

Semi-empirical Calculations on the Electronic Structures of Some Anionic σ -Complexes

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The π -electronic structures of 1,3,5-trinitrobenzene, 1,3,5-trinitrocyclohexadienide, 1,5-dinitrocyclohexadienide, 1,3-dinitrocyclohexadienide, 1,3-dinitro-4,*x*-dihydronaphthalenide, and 1,3-dinitropropenide ions have been calculated using a modification of the SCFMO-PPP method. The calculated electronic transitions agree qualitatively with experimental electronic spectra. The structures of the 1,3,5-trinitrocyclohexadienide ion and the corresponding neutral compound 3,5-dinitrocyclohexa-2,5-dienenitronic acid are discussed.

Polynitroarenes form stable anionic σ -complexes with a wide variety of nucleophiles. Most studied are complexes from 2,4,6-trinitroanisole and 1,3,5-trinitrobenzene. The chemistry, structure, and spectroscopic properties of these complexes, often called Meisenheimer complexes, have been reviewed by several authors.¹

We have carried out a semi-empirical molecular orbital calculation on the π -electron systems of some anionic σ -complexes using a modification of the Pariser-Parr-Pople method. The present work may be regarded as an extension of several previous calculations by Abe,² Caveng *et al.*,³ Hosoya *et al.*⁴ and by Strauss and Weltin.⁵

METHOD OF CALCULATION

We have used the Pariser-Parr-Pople scheme with a parameterisation method proposed by Fischer-Hjalmars⁶ and Roos and Skancke.⁷ The parameters were determined by fitting experimental data on model compounds to calculated values.⁸ The basic additions to the original PPP-scheme are the following: (a) the diagonal elements of the core operator depend on the number of π -electrons with which the atom contributes and on the neighbouring atoms; (b) the resonance integral β depends linearly on bond distances, and (c) the electron repulsion integral γ for nearest neighbours also depends linearly on

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bond distances. The proportionality constants for both β and γ are determined for each type of bond from experimental ionisation potentials and excitation energies.

The π -electron systems were all assumed to be planar, and the carbon-carbon bond lengths were iteratively fit within less than 0.01 Å to the bond-order bond-length relation

$$R_{\mu\nu} = 1.517 - 0.18 p_{\mu\nu}$$

where $R_{\mu\nu}$ is the bond length between atoms μ and ν and $p_{\mu\nu}$ is the mobile bond order between the same atoms. The carbon-nitrogen bond lengths were set equal to 1.40 Å and the nitrogen-oxygen bond lengths to 1.22 Å. However, the bond distances in the anion **2** were chosen as the average of the published X-ray data for 6,6-dimethoxy- and 6,6-diethoxy-1,3,5-trinitrocyclohexadienide ions.⁹

The saturated CH₂-groups in anions **2**–**5** were treated as described by Maggiora *et al.*¹⁰

In the calculation of the excited states, all singly excited states were mixed in a configuration interaction. The charge and bond orders in the ground state listed in Tables 1 and 2 were taken directly from the charge and bond order density matrix.

RESULTS

We have performed calculations on the π -electron system in 1,3,5-trinitrobenzene (**1**), 1,3,5-trinitrocyclohexadienide (**2**), 1,5-dinitrocyclohexadienide (**3**), 1,3-dinitrocyclohexadienide (**4**), 1,3-dinitro-4,*x*-dihydronaphthalide (**5**), and 1,3-dinitropropenide (**6**) ions. For convenience the numbering system for 1,3,5-trinitrobenzene is used for all of the compounds **2**–**6**. Thus, for example the methylene carbon in **2**–**5** is numbered C₄ (see Fig. 1).

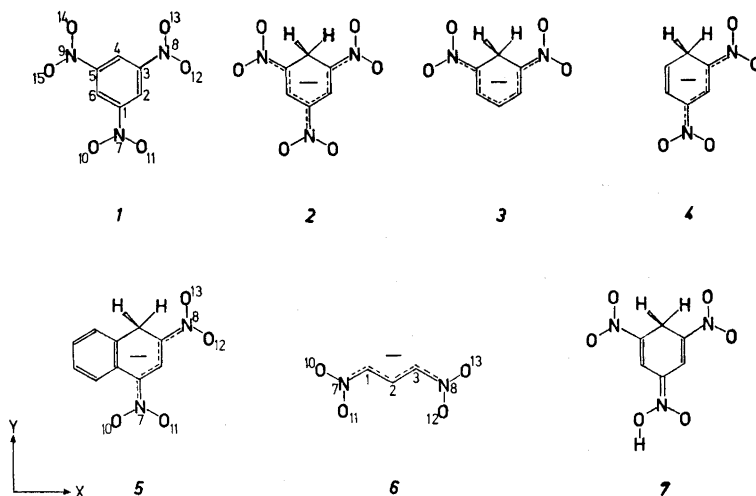


Fig. 1. Structural formulas, numbering of atoms, and choice of coordinate axes for the compounds on which calculations were made.

