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A Theoretical Study of Electrophilic Aromatic Substitution

I. The Electronic Structure of NO_2^+ *

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To study the electrophilic reactant in the nitration reaction, *ab initio* molecular orbital calculations of the nitronium ion and its protonated derivative, as well as of the corresponding isoelectronic CO_2 and CO_2H^+ systems, have been performed, with special reference to the stiffness of NO_2^+ and CO_2 to a bending of the $\widehat{OXO}$ angle. According to these calculations, the nitronium ion and carbon dioxide have comparable bending constants.

Key words: NO_2^+, electronic structure of ~ – CO_2, electronic structure of ~ – Electrophilic aromatic substitution

Many discussions of aromatic nitration have been offered in recent papers and a number of different reaction mechanisms has been proposed [1]. This is mainly due to the large amount of experimental rate data available in a lot of different solvents.

The results of the *ab initio* calculation [1d] which studied the potential surface corresponding to the interaction of ethylene with the nitronium ion, are unfortunately not conclusive and can only increase the number of interpretations of this reaction.

The nitronium ion is the most likely electrophilic reactant during the nitration reaction, but, owing to its high reactivity, experimental data about it are very few. In this paper we study theoretically, by an *ab initio* method, the NO_2^+ ion, and, as a test of the reliability of the results, parallel calculations for the isoelectronic molecule of carbon dioxide, for which a lot of experimental data are available, have been performed.

Method and Basis Sets

Our wavefunctions are MO–LCAO–SCF solutions of the Roothaan equations, where the atomic functions are Slater type orbitals. CO_2 has been studied using three different basis sets, different by the number of the included polarization atomic functions:

I. A minimal basis set: $1s$, $2s$, $2p$ atomic orbitals on C and O.
II. A minimal basis set added by five $3d$ polarization functions on the carbon.
III. An extended basis set with $1s$, $2s$, $2p$, and $3d$ orbitals on each atom.

The calculations on the NO_2^+ ion have been performed with sets I and III.

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* Dedicated to Professor H. Hartmann on the occasion of his 60th birthday.

Calculations

The geometries and the orbital exponents of the two molecules have been optimized, by searching the minimum of the total energy and using at each step of the optimizing procedure a quadratic interpolation of the calculated points.

The starting geometrical and atomic parameters were the experimental geometries:

$$CO_2: r(\text{C–O}) = 1.1613\,\text{Å}, \quad \widehat{OCO} = 180^\circ \quad [2]$$

$$NO_2^+: r(\text{N–O}) = 1.15\,\text{Å}, \quad \widehat{ONO} = 180^\circ \quad [3]$$

and the $1s$, $2s$, $2p$ STO exponents of Clementi [4].

To reduce the number of parameters to optimize, the molecules were assumed linear (this conformation was found as the more stable by preliminary calculations) and the $1s$ exponents of C, N and O were kept constant, because it is reasonable to assume that these inner orbitals do not change very much from free atoms to molecules.

At first calculations were performed with the basis set I and the experimental geometries, where the $2s$, $2p$ orbitals exponents of C, O and N, O were changed simultaneously to find a self-consistent set of values. The second step of the procedure was to optimize one parameter at a time, assuming the previous optimized values for the others. At last a new simultaneous variation of the four variables was performed.

Then the whole procedure was repeated with a new bond distance to obtain for each geometry an optimized orbital exponents set. By iterative quadratic interpolation the final geometrical and atomic parameters were found. The essential steps of the optimizing procedure are shown in Table 1 and 2 for CO_2 and NO_2^+ respectively; the final results in Table 3.

These minimal basis set optimized parameters have been kept constant in the extended basis calculations, so that the only new parameters to be optimized were the $3d$ exponents of C, N, and O. The results are shown in Table 4.

