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Novel main group-element cyclic molecules and their radical ions: are they aromatic?

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Abstract. - More than half a century ago, Erich Hückel in his classical publications forwarded the 4n + 2 rule for closed shell cyclic π systems. In the decades to follow, this intrigueing concept stimulated chemists to synthesize a manifold of then rather breath-taking molecules and molecular ions, slang-termed "aromatic" (greek: aromatikos = spicy smelling). Since then chemistry has progressed tremendously, especially by adopting a great variety of ingenious measurement methods from the physical armoury as well as by using advanced computer technology to perform quantum chemical calculations in ever higher precision for ever larger molecules. Today, highly reactive intermediates can be generated under partly extreme conditions and characterized by their spectroscopic molecular state 'fingerprints'. Concomittantly, simple chemical bonding models are more and more replaced by correlations closer to the reality of molecular states, i.e. the changes of structure with energy and charge. Molecular dynamics become important, especially to gain some insight into the largely unknown microscopic reaction pathways of medium-sized molecules. Examples predominantly from own research efforts are presented for illustration. They comprise e.g. the gasphase generation of silabenzene, tetrahedrane $\rightleftarrows$ cyclobutadiene conversions, perturbations of organic π systems by powerful main group element donor substituents as well as generation and properties of radical cations and anions with special emphasis on ion pairs and their isolation. Several total energy hypersurface calculations are presented to rationalize the experimental observations.

INTRODUCTION: PROPERTIES OF MOLECULES IN THEIR VARIOUS MOLECULAR STATES

"Where once have been the border-lines of science, there is now is its center ..."
Georg Christoph Lichtenberg (1742 - 1799)

The structures of molecules and hence their properties will change with energy and especially on acquisition or loss of electrons, generating molecular ions, which may be radicals and which also exist in numerous states of various energies (refs. 1,2 and Fig. 1: A). The individual state of a molecule or a molecular ion is characterized by the energy differences from a preceding or to a subsequent state, by its respective charge distribution i.e. its structure and by its molecular dynamics. A multitude of measurement techniques available from the physical armoury provides information both on the energy differences between and the structures of invidual molecular states (cf. examples given in Fig. 1: A). Accordingly, the total energy of the individual states of a molecule M increases from those of its stable radical anion $M^{\cdot\ominus}$ - formed, if M exhibits a negative electron affinity - via those of the neutral molecule M to those of its radical cation $M^{\cdot\oplus}$. As concerns their different structures, there are in addition to diffraction and microwave spectroscopic methods, many measurement techniques, which yield - for instance, via selection rules or from signal patterns for equivalent centers - information on their respective symmetry. And, not to forget, more sophisticated quantum chemical calculations do also provide reliable structural estimates (refs. 1-3), which are extremely valuable whenever an experimental determination is impossible.

