35. Planarization of Tetracoordinate Carbon Atom. Synthesis of 13-Oxa-14-oxo-pentacyclo [5.5.2.1.$0^{4,15}0^{10,15}$]pentadecane, a Bridged 'Tetraquinacane'

Preliminary communication

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Summary

Structural aspects of planoid deformation of tetracoordinate carbon atom, particularly those in annulenes with central carbon atom are discussed. [12]Annulene **11** with central carbon atom is proposed as compound with strong planoid deformation around the internal carbon centre. The synthesis of a saturated precursor **15** is described.

The theory of *Van't Hoff* and *Le Bel* requires 4 equal ligands of a tetracoordinate carbon atom to be arranged as a tetrahedron [1] [2]. Although the tenet is basic to organic chemistry, no test has been made of how far planoid deformation without bond breaking is possible. Experimental evidence has shown that racemization of chiral carbon compounds does not occur without breaking a bond [3].

The bonding and energetic situation of tetracoordinate tetrahedral as well as of planar carbon atom has been discussed extensively [4] [5]. In tetrahedrally coordinated carbon compounds the bonds can be described as being formed from one $2s$ and three $2p$ orbitals and an appropriate linear combination of ligand orbitals, giving rise to 4 bonding molecular orbitals, each occupied by 2 electrons, and 4 antibonding ones. For planar coordination the central carbon atom can only use one $2s$ and two $2p$ atomic orbitals for σ-bonding to the 4 ligands giving rise to 3 orbitals, occupied by 6 electrons. The orthogonal nonbonding $2p$ orbital is occupied by the remaining 2 electrons *(Fig. 1)*.

According to this bonding model, the difference in stability between the tetrahedral and the planar configuration is mainly due to the increasing energy of one of the 3 degenerate (T_2) MO's, which is correlated with the $2p$-AO of A_{2u}-symmetry in the square planar form. This suggests in terms of average C–H bond energies that the planar arrangement should be roughly 80-100 kcal/mol less stable than tetrahedrally coordinated carbon atom. It is thus not too surprising that autoracemization without bond breaking has not been observed.

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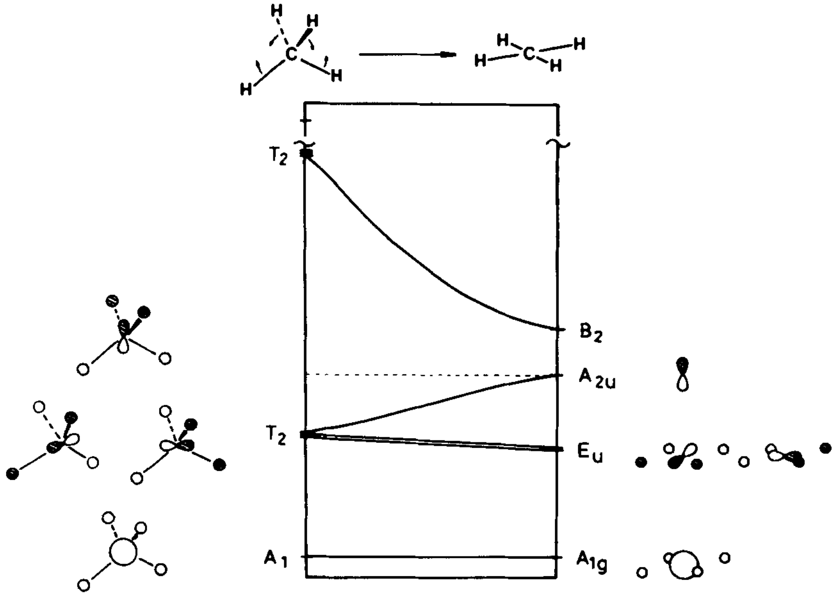


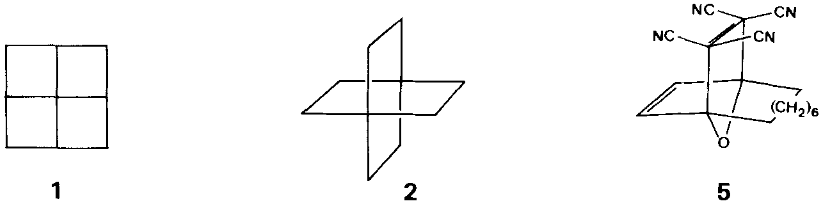
Fig. 1. *Molecular orbitals of a tetracoordinated tetrahedral or planar carbon atom*

