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The Valence Bond Description of Xylylenes

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The ground states or ortho-, meta- and para-xylylenes and low lying excited states of meta-xylylenes are investigated by the valence-bond approach. Weights of structural formulas are calculated. A criterion for biradical character is defined as the sum of the weights of biradical structures. It is found that meta-xylylene is best described as a benzene ring relatively unperturbed by the two adjacent methylene radicals, and that ortho- and para-xylylene are unequal mixtures of localized Kékulé structures and aromatic biradical structures. Surprisingly, low lying excited states of meta-xylylene deviate from the zwitterionic picture expected for singlet excited states of biradicals.

Key words: Valence bond – Diradical character – Xylylenes.

1. Introduction

Many reactive species, including transition states or intermediates of thermal or photochemical reactions, can be classified as biradicaloids, i.e. molecules which have some biradical character. Of course, an important part of the study of their electronic structure is the evaluation of this biradical character, and some criterions have been proposed, including natural orbitals occupation numbers (NOONS) [1–3] and eigenvalues of Hartree–Fock instability matrices [4]. A more natural criterion may be used, if one has the valence-bond function of the diradicaloid: the amount of biradical character is simply the sum of the weights of the biradical (long bond) structures in the wavefunction. A serious inconvenience of this criterion is that the calculation of true valence-bond functions is very costly, because one has to deal with non-orthogonal determinants, but we recently proposed a method to overcome this difficulty, by getting valence

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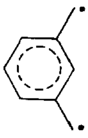
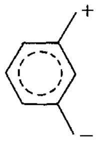
bond functions from molecular orbitals and configuration interaction coefficients [5]. Moreover, in the case of π, π biradicals, we can deal with valence bond functions built with mixed determinants, involving σ molecular orbitals and π atomic orbitals, so that the valence bond basis set, or the set of resonance structures, is reduced to π electrons.

In this paper, we apply this method to describe the electronic structure of some typical biradicaloids, the series of ortho-, meta- and para-xylylenes (**1**–**3**), by the valence-bond approach. These molecules have aroused much theoretical [1, 2, 6] as well as experimental [7] interest, and commonly asked questions concern the relative importance of biradical (**1a**–**3a**) or ionic (**1b**–**3b** or **1c**–**3c**) structures in the low-lying states. Interpretation of NMR chemical shift, based on the "Structure Representation" theory [11], of ortho- [10] and para-xylylenes [7] tends to indicate a lack of aromaticity, thus supporting structures **2d** and **3d**.


1a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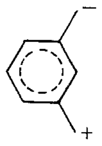
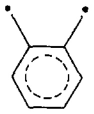
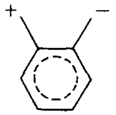
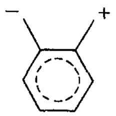
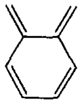
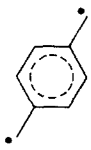

1c

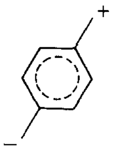

2a

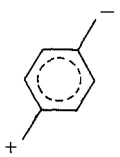

2b

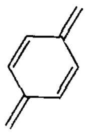

2c


2d


3a


3b


3c


3d

However, their ground states are expected to contain some biradical component [7c]. Also in favor of some biradical character are the recent PPP-full CI calculations of Dohnert and Koutecky [2], who found NOONS of approximately 0.25 and 1.75 for both ortho-and para-xylylenes, to be compared with the values 1. and 1. of a pure biradical and 0. and 2. for a pure closed shell. But it should be noted that all CC bond lengths have been set to 1.40 Å in that calculation, which certainly favors a benzene-like resonance in the rings, and should overestimate the biradical character *via* structures **1a** and **3a**. The calculations presented here are of somewhat different nature, as they explicitly measure the percentage of the wavefunction which represents a biradical. Also, the xylylenes are given geometries which should be reasonably close to equilibrium, and the calculations have been repeated with benzene-like geometries to test the sensitivity of the biradical character to geometrical distortions. Another important question concerns the electronic structure of low-lying excited states of biradicaloids. Are they zwitterionic, like excited states of biradicals? We have used the meta-xylylene, as being the most biradicaloid xylylene of the three, to investigate this problem.

