each made up to 20 ml with hexane. They were deoxygenated, sealed, and irradiated for 3 hr in the Rayonet merry-go-round, in parallel with an actinometer solution of 2-hexanone. After irradiation, tetradecane (4 mg) in hexane was added to each tube as internal standard. Samples from each tube were analyzed by vpc (QF 1, 85°) to determine the ratio (R_2) of the peak area of **5** to that of tetradecane: calibration experiments allowed this ratio to be converted to the weight of **5** produced in each tube, $0.0031R_2$ mol/l.

The actinometer solution was 2-hexanone (0.829 g) and chlorobenzene (internal standard, 1.134 g) in pentane (to 20 ml), similar to that described by Coulson and Yang.[37] The concentrations of 2-hexanone before and after irradiation were measured by vpc (DDP, 120°) relative to the internal standard; peak areas were measured using a Kent Chromalog 2 digital integrator, and were reproducible to better than 0.3%. Precision in this measurement was important, because only 5.6% (0.0232 mol/l.) of the 2-hexanone reacted in 3 hr of irradiation. Assuming a quantum yield of disappearance of 2-hexanone of 0.327,[37] values for the quantum yield of photocycloaddition can be found, $(0.327 \times 0.0031R_2)/0.0232 = 0.0437R_2$. The results, in the form of a plot of (quantum yield of **5**)$^{-1}$ *vs.* (**2**-molarity)$^{-1}$, are shown in Figure 1. Control uv spectra showed that none of the other components used (**2**, chlorobenzene, hexane, or pentane) would absorb an appreciable amount of light under the conditions used. The relative errors of the quantum yield values were estimated from the accuracy with which the vpc peak areas could be measured, and included a term due to nonuniformity of the Pyrex tubes; volumetric errors were comparably small. The absolute errors in quantum yield (±25% additionally) included the differing absorptions of 2-hexanone and acetone, inaccuracy of measurement of the conversion of 2-hexanone, and light absorption by the actinometer photoproduct (acetone). A least-squares analysis of the points in Figure 1, using a Hewlett-Packard 9100A programmable calculator, gave an intercept of 11.1 and a slope of 74.

Competition Experiments. A solution of **1** and **2** (2 ml each) in acetone (5 ml) was deoxygenated and sealed in a Pyrex tube, and irradiated for 12 hr next to the quartz reactor. Vpc (10% PEGS, 80°) showed less than 2% conversion to product, and an essentially unchanged ratio of reactants. The relative areas of the oxetane (**4** and **5**) peaks were determined. Calibration experiments, injecting known weights of oxetanes, allowed this area ratio to be converted to a molar ratio. A similar irradiation of **2** and **3** in acetone was conducted. Hence, the relative reactivities per mole of α,β-unsaturated nitrile were calculated: **1**, 19.9; **2**, 9.7; **3**, 1.0.

Fluorescence Quenching. Solutions of acetone (0.14 *M*) or cyclopentanone (0.02–0.10 *M*) with various concentrations of quencher (**1**, **2**, or **3**) were made up in Spectrosol cyclohexane; both cyclohexane and the quenchers showed negligible fluorescence. Solutions were placed in a 1-cm^2 Suprasil cell and deoxygenated by nitrogen bubbling for 30 sec, and the fluorescence spectra were recorded. The excitation wavelength was 310 nm; the intensity of emission (F) at the maximum (~410 nm for acetone, 405 nm for cyclopentanone) was compared to the intensity (F_0) in the absence of quencher. A Stern–Volmer plot was drawn of F_0/F *vs.* molarity of quencher, and the slope measured on at least four points over the lower linear portion of the curve; the results are given in Table II. For the acetone-*trans*-1,2-dicyanoethylene system in diethyl ether as solvent, the slope of the plot was 5.7 (±0.6) M^{-1}.

Acknowledgment. We thank the Science Research Council for the award of a Studentship to H. A. J. C.

Substituent Effects on Aromatic Proton Chemical Shifts. VIII. Conformational Effects of the Carbonyl Group in Benzenes and Naphthalenes

William B. Smith,* Dennis L. Deavenport, and Arthur M. Ihrig

Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. Received July 22, 1971

Abstract: The nmr parameters for a series of 2-substituted benzaldehydes and acetophenones as well as a number of 1,4-disubstituted naphthalenes are presented. The chemical shifts of the protons adjacent to the varying substituents follow the parameter *Q* as previously observed in other series. In the benzene series, the behavior of the H-6 protons is revealing about the steric requirements of the formyl and acetyl groups. Extension of the conclusions of this study to the chemical shifts of a series of 1-X-4-methoxynaphthalenes leads to the conclusion that when X is formyl there is a definite hydrogen-bond-like interaction between the oxygen and the peri hydrogen, H-8.

