[6] C. T. Foxon, M. R. Boudry, B. A. Joyce, *Surf. Sci. 44* (1974) 69.
[7] C. T. Foxon, B. A. Joyce, *Surf. Sci. 50* (1975) 434.
[8] C. T. Foxon, B. A. Joyce, *Surf. Sci. 64* (1977) 293.
[9] J. Y. Tsao, T. M. Brennan, B. E. Hammons, *Appl. Phys. Lett. 53*, (1988) 288.
[10] B. A. Joyce, J. H. Neave, P. J. Dobson, P. K. Larsen, *Phys. Rev. B 29* (1984) 814.
[11] J. H. Neave, B. A. Joyce, P. J. Dobson, N. Norton, *Appl. Phys. A 31* (1983) 1.
[12] B. A. Joyce, J. H. Neave, J. Zhang, P. J. Dobson, in P. K. Larsen, P. J. Dobson (Eds.): *Reflection High-Energy Electron Diffraction and Reflection Electron Imaging of Surfaces*, Plenum Press, p. 397.
[13] J. H. Neave, P. J. Dobson, B. A. Joyce, J. Zhang, *Appl. Phys. Lett. 47* (1985) 100.
[14] M. J. Kelly, R. J. Nicholas, *Rep. Prog. Phys. 48* (1985) 1699.
[15] M. Tanaka, K. Sakaki, *Jpn. J. Appl. Phys. 27* (1988) L2025.
[16] M. Tsuchiya, J. M. Gaines, R. H. Yan, R. J. Simes, P. O. Holtz, L. A. Coldren, P. M. Petroff, *Phys. Rev. Lett. 62* (1989) 466.
[17] H. Sakaki, M. Tanaka, J. Yoshimo, *Jpn. J. Appl. Phys. 24* (1985) L417.
[18] F. Briones, L. Gongalez, M. Recio, M. Vaquez, *Jpn. J. Appl. Phys. 26* (1987) L1125.
[19] Y. Horikoshi, M. Kawashima, H. Yamaguchi, *Jpn. J. Appl. Phys. 27* (1988) 169.

Structure-Directed Synthesis of New Organic Materials[**]

By Franz H. Kohnke, John P. Mathias, and J. Fraser Stoddart[*]

Unnatural Products
Molecular LEGO
Solvent Sensors
Zeolitic Macropolycycles
Diels-Alder Reactions

1. Preamble

The time has now been reached when the chemist can make almost anything the living world has produced. Natural product synthesis has dominated the conceptual advances in synthetic organic chemistry for more than a century now. Yet, although the deep significance and fundamental importance of natural products and the life processes that sustain and characterize them are clear, they are arguably only an infinitesimally small part of the chemical scene. Compounds which are wholly unnatural comprise an infinite variety of structures which can only be conceived and constructed thanks to the knowledge, imagination, and expertise of the chemist. The reasons for making unnatural products come from many quarters – they include evaluating chemical theories, both old and new, synthesizing exotic compounds, which, more often than not have symmetry appeal, and preparing materials with some particular structural form that might perform some highly desirable physical, chemical, or biological function.

The manufacture and manipulation of structures at a molecular level raises[1] "the possibility of maneuvering things atom by atom." The prospect is one of performing physical feats on a truly microscopic scale. The question is how to construct advanced materials that express their properties at a molecular level and then to gain access to these properties, i.e. how do we make molecules and speak to them?

Recently, rigid molecular lines or strips, with nanometer scale dimensions and composed of polyacenequinone units, have been prepared[2] by repetitive Diels-Alder reactions. Their synthesis is attractive because they could provide a range of new materials capable of forming organized monolayers and molecular electronic devices of different sorts. Artificial cell bilayer membranes, and molecular barriers and sensors all rely[3] upon the formation of surface structures with the appropriate electronic characteristics. The prospect[4] that the parent polyacenes and their cyclic analogs – the cyclacenes – constitute materials with "the possibility of possessing interesting condensed phases including high temperature superconductivity and ferromagnetism" is particularly tantalizing.

Although synthetic strategies based on a repetitive Diels-Alder methodology, involving bisdienes and bisdienophiles,[5] have much to commend themselves in the synthesis of ladder polymers, there is a need to avoid ill-defined mixtures of compounds containing molecules of differing molecular weights and different stereochemistries that are not particularly amenable to purification by chromatography or by any other means.

