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Anisotropy of the Induced Current Density (ACID), a General Method To Quantify and Visualize Electronic Delocalization

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1. Introduction

1.1. Delocalization, a Short Historical Review

1.1.1. First Developments of a Structural Theory

The problem of localized versus delocalized bonding is almost as old as chemical structure theory itself. The theory of localized bonding in organic molecules was introduced by Friedrich August Kekule[1] and Archibald Scott Cooper[2,3] in 1858. Couper was the first to draw chemical structures with localized bonds[4] (Figure 1). Kekulé used the so-called “sausage formula” in the first textbook on organic chemistry in 1861.[5]

Neither graphical representation is perfect. In Couper’s structures the hydrogens at each carbon are combined as “superatoms” without individual bonds, and in Kekulé’s “sausages” (the bulges represent the valencies) only vertical contacts are considered as bonds. However, both localized bonding descriptions for the first time assume the tetravalency of carbon and introduce carbon−carbon bonding, which at the time was a tremendous advancement over the “radical theory” advocated by Charles Gerhardt.[6] Butlerov in his paper “Einiges über die chemische Struktur der Körper” (Some Facts about the Chemical Structure of Compounds) coined and defined the term “chemische Struktur” (chemical structure) as “the manner of mutual linking of the atoms in a molecule”.[7] In 1861 Joseph Loschmidt for the first time drew structures with multiple bonds (Figure 2). His work was largely ignored at the time, probably because it was published privately by the author.[8] Richard A. C. E. Erlenmeyer coined the term “ungesättigt” (unsaturated) for compounds containing carbon−carbon multiple bonds because these compounds can add additional atoms such as bromine. Alternative graphical representations of double bonds were developed by A. Crum Brown,[9] J. Wilbrand,[10] G. C. Foster,[11] and E. Erlenmeyer.[12]

Kekulé in his “Lehrbuch der Organischen Chemie” represented double bonds by a larger overlap of his sausages (e.g., contact of two of the four bulges of carbon for a C−C double bond) (Figure 3).

Butlerov finally proved experimentally that the assumption of carbon−carbon multiple bonds is

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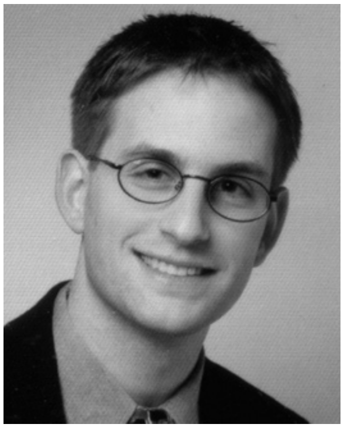

Felix Köhler was born in Idar-Oberstein, Germany, in 1973. Since 1998 he has been working toward earning his Ph.D. in the Institute of Organic Chemistry at the University of Kiel under the supervision of Prof. Herges.

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necessary to explain the chemical properties of unsaturated compounds.[13]

1.1.2. Limitations of the Localized Bonding Concept

However, compounds such as benzene that are obviously unsaturated are nevertheless different in their reactivity compared to olefins and acetylenes. When Kekulé presented his six-ring formula first with single bonds[14] and then with alternating single and double bonds,[15,16] he was aware that benzene was a special case. Expressed in modern structural theory, he realized that the localized bonding failed in explaining the properties of benzene. He suggested that the six carbon atoms are somehow combined in a common nucleus. Loschmidt used a similar explanation ("...wir behandeln denselben so, als ob er ein sechsstelliges Element wäre...") ("...we treat it as if it were a hexavalent element...").[8] Kekulé's rather fuzzy description was criticized by contemporary colleagues who tried to preserve the fixed bonding concept by proposing alternative localized structures (J. Dewar, L. Meyer, H. E. Armstrong, A. v. Baeyer, A. Claus, and A. Ladenburg).[17] Driven either by his genius or simply by the need to save his six-ring structure, Kekulé proposed a mechanical collision or vibration of the six carbon atoms exchanging double and single bonds. Even though this view might seem quite close to our understanding today, Kekulé did not have a real chance to provide an explanation on a sound physical basis. Erich Hückel later called Kekulé's "Oszillationstheorie" (oscillation theory) a "Nothypothese" (provisional hypothesis). Delocalization is a phenomenon that can be explained only by quantum theory. Probably Johannes Thiele came as close as possible to describing delocalization in terms

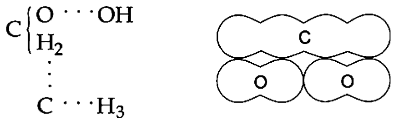
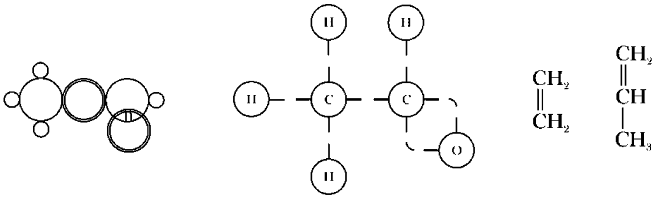


Figure 1. Couper's and Kekulé's structural formulas (CH_3-CH_2OH and CO_2) as the starting point of localized bonding theory.



methyl formate (Joseph Loschmidt)
acetaldehyde (Crum Brown)
ethene and propene (Emil Erlenmeyer)

Figure 2. First graphical representations of multiple bonds by Loschmidt (1861), Brown (1864), and Erlenmeyer (1866).

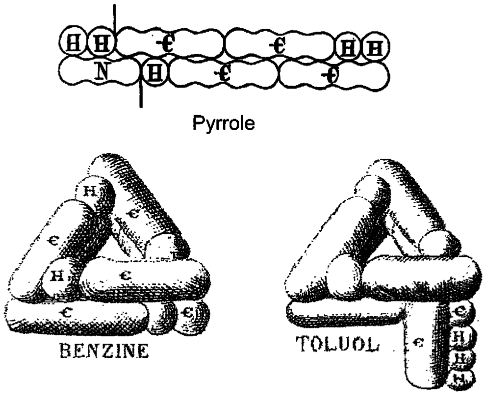


Figure 3. Kekulés “sausage” formulas of pyrrole, benzene, and toluene.

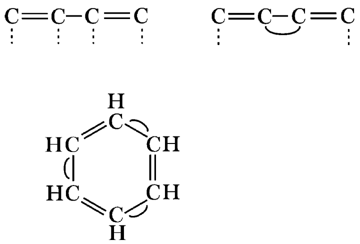


Figure 4. Thiele’s “partial valences” to explain conjugation.

of classical physics. To explain the 1,4-addition of bromine to 1,3-butadiene and related phenomena he assumed a “partial valence” at those carbons that are forming double bonds (Figure 4). In structures with alternating double and single bonds the partial valences are neighboring and can form a partial bond in addition to the single bond. In benzene this would lead to a bond equalization. Thiele for the first time used the term “conjugation” to describe the unusual reactivity of neighboring double bonds.[18]

As we know today delocalization is a phenomenon that can be adequately treated only by quantum theory. Thus, the chemical community had to wait for quantum mechanics to enter the field of chemistry. Erich Hückel published the decisive papers on delocalization in 1931[19] and 1932.[20] He explained not only aromaticity but also other forms of π conjugation.

There are two different approaches to solve the Schrödinger equation and thus to describe delocalization, the valence bond (VB) theory (developed by Heitler, London, Slater, and Pauling) and the molecular orbital (MO) theory (developed by Mulliken, Hund, and Hückel). In its simplest and most approximate application, VB theory describes delocalization by drawing mesomeric structures (mixing VB configurations). MO theory inherently considers delocalization by a linear combination of atomic orbitals giving rise to molecular orbitals that extend over a large part of the structure. Both methods, however, exhibit the drawback that they are “unanschaulich” (not easily interpretable). Moreover, in larger particularly nonplanar systems, the situation becomes complicated, and conjugative effects are difficult to extract from other phenomena.

