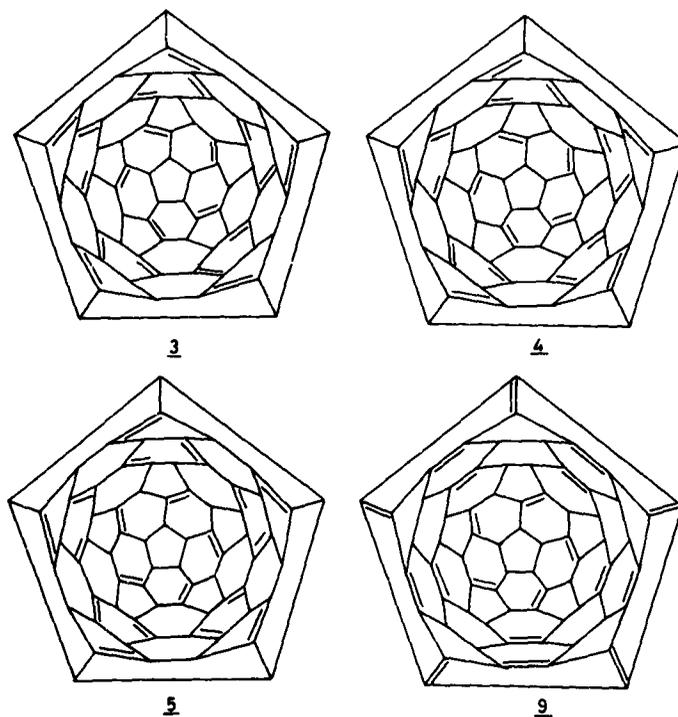
Figure 4. (a) Schlegel diagram of C_{70} emphasizing the presence of corannulene units at the top and bottom as well as the central pentaphenyl belt. (b) Atom-labelling scheme in C_{70} . Labels are omitted for symmetry-related atoms for the sake of clarity.

The most stable isomers, $\mathfrak{3}$ – $\mathfrak{5}$, may be viewed as being derived by exclusive 1,4-additions to the corannulene and pentaphenyl sub-units. While these structures have a common pattern of hydrogenation, they differ in the extent of residual conjugation and the number of eclipsing interactions involving adjacent C–H groups. The number of destabilizing eclipsing interactions are 20, 15 and 10, respectively for $\mathfrak{3}$, $\mathfrak{4}$ and $\mathfrak{5}$. However, the degree of conjugation seems to determine the relative stabilities. Isomer $\mathfrak{3}$, with five octatetraene units is computed to be the most stable, followed by $\mathfrak{4}$ and $\mathfrak{5}$ which have five hexatriene and diene units, respectively. Isomer $\mathfrak{9}$ which is computed to be nearly as stable as $\mathfrak{5}$ may also be viewed as being derived by exclusive 1,4-additions. However, the overall hydrogen addition is highly unsymmetrical in this structure, leaving a corannulene unit unaffected.

Table 1. Calculated MNDO heats of formation and relative energies (kcal/mole) of $C_{70}H_{30}$ isomers.

Isomer	Symmetry	Hydrogenation pattern*			Heat of formation	Relative energy	
		Corannulene		Penta-phenyl			
		Top	Bottom				
<u>3</u>	D_5	2a-1c	1a'-2c'	1d-10d'	406.3	0.0	
<u>4</u>	C_5	2a-1c	2a'-1c'	1d-10d'	412.7	6.4	
<u>5</u>	D_5	1a-2c	2a'-1c'	1d-10d'	417.0	10.7	
<u>9</u>	C_5	2a-1c	—	1d-10d'	418.2	11.9	
<u>10</u>	C_{5v}	1a-1b	—	10d-1d'	1d-10d'	435.7	29.4
<u>6</u>	D_5	1c-2c	1c'-2c'	1d-10d'	451.5	45.2	
<u>8</u>	C_{5v}	1a-1b	1c'-2c'	1d-10d'	453.4	47.1	
<u>1</u>	C_{5v}	1a-1b	1c'-2c'	—	458.7	52.4	
<u>7</u>	D_5	1c-2c	1c'-2c'	—	459.1	52.8	
<u>11</u>	C_{5v}	1a-1b	1a'-2b'	1d-10d'	464.4	58.1	
<u>2</u>	C_{5v}	1c-2c	—	1d-10d'	10d-1d'	481.3	75.0
		1a-1b	1a'-1b'	—			
		1c-2c					

*The location of all 30 C-H units can be generated by taking into account the additional sets related by five-fold symmetry to the pairs shown in the table.

**Figure 5.** Structures of $C_{70}H_{30}$ isomers with the least angle strain resulting from 1,4-addition to corannulene units and to the central pentaphenyl belt.

The isomer formed through Birch reduction of C_{70} is most likely to be **3** (with perhaps admixtures of **4** and **5**) for thermodynamic as well as kinetic reasons. The computed heats of formation clearly favours the formation of **3**. Since the structure is derived by exclusive 1,4-reduction of benzenoid rings, its formation is consistent with the known pattern of Birch reduction. The electronic spectrum of the experimentally isolated $C_{70}H_{30}$ is also consistent with the structural proposal. The presence of the octatetraene units will lead to relatively long wavelength absorption, as indeed noted experimentally.

It is known that Birch reduction leads to unconjugated structures. It may therefore appear surprising that **3**, which is characterized by a fair degree of delocalization, is formed by Birch reduction of C_{70} . However, it may be pointed out that no isomer of $C_{70}H_{30}$ is possible with exclusively localized double bonds (such a structure is possible for $C_{70}H_{32}$ or higher hydrides). It is conceivable that **3** does not undergo further reduction for kinetic reasons. The nature of the major product $C_{60}H_{36}$ obtained by Birch reduction of C_{60} is of interest in this context. While the original proposal was that the structure corresponds to one with an isolated double bond in each of the 12 pentagons (Haufler *et al* 1990), this view has been questioned recently (Austin *et al* 1993; Govindaraj 1993). Available experimental data and semiempirical calculations (Rathna and Chandrasekhar 1993a) are consistent with an alternative isomer with four benzenoid rings distributed in a tetrahedral arrangement. It is quite likely that Birch reductions of fullerenes in general do not entirely follow the established behaviour of planar aromatics.

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