---

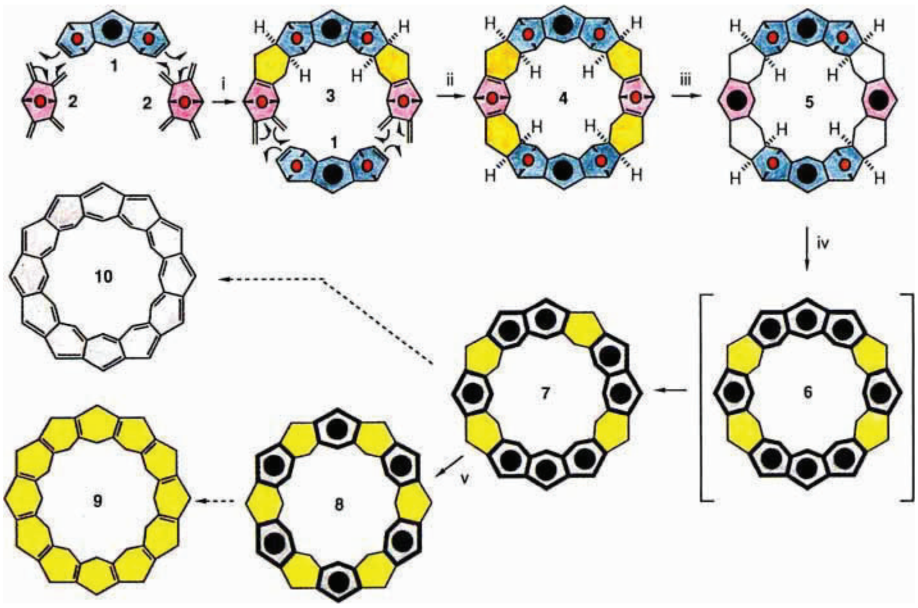
[*] Dr. J. F. Stoddart, Mr. J. P. Mathias
Department of Chemistry, The University
Sheffield S3 7HF (UK)
Dr. F. H. Kohnke
Dipartimento di Chimica Organica e Biologica
dell' Università di Messina
Salita Sperone, I-98166 Messina (Italy)

[**] We are most grateful to Dr. *N. S. Isaacs* (University of Reading) for performing all the high pressure reactions, Dr. *J. D. R. Thomas* (University of Wales College of Cardiff) for conducting the chemical sensing experiments, Mr. *P. R. Ashton* and Dr. *N. Spencer* (University of Sheffield) for recording FABMS and NMR spectra, respectively, and to Dr. *D. J. Williams* and Miss *A. M. Z. Slawin* (Imperial College London) for carrying out the X-ray crystal structure determinations. The research was supported by the University of Sheffield, the Science and Engineering Research Council, and the Ministry of Defence in the UK, and by the University of Messina in Italy. One of us (*J. F. S.*) acknowledges the award of a Research Fellowship from the Leverhulme Trust and thanks Dr. *Peter Mitchell* and Prof. *Jean-Marie Lehn* for useful discussions.

Recently, we have shown[6] that certain bisdienes and bisdienophiles, containing bicyclic ring systems, will undergo repetitive Diels-Alder reactions at their diastereotopic π-faces in a highly controllable manner,[7] not only with complete diastereoselectivity being expressed with respect to each component, but also with very high mutual diastereoselection occurring between the components, i.e. their relative reaction orientations are pre-determined. The implications of this discovery is that there are inherently simple ways of making apparently complex unnatural products from appropriate substrates. Since the pure compounds can be obtained without the need to use reagents or catalysts and result from information pre-programmed into the substrates and carried over into the products, we have referred[8, 9] to this as a form of *structure-directed synthesis*, i.e. the outcome of the reactions is dictated either by the structures of the substrates (i.e. the control is kinetic) or by the structures of the products (i.e. the control is thermodynamic). In this review, we shall outline how the principle of structure-directed synthesis can be applied to the precise and stepwise construction of new organic materials.

2. Molecular Belts

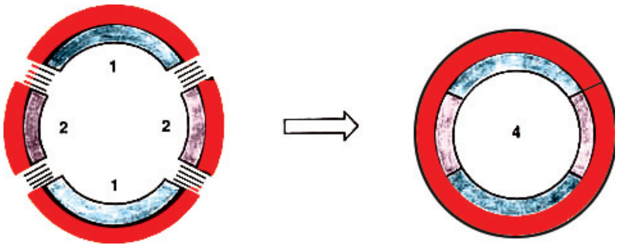
The synthesis (Scheme 1) of the macropolycycle dubbed[6] kohnkene **4** from "intelligent" substrates[10] – the bisdienophile **1** and the bisdiene **2** – is now well documented.[6, 7] The power of the synthetic approach is a double-barrelled one: a) It can be executed in discrete steps since one bisdienophile **1** will undergo cycloadditions with two bisdienes **2** under relatively mild conditions to give (78%) a discrete 2:1 adduct **3**, which can be characterized and then coaxed, under much more forcing conditions, to react remarkably efficiently (36%) in a belt-forming manner with a second bisdienophile **1**. b) Treble diastereoselectivity is expressed every time a Diels-Alder reaction occurs, such that only one product is formed after each cycloaddition step, e.g. none of the other nine configurational diastereoisomers of the 2:1 adduct **3** have been observed. It would appear that the stereoelectronic information pre-programmed into the bisdienophile **1** and the bisdiene **2** is transmitted in a domino-like fashion through all the intermediate Diels-Alder adducts to the final macropolycycle **4**. Although it has been strongly implied in the literature (see reference[7] for a discussion) that this kind of molecular recognition between bicyclic diastereofacial dienes and dienophiles is a transition state phenomenon (i.e. kinetic control is operative), the proposal remains to be vindicated or otherwise in the context of the synthesis of kohnkene **4**. Be this as it may, the practical outcome is clear: the synthetic chemist can create[7] molecular materials that are rigid, ordered, and large without having to resort to complicated multistep syntheses using expensive reagents or exotic catalysts. In this respect, unnatural product synthesis is reminiscent of prebiotic chemistry where – it has been argued[12] – certain key, relatively simple, chemical compounds served



