of the T* decay time suggests that the N–H(D) vibration seems to take an important role in the nonradiative process of T*. The isotope effect of the activation energy of the excited-state proton transfer was observed to be unusually large, though the determination of activation energy from the fluorescence rise time of T* has less accuracy. The difference of the activation energy of 1.4 kcal mol^{-1} is fortunately close to the difference of the zero-point energy between O–H and O–D vibrations.[21] Furthermore, the decay constant of T and the activation energy of T to N exhibit also unusually large deuterium isotope effect. Since any photochemical reactions and any other decay processes than that to the ground-state normal form N do not seem to be involved in the decay of T, the observed deuterium isotope effect on the decay of T may be really reflected by that of the reaction rate constant of T → N. The difference of the activation energy of this reaction was estimated to be 1.3 kcal mol^{-1}, which is consistent with that of the zero-point energy of the initial state of T.[21,22] On the other hand, the isotope effect on the proton-transfer reactions in both the ground and excited states may be interpreted in terms of the nonradiative process as a vibrational coupling between the double minimum potentials of T and N (or N* and T*). This type of nonradiative process is known as an isoenergetic transition between two upper vibrational states of T and N with an activation barrier.

Acknowledgment. We are indebted to Drs. M. Sumitani and K. Hashimoto, Institute for Molecular Science, Okazaki, for supplying an amplifier circuit of the pin photodiode.

Registry No. 7-Hydroxyquinoline, 580-20-1; methanol, 67-56-1; deuterium, 7782-39-0; methanol-d_1, 1455-13-6.

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(21) O'Ferrall, R. A. In "Proton Transfer Reactions"; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1975; p 201.

(22) Kishi, T.; Tanaka, J.; Kouyama, T. *Chem. Phys. Lett.* **1976**, *41*, 497.

Effects of Amino and Nitro Substituents upon the Electrostatic Potential of an Aromatic Ring

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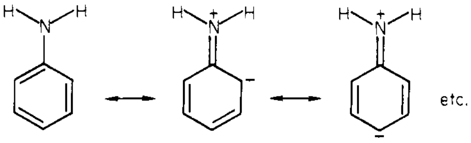
Abstract: We have calculated the electrostatic potentials of benzene, aniline, nitrobenzene, and the three isomeric nitroanilines in order to study the effects of $-NH_2$ and $-NO_2$ substituents in activating or deactivating the aromatic ring toward electrophilic attack. The potentials were computed with use of SCF STO-5G wave functions, after the molecular geometries were first optimized at the STO-3G level. (Resonance considerations are notably effective in rationalizing the changes in geometry that accompany the introduction of $-NO_2$ into aniline.) Benzene itself has extensive negative potentials (attractive toward electrophiles) above and below the aromatic ring, in the π regions. These are significantly stronger in aniline, indicating a considerable degree of activation, but are entirely eliminated in nitrobenzene. When both $-NH_2$ and $-NO_2$ are present, the deactivating influence of the latter dominates, although there remains evidence of the directing properties of $-NH_2$. An interesting feature observed in nitroaromatic potentials is a positive buildup that occurs over the $C-NO_2$ bond regions. This may indicate a possible pathway for nucleophilic attack.

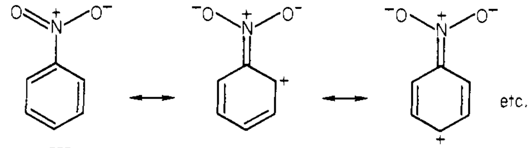
The effect of an amino substituent upon an aromatic ring is generally regarded as being a resultant of two opposing factors: an inductive withdrawal of electronic charge from the ring, coupled with a resonance donation of π charge to the ring.[1] The latter is commonly described by means of structures such as



I IIa IIb

Since it is observed experimentally that the presence of $-NH_2$ greatly activates the aromatic ring toward electrophilic attack (compared to benzene), it is concluded that the amine group is a strong π donor.[1]

In the case of the nitro group, on the other hand, both the inductive and the resonance effects are believed to result in the withdrawal of electronic charge from the ring, thus accounting for its observed deactivation toward electrophiles.[1] The resonance structures normally invoked include,



III IVa IVb

Thus, through both induction and resonance, $-NO_2$ is a charge acceptor. The inductive effect is the dominant one;[1-3] indeed it has recently been suggested that the role of structure IV may be very small.[4]

A quantitative measure of the relative roles of induction and resonance for these two substituents is given by their Taft constants, σ_I and σ_R.[5] For $-NH_2$, $\sigma_I = 0.13$ and $\sigma_R = -0.79$; for

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(1) See, for example: (a) Kemp, D. S.; Vellaccio, F. "Organic Chemistry"; Worth Publishers: New York, 1980; Chapter 20. (b) Morrison, R. T.; Boyd, R. N. "Organic Chemistry"; 4th ed.; Allyn & Bacon: Boston, 1983; Chapter 15.

(2) Baciocchi, E.; Illuminati, G. *J. Am. Chem. Soc.* **1964**, *86*, 2677.

