

THE GEOMETRIES OF TETRACOORDINATE CARBON

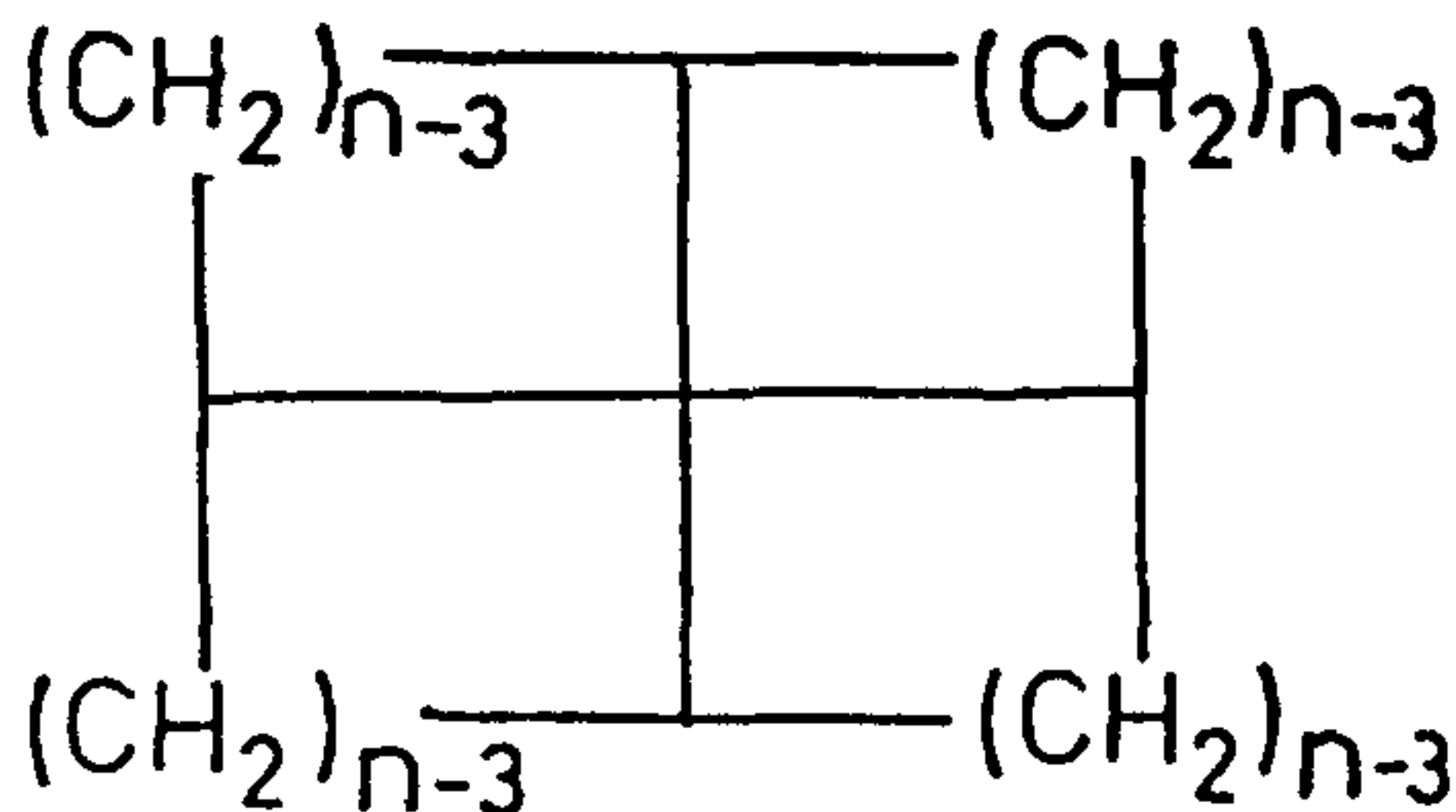
ELUVATHINGAL D. JEMMIS

School of Chemistry, University of Hyderabad, Central University P.O.,
Hyderabad 500 134, India.