2. Method

The first step is to perform, for all the molecules under study, LCAO-MO *ab initio* calculations [12], in minimal (STO-3G) basis set [13] followed by configuration interaction (CI) including all single and double excitations among the π orbitals. The SCF functions have been calculated by using the closed shell formalism for ortho- and para-xylylenes, and the Nesbet Restricted Open Shell formalism [14] for the meta-xylylene, due to its pronounced biradical character. The Gaussian 70 series of programs have been used throughout this work. Then we have projected these MO-CI wavefunctions, using a program written by us [5a], onto a basis set of Valence Bond functions $|V_m\rangle$, each of which being characteristic of a bonding structure.

This projection is not exceedingly costly for we use a simplified procedure designed to save computer-time and storage requirements. Briefly, both projection and overlap calculations are applied to "half determinants" or sets of spin orbitals of the same spin, which are much less numerous than Slater determinants, and simple formulas allow to get final valence bond functions from the results of that projection. At this stage, one has an approximate (because the CI is not complete) Valence bond function ψ for each molecule:

$$\psi = \sum_m K_m |V_m\rangle \tag{1}$$

and the weights (W_m) of the structures can be calculated using formula (2)

$$W_m = K_m^2 + \sum_{n \neq m} K_m K_n \langle V_n | V_m \rangle. \tag{2}$$

The case of conjugated molecules is particularly simple in that the valence bond description can be reduced to π orbitals, which do not mix with the σ skeleton for symmetry reasons. With this simplification, the $|V_m\rangle$ functions are not pure valence bond functions, but are built with mixed determinants, in which the σ skeleton keeps the form of molecular orbitals, while the π orbitals are pure non-orthogonal atomic orbitals. For example, if ϕ_1, ϕ_2 are σ molecular orbitals and p_1, p_2, p_3 are atomic p orbitals perpendicular to the molecular plane, the VB functions may be built with mixed determinants of the following type:

$$|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 p_1\bar{p}_1 p_2\bar{p}_3|,$$

$$|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 p_1\bar{p}_2 p_3\bar{p}_3|, \quad \text{etc} \ldots.$$

3. Ground States of Ortho-, Meta, and Para-Xylylenes

In our calculation, ortho- and para-xylylenes have been given standard bond lengths of butadiene, i.e. 1.35 Å for the formal double bonds and 1.47 Å for the formal single bonds. These values should be reasonably close to the equilibrium bond lengths, since they are similar, within 0.015 Å, to the parameters optimized by Gleicher et al. [6a] using a VBL [15] (variable bond length) semi-empirical SCF technique. On the contrary, meta-xylylene has been calculated with a benzene-like geometry, i.e. 1.40 Å for the ring bond lengths and 1.45 Å for the outer ones, since no possible Kekulé structure can be drawn for this molecule.

We define the biradical character of a molecule in a very simple way: it is the sum of the weights of all structures having at least one "long bond", i.e. two non-adjacent atoms whose atomic orbitals are connected by singlet coupling. For example, if p_1 and p_3 are the outer p atomic orbitals of ozone perpendicular to the molecular plane and p_2 is the center one, the "long-bond" structure is characterized by the function:

$$|\ldots p_2\bar{p}_2p_1\bar{p}_3| + |\ldots p_2\bar{p}_2p_3\bar{p}_1|.$$

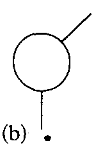
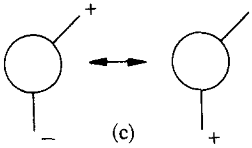
The other structures involve only covalent bonds between adjacent atoms, or electronic charges.

The results of our MO-CI + valence-bond calculations are displayed in Table 1. As expected, the meta-xylylene has, by far, the strongest biradical character (97%). The remaining structures (3%) would probably disappear if the configuration interaction were complete in the π space, since electron correlation is known to reduce the weights of ionic structures in the ground states [5a]. Perhaps surprisingly, ortho- and meta-xylylenes have also a fair amount of biradical character: 44% and 35%, respectively. Nevertheless, is should be kept in mind that all conjugated molecules have some biradical character. For example, the weights of "long bond" structures of butadiene [16], also calculated after CI in the π electrons interacting space, add to 0.12. Thus, the biradical character of o-and p-xylylenes is best estimated if compared with this of a hypothetical fully localized molecule constituted with two butadienes, whose biradical character would be: 1-(0.88)[2] = 0.23. It is then apparent that ortho-xylylene is significantly more biradical-like than para-xylylene.

