# A Theoretical Study of the Nitration of Ethylene and Benzene with the Nitronium Ion

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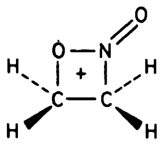
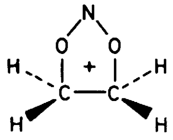
*Ab initio* and semi-empirical (MNDO, MINDO/3) studies of the interaction of $NO_2^+$ with ethylene and benzene are reported. 6-31G**//4-31G Calculations have been performed at selected points of the ethylene–nitronium ion energy hypersurface, as well as RMP2 4-31G//4-31G calculations, from which it is found that the non-classical π-complex is more stable than the classical nitro complex. Fully optimised STO-3G calculations are described for 5 stationary points of the benzene–$NO_2^+$ hypersurface; 3-21G calculations at these geometries show that the nitrito σ-complex and a 5-membered-ring structure have similar energies. 4-31G//STO-3G Calculations however show the nitro form to be the next most stable to the nitrito form. Geometry optimisation at the 3-21G level of the nitrito and nitro forms shows this finding to persist at both the 3-21G and 4-31G levels. If correlation is introduced *via* GVB/1 calculations both nitro compounds are shown to possess incipient biradicaloid character. Finally semi-empirical MINDO/3-solvaton calculations of solvation effects show that the nitro form is the most stabilised in both systems.

This work seeks to extend *ab initio* work already reported on the gas-phase nitration of ethylene, and to provide a moderately complete low-level *ab initio* study of the nitration of benzene. The types of structures considered in the two studies are the same, as are the methods of study. Neither study is definitive, but interesting new aspects of the systems are discovered. In addition to the *ab initio* data semi-empirical MINDO/3 and MNDO data are reported.

The paper is presented as two entirely separate introductions, but with a unifying discussion section.

*Ethylene.*—Bernardi and Hehre[1] originally reported STO-3G calculations on the ethylene–nitronium ion system, but they did not report the structures or absolute energies. These data now appear to be lost.[2] The essential conclusions of that work were that the 4- and 5-membered-ring systems (**I**) and (**II**) are considerably more stable than the classical (open) nitroform (**III**).


(**I**)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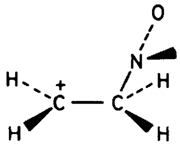
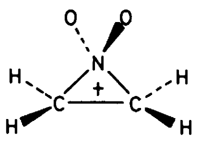
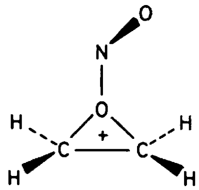

(**III**)

More recently Borisenko *et al.*[2] in a study of the cycloadditions of the nitryl cation (nitronium ion) reinvestigated these three systems at the geometry-optimised 3-21G level, at which theoretical level structure (**II**) is found to be more stable than structure (**I**), which stability sequence persists if polarisation functions are added to the heavy atoms and calculations are performed at the 3-21G-optimised geometries (6-31G*//3-21G). Further they report the characterisation of the stationary points (see also reference 3). Whilst structures (**I**) and (**II**) are stable energy minima (no negative eigenvalues of the force constant matrix), the nitro form itself is shown to be a transition state (one negative eigenvalue).

Frenking[4] has studied the migration of the nitro group *via* the π-complex (**IV**) across the carbon skeleton using the MINDO/3 method. He did not however characterise any of the stationary points on the energy hypersurface. In addition to this study of isomerisation he reported a stable nitrito-bonded form (**V**).


(**IV**)


(**V**)

At the *ab initio* level therefore the work so far reported leaves several questions unanswered, namely: (i) what roles do the nitrito form (**V**) and the π-complex (**IV**) play in the interacting system?; (ii) does a better basis set modify the conclusions reached by Borisenko *et al.*[2]?; (iii) how does correlation affect the picture?; (iv) [subsidiary to (iii)] is there evidence from MCSCF studies of a biradicaloid nature of the C–$NO_2$ bond in the nitro form (prompted by the recent interest in a radical-radical cation mechanism of the analogous aromatic–nitronium ion interaction)?

The effects of solvation have to be studied semi-empirically.

*Aromatic Nitration with Specific Reference to Benzene.*—Various gas-phase studies of aromatic nitration have appeared.[5–8] Ausloos and Lias[7] found that the major products in the gas-phase interaction of $NO_2^+$ with benzene were nitrogen dioxide and the aromatic radical-cation (70%) and, to a lesser extent, an oxygen-containing radical-cation (30%).

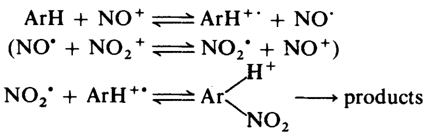
$$ArH + NO_2^+ \longrightarrow NO_2^{\cdot} + ArH^{+\cdot}$$
$$ArH + NO_2^+ \longrightarrow NO^{\cdot} + ArHO^{+\cdot}$$

With $EtONO_2NO_2^+$ as electrophile they found an ionic adduct of $NO_2^+$ and benzene (100%).

$$ArH + NO_2^+ \longrightarrow ArHNO_2^+$$

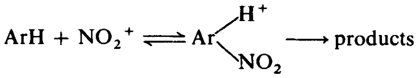
Morrison *et al.*[8] found only traces of $ArHNO_2^+$ adducts in their triple quadrupole resonance study, but Cacace[9] has observed that under their experimental conditions such ions would be formed with a large amount of internal energy, and would be expected therefore to fragment. He concludes that one cannot therefore rule out the intermediacy of such complexes in the gas phase. Schmitt, Ross, and Buttrill[10] found that the adduct formed in the reaction of nitrogen dioxide with the benzene radical-cation dimer possessed an acidic hydrogen, which was transferable to tetrahydrofuran or pyridine. So much for gas-phase studies, which highlight in general the charge-transfer pathway of reaction of free nitronium ion with the aromatic molecule.