1.2. Experimental Evidence for Delocalization

In experimental chemistry the term delocalization is mainly used to express the fact that the property of a molecule is determined by structural variations over a distance of several bonds.

The change in electronic structure can be directly measured by UV−vis or photoelectron spectroscopy[21] or indirectly by the transmission of substituent effects such as NMR shifts[22] or reactivities through the delocalized system.

In linearly conjugated polyenes the wavelength of absorption in the UV is a continuous function of the length of the π system (Figure 5). This relationship is more complicated in cyclic conjugated systems (annulenes) because they are alternatingly aromatic and antiaromatic (or nonaromatic) with an increasing number of double bonds and because they are more or less planar depending on the size and the configuration. Generally, the rule of thumb holds: the larger the delocalized π system, the more bathochromic the UV absorption if a set of molecules with a small structural variation is considered.

A very sensitive probe for delocalization is photoelectron spectroscopy. If for instance two symmetry equivalent π systems are interacting through a molecular frame of sigma bonds or through space, the orbitals split into bonding and antibonding combinations. The energy splitting is a direct measure of the strength of conjugation. A number of through-bond

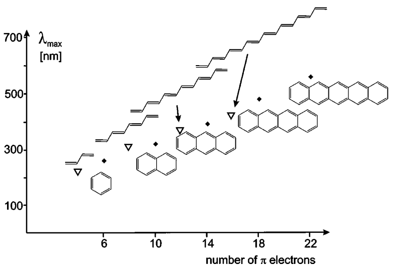


Figure 5. Electronic absorption (λ_{max} in nm) as a function of the size of the π system in linear conjugated polyenes (▽), $4n + 2$ annulenes, and linear acenes (◆).

and through-space interactions have been investigated using this tool.[21]

Substituent effects generally probe the capability of a molecular system to transmit charge effects. NMR shifts therefore are sensitive to substitution. The general rule holds that electron-withdrawing substituents cause a downfield shift and electron-donating substituents give rise to an upfield shift. The larger the distance between the substituent and the nucleus of which the chemical shift is measured, the smaller the effect. In agreement with the general view of conjugation, π systems are known to transmit substituent effects more effectively than σ systems. Similar considerations hold for the change of reactivity by distant substituents. Probably the Hammett correlation works so efficiently because the benzene ring is a very good "conductor" for charge delocalization.

Another sensitive probe for delocalization is the rate of charge separation and the lifetime of charge-separated states. Even a small conjugative coupling of the electron donor and acceptor leads to a considerable reduction of the lifetime of the excited state.[23]

Special cases are open shell systems. The delocalization of unpaired electrons (spin density) can be directly determined by the coupling with corresponding nuclei with a spin $\neq 0$ measured by ESR[24−27] (McConnel relationship in π systems). In diradicals the coupling between the two unpaired electrons and the singlet−triplet splitting is a very sensitive function of the delocalization.

1.3. Theoretical Definitions of Delocalization

Delocalization is one of the most important concepts in chemistry. Chemists use this fundamental parameter in their everyday work for explaining and predicting numerous molecular properties. The preceding section includes only an incomplete list of important effects. However, upon trying to find a rigorous definition for delocalization, we encounter the same problems as in aromaticity. This is to be expected because aromaticity is the cyclic form of delocalization and thus a special case of a much more general phenomenon. Delocalization is not a quantum theoretical observable, it cannot be directly measured, and there is no sound physical basis for a rigorous definition. Like aromaticity, it can be defined in many different ways (actually all electrons are delocalized, somehow), and one could argue that one should abandon such a fuzzy concept completely.

It would, however, be counterproductive to give up such a successful and predictive tool. The justification of concepts (unlike theories) is provided by their success in applications rather than in a reductionistic proof. On the contrary, one should search for a nonempirical method to quantify and to visualize this parameter. In the most general definition, delocalization accounts for properties that cannot be explained by the localized bonding model. There are a number of different localization schemes for orbitals developed by Foster and Boys,[28−30] Edmiston and Ruedenberg,[31−33] von Niessen,[34] and Pipek and Mezey.[35] Localized orbitals were extensively used to treat electron delocalization,[36−40] the calculation of magnetic properties, linear scaling Hartree−Fock and density functional theory methods,[41,42] and population analysis.[43] Pipek and Mezey in 1988 proposed a measure of delocalization using a similar functional as the one that has been used for localization, just by maximizing this function instead of minimizing it.[44] The authors predict a strong correlation of the reactivity and the delocalization of the orbitals of a molecular system. The AIM and ELF methods have also been extensively used to investigate delocalization in molecules.[45]

Most of the methods that were used to treat aromaticity cannot be applied to the more general phenomenon of delocalization. Aromaticity is usually quantified using the observables geometry (bond length equalization),[46] energy (aromatic stabilization energy)[47,48] and magnetic properties (magnetic susceptibility or nuclear magnetic shifts).[49−51] The application of bond length equalization and aromatic stabilization energy requires a careful choice of reference compounds that do not exhibit the kind of delocalization effect in question. This is much more difficult in noncyclic (nonaromatic) systems or even in nonplanar or σ conjugated structures. Therefore, the aromaticity measures HOMA[46] and Julg[52] probably are not suitable to be extended to treat delocalization on a general basis. Magnetic properties such as the magnetic susceptibility, the exaltation,[53−55] and anisotropy of the magnetic susceptibility[56] and the nucleus-independent shift (NICS)[57] also are restricted to cyclic delocalized (aromatic or antiaromatic) systems. Only compounds with a ring current that encloses an area of several square angstroms exhibit susceptibility exaltations that are large enough to be diagnostic of delocalization. Moreover, the magnetic parameters provide numbers and no spatial resolution of delocalization in a more complicated or larger system. Whereas the reference point for determining the NICS value in ring systems can be unequivocally defined, for example, as the "non-weighted mean of the heavy atom coordinates",[57] there is no "natural" reference point for linearly, branched, or even 3D σ conjugated or organometallic systems. To avoid the ambiguity in choosing a reference point, a method that is applicable to quantify and visualize delocalization has to be either a vector field or a scalar field.

The current density, which indicates ring currents in aromatic systems, comes closer to a more general definition of delocalization. Intuitively and as the notion implies delocalized electrons are "mobile" within a molecule. Similar to the macroscopic current that is induced by an external magnetic field in a conductor (which contains mobile electrons), currents are also induced in molecules if a magnetic field is applied.

The quantum theoretical definition of the current density in molecules $\vec{\mathbf{J}}_p^{(1)}$ can be derived from the classical definition of the flux density $\vec{\mathbf{J}}_0$ (charge times velocity) (eq 1.1) by weighing the expression by the probability density of the electron (eq 1.2) and by introducing the vector potential $\mathbf{A}$ and applying a first-order perturbation treatment to the wave function in a magnetic field (eq 1.3).

$$\vec{\mathbf{J}}_0 = -e\vec{\mathbf{v}} \tag{1.1}$$

$$\vec{\mathbf{J}}_0 = -\frac{e}{2m_e}(\Psi^* \vec{p}\Psi + \Psi\vec{p}^*\Psi^*) \tag{1.2}$$

$$\vec{\mathbf{J}}^{(1)} = -i\left(\frac{e\hbar}{2m_e}\right)\sum_{n=1}^{N}(a_n - a_n^*)(\Psi_n\nabla\Psi_0 - \Psi_0\nabla\Psi_n) - \left(\frac{e^2}{m_e}\right)\mathbf{A}\Psi_0^{\,2} \tag{1.3}$$

a_n are the coefficients in the linear combination of the wave functions Ψ_n describing the perturbation of the wave function. The resulting expression for the current can be separated in a diamagnetic and a paramagnetic contribution. However, only the total current density has a physical significance because the contribution of the individual terms depends on the gauge origin. Unfortunately, the currents that are induced in the inner shells where the electrons occupy atom-centered orbitals are several orders of magnitude larger than the so-called interatomic currents. London in 1937 for the first time introduced the term "interatomic" for currents that are not centered at an atom.[58] The large "local currents" are a problem in visualizing the currents as current density plots. Moreover, currents in π systems vanish in the nodal plane. To obtain interpretable pictures, the currents in planar systems usually are plotted as vectors projected to a sectional plane ~1 Å above the molecular plane (Figures 6 and 7). At that distance from the nuclei the local currents almost vanish and do not obscure the picture of the interatomic currents.

