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A LOOK AT MESOMERISM IN NITROBENZENE[*]

by

James P. Ritchie
Los Alamos National Laboratory
Mail Stop B214
Los Alamos, New Mexico 87545

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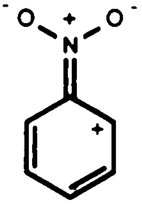
In 1959, when the X-ray structure of nitrobenzene (shown in Table I) was reported, Trotter noted that the variations of C-C bond lengths could not be explained by mesomeric structures I-III, below.[1]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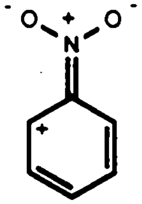
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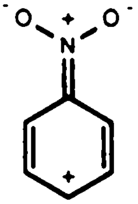
III

Structures I-III would lead to ipso (i) – ortho (o) and meta (m) – para (p) bond lengths longer than ortho – meta rather than $R(C_i - C_o) < R(C_o - C_m) > R(C_m - C_p)$, as found. The microwave structure is also shown in Table I. It confirms the pattern of ring bond length variations, although the variations are reduced in magnitude and $R(C_m - C_p)$ is only marginally less than $R(C_o - C_m)$. The ring angles from both studies are in good agreement. Thus, it has been recognized for almost thirty years that I-III cannot play a major role in determining the structure and related properties of nitrobenzene.

About that long ago, Dewar and Schmeising suggested that conjugation in polyenes was much less important than commonly believed.[2] Trotter was influenced by these ideas and pointed out the importance of changes in hybridization of the ipso carbon σ orbitals upon substitution by a group more electronegative than carbon, X.[3] Electron withdrawal from the orbital oriented toward X results in increased p character in that orbital accompanied by decreased p character (or increased s character) in the remaining ones. This leads to a shortening of the $C_i - C_o$ bond along with an opening of the $C_o - C_i - C_o$ (ipso) angle relative to benzene, as observed in nitrobenzene.[4]

In the time since these early works, mesomeric resonance structures for nitro- and other substituted benzenes have oftentimes been invoked in the literature. Molecular orbital calculations were shown to give charge distributions consistent with contributions from I-III.[5] This view readily rationalizes the observed planar structure of nitrobenzene.[6] Futher evidence for the involvement of mesomeric structures similar to I-III for substituted benzenes was obtained from correlations of atomic π orbital populations with ^{13}C chemical shifts.[7] More recently, ^{17}O shifts were initially used to argue against involvement of I-III.[8] Additional measurements of ^{17}O shifts, however, led to the opposite conclusion.[9] The latest theoretical studies have discerned only a small degree of conjugation between the nitro group and the aromatic ring.[10,11] Also, the extensive work of Taft and Topsom indicating only slight contributions

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[*] Dedicated to M. J. S. Dewar on the occasion of his seventieth birthday in recognition of his contributions to Organic Chemistry.

TABLE I

Calculated geometries and energies for planar and perpendicular nitrobenzene. Bond lengths in Angstroms, angles in degrees. Energies in kcal/mol for AM1 and delta quantities, au otherwise. Dipole moments in Debye.

	AM1			$3-21G//3-21G$			$6-31G*//6-31G*$			X – ray[b]	Microwave[c]
Quantity	Planar	Perp.	(Change)	Planar	Perp.	(Change)	Planar	Perp.	(Change)	Planar	Planar
R(C-N)	1.487	1.497	(+0.010)	1.449	1.458	(+0.009)	1.459	1.464	(+0.005)	1.486	1.493
R(N-O)	1.202	1.200	(−0.002)	1.244	1.240	(−0.004)	1.194	1.192	(−0.002)	1.208	1.227
R($C_i - C_o$)	1.404	1.401	(−0.003)	1.378	1.375	(−0.003)	1.383	1.378	(−0.005)	1.367	1.374
R($C_o - C_m$)	1.393	1.395	(+0.002)	1.381	1.383	(+0.002)	1.387	1.386	(+0.002)	1.426	1.403
R($C_m - C_p$)	1.396	1.395	(−0.001)	1.385	1.384	(−0.001)	1.387	1.386	(−0.001)	1.363	1.396
<CNO	118.9	118.7		117.6	117.0		117.7	117.1		118.0	117.8
$< C_oC_iC_o$	120.6	121.0		121.1	122.1		122.3	122.9		125.0	125.1
$< C_iC_oC_m$	119.2	119.1		118.9	118.8		118.5	118.2		116.0	117.1
$< C_oC_mC_p$	120.4	120.4		120.0	120.1		120.1	120.2		121.0	120.3
$< C_mC_pC_m$	120.1	120.1		120.4	120.2		120.5	120.3		121.0	120.2
Energy	25.3	28.8	(3.5)	−431.71216	−431.69354	(11.7)	−434.17523 (−434.27681)[a]	−434.16317 (−434.26541)[a]	(7.6 kcal) (7.2 kcal)		
Dipole	5.2	4.9		5.3	5.0		5.1 (5.1)[a]	4.7 (4.7)[a]		4.22 D[d]	

[a] Calculated with 6-311G** basis set.