(3) Ridd, J. H. In "Aromaticity"; The Chemical Society: London, 1967; Spec. Publ. No. 21, pp 149–162.

(4) Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2647. For an opposing view, see: Fraser, R. R.; Raganskas, A. J.; Stothers, J. B. *ibid.* **1982**, *104*, 6475.

(5) The more positive is σ_I, the greater is the inductive electron-attracting tendency; the more negative is σ_R, the greater is the degree of electron donation through resonance. The quoted values are taken from: Wells, P. R. "Linear Free Energy Relationships"; Academic Press: New York, 1968; Chapter 2.

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$-NO_2$, $\sigma_I = 0.63$ and $\sigma_R = 0.15$. These values are fully consistent with the above qualitative assessment of the relative inductive and resonance effects of these substituents. The net results for all these factors are in sharp contrast; they can be summarized by the generalization that aniline is approximately 10^6 times more reactive than benzene toward electrophilic attack, while nitrobenzene is less reactive than benzene to roughly the same extent.[6]

The reactivity of an aromatic ring toward electrophilic attack is reflected in the electrostatic potential that is created in the surrounding space by the molecule's nuclei and electrons. This potential is now well established as an effective guide to the reactive properties of molecules;[7,8] for example, the initial tendency of an approaching electrophile is to go to those regions or sites having the most negative potentials. An important feature of the electrostatic potential is that it is a real physical property and can be determined experimentally.[8,9]

In this paper, we shall use calculated electrostatic potentials to examine in detail the effects of $-NH_2$ and $-NO_2$ substituents in activating or deactivating the benzene ring toward electrophilic attack. Since these two groups have such powerful but opposite effects, it will be particularly interesting to observe the consequences of their being present simultaneously, in the three possible isomeric structures. Several other significant points that are brought out by these calculations will also be discussed.

Methods and Procedure

Optimized structures were computed, using GAUSSIAN70 and GAUSSIAN80 at the STO-3G level, for all of the molecules studied in this work. Nearly all of the geometrical parameters were included in these optimizations, the most notable exceptions being the N–O distances; it has been our experience that minimum basis set computations significantly overestimate the N–O bond lengths in $-NO_2$.[10] Accordingly, on the basis of the available experimental data,[11] we set these equal to 1.24 Å in the nitrobenzene and the nitroanilines.[12]

A final STO-5G wave function was computed for each optimized structure and was used for all subsequent analysis. All energies, electrostatic potentials, and other properties that are presented in this paper are therefore based on these STO-5G self-consistent-field molecular orbital wave functions.

The electrostatic potential at any point $\bar{r}$ in the space around a molecule is given rigorously by

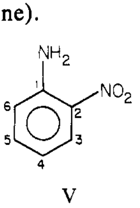
$$V(\bar{r}) = \sum_{A} \frac{Z_A}{|\bar{R}_A - \bar{r}|} - \int \frac{\rho(\bar{r}')\, d\bar{r}'}{|\bar{r}' - \bar{r}|} \qquad (1)$$

in which Z_A is the nuclear charge on atom A, located at $\bar{R}_A$, and $\rho(\bar{r})$ is the electronic density function of the molecule. In this work, $\rho(\bar{r})$ has been obtained from the STO-5G molecular wave functions. We have used the program DENPOT to evaluate $V(\bar{r})$.[13]

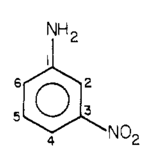
Equation 1 shows the electrostatic potential to be a sum of two terms of opposite signs, representing the effects of the nuclei and the electrons. In those regions where $V(\bar{r})$ is negative, the contribution of the electrons predominates and it is there that an electrophile is initially attracted, particularly to the point (or points) in each such region at which occurs the most negative value of the electrostatic potential, the local minimum.

Results and Discussion

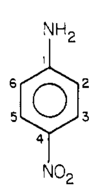
A. Structures. Our calculated structures for benzene, aniline, nitrobenzene, and the three nitroanilines (V–VII) are given in Table I. They are in good agreement with those experimentally-determined gas-phase geometries that are available (benzene and aniline).



V
(ortho)



VI
(meta)



VII
(para)

It is interesting to observe how the aniline structure is modified by introduction of the nitro group. Aniline is nonplanar; the amino hydrogens are out of the plane that contains the ring and the nitrogen. The C–C bond lenghts are all very close to 1.39 Å. Substitution of $-NO_2$ produces essentially planar systems; in none of the nitroanilines do we find an amino hydrogen to be out of the ring plane by more than approximately 0.01 Å. The C–C distances are also affected, some being lengthened by 0.01–0.02 Å and others being shortened by about the same amount.