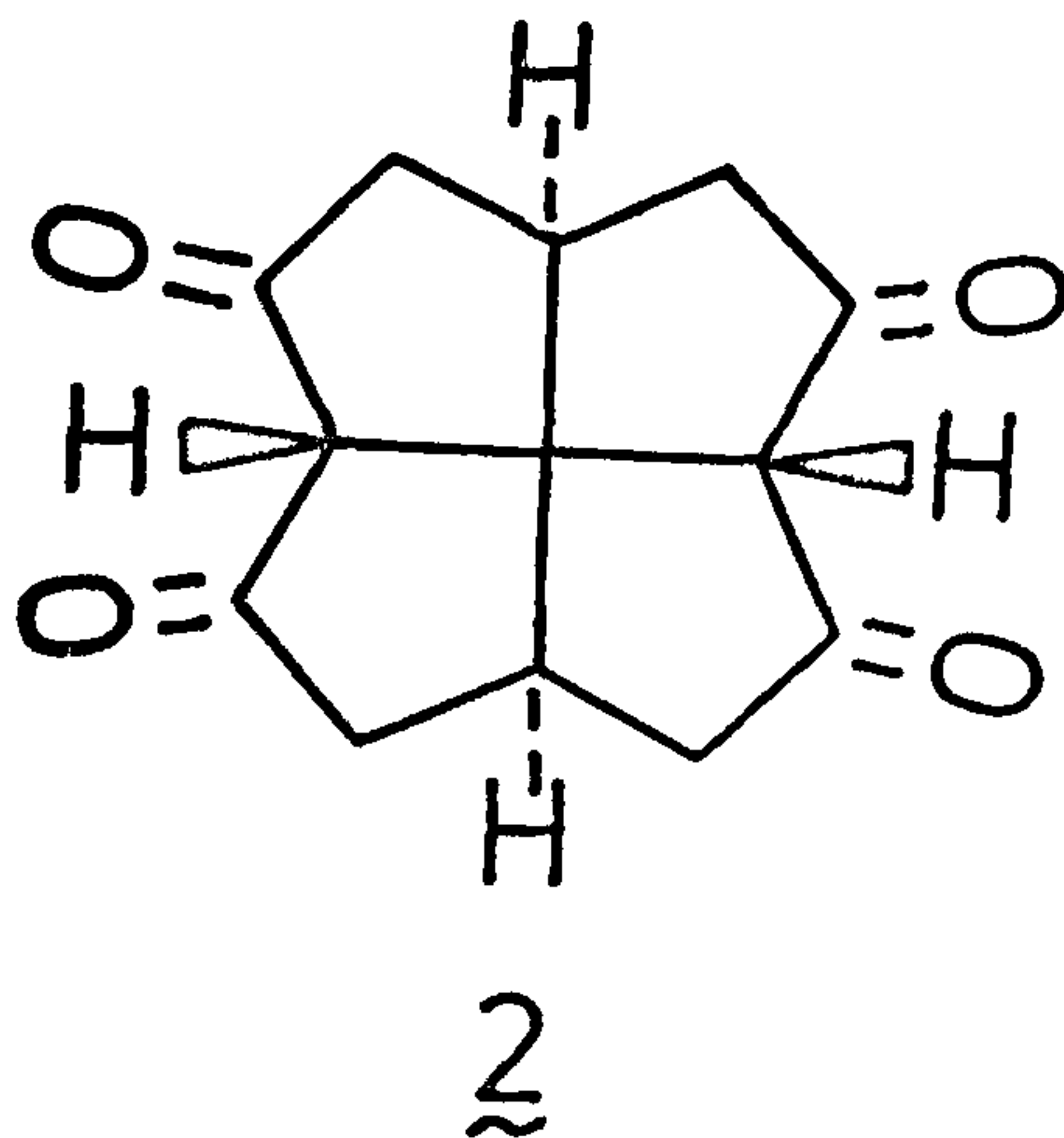
ABSTRACT

Walsh diagram for the distortion of methane ($D_{2d} \rightarrow T_d \rightarrow D_{2d} \rightarrow D_{4h}$ and $D_{4h} \rightarrow C_{4v}$) shows qualitatively the reasons for the instability of planar or pyramidal tetracoordinate carbon compounds. Various methods available for stabilization of these unusual geometries are reviewed briefly.

THE most important tenet of structural organic chemistry is the directional valence of carbon, commonly associated with the hybridization of the valence orbitals of carbon atom. Accordingly, tetracoordinate carbon prefers tetrahedral arrangement of substituents (sp^3 hybridization as in methane), tricoordinate carbon prefers trigonal planar arrangement (sp^2 hybridization as in ethylene) and bicoordinate carbon prefers linear arrangement (sp hybridization as in acetylene). Together with the concept of π -bonding these rules explain the ground state structures of most organic molecules. Even though ideal bond angles (109.47° tetrahedral, 120° trigonal planar) exist only in highly symmetric molecules such as methane and benzene deviations from ideal values are normally small. These rules were suggested, long before modern electronic structure theory was established, from experimental observations on the number of isomers of a given molecular formula, high barriers of isomerization of optical and geometric iso-



mers and tremendous intuition^{1,2}. Chemists have been trying to violate these rules. For example attempts have been made to synthesize molecules that would sterically require a planar arrangement around carbon atom. [n.n.n.n] Fenestrane (1) are common targets^{3a}. The smallest experimentally known fenestrane (2) has the central carbon atom in a distorted tetrahedral geometry^{3b,c}. Semiempirical calculation on [4.4.4.4] fenestrane shows it to be highly strained^{4,5}. Besides, the two low energy isomers of [4.4.4.4] fenestrane (3) and (4) are calculated to have non-planar arrangement of substituents around the central carbon atom. There has been several suggestions of planar tetracoordinate carbon as intermediates in the racemization of optically





active organic compounds, but no such reaction was observed.^{6,7}

The stabilization of planar tetracoordinate carbon may be better achieved by removing the factors that destabilize it rather than by the 'brute force' method used above. The electronic structure of methane in various geometries should help in identifying these factors.