In preceding papers in this series[1] it has been shown that the proton chemical shifts at C-3 in a series of 1-X-2-Y-benzenes (X is constant and Y varied) follow the previously defined, semiempirical parameter *Q*.[2] An experimental method of determining *Q* has been described,[1c] and a table of *Q* values presented.[1g,3]

For groups which are not cylindrically symmetrical about the axis of the bond to the benzene ring, two values of *Q* are required. For such instances where the group Y is flanked only by hydrogens, the *Q*(1) value obtains. When some large bulky group or a group which holds Y in some specific orientation as by a hydrogen bond is adjacent, then the H-3 chemical shift requires the *Q*(2) value of Y. The necessity of two *Q* values was first made clear for the nitro group. Subsequently, the hydroxyl and amino groups were shown to require specific *Q* values when hydrogen bonded to an ortho substituent.[1g]

---

[1] (a) W. B. Smith and G. M. Cole, *J. Phys. Chem.*, **69**, 4413 (1965); (b) W. B. Smith and S. Chiranjeevi, *ibid.*, **70**, 3505 (1966); (c) W. B. Smith and J. L. Roark, *J. Amer. Chem. Soc.*, **89**, 5018 (1967); (d) W. B. Smith and J. L. Roark, *J. Phys. Chem.*, **73**, 1043 (1969); (e) *ibid.*, **73**, 1046 (1969); (f) *ibid.*, **73**, 1049 (1969); (g) W. B. Smith, A. M. Ihrig, and J. L. Roark, *ibid.*, **74**, 812 (1970).

[2] (a) F. Hruska, H. M. Hutton, and T. Schaefer, *Can. J. Chem.*, **43**, 2392 (1965); (b) T. Schaefer, F. Hruska, and H. M. Hutton, *ibid.*, **45**, 3143 (1967).

[3] During the course of the present study, we found that the predictive utility of the *Q* value for fluorine could be improved with a value of 1.50. Whether this represents a flaw in the data used to calculate Q_F[2a] or a change in the basis of the original *Q* correlation is a moot point. Similarly, we have found that the *Q* values for methoxyl are dependent on the size of the adjacent substituent increasing with the size of Y over the range 0.4–0.8.

Here we wish to report the data on series of ortho-substituted benzaldehydes and acetophenones. The choice of these two series was dictated by the rough relationship in size of the formyl and acetyl groups to the nitro group, and the lower symmetry of the former compared to the latter. During the course of this work, data on a series of 1,4-disubstituted naphthalenes were developed. Since evidence derived from the above two series was helpful in interpreting the results from the naphthalenes, these data are also presented.

Experimental Section

The various benzaldehydes and acetophenones used in this study were all commercially available with the exception of 2-iodoacetophenone. The 2-iodo derivative was prepared in excellent yield by the standard Sandmeyer reaction from 2-aminoacetophenone.[4] Preliminary nmr examination revealed significant traces of ethanol, which was readily removed by vacuum distillation, in some of the acetophenone samples. The sample of 2-nitroacetophenone was contaminated with nonvolatile impurities and was purified by recrystallization in petroleum ether. The benzaldehydes had small but detectable traces, *ca.* 1–3%, of the corresponding benzoic acids; however, these samples were used without further purification.

While most of the 1,4-disubstituted naphthalenes were commercially available, it was necessary to prepare several. 1,4-Dimethoxynaphthalene was prepared from the corresponding dihydroxy compound by the procedure of Baker and Carlson.[5] 1-Methoxynaphthalene was converted to the 1-chloro-4-methoxy compound as per Lesser and Gad,[6] while the procedure of Buu-Hoi[7] was used for 1-methoxy-4-bromonaphthalene. Similarly, literature methods were used to prepare 1-iodo-4-methoxynaphthalene,[8] 1-cyano-4-methoxynaphthalene,[9] and 4-hydroxy-1-naphthaldehyde.[10]

1-Methoxy-4-methylnaphthalene. A solution of 20 g of 1-hydroxy-4-naphthaldehyde in 100 ml of absolute ethanol and 2 ml of acetic acid was hydrogenated at 40 psi over 4 g of palladium on charcoal. The reaction was complete after 30 hr and gave a nearly quantitative yield of 1-hydroxy-4-methylnaphthalene, mp 82–84° (lit.[11] mp 83–84°).

