Electron Pair (De)Coupling in Aniline Radical Cation and Its Implications for Organic "Mixed Valence" Systems

Padeleimon Karafiloglou*

Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

Jean-Pierre Launay*

Centre d'Elaboration de Materiaux et d'Etudes Structurales, LOE, 29 rue J. Marvig, 31055 Toulouse, France

Received: March 12, 1998

The electron pair (de)coupling induced by a $NH_2^{\bullet +}$ group to the bonds of a phenyl ring is investigated by means of polyelectron population analysis; the used density operators are built on the basis of both natural atomic orbitals (AOs) of ab initio-correlated molecular orbital (MO) wave functions, as well as the model orthogonal AOs of Parr−Pariser−Pople (PPP)+full configuration interaction (CI) ones. On the basis of two-electron, two-hole investigations, we calculate the electron pair localizations as well as the cooperation of opposite spins or charges to form bonds. The investigations of various electronic events referring to the simultaneous presence of a charge (+) and a radical center (·) lead to rules concerning the relative importance of various resonance structures. As shown, the observed quinoid (de)coupling of electron pairs of the phenyl group is in the origin of the corresponding geometrical deformations. Given these results, we investigate the key electronic reasons responsible for the localized (bi- or tristable) or delocalized behavior of monooxidized aromatic polyamines.

1. Introduction

Mixed valence systems offer the possibility of monitoring intramolecular electron transfer. Such systems are usually polymetallic complexes in which a given metal atom is present in formally different oxidation states, such as ruthenium compounds in oxidation states II and III; the most typical compound[1] is the Creutz−Taube ion $[(NH_3)_5\,Ru\,(pyrazine)\,Ru(NH_3)_5]^{5+}$. The electronic structure of mixed valence complexes is governed by competition between the electronic interaction existing between redox sites (an off-diagonal coupling term, denoted as V_{ab}) and the local distortions induced by the changes in oxidation states (electron−phonon coupling).[2] When the electronic interaction V_{ab} is weak, a **localized** ground state is observed; that is, in the case of a bimetallic ruthenium complex, the electronic structure can be written $Ru^{2+}-Ru^{3+}$. In this situation, the potential energy curve of the system exhibits two minimums. Such systems can also be called bistable because they can oscillate between the two forms $Ru^{2+}-Ru^{3+}$ and $Ru^{3+}-Ru^{2+}$. If the electronic coupling V_{ab} is large with respect to the electron−phonon coupling term, then a **delocalized** ground state occurs. The potential energy curve presents a single minimum and the electronic structure is best represented as $Ru^{2.5+}-Ru^{2.5+}$. In the earlier formulation of Robin and Day,[2a] the localized and delocalized cases were denoted class II and class III, respectively. Various types of complexes belonging to class II have been studied from both experimental and theoretical aspects.[3]

Although initially, the term mixed valence designated only polymetallic complexes, the concept of mixed valence is also valid in organic chemistry, and recent papers have been devoted to partially oxidized aromatic polyamines derived from {4-[bis-(4-ethylphenyl)amino]phenyl}-*N*,*N*,*N*′,*N*′-tetrakis(4-ethylphenyl)-[1,1′:3′,1″-terphenyl]-4,4″-diamine(p-EFTP).[4] In these systems the reduced sites of the triphenylamine type coexist with the corresponding oxidized forms (radical cations), linked around a central phenyl ring with meta connections. An analogous system is m-EFTP, where the external amine sites are linked in meta around the central 1,3,5-triphenylbenzene unit.[5] Another example of an organic mixed valence compound is the bis-(tetrathia-fulvalene).[6]

The degree of the through-bond electronic interaction between redox sites is an important factor that determines the electronic structure of the mixed valence compound. In the case of oxidized forms of p-EFTP, the electronic structure is localized (class II); that is, one can identify normal and oxidized triphenylamine sites.[4] This type of three-site localization leads to a tristable system. The electronic structure and the specific behavior of oxidized EFTP compounds can be modeled and studied by means of monooxidized symmetric aromatic diamines, $H_2N-(Ph)_3-NH_2$, that have at least one C_2 symmetry axis, the connections between the phenyl rings being either para or meta. Such a system can be represented by two electronic structures: $H_2N^{\bullet +}-(Ph)_3-NH_2$ (**I**) and $H_2N-(Ph)_3-NH_2^{\bullet +}$ (**II**).

If electronic structures **I** and **II** contribute equally to the ground state (i.e., **I**↔**II**), then the system is a usual delocalized radical cation. On the contrary, if between **I** and **II** there is an equilibrium (i.e., **I**⇄**II**), then the system is a two-site localized (bistable) radical cation, having the interesting property of the left−right charge transfer. The aim, then, of the present work is to investigate and understand the key electronic effects responsible for the localized (bi- or tri-stable) or delocalized behavior of a monooxidized aromatic polyamine. For these purposes, we shall examine first the nature of the effects induced by the $NH_2^{\bullet +}$ group to an adjacent phenyl ring and then explore

S1089-5639(98)01475-3 CCC: $15.00

the possibility that these effects can be extended to other phenyl(s) linked to the first one. This will be done in the framework of "resonance" or "mesomeric" theory by examining various types of resonance structures in the bonds of such systems and determining which are responsible for their localized or delocalized behavior.

Within the local description of a molecular system having $n_\alpha + n_\beta$ electrons and M atomic orbitals (AOs), there are $N = [M!/n_\alpha!(M - n_\alpha)!]\,[M!/n_\beta!(M - n_\beta)!]$ different ways to arrange these electrons in the AOs; in each of them, every AO is occupied by either 2 electrons or 2 holes or 1 electron and 1 hole (with opposite spins). If we are interested in the resonance structures of a bond or a functional group inside of a given molecular system, we must consider the simultaneous occupations by electrons and holes of the m AOs (where $m < M$) defining the considered moiety. This type of simultaneous occupation of the target m AOs defines an electronic event, which is characterized by a corresponding probability. For example, for two target AOs t and s, 2 electrons in t and simultaneously 2 holes in s define the ionic electronic event s(−)t(+); the probability of this event provides also the weight (or contribution) of the corresponding ionic resonance structure. The quantitative estimation of the probabilities of various types of electronic events in some target AOs of a given molecular system is the purpose of a polyelectron population analysis.

Second-quantized formalism[7] offers the possibility of going beyond the 1-electron population analysis and calculating the probabilities for various types of electronic events involving 2 or more electrons and holes, in the framework of a generalized population analysis.[8,9] The defects of a Mulliken partition, existing even in the 1-electron populations, as well as the difficult chemical interpretations of AO basis sets involving diffuse or polarization functions, are overcome by introducing the well-elaborated natural atomic orbitals (NAOs).[10,11] The combination, then, of both second quantization and NAOs[12−14] opens the way for a statistical analysis of the electronic assembly from ab initio-correlated MO wave functions, as well as calculation of the weights of resonance structures of chemical bonds, in the framework of the familiar (to a chemist) resonance or mesomeric theory. Other authors who have also gone beyond the usual 1-electron distributions, have examined the behavior of electron pairs and their localization[15] as well as the effective pair populations corresponding to the chemical bonds.[16]

For a model system to study the effects induced by a $NH_2^{\bullet+}$ group to the bonds of a phenyl ring, we have considered the radical cation of aniline (benzeneamine). Theoretical investigations of organic radicals have utilized various methods.[17] In the present work we use the usual molecular orbital (MO) wave functions as the initial materials for calculating the weights of various resonance structures and the polyelectron investigations: Each MO Slater determinant involved in a correlated MO wave function is decomposed[18] according to Moffitt's theorem,[19] and the obtained new expansions of Slater determinants are then used to calculate expectation values of second-quantized density operators. This decomposition process has been adopted not only for orthogonal AOs, but also for nonorthogonal ones.[20−22]

