6744 *J. Org. Chem.* **1995**, *60*, 6744−6755

Substituent Effects of −NO and −NO$_2$ Groups in Aromatic Systems

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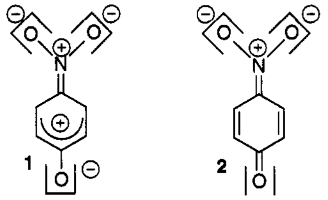
Received April 4, 1995[®]

The nitro and nitroso derivatives of methane, benzene, and Li-phenolate were theoretically investigated with the help of quantum chemical methods (SCF, MP2). Experimental densities were examined with the OIAM approach. MP2 geometries were in excellent agreement with advanced experimental data. Geometries, electron densities, atomic charges, and atomic shapes, bond orders, torsional barriers, and reaction energies were analyzed in order to elucidate the inductive and mesomeric influence of NO in comparison to NO$_2$. These influences behave partly additive with $-$I(NO) < $-$I(NO$_2$), partly nonlinear and nonadditive with $-$M(NO$_2$) < $-$M(NO). Despite some π-character of the PhNO$_2$ bond, the mesomeric influence of NO$_2$ on a nonsubstituted benzene ring is very small, but becomes enhanced by para-donors or corresponding intermolecular interactions.

1. Introduction

While nitrosobenzenes are rather neglected in organic chemistry textbooks, nitrobenzenes form the paradigm of quinoidic mesomerism through the −M effect (especially in the cases of para- and ortho-π-donors) and for the explanation of aromatic substitution reactions.[1] The view of through-resonance was supported by the dipole moment values,[2] by ^{17}O-NMR measurements of Fraser et al.,[3] by ^{15}N- and ^{17}O-NMR measurements of Craik et al.,[4] by ESR and polarography,[5] and by the low basicity of *p*-nitroaniline[6] and the high acidity of *p*-nitrophenol.[7] In general, the effects are more pronounced in para- than in meta-disubstituted compounds. By analysis of the experimental bond length alternation of *p*-nitrophenolates with the help of the simple HOSE model,[8] Krygowski et al.[9] deduced weights for contributions of the canonical structures **1** and **2** of Chart 1 to be about 20% and 10%, respectively.

Chart 1



On the other hand, the resonance view of nitrobenzenes was challenged by Lipkowitz[10] on his ^{17}O-NMR data, by the VB-analysis of MO-SCF calculations by Hiberty,[11] and by the low "resonance dipole moment" of −NO$_2$.[12] Comparison of the X-ray crystallographic geometry data of *N,N*-dialkyl-*p*-nitroaniline with 2,6- and 3,5-dimethylxylidines[13] shows that twisting the electron-donating group out of the molecular plane has a bigger influence on the ring geometry than an out-of-plane rotation of the −NO$_2$ group. Furthermore, in several organic textbooks[14] or by Exner[15] and others it was pointed out that the electron-withdrawing power of −NO$_2$ is mainly due to induction (−I effect). Low nitrobenzene π-mesomerism was also suggested by the low torsional barrier[16−18] and

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[®] Abstract published in *Advance ACS Abstracts*, September 15, 1995.

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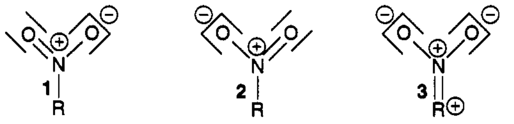
Table 1. Inductive and Resonance Constants from References 28 and 29

group	σ_I	σ_R	σ_R^-
−NO	0.34	0.33	1.46
$-NO_2$	0.56	0.19	1.27

Chart 2



large torsional amplitude.[18-20] In addition, the experimental density distribution[21] as well as Ritchie's[22] and Politzer's ab-initio calculations[23] corroborated this view.

Less is known about the nitrosobenzenes, which seems contradictory. The group electronegativity of $-NO_2$ is a little larger than that of −NO;[24-27] the same holds for the inductive substituent constant σ_I,[28,29] while the resonance constants of $-NO_2$ are the slightly smaller ones (Table 1). The larger quinoidic bond alternation in the *p*-nitrosophenolates corresponds to as much as 30% quinoidic character.[9] On the other hand, simple STO-3G calculations of the same authors indicated a stronger through-resonance of the corresponding nitro compounds.

The main difference between the nitro and nitroso groups lies in the fact that the nitro group has its own strong mesomeric effect (structure **1** and **2** in Chart 2),[9] which induces a positive charge at the nitrogen atom and, hence, is a source of increased electronegativity. The mesomeric interaction with the other part of the molecule (structure **3**) is in general reduced simultaneously and only appears in the case of the strong electron-donating property of R[30] leading to through-resonance structures of the quinoidic type in the case of p-substituted aryls. In the case of the nitroso group, in contrast, the primary mesomeric effect with the other part of the molecule dominates. In this respect, the difference between the ON and O_2N aryls is similar to the one between OCR and ^-O_2C aryls: mesomerism with the benzene ring is much more pronounced for the aryl ketones than for the benzoates.

Concerning the conflicting evidence, it should also be kept in mind that static molecular properties, dynamical molecular response properties, and reactive intermolecular properties were compared. Different intermolecular forces differently affect the observed intramolecular interactions in these compounds in different environments leading to changes in molecular geometry[31] and electronic charge distribution.[32] Furthermore, some theoretical approaches may be criticized concerning basis sets, the neglect of correlation, or the procedure of interpretation.

In order to contribute to the elucidation of the puzzling state of knowledge of the unsubstituted and substituted nitro- and nitrosobenzenes, we have performed SCF and MP2 calculations[33] of nitro and nitroso derivatives of methane, benzene, and Li phenolates of different conformations (section 2). We will analyze the energies, optimized geometries, and especially the electron density distributions using different approaches[34-36] (sections 3−6). Our summarizing conclusions are presented in section 7.

2. Calculational Methods

We have performed ab initio calculations of nitro and nitroso compounds as mentioned in the Introduction. The RHF and MP2 approahces of the GAUSSIAN 90 system have been employed.[33] Double-ζ valence basis sets with "1d/1p" polarization functions (6-31G** of Pople et al. and the split valence polarized = SVP sets of Ahlrichs et al.[37,38]) were used for the substituted phenolates, and for the smaller nitro- and nitrosomethanes and -benzenes and the unsubstituted phenolate the larger triple-ζ valence sets (6-311) with "2d1f/1p" polarization functions were used.[39] The electron density has been analyzed with the help of the independent oriented atoms approach (OIAM),[40,41] with difference and deformation density maps and projected maps,[34] with Bader's topological approach,[42] with Mulliken's populations[43] and the so-called natural populations,[44] and with the concept of potential derived charges.[45]

3. Optimized Geometries

The geometries were fully optimized both at the Hartree−Fock (SCF) and correlated MP2 levels except

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Table 2. Calculated and Experimental Geometries of Nitromethane and Nitrosomethane (Distances in pm, angles in deg). ΔSCF is the Deviation of the SCF Approximation from the More Reliable MP2 Calculation

	Nitromethane (C_s)		Nitrosomethane (C_s)	
param	MP2 (ΔSCF)	exptl[a]	MP2 (ΔSCF)	exptl[a]
C−N	149.1 (−1.2)	148.1/148.9	148.2 (−2.0)	149 (148.0)
N−O	122.8 (−3.7)	120.9/124.5	121.9 (−4.3)	122 (121.1)
$C-H_{apic/plan}$	109.0 (−0.4)	109.8	109.3 (−0.1)	(109.4)
C−H	108.7 (−0.1)		109.3 (−0.1)	
C−N−O	117.0 (0.2)	118.5	112.6 (1.3)	112.6 (113.2)
O−N−O	126.0 (−0.4)	123.3/125		
$N-C-H_{apic/plan}$	107.0 (0.5)	107.3	111.0 (−2.3)	109 (111.0)
N−C−H	107.8 (−0.3)		106.9 (1.8)	
H−C−H	112.6 (0.4)		108.1 (−0.2)	
$H-C-H_{apic/plan}$	110.6 (0.0)	111.6	111.8 (−0.3)	(109.2)

[a] Gas phase data (microwave: nitromethane,[57,60] nitrosomethane[57]); X-ray data in parentheses (nitrosomethane[61]).

Table 3. Calculated and Experimental Geometry of Benzene (D_{6h}) (See Legend of Table 2)

param	MP2 (ΔSCF)	exptl[a]
C−C	139.9 (−1.2)	139.7
C−H	108.6 (−1.0)	108.4

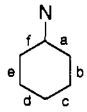
[a] Electron diffraction, X-ray diffraction.[57−59]

for the nitro- and nitrosophenolates, where only the SCF approximation was applied because of limited computational resources. Correlation is especially important for the N−O bonds, which are thereby expanded by about 6 pm, mainly because of excitations of the N-lone-pair to π^*. The results are presented in Tables 2−8. As is to be expected, the Hartree−Fock bond lengths (except for N−O) are too small by typically 1 pm; bond angles are in error by up to ±1°.

