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Valence-Bond Description of Conjugated Molecules. 3. The Through-Resonance Concept in Para-Substituted Nitrobenzenes

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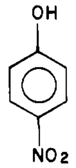
Abstract: The influence of the mesomeric interaction of a π-donor para substituent on nitrobenzene is studied by means of an analysis, in valence-bond terms, of the ab initio SCF wave functions of *p*-nitroaniline and *p*-nitrophenol. It is shown that the six-membered ring undergoes some charge transfer from the π-donor para substituent, but that the NO_2 group does not, contrary to the usual concept of "through resonance" in the valence-bond theory of resonance. A reinterpretation of the available experimental data, concerning the influence of a para substituent on the dipole moments, the negative charges on the outer oxygens, and the carbon–nitrogen bond shortenings in substituted nitrobenzenes, is suggested. Further refinements to estimate the effects of electron correlation lead to the same conclusions.

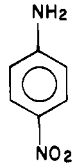
I. Introduction

The electronic structure of nitrobenzene and its various substituted derivatives has been a subject of long-standing interest for organic chemists. In particular, the description of para-substituted nitrobenzenes is one of the most widely used illustrations of the use of resonance theory in chemistry textbooks. This description has been the subject of two recent contradictory communications in this journal. Both of them were based on ^{17}O NMR chemical shifts, in complete disagreement with one another. Since NMR shifts are expected to closely parallel the variations of electronic density, comparisons of ^{17}O shifts for different substituents are an indication of the charge transfer they induce toward the oxygens atom of the nitro group. Lipkowitz[1] claimed that chemical shifts display very little variation upon change of the para substituent, from which he concluded that "the NO_2 group withdraws a constant amount of electron density from the ring regardless of what substituent is attached to the meta or para position". As a consequence, **1** and **2** should mix with **5** and **6** rather than with **7** (see Figure 1).

On the contrary, Fraser, Ragauskas, and Stothers[2] (FRS) reported chemical shifts whose sensitivity to para substituents was fully consistent with the standard belief that **2** and **7** are the only important bonding structures. While this second series covered a wider range of substituents with a better resolution of the spectra, the reason for the discrepancy between both sets of experiments remains unclear. As was noted by both groups, this problem is rather important since such considerations are underlying many qualitative descriptions of chemical reactions or interpretations of experimental data by some intuitive form of valence-bond theory, and are of widespread use in chemistry courses.

Another set of ^{15}N and ^{17}O chemical shifts for these molecules has appeared even more recently.[3] This new series, in good agreement with that of FRS, seems to reinforce the "classical" view, as claimed by the authors. Also, as FRS did, they questioned the suitability of Lipkowitz's data for such an analysis, because of the need of small concentrations and a large range of substituent types for the results to be conclusive. However, as will be discussed below, a careful examination indicates that the "through-resonance" description,[4] invoking structure **7**, is not the only way of rationalizing the experimental data in this case, and not even the best one. This prompted us to tackle the problem with a theoretical study, as experimental data have been rather well accounted for in the past by ab initio calculations[5] for this kind of molecules. For this purpose, the following two molecules have been investigated:





In section II, the theoretical methods that we have used are described in some detail; section III is devoted to a description of the computational results, and a reinterpretation of the experimental data in light of these results is attempted in section IV.

II. Theoretical Methods

The best theoretical answer to the above-addressed question lies in a valence-bond (VB) description of the relevant molecules. To be specific, by the term VB we mean the original VB theory[6] in which the functions defining bonding structures are constructed from nonorthogonalized atomic orbitals (AOs). It allows the calculation of an accurate weight for each structure, which is not possible with some other brands of VB theory like the GVB[7] or VB–SCF[8] methods, in which the AOs are allowed to mix, thus rending the bonding structure–VB function relationship rather vague. Of course, direct variational VB calculations are very expensive because the nonorthogonality of the Slater determinants complicates the computation of the Hamiltonian matrix elements; however, we have devised a computer program allowing the projection of molecular orbital (MO) wave functions, Ψ_{MO}, calculated at the SCF level or including configuration interaction, on a complete basis of VB functions V_n:[9,10]

$$|\Psi_{MO}\rangle = \Sigma_n K_n |V_n\rangle \qquad (1)$$

[†] The Laboratorie de Chimie Théorique is associated with the CNRS (ERA No. 549).

(1) K. B. Lipkowitz, *J. Am. Chem. Soc.*, **104**, 2647 (1982).

(2) R. R. Fraser, A. J. Ragauskas, and J. B. Stothers, *J. Am. Chem. Soc.* **104**, 6475 (1982).

(3) D. J. Craik, G. C. Levy, and R. T. C. Brownlee, *J. Org. Chem.*, **48**, 1601 (1983).

(4) J. Clark and D. D. Perrin, *Q. Rev. Chem. Soc.*, **18**, 295 (1964).