2. Methods and Calculations

2.1. Polyelectron Investigations. Contrary to the classical formulation of density operators, second quantization offers a simple and intuitive way of partitioning composite electronic events into simpler ones. This partition is not arbitrary but is guided by chemical intuition and can lead to the quantitative estimation of various types of correlations.[21−23] For example, the composite 2-electron, 2-hole electronic event, $a_s a_{\bar{s}}\; a_t{}^{+} a_{\bar{t}}{}^{+} a_{\bar{t}}\; a_t a_{\bar{s}}{}^{+} a_s$, representing the ionic resonance structure s(+)t(−), can be partitioned into two component electronic events: the 2-hole event, $a_s a_{\bar{s}}\; a_{\bar{s}}{}^{+} a_s{}^{+}$, representing the s(+), and the 2-electron one, $a_t{}^{+} a_{\bar{t}}{}^{+} a_{\bar{t}}\; a_t$, representing the t(−). Even though the product of these two component operators is equal to the operator of the composite electronic event, the product, $P_{0;2}[s(+)]P_{2;0}[t(-)]$, of their expectation values does not equal the expectation value of the composite operator, $P_{2;2}[s(+)t(-)]$, except when the s(+) and t(−) events are totally independent from one another. In a general case, the cooperation of (+) and (−) can be measured from the corresponding *charge* or *ionic correlation*, $I_c[s(+)t(-)]$:[23]

$$I_c[s(+)t(-)] = P_{2;2}\,[s(+)t(-)] - P_{0;2}[s(+)]\,P_{2;0}[t(-)] \quad (1)$$

Similarly, another 2-electron, 2-hole electronic event, $a_s{}^{+} a_{\bar{s}}\;\; a_t\;\; a_{\bar{t}}{}^{+} a_{\bar{t}} a_t{}^{+}\;\; a_{\bar{s}}{}^{+} a_s$, representing a covalent resonance structure, s(↑)t(↓), can be partitioned in two 1-electron, 1-hole components; this partition leads to the *spin* or *covalent correlation*, $C_c[s((\uparrow)t(\downarrow)]$:

$$C_c[s(\uparrow)t(\downarrow)] = P_{2;2}[s(\uparrow)t(\downarrow)] - P_{1;1}\,[s(\uparrow)]\,P_{1;1}\,[t(\downarrow)] \qquad (2)$$

The $I_c[s(+)t(-)]$ and $C_c[s(\uparrow)t(\downarrow)]$ provide the **degree of coooperation of opposite charge and spins**, respectively, to form chemical bond between s and t; of course, for nonequivalent s and t positions, one must consider also the correlations for the opposite occupations: $I_c[s(-)t(+)]$ and $C_c[s(\downarrow)t(\uparrow)]$.[23]

A crucial problem encountered when analyzing electronic events occurring in a molecular system is the choice of analyzers in which the second-quantized density operators must be built. For a π-system, a very good choice is the valence p_z NAOs. These orbitals are not only natural (in the Löwdin sense), but also, because of to the well-elaborated occupancy-weighted symmetric orthogonalization (OWSO) procedure,[10] have the advantage of being simultaneously orthogonal and essentially local. Of course, the σ-NAOs (or other type of σ-orbitals) can be nonlocal, provided they are orthogonal and are not used to build local density operators. Briefly, the process[12] we adopted is the following: Starting from a given correlated MO wave function, ψ(MO), we calculate the NAOs (obtained from the diagonalization of the first-order density matrix) and the corresponding wave function, ψ'(MO), in which the Slater determinants, I′, involve linear combinations of NAOs. Then, each I′ is decomposed into local Slater determinants, K, involving NAOs as 1-electron orbitals; the corresponding expansion coefficients, T_K, are calculated according to Moffitt's theorem. In these calculations, there are no approximations because the decompositions are based on identity relations and, according to Moffitt's theorem, each T_K can be calculated individually for each Slater determinant K without generating (and storing) the whole determinant basis set {K}. Consequently, without affecting the approximation level of the calculations, the decomposition process need not to be extended over the whole determinant basis set {K}; which K must be generated from the decomposition of each I′ is dictated from the chosen local operator. For example, for the ionic resonance structure s(+)t(−), we must generate only K of the type:

$$||\varphi_t\, \varphi_{\bar{t}} \cdots \chi_m||, \text{ where } \chi_m \neq \varphi_s, \varphi_{\bar{s}}$$

In the whole process the approximation level of the initial wave function, ψ(MO), is not altered; thus the calculated

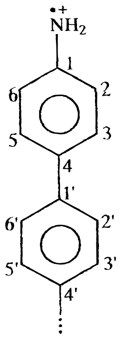

Figure 1. Numbering used for C positions.

expectation values of local density operators correspond to this wave function.

2.2. Numerical Calculations. For neutral aniline and the radical cation of aniline, two different initial MO wave functions are used in two separate series of calculations:

1. An ab initio self-consistent field (SCF) + configuration interaction (CI) wave function; we adopted the chain of computer programs involving the PSHONDO algorithm[24] and the adapted multireference CI (CIPSI) process.[25] The basis set for the SCF part is a standard double-ζ with pseudopotentials,[26] increased by one d-symmetry (5 AOs per atom) orbital at exp 0.5. The density operators are built on the p_z-valence NAOs, as described above. The effects of the AO basis sets and a comparison of minimal and extended SCF bases for polyelectron populations are given elsewhere.[12]

2. A Parr−Pariser−Pople (PPP)+full CI[27,28] wave function; in the SCF part of these calculations the one-site energies, α, and on-site Coulomb repulsion, U, for N are −15.0 and 14.09 eV, respectively; the other parameters are those of Soos and co-workers.[28] In this case the density operators are built on the model orthogonal AOs that are used in PPP as well as Hubbard[29] methods.

The C−C bond lengths of the phenyl ring in neutral aniline have rather small differences, whereas in an oxidized aromatic amine the C_2-C_3 (or C_5-C_6; for the numbering see Figure 1) bond is clearly shorter than the other C−C bonds.[30] For simplicity, in what follows we will refer to the geometries of phenyl in neutral and oxidized aniline as "aromatic" and "quinoid" respectively. The bond lengths, in Å, which are obtained from AM1[31] geometry optimizations for neutral/radical cation of aniline are $N-C_1$, 1.399/1.339; C_1-C_2, 1.414/1.452; C_2-C_3, 1.389/1.379; and C_3-C_4, 1.394/1.413, respectively; the angle of planes (HNC_1) and (NC_1C_2) is 24°/0°. For the radical cation of aniline, besides the above quinoid (relaxed) geometry, we used also another (rigid) geometry, referred to as "aromatic" in which the bond lengths are the same as those of the neutral aniline.

3. Results and Discussion

3.1. Covalent and Ionic Resonance Structures and the Corresponding Correlations. Since the mixed valence systems considered involve the $NH_2^{\bullet +}/NH_2$ groups in their extremities, we examined the effects induced by these groups on the $C{=}C$ bonds of a phenyl. To do so, we considered and compared the bonds of the neutral aniline and the radical cation of aniline. In the framework of usual MO theory, comparison of electron pairs defining $C{=}C$ bonds in two different molecular systems is very difficult, since each electron pair is shared in many MOs; these difficulties increase when CI calculations are implemented. Such a comparison is much simpler and more intuitive in the framework of resonance or mesomeric theory since, within this theory, each $C{=}C$ bond, regardless of the system in which it belongs, is composed of only two covalent [(↑)(↓) and (↓)(↑)] and two ionic [(+)(−) and (−)(+)] resonance structures.

