[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS]

A Hammett-Taft Equation for the Quantitative Relationship between the Structures and Basic Wave Number Shifts of the 2,4-Dinitrophenylhydrazones of Substituted Acetophenones[1]

LACEY E. SCOGGINS AND C. KINNEY HANCOCK

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Previously, for the 2,4-dinitrophenylhydrazones (DNP's) of nine *m*- or *p*-substituted acetophenones, it was shown that the basic wave number shifts ($\Delta\nu = 1/\lambda_{\max}^{\mathrm{CHCl_3}} - 1/\lambda_{\max}^{\mathrm{NaOH}}$) are quantitatively related to Hammett's σ-values by the equation, $\Delta\nu$ in cm.$^{-1}$ = $4700 + 2340\sigma$, with a linear correlation coefficient r of 0.993 and a standard deviation from regression s of 178 cm.$^{-1}$ The spectra of the 2,4-dinitrophenylhydrazones of eleven α-substituted acetophenones and of twelve α,(*m* or *p*)-disubstituted acetophenones have been measured in chloroform and in ethanolic sodium hydroxide solutions. The $\Delta\nu$-values for the 2,4-dinitrophenylhydrazones of the eleven α-substituted acetophenones are quantitatively related to Taft's σ^*-values by the equation, $\Delta\nu = 4620 + 730\sigma^*$, with $r = 0.953$ and $s = 124$. Multiple regression analysis of the combined data for the thirty-one 2,4-dinitrophenylhydrazones gives the excellent relationship, $\Delta\nu = 4620 + 2330\sigma + 520\sigma^*$, with multiple correlation coefficient $R = 0.986$ and $s = 166$. All of the above relations apply to the more stable *syn*-isomers of the 2,4-dinitrophenylhydrazones. The very large deviations from regression of the $\Delta\nu$-values for the *anti*-isomers of the 2,4-dinitrophenylhydrazones of three α-substituted acetophenones indicate that equation 2 may be used to establish the configurations of the 2,4-dinitrophenylhydrazones of α-substituted acetophenones.

The chloroform solution of the 2,4-dinitrophenylhydrazone of a carbonyl compound exhibits a characteristic absorption maximum ($\lambda_{\max}^{\mathrm{CHCl_3}}$) in the near ultraviolet spectrum. When this chloroform solution is made basic with alcoholic sodium hydroxide solution, there occurs immediately a large bathochromic shift to give a new absorption maximum ($\lambda_{\max}^{\mathrm{NaOH}}$). This bathochromic shift is due to the rapid removal of the *N*-hydrogen[2] and to accompanying resonance and other effects.

Previously,[3] good quantitative correlations have been shown for the relationship between the structures and basic wave number shifts ($\Delta\nu = 1/\lambda_{\max}^{\mathrm{CHCl_3}} - 1/\lambda_{\max}^{\mathrm{NaOH}}$) of the 2,4-dinitrophenylhydrazones of twenty-three aliphatic aldehydes and ketones and of the 2,4-dinitrophenylhydrazone of twenty-one *m*- or *p*-substituted benzaldehydes and acetophenones. More particularly, with reference to the present article, linear regression analysis[3,4a] of the data for the 2,4-dinitrophenylhydrazones of nine *m*- or *p*-substituted acetophenones gave

$$\Delta\nu \text{ in cm.}^{-1} = 4700 + 2340\sigma \qquad (1)$$

with a linear correlation coefficient r or 0.993[5] and a standard deviation from regression s[6] of 178 cm.$^{-1}$ In equation 1, $\Delta\nu$ = the basic wave number shift in cm.$^{-1}$, 4700 = the calculated $\Delta\nu_0$-value for unsubstituted acetophenone, 2340 = ρ = Hammett's[7] reaction constant, and σ = Hammett's[7] substituent constant.

