

Hypothetical strain-free oligoradicals

(molecular orbital theory/strained molecules/correlation diagrams)

ROALD HOFFMANN*, ODILE EISENSTEIN*, AND ALEXANDRU T. BALABAN†

*Department of Chemistry, Cornell University, Ithaca, New York 14853; and †Department of Organic Chemistry, The Polytechnic, Bucharest, Romania

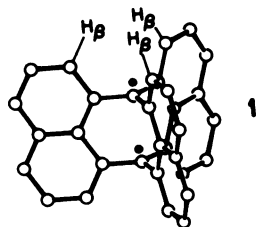
Contributed by Roald Hoffmann, July 2, 1980

ABSTRACT Several new classes of oligoradicals free of angle strain are suggested and examined by means of molecular orbital calculations. The collapse products of these hypothetical radicals are highly strained molecules. Various electronic strategies for the stabilization of these oligoradicals have been explored.

In the process of thinking about structural alternatives to graphite, (i.e., space-filling networks of trigonal carbon atoms), we have built models of several intriguing strain-free di- and oligo- or poly-radicals. These are the subject of this paper.

Oligoradicals normally would not be considered likely candidates for kinetic or thermodynamic stability. They are expected to be unstable, collapsing into classical pairwise σ -bonded structures. However, in the structures we will show in this work, the oligoradical is unstrained, whereas σ -bond formation must be accompanied by substantial strain. If the strain is large enough, perhaps the radical structure has by default a chance of existing. It would help if the collapse to a classical structure were symmetry forbidden and/or if the polyradical had its own stabilizing electronic features.

To remove some of the hypothetical nature of this discussion, consider the diradical **1**. It is the basic unit in an infinite space-filling carbon structure containing needle-like radical chains flanked by polyacene chains and surrounding large hexagonal channels. The electronic structure of that extended array will be discussed elsewhere; here let us focus on the molecule **1**.



It contains two radical centers, perfectly trigonal, mounted in the *peri*-positions of three naphthalene rings. Except for the strain known to exist between the substituents in such **1**, 8 sites on a naphthalene (1-5), this diradical is free of angle strain. Its collapse product would be a [3.3.3]propellane. Such systems are known (6, 7), but hardly with the constraint of ring fusion to a naphthalene. The strain anticipated from H_{β} - H_{β}' interaction upon σ -bond formation is likely to be very large.

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "advertisement" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

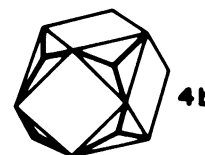
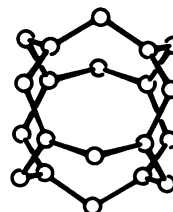
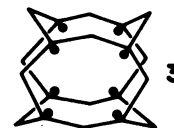
In this case there is no special stabilizing feature to the diradical, except for the guardian role of the β hydrogens, useful in limiting access to the radical site by external reagents. The radical lobes are obviously out of conjugation with the naphthalene rings. At a reasonable radical separation of 2.42 Å, a model extended Hückel calculation on **2** gives a gap of 1.65 eV between the bonding and antibonding combinations. We estimate that is enough to guarantee a low-spin singlet ground state for that geometry.



Insofar as the splitting is set primarily by through-space interaction, the collapse to the propellane is unfortunately an allowed reaction.

A cubical octaradical

Let us jump to a highly symmetrical octaradical, **3**, shown in an alternative view in **4a**. Here each radical center is at the corner of a cube. The symmetry is O_h . The polyhedral nature and geometrics of this most hypothetical species may be appreciated by drawing a cube-octahedron, **4b**, and inscribing in each triangular face a trigonal carbon atom. The angle between bonds at the juncture of two triangles is precisely the tetrahedral angle, which is why **3** is strain free.



What is the electronic structure of the octaradical? The eight radical *p* orbitals transform as $A_{1g} + T_{1u} + T_{2g} + A_{2u}$. The symmetry-adapted linear combinations are easily formed. They are shown schematically in 5.

