

Figure 13. The $(\text{CH}_3)_3\text{C}^+\text{Cl}^-$ ion pair at a C-Cl separation of 7.25 Å. The rightmost hatched oxygen indicates a water molecule that is bridging between the chloride ion and the water molecule coordinated to the carbenium carbon. The latter's hydrogens are now oriented up to accommodate the hydrogen bond in contrast to Figure 11. 7–8 hydrogen bonds with the chloride ion are also clearly visible. For additional details, see Figure 10.

kcal/mol for the interaction energies.

Again, it is seen that 1 water molecule is associated with the carbenium carbon out to $r_c = 5.25$ Å, at which point a water molecule penetrates between the ions. The decrease in the primary hydration number at 7.75 Å may be partly statistical noise since the integral of the C–O rdf is still 1.8 (Table III). However, plots of configurations from the run at $r_c = 7.75$ Å do show an increase of disorder for the water between the ions. The interaction energies for the water molecules on the carbenium carbon show reasonable variations. Up to $r_c = 5.25$ Å, the water molecule on the backside of the $t\text{-Bu}^+$ has a net attractive interaction of ca. 10 kcal/mol with the ion pair. This value is less than for the minimum in Figure 3 because the orientation of this water molecule is clearly repulsive with respect to the chloride ion. Then between $r_c = 5.25$ and 6.75 Å the attraction is much greater because the water molecule between the ions interacts favorably with both. The attraction decreases to 12–13 kcal/mol beyond $r_c = 7$ Å because the distance to the chlorine is increasing.

The number of primary water molecules for each methyl group is constant at about 3. This is 1–2 less than the number of neighbors from integrating the $\text{CH}_3\text{-O}$ rdf, so there are contributions from primary water molecules on the other solute atoms to the first band in the rdf. The average attractive interaction energy for the primary water molecules on the methyl groups is also relatively constant at 5–7 kcal/mol except for r_c below 3.75

Å. In this region, orientations of the water molecules that are particularly favorable for the cation are unfavorable for the nearby chloride ion, so the net attraction is diminished.

For the chloride ion, the primary hydration numbers are less than the integrals of the Cl–O rdfs (Table III) out to $r_c = 6.25$ Å. In this region, 1–2 water molecules with oxygens within 3.85 Å of the chlorine are closer to another solute atom. This is certainly the case for the intervening water molecule at $r_c = 5.75$ and 6.25 Å. However, beyond $r_c = 6.25$ Å the primary hydration numbers are identical with the integrals of the first peaks in the Cl–O rdfs. Thus, the separation between the ions is then great enough that the first shell of water molecules around the chlorine is distinct (Figure 13). Meanwhile, the average interaction energies for the primary water molecules on the chlorine with the ion pair become more favorable by roughly 2 kcal/mol between $r_c = 2.75$ and 7.75 Å. This is again associated with the fact that the water molecules on the backside of the chloride ion are oriented in an unfavorable way with respect to the cation. The energetic consequence is most severe at small interionic separations.

Conclusion

The present theoretical study has provided a view of the energetics and variations in hydration in the ion-pair region for the prototypical $\text{S}_{\text{N}}1$ reaction of $t\text{-BuCl}$ in water. Support was found for the existence of a contact ion pair, while solvent-separated ion pairs and “free ions” do not appear to be energetically distinct species. The Monte Carlo results predict a significant barrier between the contact and solvent-separated ion-pair regions. The insertion of a water molecule between the ions occurs at separations of 5–5.5 Å and is preceded by a buildup of water molecules off the C–Cl axis. The computations involved state-of-the-art methodology in statistical mechanics; however, they still need to be considered preliminary, particularly in view of the simplicity of the potential functions that were used. The lack of polarization is especially a concern, though the nature of the perturbation calculations is such that some compensation of errors for the reference and perturbed systems is probable. The same is true for small errors in the balance between the interionic and ion-solvent interactions. The computationally efficient extended RISM approach was again found to reveal similar qualitative trends as the simulations. The origin of the quantitative differences requires further study; the present comparisons have suggested some areas for analysis.

