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Birch Reduction of Hexaphenyl- and Pentaphenylbenzene and an X-ray Crystallography and NMR Spectroscopy Study of *cis*- and *epi*-1,2,3,4,5,6-Hexaphenylcyclohexane and of 2,3,5,6-Tetraphenyl-1,1′-bicyclohexylidene: Cannizzaro's Conundrum Revisited

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Abstract: The Birch reduction of hexaphenylbenzene yields two isomers of 1,2,3,4,5,6-hexaphenylcyclohexane. The X-ray crystal structure of the all-*cis* isomer, **1**, reveals that the severe steric crowding among the three axial phenyls is alleviated by a marked splaying out of those three aryl substituents relative to the positioning in a conventional chair structure. A second product, **2**, was identified crystallographically and by NMR spectroscopy as the 1,3-diaxial-2,4,5,6-tetraequatorial (*epi*) isomer of hexaphenylcyclohexane, in which only five of the six additional hydrogen atoms are positioned on the same face of the C_6Ph_6 precursor. A variable-temperature NMR study of the all-*cis* isomer **1** yielded a chair-to-chair inversion barrier of $\approx 19\ kcal\ mol^{-1}$, which is somewhat higher than the previously reported values for all-*cis*-1,2,3,4,5,6-$C_6H_6R_6$ in which R = Me or CO_2Me. The possible relevance to Cannizzaro's 1854 report of a product with the formula $(C_7H_6)_n$ is discussed. By contrast, Birch reduction of pentaphenylbenzene led to the formation of 2,3,5,6-tetraphenyl-1,1′-bicyclohexylidene.

Keywords: aromatic interactions · Birch reduction · conformation analysis · ring inversion · steric hindrance

Introduction

In 1854, Stanislao Cannizzaro reported that the action of a variety of compounds, including boron trifluoride, sulphuric acid, phosphorus pentoxide or zinc chloride, on benzyl alcohol or benzyl ether gave a hydrocarbon with the formula $(C_7H_6)_n$.[1] Over the following 90 years, the question of the identity of this material was the subject of more than 30 publications, and a comprehensive historical survey has been provided.[2] We are aware of only 2 substantive reports of the possible resolution of this problem: in 1941, Shriner and Berger observed that, when a large quantity of benzyl alcohol was heated for 12 h at 180 °C with boric acid, treated with NaOH and extracted with chloroform, a small amount of a pure product (m.p. 278–280 °C) could be obtained after recrystallisation from benzene.[2] A molecular-weight determination by Rast's method (depression of the freezing point of camphor)[3] gave a value of 556—$(C_7H_6)_6$ requires 540—and, in conjunction with the microanalytical results, the data led the authors to suggest that the material was "one of the isomeric 1,2,3,4,5,6-hexaphenylcyclohexanes". Subsequently, in 1956, Gerrard and Kilburn noted that, when $[PhCH_2CH(Ph)O]_4Si$ was treated with HCl, a liquid with a b.p. of 229 °C at 0.03 mm Hg was formed; this was assigned as "sym-hexaphenylcyclohexane".[4] However, in the absence of clear spectroscopic or crystallographic evidence, these claims for the existence of 1,2,3,4,5,6-hexaphenylcyclohexane remain unproven.

Our own involvement in this topic arose serendipitously as a continuation of our earlier studies on the syntheses and dynamic behaviour of sterically crowded organic and organometallic molecules,[5] in particular $[Cr(CO)_3(C_6Ph_6)]$,[6] and 1-ferrocenyl-2,3,4,5,6-penta(β-naphthyl)benzene.[7] We wished to investigate the possibility of incorporating an organoruthenium fragment directly into a polyphenylbenzene framework,[8,9] and the most common route to such [Ru(η⁶-

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arene)Cl_2]$_2$ complexes involves the Birch reduction of an arene to the corresponding 1,4-cyclohexadiene and subsequent treatment with hydrated ruthenium trichloride.[10] To this end, hexaphenylbenzene and pentaphenylbenzene were each subjected to the regular Birch conditions, and the resulting mixtures were separated by careful column chromatography. From the C_6Ph_6 reaction, two major products were isolated and identified as isomers of 1,2,3,4,5,6-hexaphenylcyclohexane. These molecules have been unambiguously characterised by X-ray crystallography, and their dynamic behaviour has been investigated by NMR spectroscopy.

Results and Discussion

Crystallographic studies: Treatment of hexaphenylbenzene (HPB) with sodium/liquid ammonia/ethanol, containing some THF to help solubilise the HPB, furnished two major products, both of which yielded crystals suitable for X-ray diffraction studies. As depicted in Scheme 1, the first compound was identified as all-*cis*-1,2,3,4,5,6-hexaphenylcyclohexane (**1**), with phenyl groups placed in alternate axial and equatorial positions on the chair framework. Figure 1 illustrates how the three axial phenyl groups in **1** find themselves in a spatially limited environment; to alleviate this steric crowding, they are markedly splayed out, such that the bonds linking these phenyl groups to the central ring make angles of 114.7, 115.6 and 117.2° with the plane defined by their attached cyclohexane ring carbon atoms (Figure 2). Of course, in a perfect chair, these angles would be 90°. Concomitantly, the axial C–H bonds are directed inwards by 78±3° such that the H–C–C–H dihedral angles average 52°. Moreover, the axial-phenyl-ring carbon bonds (average 1.527 Å) are slightly longer than the corresponding equatorial-phenyl-ring carbon bonds (average 1.511 Å). It is also noticeable that the angles within the cyclohexane ring are very different; for those carbon atoms bearing axial phenyl groups, the C–C–C angles average 107.3°, whereas the C–C–C angles for ring carbon atoms attached to equatorial phenyl groups average 117.3°. This latter observation parallels (but is noticeably greater than) the C–C–C internal angle differences found in the central ring of all-*cis*-1,2,3,4,5,6-hexamethylcyclohexane, which average 109.2° (for carbon atoms bearing axial methyl groups) and 114.7° (for carbon atoms bearing equatorial methyl groups).[11]

A second crystalline product, **2**, isolated from the Birch reduction of C_6Ph_6 was also characterised by X-ray diffraction as an isomer of 1,2,3,4,5,6-hexaphenylcyclohexane. However, in **2**, only five of the six additional hydrogen atoms are positioned on the same face of the cyclohexane ring, thus producing a molecule with two axial and four equatorial phenyl groups, as shown in Figure 3.