Calculations have also been performed with a minimal basis set of Slater type orbitals fitted by 3 gaussian functions (Basis IV) with standard exponents [5]. The optimized linear geometries and the total energies are:

$$CO_2: r(\text{C–O}) = 2.2458\ \text{a.u.} \quad E_{tot} = -185.0671\ \text{a.u.}$$

$$NO_2^+: r(\text{N–O}) = 2.2505\ \text{a.u.} \quad E_{tot} = -200.9585\ \text{a.u.}$$

Table 1. Total energies and optimized orbital exponents at different r(C–O) values

r(a.u.)	$\delta(2s_O)$	$\delta(2s_C)$	$\delta(2p_O)$	$\delta(2p_C)$	E_{tot}(a.u.)
2.1444	2.22789	1.85731	2.26161	1.78136	−186.915997
2.1944	2.22096	1.85038	2.25468	1.77443	−186.921926
2.2444	2.21437	1.84379	2.24809	1.76784	−186.921236
2.2044	2.21962	1.84909	2.25334	1.77309	−186.922281
2.2144	2.21829	1.84771	2.25201	1.77176	−186.922380
2.2244	2.21695	1.84637	2.25067	1.77042	−186.922234

Table 2. Total energies and optimized orbital exponents at different r(N–O) values

r(a.u.)	$\delta(2s_O)$	$\delta(2s_N)$	$\delta(2p_O)$	$\delta(2p_N)$	E_{tot}(a.u.)
2.1732	2.27813	2.14915	2.31916	2.10288	−203.024431
2.1232	2.28591	2.15693	2.32694	2.11066	−203.024914
2.0732	2.29418	2.16520	2.33521	2.11893	−203.017957
2.1332	2.28430	2.15532	2.32533	2.10905	−203.025368
2.1432	2.28272	2.15374	2.32375	2.10747	−203.025536
2.1532	2.28117	2.15219	2.32220	2.10592	−203.025427

Table 3. Basis I: final total energies and optimized parameters of CO_2 and NO_2^+

	CO_2		NO_2^+	
r(a.u.)	2.2128	(2.1944)[b]	2.1443	(2.1732)[e]
$O\hat{X}O$(°)	180.0	(180.0)[b]	180.0	(180.0)[e]
$\delta(1s_O)$	7.6579[c]	(7.6579)[d]	7.6579[c]	(7.6579)[d]
$\delta(2s_O)$	2.21849	(2.2458)[d]	2.28257	(2.2458)[d]
$\delta(2p_O)$	2.25221	(2.2266)[d]	2.32360	(2.2266)[d]
$\delta(1s_X)$[a]	5.6727[c]	(5.6727)[d]	6.6651[c]	(6.6651)[d]
$\delta(2s_X)$[a]	1.84794	(1.6083)[d]	2.15359	(1.9237)[d]
$\delta(2p_X)$[a]	1.77196	(1.5679)[d]	2.10732	(1.9170)[d]
E_{tot}(a.u.)	−186.922380		−203.025538	

[a] X=C or N.
[b] Experimental value [2].
[c] Not optimized value.
[d] Clementi's exponents [4].
[e] Experimental value [3].

Table 4. Basis II and III: final total energies and optimized $3d$ exponents of CO_2 and NO_2^+

	Basis	$\delta(3d_O)$	$\delta(3d_X)$	E_{tot}(a.u.)
CO_2	II		1.18596	−187.113803
	III	2.52279	1.14302	−187.185543
NO_2^+	IIII	2.55478	1.40493	−203.295783

Orbital Energies and Walsh Diagrams

Koopmans showed [6] that in the Hartree-Fock approximation the orbital energies, with reversed sign, could be used to approximate ionization energies, so that it is possible to have a direct and very simple comparison between the results of an SCF calculation of a molecule and the ionization energies measured by the ESCA method.

The experimental [7] and the calculated values (for the four basis sets taken into consideration) of the ionization energies of the CO_2 are shown in Table 5. The examination of these results shows two main disagreements between ESCA and *ab initio* values:

1) The splitting of the $3\sigma_g$ and $2\sigma_u$ levels: this splitting is not observed in the ESCA spectrum due to inherent broadening of these levels.