In view of this excellent quantitative relationship, it seemed desirable to make a similar Taft[8a] study of the 2,4-dinitrophenylhydrazones of α-substituted acetophenones and a combined Hammett-Taft study of the 2,4-dinitrophenylhydrazones of α-(*m* or *p*)-disubstituted acetophenones. It was felt that the latter study might give an insight into the nature of the interaction, if any, between the

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[1] Abstracted from the Ph.D. dissertation of L. E. S., The A. and M. College of Texas, August 1960. Present address of L. E. S., Phillips Petroleum Company, Bartlesville, Okla. Presented before the Organic Section at the 16th Southwest Regional A.C.S. Meeting, Oklahoma City, Okla., Dec. 1, 1960.

[2] F. Bohlmann, *Ber.*, **84**, 490 (1951).

[3] L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).

[4] G. W. Snedecor, *Statistical Methods*, 5th ed., The Iowa State College Press, Ames, Iowa, 1956: (a) Chap. 6, (b) Chap. 14, (c) pp. 46, 418, and 441.

[5] r is the correlation coefficient for *linear* regression (one dependent variable and one independent variable), while R is the correlation coefficient for *multiple* regression (one dependent variable and two or more independent variables). The significance level of the correlation coefficient depends on: (1) the magnitude of the correlation coefficient, (2) the number of variables, and (3) the degrees of freedom (*d.f.* = number of observations minus number of variables). Thus, for Equation 1, the r-value of 0.993 for 2 variables and 7 *d.f.* is highly significant at the 0.001 level ($r_{0\cdot001}$ = 0.898 for 2 variables and 7 *d.f.*, see R. A. Fisher and F. Yates, *Statistical Tables*, 3rd ed., Hafner Publishing Co., Inc., New York, N. Y., 1948, Table VI, p. 46). This means that there is less than one chance in one thousand of Equation 1 being a random relationship. In more useful terms, the r-value of 0.993 means that 98.6% (= 100 r^2) of the variation in $\Delta\nu$ is accounted for by Equation 1.

Similar considerations apply to the other correlation coefficients given in this article. For example, for Equation 3, the R-value of 0.989 for 3 variables and 16 *d.f.* is *exceedingly* highly significant at the 0.01 level ($r_{0\cdot01}$ = 0.662 for 3 variables and 16 *d.f.*, see G. W. Snedecor, *Statistical Methods*, 4th ed., The Iowa State College Press, Ames, Iowa, 1946, Table 13.6, p. 351). Again, this R-value of 0.989 means that 97.8% (= 100R^2) of the variation in $\Delta\nu$ is accounted for by Equation 3.

[6] One significant feature of the standard deviation s is that usually about two-thirds of the experimental values lie within ± s of the regression values.

[7] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 186 and 188.

[8] R. W. Taft, Jr., *Steric Effects in Organic Chemistry*, M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956: (a) p. 606, (b) p. 598, (c) p. 619.

TABLE I

MELTING POINTS AND SPECTRA OF THE 2,4-DINITROPHENYLHYDRAZONES OF α-SUBSTITUTED ACETOPHENONES

R_1 in DNP of $C_6H_5COR_1$	M.P.[a]	$\lambda_{max}^{CHCl_3}$, mμ	$\epsilon \times 10^{-4}$	λ_{max}^{NaOH}, mμ	$\epsilon \times 10^{-4}$	$\Delta\nu$,[b] cm.$^{-1}$	σ^*[c]
$ClCH_2$	219–220[d]	372	2.65	466	2.02	5,423	+1.050
$BrCH_2$	211–212[e]	378	2.62	473	2.14	5,313	+1.000
$BrCH_2$[f]	125–126[e]	365	2.59	466	2.23	6,121	+1.000
$C_6H_5OCH_2$	182–183[g]	380	2.62	475	2.56	5,263	+0.850
CH_3OCH_2	193–194[h]	383	2.67	471	2.63	4,879	+0.520
CH_3OCH_2[f]	106–107[i]	364	2.57	467	2.30	6,060	+0.520
$C_6H_5CH_2$	201–202[d]	382	2.69	470	2.42	4,901	+0.215
CH_3	247–248[d]	378	2.56	461	2.58	4,763	0.000
C_2H_5	187–189[j]	380	2.61	458	2.33	4,482	−0.100
n-C_3H_7	187–188[d]	382	2.72	459	2.64	4,392	−0.115
n-C_3H_7[f]	103–104[k]	370	2.52	452	2.05	4,903	−0.115
n-C_5H_{11}	166–167[d]	382	2.74	460	2.44	4,439	−0.130
i-C_3H_7	162–163[d]	368	2.46	445	1.72	4,702	−0.190
t-C_4H_9	192–193[d]	366	2.35	435	1.06	4,333	−0.300

