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Ab Initio SCF Calculations on the Molecules Nitroamine and Nitrosamine

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The electronic structures of the molecules nitroamine and nitrosamine have been investigated by a purely theoretical SCF procedure, using Gaussian type basis functions. The basis used is one consisting of seven *s*-type and three *p*-type functions for the heavy atoms, and four *s*-type and one *p*-type functions for the H-atoms. This set was contracted to a double-zeta basis. The molecules were assumed to be planar, and no geometry optimization was carried through. The results obtained are compared with a previous semi-empirical study of the π-electron systems of these molecules.

In previous papers we have performed semi-empirical studies of the π-electron systems of unsaturated nitro and nitroso compounds and of molecules containing N–N bonds within the Pariser-Parr-Pople approximation.[1,2] The necessary parameters for the nitro and nitroso group, and for the nitrogen-nitrogen bond were evaluated by means of a special scheme, previously proposed by Roos and Skancke.[3] The results obtained from the semi-empirical calculations were in satisfactory agreement with available experimental information for these systems.

One result emanating from this calculation was an unusually high polarity, predicted in both the nitro and the nitroso group.

The aim of the present work is to see if it is possible to predict the same gross features of the molecules in the mentioned semi-empirical calculations by an *ab initio* study. Particularly, we want to study the polarity in the two groups. As representative molecules, we have chosen the nitro- and nitrosamines.

DETAILS OF CALCULATIONS

The geometry of the nitroamine molecule has been determined by Tyler, who found a non-planar arrangement of the atoms.[4] We have, however, assumed a planar configuration in the present calculation. This is done in order to compare the results with our previous predictions which are based on semi-empirical π-electron calculations. Furthermore, the semi-empirical calculations do indicate that in a planar model the N–N bond is shorter than

reported in the experimental work. The dimethyl-nitroamine molecule, which is found to be planar, has a shorter nitrogen-nitrogen bond than the non-planar nitroamine.[5] Taking this into consideration, we have assumed a planar structure and the N–N bond length observed in dimethyl-nitroamine. The remaining parameters have been taken from the work of Tyler.[4]

For nitrosamine, no experimental data for the geometry are available. We have, therefore, chosen the necessary geometric parameters, partly from the work of Tyler, and partly from an investigation of dimethyl-nitrosamine.[11]

The assumed atomic coordinates are presented in Table 1.

Table 1. Molecular geometries. Coordinates in atomic units.[a]

	Nitroamine		Nitrosamine	
Atom	x	z	x	z
H(1)	1.6018	−1.0205	1.6018	−1.0205
H(2)	−1.6018	−1.0205	−1.6018	−1.0205
N(1)	0	0	0	0
N(2)	0	2.6117	0	2.5399
O(1)	2.0655	3.5749	2.0655	3.5030
O(2)	−2.0655	3.5749		

[a] The y-axis is orthogonal to the molecular plane.

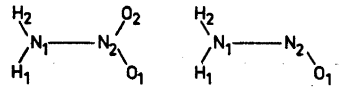

Fig. 1. Labelling of the atoms in the molecules nitroamine (I) and nitrosamine (II).

The labelling of the atoms is given in Fig. 1.

In this calculation, we have used a contracted set Gaussian functions as basis.

The orbital exponents and the contraction coefficients, which have been taken from other studies,[6,7] are presented in Tables 2 and 3.

Table 2. Orbital exponents of the basis functions.

GTO	H	N	O
s	16.7019	2038.41	2714.89
s	2.51663	301.689	415.725
s	0.567196	66.4630	91.9805
s	0.154146	17.8081	24.4515
s		5.30452	7.22296
s		0.764993	1.06314
s		0.234424	0.322679
p	0.800000	5.95461	7.75579
p		1.23293	1.62336
p		0.286752	0.365030

Table 3. Contraction coefficients.

CGTO	H	N	O
s_1	0.019060	0.004479	0.004324
	0.134240	0.034581	0.032265
	0.474490	0.164263	0.156410
s_2	1.0	0.453898	0.447813
		0.468979	0.481602
s_3		1.0	1.0
s_4		1.0	1.0
p_1		0.119664	0.129373
		0.474629	0.481269
p_2		1.0	1.0

The uncontracted Gaussian basis consists of seven s-type and three p-type functions for the heavy atoms, and four s-type and one p-type functions for the hydrogen atoms. This set is contracted to four s- and two p-type functions on the heavy atoms, and two s- and one p-type functions on the hydrogen atoms. The contraction is performed in a way which leaves some flexibility

Table 4. Symmetry-adapted functions for nitroamine (C_{2v}) and nitrosamine (C_s). For the labelling of atoms, see Fig. 1.