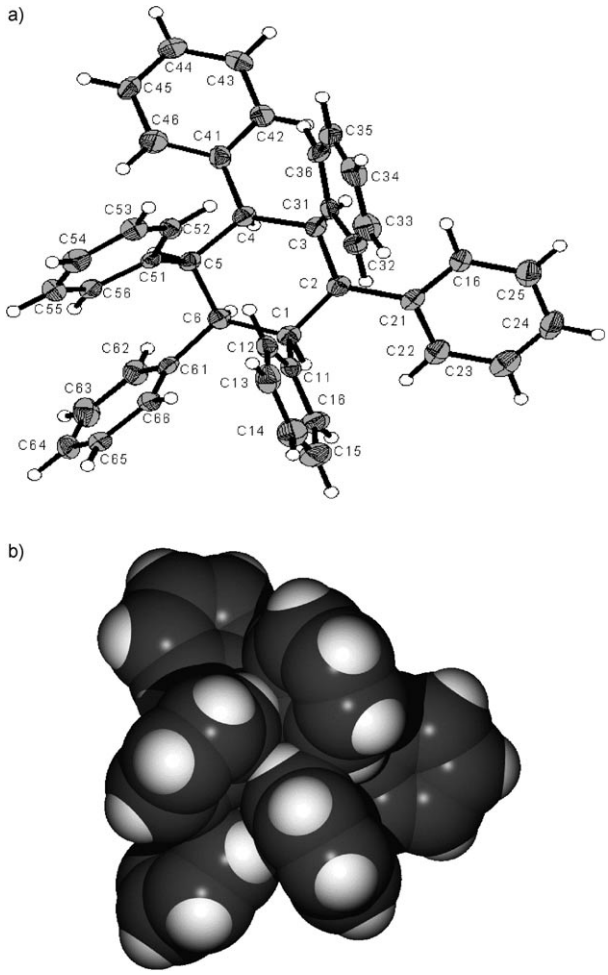


Figure 1. a) Top view of the molecular structure of all-*cis*-hexaphenylcyclohexane (**1**), with atom labelling, and b) the corresponding space-filling model.

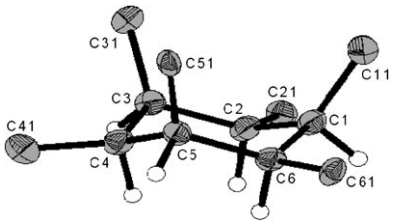
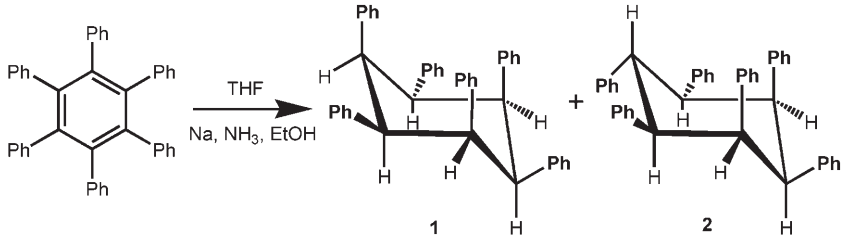


Figure 2. Side view of all-*cis*-hexaphenylcyclohexane (**1**) with only the *ipso*-carbon atoms of the phenyl rings shown.



Scheme 1. Products of the Birch reduction of hexaphenylbenzene.

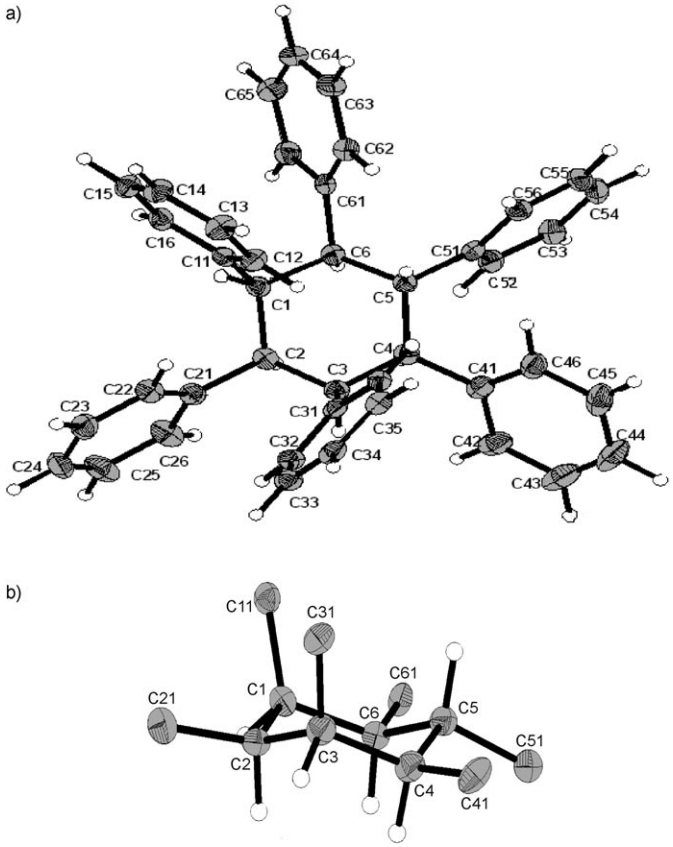


Figure 3. a) Top view of the molecular structure of 1,3-diaxial-2,4,5,6-tetraequatorial-hexaphenylcyclohexane (**2**), with atom labelling, and b) the corresponding side view with only the *ipso*-carbon atoms of the phenyl rings shown.