Table 1. Calculated atomic π -electron charges for compounds 1-6.

| Atom | Compound | | | | | |
|------|----------|-------|-------|-------|------------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| C 1 | +0.25 | +0.01 | -0.16 | +0.01 | ± 0.00 | -0.07 |
| 2 | -0.22 | -0.17 | -0.07 | -0.12 | -0.12 | -0.08 |
| 3 | | +0.08 | +0.04 | +0.04 | +0.02 | |
| 5 | | | | -0.11 | ± 0.00 | |
| 6 | | | | -0.06 | ± 0.00 | |
| N 7 | +1.27 | +1.15 | | +1.11 | +1.10 | +1.10 |
| 8 | | +1.17 | +1.10 | +1.10 | +1.10 | |
| O 10 | -0.65 | -0.72 | | -0.76 | -0.76 | -0.76 |
| 12 | | -0.71 | -0.75 | -0.75 | -0.73 | -0.74 |
| 13 | | -0.74 | -0.75 | -0.74 | -0.76 | |

Table 2. Calculated π -electron bond orders for compounds 1-6.

| Bond | Compound | | | | | |
|----------|----------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| C-C 1-2 | 0.63 | 0.52 | 0.60 | 0.57 | 0.58 | 0.66 |
| 2-3 | | 0.75 | 0.70 | 0.71 | 0.70 | |
| 1-6 | | | | 0.42 | 0.39 | |
| 5-6 | | | | 0.88 | 0.61 | |
| C-N 1-7 | 0.21 | 0.46 | | 0.52 | 0.53 | 0.56 |
| 3-8 | | 0.43 | 0.52 | 0.52 | 0.52 | |
| N-O 7-10 | 0.66 | 0.56 | | 0.52 | 0.52 | 0.51 |
| 8-12 | | 0.57 | 0.52 | 0.53 | 0.54 | 0.53 |
| 8-13 | | 0.55 | 0.52 | 0.51 | 0.51 | |

Table 3. Calculated electronic singlet transitions for the anions 2-6. See Fig. 1 for choice of axes.

| Compound | Frequency nm | Oscillator strength f | Orbital symmetries | Polarization |
|----------|-----------------|----------------------------|-----------------------|--------------|
| 2 | 589 | 0.55 | $S \rightarrow A$ | x |
| | 418 | 0.74 | $S \rightarrow S$ | y |
| 3 | 543 | 0.71 | $S \rightarrow A$ | x |
| | 310 | 0.22 | $S \rightarrow S$ | y |
| 4 | 501 | 0.55 | | |
| | 366 | 0.69 | | |
| 5 | 478 | 0.73 | | |
| | 372 | 0.18 | | |
| | 355 | 0.49 | | |
| 6 | 389 | 1.33 | $A \rightarrow S$ | x |

We have also made some attempts to calculate the π -electron structure of the neutral 3,5-dinitrocyclohexa-2,5-dienenitronic acid 7. These results will be treated separately (*vide infra*).

The calculated π -electron densities in the ground state, the π -electron bond orders, and the results concerning the electronic transitions are presented in Tables 1, 2, and 3, respectively. In Table 3 are included wavelengths for absorptions, oscillator strengths, and the symmetries of the orbitals involved. For comparison the experimentally determined absorption maxima and extinction coefficients for closely related compounds are listed in Table 4.

DISCUSSION

Validity of approximations. The reliability of the calculations is of course of crucial importance in the present work. Several approximations have been made, which will now be discussed.

Table 4. Experimentally determined electronic transitions in the visible region for some derivatives of the anionic compounds 2–6.

