Density functional study of some cation radicals

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Received 22 November 1995; accepted 4 January 1996

Density functional (DF) method is used to estimate the isotropic hyperfine coupling constants of the radical cations of pyrrole, furan and thiophene. The calculated results are in good agreement with experiment. The DF results are of a quality better than those obtained from second-order Moller-Plesset (UMP2) method with frozen core approximation.

Rao and Symons have generated the radical cations of furan, pyrrole and thiophene by ionizing radiation at low temperature (77 K) in FCCl matrices and have carried out electron spin resonance (ESR) studies. In recent years density functional (DF) methods have been successfully used to examine the spin density distributions in radical systems, the main attraction being their ability to include exchange and correlation for only a moderate cost in comparison to other post-SCF methods. In this note we present the results of our DF studies for the radical cations of pyrrole, furan and thiophene.

Computational details
The DF studies were made using two different functionals: (i) Becke's exchange with Lee, Yang and Parr's correlation functional (i.e. B-LYP) and (ii) Becke's three-parameter hybrid with Parr's correlation functional (i.e. B3-LYP).

Electron correlation effects were investigated using unrestricted second-order Moller-Plesset theory (UMP2) with frozen core approximation. 6-31G(d) basis set was used for all DF and UMP2 calculations. This basis set is small enough to study large organic systems and includes polarization functions on non hydrogen atoms that may be needed for an accurate description of radical electronic structures. The geometries were optimized by means of analytical gradients.

The hyperfine coupling constants \( a_{\text{hfc}} \) were calculated from the Fermi contact splitting term \( [0(0)] \) using Eq. (1)

\[
a_{\text{hfc}} = \frac{8}{3} \frac{\pi g_e}{g_0} g_N \beta_N Q(0)
\]

where \( g_e \) and \( g_0 \) are respectively, the isotropic \( g \) values for the molecule and free electron, \( g_N \) is the nuclear magnetogyric ratio and \( \beta_N \) is the nuclear magneton. \( g_e \) and \( g_0 \) have been taken equal to each other in the present study. The quantum chemistry package GAUSSIAN 94 was used for all calculations reported here.

Results and discussion
Our calculated results are listed in Table 1. Both functionals (B3-LYP and B-LYP) give, in general, nearly similar results. These results are

<table>
<thead>
<tr>
<th>System</th>
<th>Position</th>
<th>UMP2</th>
<th>UB3-LYP</th>
<th>UB-LYP</th>
<th>Expt</th>
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</thead>
<tbody>
<tr>
<td>Pyrrole</td>
<td>2, 5</td>
<td>-28.7</td>
<td>-16.9 (-16.9)</td>
<td>-14.7 (-14.6)</td>
<td>-13.6 (-13.6)</td>
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<tr>
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<td>3, 4</td>
<td>-3.0</td>
<td>-4.2 (-4.0)</td>
<td>-2.7 (-2.3)</td>
<td>-2.7 (-2.7)</td>
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<tr>
<td></td>
<td>N</td>
<td>-11.4</td>
<td>-1.7 (-1.6)</td>
<td>-3.8 (-3.3)</td>
<td>-2.5 (-2.5)</td>
</tr>
<tr>
<td>Furan</td>
<td>2, 5</td>
<td>-28.1</td>
<td>-17.7 (-17.7)</td>
<td>-15.0 (-15.0)</td>
<td>-14.0 (-13.9)</td>
</tr>
<tr>
<td></td>
<td>3, 4</td>
<td>-1.8</td>
<td>-5.8 (-5.6)</td>
<td>-2.7 (-2.6)</td>
<td>-2.9 (-2.7)</td>
</tr>
<tr>
<td>Thiophene</td>
<td>2, 5</td>
<td>-27.6</td>
<td>-16.4 (-16.3)</td>
<td>-13.9 (-13.6)</td>
<td>-12.8 (-12.5)</td>
</tr>
<tr>
<td></td>
<td>3, 4</td>
<td>-1.2</td>
<td>-5.6 (-5.7)</td>
<td>-2.4 (-2.4)</td>
<td>-2.7 (-2.6)</td>
</tr>
</tbody>
</table>

*See Fig. 1. Numbers in parentheses are those obtained from single-point calculations using UHF/6-31G(d) optimized geometries. UB3-LYP/6-31G(d) optimization, UB-LYP/6-31G(d) optimization.
far superior to those obtained from conventional UHF calculations (Fig. 1). Inclusion of electron correlation through unrestricted second-order Moller-Plesset theory (UMP2) with frozen core approximation improves the results to a great extent. The hyperfine coupling constants obtained from DF studies are by and large better than those obtained from UMP2 calculation. As can be seen from Table 2, DF treatment of these cations leads to much less spin contamination compared to UHF and UMP2 levels of theory\(^\text{15}\) (Table 2).

Single-point calculations have also been made using the optimized geometries obtained from UHF/6-31G(d) studies. It may be worthwhile to note that single-point results are very nearly similar to those obtained from full optimization. Geometries used seem to have little effect on the hyperfine coupling constants of the rigid systems studied here. This may enable us in future to estimate isotropic hyperfine coupling constants in larger systems. Work along this line is in progress and will be reported elsewhere.

The following points emerge from the present study: (i) DF methods like B3-LYP and B-LYP using moderate sized basis set (6-31G(d)) can give fairly reliable isotropic hyperfine coupling constants for the radical cations studied here and (ii) the spin distributions obtained from DF calculations are of a quality better than those obtained from post-SCF(UMP2) studies.

Table 2—Calculated \(S^2\) values before annihilation

<table>
<thead>
<tr>
<th>System</th>
<th>Method used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UHF (^b)</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>0.811</td>
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<tr>
<td>Furan</td>
<td>0.806</td>
</tr>
<tr>
<td>Thiophene</td>
<td>0.831</td>
</tr>
</tbody>
</table>

\(a, b, c, d\) and \(e\) are same as under Table 1.

References