Inorganica Chimica Acta, 211 (1993) 17–21

A new mechanism for the rearrangement of the icosahedral carboranes

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(Received December 14, 1992; revised March 23, 1993)

Abstract

A new mechanism which involves the anticubeoctahedron as the complementary geometry is postulated to rationalise previously reported data on the rearrangement of various icosahedral carboranes.

In a series of papers [1, 2] attempts to provide a general mechanism for the thermal rearrangements of the icosahedral carboranes have been reported. Wu and Jones [1a] suggested an extended triangle rotation (ETR) mechanism to rationalise their pyrolysis data on a bridged 1,2-carborane system and much of the previously reported data. Later, Edvenson and Gaines [2] reported elegant studies of the thermal isomerisation of regiospecifically labelled ^{10}B icosahedral carboranes. These workers presented evidence to suggest that the mechanism in closest agreement with the experimental data appears to involve a 12-vertex *nido*-intermediate. They also considered that a number of previously postulated mechanisms, including simple exchange between two boron sites, triangular face rotation in an icosahedron, diamond–square–diamond twist and rotation of pentagonal pyramids, may be facets of the *nido*-intermediate mechanism. In these papers, comprehensive reassessments of the previously reported mechanisms were made. Here, we wish to suggest a mechanism which we believe supercedes all others and provides a simple solution to a long standing problem.

Lipscomb and co-workers [3] were the first to propose a mechanism for the isomerisation of 1,2- to 1,7-carborane. Their mechanism (Scheme 1(a)), which involves a cubeoctahedral complementary geometry and a diamond–square–diamond rearrangement, could not, however, explain the further isomerisation of the 1,7- to the 1,12-form. Simply, the cubeoctahedral mechanism maintains the antipodal relationship of vertices, thereby providing an insurmountable obstacle to this final conversion. Consequently, a modified proposal was offered [4]. This considered that the triangular faces in the cubeoctahedral complementary geometry could rotate, thereby removing the restrictive antipodal relationship.

Related to this, Wu and Jones considered that rotation of a triangular face of the parent icosahedron to a form of icosahedron with D_{3h} symmetry would also produce a viable pathway. We tend to disagree; the true complementary geometry in this process is one which possesses three pentagonal faces or deviates markedly from spherical symmetry. This will be described more fully later.

Several years ago [5], we suggested that the anticubeoctahedron, which is closely related to the cubeoctahedron, would provide a highly satisfactory complementary geometry for the fluxional behaviour exhibited by the icosahedral $Fe_3(CO)_{12}$ and many of its derivatives. Like the cubeoctahedron, this polyhedron may also be derived from the icosahedron; the only difference being in the nature of the six polyhedral edges which are broken. We now wish to propose that the same polyhedron provides an entirely satisfactory complementary geometry in both the conversion of 1,2-carborane to 1,7-carborane and, more significantly, 1,7-carborane to the 1,12-form. The possibility that the anticubeoctahedron could serve as the complementary geometry in any rearrangement process has been discussed briefly on previous occasions [1]. However, as far as we are aware, no attempt has been made to employ this complementary geometry to explain the currently available data. Certainly, as late as 1990, Gaines and Edvenson [2] utilised a mechanistic pathway which does not employ any easily recognisable polyhedral intermediate and it is largely in response to that work that we make this report. Our proposed mechanism is shown in Scheme 1(b).

