[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, A. AND M. COLLEGE OF TEXAS AND THE TEXAS ENGINEERING EXPERIMENT STATION]

Spectrophotometric Studies of Some 2,4-Dinitrophenylhydrazones. III.[1] Taft and Hammett Relationships

LOUIS A. JONES[2] AND C. KINNEY HANCOCK

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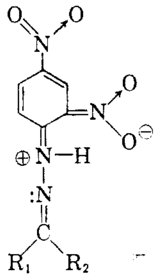
The ultraviolet and visible spectra of 21 *m*- and *p*-substituted aromatic 2,4-dinitrophenylhydrazones (DNP's) and 23 α-substituted acetaldehyde and acetone DNP's in chloroform and in alcoholic base have been determined. The difference in the absorption frequencies of these solutions, *i.e.*, $\nu_{\text{max}}^{\text{CHCl}_3} - \nu_{\text{max}}^{\text{NaOH}}$, for the aromatic DNP's were related to the Hammett substituent constants by Eq. 4: $\Delta\nu = 4835 \text{ cm.}^{-1} + 2233\sigma$ with $r = 0.977$ and $s = 274$. The aliphatic derivatives were related to Taft's σ^*-values by Eq. 6: $\Delta\nu = 4474 \text{ cm.}^{-1} + 843.9\Sigma\sigma^*$ with $r = 0.951$ and $s = 203$. By minimizing the squares along the substituent constant axis, new values were calculated for *p*-$(CH_3)_2N$ (-1.154), *p*-OH → *p*-O$^\ominus$ (-0.013 and -0.267) and *m*-OH → *m*-O$^\ominus$ (-0.014) in the aromatic series and in the aliphatic series, new constants were determined for F_3C ($+2.595 \pm 0.160$), Et_2NCH_2 (-0.066) and cyclo-C_3H_5 (-0.475). The relationship between $\Delta\nu$ and ΔF is discussed.

The shift of absorption maxima which a substituent causes in the ultraviolet absorption spectra of monosubstituted benzenes has been shown to be proportional to the difference of the Hammett substituent constants[3] in the *m*- and *p* -positions ($\Delta\sigma$).[4] More recently, the similar displacement which occurs for the disubstituted benzenes has been correlated with the Hammett substituent constants,[3] the Brown-Okamoto σ^+-values,[5] and the Taft resonance parameters[6] although for substituents with like electrical properties (*m*-orienting *vs.* m-orienting, etc.), no straightforward relationship was apparent.[7] Moreover no unique equation was found to express the relationship between substituent constants and the wave-length displacement in substituted anilines, phenols, and nitrobenzenes combined.

The ultraviolet spectra of 2,4-dinitrophenylhydrazones (DNP's) can be described in terms of increased contributions of the canonical forms I and III relative to II in the structure of the photoexcited state of the molecule compared to the ground state. The position of the absorption should be related to the electronegativities of R_1 and R_2 which would affect the electron density of the nitrogens and, in turn, the stability of the excited states. Earlier, the absorption maximum λ_{max} was empirically described as the sum of λ_{R1}, λ_{R2}, and λ_{DNP} where each term represents the "contribution" in millimicrons of the indicated moieties of the derivative.[8] However, the relationship was not applicable to substituent constants.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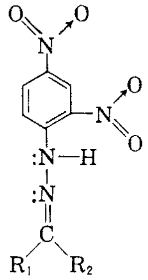
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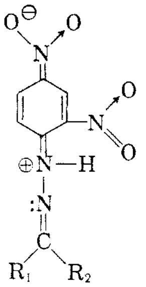
III

This communication reports a spectrophotometric examination of the chloroform and the alcoholic sodium hydroxide solutions of (a) 21 substituted aromatic DNP's, (b) 23 α-substituted acetaldehyde and acetone DNP's, and (c) the relationship of these spectra to the Hammett[3] and Taft[9] substituent constants, respectively. New constants are reported for several substituents.

EXPERIMENTAL

The procedure for preparing the derivatives and their spectra has been described.[1a]

The melting points and spectral data are contained in Tables I and II. The estimated accuracy of the wave lengths, reported to the nearest mμ, is ± 0.5 mμ.