Scheme 1. The construction of kohnkene **4** from the bisdienophile **1** (blue) and the bisdiene **2** (pink) via the 2:1 adduct **3** by a stereoelectronically-programmed set of Diels-Alder reactions – leading to the formation of new cyclohexene rings (yellow) – followed by its conversion into dideoxykohnkene **5** and [12]collarene **8** via the symmetrical (?) and unsymmetrical octahydro[12]cyclacene derivatives **6** and **7**, respectively (O = solid red). In the macropolycyclic hydrocarbons, benzenoid rings are gray/black and 1,4-cyclohexadiene rings are yellow/green. Reagents and conditions: i, PhMe, reflux, 12 h; ii, CH_2Cl_2, 10 kbars, 55–60 °C, 200 h; iii, $TiCl_4$, $LiAlH_4$, THF, room temp., 18 h; iv, HCl, Ac_2O, reflux, 16 h; v, Li/NH_3, Et_2O, EtOH, – 78 °C, 45 min.

as the building blocks for the elaboration of apparently complex biomolecules, or their biosynthetic precursors. With special structural elements of vitamin B_{12} in mind, *Eschenmoser*[11] has commented on the fact that "these outwardly complex structural elements are found to self-assemble with surprising ease under structurally appropriate preconditions". He goes on to add that "the amount of external instruction required for their formation turns out to be surprisingly small in view of the complexity of these structural elements." The prospect that the chemist might be able to create an unnatural world, using the same concepts and principles that the living world relied upon in the beginning, is an extremely exciting one indeed.

The making of kohnkene **4** has an aspect of molecular 'LEGO' about it. The rigid curved structures of the component bisdienophiles **1** and bisdienes **2**, coupled with the exclusive manner in which they interact and react with each other, dictates that a molecular-belt compound has to be the outcome. Scheme 2 is an attempt to capture visually how one doubly "intelligent" substrate, i.e. **1**, can recognize another doubly "intelligent" substrate, i.e. **2**.



Scheme 2. A diagrammatic representation of the treble diastereoselectivity exhibited by each Diels-Alder reaction between two (blue on the concave surface) bisdienophiles **1** and two (pink on the concave surface) bisdiene **2** units in the construction of kohnkene **4**. The convex surfaces, which carry the oxygen atoms, are featured in red.

Unnatural product synthesis[13] will increasingly provide incentives for major conceptual developments in the art and science of chemical synthesis, as it relates to organometallic and inorganic materials, as well as to organic ones. A recent convincing illustration is provided by the structural features of self-assembly, cooperativity, and self-self recognition that characterize[14] the new polynuclear double-stranded helicates (trimers, tetramers, and pentamers) incorporating poly(bipyridine) strands and copper(I) cations.

One of the additional challenges in synthesizing an unnatural product is to uncover a property or demonstrate a function for the new material. X-Ray crystallography of kohnkene **4** not only reveals[6] that it is a belt-like molecule with the six oxygen atoms pointing outwards, but that the rigid cavity is of the appropriate dimensions to include a benzenoid substrate oriented orthogonally (Fig. 1) between the aromatic rings at 6 and 12 o'clock with an interplanar separation of 7.9 Å. Indeed, when a piezoelectric quartz crystal was coated with kohnkene **4**, detection of aromatic vapors was achieved.[15] The response of the detection system is illustrated by a typical recorder trace for nitrobenzene (Fig. 2), the substrate for which kohnkene **4** is particularly sensitive. Whatever the precise mechanism by which nitrobenzene vapor is adsorbed on to a surface of solid kohnkene **4**, the reversible association produces a change in the mass of the quartz crystal which can be monitored by changes in the

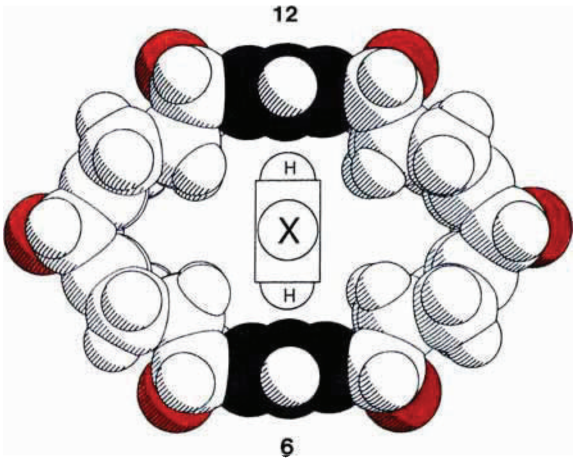


Fig. 1. Space-filling representation of the X-ray crystal structure of kohnkene **4** showing the proposed model for the rapidly-reversible inclusion of monosubstituted benzene derivatives (center) – the relative response of the piezoelectric quartz crystal is in the order, X = NO_2 > Br > Cl > H – involving stabilizing edge-to-face interactions with the aromatic rings at 6 and 12 o'clock in **4** (H = white, C = gray/black, O = red).