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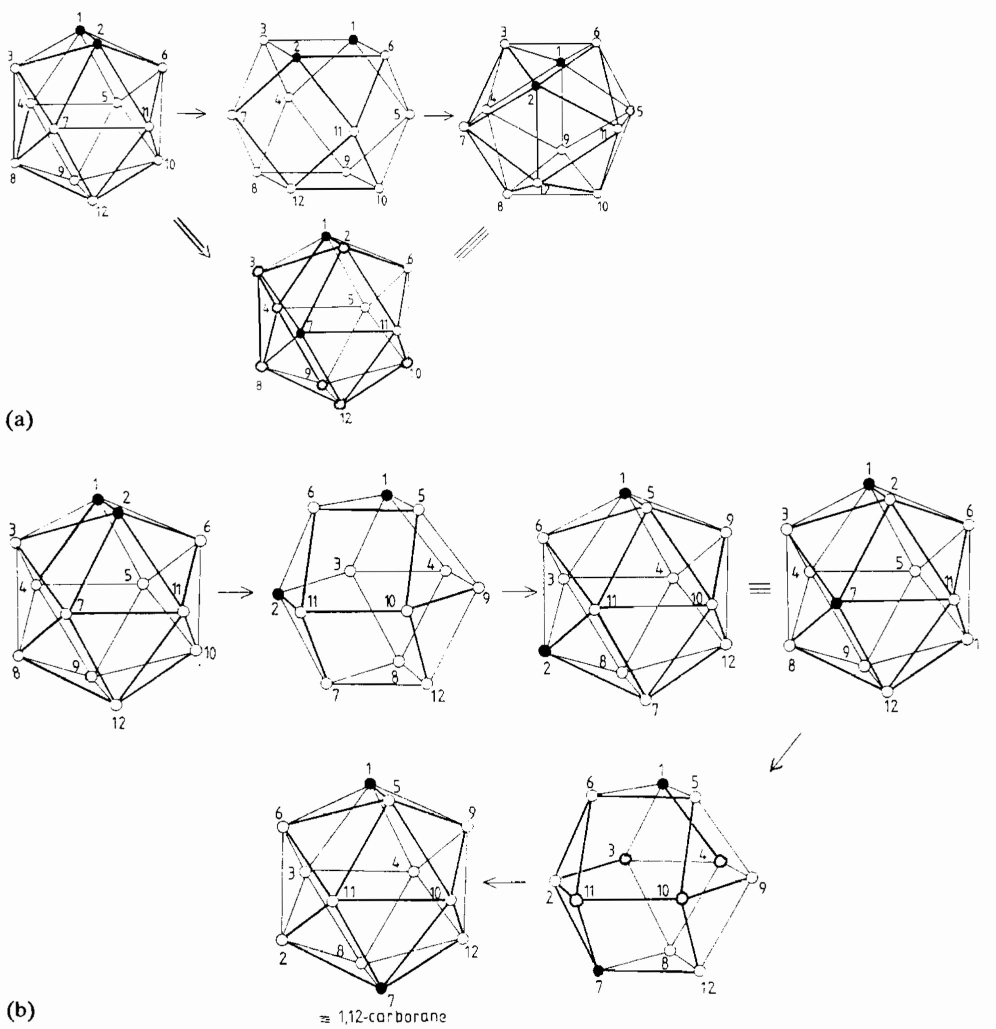


Scheme 1. (a) The interconversion of 1,2- and 1,7-carborane through a cubeoctahedral complementary geometry. (b) The interconversion of 1,2-, 1,7- and 1,12-carborane through an anticubeoctahedral complementary geometry.

The relationship between the two polyhedra (cubeoctahedron and anticubeoctahedron) is clear to see. The cubeoctahedron has a 3:6:3′ arrangement of vertices (related to ccp) and the latter a 3:6:3 relationship (related to hcp). However, there is a highly significant difference between the two mechanistic pathways; for in the case of the anticubeoctahedral mechanism the antipodal relationship of all vertices is not preserved. Consequently, this same process (Scheme 1(b)) not only rationalises the isomerisation of the 1,2- to the 1,7-form, but also the final conversion to 1,12-decacarborane (see Scheme 1(b)). The mechanism offers clear advantages over all the others offered, for the following reasons:

(1) the intermediate of complementary geometry is a simple, well-defined polyhedron;

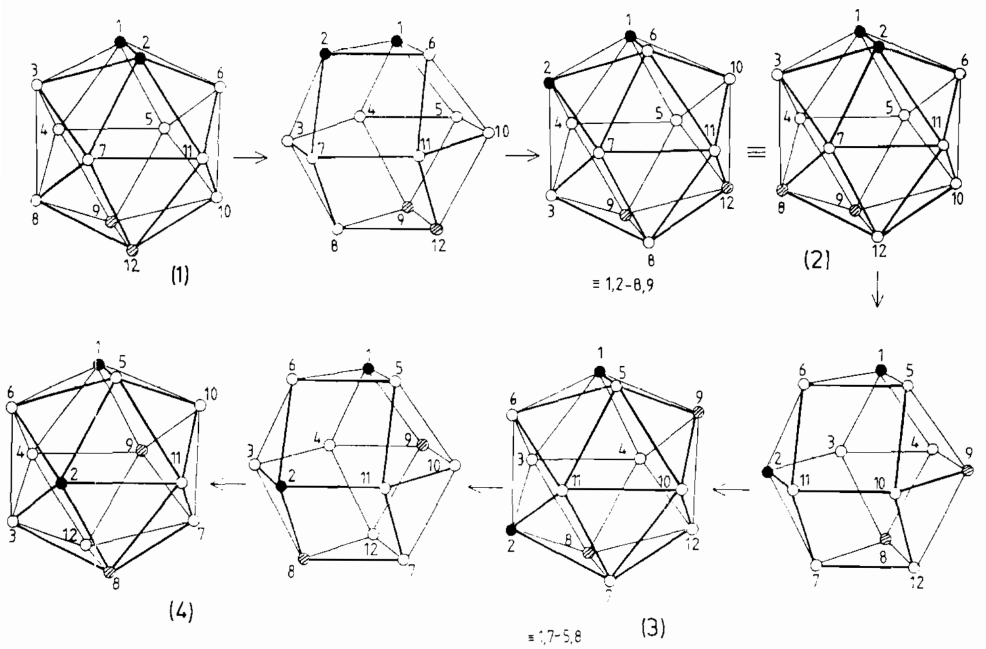
(2) the vertices of this polyhedron lie on the surface of a sphere;

