PARA-RESONANCE INTERACTIONS IN SUBSTITUTED BENZALDEHYDES
AND CORRELATIONS OF OVERTONE CARBONYL STRETCHING
FREQUENCIES WITH \( \sigma^+ \) CONSTANTS*

By G. E. Lewis†

The importance of para-resonance interactions (Ia \( \leftrightarrow \) Ib) in the conjugate
carbons of benzaldehydes containing electron-donating substituents in the para-position
has been demonstrated by Yates and Stewart,\(^1\) who found that the basicities of the
aldehydes (pK\(_{BH^+}\)) do not conform to a simple Hammett\(^2\) equation but exhibit
linear dependence on \( \sigma^+ \) values.\(^3,4\) In view of these findings, the present examination
of interrelationships of infrared carbonyl stretching frequencies of substituted
benzaldehydes and \( \sigma \) and \( \sigma^+ \) constants was undertaken. The results show that
para-resonance interactions (IIa \( \leftrightarrow \) IIb) are correspondingly important in non-
protonated benzaldehydes. Evidence for direct resonance interaction of the
aldehyde and dimethylamino groups in p-dimethylaminobenzaldehyde [IIb; X =
(CH\(_3\))\(_2\)N] has also recently been derived from low temperature n.m.r. spectra.\(^5\)

\[
\begin{align*}
\text{(Ia)} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\text{H} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\text{(Ib)} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\text{H} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\text{(IIa)} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\text{H} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\text{(IIIb)} & \quad \begin{array}{c}
\text{H} \\
\text{C=O} \\
\text{X} \\
\end{array} \\
\end{align*}
\]

In earlier studies of the fundamental carbonyl stretching frequencies of sub-
tituted benzaldehydes and related carbonyl compounds by Thompson, Needham,
and Jameson\(^6\) slight curvatures of \( \nu/\sigma \) plots were observed. Although these authors
suggested that plots of \( \nu^2/\sigma \) might be more appropriate in such cases, Rao and
Silverman\(^7\) subsequently pointed out the rationale for examination of \( \nu/\sigma^+ \) plots
from a consideration of the possibilities of strong para-resonance interactions. The
spread of frequencies in the series of benzaldehydes examined was, however, too
limited to permit a definite decision on which type of correlation was the more
satisfactory. For this reason p-dimethylaminobenzaldehyde has been included in
the present investigations and attention has been centred on measurements of

* Manuscript received February 25, 1964.
† Department of Organic Chemistry, University of Adelaide.

frequencies of overtone bands of the carbonyl group vibrations in benzaldehyde and other para-substituted derivatives because of the doubling of frequency shifts with respect to the fundamental region.

The compounds examined are listed in Table 1 together with the appropriate \( \sigma \) and \( \sigma^+ \) values, the observed frequencies of the carbonyl overtone bands (carbon tetrachloride solution) and previously recorded\(^6\) fundamental carbonyl stretching frequencies (also measured in carbon tetrachloride solution). It may be noted that the overtone frequency (3402 cm\(^{-1}\)) found for benzaldehyde itself is close to that (3404 cm\(^{-1}\)) reported earlier by Thompson and Jameson.\(^9\) In the cases of the four compounds for which the fundamental frequencies are listed, the degrees of anharmonicity of molecular motion (\(x\)) have been evaluated according to the approximation method outlined by Kaye.\(^10\) The values of \(x\) so determined are given as follows in parentheses: benzaldehyde (0·002), \(p\)-nitrobenzaldehyde (0·002), \(p\)-chlorobenzaldehyde (0·002), and anisaldehyde (0·003). It is therefore apparent that a substantially constant anharmonicity factor of low magnitude applies to this series and hence that correlations of substituent constants with overtone frequency shifts have the same significance as those with fundamental frequency shifts.

The respective correlations of the carbonyl overtone stretching frequencies (2\(v_{CO}\)) with \(\sigma^+\) (cf.4) and \(\sigma\) (cf.8) constants are illustrated graphically in Figures 1 and 2. The regression coefficients \(\rho\), standard deviations \(s_{\rho}\), correlation coefficients \(r\), and fitment of the best straight lines have been determined by the procedure given by Jaffé.\(^11\) For the 2\(v/\sigma^+\) correlation, \(\rho\) is 24·73, \(s_{\rho}\) 1·81, and \(r\) 0·982 and for the


\(^{10}\) Kaye, W., Spectrochim. Acta, 1954, 6, 257.


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**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Substituent</th>
<th>(\sigma) (cf.8)</th>
<th>(\sigma^+) (cf.4)</th>
<th>(2v_{CO})</th>
<th>(v_{CO}) (cf.8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO(_2)</td>
<td>0·778</td>
<td>0·790</td>
<td>3414</td>
<td>1713</td>
</tr>
<tr>
<td>2</td>
<td>CN</td>
<td>0·660</td>
<td>0·659</td>
<td>3409</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>0·232</td>
<td>0·150</td>
<td>3404</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>0·227</td>
<td>0·114</td>
<td>3405</td>
<td>1708</td>
</tr>
<tr>
<td>5</td>
<td>none</td>
<td>0</td>
<td>0</td>
<td>3402</td>
<td>1708</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>0·062</td>
<td>-0·073</td>
<td>3396</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>CH(_3)</td>
<td>-0·170</td>
<td>-0·811</td>
<td>3386</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>CH(_2)O</td>
<td>-0·288</td>
<td>-0·778</td>
<td>3379</td>
<td>1699</td>
</tr>
<tr>
<td>9</td>
<td>(CH(_3))(_2)N</td>
<td>-0·83</td>
<td>-1·7</td>
<td>3353</td>
<td>—</td>
</tr>
</tbody>
</table>
$2\nu_0/\sigma$ correlation $\rho 36.92$, $s_\rho 4.86$, and $r 0.943$. The $2\nu_0/\sigma^+$ plot unquestionably conforms much more closely to linearity. By contrast, the correlation coefficient for the $2\nu_0/\sigma$ plot is exceedingly poor, and the pattern of displacement of the points in Figure 2 indicates that this plot is basically curved. These findings are consistent with those of Yates and Stewart\(^1\) and demonstrate convincingly the existence of strong pararesonance interactions (IIa $\rightarrow$ IIb) in the free aldehydes.

![Fig. 1](image1)

![Fig. 2](image2)

**Fig. 1.**—Plot of carbonyl overtone stretching frequencies ($2\nu_{CO}$) of substituted benzaldehydes against $\sigma^+$ constants.

**Fig. 2.**—Plot of carbonyl overtone stretching frequencies ($2\nu_{CO}$) of substituted benzaldehydes against $\sigma$ constants. (The key to the numbers is given in Table 1.)

**Experimental**

**Materials.**—With the exception of $p$-cyanobenzaldehyde all aldehydes employed were available commercially. Each was purified immediately before use, by redistillation under reduced pressure in the case of liquids and by recrystallization in the case of solids. The method\(^1\) for converting $p$-nitrotoluene to $p$-nitrobenzaldehyde was applied to the preparation of $p$-cyanobenzaldehyde from $p$-tolunitrile. The physical constants of the product agreed with those recorded for this aldehyde by Weisler and Helmkamp.\(^1\)

**Infrared Measurements of Carbonyl Overtone Bands.**—These were carried out with a Unicam SP700 spectrophotometer. Solutions in carbon tetrachloride were examined in silica cells and at least three determinations of frequency were made in every case. Before and after each determination, frequency calibrations were made with reference to the ammonia vapour absorption spectrum.\(^1\)

