INTEGRAL INTENSITIES OF THE CARBONYL BANDS
OF A NUMBER OF PYRONES AND QUINONES*

(UDC 535-15+543.422)

M. E. Perel'son, Yu. N. Sheinker, B. E. Zaitsev, and V. A. Pozdyshev

Institute of the Chemistry of Natural Compounds, Academy of Sciences USSR
and All-Union Institute of Medicinal and Aromatic Plants
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5,
pp. 804-808, May, 1964
Original article submitted July 31, 1963

As is well known, one of the basic conditions of the formation of a stable aromatic ring is the presence of a
closed system of \((4n + 2)\) \(\pi\)-electrons in the field of the planar nucleus of the molecule, where \(n = 0, 1, 2, \ldots\). Both
the \(\pi\)-electrons of multiple bonds and unshared electron pairs of heteroatoms can take part in the formation of such a
system \([1]\). If the chemical system (planar ring) has a deficiency or surplus of \(\pi\)-electrons in comparison with the indi-
cated, its stability can be increased through their addition or removal as a result of electronic redistribution within
the molecule itself. In the particular case of nonbenzoid aromatic compounds containing an exocyclic carbonyl
group, such a redistribution can be accomplished through an increase or decrease in the negative charge on the car-
bonyl oxygen. This is manifested in a number of physical characteristics of the substance (dipole moments, bond
lengths, etc.). In the IR spectra, as has been shown \([2-4]\), such a phenomenon is accompanied by an increase or de-
crease in the integral intensity of the carbonyl band. In this report, the integral intensities of the C=O bands of a
number of pyrones and quinones are considered from this point of view.

EXPERIMENTAL

The measurements of the integral intensities of pyrones were conducted on the UR-10 spectrophotometer, spec-
tral slit width 8.2 cm\(^{-1}\). The calculation was performed according to the Wilson-Wells method. The quinones were
photographed on the IKS-14 spectrophotometer, spectral slit width 8.1 cm\(^{-1}\); the calculation was performed according
to the Burgen method. In the case of splitting of the carbonyl bands, the summary intensity is cited.

EXPERIMENTAL RESULTS AND DISCUSSION

\(\alpha\)- and \(\gamma\)-pyrones are nonbenzoid aromatic compounds, which follows both from their chemical properties \([5]\)
and from the high values of the delocalization energy of the \(\pi\)-electrons (60.8 kcal/mole for \(\alpha\)-pyrone and 60.2 kcal
per mole for \(\gamma\)-pyrone \([6]\)).

The field of the planar pyrone ring contains seven mobile electrons: four \(\pi\)-electrons of the multiple bonds,
the unshared electron pair of oxygen, and the \(\pi\)-electron of the carbonyl carbon. For the formation of a stable aro-
matic system from the six \(\pi\)-electrons, the surplus electron should be displaced in the direction of the carbonyl oxy-
gen. The integral intensity of the carbonyl band in this case should be increased in comparison with the intensity of
unsaturated lactones (for \(\alpha\)-pyrone) and \(\alpha, \beta, \alpha, \beta'\)-unsaturated ketones (for \(\gamma\)-pyrone).

Table 1 presents the positions and intensities of the bands of the C=O group of a number of derivatives of \(\alpha\-
pyrone (mainly coumarins) and \(\gamma\)-pyrone. Most of the compounds were photographed in the form of solutions in chlo-
roform, some, as a rule, the hydroxyl-compounds, in dioxane. With passage from dioxane to chloroform, the integral
intensity increases by approximately two practical units, which is probably due to the formation of hydrogen bonds.
We can see from Table 1 that the integral intensity of the carbonyl bands of \(\alpha\)-pyrone derivatives is approximately
three practical units higher than in the corresponding unsaturated six-membered lactones (in chloroform no more than
5.5 units \([9]\)). The intensity in the case of \(\gamma\)-pyrones is 1.3-1.5 units higher in comparison with \(\alpha, \beta, \alpha, \beta'\)-unsaturated
ketones (in chloroform 2.8 units). Condensation with benzene and furane rings and the introduction of hydroxyls and

* The article is published on the basis of a resolution of the Conference of Editors-in-Chief of the Journals of the
Academy of Sciences USSR from July 12, 1962 as the dissertation work of M. E. Perel'son.
TABLE 1. Position and Intensity of the C=O Bands of α- and γ-Pyrones

<table>
<thead>
<tr>
<th>Compound</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>Solvent</th>
<th>Frequency of C=O band, cm⁻¹</th>
<th>Intensity of C=O band (10⁻⁴ molecule⁻¹ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OH</td>
<td>H</td>
<td>CH₃</td>
<td>Dioxane</td>
<td>1735</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Chloroform</td>
<td>1733</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>Dioxane</td>
<td>1732</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>Chloroform</td>
<td>1733</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>H</td>
<td>OCH₃</td>
<td>Chloroform</td>
<td>1733</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>OCH₃</td>
<td>H</td>
<td>H</td>
<td>Chloroform</td>
<td>1720</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>OH</td>
<td>OCH₃</td>
<td>Chloroform</td>
<td>1722</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>H</td>
<td>OCH₃</td>
<td>Dioxane</td>
<td>1739</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>OCH₃</td>
<td>H</td>
<td>CH₃</td>
<td>-</td>
<td>Chloroform 1727</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>CH₃</td>
<td>CH₃</td>
<td>-</td>
<td>Chloroform</td>
<td>1670 *</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>OCH₃</td>
<td>OCH₃</td>
<td>OCH₃</td>
<td>Chloroform</td>
<td>1661 *</td>
<td>4.7</td>
</tr>
</tbody>
</table>

*There is no single opinion in the literature with respect to the assignment of this band in the spectra of γ-pyrones [7, 8]. Following the majority of the authors, we considered it to be the carbonyl band.

methoxyls into various positions exert a negligible influence on the carbonyl frequency and intensity. We should mention that the equal value of the intensity of the C=O bands in 4-hydroxy- and 4-methoxycoumarins confirms the conclusions drawn earlier on the basis of a study of the frequencies [10-12] of the absence of the chromone form in solutions. The values of the integral intensities of the carbonyl bands obtained can also be used for structural-analytical purposes to distinguish pyrones from the corresponding esters, lactones, and ketones.

Thus, the increase in the integral intensity in this case can be related to an increase in the negative charge on the carbonyl oxygen as a result of an intramolecular redistribution of the electrons in the formation of the aromatic system.