In solution the situation is fascinating. Perrin[11] re-awakened interest in the mechanism of aromatic nitration in solution, proposing that the products of nitration could be formed by combination of an aromatic radical-cation and $NO_2^{\bullet}$. Electron-transfer in solution is known[12] to be diffusion controlled, so that for those aromatics which could, in solution, exothermically transfer an electron to the nitronium ion an explanation was available for the observation of a limiting rate constant in the nitration of reactive aromatics. However, the encounter limit is reached with different aromatics in different solvents.[13] Eberson *et al.*,[14,15] whilst finding Perrin's rationalisation attractive, were able to discount his experimental verification of his theory, namely the results of the electrochemical nitration of naphthalene. Ridd and Draper[16] further muddied the waters in their study of nitration with ceric ammonium nitrate, in which side-chain substitution of mesitylene was observed. This reaction is supposed to pass *via* the aromatic radical-cation, and the observation of non-nuclear substitution, not observed with more conventional nitrating agents, speaks against the involvement of radical-cations in general. At this point CIDNP enters the scene. In a remarkable series of papers, Ridd and his co-workers[17–20] have shown that there are two mechanisms of nitration with nitronium ion in general; the first is nitrous acid-catalysed, and shows strong $^{15}N$ CIDNP effects (using $H^{15}NO_3$ in the reaction medium), the second being direct nitronium ion attack (Schemes 1 and 2 respectively).



$$\begin{array}{l}\mathrm{ArH} + \mathrm{NO}^+ \rightleftharpoons \mathrm{ArH}^{+\bullet} + \mathrm{NO}^{\bullet}\\ (\mathrm{NO}^{\bullet} + \mathrm{NO_2}^+ \rightleftharpoons \mathrm{NO_2}^{\bullet} + \mathrm{NO}^+)\\ \mathrm{NO_2}^{\bullet} + \mathrm{ArH}^{+\bullet} \rightleftharpoons \mathrm{Ar}\begin{array}{l}\diagup \mathrm{H}^+\\ \diagdown \mathrm{NO_2}\end{array} \longrightarrow \text{products}\end{array}$$

**Scheme 1.**



$$\mathrm{ArH} + \mathrm{NO_2}^+ \rightleftharpoons \mathrm{Ar}\begin{array}{l}\diagup \mathrm{H}^+\\ \diagdown \mathrm{NO_2}\end{array} \longrightarrow \text{products}$$

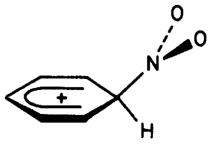
**Scheme 2.**

Under conditions (in the presence of azide ion) where the first mechanism is suppressed, *p*-nitrophenol,[18] substituted amines[19] and durene[20] show evidence for the involvement of radicals in the *direct* nitronium ion reaction; mesitylene[18] however does not. Eberson and Radner[21] have examined the application of Marcus theory[22] to the reactions in solution, and conclude that the shape change on reduction of the nitronium ion to nitrogen dioxide by the aromatic makes electron-transfer less likely in that reaction than in the corresponding nitrosonium ion reaction:

$$\mathrm{NO}^+ + \mathrm{ArH} \rightleftharpoons \mathrm{NO}{:} + \mathrm{ArH}^{+\bullet}$$

Both sets of workers conclude that dissociation into a radical pair from an *ipso* form is implicated in the observed CIDNP effects, rather than direct electron-transfer. Coupled with the evidence for the radical nature of the reactions is evidence for 1,3-shifts of the nitro group, also *via ipso*-substituted ions.

Theoretically then there are a multitude of questions in need of answers, ranging from an explanation of the variable behaviour with respect to direct nitronium ion attack, which may be evident in the gas phase as in solution, to an explanation for the mechanism of the 1,3- (or 1,5-sigmatropic?[23]) shift. Some *ab initio* work has already appeared on aromatic nitration. Politzer *et al.*[24] have performed STO-3G geometry optimisations on the nitro σ-complexes of benzene and toluene, as well as on weak complexes during early stages of the reactions. Relative to the separated reactants they find that the STO-6G//STO-3G calculations on the σ-complexes show stabilisations of around 80 kcal mol$^{-1}$. The scene is therefore set for a fuller study, herein reported. Accompanying the *ab initio* work are MINDO/3 and MNDO studies, the latter of which is not however very reliable for N,O-containing systems.