[b] Reference 1.

[c] G. Ole Sorensen, personal communication of a full substitution structure cited in Reference 6.

[d] CRC Handbook of Chemistry and Physics, 63rd ed., R. C. Weast, Ed.; pg. E-61.

from I-III has recently been reviewed.[12] Other studies will be discussed in more detail in a later section of this paper.

Despite these conflicting results, mesomeric resonance structures, such as I-III, above, are sometimes used in an unqualified or ambiguous manner to explain various properties of nitrobenzenes in several well-known texts.[13] Thus, the concept of resonance participation by nitro groups in substituted benzenes has gained widespread acceptance, oftentimes without critical examination.

To gain increased insight into the role of resonance in determining the behavior and properties of nitrobenzenes, we undertook molecular orbital calculations at higher levels than before. Calculated results are compared with observed quantities where possible. Furthermore, additional related experimental evidence concerning the structure, rotational barrier, and charge distributions in nitrobenzene is considered. These results show that the contribution of mesomeric structures to the equilibrium properties of nitrobenzene and derivatives is extremely small.

Methods

Molecular orbital calculations were performed using standard methods and computer programs. AM1 calculations[14] were performed using the MOPAC program.[15] Ab initio calculations were performed using the GAUSSIAN 82 program package[16] with the internally stored 3-21G,[17] 6-31G*,[18] and 6-311G**[19] basis sets. Geometries were completely optimized within the stated symmetry point group (C_{2v}). Initial geometry optimizations for the ab initio calculations were greatly facilitated by using a starting second derivative matrix obtained from semi-empirical calculations.

Bond points were located and characterized using the program EXTRMX.[20]

Results from Calculations

Nitromethyl anion was studied first as a simple system in which conjugation with a nitro group plays a large role. The results, shown in Chart I, were obtained with the 4-31G basis set.[21] Compared with either nitromethane or the bisected anion, there are a short C-N bond in the planar anion, characteristic of a double bond, and long N-O bonds, as expected. There is a large change in dipole moment upon rotation of the nitro group and the calculated barrier is large.

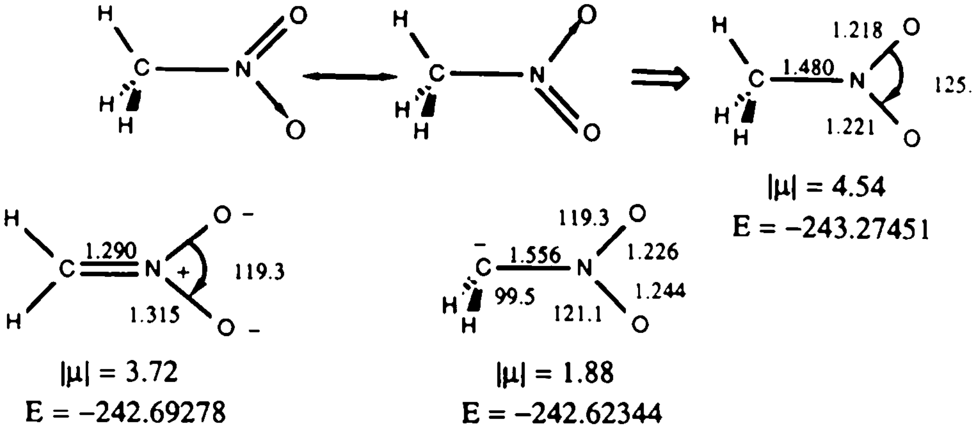


Chart I. Calculated geometries, energies, and dipole moments at 4-31G for nitromethane, planar nitromethyl anion, and nitromethyl anion with a bisecting nitro group (enforced C_s symmetry). Results for nitromethane and planar nitromethyl anion from Refs. 21a and 21b. Bond lengths in Å, angles in degrees, energies in au, and dipoles moments in Debye. The origin is taken as the center of charge ($\sum_i Z_i \vec{r}_i = 0$). The observed dipole moment for nitromethane is 3.46 D.

Calculations for nitrobenzene were performed with the plane of the nitro group both coplanar and orthogonal to the plane of the benzene ring; C_{2v} symmetry was enforced throughout. Optimized geometries, energies, and dipole moments are listed in Table I. In addition, some experimentally determined quantities are shown for comparison.