TABLE 1: Neutral Aniline Probabilities for the 2-Electron, 2-Hole Electronic Events Representing Covalent and Ionic Resonance Structures, and the Corresponding Correlations between Two 1-Electron, 1-Hole Events (in Covalent Structures) and 2-Electron and 2-Hole Events (in Ionic Structures)

resonance structure	ab initio-CI MO wave function		PPP+full CI MO wave function	
	probabilities	correlations	probabilities	correlations
C_1 (↑) C_2(↓)	0.1509	0.0702	0.1787	0.0872
C_1 (↓) C_2(↑)	0.1509	0.0702	0.1787	0.0872
C_1 (↑↓) C_2(+)	0.0757	0.0441	0.0808	0.0506
C_1 (+) C_2(↑↓)	0.1286	0.0640	0.1199	0.0711
sum	0.5061	0.2485	0.5582	0.2961
C_2 (↑) C_3(↓)	0.1700	0.0868	0.1913	0.0989
C_2 (↓) C_3(↑)	0.1700	0.0868	0.1913	0.0989
C_2 (↑↓) C_3(+)	0.1284	0.0716	0.1219	0.0762
C_2 (+) C_3(↑↓)	0.0921	0.0582	0.0974	0.0657
sum	0.5605	0.3034	0.6019	0.3398
C_3 (↑) C_4(↓)	0.1646	0.0810	0.1850	0.0929
C_3 (↓) C_4(↑)	0.1646	0.0810	0.1850	0.0929
C_3 (↑↓) C_4(+)	0.0922	0.0558	0.0973	0.0631
C_3 (+) C_4(↑↓)	0.1202	0.0670	0.1147	0.0714
sum	0.5416	0.2848	0.5820	0.3203

TABLE 2: Aniline Radical Cation Probabilities for the 2-Electron, 2-Hole Electronic Events Representing Covalent and Ionic Resonance Structures According to Aromatic or Relaxed Geometry

resonance structure	ab initio-CI		PPP+full CI	
	aromatic	relaxed	aromatic	relaxed
C_1 (↑) C_2(↓)	0.1046	0.1024	0.1023	0.0928
C_1 (↓) C_2(↑)	0.1079	0.1041	0.1310	0.1254
C_1 (↑↓) C_2(+)	0.0610	0.0564	0.0724	0.0719
C_1 (+) C_2(↑↓)	0.0880	0.0891	0.0866	0.0873
sum	0.3615	0.3521	0.3923	0.3774
C_2 (↑) C_3(↓)	0.2298	0.2348	0.2347	0.2405
C_2 (↓) C_3(↑)	0.1583	0.1618	0.1726	0.1729
C_2 (↑↓) C_3(+)	0.1282	0.1322	0.1264	0.1302
C_2 (+) C_3(↑↓)	0.1154	0.1173	0.1188	0.1197
sum	0.6317	0.6460	0.6526	0.6633
C_3 (↑) C_4(↓)	0.0767	0.0713	0.0909	0.0878
C_3 (↓) C_4(↑)	0.2035	0.2064	0.2073	0.2117
C_3 (↑↓) C_4(+)	0.1107	0.1090	0.1155	0.1132
C_3 (+) C_4(↑↓)	0.0582	0.0556	0.0636	0.0622
sum	0.4492	0.4423	0.4772	0.4749
N(↑) C_1(↓)	0.1734	0.1707	0.1451	0.1406
N(↓) C_1(↑)	0.0685	0.0775	0.0259	0.0331
N(↑↓) C_1(+)	0.2854	0.2996	0.2775	0.2807
N(++) C_1(↑↓)	0.0157	0.0162	0.0032	0.0037
sum	0.5429	0.5641	0.4517	0.4591
C_1 (↑) C_3(↓)	0.0952	0.0959	0.1077	0.1068
C_1 (↓) C_3(↑)	0.0565	0.0559	0.0434	0.0438
C_1 (↑↓) C_3(+)	0.0354	0.0338	0.0376	0.0384
C_1 (+) C_3(↑↓)	0.0550	0.0572	0.0437	0.0434
sum	0.2421	0.2428	0.2325	0.2323
C_6 (↑) C_3(↓)	0.1226	0.1220	0.1237	0.1250
C_6 (↓) C_3(↑)	0.0688	0.0677	0.0766	0.0742
C_6 (↑↓) C_3(+)	0.0487	0.0486	0.0447	0.0443
C_6 (+) C_3(↑↓)	0.0468	0.0456	0.0440	0.0442
sum	0.2869	0.2839	0.2891	0.2878

Table 1 lists the weights (or contributions) of the covalent and ionic resonance structures calculated from the expectation values of the corresponding density operators,[9] as well as the analogous correlations, for the neutral aniline bonds. Tables 2 and 3 give the weights and correlations respectively, for the radical cation of aniline. In neutral aniline, the cooperations of opposite spins or charges to form the bonds, which are

TABLE 3: Aniline Radical Cation Correlations between Two 1-Electron, 1-Hole Events in Covalent Resonance Structures, and 2-Electron and 2-Hole Events in Ionic Structures

resonance structure	ab initio-CI		PPP+full CI	
	aromatic	relaxed	aromatic	relaxed
C_1 (↑) C_2(↓)	0.0336	0.0314	0.0424	0.0393
C_1 (↓) C_2(↓)	0.0312	0.0282	0.0334	0.0321
C_1 (↑↓) C_2(+)	0.0273	0.0250	0.0344	0.0327
C_1 (+) C_2(↑↓)	0.0298	0.0284	0.0388	0.0370
sum	0.1219	0.1129	0.1490	0.1412
C_2 (↑) C_3(↓)	0.1185	0.1229	0.1229	0.1265
C_2 (↓) C_3(↑)	0.0980	0.1016	0.1059	0.1078
C_2 (↑↓) C_3(+)	0.0838	0.0873	0.0857	0.0889
C_2 (+) C_3(↑↓)	0.0744	0.0769	0.0797	0.0812
sum	0.3747	0.3887	0.3943	0.4045
C_3 (↑) C_4(↓)	0.0393	0.0365	0.0475	0.0462
C_3 (↓) C_4(↑)	0.0682	0.0665	0.0731	0.0724
C_3 (↑↓) C_4(+)	0.0551	0.0538	0.0636	0.0627
C_3 (+) C_4(↑↓)	0.0330	0.0313	0.0387	0.0376
sum	0.1956	0.1881	0.2229	0.2188
N(↑) C_1(↓)	0.1027	0.1054	0.0783	0.0826
N(↓) C_1(↑)	0.0428	0.0485	0.0149	0.0195
N(↑↓) C_1(+)	0.1086	0.1135	0.0934	0.0993
N(++) C_1(↑↓)	0.0126	0.0132	0.0026	0.0037
sum	0.2666	0.2806	0.1893	0.2052
C_1 (↑) C_3(↓)	−0.0025	−0.0022	−0.0065	−0.0064
C_1 (↓) C_3(↑)	−0.0007	−0.0004	−0.0019	−0.0020
C_1 (↑↓) C_3(+)	−0.0007	−0.0003	−0.0036	−0.0036
C_1 (+) C_3(↑↓)	−0.0025	−0.0021	−0.0067	−0.0069
sum	−0.0064	−0.0050	−0.0185	−0.0189
C_6 (↑) C_3(↓)	0.0112	0.0101	0.0119	0.0111
C_6 (↓) C_3(↑)	0.0085	0.0075	0.0100	0.0091
C_6 (↑↓) C_3(+)	0.0043	0.0037	0.0056	0.0031
C_6 (+) C_3(↑↓)	0.0058	0.0052	0.0033	0.0057
sum	0.0298	0.0265	0.0309	0.0289

measured from the corresponding correlations of Table 1, are quite close for the three C−C bonds; the sums of the covalent + ionic correlations fluctuate smoothly around 0.279. On the contrary, in the radical cation system, (Table 3), both covalent and ionic correlations differ much more from bond to bond; their sums for the C_2-C_3 bond (0.389 in relaxed geometry and ab initio level) is ∼2 or 3 times larger than for the C_3-C_4 (0.188) or C_1-C_2 (0.113) bonds. Thus $C_2-C_3 > C_3-C_4 > C_1-C_2$.