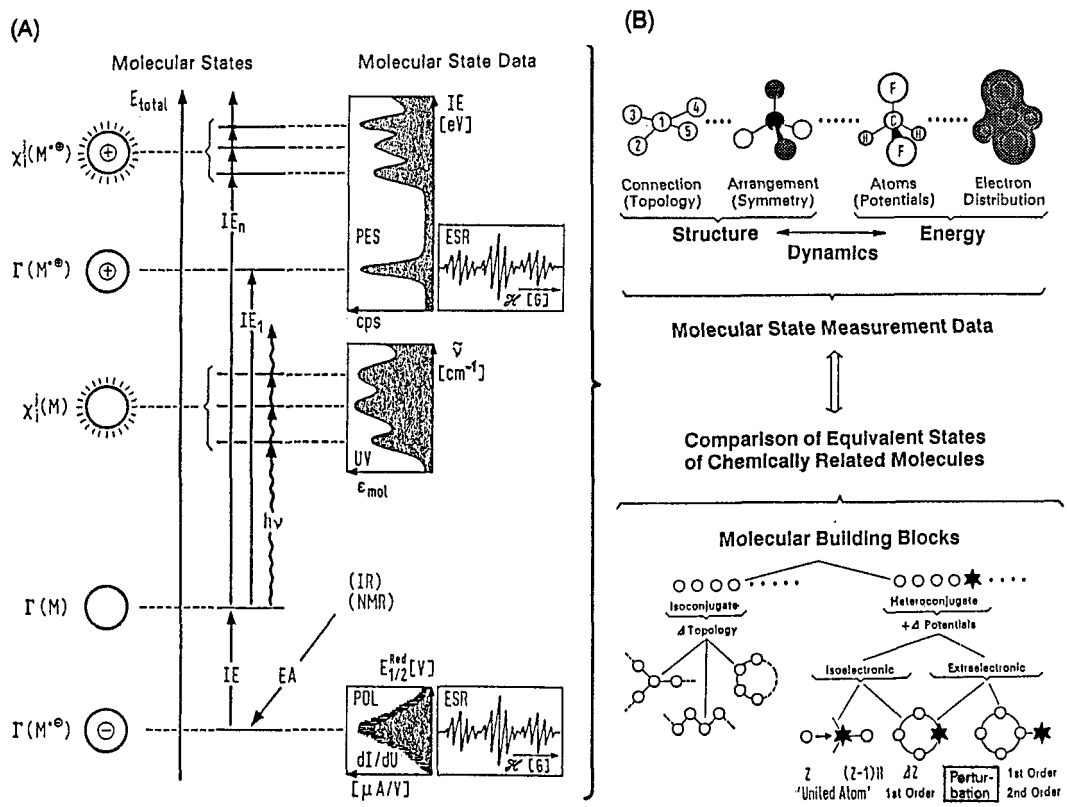


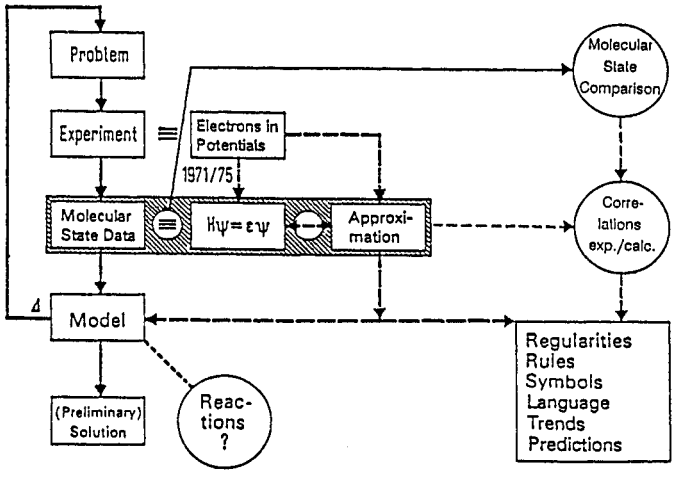
Fig. 1. (A) Selection from the multitude of molecular states comprising ground (Γ) and electronically (X_i^j) as well as vibrationally (IR) excited states of a neutral molecule M, its radical cation $M^{\cdot\oplus}$ and its radical anion $M^{\cdot\ominus}$, together with basic information as supplied by UV or PE spectra in the gasphase or by electrochemistry or ESR signal patterns in solution (see text).

Fig. 1. (B) Simplified approach to rationalize properties of molecular states by emphasizing connectivity, spatial arrangement, effective nuclear potentials and electron distribution as well as relationships between structure and energy as coupled by molecular dynamics. The comparison of equivalent states of chemically related molecules advantageously starts with the definition of molecular 'building blocks', which, if isoconjugate, may be rationalized in terms of their changing topology and, if heteroconjugate, may be discussed including the potential differences into first and second perturbation arguments (see text).

For the preparative chemist, however, the molecular states and their properties, which he measures day by day in order to identify, to analyze and to characterize his compounds (refs. 1,2), obviously are often difficult to rationalize and, therefore, quite some information inherent in his spectra remains unused. On the other hand, a simplified molecular state approach, which e.g. largely neglects the rather complicated molecular dynamics, is readily available (refs 1,2). It can be used by the chemist for his own benefit in many ways, for instance,

- ▷ to compare 'equivalent states' of 'chemically related', preferentially iso(valence)electronic molecules, thus making use of the vast general literature to stimulate his own research,
- ▷ to disentangle the multitude of known compounds and to rationalize their numerous properties by e.g. defining 'parent systems' and substituent perturbations (ref. 4),and
- ▷ to develop models based e.g. on topology and especially on symmetry considerations (Figs. 1: B and (1); refs. 1,2,4), introducing in addition effective atomic potentials from relevant experimental energy data, as well as on approximate or more rigorous quantum chemistry calculations.

All of the above suggestions have been developed, are presently applied and will be further improved by many researchers in all fields of chemistry. They fulfill most of the demands, a synthetically-minded chemist - to whom the multitude of states for any individual molecule and the numerous properties of every single state as accessible by measurement are overwhelming and largely outside the focus of his interest - would place on a suitable model (1). Above all, it must be close to experiment and to his expertise, allow to compare chemically related compounds - as he would define them -, use transparent parameters and, last but not least, should be as general and as flexible as possible. Most of these demands are met by the following scheme:



(1)

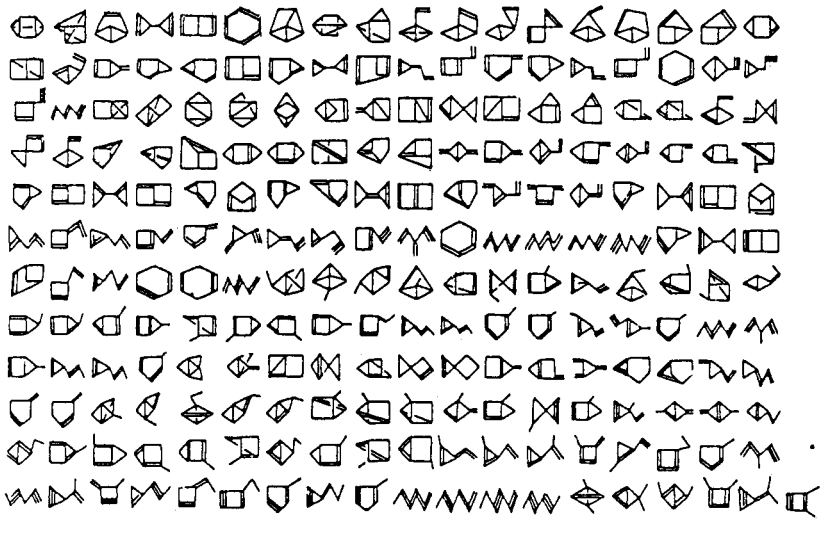
Accordingly, experimental investigation of a chemical problem yields molecualr state data, which for rationalization are best compared with equivalent ones of chemically related compounds. In addition, quantum chemical calculations - describing the behaviour of electrons in given potentials, highly correlated for small molecules and less rigorously for larger ones - are quite helpful to predict or to reproduce facts. And, frequently, they stimulate also the preparative chemist to develop models close to experiment. These, in return, should allow to detect and to verify regularities and trends. In addition, it is sincerely hoped that the quantum chemical language, treating molecules and their states as entities in terms of their total energy, their charge distribution and their dynamics will replace more and more of the rather chaotic bonding discussions based on artifically subdividing molecular entities into 'atoms in molecules' and characterizing the 'bonding between them' by identifying the topological connectivity symbols each with exactly two electrons.

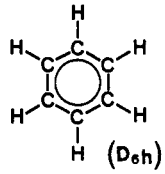
A useful simplified approach to rationalize properties of molecular states (Fig. 1: B, top) starts from the topology of the molecular skeleton, unfolded to the spatial arrangement as denoted by symmetry. Into this structural framework, energy aspects are introduced by defining effective potentials for the individual centers, representing various kinds of atoms, in such a way that the resulting electron distribution reproduces all essential details of the respective molecular structure. Of special importance is the relationship between structure and energy: there is no change in energy - especially, if coupled to addition or loss of electrons - without a corresponding change in structure and vice versa (ref. 1-3). Above all, such an approach (Fig. 1: B, bottom) must permit the comparison of experimental data within the series of compounds investigated. As concerns the comparison of equivalent states of chemically analogous molecules, practically every chemist attempts to organize his set of individual compounds by some definition of their relatedness, e.g. by principles of homology or substituent effects. Accordingly, the definition of 'molecular building blocks' and their combination within a 'molecules in molecule' treatment is recommended for molecular state comparison (Fig. 1: B, bottom). Depending upon the relative change, the distinction between iso- and hetero-conjugate and between iso- and extra-electronic systems is of course a flexible one. Often, the extent of perturbation determines the scope of a model (1), and within this scope, its quality, i.e. the deviation in correlations between observed and calculated quantities.