Abbreviations: HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

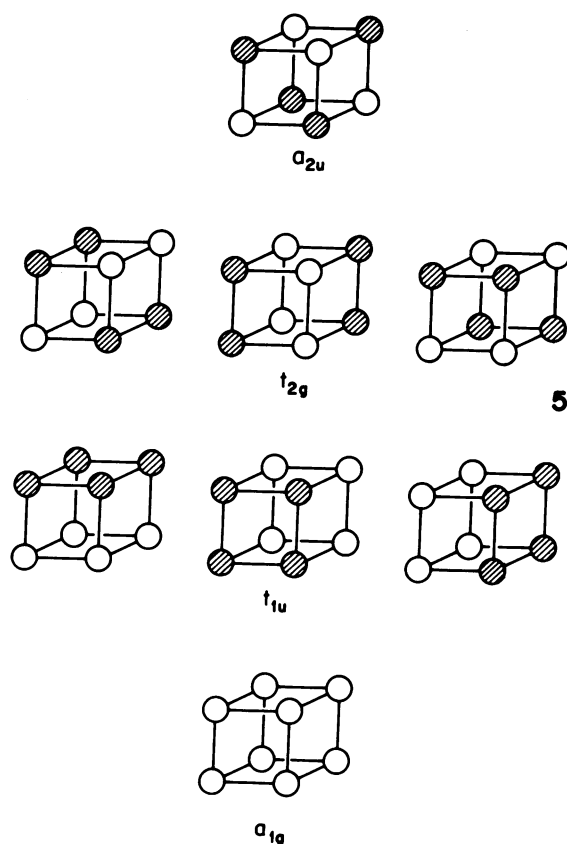


FIG. 1. Level splitting pattern for the octaradical 3.

Given the σ topology of the interaction, one would expect through-space bonding to produce the ordering $a_{1g} < t_{1u} < t_{2g} < a_{2u}$. This immediately raises the possibility of a stable closed shell structure, if the gap between t_{1u} and t_{2g} is large enough.

To estimate that gap one needs a calculation. If the C-C distance is taken as 1.52 Å, then the eight radical centers are 2.15 Å from the center of the cube. The three C-C distances (cube edge, face diagonal, and body diagonal) are 2.48, 3.51, and 4.30 Å, respectively. The corresponding overlaps of pure 2p carbon orbitals are 0.047, 0.012, and 0.004, respectively. This augurs for some splitting, but not a gigantic one. The actual outcome of an extended Hückel calculation is recorded in Fig. 1. The level ordering is as anticipated, but the t_{1u} - t_{2g} gap of 0.6 eV is disappointingly small. It is hazardous to guess whether this geometry will have a singlet ground state on the basis of this one-electron energy level scheme alone.

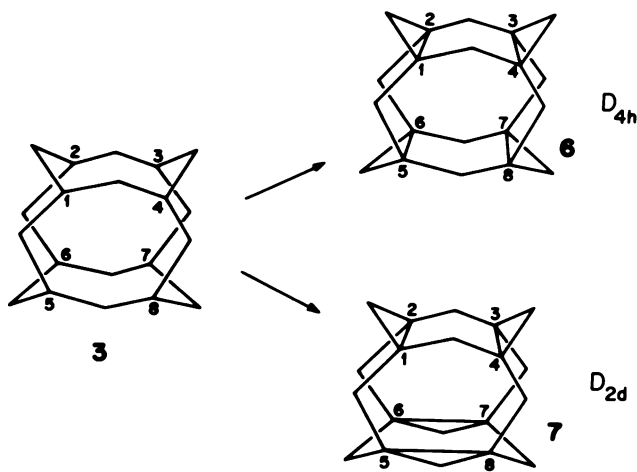
Two likely collapse modes for the octaradical lead to the highly strained D_{4h} (6) and D_{2d} (7). Schematic correlation diagrams for these reactions are easily drawn, even though we have not actually calculated the energy levels of 6 and 7. In the diagrams (Fig. 2) we make use only of the minimal essential symmetry elements—one or two planes that pass through bonds made or broken.

The reaction $3 \rightarrow 6$ entails a level crossing; it is a forbidden reaction. Unfortunately, collapse to 7 is allowed. We cannot trust extended Hückel calculations for an estimate of the relative energetics of 3 and 7. However, even if 7, or a geometry approaching 7, is more stable, there still is a role for the cubic singlet octaradical 3. Subject to symmetry constraints of the type discussed by Stanton and McIver (8), it or a slightly distorted perturbation could serve as a waypoint in a degenerate valence isomerization of 7. Such a process might be detected in the NMR spectral properties of the collapsed molecule.

