of (diene)iron complexes and useful discussions. J.S.F. also thanks the National Science Foundation (Grant 80-17045) and the Department of Energy (Contract DE-ASO5-80ER-10662) for financial support.

Registry No. I, 81277-07-8; I phosphite, 81277-08-9; II, 81277-09-0; (acrylonitrile)Fe(CO)$_3^{-\cdot}$, 81277-10-3; (butadiene)Fe(CO)$_3^{-\cdot}$, 81277-11-4; (dimethylmaleic anhydride)Fe(CO)$_3^{-\cdot}$, 81277-12-5; (dimethyl maleate)Fe(CO)$_3^{-\cdot}$, 81277-13-6; (dimethyl fumarate)Fe(CO)$_3^{-\cdot}$, 81339-51-7; (cinnamonitrile)Fe(CO)$_3^{-\cdot}$, 81277-14-7; Na$_2$Fe(CO)$_4$, 14878-31-0; methylmaleic anhydride, 616-02-4; maleic anhydride, 108-31-6; dimethylmaleic anhydride, 766-39-2; acrylonitrile, 107-13-1.

A Reassessment of Nitrobenzene Valence Bond Structures

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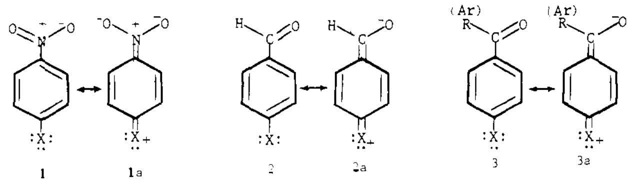
Reactivity patterns of substituted benzenes have been extensively documented by experimentalists and interpreted by theoreticians.[1] For many 1,4-disubstituted benzenes, π-electron-withdrawing effects are attenuated by direct coupling with electron-rich π donors, and deviations from the Hammett equation are found.[2] This direct resonance, termed "through conjugation", arises from the charge-separated resonance structures below. A priori one expects that as the π-donating ability of X increases, the molecular wave function can be improved by more heavily weighting the polarized valence bond structures and, accordingly, that the charge density on the oxygen of π-electron acceptors like NO$_2$, CHO, and COR(Ar) parallels the relative contribution of these polarized structures.



1 1a 2 2a 3 3a

For benzophenones, benzaldehydes, and acetophenones this expectation is borne out. The ^{17}O nuclear screening constants are highly sensitive to electronic perturbations of substituent groups, and linear correlations between ^{17}O NMR chemical shifts vs. Hammett substituent constants exist.[3] In this communication we reinterpret the electron-withdrawing behavior of the nitro group and conclude that the dipolar resonance structure **1a** is, contrary to popular belief, only a minor contributor to the total molecular wave function of para-substituted nitrobenzenes.

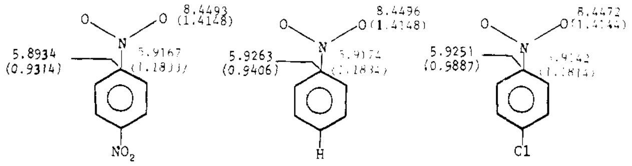
Cheng and Brown found that nitrogen-14 quadrupole coupling constants (a precise measure of electron density)[4] correlated linearly with the Hammett substituent parameter, σ.[5] The nuclear quadrupole coupling constants of natural abundance ^{17}O were also reported,[6] and it is apparent that all meta- and para-substituted nitrobenzenes show negligible differences in nuclear quadrupole coupling constants for oxygen. In other words, the electron density of oxygen is invariant to substitution in the meta and para positions!