There are several problems in applying the current density as a general delocalization measure. The current density is a vector field. A vector is assigned to each point in space. Therefore, a visualization is restricted to a more or less arbitrarily chosen sectional plane in which for a grid of points the vectors are projected. The length of the vectors is proportional to the magnitude of the current. Therefore, the current density plots usually are only applied to planar or nearly planar systems. Fowler and Steiner in a series of papers have proven the power of ring current mapping[59] as a tool for visualizing and understanding aromaticity in a large number of systems.[60−69] Current density plots are an indispensable tool to investigate aromaticity. However, in systems without cyclic conjugation such as linear or branched polyenes or in nonplanar systems the topology of the currents can be extremely complicated and thus difficult to interpret. The situation is aggravated by the fact that the current density depends on the relative orientation of the magnetic field and the molecular system. Again, in cyclic planar molecules this problem is less severe. The "natural" choice is to apply the magnetic field orthogonal to the sectional plane, which is parallel to the molecular plane.

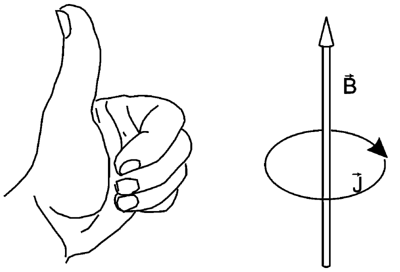


Figure 6. "Left-hand rule" to determine the direction of the currents induced by a magnetic field in a conductor.

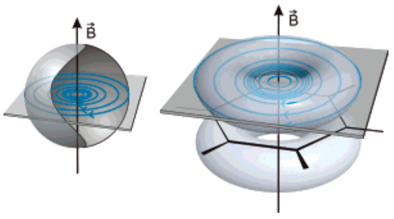


Figure 7. Current density (blue circles) in the xy-plane of a ground-state hydrogen atom ("local current") and in benzene in a plane 1 Å above the molecular plane ("interatomic current").

1.4. ACID Method

1.4.1. Definition of ACID Scalar Field

The "density of delocalized electrons" is a concept that is intuitively used to explain the electronic structure of benzene, allyl cation, enolate, and other conjugated systems in organic and inorganic textbooks. Expressions such as "...delocalized electrons form a π cloud"[71,72] or the "electrons are smeared out" are used for didactic purposes. Figures presenting a qualitative plot of the "density of delocalized electrons" are used in almost all undergraduate textbooks (Figure 8).

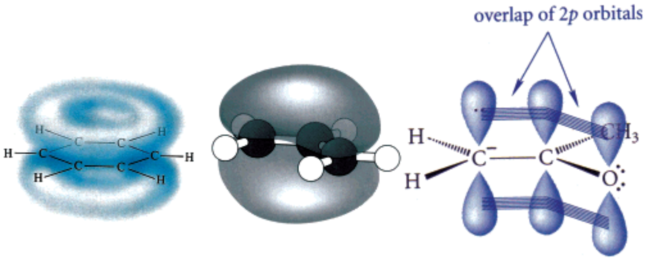


Figure 8. "Didactic" illustrations of delocalized electrons in textbooks (benzene,[71] allyl cation,[73] and the enolate anion of acetone[74]). Reprinted with permission from ref 71, Copyright 1994 W. H. Freeman; from refs 73 and 74, Copyright 2002 Oxford University Press.

Unfortunately, however, there is no rigorous way to separate the total electron density in a density of localized and delocalized electrons. Like aromaticity, bond order, point charge, and other important concepts in chemistry, a definition for the density of delocalized electrons has to be derived from more fundamental quantum theoretical parameters. From a puristic point of view one could argue for avoiding such nonobservables. Such a rigorous reductionistic viewpoint, however, is not helpful in experimental sciences such as chemistry. We therefore think that the routinely used and successful but fuzzy concept of the density of delocalized electrons should not be abandoned but rather be put on a sound physical basis. A nonempirical definition should be of great value for interpreting and predicting numerous properties of molecular systems. Synthetic chemists and application-oriented theorists need tools for the visualization and quantification of parameters that describe electronic structure and bonding in various molecular systems.

As in the case of aromaticity, magnetic properties are a good starting point for a general description of delocalization. To this end we decided to analyze the properties of the current density. A density of delocalized electrons should have the same mathematical and physical properties as the total electron density of a molecular system. Hence it should be

- a scalar field,
- invariant under similarity transformations,
- independent of the relative orientation of the molecule and the magnetic field,
- of the same symmetry as the total wave function, and
- linearly independent of the total electron electron density.

Moreover, the parameter should be generally applicable, not only for aromatic systems but also for any kind of conjugation (through bond, through space) and for any kind of system (ground state, excited state, transition state).

In analogy to the anisotropy of the magnetic susceptibility, which is a powerful measure of aromaticity, we decided to investigate the anisotropy of the current (induced) density (ACID).[70] The analysis of the anisotropy of the induced current density proves that the above conditions are met. The induced current density $\vec{\mathbf{J}}^{(1)}$ is given by

$$\mathbf{T}:\ \mathbf{T}_{\nu\mu} = \frac{\partial J_\nu}{\partial B_\mu}(\text{at } B = 0) \qquad \vec{\mathbf{J}}^{(1)} = \mathbf{T}\vec{\mathbf{B}} \tag{1.4}$$

$\mathbf{T}$ is a tensor of second rank,[75] and we defined the anisotropy $\Delta\mathbf{T}^{(1)}$ as the standard deviation of the eigenvalues e_i

$$\Delta\mathbf{T}^{(1)^2} = \sum_i (e_i - \bar{e})^2 \tag{1.5}$$

with

$$\bar{e} = \frac{1}{n}\sum_i e_i \qquad \text{and} \qquad \sum_i e_i = \text{tr}\,\mathbf{T}$$

we obtain

$$\Delta\mathbf{T}^{(1)^2} = \text{tr}(\mathbf{T}^2) - \frac{1}{n}(\text{tr}\,\mathbf{T})^2 \tag{1.6}$$

Any real matrix $\mathbf{T}$ can be decomposed into a symmetric and antisymmetric part $\mathbf{T} = \mathbf{T}_\text{S} + \mathbf{T}_\text{A}$. The anisotropy of $\mathbf{T}$ therefore can be written as

$$\Delta\mathbf{T}^{(1)^2} = \Delta\mathbf{T}_\text{S}^{(1)^2} + \text{tr}\,\mathbf{T}_\text{A}^{(1)}\mathbf{T}_\text{A}^{(1)^+} \tag{1.7}$$

We neglect the contribution of the antisymmetric part, and we obtain an analytical solution for the symmetric contribution:

$$\Delta\text{T}_\text{S}^{(1)^2} = \frac{1}{3}[(t_{xx} - t_{yy})^2 + (t_{yy} - t_{zz})^2 + (t_{zz} - t_{xx})^2] + \frac{1}{2}[(t_{xy} + t_{yx})^2 + (t_{xz} + t_{zx})^2 + (t_{yz} + t_{zy})^2] \tag{1.8}$$

Wallenborn et al. used a similar formula, however, without derivation or substantiation.[76] In contrast to other methods[77] the formula includes the off-diagonal elements of the current density tensor (t_{nk}, $n \neq k$). In asymmetric tops or systems with $D_{\infty h}$ or $C_{\infty v}$ symmetry two of the diagonal elements of $\mathbf{T}$ are identical and the anisotropy takes the known form

$$\Delta\mathbf{T}^{(1)}{}_{\text{asymm.top}} = (t_{zz} - t_{xx}) \tag{1.9}$$

1.4.2. Properties of ACID

By dropping the antisymmetric contributions to the anisotropy the diamagnetic current density always vanishes at all points in space regardless of the choice of the gauge origin.[70] This is an important property because the diamagnetic current density is a linear function of the total electron density. Thus, the anisotropy of the induced current density (ACID) exclusively is a function of the paramagnetic part of the current density, which is determined by the perturbation of the wave function by the magnetic field. This makes sure that the ACID function can be small or even zero at points in space where the total electron density is large. We could also prove that the ACID scalar field has the same symmetry as the wave function and hence the same symmetry as the molecule. Atomic orbitals as models for perfectly localized systems give rise to a zero ACID at all points in space because a natural gauge origin can be chosen in such a way (at the nucleus) that the paramagnetic term of the current density vanishes. Spherical systems also give rise to perfectly isotropic current density tensors. Hence, the strong local currents that are induced in the inner shells of the atoms in a molecule almost completely vanish and the ACID function represents mainly anisotropies of "interatomic currents" and hence the delocalized electrons.