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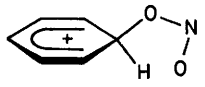

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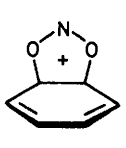

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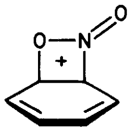

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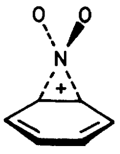

(X)

## Methods

The following *ab initio* programmes have been used variously during the progress of this work: ATMOL/3,[25] Monstergauss,[26] Gaussian-80,[27] and GAMESS.[28] Gaussian-80 was used on the University of Lancaster VAX 11-785, whilst ATMOL, Monstergauss and GAMESS were used on the Cyber 205 supercomputer at the University of Manchester Regional Computer Centre. Also used were MINDO/3[29] and MNDO.[30] Solvent effects were treated using the solvaton model of Klopman,[31] which was later modified for inclusion into SCF programmes by Germer.[32] The formulae used for the Hamiltonian matrix elements are as described by Rauscher *et al.*,[33] with the exception that the atomic charge-solvaton distance is given by the empirical formula:

$$R_{AS} = R_{VDW}(1 - \alpha|Q_S|)\ (\alpha = 0.65)$$

where $R_{VDW}$ is the van der Waals radius of atom A, and where $Q_S$ is the solvaton charge. This formula reduces the atom–solvaton distance in the one-centre integrals irrespective of the sign of the charge on the atom. In the oxygen-containing systems negative charges in the formula of Rauscher *et al.* reduce the one-centre terms rather than increase them.

## Results

We have taken the unusual step of recording the full optimised *Z*-matrices of most of the structures discussed. Such data are usual for input to the *ab initio* programs used here (apart from ATMOL), as well as to their derivatives, and to

**Table 1**. Energies (hartree) of the structures (**I**)—(**V**) (ethylene related)

| Structure | STO-3G//STO-3G | 4-31G//4-31G[a] | 6-31G//4-31G | 6-31G*//4-31G | 6-31G**//4-31G |
|---|---|---|---|---|---|
| (**I**) (4-Ring) | −278.246 15 | −281.341 10(0) | −281.631 91 | −281.798 53 | −281.805 27 |
| (**II**) (5-Ring) | −278.295 14 | −281.358 00(0) | −281.648 13 | −281.821 16 | −281.827 72 |
| (**III**) (Nitro) | −278.074 10 | −281.272 38(1) | −281.564 66 | −281.720 73 | −281.727 71 |
| (**IV**) ($\pi$-Complex) | −278.065 85 | −281.259 77(1) | −281.549 68 | −281.711 41 | −281.718 57 |
| (**V**) (*O*-Nitroso) | −278.234 33 | −281.108 97 | — | — | — |
| (**III**) (Nitro) | −278.148 73* | — | — | — | — |
| (**III**) (Nitro) | −278.224 75† | −281.275†,‡ | — | — | — |

* Spin contaminated UHF energy. † Spin contaminated UHF triplet energy. ‡ The optimisation shows that the triplet is dissociative. [a] The numbers in brackets are the critical point indices; 1 indicates a transition state and 0 a stable minimum.

**Table 2**. Correlated RMP2/4-31G//4-31G data* for the ethylene–$NO_2^+$ system

| Structure | Energy (hartree) | $\Delta\varepsilon_{corr.}$ (hartree) |
|---|---|---|
| (**I**) | −281.905 23 | −0.564 13 |
| (**II**) | −281.909 75 | −0.551 75 |
| (**III**) | −281.840 44 | −0.568 06 |
| (**IV**) | −281.883 14 | −0.610 76 |

[a] Frozen core; orbitals 6-53 active in the correlation calculations.

**Table 3**. Structure of the ethylene–$NO_2^+$ nitro compound (**III**)*

| Geometric variable | STO-3G | 4-31G | GVB/1:4-31G |
|---|---|---|---|
| $r_{CC}$ | 1.4612 | 1.4719 | 1.4742 |
| $r_{CN}$ | 1.6671 | 1.5575 | 1.5177 |
| $r_{NO_1}$ | 1.2573 | 1.2059 | 1.2441 |
| $r_{NO_2}$ | 1.2573 | 1.2059 | 1.2437 |
| $r_{C_1H_1}$ | 1.0934 | 1.0758 | 1.0750 |
| $r_{C_1H_2}$ | 1.0934 | 1.0766 | 1.0755 |
| $r_{C_2H_3}$ | 1.1100 | 1.0780 | 1.0778 |
| $r_{C_2H_4}$ | 1.1100 | 1.0780 | 1.0778 |
| $<NC_1C_2$ | 101.721 | 103.153 | 98.524 |
| $<O_1NC_1$ | 114.146 | 115.205 | 116.709 |
| $\tau(O_1NC_1C_2)$ | 93.369 | 89.377 | 90.583 |
| $<O_2NC_1$ | 114.146 | 115.379 | 116.806 |
| $\tau(O_2NC_1C_2)$ | 270.954 | 270.083 | 269.097 |
| $<H_1C_1C_2$ | 114.313 | 113.604 | 114.231 |
| $\theta(H_1C_1N)$ (−1)† | 105.072 | 106.060 | 107.762 |
| $\theta(H_2C_1N)$ (+1)† | 104.801 | 105.756 | 107.670 |
| $<H_2C_1C_2$ | 114.313 | 113.338 | 114.096 |
| $<H_3C_2C_1$ | 121.286 | 120.790 | 120.622 |
| $\tau(H_3C_1C_1H_2)$ | —26.014 | —27.158 | —28.249 |
| $<H_4C_2C_1$ | 121.286 | 120.932 | 120.916 |
| $\tau(H_4C_2C_1H_1)$ | 23.808 | 23.840 | 25.048 |

* See the Results section for a description of the *Z*-matrix parameters $\tau$ and $\theta$. The other parameters are self-explanatory. † Additional parameter specifying position of H1 or H2. The atom N2 is the second carbon (see Results section).

some semi-empirical programs. However, it behoves us here to give a brief description of this mode of presentation of the atomic co-ordinate data.

