Letter

The Carcerand, an Organic Structure on a Minimal Surface

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Structures in the solid state can be readily explained by topological reasoning. The positions of atoms in space can be viewed as governed by their arrangement on, or on either side of, particular surfaces. In recent years it has been shown that a majority of these surfaces share a profound quality: they are periodic minimal surfaces.[1-6] In the classical works on differential geometry one can distinguish between a number of discrete periodic minimal surfaces named according to a nomenclature of their own, e.g. the so-called P-surface of Schwarz[7] (Fig. 1).

A minimal surface can be recognized in that every point on the surface is a saddle point. By applying concepts of differential geometry a minimal surface can be said to have negative Gaussian curvature and zero mean curvature.[8] In a chemical compound with sp^3 *i.e.* saddle, or similar units these latter provisions will profoundly influence the structure, e.g. zero mean curvature minimizes the interactions with the surroundings. Periodicity on the other hand, obviously provides long-range structural integrity. The validity of this reasoning has been convincingly demonstrated for a number of solid-state structures ranging from inorganic structures, e.g. zeolites,[6] to natural products, e.g. starch.[9] Thus, it has been shown that particular structures can be fitted to particular periodic minimal surfaces, e.g. zeolite A can be fitted to the P-surface.

When considering small to medium-sized molecular compounds, notably organic substances, the topological approach becomes less perceptible in that the surface distended by the carbon backbone can be difficult to recognize. If, however, the size of a molecule is allowed to increase, e.g. by including several surface-carrying units such as aromatic rings, the surface can be readily apprehended.

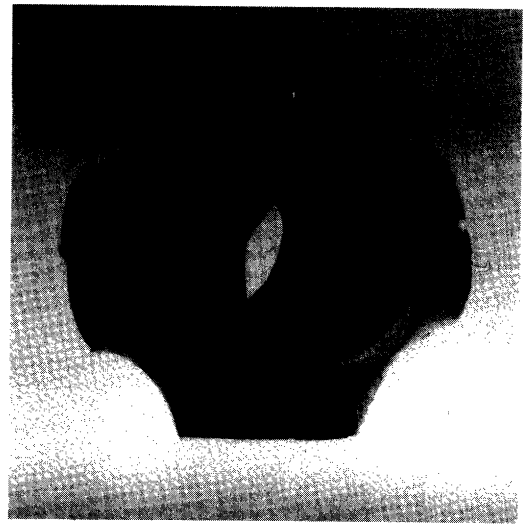
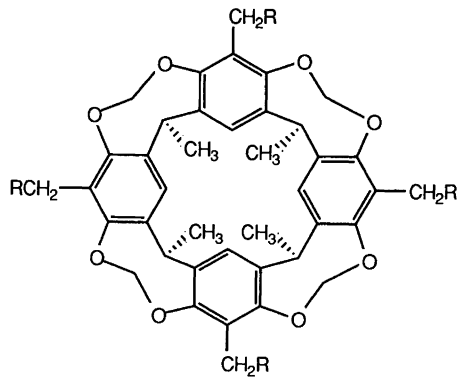


Fig. 1. The P-surface.

Recent developments in the field of organic complexing agents have resulted in numerous elaborate structures carrying onomatopoetic names such as cryptands, spherands, cavitands, carcerands etc. The names are obviously chosen so as to imply certain qualities with respect to molecular organization and capacity. Unfortunately, in a geometrical sense, the names are highly misleading in that the reader is tempted to assume a close-to-spherical geometry of the molecules. Spherical geometry implies positive Gaussian curvature *and* non-zero mean curvature.



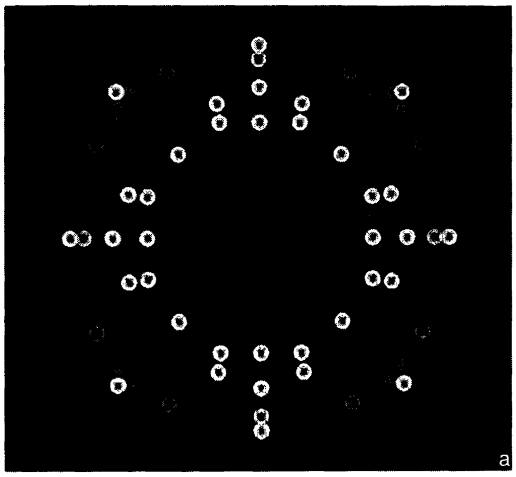
R=Cl or R=SH

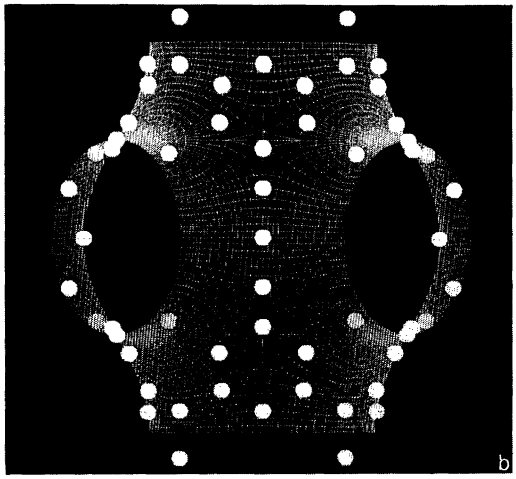
Fig. 2. The cavitand precursors for carcerand synthesis.