Table 5. Comparison of theoretical and experimental ionization energies of CO_2. All values in eV

Orbital	ESCA ionization energies [7]	MO–LCAO–SCF orbital energies			
		Basis I	Basis II	Basis III	Basis IV
$1\pi_g$	13.8	10.7	14.1	13.4	10.6
$1\pi_u$	17.6	17.0	18.8	18.1	17.2
$3\sigma_u$	18.1	16.1	18.7	18.6	16.0
$4\sigma_g$	19.4	18.5	20.9	20.9	18.5
$2\sigma_u$	37.6	37.5	40.0	39.0	37.5
$3\sigma_g$	37.6	39.3	41.6	40.7	39.3
$2\sigma_g$	297.5	309.4	312.2	311.2	306.5
$1\sigma_g$	541.1	561.0	566.8	565.4	553.8

Table 6. Orbital energies of NO_2^+. All values in eV

Orbital	MO–LCAO–SCF orbital energies		
	Basis I	Basis III	Basis IV
$1\pi_g$	21.8	23.9	22.9
$1\pi_u$	30.6	31.2	30.8
$3\sigma_u$	28.6	30.8	29.6
$4\sigma_g$	32.1	34.0	33.8
$2\sigma_u$	51.4	52.1	51.3
$3\sigma_g$	55.4	56.0	55.0
$2\sigma_g$	442.2	444.1	441.9
$1\sigma_g$	573.7	577.2	570.9

Table 7. Total energies and total orbital energies at different $\widehat{OXO}$ angles of CO_2 and NO_2^+

$\widehat{OXO}$	CO_2		NO_2^+	
	E_{tot}(a.u.)	E_{orb}(a.u.)	E_{tot}(a.u.)	E_{orb}(a.u.)
180°	−186.9224	−58.7607	−203.0255	−68.4521
170°	−186.9201	−58.7572	−203.0235	−68.4521
160°	−186.9127	−58.7462	−203.0169	−68.4506
150°	−186.8995	−58.7277	−203.0048	−68.4462
140°	−186.8786	−58.6977	−202.9853	−68.4371
130°	−186.8473	−58.6528	−202.9551	−68.4197
120°	−186.8014	−58.5875	−202.9090	−68.3888
110°	−186.7338	−58.4940	−202.8383	−68.3377
100°	−186.6382	−58.3598	−202.7205	−68.2561
90°	−186.4788	−58.1685	−202.5544	−68.1294

2) The ordering of the $3\sigma_u$ and $1\pi_u$ levels is reversed for the Basis I, II, and IV ($\Delta E = 0.90$ eV, $\Delta E = 0.10$ eV, $\Delta E = 1.20$ eV respectively) in respect to the ESCA one, but it is correct for the extended basis set ($\Delta E = -0.50$ eV), i.e. in these SCF calculations the contributions of the d orbitals of the oxygens (d_{xy} to $1\pi_u$ and d_{yz} to $3\sigma_u$) are essential to reproduce the order of the experimental data.

In Table 6 are shown the results for the nitronium ion; the $1\pi_u$ level is always more stable than the $3\sigma_u$.

