J. Am. Chem. Soc. **1982**, *104*, 2645–2647 2645

Spectrometry Laboratory (NIH PHS HHS GM-27029). T.K.J. thanks the University of Illinois for a Fellowship.

Registry No. 3a, 81255-86-9; **3b**, 81255-87-0; **3c**, 81255-88-1; **3d**, 59376-60-2; **3e**, 81255-89-2; **3f**, 81255-90-5; **3g**, 59376-62-4; **4a**, 23668-30-6; **4a** DNP, 1160-37-8; **4b**, 81255-91-6; *cis*-**4c**, 81255-92-7; *trans*-**4c**, 81255-93-8; **4d**, 23033-96-7; **4d** DNP, 23034-00-6; **4e**, isomer 1, 81255-94-9; **4e**, isomer 2, 81255-95-0; *cis*-**4f**, 33765-38-7; *trans*-**4f**, 32556-65-3; **4g**, 81255-96-1; **5a**, 6140-65-4; **5b**, 1192-88-7; **5c**, 6140-67-6; **5d**, 123-73-9; **5e**, 78-85-3; **5f**, 497-03-0; **5g**, 14371-10-9; **6a**, 81255-97-2; **6b**, 81255-98-3; **6c**, 81255-99-4; **6d**, 81256-00-0; **6e**, 81256-01-1; **6f**, 81256-02-2; **6g**, 81256-03-3; **7b** oxime, 81256-04-4; *cis*-**7c** DNP, 81256-05-5; *trans*-**7c** DNP, 81256-06-6; (*E*)-(2-bromoethenyl)trimethylsilane, 13682-94-5.

An ESR Study of Olefin Iron Carbonyl Radical Anions

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Recently we reported an electron spin resonance study of a series of iron carbonyl radical anions $Fe_n(CO)_m^{-}\cdot$ (n = 2–4), which are formed in the reduction of $Fe(CO)_5$ by alkali metals as well as in the chemical one-electron oxidation of iron carbonylate dianions in THF.[1] Despite considerable effort, we failed to observe the ESR spectrum of the simplest member of this family, the 17-electron $Fe(CO)_4^{-}\cdot$ radical anion,[2] although many observations strongly implicated its involvement as a short-lived reaction intermediate.[3] We now find that the closely related (π-olefin)-$Fe(CO)_3^{-}\cdot$ radical anions are sufficiently stable, for certain olefins, to be studied by ESR. These radical anions exist in equilibrium with their diamagnetic dimers and are substitutionally labile as recently observed for other 17-electron species.[4]

Depending on the reaction temperature, time, and stoichiometry, three paramagnetic species can be obtained by reaction of saturated THF solutions of disodium tetracarbonylferrate,[5] $Na_2Fe(CO)_4$, with dilute THF solutions of methylmaleic anhydride (~0.02 M). With excess $Fe(CO)_4^{2-}$ at −80 °C, the spectrum of the thermally labile radical anion of this activated olefin is observed consisting of a quartet of doublets (ΔH ~ 0.2 G) for the three methyl protons (7,06 G) and the single vinylic proton (5.77 G). The radical anion $Fe_2(CO)_8^{-}\cdot$ is also formed (g = 2.0385).[1] If the reaction is carried out at room temperature with excess olefin, $Fe_2(CO)_8^{-}\cdot$ and a third species are produced as evidenced by the observation of a doublet partially overlapped by the $Fe_2(CO)_8^{-}\cdot$ line. Longer reaction times at room temperature lead to spectra in which this doublet (a^H = 3.6 G, ΔH = 2.3 G, g = 2.0407, −80 °C)[6] is unencumbered by other resonances. In view of the collective evidence presented below, this doublet spectrum is assigned to (methylmaleic anhydride)$Fe(CO)_3^{-}\cdot$ (I) in which the unpaired electron resides mostly on iron and interacts weakly with only the vinylic proton of the olefin.[7] This is in sharp contrast to the uncomplexed organic radical anion in which the hyperfine interaction with the methyl protons (7.06 G) is the major one. The observation of the free organic radical anion implies the initial formation of $Fe(CO)_4^{-}\cdot$, which either undergoes ligand substitution to give I[8] (reaction 1) or dimerizes to $Fe_2(CO)_8^{2-}$.