Stabilizing the octaradical

The simplistic approach to conferring greater stability on the cubical structure focuses on the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), between t_{1u} and t_{2g} , and on lowering the energy of the HOMO, t_{1u} . The cause for concern about the t_{1u} is that this orbital is *destabilized* in the molecule. Counting up bonding and antibonding contributions in the symmetry-adapted linear combinations of 5 would indicate that there are more bonding than antibonding contributions in the t_{1u} set. Our estimate, based on model calculations of eight cubically disposed C p orbitals is that the net through-space stabilization in the t_{1u} should be ≈ 0.3 eV. In fact the t_{1u} may be seen from Fig. 1 to be ≈ 1.25 eV destabilized relative to the reference point of -11.4 eV for a free carbon 2p orbital.

This destabilization is the result of through-bond coupling



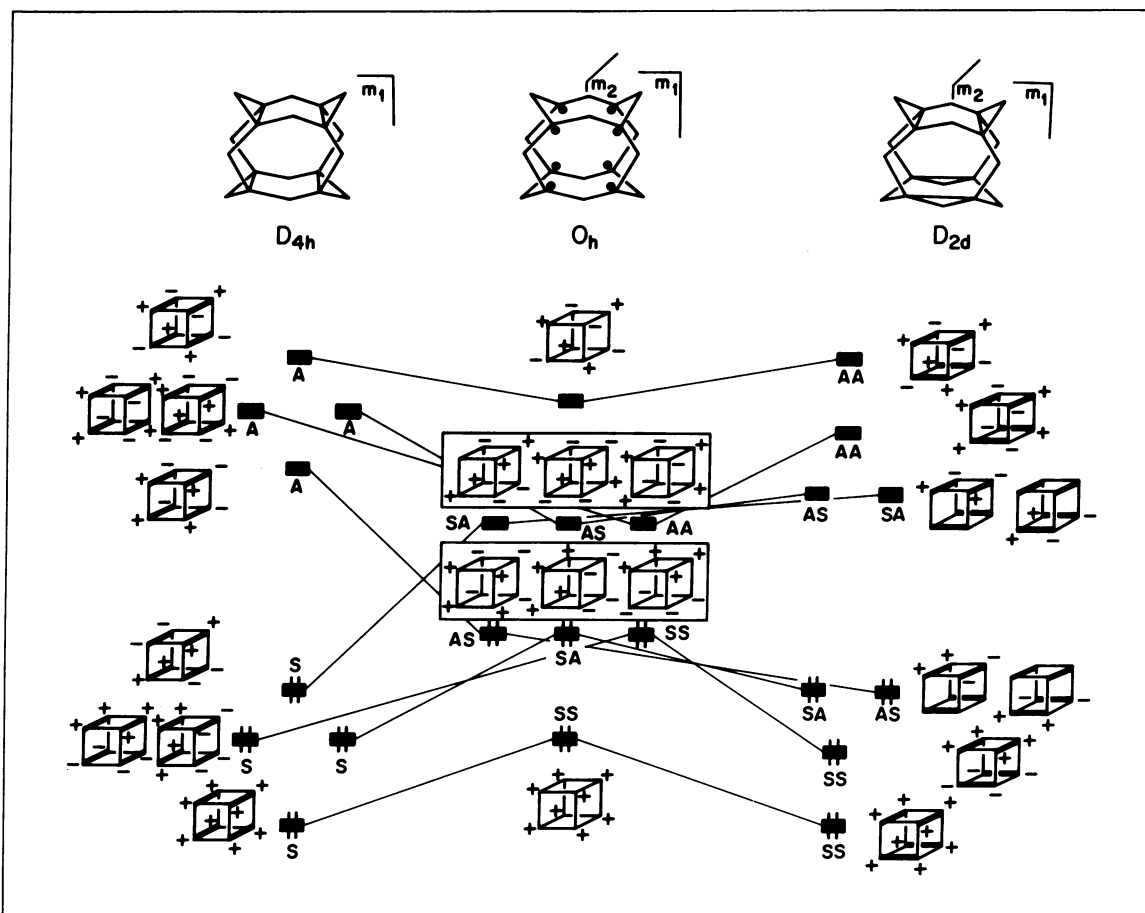
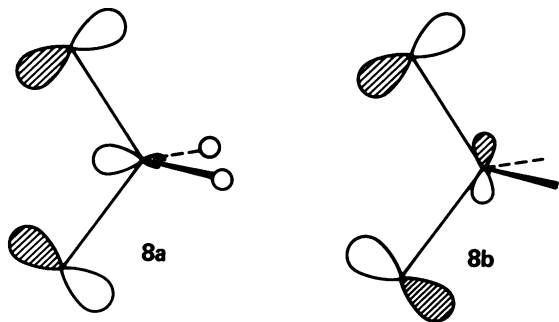