The DNP of ethyl glyoxylate in basic solution gave two peaks $\lambda_1 = 369$ mμ, $\epsilon = 1.83 \times 10^4$; $\lambda_2 = 446$ mμ, $\epsilon = 1.42 \times 10^4$. The longer wave-length absorption increased with the passage of time and shifted to 450 mμ while the shorter wave-length absorption disappeared. Since this probably

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(1) (a) Part I, L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956). (b) Part II. L. A. Jones and C. K. Hancock, *J. Am. Chem. Soc.*, **82**, 105 (1960). This present article is taken in part from a dissertation by L. A. Jones submitted to the Graduate School of the A. and M. College of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May 1959. Presented at the American Chemical Society Meeting, Atlantic City, N. J., September 15, 1959.

(2) Present address: Research Laboratories, Brown and Williamson Tobacco Corp., Louisville 1, Ky.

(3) (a) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188. (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(4) L. Doub and J. M. Vandenbelt, *J Am. Chem. Soc.*, **69**, 2714 (1947).

(5) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957). See also Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(6) R. W. Taft in *Steric Effects in Organic Chemistry*, M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13, p. 595.

(7) C. N. R. Rao, *J. Sci. and Ind. Res.*, **17B**, 56 (1958) and references cited therein.

(8) G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

(9) Ref. 6, p. 619.

TABLE I

PHYSICAL CONSTANTS OF SUBSTITUTED AROMATIC 2,4-DINITROPHENYLHYDRAZONES

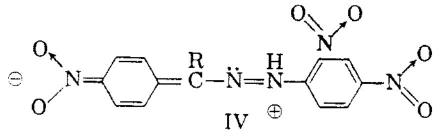
No.	2,4-Dinitrophenylhydrazone of	M.P. (Uncorr.)	$\lambda_{max}^{CHCl_3}$ mμ	$\epsilon \times 10^{-4}$	λ_{max}^{NaOH} mμ	$\epsilon \times 10^{-4}$	$\Delta\nu$[a]	σ[b]
1	*p*-NO_2-acetophenone	257–258[c]	382	3.48	540	3.75	7659	+1.270
2	*p*-NO_2-benzaldehyde	319–320[d]	381	3.69	537	4.52	7625	+1.270
3	*m*-NO_2-acetophenone	227–228[e]	363	2.74	473	2.87	6406	+0.710
4	*m*-NO_2-benzaldehyde	285–286d[d]	369	3.12	481	3.27	6310	+0.710
5	*p*-Cl-acetophenone	235–236[d]	377	2.95	465	2.87	5020	+0.227
6	*p*-Cl-benzaldehyde	264–265[e]	375	3.30	468	3.70	5299	+0.227
7	*m*-MeO-benzaldehyde	218–219[f]	369	3.08	469	3.39	5778	+0.115
8	Acetophenone	247–248[d]	377	2.76	461	2.66	4833	0.000
9	Benzaldehyde	238–239[d]	378	3.03	462	3.19	4810	0.000
10	*p*-OH-benzaldehyde	271–272d[d]	387	2.85	475	2.91	4788	−0.013[g]
11	*m*-OH-benzaldehyde	256–257[h]	377	2.99	460	3.12	4786	−0.014[g]
12	*p*-CH_3CONH-benzaldehyde	—[i]	390	—	480	—	4808	−0.015
13	*m*-NH_2-acetophenone	265–266[j]	381	2.89	460	2.57	4508	−0.161
14	*m*-NH_2-benzaldehyde	270–271d[k]	381	2.90	467	3.29	4834	−0.161
15	*p*-CH_3-acetophenone	257–258[d]	380	2.75	458	2.45	4481	−0.170
16	3,4-$(CH_3)_2$-acetophenone	251–252[l]	385	2.86	458	2.53	4140	−0.239
17	*p*-OH-acetophenone	258–259d[m]	387	2.73	462	2.54	4195	−0.267[g]
18	*p*-MeO-acetophenone	227–228[d]	392	2.74	460	2.56	3771	−0.268
19	*p*-MeO-benzaldehyde	251–252[n]	387	3.05	470	3.19	4563	−0.268
20	*p*-NH_2-acetophenone	258–259d[o]	403	2.68	461	2.61	3122	−0.660
21	*p*-$(CH_3)_2N$-benzaldehyde	233–234[d]	434	3.02	478	3.88	2120	−1.154[g]