In closing this essential introductory part it shall be pointed out that by adding the time-scale, molecular dynamics within the numerous (3n - 6) degrees of freedom of molecules becomes important - especially to improve our rather rudimentary insight into microscopic reaction pathways.

PERIMETER TOPOLOGY AND HÜCKEL'S 4n + 2 RULE

The artifical subdivision of molecular entities into 'atoms in molecules' and especially the discussion of the 'bonding between them' by identifying topological connection lines of the chemical shorthand notation with each exactly two electrons can lead to ridiculous consequences: Thus the beautiful hexagonal skeleton of benzene, one out of 217 potential C_6H_6 topological isomers (ref. 1) and the only one exhibiting D_{6h} symmetry, is fictitiously distorted to D_{3h} or even C_{2v} symmetry as displayed on many postal stamps, e.g.:





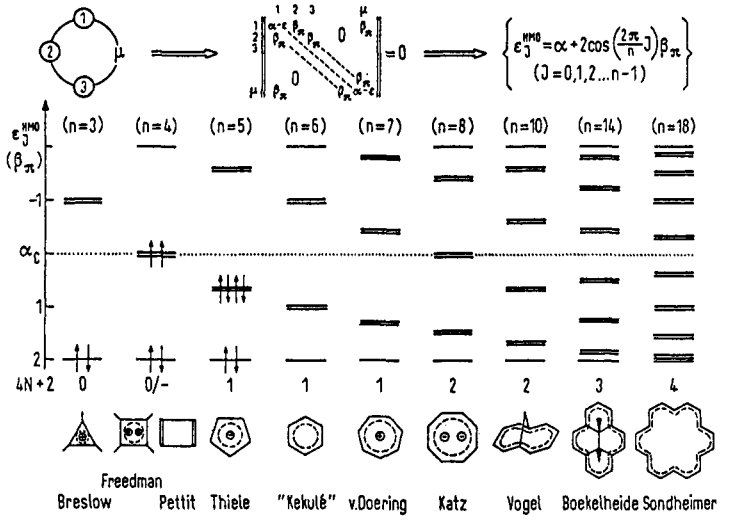
(D_{6h})

(2)

(C_{2v})

Worse, however, the wrong assumption of each 3 'single' and 'double' bonds results in a huge discrepancy between expected and observed enthalpies of formation, with the astonishment about it being directly proportional to the impertinence of defining this aberration from the experimentally determined C_6H_6 gasphase structure as 'resonance energy'.

Contrary to these futile excercises far from the reality of molecular states (Fig. 1 and (1)), the topology-based Hückel concept (ref. 6) for cyclic π systems known as perimeters (ref. 4) has been proven to be most valuable by stimulating the synthetic efforts for numerous and often surprising novel benzoid and non-benzoid π systems (ref. 2), e.g. the prototype ones displayed in (3). For rationalization, one best starts with approximate solutions of the Schrödinger equation (1) by applying the variation principle, in which a secular determinant is passed (3), which incorporates the topology of the respective molecule. Thus in the HMO approximation (ref. 4) for cyclic π systems, the main diagonal contains the energy terms $(\alpha - \varepsilon)$ and the off-diagonal elements represent the π interactions β_π assumed to be equal between all connected centers. The solutions of the corresponding eigenvalue polynomials (ref. 4) can be derived in closed form (3). The general formula resulting for the eigenvalues ε_J^{HMO} furnishes energy-level schemes in units of β_π which display the following features: regardless of the number of centers J = n, one eigenvalue $\varepsilon_J^{HMO} = \alpha + 2\beta$ is always obtained for J = O; pairs of degenerate eigenvalues $\varepsilon_J^{HMO} = \varepsilon_{J-n}^{HMO}$ result from the cosine term for values $0 < J < n-1$; and finally $\varepsilon_{n-1}^{HMO} = \alpha - 2\beta$ follows for J = n-1 in all even-numbered, and hence alternant, perimeters. On introducing the electrons, one recognizes that closed shells with spin-paired electrons ($\uparrow\downarrow$) are obtained only, if their number satisfies Hückel's $4n + 2$ rule. The corresponding compounds may be charged , they exhibit characteristic properties, and have been systematically synthesized in large numbers.



(3)

It should also be pointed out that even-numbered perimeters are also alternant π systems (ref. 4). The fascinating topological criterion for alternancy can be formulated such that labeling of the individual centers of a system with "*" or "o" leads only to "* - o" connections. Among the numerous consequences of such a topological alternancy(ref. 4), the pairwise occurence of molecular orbitals Ψ_J and Ψ_{n-J} for even-numbered cyclic π-electron systems (3) is especially striking. In this context it should also be emphasized that the calculated virtual and unoccupied molecular orbitals can also be correlated with experimental data (ref. 4) as demonstrated here for the electron affinities determined by electron transmission spectroscopy (Fig. 2: A) as well as for the ionization energies of dodecamethyl cyclohexasilane (ref. 1), a topologically equivalent σ system with 6 SiSi bonds, in which by using a linear combination of bond orbitals all 6 resulting molecular orbitals are occupied (Fig. 2: B).