These changes can be rationalized very satisfactorily in terms of resonance considerations. Since $-NO_2$ has a strong tendency to withdraw electronic charge from the ring, especially by induction, its presence can be expected to strengthen the electron-donating action of the $-NH_2$ and therefore to increase the effects described by structures such as IIa and IIb. In these, the nitrogen is sp^2 hybridized, with the amino hydrogens in the ring plane. Also, the C_1–C_2 and C_1–C_6 bonds have no double-bond character in these structures, which should tend to lengthen them somewhat relative to aniline. These considerations apply to all three nitroanilines. With regard now to the ortho isomer, its description should include a particularly important contribution from structure IIa, which accounts for the shortening of the C_3–C_4 and C_5–C_6 bonds in this molecule. IIb should play a similar role in the case of *p*-nitroaniline, and indeed it is now the C_2–C_3 and C_5–C_6 bonds that show marked decreases in length. Thus, the various structural effects that were pointed out as following from the substitution of $-NO_2$ in aniline can all be interpreted by invoking the contributions of IIa and IIb.

The $C-NH_2$ and $C-NO_2$ distances can also be viewed as reflecting the role of resonance. Already in aniline, the $C-NH_2$ bond length, 1.418 Å, is well below its average value in aliphatic systems, 1.472 Å,[14] due to the participation of IIa and IIb. In the nitroanilines, this distance is yet further shortened (Table I), again indicating the increased importance of these structures. In contrast, all of the $C-NO_2$ bond lengths confirm that resonance such as is shown in IVa and IVb is of minor importance.

Finally, there is evidence indicating the existence of an ON-O···HNH intramolecular hydrogen bond in *o*-nitroaniline. The optimized O···H distance is 1.78 Å, which is well within the normal range for hydrogen bonds,[15] and the atomic charges (calculated by the Mulliken population analysis procedure[16]) are also consistent with this conclusion. The hydrogen is approximately 0.05 electron unit more positive than are the other amino hydrogens in the nitroanilines, while the oxygen is roughly 0.02 electron units more negative than its typical values.

B. Electrostatic Potentials. 1. Benzene and Aniline. Figure 1 shows the electrostatic potential of unsubstituted benzene. It is positive everywhere in the plane of the ring, but there are very large negative regions above and below this plane, extending well beyond the ring itself. These are of course interpreted as being due to the π electrons of the molecule.

In aniline, these π regions are notably more negative, especially on the side of the ring plane that is opposite to the amino hydrogens (Figure 2). (There are generally positive electrostatic potentials

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(6) Reference 1b, p 598.

(7) For recent reviews, see: (a) Scrocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 116. (b) Politzer, P.; Daiker, K. C. In "The Force Concept in Chemistry"; B. M. Deb, Ed.; Van Nostrand-Reinhold: New York, 1981; Chapter 7.

(8) Politzer, P.; Truhlar, D. G.; Eds. "Chemical Applications of Atomic and Molecular Electrostatic Potentials"; Plenum Press: New York, 1981.

(9) Stewart, R. F. *Chem. Phys. Lett.* 1979, *65*, 335; Bentley, J. *J. Chem. Phys.* **1979**, *70*, 159.

(10) Politzer, P.; Domelsmith, L. N.; Sjoberg, P.; Alster, J. *Chem. Phys. Lett.* **1982**, *92*, 366.

(11) Trueblood, K. N.; Goldish, E.; Donohue, J. *Acta Crystallogr.* **1961**, *14*, 1009. Wyckoff, R. "Crystal Structures", 2nd ed.; Interscience: New York, 1969; Vol. 6.

(12) Fortunately, the calculated electrostatic potential is not critically sensitive to small changes in geometrical parameters; for example, we have found that variations of 0.02 Å in bond lengths have no significant effect upon our computed potentials.

(13) Peeters, D.; Sana, M. *QCPE* **1978**, *11*, 360.

(14) Sutton, L. E., Ed. "Tables of Interatomic Distances and Configuration in Molecules and Ions"; The Chemical Society: London, 1965; Spec. Publ. No. 18, supplement.

(15) Kollman, P.; McKelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975**, *97*, 955.

(16) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

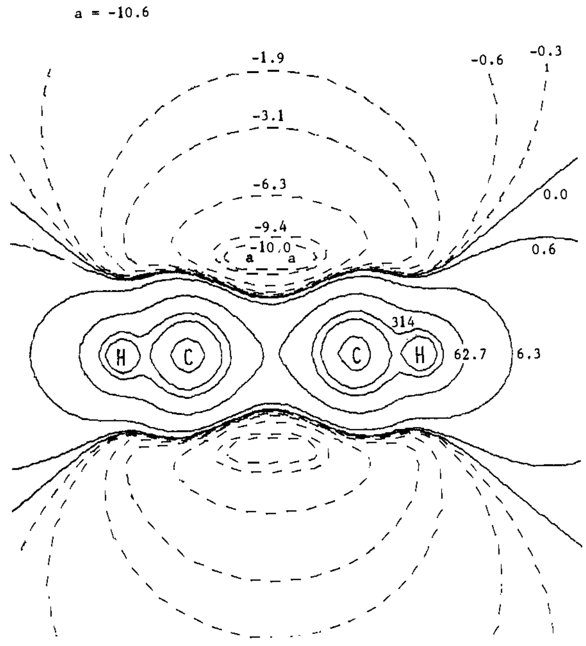

Figure 1. The electrostatic potential of benzene in the symmetry plane through carbons, perpendicular to the molecular plane. Positions of potential minima are indicated by a, with the corresponding value (in kcal/mol) given at the top of the figure. The innermost carbon and hydrogen contours have values of 627 and 3136 kcal/mol.