FIG. 2. Correlation diagram for the collapse of 3 (center) to two alternative isometric structures with fully formed σ bonds. The energy level ordering in these σ -bonded structures 6 (left) and 7 (right) is schematic and is not based on a detailed calculation. The + and - signs stand for orbital phases in σ or σ^* levels localized along the dark cube edges. Though relatively high (D_{4h} or D_{2d}) symmetry is maintained along the reaction paths, the levels are classified as symmetric (S) or antisymmetric (A) only with respect to the essential symmetry planes m_1 and m_2 .

with orbitals of the intervening CH_2 groups. There are two types of such destabilizing interactions, 8a and 8b, operating across locally symmetric or antisymmetric edge components of t_{1u} .



A similar destabilizing through-bond coupling affects the energy of the other molecular orbitals of 3 as well.

Our goal then might be reformulated as the increase of the through-space interaction (increasing the t_{1u} - t_{2g} gap) and decrease of the through-bond coupling, if possible, in the t_{1u} HOMO alone. We tried to increase the through-space interaction by making the radical center orbitals more diffuse. This was accomplished by changing the Slater exponent of the radical center carbons from 1.625 to 1.3 (a value close to that

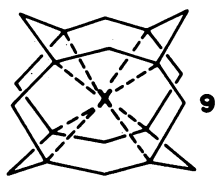
of boron). The HOMO-LUMO gap did increase to 1.9 eV, a desired effect, but all the levels moved up in energy. This suggests a substantial and undesired increase in the through-bond destabilization.

Through-bond coupling can be manipulated by introducing substituents on the CH_2 bridges or by changing the bridging carbon to a heteroatom. For reasons of computational economy, we were constrained to simulation of the effect by modification of the electronegativity of the bridging carbon. A decrease in through-bond coupling is desirable, and this might be achieved by σ -electron-withdrawing substituents on the bridge, modeled by a more electronegative bridging carbon. Calculations confirm this line of reasoning, but the overall effect is small. For instance, endowing the bridging carbons with the extended Hückel parameters of nitrogen lowers the HOMO by ≈ 0.05 eV and increases the HOMO-LUMO gap to 0.75 eV. We do not judge these perturbations to be very effective. More drastic measures are called for.

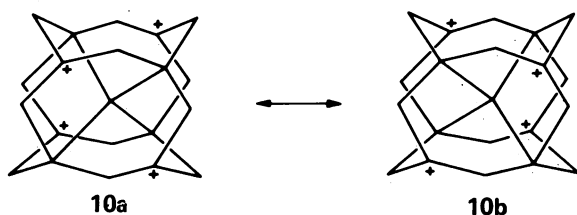
Possible use of the octaradical as a cage

Molecule 3 has the geometrical features of a cubical cryptate. Ideally the atom that it could encapsulate should provide orbitals of appropriate symmetry to stabilize the octaradical a_{1g} and t_{1u} orbitals and destabilize the LUMO t_{2g} . The system

under discussion is 9.



A C^{4+} atom seems to be a good candidate for the central atom X. It has low-lying empty s and p orbitals of a_{1g} and t_{1u} symmetry, respectively. Indeed, a calculation of the octaradical including a C^{4+} in its center (Fig. 3) shows a stabilization of 1.2 eV in t_{1u} , and even more in a_{1g} . The central C has no d orbitals to match the symmetry of the octaradical t_{2g} , so a substantial HOMO-LUMO gap results. A classical representation of this most hypothetical tetracation is given by the resonance structures 10a and 10b.



A similar stabilizing effect would be expected for main-group central atoms isoelectronic with C^{4+} , provided their low-lying s and p orbitals are diffuse enough to overlap strongly with a_{1g} and t_{1u} . Alkali cations may be unfavorable in this respect because their s and p orbitals lie at high energy.