Table I. ^{17}O NMR Chemical Shifts for Substituted Nitrobenzenes

compound	chemical shift (ppm from H$_2$O)[a]
nitrobenzene	568
p-fluoronitrobenzene	-, 573[b]
p-chloronitrobenzene	574
m-chloronitrobenzene	574, 567[b]
p-nitroanisole	570, 571[b]
m-dinitrobenzene	574, 570[b]
m-nitrobenzaldehyde	568,
m-nitrotoluene	572, 574[b]
p-nitrotoluene	573, 568[b]
sym-trinitrobenzene	-, 571[b]

[a] Chemical shifts were measured with a modified Varian XL-100 spectrometer either at room temperature or at 40 °C. All spectra were recorded neat or in benzene or chloroform. Although the NMR lines are invariably broad due to the quadrupole relaxation (approximately 35 ppm at half-height), the signal to noise ratio was above 5 for all spectra. Standard deviation of all absorption was ±5 ppm. [b] Christ, H. A.; Diehl, P. *Helv. Phys. Acta* 1963, *36*, 170.

Chart I



To further probe the electronic environment of the nitro oxygens, we present ^{17}O NMR[7] data in Table I. Due to the large quadrupole coupling constant and low natural abundance (0.37%) of oxygen-17, the chemical shifts have a rather large standard deviation. However, the chemical shifts are constant within experimental uncertainty.

The nuclear magnetic shielding can be approximated as a sum of paramagnetic and diamagnetic terms with the former principally responsible for the ^{17}O chemical shifts, i.e., $\sigma \simeq \sigma_p \simeq -{}^2/_3(eh/mc)^2\Delta E^{-1}\langle r^{-3}\rangle P_u$.[3c] One group claims that the $\langle r^{-3}\rangle_{2p}$ term be invoked to explain observed ^{17}O shifts[3b] while another concludes that the ΔE^{-1} term is the dominant factor.[3c] We point out that as the substituent orbitals mix with the aromatic ring orbitals, there will be a HOMO-LUMO gap change[1] (i.e., $\Delta E_{n\rightarrow\pi^*}$ changes) with a concomitant change in $\langle r^{-3}\rangle_{2p}$. These terms are inseparable. Attempts at separating them is phenominologically unsound and results in a gross oversimplification that may be misleading.

In any event, one may anticipate that whatever mechanism is responsible for the large changes in ^{17}O chemical shifts for substituted benzophenones,[3a,b] benzaldehydes[3c] and acetophenones[3c] should be operative in the nitrobenzene derivatives listed in Table I. Such an assumption, however, is not correct. The strong electron-withdrawing ability of the nitro group may be considered as the net result of a very low-lying, symmetric, unoccupied π orbital with a very large coefficient at nitrogen and very little contributions from the two oxygens. As would thus be expected from this perturbation molecular orbital (PMO) approach, most of the change in electron density in the NO$_2$ function would be centered at nitrogen with little change at the oxygens. Our computational results (see below) indicate that the (Mulliken) electron density on the nitrogen does not change. Clearly then, the benzene and nitro π systems are only weakly coupled, and resonance structures like **1a** are minor contributors to the molecular wave function.

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(1) For leading references see: Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1981**, *13*, 1.

(2) See, for example: Johnson, C. D. "The Hammett Equation"; Cambridge University Press: London, 1973.

(3) (a) Buchanan, G. W.; Stothers, J. B.; Wu, S. T. *Can. J. Chem.* **1967**, *45*, 2955. (b) Sardella, D. J.; Stothers, J. B. *Ibid.* **1969**, *47*, 3080. (c) St. Amour, T. E.; Burgar, M. I.; Valentine, B.; Fiat, D. *J. Am. Chem. Soc.* **1981**, *103*, 1128.

(4) The nuclear quadrupole double resonance (NQDR) method is a very sensitive probe of electronic environment about nuclei. For leading references see: (a) Lucken, C. E. A. "Nuclear Quadrupole Coupling Constants"; Academic Press: New York, 1968. (b) Brown, T. L.; Cheng, C. P. *Symp. Faraday Soc.* **1979**, *13*, 75. (c) Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 2327. (d) Hsieh, Y.-N.; Rubenacker, G. V.; Cheng, C. P.; Brown, T. L. *Ibid.* **1977**, *99*, 1384. (e) Edmonds, D. T. *Phys. Rep.* **1977**, *29*, 233.