The most reliable experimental structure determinations (gas phase electron diffraction and microwave spectroscopy, crystal X-ray diffraction) are in good agreement with the present theoretical results (see Tables 2−4). In order to achieve this agreement both accounting for correlation (MP2) and use of more extended basis sets than previous authors and comparison with modern experimental data and structural parameters obtained by sophisticated data analysis are of importance. The accuracy of the calculations is expected to be a few tenths of a pm/deg concerning bond lengths/angles, respectively.

Since it is not very clear to compare the six individual bond lengths of the benzene rings of different compounds directly, we will analyze linear combinations. A C_6 skeleton of D_{6h}-symmetry possesses 12 irreducible deformations: three are of ring puckering type (b_{2g},e_{2u}), three are of bond angle bending type (b_{1u},e_{2g}), and six are of bond stretching type, namely (see Chart 3):

Chart 3



$$a_{1g} = (a + b + c + d + e + f)/6 =$$
average bond length

$$b_{2u} = (a - b + c - d + e - f)/6 =$$
Kekule bond alternation

$$e_{2g} = (a - 2b + c + d - 2e + f)/4 =$$
quinoidic bond alternation

$$e_{1u} = (a - c - d + f)/4 =$$
up−down (ipso-para) asymmetry

We also give these a_{1g}, e_{2g}, and e_{1u} parameters in Tables 4−8. For left-right symmetric rings, b_{2u} is zero. b_{2u} is small in all the present cases. We note that these parameters are related to Krygowski's[31,46] aromaticity parameters HOMA and BAC. In the case of left−right

Table 4. Calculated and Experimental Geometries of Planar (‖) and 90°-Torsioned (⊥) Nitrobenzene (C_{2v}) (Equivalent Atoms or Bonds Are Separated by /. See Legend of Table 2)

param	MP2 (ΔSCF) ‖	exptl[a] ‖	MP2, ⊥	exptl,[b] ⊥
C1−N	147.1 (−0.7)	148.6,147.8/149.2 (147.1)	146.1	
N−O	124.2 (−5.8)	122.3,121.8/122.7 (123.1)	124.4	
C1−C2/C6	139.3 (−0.7)	139.6,139.1/138.4 (139.2)	139.1	
C2−C3/C5−C6	139.5 (−0.8)	141.0,139.1/141.2 (139.0)	139.6	
C4−C3/C5	139.7 (−0.7)	141.0,139.1/139.5 (139.4)	139.7	
a_{1g}	139.5 (−0.7)	140.5,139.1/139.7 (139.2)	139.5	
e_{2g}	0 (0.1)	−0.7, 0.0/−2.2 (0.3)	−0.2	
e_{1u}	−0.2 (0.0)	−0.7, 0.0/−0.6 (−0.1)	−0.3	
C2−C1−C6	122.7 (−0.5)	123.4,125.1/125.0 (122.7,122.7)	123.0	123.4
C1−C2−C3	118.1 (0.5)	117.7,115.7/117.1 (118.2,118.1)	118.1	117.8
C2−C3−C4	120.5 (−0.4)	120.5,122.5/120.3 (120.3,120.3)	120.3	120.1
C3−C4−C5	120.0 (0.4)	120.2,118.3/120.2 (120.4,120.5)	120.2	120.7
C2−C1−N	118.6 (0.3)	118.3,117.5/117.5 (118.7)	118.5	
O−N−O	124.7 (0.2)	125.3,123.4/124.4 (123.2)	125.9	

[a] Electron diffraction/microwave data of the molecule,[16,18,57,62] X-ray data of the crystal[18,21] in parentheses (averages of equivalent bonds).
[b] Derived from X-ray data.[18]

Table 5. Calculated and Experimental Geometries of Planar (||) and 90°-Torsioned (⊥) Nitrosobenzene (C_s) (C-Atoms with the Lower Numbers Are on the Same Side as the O-Atom. See Legend of Table 2)

param	MP2 ‖(ΔSCF)	exptl,[a] ‖	MP2, ⊥
Cl−N	144.3 (−1.2)	(147)	146.2
N−O	124.5 (−7.4)	(122)	124.3
C1−C2	139.7 (−1.0)	137.3	139.3
C1−C6	140.0 (−0.6)	137.5	
C2−C3	139.5 (−0.5)	138.4	139.6
C5−C6	139.1 (−0.8)	138.0	
C4−C3	139.7 (−1.0)	136.9	139.7
C4−C5	140.2 (−0.7)	137.3	
a_{1g}	139.7 (−0.8)	137.6	139.5
e_{2g}	0.6 (−0.2)	−0.9	−0.1
e_{1u}	−0.1 (0.0)	0.1	−0.2
C1−C2−C3	119.2 (0.5)	118.0	118.7
C2−C3−C4	119.8 (−0.2)	118.8	120.3
C3−C4−C5	120.0 (0.6)	120.0	120.0
C4−C5−C6	120.3 (−0.2)	120.6	
C5−C6−C1	118.6 (0.5)	118.3	
C2−C1−C6	121.3 (−0.2)	122.2	121.9
C2−C1−N	114.6 (1.1)		119.0
C1−N−O	114.1 (2.0)	(116)	111.3

[a] X-ray data,[63] because of strong NO-dimer interactions in the crystal, the C1−N−O entity is not comparable with the free monomer. Data in parentheses: microwave.[57]

Table 6. Calculated and Experimental Geometry of Li Phenolate (C_{2v}) (See Legend of Table 2)

param	MP2(ΔSCF)	exptl[a]
Li−O	162.2 (3.3)	
O−C4	132.3 (−3.5)	132.1
C1−C2/C6	140.0 (−0.9)	139.0
C2−C3/C5−C6	139.7 (−1.2)	139.3
C4−C3/C5	140.0 (1.2)	141.4
a_{1g}	139.9 (−0.3)	139.9
e_{2g}	0.3 (1.3)	1.0
e_{1u}	0.0 (−1.0)	−1.3
C2−C1−C6	117.3 (0.8)	117.3
C1−C2−C3/C1−C6−C5	120.6 (0.6)	120.3
C2−C3−C4/C4−C5−C6	121.3 (0.0)	122.7
C3−C4−C5	118.9 (−2.4)	117.1
O−C4−C5/C3	121.3 (0.5)	121.5

[a] X-ray diffraction of Na phenolate monohydrate crystal.[64] The molecular C_{2v} symmetry is broken in the solid.

Table 7. Calculated and Experimental Geometries of Planar (||) and 90°-Torsioned (⊥) Li *p*-Nitrophenolate (C_{2v}) (Values in Parentheses: with Estimated Correlation Correction. (Nearly) Equivalent Atoms or Bonds Are Separated by /. See Legend of Table 2)

param	HF, ‖	exptl,[a] ‖	HF, ⊥
Li−O	165.0 (162)		164.4 (161)
O−C4	128.1 (131.5)	129.5	128.8 (132)
C1−N	144.4 (145)	143.0	146.5 (147)
N−O	118.9 (124.5)	123.8/125.3	118.5 (124)
C1−C2/C6	139.3 (140.1)	132.2/141.8	138.3 (139.1)
C2−C3/C5−C6	137.8 (138.8)	135.8/141.7	138.2 (139.2)
C4−C3/C5	141.5 (141.4)	140.9/142.7	141.1 (141.0)
a_{1g}	139.5 (140.1)	136.3/142.1	139.2 (139.8)
e_{2g}	2.6 (2.0)	0.8/0.6	1.5 (0.9)
e_{1u}	−1.1 (−0.7)	−4.3/−0.5	−1.4 (−1.0)
C2−C1−C6	120.4	121.1	121.2
C1−C2−C3/C1−C6−C5	119.8	119.2/121.2	119.4
C2−C3−C4/C4−C5−C6	121.3	119.0/122.0	121.5
C3−C4−C5	117.3 (119.5)	117.4	117.2 (119.5)
N−C1−C2/C6	118.0	118.9/120.0	119.4
O−N−O	123.9	121.3	125.0

[a] X-ray diffraction of Na *p*-nitrophenolate dihydrate crystal.[32] The molecular C_{2v} symmetry is broken in the solid. Further nitrophenolates were investigated in refs 9, 66, and 67.