DISTORTIONS OF METHANE

What happens when methane is distorted away from tetrahedral geometry? A Walsh dia-

gram may be constructed for the change D_{2d} (5) \rightarrow T_d (6) \rightarrow D_{2d} (7) \rightarrow D_{4h} (8) by increasing the angle α ^{8,9}. Figure 1 shows this diagram together with the distortion D_{4h} (8) \rightarrow C_{4v} (9) brought by increasing β . The lowest occupied molecular orbital shown in the diagram does not change considerably during the various distortions. The triply degenerate orbital splits into a set of two and one in either of the D_{2d} geometries. The nodal properties of the molecular orbitals involved explain the changes in energy of each MO during the distortions. For example the b_2 orbital in D_{2d} (a_{2u} in D_{4h}) goes up in energy for the distortions $D_{2d} \rightarrow T_d \rightarrow D_{2d} \rightarrow D_{4h}$ and comes down in energy during pyramidalization ($D_{4h} \rightarrow C_{4v}$, figure 1). The changes in this mole-

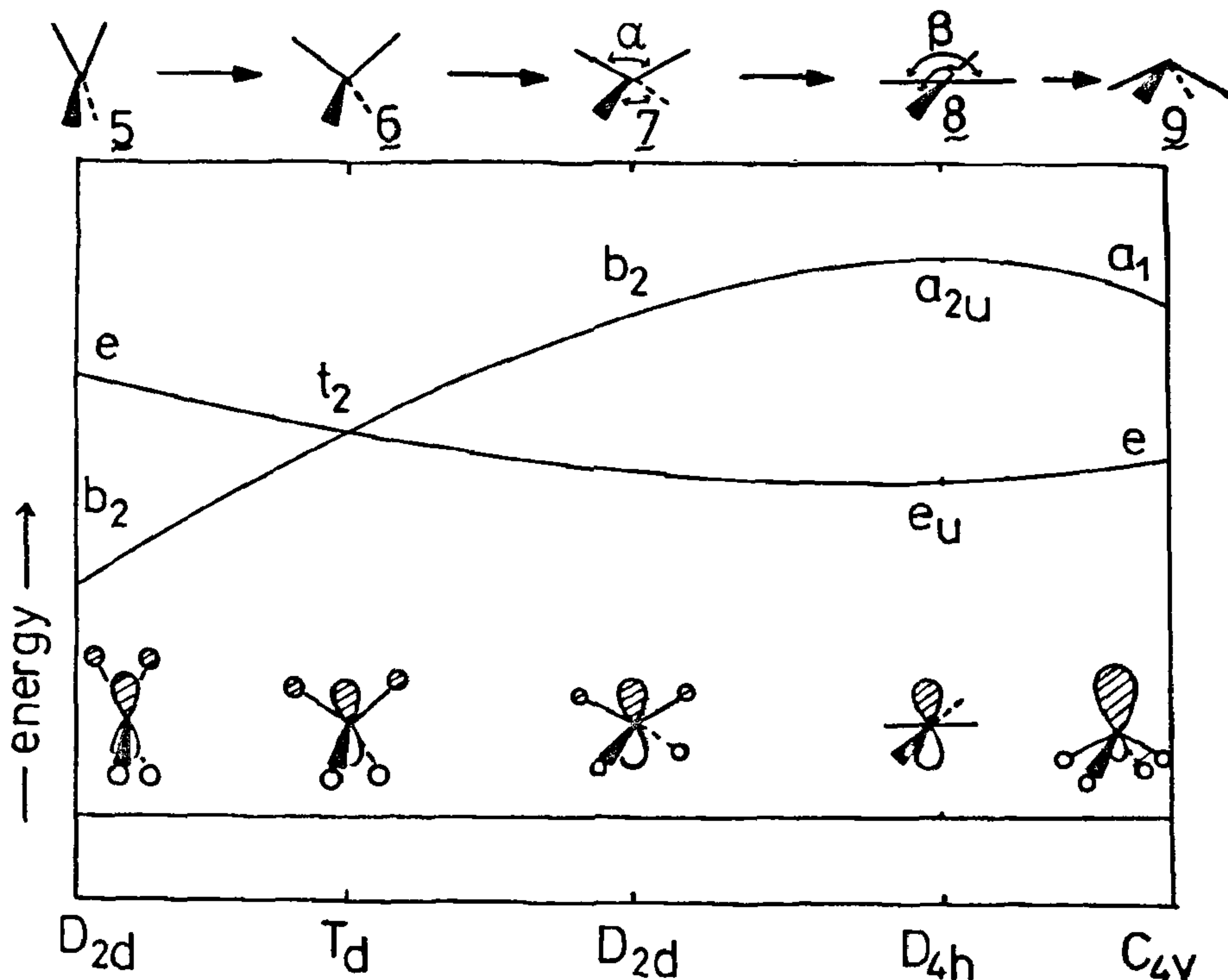
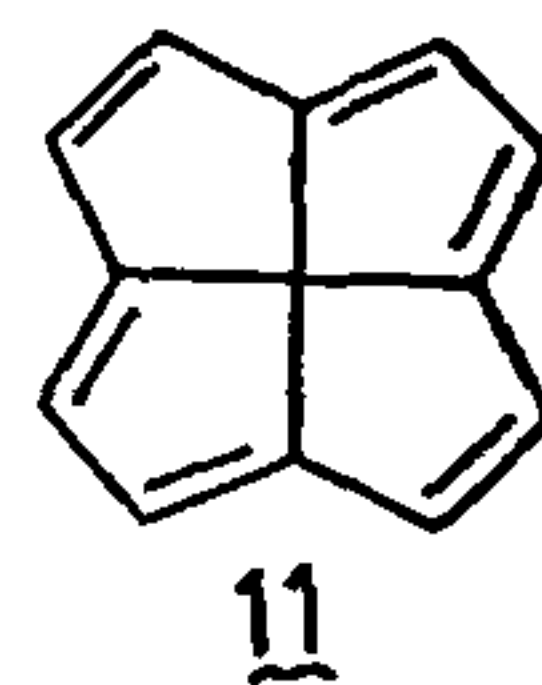
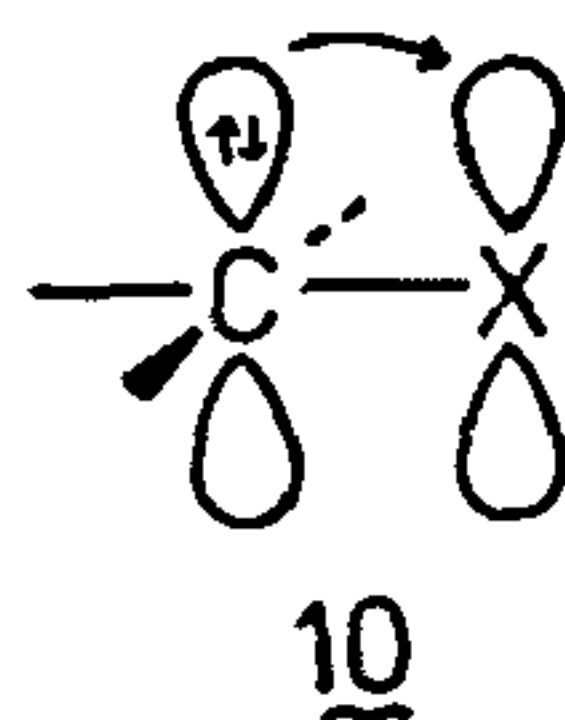


Figure 1. Walsh diagram (in fact a combination of two Walsh diagrams) for the distortion of CH_4 through various geometries. The first part ($D_{2d} \rightarrow T_d \rightarrow D_{2d} \rightarrow D_{4h}$) is obtained by the change of α . Increase of β gives the second part ($D_{4h} \rightarrow C_{4v}$). The molecular orbital pictured at the lower part corresponds to that of b_2 orbital (in D_{2d} and a_{2u} in D_{4h}).