| Compound | Solvent | Absorption maxima ϵ_1 , | | | | Ref. |
|---|-----------------|----------------------------------|------------------------------------|-------------|-------------------|------|
| | | λ_1 , nm | $\text{l mol}^{-1} \text{cm}^{-1}$ | λ_2 | ϵ_2 | |
| 1,3,5-Trinitrocyclohexadienide ion 2 | acetonitrile | 478 | 3.1×10^4 | 585 | 1.5×10^4 | 18 |
| 6-Methyl-1,3,5-trinitrocyclohexadienide ion 2 | acetonitrile | 470 | 3.2 | 572 | 1.5 | 19 |
| 6-Butyl-1,3,5-trinitrocyclohexadienide ion 2 | acetonitrile | 474 | 3.2 | 568 | 1.5 | 19 |
| 5-Cyclopentadienyl-1,3,5-trinitrocyclohexadienide ion 2 | ethanol | 464 | 3.0 | 550 | 1.3 | 20 |
| | pyridine | 470 | 3.0 | 573 | 1.5 | |
| 6(2,6-Dimethoxyphenyl)-1,3,5-trinitrocyclohexadienide ion 2 | ethanol | 471 | 2.8 | 554 | 1.1 | 15 |
| | pyridine | 475 | 2.8 | 585 | 1.3 | |
| 6-Methoxy-1,3,5-trinitrocyclohexadienide ion 2 | methanol | 425 | 3.1 | 495 | 2.1 | 21 |
| 6,6'-Dimethoxy-1,3,5-trinitrocyclohexadienide ion 2 | methanol | 414 | 2.6 | 487 | 1.8 | 22 |
| | acetone | 420 | 2.9 | 494 | 1.9 | |
| | acetonitrile | 421 | 2.9 | 494 | 1.9 | |
| | tetrahydrofuran | 407 | 2.5 | 504 | 2.1 | |
| 6,6'-Dimethoxy-1,5-dinitrocyclohexadienide ion (analogue of 3) | methanol | 584 | 2.3 | | | 23 |
| 6,6'-Dimethoxy-1,3-dinitrocyclohexadienide ion (analogue of 4) | methanol | 495 | 2.6 | | | 23 |
| 4,4'-Dimethoxy-1,3-dinitro-dihydronaphthalenide ion (analogue of 5) | methanol | 495 | 2.6 | | | 24 |
| 4,4,6-Trimethoxy-1,3,5-trinitrocyclohexenide ion (analogue of 6) | methanol | 482 | 2.4 | | | 22 |

1. The π - σ -separation is probably less valid in the presence of nitro groups than for simple conjugated aromatic hydrocarbons, since the very low π -electron density on the nitrogen in a nitro group is compensated by a high σ -electron charge.¹¹ A charge transfer to the nitro group on excitation should thus effect the σ -core. However, this error is partly compensated for by the parameterisation made in Ref. 8.

2. The parameters are fitted to experimental data from neutral molecules, and consequently the use of these parameters in calculations on ions introduces some uncertainty. However, it has been noted that the extension of the PPP-approximation to ions is at least sounder than the corresponding extension of the Hückel approximation.¹²

3. As a consequence of the π -approximation, calculations cannot be made on compounds 2–5 with different substituents at C₄. This limitation is not severe, as substituents at C₄ in the σ -complex do not considerably affect the electronic spectrum (Table 4). It is therefore assumed that the comparison of calculated electronic spectra for compounds 3–5 with experimental spectra of compounds with different substituents at C₄ is relevant.

4. Another difficulty in relating experimental and calculated electronic spectra for ionic species is the influence of the solvent, and particularly the presence of ion-pairs. If the σ -complexes exist as ion pairs in solution this could affect the wavelength for absorption. Experimentally the electronic absorptions are little affected by the positive ion but depend on the solvent (Table 4). This does not seem to be easily related to the polarity, and consequently the ion-pair is assumed to be of minor importance.

It should be borne in mind that since the π -electron density is difficult to correlate with any observable quantity, it should be the least reliable of the calculated quantities and should only be used for comparison in a series of similar compounds.

The electronic structure of the Meisenheimer complexes. The electronic structures of the Meisenheimer complexes have been a matter of some dispute.¹ The question is whether the most relevant valence bond form of the anion 2 is 2a or a combination of 2a, b, and c, written as 2 (see Fig. 2). Valence bond

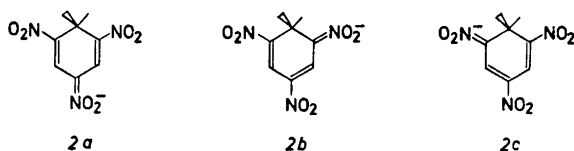


Fig. 2. Possible resonance structures of the anion (2).

forms in which the charge is located on the ring carbons seem to be of minor importance. From Tables 1 and 2 it may be inferred that both forms are important, and that there is a small but significant preference of 2a over 2b and c. The π -electron charges and bond-orders for the three nitro groups are very similar but the carbon-carbon bond between atoms 2 and 3 has more double bond character than in the parent compound, 1,3,5-trinitrobenzene.

This conclusion seems to be in agreement with the result of the calculations by Hosoya *et al.*⁴

The X-ray structure determinations of Meisenheimer complexes of type 2 have shown that the 1–7 C–N bond is significantly shorter than the 3–8 bond.⁸ This has been taken as evidence for the preference of structure 2a over 2. In the crystal lattice the anion may be heavily perturbed. It seems possible that the anion in solution has more equal carbon-nitrogen bonds and nitro groups.