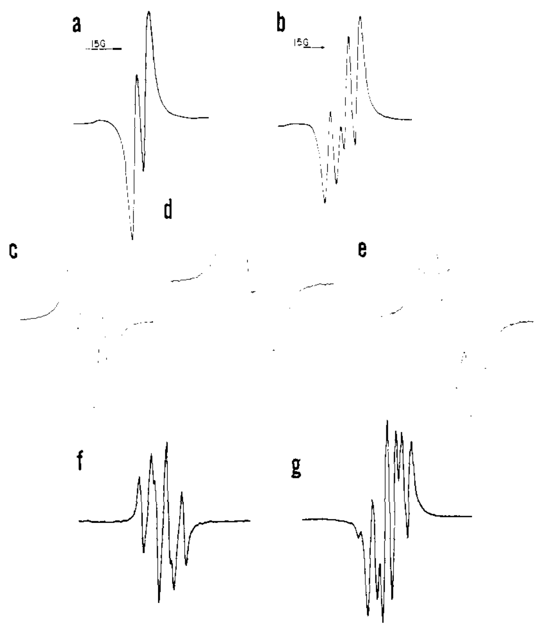
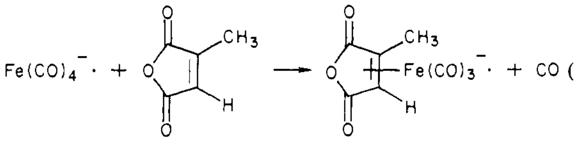


Figure 1. ESR spectra of (a) (methylmaleic anhydride)$Fe(CO)_3^{-}\cdot$ in THF at −80 °C; (b) (methylmaleic anhydride)$^{57}Fe(CO)_3^{-}\cdot$ in THF at −80 °C; (c) (maleic anhydride)$Fe(CO)_3^{-}\cdot$ in THF/HMPA (9:1 v/v) at −80 °C; (d) (maleic-d_2 anhydride)$Fe(^{13}CO)_3^{-}\cdot$ at −80 °C (same solvent); (e) (methylmaleic anhydride)$Fe(^{13}CO)_3^{-}\cdot$ at −80 °C (same solvent); (f) (acrylonitrile)$Fe(CO)_3^{-}\cdot$ at −90 °C (same solvent); (g) (butadiene)$Fe(CO)_3^{-}\cdot$ at −100 °C in THF/HMPA (2:1 v/v).



(1)

Similar results were obtained with maleic and dimethylmaleic anhydrides. The maleic anhydride iron tricarbonyl radical anion (II) gives a triplet appropriate for two equivalent vinylic protons (a^H = 3.5 G, g = 2.0412, ΔH = 1.8 G, −80 °C), while the dimethylmaleic anhydride analogue produces only a single line (g = 2.0389, ΔH = 3.0G, −70 °C). The lack of hyperfine structure in the latter case is in sharp contrast to the septet for the six methyl

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[1] Krusic, P. J.; San Filippo, J., Jr.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129–2131.

[2] $Fe(CO)_4^{-}\cdot$ has been studied by matrix-isolation IR [Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1–58. Burdett, J. K. *J. Chem. Soc., Chem. Commun.* **1973**, 763–764] and in the gas phase by mass spectrometry and ion cyclotron resonance [Dunbar, C. R.; Ennever, J. F.; Fackler, J. P., Jr. *Inorg. Chem.* **1973**, *12*, 2734–2736. Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 3671–3673. Dunbar, R. C.; Hutchinson, B. B. *Ibid.* **1974**, *96*, 3816–3820. Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 47–55. Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569–5573].