(5) Some major references follow: (a) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 159 (1976); (b) A. Pross, and L. Radom, *ibid.* **13**, 1 (1981); (c) R. D. Topsom, *Acc. Chem. Res.*, **16**, 292 (1983); (d) D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.*, **14**, 1 (1983), (e) W. F. Reynolds, *ibid.*, **14**, 165 (1983).

(6) J. C. Slater, *Phys. Rev.*, **37**, 481 (1931); L. Pauling, *J. Am. Chem. Soc.*, **53**, 1367 (1931). Several groups have brought this method to a high level of accuracy; see, for example, the review by G. A. Gallup, R. L. Vance, J. R. Collins, and J. M. Norbeck, *Adv. Quant. Chem.*, **16**, 229 (1982).

(7) W. A. Goddard III, T. H. Dunning, W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).

(8) J. H. Van Lethe and G. G. Balint-Kurti, *J. Chem. Phys.*, **78**, 5699 (1983).

(9) P. C. Hiberty and C. Leforestier, *J. Am. Chem. Soc.*, **100**, 2012 (1978); P. C. Hiberty, Thèse d'Etat, Orsay, France, 1978.

(10) The complete basis of VB functions is determined by the graphical method of G. Rumer, *Gottingen Nachr.*, 377 (1932).

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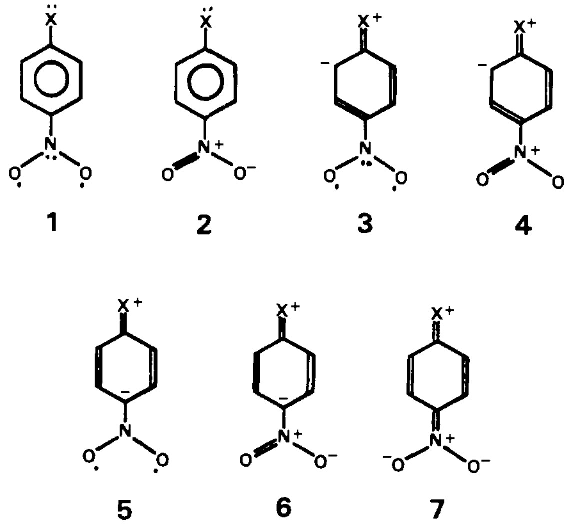

Figure 1. Main structures for para-substituted nitrobenzenes.

and the calculation of an accurate weight W_n for each structure represented by V_n, using Chirgwin and Coulson's formula:[11]

$$W_n = K_n^2 + \sum_{m\neq n} K_m K_n \langle V_m | V_n \rangle \qquad (2)$$

It should be noted that this analysis of MO wave functions in terms of bonding structures is nothing but a translation of Ψ_{MO} into the VB language. Indeed, the MO determinants and the VB functions span the same linear space; thus, we do not change Ψ_{MO} but simply express this wave function in a new basis set. There are *no* approximations in that process; thus there can be no contradictions between this analysis and calculated net charges or dipole moments,[12] all the more as the population analysis using eq 2 is rigorously equivalent[13] to the well-known Mulliken population analysis in MO theory.[14]

In a first step, we simply analyzed SCF–MO wave functions, at the ab initio level. Indeed, the relation of such calculations to NMR data is well documented in the literature of the past 10 years. Linear relations are generally found between chemical shifts and calculated electron densities. They also yield good values for the dipole moments and the geometrical parameters, and should reasonably describe the bonding structure of delocalized systems as shown by the well-known correlations between bond lengths and bond orders in the conjugated molecules.

Most of the ab initio calculations published to date on aromatic molecules have used minimal basis sets of atomic functions. Two different ways have been followed to investigate their deficiencies in VB calculations. (i) Norbeck and Gallup[15] studied the effects of scaling the AO exponents of a minimal basis set on the structural weights for first-row hydrides. (ii) We have compared the minimal STO-3G[16] and the split-valence 4-31G[17] basis sets for 17 1,3-dipoles; [18] in both cases, substantial effects were found on the detailed description of the molecules, altering some structural weights by some 20–30%. This error is obviously not large enough to modify the conclusions of the present study. Qualitatively, one might predict the weights of **2**, **4**, **6**, and **7** to increase slightly upon basis set extension, but the ratio **6** vs. **7** should not be altered significantly. Therefore, the STO-3G basis set is adequate for our purpose and has been used throughout.

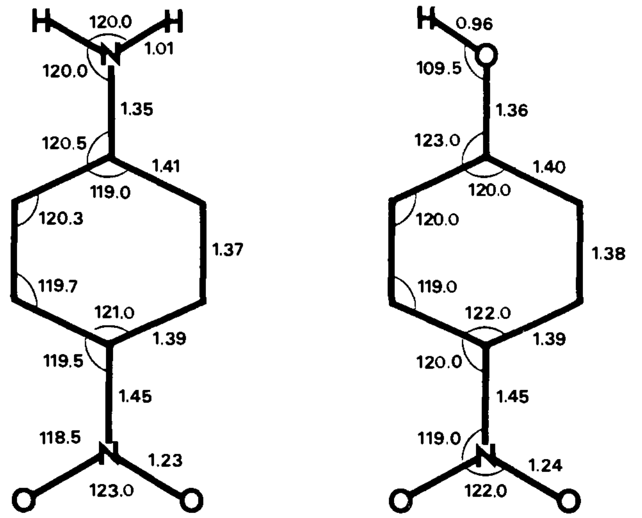

Figure 2. Experimental geometries for nitrophenol and nitroaniline.