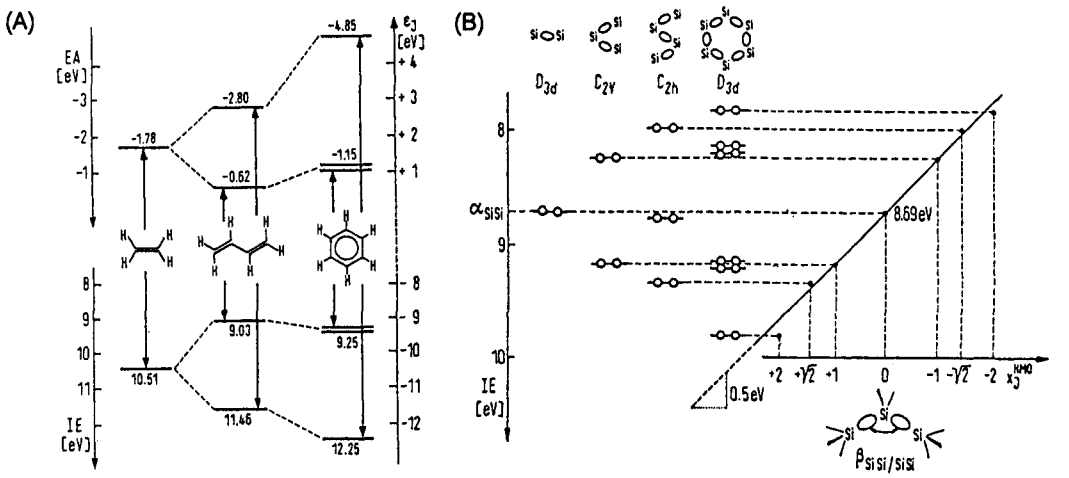
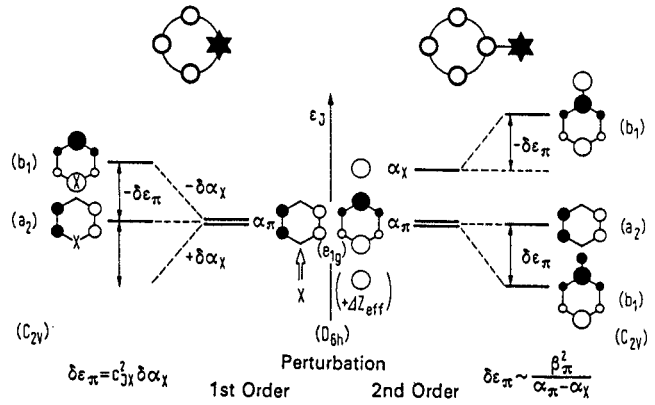


Fig. 2 (A). Electron affinities EA determined by electron transmission spectroscopy and plotted together with PE spectroscopic ionization energies IE along a molecular orbital eigenvalue ε_J scale demonstrate that an object/mirror image between the respective molecular states result, further substantiating the alternancy of the π systems shown, which includes the C_6H_6 benzene perimeter.

Fig. 2 (B). Comparison of the lowest PE ionization energies of methylpolysilanes $R(SiR_2)_nR$ and $(SiR_2)_n$ with the resulting correlation centered around α_{SiSi}, the first vertical ionization energy of hexamethyldisilane. The splitting patterns correspond to the HMO eigenvalue schemes of isoconjugate chains (Fig. 1: B) and rings (3) with fully occupied orbitals and the slope of the regression line affords the interaction parameter $\beta_{SiSi/SiSi}$ = 0,5 eV. For all compounds shown, the inherent alternancy results in pairwise correspondence around the center α_{SiSi}.

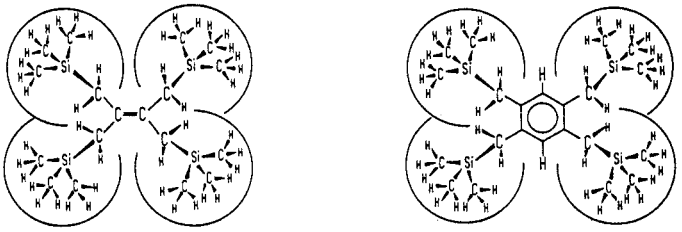
An outline of the Hückel concept for $(4n + 2)\pi$ perimeter compounds would be incomplete without indicating at least their first and second order π perturbations by substitution (Fig. 1: B; refs. 2,4):



(4)

Obviously, substitution within and of the benzene ring, chosen here as representative examples, lowers the molecular symmetry, e.g. $D_{6h} \rightarrow C_{2v}$, thereby removing the degeneracy of its highest occupied e_{1g} molecular orbitals. Within the HMO approximation (ref. 4), 1st order perturbation occurs via a change in potential $-\delta\alpha_X$ (X = donor) or $+\delta\alpha_X$ (X = acceptor) and raises $-\delta\varepsilon_\pi$ or lowers $+\delta\varepsilon_\pi$ the respective perturbed molecular orbital, whose composition is regarded approximately as being unchanged. On substitution in a nodal plane, i.e. with a coefficient $c_{JX} = 0$ at the substitution center X, $\delta\varepsilon_\pi$ remains equal to zero. Frequently, 1st order perturbations are isoelectronic (Fig. 1: B), i.e. an atom X at the respective substitution center is replaced by another atom or another group of atoms of different nuclear charge $Z_{eff}(X)$. On the contrary, 2nd order perturbation occurs in the HMO approximation (ref. 4) on mixing orbitals of the same symmetry class, i.e. construction of the linear combination $\Psi = c_J\Psi_J + c_K\Psi_K$ for the complete system. The change in orbital eigenvalues $+\delta\varepsilon_\pi$ is directly proportional to the square of the perturbing interaction β^2_{JK} and inversely proportional to the separation of the starting orbitals $\alpha_\pi - \alpha_X$. In general, 2nd order perturbations are extra-electronic (Fig. 1: B), i.e the π system is extended by one or more centers.