[3] For example, $Fe(CO)_4^{-}\cdot$ must be formed in the reaction of $Fe(CO)_4^{2-}$ with alkyl iodides (but not bromides or chlorides) since we detected the ESR spectra of the corresponding alkyl radicals (n-butyl, isopropyl, and *tert*-butyl) by mixing in the ESR cavity 0.1 M $Na_2Fe(CO)_4$ in 9:1 v/v THF/HMPA with 0.2 M alkyl iodide in THF at flow rates of about 9 mL/min. Cf.: Krusic, P. J.; Fagan, P. J.; San Filippo, J. Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250–252.

[4] See, for example: Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095–4103.

[5] Commerical disodium tetracarbonylferrate dioxanate, $Na_2Fe(CO)_4\cdot 1.5C_4H_8O_2$ was used. All operations and reactions were carried out in a nitrogen glovebox. Solvents were rigorously dry and deoxygenated.

[6] The line widths of all iron carbonyl radical anions of this work are strongly temperature dependent and are narrowest at about −80 °C.

[7] Paramagnetic olefin–transition-metal complexes are rare. See: Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179–190 and references cited therein.

[8] The displacement of CO from $Fe(CO)_4^{-}\cdot$ by maleic anhydride and its methyl-substituted derivatives has been recently observed in the gas phase by negative ion mass spectrometry. Weddle, G. H.; Ridge, D. P., private communication.

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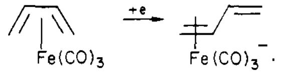
protons (6.28 G) observed for the uncomplexed dimethylmaleic anhydride radical anion, which was obtained at −80 °C with excess $Fe(CO)_4^{2-}$. The concentration of II is strongly and reversibly temperature dependent, increasing as the temperature increases. Concomitantly, the solutions display an equally reversible thermochromism, turning red below −80 °C. These phenomena are associated with an equilibrium between the iron–olefin radical anion and its diamagnetic dimer.[9] This behavior is exhibited to a lesser degree by the monomethyl-substituted analogue and not at all by the dimethyl analogue. We conclude that the latter do not dimerize as readily as II.

Other activated olefins, for example, dimethylmaleate and dimethylfumarate [$a^H = 5.0$ G (2 H), $g = 2.0394$ at −80 °C for both] and cinnamonitrile [$a^H = 4.6$ G (2 H), $g = 2.0387$] behave similarly. Acrylonitrile reacts at −80 °C with $Fe(CO)_4^{2-}$ to give the spectrum of Figure 1f ($g = 2.0389$) consisting of a triplet (5.6 G) of doublets (4.4 G) for two equivalent or nearly equivalent protons and a unique proton; no resolvable interaction with the nitrogen nucleus was observed. In all cases, only the protons directly attached to the double bond can be accounted for by the observed hyperfine structures.

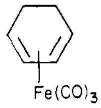
The (olefin)tricarbonyliron radical anions described above can also be generated from the corresponding (olefin)$Fe(CO)_4$ complexes by reduction with Na/K alloy or with equimolar solutions of sodium naphthalide in THF.[10] If a small excess of trimethylphosphite, $P(OCH_3)_3$, is added prior to reduction with Na/K alloy, the phosphite-monosubstituted analogues are obtained. These species display an additional doublet due to the presence of one phosphorus nucleus in the coordination sphere of iron. We attribute this result to the inherent substitutional lability of these 17-electron species. For the methylmaleic anhydride analogue [$a^P = 12.5$ G, $a^H = 3.2$ G (doublet), $g = 2.0418$ at −80 °C] the phosphorus splitting is remarkably temperature dependent ($a^P = 18.3$ G at −6 °C), This is undoubtedly a manifestation of stereochemical fluxionality: the observed phosphorus splitting is the average of two (or more) widely different values for phosphorus atoms in different stereochemical sites, weighted by the temperature-dependent populations of each site.