[a] $\Delta\nu = \nu_{max}^{CHCl_3} - \nu_{max}^{NaOH}$. [b] σ-values taken from ref. 3 (b). [c] Calcd. for $C_{14}H_{11}N_5O_6$: N, 20.3. Found: N 20.8. [d] Ref. 8. [e] N. D. Cheronis and J. B. Entrekin, *Semimicro Qualitative Organic Analysis*, Interscience Publishers, Inc., New York, N. Y., 1957, pp. 582–587. [f] J. B. Bowen and E. M. Wilkinson, *J. Chem. Soc.*, 750 (1950). [g] Calcd. from Eq. 5. [h] I. Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, Vol. II. [i] Data taken from K. Yamaguchi, S. Fukushima, T. Tabata, and M. Ito, *J. Pharm. Soc. (Japan)*, **74**, 1335 (1954). No extinction coefficients reported. Acetone used as neutral solvent, 1% alcoholic sodium hydroxide as basic solvent. [j] Calcd. for $C_{14}H_{13}N_5O_4$: N 22.2. Found: 22.5. [k] Calcd. for $C_{13}H_{11}N_5O_4$: N 23.3. Found: N 23.4. [l] Calcd. for $C_{16}H_{16}N_4O_4$: N 17.1. Found: 16.8. [m] Ref. e, pp. 663–668. [n] Ref. 1(a). [o] W. Borsche and H. Groth, *Ann.*, **549**, 238 (1941).

represents the hydrolysis of the ester, only the original long wave-length maximum is reported in Table II.

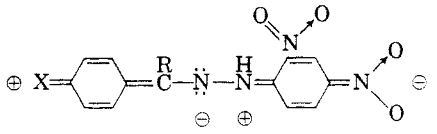
RESULTS AND DISCUSSION

A. *Aromatic derivatives.* The *p*-substituted DNP's absorbed at longer wave lengths in chloroform solution than benzaldehyde DNP (377 mμ) or acetophonone DNP (378 mμ), and, as the substituent constants decreased, the extinction coefficients also decreased and became more nearly equal (Table I). Despite the large positive σ-value of the *p*-NO_2 group which would be expected to decrease the weights of I and III and cause absorption at shorter wave lengths, the derivatives so substituted absorbed at 381–382 mμ, probably due to the contribution of IV to I, II, and III which further stabilizes the excited state.



IV

The less electronegative groups can stabilize the excited state by V and, as the availability of the electrons in the substituent increases,



V

the contribution of V to the hybrid must also increase, thus accounting for the absorption maxima of the *p*-NH_2- and *p*-$(CH_3)_2N$-substituted derivatives (Table I).

The excitation energy of the *m*-substituted DNP's is considerably higher than that of the *p*-substituted DNP's with the same group. Although *p*-quinoid structures can be written for the latter derivatives, the *m*-substituent cannot contribute in a similar manner to the stability of the excited state. Hence, the inductive effect described elsewhere[10] lessens the contribution of I and III to the hybrid unless the substituent is extremely electron rich (as in *m*-NH_2 groups).

In basic solution, the acidic *N*-hydrogen is removed and the excited state is stabilized since no separation of charge is required.[1b] Those groups with positive σ-values absorbed at the longest wave length due to the increased weight of the anion of IV. Conversely, the anion of V can contribute only slightly more to the excited state than

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(10) Ref. 3b, p. 230.