As only π electrons may undergo significant delocalization in these molecules, the VB basis is restricted, in what follows, to π electrons and π orbitals; i.e., the VB functions are constructed with mixed determinants in which the σ electrons are frozen into MOs, while π electrons are associated with AOs. In other words, we have performed a π-only VB analysis,[19] with π electrons moving in a σ field calculated at the SCF level. It should be noted that the effects of using (i) the minimal basis set and (ii) mixed determinants with σ MOs have been shown, in the case of ozone, to be of the same order of magnitude, but cancelling each other.[20]

The reliability of these calculations can be further assessed by comparing various calculated properties with their experimental values. Among these, the dipole moments certainly constitute a key point since **6** and/or **7** are expected to bring a large contribution to it. A necessary condition for any method to be relevant here is thus that it gives a satisfactory value for the dipole moment of the molecule under study. Previous calculations on monosubstituted benzenes[21] have shown that calculated values are generally slightly smaller than the experimental ones, but that the trends are well reproduced. Using experimental geometries,[22] displayed in Figure 2, we have calculated the dipole moments of nitrobenzene, *p*-nitrophenol, and *p*-nitroaniline; our values, respectively 3.95, 4.49, and 6.20 D, are in good agreement with experimental data.[23]

One can also evaluate the mesomeric component of the dipole moment of nitrobenzene, by comparing its calculated value in the latter molecule with that of nitromethane. Using experimental geometries,[24] we have found a difference of 0.86 D between the two molecules, quite in agreement with the experimental value of about 1 D. Thus SCF calculations meet the condition expressed above concerning dipole moments.

Another parameter of interest is the barrier to rotation around the bond linking the ring to the substituent, because it gives a rough estimate of its partial double-bond character. A systematic in-

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(11) B. H. Chirgwin and C. A. Coulson, *Proc. R. Soc. London, Ser. A*, **201**, 196 (1950). Another definition of the structural weights has been proposed: G. A. Gallup and J. M. Norbeck, *Chem. Phys. Lett.*, **21**, 495 (1973).

(12) Note, however, that these properties cannot be accurately calculated from the results shown in Tables I and II alone, since, by necessity, many minor structures are not displayed here.

(13) A. C. Hurley, *Proc. R. Soc. London, Ser. A*, **248**, 119 (1958).

(14) R. S. Mulliken, *J. Chem. Phys.*, **51**, 1833 (1955).

(15) J. M. Norbeck and G. A. Gallup, *Int. J. Quantum Chem.*, **7**, 161 (1973).

(16) W. J. Hehre, R. F. Stewart, and J. A. Popel, *J. Chem. Phys.*, **51**, 2657 (1969).

(17) R. Dithfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(18) P. C. Hiberty and G. Ohanessian, *J. Am. Chem. Soc.*, **104**, 66 (1982).

(19) This restriction to π electrons is made in all descriptions of aromatic molecules by means of resonance structures, that is, both qualitative uses of resonance theory and VB calculations.

(20) P. C. Hiberty, *Isr. J. Chem.*, **23**, 10 (1983).

(21) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).

(22) For nitrobenzene: F. di Rienzo, A. Domenicano, and L. Riva di Sanseverino, *Acta Crystallogr., Sect. B.*, **36**, 586 (1980); for nitrophenol: P. Coppens and G. M. J. Schmidt, *Acta Crystallogr.*, **18**, 654 (1965); for nitroaniline: K. N. Trueblood, E. Goldish, and J. Donohue, *ibid.*, **14**, 1009 (1961). The geometric parameters have been slightly modified, when necessary, so as to recover the exact C_{2v} symmetry.

(23) A. L. McClellan, Tables of Experimental Dipole Moments, Rahara, El Cerrito, 1974.

(24) For nitromethane: A. P. Cox and S. Waring, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1060 (1972).