1.4.3. Visualization of ACID

For the visualization of the ACID scalar field isosurfaces are plotted in a similar way as usually done for the total electron density or the boundary surface of molecular orbitals. If not stated otherwise, all ACID isosurfaces in this review are plotted at a standard isosurface value of 0.05. To distinguish between anisotropies caused by diatropic and paratropic ring currents, we plot the current density vectors onto the ACID isosurface. The length of the arrows indicates the absolute value of current density at the point of its origin.

1.4.4. Quantification of Conjugation by Topological Analysis of ACID

Because ACID has the properties of an electron density, the AIM methods developed by Bader et al.[78]

for analyzing the total electron density can also be applied to the ACID density of delocalized electrons. To quantify delocalization effects we define the critical isosurface value (CIV) between two groups or atoms as the ACID value at the "delocalized critical point", r_{dcp}. At this point the gradient of the ACID scalar field $\Delta\mathbf{T}_S{}^{(1)}$ is zero.

$$\nabla(\Delta\mathbf{T}_{\mathrm{S}}{}^{(1)}(\vec{r}_{\mathrm{dcp}})) = 0 \tag{1.10}$$

$$\nabla^2(\Delta\mathbf{T}_{\mathrm{S}}{}^{(1)}(\vec{r}_{\mathrm{dcp}})) = \lambda_1 + \lambda_2 + \lambda_3 \tag{1.11}$$

Analogous to the definition of the bond critical point in AIM the Laplacian of the ACID scalar field $\nabla^2(\Delta\mathbf{T}_{\mathrm{S}}{}^{(1)}(\vec{\mathrm{r}}_{\mathrm{dcp}}))$ at r_{dcp} has two negative and one positive eigenvalue λ_n. Hence, a high CIV indicates a strong delocalization.

1.4.5. Computational Details

The ACID method currently is implemented in Gaussian 98[79] and Gaussian 03 programs. We applied the continuous set of gauge transformation (CSGT) method of Bader et al.[80−82] to calculate the current densities. Link 1002 was modified to write the current density, which was transformed into a rectangular grid and visualized as a cub-file with Gaussview or Povray. If not stated otherwise, all molecules in this review were optimized at the B3LYP/6-31G* level of theory. The CSGT calculations were performed at the same level as the optimizations. Copies of the ACID program can be obtained free of charge from the author.

2. Simple π Conjugation

Typical delocalized systems are π rather than σ conjugated. This fact should also be represented in the ACID scalar field of the corresponding systems. The simplest model of a σ bond are the two interacting s orbitals in the ground state of the hydrogen molecule (Figure 9). The $\Pi_u{}^2$ excited state of the hydrogen molecule represents the simplest case of a bonding π orbital.

The ACID values in the π bond are several orders of magnitude higher than in the σ bond. The very small anisotropies in σ bonds are of toroidal shape. Usually they are only visible if the ACID isosurface is plotted at very small isosurface values. Π Bonds generally exhibit large anisotropies of the current density tensor, the largest ACID values being located between two atoms.

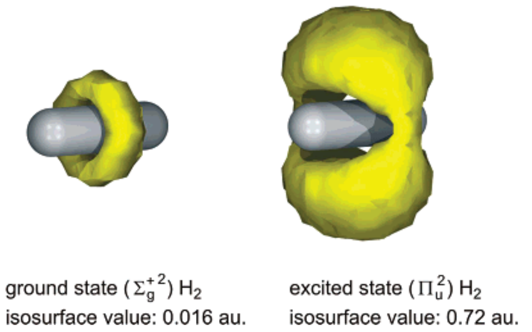


Figure 9. ACID scalar field of a prototype σ and π bond.

2.1. Linear Systems

2.1.1. Alkanes, Alkenes, Polyenes

The series butane, 1-butene, and butadiene comprises an instructive example to illustrate the properties of ACID in unsaturated hydrocarbons.

According to the general conception there are almost no delocalized electrons in saturated hydrocarbons such as n-butane. This is represented by small ACID values around the nuclei and bonds. At the standard isosurface value of 0.05 only small areas of toroidal topology between the bonded nuclei (C−C and C−H) are visible, whereas double bonds (see 1-butene in Figure 10) exhibit ACID values that are much larger. Interpreted in usual terms this means that the two electrons in a double bond are delocalized over both p orbitals of the sp^2 carbon atoms. In linearly π conjugated molecules such as butadiene the delocalization is represented by a continuous boundary of the ACID isosurface including all sp^2 carbon atoms. In agreement with the general interpretation of conjugation, the critical isosurface value (CIV) and hence the density of delocalized electrons are lower for the single bond between the double bonds than within the double bonds.

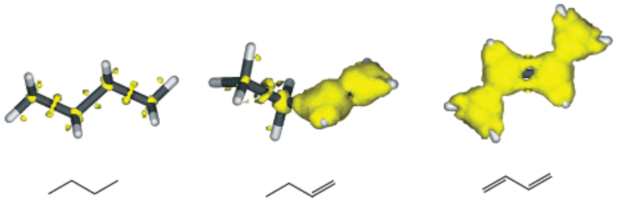


Figure 10. ACID isosurface plots of butane, 1-butene, and 1,3-butadiene.

The conjugation of two double bonds should decrease if the system is distorted from planarity. In agreement with this interpretation the CIVs of the π system in planar *cis*- and *trans*-1,3-butadiene are 0.0744 and 0.0755 (actually there is a higher conjugation in the *cis* isomer) and are considerably lower in the 90° distorted transition state of the isomerization (Figure 11).

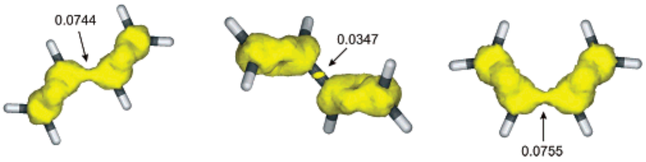


Figure 11. ACID isosurface in cis, trans, and 90° distorted 1,3-butadiene.