These results show a clear differentiation of the bonding in the radical cation system: The opposite spins and charges cooperate strongly to form a bond between C_2 and C_3 but weakly between C_1 and C_2. This differentiation can be also determined by examining the weights of covalent or ionic resonance structures given in Table 2; furthermore, the sums of these weights (two covalent + two ionic for each bond) provide a measure of localization of electron pairs[13,22,32] (in the limit case of a totally localized bond, according to fourth-order anticommutation relation,[22] this sum equals 1). This measure also follows the above ordering: 0.646, 0.442, and 0.352 for C_2-C_3, C_3-C_4, and C_1-C_2, respectively. In neutral aniline, the electron pair localizations for these bonds fluctuate smothly around 0.536. Consequently, we can conclude, from both the cooperations of opposite spins or charges and the electron pair localizations, that the $NH_2^{\bullet+}$ imparts to the phenyl ring an enhanced *coupling* for the electron pairs in C_2-C_3 (or C_5-C_6) and a *decoupling* for the electron pairs in C_1-C_2 (or C_1-C_6) and C_3-C_4 (or C_5-C_4).

Since the cooperation of opposite spins and charges to form bonds is intrinsically related to the relative importance of various resonance structures (see Section 3.2), we extended the polyelectron investigations to some couples of AOs that refer to typical nonvicinal positions. We found that both covalent and ionic correlations are extremely small and even negative, showing the very unfavorable nature of the corresponding cooperations. For example, the correlation (covalent + ionic) for positions C_6-C_3 is only 0.027, and the corresponding value for C_1-C_3 is negative: −0.005.

Another feature of the radical cation of aniline is the nature of its $N-C_1$ bond. Both the weight of the ionic N(↑↓)-C_1(+) resonance structure (0.300) and that of the covalent N^+(↑)-C_1(↓) one (0.171) are important, but the former is greater, revealing an ionic nature for this bond. Furthermore, the sum of the weights of the two ionic structures (measuring the ionicity of this bond), 0.316, is greater than the sum of the two covalent ones (measuring its covalency), 0.248.

Even though the above conclusions are drawn from results of polyelectron investigations, starting from ab initio MO wave functions, examination of the results from the PPP+full CI wave functions (Tables 1−3) leads to identical conclusions. The good agreement between these two initial MO wave functions allows us to conclude that the electron pair (de)coupling, induced in the phenyl ring by the $NH_2^{\bullet+}$ group, is controlled by electron pair reorganizations occurring essentially in the π system.

3.2. Rules for the Relative Importance of Various Resonance Structures. A radical cation system by definition refers to the simultaneous presence of a radical center (·) and a positive charge (+). However, neither the usual delocalized pictures of MO theory nor the 2-electron distributions can provide information for such basic features of a radical cation system. Within the polyelectron population analysis, the probabilities to find simultaneously (+) and (·) in various positions, C_x and C_y respectively, of the radical cation can be calculated from the expectation values of the corresponding density operators:[13]

$$a_y^{+} a_{\bar{y}} a_x a_{\bar{x}}\, a_{\bar{x}}^{+} a_x^{+} a_{\bar{y}}^{+} a_y \tag{3}$$

Apart from these 1-electron, 3-hole electronic events, in the case of radical cation of aniline the simultaneous presence of (·) and (+) should also be associated with the two most probable occupations for the N atom:

1. The N involves an electron pair, consequently, the (·) and (+) must be located in various positions of the carbon atoms of the phenyl: N(↑↓)...C_x(+)...C_y(↑) (see resonance structures A of Figure 2). The probabilities for these 3-electron, 3-hole electronic events are calculated from the expectation values of the following density operators:

$$a_y^{+} a_{\bar{y}} a_x a_{\bar{x}} a_N^{+} a_{\bar{N}}^{+} a_{\bar{N}} a_N a_{\bar{x}}^{+} a_x^{+} a_{\bar{y}}^{+} a_y \tag{4}$$

These operators are derived directly from $a_N^{+} a_{\bar{N}}^{+} a_{\bar{N}} a_N$, which corresponds to the 2-electron event N(↑↓), and the density operators given in (3).

2. The N involves one electron [and then the (+) charge]; given this, the most probable occupation for the adjacent C_1 atom is an electron with opposite spin (the covalent pair in $N-C_1$), while another carbon atom of the phenyl ring bears the single electron: N^+(↑)−C_1(↓)...C_y(↑) (see resonance structures B of Figure 2). The associated density operators are derived from $a_y^{+} a_{\bar{y}} a_{\bar{y}}^{+} a_y$, which corresponds to the 1-electron, 1-hole events C_y(↑), and $a_N^{+} a_{\bar{N}} a_1 a_{\bar{1}}^{+} a_{\bar{1}} a_1^{+} a_{\bar{N}}^{+} a_N$, which corresponds to the covalent pair in $N-C_1$:

$$a_y^{+} a_{\bar{y}} a_N^{+} a_{\bar{N}}\, a_1\, a_{\bar{1}}^{+} a_{\bar{1}}\, a_1^{+} a_{\bar{N}}^{+} a_N a_{\bar{y}}^{+} a_y \tag{5}$$

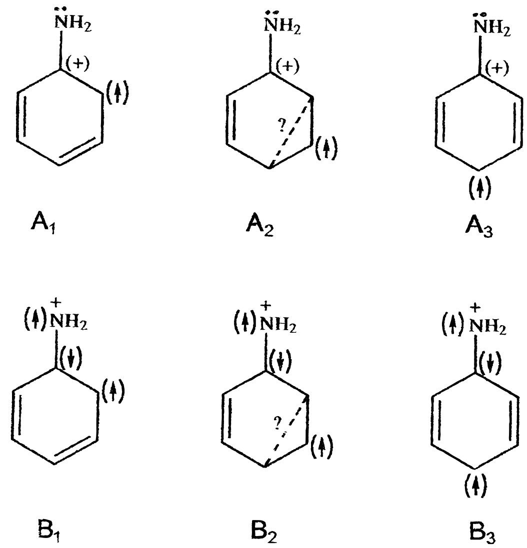

Figure 2. Some resonance structures for an aniline radical cation. Structures A_1 to A_3 involve an electron pair in N and an ionic electronic event between N and the adjacent C atom; structures B_1 to B_3 involve one electron in N and a covalent electronic event between N and the adjacent C atom.

TABLE 4: Aniline Radical Cation Probabilities for Electronic Events Involving (·) and (+), Calculated from the Expectation Values of Density Operators (3), (4), and (5)

density			figure	ab initio-CI		PPP+full CI	
operator	x	y	scheme	aromatic	relaxed	aromatic	relaxed
(5)	–	2	2-B_1	0.0907	0.0872	0.0899	0.0810
(5)	–	3	2-B_2	0.0440	0.0436	0.0396	0.0358
(5)	–	4	2-B_3	0.0803	0.0825	0.0762	0.0765
(4)	1	2	2-A_1	0.1379	0.1432	0.1296	0.1308
(3)	1	2	2-A_1	0.1458	0.1503	0.1430	0.1435
(4)	2	1		0.0868	0.0856	0.1010	0.1088
(3)	2	1		0.1014	0.1006	0.1187	0.1159
(4)	1	3	2-A_2	0.0776	0.0813	0.0671	0.0678
(3)	2	3	2-A_2	0.0862	0.0889	0.0857	0.0864
(4)	3	1		0.0546	0.0540	0.0605	0.0601
(3)	3	1		0.0786	0.0788	0.0778	0.0782
(4)	1	4	2-A_3	0.1458	0.1572	0.1356	0.1417
(3)	1	4	2-A_3	0.1584	0.1688	0.1562	0.1615
(4)	4	1		0.0860	0.0866	0.1005	0.1117
(3)	4	1		0.1126	0.1130	0.1236	0.1300
(4)	4	3	3-A_4	0.0699	0.0704	0.0654	0.0670
(3)	4	3	3-A_4	0.1079	0.1080	0.1043	0.1053
(4)	3	4		0.0810	0.0833	0.0794	0.0822
(3)	3	4		0.1288	0.1328	0.1258	0.1292
(4)	6	3	3-A_5	0.0428	0.0426	0.0484	0.0463
(3)	6	3	3-A_5	0.0695	0.0681	0.0729	0.0710
(4)	3	6		0.0552	0.0558	0.0640	0.0641
(3)	3	6		0.0959	0.0962	0.0931	0.0988
(4)	2	3	3-A_6	0.0273	0.0267	0.0259	0.0255
(3)	2	3	3-A_6	0.0456	0.0436	0.0453	0.0438
(4)	3	2		0.0323	0.0320	0.0318	0.0308
(3)	3	2		0.0572	0.0557	0.0566	0.0559

Since the electronic events represented by density operators (5) are also 3-electron, 3-hole events, their probabilities can be compared with the previous ones involving the $N(\uparrow\downarrow)$.