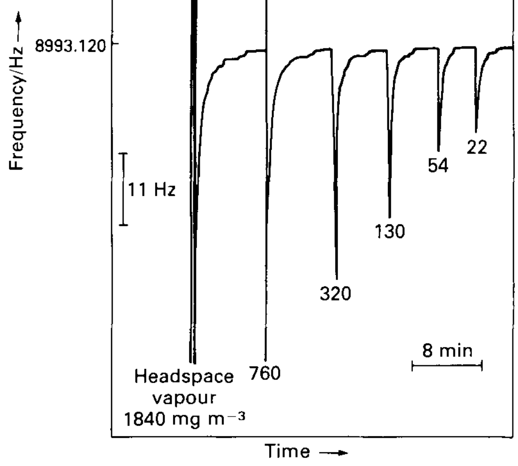


Fig. 2. A typical recorder trace of a calibration for nitrobenzene vapor using a piezoelectric quartz crystal (gold electrode) coated with kohnkene **4**. Reproduced from *Anal. Proc. 26* (1989) 14, by permission of the publishers.

frequency of its oscillation. This extremely sensitive technique for monitoring gaseous products[16] represents one of the most immediate applications of new organic materials with zeolitic properties.

The model proposed in Figure 1 for the interaction of a monosubstituted benzene derivative with kohnkene **4** involves edge-to-face stabilizing interaction[17] between the substrate and the aromatic rings at 6 and 12 o'clock. In the case of nitrobenzene, the electron-withdrawing nitro group would only serve to enhance any stabilization through edge-to-face interactions involving slightly electron deficient – or δ^+ – hydrogen atoms on the substrate molecules and the π-electron systems of the two aromatic rings in kohnkene **4**. The dideoxy derivative **5**, obtained[18] on deoxygenation of kohnkene **4** ranks as an equally sensitive but much more universal type of sensor for a range of aromatic vapors including those of toluene, 2-nitrotoluene, 3-nitrotoluene, benzene, chlorobenzene, bromobenzene, and nitrobenzene.[15] X-Ray crystallography (Fig. 3) shows that the interplanar distance between the planes of the aromatic rings at 6 and 12 o'clock is 9.6 Å, whilst that between the planes of the aromatic rings at 3 and 9 o'clock is marginally less at 8.9 Å. The most striking feature of the solid state structure is that a disordered water molecule is positioned within its Celtic-cross like cavity such that its hydrogen atoms are more than 2.7 Å away from any potentially interactive sites within the rigid hydrophobic cavity. Attempts to reach (Scheme 1) [12]beltene[19] **9** and [12]cyclacene[20] **10** have so far only proved to be partially successful. Dehydration of dideoxykohnkene **5**, under conditions of thermodynamic control, led, not to the highly symmetrical octahydro[12]cyclacene derivative **6**, containing two benzene and two anthracene units, but rather to the much less symmetrical isomer **7** comprised of one benzene, one anthracene, and two naphthalene units. The isomer **7** was converted by means of a Birch reduction into [12]collarene **8** with six 'insulated' benzene rings. Apart from [12]cyclacene **10**, all the other hydrocarbons, i.e. **7**–**9**, in Scheme 1 are characterized by π-electron systems which are localized or delocalized in a plane perpendicular to that of the macropolycycle. Exploiting their coordination chemistry towards transition metals might uncover some novel organometallic materials.

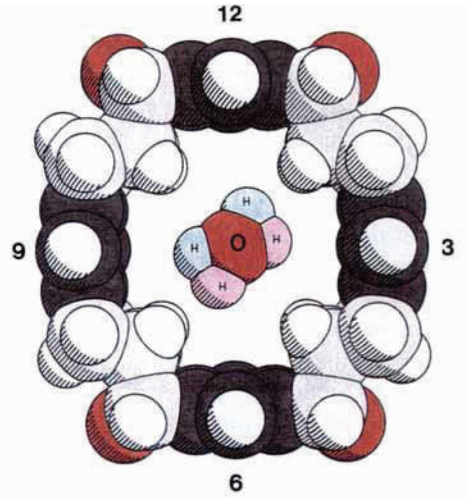
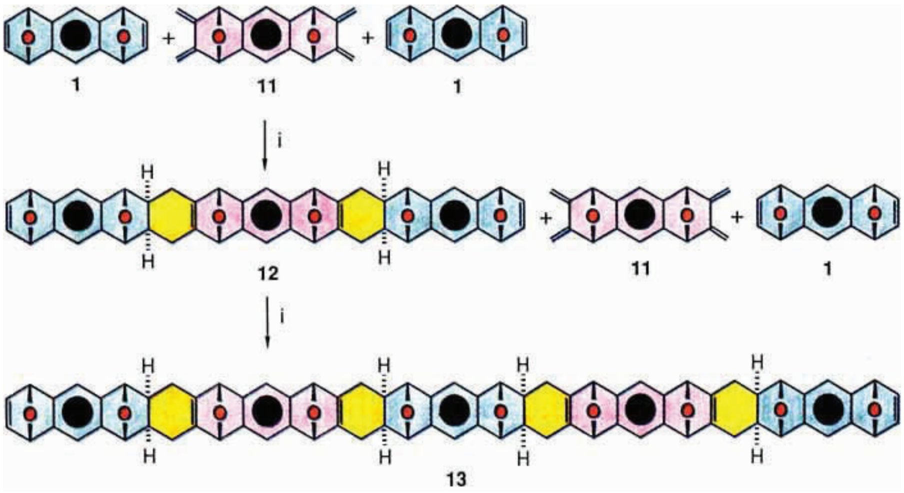


Fig. 3. Space-filling representation of the X-ray crystal structure of dideoxykohnkene **5**. In the disordered water molecule, which is included in the middle of **5**, half the molecules have their hydrogen atoms located in positions shaded pink and half in positions shaded blue (H = white, C = gray/black, O = red).