As a closing remark, the reality of molecular states shall be emphasized again (cf. Introduction), which might well put some limits to oversimplified model approaches (1), requiring at least their adjustment or reparametrization. Thus, in the example of the tetrakis(trimethylsilylmethyl)-substituted ethylene and benzene derivatives $C_{18}H_{44}Si_4$ and $C_{22}H_{46}Si_4$



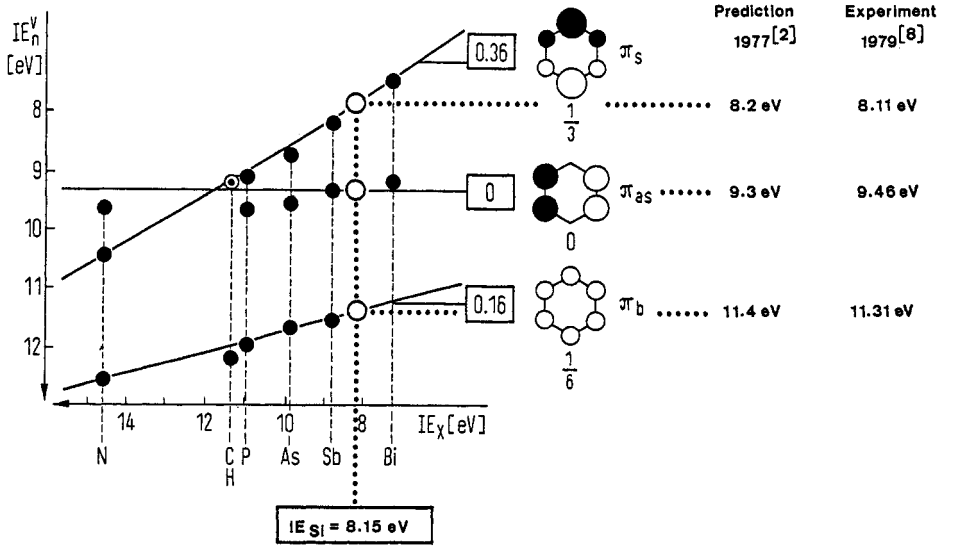
(5)

chosen for illustration, both the different central π systems are surrounded each tetrahedrally by four bulky $(H_3C)_3SiCH_2$ groups. The energy differences between the ground states of the neutral molecules and their radical cations almost coincide at 7.15 eV and 7.10 eV, providing evidence - further substantiated by the rather similar ESR spectra of their radical cations (ref. 7) - that the positive charge generated is delocalized over the molecular skeleton including the $(H_3C)_3SiCH_2$ substituents. In other words: here the benzene and ethene π subunits lose their individuality or, as pointed out repeatedly, molecules and molecular ions are better rationalized as entities, exhibiting a specific charge distribution and, therefore, structure in their respective molecular states along the total energy scale (Fig. 1: A).

Along these lines, three additional examples of investigations by the Frankfurt PES and ESR/ENDOR group will be discussed in some detail: the generation of silabenzene in the gasphase (ref. 8), the oxidation of tetrakis(tert.butyl)tetrahedrane in solution (ref. 9) and the structure of tetraphenyl ethylene dianion in the solid state (ref. 10).

NOVEL MAIN-GROUP ELEMENT CYCLIC COMPOUNDS I: THE GENERATION OF SILABENZENE IN THE GASPHASE

The story starts with the prediction of the π ionisation energies of the then still unknown compound H_5C_5SiH (ref. 2) to facilitate its PE spectroscopic detection in a gas flow under reduced pressure (ref. 11). This could be reliably achieved by inserting the silicon atom ionisation energy in a most elegant molecular state correlation for benzene and group V heterobenzenes from the literature (for details cf. ref. 2):



(6)

The best-suited precursor proved to be 1-sila-2,5-cyclohexadiene (ref. 8c), which upon heating in a specially designed short-path pyrolysis apparatus (Fig. 3:A) above 1050 K selectively splits off H_2 to yield the target molecule H_5C_5SiH, identified by its PE spectroscopic 'molecular state fingerprint' (Fig. 3: B). The radical cation state sequence assigned via Koopmans correlation, $IE_n^v = -\varepsilon_j^{SCF}$, based on ab initio SCF calculations with a nearly saturated basis set, is almost analogous to that of benzene. The first ionization energies are lowered, e.g. the first one by 1,14 eV, due to the smaller effective nuclear charge of Si (ref. 8c). The iso(valence)electronic relationship between the two cyclic π systems can be further substantiated by a comparison of their UV spectra (Fig. 3:C), with the bathochromically shifted one of H_5C_5SiH recorded after trapping in a low-temperature argon matrix. Thus, all molecular state data recorded prove that the novel main group element cyclic compound is indeed a 'sila'-benzene (refs. 1,2,8).

To rationalize the rather high H_2 elmination temperature of 1050 K (Fig. 3:B) under nearly unimolecular reaction conditions ($p \sim 10^{-5}$ torr), an approximate energy hypersurface calculation for an intramolecular H_2 split-off has been calculated. With $(3 \cdot 14 - 6) = 36$ degrees of freedom for the 14 atom precursor molecule, drastic assumptions had to be made for an appropriate cut through the presently untreatable 36-dimensional hyperspace. Therefore, a plane of symmetry is introduced by choosing the 1,4-disila derivate, and as internal coordinates, assumed to represent the dominant molecular dynamics, the H···H distance as well as the dihedral angles ω between the CSiC triangles and the plane containing the C=C bonds are selected. Their variation by about a 1000 independent MNDO calculations, each