Table I. Calculated Weights of Structures **1**–**7** for Nitrophenol

	p-nitrophenol						
	1	**2**	**3**	**4**	**5**	**6**	**7**
covalents SCF level	0.239	0.607	0.028	0.071	0.014	0.037	0.005
covalents + monoionics SCF level	0.251	0.639	0.019	0.049	0.010	0.028	0.004
covalents estimated CI	0.422	0.501	0.023	0.028	0.011	0.014	0.001
covalents + monoionics estimated CI	0.424	0.507	0.021	0.025	0.009	0.012	0.001

Table II. Calculated Weights of Structures **1**–**7** for *p*-Nitroaniline

	p-nitroaniline						
	1	**2**	**3**	**4**	**5**	**6**	**7**
covalents SCF level	0.214	0.549	0.041	0.107	0.021	0.062	0.007
covalents + monoionics SCF levels	0.230	0.590	0.029	0.075	0.016	0.048	0.011
covalents estimated CI	0.398	0.477	0.035	0.043	0.019	0.025	0.002
covalents + monoionics estimated CI	0.406	0.480	0.033	0.040	0.016	0.021	0.003

vestigation of monosubstituted benzenes[21] has shown that calculated values are in good agreement with experimental ones, generally a little higher. For example, the value obtained for nitrobenzene is 5.74 kcal/mol, to be compared with an estimation from the microwave spectrum of (3 ± 1.5) kcal/mol.[25] Therefore, the SCF function is an appropriate tool for the study of the relative importance of **6** and **7**. Incidentally, such barriers are much like those of single bonds, while barriers for double bonds are generally higher by an order of magnitude.

However, despite these encouraging data, some care should be exercised when calculating structural weights at the SCF level. Indeed, it is well known that, if the SCF wave functions correctly describe the average positions of the electrons, it quite overestimates the zwitterionic:covalent ratio for each bond. As a consequence, the weights of structures involving four formally purely covalent bonds, like structures **1**–**7**, must be considered as relative values rather than absolute ones. With this restriction in mind, we have recently demonstrated[26] that relative structural weights can be reasonably approximated at the SCF level. For example, the ratio of Kekulē vs. Dewar structures of benzene is 2.34 in the SCF configuration, to be compared with the value 2.02 in a complete VB calculation, i.e., including full correlation of π electrons, by Simonetta.[27]

On the other hand, a further restriction must be imposed for π systems having more electrons than AOs, which is the case here. Indeed, the SCF wave functions also overestimate the weights of structures bearing formal charges with respect to the formally neutral ones,[9,18] despite the fact that both types of structures have the same number of covalent bonds or electron pairs. Thus, comparisons of structural weights at the SCF level are strictly valid only among the sets of structures **2**, **3**, **5** or **4**, **6**, **7**. So, the SCF level is sufficient for one of the purposes of the present work, which is to settle the contradictory statements of Lipkowitz and FRS about the relative importance of structures **6** and **7**; however, we also wanted to have an overall VB description of para-substituted nitrobenzenes in terms of structures **1**–**7**, thus needing "absolute" structural weights for any structure, regardless of the number of its formal charges. Now these absolute weights can be obtained only if the electron correlation effects are properly taken into account. Ideally, the best course to take would be to perform a full configuration interaction (CI) calculation among the space of the π MOs, but such a CI involves some 44 100 determinants and would be quite costly, as also the projection of the resulting wave function. However, we recently devised a much simpler method to estimate the effects of electron correlation on the structural weights, which is described in detail elsewhere.[28] Briefly, it assumes that the effect of the CI is to increase the weights of covalent bonds or singlet-coupled diradicals and to diminish those of ionic bonds, by factors which are transferable from one molecule to another. Thus, each type of bond, or small group of bonds, can be given a multiplier,[29] depending only on its covalent or ionic nature, the atoms it connects, and the bond length, and the weight of a structure is very simply calculated as its weight in the SCF configuration, multiplied by the product of each bond multiplier. This method not only yields the correct ratios between the structural weights, but it also gives the absolute weights in very reasonable agreement with the results of the full CI calculation. As an example, the absolute weights of the Kekulē and Dewar structures of benzene are estimated to be respectively 0.20 and 0.11, to be compared with the full CI values[27] 0.22 and 0.11. More generally, all estimated absolute weights for significant structures of benzene agree with the exact ones within a relative error margin of 10%.

III. Results

All calculations have been performed using experimental geometries[21] (Figure 2). The resonant structures of interest in connection with the questions discussed in this paper are displayed in Figure 1. All of them should be understood as "symmetrized", so, for example, **4** includes the four structures **4a**–**d**. Moreover, structures **1** and **2** summarize all possible neutral arrangements on the ring (i.e., two Kekulē and three Dewar structures). The structural weights, calculated at the ab initio SCF level[30] and

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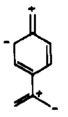
(25) J. H. Hog, L. Nygaard, and G. O. Sorensen, *J. Mol. Struct.*, **7**, 111 (1970). Other comparisons between theoretical and experimental barriers can be found in ref 21 and in: T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 289 (1974).

(26) P. C. Hiberty and G. Ohanessian, *Int. J. Quantum Chem.*, in press (paper I of this series).

(27) (a) G. F. Tantardini, M. Raimondi, and M. Simonetta, *J. Am. Chem. Soc.*, **99**, 2913 (1977); (b) J. M. Norbeck and G. A. Gallup, *ibid.*, **96**, 3386 (1974).

(28) P. C. Hiberty and G. Ohanessian, *Int. J. Quantum Chem.*, in press (paper II of this series).

