$C_{71}H_2$ Cyclopropanes and Annulenes: Synthesis and Characterization

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Addition of diazomethane to a toluene solution of C_{70} affords a mixture of isomeric pyrazolines, which, upon photolysis, furnish two isomeric $C_{71}H_2$ cyclopropanes; thermolysis of the mixture produces two isomeric annulenes.

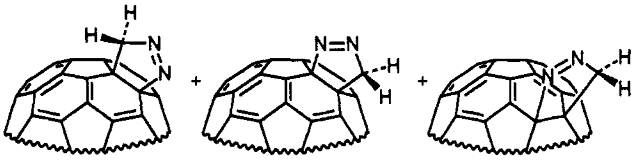
The unique structures of C_{60} and its derivatives have sparked intense research activity, bridging the disciplines of chemistry, physics and materials science.[1] We have previously prepared and characterized the prototypical fullerene epoxide ($C_{60}O$, **1**) and cyclopropane ($C_{61}H_2$, **2**).[2,3] In the latter study, photolysis of pyrazoline **3**, prepared *via* addition of diazomethane to C_{60}, furnished a 3 : 4 mixture of **2** and the isomeric annulene **4**.[3] Alternatively, as observed by Wudl *et al.*,[4] thermolysis of **3** leads to **4** as the major product (>20 : 1). Whereas C_{60} contains only two types of bonds, C_{70} embodies no fewer than eight; half of these could lead to regioisomeric adducts with unsymmetrical reagents such as CH_2N_2. In this communication, we describe the synthesis, isolation, and characterization of two $C_{71}H_2$ cyclopropanes and two isomeric annulenes, the first methylenated C_{70} derivatives.[5–7]

By analogy with the chemistry of C_{60},[1–4] initial addition of CH_2N_2 to C_{70} was expected to involve one or more of the four types of 6,6 ring fusions (i–iv, Fig. 1). The X-ray crystal structure[8] of the clathrate $C_{70}\cdot 6S_8$, in agreement with earlier *ab initio* calculations on the isolated fullerene,[9,10] revealed that i and ii are by far the shortest bonds in C_{70}, suggesting that they would prove to be the most reactive. These studies also disclosed that iv, a 6,6 single bond in most canonical representations of the molecule, is in fact the longest bond type and a highly unlikely site for CH_2N_2 addition.[7c] Importantly, Hawkins *et al.*[5] observed that bond i is more reactive than ii, even though the bond order for ii is slightly higher. They attributed this striking result to greater local curvature (*i.e.* pyramidalization)[11] at the carbons joined by bond i.[5,7d]

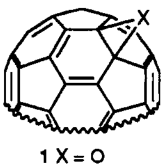
Treatment of a toluene solution of C_{70} (60 mg, 0.7 mmol dm^{-3}) with 230 µl of ethereal diazomethane (0.071 mmol, 0.31 mol dm^{-3}) at 0 °C for 1 min furnished a mixture of pyrazoline adducts which was isolated in 34% yield *via* column chromatography on silica gel. The 500 MHz ^1H NMR spectrum ($CDCl_3$) revealed the formation of three isomers, **5a** (s, δ 6.29), **5b** (s, δ 5.92), and **6** (d, δ 5.83, J_{HH} 19 Hz; d, δ 6.11, J_{HH} 19 Hz), in a *ca.* 12 : 1 : 2 ratio. Apart from the product of an improbable addition to bond iv, **5a** and **5b** are the only pyrazolines derivable from C_{70} that contain symmetry-equivalent hydrogens, consistent with the observed singlets. The structure assignments are also in accord with the conversions of the isomers to specific cyclopropanes and annulenes (see below), as well as the expectation that addition would occur primarily or exclusively at bonds i and ii. The formation of **5a** and **5b** in unequal amounts appears to be the first well-characterized[7a,e] regioselective reaction at a fullerene bond. Interestingly, CH_2N_2 is much more discriminating than OsO_4[5] in addition to bonds i and ii.

Photolysis and thermolysis of the pyrazolines generated four isomeric methylene derivatives of C_{70}, two cyclopropanes and two annulenes. They were identified by NMR analysis, augmented as appropriate by the recognition that only specific combinations of $C_{71}H_2$ hydrocarbons could arise from three common precursors. Symmetry considerations proved critical in the correlation of NMR data with structure. For example, symmetry arguments permit straightforward NMR differentiation among the four possible 6,6 cyclopropanes **7–10** (Fig. 2); similar analyses serve to distinguish certain pyrazolines and annulenes as well as 6,5 cyclopropane structures. These interpretations of the NMR spectra rely upon the reasonable assumption that the inequivalent protons and carbons in unsymmetrical C–CH_2–C moieties will be resolved at high field.