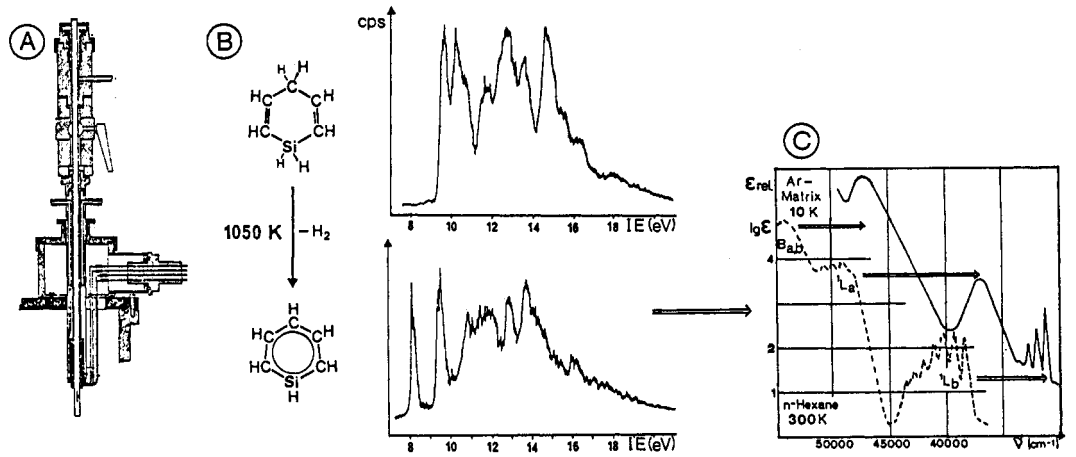
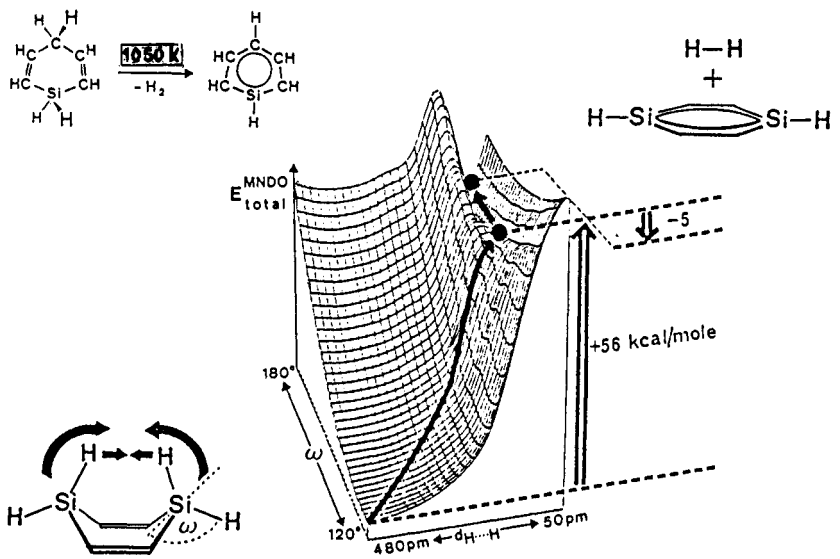


Fig. 3. PE spectroscopic detection of silabenzene (B) after heating the precursor, 1-sila-2,5-cyclohexadiene above 1050 K in a specially designed short-path pyrolysis apparatus (A) as well as its UV spectrum (C), recorded after isolation in a 10 K Ar matrix (for comparison UV spectrum of C_6H_6 in broken lines)

geometry-optimized by the Davidson/Fletcher/Powell subroutine of the program used, generates the following folded energy hypersurface (ref. 1):



(7)

From the total energy hypersurface calculated to approximate the anticipated intramolecular H_2 elimination from sila-hexadiene to sila-benzene derivates the following details can be gathered: The precursor molecule, for which a boat conformation is predicted, sits in a rather deep potential well. On distortion by both shortening the H···H distance and, independently, deforming the molecular Si_2C_4 skeleton, it climbs the potential wall to eventually reach a transition state saddle point, situated at approximately $d_{H\cdots H} \sim 90$ pm and $\omega \sim 150$. Then on relaxation into a potential trough, H_2 splits off and disila-benzene forms, which according to the calculations is only slightly stabilized. Altogether, the approximated activation barrier of ~ 56 kcal/mole does correspond well with the rather high H_2 elimination temperature of 1050 K determined experimentally (ref. 8c). And, if the rather crude hypersurface (7) would at least cover some facets of the molecular dynamics involved in the presumably intramolecular thermal fragmentation, then the essential rôle of storing internal energy along the real microscopic pathway becomes obvious.

NOVEL MAIN-GROUP CYCLIC COMPOUNDS II: THE OXIDATION OF A TETRAHEDRANE TO A CYCLOBUTADIENE RADICAL CATION IN SOLUTION

Tetrahedrane $(CR)_4$, the 4 carbon center cluster, has been synthesized with bulky tert.butyl substituents R in 1978 (ref. 12) and an interesting valence isomerization observed: on melting, the C_4 cluster rearranges to the thermodynamically more stable cyclobutadiene derivative, which on photochemical energy uptake forms again the tetrahedrane skeleton (Fig. 4: A). Both valence isomers exhibit low first vertical ionization energies of only 7,5 eV and 6,35 eV, respectively and, therefore, are readily oxidized in solution by the selective one-electron oxidizing system $AlCl_3/H_2CCl_2$ (ref. 7). The result, however, is puzzling: for both compounds, the tetrakis(tert.butyl) cyclobutadiene radical cation is identified as one-electron oxidation product by its ESR spectrum (Fig. 4: B and ref. 9).