(5) Cheng, C. P.; Brown, J. L. *J. Magn. Reson.* **1977**, *28*, 391.

(6) Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6418.

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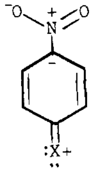
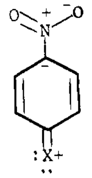
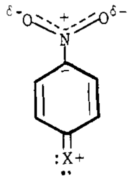
The nitro group is unique; based upon NQDR and NMR results it appears that the NO$_2$ group withdraws a constant amount of electron density from the ring regardless of what substituent is attached to the meta or para position. To further emphasize the unique electron-withdrawing properties of the nitro group, we focus our attention on the N–O vs. C–O bond order. Since force constants are related to bond order, we anticipate a linear correlation of IR stretching frequencies with Hammett σ values.[8] For substituted benzaldehydes and acetophenones this is observed.[3c] In contrast, the nitro asymmetric stretch correlates poorly with the Hammett σ values, and the symmetric stretching frequency is completely invariant to substitution.[9]

To better understand the nitro group's electron-withdrawing ability, we have carried out several ab initio molecular orbital calculations with an STO-3G basis set.[10] Total electron densities (Mulliken population analysis) and the corresponding π component (in parentheses) are summarized in Chart I. It is apparent that the charge density on oxygen and nitrogen is independent of substituent. Even the π-electron density, which by invoking canonical structure **1a** should show a large change, is likewise invariant to substituent.

All of the available evidence points to the conclusion that the electronic environment of oxygen in nitrobenzene derivatives does not depend on meta and para substituents. We conclude that the nitro group withdraws a constant amount of electron density from the benzene ring whether the ring is electron rich or electron deficient. Consequently resonance structure **1a**, considered by many as a major contributor to the nitrobenzene resonance hybrid,[11] is not a valid structure for the description of para-substituent lone-pair delocalization. Instead, we invoke valence bond structure **5** to describe the chemical and physical properties of nitrobenzenes.


4


4a


5

The salient feature of **5** is that the nitro group resonance is not disrupted. The NO$_2$ group has two stable and energetically degenerate valence bond structures, **4** and **4a**. The loss of the NO$_2$ resonance more than offsets the system's drive to use **1a** in the molecular wave function.

Valence bond structure **5** is consistent with the physical characteristics of substituted nitrobenzenes. It allows for para-substituent lone-pair delocalization into the ring and accounts for the typically large dipole moments. Further, it explains the peculiarities observed in the IR stretching frequencies and ^{17}O NMR chemical shifts. Finally, it clarifies the NQDR results (the most sensitive and direct probe of electron density).

Because the nitrogen is directly attached to the carbanionic center, the electron density around the nitrogen atom will vary with the substituent's ability to localize charge at the point of NO$_2$ attachment. This is simply an inductive effect, not a mesomeric affect. Hence, a plot of *ehqQ* for nitrogen should, and does, correlate with σ.[6] The oxygens, since they are shielded from the carbanionic center by the nitrogen, are oblivious to the degree of negative charge buildup, and consequently *ehqQ* for oxygen is independent of σ.[6]

Invoking resonance structure **1a** localizes two negative charges near one another and disrupts the NO$_2$ group resonance. Our conclusion, contrary to popular belief, is that valence bond structure **1a** is not a major contributor to the molecular wave function of neutral nitrobenzenes and that **5** is.[12]

Acknowledgment. We thank Dr. C. P. Cheng for bringing the NQDR results to our attention. We also thank the Indiana University Bloomington staff for making their NMR spectrometer available to us and acknowledge the Indiana University Computer Network for generous use of their facilities.