TABLE II

PHYSICAL CONSTANTS FOR R_1—CO—R_2 2,4-DINITROPHENYLHYDRAZONES

No.	R_1	R_2	M.P. (Uncorr.)	$\lambda_{max}^{CHCl_3}$ mμ	$\epsilon \times 10^{-4}$	λ_{max}^{NaOH} mμ	$\epsilon \times 10^{-4}$	$\Delta\nu$[a]	σR_1*[b]	σR_2*[b]	$\Sigma\sigma$*
1	F_3C	H	149–150[c]	329	2.17	436	2.84	7459	+2.755[d]	+0.490	+3.245
2	F_3C	CH_3	135–136[e]	338	2.10	437	2.57	6703	+2.435[d]	0.000	+2.435
3	$C_2H_5O_2C$	H	126–127[f]	349	3.20	446	2.25	6231	+1.900[g]	+0.490	+2.390
4	$ClCH_2$	H	156–157[h]	345	2.31	435(500)[i]	2.23(1.30)[i]	5997	+1.050	+0.490	+1.540
5	$C_6H_5OCH_2$	H	129–130[f]	348	2.41	433(500)	2.46(1.44)	5641	+0.850	+0.490	+1.340
6	$ClCH_2$	CH_3	125–126[j]	351	2.46	431(517)	2.50(1.55)	5288	+1.050	0.000	+1.050
7	H	H	164–165[k]	345	2.09	430(500)	1.73(1.05)	5730	+0.490	+0.490	+0.980
8	$C_6H_5CH_2$	H	121–122[k]	355	2.42	430(510)	2.25(1.23)	4913	+0.215	+0.490	+0.705
9	$C_6H_5(CH_2)_2$	H	154–155[k]	355	2.22	433(515)	2.22(1.24)	5074	+0.080	+0.490	+0.570
10	CH_3	H	146–147[l]	355	2.22	431(519)	2.19(1.28)	4967	0.000	+0.490	+0.490
11	CH_3CH_2	H	—[m]	356	2.25	431(520)	2.25(—)	4888	−0.100	+0.490	+0.390
12	$CH_3(CH_2)_2$	H	—[m]	358	2.10	426(520)	2.04(—)	4459	−0.115	+0.490	+0.375
13	$(CH_3)_2CH$	H	—[m]	357	2.18	428(523)	2.51(—)	4647	−0.190	+0.490	+0.300
14	$C_6H_5CH_2$	CH_3	154–155[n]	360	2.46	434(527)	2.23(1.34)	4736	+0.215	0.000	+0.215
15	$C_6H_5(CH_2)_2$	CH_3	129–130[j]	364	2.40	440(526)	2.54(1.38)	4646	+0.080	0.000	+0.080
16	CH_3	CH_3	125–126[k]	362	2.15	432(530)	2.12(1.28)	4325	0.000	0.000	0.000
17	Et_2NCH_2	CH_3	85.0–85.5[f]	362	2.43	430(525)	2.21(1.37)	4368	−0.066[d]	0.000	−0.066
18	CH_3CH_2	CH_3	—[m]	365	2.16	430(532)	2.17(—)	4141	−0.100	0.000	−0.100
19	$(CH_3)_2CH$	CH_3	—[m]	363	2.27	430(532)	2.21(—)	4292	−0.190	0.000	−0.190
20	CH_3CH_2	CH_3CH_2	—[m]	365	2.18	430(530)	2.16(—)	4141	−0.100	−0.100	−0.200
21	cyclo-C_6H_{11}	cyclo-C_6H_{11}	151.0–151.5[o]	370	2.41	438(535)	2.14(1.30)	4196	−0.150	−0.150	−0.300
22	$(CH_3)_2CH$	$(CH_3)_2CH$	87–88[p]	365	2.45	435(535)	2.17(1.33)	4408	−0.190	−0.190	−0.380
23	cyclo-C_3H_5	CH_3	155–156[q]	370	2.42	434(525)	2.36(1.42)	3986	−0.475[d]	0.000	−0.475

[a] $\Delta\nu = \nu_{max}^{CHCl_3} - \nu_{max}^{NaOH}$. [b] σ*— values taken from ref. 9. [c] F. Brown and W. K. R. Musgrave, *J. Chem. Soc.*, 5049 (1952). [d] Calcd. from Eq. 7. [e] R. N. Hazeldine, *J. Chem. Soc.*, 3565 (1953). [f] L. A. Jones, C. K. Hancock, and R. B. Seligman, unpublished data. [g] Calcd. from $\sigma^*_{CH_3O_2C} + \sigma^*_{Et}$ in Ref. b. [h] F. Weygand, G. Eberhardt, H. Linden, F. Schafer, and I. Eigen, *Angew. Chem.*, **65**, 525 (1953). [i] Data in parenthesis indicate secondary maxima. [j] Ref. 8. [k] Ref. 1(a). [l] W. M. D. Bryant, *J. Am. Chem. Soc.*, **60**, 2814 (1938). [m] Data taken from Ref. 1(a). No extinction coefficients were reported for the secondary maxima in basic solution. [n] F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953). [o] Calcd. for $C_{19}H_{24}N_4O_4$: N 15.1. Found: N 15.1. [p] Calcd. for $C_{13}H_{18}N_4O_4$: N 19.0. Found: N 18.9. [q] M. F. Hawthorne, *J. Org. Chem.*, **21**, 1523 (1956).

originally since energy is still required for charge separation. The *m*-substituted DNP's absorbed in the same region as the unsubstituted derivatives, indicating the inductive effect does not favor stabilization of the excited state.

