

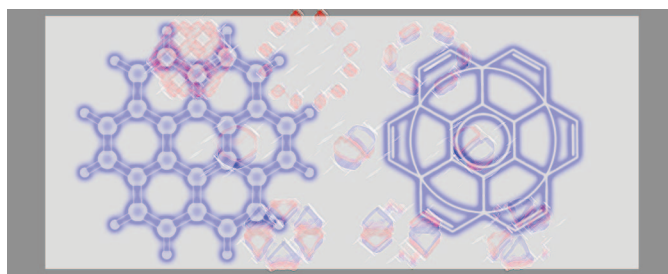
Revealing Intuitively Assessable Chemical Bonding Patterns in Organic Aromatic Molecules via Adaptive Natural Density Partitioning

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The newly developed adaptive natural density partitioning (AdNDP) method has been applied to a series of organic aromatic mono- and polycyclic molecules, including cyclopropenyl cation, cyclopentadienyl anion, benzene, naphthalene, anthracene, phenanthrene, triphenylene, and coronene. The patterns of chemical bonding obtained by AdNDP are consistent with chemical intuition and lead to unique, compact, graphic formulas. The resulting bonding patterns avoid resonant description and are always consistent with the point symmetry of the molecule. The AdNDP representation of aromatic systems seamlessly incorporates localized and delocalized bonding elements.

Introduction

In contemporary chemistry, there is a well-established intuitive way of thinking of chemical bonding in organic aromatic molecules. For many organic molecules, the Lewis formula is the simplest and most powerful way to represent the real chemical species. Lewis developed this way of representing chemical species before the formulation of quantum mechanics. He developed this description of molecules on the basis of generalizations of numerous experimental facts. Today, the Lewis formula is an essential part of the chemical language, and it is impossible to imagine modern chemistry without Lewis models of molecules. Quantum chemistry introduced its own language to chemistry on the basis of canonical Hartree–Fock or Kohn–Sham molecular orbitals. These two languages are different. The Lewis representation of molecules is based on localized bonding elements such as lone pairs and two-center two-electron (2c-2e) bonds, while in the quantum chemical description of molecules, two-electron objects such as molecular orbitals (MOs) are delocalized over entire molecules. In the 1960s, there was a major breakthrough in quantum chemistry

when Foster and Boys,¹ Edmiston and Ruedenberg,² and later Pipek and Mezey³ and Weinhold⁴ proposed their schemes for obtaining localized orbitals from completely delocalized ones. These schemes allow us to make a connection between two very different chemical languages: the rigorous language of the delocalized MOs and the intuitive language of the localized bonding elements such as lone pairs and 2c-2e bonds. In Figure 1, we present the structure of formic acid, its Lewis representation, canonical MOs describing the formic acid molecule, and the corresponding localized orbitals obtained by the natural bond orbital (NBO) analysis introduced into chemistry by Weinhold.⁵ One can see that all of the elements of the Lewis structure such as lone pairs on oxygen, 2c-2e σ bonds (C–H and C–O), and 2c-2e π bond (C=O) have been recovered by the NBO analysis.

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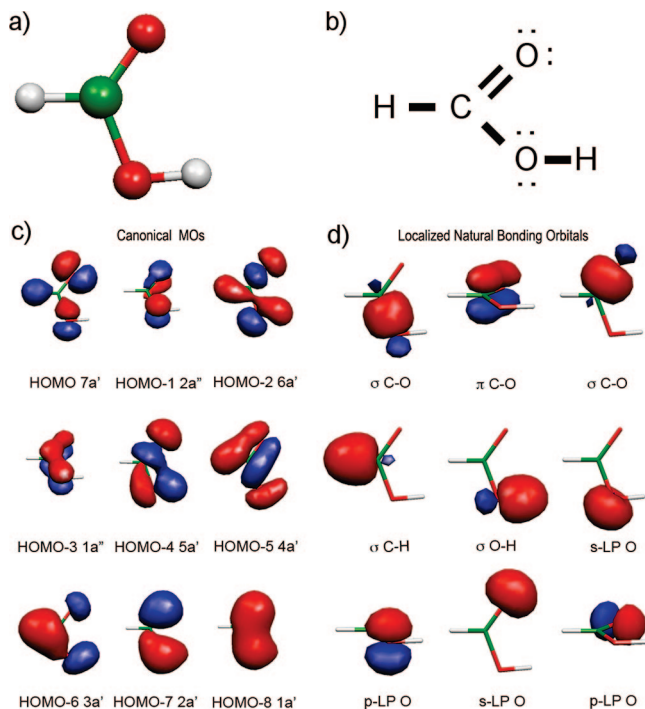


FIGURE 1. (a) Structure of a molecule of formic acid. (b) Lewis representation of a molecule of formic acid. (c) Canonical MOs of formic acid. (d) Localized natural bonding orbitals of formic acid.

Thus, we have a quantum mechanical justification for the intuitive Lewis description of organic molecules.

The bonding pattern of benzene is easily represented with a set of localized 2c-2e σ bonds between neighboring carbon atoms and between carbon and adjacent hydrogen atoms supplemented with a set of three completely delocalized π -canonical molecular orbitals (CMOs) with contributions from the carbon atoms only. The benzene molecule is π aromatic according to Hückel's $4n + 2$ rule. The strategy of combining the localized and delocalized bonding can be extended to other organic aromatic molecules. The above-mentioned intuitive chemical bonding pattern of benzene is taught in general chemistry classes, although there is not a single chemical theoretical tool that allows extraction of this particular bonding pattern from the molecular orbital (MO) wave function. The application of the standard NBO analysis to the benzene molecule leads to the recovery of the framework of six 2c-2e carbon-carbon σ bonds and six 2c-2e carbon-hydrogen σ bonds. The π -electronic subsystem also is represented in terms of three 2c-2e π bonds, i.e., one of the resonance Kekulé structures is formed. Apparently, this bonding interpretation is not consistent with the above-mentioned picture combining the localized 2c-2e C-C and C-H σ bonds and the delocalized C-C π bonding.