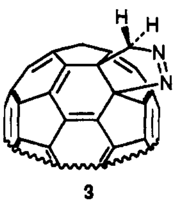
Irradiation of the pyrazoline mixture (5 µmol dm^{-3}, toluene–hexane, 10 : 1) through Pyrex for 25 min followed by



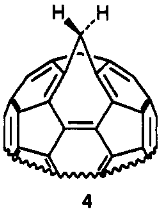
5a **5b** **6**
(12:12)



1 X = O
2 X = CH_2



3



4

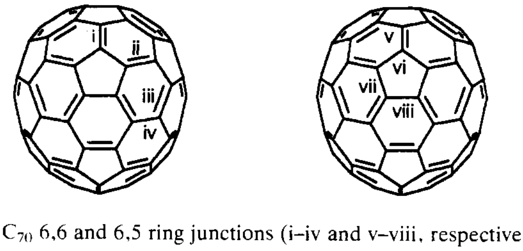
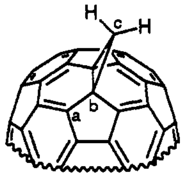
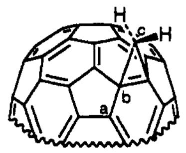


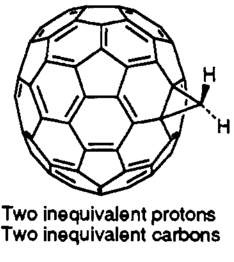
Fig. 1 C_{70} 6,6 and 6,5 ring junctions (i–iv and v–viii, respectively)



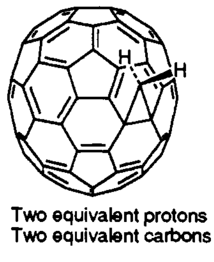
7 Two equivalent protons
Two inequivalent carbons



8 Two inequivalent protons
Two equivalent carbons

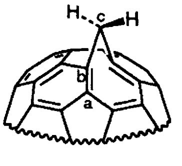


9 Two inequivalent protons
Two inequivalent carbons

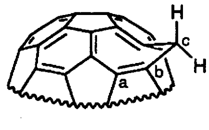


10 Two equivalent protons
Two equivalent carbons

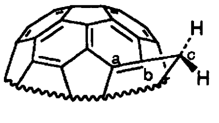
Fig. 2 Symmetry-dependent NMR characteristics of the protons and skeletal cyclopropane carbons for the four possible 6,6 isomers **7–10**



12 (Major)



13 (Minor)



14 (Not detected)

silica gel filtration (1 : 1 hexane/toluene) and concentration afforded a dark-brown solid. The 500 MHz ^1H NMR spectrum ($CS_2/CDCl_3$) revealed that two principal products were formed in a 7 : 1 ratio, accompanied by traces (<2%) of a third compound which proved to be annulene **12**. After separation *via* normal-phase HPLC (Dynamax 60-A Si column, 100% hexane; 25% combined yield), laser desorption time of flight (LDTOF) MS of both species showed $C_{71}H_2$ parent ions at 854, as well as less intense peaks at 840 (C_{70}).

The NMR spectra of the major isomer define the cyclopropane structure **7** unambiguously. The only ^1H absorption is a methylene singlet at δ 2.88 (*cf.* δ 3.93 for **2**).[3] The ^{13}C NMR spectrum [CS_2/[$^2H_6$]acetone, *ca.* 70 mmol dm^{-3} $Cr(acac)_2$] of isotopically enriched material (10–15% $^{13}C_{70}$, 100% $^{13}CH_2$) consists of 38 peaks, with 35 resonances between δ 130 and 156. Two peaks at δ 62.6 and 64.1 are assigned to the inequivalent skeletal cyclopropane carbons; the methylene carbon appears at δ 13.8. The J_{CH} and $J_{C_{bc}}$ coupling constants (168.0 and 22 Hz) are also typical of cyclopropanes (160–170 and 10–22 Hz).[12] Of the eight conceivable cyclopropane derivatives of C_{70}, only **7** contains equivalent protons and inequivalent cyclopropane carbons. Isomer **7** would derive principally from **5a**, and also from **5b** unless the latter unexpectedly failed to yield a cyclopropane.