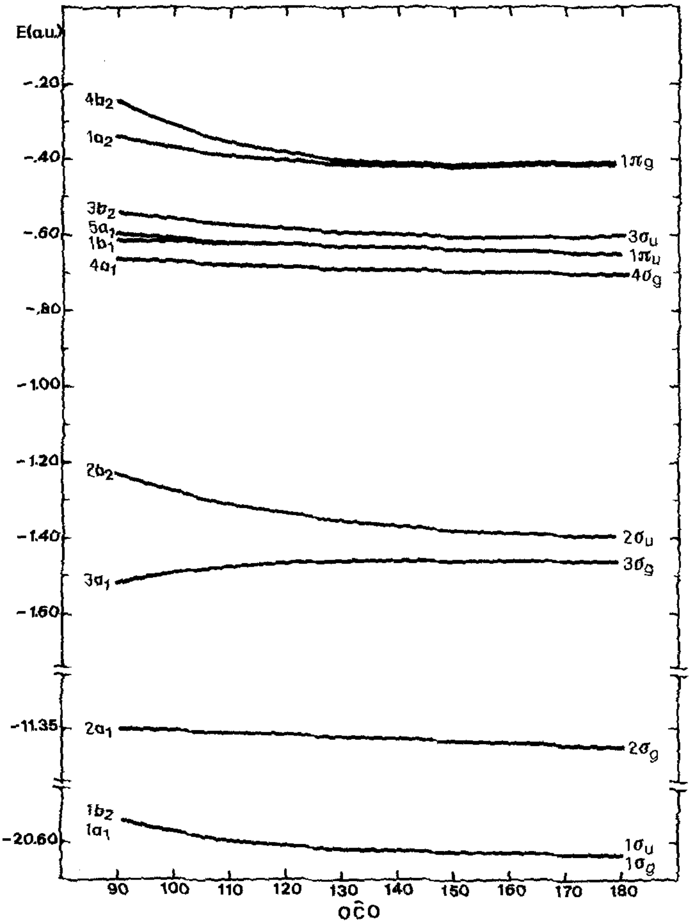

Fig. 1. *Walsh diagram for ground state of* CO_2

By using the optimized geometries and the orbital exponents of the Basis I, the influence of the variation of the $\widehat{OXO}$ angle has been studied to see, in a first approximation, whether the two molecules have the same stiffness to a bending of the molecular angle. The $\widehat{OXO}$ angle has been varied by steps of 10° and the total molecular and orbital energies are shown in Table 7 and Figs. 1 and 2. The trends of the two diagrams are very similar, so that the carbon dioxide molecule and the nitronium ion are expected to have a comparable behaviour.

Bending Constants

The bending constants of the two isoelectronic systems have been calculated by means of numerical derivation. To test the influence of a possible numerical error, the bending constants have been calculated for a few slightly different bent conformations, e.g. the linearity shifts (α) were 1–5° for the set I calculations. The reasonable reproducibility of the results (Table 8) assures that total energies were calculated with sufficient accuracy.