We recently developed a new theoretical tool for analysis of chemical bonding in the chemical systems of the general type which is called adaptive natural density partitioning (AdNDP).⁶ This approach leads to partitioning of the charge density into elements with the highest-possible degree of localization of electron pairs such as the n -center two-electron (nc -2e) bonds, which include core electrons, lone pairs (LPs), 2c-2e bonds, etc. If some portion of the density cannot be localized in this manner, it is represented using completely delocalized objects, similar to canonical MOs, naturally incorporating the idea of the completely delocalized bonding. Thus, AdNDP achieves a

seamless description of different types of chemical bonds. We would like to stress that the AdNDP method is not a tool for assessment of aromaticity in molecules. Its primary goal is to reveal if there is delocalized bonding in a particular system. Also, AdNDP is not relying on Bader's atoms-in-molecule theory, Gillespie's Laplacian condition, or others for partitioning of atoms or bonds in molecules. AdNDP is a tool that provides partitioning of electron density (see ref 6 for details). AdNDP has been successfully applied to the analysis of chemical bonding in boron clusters.⁶

There are various chemical theoretical approaches to the assessment of aromaticity. The most recent review of the existing techniques can be found in refs 7–9. The three-center bond index was first proposed by Giambiagi et al.¹⁰ and also independently by Sannigrahi and Kar.¹¹ Other electron-sharing indexes such as Fulton's electron sharing index (ESI),^{12,13} Mayer's bond orders,^{14–18} and delocalization indexes (DI)^{19,20} were reviewed by E. Matito et al.²¹ Various aromaticity indices are used to probe delocalized bonding such as para-delocalization index (PDI),²² the aromatic fluctuation index (FLU),²³ MO multicenter bond index (MCI),^{24,25} etc. Six-center bond index as a measure of aromaticity was proposed by Ponec and co-workers.^{26,27} Ponec et al.²⁸ further demonstrated that homoaromaticity and nonhomoaromatic and antihomoaromatic systems can be characterized quantitatively using MCI. Normalized variants of MCI were developed by Cioslowski et al.²⁹ Chattaraj and co-workers³⁰ studied efficiency of the multicenter indices in providing insights into the bonding, reactivity, and aromaticity in all metal aromatic and antiaromatic compounds. Chattaraj and co-workers³¹ described the stability and reactivity of aromatic and antiaromatic compounds on the basis of the maximum hardness and the minimum polarizability principles. There are probes for aromaticity and antiaromaticity based on

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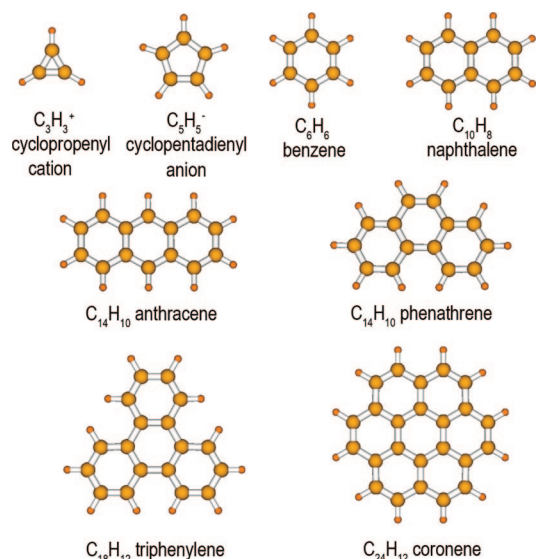


FIGURE 2. Structures of cyclopropenyl cation, cyclopentadienyl anion, benzene, naphthalene, anthracene, phenanthrene, triphenylene, and coronene.

the response to the presence of an external magnetic field. These probes include the nuclear independent chemical shift (NICS) pioneered by Schleyer and co-workers,^{32,33} the aromatic ring-current shieldings (ARCS)³⁴ and the gauge-including magnetically induced current (GIMIC)³⁵ proposed by Sundholm and co-workers, and maps of current density induced by a perpendicular magnetic field developed by Fowler and co-workers.³⁶

In the present study, we use the AdNDP novel approach for the analysis of the MO wave function of the selected organic aromatic systems, including cyclopropenyl cation, cyclopentadienyl anion, benzene, naphthalene, anthracene, phenanthrene, triphenylene, and coronene (Figure 2). We show that the obtained description of chemical bonding is indeed a combination of localized 2c-2e C–C and C–H σ bonds and delocalized C–C π bonding in agreement with the intuitive assessment of the chemical bonding in these systems.

Theoretical Methods

The detailed description of the AdNDP algorithm can be found elsewhere.⁶ From the computational point of view, AdNDP is a generalization of the NBO analysis by Weinhold.⁵ AdNDP performs analysis of the first-order reduced density matrix with the purpose of obtaining its local block eigenfunctions with optimal convergence properties for describing the electron density. The local blocks of the first-order reduced density matrix correspond to the sets of n atoms (from one to all the atoms of the molecule) that are tested for the presence of a two-electron object (nc -2e bonds, including core electrons and lone pairs as a special case of $n = 1$) associated with this particular set of n atoms. The n atomic sets are formed and checked in an exhaustive manner, so that the recovered nc -2e