Several theoretical calculations for nitrobenzene have appeared previously. The AM1 results shown in Table I differ importantly from the previous MINDO/3 calculation[22] in that the nitro group is predicted to be coplanar with the benzene ring. Also, the calculated H_f is too large compared with the experimental result of 16.1 kcal.[23] Indeed, it has previously been found necessary to include a -10 kcal per $C - NO_2$ group correction to AM1 H_f's.[24]

The ab initio results in Table I extend previous calculations at the STO-3G,[5,25,26,27,28] 3-21G,[26] 4-31G,[26,29] and 6-31G[11,30] levels; some of these used partially optimized geometries.

Geometry: The calculated geometries shown in Table I show no serious failings in an absolute sense - most errors in bond lengths and angles being within usual bounds. Nevertheless, in addition to R(C-N) being systematically too short in the ab initio calculations, there is a serious failure by all methods to reproduce the observed bond length variations within the nitrobenzene ring. Thus, AM1 gives $C_i - C_o > C_o - C_m < C_m - C_p$; the pattern expected in structures I-III. STO-3G results show only minor variations of less than 0.002 Å within the ring.[25,28] Although the 3-21G calculation correctly predicts $C_i - C_o < C_o - C_m$, 6-31G,[30] and 6-31G* calculations give $C_i - C_o$ and $C_o - C_m$ equal.

Distortions of the ipso angle in substituted benzenes has attracted considerable attention.[28,30-32] The calaulations apparently underestimate the ipso angle somewhat. Nevertheless, all calculations in Table I correctly predict that the strongly electronegative nitro group causes an opening of the ipso angle accompanied by a closing of the adjacent angle relative to that in benzene. Recent calculations for a variety of substitutents show this to be a general effect,[30,31] in accord with the arguments of Trotter.[3]

Optimized geometries of nitrobenzene in which the nitro group is held orthogonal to the ring appear in Table I. These show more clearly the expected bond length variation brought about by an electronegative group with minimal resonance interactions. Thus, both 3-21G and 6-31G* C-C bond lengths show $C_i - C_o < C_o - C_m$. In addition, as Politzer found with the 6-31G basis set,[11] the calculated bond length changes brought about by nitro group rotation appear to result from a loss of resonance interactions present in the coplanar geometry. This leads to a shortening of the N-O, $C_i - C_o$, and $C_m - C_p$ bonds together with a lengthening of the C-N and $C_o - C_m$ bonds; however, none of the changes exceeds 0.01 Å at any level, while at 6-31G* the largest change is 0.005 Å.

Rotational Barrier: A presumed two-fold rotational barrier was obtained as the energy difference between the coplanar and orthogonal configurations. At the AM1 level, force constant calculations indicated the orthogonal configuration to be a bona fide transition state and that the zero point energy difference between the two configurations is about 0.5 kcal. The AM1 barrier of 3.5 kcal is in good agreement with experimentally determined barriers of 2.8-3.3 kcal.[6,33,34]

It has been previously shown that minimal basis set ab initio calculations give reasonable rotational phenyl-X barriers.[5] Unfortunately, bigger basis sets yield much higher barriers that only slowly improve with increasing size. Thus, the $C - NO_2$ rotational barrier at STO-3G has been calculated as between 5.0 and 5.5 kcal, depending upon geometrical details.[5,26,27] Using a fixed geometry for the benzene ring, values of 11.9 and 10.0 kcal were obtained using 3-21G and 4-31G basis sets, respectively.[26] At 6-31G, the barrier is 8.5 kcal.[11]

The results in Table I show similar trends in that the 3-21G//3-21G barrier is seriously overestimated. The 6-31G*//6-31G* and 6-311G**//6-31G* barriers show some improvement, but are still too large. Similar failings at 6-31G* for nitroethene have been observed.[27]

Charge Distribution: Dipole moments shown in Table I are too large compared with the handbook value of 4.2 D. In contrast, STO-3G gives 4.3 D.[5] Interestingly, the dipole moments in Table I for the orthogonal configuration are still significantly larger than the observed dipole. Also, as shown in Chart I, 4-31G calculations overestimate the dipole moment of nitromethane. Taken together, these results show an exagerated σ withdrawing effect of the nitro group.

Results of Mulliken analysis performed at various levels are shown in Table II for the planar and perpendicular configurations of nitrobenzene.

TABLE II

Mulliken analysis for nitrobenzene with the plane of the nitro group fixed planar and perpendicular to the plane of the benzene ring. All orbitals on ring and nitro group constituent atoms transforming as -1 with respect to the plane of the fragment are considered π. This means the plane orthogonal to the ring plane for the nitro group in the rotated geometries.