An alternative method of preparation, particularly suitable for isotopic-labeling studies, employs minute amounts of $Fe(CO)_5$ in THF (<1 μL/mL). Following exhaustive reduction at room temperature with a small excess of Na/K alloy, the resulting solution is filtered and treated with an excess of activated olefin. The spectrum of I obtained in this manner is shown in Figure 1a. A parallel experiment with $^{57}Fe(CO)_5$[1] gave the spectrum of Figure 1b, which clearly shows an additional doubling of 5.5 G obviously caused by a *single* ^{57}Fe nucleus of spin $^1/_2$. Alternatively, these species can be prepared by addition of sodium naphthalide in THF to a dilute equimolar THF solution of activated olefin and $Fe(CO)_5$ (1 μL/mL). Spectra of improved resolution are obtained by adding small amounts of hexamethylphosphoramide to the solvent (~10% by volume). The spectrum of (maleic anhydride)$Fe(CO)_3^{-}\cdot$ obtained by this procedure is shown in Figure 1c. A parallel experiment with maleic-d_2 anhydride and 92% ^{13}C-enriched $Fe(CO)_5$[11] yielded the partially resolved quartet of Figure 1d (3.3 G). Since deuteration causes the proton hyperfine structure to collapse into a single line at this resolution, the quartet unambiguously establishes the presence of *three equivalent* ^{13}CO ligands. This equivalence persists to a least −115 °C judging by the absence of line width effects other than a progressive broadening of all lines on lowering the temperature. Similar treatment of methylmaleic anhydride and 92% ^{13}C-enriched $Fe(CO)_5$ produced the quintet of Figure 1e (3.6 G). This demonstrates again the presence of three equivalent ^{13}C nuclei which in this case have the same coupling as the single vinylic proton of I. We believe that the equivalence of three CO ligands is dynamic in nature and that it need not reflect the symmetry of the static molecular structure.[12]

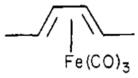
The formation of these olefin–iron radical anions is not limited to strongly activated olefins. We find that a series of closely related species is obtained by treatment at −80 °C of simple (diene)tricarbonyliron complexes in THF/HMPA (~2:1 (v/v) with finely dispersed Na/K alloy suspensions in THF or with equimolar solutions of sodium naphthalide in THF. (Butadiene)tricarbonyliron yields the spectrum of Figure 1 g, which is a partially resolved triplet of doublets [5.2 G (2 H), 3.3 G (1 H), $g = 2.0395$, −100 °C]. We conclude that one-electron reduction causes the detachment of one of the π-bonded double bonds rather than the loss of a CO ligand to establish a 17-electron configuration around the iron.[13,14] Only the protons attached to one of the double bonds give rise to resolvable hyperfine structure (eq 2). This interpretation is consistent with the results for the iron diene complexes III–VI.[15] The first three gave very similar triplets for the two protons attached to one of the double bonds (III, 3.6 G, $g = 2.0393$; IV, 3.4 G, $g = 2.0401$; V, 5.4 G, $g = 2.0389$, −100 °C) while VI gave a triplet of doublets identical with that of the butadiene analogue. Evidently, the more substituted double bond detaches itself from the iron center. These species are all substitutionally labile since in each case addition of acrylonitrile replaces the spectrum of the diene paramagnetic complex with that of the acrylonitrile analogue.



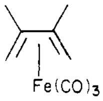
(2)



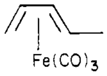
III



IV



V



VI

Acknowledgment. We are grateful to B. F. Gordon and D. J. Jones for able technical assistance, To Professor B. Hutchinson for a sample of $^{57}Fe(CO)_5$, and to Dr. T. H. Whitesides for samples

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[9] Similar effects were observed for the (allyl)$Fe(CO)_3\cdot$ radical, which exists in equilibrium with its diamagnetic dimer: Muetterties, E. L.; Sosinsky, B. A.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299–5370.