Numerical calculations at different levels of sophistication have lead to values of 95-250 kcal/mol for this configurational change in methane [5i]. Recently it has been proposed that the D_{4h}-structure of methane is on top of a flat energy maximum, whereas a tetragonal pyramidal structure of C_{4v}-symmetry corresponds to a saddle point on the potential energy surface [6].

Despite these numerical aspects, various structures containing carbon centers with possibly planar coordination such as fenestranes (**1**) [7] and [2.2.2.2] paddlanes (**2**) [8] have been proposed, but none of these has as yet been prepared. It also seems that no processes involving a planar transition state are yet known. For example, thermal geometrical isomerizations of cyclopropanes occur by 2-centre epimerizations [9]. However, a transition state with planar tetracoordinate carbon has recently been proposed for the stereospecific reaction of 1-methyl-2,3-di(*t*-butyl)-thiirenium ion (**3**) with chloride ions giving **4** [10].

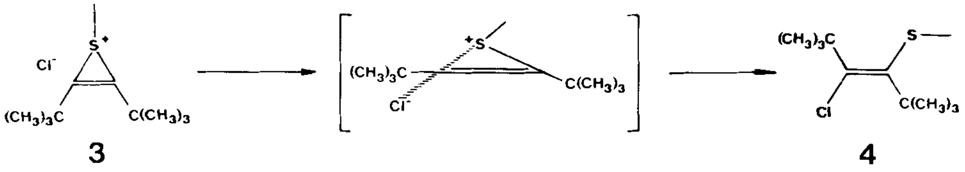
Short of cases where complete planarity could occur, the question remains of how far planoid distortion of the ligands of tetracoordinate carbon atom can be realized experimentally. Although the paddlane (**5**) has been prepared [11], the geometry around the bridgehead carbon atom has not been reported.

Scheme 1

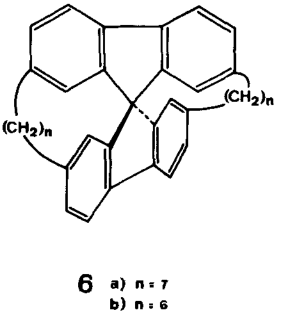


1 **2** **5**

Scheme 2



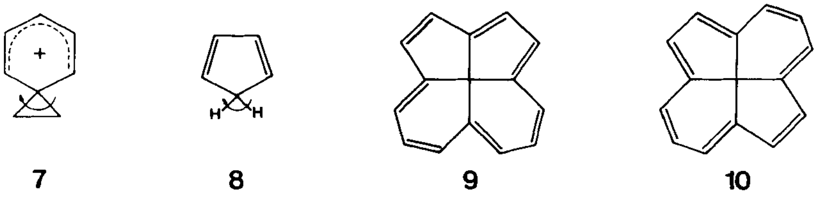
Scheme 3



In this context, X-ray structure analysis of the vespirenes **6a** and **6b** *(Scheme 3)* prepared by *Prelog & Haas* [12], shows planoid distortion at the central carbon²). Such structures certainly merit further attention.

Stabilization of planar, tetracoordinate carbon. The stability of the planar configuration is enhanced by interaction between the 2*p*-AO of planar tetracoordinate carbon and π-MO's of appropriate ligands. Computer-assisted investigations have shown that the hypothetical transition states of rotational barriers in compounds like **7** and **8** *(Scheme 4)* are stabilized by π-delocalization; molecules **9** and **10** possess closed-shell π-systems if planar [5b, c]. The energy difference between planar and tetrahedral arrangements should also be effectively reduced by ligands such as SiR_3, BR_2 or Li [5b], *i.e.* by ligands which combine reduced electron demand in σ-bonding with π-acceptor properties³). It has been proposed that lithium should be especially effective in stabilizing planar, tetracoordinate carbon atom; for example, 1,1-dilithiocyclopropane should prefer a planar arrangement [5i]. The potential for stabilization of tetracoordinate carbon atom with planar arrangement of the ligands is not limited to the above mentioned elements. The first compound