The axial substituents in **2** are disposed in a 1,3 fashion, thereby generating a system with C_s symmetry on the NMR timescale. However, in the solid state, this mirror symmetry is broken as the two axial phenyl groups have quite different orientations relative to the central ring. Analogously to the all-*cis* isomer **1**, the bonds in **2** linking the axial phenyl groups at the C1- and C3-positions on the central ring make angles of 115.1 and 114.6° with the plane defined by the cyclohexane ring carbon atoms C1, C3 and C5. However, overall, there appears to be less steric strain in **2** than that engendered in **1**, and the C−C−C angles within the cyclohexane ring of **2** are somewhat less perturbed (Table 1).

A search of the Cambridge Crystallographic Database revealed only three other hexasubstituted all-*cis* cyclohexanes: 1,2,3,4,5,6-hexamethylcyclohexane,[11] 1,2,3,4,5,6-hexa(methoxycarbonyl)cyclohexane, $C_6H_6(CO_2Me)_6$ and the corresponding hexacarboxylic acid $C_6H_6(CO_2H)_6$.[12] In each of these systems, the C−C−C angles within the cyclohexane ring are larger for the carbon atoms bearing the equatorial substituents. Another isomer of $C_6H_6(CO_2Me)_6$, in which only one of the ester substituents occupies an axial site, has also been structurally characterised; likewise, in 1-ethoxycarbonyl-2,3,4,5,6-penta(methoxycarbonyl)cyclohexane, only the ethyl ester is axial.[12] Interestingly, 1,2,3,4,5,6-hexa(isopropyl)cyclohexane has been crystallographically characterised as the all-*trans* isomer in which, perhaps surprisingly, all of the alkyl groups occupy axial sites, probably because of unacceptable torsional strain in the all-equatorial conformer.[13] However, in all-*trans*-1,2,3,4,5,6-hexaethylcyclohexane, the six alkyl groups occupy equatorial sites, which results in an essentially idealised chair structure with cyclohexane carbon–carbon distances of 1.552 Å and C−C−C angles of 108.4°.[14]

Table 1. Bond angles in all-*cis*-1,2,3,4,5,6-hexaphenylcyclohexane (**1**), 1,3-diaxial-2,4,5,6-tetraequatorial-hexaphenylcyclohexane (**2**) and 1,2,3,4,5,6-hexaethylcyclohexane (**7**).

Angle [°]	1	2	7
ring C-C-C (axial)	108.2, 107.3, 106.7	109.5, 107.6	–
ring C−C−C (equatorial)	117.9, 117.2, 117.1	117.1, 114.7, 114.7, 109.0	108.4

NMR spectroscopic data: The 600 MHz ^{1}H NMR spectrum of **2** in CD_2Cl_2 (Figure 4) confirms that the 1,3-diaxial-2,4,5,6-tetraequatorial conformation is retained in solution. The single axial proton at the C2-position exhibits a $J=6.0$ Hz triplet at $\delta=4.45$ ppm, thereby showing coupling to its two equatorial neighbours, whereas the single axial proton at the C5-position is a $J=12.0$ Hz triplet at $\delta=4.83$ ppm coupled to the two adjacent axial hydrogen atoms. The two equatorial protons H1 and H3 appear as a pseudo-triplet at $\delta=3.80$ ppm with $J=6.0$ Hz couplings to the axial hydrogen atoms at the C2/C6- and C2/C4-positions, respectively; finally, the axial protons at the C4- and C6-positions exhibit, at $\delta=4.13$ ppm, a doublet ($J=12.0$ Hz) of doublets ($J=6.0$ Hz) that is appropriate for interactions with one axial and one equatorial hydrogen atom. The ^{13}C NMR spectrum of **2** was readily assigned by standard ^{1}H–^{13}C 2D techniques.

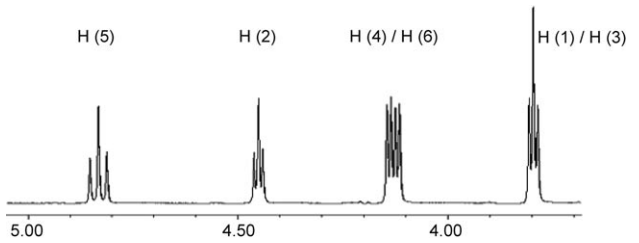


Figure 4. The cyclohexane region of the 600 MHz ^{1}H NMR spectrum of **2**.

The barrier for the chair-to-chair inversion in cyclohexane itself was evaluated as 10.8 kcal mol^{-1} in a now classic paper by Anet and Bourn in which coalescence of axial and equatorial proton sites in deuterium-decoupled [D_{11}]cyclohexane was monitored.[15] The corresponding value of 17.3 kcal mol^{-1} for the ring flip in all-*cis*-1,2,3,4,5,6-hexamethylcyclohexane was initially obtained from ^{1}H NMR peak coalescence of the axial methyl resonances, but no mention was

made of the cyclohexyl ring protons.[16] Subsequently, the magnitude of this barrier was confirmed by ^{13}C NMR spectroscopic data on both the methyl and ring carbon atoms,[17] and values calculated by using empirical force fields have also been reported.[18] The equilibrium ratios of eight geometric isomers of 1,2,3,4,5,6-$C_6H_6Me_6$ at 250 °C have been determined by gas chromatography.[19] The barrier for the corresponding chair-to-chair interconversion process in all-*cis*-1,2,3,4,5,6-hexa(methoxycarbonyl)cyclohexane was also found to be 17 kcal mol^{-1}.[20]

The ^1H NMR spectrum of all-*cis*-hexaphenylcyclohexane (**1**) was recorded in deuteriochloroform at 11.7 T (500 MHz) and exhibited a slightly broadened singlet in the aliphatic region at room temperature. However, upon cooling of the solution to −45 °C, the singlet gradually decoalescenced into two triplets at $\delta = 4.53$ and 4.58 ppm with $^3J_{HH} = 4.5$ Hz, a value in the normal range for axial–equatorial couplings. By contrast, the room-temperature ^{13}C NMR spectrum at 125 MHz revealed cyclohexane ring carbon peaks at $\delta = 57.3$ and 49.4 ppm, each of which broadened and disappeared into the baseline at 90 °C; simulation of the variable-temperature spectra yielded a cyclohexane ring inversion barrier of 19 ± 0.5 kcal mol^{-1}. The relatively small increase in the barrier for ring inversion in **1** over the previously reported value of ≈ 17 kcal mol^{-1} for both the hexamethyl and hexaester analogues described above is perhaps somewhat surprising considering the very severe steric crowding observed in **1**. However, even though the transition state for the chair-to-chair inversion of **1** will undoubtedly be extremely congested, we note that the ground-state energy must also be raised, and the barrier value derived by NMR methods is merely the difference between them.