[a] Corr. [b] $\Delta\nu = \nu_{max}^{CHCl_3} - \nu_{max}^{NaOH}$. [c] Ref. 8c. [d] G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953). [e] Ref. 10a. [f] *anti*-Isomers. [g] C. O. Guss, *J. Am. Chem. Soc.*, **71**, 3460 (1949). [h] P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952). [i] *Anal.* Calcd. for $C_{15}H_{14}N_4O_5$: N, 16.96. Found: N, 16.85. [j] T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 2607 (1932). [k] *Anal.* Calcd. for $C_{16}H_{16}N_4O_4$: N, 17.07. Found: N, 17.21.

effect of substitution in the aliphatic portion and the effect of simultaneous substitution in the aromatic portion of the same molecule. The result would be of comparative value in connection with previous studies[9] which showed, for the diphenyl–diazomethane–benzoic acid reaction, that the effect of substitution in one reactant is independent of the effect of simultaneous substitution in the other reactant.

The problem is somewhat complicated by the possible existance of *syn*- and *anti*-forms of the 2,4-dinitrophenylhydrazones of substituted acetophenones. Ramirez and Kirby[10a] have isolated both the *syn*- and *anti*-forms of the 2,4-dinitrophenylhydrazones of several α-substituted acetophenones and have assigned[10b] the term "*syn*-" to that isomer having the 2,4-dinitroanilino group and the α-substituent on the same side of the C=N bond. The *syn*-form is the more stable and is the isomer obtained from the preparation by Johnson's method.[11] Steric hindrance in the *anti*-form prevents coplanarity of the C=N group with the benzene ring and destabilizes this form.

RESULTS AND DISCUSSION

Using the values given in Table I for the *syn*-forms of the 2,4-dinitrophenylhydrazones of eleven α-substituted acetophenones, linear regression analysis[4a] gives

$$\Delta\nu = 4620 + 730\sigma^* \qquad (2)$$

with $r = 0.953$ and $s = 124$, where $730 = \rho^* =$ Taft's[8a] polar reaction constant and $\sigma^* =$ Taft's[8a] polar substituent constant. Even though the relationship given by Equation 2 is good, attempts to improve it were made by including steric substituent constants[8b] and/or hyperconjugative resonance effects (*i.e.*, the number of α-hydrogens) as independent variables along with σ^*-values in multiple regressing analyses[4b]; however, none of these analyses showed any significant improvement.

The $\Delta\nu$- and σ^*-values from Table I for *syn*-2,4-dinitrophenylhydrazones are plotted as circles in Fig. 1 along with the regression line defined by