The label (L) specifies the current atom or dummy centre (denoted by X in the atom column). N1 is the centre from which L is distant the value appearing in the Length column. N2 is the next centre away from N1, the angle $\alpha$ being the angle LN1N2. It is with N3 and $\beta$ that some further explanation is necessary. Normally, unless otherwise indicated, $\beta$ is the dihedral angle between the planes LN1N2 and N1N2N3. The angle is positive if the vector $\overrightarrow{N1L}$ has to be rotated clockwise to 'eclipse' vector $\overrightarrow{N2N3}$, negative if the rotation has to be anticlockwise. This description is sufficient for all but the nitro form of the ethylene system (Table 3). In that Table $\tau$ denotes a torsion angle as just described. For the angles marked $\theta$ N3 specifies a nucleus for which a second internuclear angle LN1N3 is defined, and $\theta$ is the magnitude of this angle in degrees. There are, however, two possible positions of nucleus N3. If the triple vector product $(\overrightarrow{N1L})\cdot(\overrightarrow{N1N2} \leqslant \overrightarrow{N1N3})$ is positive then an additional parameter is set equal to +1, if negative to −1. This additional parameter is given in brackets in Table 3 (it is normally zero for the dihedral angle specification).

The alternative descriptions in terms of additional bond angles rather than the torsional angles given here are available on request, as are the *Z*-matrices of the remaining benzene–$NO_2^+$ stationary points.

Tables 1—7 contain the energies, structures and charge distributions of the ethylene systems described. Tables 8—12 contain the benzene energetic data and selected structures. Table 13 contains selected semi-empirical data. Wavenumbers of vibration of the various (*ab initio*) stationary points characterised are available on request.

## Discussions

Consider first the ethylene data. The 5- and 4-membered-ring structures have already been established[2] to be stable intermediates, and the nitro form to be a transition state at the 3-21G level. These conclusions are unmodified using the 4-31G basis set. Additionally the $\pi$-complex is also found to be a transition state, above the nitro form in energy at the SCF level. This finding is in agreement with Frenking's MINDO/3 study[4] (but see below). The *O*-nitroso form is found to be of high energy at the 4-31G level, although a nitrito-like form with close to $C_s$ symmetry of much lower energy was found, but the optimisation did not converge (oscillations set in). Of particular note are the strongly destabilised nitro form at the SCF level, and the strongly stabilised 4- and 5-membered-ring structures. Introduction of correlation energy by second-order Møller–Plesset perturbation theory[34] modifies the predicted stability sequence such that the $\pi$-complex is now lower in energy than the nitro form. This appears to be another example where a non-classical ion is more stable than the corresponding classical ion in the gas phase (found also to be true in protonation,[35] fluorination,[35] chlorination[35] and bromination[36]). Of the other species the nitro form is (slightly) the most stabilised. It is to a discussion of this species that we now turn.

The change in basis set from STO-3G to 4-31G leads to a marked reduction in the C–$NO_2$ bond length from 1.67Å to 1.56Å. It was suspected that this bond, and indeed the nitro group as a whole, would be subject to correlation effects, so it was decided to perform Generalised Valence Bond[37] calculations (specifically GVB/1). Firstly the Boys localised orbitals were found for the ion. The bonding and antibonding orbitals relating to the C–$NO_2$ bond were then found by inspection, and

**Table 4.** Ethylene $\pi$-complex; $Z$-matrices

| Label (L) | Atom | N1 | Length (Å) STO-3G | 4-31G | N2 | $\alpha$ (°)* STO-3G | 4-31G | N3 | $\beta$ (°)† STO-3G | 4-31G |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Dummy | — | — | — | — | — | — | — | — | — |
| 2 | C | 1 | 1.0 | 1.0 | — | — | — | — | — | — |
| 3 | Dummy | 2 | 0.6965 | 0.6965 | 1 | 90.0 | 90.0 | — | — | — |
| 4 | N | 3 | 1.9063 | 1.9361 | 2 | 90.0 | 90.0 | 1 | 180.0 | 180.0 |
| 5 | O | 4 | 1.2415 | 1.1775 | 3 | 111.672 | 111.553 | 2 | 90.162 | 90.011 |
| 6 | O | 4 | 1.2415 | 1.1775 | 3 | 111.670 | 111.618 | 2 | 270.160 | 269.978 |
| 7 | C | 3 | 0.6959 | 0.6965 | 4 | 90.0 | 90.0 | 5 | 270.168 | 270.040 |
| 8 | H | 7 | 1.0956 | 1.0736 | 3 | 120.951 | 120.788 | 4 | 92.736 | 91.912 |
| 9 | H | 7 | 1.0956 | 1.0736 | 3 | 120.951 | 120.788 | 4 | 267.266 | 267.726 |
| 10 | H | 2 | 1.0956 | 1.0736 | 3 | 120.951 | 120.788 | 4 | 267.266 | 267.726 |
| 11 | H | 2 | 1.0956 | 1.0736 | 3 | 120.951 | 120.788 | 4 | 92.736 | 91.912 |

[a] $\alpha$: angle LN1N2. † $\beta$: torsion angle LN1N2N3.