	3-21G//3-21G			6-31G*//6-31G*			6-311G**//6-31G*		
	Planar	Perp.		Planar	Perp.		Planar	Perp.	
q_σ									
C_i	0.398	0.388		0.276	0.268		0.263	0.202	
C_o	-0.267	-0.209		-0.238	-0.181		-0.105	-0.047	
C_m	-0.237	-0.244		-0.207	-0.220		-0.100	-0.102	
C_p	-0.270	-0.253		-0.229	-0.207		-0.120	-0.110	
N	0.290	0.316		0.576	0.550		0.460	0.421	
O	-0.411	-0.444		-0.472	-0.477		-0.403	-0.408	
q_{tot} (NO_2)	-0.586	-0.586		-0.419	-0.412		-0.094	-0.409	
N_π			Δ			Δ			Δ
C_i	1.131	1.077	-0.054	1.123	1.060	-0.063	1.189	1.054	-0.135
C_o	0.926	0.986	0.060	0.923	0.996	0.073	0.926	0.991	0.065
C_m	1.010	0.989	-0.021	1.010	0.986	-0.024	1.005	0.981	-0.024
C_p	0.941	0.974	0.033	0.943	0.981	0.038	0.941	0.977	0.036
N	1.104	1.137	0.033	1.055	1.064	0.009	1.086	1.106	0.020
O	1.475	1.439	-0.036	1.498	1.472	-0.026	1.481	1.454	-0.027
N_π (ring)	5.944	6.001	0.057	5.950	6.005	0.055	5.992	5.975	-0.017
N_π (NO_2) + N_π (ring)	9.998	10.016	0.018	10.001	10.013	0.012	10.040	9.989	-0.051

In the planar geometry, N_π is always less than 1.0 at the ortho and para positions, while N_π is close to one at the meta position. In addition, at all levels, the σ charges are polarized in the opposite sense of the π system; i.e., q_σ at the ipso carbon is always greatest, while that at the meta position is less negative than that at the ortho or para positions. Although these results seem quite consistent with I-III, π-induction and π-polarization effects can give rise to alternating charges in a cyclic system.[35]

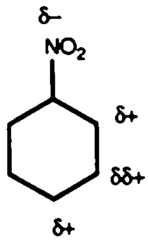
Perpendicular geometries were studied to determine the importance of π-induction.[36] This effect results primarily from the substitution of a carbon in benzene with a more electronegative atom; e.g. pyridine. It results in the familiar pattern of alternating charge. In addition, the perpendicular geometries allow the study of σ - π mutual polarization, free of resonance effects with the nitro group.

Unfortunately, different basis sets gave different results. Thus, at the 3-21G level, $N_\pi(C_i)$ > $N_\pi(C_m)$ > $N_\pi(C_o)$ > $N_\pi(C_p)$; however, the σ system shows a classic induction effect, with the charge increasing with increasing distance from the nitro group. At 6-31G*, while N_π now decreases with increasing distance, q_σ is more negative at the meta position than at the ortho or para systems. At 6-311G**, q_σ shows the classical inductive effect, increasing with increasing distance from the nitro group; the π system shows a similar effect with distance, only now the polarization is reversed. At 6-311G**, Equation 1 was found to relate the σ and π charge distributions quite accurately ($r^2 = 0.998$).

$$N_\pi(C_x) = 0.245 \bullet q_\sigma(C_x) + 1.004$$
$$x = i, o, m, p \qquad (1)$$

To separate the σ-induced π polarization from other effects, the difference of N_π in the two geometries was examined. The results, shown in Table II exhibit the largest changes at the ipso and ortho positions, while lesser changes occur at the meta and para position. In addition, the sign of the change alternates in going around the ring. This qualitative result is obtained by all three models with varying quantitative details. Thus, it is observed that the population depletion at the para carbon is less than that at the ortho position.

The above result suggests the dominant contribution of π-polarization effects. The classic charge pattern written for mesomeric conjugation is shown by IV.[37] Clearly, the calculated charges do not support this structure, because $N_\pi(C_m)$ is always greater than one. Also, the difference in $N_\pi(C_m)$ in the planar and perpendicular forms is always negative and of similar magnitude as that at the para positions. Traditionally, structure V might be written to symbolize the observed polarization. We suggest that structure VI may serve the same purpose, but it has the advantage of underscoring the fundamental relations between σ and π conjugation.[38] It is also consistent with the available observed structural data for nitrobenzene.