The results for the expectation values of density operators (3),(4), and (5) from both types of initial MO wave functions are given in Table 4. The first conclusion apparent from Table 4 is that the $N(\uparrow\downarrow)-C_1(+)...C_y(\uparrow)$ electronic events are clearly more important than the corresponding event (see Figure 2) $N^+(\uparrow)-C_1(\downarrow)...C_y(\uparrow)$; the probabilities for the former are greater by 54%, 76%, and 82% for $y = 2$, 3, and 4, respectively. Examining further the probabilities of all the electronic events given in Table 4, we can summarize the main trends by the following rules concerning the relative importance of various resonance structures of the radical cation of aniline. Most favorable are those resonance structures in which:

1. The $N-C_1$ bond involves the ionic event $N(\uparrow\downarrow)-C_1(+)$;
2. The location of (+) and (·) is such that the remaining electrons can be coupled by pairs in vicinal positions; and
3. The positions C_2-C_3 or (and) C_6-C_5 are occupied by an electron pair or pairs.

The first "or" of rule 3 can be considered a consequence of rules 1 and 2. The most favorable resonance structure is 2A-3, which satisfies rules 1 and 2 and both requirements of rule 3. Figure 3 gives the classification of some typical resonance structures involving $N(\uparrow\downarrow)$ and the couple (·) (+) in various C positions, according to their relative importance. The rules presented above are valid for both levels of the initial MO wave function (ab initio or PPP+full CI). For example, according to rule 1, resonance structures 2-A_1,2-A_2, and 2-A_3 have a greater contribution than the corresponding 2-B_1, 2-B_2, and 2-B_3 structures or the 3-A_4, 3-A_5, and 3-A_6; from rule 2, 2-A_2 has a smaller contribution than 2-A_1 or 2-A_3, and that of 2-B_2 is smaller than 2-B_1 or 2-B_3 ; according to rule 3, 2-A_3 has greater contribution than 2-A_1, 3-A_4 greater than 3-A_5 or 3-A_6, and so forth.

The above trends for the most favorable resonance structures are completely coherent with the nature of the electron pair (de)-coupling found in Section 3.1. This is because the cooperation of opposite spins or charges depends intrinsically on the location of (·) and (+) in various positions, and vice versa. For example, the high probability for $C_1(+)C_4(\uparrow)$ is related to the ionic nature of the $N-C_1$ bond [i.e., the strong cooperation of $C_1(+)$ and $N(\uparrow\downarrow)$] or to the enhanced electron pair decoupling in C_1-C_2 and C_3-C_4, and so forth.

As discussed previously (Section 3.1), the good agreement between the results obtained by using ab initio or PPP+full CI initial MO wave functions shows that the relative importance of various resonance structures is also controlled by electronic events occurring essentialy in the π-system.

3.3. Relation of Electron Pair (De)Coupling and Bi- (or Tri-) Stability. In this section we examine the relation between the electron pair (de)coupling and the geometrical deformations provoked by a $NH_2^{\bullet+}$ group on the bonds of a phenyl ring. We then investigate how the extension of this (de)coupling and the geometrical deformations along an aromatic polyamine can determine whether such a system is delocalized or shows two- (or three-) site localization, that is, bi- (or tri-) stability.

3.3.1. Electron Pair (De)Coupling as the Key Reason for Geometrical Deformations. The results and conclusions presented in previous sections are based on calculations (in both ab initio and PPP+full CI levels) performed by considering the relaxed geometry of aniline radical cation, which involves a quinoid deformation. Since the electron pair (de)coupling found represents also a quinoid reorganization of electron pairs, one might rush to the conclusion that the quinoid geometry used is the key reason for the observed effects on electron pairs. An opposite assumption would be that the electron pair (de)coupling is specifically due to the radical cation behavior of the considered topology (i.e., to the electron withdrawing from a topology of aniline), and in this sense, the quinoid reorganization of electron pairs would be the key reason provoking the corresponding geometrical deformations. To check which point of view is correct, we repeated all calculations for the radical cation in the geometry referred in Tables 2−4 as aromatic (see also Section 2), in which the bonds of the phenyl ring are identical to those of the neutral aniline.

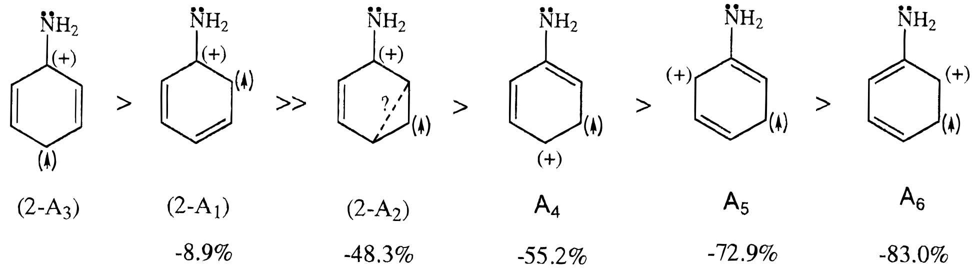

Figure 3. Classification of some typical resonance structures involving an electron pair in N and the (+) and (·) in various C positions; the numbers give the percentage decrease (in relaxed geometry and ab initio-CI calculations) of the expectation values of operators (4) with respect of the most favorable structure 2-A$_3$, which involves C$_1$(+) and C$_4$(·).

The differences, Δ(g), between the results found for the radical cation of aniline in the quinoid (i.e., relaxed) and aromatic geometries with respect to electron pair localizations and correlations (covalent + ionic) indicate what amount of the reorganization of electron pairs is due to geometrical (g) deformations. The differences, Δ(rc), for the same quantities between the radical cation in aromatic geometry and the neutral aniline indicate the corresponding amount that is due only to the electron withdrawing without any relaxation, that is, to the radical cation (rc) behavior of aniline topology. Some typical values for Δ(g)/Δ(rc), given as percentages of the results for the neutral/radical cation in aromatic geometry, are as follows: for electron pair localizations, $C_1-C_2 = -2.6\%/-28.6\%$, $C_2-C_3 = 2.3\%/12.7\%$, and $C_3-C_4 = -1.5\%/-17.1\%$; for correlations (covalent + ionic), $C_1-C_2 = -7.4\%/-50.9\%$, $C_2-C_3 = 3.7\%/23.5\%$, and $C_3-C_4 = -3.8\%/-31.3\%$.

These Δ(g)/Δ(rc) values are obtained from the ab initio wave functions, but quite similar are the correspnding values obtained from the PPP+full CI wave functions. The amount of electron pair (de)coupling which is attributable to geometrical deformations (Δ(g) for both electron pair localizations and correlations, is much smaller than that which is attributable to the radical cation behavior of aniline [i.e., with respect to the corresponding Δ(rc)]. Therefore, the main effects observed on electron pairs in relaxed geometry are due almost exclusively to the radical cation behavior of the considered topology. The same conclusion can be drawn by comparing the results for both geometries given in Table 4: The probabilities for all the considered electronic events vary very little between aromatic and quinoid geometries, whether for ab initio or PPP+full CI wave functions. All these results lead to the conclusion that the quinoid electron pair (de)coupling is, in fact, the key reason for the geometrical deformations. This conclusion is in good agreement with the behavior of electron pairs (covalent + ionic) observed in the radical cation of a polyene with a linear topology;[13] in that case, also, the enhanced electron pair delocalization or localization for formal simple or double bonds, respectively, occured even in a rigid geometry with alternating bond lengths.