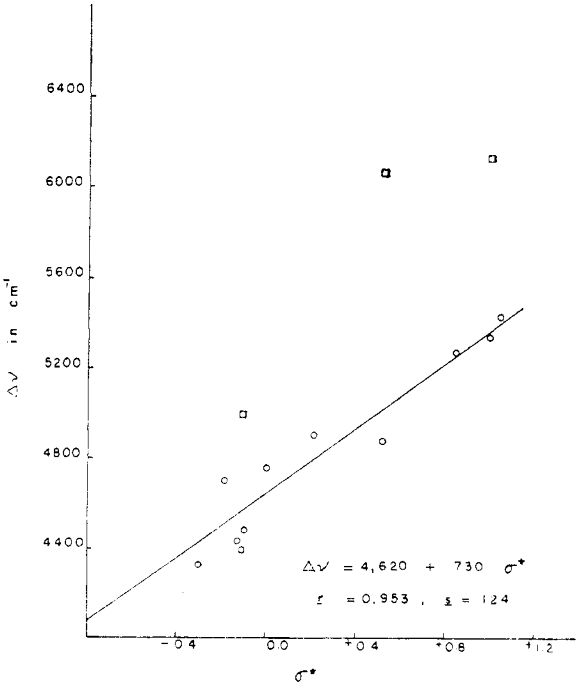

Fig. 1. Relationship between the basic wave number shifts $\Delta\nu$ and Taft's polar substituent constants σ^* for the 2,4-dinitrophenylhydrazones of eleven α-substituted acetophenones. Circled points represent *syn*-DNP's. Squared points represent *anti*-DNP's. The line drawn is the line defined by equation 2 for the eleven *syn*-DNP's

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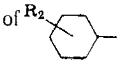
(9) C. K. Hancock and J. S. Westmoreland, *J. Am. Chem. Soc.*, **80**, 545 (1958); C. K. Hancock, R. F. Gilby, Jr., and J. S. Westmoreland, *J. Am. Chem. Soc.*, **79**, 1917 (1957).

(10) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*: (a) **75**, 6026 (1953); (*b*) **76**, 1037 (1954).

(11) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

TABLE II

MELTING POINTS AND SPECTRA OF THE 2,4-DINITROPHENYLHYDRAZONES OF α, (m OR p)-DISUBSTITUTED ACETOPHENONES

DNP of  R₁	R₂	M.P.[a]	$\lambda_{\text{max.}}^{\text{CHCl}_3}$ mμ	$\epsilon \times 10^{-4}$	$\lambda_{\text{max.}}^{\text{NaOH}}$ mμ	$\epsilon \times 10^{-4}$	$\Delta\nu$,[b] cm.$^{-1}$	σ[c]	σ^*[d]
$ClCH_2$	m-NO_2	200–201[e]	368	2.64	492	2.77	6,849	+0.710	+1.050
CH_3OCH_2	m-NO_2	247 d.[f]	377	2.86	496	3.12	6,364	+0.710	+0.520
n-C_3H_7	m-NO_2	174–176[g]	373	2.54	487	2.26	6,276	+0.710	−0.115
C_2H_5	m-NO_2	206–207[h]	372	2.67	484	2.53	6,221	+0.710	−0.100
$BrCH_2$	p-Br	220–221[i]	379	2.70	481	2.50	5,595	+0.232	+1.000
$ClCH_2$	p-C_6H_5	222–223[j]	385	2.95	478	2.31	5,053	+0.009	+1.050
$BrCH_2$	p-C_6H_5	229–230[i]	388	2.55	479	2.15	4,896	+0.009	+1.000
C_2H_5	p-Cl	221–222[k]	380	2.80	470	2.65	5,039	+0.227	−0.100
$BrCH_2$	p-CH_3	205–206[l]	384	2.74	466	2.28	4,583	−0.170	+1.000
C_2H_5	m-CH_3O	190–191[m]	381	2.69	462	2.36	4,602	+0.115	−0.100
C_2H_5	p-CH_3	204–205[n,o]	385	2.60	457	2.46	4,092	−0.170	−0.100
C_2H_5	p-CH_3O	194–195[n]	390	2.52	459	2.19	3,855	−0.268	−0.100