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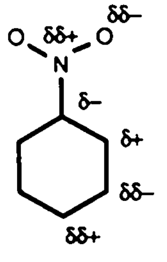
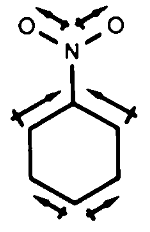


V



VI

Despite the above discussion, inconsistencies in the Mulliken analysis have been long recognized.[39] Other results in Table II show that the total N_π(ring) and $q_{tot}(NO_2)$ do not always behave as expected. For example, while N_π(ring) is greater in the perpendicular geometry at 3-21G and 6-31G*, the situation reverses unexpectedly at 6-311G**. Likewise, the total charge on the nitro group is larger in the perpendicular geometry at 6-311G**. An additional problem in the analysis is that the number of electrons assigned as π electrons is not constant for the two geometries. This indicates that σ - π separation we have employed is questionable. All these problems make it quite difficult to assign in any absolute sense the amount of electron transfer to the nitro group in either geometry.

Because of the many difficulties associated with analyzing Mulliken charges, a critical point analysis of the electron density was undertaken. As Bader and 10 workers have shown, increased bond order leads to an increase of electron density at the bond critical point (ρ_c).[40] The presence and relative magnitudes of π bonding can also be detected by calculation of curvatures of the electron density at the bond point.[41] Softer curvatures (that is, more nearly zero eigenvalues of the second derivative matrix of the electron density with respect to the cartesian coordinates) in the plane of the π bond arise from a build-up and resulting less rapid drop-off in electron density associated with increased double bond character. The ellipticity, ϵ, is a convenient measure of the deviation from cylindrical symmetry of the electron density at the bond critical point. It is defined as $\epsilon = (\lambda_1/\lambda_2) - 1$.

The results of this analysis for the heavy atom bonds in nitrobenzene are shown in Table III. Only very small changes in the value of ρ_c are brought about by rotation of the nitro group. Particularly significant are the quantities associated with the C-N bond. The value of ρ_c is essentially the same in both the perpendicular and planar configurations. The curvatures show unusual behavior. In the perpendicular geometry, the soft curvature for the C-N bond point points in the y direction; ie, it lies in the plane of the ring. This indicates that the C-N bond deviations from cylindrical symmetry are determined by factors other than conjugation with the benzene ring.[*] In any case, the ellipticity is less for the planar geometry. Both of these observations are inconsistent with increased double-bond character in the C-N bond in the planar geometry. Elsewhere in the molecule, the values of ρ_c and ϵ for the ring bonds are not interpretable in terms of structures I-III. Significant involvement of these forms would lead to greater single bond character in the $C_i - C_o$ and $C_m - C_p$ bonds in the planar form. An increase in the double bond character in the $C_o - C_m$ bond would also occur. These changes could be detected by decreases in ϵ and ρ_c in the former case and increases in these quantities for the latter case. None of this behavior is observed. Some differences consistent with increased single bond character of the N-O bond can be noted, however.

TABLE III

Curvatures ($\lambda_1, \lambda_2, \lambda_3$), ellipticity ($\epsilon$), and value of electron density calculated at bond points (ρ_c) for nitrobenzene at 6-31G*//6-31G*. All quantities in au. The ellipticity (ϵ), is defined as $\epsilon = (\lambda_1/\lambda_2) - 1$. The letter after λ_2 indicates its direction. The molecule is in y-plane with x = 0.

Bond	λ_1	λ_2	λ_3	ϵ	ρ_c
O-N					
para.	-1.426	-1.262 (x)	1.295	0.130	0.548
perp.	-1.441	-1.262 (y)	1.288	0.142	0.551
C-N					
para.	-0.539	-0.496 (x)	0.449	0.088	0.269
perp.	-0.561	-0.503 (y)	0.443	0.114	0.270
$C_i - C_o$					
para.	-0.722	-0.579 (x)	0.256	0.246	0.330
perp.	-0.721	-0.566 (x)	0.242	0.273	0.330
$C_o - C_m$					
para.	-0.710	-0.579 (x)	0.266	0.225	0.328
perp.	-0.706	-0 575 (x)	0.266	0.229	0.327
$C_m - C_p$					
para.	-0.708	-0.581 (x)	0.270	0.219	0.327
perp.	-0.708	-0.578 (x)	0.269	0.225	0.327

[*] For some possible alternatives see: a) D. Cremer; E. Kraka *Croatica Chimica Acta* **57**, 1259 (1984). b) J. P. Ritchie *J. Comput. Chem.* **7**, 1 (1986).

We also note that a critical point arising from the existence of an O-ortho H hydrogen bond was sought but not found at 6-31G*.