(3) the rearrangement process also involves the familiar diamond–square–diamond process;

(4) most, if not all, of the available experimental data is readily explained;

(5) most importantly, the same soft mode, or method of interconversion, is employed in both the first conversion from 1,2- to 1,7- and the second from 1,7- to 1,12-. This is of the utmost importance. If a species has a low-frequency vibrational mode (i.e. one with a large amplitude), it is likely that the structure will vary most along the pathway followed by that vibration. It is unlikely that the same fundamental geometric species will change this mode from one step to another. Thus, the model presented had the clear advantage that the process of conversion from 1,2- through 1,7- to 1,12- is continuous; this is not meant to imply that the energies will be the same for each independent step. We are currently exploring the crystal structures of a range of carborane derivatives with a view to establishing any mode of distortion which these compounds exhibit.

In the conversion of the icosahedron to an anticubeoctahedron there are ten different sets of edges which



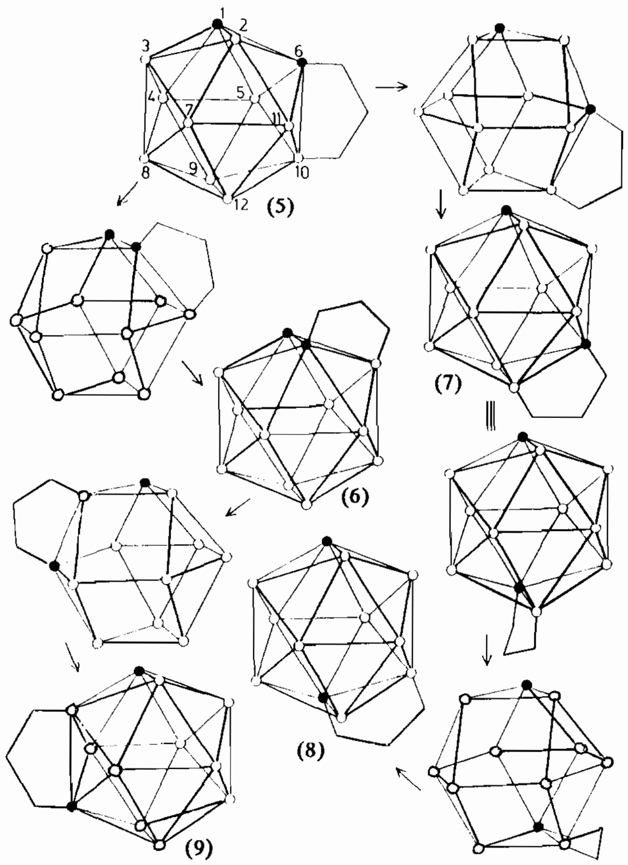
Scheme 2. The thermal rearrangement of 1,2-dimethyl-9,12-dichloro-1,2-carborane.

can be broken, although pairs of these sets are related by mirror symmetry. For an isolated icosahedron, these ten sets are degenerate. However, if vertices undergo substitution, e.g. B by C, then this degeneracy is removed. Thus, in 1,2-$C_2B_{10}H_{12}$ three modes are expected and hence, three different pathways to interconversion exist. All involve an anticubeoctahedral complementary geometry, but require different energies. So a clear relationship emerges between the molecular symmetry and the possible reaction pathways. This point we shall develop in detail in a full report of this work.

In this communication we shall simply *apply* our suggested new approach to those cases which have previously provided problems and a more detailed examination will be given in a forthcoming paper.