Table 8. Calculated and Experimental Geometries of Planar (||) and 90° Torsioned (⊥) Li *p*-Nitrosophenolate (C_s) (C-Atoms with the Lower Numbers Are on the Same Side as the O-Atom. See Legend of Table 2)

param	HF, ‖	exptl,[a] ‖	HF, ⊥
Li−O	164.7 (161.5)		163.7 (160.5)
O−C4	128.2 (131.5)	128.1	129.3 (132.5)
C1−N	140.6 (142)	135.9	144.9 (146.5)
N−O	118.0 (125)	128.2	116.9 (124)
C1−C2	140.1 (141)	142.4	138.6 (139.4)
C1−C6	139.5 (140.2)	142.2	
C2−C3	137.5 (138.2)	136.5	138.4 (139.3)
C5−C6	137.5 (138.5)	136.1	
C3−C4	141.6 (141.6)	142.4	141.1 (141)
C4−C5	141.6 (141.4)	142.6	
a_{1g}	139.6 (140.2)	140.4	139.4 (140.0)
e_{2g}	3.2 (2.7)	6.1	1.4 (1.0)
e_{1u}	−0.9 (−0.5)	−0.1	−1.2 (−0.8)
C2−C1−C6	119.3	119.0	119.9
C1−C2−C3	120.5	120.3	118.7
C5−C6−C1	120.7	121.0	
C2−C3−C4	121.0	120.1	121.5
C4−C5−C6	121.0	121.2	
C3−C4−C5	117.6	118.2	116.9
C2−C1−N	116.8	115.9	120.1
C1−N−O	117.2 (116)	117.2	114.5 (113)
O−C4−C3	121.2 (123.5)	121.1	121.5 (124)

[a] X-ray diffraction of *p*-nitrosophenolate hydrate crystals.[32] The values given here are for the Mg hexahydrate.

symmetric rings, the relations are

$$\mathrm{BAC} = 1 - \mathrm{const}\sqrt{e_{2g}^2 + e_{1u}^2}$$

$$\mathrm{HOMA} = 1 - \mathrm{const}[e_{2g}^2 + 3e_{1u}^2 + 1/2(a_{1g} - d^{\mathrm{opt}})^2]$$

where d^{opt} is an optimized reference value of the C−C bond length.[31]

3.1 Nitrobenzene (Table 4). The most reliable experimental structures are the electron diffraction data of Domenicano et al.[18] (first experimental entry in Table 4) and the X-ray diffraction data of Boese et al.[21] (first entry in parentheses in Table 4). The latter ones agree best with our calculations concerning the CNO_2 grouping, the benzene bond lengths, and the benzene bond angles.

Upon rotation of the NO_2 group of nitrobenzene 90° out of the molecular plane, intramolecular nonbonded and mesomeric interactions are reduced: the C−N bond contracts by 1 pm, and the ONO angle opens by 1°. (Politzer,[23] applying the Hartree−Fock approximation and neglecting polarization functions, found the opposite bond length trend.) The benzene ring is hardly changed by $-NO_2$ torsion. The accuracy of theoretical, and especially of experimental, structure determinations is still not sufficient to draw conclusions on the change of electronic structure of nitrobenzene upon NO_2 rotation. This reservation also holds with respect to the comprehensive review on nitrobenzene by Ritchie.[22]

The ring angle at the ipso-C1 is nearly 3° wider than 120°, according to the Walsh−Bent rule[47] typical for a strongly electronegative substituent. There is nearly no bond length alternation in the benzene ring. Thus, the geometric parameters are compatible with dominantly inductive action of the nitro group and insignificant $O_2^{\delta-}N = C_6^{\delta+}H_5$ mesomerism in the copolanar form.

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(46) Krygowski, T. M.; Ciesielski, A.; Cyranski, M. *Chem. Papers (Bratislava)*, in press.

(47) Walsh, A. D. *Discuss. Farad. Soc.* **1947**, *2*, 18−24. Bent, H. A. *Chem. Rev.* **1961**, *61*, 275−311.

3.2 Nitrosobenzene (Table 5). The benzene ring angle at the ipso-C is only 2° larger than 120° for "vertical" −NO. Upon planarization of the nitroso group, there appears a weak quinoidic bond length alternation in the benzene ring of about 0.67 pm (compare the e_{2g} parameters for $\parallel$ and $\perp$), and the C−N bond contracts by 2 pm, corresponding to about 10% double bond character according to the standard bond length−bond order correlation. These geometric parameters are compatible with a smaller −I but larger −M effect for planar −NO than for planar $-NO_2$. For vertical −NO, the nitrogen σ-lone pair might even act as a weak π-donor to the benzene ring.

3.3 Li Phenolate (Table 6). This molecule shows small bond length alternation (which is strongly exaggerated by the SCF approximation) and a bond angle reduction at the ipso-C of 3° (i.e., C4; C1 is reserved for $-NO_x$ substitution). This corresponds to some quinoidic mesomerism (+M effect of −OLi) and to the +I properties of −OLi, respectively.

3.4 Li Nitrophenolate (Table 7). Planarization of the nitro group shortens the C−N bond by 2 pm. It also enhances the quinoidic bond length alternation over the values of nitrobenzene and phenolate and increases the average benzene C−C bond length. This suggests that a +M π-donor (as LiO−) synergetically *induces* through-resonance to a planar $-NO_2$ group, as already pointed out by Hiberty and Ohanessian.[11]

3.5 Li Nitrosophenolate (Table 8). Planarization of the nitroso group shortens the C−N bond by as much as 4 pm and also enhances the quinoidic bond length alternation overadditively (compare also ref 31). That is, the +M phenolate synergetically *enhances* the already existing benzene−planar nitroso resonance.

4. Shape of Atoms in Molecules

Atoms with an open degenerate valence shell may carry different amounts of electronic charge in their different valence AOs. We have developed a procedure to determine the orientation and occupancy (W_i) of the AOs of *independent atoms* in their electronic ground configuration, which optimally reproduces the electron density in a given molecule.[40] If the AOs of an atom in a molecule are, as usual, not evenly populated, the independent atom is *not* spherical. Namely:

Quantum mechanically, particles have momentum and angular momentum and, complementarily, position and orientation. An unperturbed independent atom with specified momentum in free space has a completely uncertain position. Concerning its shape and the corresponding orientation in space, there exist different possibilities. An atom with closed shells or with an open s shell (or in an S or 0 or 1/2 state) is spherical. Atoms with open p or d shells with *degenerate* ground configuration may in general have a manifold of shapes, which may be specified even in free space.

When one thinks of a molecule or crystal as being composed of atoms, it is appropriate at first to specify the shape and orientation of the independent atoms in free space. This prerequisite of the atomic model of matter is often overlooked. Second, one constrains the atomic positional distributions to the regions around their equilibrium positions, when they become bound. According to Heisenberg's uncertainty principle, at least the zero-point energy must be supplied in this step. Now one has the so-called "independent atom promolecule (procrystal)" model. In the final step the interaction between the oriented and positioned independent atoms is switched on, yielding "chemically bound atoms in the molecule". The accompanying change of the electron density is called "chemical deformation density".[40,41,51]

Table 9. AO-Occupancies *W* (from SCF Densities, MP2 Values in parentheses) and *q* and *a* Parameters of Atomic p-Shells of Independent Oriented Ground Configuration Atoms in Ethane, Ethene, Nitromethane, and Nitrosomethane

molecule	AO[a]	*W*
C_2H_6 $^1A_{1g}$	$Cp_{\sigma(CC)}$	0.62
$q(C) = -0.08$	$Cp_{\sigma'\sigma''}$	0.69
C_2H_4 ^1A_g	$Cp_{\sigma(CC)}$	0.92
$q(C) = -0.57$	$Cp_{\sigma'(CH)}$	0.80
$a(C) = 0.12$	Cp_π	0.28
CH_3NO_2 $^1A'$	$Cp_{\sigma(CN)}$	0.36 (0.41)
$q(C) = -0.46\ (-0.39)$	$Cp_{\sigma',\sigma''}$	0.82 (0.80)
	$Np_{\sigma(NC)}$	1.17 (1.09)
$q(N) = -0.54\ (-0.24)$	$Np_{\sigma'(NO)}$	1.21 (1.07)
	Np_π	0.65 (0.84)
	$Op_{\sigma(ON)}$	1.09 (1.16)
$q(O) = 0.55\ (0.47)$	Op_n	1.70 (1.65)
	Op_π	1.21 (1.20)
CH_3NO $^1A'$	$Cp_{\sigma(CN)}$	0.47 (0.49)
$q(C) = -0.30\ (-0.27)$	$Cp_{\sigma'}$	0.77 (0.76)
	$Cp_{\sigma''}$	0.76 (0.75)
	Np_σ	1.06 (1.02)
$q(N) = -0.77\ (-0.57)$	Np_n	1.45 (1.36)
$a(N) = 0.39\ (0.34)$	Np_π	0.49 (0.62)
	$Op_{\sigma(ON)}$	1.24 (1.27)
$q(O) = 0.71\ (0.63)$	Op_n	1.80 (1.75)
$a(O) = 0.29\ (0.29)$	Op_π	0.95 (0.98)

[a] $Ap_{\sigma(AB)}$ refers to a p-AO on A pointing along the σ-bond toward atom B. Ap_π and Ap_n indicate p-AOs vertical to the σ-bond in the π-direction and in the lone-pair direction, respectively.