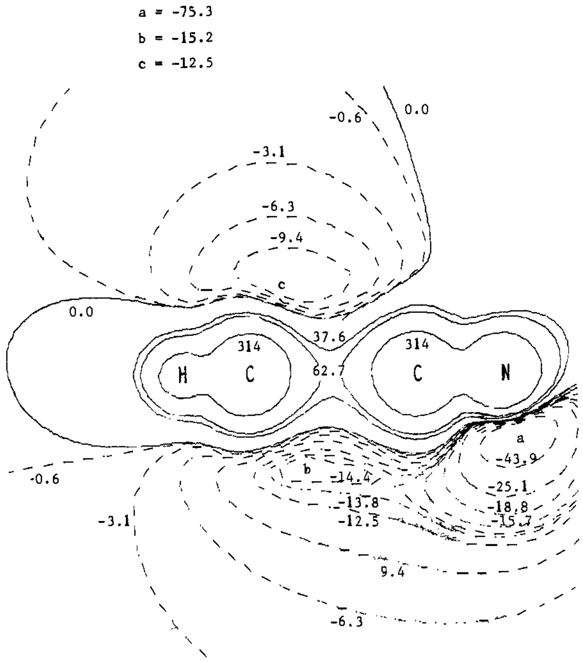

Figure 2. The electrostatic potential of aniline in the symmetry plane perpendicular to the plane of the ring. Positions of potential minima are indicated by a, b, and c, with the corresponding values (in kcal/mol) given at the top of the figure. The positive region in the upper right portion of the figure is due to amino hydrogens.

associated with hydrogen atoms.[7b]) This supports the usual description of the amine group as a π donor and a strong activator of aromatic rings.

The very considerable extent of the negative potential above the ring in aniline (as in benzene) can be seen in Figure 3. It favors the ortho and para positions as sites for electrophilic attack upon the ring, in agreement with the known directing properties of $-NH_2$. Furthermore, it is clear that such attack is most likely to occur via the π regions.

A major feature in the electrostatic potential of aniline is the strong negative region associated with the nitrogen, which can be attributed to the effect of its lone pair. This negative potential,

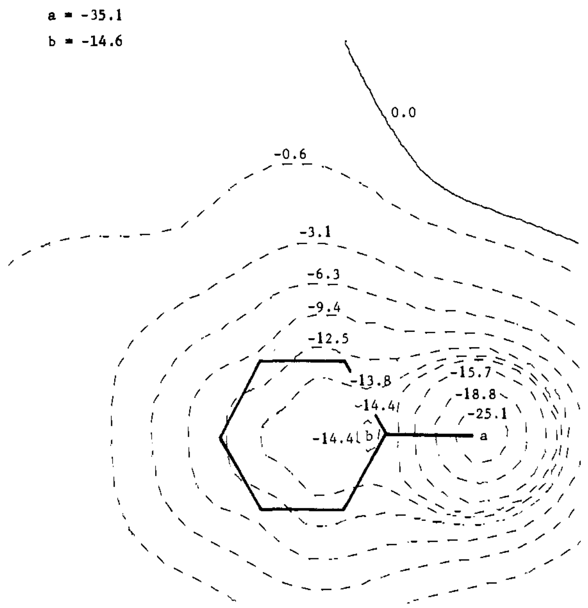

Figure 3. The electrostatic potential of aniline in the plane 1.75 Å above the ring plane on the side opposite to the amine hydrogens. The locations of the ring and the nitrogen are indicated. Potential minima occur at points a and b, with the corresponding values (in kcal/mol) given at the top of the figure.