Molecular modelling of 1,2,3,4,5,6-hexaphenylcyclohexane isomers: The structures, relative energies and interconversions of 1,2,3,4,5,6-cyclohexanes bearing six equivalent groups, $C_6H_6R_6$, have long fascinated the stereochemical community. Pioneering studies on the inositols, $C_6H_6(OH)_6$,[21] and on the isomers of hexachlorocyclohexane[22] are now classic. Subsequently, elegant work by Farina and co-workers elucidated the relative stabilities of the analogous hexaesters, $C_6H_6(CO_2Me)_6$, and revealed that the base-promoted epimerisation followed the sequence *cis*→*epi*→*muco*⇄*chiro*⇄*myo*⇄*scyllo*.[12c]

In an attempt to estimate the strain inherent in the *cis* and *epi* isomers of 1,2,3,4,5,6-hexaphenylcyclohexane (**1** and **2**, respectively), the heats of formation of the eight possible hexahydro derivatives of hexaphenylbenzene were evaluated.[23] Thus, there is one possible isomer of $C_6Ph_6H_6$ for addition of all six hydrogen atoms to the same face, and likewise for a 5:1 facial distribution; however, placement of only two or three hydrogen atoms on the same face gives rise to three isomers each, as illustrated in Figure 5, which also lists the appropriate nomenclature for such systems. Not surprisingly, the *scyllo* (all-equatorial) structure is the most favourable, as in $C_6H_6Et_6$,[14] and is taken as the zero to which all the others are compared. The *myo* isomer of

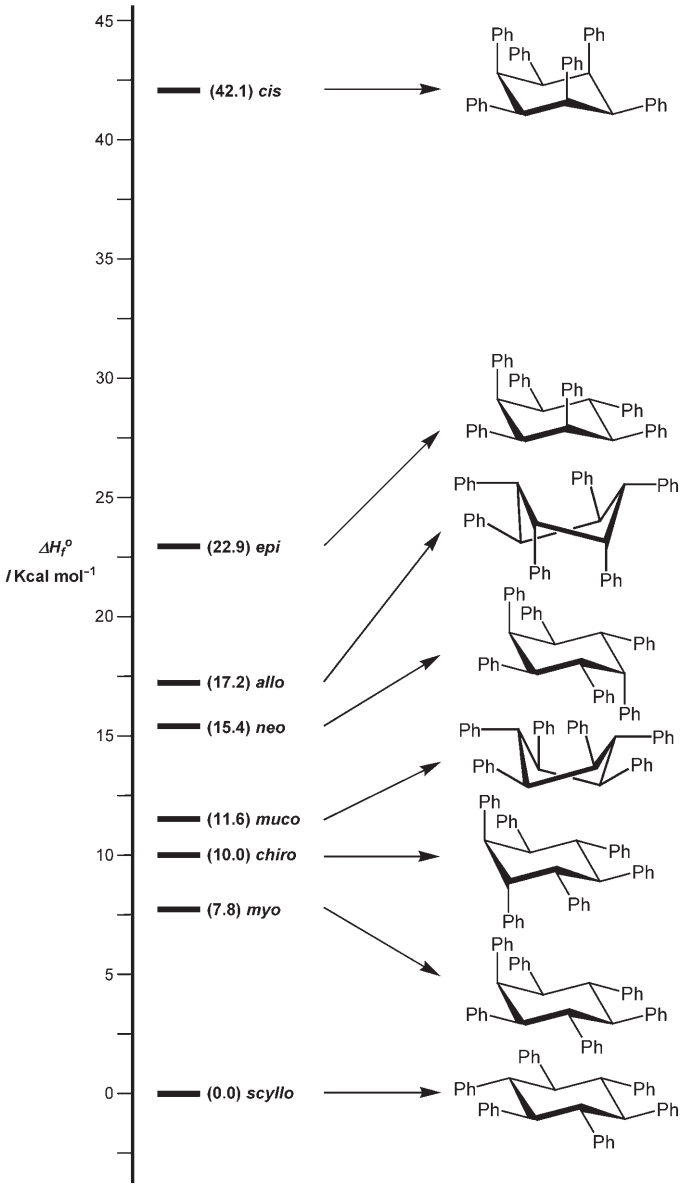


Figure 5. Calculated heats of formation (ΔH_f^0) of isomers of 1,2,3,4,5,6-hexaphenylcyclohexane.

$C_6H_6Ph_6$ (which possesses a single axial phenyl substituent) lies only 7.8 kcal mol^{-1} above the ground state, and this structure has been observed by X-ray crystallography in some $C_6H_6(CO_2R)_6$ cases.[12] Interestingly, in the $C_6H_6Ph_6$ system, it transpires that the *muco* and *allo* isomers prefer to adopt the twist-boat structure. Experimentally, however, the apparently extremely disfavoured *cis* structure, which lies more than 42 kcal mol^{-1} above the ground state, is the major product of the Birch reduction of hexaphenylbenzene, with the *epi* isomer at almost 23 kcal mol^{-1} above the ground state as the only other isolable product.