[a] Corr. [b] $\Delta\nu = \nu_{\text{max}}^{\text{CHCl}_3} - \nu_{\text{max}}^{\text{NaOH}}$ [c] Ref. 7. [d] Ref. 8c. [e] *Anal.* Calcd. for $C_{14}H_{10}ClN_5O_6$: N, 18.44. Found: N, 18.60. [f] *Anal.* Calcd. for $C_{15}H_{13}N_5O_7$: N, 18.66. Found: N, 18.79. [g] *Anal.* Calcd. for $C_{16}H_{15}N_5O_6$: N, 18.76. Found: N, 18.51. [h] *Anal.* Calcd. for $C_{15}H_{13}N_5O_6$: N, 19.49. Found N, 19.50. [i] Ref. 11. [j] *Anal.* Calcd. for $C_{20}H_{15}ClN_4O_4$: N, 13.64. Found: N, 13.39. [k] Note d, Table I. [l] K. Yamaguchi, S. Fujii, T. Tabata, and S. Kato, *J. Pharm. Soc. Japan*, **74,** 1328 (1954). [m] W. S. Johnson, C. A. Erickson, and J. Ackerman, *J. Am. Chem. Soc.*, **74,** 2251 (1952). [n] N. M. Cullinane, S. J. Chard, and D. M. Leyshon, *J. Chem. Soc.*, 376 (1952). [o] *Anal.* Calcd. for $C_{16}H_{16}N_4O_4$: N, 17.07. Found N, 17.04.

Equation 2. Also plotted in Fig. 1 as squares are the $\Delta\nu$- and σ^*-values for the *anti*-2,4-dinitrophenylhydrazones of α-bromoacetophenone, α-methoxyacetophenone, and n-butyrophenone. In Fig. 1 it is apparent that the experimental $\Delta\nu$-values for the *anti*-2,4-dinitrophenylhydrazones deviate widely from regression; in fact, these deviations are so great that Equation 2 may serve as a criterion for establishing the configuration of 2,4-dinitrophenylhydrazones of α-substituted acetophenones.

The data used to obtain Equations 1 and 2 were combined and submitted to multiple regression analysis[4b] to obtain[12]

$$\Delta\nu = 4660 + 2350\sigma + 700\sigma^* \qquad (3)$$

with multiple correlation coefficient $R^5 = 0.989$ and $s = 153$. "Student's" t-tests[4c] show that the parameters 2350 and 700 of equation 3, as well as the corresponding parameters of equations 4 and 5, are all highly significant at the 0.001 level.[13]

A similar treatment of the data from Table II for the 2,4-dinitrophenylhydrazones of twelve α, (m or p)-disubstituted acetophenones gives the excellent relationship

$$\Delta\nu = 4510 + 2460\sigma + 470\sigma^* \qquad (4)$$

with $R = 0.996$ and $s = 91$.

A comparison of Equations 3 and 4 indicates that there may be interaction between the effect of α-substitution and the effect of simultaneous m- or p-substitution. In order to test for such interaction, if any, all of the data for equations 1, 2, and 4 were combined and first submitted to analysis of the multiple regression[4b] of $\Delta\nu$ on σ and σ^* to obtain

$$\Delta\nu = 4620 + 2330\sigma + 520\sigma^* \qquad (5)$$

with $R = 0.986$ and $s = 166$.

Then, the interaction factor[14] $\sigma.\sigma^*$ was included in the multiple regression analysis to obtain

$$\Delta\nu = 4620 + 2340\sigma + 530\sigma^* - 90\sigma.\sigma^* \qquad (6)$$

with $R = 0.986$ and $s = 169$. "Students'" t-tests[4c] show that the parameters 2340 and 530 are both highly significant at the 0.001 level while the interaction parameter 90 is not significant even at the 0.500 level. Consequently, it is indicated that the polar effect of α-substitution in the 2,4-dinitrophenylhydrazone of an acetophenone is independent of the polar effect of simultaneous m- or p-substitution. However, though statistically insignificant, the differences between Equations 3 and 4 remain and it is believed that they are largely the result of a weighting effect of the much larger ρ-value as compared to the ρ^*-value. Also, they may be partially due to a somewhat better precision of the Hammett relation over that of the Taft relation.

Of the data used in this article, not only the $\Delta\nu$-values but also the σ- and σ^*-values are subject to uncertainties. For example, both Hammett[7] and Taft,[8c] in their compilations, list median deviations of σ- and σ^*-values. Consequently, it should be expected that the parameters of equations 3, 4, and 5 will not be the same since different sets of data (each set being subject to uncertainties in the values of all the variables involved) were used in

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(12) Multiple regression Equation 3 defines a multiple regression *plane*. The deviations from regression are deviations from this plane. Similar considerations apply to Equations 4 and 5. Equation 6 is more complex, involving four dimensions (one dependent variable and three independent variables).