The ^1H NMR spectrum of the minor photolysis product contains doublets at δ 2.56 and 2.82 (J_{HH} 6.5 Hz), consistent with inequivalent cyclopropane hydrogens. The ^{13}C spectrum of an isotopically enriched sample contains 36 downfield resonances (δ 126–151), as well as peaks at δ 56.8 and 15.0, which correspond to two equivalent skeletal cyclopropane carbons and the methylene carbon, respectively. The J_{CH} and $J_{C_{bc}}$ values, 167.8 and 22 Hz, proved to be nearly identical to the analogous couplings for **7**. These data are consistent with the likely 6,6 cyclopropane structure **8**, derivable from pyrazoline **6**, but they do not exclude the isomeric 6,5 cyclopropane **11** (structure not shown) at bond v (Fig. 1) which could arise (with 7) *via* **5a**. The formation of **11** would require that **6** give no cyclopropane; moreover, a 6,5 cyclopropane structure finds no precedent in the chemistry of C_{60} diazoalkane adducts.

Thermolysis of the pyrazoline mixture was initially achieved by heating a *ca.* 0.05 mmol dm^{-3} solution in toluene–hexane (10 : 1) at 70 °C for 0.5 h. Concentration afforded a 4 : 1 (^1H NMR) mixture of products in 33% overall yield from C_{70}. The isomers were separated *via* normal-phase HPLC (Dynamax 60-A Si column, hexane), and both LDTOF MS showed parent and fragment ions at 854 and 840 ($C_{71}H_2$ and C_{70}).

NMR analysis established that the two new $C_{71}H_2$ isomers are annulenes. The ^1H NMR spectrum of the major isomer consists of doublets at δ 2.91 and 6.52 (J_{HH} 9.8 Hz), very similar to the corresponding data for the $C_{61}H_2$ 6,5 annulene **4** (doublets at δ 2.87 and 6.35, J_{HH} 9.7 Hz).[4] The ^{13}C NMR spectrum of the major annulene contains 37 peaks between δ 118.0 and 153.4. The remaining signal at δ 34.0 is assigned to the methylene carbon; no other resonances appear upfield of δ 118. In addition, the J_{CH} and $J_{C_{bc}}$ coupling constants (measured with isotopically enriched material, 10–15% $^{13}C_{70}$ and 100% $^{13}CH_2$) proved to be 150.2, 145.7 and 32 Hz, characteristic of methano-bridged fullerenes[13] (*cf.* 147.0, 145.0 and 32 Hz for **4**[3,4]). Structure **12** for the major annulene derives from its symmetry, in conjunction with the structure of **7** and the requirement that **7** and the major annulene both arise principally (or exclusively) *via* the major pyrazoline. In addition, the major pyrazoline must be **5a** rather than **5b**; we therefore assign structure **5b** to the minor pyrazoline with equivalent hydrogens.

The ^1H NMR spectrum of the minor annulene contains doublets at δ 2.78 and 5.23 (J_{HH} 10.0 Hz, J_{CH} 149.8 and 146.4 Hz); to date, attempts to obtain a ^{13}C NMR spectrum have been frustrated by the scarcity and low symmetry of this compound. The structure assignment rests upon direct ^1H NMR observation of the pyrazoline thermolysis. Both **5a** and **6** are considerably more labile than **3**, furnishing **12** and the minor annulene, respectively, within *ca.* 10 h in solution at room temp. In contrast, **5b** is transformed to the minor annulene only upon heating. The conversion of both minor pyrazolines to the same annulene, in conjunction with the earlier assignment of structure **5b**, indicates that the second minor pyrazoline is **6** and that the minor annulene is **13** rather than **14** (**14** could be generated from **6** but not from **5b**).

The UV spectra of **7**, **8**, **12** and **13** also serve to distinguish between 6,6 closed structures and 6,5 open systems.[14] Both in this work and in our previous studies of $C_{60}O$[2] and the $C_{61}H_2$ isomers,[3] we have observed that the UV fine structure patterns of 6,5 annulenes closely resemble those of C_{60} and C_{70}, whereas the spectra of 6,6 closed systems differ significantly.

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