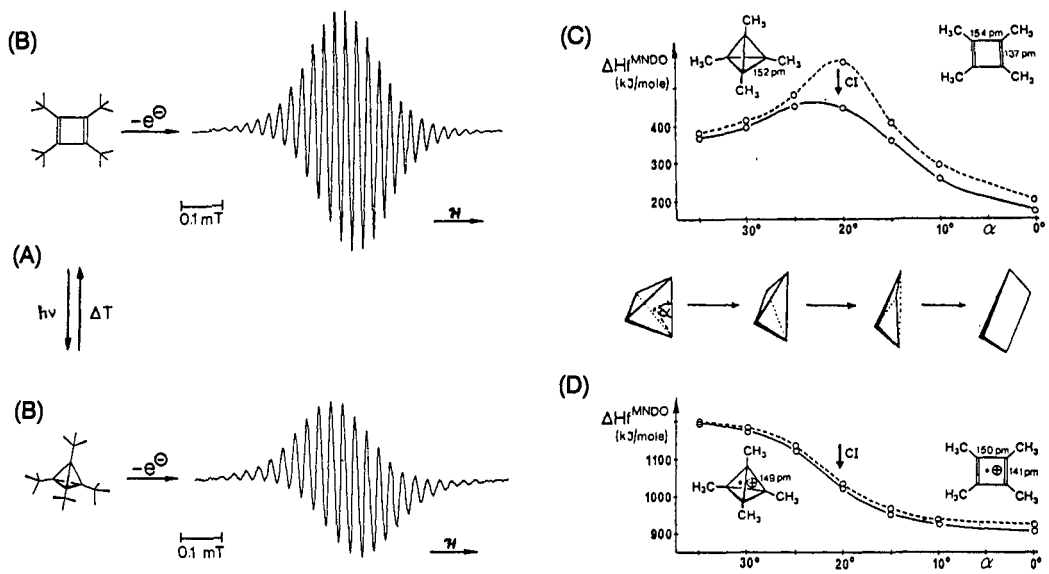


Fig. 4. Tetrakis(t.butyl) tetrahedrane ⇄ cyclobutadiene valence isomerizations: (A) Photochemical generation of the C_4 cluster and its thermal opening to the 4 center π system, (B) one-electron oxidation of both neutral isomers by the selective $AlCl_3/H_2CCl_2$ redox reagent to the π radical cation, identified by identical ESR spectra as well as one-dimensional hypersurfaces along the tetrahedrane angle α coordinate for (C) thermal and photochemical interconversion and (D) rearrangement of the tetrahedral to the rectangular C_4 skeleton in the radical cation (see text).

In the order to further substantiate the ESR spectroscopic result (Fig. 4:B) and to gain more insight into both the thermal rearrangement of the neutral tetrahedrane and the structural change accompanying its one-electron oxidation to the cyclobutadiene radical cation formed, MNDO closed and open shell hypersurface calculations have been performed chosing the tetramethyl derivates as model systems to lay bare the electronic effects, which might be obscured by the steric requirement of the bulky tert.butyl groups (Fig. 4: C and D; refs. 3,9). To facilitate the calculations, a single isomerization coordinate α, along which the tetrahedron is flattened to a rectangle, has been selected. This choice of α, defines an isomerization, in which D_2 symmetry is conserved along the rearrangement path and thus removes the restriction within $D_{2d} \rightarrow C_S$ or $D_{2d} \rightarrow C_2$ approaches, which would lead to symmetry-forbidden orbital crossings. Furthermore, the D_2 deformation corresponds closely to the E-type normal vibrations in the ground state $\tilde{X}(^2E)$ of a tetrahedral radical cation, which contribute to the PE spectroscopically observed Jahn/Teller splitting.

The approximate though rather elegant only one-dimensional MNDO cuts through - with respect to the degrees of freedom exhibited by the 20 atom ensemble $(C(CH_3))_4$ - its $(3 \cdot 20) - 6 = 54$ dimensional hyperspace, nevertheless reproduce all essential experimental findings for both the neutral valence isomers and their radical cations (Fig. 4: C and D; refs. 3,9). They predict that the 4 center π system should be thermodynamically more stable than the C_4 cluster, separated by an activation barrier - calculated including configuration interaction (Fig. 4: CI) - to be approximately 80 kJ/mole and satisfactorily close to the 107 kJ/mole determined experimentally (ref. 12). Thus the one-dimensional energy hypersurface for the neutral valence isomers (Fig. 4:C) allows to rationalize straightforwardly both the thermal C_4 cluster opening and its photochemical formation. As concerns the corresponding radical cations $(C(CH_3))_4^{\cdot\oplus}$, no barrier is calculated for the isomerization of the oxidized tetrahedrane to the still rectangular 4 center π system, in which according to the MNDO calculations the positive charge is delocalized more effectively.

Summarizing, the ESR observation, puzzling at first glance, that one-electron oxidation of both the tetrakis(tert.butyl)-substituted tetrahedrane and its cyclobutadiene isomer yield the radical cation of the latter, based on the approximate energy hypersurface calculations finds a simple explanation. It has to be pointed out, however, that additional valence isomers $(CR)_4$ - cf. the 217 of the C_6H_6 ensemble (2) - e.g. cyclopropenyl carbene are found in local energy minima, if other cuts through the 54-dimensional hyperspace are calculated (ref. 3,9) in agreement with additional experimental results (ref. 9,12)

NOVEL MAIN-GROUP CYCLIC COMPOUNDS III: THE TETRAPHENYLETHYLENE DIANION AND ITS CRYSTAL STRUCTURE

The increasing ability to manually master difficile reaction conditions allows the preparative exploration of ever more shallow potential troughs, for instance in the syntheses of air-, temperature- and sometimes light-sensitive organic compounds of alkaline metals. Their rather complex crystal structures, frequently and even after long elaboration, convey 'fairy tale'- like impressions, which no longer can be rationalized by usual bonding considerations. In our investigations on the formation of ion pairs in aprotic solution (ref. 1,5,10,13), tetraphenylethylene has been reacted under argon and strictly aprotic conditions with a vacuum-destilled sodium mirror and yielded green crystals with a metallic luster (Fig. 5).

The following facets of the rather surprising band structure of tetraphenylethylene dianion are emphasized (ref. 10): The two $(H_5C_6)_2C$ molecular halves are twisted by 56^o and the connecting bond is elongated relative to the neutral compound by 13 pm to the single CC bond distance of 149 pm (Fig. 5: B). As concerns the charge distribution, MNDO calculations predict each 1/6 at the central carbons and each 1/6 in every phenyl ring. The twofold diethylether-solvated Na 1 (Fig. 5: C) displays 6 additional coordination contacts along the 'zig-zag' carbon chain starting from phenyl ring I at C 1 and streching via the C1-C2 bond to the C_6H_5 substituent III, which both - as demonstrated by their ipso angles of only 113^o and 114^o - are considerably distorted. The sandwiched Na 2 (Fig. 5: D), which establishes the band structure between the tetraphenylethylene dianion subunits, exhibits a 10- to 14-fold coordination predominantly with the phenyl rings I and III, which are already involved in the Na 1 bonding (Fig. 5: C).