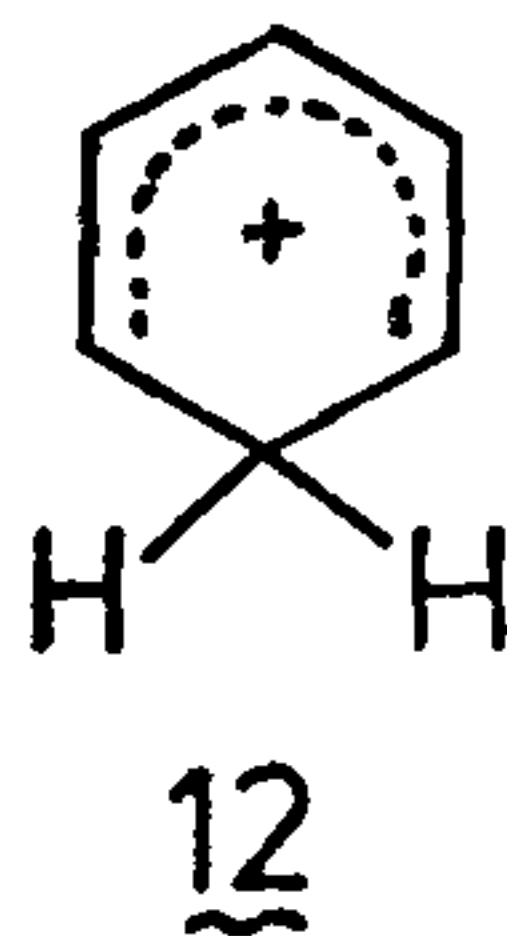
cular orbital at various points along the process is shown in the lower part of figure 1. Initially the MO loses C-H bonding character, becoming a totally nonbonding p orbital in **8**. Further distortion to **9** brings in some C-H bonding (figure 1 extreme right). In this one electron picture the minimum energy geometry of methane corresponds to the optimum point taking into account of all the occupied levels. This treatment of distortions of methane shows the reasons for the instability of planar methane¹⁰⁻¹². Two electrons that contribute to C-H binding in **6** are nonbonding in **8**. Consequently carbon atom acquires more negative charge. Each C-H bond is weaker because there are only six electrons to form the four C-H bonds. The large destabilization of planar methane (**8**) has been confirmed by numerical calculations¹², the best estimate being 150 kcal/mol relative to **6**. In view of the high energy of square planar methane it is not surprising that no racemization of an optically active organic compound is known to take place via a planar carbon species.