There is a recent controversy whether there is a conjugation between adjacent triple bonds (−C≡C−C≡C−) in polyynes.[83−85] The ACID analysis predicts a small conjugation (CIV = 0.014) which, however, is different from zero (in contrast to the findings of Rogers et al.).[83,84]

2.2. Cyclic Systems

2.2.1. Benzene

Cyclicly conjugated systems are either aromatic or antiaromatic. According to the ACID analysis the

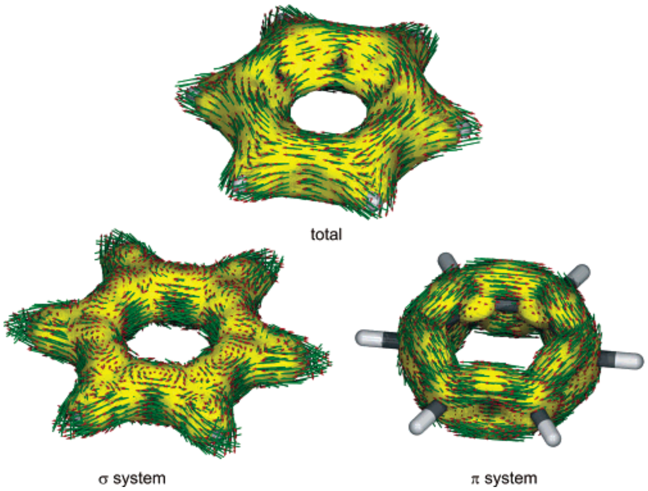


Figure 12. ACID isosurfaces of benzene separated into the σ and π contribution. Current density vectors are plotted onto the ACID isosurface to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

prototype system benzene exhibits both π and σ delocalization. The current density vectors plotted onto the ACID isosurface indicate a strong diatropic ring current in the π system above and underneath the ring and—interestingly—a weak paratropic ring current in the molecular plane mainly located inside the six-membered ring (Figure 12).[86−88] The strong σ conjugation might seem to be counterintuitive; however, there is evidence that the delocalized σ and not the π system is the decisive factor that favors the D_{6h} over the D_{3h} (cyclohexatriene) structure in benzene.[89,90]

2.2.2. Heterobenzenes

According to the ACID analysis, the aromatic character decreases in the series pyridine, phosphinine, silabenzene. This is in agreement with theoretical investigations[91−94] and the relative reactivity of these systems.[95,96] There is almost no cyclic conjugation and therefore no aromaticity in silabenzene. The pentadienyl system in silabenzene, however, exhibits a strong linear conjugation. The iridabenzene (Figure 13, bottom right) synthesized by Haley et al.[97] definitely has aromatic character.

2.2.3. Cycloalkanes

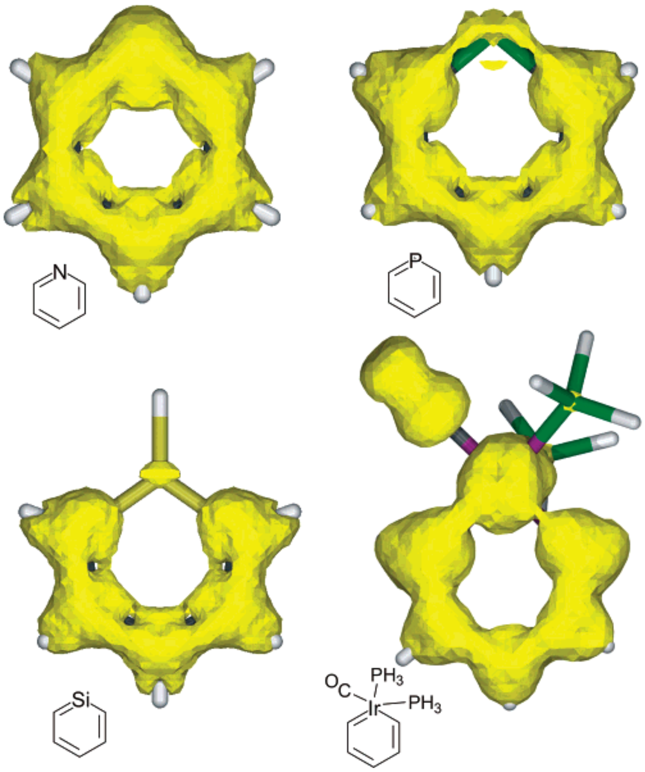


Figure 13. ACID plots of pyridine, phosphinine, silabenzene, and iridabenzene.

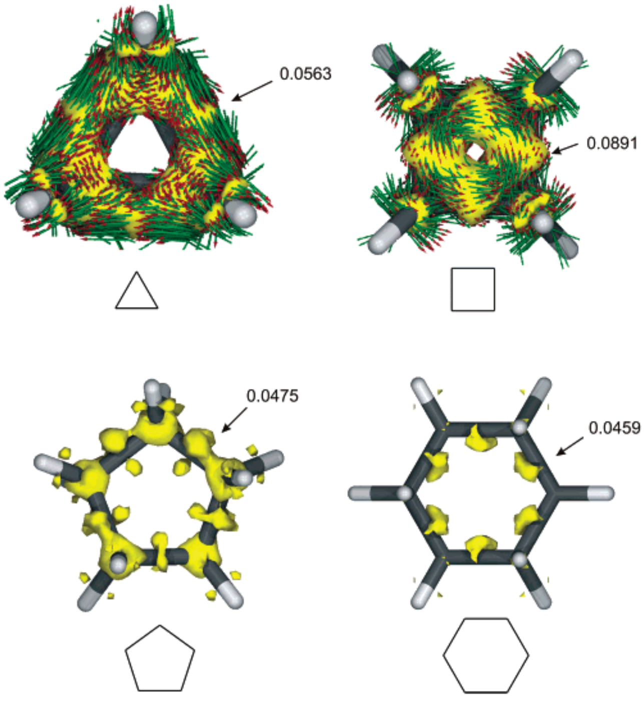


Figure 14. ACID isosurfaces of cyclopropane, cyclobutane, cyclopentane, and cyclohexane. Current density vectors are plotted onto the ACID isosurface of cyclopropane and cyclobutane. CIV values are given for the cyclic delocalized systems. Cyclopropane exhibits σ aromaticity and cyclobutane antiaromaticity.

Among the cycloalkanes, cyclopropane and cyclobutane are exceptions (Figure 14). Whereas cyclopentane and higher cycloalkanes exhibit ACID isosurfaces with a very low degree of conjugation similar to n-alkanes, cyclopropane and cyclobutane are less “innocent”. In agreement with other magnetic data (diamagnetic susceptibility, highfield shift in ^{1}H NMR and NICS (−42.8)), cyclopropane exhibits a considerable amount of delocalization.[98−107] The critical isosurface value (CIV = 0.0563), however, is much lower than the value of benzene (CIV = 0.0739). The current density plotted onto the ACID isosurface indicates a strong diamagnetic ring current in the ring plane and hence σ aromaticity. In contrast to cyclopropane, cyclobutane is antiaromatic.[108−116] The ACID plot and the current density vectors (Figure 14) exhibit a strong paratropic ring current and thus antiaromaticity. However, the paramagnetic properties most probably are exaggerated for reasons that are due to an inadequate electronic description[117,118] by the DFT method and the magnetic properties that are calculated using the CSGT approach.[80,81] This is probably also true for magnetic susceptibilities and NICS values calculated at the same level of theory.

2.3. Polycyclic Systems

2.3.1. Naphthalene

Concurrent with the general view and current density plots[119−121] the π system of polycyclic aromatics such as naphthalene and azulene rather look like [10]annulenes than a composition of separate rings. The central C−C bond is not part of the delocalized π system, and the diamagnetic ring current is restricted to the periphery (Figure 15).

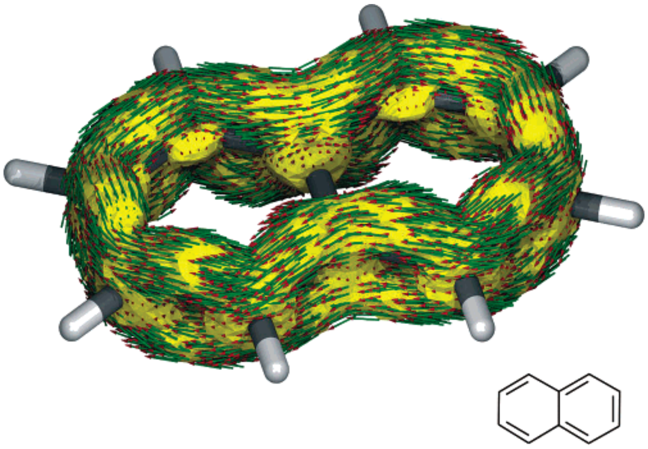


Figure 15. ACID of the π system of naphthalene. The current density vectors plotted onto the ACID isosurface indicate a strong diatropic ring current in the [10]annulene periphery.