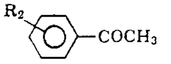
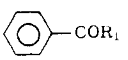
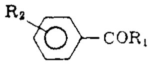
(13) The calculated "Students" t-value for the parameter 2350 of Equation 3 is 25.48. The $t_{0.001}$ value for 16 $d.f.$ is 4.02 (see Ref. 4c). Therefore, the parameter 2350 of Equation 3 is very highly significant beyond the 0.001 level of probability. In practical terms, this means that there is much less than one chance in one thousand that the parameter 2350 is a random value. Similar considerations apply to "Students'" t-tests on other parameters of Equations 3, 4, and 5.

(14) S. I. Miller, *J. Am. Chem. Soc.*, **81,** 101 (1959)

calculating these three equations. Even though the three parameters of Equations 3, 4, and 5 are somewhat different, still there is no statistically significant difference between these three equations; in fact, there is no practical difference as illustrated in Table III in a comparison of results calculated by Equations 3 and 5. As shown in the following paragraph, the differences, shown in Table III, between the average deviations from regression calculated by Equations 3 and 5 are less than the experimental uncertainty in the observed Δν-values. In view of the above, Equation 5 is a useful, general equation for the 2,4-dinitrophenylhydrazones of: *m*- or *p*-substituted acetophenones (I), α-substituted acetophenones (II), and α, (*m* or *p*)-disubstituted acetophenones (III). If it is not desired to make such general use of Equation 5, then use may be made of Equation 3 for I and II and of Equation 4 for III.

TABLE III

A COMPARISON OF THE AVERAGE DEVIATION OF EXPERIMENTAL Δν-VALUES FROM Δν-VALUES CALCULATED BY EQUATIONS 3 AND 5

DNP's of	Av. Dev. (cm.$^{-1}$) for Δν Calcd. By: Eq. 3	Eq. 5
	139	161
	103	149
	221	115

As illustrated in Fig. 2, a very good fit for all of the data (thirty-one 2,4-dinitrophenylhydrazones) is provided by Equation 5. Comparing experimental Δν-values with Δν-values calculated by Equation 5, the average deviation is 139 cm.$^{-1}$, the maximum deviation is 266 cm.$^{-1}$, and only six deviations exceed 200 cm.$^{-1}$ If a possible error of ±1 mμ in measuring the absorption maxima be assumed, then as shown below, the average deviation from regression of 139 cm.$^{-1}$ only slightly exceeds the experimental uncertainty in the value of Δν. For example, suppose that the true $\lambda_{max}^{CHCl_3}$ and λ_{max}^{NaOH} values for a particular 2,4-dinitrophenylhydrazone are 380 and 470 mμ (these being the averages of the maxima for all of the thirty-one 2,4-dinitrophenylhydrazones involved in this study). Then, the true Δν-value for this 2,4-dinitrophenylhydrazone would be 5039 cm.$^{-1}$ If, instead, the observed values of $\lambda_{max}^{CHCl_3}$ and λ_{max}^{NaOH} had been 379 and 471 (or 381 and 469) mμ, then Δν would have been 5154 (or 4925) cm.$^{-1}$ This amounts to an uncertainty of ±115 cm.$^{-1}$ in the observed Δν-value.

