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MO STUDIES ON THE STRUCTURE OF THIANTHRENE AND ITS CATION RADICALS (THE GROUND STATE AND FIRST EXCITED STATES) AND SOME OF THEIR CHEMICAL PROPERTIES

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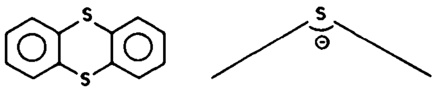
Abstract - The geometry of thianthrene and its cation radicals (the ground state and first excited state) has been studied. *Ab initio* calculations on thianthrene indicate a folded structure. *Ab initio* and energy weighted maximum overlap on the thianthrene cation radical and its first excited state reveal a structure very similar to the closed shell system. The results obtained are discussed in relation to the chemical properties of thianthrene.

Thianthrene (Ia) has been the subject of a number of structural and dynamic studies. In the crystal, each of the phenylene groups and the two sulfur atoms are coplanar, and the two planes intersect along the S-S line. The molecule thus assumes a folded C_{2v} conformation with a dihedral angle at θ = 131°[1] (Figure 1).

The structure of the thianthrene cation radical ($Ia^{+\bullet}$) has been discussed in relation to the results obtained by measurement of the g-tensor.[2] The components of the g-tensor were found to be 2.0048, 2.0086 and 2.0142, which is not compatible with a completely planar structure, and it has therefore been assumed that the radical cation is non-planar.[2]



Ia

Fig. 1. Thianthrene

The structure of the excited thianthrene cation radical ($Ia^{+\bullet *}$) has to our knowledge never been discussed, but it has recently been found that electron-transfer fluorescence quenchings of $Ia^{+\bullet *}$ by added donors give very high reorganization energies.[3] The quenching data which were treated in terms of the Marcus theory gave a high $\Delta\underline{G}_0^{\neq}$ (15.3 kcal·mole^{-1}),[3] which indicates bond and/or solvent reorganization due to the addition of the electron to $Ia^{+\bullet *}$.

In attempts to throw some light over the structures of Ia, $Ia^{+\bullet}$ and $Ia^{+\bullet *}$ and some of their chemical properties this paper presents a study using MO calculations for these purposes.

RESULTS AND DISCUSSION

The present investigation is based on *ab initio* (Gaussian 80)[4] and energy weighted maximum overlap (EWMO)[5] calculations. The bond lengths for Ia were taken from the literature.[1]

The total energy, E for Ia as a function of the dihedral angle, θ, has been calculated using an STO-3G basis set (Gaussian 80) and the result is shown in Fig. 2.

It appears from Fig. 2 that the total energy for Ia has a minimum for θ = 130°, in accordance with the results from X-ray crystallographic investigations[1] and earlier calculations:[6] In these calculations, the total energy, E was given as: $E = E_\sigma + E_\pi + E_s$, where it was assumed that the σbond energy is given by a constant quantity and E_s and E_π are the strain and π-electron binding energy, respectively. From the results in Fig. 2 the energy of the barrier for turning the molecule inside out can be calculated to be about 15 kcal·mole^{-1}. This value is in reasonable agreement with the experimental result where analysis of the inversion barrier using different harmonic vibrations gave an inversion barrier of 4-7 kcal·mole^{-1}. Using *ab initio* calculations with an extended basis set (4-31G)* gives a result (~10 kcal·mole^{-1}) which is in better accordance with the experimental result.[1] The dihedral angle found for Ta is also in good agreement with dipolemoment analysis of Ta in benzene solution which indicates a dihedral angle of 144° ± 8°.[7]

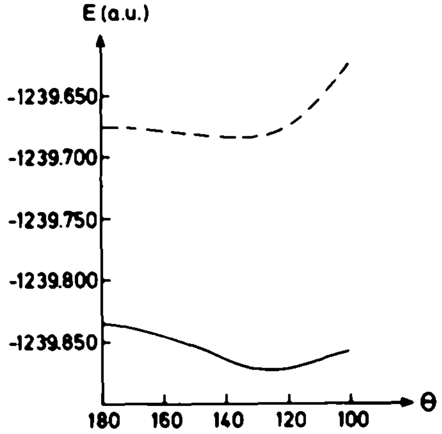


Fig. 2. The total energy, E as a function of the dihedral angle, Θ, for thianthrene (basis set: STO-3G, full line) and the thianthrene cation radical (UHF, basis set: STO-3G, dotted line).