bonding elements always correspond to the point group symmetry of the system after these bonding elements are superimposed onto the molecular frame. For the given n atomic block those eigenvectors are accepted whose occupation numbers (eigenvalues) exceed the established threshold value, usually close to 2.00 lel. Thus Lewis's idea of an electronic pair as the essential element of bonding is preserved. The AdNDP procedure is numerically efficient because it involves only a series of diagonalizations of density matrix blocks. It is unbiased in the sense that no preliminary ideas of the bonding pattern are required to perform analysis. The AdNDP code is a stand-alone program that uses output from Gaussian 03. The geometry optimization and normal-mode analysis for the studied systems were carried out using the hybrid density functional B3LYP³⁷ method with the 3-21G basis set³⁸ as implemented in Gaussian 03.³⁹ The density matrix used for the basis of the natural atomic orbitals as well as for the transformation between atomic orbital and natural atomic orbital basis sets, which are used by the AdNDP program, was generated at the B3LYP/3-21G level of theory by means of the NBO 3.0 code⁴⁰ incorporated into Gaussian 03. It is known that the results of NBO analysis do not generally depend on the quality of the basis set, so the choice of the level of theory for the AdNDP application is adequate. The visualization of the results of the calculations is performed using MOLEKEL 4.3⁴¹ and MOLDEN 3.6.⁴²

Theoretical Results

$C_3H_3^+$. The cyclopropenyl cation, $C_3H_3^+$, is the simplest organic aromatic system with two π electrons satisfying Hückel's $4n + 2$ rule for $n = 0$. The straightforward application of the standard NBO analysis accepting only LPs and 2c-2e bonds leads to a bonding pattern including three 2c-2e C–C σ bonds and three 2c-2e C–H σ bonds in the σ -bonding framework. There is just one MO responsible for π bonding. The NBO analysis leads to the representation of the π -electronic system in terms of three low-occupancy (0.66 lel) LPs on carbon atoms. If NBO is allowed to accept 3c-2e bonds, the π -electronic system is represented as a 3c-2e π bond involving carbon atoms. This picture is indeed the one corresponding to the intuitive representation of the chemical bonding in $C_3H_3^+$. The application of AdNDP leads to the bonding pattern shown in Figure 3a. There are three C–C σ bonds (superimposed on the single molecular framework) with an occupation number of ON =

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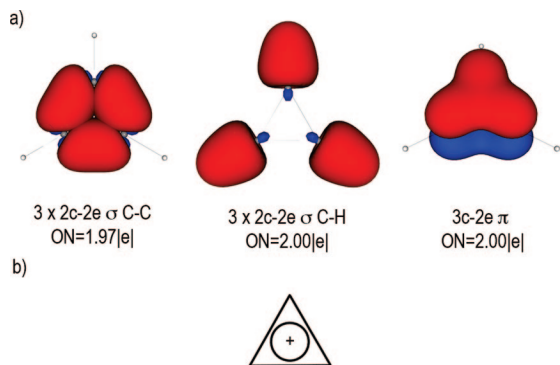


FIGURE 3. (a) AdNDP bonding pattern for $C_3H_3^+$. (b) Symbolic representation of $C_3H_3^+$.

1.97 lel, three C–H σ bonds (superimposed on the single molecular framework) with ON = 2.00 lel, and one 3c-2e π bond with ON = 2.00 lel involving three carbon atoms. In order to test the sensitivity of the ON numbers to the basis set, we performed AdNDP calculations of $C_3H_3^+$ with the 6-31G* and 6-311++G** basis sets. The ONs for 2c-2e C–C σ bonds are 1.98 lel (6-31G*) and 1.97 lel (6-311++G**), and the ONs for the 3c-2e C–C π bond are 2.00 lel for both basis sets. As expected, the results of the AdNDP analysis did not show significant dependence on the basis set. The occupation numbers here are very close to the ideal values of 2.00 lel. These results are in perfect agreement with the above-mentioned NBO results. This representation almost ideally corresponds to the concept of the chemical bond as an object involving a perfect electron pair. The results of the analysis can be expressed in a compact way by a graphical formula in Figure 3b.

The consistency between the AdNDP and NBO results in this case is due to the fact that bonding can be described by a combination of 2c-2e and 3c-2e bonds. NBO analysis is indeed considered as a standard within the ranges of its applicability, so this consistency is very important for benchmarking the performance of AdNDP. Like in the conventional NBO analysis, the portions of the electron density responsible for the deviation of the occupation number from the ideal value of 2.00 lel, such as 1.97 lel for the 2c-2e C–C σ bond, are the low occupation orbitals, also called the “Rydberg” orbitals according to NBO terminology.

$C_5H_5^-$. The bonding in a cyclopentadienyl anion is expected to be represented as a combination of five 2c-2e C–C σ bonds forming a cycle, five 2c-2e C–H σ bonds, and a delocalized part involving three π MOs. The bonding pattern revealed by AdNDP (Figure 4a) is in agreement with this description. There are five peripheral 2c-2e C–C σ bonds with ON = 1.99 lel (superimposed on the single molecular framework), five 2c-2e C–H σ bonds with ON = 1.98 lel (superimposed on the single molecular framework), and three 5c-2e delocalized π bonds with ON = 2.00 lel responsible for the π aromaticity of $C_5H_5^-$, which closely resemble parental canonical MOs. From the technical point of view, these three 5c-2e delocalized π bonds were found during the search including all ten atoms. Apparently, only five carbon atoms have non-zero contributions to these bonds, so they are designated as 5c-2e. The same logic is applied in other similar cases. Because the current version of the NBO program does not perform a search beyond three center bonds, it recovers one of the resonant structures (Figure 4b) with the π system represented by two 2c-2e C–C π bonds and a π LP. On the other hand, the results of AdNDP are consistent with the single