Scheme 4



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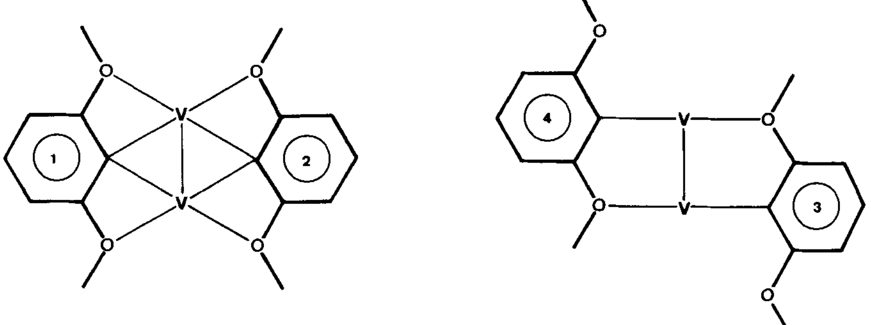
²) We thank Prof. *Prelog* for communication of these results prior to publication.

³) This bonding model has analogy in transition metal complexes. For example, in carbonyl complexes $:\overset{\ominus}{C}\equiv\overset{\oplus}{O}$ is simultaneously σ-donator and π-acceptor.

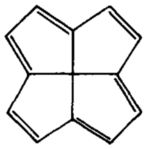
Scheme 5. *Two different planes of coordination in V_2(2,6-dimethoxyphenyl)$_4$ · 2THF*



containing planar, tetracoordinate carbon prepared is V_2(2,6-dimethoxyphenyl)$_4$ · 2THF [13]. As shown by X-ray analysis, the structure of this complex contains a plane common to one phenyl ring and 2 vanadium ligands *(Scheme 5)*.

Restricting possible model compounds to hydrocarbons, it is clear from the preceding arguments that an appropriate compound must contain structural elements which provide a considerable amount of bond angle deformation as well as a π-system for effective delocalization of an adjacent electron pair. We propose, therefore, tetracyclo$[5.5.1.0^{4,13}0^{10,13}]$tridecahexaene (**11**), a [12]annulene containing a symmetrically bound carbon centre, as a molecule with extensively planarized carbon atom[4] *(Scheme 6)*.

Scheme 6



11

Because of the pronounced tendency of carbon atom for covalent bonding, the bridgehead double bonds in **11** should exert a *planarizing force* on the adjacent σ-bonds to the central atom. Concomitant with the resulting strain localized to a large extent around the central carbon atom, the π-bonds of the annulene periphery should stabilize the electron pair of the developing $2p$-orbital. These 2 countercurrent effects, build-up of strain and stabilization by π-delocalization, could result in a structure containing a planoid tetracoordinate carbon atom. If the stabilization does not compensate the strain completely, racemization of monosubstituted derivatives of **11** should occur readily.

HMO-Aspects. The choice of **11** as a model compound in preference to other annulene ring systems with an internal carbon centre is illustrated by HMO-calculations. Assuming planarity, the interaction between the doubly occupied $2p$-orbital of the central carbon atom and a peripheral annulene π-system *(Scheme 7)* leads to

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[4] Some of the structural features of **11** have been discussed [5b].

Scheme 7

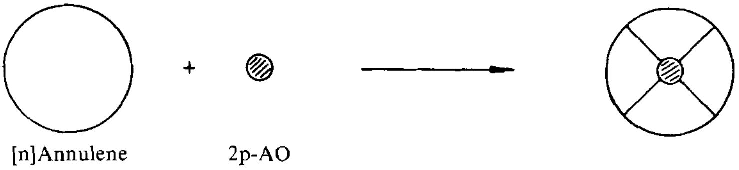

Table. *Delocalization energies of a* [*n*]*annulene with planar, central carbon atom*

n-Value of the [n]Annulene	Delocalization energy [β]	Delocalization energy [β] per peripheral double bond
8	1.657	0.414
10	1.950	0.39
12	2.646	0.44
14	2.939	0.418

conjugative stabilization. It is evident that the delocalization energy[5]) depends on the annulene ring system; it increases with increasing size of the annulene system (*cf.* the *Table*).