The distance between cube center and radical carbon of 2.15 Å is not very well suited to a central C atom, but it is typical of transition metal-carbon separations. Fig. 4 shows the interaction diagram for a typical metal atom, iron, in the middle of the cage. Although the metal d functions are most effective at de-

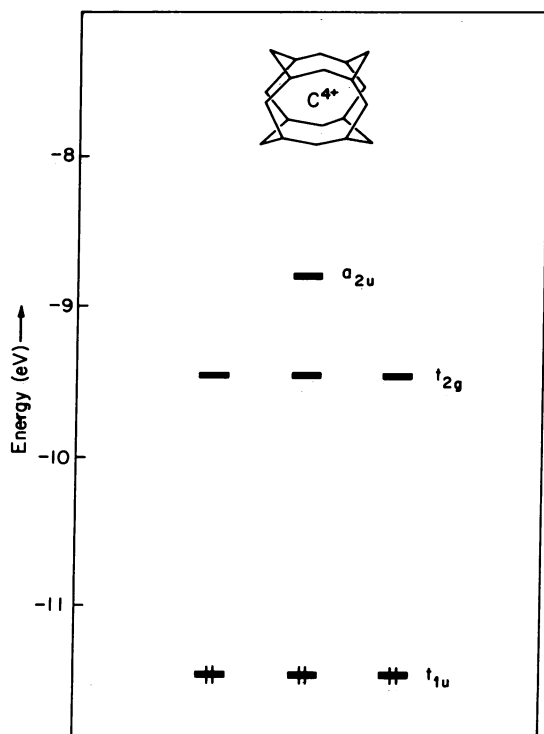


FIG. 3. Energy levels of the octaradical after interaction with a central C^{4+} .

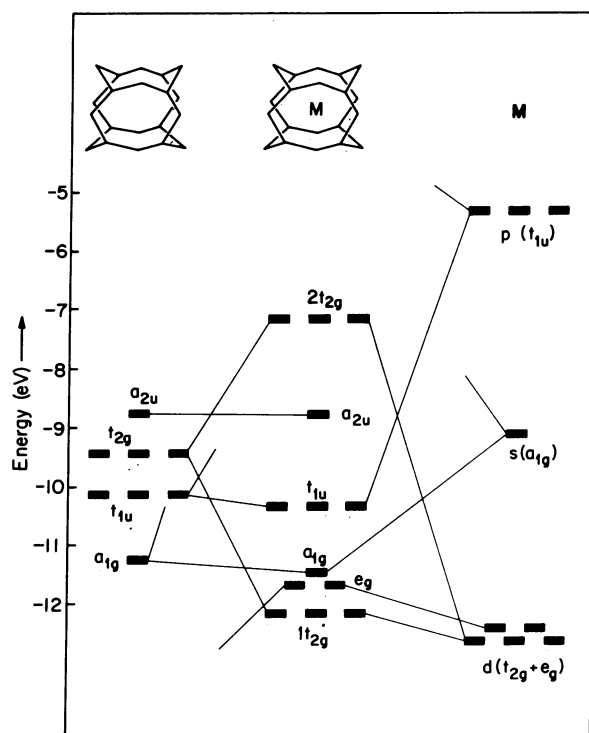
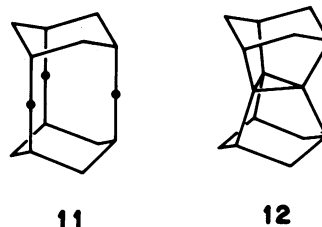


FIG. 4. Interaction diagram for the octaradical (left) with a central iron atom (right).

stabilizing the octaradical t_{2g} LUMO, the interaction of a_{1g} and t_{1u} with metal s and p orbitals is very weak. If the iron atom parameters are typical, then closed-shell low-spin configurations will be obtained for a neutral $C_{20}H_{24}M$, in which M is a d^4 (t_{1u} empty) or a d^{10} (t_{1u} filled) transition metal center. It has not escaped our attention that the low-lying a_{2u} orbital of the cage has the proper symmetry to interact with a central metal f orbital, but detailed examination of the case for which M is an actinide must await the future.

A carbenoid triradical

The two previously discussed molecules made use of sp^2 radical centers and of sp^2 or sp^3 units for the framework of the molecule. An alternative construction principle makes use of linear sp diradical centers, i.e., carbenes. Molecule 11 is an example. It contains a triangle of linear two-coordinate atoms suspended between two cyclohexanes. The attachment to the cyclohexane axial sites is free of strain, but one cannot say that such a tri-carbene is strain free because carbenes, be they singlet or triplet, are bent (9).



It may be easily seen that repetition of the motif 11 can fill space. The extended structure would be composed of alternating layers of diamond-like cyclohexane rings and triangular nets of carbenoid carbons. The electronic structure of this hypothetical material will be described elsewhere.