This compound was converted to the known methoxy analog by the method of Baker and Carlson.[5]

4-Methoxy-1-acylnaphthalenes. The method of Kindler and Li[12] was adopted to the preparation of the acetyl, propionyl, isobutyryl, and pivalyl compounds by the acylation of methoxynaphthalene in carbon disulfide. The work-up procedure was varied in that the carbon disulfide solvent was decanted from the solid aluminum chloride addition complex. The complex was dissolved in acetone (minimum amount) and treated with an excess of water. Extraction with ether and crystallization from hexane gave the pure products. The acetyl and propionyl compounds were not new compounds.[12]

For 4-methoxy-1-isobutyrylnaphthalene the mp was 100–101°. *Anal.*[13] Calcd for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02. Found: C, 78.92; H, 7.14.

The melting point for 4-methoxy-1-pivalylnaphthalene was 92–94°. *Anal.* Calcd for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44. Found: C, 79.27; H, 7.51.

4-Methoxy-1-bromonaphthalene-*8*-^2H. Scheme I. A solution of 11.1 g of 1-naphthol-5-sulfonic acid sodium salt in 50 ml of 5% of sodium deuterioxide was allowed to react with 28 g of sodium amalgam for 2 hr.[14] The reaction mixture was neutralized with a solution formed by treating 20 ml of phosphorus oxychloride with 40 ml of deuterium oxide. An ether extract of the reaction solution was dried (magnesium sulfate) and evaporated to yield 5.1 g of 1-hydroxynaphthalene-*5*-^2H. The latter was brominated[7] and methylated[5] to give the desired 4-methoxy-1-bromo-*8*-^2H compound.

Scheme II. A solution of 40 g of 5-amino-1-naphthol in 100 ml of 35% hydrochloric acid and 100 ml of water was cooled to −10° and treated with a concentrated solution containing 17.6 g of sodium nitrite. The red froth which formed was dispersed from time to time by the addition of small amounts of ether. An excess of aqueous potassium iodide was added and the mixture allowed to come to room temperature. Work-up gave a 52% yield of 5-iodo-1-naphthol, mp 130–131°.

The iodo–hydroxy compound was methylated.[5] The 5-iodo-1-methoxynaphthalene (10 g) was allowed to react with 2 g of magnesium turnings in 50 ml of ether. The resultant Grignard reagent was hydrolyzed with deuterium oxide, and the resultant 1-methoxynaphthalene-*5*-^2H was brominated in the 4 position as above.

Comparison of the nmr spectra of the two deuterated products above with 1-bromo-4-methoxynaphthalene showed that H-8 had been replaced by deuterium in each case. The products from both schemes showed very small amounts of impurity in the form of the undeuterated compound.

Nmr Determination. All nmr spectra were determined on a Varian HA-100. Solutions (10% w/v) in carbon tetrachloride and DMSO-d_6 containing a small amount of TMS were degassed at *ca.* 10^{-4} Torr and sealed under vacuum. The methyl groups, methoxy groups, aldehyde protons, and phenolic hydrogens were decoupled with the aid of a Hewlett-Packard 200 CD audio oscillator. The fluorine spectra of 2-fluoroacetophenone and 2-fluorobenzaldehyde were run at 94.1 MHz in the HA mode using 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as an internal standard.

All spectra were taken at least five times and the line positions averaged. The parameters were determined using previously stated techniques.[1] The complex spectra were fitted using LAOCOON II.[15] Generally the spectra in this investigation provided 28 to 40 lines out of a possible maximum of 56. All observable transitions were used in the computer fitting of every spectrum. The root-mean-square deviations for the calculated and experimental lines were routinely 0.05 Hz or less.

Results

The chemical shifts and coupling constants are presented in Tables I and II for a series of benzaldehydes and acetophenones. The chemical shifts were assigned on the basis of the splitting patterns, long-range coupling constants,[16,17] correlations from previously established *Q* parameters,[1] and the additivity rules of Martin and Dailey.[18]

The aldehyde proton signal in the benzaldehydes appears as a doublet (J = 0.6–0.8 Hz) except for the bromo and methyl isomers which display the pattern of an unsymmetrical triplet ($J \sim$ 0.3–0.4 Hz). A detailed computed analysis of the aromatic and aldehyde protons in the bromo compound revealed that the triplet appeared as an excellent example of virtual coupling.[19] For the methyl compound, spin coupling suggested that the aldehyde proton coupled about equally to H-3 and H-5 with a small, but finite, coupling to H-6.