However, the delocalization energy per peripheral double bond in this series is largest for n = 12 and suggests that [12]annulene with a central carbon atom is a suitable model compound. Also, the sequence of MO resulting from the interaction between the π-system of [12]annulene and a 2p-orbital of the internal carbon centre is unique (*cf. Fig. 2*).

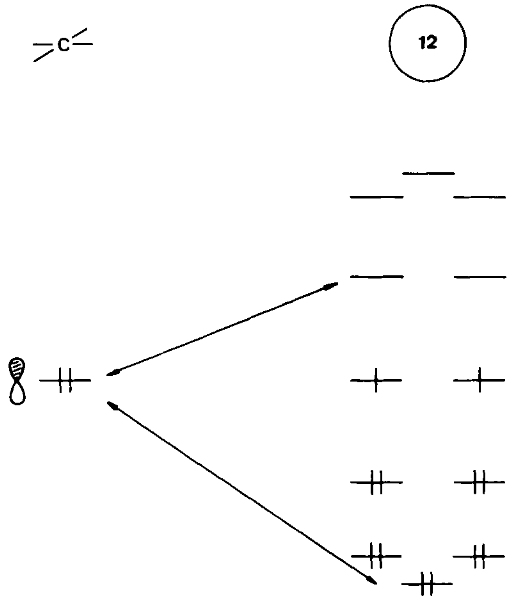

Fig. 2. *Interaction between the* π*-system of* [12]*annulene and a* 2p*-orbital of the central carbon atom*

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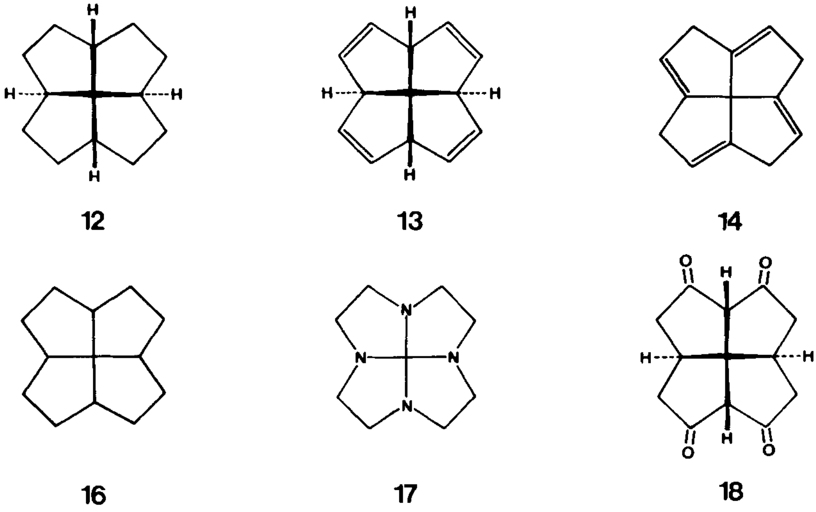
[5]) For a definition see [14].

Besides the interaction with the lowest bonding π-MO - which occurs with all annulene ring systems regardless of size - the $2p$-AO can only interact with one of the 2 degenerate MO's of the lowest *antibonding* set. Hence, the highest occupied MO's of the tetracyclic π-system of **11** are exclusively localized in the peripheral π-system and the stabilization of the electron pair of the $2p$-AO at the central, planar tetracoordinate carbon is independent of the number of electrons in these 2 nonbonding MO's. This suggests that the demand for π-electrons of the periphery could appropriately be adjusted by oxidation or reduction.

Force field results. Strain energy and angle deformation of structures like **12** and the unsaturated derivatives **13** and **14** have been explored by force field calculations6). As expected, the incorporation of bridgehead double bonds induces additional strain and leads to a weakening of the σ-bonds towards the central carbon atom. In case of complete planarization of the internal carbon centre the delocalized π-system of **14** would be stabilized by 2.5 β. Since this value is close to that found for **11** (*cf.* the *Table*), **14** is itself an attractive synthetic target. Finally, tetracyclo $[5.5.1.0^{4,13}0^{10,13}]$trideca-2,5,8,11-tetraene (**13**) has been proposed as molecule of synthetic interest [15].