C_{2v} Repr.	Sym. orb.	Multipl.	C_s Repr.	Sym. orb.	Multipl.
a_1	sH(1)+sH(2)	2	a'	sH(1)	2
	sN(1)	4		sH(2)	2
	sN(2)	4		sN(1)	4
	sO(1)+sO(2)	4		sN(2)	4
	xO(1)−xO(2)	2		sO(1)	4
	zO(1)+zO(2)	2		xN(1)	2
	zN(1)	2		xN(2)	2
	zN(2)	2		xO(1)	2
	xH(1)−xH(2)	1		zN(1)	2
	zH(1)+zH(2)	1		zN(2)	2
				zO(1)	2
a_2	yO(1)−yO(2)	2		xH(1)	1
	yH(1)−yH(2)	1		xH(2)	1
				zH(1)	1
b_1	sH(1)−sH(2)	2		zH(2)	1
	sO(1)−sO(2)	4			
	xO(1)+xO(2)	2	a''	yH(1)	1
	xN(1)	2		yH(2)	1
	xN(2)	2		yN(1)	2
	zO(1)−zO(2)	2		yN(2)	2
	xH(1)+xH(2)	1		yO(1)	2
	zH(1)−zH(2)	1			
b_2	yO(1)+yO(2)	2			
	yN(1)	2			
	yN(2)	2			
	yH(1)+yH(2)	1			

in the valence shells. An MO-SCF calculation with such a basis should be rather well adapted for a description of molecular ground states without any further optimization of the orbital exponents. The effect of including polarization functions in the basis has previously been investigated. The result is that p-orbitals on the hydrogen atoms seem to be more important than the d-orbitals on oxygen and nitrogen.[6,7] As we for computational reasons are forced to limit our basis, we have included p-orbitals on the hydrogen atoms and neglected polarization functions on the heavy atoms. Calculations without p-orbitals on the hydrogen atoms are also performed for comparison.

With the adapted structures, nitroamine and nitrosamine belong to the symmetry groups C_{2v} and C_s, respectively. The symmetry orbitals are presented in Table 4. The transformation to symmetry orbitals is necessary as the program is performing the calculation with symmetry orbitals and the presented expansion coefficients refer to these orbitals.

The calculations were performed by means of the IBMOL programme,[8] version IV.

Table 5. Total electronic energies. Values in a.u.

	Nitroamine	Nitrosamine
No p on H	−259.1508	−184.4986
p on H	−259.1724	−184.5197

Table 6. Orbital energies for nitrosamine in a.u.

Orbital	Orbital energy	Nature of orbital
1 (1a')	−20.6112	1s O
2 (2a')	−15.7456	1s N(2)
3 (3a')	−15.6328	1s N(1)
4 (4a')	− 1.5590	σ (N−O)
5 (5a')	− 1.2572	σ (N−N)
6 (6a')	− 0.9267	σ (N−H)
7 (7a')	− 0.7569	σ (N−H)
8 (8a')	− 0.7081	σ Oxygen lone pair
9 (1a'')	− 0.6340	π
10 (9a')	− 0.5938	σ
11 (2a'')	− 0.4274	π oxygen and nitrogen lone pair mixed
12 (10a')	− 0.4143	σ

RESULTS AND DISCUSSION

The results obtained are presented in Tables 5 – 12.

In Table 5, the total electronic energies calculated with and without inclusion of p-functions on the hydrogen atoms are given.

Table 7. Orbital energies for nitroamine in a.u.

Orbital	Orbital energy	Nature of orbital
1 ($1a_1$)	−20.6202	1*s* O
2 ($1b_1$)	−20.6202	»
3 ($2a_1$)	−15.9027	1*s* N(2)
4 ($3a_1$)	−15.6534	1*s* N(1)
5 ($4a_1$)	− 1.6753	σ (N−O)
6 ($2b_1$)	− 1.4545	σ (N−O)
7 ($5a_1$)	− 1.2699	σ (N−N)
8 ($6a_1$)	− 0.9310	σ (N−H)
9 ($7a_1$)	− 0.7903	σ lone pair oxygen
10 ($3b_1$)	− 0.7690	σ (N−H)
11 ($1b_2$)	− 0.7675	π
12 ($4b_1$)	− 0.6832	σ lone pair oxygen
13 ($8a_1$)	− 0.5011	σ »
14 ($5b_1$)	− 0.4949	σ »
15 ($2b_2$)	− 0.4661	π
16 ($1a_2$)	− 0.4521	π

In Tables 6 and 7, the calculated orbital energies are presented. In addition, we have indicated the nature of each orbital in terms of π-bonds and more or less localized σ-bonds. The three lowest orbitals in nitrosamine are clearly the inner shell *s*-orbitals on the three heavy atoms. Furthermore, the three highest occupied σ-orbitals seem to be responsible for the lone pairs on nitrogen and oxygen. The expansion coefficients and the population analysis do indicate that the lowest of these, $8a'$, describes an oxygen lone pair, and that the other two are combinations of the other oxygen lone pair and the nitrogen lone pair. The remaining σ-orbitals are more complex, but the overlap population does indicate that the two lowest, $5a'$ and $4a'$, are mainly responsible for the σ(N−O) and σ(N−N) bonds, respectively, and that the remaining two are a mixture of the two σ(N−H) bonds.