1. The thermal rearrangement of 1,2-dimethyl-9,12-dichloro-1,2-carborane

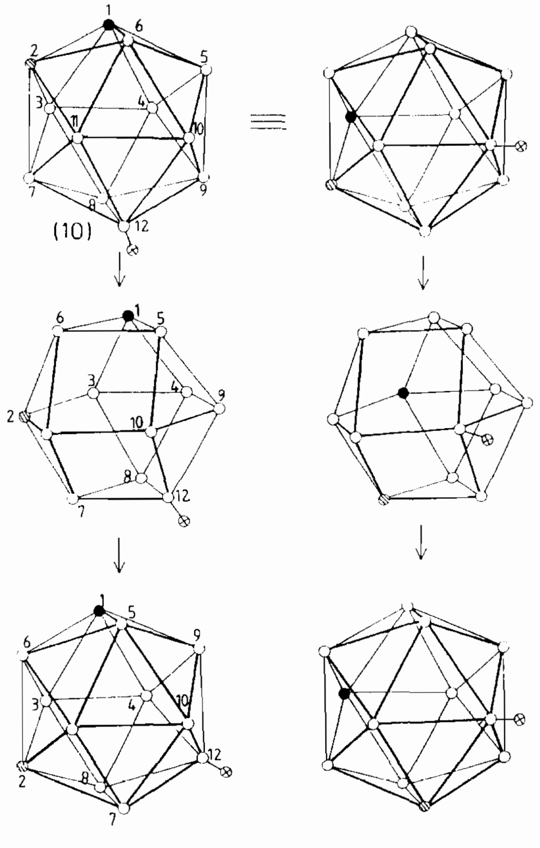
Hart and Lipscomb [6] examined the thermal arrangement of the dilabelled molecule, 1,2-dimethyl-9,12-dichloro-1,2-carborane (**1**) and found that the principal compound formed was 1,7-dimethyl-5,12-dichloro-1,7-carborane (**4**). One of the initial products was, however, 1,2-dimethyl-8,9-dichloro-1,2-carborane (**2**). These observations are totally in accord with our proposed mechanism given in Scheme 2. Interestingly, according to our method, the compound 1,7-dimethyl-5,8-dichloro-1,7-carborane (**3**) is expected as a second intermediate in the rearrangement sequence from **1**→**2**→**3**→**4**.



Scheme 3. The thermal rearrangement of the bridged 1,2-carborane **5**.

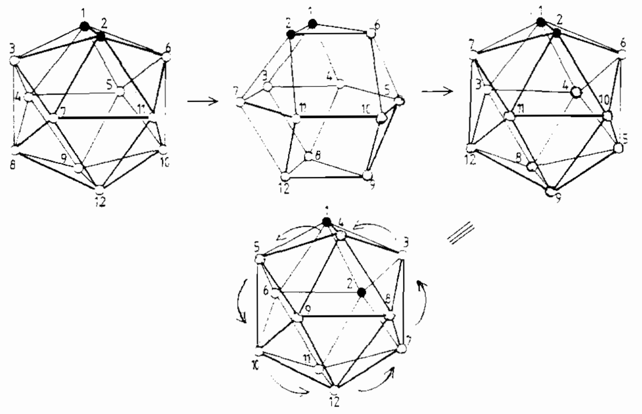
2. *The thermal rearrangement of the bridged 1,2-carborane (5)*

In an elegant sequence of experiments Wu and Jones [1] examined the products of the thermal rearrangement of the bridged 1,2-carborane **5** and found the four possible isomer products **6**, **7**, **8** and **9**. Again, the formation of these products is in line with our predictions according to Scheme 3. The sequence of pathways to isomerisation also takes account of the product distribution observed.



(11) (12)

Scheme 4. The thermal rearrangement of 12-Cl-1,2-CHPB$_{10}$H$_9$ to form 9-Cl-1,7-CHPB$_{10}$H$_9$.



Scheme 5. The thermal isomerisation of regiospecifically ^{10}B-labelled icosahedral carborane.

3. *The thermal rearrangement of 12-Cl-1,2-CHPB$_{10}$H$_9$ to form 9-Cl-1,7-CHPB$_{10}$H$_9$ and 12-Cl-1,7-CHPB$_{10}$H$_9$*

The thermal rearrangement of 12-Cl-1,2-CHPB$_{10}$H$_9$ (**10**) to 9-Cl-1,7-CHPB$_{10}$H$_9$ (**11**) and 12-Cl-1,7-CHPB$_{10}$H$_9$ (**12**), which has apparently raised severe mechanistic problems in the past [7], would appear to follow two rearrangement processes as outlined in Scheme 4.

4. *The thermal isomerisation of regiospecifically ^{10}B-labelled icosahedral carborane*

The recently reported [2] movement of ^{10}B at 350 °C in 1,2-C$_2$B$_{10}$H$_{10}$ is entirely consistent with the mechanistic approach reported here. According to Scheme 5, preferential enrichment at sites, 3, 6, 4, 5, 7 and 11 will occur, followed by further occupancy of sites 8,10 and 9,12. Rearrangement of the 1,2-isomer to the 1,7-isomer may occur by a process similar to those outlined above and the expected substitution pattern generated as a consequence of the rearrangement is exactly as observed.

Conclusions

The new scheme appears to offer a surprisingly simple solution to a long-standing problem. Certainly, it easily explains the conversion 1,2-, 1,7- and 1,12-carborane and some other related rearrangements. We are currently exploring the full potential of this mechanism and the means by which it may be justified experimentally. We also consider that a number of the other mechanisms which have been proposed are inappropriate for reasons we shall discuss in full in a comprehensive report of this work. In making these proposals we recognise that the conversion 1,2- to 1,7- and 1,7- to 1,12- need not necessarily follow the same mechanistic pathway.

Acknowledgements

We thank the SERC, NATO and The University of Edinburgh for financial support.

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