The simplest way to stabilize **8** will be to remove the two nonbonding electrons. The Walsh diagram clearly indicates D_{4h} as the preferred structure of CH_4^{+2} . Theoretical studies at various levels show the D_{4h} structure to be an energy minimum with substantial barrier for decomposition to CH_3^+ and H^+ . CH_4^{+2} has been characterized experimentally¹⁴. Despite the increased interest in dications, CH_4^{+2} is a very uncommon species. Let us look at ways of stabilizing planar tetracoordinate carbon compounds that provide a formal octet of electrons around carbon.

Hoffmann, Alder and Wilcox first realized the importance of bringing the lone pair on the central carbon in **8** back into bonding¹⁰. This can be achieved in the planar geometry by substituting hydrogens with groups having acceptor orbitals (**10**). Thus C-X π -bonding increases, reducing the charge localization on carbon. Suggestions were made to locate carbon in the middle of an annulene perimeter¹⁰ as in **11**. Calculations using semi-empirical methods showed that these are too strained to be experimentally accessible¹⁵

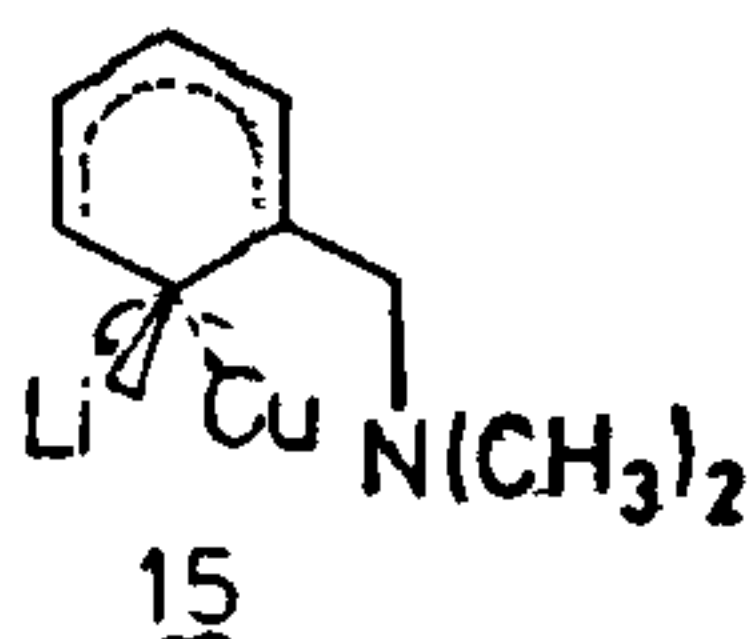
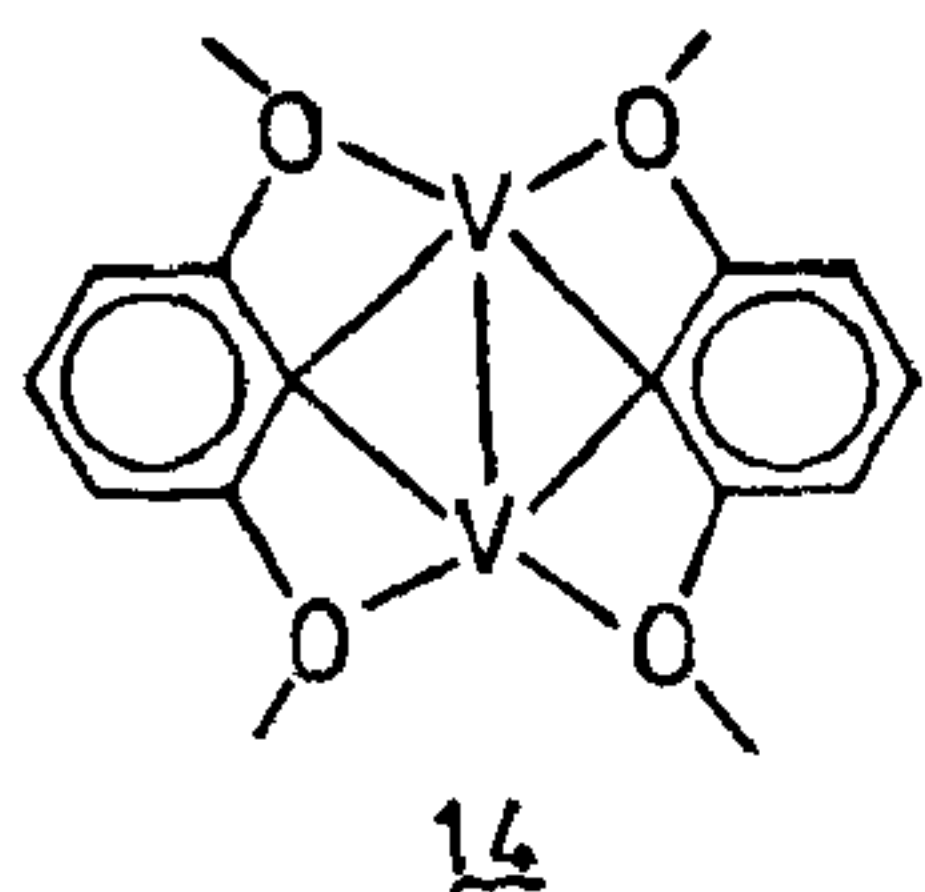


