Topological Organic Chemistry. Polyhedranes and Prismanes

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The paper discusses two classes of regular, three-dimensional, organic solids—polyhedranes and prismanes—all of whose boundaries are defined by nets of tetrahedrally hybridized carbon atoms. The topic is defined, the various representatives of each class are enumerated, the geometric dimensions of all examples are calculated and tabulated, and some conjecture of chemical properties is presented.

Only a few authors have reported the role that the carbon atom might play in establishing the boundaries or limits of geometrical solids. The end papers of the modern organic chemistry textbook by Cram and Hammond[1] contain pictures of a tetrahedron, a truncated tetrahedron, a cube, and a triangular prism with vertices of carbon atoms and edges of carbon–carbon bonds. Roberts and Caserio[2] refer to the tetrahedron-shaped molecule as tricyclobutane and recognize the triangular prismoid molecule as Ladenburg's benzene. Freedman and Petersen[3] reported the synthesis of a possible octaphenylcubane, and Eaton and Cole[4] have reported the preparation of dicarboxylic acid derivatives of cubane, as well as of cubane itself. Woodward, *et al.*,[5] have referred to dodecahedrane as a possible synthetic objective.

It is the purpose of this paper to outline and discuss all related, regular, polyhedron-type organic chemicals of potential existence, within the bounds of the restrictions stated below. The cubane (hexahedrane) derivative mentioned earlier is one of the simplest examples of these compounds.

Only such solid forms as convex solids with regular planar faces like a cube, for example, and not like a saddle are considered. Only such solid forms as are possible organic compounds are considered, limiting the discussion to hydrocarbons and simultaneously rejecting mere frameworks of carbon atoms to which no other atoms can be bonded. In order to fulfill these conditions, each carbon atom of a molecule must utilize three of its valences in bond formation to adjacent carbon atoms, thus outlining the form of the solid. This of necessity permits only one valence for bonding to another atom, which, as already stated, is the hydrogen atom in this analysis. Thus, every three-dimensional molecule being considered has equal numbers of carbon and hydrogen atoms and possesses the empirical formula of C_nH_n in all cases.

The two great classes of regular solids which fulfill all of these conditions are some of the polyhedra and all of the regular prisms. These are discussed in the order named.

The first great class of topologically defined regular solids is the polyhedra, of which there are four groups or types. Of the five regular (Platonic) polyhedra—tetrahedron, hexahedron (a cube, also a square prism), octahedron, icosahedron, and dodecahedron—only three may serve as topological models of organic polyhedranes within the limits outlined. These are the tetrahedron (Figure 1), the cube (Figure 2), and the dodecahedron (Figure 3); each has three edges that meet at each vertex and in a hydrocarbon polyhedrane allow for one exterior carbon–hydrogen bond at every carbon atom of the molecule. The octahedron with four edges meeting at each vertex and the icosahedron with five edges meeting at each vertex can not serve as frameworks for the C_nH_n molecules to which this topic is restricted. (There are, of course, other elements than carbon whose valences would conceivably permit their incorporation into the matrix or framework represented by the last two Platonic polyhedra named above.)

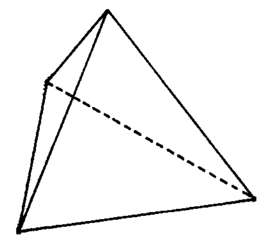

Figure 1.

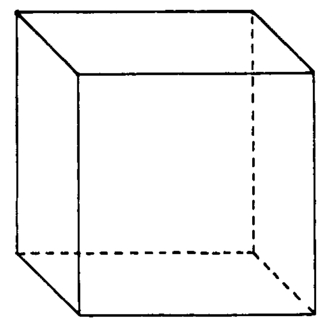

Figure 2.

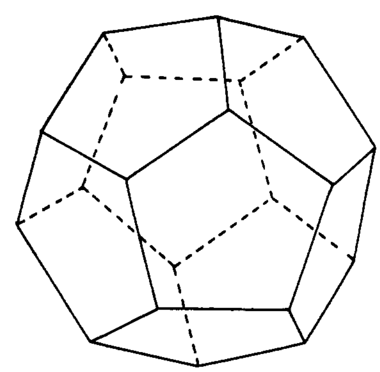

Figure 3.

