All-Valence Electron Study of Some Pyrones:
EHT Bond Orders & Carbonyl Bond Stretching Frequencies

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Received 27 October 1977

Extended Hückel theory (EHT) has been used to compute the bond orders for C=O bonds in some pyrones. The computed bond orders are found to be well correlated to the IR stretching frequencies of these bonds.

Theoretical study of α-pyrene (I), γ-pyrene (II) and of pyrone derivatives, viz. coumarin (III), chromone (IV) and isocoumarin (V), has been drawn considerable attention in recent years since a great wealth of experimental data is available for these systems. Some of the benzo-pyrene (coumarin) derivatives are known to be tunable dye lasers and we have earlier studied the π-electronic structure of these systems with a view to understanding the effect of various substituents on the π-electronic structures of these systems both in ground and excited states.

In this communication we report the results of our all-valence electron calculations for pyrones and some of their derivatives (Table 1). The extended Hückel theory (EHT) of Hoffmann has been used for the present study and standard parameters are used for estimating the diagonal matrix elements ($H_{ii}$). Off-diagonal matrix elements are obtained using Wolsberg-Helmholtz relation:

$$H_{ij} = (K/2)S_{ij}(H_{ii} + H_{jj})$$

where $K = 2.0$ and $S_{ij}$ is the overlap integral.

Calculated EHT bond order for the carbonyl bond is expected to be a rough measure of the strength of the bond. In view of this fact, some relationship is expected between the calculated C=O bond orders ($P_{C=O}$) and observed C=O stretching frequencies. A least squares fit analysis gives a linear relation of the form:

$$v_{C=O} (cm^{-1}) = 2050 P_{C=O} - 189$$

References

6. MACPHERSON, E. J. & SMITH, J. G., Can. J. chem., 48 (1970), 1904. These workers report that the dienion of benzophenone azine behaves chemically as if it has the 1,2-dienion structure. The hydrolysis product is N-benzhydrbenzohenothenone hydrazone.

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### Table 1 — Calculated EHT Carbonyl Bond Orders and IR Carbonyl Stretching Frequencies

<table>
<thead>
<tr>
<th>System</th>
<th>( P_{C=O} )</th>
<th>( \nu_{C=O} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Pyrone (I)</td>
<td>0.927</td>
<td>1711</td>
</tr>
<tr>
<td>( \gamma )-Pyrone (II)</td>
<td>0.901</td>
<td>1658</td>
</tr>
<tr>
<td>Coumarin (III)</td>
<td>0.935</td>
<td>1728</td>
</tr>
<tr>
<td>Chromone (IV)</td>
<td>0.908</td>
<td>1672</td>
</tr>
<tr>
<td>IsoCoumarin (V)</td>
<td>0.943</td>
<td>1744</td>
</tr>
<tr>
<td>3-Me-Coumarin</td>
<td>0.932</td>
<td>1722</td>
</tr>
<tr>
<td>3-OH-( \alpha )-Pyrone</td>
<td>0.915</td>
<td>1687</td>
</tr>
</tbody>
</table>

(a) Obtained using Eq. 2.  
(b) Obtained from ref. 13-15.

The carbonyl stretching frequencies obtained using Eq. (2) are given in Table 1 along with available experimental data. The correlation coefficient is found to be 0.98 and excellent agreement between the calculated and experimental stretching frequencies can be seen.

Studies are in progress in our laboratory to correlate other bond stretching frequencies with EHT bond orders. Initial results obtained for some systems containing C=S bond appear quite promising. These results will be reported elsewhere.

### References