The quadrupolar parameter of an open p-shell of an independent atom is defined as

$$q = W_1 - (W_2 + W_3)/2$$

where it is assumed that W_2 and W_3 are the two most similar p-AO occupancies. If $W_2 = W_3$, the atom is axially symmetric, and the so-called asymmetry parameter

$$a = W_2 - W_3$$

vanishes. For instance, the F-atom has a $2p^5$ ground configuration. In F_2, the respective state of F is $2p_x^2\ 2p_y^2\ 2p_z^1$, if the z-axis is chosen parallel to the F−F bond. Then $W_2 = W_3 = 2$, $W_1 = 1$, $a = 0$, and $q = -1$. We have $q < 0$ for oblate disklike atoms (as F in F_2) and $q > 0$ for prolate cigar-like shapes (as $B(2p_x^0\ 2p_y^0\ 2p_z^1)$ in BH).[48] Our results are given in Tables 9−14.

4.1 Nitromethane and Nitrosomethane (Table 9). While the carbon in CH_4 is spherical because of symmetry reasons, and nearly so in ethane, it is oblate in nitrosomethane ($q \approx -0.3$) and even more so in nitromethane ($q \approx -0.4$). It is known that electron-rich substituents X make the carbon atom flat according to the relation $q_{HF} = 0.26\cdot(2.2 - \eta_x)$,[48] where η_x is the electronegativity of the ligand X. From this relation, we obtain for NO_2 $\eta \approx 4.0$ and for NO $\eta \approx 3.4$ Pauling units. This is consistent with −NO having a −I influence and $-NO_2$ an even larger influence. These electronegativity

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(48) Schwarz, W. H. E.; Lin, H. L.; Irle, S.; Niu, J. E. *THEOCHEM* **1992**, *255*, 435−459.

Table 10. AO-Occupancies and q Parameters of Atomic p-Shells of Independent Oriented Ground Configuration Atoms in Butadiene, Benzene, and Li Phenolate

molecule	AO[a]	W
tr-C_4H_6 (planar)	$p_{\sigma(CC)}$	0.90
$q(C_1) = -0.56$	$p_{\sigma(CH)}$	0.80
$\alpha(C_1) = 0.10$	p_π	0.29
$q(C_2) = -0.52$	p_σ	0.93
$\alpha(C_2) = 0.18$	$p_{\sigma'}$	0.75
	p_π	0.32
C_6H_6 $^1A_{1g}$	$p_{t(CC)}$	0.86
$q(C) = -0.52$	$p_{r(CH)}$	0.82
$\alpha(C) = 0.04$	p_π	0.32
C_6H_5OLi $^1A_1$	$p_{t(CC)}$	0.81
C-para	$p_{r(CH)}$	0.79
$q = -0.40$	p_π	0.40
C-meta	$p_{t(CC)}$	0.92
$q = -0.60$	$p_{r(CH)}$	0.81
	p_π	0.27
C-ortho	$p_{t(CC)}$	0.83
$q = -0.37$	$p_{r(CH)}$	0.75
	p_π	0.42
C-ipso	$p_{t(CC)}$	0.93
$q = -0.69$	$p_{r(CO)}$	0.86
	p_π	0.21
O	$p_{\sigma(OC)}$	1.15
$q = -0.28$	p_n	1.49
	p_π	1.36

[a] $p_{r,t,\pi}$ mean p-orbitals pointing radially out of the ring, tangentially, and vertically, respectively.

Table 11. AO-Occupancies and q Parameters of Atomic p-Shells of Independent Oriented Ground Configuration Atoms in Coplanar (Vertical in Parentheses) Nitrobenzene

atom	AO	W	W_{exp}
C-para	$p_{t(CC)}$	0.88 (0.86)	0.9
$q = -0.60\ (-0.56)$	$p_{r(CH)}$	0.85 (0.84)	0.7
$q_{exp} = -0.4$	p_π	0.27 (0.30)	0.4
C-meta	$p_{t(CC)}$	0.86 (0.87)	0.7
$q = -0.54\ (-0.56)$	$p_{r(CH)}$	0.83 (0.83)	1.1
$q_{exp} = -0.7$	p_π	0.31 (0.30)	0.2
C-ortho	$p_{t(CC)}$	0.84 (0.82)	1.1
$q = -0.61\ (-0.54)$	$p_{r(CH)}$	0.90 (0.87)	0.6
$q_{exp} = -0.5$	p_π	0.26 (0.31)	0.3
C-ipso	$p_{t(CC)}$	0.99 (1.03)	1.2
$q = 0.49\ (0.55)$	$p_{r(CN)}$	0.48 (0.50)	0.2
$q_{exp} = 0.8$	p_π	0.53 (0.46)	0.6
N[a]	$p_{\sigma'(NO)}$	1.18 (1.18)	1.1
$q = -0.52\ (-0.52)$	$p_{\sigma(NC)}$	1.17 (1.17)	1.3
$q_{exp} = -0.6$	p_π	0.65 (0.65)	0.6
O	$p_{\sigma(ON)}$	1.04 (1.05)	1.2
$q = 0.58\ (0.61)$	p_n	1.72 (1.74)	1.5
$q_{exp} = 0.2$	p_π	1.24 (1.21)	1.3

[a] $Np\pi$ and $Cp\pi$ are parallel for the coplanar conformation but orthogonal in the torsioned vertical conformation.

values lie within the rather wide range given by other authors (see Table 15). According to our q values, −NO_2 is more electronegative than −NO by 0.6 units, while the literature values are less different.

In general, electron correlation tends to smooth the HF-density fluctuations.[49,50] This trend is also seen here: the atomic quadrupolarities are lower at the MP2 than at the SCF level. However, the trends are similar.

Table 12. AO-Occupancies and q and a Parameters of Atomic p-Shells of Independent Oriented Ground Configuration Atoms in Coplanar (Vertical in Parentheses) Nitrosobenzene

atom[a]	AO	W
C-para	$p_{t(CC)}$	0.89 (0.86)
$q = -0.60\ (-0.54)$	$p_{r(CH)}$	0.84 (0.83)
	p_π	0.27 (0.31)
C-meta	$p_{t(CC)}$	0.86 (0.88)
$q = -0.52\ (-0.57)$	$p_{r(CH)}$	0.82 (0.83)
	p_π	0.32 (0.29)
C-ortho	$p_{t(CC)}$	0.87 (0.85)
$q = -0.60\ (-0.51)$	$p_{r(CH)}$	0.86 (0.82)
	p_π	0.27 (0.33)
C-ipso	$p_{t(CC)}$	0.94 (1.01)
$q = 0.41\ (0.52)$	$p_{r(CN)}$	0.61 (0.60)
	p_π	0.45 (0.39)
N	p_σ	1.04 (1.05)
$q = -0.74\ (-0.75)$	p_n	1.45 (1.45)
$a = 0.41\ (0.40)$	p_π	0.51 (0.50)
O	$p_{\sigma(ON)}$	1.19 (1.21)
$q = 0.73\ (0.79)$	p_n	1.82 (1.86)
$a = 0.20\ (0.28)$	p_π	0.99 (0.93)

[a] Both ortho and meta atoms are so similar that only one entry is given for each one.

Table 13. AO-Occupancies and q Parameters of Atomic p-Shells of Independent Oriented Ground Configuration Atoms in Coplanar (Vertical in Parentheses) p-Li Nitrophenolate

atom[a]	AO	W
C-para	$P_{t(CC)}$	0.95 (0.93)
$q = -0.75\ (-0.70)$	$p_{r(CO)}$	0.88 (0.87)
	p_π	0.17 (0.20)
C-meta	$p_{t(CC)}$	0.82 (0.82)
$q = -0.37\ (-0.40)$	$p_{r(CH)}$	0.76 (0.78)
	p_π	0.42 (0.40)
C-ortho	$p_{t(CC)}$	0.90 (0.88)
$q = -0.67\ (-0.58)$	$p_{r(CH)}$	0.88 (0.84)
	p_π	0.22 (0.28)
C-ipso	$p_{t(CC)}$	0.90 (0.97)
$q = 0.35\ (0.46)$	$p_{r(CN)}$	0.48 (0.47)
	p_π	0.62 (0.56)
N	$p_{\sigma'(NO)}$	1.20 (1.20)
$q = -0.56\ (-0.56)$	$p_{\sigma(NC)}$	1.17 (1.17)
	p_π	0.63 (0.63)
O(nitro)	$p_{\sigma(ON)}$	1.09 (1.11)
$q = 0.52\ (0.55)$	p_n	1.68 (1.70)
	p_π	1.23 (1.19)
O(phenolate)	$p_{\sigma(OC)}$	1.16 (1.15)
$q = -0.26\ (-0.28)$	p_n	1.50 (1.49)
	p_π	1.34 (1.36)

[a] Para, etc. refer to the nitro group.