Table 1 also shows that the biradcial character of o- and p- xylylene is quite sensitive to the correctness of the geometry. Indeed, when a benzene-like geometry is used, with ring bonds of 1.40 Å, the biradical characters rise to 74% and 56%, respectively.

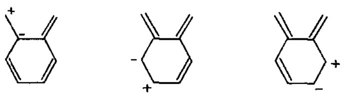
Although no less than 4900 structural formulas compose the canonical basis set for the xylylenes, it is possible to describe them with only a few of them. For example, 74% of meta-xylylene's wavefunction is representative of a long bond between outer carbons; in these structures, the other bonds, connecting the ring carbons, are not only of Kékulé-type, but in benzene itself Kékulé structures

Table 1. Structural weights of xylylenes, (a) sum of the weights of all structures having at least one "long bond"; (b) sum of the weights of all structures having a "long bond" connecting the outer carbons; (c) sum of the weights of all structures in which outer carbons are oppositely charged.

	Biradical character (a)	 (b)	 (c)
ortho-xylylene equilibrium geometry	0.437	0.104	0.068
ortho-xylylene benzene-like geometry	0.735	0.278	0.030
para-xylylene equilibrium geometry	0.354	0.074	0.044
para-xylylene benzene-like geometry	0.563	0.257	0.025
meta-xylylene singlet S_0	0.972	0.729	0.0
meta-xylylene singlet S_1	0.968	0.002	0.060
meta-xylylene singlet S_2	0.760	0.022	0.109

represent only 22% of the total [16, 17]. Thus the ground state of meta-xylylene can be conveniently described as a benzene, keeping its aromaticity, to which two methylene radicals would be attached.

Ortho- and para-xylylenes, also, may be described very simply if one remembers that what is called a chemical bond is never purely covalent at short distance, but involves some zwitterionic component. Thus the weight of structure **2d**, in ortho-xylylene for example, is best estimated by adding the weight of the purely covalent structure to those of structures involving ionic bonds between atoms connected by formal double bonds in **2d**:



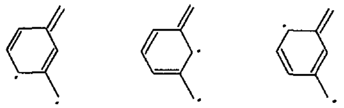
This way, the classical structure **2d** represents 55% of ortho-xylylene's wavefunction, almost the totality of structures involving no long bond. Benzenoid biradical structure **2a**, on the other hand, in only 10% of the total.

Expectedly, since para-xylylene has less biradical character than ortho-xylylene, it is also found less delocalized. Indeed, the classical structure **3d**, taken in the above described extended meaning, is a very good description of para-xylylene, with a weight of 64%, *versus* 7% for benzenoid **3a**.

4. Low-Lying Excited States of Meta-Xylylene

It is well known that the low-lying singlet states S_1 and S_2 of a biradical are zwitterionic [18] in nature, if these states are built by excitation among frontier orbitals. As the ground state of meta-xylylene is best represented as a localized biradical, it can be asked whether or not low-lying excited states can be described in terms of the zwitterionic structures **1b** and **1c**. To answer this question, we performed a Valence-Bond projection for the S_1 and S_2 excited states of meta-xylylene, S_1 being defined as the state whose major component is the single excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied one (LUMO), and S_2 involving a combination of the SCF configuration and the double excitation from HOMO to LUMO. For the MO calculation, we kept the benzenoid geometry, since no Kékulé structure can be drawn for this molecule.

The results are somewhat surprising in that the expected zwitterionic structures **1b** and **1c** have a rather weak weight in both S_1 and S_2 states. Only 6% of these structures contribute to S_1, which is almost a pure biradical, although involving no contribution from **1a**. In fact, S_1 is best represented as a mixture of biradical structures of the following type:



S_2 has significantly less biradical character (76%), but still very little contribution from **1b**–**1c** (11%).

5. Conclusion

Despite the considerable number of structures that can be drawn for the xylylenes, their ground states can be represented by very few of them. Grossly, meta-xylylene is a benzene substituted by two methylenes interacting relatively little with the ring. Para-xylylene is best represented by the localized Kékulé structure **3d** with a small contribution from the aromatic biradical structure **3a**, in the ratio 9 : 1. This ratio goes down to 5 : 1 for ortho-xylylene, in agreement with its significant biradical character. S_1 and S_2 excited states of meta-xylylenes, on the other hand, depart from the zwitterionic picture expected for low-lying states of biradicals.

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