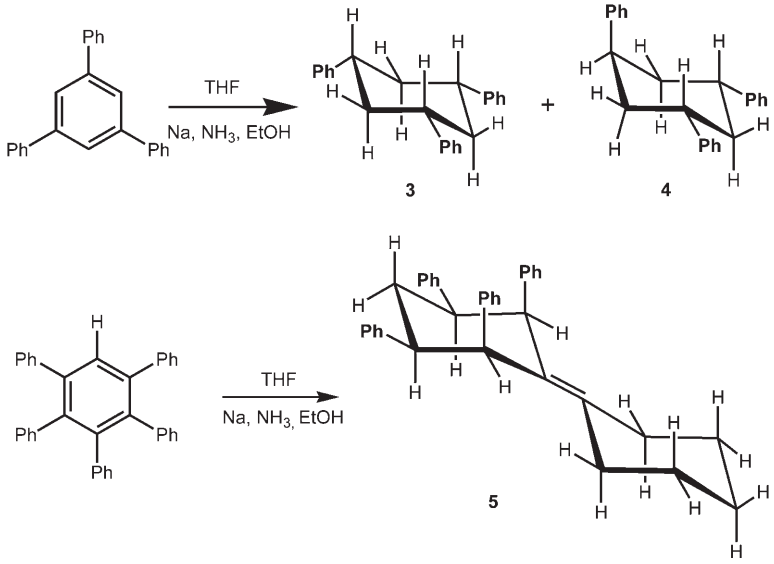
Other all-*cis* products, such as the 1,2,3,4,5,6-hexaester- and hexamethyl-cyclohexane derivatives mentioned previously, were prepared either from stereochemically rigid precursors or by catalytic hydrogenation on a metal surface,

whereby location of all six hydrogen atoms on the same face is readily explicable. At first sight, it is difficult to rationalise the formation of **1** and **2** from hexaphenylbenzene during the course of a Birch reduction, which presumably proceeds through successive additions of electrons and protons.[24] Assuming that the first stereodefining event is the second protonation reaction leading to either *cis*- or *trans*-hexaphenyl-1,4-dihydrobenzene, one might envisage that the precursor anion, being extensively delocalised, is a relatively flat species and that protonation *trans* to the phenyl substituent at the one tetrahedral centre is kinetically favoured because the phenyl group effectively shields one of the faces. While it has been reported that Birch reduction of 1,4-diphenylbenzene yields a substantial proportion of the *trans* isomer,[25] the presence of the four additional bulky phenyl substituents in the present substrate would presumably enhance the stereoselectivity for the *cis* product. Moreover, under these low-temperature conditions and in a strongly solvating medium, it is likely that protonation is irreversible, that is, that the reaction is under kinetic control. Once the first *cis* protonation has occurred, subsequent proton transfers would be even more likely 1) to be under kinetic control and 2) to occur selectively on the more exposed face, that is, *cis* to the already present hydrogen atoms.

An additional factor which may partly compensate for the increasing steric crowding that develops as the reaction proceeds is the potential for attractive edge-to-face aromatic interactions. As emphasised by Jennings et al.,[26] this phenomenon may play a greater role than is generally appreciated in such diverse areas as protein folding,[27] host–guest binding in supramolecular assemblies[28] and other molecular-recognition processes.[29] Experimental and theoretical estimates indicate that these interactions are energetically attractive by approximately 1.5–2.0 kcal mol^{-1}[26] and are more likely to be evident in solution at low temperatures or in the crystalline state, when conformational entropy effects are minimised. In support of such a hypothesis, we note that the space-filling view of **1** (Figure 1b) reveals that the three axial phenyl groups exhibit two edge-to-face orientations and one offset-parallel-stacking interaction.

Interestingly, the very recently reported structure of an approximately C_3-symmetric benzene trimer (as part of a supramolecular trimeric zinc–porphyrin complex) exhibits ring centroid separations of 5.04, 4.93 and 5.33 Å, with dihedral angles between the phenyl rings of 82.0, 75.3 and 55.8°.[30] These values compare favourably with the optimised C_{3h} geometry of the cyclic benzene trimer, which is calculated to have ring centroid separations of 4.8 Å.[31,32] Gratifyingly, the corresponding distances between the centroids of the three axial phenyl substituents in **1** are 4.89, 4.90 and 5.15 Å, with dihedral angles of 73.6, 77.4 and 27.4°, values that again suggest an attractive interaction between the aryl rings.

To probe the generality of this unexpected addition of six hydrogen atoms to a multiply substituted arene under Birch conditions, several other aromatic systems were investigated. Not unexpectedly, the electron-rich systems of 1,3,5-trimethoxybenzene and 1,3,5-triferrocenylbenzene[33] were unresponsive and were recovered unchanged. However, as shown in Scheme 2, Birch reduction of 1,3,5-triphenylbenzene yielded two known isomeric 1,3,5-triphenylcyclohexanes: 1,3,5-*e*,*e*,*e*-$C_6H_9Ph_3$ (**3**) was readily identified by the simplicity of its ^{1}H and ^{13}C NMR spectra, whereas the corresponding 1,3,5-*a*,*e*,*e* isomer **4** was characterised by X-ray crystallography, the results of which are depicted in Figure 6. The ^{1}H NMR spectrum of **4** at room temperature exhibited slightly broadened signals that did not decoalesce fully even at −80 °C, a result suggesting that chair-to-chair interconversion of the *e*,*e*,*a* and *a*,*a*,*e* isomers has a low barrier. This observation is consonant with a previous report on the NMR spectra of **3** and **4** derived from the electrochemical reduction of 1,3,5-triphenylbenzene.[34]



Scheme 2. Products of the Birch reductions of 1,3,5-triphenylbenzene and of pentaphenylbenzene.

The Birch reduction of pentaphenylbenzene required the presence of additional THF to help solubilise the arene. Although the reaction proceeded only to the extent of ≈5% conversion, the product, **5**, was obtained in ≈95% yield, based on C_6Ph_5H consumed. The unambiguous identification of **5** was secured by X-ray crystallography: **5** was revealed to be a 1,1′-bicyclohexylidene in which one of the cy-