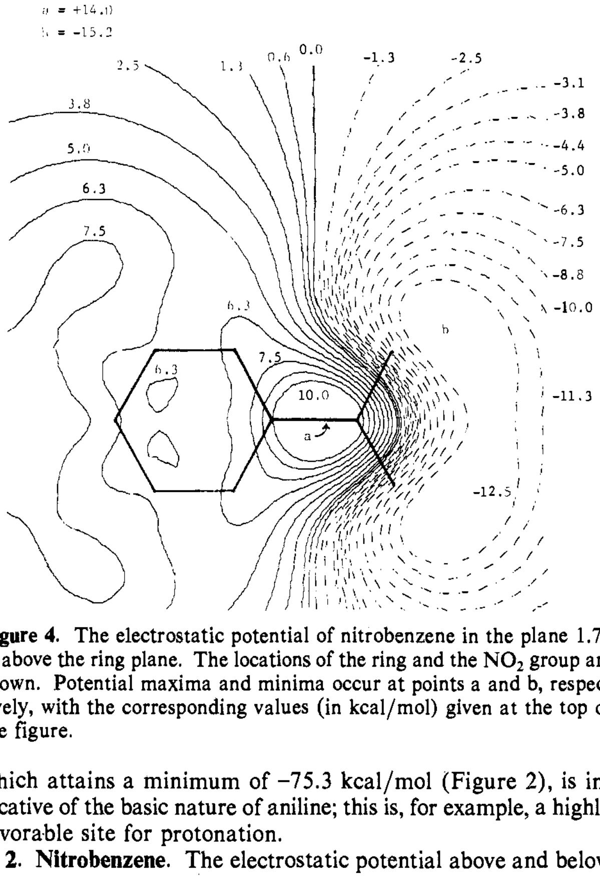

Figure 4. The electrostatic potential of nitrobenzene in the plane 1.75 Å above the ring plane. The locations of the ring and the NO_2 group are shown. Potential maxima and minima occur at points a and b, respectively, with the corresponding values (in kcal/mol) given at the top of the figure.

which attains a minimum of −75.3 kcal/mol (Figure 2), is indicative of the basic nature of aniline; this is, for example, a highly favorable site for protonation.

2. Nitrobenzene. The electrostatic potential above and below the aromatic ring of nitrobenzene (Figure 4) is in sharp contrast to what is seen for benzene and aniline and is testimony to the electron-withdrawing power of the nitro group. There are now no negative regions associated with the ring; it has been greatly deactivated toward electrophilic attack. (However, there can be seen less positve, less deactivated channels leading to the meta positions, consistent with the established directing tendencies of $-NO_2$.)

Nitrobenzene's only negative potentials are those due to the oxygens and are centered in the molecular plane (see Figure 5). There are two minima near each oxygen, with values of −42.8 and

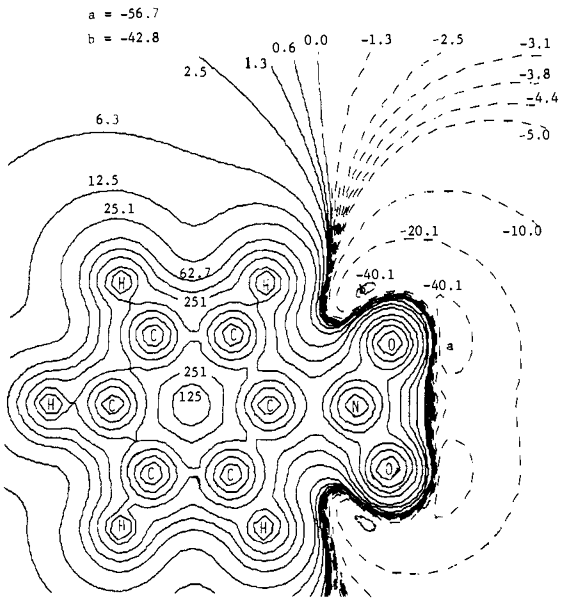

Figure 5. The electrostatic potential of nitrobenzene in the molecular plane. Positions of potential minima are indicated by a and b, with the corresponding values (in kcal/mol) given at the top of the figure. The approximately spherical contours around the nuclei have values of 627, 1254, 2509, and 6272 kcal/mol.

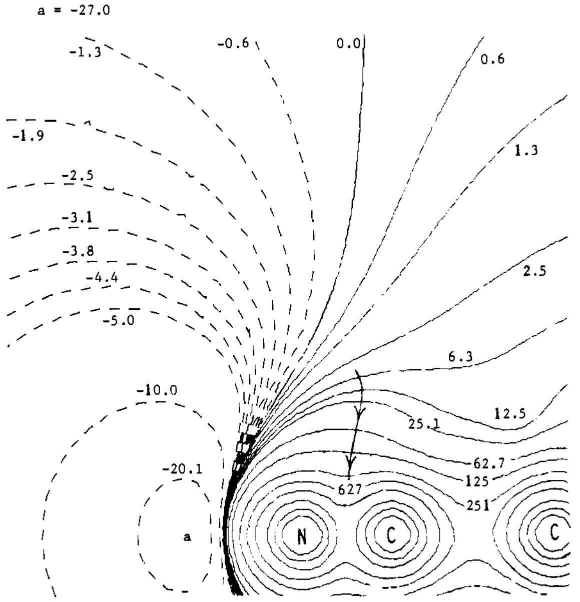

Figure 6. The electrostatic potential of nitrobenzene in the symmetry plane perpendicular to the plane of the molecule. One of the electric field lines of force has been sketched. It indicates the direction of the electrostatic force that would be felt by a negative point charge. The potential minimum is at the point a, with its value (in kcal/mol) given at the top of the figure. The remaining positive contour values are 1254, 2509, 6272, and 15 680 kcal/mol.

−56.7 kcal/mol; these can be regarded as reflecting the lone pairs of the oxygens.

Figure 4 reveals an interesting feature of the electrostatic potential of nitrobenzene. There is a planar maximum located approximately over the midpoint of the C–N bond. This is rather unusual; significant buildups of positive potential generally occur over the positions of nuclei, but not over bonds. A side view, in Figure 6, shows that the electric field has lines of force (one has been sketched, for a negative point charge) that lead to the C–N bond region. We have found this in a number of nitroaromatics. The implications of these positive pathways as possible routes for nucleophilic attack are being studied.