(1) D. J. Cram and G. S. Hammond, "Organic Chemistry," 2d Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(2) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 1126.

(3) H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962). The author thanks the Editor-in-Chief for referral to the recently reported proof that the octaphenylcubane was octaphenylcyclooctatetraene: see G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *ibid.*, **86**, 4725 (1964).

(4) P. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 962 3157 (1964).

(5) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *ibid.*, **86**, 3162 (1964).

TABLE I
PHYSICAL DIMENSIONS OF POLYHEDRANES

Name	Formula	Vertices (C atoms)	Edges (C–C bonds)	No. of faces (all regular)	Face angle(s)	Exterior isoclinal angle, ϕ	Total angular strain per carbon atom, $\Sigma\angle S/C$	Adjacent H–H distance, Å.
Tetrahedrane	C_4H_4	4	6	Triangle, 4	60° (ρ,ω)	144° 44′	254° 12′	3.32
Cubane	C_8H_8	8	12	Square, 6	90° (ρ,ω)	125° 16′	105° 48′	2.80
Truncated tetrahedrane	$C_{12}H_{12}$	12	18	Triangle, 4	60° (ρ)			
				Hexagon, 4	120° (ω)	115° 15′	87° 53′	2.47
Dodecahedrane	$C_{20}H_{20}$	20	30	Pentagon, 12	108° (ρ,ω)	110° 54′	8° 42′	2.32
Truncated octahedrane	$C_{24}H_{24}$	24	36	Square, 6	90° (ρ)			
				Hexagon, 8	120° (ω)	108° 26′	43° 38′	2.23
Truncated cubane	$C_{24}H_{24}$	24	36	Triangle, 8	60° (ρ)			
				Octagon, 6	135° (ω)	106° 20′	109° 56′	2.15
Truncated cuboctahedrane (rhombicuboctahedrane)	$C_{48}H_{48}$	48	72	Square, 12	90°			
				Hexagon, 8	120°			
				Octagon, 6	135°	102° 27′	76° 35′	2.01
Truncated icosahedrane	$C_{60}H_{60}$	60	90	Pentagon, 12	108° (ρ)			
				Hexagon, 20	120° (ω)	101° 39′	45° 59′	1.98
Truncated dodecahedrane	$C_{60}H_{60}$	60	90	Triangle, 20	60° (ρ)			
				Decagon, 12	144° (ω)	99° 41′	146° 53′	1.91
Truncated icosidodecahedrane (rhombicosidodecahedrane)	$C_{120}H_{120}$	120	180	Square, 30	90°			
				Hexagon, 20	120°			
				Decagon, 12	144°	97° 33′	100° 17′	1.83

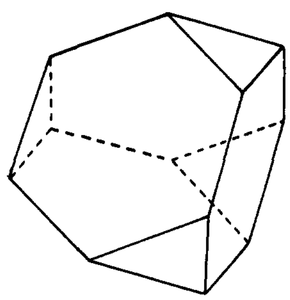

Figure 4.

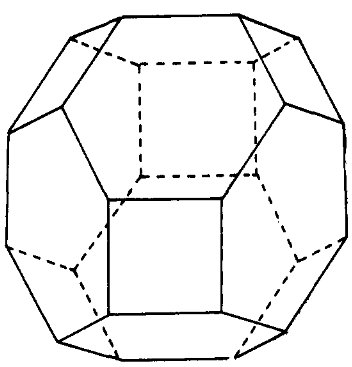

Figure 5.

None of the four Kepler–Poinsot, or stellated, polyhedra has any utility for this consideration, for all have four or more edges meeting at each vertex.