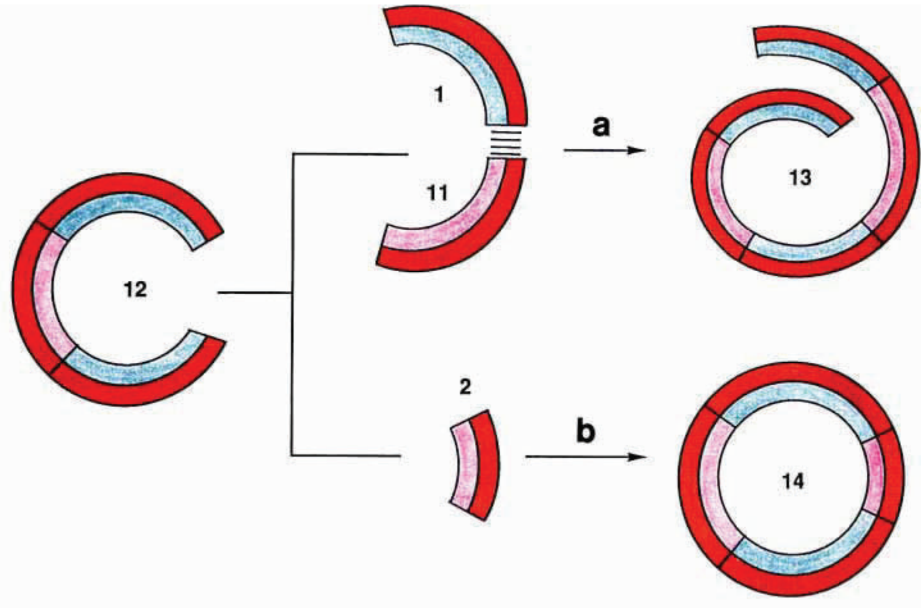
3. Molecular Strips

The power of any synthetic approach to new materials lies ultimately in its generality. One might ask – is it possible to replace **1** and **2** by other bisdienophiles and bisdienes and still

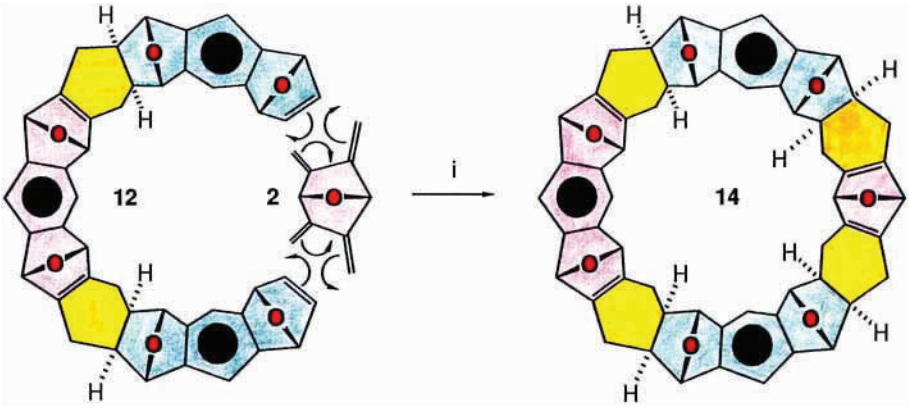


Scheme 3. The construction of the 2:1 adduct **12** and the 3:2 adduct **13** with the all-*syn* configurations from the bisdienophile **1** (blue) and the extended bisdiene **11** (pink) by repetitive Diels-Alder reactions. The newly-formed cyclohexene rings are highlighted in yellow (O = solid red). Reagents and conditions: i, CH_2Cl_2, 10 kbars, 50 °C, 6 days.

retain stereoelectronic control of the repetitive Diels-Alder reactions? The answer is by and large – yes, but the outcome is a little different.[8] Instead of constructing molecular belts, one obtains (Scheme 3) using **1** and the extended bisdiene **11** in place of **2**, molecular strips in the form of a 2:1 adduct **12** and a 3:2 adduct **14**, which coils up like a spring – at least, so ^{1}H NMR spectroscopy in solution indicates. In Scheme 4 an attempt is made to rationalize what might be happening in this series of repetitive Diels-Alder reactions. The bisdiene **11** is obviously too large to fit into the 'gap' in the 2:1 adduct **12** and so the route to the 3:2 adduct **13** is an inevitable outcome. However, despite the fact that a [16]cyclacene derivative has not been isolated, the [14]cyclacene derivative **14**, resulting from reaction of the 2:1 adduct **12** with the smaller bisdiene **2** (Scheme 5) is formed with remarkable ease. These preliminary observations hold out the promise that it should be possible to construct molecular strips of varying sizes and shapes in a highly controlled manner. Considerable thought and effort has already been invested[2–4] in the applications to materials science of rigid molecular lines and strips.



Scheme 4. A diagrammatic representation of the construction by repetitive Diels-Alder reactions of a) the 3:2 adduct **13** from three bisdienophile **1** (blue on the concave surface) and two extended bisdiene **11** units (pink on the concave surface) and of b) the [14]cyclacene derivative **14** from the bisdiene **2** unit (pink on the concave surface) – both having the 2:1 adduct **12** as a common intermediate. The convex surfaces, which carry the oxygen atoms, are featured in red.