2.3.2. Coronene

Coronene in principle can be written in two different D_{6h} or D_{3h} (and several less) symmetrical mesomeric structures: (a) a bis-annulenoid structure with a diamagnetic [18]annulene periphery and a diamagnetic central benzene ring or (b) a radialene structure with an [18]annulene periphery as in (a) but with a nonaromatic central benzene ring. The ACID plot of the π system (Figure 16) indicates that structure b with a weak paramagnetic ring current in the central six-membered ring provides a better description of the electronic structure than (a). The ACID analysis is in agreement with the NICS values of the peripheral and the central ring of coronene[122] and the ring current analysis of several independent groups.[123−125]

2.3.3. Porphine

On the basis of its reactivity (the double bonds of the unprotonated pyrrol rings are reduced and oxidized)[126−131] and magnetic properties (NMR, NICS, and current density maps),[132−137] porphine can be viewed as an [18]annulene derivative.[138]

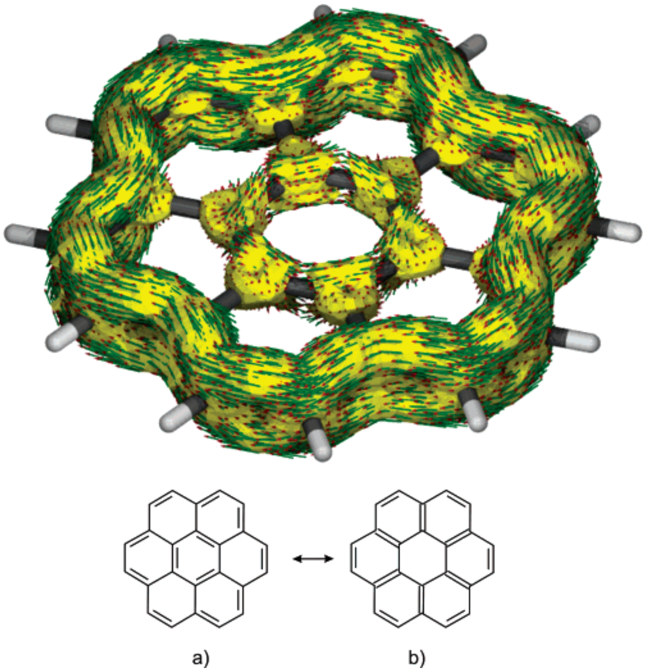


Figure 16. ACID of the π system of coronene. The current density vectors plotted onto the ACID isosurface indicate a strong diatropic ring current in the [18]annulene periphery and a weak paratropic ring current in the central benzene ring. Hence, the mesomeric structure (b) is a better representation of the electronic structure.

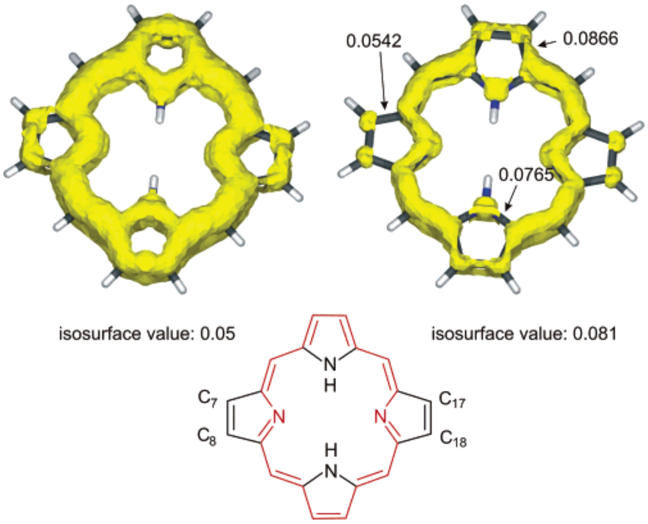


Figure 17. ACID plots of porphine at isosurface values of 0.05 and 0.081. CIVs representing the strength of delocalization) are given for selected bonds.

At the standard isosurface value of 0.05 the delocalized system includes all bonds (Figure 1, left). Upon increasing the isosurface value to 0.0542 the C7−C8 and the C17−C18 double bonds are isolated; at 0.081 the 1,10-diaza[18]annulene part remains as a continuous isosurface, which exhibits a strong diamagnetic ring current (Figure 17, right).

2.3.4. Indigo

Indigo is one of the oldest organic dyes. It has a deep blue color, and the reduced form, leuco indigo, is colorless. The reason for the difference in color is not obvious at first glance because both systems are planar and, at least from a formal point of view, fully conjugated (Figure 18). There are two different explanations for the long wavelength absorption of indigo. If a partial negative charge is assumed at the carbonyl oxygen, an antiaromatic character of the positively charged five-membered rings and thus a

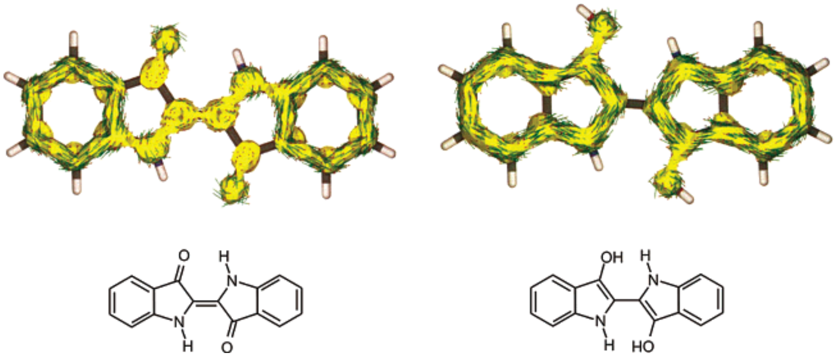


Figure 18. ACID plot of indigo and leuco indigo.

bathochromic shift can be assumed.[139] An alternative explanation is based on the cross-conjugated donor−acceptor system including the central double bond, both carbonyl, and both amino groups (H-chromophore).[140] The ACID analysis and recent high-level ab initio calculations[141] are in favor of the latter concept. There is only a very small paratropic ring current in the five-membered rings and thus no marked antiaromaticity. The ACID plot of indigo at the standard isosurface value of 0.05 exhibits a linear conjugated system connecting both benzene rings. The carbonyl groups are included at lower isosurface values (0.035). Leuco indigo is best described by two independent indole units.

3. Through-Bond Conjugation

π systems that are not directly conjugated may interact either through space or through bonds.[142−147] Even though sp^3 hybridized carbons usually act as insulators, σ systems of suitable symmetry can act as a relay[148] transmitting substituent effects, charge transfer, or other effects through bond.[149]

3.1. Conjugation of π Systems through Several σ Bonds

3.1.1. Stelladiene

In stellenes, a six-membered ring fixed in twist conformation (within the tricyclo[3.3.0.^{1,5}0^{3,7}]octane system) provides a suitable σ framework for the through-bond conjugation of two exocyclic double bonds.[148,150,151] The σ conjugation is clearly visible in the ACID plot of stelladiene (Figure 19).

As predicted by Gleiter et al.[148] using a MO analysis (see orbitals b_2 and b_3 in Figure 19), the delocalized system involves four σ bonds including the central CH_2 group instead of using the shorter path with three σ bonds via the “diagonal” C−C bonds of the stellane framework.

3.1.2. Conjugated Donor Acceptor Systems

Trans-fused norbornane rings are effective in transmitting electron transfer via σ conjugation. Cis or gauche bend configurations decrease the conjugation. If one end of such a σ framework is substituted by an electron donor and the other end by an electron acceptor, the “degree” of conjugation can be measured as a function of the rate of charge separation.[152] The ratio for the charge separation (k_{cs}) of the two donor acceptor systems without and with the “bend” is 14:1, and hence the bend structure should exhibit a less pronounced conjugation. This is reflected by the CIVs of the corresponding bonds neighboring the cis bend (Figure 20). With a CIV of 0.026 and 0.040 the conjugation in the trans norbornyl unit is considerably larger than in the corresponding cis-fused norbornyl (CIV = 0.024 and 0.020).