Several of the fourteen Archimedian polyhedra can serve as models for polyhedranes. These are the truncated tetrahedron (Figure 4), truncated octahedron (Figure 5), truncated cube, truncated cuboctahedron (rhombicuboctahedron), truncated icosahedron, truncated dodecahedron, and the truncated icosidodecahedron (rhombicosidodecahedron).[6]

The following Archimedian polyhedra cannot serve as topological models for polyhedranes because four or more edges meet at some or all of the vertices of the latter polyhedra: the cuboctahedron, the small rhombicuboctahedron, the snub cube, the icosidodecahedron, the small rhombicosidodecahedron, the snub dodecahedron, and a new, as yet not named, polyhedron similar to the rhombicuboctahedron.[7] For the same reason none of the fourth class of polyhedra, the dual Archimedian solids, can serve as polyhedrane models.[8]

Table I contains data concerning the polyhedranes. Vertices (carbon atoms, and therefore molecular formula), edges (carbon–carbon bonds), number and type of regular faces, and face angles have been extracted from references.[7,8]

The exterior isoclinical angle (ϕ), the presumed equal angle which each exterior hydrogen atom makes with the three bonds (edges) that meet at each carbon atom (vertex), is calculated. The primary requisites for the calculation of the exterior isoclinal angle are two. The value of θ, the interior isoclinal angle, is calculated by determining the inverse ratio of the carbon–carbon bond distance to its projection into a plane formed by three adjacent carbon atoms of the solid. With θ known, ϕ is easily computed, for it is the supplement of θ.[6] Derivation gives

$$\sin \phi = \frac{\sin \omega/2}{\sqrt{1 - \frac{\sin^2 \rho/2}{4 \sin^2 \omega/2}}}$$

where ρ is the face angle of the one nonidentical face, and ω is the face angle of the two identical faces meeting at any given carbon atom of a polyhedrane.

(6) (a) A more detailed form of this paper[6b] (or extended version, or material supplementary to this article) has been deposited as Document number 8315 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. (b) This includes a general derivation for the value of ϕ and drawings of all possible polyhedranes.

(7) V. G. Ashkinuze, cited in L. A. Lyusternik, "Convex Figures and Polyhedra," T. J. Smith, Transl., Dover Publications, New York, N. Y., 1963, p. 149.

(8) H. M. Cundy and A. P. Rollett, "Mathematical Models," 2d Ed., Oxford Press, Amen House, London, 1961, pp. 70–160.

In tetrahedrane, cubane, and dodecahedrane all vertex angles of each are the same, and the expression for the calculation of ϕ is

$$\sin \phi = \frac{2 \sin \omega/2}{\sqrt{3}} = \frac{2 \sin \rho/2}{\sqrt{3}}$$

The total angular strain per carbon atom ($\Sigma \angle S/C$) is computed in degrees for the purpose of reducing to a common base all positive and negative strains about each carbon atom of every molecule. The total angular strain per carbon atom, as defined within this paper, is computed by summing the six individual angle strains ($\angle S$) about each carbon atom; $\angle S$ is the deviation from 109° 28′, computed in such a fashion as to be positive in all instances. Hence, angles smaller than or equal to 109° 28′ are subtracted *from* 109° 28′ to determine individual angle strain; the opposite procedure is used for angles larger than 109° 28′.

The most extreme value of total angular strain about a carbon atom, according to this definition, is observed about a carbon atom of acetylene (Figure 6).

$$\Sigma \angle S/C, \text{acetylene} = \angle S \angle ACE + \angle S \angle ACB + \angle S \angle ACD + \angle S \angle DCB + \angle S \angle BCE + \angle S \angle DCE$$

$$\Sigma \angle S/C, \text{acetylene} = (180° - 109° 28')3 + (109° 28' - 0°)3 = 540°$$

The least value of total angular strain is observed in a molecule of methane (Figure 7).

$$\Sigma \angle S/C, \text{methane} = (109° 28' - 109° 28')6 = 0°$$

In column 8 of Table I are listed the total angular strains per carbon atom for each of the polyhedranes.