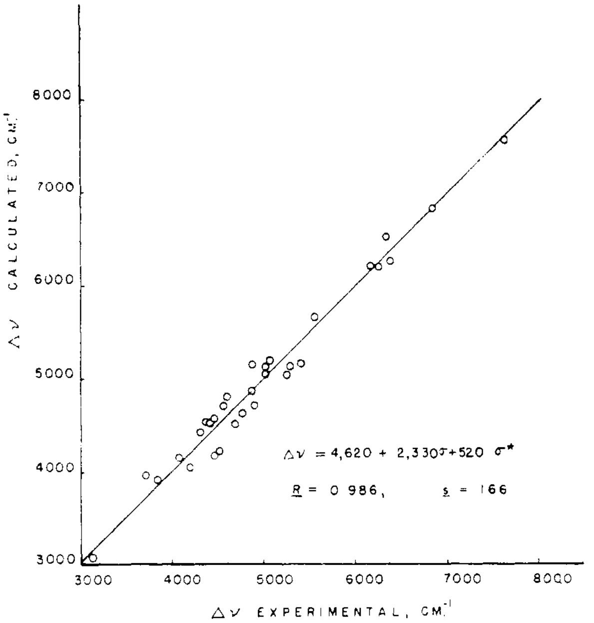


Fig. 2. Relationship between the Δν-values calculated by Equation 5 and the observed Δν-values for the 2,4-dinitrophenylhydrazones of thirty-one α- and/or (*m* or *p*)-substituted acetophenones

In all regression analyses involved in this article, statistical quantities were calculated from regression Equations 1 to 8, inclusive, in which wave numbers were given to the nearest cm.$^{-1}$ In all of these equations as given in this article, the wave numbers are given to the nearest 10 cm.$^{-1}$ In view of the experimental uncertainties discussed in the paragraph above, the wave numbers calculated by Equations 1 to 6, inclusive, are probably significant only to the nearest 100 cm.$^{-1}$

The results shown in Fig. 1 indicate that equation 2 may serve as a criterion for establishing the configuration of the 2,4-dinitrophenylhydrazones of α-substituted acetophenones. For example, the σ*-value is the same for the *syn*- and *anti*- forms of the 2,4-dinitrophenylhydrazone of a particular α-substituted acetophenone. Therefore, if the σ*- and Δν-values for the particular 2,4-dinitrophenylhydrazone of an α-substituted acetophenone are plotted and the resulting point lies reasonably close to the line defined by equation 2, then the 2,4-dinitrophenylhydrazone is very likely the *syn*-isomer. On the other hand, if the resulting point deviates quite seriously from the line defined by equation 2, then the 2,4-dinitrophenylhydrazone is very likely the *anti*-isomer. Similar considerations probably also apply to Equations 1, 3, 4, and 5. Also, there is some indication in Fig. 1 that the points for a sufficient number of the *anti*- 2,4-dinitrophenylhydrazones of α-substituted acetophenones may reasonably define a straight line of significantly different slope and intercept from that of the line defined by Equation 2. Presently, studies are under way for investigating these latter two points.

It is apparent that Equation 5 may be used to calculate undetermined Δν-values for the 2,4-

dinitrophenylhydrazones of α- and/or (*m* or *p*)-substituted acetophenones of known structure for which σ- and/or σ*-values are known.

A rearrangement of Equation 1 or 2 should not be used to calculate new σ- or σ*-values from experimental Δν-values since not only the Δν-values but also the σ- or σ*-values are subject to uncertainties. Equations 1 and 2 were obtained by minimizing the squares of the deviations of the Δν-values. Minimizing the squares of the deviations of σ-values, linear regression reanalysis of the data[3] used to obtain equation 1 leads to

$$\sigma = -1.983 + 0.000422\Delta\nu \qquad (7)$$

with $r = 0.993$ and $s = 0.077$ log units. Equation 7 is useful for calculating new σ-values from experimental Δν-values for 2,4-dinitrophenylhydrazones of *m*- or *p*-substituted acetophenones. Because of the nearness to unity of the *r*-value of 0.993, Equation 7 does not deviate seriously from the equation, $\sigma = -2.004 + 0.000427\Delta\nu$, obtained by rearrangement of Equation 1. Similarly, by minimizing the squares of the deviations of σ*-values, linear regression re-analysis of the data of Table I leads to