Despite of the rather unique structure discovered for $[(H_5C_6)_2{}^{\delta\ominus}C\text{-}C{}^{\delta\ominus}(C_6H_5)_2\ Na^{\oplus}(OR_2)_2\ Na]_\infty$, some facets of it do parallel known structures of other organo alkaline metal compounds (for details cf. ref. 10). Referring to these more general aspects, the following speculation concerning the formation of the title ion pair, which are supported by other literature observations (ref. 10), are appropriate: The tetraphenylethylene radical anion, generated first by single electron transfer, suffers only small structural changes. Due to its excessive sterical shielding, which is comparable to that in the neutrale molecule, it forms even in ether solution only 'solvens-separated' radical ion pairs ($M^{\cdot\ominus}_{solv.}\cdots Me^{\oplus}_{solv.}$) and,

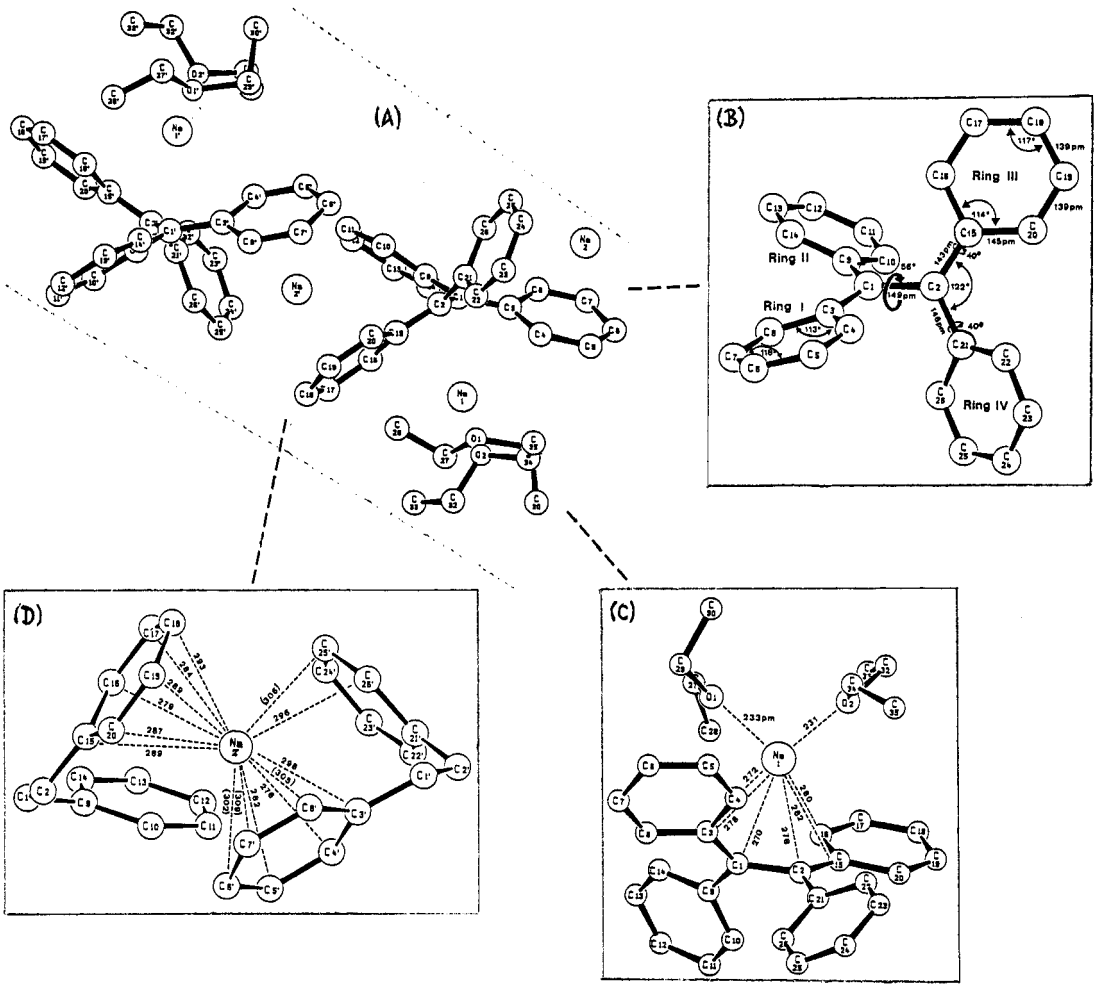


Fig. 5. Band structure of tetraphenylethylene dianion at 200 K (A) as well as enlarged sections displaying the twisted tetraphenylethylene skeleton (B) as well as the contact distances from the ether solvated sodium counter cation (C: Na 1) and from the sandwiched one (D: Na 2) to the nearest carbon centers of the dianion moiety (see text).

therefore, readily disproportionates via $2\ M^{\cdot\ominus} \rightleftarrows M + M^{\ominus\ominus}$. The resulting dianion, in contrast to the preceding radical anion, changes its structure tremendously (Fig. 5:B), laying bare its central CC bond and, therefore, can be additionally stabilized as a contact ion pair $[M^{\ominus\ominus}Me^{\oplus}]^{(n-1)\oplus}_{solv.}$. Under the reaction conditions selected, this crystallizes in the tetraphenylethylene dianion/disodium counter cation band structure determined by X-ray diffraction (Fig. 5:A).

CONCLUDING REMARKS

This rather incomplete summary of the fascinating world of cyclic π systems (ref. 14) has emphasized their molecular entity as measured by numerous different spectroscopic techniques. The resulting molecular state data, therefore, should be rationalized by models as close to the experimental reality as possible. Fortunately, the Hückel π molecular orbital approach, largely based on topological connectivities and extendable by 1st and 2nd order perturbations, provides an elegant starting point. For the structural changes observed on changing energy and charge, however, more advanced quantum chemical approaches like energy hypersurface calculations are indispensable.

Facets of todays advanced preparative methods to generate, to characterize and partly also to isolate reactive molecules have been illustrated by the gasphase investigations of silabenzene, the oxidation of tetrahedrane in aprotic solution and the crystal band structure of the disodium salt of tetraphenyl ethylene dianion. Referring to the title question "are they aromatic?" it is - jokingly - admitted that there has been no chance to 'sniff the smell' of any of these either unbottable or rather air-sensitive compounds. On the other hand, the charge delocalization over the molecular skeletons and especially within the cyclic π systems has been proven beyond doubt as well as the structural changes with energy and charge. By pointing to the reality of molecular states, therefore, it is hoped that further investigation of the intrigueing compounds with cyclic π systems could be stimulated, especially with respect to their dynamic behaviour and to their largely unknown microscopic reaction pathways.

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