(29) The significance of these multipliers can be illustrated with the trivial example of ethylene. At the SCF level, the weights of the covalent and zwitterionic structures are both equal to 0.5. The exact weights, respectively 0.8 and 0.2, are related to the SCF ones by the multipliers 1.6 and 0.4.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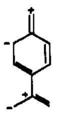
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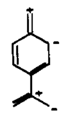
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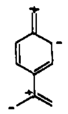
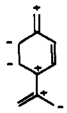

4d

normalized to unity, of structures **1**–**7** are displayed in the first rows of Tables I and II. It should be noted that, in these rows, the formal bonds are considered as purely covalent. Thus, the analysis is restricted to the structures involving four covalent bonds. The inconvenience of this restriction is that it ignores the major class of strutures,[31] this constituted by the "monoionics", i.e., structures in which one of the four covalent bonds is replaced by a zwitterionic bond. Thus, to make sure that such a restriction was not altering our results, we performed another VB analysis including the monoionics, whose results are displayed in the second rows of the tables; this procedure takes a much larger number of structures into account, and amounts to adding to each covalent bond its zwitterionic component.

To take explicitly into account the most significant part of these zwitterionic terms, we have added all structures which are monoionic with respect to the parent structures of Figure 1. Each covalent bond ($A{=}B$) is thus replaced by the two ionic ones that can be deduced from it ($A^{+}{-}B^{-}$ and $A^{-}{-}B^{+}$), e.g., the six structures (I–VI) in the case of **4A**, this treatment being restricted to the aniline or phenol fragment. This way **1** groups 5 neutral and 30 monoionic structures, **2** twice as many as **1** (because there are two symmetric zwitterions for the nitro groups, $O^{-}{-}N^{+}{=}O$ and $O{=}N^{+}{-}O^{-}$, associated with each structure of the ring, instead of only one long bond in **1**), and so on. In a few cases, there is an ambiguity as several monoionic structures can be associated with two parent covalent structures. For example, structure II was derived from **4a**, but can also be related to **6**. In such cases, the ionic weight has been shared among both structures, in proportion to their relative covalent weights.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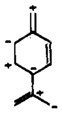
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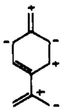
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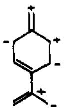
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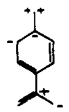
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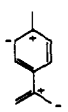
VI

An examination of Tables I and II shows that including the monionics does not significantly modify the results of the restricted VB analysis. However, we will base the discussion on the structural weights arising from the analysis including the monoionics, for two reasons: (i) it takes a much larger number of structures into account, and (ii) it makes more sense because it amounts to considering each bond as partly ionic, as it is in reality: with the exception of "long bonds" (singlet coupled diradicals), purely covalent bonds do not exist.

The structural weights calculated after estimation of electron correlation effects are displayed in the last two rows of Tables I and II. It is interesting to visualize these effects, column by column. As electron correlation is introduced, the weight of **2** decreases to the benefit of **1**, as expected since the former has two formal charges while the latter has a long bond. Similarly, the weights of **4**, **6**, and **7** significantly decrease under CI effects, as they have four formal charges, while the weights of **3** and **5** remain unaffected because the presence of two formal charges compensates for that of a long bond.

One can see from the tables that, among **1**–**7**, the structures exhibiting no charge transfer from the ring to the nitro group are by far the most important ones. However, this result is not in itself sufficient to conclude that the charge transfer is weak in nitrophenol and nitroaniline; indeed, many structurs have not been displayed here,[32] some of them being long-bond structures capable of contributing to some charge transfer. Therefore, we have performed a Mulliken π-electron population analysis of the total wave function (see Figure 3), which confirms that the charge transfer to NO_2 (0.030 electron in nitrophenol and 0.037 electron in aniline) is indeed small as compared to population variations corresponding to polarization within the ring and the nitro group. These values are in agreement with those of von Nagy-Felsobuki et al.[33] (0.028 electron in nitroaniline) reported for fully optimized STO-3G structures, and those of Reynolds et al.[34] (0.044 electron) using standard geometries. This should not be considered contradictory with the fact that p-nitroaniline is a weaker base than aniline. Pross and Radom have shown[5b] that this difference is mainly due to an unfavorable interaction between NH_3^+ and NO_2 in the ammonium ion rather than to a favorable interaction between NH_2 and NO_2 in p-nitroaniline as could be thought using **7**. Pross and Radom evaluated this resonance to represent only 20% of the reduction in aniline basicity brought about by the nitro group, the charged group–neutral group interactions being significantly greater than those between two neutral groups. We end this general description by noting that, as expected, NH_2 is found to be a stronger π-electron donor than OH (by comparing the weights of structures **3**–**7** in both cases).