Assessment of the Calculations

The results in Chart I demonstrate unambigously the effects of charge delocalization onto a nitro group. The geometry of the planar nitromethyl anion clearly indicates a C-N double bond, while the N-O bonds are lengthened as expected. There is significant transfer of electron density onto the nitro group, as evidenced by the large calculated change in dipole moment upon rotation of the nitro group. There is also a large barrier to rotation about the C-N bond, consistent with its double bond character. Similar effects are well-known in other systems such as allyl and the nitro group itself.

The effects noted above, although present, are much diminished in calculations for nitrobenzene. Unfortunately the calculations reported in this paper do not reproduce many important properties of nitrobenzene and overestimate those associated with delocalization of charge onto the nitro group. The calculated geometries differ in ways from those observed suggesting an overestimation of resonance interaction with the nitro group. The observed alterations of C-C bond lengths was not reproduced by the planar calculations, but the perpendicular geometry showed shortened $C_i - C_o$ bonds. The rotational barrier and dipole moments are both seriously overestimated in the calculations. Seemingly reasonable values for these quantities obtained at STO-3G must be tempered by the realization that the geometry is poorly predicted and that an unjustified coincidental cancellation of errors must be responsible for its good performance. Thus, it is well known that extended basis sets are required to obtain electron distributions similar to those found in X-ray structures.[42] The Mulliken analysis showed that the calculated charge distributions did not correspond to classical ideas about mesomerism.

Because the calculations do not reproduce many of the relevant properties of nitrobenzene accurately, it is necessary to consider additional experimental data to determine the relative contributions of mesomeric resonance structures and polarization effects.

Relevant Selected Experimental Data

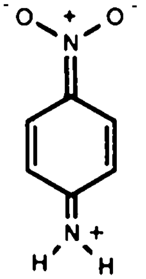
Before proceeding with a discussion of the importance of structures I-III, it is useful to consider the question being asked a little more carefully. The discussion is limited to neutral, even numbered electron, singlet molecules in their equilibrium ground state geometry. Excited states, charge bearing species, and transition states may well include greater contributions from mesomeric resonance structures. Thus much spectroscopic, reactivity, and acidity measurements are either unsuited or only indirectly useful for analysis of the ground state properties of nitrobenzene and its derivatives. Bearing this in mind, we proceed to consider some selected experimental results.

As Trotter originally noted, the structure of nitrobenzene is not in accord with expectations from I-III.[1,3] Additional evidence can be obtained by comparing the microwave structures of nitrobenzene (shown in Table I) and nitromethane.[43] Both the C-N and N-O bonds are very similar in the two structures: R(C-N) = 1.498 and R(N-O) = 1.224 Å in nitromethane while R(C-N) = 1.493 and R(N-O) = 1.227 Å in nitrobenzene. Consequently, despite the $sp^2 - NO_2$ bond in nitrobenzene compared with the $sp^3 - NO_2$ bond in nitromethane, there is little structural manifestation of significantly decreased $C - NO_2$ or increased O-N bond order as expected from I-III.

Most structural data for nitrobenzene derivatives and related compounds comes from crystal studies. It appears, however, that crystal forces may exert geometry alterations at least as large as those expected from resonance considerations. Indeed, the crystal may cause increased importance of resonance structures not contributing to the gas phase structure. An interesting possible example of this was found by comparing the calculated and X-ray structure of nitroguanidine.[44] Furthermore, crystal studies show the two N-O bond lengths in nitromethane to differ from one another by up to 0.02 Å.[45,46] These differences arise because of dissimilar crystal environments and the asymmetric formation of hydrogen bonds. Oxygens of the nitro group provide hydrogen bond acceptors and evidence is beginning to show that these form C-H ·· O hydrogen bonds in the crystal.[47,48]

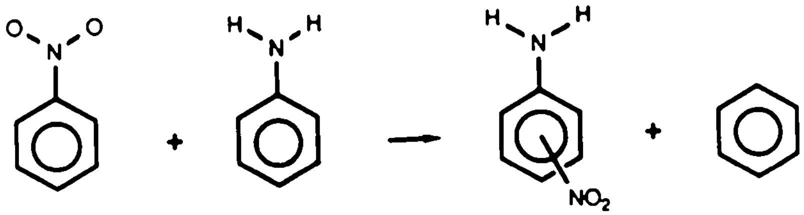
Despite these difficulties, systematic studies of crystal structures have provided interesting results. Holden and Dickinson showed from a study of 104 aromatic nitro groups that there is no systematic relationship between the interplanar angle and the $C - NO_2$ bond length.[49] From another study of selected crystal structures, Sorriso finds a correlation coefficient (r) = -0.44 for C-N vs. N-O bond lengths, but 0.88 for C-N bond length versus ONO angle.[50] This, according to the interpretation of Coppens[51] and Bartell[52] indicates dominance of steric crowding of the ortho substituent. Consequently, there is no systematic structural evidence of the mesomeric effect.