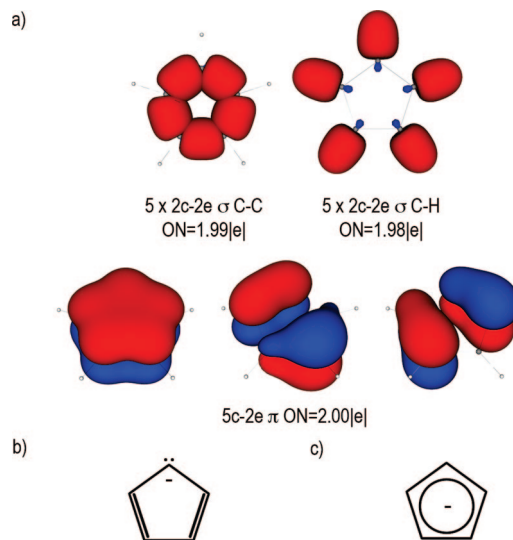


FIGURE 4. (a) AdNDP bonding pattern for $C_5H_5^-$. (b) Symbolic representation of the resonant structure of $C_5H_5^-$ according to NBO. (c) Symbolic representation of $C_5H_5^-$ according to AdNDP.

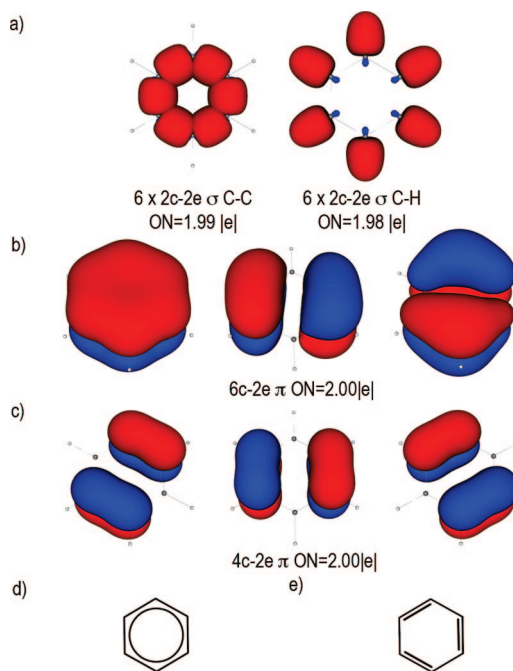


FIGURE 5. (a) σ -Bonding pattern for C_6H_6 according to AdNDP. (b) First possible π -bonding pattern for C_6H_6 according to AdNDP. (c) Second possible π -bonding pattern for C_6H_6 according to AdNDP. (d) Symbolic representation of C_6H_6 according to AdNDP. (e) Symbolic representation of C_6H_6 according to NBO.

symbolic representation (Figure 3c), which is widely accepted in the literature.

Benzene. Benzene is a prototypical aromatic molecule. The bonding is described as a combination of the localized (six 2c-2e C–C σ bonds forming the cycle and six 2c-2e C–H σ bonds) and delocalized (three π MOs) bonding objects. AdNDP (Figure 5a) recovers the pattern of six 2c-2e C–C (ON = 1.99 lel, superimposed on the single molecular framework) and six 2c-2e C–H (ON = 1.98 lel, superimposed on the single molecular framework) bonds as well as NBO. AdNDP provides two solutions to the representation of the delocalized π bonding in the benzene molecule. The first one (Figure 5b) includes three 6c-2e bonds (ON = 2.00 lel) closely resembling the parental

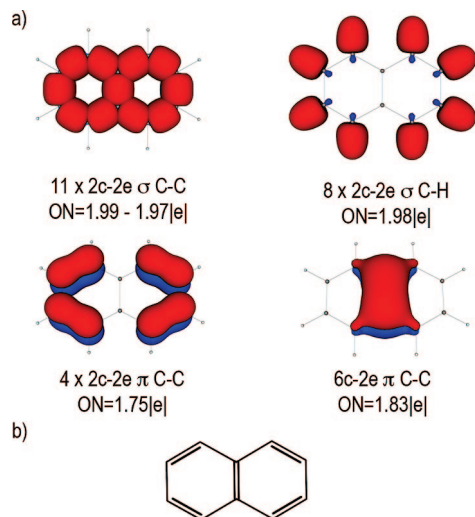


FIGURE 6. (a) AdNDP bonding pattern for naphthalene. (b) Symbolic representation of naphthalene according to AdNDP.

canonical MOs. The second one (Figure 5c) includes three $4c-2e$ bonds (ON = 2.00|e|). Both representations are correct as far as the AdNDP algorithm is concerned. It is up to the researcher to select a particular description of the chemical bonding. In the present study, in order to preserve the unified descriptive approach to the aromatic systems like $C_5H_5^-$ and $C_7H_7^+$, we will preserve the first representation. It does not seem possible to obtain the representation of the second type for $C_5H_5^-$ and $C_7H_7^+$. The six C–C and six C–H σ bonds, together with three $6c-2e$ π bonds (panels a and b of Figure 5, respectively), agree with the commonly used symbolic representation of benzene (Figure 5d). NBO analysis of benzene leads to one of two resonant Kekulé structures (Figure 5e).

AdNDP has elucidated the delocalized π bonding in all three of the above-mentioned monocyclic systems: cyclopropenyl cation, cyclopentadienyl anion, and benzene. The presence of the π bonds delocalized over all the carbon atoms that closely resemble canonical π MOs makes it possible to apply Hückel's $4n + 2$ rule and assign π aromaticity to these systems.