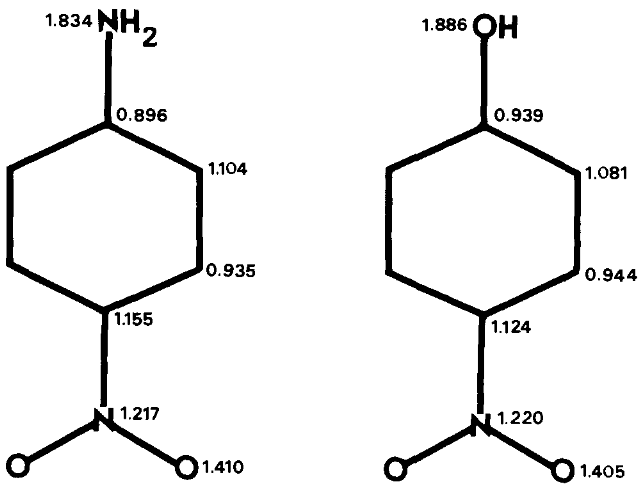

Figure 3. Calculated net π-electron population, from a Mulliken population analysis of MOs, for nitrophenol and nitroaniline.

It is instructive to compare the net charges displayed in Figure 3 with the structural weights of structures **3**–**7**. Taking nitroaniline as an example, one sees that the weights of structures **3**–**7**, all bearing a positive charge on the NH_2 group, sum to 0.179, in good agreement with the calculated net charge on Figure 3. On the contrary, the weights of structures **5**–**7** account for a charge transfer of only 0.011 e on the NO_2 group and a negative charge of only 0.064 e on the carbon adjacent to it, vs. 0.037 and 0.155 e, respectively, according to the π-Mulliken population analysis displayed on Figure 3. In fact, this apparent discrepancy illustrates two effects which are usually neglected in intuitive valence-bond reasoning.

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(30) We have used the GAUSSIAN 70 program: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, No. 236, Indiana University, Bloomington, Ind.

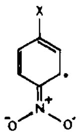
(31) Indeed, the class of purely covalent structures represents a smaller and smaller part of the wave function as the molecule gets bigger. For example, the weights of the purely covalent structures, at the SCF level, add to 0.23 in butadiene, 0.07 in benzene,[26] and 0.06 in the molecules studied here. By contrast, the joined covalent and monoionic weights add to 0.37 at the SCF level. When CI effects are taken into account, the purely covalent structures are still minor, with weights adding to about 0.21, while some 80% of the wave function is taken into account when monoionics are included.

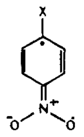
(32) As suggested by a referee, other structures can be invoked to complete the descriptions given in Tables I and II. For example, one may consider an electron donation to the NO_2 group from the carbon ipso to the donor group (instead of the donor group itself as in **7**). The weight of this structure is approximately three times that of **7** at the SCF level and its half at the CI level for p-nitroaniline. By the way, it has been included in our treatment as a monoionic associated with **7**. It should be remembered that there are many small contributors to the wave function among which **7** was selected for the purpose of the present work.

(33) E. von Nagy-Felsobuki, R. D. Topsom, S. Pollack, and R. W. Taft, *J. Mol. Struct.* (*Theochem.*) **88**, 255 (1982).

(34) W. F. Reynolds, P. Dais, D. W. Mac Intyre, R. D. Topsom, S. Marriott, E. von Nagy-Felsobuki, and R. W. Taft, *J. Am. Chem. Soc.*, **105**, 378 (1983).

The first one is the contribution of "long bonds" or spin-paired diradical structures. Indeed, the sum of the weights of the long-bond structures contributing to negative charge transfer on the NO_2 group is 0.013 which is far from being negligible since it is slightly larger than the weight of the classical structure **7**. Most of these structures (**8–10**) display a long bond between an oxygen and a carbon of the ring. It is worth noting that the importance of long bonds in the electronic structure of conjugated molecules has been established many years ago by Harcourt[35] on the basis of rigorous calculations.


8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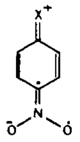
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The second effect lies in the polarity of the formal double bonds, reflecting that the two zwitterionic components of a given bond many have unequal weights, if the atoms it connects have different electronegativities. In the case of structures **6** and **7**, the π bond connecting the ring to the positively charged nitrogen of the nitro group is, as one expects, polarized so as to bring some electron density toward the nitrogen cation. This effect brings a partial negative charge of 0.013 e on the NO_2 group. Thus, the charge transfer on NO_2 is due to three factors of approximately equal importance: the classical structure **7**, the long bonds, and the short-bond polarization.

The same effects are responsible for the positive net charge on the NH_2 group. Once again, the long-bond structures contributing to this charge transfer are very important, approximately as much as the sum of structures **3–7**. The $C{=}N^+$ bond is also quite polarized, but this polarization brings some negative charge on the nitrogen and now compensates for the effects of long bonds. This explains why there is no apparent discrepancy between Table II and Figure 1 as regards the NH_2 group.

Some similar effects explain the negative charge on the carbon adjacent to the nitro group. In addition to **5**, other long-bond structures bring a contribution of 0.022 e. One also expects the bonds linking this carbon to neighboring ones to be moderately polarized by the presence of a neighboring positively charged nitrogen. However, as there are two such C–C bonds, the polarization effect is still strong and brings 0.067 e.