**Table 5.** Ethylene 5-ring; $Z$-matrices*

| Label (L) | Atom | N1 | Length (Å) STO-3G | 4-31G | N2 | $\alpha$ (°) STO-3G | 4-31G | N3 | $\beta$ (°) STO-3G | 4-31G |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Dummy | — | — | — | — | — | — | — | — | — |
| 2 | C | 1 | 0.8640 | 0.9044 | — | — | — | — | — | — |
| 3 | O | 2 | 1.4624 | 1.5348 | 1 | 106.967 | 105.279 | — | — | — |
| 4 | N | 3 | 1.3280 | 1.2565 | 2 | 112.642 | 113.626 | 1 | 0.0 | 0.0 |
| 5 | O | 4 | 1.3280 | 1.2565 | 3 | 110.816 | 111.907 | 2 | 0.0 | 0.0 |
| 6 | C | 5 | 1.4624 | 1.5348 | 4 | 112.642 | 113.626 | 3 | 0.0 | 0.0 |
| 7 | H | 6 | 1.1057 | 1.0731 | 5 | 106.222 | 104.781 | 4 | 242.689 | 239.537 |
| 8 | H | 6 | 1.1057 | 1.0731 | 5 | 106.222 | 104.781 | 4 | 121.544 | 120.496 |
| 9 | H | 2 | 1.1057 | 1.0731 | 3 | 106.222 | 104.781 | 4 | 242.689 | 239.537 |
| 10 | H | 2 | 1.1057 | 1.0731 | 3 | 106.222 | 104.781 | 4 | 121.544 | 120.496 |

* See base of Table 4.

**Table 6.** Ethylene 4-ring; $Z$-matrices*

| Label (L) | Atom | N1 | Length (Å) STO-3G | 4-31G | N2 | $\alpha$ (°) STO-3G | 4-31G | N3 | $\beta$ (°) STO-3G | 4-31G |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Dummy | — | — | — | — | — | — | — | — | — |
| 2 | C | 1 | 0.9044 | 0.9044 | — | — | — | — | — | — |
| 3 | O | 2 | 1.4911 | 1.5285 | 1 | 90.004 | 90.014 | — | — | — |
| 4 | N | 3 | 1.4095 | 1.3462 | 2 | 90.641 | 91.600 | 1 | 0.0 | 0.0 |
| 5 | O | 4 | 1.2199 | 1.1501 | 3 | 125.848 | 126.064 | 2 | 180.0 | 180.0 |
| 6 | C | 4 | 1.5506 | 1.5257 | 3 | 94.875 | 95.690 | 2 | 0.0 | 0.0 |
| 7 | H | 6 | 1.0983 | 1.0779 | 4 | 110.470 | 110.156 | 3 | 242.727 | 242.315 |
| 8 | H | 6 | 1.0983 | 1.0779 | 4 | 110.470 | 110.156 | 3 | 117.272 | 117.685 |
| 9 | H | 2 | 1.0965 | 1.0714 | 3 | 110.572 | 108.565 | 4 | 242.727 | 242.162 |
| 10 | H | 2 | 1.0965 | 1.0714 | 3 | 110.572 | 108.565 | 4 | 117.272 | 117.838 |

* See base of Table 4.

**Table 7.** Mulliken net atomic charges for the ethylene $+NO_2^+$ nitro form

| Atom | Basis STO-3G | 6-31G | 6-31G* | 6-31G** |
|---|---|---|---|---|
| $C_1$ | −0.077 | −0.280 | −0.300 | −0.197 |
| $C_2$ | +0.179 | +0.101 | +0.040 | +0.145 |
| N | +0.216 | +0.332 | +0.520 | +0.514 |
| $O_1$ | −0.051 | −0.280 | −0.342 | −0.343 |
| $O_2$ | −0.053 | −0.280 | −0.343 | −0.343 |
| $H_1$ | +0.177 | +0.347 | +0.343 | +0.293 |
| $H_2$ | +0.178 | +0.349 | +0.345 | +0.295 |
| $H_3$ | +0.215 | +0.355 | +0.369 | +0.319 |
| $H_4$ | +0.215 | +0.354 | +0.369 | +0.318 |

the orbitals reordered so that the selected bonding orbital was put top of the occupied orbitals (the strong component of the GVB pair), and the antibonding orbital bottom of the virtual set (the weak component of the GVB pair). GVB/1 Calculations, corresponding to a 2 determinant MCSCF level, were then performed using the vectorised GAMESS package. A significant energy reduction was found (0.07 hartree) but more interestingly incipient biradicaloid character was found (GVB coefficients −0.946 and +0.324). Geometry optimisation, however, does not much reduce the energy. Increasing the C–$NO_2$ bond length by approximately 5 and 10% leads to very little change in the two GVB coefficients; geometry optimisation at these extensions shows that the energy change is small (*ca.* 6 kcal mol$^{-1}$, or 25 kJ mol$^{-1}$ out to the 10%