Some stabilization of the planar structure was obtained by incorporating the lone pair into an aromatic system^{10,12} e.g. **12** and **13**. However the calculated energy difference between planar and tetrahedral arrangements was still very large. The delocalization of the lone pair may be enhanced by increasing the charge on the central carbon atom. This is best done by selecting substituents which are more electropositive than carbon but are also π -acceptors. Boron, beryllium, lithium and silicon are ideal substituents¹⁰. Accordingly extensive calculations have been carried out on various methane derivatives. Let us consider a specific example, CH_2Li_2 . Calculations at various levels indicate that the planar tetrahedral energy difference is low enough for planar methane derivatives is 90° . This is a solid, first prepared in 1959,¹⁷ but its structure is not known. Like other organolithium compounds CH_2Li_2 may be polymeric in the solid state. Model calculations indicate that intermolecular association decreases the energy differ-



ence between planar and tetrahedral arrangements¹⁸. The only well characterized molecule with a planar tetracoordinate carbon has two metal substituents, (**14**)¹⁹. A rearrangement via planar tetracoordinate carbon has been suggested for compound **15**, in solution²⁰.

Introduction of small rings also should help to stabilize the planar form as the 'normal' angle in planar methane derivatives is 90° . This is

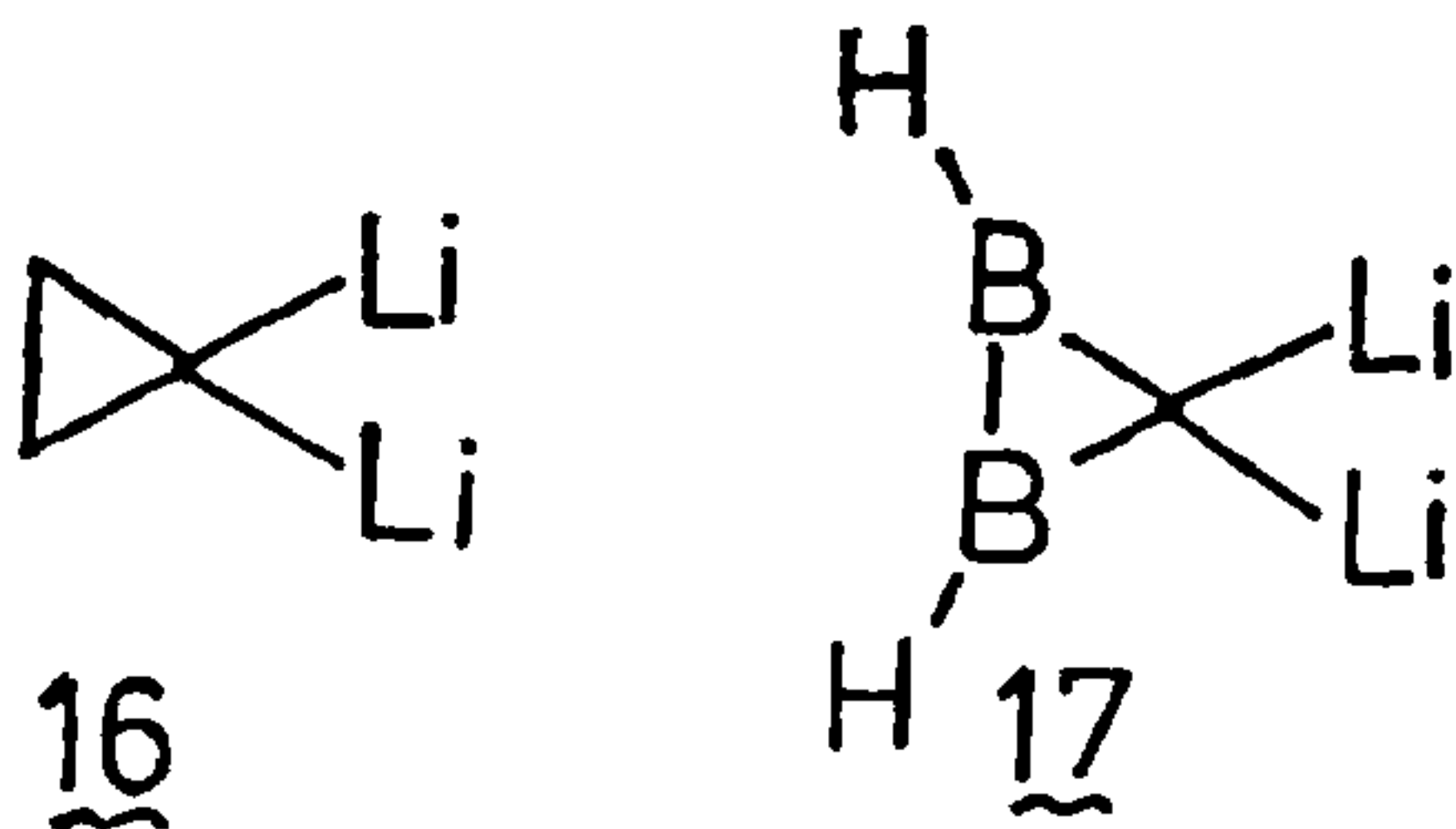


another way of looking at the traditional brute force approach. Best possible candidates will be obtained by incorporating all the three ways of stabilizing the planar carbon: π -acceptance, and σ -donation by electropositive substituents, and strain effects. Molecules 16 and 17 that take advantage of all the three effects are calculated to favour planar arrangement at the carbon having electropositive substituents^{12,21}. These are not yet known, but the ingenuity of the experimentalist is boundless.

Another tetracoordinate geometry available for carbon is square pyramidal. The Walsh diagram (figure 1) shows that a square pyramidal tetracoordinate CH_4 (9) will be more stable than

8 and will have a lone pair as in ammonia. The all cis isomer of [4.4.4.4.] fenestrane, 4, is calculated to have a square pyramidal arrangement at the central carbon atom^{4,5}. The pyramidal structure 18 has been calculated to be an energy minimum on the potential energy surface of C_5H_4 but no experimental evidence is yet available for its structure^{22,23}.

The problem of planar tetracoordinate carbon may appear esoteric, but part of the uncommonness of this problem lies in the training of chemists. Every undergraduate student learns about the inversion of ammonia as an isolated experimental observation. One rarely hears of the possible linear inversion of water or the 'inversion' of methane (hydrides of two atoms adjacent to nitrogen in the periodic table). It may be argued that the barrier for NH_3 inversion is in the range easily accessible in the laboratory. Should easy accessibility alone be a reason to study one system and ignore another? It is possible to find substituents to raise the barrier in tricoordinated nitrogen and to lower the barrier for linear inversion in dicoordinate oxygen. So 'easy accessibility' is variable. What is required is a wider outlook towards chemistry so that problems will not be dealt in isolation. Wherever possible theoretical methods available may be used to bring different aspects of chemistry together.