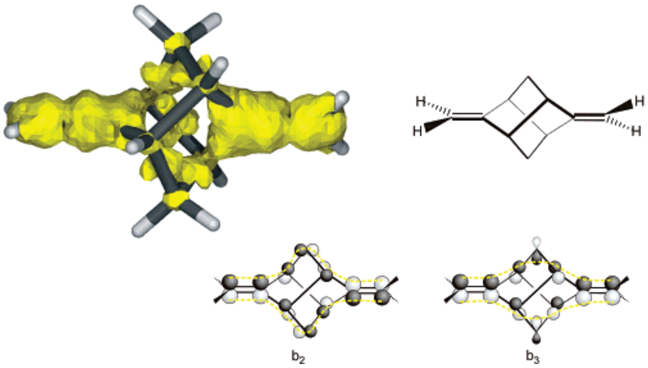


Figure 19. ACID of p-stelladiene. Even though the two exocyclic double bonds are orthogonal and separated by three σ bonds, there is a considerable through-bond conjugation via the MO’s b_2 and b_3. The ACID isosurface exhibits a continuous boundary surface involving the two π bonds and two pathways with four σ bonds each.

3.2. Hyperconjugation

3.2.1. Ethane

The prototype system that has the potential to exhibit hyperconjugation is ethane. There is considerable disagreement whether the rotational barrier in ethane arises from the van der Waals repulsion of the hydrogen atoms and thus the destabilization of the eclipsed conformation or from hyperconjugative stabilization of the staggered conformation.[153−157] The ACID analysis surprisingly predicts a slightly stronger hyperconjugation of the eclipsed compared to the staggered conformation and thus is in favor of explanations other than hyperconjugation. At low isosurface values the toroidal ACID densities of the C−C and C−H bonds merge to form a continuous boundary surface that represents six hyperconjugative relationships with a CIV of 0.0348 for the staggered conformation and a CIV of 0.0370 for the eclipsed conformation (Figure 21).

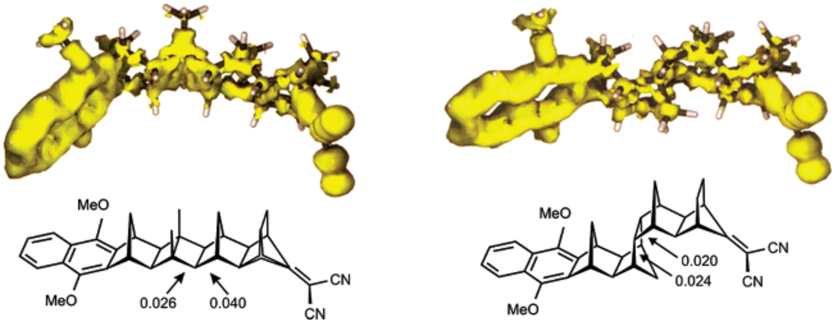


Figure 20. ACID plot of a donor acceptor system with all-trans fused norbornane rings and a system with a cis bend. CIVs are given for the cis bend and the corresponding trans fusion.

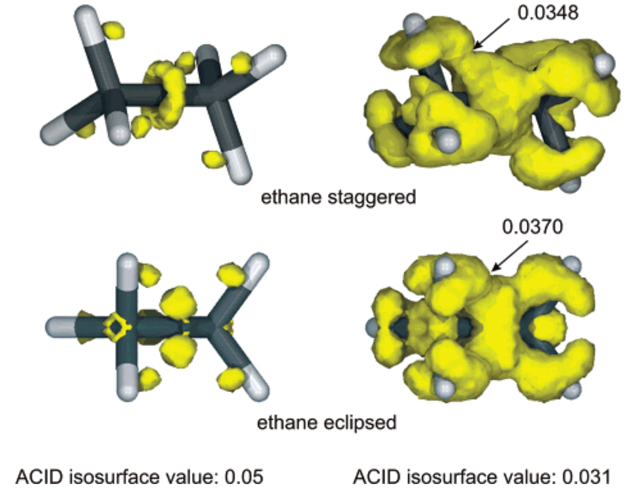


Figure 21. ACID plots of staggered and eclipsed ethane at the standard isosurface value of 0.05 (left) and a lower value of 0.031 (right). CIVs are given for the critical points representing the hyperconjugation.

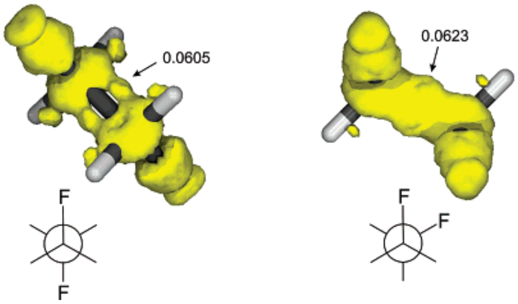


Figure 22. ACID plot of 1,2-difluoroethane in anti and gauche conformations. CIVs represent the strength of the hyperconjugation between the σ_{CH} and σ^*_{CF} orbitals, explaining the preference of the gauche conformation.

3.2.2. 1,2-Difluoroethane

1,2-Difluoroethane in the gas phase prefers the gauche conformation,[158−176] whereas 1,2-dichloroethane and 1,2-dibromoethane are more stable in the anti conformation because of the sterical repulsion of the halogens and the zero dipole moment. According to theoretical investigations the gauche conformation[177−180] of 1,2-difluoroethane (Figure 22) is stabilized by hyperconjugation[181−184] of the donor σ_{CH} and the acceptor σ_{CF}^* orbitals.[185,186] This is confirmed by the ACID analysis. The CIV of anti difluoroethane is smaller (0.0605) than the CIV of the gauche isomer (0.0623).

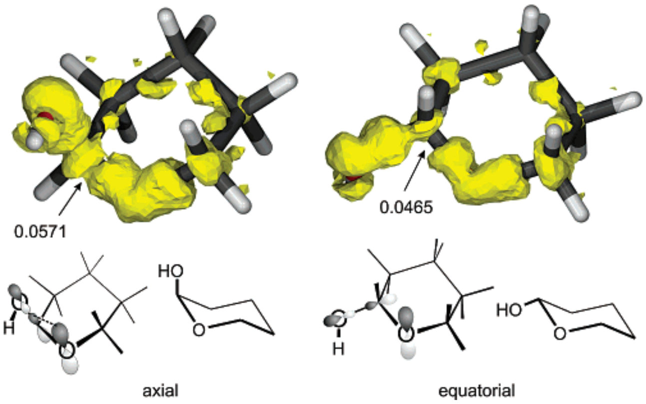


Figure 23. ACID isosurface of 2-hydroxytetrahydropyran. CIVs reveal a more pronounced conjugation in the axial than in the equatorial conformation.

3.2.3. Anomeric Effect in 2-Hydroxytetrahydropyrane

A special case of hyperconjugation is the anomeric effect, which was first observed in sugars. Conjugation between the lone pair of the ring oxygen and the exocyclic C−O σ^* bond of the neighboring OH group is more effective if the OH group occupies the axial compared to the equatorial position. Glucose is more stable in the α conformation (axial OH in 1-position) than in β conformation (equatorial OH) in the gas phase.[187,188] Because of the more effective solvation, the equilibrium in water is shifted toward the β conformation (36:64%).[189]

We chose 2-hydroxytetrahydropyrane as a suitable model to study the anomeric effect.[190] The different extents of conjugation are clearly visible in the ACID plot of the axial and the equatorial conformations (Figure 23). At the standard isosurface value of 0.05 there is a continuous boundary surface in the conjugating C−O−C part of the structure (CIV = 0.0571), and in the equatorial conformation the lone pair oxygen and the exocyclic C−O bond are clearly separated (CIV = 0.0465).