Therefore and because of reasons of computational resources, we will be content with HF results for the other molecules.

4.2 Benzene and Li Phenolate (Table 10). At first, a paradox must be explained. Carbon atoms are nearly spherical ($q \approx 0$) in singly bonded tetrahedral nonpolar compounds. When bonded to electron-rich ligands, the carbon becomes disklike, *vertical* (!) to the C−X bond, (see above). In the case of trigonal carbons, the π-bond overlaying a σ-bond compresses the latter. While this reduces the σ-contribution to the bond energy, it increases the σ-overlap and therefore the electron density accumulation on the σ-bond path. On the other hand, π-electron

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(50) Irle, S. Diploma thesis, Siegen, 1992.

Table 14. AO-Occupancies and q and a Parameters of Atomic p-Shells of Independent Oriented Ground Configuration Atoms in Coplanar (Vertical in Parentheses) *p*-Li Nitrosophonolate

atom[a]	AO	W
C-para	$p_{t(CC)}$	0.95 (0.93)
$q = -0.75$ (-0.69)	$p_{r(CO)}$	0.88 (0.86)
	p_{π}	0.17 (0.21)
C-meta	$p_{t(CC)}$	0.82 (0.83)
$q = -0.37$ (-0.40)	$p_{r(CH)}$	0.76 (0.77)
	p_{π}	0.42 (0.40)
C-ortho	$p_{t(CC)}$	0.91 (0.87)
$q = -0.67$ (-0.55)	$p_{r(CH)}$	0.87 (0.83)
	p_{π}	0.22 (0.30)
C-ipso	$p_{t(CC)}$	0.84 (0.94)
$q = 0.26$ (0.41)	$p_{r(CN)}$	0.62 (0.59)
	p_{π}	0.54 (0.47)
N	p_{n}	1.44 (1.45)
$q = -0.77$ (-0.78)	p_{σ}	1.07 (1.07)
	p_{π}	0.49 (0.48)
O(nitroso)	$p_{\sigma(ON)}$	1.22 (1.27)
$q = 0.66$ (0.73)	p_{n}	1.77 (1.82)
	p_{π}	1.01 (0.91)
O(phenolate)	$p_{\sigma(OC)}$	1.16 (1.14)
$q = -0.26$ (-0.29)	p_{n}	1.50 (1.49)
	p_{π}	1.34 (1.37)

[a] Para, etc. refer to the nitroso group. Both ortho and both meta atoms are so similar that only one entry is given for each one.

densities are more diffuse and less apparent than σ-densities. Consequently, the density in π-bonded systems is well approximated by a promolecule of atoms with *low* p_{π}-occupancy and high p_{σ}-occupancy. That is, the nonpolar trigonal carbon is also disklike; however, it is *coplanar* to the bond plane. Finally, we note that, obviously, AO *populations* derived from theoretical *wavefunctions* (e.g., Mulliken populations) and the present AO *occupancies* derivable from experimental[41,51] or theoretical *densities*[40,48,50] are by definition two different quantities.

So, in general, the aromatic carbons are disklike.[41,50] In benzene itself, $q = -0.52$. The central carbon atoms in butadiene have the same q values but are less cylindrical ($a = 0.18$) than in benzene ($a = 0.04$). In passing, we note that the parameters of the terminal C-atoms of butadiene are similar to those of ethene.

In Li phenolate, the q values "oscillate" about the value of $q = -0.5$ along the ring (+M effect). The large π-density on the oxygen corresponds to a reduced π-occupancy of the pπ-AO of the ipso-carbon with more negative q value. Also the meta-q is more negative than in benzene, while the q values and pπ-occupancies of the ortho and para carbons are higher. The negative q value of the ipso-C indicates the low electronegativity (+I effect) of $-$OLi.

4.3 Nitrobenzene (Table 11). In nitrobenzene, the theoretical q values (≈ -0.55) are similar to the benzene value, except for the ortho- and para-carbons of the coplanar structure ($q \approx -0.60$). This is an indication of a NO_2/C_6H_5 π-interaction in the planar configuration of a type opposite that in the Li phenolate (weak $-$M effect). There is a significant inductive transfer of electron density from the $p_{\sigma(CN)}$-AO of the ipso-carbon to the other two Cp-AOs, corresponding to the large group electronegativity of $-NO_2$ of ~4 (see Table 15). The p_{π} occupancy of the ipso-carbon is reduced as for the other carbons, but less so in coplanar geometry. This again indicates some $O_2^{\delta-}N = C_6^{\delta+}H_5$ character. The N and O atoms change rather little upon $-NO_2$ rotation.

The recent experimental X-ray diffraction data of Boese et al.[21] have also been analyzed. Despite the high quality of the geometric parameters of the atomic cores (Table 4), the accuracy of the valence density parameters (W_{exp} and q_{exp} in Table 11) is only sufficient to reproduce the dominant trends. The pπ-occupancies of the benzene carbons and of the nitro nitrogen are low; the ipso-carbon has also a low p-occupancy toward the nitro group.

4.4 Nitrosobenzene (Table 12). The atomic shapes in nitroso- and nitrobenzene are qualitatively similar. There is comparatively low π-occupancy at the ortho- and para-positions and relatively high π-occupancy on the ipso-carbon for the coplanar geometry, while less occupancy variation occurs for the vertical conformer. Thus, according to the atomic shape criterion, planar nitrosobenzene undergoes mesomerism similar to that of nitrobenzene. However, the variation of the q-values upon 90°-torsion is larger for the nitroso (~15%) than for the nitro compound (~10%), indicating somewhat larger $-$M effect for the $-$NO group. The inductive influence of $-$NO, as determined from the p_t/p_r asymmetry of the ipso-carbon, corresponds to an electronegativity of ~3.5.

4.5 Li Nitro- and Nitrosophenolates (Tables 13 and 14). A detailed comparison of occupancies and q parameters of the *carbon atoms* with those of Li phenolate and of nitro- and nitrosobenzene shows that the substituent effects on the density are approximately additive. *No synergic* effects on the carbon atoms are apparent. While the inductive effects are of the order $-I(NO_2) > -I(NO) > +I(OLi)$, the mesomeric effects vary according to $+M(OLi) > -M(NO) > -M(NO_2)$.

Concerning the q values of the *N and O atoms*, they are quite similar in the five nitro compounds ($q(N) = -0.5_3$, $q(O) \approx +0.5_6$) and nitroso compounds ($q(N) = -0.7_6$, $q(O) \approx +0.7_3$) with one exception: the q value and asymmetry of N is significantly modified by the strong mesomeric interaction of $-$NO with the benzene ring and through-resonance to $-$OLi in planar Li nitrosophenolate.

The 2p-AO occupancies, and also the 2p-AO directions, are presented in graphical form in Figure 1 for benzene and Li nitrophenolate. The "rotation" of the carbon AOs in the benzene ring upon substitution is obvious. No additional interesting trends could be found within the set of molecules (see for instance the projected chemical difference density maps in Figure 2[34,40,48]). Therefore, no further graphs are shown.

5. Atomic Charges and Bond Orders

5.1 Effective Charge Transfer. There exist many experimentally and theoretically based charge scales in the literature. Despite their quite different conceptual bases, a factor analysis of 36 charge scales has shown that there is only *one* principal component which covers more than 90% of the charge value variations.[52] Namely, the different charge definitions mainly differ in their effective charge units and only slightly in the relative

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(52) Meister, J.; Schwarz, W. H. E. *J. Phys. Chem.* **1994**, *98*, 8245–8252.