Electronic transitions. The electronic transitions above 200 nm for 1,3,5-trinitrobenzene were calculated to be at 288, 240, 230 (degenerate), and 217 nm (degenerate) with oscillator strengths of 0.00, 0.00, 0.49, and 0.07, respectively. The results are somewhat different from those of Peacock and Wilkinson,¹³ who used a similar method of calculation. The lack of characteristic absorption of 1,3,5-trinitrobenzene make it though of little value for the estimation of the reliability of the present method of calculation. For a discussion of calculated and experimental spectra, see Ref. 13.

The agreement between calculated and observed absorption wavelengths for compounds 2–5 is quite acceptable. Both the absolute magnitudes and relative trends are reproduced with good accuracy.

The discrepancy between calculated and experimental values found for 1,3-dinitropropenide ion (6) indicates that the reduction of 4,4,6-trimethoxy-1,3,5-trinitrocyclohexanide ion to the π -system 6 to account for its electronic spectrum as in Ref. 5, is an oversimplification.

Comparison of the lowest excitations in 1,3,5-trinitrocyclohexadienide (2) and 1,5-dinitrocyclohexadienide (3) ions reveals some interesting features. The lowest excitation is of $S \rightarrow A$ type in both compounds, which implies that the excited state has lost electrons in the symmetry plane. The second lowest transition is of $S \rightarrow S$ type, and the calculations show that there is an increase in electron density in the symmetry plane. These results are in agreement with the observation that removal of the nitro group in the symmetry plane at C₁ in ion 2 to give 3 results in a greater change in the energy for the second excitation than in the first (see Tables 3 and 4). The influence of a strongly electronegative group such as a nitro group is of course greater when there is an increase in electron density at the α -carbon than when there is a decrease in electron density.

Destruction of the symmetry, as in 1,3-dinitrocyclohexadienide ion (4), results in mixing of the two lowest excited states mentioned above.

The fusion of an aromatic ring to system 4, as in 1,3-dinitro-4, x -dihydro-naphthalide ion (5), does not increase the absorption wavelength, but gives rise to a new absorption band at 372 nm, involving primarily a charge transfer from the nitro groups to the unsubstituted benzene ring.

All other transitions in compounds 2–5 involve both a redistribution of electron density within the cyclohexadienyl ring and an increase in electron density on the nitrogens. Hosoya *et al.*⁴ characterized these transitions as charge transfers from the ring to the nitro groups, which seems to be a slight oversimplification.

The structure of 3,5-dinitrocyclohexa-2,5-dienenitronic acid. In analogy with

other salts of nitronic acids,¹³ Meisenheimer compounds could give cyclohexadienenitronic acids or nitrocyclohexadienes on protonation, but other reactions usually occur. The nucleophile used to generate the Meisenheimer compounds can be protonated to give a good leaving group. Polymerisations⁵ or decompositions to polynitroarenes¹⁴ have also been reported. However, we have isolated or spectroscopically observed nitronic acids from protonation of some Meisenheimer anions of type 2 with or without substituents at C₄.¹⁵⁻¹⁷ These acids have not been observed to tautomerize to the corresponding nitro compounds. The structures of the nitronic acids have been proposed, on the basis of their NMR and infrared spectra only, to be 3,5-dinitrocyclohexa-2,5-dienenitronic acids 7. The visible spectra of the acids are insensitive to substituents at C₄ but differ substantially from the spectra of the corresponding anions of type 2. Only one absorption at about 365 nm with $\epsilon = 1.8 \times 10^4$ was observed.

Some calculations to attempt to reproduce this spectrum were carried out, but severe problems concerning the choice of suitable parameters arose since no calculations on simpler nitronic acids have been made. Complete withdrawal of oxygen O₁₀ (7) from the conjugate system, equivalent to an out-of-plane O-H bond, resulted in two calculated absorption maxima at 448 nm and 358 nm with oscillator strengths of 0.17 and 0.74, respectively. The first absorption was essentially *x*-polarized and the second *y*-polarized. A less drastic approximation, using atomic parameters for singly-bonded oxygen for O₁₀, gave similarly two calculated absorptions at 517 nm and 395 nm with oscillator strengths of 0.21 and 0.81, respectively, with the same polarisations as above. Nitronic acids of type 7 are thus predicted to give two absorptions at longer wavelength, in contrast to experiment. The discrepancy between calculated and observed electronic transitions might be due to the coincidence of the two absorptions or possibly to incorrectly assigned structures for the compounds isolated from the protonation of Meisenheimer complexes from 1,3,5-trinitrobenzene.

The parameterisation of the PPP-scheme used in this work is well suited to account for the spectral properties of Meisenheimer complexes and probably also for their π -electron distribution. The calculations give two kinds of information which are difficult to obtain by experiments.

The π -electron distribution in the ground state is obtained making possible a better understanding of the chemical behaviour of the Meisenheimer compounds. The electronic structure of the excited states is obtained, which makes it possible to rationalize the spectra.

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