procedure[11] for the preparation of a 3,5-dinitrobenzoate, 0.15 g. of a cream-colored solid was obtained, which melted at 109–111° and did not depress the m.p. of an authentic sample of benzyl 3,5-dinitrobenzoate [reported m.p.[12] 113–113.5° (corr.)].

Department of Chemistry
State University of Iowa
Iowa City, Iowa

---

(11) J. H. Brewster and C. J. Ciotti, Jr., *J. Am. Chem. Soc.*, **77**, 6214 (1955).

(12) R. E. Buckles and J. E. Maurer, *J. Org. Chem.*, **18**, 1585 (1953).

Transmission through the Phenylamino-Group of the Effect of Substituents in the Benzene Ring

D. G. O'Sullivan and P. W. Sadler

Received May 21, 1956

The carbonyl group possesses a stretching frequency in the 1800–1650 cm.$^{-1}$ region of the infrared spectrum.[1,2] Certain sets of compounds containing the substituted benzoyl group give carbonyl maxima which are linear functions of the σ values of the substituents.[3,4,5] The latter numbers are monotonically related to the decrease of electron density in the region of the particular benzene-ring carbon atom, produced by a substituent in either the *meta*- or *para*-position.[6] The effect of substituents may, however, be further transmitted through an NH group attached to the benzene ring as is shown by the tabulated carbonyl frequencies of *meta*- and *para*-substituted acetanilides and *iso*nitrosoacetanilides. For comparison, carbonyl frequencies of substituted acetophenones and benzophenones[4] are also included in Table I. Amongst other compounds that show this effect are benzoic acid monomers and dimers,[3] benzoyl peroxides,[7] and isatins.[8] The carbonyl frequencies of all these compounds in solution approximately obey the equation $\nu - \nu_0 = 15\sigma$, where $\nu_0 = 1684$ (acetanilides), 1680 (*iso*nitrosoacetanilides), 1690 (acetophenones), 1663 (benzophenones), 1742 (benzoic acid monomers), 1696 (benzoic acid dimers), and 1740 (isatins). The good correlation between carbonyl frequency and σ function in acetanilides occurs despite the very extensive hydrogen bonding, presumably involving the carbonyl group, that is present in these compounds. Of the compounds examined, only *p*-phenylacetanilide exhibits an unusual carbonyl absorption, which may arise from partial hydrogen bonding.

TABLE I

Carbonyl Stretching Frequencies of Acetanilides A, Isonitrosoacetanilides B, Acetophenones C, and Benzophenones D, with the σ Values of Their Substituents

Substituent	σ	Carbonyl Frequencies A[a]	B[a]	C[b]	D[b]
p-NH_2	−0.660			1677	1651
p-MeO	−0.268	1678		1684	1658
p-Me	−0.170	1682	1677		1661
m-Me	−0.069	1683	1679		
None	0	1685	1680	1692	1664
p-Ph	0.009	1682 1686sh.			
p-F	0.062	1685	1680		
m-MeO	0.115	1686	1682		
p-Cl	0.227	1688	1683	1692	1666
m-F	0.337	1689	1685		
m-I	0.352	1690	1685		
m-Cl	0.373	1690	1686		
m-NO_2	0.710	1696	1690	1701	

[a] In chloroform. [b] In carbon tetrachloride.

Certain physical properties and many chemical reaction rates may be correlated with σ values of substituents. As an illustration, in Table II, rates of de-acylation of substituted *o*-nitroacetanilides[9–12] are compared with the carbonyl frequencies of the corresponding acetanilides. It has been shown that the nitro-group in the *ortho*-position exerts a constant effect in all cases, so that the comparison is valid.[9–12]

TABLE II

σ-Values and Carbonyl Frequencies (ν) of Acetanilides Compared with Rates of De-acylation (ρ) of Corresponding *o*-Nitroacetanilides

Substituent	σ	ρ	ν
p-NH_2	−0.660	0.06	
p-MeO	−0.268	0.6	1678
p-Me_2N	−0.205	0.06	
p-Me	−0.170	0.6	1682
m-Me	−0.069	1	1683
None	0	1	1685
p-Cl	0.227	4	1688
p-Br	0.232	4	
m-Cl	0.373	10	1690
m-Br	0.391	10	
m-NO_2	0.710	12	1696
p-NO_2	1.27[a]	18	

[a] Value quoted by Hammett[5] for derivatives of *p*-nitroaniline.

---

(1) Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., London, 1954.

(2) Jones and Sandorfy, *Chemical Applications of Spectroscopy* (Editor: W. West), Interscience Publishers, New York, 1956, p. 443.

(3) Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

(4) Fuson, Josien, and Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954).

(5) Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, p. 188.

(6) Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).

(7) Davison, *J. Chem. Soc.*, 2456 (1951).

(8) O'Sullivan and Sadler, *J. Chem. Soc.* (in the press).

(9) Wepster and Verkade, *Rec. trav. chim.*, **67**, 411 (1948).

(10) Wepster and Verkade, *Rec. trav. chim.*, **67**, 425 (1948).

(11) Wepster and Verkade, *Rec. trav. chim.*, **68**, 77 (1949).

(12) Wepster and Verkade, *Rec. trav. chim.*, **68**, 88 (1949).