**Table 8.** STO-3G Structure of the benzene (nitrito) σ-complex *Z*-matrix*

| Label (L) | Atom | N1 | Length (Å) | N2 | α (°) | N3 | β (°) |
|---|---|---|---|---|---|---|---|
| 1 | H | — | — | — | — | — | — |
| 2 | C | 1 | 1.0972 | — | — | — | — |
| 3 | C | 2 | 1.4235 | 1 | 118.398 | — | — |
| 4 | C | 3 | 1.3543 | 2 | 119.114 | 1 | 179.025 |
| 5 | C | 4 | 1.5136 | 3 | 122.139 | 2 | 3.412 |
| 6 | C | 5 | 1.5136 | 4 | 113.933 | 3 | −6.731 |
| 7 | C | 6 | 1.3542 | 5 | 122.148 | 4 | +6.734 |
| 8 | H | 3 | 1.0829 | 2 | 119.357 | 1 | 0.648 |
| 9 | H | 7 | 1.0829 | 2 | 119.347 | 8 | 0.505 |
| 10 | H | 4 | 1.0932 | 3 | 121.140 | 8 | 0.019 |
| 11 | H | 6 | 1.0932 | 7 | 121.135 | 9 | −0.153 |
| 12 | H | 5 | 1.1127 | 6 | 106.284 | 11 | 68.296 |
| 13 | O | 5 | 1.4542 | 6 | 111.114 | 11 | 311.343 |
| 14 | N | 13 | 1.4368 | 5 | 114.349 | 12 | −0.327 |
| 15 | O | 14 | 1.2158 | 13 | 113.002 | 5 | 0.024 |

* See base of Table 4.

**Table 9.** STO-3G Structure of the benzene (nitrito) σ-complex *Z*-matrix*

| Label (L) | Atom | N1 | Length (Å) | N2 | α (°) | N3 | β (°) |
|---|---|---|---|---|---|---|---|
| 1 | H | — | — | — | — | — | — |
| 2 | C | 1 | 1.0976 | — | — | — | — |
| 3 | C | 2 | 1.4270 | 1 | 118.426 | — | — |
| 4 | C | 3 | 1.3527 | 2 | 119.239 | 1 | 178.517 |
| 5 | C | 4 | 1.5088 | 3 | 121.530 | 2 | 2.932 |
| 6 | C | 5 | 1.5081 | 4 | 115.053 | 3 | −5.351 |
| 7 | C | 6 | 1.3534 | 5 | 121.669 | 4 | 5.181 |
| 8 | H | 3 | 1.0835 | 2 | 119.285 | 1 | −0.068 |
| 9 | H | 7 | 1.0835 | 2 | 119.407 | 1 | −0.160 |
| 10 | H | 4 | 1.0931 | 3 | 121.619 | 8 | 0.412 |
| 11 | H | 6 | 1.0937 | 7 | 121.953 | 9 | −0.267 |
| 12 | H | 5 | 1.1052 | 6 | 107.604 | 11 | 64.079 |
| 13 | N | 5 | 1.5765 | 6 | 109.905 | 11 | 311.350 |
| 14 | O | 13 | 1.2695 | 5 | 116.608 | 12 | 108.572 |
| 15 | O | 13 | 1.2688 | 5 | 115.507 | 12 | 289.432 |

* See base of Table 4.

**Table 10.** 3-21G Structure of the benzene (nitrito) σ-complex *Z*-matrix*

| Label (L) | Atom | N1 | Length (Å) | N2 | α (°) | N3 | β (°) |
|---|---|---|---|---|---|---|---|
| 1 | H | — | — | — | — | — | — |
| 2 | C | 1 | 1.0734 | — | — | — | — |
| 3 | C | 2 | 1.4096 | 1 | 118.353 | — | — |
| 4 | C | 3 | 1.3496 | 2 | 118.996 | 1 | 177.042 |
| 5 | C | 4 | 1.4820 | 3 | 120.924 | 2 | 6.578 |
| 6 | C | 5 | 1.4820 | 4 | 115.595 | 3 | −13.132 |
| 7 | C | 6 | 1.3496 | 5 | 120.924 | 4 | 13.142 |
| 8 | H | 3 | 1.0693 | 2 | 119.577 | 1 | −0.009 |
| 9 | H | 7 | 1.0693 | 2 | 119.577 | 8 | −0.009 |
| 10 | H | 4 | 1.0720 | 3 | 121.922 | 8 | 0.031 |
| 11 | H | 6 | 1.0720 | 7 | 121.922 | 9 | 0.031 |
| 12 | H | 5 | 1.1064 | 5 | 104.298 | 11 | 75.816 |
| 13 | O | 5 | 1.4373 | 6 | 111.601 | 11 | 318.451 |
| 14 | N | 13 | 1.4835 | 5 | 116.477 | 12 | −0.638 |
| 15 | O | 14 | 1.1651 | 13 | 113.024 | 5 | −0.014 |

* See base of Table 4.

extension). As expected the optimised C–C bond length at $r_{C\text{-}NO_2}$ = 1.7 Å is reduced quite considerably (to 1.43 Å) towards the ethylene value.