Scheme 5. The construction of the [14]cyclacene derivative **14** by two stereoelectronically-programmed Diels-Alder reactions from the bisdiene **2** and the 2:1 adduct **12**. Fragments derived from bisdienophile **1** units are shown in blue and those derived from bisdiene (**2** and **11**) units are shown in pink. Cyclohexene rings, resulting from Diels-Alder reactions, are highlighted in yellow (O = solid red). Reagents and conditions: i, PhMe, reflux, 17 h.

4. Molecular Cages

The relatively recent construction of carcerands[21] – hollow container-like molecules (Fig. 4), which can imprison smaller molecules to form so-called carceplexes – raises the prospect of new organic materials with exciting properties and exotic applications,[13, 21] e.g. slow release biodegradable molecular encapsulants for pharmaceuticals and agrochemicals or metabolism-resistant molecular shells, containing radiation-emitting guests, attached to immunoproteins for use in cancer therapy. Incarcerated molecules inside soluble carcerands[21] give very unusual NMR spectra. They indicate that the inside of the carcerand is a new phase – the incarcerated molecules plus 'vacuum' – whose properties are a function of the degree of occupancy of the interior of the carcerand by the imprisoned molecules. At the end of their recently-published communication, *Sherman* and *Cram*[22] speculate: "The carceplexes represent a new state of matter whose guest-mobility with respect to the host is subject to design, and whose physical properties are subject to molecular level manipulation. Several potential applications of carceplexes to materials science problems are envisioned, and are being examined."

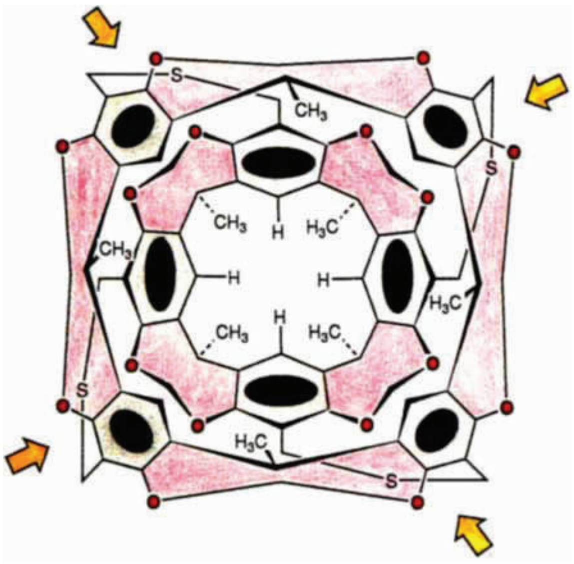
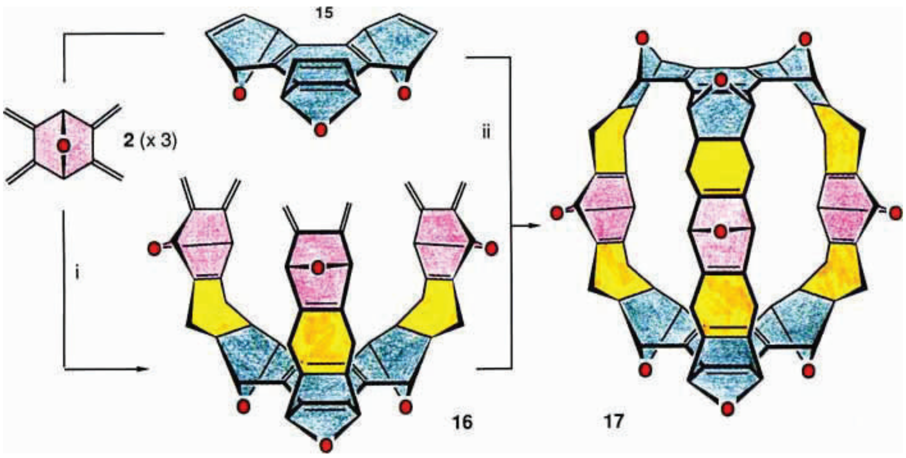


Fig. 4. Looking through the portals along the four-fold axis of the structural formula of *Cram*'s carcerand which is shaped like an American football. The arrows indicate the four carbon–sulfur bonds formed during the last step of the synthesis which brings together two cavitands each composed of alternating resorcinol (gray/black) and 8-membered acetal rings (pink) (O = solid red).

The recognition[23] that the basic carcerand topology is such that its atoms can be assembled on a minimal surface, may assist in the design and syntheses of other organic molecules. However, incentives for designing and synthesizing new materials come from many quarters. The cage compound **17**, which we have called[9] trinacrene after an old name (Trinacria) for Sicily, can be constructed via the 3:1 adduct **16** in two steps from the bisdiene **2** and the all-*syn* trisdienophile **15** (Scheme 6). The synthesis of trinacrene **17**, relying on repetitive Diels-Alder reactions as it does, is once again one that can be performed under tight stereochemical control. It is within the realms of possibility to adapt structure-directed approaches of this kind towards rational and total syntheses of carbon clusters,[24] including the C_{60} compound (Fig. 5) which has been christened buckminsterfullerene or footballene.



Scheme 6. The construction of trinacrene **17** via the 3:1 adduct **16** by a stereo-electronically-programmed set of Diels-Alder reactions from the bisdiene **2** (pink) and the all-*syn* trisdienophile **15** (blue). Newly-formed cyclohexene rings are highlighted in yellow (O = solid red). Reagents and conditions: i, PhMe, reflux, 16 h; ii, CH_2Cl_2, 10 kbars, 50 °C, 6 days.