The results obtained by Richards and Thompson[13] on some substituted acetanilides in dioxane, suggest that similar carbonyl frequency shifts occur in this solvent. However, the work of these authors[13] shows that much bigger shifts occur with solid acetanilides and this is also apparent with solid acetophenones.[14] Substituted oxindoles[15] have carbonyl maxima that obey the equation $\nu - \nu_0 = 37.5\sigma$, ν_0 possessing the value 1725 $cm.^{-1}$ It is likely that the augmentation of the effect in the latter cases arises from the absence of free rotation about the Ph—N—C bonds in oxindoles, and in acetanilides and acetophenones in the solid state. As a result, the position of the carbonyl group is fixed, presumably in the plane of the benzene ring. The coplanarity assists the transmission of substituent effects. It is not clear why the shifts are small with substituted isatins.

Certain other features, present in the infrared spectra of substituted acetanilides in chloroform, now are briefly mentioned. All these compounds exhibit a single, very broad, band in the 3500–3200 $cm.^{-1}$ region, indicating that hydrogen bonding (presumably intermolecular) is very extensive in this solvent.[13] In most cases there was no evidence of any distinct maximum arising from an unassociated NH group, and, consequently, it was not possible to gain any information on the effect of substituents on the NH frequency. It is of interest to note, however, that Flett[3] has examined the NH_2 frequencies of substituted anilines in carbon tetrachloride. The symmetric and asymmetric stretching vibrations of the NH_2 group give rise to two maxima in the 3535–3400 $cm.^{-1}$ region. Substituents have a marked influence on the frequency maxima, the effect being more pronounced on the asymmetric mode. In each case, an approximately linear relationship exists between NH_2 frequency and σ value for those substituents possessing a σ value greater than -0.2.

The aromatic C—C stretching vibration is present in acetanilides close to 1610 $cm.^{-1}$, and this maximum undergoes splitting when *meta-* or weakly *ortho-para-*directing substituents are attached to the ring. Unassigned bands appear in the 1350–1300 $cm.^{-1}$ region, some of which may be related to the Ph—N stretching mode.

EXPERIMENTAL

The infrared spectra were determined in chloroform using a Perkin-Elmer 21 double-beam recording spectrometer with a rock-salt prism.

Courtauld Institute of Biochemistry,
The Middlesex Hospital,
London, W. 1, England.

---

[13] Richards and Thompson, *J. Chem. Soc.*, 1259 (1947).

[14] Soloway and Friess, *J. Am. Chem. Soc.*, **73**, 5000 (1951).

[15] Kellie, O'Sullivan, and Sadler, *J. Chem. Soc.* (in the press).

The Nuclear Magnetic Resonance Spectrum of Helvolic Acid

Norman L. Allinger[1]

Received May 23, 1956

A tentative structure was recently proposed for helvolic acid[2] in which all of the known groupings were accounted for with the exception of the location of one carbon atom. It is the purpose of this report to offer evidence for the position of this remaining atom.

The C-methyl analysis of helvolic acid gave a value of 3.62 C-methyls per mole.[2] This number is rather high to represent four, and can best be taken as indicative of five such methyls per molecule. The formula proposed earlier[2] would be predicted to give four C-methyls,[3] two from the acetoxyl groups, one from C_{18}, and one from the acetone resulting from cleavage of the side chain. The extra carbon atom would thus appear likely to be present as a methyl group.

Ordinarily extra carbon atoms in steroids are found as alkyl groups at C_{24}. The ultraviolet spectra of helvolic acid and its derivatives did not, however, appear consistent with a methyl group at this position. On the other hand, there was available some evidence which appeared to indicate that no hydrogen atom was present at C_{24}. There was no hydrogen out-of-the-plane bending band near 12 μ in the infrared spectrum, and there was no strong band in the 6μ region which could be attributed to the carbon-carbon double bond stretching absorption. The stretching absorption is ordinarily very intense for a double bond of the mesityl oxide type,[4] while it might be expected to be weak if a nearly symmetrical arrangement around the double bond existed, as it would if a C_{24} methyl were present. In view of the conflicting evidence, location of the extra carbon was not specified in the original formulation.

Recently nuclear magnetic resonance spectra have been used to locate the positions of double bonds in molecules by determining the number of hydrogens present on the double bonds,[5] and the success of this technique is dependent on the fact

---

[1] National Science Foundation Post Doctoral Fellow, 1955–1956. Present address: Chemistry Department, Wayne State University, Detroit, Michigan.

[2] Cram and Allinger, *J. Am. Chem. Soc.*, **78**, in press (1956).

[3] Eisenbraun, McElvain, and Aycock, *J. Am. Chem. Soc.*, **76**, 607 (1954).

[4] (a) Bellamy, *The Infrared-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954, p. 37; (b) Djerassi, Bowers, and Khastgir, *J. Am. Chem. Soc.*, **78**, 1729 (1956).

[5] (a) Dauben and Hance, *J. Am. Chem. Soc.*, **77**, 2451 (1955); (b) Corey, Burke, and Remers, *J. Am. Chem. Soc.*, **77**, 4941 (1955); (c) Ettlinger and Kennedy, *Chemistry & Industry*, 166 (1956).