It is interesting to examine the adjacent hydrogen–hydrogen distance for each of the polyhedranes. This distance, the last column of values in Table I, gives an indication of the nonbonding interactions between the adjacent hydrogen atoms that cover the surface of the carbon net which constitutes each of the polyhedranes. The values for the radius of the sphere of action of a hydrogen atom vary. Those by P. H. Hermans,[9] 1.10 Å. in many organic compounds, should be kept in mind when one examines the hydrogen–hydrogen bond distance columns of the tables.

Since any adjacent set of hydrogen–carbon bonds lies in the same plane, the calculation of adjacent hydrogen–hydrogen distance in any polyhedrane is relatively simple. For these calculations Pauling[10] values of a carbon–carbon bond distance of 1.54 Å. and a hydrogen–carbon bond distance of 1.09 Å. are assumed. No doubt these values would vary somewhat from the tetrahedrane molecule with its highest degree of strain within the carbon matrix of the molecule, to dodecahedrane with the lowest apparent degree of angular strain about each carbon atom of the net. The differences, however, would probably not be great, no greater in most instances than comparative carbon–carbon bond distance differences between carbon atoms of ethane (1.54 Å.) and of cyclopropane (1.53 Å.). An obvious advantage of such assumption is the common point of view taken in determining these hydrogen–hydrogen distances for every polyhedrane molecule;

(9) P. H. Hermans, "Theoretical Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1954, pp. 4, 5.

(10) L. Pauling, "The Nature of the Chemical Bond," 3d Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 222, 224.

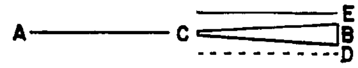

Figure 6.

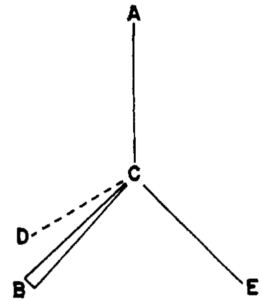

Figure 7.

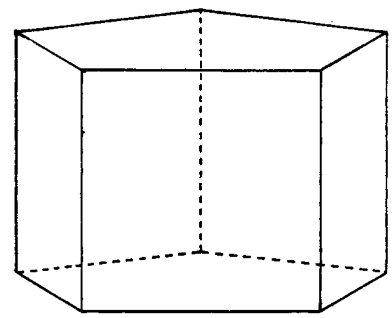

Figure 8.

only the topological variations due to geometry are compared.

Certain general conclusions are drawn from Table I. It is expected that the first two and last four members of the polyhedrane series would be less stable than the middle members of the series. Several factors contribute to this conclusion. Positive strain of high order is evident from the compressed face angles of both tetrahedrane and cubane. The exterior isoclinal angle is very much above the value of 109° 28′ for tetrahedrane and cubane and is somewhat low for the last four members of the polyhedrane series. The total angular strain per carbon atom is very high for the first members of the series, reaching a minimum for dodecahedrane and again increasing in value, with rather low values also for truncated octahedrane and truncated icosahedrane. The three points mentioned thus far indicate a maximum stability toward the center of the table at dodecahedrane, with stability decreasing at each extreme end of the table.

Instability due to hydrogen–hydrogen nonbonding interactions, however, shows a constantly increasing trend to higher values from simplest to most complex of the polyhedranes. At about the fifth or sixth member of the series, the adjacent hydrogen–hydrogen distances decrease enough to contribute to the instability of the polyhedranes.

Dodecahedrane is the one substance of the series with almost ideal geometry, physically the molecule is practically a miniature ball bearing! One would expect the substance to have a low viscosity, a low thermal coefficient of viscosity, a high melting point but low boiling point, high thermal stability, a very simple infrared spectrum, and perhaps an aromatic-like p.m.r. spectrum. Chemically one might expect a relatively