Close inspection of molecular models and X-ray structures reveals that all the above-mentioned structures have negative Gaussian curvature and zero mean curvature. Thus the atoms are assembled on a *minimal surface.*

The most striking and unambiguous evidence for the presence of minimal surfaces in organic structures is provided by the carcerand of Cram.[10] The carcerand was constructed from two closely related cavitands: one with four benzylic chlorines and one with four benzylic sulfides (Fig. 2).

The cavitands were allowed to react in DMF, with Cs_2CO_3 present to neutralize the hydrogen chloride formed, whereupon the carcerand precipitated, encapsulating the different substances present in the solution. If one supposes that the starting cavitands are not bowl-shaped (Cram's terminology) but rather shaped as part of a catenoid (this is validated by studies of both models and X-ray structures) it can easily be seen that the carcerand can be fitted to the P-surface (*vide supra*). A slight tetragonal contractive distortion of the P-surface is necessary in order to consummate the alignment of the carcerand (Fig. 3). This distorsion is mathematically sound and preserves the overall features of the surface.[11] The contrac-





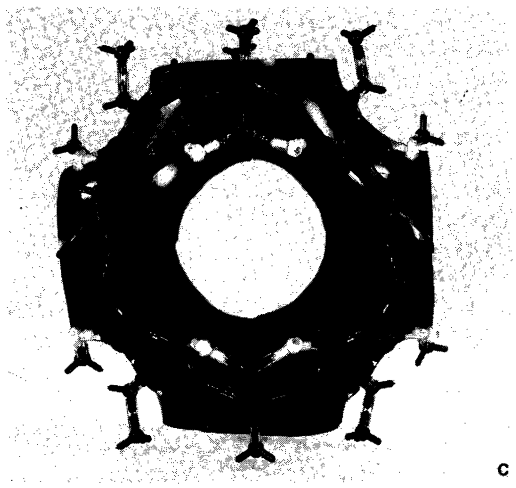


Fig. 3. The carcerand fitted to the P-surface; (a) and (b) Computer graphics. (c) Molecular model built on a plastic model of the P-surface.

tion results in an enlargement of the top and bottom ports, while the remaining four ports adopt elliptical shapes.

The role of Cs_2CO_3, or rather the caesium ion, may be more subtle than perhaps originally anticipated. In the crystal structure of CsCl the zero potential is distributed in the lattice on a surface that has been demonstrated to be equivalent to the P-surface.[5] One can then argue that if the CsCl formed attains a disposition in solution that resembles the solid state, then CsCl can be regarded as a template on which the emanating carcerand is contrived; the organic residues, in avoiding the vicinity of either Cs^+ or Cl^-, are forced to stay on the zero potential surface. Together with the expedient preorganization in the starting cavitands, strong synergism would be expected, resulting in a substantial yield increase. It would be interesting to undertake a study in which Cs_2CO_3 was exchanged for either Na_2CO_3 or K_2CO_3. Neither of the compounds NaCl or KCl have zero potential surfaces that can be fitted to the P-surface, resulting perhaps (in the absence of cooperative effects) in diminishing yields.

Another structure that can be fitted to the P-surface is also related to cavitands. This compound (vase-shaped in Cram's terminology, 10a in Ref. 12) lacks one of the catenoid-like parts but nevertheless fits perfectly to the remaining parts of the P-surface.

One can speculate why the formation of the carcerand is relatively straightforward when tremendous difficulties were encountered before the synthesis of e.g. dodecahedrane was finally achieved. The reason is the geometry: dodecahedrane is truly spherical, i.e. all relevant bonds protrude from the *same side* of the surface, and thus structural congestion increases as the sphere is closed. The carcerand is composed entirely of saddles, i.e. all relevant bonds protrude from *both sides* of the surface, and thus there will be no problems of congestion. Hence, *if an* sp^3*-hybridized carbon is identified as a saddle, any synthetic activity aiming to confer spherical geometry to an assemblage of such carbons will be severely thwarted and* vice versa.

Apart from aiding in structure elucidation and providing synthetic guidance, a topological approach to organic structures can possibly illuminate the forces responsible in host-guest relationships. It is well established that the effect of zeolites on sorbate molecules can be related to the curvature of the surface distended by the sorbent.[13,14] The curvature is a measure of the degree of focusing of total van der Waals forces. There are reasons to believe that organic sorbents, or hosts, can be treated analogously.

Cram, for one, points to the faculty of cavitands to enable a number of functional groups to converge on one another and act cooperatively.[15]

If the term functional group is taken to include any part of a molecule that can contribute to total van der Waals activity and that this activity is confined to a saddle surface, the dissimilarities between e.g. zeolites and organic compounds vanish. Thus, by determining the curvature of an organic host one can get a measure of its ability to intercept different guests.

By studying the topology of molecules one can collect information on their structure, synthetic availability and sorbent quality. In recognizing a majority of organic hosts as contrived of minimal surfaces we have gained access to a powerful means of understanding and elucidating the features of complex organic molecules. Work is in progress in this laboratory on the topologies and hence properties of podands, coronands, cryptands, spherands, cavitands, natural products etc. and will be published in the near future. The particular effect of caesium ions in organic reactions,[16] the so-called "Caesium Effect", will also be subject to further examination.

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