Quantitative treatment. As indicated in Table I (and also Table II), neither the chloroform solution data nor the alcoholic sodium hydroxide solution data are independently related to the substituent constants suggesting that a change of "mechanism" may be involved. Since no mechanistic change can be present in these spectra, the substituents themselves must contribute to the stability of the excited states in different ways as previously shown in IV and V.

However, using the statistical treatment described by Jaffé,[3b] the difference in the absorption frequencies in chloroform and alcoholic base, $\nu_{max}^{CHCl_3} - \nu_{max}^{NaOH}$, of the benzaldehyde DNP's[11] were related to the Hammett substituent constants[12] by the equation

$$\Delta\nu = 4764 \text{ cm.}^{-1} + 2500\sigma \qquad (1)$$

with a correlation coefficient r of 0.929 and standard deviation s equal to 590. The p-$(CH_3)_2N$-benzaldehyde DNP showed serious deviation, the experimental and calculated $\Delta\nu$-values being 2120 and 3264 cm.$^{-1}$, respectively, or a 54% deviation. Omitting this derivative from the calculations, Eq. 2 was obtained with r = 0.971 and s = 268. The decrease in the standard deviation

$$\Delta\nu = 5041 \text{ cm.}^{-1} + 1970\sigma \qquad (2)$$

was statistically significant although only a slight increase in the correlation coefficient was obtained.

Repeating the statistical treatment using the substituted acetophenone DNP's gave

$$\Delta\nu = 4698 \text{ cm.}^{-1} + 2344\sigma \qquad (3)$$

with r = 0.993 and s = 178. Comparison of equations 1 and 3 showed the slopes and intercepts to be similar, despite the serious deviation of the p-$(CH_3)_2N$-substituted derivative. Hence, all of the data for the 17 substituted aromatic DNP's were statistically combined to give

$$\Delta\nu = 4835 \text{ cm.}^{-1} + 2233\sigma \qquad (4)$$

with r = 0.977 and s = 274. A plot of the experimental $\Delta\nu$-values *versus* the substituent constants and the line described by Eq. 4 are shown in Fig. 1.

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(11) The substituted phenols were omitted in these calculations since —OH → —O^- in basic solution.

(12) For the p-NO_2 group, the σ^- value of +1.270 (same as σ* but redefined in reference given) was used since an appreciable difference in conjugation of the substituent and the reaction site exists between the ground and the excited states of the molecule. This is the condition given by H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958).

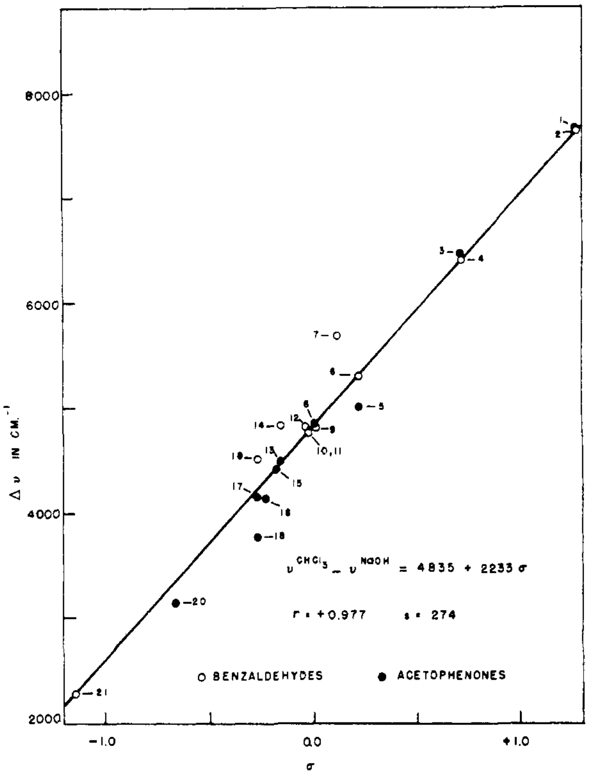

Fig. 1. Relationship between the experimental $\Delta\nu$-values and σ-values. Numbers refer to the compounds in Table 1.