$$\sigma^* = -5.754 + 0.00125\Delta\nu \qquad (8)$$

with $r = 0.953$ and $s = 0.163$. Because of the greater deviation from unity of the *r*-value of 0.953, Equation 8 deviates considerably from the equation, $\sigma^* = -6.365 + 0.00138\Delta\nu$, obtained by rearrangement of Equation 2. Equation 8 is fairly good for calculating new σ*-values from experimental Δν-values for 2,4-dinitrophenylhydrazones of α-substituted acetophenones. Provided R is not conjugated with the carboxyl group, it is better to calculate σ* for R from the rate constant for the reaction of RCO_2H with diphenyldiazomethane.[15] The fairly good fit of equation 8 compared to the very good fit of Equation 7 may result from: (1) a smaller range of 1,788 cm.$^{-1}$ in Δν-values for equation 8 compared to a range of 4,537 cm.$^{-1}$ in Δν-values for equation 7, (2) a somewhat better general precision of the Hammett relation over that of the Taft relation, and (3) the considerable deviation of the data for the 2,4-dinitrophenylhydrazone of isobutyrophenone from Equation 8, 41% of the variance of the deviations of eleven values being due to this single value.

Finally, in some cases, equation 5 may serve as an aid in confirmation of structure. As a simple example, supposed that a Δν-value of 3771 cm.$^{-1}$ is found[3] for the 2,4-dinitrophenylhydrazone of a particular methoxy-substituted acetophenone. If this methoxy group were in the *p*-position (σ for *p*-CH_3O = -0.268), the Δν-value calculated by Equation 5 would be 3996 cm.$^{-1}$ If in the *m*-position (σ for *m*-CH_3O = $+0.115$), the calculated Δν-value would be 4888 cm.$^{-1}$ If in the α-position (σ* for CH_3OCH_2 = $+0.520$), the calculated Δν-value would be 4890 cm.$^{-1}$ Of course, the presence of the methoxy group in the *o*-position is not ruled out, but of the *p*-, *m*-, and α-positions, the above data strongly indicate that the methoxy group is in the *p*-position.

EXPERIMENTAL

α-Substituted acetophenones. α-Phenoxyacetophenone, α-phenylacetophenone, and pivalophenone were prepared, respectively, by treating: (1) potassium phenoxide with α-chloroacetophenone,[16] (2) phenylacetyl chloride with benzene and anhydrous aluminum chloride, and (3) *tert*-butylmagnesium chloride with benzoyl chloride in tetrahydrofuran.

α, (m or p)-Disubstituted acetophenones. α-Bromo-*p*-methylacetophenone was prepared by bromination of *p*-methylacetophenone in glacial acetic acid.[17] *m*- and *p*-Methoxypropiophenones were prepared by treating *m*- and *p*-hydroxypropiophenones with dimethyl sulfate in sodium hydroxide solution. α-Chloro-*m*-nitroacetophenone, *m*-nitrobutyrophenone, *m*-nitropropiophenone, and α-methoxy-*m*-nitroacetophenone were prepared by nitration[18] of the appropriate α-substituted acetophenone.

The other eight α-substituted acetophenones and five α, (*m* or *p*)-disubstituted acetophenones used in this study were obtained from commercial sources.

Preparation of 2,4-dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazones were prepared by Johnson's[11] method and were recrystallized until a constant melting point was obtained from two or more solvents (acetic acid, benzene, chloroform, dioxane, or toluene). The melting points are shown in Tables I and II.

anti-Isomers of 2,4-dinitrophenylhydrazones. The *syn*-isomers of the 2,4-dinitrophenylhydrazones of α-bromoacetophenone, α-methoxyacetophenone, and *n*-butyrophenone were isomerized to the *anti*-form by the method of Ramirez and Kirby,[10a] except that the *anti*-isomers were recrystallized from 95% ethanol. The melting points are shown in Table I. The *anti*-isomers were easily reconverted to the *syn*-forms by refluxing 2 g. in 20 ml. of ethanol with a few drops of concentrated hydrochloric acid. Mixtures of the reconverted and orginal *syn*-forms showed no depression in melting point.

Measurement of spectra. Neutral and basic solutions of the 2,4-dinitrophenylhydrazones were prepared at 25° by a previously described method[19] and the spectra were measured with a Beckman DK-1 recording spectrophotometer. The spectral results are shown in Tables I and II.

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COLLEGE STATION, TEX.

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