3.3.2. Extension of Electron Pair (De)Coupling to Other Phenyl(s) of an Aromatic Polyamine. The notion of "functional group" is one of the most basic concepts in chemistry.[33] One of the advantages of the frequently used resonance or mesomeric theory is that it allows deduction of the properties of large systems on the basis of the resonance structures of functional groups. In this context, given the results of previous sections, one can deduce whether the electron pair (de)coupling and the corresponding geometrical deformations can be extended to other phenyl(s), and then determine whether the electronic situation favors either a delocalized or a localized (bi- or tristable) behavior. In a general case, the (+) as well as the (·), both of which characterize any radical cation system, can be considered to be responsible for an electron pair (de)coupling. In the present case, however, we determined that the (·) was more influential in causing the (de)coupling of a second phenyl linked to aniline. This is because the (+) is mainly located in the $N-C_1$ bond: The (↑↓) of N cooperates strongly with the (+), forming the ionic bond $N(\uparrow\downarrow)-C_1(+)$. Furthermore, the spin cooperation within the covalent structure $N^+(\uparrow)-C_1(\downarrow)$, is also not negligible.

Since in p-EFTP topology each amino group is linked in para position to a biphenyl, one must examine, first, whether in a system of the type $H_2N^{\bullet+}-Ph_1-Ph_2$ (para) the electron pair (de)coupling of Ph$_1$ can be extended to Ph$_2$. According to Section 3.2, the most favorable structures for $H_2N^{\bullet+}-Ph_1$ group are those of the type 2-A$_3$ and 2-A$_1$ (see Figure 3), which exhibit the (·) in C$_4$ and in C$_2$, respectively. After structure 2-A$_3$ (the other structure, 2-A$_1$, should be considered for ortho substitutions, which are not examined in the present work), the (·) of C$_4$ can be coupled with an electron in $C_{1'}$ (for the numbering see Figure 1), causing an enhanced coupling in $C_4-C_{1'}$ and a subsequent decoupling in $C_{1'}-C_{2'}$ and $C_{1'}-C_{6'}$. According to rule 3 of Section 3.2, we expect an enhanced coupling in $C_{2'}-C_{3'}$ or (and) $C_{6'}-C_{5'}$, as well as a decoupling in $C_{3'}-C_{4'}$ and $C_{5'}-C_{4'}$. This electron pair reorganization represents a trend toward a quinoid (de)coupling in Ph$_2$, which, according to Section 3.3.1, must cause quinoid geometrical deformations in Ph$_2$. All these predictions for Ph$_2$ are verified by polyelectron investigations within the PPP+full CI wave function and by geometrical optimizations in the AM1 level in the considered topology of para biphenylamines: For example, the (covalent + ionic) correlations, 0.219, 0.351, and 0.282, for the vicinal positions $C_{1'}-C_{2'}$, $C_{2'}-C_{3'}$, and $C_{3'}-C_{4'}$, respectively, show the trend toward the quinoid (de)coupling; the same quantities for nonvicinal positions are very small or negative (see Section 3.1 and rule 2 of Section 3.2), (e.g.) 0.054 or −0.026 for $C_{6'}-C_{3'}$ or $C_{1'}-C_{3'}$ (which involve the meta position, $C_{3'}$). The lengths (in Å) of bonds between the same vicinal positions obtained by AM1 show also a trend toward the quinoid deformation: 1.416, 1.388, and 1.398 for $C_{1'}-C_{2'}$, $C_{2'}-C_{3'}$, and $C_{3'}-C_{4'}$, respectively.

To investigate the possibility that the electron pair (de)coupling is extended to a third phenyl, Ph$_3$, as well as the electronic reasons leading to the localized behavior of p-EFTP, we have to consider the radical cation of triphenylenediamine, $H_2N^{\bullet+}-Ph_1-Ph_2-Ph_3-NH_2$, or TPDA (pmp), involving para, meta, and para connections for Ph$_1$, Ph$_2$, and Ph$_3$, respectively. For comparative purposes, we consider also the all-para isomer, TPDA (ppp). In the (ppp) isomer, for the same reasons presented above concerning the (de)coupling induced from C$_4$ to Ph$_2$, we expect also that a similar electron pair (de)coupling will be induced from $C_{4'}$ (of Ph$_2$) to Ph$_3$; this is shown schematically in resonance structures A$_2$ and A$_3$ of Figure 4. In contrast, in the (pmp) isomer, the extension of the (de)coupling from Ph$_2$ to Ph$_3$ is not favorable in the ground state: in this

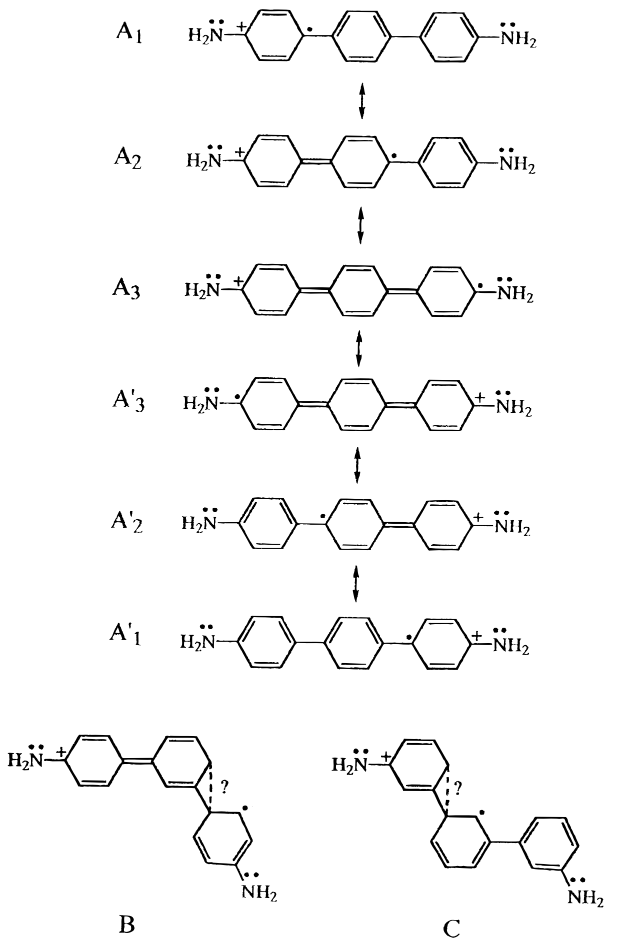

Figure 4. (A) Electron pair (de)coupling in the three phenyl rings of an all-para triphenyldiamine radical cation. (B, C) Typical unfavorable resonance structures preventing the electron pair (de)coupling in the third and second phenyl rings of para,meta,para (B) and all-meta (C) isomers.

system, the resonance structures of type B (of Figure 4) are unfavorable because, regardless of the location of (•), they refer always to couples of AO positions in which, according to Section 3.1, the spin and charge correlations are very small or negative (see also rule 2 of Section 3.2). Consequently, structures of type B (and the related unfavorable correlations) prevent the electron pair (de)coupling of Ph$_3$, and in this sense are responsible for the localized behavior of the (pmp) isomer.

Further, in the (ppp) isomer, the (de)coupling of Ph$_1$, Ph$_2$, and Ph$_3$ (represented schematically by structures A$_1$, A$_2$, and A$_3$) that is induced when the (+) is located in Ph$_1$, is **completely coherent** with the (de)coupling that is induced when the (+) is located in Ph$_3$ (represented by structures A$_{1'}$, A$_{2'}$, and A$_{3'}$). The opposite holds for the (pmp) isomer: The electronic and the associated geometrical effects induced in Ph$_3$ in the case when the (+) is in Ph$_1$ **are not coherent** with the effects produced in Ph$_3$ when the (+) is located on this ring. In the former case, there is no important (de)coupling for Ph$_3$, essentially because of the unfavorable behavior of structures of type B, and consequently the geometry of the group Ph$_3$−NH$_2$ should not differ much from that of the neutral aniline; in the latter case, however, the geometry of Ph$_3$−NH$_2$ should be similar to that of the radical cation of aniline. Thus, even though the (ppp) isomer must be a delocalized radical cation, clearly the (pmp) isomer must be a two-site localized (bistable) structure.