By minimizing the squares of the deviations along the σ-axis,[3b] Eq. 5 was obtained

$$\sigma = 4.274 \times 10^{-4}\Delta\nu - 2.059 \qquad (5)$$

Substitution of the $\Delta\nu$-value for the p-$(CH_3)_2N$-benzaldehyde DNP in Eq. 5 yielded a σ- value of -1.154. Jaffé[3b] has presented evidence that the substituent constant for the p-$N(CH_3)_2$ group should have a range of values dependent on the nature of the side chain, in this case the $=N—NH—C_6H_3(NO_2)_2$ group of I, II, III, and V. It is apparent that this moiety is strongly electron withdrawing and the resonance stabilization of the excited state is considerably affected by the increased electron density of the p-$N(CH_3)_2$ group. The most negative value for the substituent constant previously reported is -0.972[3b] and the value -1.154 determined here is within the precision of the Hammett equation.

The substituent constant for the p-OH → p-$O^{\ominus}$ group was calculated from Eq. 5 to be -0.013 and -0.267 for the benzaldehyde and acetophenone derivatives, respectively. It should be noted that the formation of this ion in basic solution involves the loss of *two* protons whereas other derivatives lose only one, possibly accounting for the large differences observed. The m-OH → m-$O^{\ominus}$ σ-value was calculated to be -0.014 from Eq. 5 suggesting that the inductive effect encountered from m-substituents has little effect on the stability of the excited state. However, the limitations observed above for the p-OH → p-$O^{\ominus}$ group would probably apply also.

Some discussion concerning the deviations of the DNP's of p-Cl- and p-MeO-acetophenone and m-MeO-benzaldehyde from the straight line in Fig. 1 appears warranted. The methoxy substituents are noted for their substituent constant deviations and have been discussed in some detail.[13] However, in addition to the usual reasons for these deviations, the problem of *syn*- and *anti*-isomers must also be considered. In a previous work,[1a] the *syn*- and *anti*-isomers of 2-furaldehyde DNP were prepared and their spectra obtained in chloroform and alcoholic sodium hydroxide solutions. The *syn*-DNP yielded a $\Delta\nu$-value of 5237 cm.$^{-1}$ while the *anti*-form gave a $\Delta\nu$-value of 4542 cm.$^{-1}$, indicating that the isomeric modifications can have considerable effect on the spectra. These results suggest that the deviations noted for m- and p-OH → $O^{\ominus}$, p-Cl, and m- and p-MeO substituted aromatic DNP's may be due to *syn*- and *anti*-modifications as well as substituent constant deviations. As will be shown, the isomeric modifications are not as important in the aliphatic series.

B. *Aliphatic derivatives.* Since no resonance (except hyperconjugation) can be involved within the substituents R_1 and R_2 of I, II, and III for the aliphatic DNP's, the excitation energy must depend on the ability of these substituents to aid in the shift of electron density towards the nitro groups. Table II shows that, as the substituents became less positive, the absorption maxima of these derivatives in chloroform shifted to the red although little change in the extinction coefficients was apparent. The bathochromic shift of 5 to 11 mμ noted in the comparison of correspondingly substituted aldehyde and acetone DNP's has been previously attributed to hyperconjugation of the methyl groups.[14]

The absorption maxima in basic solution were located between 426 and 446 mμ, and, as in the chloroform solution spectra, the extinction coefficients were quite similar. DNP's with more positive substituents did not exhibit the secondary absorption maxima previously reported to be characteristic of the aliphatic derivatives.[1a] In those cases where the secondary maxima were observed, changes in the absorption wave lengths or the extinction coefficients were not appreciable. Hyperconjugation affected the maxima to a lesser extent than in chloroform although the secondary maxima were more sensitive to this effect as indicated in Table II.

Quantitative treatment. A statistical treatment of the $\Delta\nu$-values and σ^*-values[9] (Table II) gave

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(13) Ref. 6, p. 578.