Naphthalene. According to Hückel's $4n + 2$ rule for aromaticity, naphthalene, $C_{10}H_8$ (Figure 2), is π aromatic with 10 delocalized π electrons. However, it should be realized that the $4n + 2$ rule was not originally designed for the description of polycyclic systems, and certain modifications might be necessary. For instance, Platt⁴³ proposed that the $4n + 2$ rule be applied to the peripheral carbon atoms only. Clar⁴⁴ proposed an alternative representation of aromaticity. Clar's rule suggests that the most important structures of the polycyclic aromatic hydrocarbons (PAHs) are those with the largest number of disjoint benzene-type moieties (π -aromatic sextets). Naphthalene, however, cannot be represented using a single Clar's structure and requires invoking resonance between two Clar's structures, each containing a π sextet (inscribed in a solid circle) in one of the six-atomic cycles.

AdNDP analysis (Figure 6a) reveals the expected σ -bonding framework including eleven $2c-2e$ C–C σ bonds (ON = 1.99–1.97|e|, superimposed on the single molecular framework) and eight $2c-2e$ C–H σ bonds (ON = 1.98|e|, superimposed on the single molecular framework). The π -bonding framework

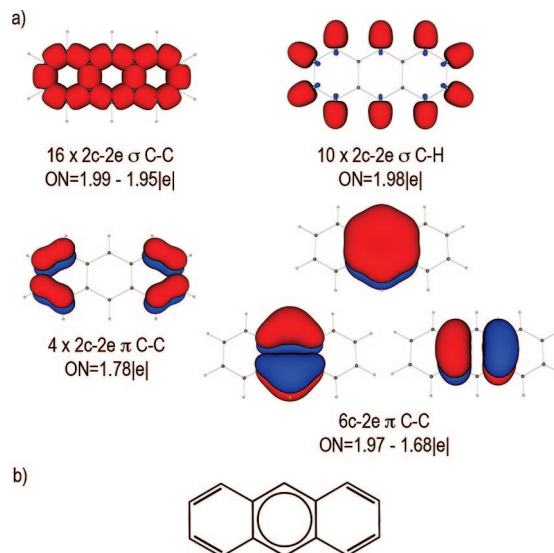


FIGURE 7. (a) AdNDP bonding pattern for anthracene. (b) Symbolic representation of anthracene according to AdNDP.

consists of four $2c-2e$ C–C π bonds (ON = 1.75|e|, superimposed on the single molecular framework) and one $6c-2e$ C–C π bond (ON = 1.83|e|) with two central atoms being the major contributors to the latter. The deviations of the occupation numbers of the π bonds from the ideal value of 2.00|e| are signatures of the conjugation between the recovered π bonds. This bonding picture is close to one of the Kekulé structures of naphthalene (Figure 6b), which was previously reported by England and Ruedenberg.⁴⁵ The difference is that the central C–C π bond is two-center in the Kekulé formula and six-center in the AdNDP description. AdNDP analysis did not reveal Clar's structures for naphthalene because one of the goals of this method is to avoid a resonant description of chemical bonding. Instead, a single structural representation is sought for the given molecular system. The single Kekulé-like structure with conjugated π bonds is consistent with the appreciable C–C bond length alternation from 1.367 to 1.419 Å observed experimentally for this molecule.⁴⁶

Anthracene. Anthracene, $C_{14}H_{10}$ (Figure 2), is a π -aromatic molecule with 14 π electrons. The results of the AdNDP analysis (Figure 7a) include 16 $2c-2e$ C–C σ bonds (ON = 1.99–1.95|e|, superimposed on the single molecular framework) and 10 $2c-2e$ C–H σ bonds (ON = 1.98|e|, superimposed on the single molecular framework). The π bonding is represented as a combination of four $2c-2e$ C–C π bonds (ON = 1.78|e|, superimposed on the single molecular framework) and three $6c-2e$ C–C π bonds (ON = 1.97–1.68|e|). The $6c-2e$ π bonds, involving six carbon atoms of the central ring fragment, are similar to the three $6c-2e$ π bonds found in benzene (Figure 5b). These bonds were obtained by the application of the AdNDP procedure to the manually specified molecular fragments. This user-directed form of the AdNDP analysis is analogous to the directed search option of the standard NBO code. The choice of the fragments for the directed AdNDP procedure was performed on the basis of the assessment of the residual density after the removal of the density associated with the accepted $2c-2e$ σ bonds and π bonds. The residual density

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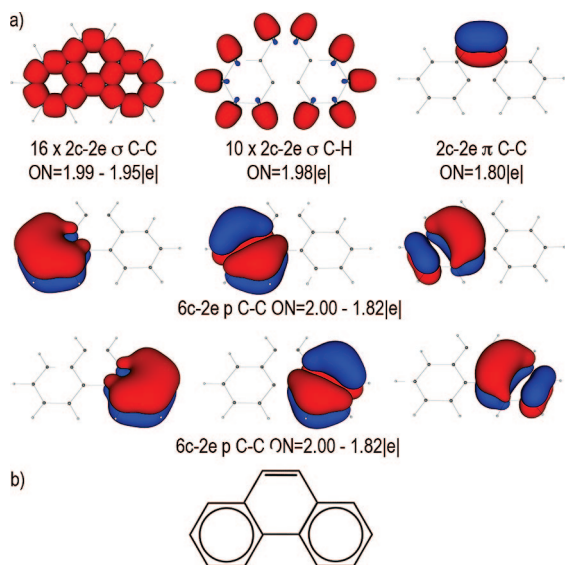


FIGURE 8. (a) AdNDP bonding pattern for phenanthrene. (b) Symbolic representation of phenanthrene according to AdNDP.