Because of the mutual conjugation exhibited by p-nitroaniline (VII), it occupies a central place in theories of mesomerism. As a result, its properties and the properties of related molecules have been studied extensively. We present a few results intended to suggest that the role of I-III and VII must be strictly limited.



VII

As Liebman points out, thermochemical evidence does not indicate a significant stabilization of p-nitroaniline due to mesomeric effects.[53] The heats of reaction for the simple exchange reactions shown below were calculated from observed heats of formation of the reactants and products.[23] The results reveal that m- and p-nitroanilines are only slightly stabilized relative to reactants and by nearly equal amounts.



3-nitro: H_r = -3.2 kcal

4-nitro: H_r = -3.0 kcal

Thus, no stabilization energy resulting from mutual conjugation has been observed. As a direct consequence of this, the stronger acidity of p-nitroanilinium ion as compared with the meta compound should not be explained by stabilisation resulting from VII. Taagepera et al. have previously showed a similar result and attribute the acidity of the p-nitroanilinium ion to field/inductive destabilization of the ion.[54]

In passing it is interesting to compare the strucutres of meta- and p-nitroaniline.[55] Both molecules are found to be essentially planar, and Trueblood, Goldish, and Donohue comment upon the large thermal parameters as indicating easy rotation of the nitro group in the para isomer.[55b] The C_{ar} - NH_2 bond is shorter in the para isomer (1.371 vs. 1.406 Å), as VII would suggest. The nitro group geometry, however, is not so simply explained. Although the O-N bonds are shorter in the meta isomer (1.242 and 1.211 Å vs. 1.246 and 1.247 Å) so is the C_{ar}-NO_2 bond (1.440 vs. 1.460 Å). It should be noted that both $C - NO_2$ bond lengths are appreciably shorter than those in nitrobenzene.

Because dipole moments have been measured for decades, they have been frequently used in discussions of mesomerism. Typically, a mesomeric moment is obtained as the difference between the dipole moment of nitrobenzene and a suitable model for which mesomerism is not possible.[13a] Gaseous nitromethane[4] ($\mu = 3.46$ D) and *t*-nitrobutane[56] ($\mu = 3.71$) are usually used and result in large mesomeric moments. It seems, however, that this comparison is unwarranted as it does not account for the differences in polarisability of the hydrocarbon fragment. The polarisability is important in that dipole moments can be induced by the field effect as shown in Equation 2.

$$\vec{\mu}_{\text{induced}} = \overleftrightarrow{\alpha} \cdot \vec{E} \qquad (2)$$

Tensor polarisabilities for methane, iso-butane, and benzene are shown in Table IV and are highly suggestive. Benzene is much more polarizable than is either methane or *iso*-butane. Consequently, there is no reason to believe that, say, *t*-nitrobutane and a nitrobenzene with a rotated nitro group should have equal dipole moments.

TABLE IV

Tensor and average polarizabilities for methane, iso-butane, and benzene. Units are A^3. $\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

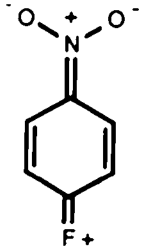
Compound	α_{xx}	α_{yy}	α_{zz}	α
CH_4	1.13	1.13	1.13	1.13[a]
	2.62	2.62	2.62	2.62[b]
C_4H_{10}	2.62	3.41	2.44	2.82[a]
C_6H_6	13.19	13.50	9.00	9.20[a]
	14.10	14.10	8.50	10.40[b]

[a] F. T. Marchese and H. H. Jaffe Theoret. *Chim. Acta* **45**, 241 (1977). Calculated values.

[b] N. J. Bridge and A. D. Buckingham *Proc. Royal Soc.* **295A**, 334 (1966). Observed values.

To determine mesomeric moments more accurately, Exner has measured and compared the dipole moments of nitrobenzene and 2,4,6-trimethylnitrobenzene in benzene solution.[57] In the latter compound, steric effects cause the nitro group to rotate, inhibiting conjugation. The difference in these compounds' dipole moments, 0.3 D, is relatively small compared with the measured dipole moment of nitrobenzene of 3.95 D. Topsom comments that although the effect is small on a relative basis, 0.3 D is still a fairly large contribution in an absolute sense.[12b] For comparison, the dipole moment of toluene, which is not usually considered to be very polar, is 0.36 D. As Exner points out, the effect could be explained in terms of the unequal polarisabilities of the benzene nucleus, similar to that shown in Table III. In addition, the anisotropic field associated with the nitro group and the changed dielectric constant near the nitro group of a methyl group versus hydrogen is bound to have an effect. The dielectric argument is surely important, as it is well known that dipole moments are solvent and phase dependent. Indeed, the dipole moment of nitrobenzene differs by 0.27 D in benzene and the gas phase.