(14) H. C. Barany and M. Pianka, *J. Chem. Soc.*, 2217 (1953).

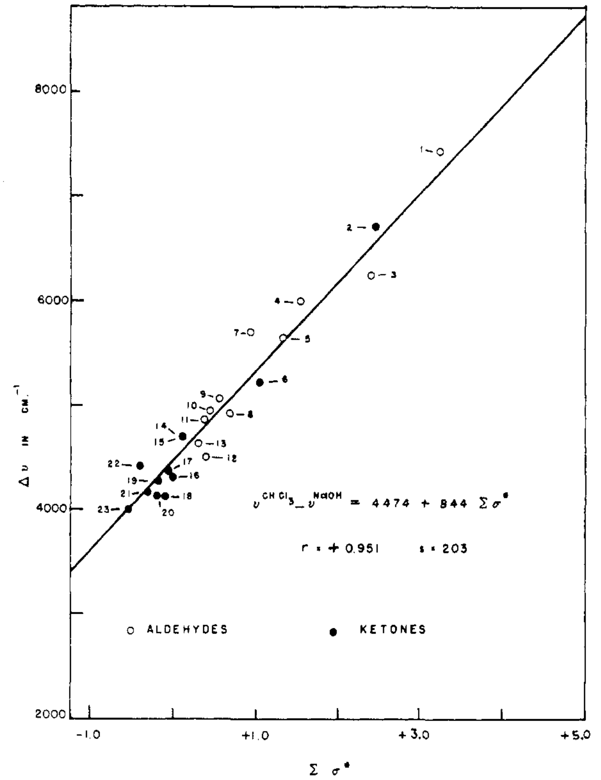

Fig. 2. Relationship between the experimental $\Delta\nu$-values and $\Sigma\sigma$-values. Numbers refer to the compounds in Table II

$$\Delta\nu = 4474 \text{ cm.}^{-1} + 843.9\Sigma\sigma^* \qquad (6)$$

with $r = 0.951$ and $s = 203.4$. The regression line and the experimental $\Delta\nu$-values and $\Sigma\sigma^*$-values are shown in Fig. 2.

The squares of the deviations along the $\Sigma\sigma^*$-axis were minimized[3b] and Eq. 7 this obtained:

$$\Sigma\sigma^* = 1.071 \times 10^{-3}\Delta\nu - 4.744 \qquad (7)$$

The experimental $\Delta\nu$-values obtained for the F_3C-substituted DNP's yielded, when substituted in Eq. 7, σ^*-values of $+2.756$ and $+2.436$ (Table II) for the F_3C-group. The average value of $+2.595 \pm 0.160$ is in reasonable agreement with the σ^*-value of $+2.79$ calculated by the method of Brown.[15]

In a similar manner a σ^*-value of -0.066 was calculated for the Et_2NCH_2 group.

On the basis of its apparent ability to conjugate with aromatic systems,[16] carbonyl groups,[17] and double bonds,[18] the cyclopropyl group has been placed between a vinyl and a saturated group from ultraviolet studies. The effects on chemical reactions resulting from conjugation of this group with carbonyl groups,[19] double bonds,[20] and carbonium ions[21] further supports an electron release which has been attributed to a possible hyperconjugative release mechanism.[19b,21c] Substitution of the spectral data for methylcyclopropyl ketone DNP in equation 7 gives a σ^*-value of -0.475 in agreement with the above results.

Conversely, some ultraviolet studies have shown that the cyclopropyl group does not give the expected bathochromic shift[22,16b] and, further, the pK_a's of a series of *m*- and *p*-substituted hydrocinnamic and *trans*-2-phenylcyclopropanecarboxylic acids were similar but radically different from those of the *trans*-cinnamic acids.[22] The electronegativity of the three-membered ring has been predicted[23] and, in support of these data, a σ^*-value of $+0.11$ has been determined.[15]

The value determined here appears reasonable since (1) the spectra in chloroform and in alcoholic sodium hydroxide solutions were similar in *all* respects to the other aliphatic derivatives (Table II) and (2) the σ^*-values of alicyclic rings decrease in value as the ring size decreases.[9] That no ring opening occurred in basic solution is apparent by comparison of the spectra of olefinic derivatives in basic solution.[1a] It seems likely that in view of the conflicting experimental evidence, the cyclopropyl group may have dual substituent constants dependent on the electron demands of adjacent groups and/or the type of reaction involved.