is primarily concentrated over the central six-atomic fragments (Supporting Information), so it is natural to perform the directed search procedure for this central six-atomic cycle. The deviation of the occupation numbers of the C–C π bonds in this case is due also to their conjugation. The appropriate symbolic representation consistent with the AdNDP results is the generally accepted Clar's structure shown in Figure 7b. In this structure, the delocalized π sextet, represented by a solid inner circle, is associated with the central cyclic fragment. According to the experimental data,⁴⁷ the bond alternation within the central cyclic fragment is indeed smaller (from 1.392 to 1.441 Å) than that within two peripheral cycles (from 1.366 to 1.460 Å), which is in agreement with Clar's structure (Figure 7b). The calculated NICS_{zz} values for the outer rings are –9.2 ppm (0.0 Å), –18.3 ppm (0.5 Å), and –26.0 ppm (1.0 Å), and for the inner ring, the values are –18.5 ppm (0.0 Å), –28.2 ppm (0.5 Å), and –34.7 ppm (1.0 Å). Here and elsewhere, the NICS_{zz} values are calculated at the B3LYP/6-311++G** level of theory. Thus, this NICS description is consistent with our conclusions based on the AdNDP analysis.

Phenanthrene. Phenanthrene, C₁₄H₁₀ (Figure 2), is an isomer of anthracene and is also π aromatic with 14 π electrons. The results of the AdNDP analysis are presented in Figure 8. According to the AdNDP results, the σ -bonding framework consists of 16 C–C σ bonds (ON = 1.99–1.95|e|, superimposed on the single molecular framework) and 10 2c-2e C–H σ bonds (ON = 1.98|e|, superimposed on the single molecular framework). The π -bonding framework consists of one 2c-2e C–C π bond (ON = 1.80|e|) with contributions from the two upper carbon atoms of the central six-atomic ring and six 6c-2e C–C π bonds (ON = 2.00–1.82|e|) involving carbon atoms of the two peripheral six-atomic cyclic fragments. The latter six 6c-2e π bonds were obtained using an AdNDP directed search, according to the procedure described in the section for the anthracene molecule. The residual density is primarily concentrated over the two outer six-atomic fragments (Supporting Information), hinting to the choice of the fragments for the user-

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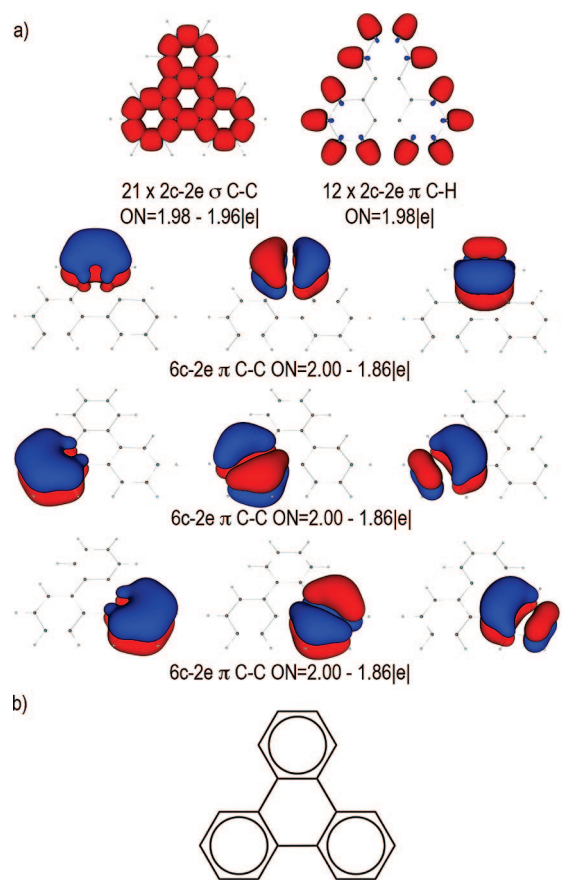


FIGURE 9. (a) AdNDP bonding pattern for triphenylene. (b) Symbolic representation of triphenylene according to AdNDP.

directed AdNDP search. The six 6c-2e π bonds form two groups. Each of these groups is located over one of the two peripheral six-atomic rings and includes three 6c-2e π bonds similar to the π bonds of the benzene molecule as shown in Figure 5b. The appropriate symbolic representation consistent with the AdNDP results is the generally accepted Clar's structure of the phenanthrene shown in Figure 8b. This structure contains two disjointed delocalized π sextets represented by solid inner circles, which are associated with the peripheral cyclic fragments. This graphical formula agrees with the experimentally observed⁴⁸ bond length alternations, which are smaller in the two peripheral cycles (from 1.369 to 1.412 Å) and larger in the central cycle (from 1.334 to 1.434 Å). The calculated NICS_{zz} values for the outer rings are –12.5 ppm (0.0 Å), –21.9 ppm (0.5 Å), and –29.1 ppm (1.0 Å), and for the inner ring, the values are –1.5 ppm (0.0 Å), –10.8 ppm (0.5 Å), and –20.4 ppm (1.0 Å). Thus, this NICS picture is consistent with our conclusions based on the AdNDP analysis.