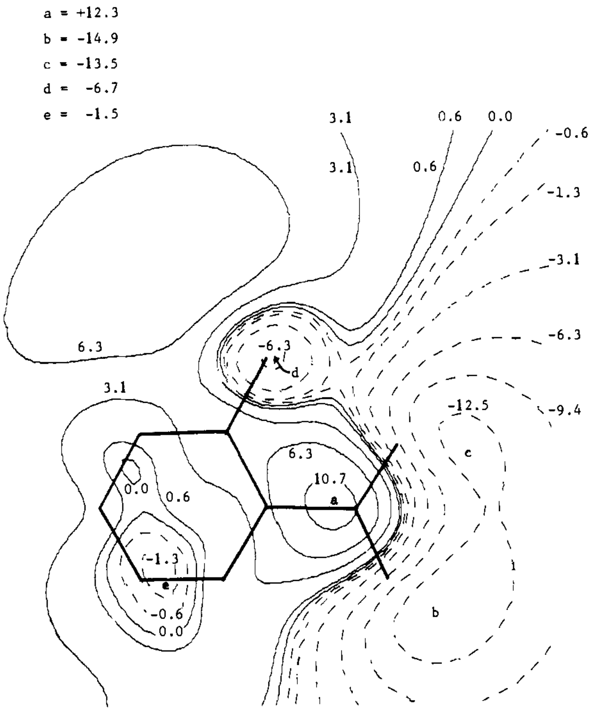

Figure 7. The electrostatic potential of *o*-nitroaniline in the plane 1.75 Å above the ring plane. The locations of the ring, the nitrogens, and the oxygens are indicated. A potential maximum occurs at the point a, with minima at b, c, d, and e. The corresponding values (in kcal/mol) are given at the top of the figure.

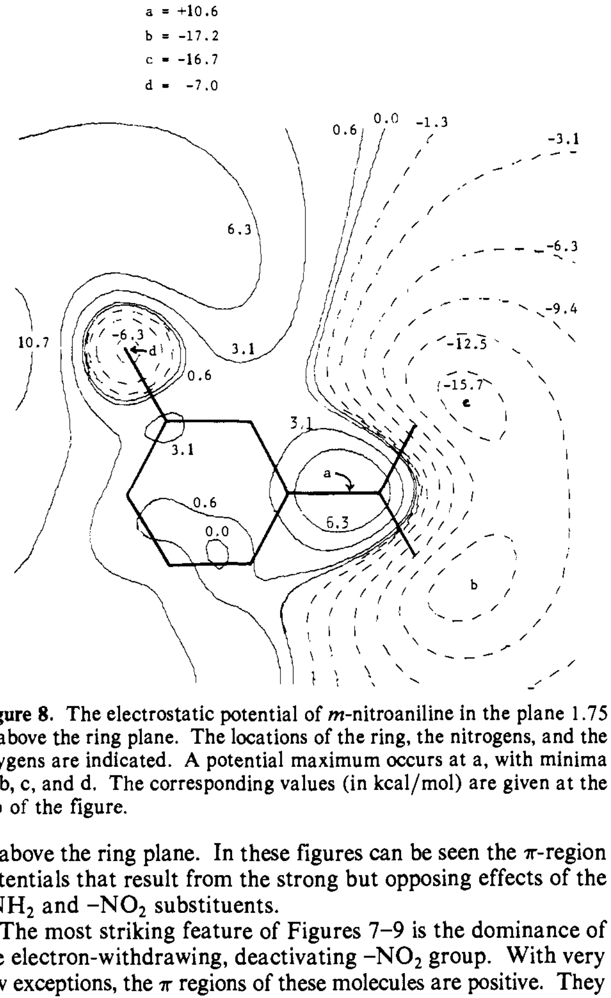

Figure 8. The electrostatic potential of *m*-nitroaniline in the plane 1.75 Å above the ring plane. The locations of the ring, the nitrogens, and the oxygens are indicated. A potential maximum occurs at a, with minima at b, c, and d. The corresponding values (in kcal/mol) are given at the top of the figure.

3. Nitroanilines. Figures 7–9 show the electrostatic potential of each of the three isomeric nitroanilines in a plane that is 1.75 Å above the ring plane. In these figures can be seen the π-region potentials that result from the strong but opposing effects of the $-NH_2$ and $-NO_2$ substituents.

The most striking feature of Figures 7–9 is the dominance of the electron-withdrawing, deactivating $-NO_2$ group. With very few exceptions, the π regions of these molecules are positive. They should certainly be much less reactive toward electrophilic attack than aniline or benzene, although not to the level of nitrobenzene.