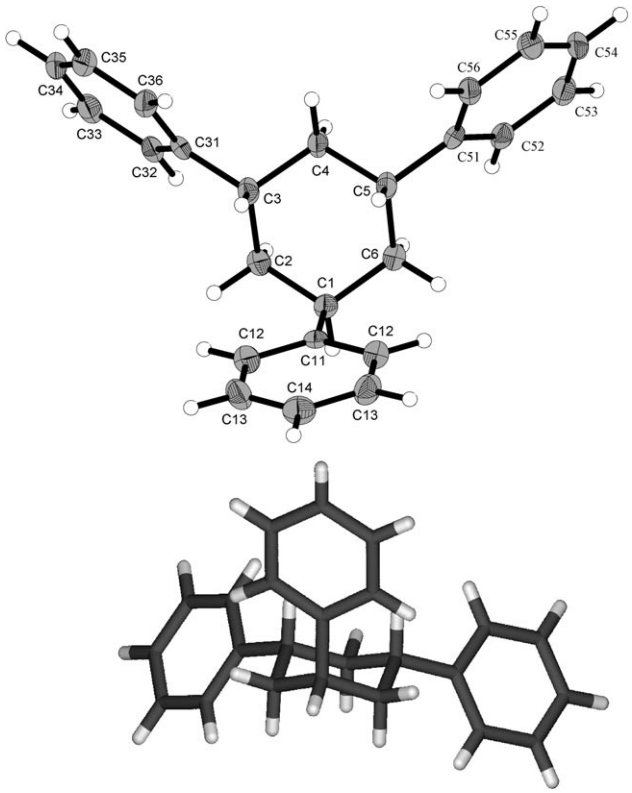


Figure 6. Top and side views of the structure of *a*,*e*,*e*-1,3,5-triphenylcyclohexane.

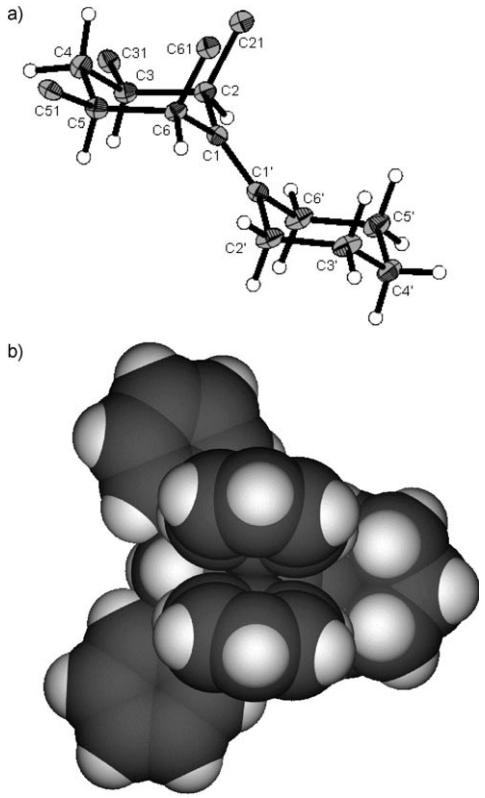


Figure 7. Side view of 2,3,5,6-tetraphenyl-1,1′-bicyclohexylidene (**5**), with only the *ipso*-carbon atoms of the phenyl rings shown, and a top view of the corresponding space-filling model.

clohexylidenes bears four phenyl groups, all on the same face of the ring (Figure 7). It is evident that the peripheral *ortho*- and *meta*-phenyl groups of the C_6Ph_5H precursor have not been reduced, whereas both the central ring and the *para*-phenyl substituent each now have five additional hydrogen atoms. As with *cis*-$C_6Ph_6H_6$, all of the additional hydrogen atoms are situated on the same face of the central ring. The ^1H and ^{13}C NMR spectra of **5** were readily assigned by conventional two-dimensional techniques.

It is instructive to compare the structure of **5** with that of the parent 1,1′-bicyclohexylidene, $H_{10}C_6{=}C_6H_{10}$ (**6**), which has approximate C_{2h} symmetry.[35] In the tetraphenylated cyclohexylidene ring of **5**, the C−C−C angles at carbon atoms C2 and C6, which bear axial phenyl groups, are 108.2 and 109.9°; the corresponding angles in **6** are 111.9 and 112.3°. Moreover, the C−C−C angles at carbon atoms C3 and C5, which bear equatorial phenyl groups, are 113.1 and 113.4°, somewhat larger than the corresponding angles (111.1 and 111.2°) found in 1,1′-bicyclohexylidene itself. As in the hexaphenylcyclohexanes **1** and **2**, the axial phenyl groups in **5** are splayed out and the angles made by the bonds linking them to the cyclohexylidene ring with the plane defined by the ring carbon atoms C2, C4 and C6 are 104.8 and 106.9°. In **6**, the corresponding angles for bonds linking hydrogen atoms to the cyclohexylidene ring are 90.3 and 92.0°, values very close to those expected for the perfect chair. The carbon–carbon bond lengths in the phenylated bicyclohexylidene ring in **5** (average 1.538 Å) are somewhat longer than those in **6** (average 1.521 Å). The double bond between the two cyclohexylidenes has lengthened from 1.339 Å in **6** to 1.346 Å in **5**, but the metric parameters of the hydrogenated cyclohexylidene ring in **5** show little deviation from those of the parent compound.

Conclusion

The Birch reaction of hexaphenylbenzene with sodium in liquid ammonia does not yield a 1,4-cyclohexadiene but rather reduces the central ring to yield primarily all-*cis*-1,2,3,4,5,6-hexaphenylcyclohexane (**1**), along with a lesser amount of the 1,3-diaxial-2,4,5,6-tetraequatorial isomer **2**. The formation of these sterically crowded *cis* and *epi* molecules, rather than the thermodynamically favoured all-equatorial (*scyllo*) isomer, raises interesting mechanistic problems. These products, quite apart from their intrinsic structural interest, are also noteworthy because they have been the source of some controversy for more than 150 years. While the identity of Cannizzaro's original product remains an enigma, if it were indeed one of the isomers of 1,2,3,4,5,6-hexaphenylcyclohexane, it may have been the energetically favoured all-equatorial structure, which apparently is not produced under the low-temperature Birch conditions, in which kinetic factors presumably dominate. In the total absence of any structural or spectroscopic data from

the earlier work, the only viable historical links are the melting points of the products. In all of the studies over the past 150 years, the only reported melting point (278–280 °C) is that of the crystalline product reported by Shriner and Berger;[2] clearly, this does not correlate with those found here (190–191 °C for *cis*-**1**, 216–217 °C for *epi*-**2**), thereby showing that these products are different from the material reported in 1941.