In the light of this analysis, one may speculate further on the effects of CI on the charge transfers and the dipole moment. We have already seen that the long-bond structural weights are unaffected by electron correlation; on the other hand, the polarity of the covalent bonds should also be weakly modified by CI effects, as shown by the good overall agreement between calculated and experimental values for dipole moments in the literature. As an important consequence, the fact that **6** and **7** have their weights reduced when electron correlation is introduced should only result in small decreases of charge transfers and dipole moment in nitrophenol and nitroaniline, since **6** and **7** are not major contributors to these observables.

Concerning the central question of this study, the importance of the so-called "through-resonance effect", we find that structure **6** is significantly more important than **7** in both nitrophenol and nitroaniline. Indeed, **6** is respectively seven and five times as important as **7** is in nitrophenol and nitroaniline, according to the VB analysis of the SCF wave functions, the monoionics being included. This tendency is confirmed at all levels of the theory, regardless of the inclusion of monoionics and the electron correlation effects.

It should be noted that this result, implying that **6** is more stable than **7**, is not counterintuitive since the stabilizing allylic-type resonance of the nitro group is lost in **7**. The benzene-induced polarization certainly modifies this resonance, which is described in VB terms by a balance between the diradical and octet zwitterionic structures (other zwitterions being of minor importance), since we have seen that the diradical:zwitterion ratio changes under the substituent influence. But the resonance is not disrupted as it is in **7**, which should make a significant difference.

We also note that both **6** and **7** are relatively minor components among **1–7**, with weights of 2.8 and 0.4% for *p*-nitrophenol, and 4.8 and 1.1% for *p*-nitroaniline, at the SCF level. More, these values should be considered as higher limits, since electron correlation can only diminish these weights.

IV. Discussion

We are now going to discuss the relevance of our results to the interpretation of experimental data. First, **7** is generally used to explain the dipole moment difference between nitrobenzene and its π-donor *para* substituted derivatives. Indeed, the dipole moment associated with **7** is considerable and can be roughly estimated to 32 D. However, **6** also has quite a large dipole moment of approximately 23 D, and could be used just the same way to account for experimental tendencies. Thus, dipole moment considerations cannot be used to distinguish in any way between **6** and **7**. Another contribution to the dipole moment is the polarization of the six-membered ring; this interpretation is suggested by the Mulliken π-electron population analysis displayed in Figure 2, which shows that the ring polarization is significantly more important than the charge transfer. Lastly, we have seen in the preceding section that long-bond structures and covalent bond polarities each contribute as much as classical resonant structures to the dipole moment.

Another result that has been invoked as a proof of the importance of **7** is the shortening of the bond linking the ring to the nitro group as one goes from nitrobenzene to *p*-nitroaniline. This again is not conclusive, since this bond is ionic in **6**, and it is well known that such a bond, though formally drawn as a single one, is almost as short as a double bond. As an example, such an ionic bond has the length 1.416 Å in the pyramidalized geometry of the zwitterionic state of twisted ethylene,[36] vs. 1.54 Å for a single C–C bond length.

The values of ^{17}O NMR chemical shifts were the key points of FRS's paper, and were claimed to discriminate between **6** and **7** in favor of the latter. However, their results do not imply the importance of **7**, but only that there is an increase of electron density around the oxygen atoms. Once again, this result is consistent with structure **6** as well. The point is that the π system of the nitro group is polarized by the presence of a negative charge on the adjacent carbon of the ring; thus, the zwitterionic:diradical ratio of the nitro group is increased, so that there appears a partial positive charge on the nitrogen and partial negative charges on the terminal oxygens. This is also consistent with the correlated decrease of electron density around the nitrogen nucleus of the nitro group, which has been shown by ^{15}N NMR spectra.[3] In fact, both **6** and **7** could be invoked for the interpretation of ^{15}N and ^{17}O NMR shifts. The folllowing question then emerges: is there any experimental way to discriminate between both structures, so that the importance of **6** could be definitively proved or rejected? The answer is yes, and the way is ^{13}C NMR spectroscopy. This is simply because the only clear and experimentally measurable difference between **6** and **7** appears to be the negative charge on the carbon ipso to the nitro group in **6**, which does not exist in **7**. It is thus clear that a participation of **6** to the wave function implies a variation of shift at this position, while **7** does not. A comprehensive study of the ^{13}C NMR spectra of 1,4-disubstituted benzenes has been published recently.[37] It clearly appears that the above-mentioned variation of shift does exist, so that **6** is indeed

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(35) Some major references follow: (a) R. D. Harcourt, *Aust. J. Chem.*, **22**, 279 (1969); (b) R. D. Harcourt and A. Harcourt, *J. Chem. Soc., Faraday Trans. 2*, **70**, 743 (1974); (c) R. D. Harcourt, *Theor. Chim. Acta*, **2**, 437 (1964); **4**, 202 (1966); (d) R. D. Harcourt, *ibid.*, **6**, 131 (1966); (e) R. D. Harcourt, *Int. J. Quantum Chem.*, **4**, 173 (1970); (f) R. D. Harcourt and J. F. Sillitoe, *Aust. J. Chem.*, **27**, 691 (1974); R. D. Harcourt, "Lecture Notes in Chemistry", Vol. 30, Springer, New York, 1982.