Table I. Calculated Structures[a]

molecule	energy (STO-5G), hartrees	distances, Å		angles, deg	
benzene	−229.9900	C–C	1.386 (1.396)	C-C-C	120^b (120)
		C–H	1.083^b (1.083)	H-C-C	120^b (120)
aniline	−284.8047	C_1-N	1.418 (1.402)	N-C_1-C_2	119.8 (120.3)
		C_1-C_2	1.392 (1.397)	H-C_4-C_3	119.9 (120.6)
		C_2-C_3	1.394 (1.394)	H-N-H	113.0 (113.1)
		C_3-C_4	1.387 (1.396)	H-C_2-C_3	119.8 (120.1)
		N-H	1.020 (1.001)	H-C_3-C_2	120.0^b (120.0)
		C_2-H	1.080 (1.082)	H-N-H, N-ring (dihedral)^c	36.5 (37.5)
		C_3-H	1.086 (1.083)		
		C_4-H	1.086 (1.080)		
nitrobenzene	−432.5183	C_1-N	1.517	O-N-C	117.5
		C_1-C_2	1.387	H-C_4-C_3	119.7
		C_2-C_3	1.385	N-C_1-C_2	118.9
		C_3-C_4	1.389	H-C_2-C_1	119.5
		N-O	1.240	H-C_3-C_2	119.8
		C-H	1.083		
o-nitroaniline	−487.3350	C_1-NH_2	1.383	C_1-C_2-C_3	121.9
		C_2-NO_2	1.511	C_2-C_3-C_4	120.1
		C_1-C_2	1.403	C_1-C_6-C_5	120.8
		C_2-C_3	1.394	C_6-C_1-C_2	116.9
		C_3-C_4	1.374	O_a-N-C_2^{d}	119.8
		C_4-C_5	1.399	O_b-N-C_2^{d}	117.1
		C_5-C_6	1.373	H_a-N-C_1^{d}	116.5
		C_1-C_6	1.412	H_b-N-C_1^{d}	120.6
		N-H_a^{d}	1.018	N-C_2-C_3	117.2
		N-H_b^{d}	1.013	N-C_1-C_2	121.3
		N-O^b	1.240	H-C_3-C_4	121.8
		C_3-H	1.084	H-C_4-C_5	120.5
		C_4-H	1.080	H-C_5-C_6	119.1
		C_5-H	1.084	H-C_6-C_1	118.3
		C_6-H	1.081		
m-nitroaniline	−487.3309	C_1-NH_2	1.401	C_1-C_2-C_3	118.8
		C_3-NO_2	1.519	C_2-C_3-C_4	122.8
		C_1-C_2	1.397	C_3-C_4-C_5	118.1
		C_2-C_3	1.382	C_2-C_1-C_6	119.1
		C_3-C_4	1.381	O_a-N-C_3^{d}	117.6
		C_4-C_5	1.389	O_b-N-C_3^{d}	117.5
		C_5-C_6	1.382	H_a-N-C_1^{d}	120.8
		C_1-C_6	1.403	H_b-N-C_1^{d}	120.7
		N-H	1.012	N-C_1-C_6	120.5
		N-O^b	1.240	N-C_3-C_4	119.0
		C-H^b	1.083	H-C-C^b	120.0
p-nitroaniline	−487.3558	C_1-NH_2	1.396	C_1-C_2-C_3	120.2
		C_4-NO_2	1.510	C_2-C_3-C_4	119.4
		C_1-C_2	1.404	C_3-C_4-C_5	121.4
		C_2-C_3	1.379	O-N-C_4	117.6
		C_3-C_4	1.388	H-N-C_1	120.8
		N-H	1.013	N-C_1-C_2	120.3
		N-O^b	1.240	N-C_4-C_5	119.3
		C_2-H	1.080	H-C_2-C_1	119.3
		C_3-H	1.084	H-C_3-C_2	121.4

[a] Experimentally-determined gas-phase values are in parentheses. These are taken from: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, *8*, 619. Except for aniline, all of the molecules in Table I were found to be essentially planar. [b] Assumed value. [c] This value refers to the angle between the H-N-H and the N-ring planes. [d] H_a is the amino hydrogen closest to the nitro group; O_a is the nitro oxygen closest to the amino group.

The strong activating influence of $-NH_2$ has been overwhelmed.

The only sizable negative potential in any of these π regions appears in *o*-nitroaniline (V), above position 4 (Figure 7). Accordingly, within the group of nitroanilines, this should be a likely site for electrophilic attack on the aromatic ring, although the magnitude of this potential is only one-eighth of the value at the corresponding position in aniline.

Positions 4 and 6 in *o*-nitroaniline and 2 and 6 in *p*-nitroaniline (VII) are sites at which the directive influences of the $-NH_2$ and $-NO_2$ substituents in these molecules are expected to reinforce each other.[17] (This is not true of any position in *m*-nitroaniline.) As pointed out above, only the first of these sites has a significant negative region associated with it; however, the potential in the neighborhood of each of the others is close to zero or only weakly positive. This applies also to position 4 in *m*-nitroaniline (VI) (see Figure 8).

On the whole, Figures 7–9 indicate that to whatever extent the nitroanilines do undergo electrophilic substitution, it is expected to be governed by the directing properties of the amine group.[19] However, the rates and extents of such reactions should be considerably reduced compared to aniline and benzene.