[10] Similar reductions with potassium mirrors of several (olefin)$Fe(CO)_4$ complexes, including the maleic anhydride analogue, were reported before: Dessy, R. E.; Charkoudian, J. C.; Abeles, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 3947–3956. The observed ESR spectra were erroneously assigned to (olefin)$Fe(CO)_4^{-}\cdot$ radical anions.

[11] Obtained from Pressure Chemical Co.

[12] The powder spectra of these species in frozen samples are appropriate for almost axially symmetric **g** tensors. For example, the powder spectrum of (dimethylfumarate)$Fe(CO)_3^{-}\cdot$ in a 2-methyltetrahydrofuran glass at −170 °C reveals three different principal values of the **g** tensor: $g_1 = 2.0599$, $g_2 = 2.0511$, and $g_3 = 2.0063$. The feature corresponding to g_3 also shows a 1:2:1 triplet splitting of about 3 G. The g_1 and g_2 features are broader and could not be further resolved.

[13] An analogous process was observed in the electrochemical reduction of benzylidene acetone tricarbonyliron, a heterodiene analogue, in which a conjugated carbonyl group replaces one of the two ene groups. This compound undergoes *two reversible* one-electron reduction steps. The radical anion formed in the first step is entirely analogous to the species reported here. The ESR spectrum for two protons ($a^H = 3.8$ G; $g = 2.0384$) indicates that one-electron reduction was accompanied by the detachment of the ketone group from the coordination sphere of iron: El Murr, N.; Riveccie, M.; Dixneuf, P. *Chem. Commun.* **1978**, 552–553.

[14] A closely related radical anion was obtained by γ irradiation of dicarbonyl(cyclohexadiene)(triphenylphosphine)iron in 2-methyltetrahydrofuran glasses at 77 K and was characterized by ESR. Its powder spectrum is in good agreement with those of the species discussed here.[12] Interestingly, the g_2 components of the powder spectrum displayed a poorly resolved triplet structure of about 4 G, appropriate for a coupling to two protons. In the light of our observations, it is probable that the two protons are those associated with one of the double bonds of the cyclohexadiene ligand. It appears, therefore, that even in the solid state the attachment of an electron has caused the dechelation of the second double bond in order to achieve a 17-electron configuration: Anderson, O. P.; Symons, M. C. R. *Inorg. Chem.* **1973**, *12*, 1932–1934.

[15] Easy electron attachment by thermalized electrons in the gas phase to simple (diene)tricarbonyliron compounds to give the molecular radical anions has been observed by negative ion mass spectrometry: Blake, M. R.; Garnett, J. L.; Gregor, I. K.; Wild, S. G. *Chem. Commun.* **1979**, 496–497.

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; $Na_2Fe(CO)_4$, 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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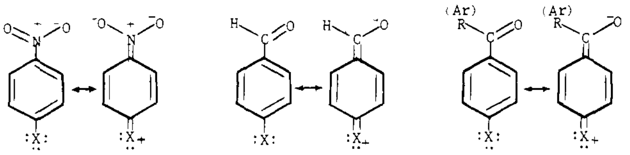
Reactivity patterns of substituted benzenes have been extensively documented by experimentalists and interpreted by theoreticians.[1] For many 1,4-disubstituted benzenes, π-electron-withdrawing effects are attenuated by direct coupling with electron-rich π donors, and deviations from the Hammett equation 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.

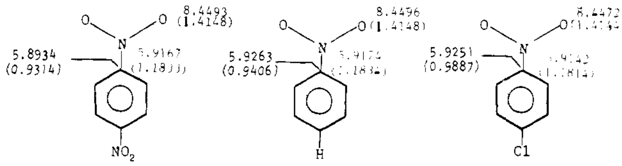
Cheng and Brown found that nitrogen-14 quadrupole coupling constants (a precise measure of electron density)[4] correlated linearly with the Hammett substituent parameter, σ.[5] The nuclear quadrupole coupling constants of natural abundance ^{17}O were also reported,[6] and it is apparent that all meta- 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_2O)[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.

(7) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246.

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