For the molecule nitroamine, the situation seems to be somewhat analogous. The four lowest occupied orbitals are the inner shells. The other molecular orbitals are composite orbitals, and accordingly more difficult to interpret. A consideration of the expansion coefficients and the population analysis leads to an indication of which orbitals give the greatest contribution to the different bonds in the molecule. This is indicated in column 3 in Table 7.

To a large extent the predicted energies of the π-orbitals and the lone pair orbitals are in the same region. Some of the energy differences calculated are too small to serve as a reliable guide for the assignment of measured ionization potentials. In nitrosamine, the separation between the lowest lone pair and the highest occupied σ(N−H) orbital is 0.05 a.u., and the separation between the lowest π-orbital and the same σ(N−H) orbital is 0.13 a.u. (see Table 6).

In nitroamine, however, one lone pair is found between the two σ(N−H) orbitals, and the lowest π-orbital is almost degenerate with the highest of these. The lowest π-orbital is almost completely delocalized in both the molecules. This explains its very low energy in nitroamine.

The overlap and the gross atomic populations are given in Tables 8−11.

Table 8. Overlap population for nitrosamine.

	Total overlap population					π-Electron overlap population				
	H(1)	H(2)	N(1)	N(2)	O(1)	H(1)	H(2)	N(1)	N(2)	O(1)
H(1)	0.5210					0.0006				
H(2)	−0.0298	0.4769				0.0000	0.0007			
N(1)	0.3424	0.3800	6.4921			0.0094	0.0100	1.6995		
N(2)	−0.0176	−0.0226	0.1538	6.3517		0	0	0.0601	0.6226	
O(1)	0.0122	0.0038	−0.1258	0.2300	8.3053	0	0	−0.0193	0.1725	1.2100

Table 9. Overlap population for nitroamine.

	Total overlap population						π-Electron overlap population					
	H(1)	H(2)	N(1)	N(2)	O(1)	O(2)	H(1)	H(2)	N(1)	N(2)	O(1)	O(2)
H(1)	0.4613						0.0007					
H(2)	−0.0263	0.4613					0.0000	0.0007				
N(1)	0.3762	0.3762	6.4133				0.0109	0.0109	1.8056			
N(2)	−0.0236	−0.0236	0.2204	5.9766			0.0001	0.0001	0.0255	0.8446		
O(1)	0.0099	0.0035	−0.1177	0.1686	8.3877		0	0	−0.0119	0.1167	1.5123	
O(2)	0.0035	0.0099	−0.1177	0.1686	−0.7182	8.3877	0	0	−0.0119	0.1167	0.0281	1.5123

Table 10. Gross atomic population for nitrosamine.

	p-Orbitals on H			No *p*-Orbitals on H		
	π-Charge	σ-Charge	Total charge	π-Charge	σ-Charge	Total charge
H(1)	0.01007	0.81819	0.82826	0	0.6634	0.6634
H(2)	0.01072	0.79766	0.80838	0	0.64699	0.64699
N(1)	1.75968	5.48287	7.24255	1.78706	5.78067	7.56773
N(2)	0.85830	5.84001	6.69531	0.85530	5.84219	6.69252
O(1)	1.36420	7.0613	8.4255	1.36261	7.06381	8.42642

Table 11. Gross atomic population for nitroamine.

	p-Orbitals on H			No *p*-orbitals on H		
	π-Charge	σ-Charge	Total charge	π-Charge	σ-Charge	Total charge
H(1)	0.01166	0.78941	0.80107	0	0.63337	0.63337
H(2)	0.01166	0.78941	0.80107	0	0.63337	0.63337
N(1)	1.82904	5.32167	7.15071	1.85698	5.64824	7.50522
N(2)	1.10359	5.38346	6.48705	1.09988	5.36066	6.46054
O(1)	1.52202	6.85806	8.38008	1.52157	6.86216	8.38373
O(2)	1.52202	6.85806	8.38008	1.52157	6.86216	8.38373

The predicted populations in an *ab initio* calculation are very sensitive to the choice of basis. This is illustrated by the comparison of the results obtained with and without p-orbitals on the hydrogen atoms (see Tables 10 and 11). Systematic studies of basis sets in this context have, however, indicated that further extension of the basis is not as important as the inclusion of p-orbitals on the hydrogen atoms.[6,7]

Our calculated dipole moment for nitroamine, 4.42 D, exceeds the measured one of 3.78 D.[9] This discrepancy, which has the expected sign, is small enough to be accounted for in terms of polarization functions on the heavy atoms.