The structure of Ta$^{\cdot+}$ has to our knowledge only been discussed in relation to ESR spectroscopy from which it was assumed that it was non-planar.[2]

The total energy, E (UHF, STO-3G) of Ta$^{\cdot+}$ as a function of the dihedral angle, Θ, is shown as the dotted line in Fig. 2. This curve reaches also a minimum at Θ ± 130°. Compared with Ta, it appears that the total energy increases very rapidly for smaller dihedral angles, whereas a slower increase is observed for larger angles. Using the results for Ta$^{\cdot+}$ from Fig. 2 the inversion barrier is found to be about 6 kcal·mole^{-1}, a result which remains to be verified spectroscopically or calometrically.

Further support for a dihedral angle at about 130° for Ta$^{\cdot+}$ comes from EWMO calculations of the principal components of the g-tensor[5c, 8] (g_{11}, g_{22}, and g_{33}). Figure 3 exhibits the results of the variation of the EWMO g-tensor principal values as a function of the dihedral angle Θ.

A good agreement with experimental results is obtained for the two first components of the g-tensor (g_{11} and g_{22}) for Θ = 130°, whereas for g_{33} no agreement is found. These results indicate, together with the UHF *ab initio* calculations of Ta$^{\cdot+}$ in Fig. 2 that this cation radical probably has a structure which is very similar to that of the closed shell system.

Before we proceed to the structure of Ta$^{\cdot\cdot+}$ a small part of theory is necessary: In the discussion of features of radicals with one unpaired electron spin, a fundamental notation is the separation of the electronic energy:

$$E(j, N \pm 1) = E(0,N) \pm e(j) \qquad (1)$$

where E(0,N) represents the closed shell energy of the reference state and e(j) is the energy difference between the radical and the ground state. This difference can be obtained by the electron propagator;[5] the EWMO model was originally presented as an approximative way of estimating the propagator. It is assumed that conformational changes and other perturbations of the e-

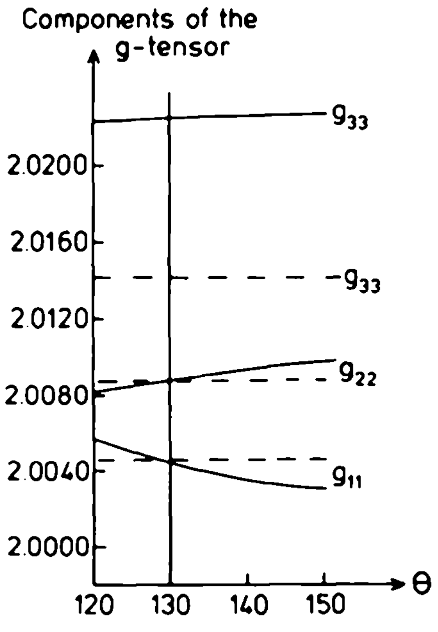


Fig. 3. Variation in the EWMO g-tensor principal values as a function of the dihedral angle, Θ (full line). The experimental values are given as the dotted line.[2]

lectronic system induce changes in F(O,N) as well as the singly occupied and excited states.[9] The relative position of the states is determined by the latter only and it is expected to obtain useful information from the possible degeneracies and near degeneracies in the molecular orbitals of the effective hamiltonian in the way one usually uses molecular orbital theory.

The changes in EWMO orbital energy for the highest doubly occupied MO(HDOMO), the highest singly occupied MO(HSOMO) and the lowest unoccupied MO(LUMO) as a function of the dihedral angle, θ, are shown in Fig. 4.

From Fig. 4 it appears that the HSOMO energy, which represents the Ia($Ia^{+\bullet}$) system, exhibits a minimum of energy at a dihedral angle at about 125°. These results are in good accordance with the results obtained by the *ab initio* calculations above for Ia and $Ia^{+\bullet}$. With regard to the LUMO state which represents the excited structure of $Ia^{+\bullet}$($Ia^{+\bullet *}$), it is seen that it has a maximum in energy at a dihedral angle at about 120° and that a small decrease in MO energy takes place for both smaller and larger angles. A few words about the other occupied MOs should be mentioned here: MOs located at lower energies (not shown in Fig. 4) exhibits a nearly similar curvature as the HDOMO and HSOMO - a minimum in energy at a dihedral angle at about 125°-140° or remains more or less flat. From the LUMO state it should thus be expected that the structure of $Ia^{+\bullet *}$ is very similar to that of Ia^{+} and Ia. The experimentally found excitation energy (2.13 ev[10]) corresponds to some extent to the calculated excitation energy at a dihedral angle at about 130°-140°. Further support for geometry of $Ia^{+\bullet *}$ very similar to that of $Ia^{+\bullet}$ comes also from the relative small Stokes shift (1029 cm^{-1}).[11]