Extension of this reaction to 1,3,5-triphenylbenzene and pentaphenylbenzene reveals that, under these conditions, the expected 1,4-hexadienes are not the observed products. Current studies are focussed on Birch reductions of other hindered arenes to investigate the generality of these observations.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 400, 500 or 600 MHz spectrometers. NMR simulations were carried out by using the multisite EXCHANGE program generously provided by Professor R. D. McClung (University of Alberta). All reactions were carried out under an atmosphere of dry nitrogen. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

Birch reduction of hexaphenylbenzene: In a typical reaction, ammonia (15 mL) was condensed onto hexaphenylbenzene (HPB) (1600 mg, 2.99 mmol) in EtOH (3 mL) and dry THF (20 mL). When sodium (350 mg, 15.22 mmol) was added in small pieces over a period of 1 h, the solution became light purple; it was then maintained at reflux at −33 °C for 2 h before being allowed to warm to room temperature. Addition of water and filtration led to the formation of a white solid that was washed with Et_2O to yield unreacted HPB (870 mg, 1.63 mmol; 54 % recovery). The organic layer was washed with water and dried over $MgSO_4$ to yield a white solid (670 mg, 1.24 mmol; 91 % based on HPB consumed). Extensive chromatographic investigation revealed that optimal separation was achieved on a long, thin silica column by using exactly 7 % diethyl ether in pentane as the eluent. This procedure yielded two white crystalline products, **1** (308 mg, 0.57 mmol; 46 %) and **2** (214 mg, 0.40 mmol; 32 %), each suitable for an X-ray crystallography study.[36]

Data for 1: M.p. 190–191 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.14–7.07 (12 H, m; equatorial Ph *ortho*- and *meta*-H), 7.05–7.01 (3 H, m; axial Ph *para*-H), 6.94–6.88 (3 H, m; equatorial Ph *para*-H), 6.79 (6 H, t, J = 7.5 Hz; axial Ph *meta*-H), 6.73 (6 H, d, J = 7.5 Hz; axial Ph *meta*-H), 4.50 ppm (6 H, br s; H1–H6); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 143.0 (axial Ph *ipso*-C), 139.8 (equatorial Ph *ipso*-C), 133.3 (axial Ph *ortho*-C), 130.0 (equatorial Ph *ortho*-C), 127.9 (equatorial Ph *meta*-C), 127.7 (axial Ph *para*-C), 126.7 (axial Ph *meta*-C), 126.5 (equatorial Ph *para*-C), 57.3 (C1, C3, C5), 49.3 ppm (C2, C4, C6); elemental analysis: calcd for $C_{42}H_{36}\cdot(Et_2O)_{1.2}$: C 89.27, H 7.68; found: C 89.16, H 7.59.

Data for 2: M.p. 216–217 °C; ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 7.38 (2 H, d, J = 7.5 Hz; H52, H56), 7.15 (4 H, d, J = 7.5 Hz; H42, H46, H62, H66), 7.06 (4 H, d, J = 7.0 Hz; H12, H16, H32, H36), 7.08–7.05 (1 H, m; H24), 7.03 (2 H, t, J = 7.5 Hz; H53, H55), 6.98 (2 H, t, J = 7.0 Hz; H14, H34), 6.93 (4 H, t, J = 7.0 Hz; H13, H15, H33, H35), 6.94–6.91 (2 H, m; H23, H25), 6.91 (4 H, t, J = 7.5 Hz; H43, H45, H63, H65), 6.87 (1 H, t, J = 7.5 Hz; H54), 6.81 (2 H, t, J = 7.5 Hz; H44, H64), 6.41 (2 H, d, J = 7.5 Hz; H22, H26), 4.83 (1 H, t, J = 12 Hz; H5), 4.45 (1 H, t, J = 6 Hz; H2), 4.13 (2 H, dd, J = 6, 12 Hz; H4, H6), 3.80 ppm (2 H, t, J = 6 Hz; H1, H3); ^{13}C NMR (CD_2Cl_2, 150 MHz): δ = 144.0 (C51), 142.1 (C41, C61), 142.0 (C21), 139.1 (C11, C31), 133.3 (C12, C16, C32, C36), 131.9 (C22, C26), 130.4 (C42, C46, C52, C56, C62, C66), 127.4 (C43, C45, C63, C65), 127.3 (C23, C25), 126.8 (C13, C15, C33, C35, C53, C55), 126.7 (C24), 126.3 (C14, C34), 126.0 (C54), 125.5 (C44, C64), 57.0 (C4, C6), 56.7 (C2), 54.7 (C1, C3), 43.7 ppm (C5); elemental analysis: calcd for $C_{42}H_{36}\cdot(Et_2O)_{0.33}$: C 92.04, H 7.02; found: C 91.92, H 7.29; IR (KBr): $\tilde{\nu}$ = 3056, 3023, 2923, 2850, 1598, 1492, 1448 cm^{-1}.

Birch reduction of 1,3,5-triphenylbenzene: In similar fashion to the method described above, ammonia (100 mL) was condensed onto 1,3,5-triphenylbenzene (5 g, 16.3 mmol) in EtOH (25 mL) and THF (30 mL). Sodium (5.25 g, 228.3 mmol) was added over a period of 30 min. The reaction mixture was allowed to reflux at −33 °C for 1 h, warmed to room temperature, hydrolysed with water and extracted with CH_2Cl_2. The solvent was then removed, and the residue was recrystallised from hexane/CH_2Cl_2 (50:50) to yield a yellow crystalline product (0.83 g, 2.65 mmol; 16.3 %). Further recrystallisations yielded the known compounds 1,3,5-*e*,*e*,*e*-triphenylcyclohexane (**3**) and 1,3,5-*a*,*e*,*e*-triphenylcyclohexane (**4**), the latter as X-ray quality crystals.

Data for 3: M.p. 74–77 °C (literature value:[34] 75–77 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78–7.18 (15 H, m; Ph H) 2.97 (3 H, t, J = 12 Hz; H1a, H3a, H5a), 2.22 (3 H, br d, J = 12 Hz; H2e, H4e, H6e), 1.76 ppm (3 H, q, J = 12 Hz; H2a, H4a, H6a).