Semi-empirical MNDO data (Table 13) predicts that the triplet state of the nitro form should be lower in energy than the singlet state; MINDO/3 shows that the triplet state is above the singlet, but only by 35 kcal mol$^{-1}$ (138 kJ mol$^{-1}$). It seems that the two states are close. It was therefore decided to perform *ab initio* UHF STO-3G calculations at the RHF STO-3G optimised geometry. The obvious solution was found as well as a lower-energy, slightly spin-contaminated [$S(S + 1) = 0.126$] singlet 0.074 hartree below the former. At the same geometry the UHF triplet solution (rather more spin-contaminated [$S(S + 1) = 2.424$] was a further 0.025 hartree below this. Geometry

**Table 11.** 3-21G Structure of the benzene (nitrito) σ-complex *Z*-matrix*

| Label (L) | Atom | N1 | Length (Å) | N2 | α (°) | N3 | β (°) |
|---|---|---|---|---|---|---|---|
| 1 | H | — | — | — | — | — | — |
| 2 | C | 1 | 1.0735 | — | — | — | — |
| 3 | C | 2 | 1.4121 | 1 | 118.380 | — | — |
| 4 | C | 3 | 1.3478 | 2 | 119.314 | 1 | 176.505 |
| 5 | C | 4 | 1.4826 | 3 | 119.876 | 2 | 7.566 |
| 6 | C | 5 | 1.4826 | 4 | 116.733 | 3 | −14.962 |
| 7 | C | 6 | 1.3478 | 5 | 119.876 | 4 | 14.973 |
| 8 | H | 3 | 1.0694 | 2 | 119.602 | 1 | 0.001 |
| 9 | H | 7 | 1.0694 | 2 | 119.602 | 1 | 0.001 |
| 10 | H | 4 | 1.0707 | 3 | 122.846 | 8 | 0.009 |
| 11 | H | 6 | 1.0707 | 7 | 122.846 | 9 | 0.009 |
| 12 | H | 5 | 1.1022 | 6 | 105.279 | 11 | 74.815 |
| 13 | O | 5 | 1.5113 | 6 | 112.340 | 11 | 322.971 |
| 14 | N | 13 | 1.2318 | 5 | 115.710 | 12 | 271.795 |
| 15 | O | 13 | 1.2318 | 5 | 115.710 | 12 | 87.949 |

* See base of Table 4.

**Table 12.** Energies (hartree) of the structures (**VI**)—(**X**) (benzene related)

| Structure | STO-3G//STO-3G* | 3-21G//STO-3G | 4-31G//STO-3G | $\left.\begin{matrix}\text{3-21G}\\ \text{4-31G}\end{matrix}\right\}$//3-21G |
|---|---|---|---|---|
| (**VI**) (Nitro) | −428.931 76 (1) | −431.958 64 | −433.763 16 | −431.968 64<br>−433.777 10 |
| (**VII**) (Nitrito) | −429.016 00 (2) | −432.003 61 | −433.789 64 | −432.011 21<br>−433.800 24 |
| (**VIII**) (5-ring) | −429.062 05 (0) | −431.990 58 | −433.759 54 | — |
| (**IX**) (4-ring) | −429.014 25 (2) | −431.960 26 | −433.739 86 | — |
| (**X**) (π-Complex) | −428.898 89 (2) | −431.920 62 | −433.720 76 | — |

* The figure in brackets is the critical point index; 2 indicates a super-saddle point, 1 a saddle point, and 0 a true minimum.

**Table 13.** Optimised semi-empirical energetic data ($\Delta H_f^{298}$) (kJ mol$^{-1}$)

| | | | MINDO/3* | |
|---|---|---|---|---|
| Species | State | MNDO | ε = 1 | ε = 50 |
| (**VI**) | Singlet | 947.5 | 875.5 | 413.4 |
| (**VII**) | Singlet | 923.2 | 751.2 | 356.3 |
| (**VIII**) | Singlet | 866.3 | 694.1 | 284.5 |
| (**II**) | Singlet | 755.3 | 618.1 | 163.7 |
| (**III**) | Singlet | 1 030.0 | 923.4 | 369.8 |
| (**II**) | Triplet | 1 015.7 | 768.8 | 282.2 |
| (**III**) | Triplet | 980.9 | 1 061.7 | 558.3 |

* MINDO/3-Solvaton calculations (ε = 1, gas phase)

optimisation of the triplet reduces the C–$NO_2$ bond length from the singlet value of 1.67 Å to 1.58 Å, and increases the NO bond lengths to 1.39 Å, giving a final energy of −278.224 75 hartree, with $S(S + 1) = 2.682$. At the 4-31G level the triplet state seems to be dissociative into $NO_2^{\bullet}$ and $C_6H_6^{+\bullet}$, but to have about the same energy as the (optimised) RHF singlet, in fact slightly lower. To clarify the state ordering of the nitro form-configuration interaction calculations on both the closed shell singlet and on the lowest triplet state were performed at the 4-31G-optimised geometry, using the 4-31G basis set and frozen core orbitals. A 114 003 configuration all singles and doubles calculation using the DIRECT module of the ATMOL package from the (putative) ground state gave an energy of −281·761 32 hartree; the Davidson correction for quadruple excitations with a root determinant CI coefficient of 0.9256 gives a further lowering of 0.070 05 hartree, to −281.831 37 hartree. Using RHF triplet state vectors in a 460 587 configuration all 1 + 2 calculation from the lowest triplet state an energy of −281.715 34 hartree was found. From this evidence therefore it is improbable that the triplet state lies below the singlet state (at this geometry).