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Examination of Some Effects of NO_2 Rotation in Nitrobenzene

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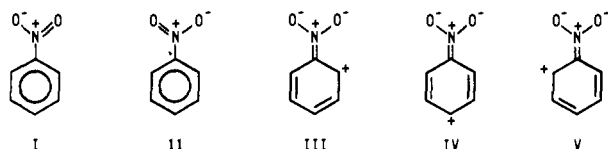
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Abstract: A computational analysis has been made of some of the effects of rotating the NO_2 group of nitrobenzene by 90° from its equilibrium position in the plane of the aromatic ring. An ab initio SCF approach was used to compute the optimized structures and molecular electrostatic potentials of these two forms of nitrobenzene. A comparison of the calculated structures indicates that there is only a very small degree of conjugation between the nitro group and the aromatic ring in the equilibrium form of the molecule. Chemical consequences of NO_2 rotation are expected to include a decreased reactivity toward nucleophiles, but a slightly greater susceptibility to electrophilic attack.

I. Conjugation in Nitrobenzene

Nitrobenzene is commonly described in terms of resonance structures such as I–V. The NO_2 group is strongly electron

withdrawing; this is usually attributed to induction and also the contributions of structures III–V, and accounts for the observed deactivation of the aromatic ring toward electrophilic attack.¹



In this withdrawal of charge from the ring, the role of induction is by far the dominant one.¹⁻³ One quantitative indication of this is provided by the Taft substituent constants.⁴ The nitro group has one of the largest listed values for σ_1 , which measures the extent of inductive electron attraction, whereas its σ_R , reflecting the resonance effect, is relatively small in magnitude.

In a recent analysis of some para-substituted nitrobenzenes, Lipkowitz concluded that conjugation between the NO_2 and the ring occurs only to a small extent, significantly less than has been generally believed.⁵ This view has subsequently been both challenged⁶ and supported.⁷ If Lipkowitz's conclusion is valid, it suggests—for nitrobenzene itself—that structures III–V are of little importance.

This would have significant implications for the interpretation and prediction of the properties of nitro aromatics. In the ground state of nitrobenzene, the NO_2 group is in the plane of the ring.^{8,9} However, the presence of substituents, especially in the ortho positions, can force the NO_2 to rotate (around the C–N bond) out of this plane, by as much as 70° .¹⁰⁻¹² (In the crystalline state, intermolecular forces can also be a factor in causing such rotation.) Such disruption of the coplanarity of the nitro group and the ring would diminish whatever conjugation is present, as represented by structures III–V, and would correspondingly affect the properties of the molecule. Indeed a number of experimental observations (involving, for instance, electronic, NMR, and ESR spectra) have been interpreted on this basis.¹³

It is important to recognize, however, that interference with conjugation is not the only reason why rotation of the NO_2 may lead to some changes in molecular properties. It has been proven rigorously that any change in the relative positions of the nuclei of a system will alter its electronic density distribution.¹⁴ This comes about in response to the new nuclear potential that is then felt by the electrons. It is to be expected, therefore, that there will be some changes in the properties of the system, independent of any resonance or conjugation considerations.

Our objectives in this study have been to determine how rotation of the NO_2 in nitrobenzene through 90° around the C–N bond affects (a) the geometry of the system (i.e., bond lengths and bond angles) and (b) its electrostatic potential. We have accordingly computed optimized structures for nitrobenzene in both its planar equilibrium configuration and also in the rotated form in which the NO_2 group is perpendicular to the plane of the ring. The molecular electrostatic potential, which is a very sensitive indicator of the charge distribution in a system, was then calculated for both states.