Data for 4: M.p. 45–46 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.49 (2 H, d, J = 7.5 Hz; H12, H16), 7.38 (2 H, t, J = 7.5 Hz; H13, H15), 7.29 (4 H, t, J = 7.5 Hz; H33, H35, H53, H55), 7.24 (4 H, d, J = 7.5 Hz; H32, H36, H52, H56), 7.23 (1 H, m; H14), 7.18 (2 H, t, J = 7.5 Hz; H34, H54), 3.46 (1 H, br s; H1e), 2.94 (2 H, t, J = 12.4 Hz; H3a, H5a), 2.56 (2 H, d, J = 13.5 Hz;

Table 2. Crystallographic data for **1**, **2**, **4** and **5**.

	1	**2**	**4**	**5**
empirical formula	$C_{42}H_{36}$	$(C_{42}H_{36})_2\cdot C_4H_{10}O$	$C_{24}H_{24}$	$C_{36}H_{36}$
M	540.71	1155.54	312.43	468.65
crystal system	triclinic	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$Cmc2_1$ (no. 36)	$P\bar{1}$ (no. 2)
a [Å]	10.4765(13)	11.4883(14)	18.529(6)	8.6361(13)
b [Å]	11.9433(15)	12.1143(15)	12.284(4)	8.7002(13)
c [Å]	13.6128(17)	12.4502(16)	7.531(2)	18.212(3)
α [°]	99.031(2)	91.267(2)	90	102.079(3)
β [°]	109.107(2)	92.944(2)	90	91.945(3)
γ [°]	105.647(2)	113.853(2)	90	108.257(3)
V [Å^3]	1492.4(3)	1580.9(3)	1714.1(9)	1263.4(3)
Z	2	1	4	2
ρ_{calcd} [g cm^{-3}]	1.203	1.214	1.211	1.232
T [K]	100(2)	100(2)	100(2)	100(2)
μ [mm^{-1}]	0.068	0.069	0.068	0.069
$2\theta_{max}$ [°]	44.00	52	50	52
reflections measured	8502	12808	3708	10578
reflections used (R_{int})	3638 (0.0298)	6113 (0.0216)	841 (0.0502)	4927 (0.0278)
parameters	379	570	115	469
final R values ($I > 2\sigma(I)$):				
R_1	0.0543	0.0454	0.0401	0.0624
wR_2	0.1278	0.1199	0.0920	0.1467
R values (all data):				
R_1	0.0703	0.0568	0.0460	0.0763
wR_2	0.1376	0.1359	0.0950	0.1537
GoF on F^2	1.081	1.063	1.078	1.079

H2e, H6e), 2.07 (1H, m, $J=12.4$ Hz; H4e), 2.03 (2H, td, $J=13.5$, 5 Hz; H2a, H6a), 1.73 ppm (1H, q, $J=12.4$ Hz; H4a); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=146.0$ (C31, C51), 142.8 (C11), 127.6 (C13, C15), 127.5 (C33, C35, C53, C55), 126.6 (C12, C16), 125.4 (C32, C36, C52, C56), 125.2 (C34, C54), 124.7 (C14), 41.32 (C4), 38.23 (C3, C5), 36.44 (C1), 36.17 ppm (C2,C6); IR (CH_2Cl_2): $\tilde{\nu}=3064$, 3029, 1600, 1494, 1452 cm^{-1}.

Birch reduction of pentaphenylbenzene: In similar fashion to the method described above, ammonia (18 mL) was condensed onto pentaphenylbenzene (4 g, 8.73 mmol) in EtOH (4 mL) and THF (100 mL). The reaction mixture was then treated with sodium (0.95 g, 41.32 mmol). Hydrolysis and extraction with CH_2Cl_2 yielded a yellow solid (3.59 g). Recrystallisation of the crude product from Et_2O furnished white crystals of 2,3,5,6-tetraphenyl-1,1′-bicyclohexylidene (**5**; 0.21 g, 0.44 mmol; 5.1%).

Data for 5: M.p. 236–237 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta=7.45$ (4H, d, $J=7.5$ Hz; H32, H36, H52, H56), 7.27 (4H, t, $J=7.5$ Hz; H33, H35, H53, H55), 7.14 (2H, t, $J=7.5$ Hz; H34, H54), 6.76 (4H, d, $J=6.5$ Hz; H22, H26, H62, H66), 6.68 (2H, t, $J=6.5$ Hz; H24, H64), 6.63 (4H, t, $J=6.5$ Hz; H23, H25, H63, H65), 5.01 (2H, d, $J=5.0$ Hz; H2e, H6e), 3.49 (2H, td, $J=12.0$, 4.0 Hz; H3a, H5a), 3.26 (1H, q, $J=12.8$ Hz; H4a), 2.79 (1H, dt, $J=12.7$, 3.3 Hz; H4e), 2.66–2.74 (4H, m; H2′a, H2′e, H6′a, H6′e), 1.78–1.82 ppm (6H, m; H3′a, H3′e, H4′a, H4′e, H5′a, H5′e); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=144.2$ (C31, C51), 141.2 (C21, C61), 135.5 (C1′), 134.8 (C1), 129.6 (C22, C26, C62, C66), 128.3 (C33, C35, C53, C55), 127.3 (C23, C25, C63, C65), 126.9 (C32, C36, C52, C56), 125.8 (C34, C54), 124.5 (C24, C64), 46.7 (C3, C5), 44.6 (C2, C6), 32.0 (C2′, C6′), 28.9 (C3′,C5′), 27.4 (C4′), 26.9 ppm (C4); IR (CH_2Cl_2): $\tilde{\nu}=3079$, 3056, 2983, 1602, 1496 cm^{-1}; elemental analysis: calcd for $C_{36}H_{36}$: C 92.26, H 7.74; found: C 92.24, H 7.82.

X-ray crystallography measurements for 1, 2, 4 and 5: Crystal data (Table 2) were collected by using a Bruker SMART APEX CCD area detector diffractometer, and absorption corrections were performed by using the program SADABS.[37] The structures were solved by direct methods with the SHELXS-97[38] software and refined by full-matrix least-square calculations on F^2 for all data with the SHELXL-97 software.[39] CCDC 631099 (**1**), CCDC 631100 (**2**), CCDC 647380 (**4**) and CCDC 647381 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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