The charge distributions for varying basis set size for the nitro form are presented in Table 7. The 6-31G** distribution is seen to be markedly different with respect to the unpolarised basis set; the positive charge on the nitrogen increases appreciably. Realistic descriptions of nitro group-containing compounds would seem to require at least this level of basis set. It is worth pointing out that $NO_2^+$ at good quality basis set level has no nucleophilic centres; both N (*ca.* +0.6) and O (*ca.* +0.2) are electrophilic in nature.

Although no data have been reported on the nitration of ethylene in solution, MINDO/3-solvaton calculations (Table 13) show that the nitro form would be appreciably stabilised by solvation; a differential stabilisation of 25 kcal mol$^{-1}$ (105 kJ mol$^{-1}$) relative to the 5-membered-ring structure is indicated (for ε = 50).

Considering now the benzene–nitronium interaction, for which a 6-31G** calculation would be a 156 orbital problem, very definitely a non-trivial calculation. The number of geometric variables makes geometry optimisation at higher than the STO-3G level exceedingly expensive even with vector code; the nitro and nitrito forms have, however, been selected for (symmetry constrained) geometry optimisation at the 3-21G level. The emergence of the nitrito form as a stable structure on the benzene–nitronium ion hypersurface seems to be due to a strong stabilising interaction between the terminal oxygen of the nitrito group and the hydrogen at the seat of substitution (preserving *ca.* $C_s$ symmetry). One can conjecture that the oscillations encountered in the ethylene study of the nitrito form were between in fact two nitrito forms in which the ONO group lies not *between* the two hydrogens of one $CH_2$ group but over one or the other, preserving in this way a similar type of stabilising interaction to that found in the benzene study.

The energy ordering of the five species discovered is markedly dependent upon basis set size and quality, the 3-21G//STO-3G calculations being at variance with the 4-31G/STO-3G ones in the positioning of the nitro group in the sequence. The 3-21G and 4-31G calculations, however, at both STO-3G-optimised geometries and at (symmetry constrained) 3-21G-optimised geometries show that the nitrito form is the most stable species. One can therefore rationalise the gas-phase formation of $C_6H_6O^{+\bullet}$ in the reaction of benzene with the nitronium ion[7] as being due to the loss of nitric oxide from the vibrationally excited nitrito form. With $EtONO_2NO_2^+$ benzene forms an adduct of σ-complex stoicheiometry,[7] which is likely to be an isomerising mixture of the lower-energy forms. This reaction is less exothermic than the nitronium ion reaction, so that the product ions are formed with less internal energy for fragmentation. We will return to the nitrito form later. A GVB/1 calculation on the nitro compound reveals an increasing tendency towards biradical nature ($C_1 = 0.899$, $C_2 = -0.438$, $\Delta E = 0.12$ hartree), although these results are for the STO-3G basis set. Marked geometry changes are found, however, on introducing correlation in this two determinant treatment; thus the C–N bond length reduces to 1.48 Å, and the NO bond lengths increase to 1.35 Å. It is clear that theoretical predictions for nitro group-containing systems are sensitive to both basis set and correlation effects. In solution differential solvation is also important (*vide infra*). The correct energetic ordering of the various species is expected therefore to be an unusually difficult problem (a GVB/1 calculation on the nitrito form also shows correlation effects on the structure, but they are less marked and the energy reduction is smaller than in the nitro case).

As in the ethylene problem semi-empirical data indicate that the triplet states of the various benzene complexes are within 30 kcal mol$^{-1}$ (125 kJ mol$^{-1}$) of the ground singlet state. Geometry-optimised UHF STO-3G calculations on the nitro form triplet state give an energy about 0.05 hartree below the singlet state. Again it is clear that the proximity of the states requires a higher level of basis set as well as appreciable configuration interaction for a clear statement of which is the lowest-energy state of the classical nitro form. Induced spin-orbit interactions may therefore be implicated in the Perrin mechanism,[11] and the solvent may play a rôle other than that of stabilising ionic species in solution. For a discussion of this latter point let us consider again the semi-empirical data reported in Table 13. Crude though they may be the MINDO/3-solvaton calculations show that the nitro form is stabilised by 15 kcal mol$^{-1}$ (63 kJ mol$^{-1}$) in a medium of dielectric constant 50 with respect to the 5-membered ring, and by a greater amount relative to the nitrito form. It appears therefore that solvation may be the cause of the (well known) appearance of nitro Wheland intermediates in solution; without it the nitrito form would predominate. Of interest here are the recent reports by Hartshorn *et al.*,[38] and by Ridd, Sandall *et al.*,[39] of the observation in *ipso*-nitration of a nitro–nitrito equilibrium. The medium (chloroform) is such ($\varepsilon = 5$) that the differential stabilisation of the nitro form is less than maximal, and the two forms coexist.

In conclusion we note the importance of correlation effects in these systems, both on energetic ordering and on the emergence of biradicaloid character, and the possibly critical role of solvation in determining the most stable form in solution.

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