(36) B. R. Brooks and H. F. Schaefer, *J. Am. Chem. Soc.*, **101**, 307 (1979).

(37) J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sadek, and R. W. Taft, *J. Org. Chem.*, **45**, 2429 (1980).

necessary to describe the electronic structure of our molecules.

We are thus led to a new picture of 1,4-disubstituted benzenes with a π donor and a nitro group: while an interaction between both groups does exist (as proved by the non-additivity of ^{13}C shifts at ipso positions), it does not go through a charge transfer from one substituent to the other one, but rather through a charge transfer to the ring, inducing a polarization of the π system of the nitro group.

Thus, our calculations support Lipkowitz's proposal of the predominance of **6** over **7**. However, it should be emphasized that this is not contradictory with the results of FRS's experiments, whose validity is not in doubt. Rather, we interpret the calculated and experimentally observed accumulation of charge on the outer oxygens, under the influence of π-donor para substituents, in a way which departs from the traditionally accepted view, since we show that charge transfer to the ring is necessary and sufficient to account for all experimental data.

Lastly, it should be kept in mind that the discussion presented in this paper applies to molecules in the gas phase. Using a polar solvent like acetonitrile, as FRS did, should certainly increase the structural weights of **6** and **7**, and probably that of **7** more than that of **6** since in the former the negative charges are exposed to solvent effects more than in the latter. These intuitive predictions are supported by the experimental finding that the influence of solvent polarity on ^{13}C shifts is not negligible,[38] and the same should hold true for ^{15}N and ^{17}O as well. Also, in proton–donor solvents, structure **7** is favored, as shown by UV spectroscopy.[39] Thus, our conclusions invalidating the classical interpretation of the "through-resonance" effect should be tempered when polar solvents are employed.

Acknowledgment. Professor J. Jullien is gratefully acknowledged for a fruitful discussion.

Registry No. *p*-Nitroaniline, 100-01-6; *p*-nitrophenol, 100-02-7.

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Electron-Transfer-Sensitized C–C Bond Cleavage. Facile Homolytic Fission via Geminate Back Electron Transfer in Photogenerated Ion Pairs[1]

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Abstract: Several organic substrates (donors) known to undergo oxidative C–C bond cleavage upon steady-state irradiation under electron-transfer photosensitization have been examined by 337.1 nm laser flash photolysis for photoproduction of substrate radicals/radical cations and sensitizer triplet as a result of charger-transfer interaction with 1,4-dicyanonaphthalene (DCN) singlet (acceptor). The transient-absorption phenomena and quantitative estimates of electron-transfer-mediated yields show that for substrates such as 1-(diphenylmethyl)cyclohepta-2,4,6-triene and aryl-substituted pinacols and pinacol–ethers characterized by relatively unstable, short-lived, radical cations, a substantial fraction of arylmethyl radicals are generated fast via back electron transfer in the photogenerated ion pair. In other cases, we have observed longer lived radical cations (solvated) that either undergo intramolecular electron transfer leading to C–C bond fragmentation (e.g., with 1,1,2,2-tetraphenylethane) or diffusional back donation of electron from the DCN radical anion (e.g., with *p*-methoxy- and *p*-methyl-substituted bibenzyls). Within small groups of closely related quenchers, radical and radical ion yields are found to depend systematically on the structures, chemical nature, and oxidation potentials of the substrates.

In electron transfer (ET) sensitized photoreactions involving organic substrates in a polar medium, important roles are usually played by ET-derived radical ions (solvated). While fast chemical transformations in the form of isomerization and bond cleavage can occur in short-lived primary intermediates such as exciplexes[3] and ion pairs (solvent shared),[3] the solvated radical ions usually enjoy longer lifetimes and hence are susceptible to various bimolecular reactions as well as back donation of electron at the time scale of diffusion. In many instances, intramolecular ET occurs within the radical ion leading to cleavage of a relatively weak bond and consequent formation of a radical and an ion with lifetimes and chemical affinities different from those of the parent species. Studying the kinetic and spectral behaviors of transient radicals and radical ions and modes of their generation following photoexcitation is an integral part of understanding the mechanisms of photosensitized organic reactions[4] involving charge-transfer interactions.

Oxidative C–C bond cleavage effected by ET to excited-state cyanoaromatics (acceptors) is well-recognized.[4] In a recent paper,[5] we have presented a detailed account of 1,4-dicyanonaphthalene (DCN) sensitized steady-state photolyses of several systems containing C–C bonds flanked by aryl substituents. We have shown that the yields of final photoproducts (aldehydes/ketones)

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