Table 15. Electronegativities of −NO and −NO$_2$ in Pauling Units

	Bratsch[25] or Sanderson[26]	Inamoto and Masuda[27]	Huheey[24]		this work, from q	
			to Csp^3	to Csp^2	to Csp^3	to Csp^2
−NO	3.2	3.6	4.2	4.7	3.4	3.6
−NO$_2$	3.3	3.4	4.3	4.8	4.0	4.2

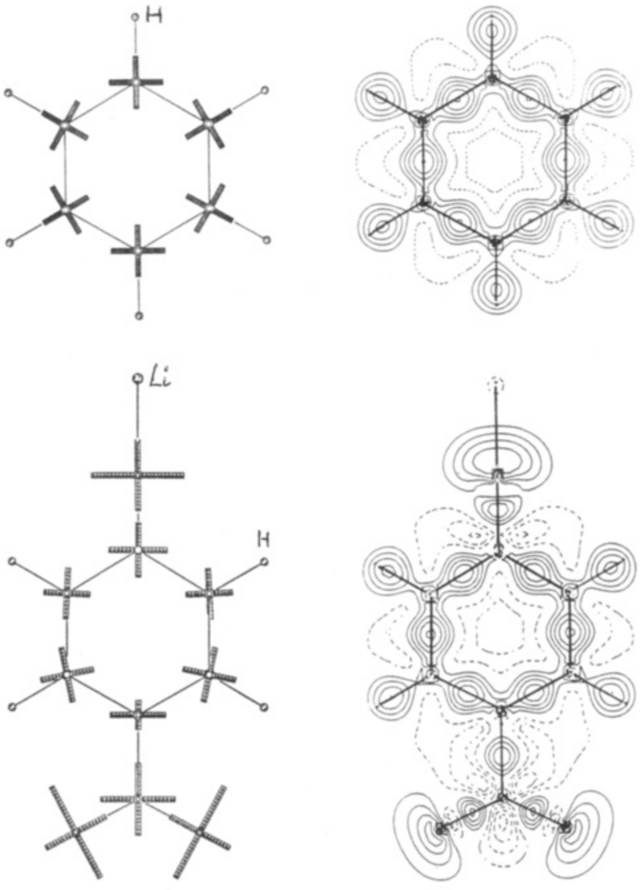

Figure 1. Benzene (top) and planar Li nitrophenolate (bottom). Left: the lengths and directions of the sticks represent the occupancies and orientations, respectively, of the 2p-orbitals of the atomic ground configuration, which optimally approximate the electron density of the molecule. Right: The corresponding difference density (CDD as defined in refs 34, 40, and 48) projected onto the molecular plane. The distance of contour lines is 0.1 e/Å^2.

orders of charge values. That is: it has been found empirically[52] that the conceptual differences between different definitions of atomic charges are comparatively small. The largest amount of physical information is carried by the dominant factor, which is the weighted average of the conceptually and physically different charge scales.

To this end we have used the charge values of five theoretical scales. The classical Mulliken gross charges (MC)[43] and the similar, but somewhat less basis set sensitive, natural charges (NC)[44] both depend on the wavefunction, i.e., on the one-particle density *operator*. The charges simulating the molecular electrostatic potential (CHELPG)[45] and the ones defined by Bader (BC)[42] are derived from the one-particle density *function*. While the MC, NC, and CHELPG are of a comparable order of magnitude, the Bader charges are about three times as large (see Table 16). One drawback of Bader's definition is that a superposition of *neutral*, *spherical*, *unperturbed* atoms may already yield large BC. Maslen and Spackman[53] suggested that these artifacts be subtracted. We have modified Maslen's approach by using the oriented (instead of the spherically averaged) neutral independent atoms as the reference (MMC = modified Maslen charges).[48,50,53] The mean values of these five charge scales (BC with weight 0.33) are presented in the last block of Table 16. Statistical and systematic errors and specific factors are reduced in these averaged values, and only they will now be discussed.

LiO−, vertical −NO, and vertical −NO$_2$ causes flows of 0.12, 0.23, and 0.28 e, respectively, out of the ring. The effects are roughly additive. Their order is consistent with the order of inductive effects derived in section 4.

When −NO$_x$ is rotated into the ring plane, the charge on the ring increases by +0.03 e for both nitro- and nitrosobenzene. In the phenolates, however, this effect is larger, especially for nitrosophenolate. This is another example for the synergic through-resonance occurring for the nitro and more so for the nitroso compounds.

5.2 Charges on the Nitro and Nitroso Groups. Average charge distributions on the atoms of the nitro and nitroso groups in the different molecules are displayed in Table 17. First, we note the larger negative charge on oxygen and especially the large positive charge on nitrogen in −NO$_2$, as compared to −NO. This supports the description of the nitro group by Chart 2 as well as the larger electronegativity and −I effect of nitro than nitroso.

Second, the charges on oxygen are in general more influenced than those on nitrogen. Planarization increases the negative O charge more on nitroso than on nitro, especially in the case of *p*-LiO− substitution.

5.3 Bond Orders. Mayer-[36] and AOM-bond orders[35] are presented in Figure 2. Natural bond orders[44] are rather similar to the Mulliken[43] or Mayer ones, but show even less variation in general and are not displayed here.

Only three trends are obvious: The N−O bond order in −NO is about 0.2 larger than in −NO$_2$. The PhNO$_x$ bond order increases by about 0.1 when NO$_x$ is rotated from the vertical to the planar conformation. A quinoidic bond order alternation of about 0.1 is brought about by LiO−, and the weak bond order alternation due to planar −NO and the even weaker one due to −NO$_2$ is enhanced to about 0.2 in the p-LiO−NO$_x$ compounds. So, according to the present criterion, the very small resonance of −NO$_2$, and the small resonance of −NO with the benzene ring, are overadditively increased by the strongly mesomeric donor LiO−.

5.4 Bader's Bond Ellipticities. Bader defined the bond ellipticity ϵ[42,54] and suggested it as the measure of π-character of the bond. We have calculated them using the HF/SVP approach for all molecules for consistency reasons. We chose the ϵ-values of $H_2C{=}CH_2$ (0.418), $H_2C{=}NH$ (0.226), and $HN{=}O$ (0.383) as 100% reference values and display the percent ellipticities of the 10 benzene derivatives in Figure 3. The ϵ-value for the C−C bond in benzene is 0.233/0.418 = 56%. The ellipticities

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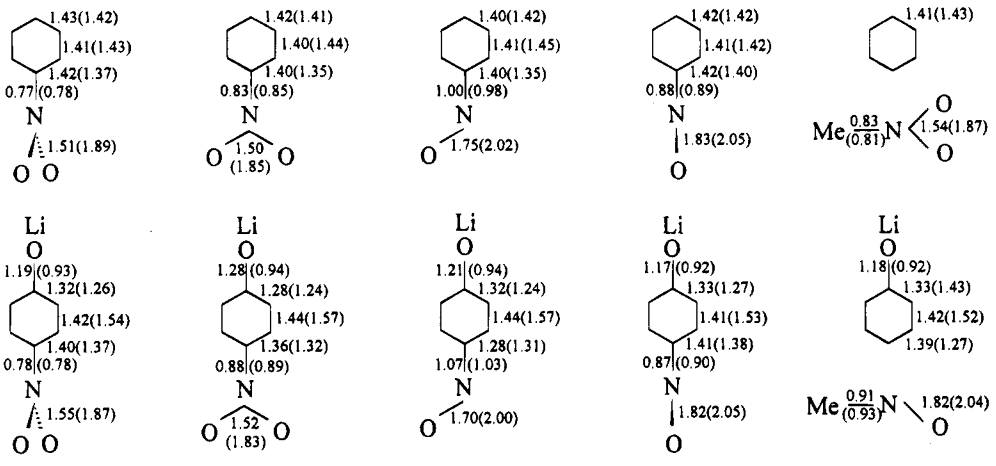

Figure 2. Mayer bond orders (AOM bond orders in parentheses). Left−right averages are given for the planar nitroso compounds.

Table 16. Charges on the Donor, the Ring, and the Acceptor (in $10^{-2}|e|$) According to Different Charge Definitions

	Mulliken MC,[43]			Weinhold et al. NC,[44]			el. stat. pot. CHELPG,[45]			mod. Maslen MMC,[48,50,53]			Bader BC,[42]			avg charge[a]		
method	LiO	Ph	NO_x	LiO	Ph	NO_x	LiO	Ph	NO_x	LiO	Ph	NO_x	LiO	Ph	NO_x	LiO	Ph	NO_x
nitrobenzene, ∥		36	−36		30	−30		19	−19		47	−47		68	−68		30	−30
nitrobenzene, ⊥		36	−36		27	−27		10	−10		46	−46		66	−66		27	−27
nitrosobenzene, ∥		23	−23		22	−22		37	−37		30	−30		57	−57		25	−25
nitrosobenzene, ⊥		21	−21		16	−16		32	−32		28	−28		49	−49		23	−23
nitrophenolate, ∥	4	34	−38	−9	42	−33	−12	28	−16	−14	65	−51	−58	132	−74	−10	43	−33
nitrophenolate, ⊥	2	36	−38	−10	37	−27	−13	19	−6	−16	63	−47	−58	124	−66	−11	41	−30
nitrosophenolate, ∥	4	22	−26	−9	36	−27	−8	50	−42	−15	58	−43	−58	126	−68	−9	42	−33
nitrosophenolate, ⊥	0	22	−22	−11	27	−16	−13	45	−32	−18	49	−31	−59	111	−52	−12	35	−23
phenolate	1	−1		−12	12		−15	15		−16	16		−60	60		−12	12	

[a] Bader charges with weight 0.33.