Contributions from I-III predict a rotational barrier. As mentioned, the observed barrier in nitrobenzene is 2.8–3.3 kcal.[33,34] This is surprisingly small, especially in comparison with the barrier in ethane, which is observed to be in the same range – 2.93 kcal.[58] Measurements of the nitro group rotational barrier in 3- and 4-fluorobenzene have also been obtained.[34] In the para isomer, the π donating fluorine can interact with the nitro group as shown in VIII. This should lead to a larger rotational barrier than in nitro benzene. The barrier to internal rotation was found to be 3.5 kcal for the para isomer, only slightly larger than the observed barrier in nitrobenzene (actually within experimental error). However, the observed barrier was 4.1 kcal for the 3-fluoro isomer; i.e., larger than for the para isomer. Thus, these measurements are additional direct evidence against the importance of the mesomeric forms shown in VIII.



VIII

Correlations of NMR chemical shifts with calculated Mulliken π populations are often rationalized by structures I-III.[7-10,59] It is not certain, however, that the calculated Mulliken charges arise only or even largely from charge transfer to the nitro group. Indeed, we showed above that the π charge distribution in nitrobenzene was not primarily due to mesomeric structures I-III. As Hiberty and Ohanessian point out,[10] the NMR experiment measures depletion or accumulation of charge and that resonance effects are not the only means by which charge can be transferred to an atom. Thus, the polarization mechanism is only one of several effects that could cause the observed shifts. Untangling the various effects is difficult and, to be sure, many attempts have been made.[7-10,59] Typically, a correlation with LFER parameters is observed and interpreted in terms of resonance, field, inductive, etc., effects. A basic limitation of these approaches is that they are largely empirical attempts to describe the several mutually dependent and complicated phenomena in a simple manner. So, it has been shown that π-induction and π resonance behave quite similarly.[36] It is quite likely then that σ_r represents a mixture of these effects. Indeed, the several σ_r scales in existence is evidence of this.

Another point concerning the NMR data is that magnetic shielding tensors include a paramagnetic as well as a diamagnetic term.[60] The paramagnetic term, as usually expressed, includes a mean excitation term, accounting for mixing of the ground state with excited states brought about by interaction with the magnetic field. Calculations for simple carbonyl compounds have shown that excited states are important to the interpretation of ^{17}O chemical shifts.[61] Thus at least for ^{17}O shifts, and possibly other nuclei, correlations with σ_+ and σ_r values, while informative, may not indicate the contribution of nitro group resonance in the ground states of substituted nitrobenzenes.

A final piece of information is that a correlation of ^{17}O shifts of several nitroaromatics with rotation angles as found in the X-ray structure has been observed.[62] As mentioned previously the $C-NO_2$ bond lengths and $C-NO_2$ torsional angles don't correlate well[49] suggesting that mesomeric structures are not responsible for the observations.

Summary and Conclusion

There is considerable evidence against the involvement of resonance structures I-III in describing the ground state properties of nitrobenzenes. It was found that RHF calculations, even with extended basis sets, do a poor job of reproducing important properties of nitrobenzene such as the geometry, rotational barrier, and dipole moment. Mulliken populations supplemented by a bond point characterization were found to be more consistent with a π-polarization effect.

Consideration of experimental data showed that mesomeric resonance forms of the sort indicated in I-III were not important in describing many ground state properties. Thus the structural predictions of I-III are not observed. The rotational barrier for nitrobenzene is not very large, contrary to expectations from I-III. In addition, 3- and 4-fluorobenzene do not show rotational barriers that can be rationalized with mesomerism. The mesomeric contribution to the dipole moment has been shown to be small and possibly attributable to other factors. Finally, there is no thermochemical evidence of stabilization from mesomerism.

The utility of any model lies in its capability to rationalize observed chemical behavior and properties and to make predictions. Mesomeric structures rationalize some data quite well. Dipole moments of mutually conjugated compounds, for example, and no new explanation of this phenomenon is offered here. Nevertheless, commonly used (actually overused) structures I-III, VII, and VIII and probably similar ones are quite misleading. Mesomerism is clearly not a dominating effect for determining many chemical properties. We suggest that structure V or VI represents a more accurate description of the charge distribution in nitrobenzene without being misleading.

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