II. Methods

The geometry optimizations were carried out with the GAUSSIAN 82 program at the 6-31G level.¹⁵ The resulting structures were

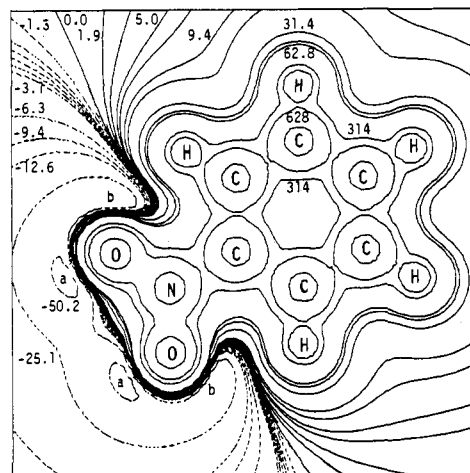


Figure 1. Calculated electrostatic potential of planar equilibrium nitrobenzene in the molecular plane. Dashed contours correspond to negative potentials; all values are in kcal/mol. The most negative points are indicated by a and b, and have the following values: a, -59 kcal/mol; b, -45 kcal/mol.

then used to compute the STO-5G electrostatic potentials.

The electrostatic potential $V(\vec{r})$ that is created at any point \vec{r} in the space around a molecule by its nuclei and electrons is given rigorously by the equation:

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}') d\vec{r}'}{|\vec{r}' - \vec{r}|} \quad (1)$$

Z_A is the nuclear charge on atom A, located at \vec{R}_A , and $\rho(\vec{r}')$ is the molecular electronic density function.

$V(\vec{r})$ provides an effective means for interpreting and predicting chemical reactive behavior, especially toward electrophiles.^{16,17} Equation 1 shows that $V(\vec{r})$ is negative in those regions in which the effects of a molecule's electrons are dominant, and it is to these regions that an approaching electrophile is initially attracted, especially to those points at which $V(\vec{r})$ attains its most negative values (local minima). The electrostatic potential is a real physical property, which can be determined experimentally as well as computationally.¹⁸ Extensive investigations have confirmed that satisfactory electrostatic potentials can be obtained with ab initio SCF procedures using minimum basis sets, such as the STO-5G.^{17,19-21}

III. Results and Discussion

A. Structures. Experience has shown that the optimized geometries of aromatic molecules tend to reflect the role played by resonance in those systems.²²⁻²⁴ This is particularly true when split-valence basis sets are used for the optimization, as in the present work. In view of this, it is significant that the structures calculated for the two forms of nitrobenzene are extremely similar, the largest difference being a $0.01\text{-}\text{\AA}$ increase in the $\text{C}_1\text{-N}$ bond length that accompanies NO_2 rotation. This, together with simultaneous slight shortenings of the N–O and $\text{C}_1\text{-C}_2$ bonds (0.003 and 0.005 \AA , respectively), suggests a small contribution to the equilibrium planar form from structures III–V, in which the double

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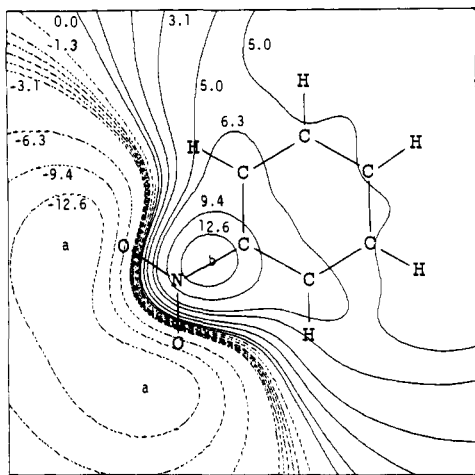


Figure 2. Calculated electrostatic potential of planar equilibrium nitrobenzene in plane 1.75 Å above molecular plane. Dashed contours correspond to negative potentials; all values are in kcal/mol. The planar minima and maxima are indicated by a and b, respectively, and have the following values: a, -16 kcal/mol; b, +15 kcal/mol (above the C-NO₂ bond).

bond character has increased for the C₁-N and decreased for the C₁-C₂ and N-O bonds. However, the magnitude of these differences indicate that the extent of the conjugation with the aromatic ring is very small. In aniline, for example, resonance between the NH₂ and the ring shortens the C-NH₂ distance by fully 0.07 Å compared to its average (aliphatic) value.²⁵