The carbene-like carbons of 11 are 2.515 Å apart in our model. A calculation on the molecule gives as the frontier orbitals the typical Walsh-type pattern (10) of Fig. 5. The HOMO-LUMO gap is only 0.65 eV. As in the other molecules

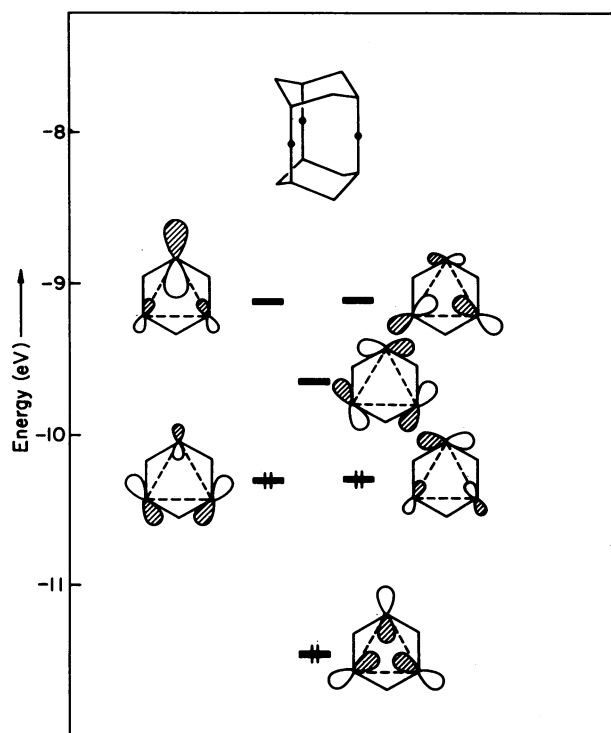


FIG. 5. Top view, onto the median horizontal mirror plane, of the orbitals of 11.

reported here, these orbitals are destabilized by through-bond interaction. The Walsh pattern of interaction unfortunately guarantees that collapse to 12, a three-membered ring sandwiched between cyclohexanes, is an allowed reaction. A related molecule, triaxane, built up of a three-membered ring atop a single cyclohexane ring, has been synthesized (11).

The calculations reported here are of the extended Hückel

type, with standard carbon and hydrogen parameters (12) and with parameters for iron taken from ref. 13. For a theoretical study of other carbon network alternatives to graphite, the reader is directed to ref. 14.

The angular relationships in a cube-octahedron, 4b, were pointed out to us by Frank Delk. The ORTEP plots were generated by Bruce Tagle. The drawings were skillfully rendered by J. Jorgensen. We are grateful to the National Science Foundation for its support of this work through Research Grants CHE 7828048 and DMR 7681083, the latter to the Materials Science Center at Cornell University.

- Bright, D., Maxwell, L. E. & de Boer, J. (1973) *J. Chem. Soc. Perkin Trans. 2*, 2101-2105.
- Jameson, M. B. & Penfold, B. R. (1965) *J. Chem. Soc.*, 528-536.
- Jungk, A. E. (1972) *Chem. Ber.* 105, 1595-1613.
- Einspahr, H., Robert, J. B., Marsh, R. E. & Roberts, J. D. (1973) *Acta Crystallogr.* B29, 1611-1617.
- Handal, J., White, J. G., Franck, R. W., Yuh, Y. H. & Allinger, N. L. (1977) *J. Am. Chem. Soc.* 99, 3345-3349.
- Ginsburg, D. (1975) *Propellanes, Structure and Reactions* (Verlag Chemie, Weinheim, W. Germany).
- Drouin, J., Leyendecker, F. & Conia, J. M. (1975) *Tetrahedron Lett.*, 4053-4056.
- Stanton, R. E. & McIver, J. W., Jr. (1975) *J. Am. Chem. Soc.* 97, 3632-3646.
- Harrison, J. F. (1971) in *Carbene Chemistry*, ed. Kirmse, W. (Academic, New York), 2nd Ed., pp. 159-193.
- Hoffmann, R. (1971) *Special Lectures at 23rd International Congress of Pure and Applied Chemistry* (Butterworths, London), Vol. 2, pp. 233-250.
- Nickon, A. & Pandit, G. D. (1968) *Tetrahedron Lett.*, 3663-3666.
- Hoffmann, R. (1963) *J. Chem. Phys.* 39, 1397-1412.
- Albright, T. A., Hofmann, P. & Hoffmann, R. (1977) *J. Am. Chem. Soc.* 99, 7546-7557.
- Balaban, A. T., Rentia, C. C. & Ciupitu, E. (1968) *Rev. Roum. Chim.* 13, 231-247; erratum, 1233.