4. Through-Space Conjugation

4.1. Homoconjugation

4.1.1. Cycloheptatriene and Triquinacene

Homoaromaticity is another important type of conjugative interaction.[191,192] In a number of cases it had been the subject of controversial discussions.[193] Homoconjugation has been invoked to explain ther-

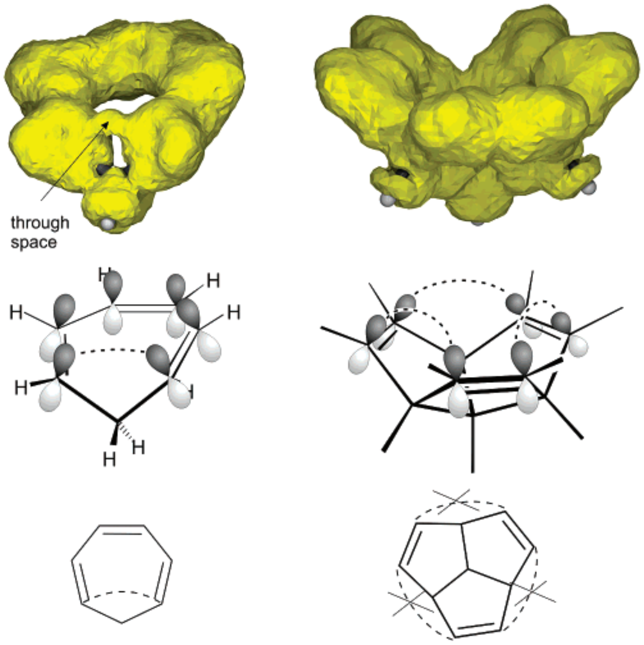


Figure 24. ACID plots of cycloheptatriene and triquinacene at an isosurface value of 0.027. There is through-space conjugation in the cycloheptatriene bridging the CH_2 group but no homoconjugation in triquinacene.

modynamic[194] and NMR data of cycloheptatriene.[195] The ACID plot at an isosurface value of 0.014 clearly confirms the through-space interaction bridging the CH_2 group (Figure 24) and forming a six-electron homoaromatic system (there is also through-bond conjugation involving the CH_2 group). The situation is different in triquinacene. Neither experimental (heats of hydrogenation, enthalpy of formation, spectroscopic and structural data) nor theoretical investigations find evidence of homoaromaticity.[196] This is in agreement with the ACID analysis. Even at very low isosurface values, there is no through-space interaction between the double bonds and hence no trishomoaromaticity.

4.2. Spiroconjugation

A very well investigated example of through-space interaction is spiroconjugation.[197−199] Two orthogonal π systems joined by a common tetrahedral atom interact through space. In closed shell systems, the interaction is stabilizing if $4n + 2$ electrons are involved (if one π system has an even and the other an odd number of double bonds) and zero or destabilizing if $4n$ electrons are delocalized. This effect is clearly represented in the ACID plot of spiro[2.4]-hepta-1,3,6-triene and spiro[4.4]nona-1,3,6,8-tetraene (Figure 25). There is a strong conjugation in the [2.4]-spiro framework (left) but no continuous isosurface (at the standard isosurface value of 0.05) in the [4.4]-spiro compound (right).

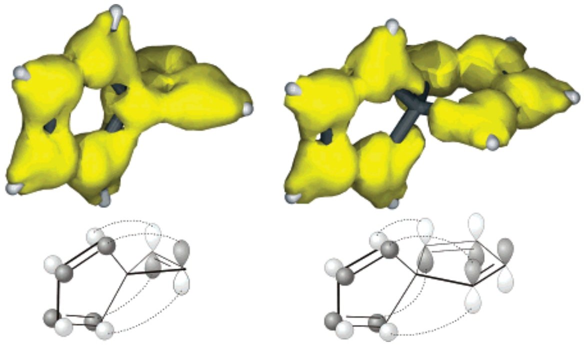


Figure 25. ACID isosurface of spiro[2.4]hepta-1,3,6-triene (left) and spiro[4.4]nona-1,3,6,8-tetraene (right). The through-space interaction is energetically favorable in the [2.4]spiro compound, because the ethylene LUMO and butadiene HOMO interact in a bonding combination. In the [4.4]spiro compound the interaction is zero or destabilizing because only the occupied HOMOs of both butadiene units interact. The bonding as well as the antibonding combination is occupied (only the bonding combination is shown).

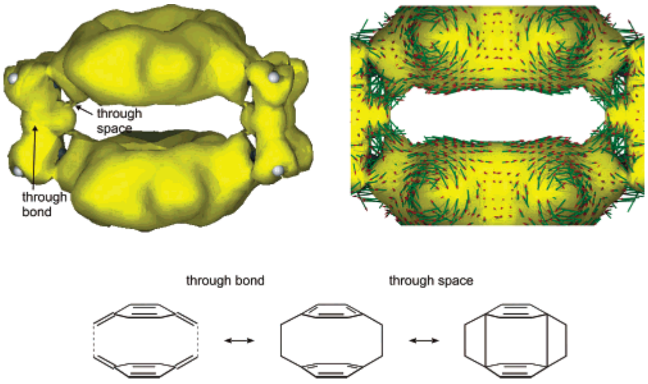


Figure 26. ACID plot of [2,2]paracyclophane at an isosurface value of 0.027 (left). The ACID boundary surface indicates a strong through-bond interaction (MO scheme, bottom left) and a weaker through-space interaction (quinoid mesomeric structure with cyclobutane rings, bottom right). Current density vectors are plotted onto the ACID isosurface (right). The magnetic field is perpendicular with respect to the plane defined by the four sp^3 bridge atoms. There is a strong (counterclockwise) paratropic ring current in the bishomo[8]annulene path, indicating a considerable destabilizing antiaromaticity in [2,2]paracyclophane.

4.3. Paracyclophane

There is strong evidence that the two benzene rings in [2,2]paracyclophane are in conjugation. The small HOMO−LUMO gap (UV, $\lambda_{max} = 302$ nm)[200] and the photoelectron spectrum[201,202] indicate a strong through-bond or through-space interaction. Substituents at the benzene rings affect not only the ^1H NMR chemical shift of the ortho protons but also the chemical shifts of the opposing unsubstituted ring.[203] There is no general agreement whether the conjugation between the two rings is through bond or through space. The through-bond conjugation of the σ^* orbitals of the ethane bridges with benzene π orbitals of suitable symmetry is illustrated by a mesomeric structure with two nonbonded *p*-xylylene units (Figure 26). The close proximity of the benzene rings, which is well below the sum of the van der Waals radii of the opposing carbon atoms (2.78 and 3.09 Å), also suggests a considerable transannular π π overlap. This through-space interaction can be represented by a quinoid mesomeric structure with two cyclobutane rings (Figure 26, bottom right). According to the analysis of the ACID density there is a strong through-bond interaction (the ACID isosurface includes the CH_2CH_2 bridges) and a weaker through-space interaction (ACID isosurface that connects the ipso carbon atoms). The through-space interaction between the remaining ortho carbon atoms is very weak.

Interestingly, there is a paratropic ring current in the bishomo [12]annulene periphery of the [2,2]-paracyclophane. The through-bond interaction between the two benzene rings closes the structure to a bishomo conjugated 12-membered ring, and through-space interaction creates an antiaromatic 8-membered ring. Hence, [2,2]paracyclophane is not only destabilized by the high ring strain but also suffers from antiaromaticity.

5. Conclusion

The ACID method is an intuitive and generally applicable method for the investigation and visualization of delocalization and conjugation (π, σ, through-bond, and through-space conjugation) in ground, excited, and transition states[204−209] and organometallic compounds.[210] It is directly derived from a quantum theoretical quantity and does not include empirical parameters that have to be fitted. As a tool for the investigation of molecular properties, ACID is complementary to the electrostatic surface and the electron density that provide information about charge and steric interactions. In the prototype examples for different types of delocalization presented in this review, the ACID analysis is in agreement with previous alternative theoretical investigations.

6. Acknowledgments

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