Registry No. Nitrobenzene, 98-95-3; *p*-fluoronitrobenzene, 350-46-9; *p*-chloronitrobenzene, 100-00-5; *m*-chloronitrobenzene, 121-73-3; *p*-nitroanisole, 100-17-4; *m*-dinitrobenzene, 99-65-0; *m*-nitrobenzaldehyde, 99-61-6; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0; *sym*-trinitrobenzene, 99-35-4.

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(8) For leading references of LFER's for aromatic systems with infrared spectral data see: (a) Rao, C. N. R. "Chemical Applications of Infra Red Spectroscopy"; Academic Press: New York, 1963. (b) Katritzky, A. R.; Topsom, R. D. "Advances in Linear Free Energy Relations"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972. (c) Brownlee, R. T. C.; Topsom, R. D. *Spectrochim. Acta* **1975**, *31A*, 1677. (d) Brownlee, R. T. C.; DiStefano, J.; Topsom, R. D. *Ibid.* **1975**, *31A*, 1685.

(9) There appears to be a lack of agreement on whether or not ν_{sym} correlates with the Hammett substituent parameter. Also, the nature of the interactions giving rise to the nitro IR shifts has yet to be firmly established. Pertinent references: (a) Brown, J. F., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 6341. (b) Kross, R. D.; Fassel, V. A. *Ibid.* **1956**, *78*, 4225. (c) Brownlee, R. T. C.; Cameron, D. G.; Topsom, R. D.; Katritzky, A. R.; Pozharsky, A. F. *J. Chem. Soc., Perkin 2* **1974**, 247. (d) Exner, O.; Kovac, S.; Solcaniova, E. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2156.

(10) The molecular orbital calculations were performed with PHANTOM by D. Goutier, R. Macaulay, and A. J. Duke, *QCPE* **1974**, No 241, Indiana University, Bloomington, IN. Standard bond lengths and bond angles were used. The Dacre–Elder formalism was adapted with C$_1$–C$_4$ defining the plane of symmetry. Oscillations in the SCF part were damped with a weighting factor of 0.50 for the new density matrix.

(11) See for example: Wiberg, K. B. "Physical Organic Chemistry"; Wiley: New York, 1964; p 288. Hine, J. "Physical Organic Chemistry", 2nd ed.; McGraw Hill: New York, 1962; p 88. Hirsch, J. A. "Concepts in Theoretical Organic Chemistry"; Allyn and Bacon: Boston, 1974; p 101. Lowry, T. H.; Richardson, T. H. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 64.

(12) The only molecule for which resonance structure **1a** has been seriously proposed is *p*-nitrophenolate. We would like to include in Table I *p*-nitrophenol and the corresponding anion. However, the ionized species, unlike the neutral phenol, is insoluble in most solvent systems we tried. Furthermore, even if the natural abundance ^{17}O chemical shift could be obtained, we would be uncertain of the contributions from contact ion pairing. Our conclusions unfortunately are limited to neutral species only.

Heats of Formation of the Ionic and Neutral Enols of Acetaldehyde and Acetone

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Theoretical[1,2] and experimental[3,4] results are in agreement that the enol radical cations of acetaldehyde and acetone are much more stable thermodynamically than their corresponding keto forms. This is in marked contrast to the neutral tautomeric pairs, in which the keto forms are generally more stable. Recently reported values for heats of formation, ΔH_f, and ionization energies, IE, for the ions and their neutral counterparts are given in Table I. Although the ΔH_f (neutral) and IE results for the enol of acetaldehyde (vinyl alcohol) are in reasonable agreement, the estimated IE values[7-9] for the enol of acetone show a wide

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(1) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443.

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(9) Bentley, T. W.; Johnstone, R. A. W. *Adv. Phys. Org. Chem.* **1970**, *8*, 242.

(10) Pollack, S. K.; Hehre, W. J.; *J. Am. Chem. Soc.* **1977**, *99*, 4845. Hehre (private communication) has remeasured ΔH_f[CH$_2$=C(OH)CH$_3$] and now reports it to be 44 ± 2 kcal mol^{-1}.

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