The calculated moment for nitrosamine is 3.83 D. No experimental value seems to be available.

In this calculation we have tried to relate the overlap populations and the gross atomic populations to available experimental measurements and to conclusions based on these.

Considering the overlap population, we have obtained the values 0.2204 and 0.1538 for the nitrogen-nitrogen bond in nitro- and nitrosamine, respectively.

If there is any correlation between this population and the bond distance, one should expect a shorter N – N bond length in the nitro compound.

These results are, however, in disagreement with the conclusions reached by an electron-diffraction study of the dimethyl-nitro- and dimethyl-nitrosamine,[5,10] where the N – N bond was found to be significantly shorter in the nitroso compound. Nor is it reasonable that the methyl groups should be responsible for a change of this kind.

On the other hand, by considering the π-electron overlap population alone in the same region we find the values 0.0601 and 0.0255 for the nitrose and the nitro compound, respectively. Regarding the hybridization and the σ population on the nitrogen atoms as nearly the same in the two molecules, this π-electron overlap population would indicate a difference in the N – N bond length in the two molecules, being in agreement with experiment.

In the nitrogen-oxygen bonds, the π-electron contribution to the overlap population is of a substantial relative magnitude in both the molecules (see Tables 8 and 9). The total overlap populations in the two molecules are different, but not more than expected. We obtained a high polarity in both the nitro and the nitroso group, as revealed by Tables 10 and 11.

By comparing the influence of the nitro and the nitroso group on the amino group, one may conclude that the nitro group has a greater electron affinity than the nitroso group. This is in contradiction to previous results,[5,10,11] but, considering the π-electron distribution alone, one would reach the opposite conclusion.

An interesting feature concerning the population analysis is the σ- and π-charge on the nitrogen atoms in the nitro and nitroso group. Even if the total charges on these atoms are not too different, the σ- and π-charges are significantly redistributed, going from a pyrrole to a pyridine nitrogen. This is important for a discussion of the core potential in semi-empirical calculations, including the π-electrons only.

COMPARISON BETWEEN SEMI-EMPIRICAL AND *AB INITIO* CALCULATIONS

As mentioned above, we have previously performed a semi-empirical study of the π-electron systems of the same two molecules by using a recently suggested parameter scheme.[1,2] This enables us to compare some of the results obtained in that work with those of the present calculations.

The two highest occupied orbitals in nitroamine are found to be degenerate in the semi-empirical calculation, as shown in Table 12. These orbitals are

Table 12. π-Orbital energies (in a.u.) for nitroamine and nitrosamine, obtained by the semi-empirical calculations.[1,2] Corresponding energy values, obtained by the present calculations, in parentheses.

Nitroamine	Nitrosamine
−0.6314 (−0.7675)[a]	−0.4116 (−0.6340)[b]
−0.4568 (−0.4661)	−0.3932 (−0.4274)
−0.4568 (−0.4521)	

[a] Values taken from Table 5.
[b] Values taken from Table 6.

slightly separated in the *ab initio* calculation, but the obtained values are very close to the semi-empirical one. The highest occupied orbital in nitrosamine is also nicely reproduced in this calculation, but for the lower orbital in both molecules we obtain rather different values by the two calculations.

The obtained π-electron charges in the *ab initio* and the semi-empirical calculations are comparatively the same, but the predicted polarity is larger in the semi-empirical calculation than in the *ab initio* calculation. The π-electron contributions to the dipole moments in the *ab initio* calculation are 1.37 D, and 1.18 D for nitro- and nitrosamine, respectively. The corresponding values obtained by the semi-empirical calculation are 5.39 D and 5.03 D. The *ab initio* values are here more reasonable, as the total experimental value for nitroamine is 3.78 D, which is less than the semi-empirically calculated π-electron contribution alone. The difference between the charge on the oxygen atoms belonging to either a nitro or a nitroso group is, however, approximately the same in the two calculations.

An interesting feature in this comparison is the electron affinity of the nitro and nitroso group discussed above. The conclusions based on the π-electron results from the two calculations are the same, leaving a greater electron affinity to the nitroso group.

Other properties which may be correlated in these two calculations are the overlap population in the *ab initio* calculation and the bond order in the semi-empirical calculation. These quantities, too, are giving qualitatively the same picture in the two methods. We obtained in the present work a greater π-electron overlap population between the nitrogen atoms in the nitrosamine

than in the nitroamine, just as for the bond order in the semi-empirical work, where we concluded that this bond is shorter in the nitroso than in the nitroamine.

This comparison shows that at least qualitatively, it is possible to obtain the same results by the two different methods. However, one should bear in mind that the semi-empirical calculations are based on an assumed orthogonal basis.

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