Table 17. Average Charge Values on N and O

	nitro		nitroso	
molecule	N	O	N	O
$MeNO_x$	0.47	−0.37	0.00	−0.25
$PhNO_x(\perp)$	0.43	−0.36	0.00	−0.23
$PhNO_x(\parallel)$	0.40	−0.35	0.00	−0.28
$LiOPhNO_x(\perp)$	0.50	−0.40	0.01	−0.24
$LiOPhNO_x(\parallel)$	0.47	−0.40	−0.01	−0.32

of the C−O bonds in $H_2C{=}O$ and in RPhOLi are low (≤ 0.1) and are not displayed.

The only remarkable trends are the following: $\epsilon(C_{ortho}-C_{meta})$ increases by about 20% when LiO− is introduced; also ϵ(C−N) increases if the NO− and especially the NO_2− groups are coplanar. This is another indication of $LiOPhNO_x$ through-resonance. Although the $PhNO_2$ bond has more Bader π-character than the PhNO bond, its value for the planar benzene derivative at least *in comparison to* the methyl or vertical benzene derivatives is larger for −NO than for $-NO_2$.

The N−O bond is, unexpectedly, more elliptic in NO_2 ($\epsilon \approx 35\%$) than in NO ($\epsilon \approx 20\%$). The $C_{ipso}-C_{ortho}$ ϵ value increases from benzene ($\epsilon = 55\%$) to the planar ($\epsilon \approx 60\%$) and further to the torsioned compounds ($\epsilon \approx 67\%$). No other clear, significant changes occur in the ring. These "Bader-features" are not easily fitted into the picture we have developed so far.

5.5 Ellipticities of DD Plots. In Figure 4 we present difference densities (DD) of nitrobenzene with respect to a procrystal of spherically averaged atoms, generated from the experimental X-ray diffraction data of Boese et al.[21] The upper figures show the DD on cuts vertically through the bonds at their midpoints; they are nearly indentical with Figure 6 of the original authors. If these plots are rotated by 90° and subtracted, one obtains empty plots for axially symmetric σ-bonds. The stronger the π-character of the bond, the larger the quadrupolar feature, as shown in the lower diagrams of Figure 4. The maxima of these bond-density ellipticities are given in Table 18, together with the corresponding $\sigma-\pi$ bond orders.

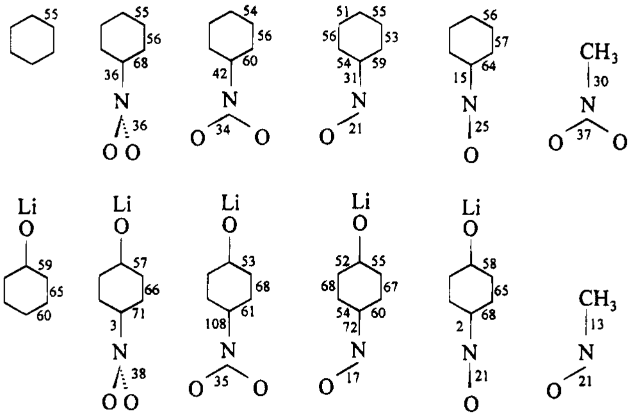

Figure 3. Bader's bond ellipticities in percent of the values for $H_2C{=}CH_2$ ($\epsilon = 0.418$), $H_2C{=}NH$ ($\epsilon = 0.226$), and $NH{=}O$ ($\epsilon = 0.383$).

According to the density criterion, there exists some mesomerism between benzene and coplanar $-NO_2$, though there is no indication of quinoidic character of the benzene ring. An increase of ellipticity of the C1−C2 and C1−C6 bonds in comparison with the other C−C bonds in the ring is in line with the electronegativity effect of the NO_2 group (Walsh−Bent rule[47]) leading to a shortening of the former bonds and to their increased bond order. A tendency to antiquioidic π-bond orders is sometimes

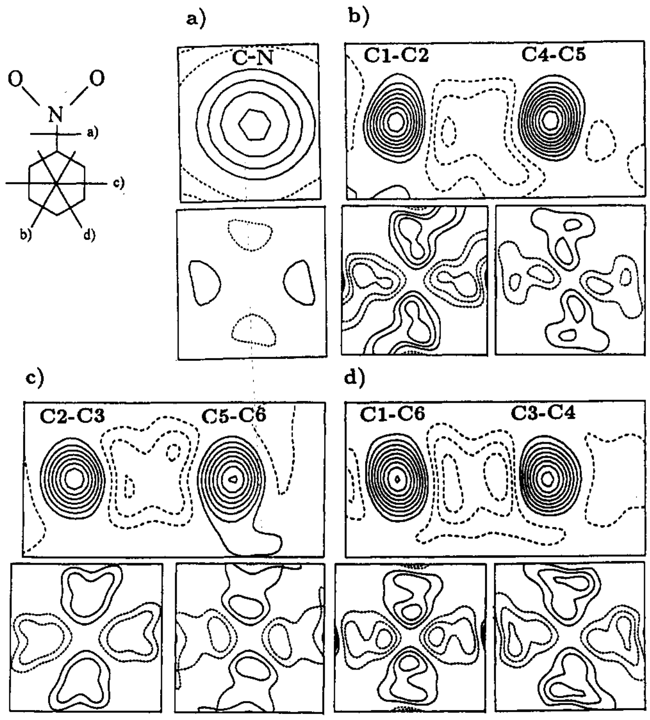

Figure 4. Difference density (DD) maps of nitrobenzene with respect to a procrystal of spherically averaged atoms, on cuts vertical to the molecular plane though the midpoints of bonds, as shown in the left top diagram. Under each DD map, the difference between this map and the same map rotated by 90° is shown ($\Delta\Delta h$), indicating the π-bond ellipticity. Contour line values are $\pm 0.05n$ e/Å^3, $n = 1, 2, 3, \ldots$.

Table 18. Bond Ellipticities of Density Plots, Based on Experimental X-ray Scattering Data of Nitrobenzene[21]

bond	$\Delta\Delta\varrho$ (e/Å^3)	corresponding bond oder
C−N	0.06	1.2
C1−C2	0.16	
C1−C6	0.18	1.6
C2−C3	0.15	
C6−C5	0.14	1.5
C3−C4	0.13	
C5−C4	0.12	1.4

observed as a consequence of σ-electron invoked shortening of the ipso-ortho bonds.[55]

Table 18 demonstrates a right−left asymmetry of the benzene ring in crystalline nitrobenzene. There exist three O···H contacts between the $-NO_2$ group of one molecule and the benzene ring of other molecules (Figure 5), which are slightly shorter (256−258 pm) than the sum of van der Waals radii (260 pm). While oxygen O1 forms two hydrogen contacts slightly above and below the NO_2-plane at N−O···H angles of 162° and 141° with H'_4 and H''_3, oxygen O2 forms a contact quite off the NO_2 plane with H'''_2 at an N−O···H angle of 135°. The latter interaction had already been mentioned by Boese et al.[21]

6. Energies

6.1 Torsional Barriers. It is known from the literature[20,23] that torsional barriers of nitro compounds, reasonably accurate for comparison with experiment, can only be obtained at the MP2 level of theory. Our SCF and MP2 calculations are summarized in Tables 19 and 20. Our results on $PhNO_x$ confirm the literature values.

At the less accurate SCF level of approximation, the barrier of $PhNO_2$ is as large as 7−8 kcal/mol, while that of PhNO is even larger, 8−9 kcal/mol. Neglecting the nonbonded interactions, this would indicate significant resonance in nitrosobenzene and nearly so in nitrobenzene. However, these effects are reduced by electron correlation: by more than 1 kcal/mol in PhNO, but by ~3.5 kcal/mol in $PhNO_2$. Our barrier for $PhNO_2$ (4.5 kcal/mol) is in good agreement with the best other theoretical calculation (4.6 kcal/mol[20]) and experimental determination (4.0 kcal/mol[18]). So, the resonance seems to be considerably weaker in nitrobenzene at the correlated level.

The correlation effects are very similar in the phenolates which have so far not been investigated in this context. The p-LiO substitution enhances the torsional barrier by ~2.5 kcal/mol for the nitro compounds and by ~4.5 kcal/mol for the nitroso compounds, showing that through-resonance is more important for nitroso- than for nitroaryls, with respect to the torsional barriers.