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(17) In agreement with this expectation, the nitration of *p*-nitroaniline is found to occur at position 2 or 6.[18]

(18) Hartshorn, S. R.; Ridd, J. H. *J. Chem. Soc. B* **1968**, 1068.

(19) Our results support the generalization[1b,20] that in disubstituted benzenes, a strongly activating substituent, such as $-NH_2$, usually exerts the controlling directive influence, even though the system may be overall deactivated because of the presence of the other group.

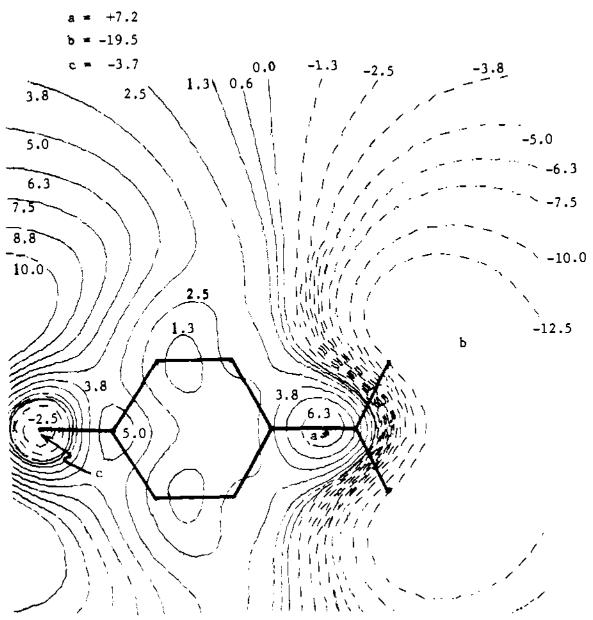

Figure 9. The electrostatic potential of *p*-nitroaniline in the plane 1.75 Å above the ring plane. The locations of the ring, the nitrogens, and the oxygens are indicated. There is a potential maximum at the point a, with minima at b and c. The corresponding values (in kcal/mol) are given at the top of the figure.

The negative potentials above the amine groups in Figures 7–9 are much weaker than those in aniline (Figure 3), which is consistent with the considerably greater basicity of the latter.[21-23] The difference in the potentials can be attributed in part to the amino nitrogen adopting a planar configuration in the nitroanilines and in part also to the strong electron-attracting power of the $-NO_2$, which stimulates a greater degree of electronic charge donation by the $-NH_2$.

Figures 7–9 all show the same interesting feature as did nitrobenzene (Figure 4): a planar maximum over the $C-NO_2$ bond, reflecting a buildup of positive potential over this bond region. This effect is smaller for the nitroanilines than for nitrobenzene, consistent with the idea that the presence of $-NH_2$ results in a greater concentration of electronic charge in the nitro portion of each molecule. Within the group of nitroanilines, the magnitude of this $C-NO_2$ planar maximum decreases in the order ortho > meta > para.[23]

Summary

The electrostatic potential has been used as a means for examining the degrees of activation or deactivation of aromatic rings toward electrophilic attack that result from the presence of $-NH_2$ and/or $-NO_2$ substituents. Whereas $-NH_2$ activates the ring, by strengthening the negative potentials already present in the π regions of benzene, $-NO_2$ has the opposite effect; nitrobenzene has no negative regions above or below the ring and is greatly deactivated. When both substituents are present simultaneously, the deactivating tendency is very much the dominant one, although the ortho and para directing properties of $-NH_2$ are still evident, with the particular emphasis on position 4 in *o*-nitroaniline.

An interesting observation is that a buildup of positive potential occurs over the $C-NO_2$ bond regions in these nitroaromatics. The possibility that this may indicate a significant route for nucleophilic attack is being investigated.

Finally, resonance considerations, particularly involving π-charge donation by $-NH_2$ coupled with electron withdrawal by $-NO_2$, have been shown to be an effective means of rationalizing the changes in geometry that accompany the substitution of $-NO_2$ into aniline.

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Registry No. Benzene, 71-43-2; aniline, 62-53-3; nitrobenzene, 98-95-3; *o*-nitroaniline, 88-74-4; *m*-nitroaniline, 99-09-2; *p*-nitroaniline, 100-01-6.

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(20) Geissman, T. A. "Principles of Organic Chemistry"; 4th ed.; W. H. Freeman & Co.: San Francisco, 1977; p 688.

(21) Bolton, P. D.; Johnson, C. D.; Katritzky, A. R.; Shapiro, S. A. *J. Am. Chem. Soc.* **1970**, *92*, 1567.

(22) Weast, R. C., Ed. "Handbook of Chemistry and Physics"; 58th ed.; CRC Press: West Palm Beach, FL 1977.

(23) In examining the electrostatic potentials of the nitroanilines, it should be borne in mind that the $-NH_2$ and $-NO_2$ contributions overlap in the case of *o*-nitroaniline, which significantly complicates comparisons with the other isomers.