TABLE II

Physical Dimensions of Prismanes

Name	Formula	Vertices (C atoms)	Edges (C–C bonds)	No. faces (all regular)	Face angle(s)	Exterior isoclinal angle, ϕ	Total angular strain per carbon atom, $\Sigma\angle S/C$	Adjacent H–H distance, Å.
Triprismane	C_6H_6	6	9	Triangle, 2	60°	130° 54′	152° 42′	2.97
				Square, 3	90°			
Quadriprismane (cubane)	C_8H_8	8	12	Square, 6	90°	125° 16′	105° 48′	2.80
Pentaprismane	$C_{10}H_{10}$	10	15	Pentagon, 2	108°	120° 27′	73° 21′	2.65
				Square, 5	90°			
Hexaprismane	$C_{12}H_{12}$	12	18	Hexagon, 2	120°	116° 34′	70° 46′	2.52
				Square, 6	90°			
Heptaprismane	$C_{14}H_{14}$	14	21	Heptagon, 2	128° 34	113° 36′	70° 26′	2.42
				Square, 7	90°			
Octaprismane	$C_{16}H_{16}$	16	24	Octagon, 2	135°	110° 57′	68° 55′	2.32
				Square, 8	90°			
Nonaprismane	$C_{18}H_{18}$	18	27	Nonagon, 2	140°	108° 53′	71° 13′	2.25
				Square, 9	90°			
Decaprismane	$C_{20}H_{20}$	20	30	Decagon, 2	144°	107° 10′	80° 22′	2.18
				Square, 10	90°			
Undecaprismane	$C_{22}H_{22}$	22	33	Undecagon, 2	147° 16′	105° 44′	87° 56′	2.13
				Square, 11	90°			
Dodecaprismane	$C_{24}H_{24}$	24	36	Dodecagon, 2	150°	104° 31′	94° 19′	2.09
				Square, 12	90°			
Tridecaprismane	$C_{26}H_{26}$	26	39	Tridecagon, 2	152° 19′	103° 26′	99° 53′	2.05
				Square, 13	90°			
Tetradecaprismane	$C_{28}H_{28}$	28	42	Tetradecagon, 2	154° 17′	102° 32′	104° 33′	2.01
				Square, 14	90°			
n-Prismane	$C_{2n}H_{2n}$[a]	$2n$[a]	$3n$[a]	*n*-Agonal, *n*	180°			
				Square, *n*	90° (approaches)	90° (approaches)	167° 52′ (approaches)	1.54 (approaches)

[a] *n* is the number of carbon atoms in each face.

easy (for an aliphatic hydrocarbon) removal of a tertiary proton from the molecule, for the negative charge thus deposited on the molecule could be accommodated on any one of the twenty completely equivalent carbon atoms, the carbanion being stabilized by a "rolling charge" effect that delocalizes the extra electron.

The second great subclass of regular organic solids, the prismanes, is considered next. All regular prisms, solids with two parallel faces of regular polygons, all of whose sides are equal in length and are joined at planar dihedral right angles, fulfill the requirements earlier established in this paper. Figure 8 pictures the carbon skeleton of one of the simplest regular prisms, a pentagonal prism or pentaprismane. Although theoretically this subtopic has no limitation, for practical purposes the survey is limited to prisms whose regular polygonal ends, or faces, are no larger than a tetradecagon. The last line of Table II shows data for the *n*th member of the prismane series of hydrocarbons, with *n* sides of the polygonal faces meeting each vertical edge of the prism at a limiting valence bond angle of 180°.

The data listed in Table II are obtained in the same general fashion as those described for Table I. Each prismane has sides whose face angles by definition are always 90°. This fixes the value for ω, in the earlier described expression, at a constant value, thereby considerably simplifying the calculation of the internal isoclinal angle (θ) to

$$\sin \theta = \frac{1}{\sqrt{2 - \sin^2 \rho/2}}$$

and hence its supplement, the external isoclinical angle (ϕ).

The quadriprismane of Table II is identical with cubane of Table I.

A general trend for the most stable prismanes to exist in the middle of the table centered about values cited for octaprismane is observed again in Table II. However, values for face angle distortion, total angular strain per carbon atom, and hydrogen–hydrogen opposition are by no means so low for the octaprismane of Table II as they were for dodecahedrane of Table I.

Examination of Table II, as could be anticipated, shows data for end face angles with considerable positive strain in the first two members of the series, merging rather abruptly through only one relatively strain-free substance, pentaprismane, into substances with end face angles of constantly increasing negative strains.