C. *Theoretical discussion.* The instantaneous color developed by DNP's in basic solution has been shown to disappear with the passage of time and the rate appears to be a function of R_1 and R_2 in I.[1a] The reaction proceeds with the evolution of nitrogen and the end products are, for the most part, polymers.[24] The over-all reaction can be represented by

$$\text{DNP} + \text{OH}\ominus \xrightarrow{\text{fast}} \text{DNP}\ominus \xrightarrow[\text{r.d.}]{\text{OH}} \text{products}$$

where the rate-determining step occurs *after* the formation of the anion or intermediate. From these data, Fig. 3 can be said to represent the free energy requirements of the reactions involved.

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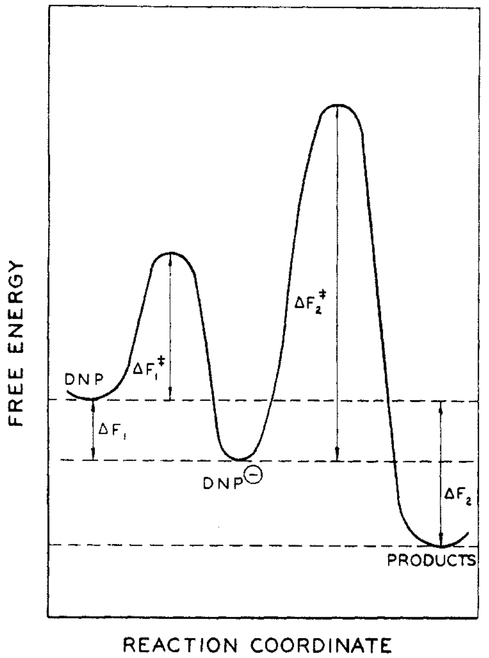

Figure 3

The $\Delta F_1\ddagger$ in Fig. 3 cannot be determined due to the very rapid formation of $DNP^{\ominus}$ and the lower free-energy of this intermediate implies a stability greater than that of the reactant in basic solution as well as a high concentration, in accord with the experimental results. The $\Delta F_2\ddagger$ values are being determined by kinetic studies at the present time.

The ΔF_1 term represents the difference in free-energy content of the product (in this case, $DNP^{\ominus}$) and the reactant states and, as such, is proportional to the ionization constant. The relationship of this free-energy term and the Hammett equation has been discussed.[25] However, in the present investigation, the absorption spectra of the reactant (DNP in chloroform) and the product (DNP in alcoholic base) were determined and the difference $\nu_{max}^{CHCl_3} - \nu_{max}^{NaOH}$ related to the Hammett substituent constants. With these $\Delta\nu$- values, the change in energy $E^{NaOH} - E^{CHCl_3}$ was calculated to range from -21.9 kcal./mol. (p-NO_2 compound) to -6.05 kcal./mol. (p-$(CH_3)_2N$ compound). Since the ΔF_1 values would also be negative, it is apparent that the energy differences (and hence the $\Delta\nu$-values), being *linearly related* to the Hammett substituent constants, must also be linearly related to ΔF_1. Comparison of the $\Delta\nu$- values and some pK_a's of DNP's[26] suggests that $\Delta\nu$ is the more sensitive measure of the free-energy changes involved.

The same arguments may be applied to the Taft relationship found for aliphatic DNP's. In addition, the condition "that all effects other than polar must remain nearly constant within the given reaction series"[27] for the Taft equation to hold applies here also. Hence, the hyperconjugation found in ketone DNP's disappears in the determination of $\Delta\nu$, indicating the effect is of the same order of magnitude in the DNP and $DNP^{\ominus}$ spectra. Further, the spectral data previously obtained for the mono-DNP's of aliphatic 1,2-dicarbonyl compounds[1b] could not be used since the $\Delta\nu$-values contain not only the polar effect of R—CO— but also the effect of hydrogen bonding with the N-hydrogen which abnormally lowers the ground state in chloroform solution but disappears in basic solution.[1b] In addition, the removal of the N-hydrogen in basic solution permits resonance interaction of the substituent with the 2,4-dinitrophenyl group, obscuring any polar effects.

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