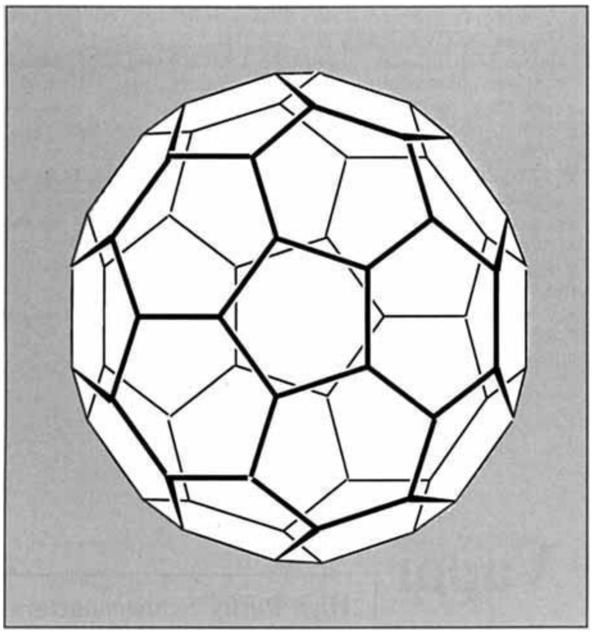


Fig. 5. The structural formula of buckminsterfullerene or footballene, a C_{60} species composed of 12 pentagonal and 20 hexagonal rings in the shape of a pentagonal dodecahedron.

Fig. 6. Birds in flight – natural and unnatural forms functioning.

5. Outlook

The structure-directed synthesis of unnatural products is set to undergo rapid development during the next few years. It will provide a relatively straightforward means for the creation of a vast number of very large, organized, and functional structures. Opportunities beckon presently for the production of molecules with form – that look like ball bearings, beads and threads, belts, cages, chains, chimneys, clefts, coils, collars, knots, ladders, nets, springs, stacks, strips, washers, and wires – and concurrently and subsequently for molecules with function – that work like abacuses, capacitors, catalysts, circuits, clocks, conductors, dynamos, membranes, motors, nuts and bolts, resistors, screws, semiconductors, sensors, shuttles, superconductors, and switches.[25] Some of these postulated developments in molecular engineering may seem rather bizarre, but, actually, the notion that mechanical and electronic devices can operate at a molecular level has already been demonstrated in biological systems. For example, the smallest known[26] rotatory mechanical devices – either natural or artificial – are the bacterial ion-driven flagellar motors, which are unique to the fields of biology and engineering.

The form and function of unnatural products is infinite. As invention, rather than discovery, becomes more and more the hallmark of chemical research, unnatural products with form and function will result. Natural products serve only to reveal some of what is possible and they certainly do not have a monopoly on the means of realizing the possibilities. If you want to reach for the sky (Fig. 6) then wings – but without feathers – might be all you need to help you on your way.

Received: June 2, 1989

[1] R. P. Feynman, *Saturday Reviews 432* (1960) 45.
[2] P. W. Kenny, L. L. Miller, *J. Chem. Soc. Chem. Commun. 1988*, 84; P. W. Kenny, L. L. Miller, S. F. Rak, T. H. Jozekiak, W. C. Christopfel, J.-H. Kim, R. A. Uphaus, *J. Am. Chem. Soc. 110* (1988) 4445 and references therein.
[3] I. Rubenstein, S. Steinberg, Y. Tor, A. Shanzer, J. Sagiv, *Nature London 332* (1988) 426.
[4] S. Kivelson, O. L. Chapman, *Phys. Rev. B28* (1983) 7236.
[5] K. Blatter, A.-D. Schlüter, G. Wegner, *J. Org. Chem. 54* (1989) 2396.
[6] F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Angew. Chem. Int. Ed. Engl. 26* (1987) 892; *Angew. Chem. 99* (1987) 941; J. F. Stoddart, *Chem. Br. 24* (1988) 1203; *J. Incl. Phenom. 7* (1989) 227; L. Milgrom, *New Sci. 1641* (3 Dec. 1988) p. 61.
[7] P. Ellwood, J. P. Mathias, J. F. Stoddart, F. H. Kohnke, *Bull. Soc. Chim. Belg. 97* (1988) 669; F. H. Kohnke, J. F. Stoddart, *Pure Appl. Chem. 61* (1989) 1581.
[8] P. R. Ashton, N. S. Isaacs, F. H. Kohnke, J. P. Mathias, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl. 28* (1989) in press; *Angew. Chem. 101* (1989) in press.
[9] P. R. Ashton, N. S. Isaacs, F. H. Kohnke, G. Stagno d'Alcontres, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl. 28* (1989) in press; *Angew. Chem. 101* (1989) in press.

[10] C. Mahaim, P.-A. Carrupt, J.-P. Hagenbuch, A. Florey, P. Vogel, *Helv. Chim. Acta 63* (1980) 1149; H. Hart, N. Raja, M. A. Meador, D. L. Ward, *J. Org. Chem. 48* (1983) 4357.

[11] S. L. Miller, L. E. Orgel: *The Origin of Life on the Earth,* Prentice-Hall, Englewood Cliffs, New Jersey, USA 1974; for a contemporary view on the origin of life, see G. Wächtershäuser, *Microbiol. Rev. 52* (1988) 452.