- (a) van't Hoff, J. H., *Arch. Neerl. Sci. Exactes Nat.*, 1874, 445, translated in 'Classics in the Theory of Chemical Combinations', Benfey, O. T. (ed), Dover Publications, New York, N. Y. 1963, (b) Le Bel, J. A., *Bull. Soc. Chim. Fr.*, 1874, 22, 337, (c) A historical review is given in 'van't Hoff-Le Bel Centennial', (ed.), Ramsay, O. E. American Chemical Society Symposium Series 12, Washington, 1975.
- van't Hoff, J. H. 'La Chimie dans L'Espace', Bazenijk, Rotterdam, 1875, see 'The Arrangement of Atoms in Space', 2nd Ed., Longmans, Green and Co., New York, 1898.
- (a) Keese, R., *Nachr. Chem. Tech. Lab.*, 1982, 30, 844. This reference is a review with special importance given to fenestrans. (b) Mitschka, R., Cook, J. M. and Weiss, U. *J. Am. Chem. Soc.*, 1978, 100, 3973. (c) Han, W. C., Takahashi, K., Cook, J. M., Weiss, U. and Silverton, J. V., *J. Am. Chem. Soc.*, 1982, 104, 318.

4. Wurthwein, E. U., Chandrasekhar, J., Jemmis, E. D. and Schleyer, P. V. R., *Tetrahedron Lett.*, 1981, **22**, 843.
5. Minkin, V. I., Minyaev, R. M. and Natanson, V. I., *Zh. Org. Khim.*, 1980, **16**, 673.
6. Werner, A., 'Lehrbuch der Stereochemie', Fischer, G., Jena, 1904.
7. Smith, F. T., *J. Chem. Phys.*, 1958, **29**, 235.
8. Gimarc, B. M., 'Molecular Structure and Bonding', Academic Press, New York, 1979.
9. Buenker, R. J. and Peyerimhoff, S. D., *Chem. Rev.*, 1974, **74**, 127.
10. Hoffmann, R., Alder, R. W. and Wilcox, Jr., C. F., *J. Am. Chem. Soc.*, 1970, **92**, 4992.
11. Hoffmann, R., *Pure Appl. Chem.*, 1971, **28**, 181.
12. Collins, J. B., Dill, J. D., Jemmis, E. D., Apeloig, Y., Schleyer, P. v. R., Seger, R., and Pople, J. A., *J. Am. Chem. Soc.*, 1976, **98**, 5419.
13. Pople, J. A., Tidor, B. and Schleyer, P. v. R., *Chem. Phys. Lett.*, 1982, **88**, 533.
14. Ast, T., Porter, C. J., Proctor, C. J. and Beynon, J. H., *Chem. Phys. Lett.*, 1981, **78**, 439.
15. Chandrasekhar, J., Wurthwein, E. U. and Schleyer, P. v. R., *Tetrahedron*, 1981, **37**, 921.
16. (a) Janoschek, R., *The Jerusalem Symposium on Quantum Chemistry and Biology*, Vol. X, 1977, (b) Laidig, W. D. and Schaefer, H. F. III, *J. Am. Chem. Soc.*, 1978, **100**, 5972.
17. Ziegler, K., Nagel, K. and Patheiger, M., *Z. Anorg. Allg. Chem.*, 195, **282**, 345.
18. Jemmis, E. D., Schleyer, P. v. R. and Pople, J. A., *J. Organomet. Chem.*, 1978, **154**, 327.
19. Cotton, F. A. and Millar, M., *J. Am. Chem. Soc.*, 1977, **99**, 7886.
20. Koten, G. V. and Noltes, J. G., *J. Am. Chem. Soc.*, 1979, **101**, 6593.
21. Krogh-Jespersen, K., Cremer, D., Poppinger, D., Pople, J. A., Schleyer, P. V. R. and Chandrasekhar, J., *J. Am. Chem. Soc.*, 1979, **101**, 4843.
22. Jemmis, E. D. and Schleyer, P. v. R., *J. Am. Chem. Soc.*, 1982, **104**, 4781.
23. Minkin, V. I. and Minyaev, R. M., *Zh. Org. Khim.*, 1979, **15**, 1569.

ANNOUNCEMENT

SACRAMENTO PEAK OBSERVATORY, NEW MEXICO

The National Solar Observatory sponsored by the National Science Foundation, announces the availability of a limited number of Summer Research Assistantships for graduate students and well qualified undergraduates (Seniors). The Observatory, with facilities in the Sacramento mountains in south-central New Mexico and at Kitt Peak in south-central Arizona, has on-going research programs in solar physics, space instrumentation, solar terrestrial relations, and stellar astrophysics. Students selected will be given the opportunity to work closely with one of the observatory staff members on a research program of mutual interest. Stipends will be commensurate with the student's academic standing. Travel within

North America will be provided.

Application forms for the Summer Research Assistantship program may be obtained from: Dr. Stephen L. Keil, National Solar Observatory, Sunspot, New Mexico 88349.

Inquiries for additional information on the facilities and staff research interests may also be addressed to Dr. Keil. In addition to the application form, each applicant should send a letter detailing research interests and experience, transcripts from all colleges and universities attended, and two letters of recommendation to the above address. Application materials are due by 1 February 1984, while announcements of selections will be made by 16th March 1984.