Scheme 8



Synthesis of 13-oxa-14-oxopentacyclo $[5.5.2.1.0^{4,15}0^{10,15}]$pentadecane (**15**, *Scheme 10*). As the first step towards the synthesis of model compounds for tetracoordinate, planoid carbon atom, particularly **11** and **14**, the preparation of the saturated, functionalized precursor **15**, a disubstituted derivative of tetracyclo$[5.5.1.0^{4,13}0^{10,13}]$-tridecane (**12**) (tetraquinacane)7) is reported.

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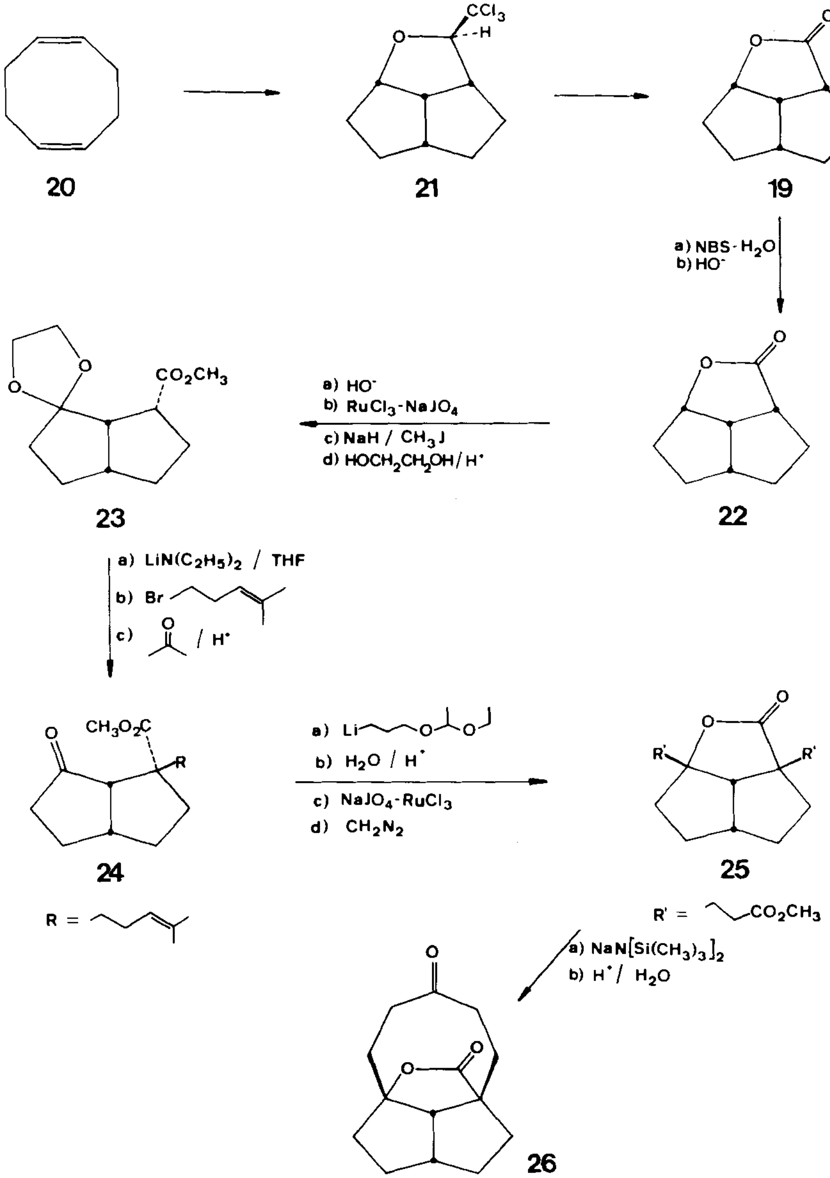
6) We thank Dr. *O. Ermer*, Universität Bochum, for these results. A detailed discussion of force field calculations in this area will be published in due course.