Triphenylene. Triphenylene, C₁₈H₁₂ (Figure 2), is π aromatic with 18 π electrons. The results of the AdNDP analysis are presented in Figure 9. According to the AdNDP partitioning, the σ -bonding framework consists of 21 C–C σ bonds (ON = 1.98–1.96|e|, superimposed on the single molecular framework) and 12 2c-2e C–H σ bonds (ON = 1.98|e|, superimposed on the single molecular framework). The π -bonding framework consists of the nine 6c-2e C–C π bonds (ON = 2.00–1.86|e|) involving carbon atoms of the three peripheral six-atomic cyclic fragments. These 6c-2e π bonds were obtained using an AdNDP

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directed search, according to the procedure described in the section for the anthracene molecule. These bonds form three groups. Each of these groups is located over one of the three peripheral six-atomic rings and includes three 6c-2e π bonds similar to those of the π bonds of the benzene molecule as shown in Figure 5b. The appropriate symbolic representation consistent with the AdNDP results is the generally accepted Clar's structure of the triphenylene shown in Figure 9b. The Clar's structure of triphenylene contains three disjointed delocalized π sextets represented by solid inner circles, each associated with one of three peripheral cyclic fragments. The bond alternations within these peripheral cycles (from 1.373 to 1.415 Å) are comparable with the bond alternations within the central ring (from 1.415 to 1.468 Å) according to the experimental results.⁴⁹ This fact is consistent with the absence of the formally double bonds in the obtained bonding description. The calculated NICS_{zz} values for the outer rings are -8.9 ppm (0.0 Å), -18.6 ppm (0.5 Å), and -26.4 ppm (1.0 Å), and for the inner ring, the values are 12.2 ppm (0.0 Å), 2.6 ppm (0.5 Å), and -10.1 ppm (1.0 Å). As in the two previous cases, the NICS picture is consistent with our conclusions based on the AdNDP analysis.

Coronene. Coronene, C₂₄H₁₂ (Figure 2), has 18 valence π electrons. This molecule sometimes is considered to be superaromatic.⁴⁴ This means that three Clar's sextets are mobile and can migrate into the neighboring outer six-atomic cyclic fragments giving rise to the "ring of rings". The single Clar's structure is a resonance structure in this case and is not symmetry consistent. Also, the applicability of the traditional "annulene-within-an-annulene" model in which both the internal six-atomic rings and external 18-atomic rings attain an aromatic $4n + 2$ Hückel electron count has been discussed.⁵⁰ The results of the AdNDP analysis are presented in Figure 10. According to the AdNDP partitioning, the σ -bonding framework consists of 30 C-C σ bonds (ON = 1.99–1.95 lel, superimposed on the single molecular framework) and 12 2c-2e C-H σ bonds (ON = 1.98 lel, superimposed on the single molecular framework). The π -bonding framework consists of the six 2c-2e C-C π bonds (ON = 1.76 lel, superimposed on the single molecular framework), three 6c-2e C-C π bonds (ON = 1.87–1.67 lel) involving carbon atoms of the central six-atomic cyclic fragment, and three 24c-2e C-C π bonds (ON = 2.00 lel) involving all carbon atoms. The 6c-2e and 24c-2e π bonds were obtained using an AdNDP directed search, according to the procedure described in the section for the anthracene molecule. The appropriate symbolic representation consistent with the AdNDP results for the coronene molecule is shown in Figure 10b. The graphic formula in Figure 10b has never been suggested before to the best of our knowledge. We used the outer circle in the schematic representation to designate three 24c-2e C-C π bonds (ON = 2.00 lel) responsible for π bonding between the inner six-atomic ring and the outer 18-atomic fragment. This element of the schematic representation is analogous to the circle inscribed in the conventional formula of benzene, which stands for three 6c-2e C-C π bonds of benzene. This is neither a superaromatic Clar's structure nor an annulene-within-an-annulene representation.

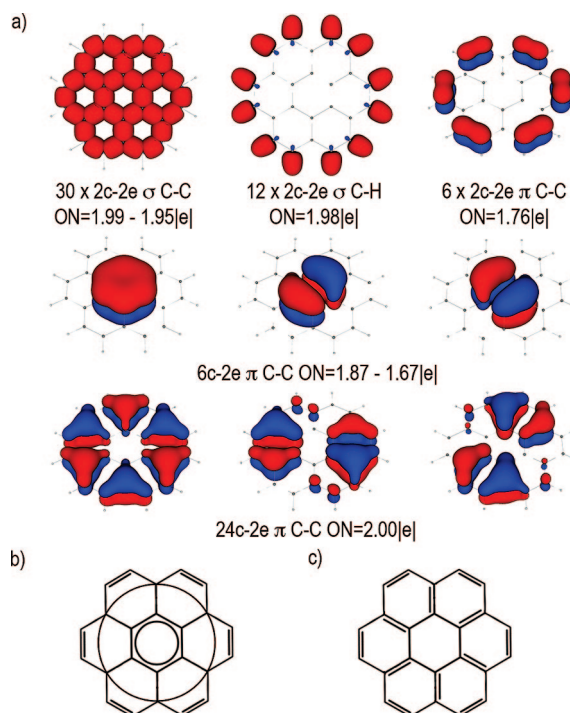


FIGURE 10. (a) AdNDP bonding pattern for coronene. (b) Symbolic representation of coronene according to AdNDP. (c) Symbolic representation of coronene according to England and Ruedenberg (ref 45).

If the threshold value for the acceptance of the 2c-2e bonds is lowered to 1.55 lel, the AdNDP analysis recovers a single Kekulé structure (Figure 10c) previously reported by England and Ruedenberg.⁴⁵ We believe the graphic formula in Figure 10b is a better representation of the chemical bonding in coronene than the graphic formula in Figure 10c because it corresponds to the higher values of the occupation numbers. The deviations of the ONs of the recovered π bonds from the ideal value of 2.00 lel are an indication of a significant conjugation between the π bonds.