[12] A. Eschenmoser, *Angew. Chem. Int. Ed. Engl. 27* (1988) 5; *Angew. Chem. 100* (1988) 5.

[13] J. F. Stoddart, *Nature London 334* (1988) 10.

[14] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevier, D. Moras, *Proc. Nat. Acad. Sci. USA 84* (1987) 2565; J.-M. Lehn, A. Rigault, *Angew. Chem. Int. Ed. Engl. 27* (1988) 1095; *Angew. Chem. 100* (1988) 1121.

[15] M. A. F. Elmosalamy, G. J. Moody, J. D. R. Thomas, F. H. Kohnke, J. F. Stoddart, *Anal. Proc. London 26* (1989) 12.

[16] G. G. Guilbault, J. Ngeh-Ngwainbi in G. G. Guilbault, M. Mascini (Eds.): *Analytical Uses of Immobilised Biological Compounds for Detection, Medical, and Industrial Uses (NATO ASI Ser., Ser. C; Math. Phys. Sci. Vol. 226)* Reidel, Lancaster 1988, p. 187.

[17] S. K. Burley, G. A. Petsko, *Science Washington DC 229* (1985) 23; *J. Am. Chem. Soc. 108* (1986) 7995.

[18] P. R. Ashton, N. S. Isaacs, F. H. Kohnke, A. M. Z. Slawin, C. M. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem. Int. Ed. Engl. 27* (1988) 966; *Angew. Chem. 100* (1988) 981.

[19] R. W. Alder, R. B. Sessions, *J. Chem. Soc. Perkin Trans. 2 (1985)* 1849.

[20] A. T. Balaban, *Pure Appl. Chem. 52* (1980) 1409.

[21] D. J. Cram, S. Karbach, Y. H. Kim, L. Baczynskyj, K. Marti, R. M. Sampson, G. W. Kalleymeyn, *J. Am. Chem. Soc. 110* (1988) 2554.

[22] J. C. Sherman, D. J. Cram, *J. Am. Chem. Soc. 111* (1989) 4527; see also M. W. Browne, *The New York Times,* 21 March 1989.

[23] Z. Blum, S. Lidin, *Acta Chem. Scand. B42* (1988) 332.

[24] H. W. Kroto, *Science Washington DC 242* (1988) 1139.

[25] J.-M. Lehn, *Angew. Chem. Int. Ed. Engl. 27* (1988) 89; *Angew. Chem. 100* (1988) 91.

[26] P. Mitchell, *FEBS Lett. 176* (1984) 287.

Metal Organic Chemical Vapor Deposition (MOCVD) Perspectives and Prospects[**]

High Purity Semiconductors
Heteroepitaxy
Low-Dimensional Structures
Precursors for III–V Growth
Electronic Ceramics
Thin Films

By John O. Williams[*]

1. Introduction

This paper reviews the progress that has been made over the past decade in the use of metal organic chemical vapor deposition (MOCVD) for the preparation of high purity, epitaxial layers of a wide range of semiconductor materials: it also considers an extension of the technique to the preparation of thin film electronic ceramics and archetypal high temperature oxide superconductors.

It is now over a decade since the pioneering work of *Manasevit* and coworkers[1,2] gave rise to the remarkable interest subsequently shown in processes that use metal-organic compounds for the production of semiconductor materials. Since 1981 four international conferences have been held on the topic,[3] numerous workshops have been organized and nowadays, for certain key III–V materials systems (and to a lesser extent narrow band gap II–VI analogs), MOCVD or metal organic vapor phase epitaxy (MOVPE) is an accepted production technique yielding novel electronic and optoelectronic devices.[4–6] In many of these cases, MOVPE compares favorably with molecular beam epitaxy (MBE) and for certain materials particularly those containing phosphorus, MOVPE can produce superior materials. MOVPE is capable of producing thin layered structures – the so-called quantum wells and superlattices – and the technique can be used for atomic layer epitaxy (ALE)[7] and in the preparation of layered crystals (LC).[8]

One area where MOCVD has not developed to the same extent as MBE is the in situ monitoring of the deposition reactions. Despite recent progress[9,10] our understanding of the basic processes occurring in MOCVD is not very advanced and monitoring techniques are only currently being developed unlike in the case of, for example, reflection high energy electron diffraction (RHEED) in MBE to monitor and control atomic layer deposition.[11] In addition, since compounds are used as precursors in MOCVD, a great effort has to be expended in order to achieve the required levels of high purity and safety/convenience of the growth process. Many innovative preparation and purification routes have been developed[12,13] for the most common precursors and over the past two years, safer and less toxic chemicals have been studied as alternative starting materials.[14,15] With an improved understanding of the growth mechanisms, we can look forward to a period of considerable innovation in the use of the MOCVD technique and it is interesting to note

---

[*] Prof. J. O. Williams
Solid State Chemistry Group
Department of Chemistry
UMIST, PO Box 88
Manchester M60 1QD (UK)

[**] I would like to thank members of the UMIST Solid State Chemistry Group and the UK JOERS Consortium on InP-based materials for numerous stimulating discussions. The financial support of the SERC, US Air Force, Thorn EMI CRL, Air Products Ltd. and Johnson Matthey Ltd. is also gratefully acknowledged.