7) In analogy to triquinacane, we propose the name tetraquinacane for the saturated ring system tetracyclo$[5.5.1.0^{4,13}0^{10,13}]$tridecane (**12**) to indicate that 4 5-membered rings are connected by a common carbon atom. Of the 6 possible stereoisomers, the all-*cis* isomer **12** with D_{2d}-symmetry contains only *cis*-fused cyclopentane rings; it appears to be the least strained isomer.

Structures with 2 or more cyclopentane rings fused in an *ortho* and *peri* fashion have recently attracted attention, with the synthesis of triquinacene [16], peristylane [17] and related structures [18]. The first example of general structure **16** to be prepared is 1,4,7,10-tetraazatetracyclo$[5.5.1.0^{4,13}0^{10,13}]$tridecane (**17**) [19]. During the final stage of this work, a short and elegant synthesis of the tetraketone **18** has been published [20].

Scheme 9

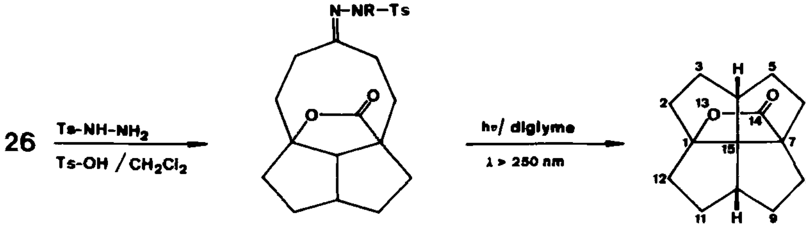


Starting material for the synthesis of **15** was the substituted oxatriquinacane **19**, which is readily available from cycloocta-1,5-diene **20** *via* **21** [21][8]).

The bromohydrin which is formed by reaction of **19** with *N*-bromosuccinimide in the presence of water gave upon treatment with base the lactone **22** in over 88% yield. Ruthenium (VIII)-catalyzed oxidation [22] of **22** under basic conditions followed by alkylating esterification [23] and treatment with ethyleneglycol yielded the acetalester **23** (39%), which, after base-induced alkylation with 4-methyl-pent-3-enylbromide and hydrolysis gave stereospecifically the ketoester **24** in 59% yield. Hydroxypropylation [24] of **24** furnished a 2-oxa-3-oxotriquinacane with 2 side-chains in configurationally fixed orientation. Both side-chains were oxidized simultaneously with ruthenium (VIII)oxide and gave after treatment with diazomethane the diester **25** (31%). The configuration of **25** is defined by the presence of the lactone bridge. Diester **25** was converted by *Dieckmann* condensation [25] to a mixture of isomeric *β*-ketoesters, which furnished after hydrolysis and decarboxylation the keto-lactone **26** in 67% yield.

Reaction of **26** with *p*-toluenesulfonylhydrazide in refluxing methylene chloride and removal of water furnished the corresponding *p*-toluenesulfonylhydrazone **27** (83%), leaving the lactone bridge unaffected.

Scheme 10



27

a) R = H
b) R = K

15

Photolysis of the dry potassium salt **27b** in diglyme yielded the tetraquinacane derivative **15** as the main product. The structure of **15** is supported by spectral data; in particular the C_s-symmetry is revealed by its ^{13}C-NMR. spectrum, which shows signals at 183.4, 101.8, 81.3 and 64.3 [quarternary carbon atoms C(14), C(1), C(7), C(15)], 50.3, 37.2, 36.8, 31.8 and 29.1 [C(4)/C(10) and (not assigned) C(2)/C(12), C(3)/C(11), C(5)/C(9), C(6)/C(2)].

The synthesis of **15**, an all-*cis* stereoisomer of the tetraquinacane family, has been achieved. Compounds like **15**, now becoming available, allow the investigation of hydrocarbons with the tetraquinacane skeleton. The specific functionality at 2 bridgeheads is well suited for the preparation of new bridgehead olefins and annulenes with central carbon atom. Strong planoid deformation at the central carbon atom of these compounds is to be expected.

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[8]) A full account of this work will appear in Helv.

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