Discussion

If we assume that an electron pair in a closed-shell system is the essential element of chemical bonding, then AdNDP is an ideal theoretical tool for transforming the MO wave function description of the electronic structure into a description operating with LPs, 2c-2e bonds, 3c-2e bonds, and so on, up to nc -2e bonds, where n is the total amount of atoms in a given molecule. The application of the AdNDP analysis to the MO wave function of organic monocyclic systems, such as cyclopropenyl cation, cyclopentadienyl anion, and benzene, for the first time revealed chemical bonding patterns that are in agreement with generally accepted, intuitively assessable, chemical representations. The AdNDP analysis recovers only 2c-2e C-C and C-H bonds with almost ideal ONs within 1.97–2.00 lel in the σ -bonding framework. The π -bonding framework is represented by means of multicentered nc -2e π bonds delocalized over all carbon atoms. The amount of the obtained nc -2e π bonds agrees with Hückel's $4n + 2$ counting rule for the monocyclic aromatic systems. The delocalized π bonding in the AdNDP representation can be designated naturally by a solid circle inscribed in the framework of the peripheral C-C σ bonds. The overall AdNDP-bonding picture is consistent with the single-most

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compact graphic formula of the monocyclic aromatic molecules accepted in the literature. Thus, AdNDP seamlessly reconciles localized and delocalized bonding descriptions.

For the polycyclic systems, the accepted bonding patterns are more complicated and somewhat controversial. For example, the naphthalene molecule is sometimes represented as two merged benzene rings with two solid circles within each six-atomic cycle, sometimes as a resonance of two Clar's structures and sometimes as a single Kekulé structure. Each of these representations has its pros and cons. According to the NICS study of the naphthalene molecule,⁵¹ each of the rings exhibits aromatic magnetic properties comparable to those of the benzene ring. Nevertheless, there are noticeable bond length alternations consistent with those of the single Kekulé structure description involving formally single and double bonds. The AdNDP provides a description that is closer to the single Kekulé structure but involves a 6c-2e central C–C π bond instead of a 2c-2e bond.

Anthracene, phenanthrene, and triphenylene can be represented using a single Clar's structure according to the AdNDP results. This bonding description is consistent with the graphic formulas accepted in the literature and confirmed by a variety of aromaticity indices (ref 52 and references therein).

Coronene is the most controversial molecule among the PAHs considered in the present study. According to Clar,⁴⁴ this molecule is superaromatic. According to the magnetic criteria such as NICS²⁶ and current-density maps,⁵⁰ the outer circuit of coronene is aromatic, while the inner circuit is either nonaromatic or antiaromatic. However, Aihara⁵³ stated that on the basis of the bonding resonance energies, all rings in coronene, including the central one, are aromatic. The AdNDP provides a description of the coronene molecule that neither is superaromatic in Clar's sense, nor implies antiaromaticity of the central six-atomic fragments, nor is an annulene-within-an-annulene representation. The π -bonding subsystem consists of three parts: the set of six 2c-2e C–C peripheral π bonds, the three π bonds delocalized over the central six-atomic cycle, and the three delocalized π bonds responsible for the bonding between the inner six-atomic and outer 18-atomic cycles. The deviation of the ONs of these π bonds from the ideal value suggests strong conjugation of the π -bonding system.

According to the request of one of the reviewers, we performed AdNDP analysis for a prototypical antiaromatic system (cyclo-butadien) and a nonaromatic system (cyclopentadien). The results of the analyses are included in the Supporting Information. For both systems, the expected classical descriptions were obtained, i.e., all the identified bonding elements are 2c-2e, either σ bonds (C–C and C–H) or π bonds (C–C) with occupation numbers close to the ideal value of 2.00 lel. Thus, there is no qualitative difference between these particular antiaromatic and nonaromatic systems according to the AdNDP results.

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Conclusions

The patterns of chemical bonding obtained by AdNDP are consistent with chemical intuition and lead to unique compact graphic formulas. The deviations of the obtained ONs from the ideal value of 2.00 lel show how close the recovered bonding pattern is to the perfect bonding description. Any model of chemical bonding is intrinsically deficient as it invokes certain approximations and is just a model after all. The AdNDP method was designed with the intention to avoid resonant descriptions and provide a chemical bonding pattern always consistent with the point symmetry of the molecule. Indeed, when the bonds recovered by AdNDP are superimposed on the single nuclear framework, the latter requirement is met. The significant advancement made in the current study is that bonding patterns and formulas are obtained from the MO wave function via a unified and well-defined quantum chemical procedure. Just like standard NBO analysis allows one to obtain Lewis structures from MO wave function in a rigorous manner, AdNDP provides a description of aromatic systems seamlessly incorporating localized and delocalized bonding elements. However, it should be kept in mind that AdNDP is not a probe for aromaticity. Instead, it provides information about the degree of delocalization for the electron pairs responsible for chemical bonding. The final assessment of the aromaticity of a particular system with delocalized bonding resides with the researcher. In the present study of a selected set of organic aromatic molecules, it was possible to reveal bonding patterns, including a localized σ framework (2c-2e C–C and C–H σ bonds) and a delocalized π framework. For the monocyclic aromatic molecules, such as cyclopropenyl cation, cyclopentadienyl anion, and benzene, the completely delocalized π bonding is consistent with Hückel's $4n + 2$ rule. For the polycyclic aromatic molecules, such as anthracene, phenanthrene, and triphenylene, the obtained representations are essentially Clar's structures. For the naphthalene molecule, the AdNDP bonding pattern is consistent with results of England and Ruedenberg.⁴⁹ Finally, the coronene molecule neither is superaromatic in Clar's sense, nor implies antiaromaticity of the central six-atomic fragment, nor is an annulene-within-an-annulene representation. The AdNDP representation of coronene is novel and incorporates two delocalized π systems, one of which is associated with the internal six-atomic ring and the other connecting the internal ring with the rim atoms.

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Note Added after ASAP Publication. Throughout the text and Supporting Information of the version published ASAP November 4, 2008, the $C_3H_3^+$ cation was referred to as cyclopropyl cation instead of cyclopropenyl cation; the corrected version was published on the Web November 13, 2008.

Supporting Information Available: Table of Cartesian atom coordinates and absolute energies of the studied molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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