The opposite properties of the radical cations of the two isomers, reflected essentially in the opposite behaviors of Ph$_3$, can be verified easily by means of AM1 geometrical optimizations in their ground states. The bond lengths obtained for Ph$_1$ and Ph$_2$ are rather similar in the two isomers, but those for Ph$_3$ are not: The ring in (ppp) is identical to Ph$_1$, whereas that in (pmp) is quite similar to the phenyl ring of the neutral aniline (see Section 2.2). Thus, after geometry optimization, the (pmp) isomer exhibits a broken symmetry, that is, one end of the molecule presents the geometrical features of an aniline radical cation, while the other is reminiscent of a neutral aniline, in agreement with its localized (bistable) nature. An analogous behavior has been described for the monoradical cations of several bis(tetrathia-fulvalenes).[6] In contrast, the (ppp) isomer remains symmetrical. The bond lengths, in Å, for the (ppp)/(pmp) isomers are as follows [for (pmp) we give the average values for the noncompletely equivalent bonds situated on both sides of the $C_1{-}C_4$ or $C_{1'}$-$C_{4'}$ axis]:

Ph$_1$, $C_N{-}C_1 = 1.355/1.341$; $C_1{-}C_2 = 1.432/1.444$; $C_2{-}C_3 = 1.373/1.363$; $C_3{-}C_4 = 1.422/1.437$

Ph$_2$, $C_{1'}{-}C_{2'} = 1.424/1.427$; $C_{2'}{-}C_{3'} = 1.374/1.386$; $C_{3'}{-}C_{4'} = 1.424/1.405$; $C_4{-}C_{1'} = 1.425/1.416$

Ph$_3$(pmp only), $N{-}C_{1''} = 1.382$; $C_{1''}{-}C_{2''} = 1.415$; $C_{2''}{-}C_{3''} = 1.388$; $C_{3''}{-}C_{4''} = 1.401$.

The above results clarify the electronic reasons leading to the three-site localization in an oxidized aromatic triamine, such as p-EFTP: The topology of this system, besides the two aminophenylene groups of the above studied TPDA (pmp), involves another Ph$_4$−NH$_2$ group linked in meta connection to the central Ph$_2$ (in C_3 symmetry around Ph$_2$). Similarly, we can understand the localized behavior of the topology of m-EFTP, in which the Ph$_2$ is connected in meta position with Ph$_1$−H$_2$N. In this topology, to find the (•) in Ph$_2$, one must consider resonance structures of the type C (Figure 4), which involve necessarily unfavorable covalent and ionic correlations. Furthermore, for the same reasons as above, the electron pair (de)coupling and the corresponding geometrical deformations of Ph$_2$ and Ph$_3$ in the ground electronic state are not coherent for the two cases in which the (+) is located in the extreme phenyls, Ph$_1$ and Ph$_3$.

4. Conclusion

Within the local description of a molecular system provided by resonance or mesomeric theory, we investigated electrons and holes in (local) AO positions, instead of (delocalized) occupied and vacant MOs, as is usually done in MO theory. Because resonance structures are closer to the traditional chemical formulas, this type of investigation provides a more intuitive (from the chemical point of view) description of chemical bonding. The combination of both NAOs and second quantization can lead to polyelectron investigations by using ab initio-correlated MO wave functions. The methodology used allows the calculation not only of the weights of covalent and ionic resonance structures, but also of the degree of cooperation of opposite spins or charges to form chemical bonds, by means of the corresponding covalent and ionic correlations.

Polyelectron investigations in aniline (neutral and radical cation) revealed that the oxidized amino group has the following effects on a phenyl ring: It removes the quasi-uniform correlations existing in neutral aniline, inducing regions of high and low spin or charge correlations; and it produces a differential localization of electron pairs. Both effects show a quinoid (de)coupling of the electron pairs, which, as shown in Section 3.3.1, is the driving force for the corresponding geometrical deformations.

To investigate what characterizes any radical cation system [i.e., the simultaneous presence of (•) and (+)], we used density operators (3), (4), and (5). The most important resonance structure we found was 2-A_3, which exhibited the (•) and (+) in C_4 and C_1, respectively. The main trends determined from examination of the expectation values of the density operators used can be summarized in the rules of Section 3.2.

The importance of resonance structure 2-A_3 is in agreement with the electrochemical behavior of anilines upon oxidation, in particular the frequent occurrence of tail-to-tail coupling, which can be assigned to the existence of a radical cation with unpaired electron density in the para position.[34] Another experimental clue is provided by the spin densities obtained from the electron paramagnetic resonance hyperfine coupling constants with protons. The aniline radical cation is not stable enough to be accurately measured, but the related triphenylaminium radical cation exhibits spin densities of 0.084, −0.045, and 0.123 in ortho, meta, and para positions, respectively.[35] This again stresses the importance of structure 2-A_3 and the very minor contribution of structure 2-A_2; in general, these experimental results are in good agreement with the ordering 2-A_3 > 2-$A_1 \gg$ 2-A_2, found in Section 3.2 (see Figure 3 and Table 4).

The good agreement between calculations obtained for initial MO wave functions ab initio-CI and those obtained for PPP+full CI shows that the observed effects are controlled essentially by the π-system.

The localized (bi- or tri-stable) or delocalized behavior of a monooxidized aromatic polyamine depends essentially on whether the (quinoid) electron pair (de)coupling, and the associated geometrical deformations induced by the $NH_2^{\bullet+}$ group to the first phenyl ring, can be extended to the other phenyl rings of the system. For example, in the (pmp) isomer of $NH_2^{\bullet+}-Ph_1-Ph_2-Ph_3-NH_2$, to obtain the electron pair (de)coupling of the third phenyl, one must consider resonance structures in which the (•) is located in this ring (e.g., structure B of Figure 4). This type of resonance structure is unfavorable in the ground state, since all electrons cannot be coupled by pairs in vicinal positions, leaving necessarily at least one electron pair with very small or negative covalent and ionic correlations (see also rule 2 of Section 3.2). By assuming that the (+) is located in Ph_1 [essentially in C_1, given its strong correlation with N(↑↓)], it is not possible to find at least one resonance structure in which the (•) is located in Ph_3 and at the same time all the remaining electrons are coupled by pairs in vicinal positions. This is a purely topological effect and can be considered to be the origin of the localized (bistable) behavior of the (pmp) isomer. In contrast, the (ppp) isomer is a delocalized radical cation, since all electrons can be coupled by pairs in vicinal positions (and in quinoid manner), regardless of on which phenyl ring the (•) is located (see Figure 4). Consequently, resonance structures of the type B or C (Figure 4), and the related electron pairs having unfavorable covalent and ionic correlations, are the key reasons why the electron pair (de)coupling cannot be extended to the whole system and, therefore, account for the localized behavior of p-EFTP or m-EFTP.

Acknowledgment. J. Bonvoisin and M. Van der Auweraer are acknowledged for helpful and stimulating discussions and European Community Network CHRX-CT94-0538 “Electron and Energy Transfer in Model Systems” for financial support.

References and Notes

(1) See, e.g., reviews by (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273.

(2) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (b) The detailed calculation showing the competition between electronic coupling and electron−phonon coupling is in Wong, K. Y.; Schatz, P. N. *Progr. Inorg. Chem.* **1981**, *28*, 369.

(3) (a) Ribou, A.-C.; Launay, J.-P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735. (b) Patoux, C.; Coudret, C.; Launay, J.-P.; Joachim, C.; Gourdon, A. *Inorg. Chem.*, **1997**, *36*, 5037. (c) Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.*, in press.