The geometry of our planar form is in excellent agreement with the results of an earlier 6-31 G optimization,²⁶ and also agrees well, overall, with experimentally determined structures.²⁷ Our calculated energy barrier for the C-NO₂ rotation is 8.5 kcal/mol, compared to observed values which range from 2.8 to 3.3 kcal/mol.²⁸

B. Electrostatic Potentials. In the molecular plane of the equilibrium for nitrobenzene, there is a large region of negative electrostatic potential that can be attributed to the lone pairs of the oxygens (Figure 1). The most negative values (local minima) are -45 and -59 kcal/mol. When the NO₂ group is rotated, this negative region remains very similar in form, with the minima now being -49 and -57 kcal/mol. We feel that a comparison of the potentials for the equilibrium and the rotated forms should be based on the -59 and -57 values, since the -45 for the planar system probably reflects some positive contribution from the neighboring hydrogens which is not present when the NO₂ is perpendicular to the ring. Thus we view the oxygen potentials as being slightly more negative in the equilibrium planar form. This could be due to a rearrangement of electronic density that is independent of any conjugation, although it is also consistent with very minor contributions from structures III-V.

Because of the electron-withdrawing power of the nitro group, the electrostatic potential is positive above and below the aromatic ring, for both the planar and the rotated forms of nitrobenzene (Figure 2). The effects of rotating the NO₂ are shown in Figure 3, which presents the difference obtained by subtracting the potential of the rotated form from that of the equilibrium structure, in a plane 1.75 Å above the ring. It can be seen that the deactivation of the ring toward electrophilic attack is stronger in the equilibrium form, as is also the meta-directing tendency of the

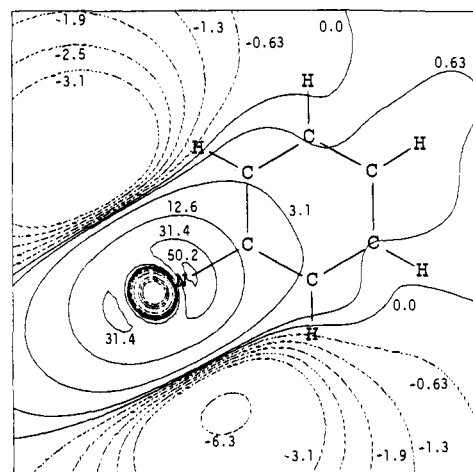


Figure 3. Calculated difference in electrostatic potentials, planar equilibrium nitrobenzene minus rotated perpendicular form, in plane 1.75 Å above the plane of the aromatic ring. Dashed contours correspond to negative values, in kcal/mol.

NO₂ group. For example, rotation of the latter by 90° weakens the positive potential near the meta carbons by about 0.63 kcal/mol (Figure 3).

Another point of interest is related to the buildup of positive potential that we have found above the C-NO₂ bond regions of nitro aromatics^{23,29} (see Figure 2) and also nitroacetylenes.³⁰ A detailed analysis showed that these regions can serve as pathways for nucleophilic attack.²⁹ An examination of the electrostatic potential of rotated nitrobenzene, at 1.75 Å from the ring plane and again at 1.75 Å from the NO₂ plane, shows no sign of such a positive buildup. This suggests that reactivity toward nucleophiles should diminish as the degree of NO₂ rotation increases, particularly when the nucleophile is charged, making electrostatic factors more significant. Experimental observations of the "ortho effect" in nucleophilic substitutions are in accord with this prediction.³¹

IV. Conclusions

The results of our analysis are indicative of a very minor degree of conjugation between the nitro group and the aromatic ring of nitrobenzene. Perhaps the various experimental observations of significant changes in properties accompanying rotation of the NO₂ should be reassessed; they may be due to rearrangements of the electronic density arising from the new nuclear configuration but not primarily reflecting a disruption of conjugation.

From the standpoint of chemical reactivity, an important consequence of NO₂ rotation is the elimination of the positive potential buildup above the C-NO₂ bond, leading to a predicted (and observed, in related systems³¹) decrease in reactivity toward nucleophiles. At the same time, however, the aromatic ring becomes slightly more susceptible to electrophilic attack.

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