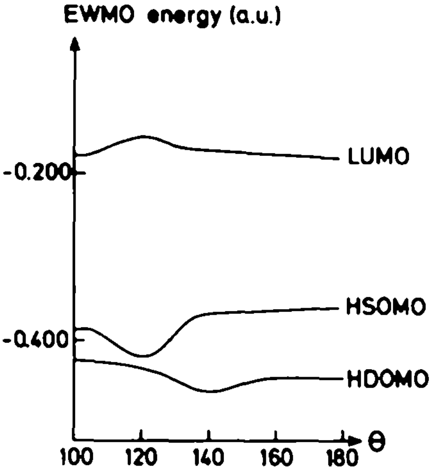
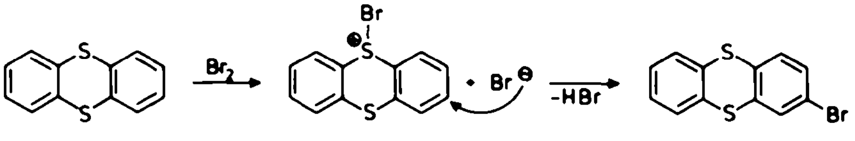


Fig. 4. Variation in EWMO orbital energies (HDMO: highest doubly occupied molecular orbital; HSOMO: highest singly occupied molecular orbital; LUMO: lowest unoccupied molecular orbital) as a function of the dihedral angle, θ.

Let us now return to some of the chemical properties of Ia and $Ia^{+\bullet *}$, and the attention will here be focused on the halogenation of Ia[12] and the quenching of $Ia^{+\bullet *}$ by electron donors.[3,11]

Bromination of Ia leads to 2-bromo-Ia exclusively:



I

Scheme 1

It has been reported that addition of bromine to the Ia solution gives an initial red colour which was refluxed until the colour was yellow.[12] The initial red solution might indicate that the first step is an electrophilic attack of a bromonium ion on sulfur in Ia giving a bromo-sulfonium ion, I, which by reaction with bromide leads to 2-bromo-Ia (Scheme I).

Fig. 5 shows the HOMO and LUMO coefficients for Ta (only left side shown).

It appears that sulfur has the largest HOMO coefficient, or in other words: Sulfur is most preferred for an electrophilic attack by the bromonium ion leading to a bromo-sulfonium ion (I, Scheme 1), whereas the LUMO is mainly located as shown in Fig. 5, which supports the next step being a nucleophilic bromide attack on carbon no. 2 in Ta (Scheme 1).


HOMO LUMO

Fig. 5. HOMO and LUMO of thianthrene (STO-3G basis set).

The HOMO and LUMO states (as well as other unoccupied states located immediately above the LUMO state) lead to a discussion of the large reorganization energy, $\underline{\Delta G}_0^{\neq}$ (15.3 kcal•mole^{-1}) for Ta+•* as an electron acceptor.[3] In the ground state of Ta+• the unoccupied electron is mainly located on the two sulfur atoms (0.63) relative to 0.185 on each of the two phenyl rings, whereas in the LUMO state, which corresponds to Ta+•*, the charge density on sulfur equals to 0 and 0.50 on each of the two phenyl rings. Unoccupied states immediately above the LUMO state give a nearly similar charge density picture as the LUMO state. The reorganization of the electron density from the central ring in Ta+• to the side rings in Ta+•* might then cause a solvent reorganization which can explain the large $\underline{\Delta G}_0^{\neq}$.

It might be concluded that *ab initio* calculations of the total energy for thianthrene give a minimum in energy at a dihedral angle which is in agreement with the structure found by experimental investigations. *Ab initio*, as well as energy weighted maximum overlap calculations predict the structure of the cation radical and the excited cation radical of thianthrene obtained to have a similar structure to the closed shell system. The calculations predict the sulfur in thianthrene to be most reactive towards an electrophilic attack, and position 2 to be most reactive towards nucleophilic attack, which is in accordance with the experimental results. The relatively large reorganization energy for thianthrene obtained in fluorescence quenching experiments might be explained from a sudden polarization in the excited state of its cation radical.

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