(4) (a) Bonvoisin, J.; Launay, J.-P.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1994**, *98*, 5052. (b) Bonvoisin, J.; Launay, J.-P.; Verbouwe, W.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1996**, *100*, 17079.

(5) (a) Van der Auweraer, M.; De Schryver, F. C.; Verbeek, G.; Geelen, C.; Terrell, D.; De Meutter, S. Eur. Patent EP 349034. (b) Verbeek, G.; Depaemelaere, S.; Van der Auweraer, M.; De Schryver, F. C.; Vaes, A.; Terrell, D.; De Meutter, S. *Chem. Phys.* **1993**, *176*, 195.

(6) Lahlil, K.; Moradpour, A.; Bowlas, C.; Menou, F.; Cassoux, P.; Bonvoisin, J.; Launay, J.-P.; Dive, G.; Dehareng, D. *J. Am. Chem. Soc.* **1995**, *117*, 9995.

(7) (a) Avery, J. *Creation and Annihilation Operators*; McGraw-Hill: New York, 1976. (b) Surjan, P. R. *Second Quantized Approach to Quantum Chemistry*; Springer: Berlin, 1989.

(8) (a) Karafiloglou, P. *Chem. Phys.* **1988**, *128*, 373. (b) Karafiloglou, P.; Parrondo, R. M.; Sanchez-Marcos, E. QCPE program 638. *QCPE Bull*. **1993**, *13(4)*, 64.

(9) (a) Karafiloglou, P. *Chem. Phys.* **1990**, *140*, 373. (b) Karafiloglou, P.; Kapsomenos, G. *Theor. Chim. Acta* **1994**, *88*, 395.

(10) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899, and references therein.

(11) (a) Reed, A. E.; Weinhold, F. *J. Chem. Phys*. **1983**, *78*, 4066. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735. (c) Nemukhin, A. V.; Weinhold, F. *J. Chem. Phys*. **1993**, *98*, 1329. (d) King, B. F.; Weinhold, F. *J. Chem. Phys*. **1995**, *103*, 333.

(12) Parrondo, R. M.; Karafiloglou, P.; Sanchez-Marcos, E. *Int. J. Quantum Chem.* **1994**, *52*, 1127.

(13) Karafiloglou, P.; Kapsomenos, G. *Chem. Phys.* **1995**, *196*, 69.

(14) Parrondo, R. M.; Karafiloglou, P.; Pappalardo, R. R.; Sanchez-Marcos, E. *J. Phys. Chem.* **1995**, *99*, 6461.

(15) (a) Savin, A.; Becke, A. D.; Flad, J.; Nesper, R.; Preuss, H.; Von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 409. (b) Savin, A.; Jepsen, O.; Flad, J.; Andersen, O. K.; Preuss, H.; Von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 187. (c) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683. (d) Boyd, R. J.; Ugalde, J. M. In *Computational Chemistry: Structure, Interactions and Reactivity;* Fraga, S, Ed.; Studies in Physical and Theoretical Chemistry 77(A); Elsevier: Amsterdam, 1992; p 273. (e) Bader, R. F. W.; Streitwieser, A.; Neuhaus, A.; Laidig, K. E.; Speers, P. *J. Am. Chem. Soc.* **1996**, *118*, 4959.

(16) (a) Strnad, M.; Ponec, R. *Int. J. Quantum Chem.* **1994**, *49*, 35. (b) Ponec, R.; Strnad, M. *Int. J. Quantum Chem.* **1994**, *50*, 43. (c) Ponec, R.; Bochicchio, R. C. *Int. J. Quantum Chem.* **1995**, *54*, 99. (d) Ponec, R.; Jug, K. *Int. J. Quantum Chem.* **1996**, *60*, 75. (e) Ponec, R. *Int. J. Quantum Chem.* **1997**, *62*, 171.

(17) (a) Eriksson, L. A.; Lunell, S.; Boyd, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 6896. (b) Boyd, S. L.; Boyd, R. J. *J. Phys. Chem.* **1994**, *98*, 1856 and 11705. (c) Martell, J. M.; Boyd, R. J. *J. Phys. Chem.* **1995**, *99*, 13402. (d) Martell, J. M.; Boyd, R. J.; Eriksson, L. A. *J. Phys. Chem.* **1995**, *99*, 623. (e) Wang, J.; Laaksonen, A.; Eriksson, L. A.; Boyd, R. J. *J. Chem. Phys.* **1995**, *103*, 8166. (f) Dong, X. C.; Salhi-Benachenhou, N.; Lunell, S. *J. Mol. Struct.* (THEOCHEM) **1997**, *392*, 111. (h) Fängström, T.; Lunell, S.; Engels, B.; Eriksson, L. A.; Shiotani, M.; Komaguchi, K. *J. Chem. Phys.* **1997**, *102*, 297.

(18) (a) Karafiloglou, P.; Akrivos, P. *Chem. Phys.* **1988**, *127*, 41. (b) Karafiloglou, P.; Theodorakopoulos, G.; Petsalakis, I. D. *J. Mol. Struct.* (THEOCHEM) **1988**, *180*, 31. (c) Karafiloglou, P.; Kapsomenos, G. *J. Mol. Struct.* (THEOCHEM) **1989**, *184*, 213. (d) Bachler, V. *Theor. Chim. Acta* **1997**, *92*, 223.

(19) (a) Moffitt, W. *Proc. R. Soc.* **1953**, *A218*, 486. (b) Karafiloglou, P.; Ohanessian, G. *J. Chem. Educ.* **1991**, 68, 583. (c) Karafiloglou, P. *J. Solid State Chem.* **1992**, *99*, 29. (d) Karafiloglou, P.; Kapsomenos, G. *J. Mol. Struct.* (THEOCHEM) **1995**, *337*, 241.

(20) Sanchez-Marcos, E.; Karafiloglou, P.; Fernandez-Sanz, J. *J. Phys. Chem.* **1990**, *94*, 2763.

(21) Parrondo, R. M.; Karafiloglou, P.; Sanchez-Marcos, E. *Int. J. Quantum Chem.* **1993**, *47*, 191.

(22) Karafiloglou, P.; Sanchez-Marcos, E. *Int. J. Quantum Chem*. **1992**, *44*, 337.

(23) Karafiloglou, P. *J. Mol. Struct.* (THEOCHEM) **1998**, *428*, 221.

(24) Pelissier, M.; Komiha, N.; Daudey, J. P. *J. Comput. Chem.* **1988**, *9*, 298.

(25) Laboratoire de Physique Quantique, Programme PSHONDO+CIPSI, Université Paul Sabatier, Toulouse, France.

(26) Durand, P.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283.

(27) Dohnert, D.; Koutecky, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789.

(28) (a) Ducasse, I. R.; Miller, T. E.; Soos, Z. G. *J. Chem. Phys.* **1982**, *76*, 4094. (b) Ramasesha, S.; Soos, Z. G. *J. Chem. Phys.* **1984**, *80*, 3278.

(29) (a) Fortunelli, A.; Painelli, A. *J. Chem. Phys.* **1997**, *106*, 8051. (b) Fortunelli, A.; Painelli, A. *Phys. Rev. B* **1997**, *55*, 16088.

(30) Brown, G. M.; Freeman, G. R.; Walter, R. I. *J. Am. Chem. Soc.* **1977**, *99*, 6910.

(31) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(32) Karafiloglou, P. *Chem. Phys.* **1997**, *214*, 171.

(33) Patai, S. *Patai's 1992 Guide to the Chemistry of Functional Groups*; J. Wiley: Chichester, U.K., 1992.

(34) Lund, H.; Baizer, M. M., Eds. *Organic Electrochemistry*, 3rd ed.; Marcel Dekker: New York, 1991; Chapter 15.

(35) (a) van Willigen, H. *J. Am. Chem. Soc.* **1967**, *89*, 2229. (b) Mohammad, M.; Sundheim, B. R. *Theor. Chim. Acta* **1968**, *10*, 222.