6.2 Isodesmic Reactions. We have investigated the isodesmic reactions

$$\mathrm{LiOPh} + \mathrm{PhNO}_x = \mathrm{LiOPhNO}_x + \mathrm{Ph}$$

for the planar conformations. Geometries were optimized using the SVP basis at the SCF level. Energies were then calculated at the MP2 level. The following reaction energies were obtained (the less accurate SCF values are in parentheses)

$$\text{for } -\mathrm{NO}_2\text{:}\quad -5.7 \text{ kcal/mol } (-8.5 \text{ kcal/mol})$$

$$\text{for } -\mathrm{NO}\text{:}\quad -6.3 \text{ kcal/mol } (-7.1 \text{ kcal/mol})$$

Accordingly, the donor−acceptor interaction through the ring is important and stabilizes the disubstituted aromatics by about 6 kcal/mol. This effect is bigger for −NO at the MP2 level. (It is still smaller for −NO at the SCF level of approximation, so correlation is again important concerning the trends.) These results should only be taken as qualitatively correct because of limited correlation, limited basis sets, and basis superposition defects.

7. Conclusions

The *molecular geometries* indicate a smaller −I effect of −NO than of $-NO_2$. Only coplanar −NO causes some mesomeric bond length alternation in the ring which is enhanced by a para-donor (LiO−) which itself exerts +I and +M effects. Para-LiO− induces some through-resonance to coplanar $-NO_2$.

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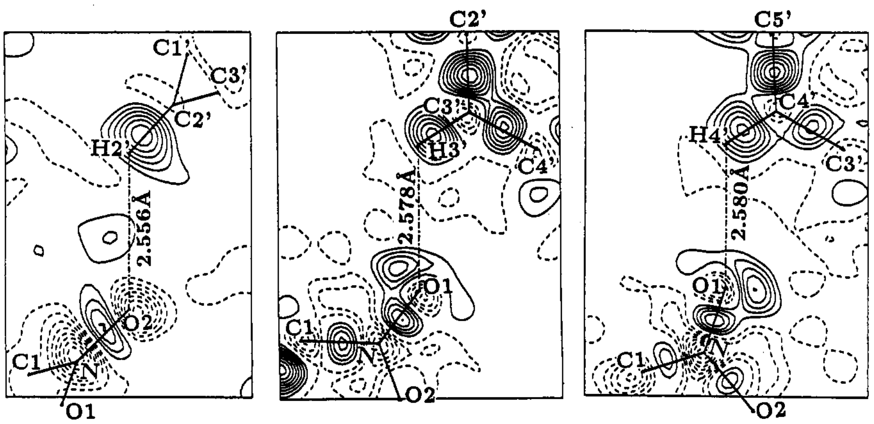

Figure 5. Difference density maps of O⋯H contacts in crystalline nitrobenzene. Contour line values ±0.05*n* e/Å^3, *n* = 1, 2, 3, ….

Table 19. Total Molecular Energies (au) of DPhA Molecules

D	A	HF/6-311G**//MP2/6-31G*	MP2/6-311G**//MP2/6-31G*	E_{cor}[a]	ΔE_{cor}[b]
H	∥, NO_2	−434.265 524	−435.671 634	−1.406 110	
H	⊥, NO_2	−434.252 862	−435.664 374	−1.411 512	−3.39
H	∥, NO	−359.417 852	−360.604 674	−1.186 822	
H	⊥, NO	−359.404 202	−360.592 702	−1.188 500	−1.05
		HF/SVP//HF/SVP	MP2/SVP//HF/SVP		
LiO	∥, NO_2	−515.555 962	−517.043 233	−1.487 271	
LiO	⊥, NO_2	−515.538 774	−517.031 842	−1.493 068	−3.64
LiO	∥, NO	−440.782 861	−442.069 257	−1.286 396	
LiO	⊥, NO	−440.761 863	−442.050 080	−1.288 217	−1.14

[a] $E_{cor} = E_{MP2} - E_{HF}$. [b] $\Delta E_{cor} = E_{cor}(\perp) - E_{cor}(\parallel)$ (kcal/mol).

Table 20. Rotational Barriers (kcal/mol) of Nitrobenzene and Nitrosobenzene

D	A	HF/6-311G**//MP2/6-31G*	MP2/6-311G**//MP2/6-31G*	exptl	others calcd
H	NO_2	7.9	4.5	2.8–4.0[16–18]	3.5–5.8[20,22,68–70]
H	NO	8.6	7.5	4 ± 1[19]	4.8–10.4[69,70]
		HF/SVP//HF/SVP	MP2/SVP//HF/SVP		
LiO	NO_2	10.8	7.1		
LiO	NO	13.2	12.0		

The *electron density* seems to be a more sensitive indicator of subtle substituent effects, while the ring geometry is nearly unaffected by a single $-NO_x$ substituent. A small +I effect of LiO−, a medium −I effect of −NO, a larger −I effect of $-NO_2$, a large +M effect of LiO−, a medium −M effect of coplanar −NO, and a weak −M effect of coplanar $-NO_2$ could be deduced from the *shapes of the oriented independent atoms* in the molecules (OIAM approach[41,48]).

Another feature of the electron density is the *bond ellipticity*. Bader's ellipticity parameter indicates an M effect by LiO−, more π-character of the $C-NO_2$ than of the C−NO bond, but a larger M effect in planar PhNO than in planar $PhNO_2$, and strong through-resonance in $LiOPhNO_x$, especially for the nitro compound. The bond ellipticity as defined in section 5.5 also indicates some π-character of the planar $PhNO_2$ bond.

Total densities and the various kinds of other *difference density* maps are less informative in this respect, independent of whether planar cuts or projections onto planes are considered. Namely, in the traditional densities and difference densities, the interesting features are buried under the large atomic core densities and under the valence shell quadrupolar features. Furthermore, chemical deformations accompanying bond formation are not very specific,[48] the main information being contained in the shapes of the independent atoms' valence shells.

The most reliable *atomic charges* correspond to the principal component or average of many different charge scales (being based on different quantities such as electron density, wave function, electrostatic potential, etc.). The charges indicate additive I effects increasing in the order LiO < NO < NO_2, and nonadditive M effects especially in the case LiO/NO(∥). Otherwise the +M effects of NO and NO_2 appear similar.

Bond orders are usually derived from the wavefunction. They indicate M effects of the order NO_2 < NO < LiO and strong enhancement for double para-substitution by LiO and NO_x.

Finally, molecular *energy differences* indicates stronger M effect and stronger enhancement of resonance by *p*-LiO− for −NO than for $-NO_2$. Electron correlation is important especially for the nitro compounds.

In summary, the description of even the selected set of observables (geometry, energy, density, etc.) by just two parameters (inductive and mesomeric effects) is only a projection of the real world onto a two-dimensional "flatland". It gives a rough overview of the real behavior, in most cases corresponding to additive inductive influences of the order LiO ≪ NO < NO_2, to mesomeric influences of the order LiO > NO(∥) > NO_2(∥), and to strong and diverse nonlinear (nonadditive) through-resonance effects.

However, it must be remembered that the observables are of different sensitivity to these theoretical constructs. For instance, the strong electronegativity of O may result in the −I effect for one observable, while the electron-richness of LiO may dominate and result in the +I effect for another observable. Similarly, the order of NO and NO_2 with respect to I and M effects on different observables is not always the one given above. For instance, if one property depends on the parameter value X and another property depends on the change, sensitivity, derivative X′ of this parameter, we may easily encounter different orders, namely $X_1 < X_2$ but $X'_2 > X'_1$. We remind the reader here, for intance, of the C−N ellipticity discussed in section 5.3.

The overall result is that NO_2 may be *described* as being somewhat more electronegative than NO, while exerting a smaller mesomeric effect than NO in the coplanar arrangements. We do not support those textbooks which take nitrobenzene as a paradigm for the +M effect, while benzonitrile indeed exhibits this kind of resonance according to several criteria.[65]

However, these "effects", especially the mesomeric ones, are nonlinear, even nonadditive, i.e., their order with respect to the investigated changes (additional substituents; most probably also different surroundings, solvents, hydrogen bonds) and with respect to the property or observable under discussion is not always the same.

Since chemical concepts are based on some general views and on the attempt of a severe reduction of the richness of chemistry, they are bound to limited applicability. On one hand not all phenomena of reality are explainable in terms of simple concepts; on the other hand, not all chemical concepts can rigorously be correlated with the fundamental theory of matter, that is to say with reality. Nevertheless, it is valuable to recall that Coulson[56] very highly estimated the value of "primitive patterns of understanding" for the interpretation of complex chemical phenomena. At least at the beginning steps of study of chemical problems they open fruitful ways, and then they often become insufficient and more advanced tools must be introduced.

Acknowledgment. W.H.E.S. gratefully acknowledges the overwhelming hospitality he experienced in Olsztyn and in Warszawa. We thank R. Boese for his X-ray data set and A. Maercker for valuable comments. This work has financially been supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie (W.H.E.S.), and by the Polish grant BST/24/94 (to T.M.K.).

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