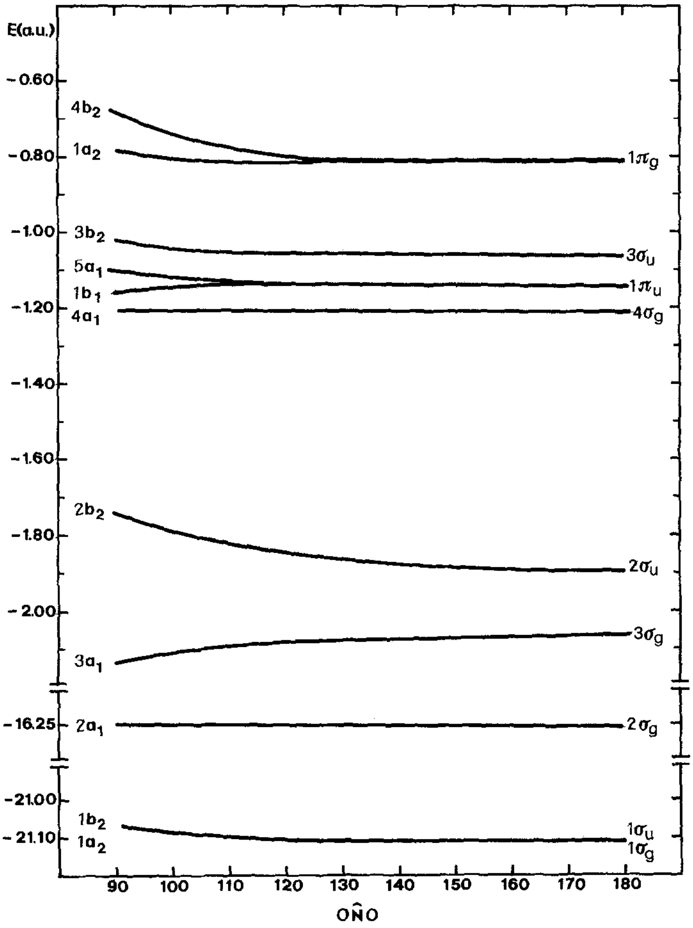

Fig. 2. Walsh diagram for ground state of NO_2^+

Table 8. Calculated bending constants of CO_2 and NO_2^+

Basis	α	CO_2 K_{δ/l^2} (mdyne/Å)	NO_2^+ K_{δ/l^2} (mdyne/Å)
I	1°	0.47	0.44
	2°	0.48	0.46
	3°	0.48	0.46
	4°	0.49	0.46
	5°	0.49	0.46
II	1°	0.83	
	2°	0.82	
III	1°	0.83	0.78
	2°	0.87	

The experimental value of the CO_2 bending constant is 0.58 mdyne/Å; the calculated value with the Basis I (0.47–0.49 mdyne/Å) is smaller than the expermental, but it is in a better agreement than that obtained with the Basis IV (0.42 mdyne/Å).

To have a further comparison between calculations adopting the two different orbital types (STO and STO-3G), an STO-3G calculation on the NO_2^+ ion was performed and a value of 0.33 mdyne/Å was found. This result has to be compared with the NO_2^+ data shown in Table 8.

As the CO_2 experimental bending constant is larger than the calculated value, polarization functions were introduced according to the procedure followed in the case of the C_3 molecule [8]. At first five 3*d* orbitals were added on the three atoms of the studied systems and too high values (Table 8) were obtained, with comparable values for CO_2 and NO_2^+. Then the extended basis was reduced including only polarization functions on the carbon atom, and no significant change in results was found (Table 8). That seems to suggest that a standard, generalized use of polarization functions is not worth-while, but its usefulness must be tested case by case.

The similar behaviour of CO_2 and NO_2^+ as far as bending constant is concerned, suggests that the difference in stiffness has no significance in the explanation of the difference in electrophilic power for the two species.

Protonated Nitronium Ion and Carbon Dioxide

To check the possibility that the electrophilic reactant during the nitration reaction could be the protonated nitronium ion [9], calculations with the Basis IV have been performed on the singlet and triplet states of $ONOH^{++}$ and on the singlet state of the isoelectronic $OCOH^+$ ion.

All geometrical parameters of these ions have been optimized as experimental data are not available: results are shown in Table 9. According to these calculations it seems that it is possible to protonate carbon dioxide molecule, but not the nitronium ion. In fact there was no convergence on the density matrix of the singlet state of $ONOH^{++}$ and the same hypothetical ion in its triplet state was broken into O^+ and NOH^+.

However we must remember that these results are for isolated species and might be reversed when interaction with solvent molecules is present.

Table 9. $OCOH^+$ (singlet) and $ONOH^{++}$ (triplet) optimized geometries. Both ions are planar. Bond lengths in a.u.

	$O_{(1)}CO_{(2)}H^+$	$O_{(1)}NO_{(2)}H^{++}$
$r(X\text{–}O_{(1)})^a$	2.1812	∞
$r(X\text{–}O_{(2)})^a$	2.4516	2.7538
$r(O_{(2)}\text{–}H)$	1.9053	1.9745
$\vartheta(O_{(2)}CO_{(1)})$	171.8°	
$\vartheta(XO_{(2)}H)^a$	111.9°	110.2°
E_{tot}(a.u.)	−185.3735	−201.2577

[a] X=C or N.

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