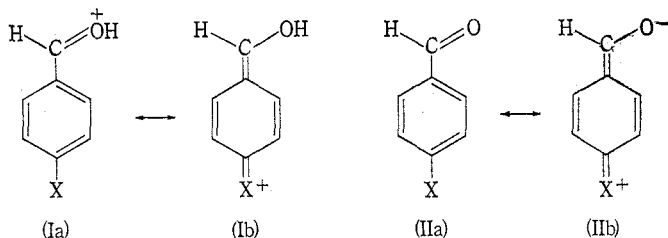


# PARA-RESONANCE INTERACTIONS IN SUBSTITUTED BENZALDEHYDES AND CORRELATIONS OF OVERTONE CARBONYL STRETCHING FREQUENCIES WITH $\sigma^+$ CONSTANTS\*

By G. E. LEWIS†

The importance of *para*-resonance interactions (Ia  $\leftrightarrow$  Ib) in the conjugate acids of benzaldehydes containing electron-donating substituents in the *para*-position has been demonstrated by Yates and Stewart,<sup>1</sup> who found that the basicities of the aldehydes ( $pK_{BH^+}$ ) do not conform to a simple Hammett  $\rho\sigma$  equation but exhibit linear dependence on  $\sigma^+$  values.<sup>3,4</sup> 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<sub>3</sub>)<sub>2</sub>N] has also recently been derived from low temperature n.m.r. spectra.<sup>5</sup>



In earlier studies of the fundamental carbonyl stretching frequencies of substituted benzaldehydes and related carbonyl compounds by Thompson, Needham, and Jameson<sup>6</sup> 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<sup>7</sup> 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

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† Department of Organic Chemistry, University of Adelaide.

<sup>1</sup> Yates, K., and Stewart, R., *Canad. J. Chem.*, 1959, **37**, 664.

<sup>2</sup> Hammett, L. P., "Physical Organic Chemistry." Ch. 7. (McGraw-Hill: New York 1940.)

<sup>3</sup> Deno, N. C., and Evans, W. L., *J. Amer. Chem. Soc.*, 1957, **79**, 5804.

<sup>4</sup> Brown, H. C., and Okamoto, Y., *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

<sup>5</sup> Anet, F. A. L., and Ahmad, M., *J. Amer. Chem. Soc.*, 1964, **86**, 119.

<sup>6</sup> Thompson, H. W., Needham, R. W., and Jameson, D., *Spectrochim. Acta*, 1957, **9**, 208.

<sup>7</sup> Rao, C. N. R., and Silverman, G. B., *Current Sci.*, 1957, **26**, 375.

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<sup>6</sup> fundamental carbonyl stretching frequencies (also measured in carbon tetrachloride solution). It may be noted that

TABLE 1  
SUBSTITUENT CONSTANTS ( $\sigma$  AND  $\sigma^+$ ) AND FREQUENCIES ( $\text{cm}^{-1}$ ) OF INFRARED OVERTONE ( $2\nu_{\text{CO}}$ ) AND FUNDAMENTAL ( $\nu_{\text{CO}}$ ) BANDS OF CARBONYL STRETCHING VIBRATIONS IN SUBSTITUTED BENZALDEHYDES

No.	<i>para</i> -Substituent	$\sigma$ (cf. <sup>8</sup> )	$\sigma^+$ (cf. <sup>4</sup> )	Frequencies ( $\text{cm}^{-1}$ ) (in $\text{CCl}_4$ )	
				$2\nu_{\text{CO}}$	$\nu_{\text{CO}}$ (cf. <sup>6</sup> )
1	$\text{NO}_2$	0.778	0.790	3414	1713
2	CN	0.660	0.659	3409	—
3	Br	0.232	0.150	3404	—
4	Cl	0.227	0.114	3405	1708
5	none	0	0	3402	1708
6	F	0.062	-0.073	3396	—
7	$\text{CH}_3$	-0.170	-0.311	3386	—
8	$\text{CH}_3\text{O}$	-0.268	-0.778	3379	1699
9	$(\text{CH}_3)_2\text{N}$	-0.83	-1.7	3353	—

the overtone frequency ( $3402 \text{ cm}^{-1}$ ) found for benzaldehyde itself is close to that ( $3404 \text{ cm}^{-1}$ ) reported earlier by Thompson and Jameson.<sup>9</sup> 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.<sup>10</sup> 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 ( $2\nu_{\text{CO}}$ ) with  $\sigma^+$  (cf.<sup>4</sup>) and  $\sigma$  (cf.<sup>8</sup>) 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.<sup>11</sup> For the  $2\nu/\sigma^+$  correlation,  $\rho$  is 24.73,  $s_\rho$  1.81, and  $r$  0.982 and for the

<sup>8</sup> McDaniel, D. H., and Brown, H. C., *J. Org. Chem.*, 1958, **23**, 420.

<sup>9</sup> Thompson, H. W., and Jameson, D. A., *Spectrochim. Acta*, 1958, **13**, 236.

<sup>10</sup> Kaye, W., *Spectrochim. Acta*, 1954, **6**, 257.

<sup>11</sup> Jaffé, H. H., *Chem. Rev.*, 1953, **53**, 191.

$2\nu/\sigma$  correlation  $\rho$  36.92,  $s_\rho$  4.86, and  $r$  0.943. The  $2\nu/\sigma^+$  plot unquestionably conforms much more closely to linearity. By contrast, the correlation coefficient for the  $2\nu/\sigma$  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<sup>1</sup> and demonstrate convincingly the existence of strong *para*-resonance interactions ( $\text{IIa} \leftrightarrow \text{IIb}$ ) in the free aldehydes.

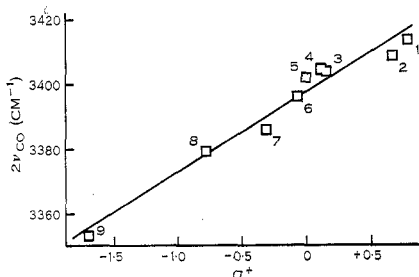


Fig. 1

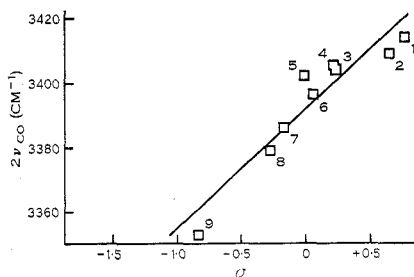


Fig. 2

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

Fig. 2.—Plot of carbonyl overtone stretching frequencies ( $2\nu_{\text{CO}}$ ) 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<sup>12</sup> 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.<sup>13</sup>

**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.<sup>14</sup>

<sup>12</sup> Lieberman, S. V., and Connor, R., in "Organic Syntheses." Coll. Vol. 2, p. 441. (Ed. A. H. Blatt.) (John Wiley: New York 1943.)

<sup>13</sup> Weisler, L., and Helmkamp, R. W., *J. Amer. Chem. Soc.*, 1945, **67**, 1167.

<sup>14</sup> Downie, A. R., Magoon, M. C., Purcell, T., and Crawford, B., *J. Opt. Soc. Amer.*, 1953, **43**, 941.