Spin decoupling was used to demonstrate that the aldehyde proton is coupled to H-5 in all compounds except for the hydroxy and amino isomers where the coupling was to H-3. An extremely small H–F coupling ($J < 0.2$ Hz) is observed between the aldehyde proton and the fluorine in *o*-fluorobenzaldehyde.

---

(4) D. A. Shirley, "Preparation of Organic Intermediates," Wiley, New York, N. Y., 1951.

(5) B. R. Baker and G. H. Carlson, *J. Amer. Chem. Soc.*, **64**, 2657 (1942).

(6) R. Lesser and G. Gad, *Ber.*, **56**, 963 (1923).

(7) Ng. Ph. Buu-Hoi, *Recl. Trav. Chim. Pays-Bas*, **73**, 197 (1954).

(8) F. G. Baddar, L. S. Et-Assal, and V. B. Baghos, *J. Chem. Soc.*, 986 (1958).

(9) P. Karrer, A. Rebmann, and E. Zeller, *Helv. Chim. Acta*, **3**, 261 (1920).

(10) R. Adams and I. Levine, *J. Amer. Chem. Soc.*, **45**, 2373 (1923).

(11) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 5628 (1956).

(12) K. Kindler and T. Li, *Ber.*, **74**, 321 (1941).

(13) Microanalyses by M-H-W Laboratories, Garden City, Mich.

(14) P. Lucht and P. Friedlander, *Ber.*, **26**, 3028 (1893).

(15) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(16) G. J. Karabatsos and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 3887 (1963).

(17) S. Forsen and A. Hoffman, *J. Mol. Spectrosc.*, **20**, 168 (1966).

(18) J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

(19) See, for instance, E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 163.

Table I. Parameters for the Ortho-Substituted Benzaldehydes[a]

Ortho substituent	δ_3	δ_4	δ_5	δ_6	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}	δ Ald-H
NH_2	6.54	7.17	6.61	7.35	8.36	1.03	0.49	7.10	1.60	7.79	9.77
OH	6.90	7.43	6.92	7.45	8.45	1.02	0.41	7.26	1.77	7.73	9.82
OCH_3	6.81	7.43	6.93	7.72	8.43	0.93	0.32	7.35	1.86	7.71	10.38
CH_3	7.17	7.47	7.27	7.68	7.57	1.26	0.55	7.33	1.58	7.62	10.15
F[b]	7.13	7.56	7.23	7.82	8.40	1.00	0.42	7.38	1.91	7.76	10.33
Cl	7.40	7.47	7.34	7.86	8.03	1.15	0.53	7.31	1.74	7.70	10.42
Br	7.59	7.39	7.39	7.86	8.12	1.03	0.38	7.33	1.95	7.67	10.29
I	7.89	7.23	7.42	7.82	7.94	1.13	0.37	7.35	1.82	7.76	9.97
NO_2	8.15	7.75	7.78	7.88	8.18	1.15	0.45	7.44	1.49	7.69	10.03

[a] Coupling constants are in Hz. Solutions in carbon tetrachloride. [b] The chemical shift of the fluorine is 9.28 ppm upfield from TCTFB. Values for the coupling constants in Hz to fluorine are J_{3F} = 10.37, J_{4F} = 5.36, J_{5F} = −0.19, and J_{6F} = 6.98.

Table II. Parameters for the Ortho-Substituted Acetophenones[a]

Ortho substituent	δ_3	δ_4	δ_5	δ_6	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
NH_2	6.51	7.11	6.49	7.56	8.25	1.13	0.47	6.69	1.58	8.06
	6.77	7.23	6.54	7.71	8.38	1.19	0.42	6.95	1.56	8.15
OH	6.85	7.36	6.77	7.61	8.37	1.20	0.42	7.20	1.67	8.02
	6.97	7.53	6.97	7.89	8.36	1.19	0.37	7.25	1.69	8.02
OCH_3	6.87	7.33	6.89	7.63	8.35	0.99	0.38	7.34	1.88	7.73
	7.15	7.53	7.02	7.60	8.41	1.09	0.39	7.14	1.86	7.64
CH_3	7.14	7.25	7.15	7.60	7.64	1.30	0.47	7.39	1.44	7.87
	7.28	7.42	7.31	7.79	7.79	1.32	0.60	7.36	1.42	7.77
F	7.07	7.45	7.15	7.82	8.32	1.14	0.36	7.29	1.90	7.81
	7.33	7.67	7.34	7.83	8.35	1.11	0.35	7.34	1.86	7.83
Cl	7.34	7.32	7.25	7.47	8.01	1.09	0.45	7.37	1.79	7.61
	7.53	7.52	7.46	7.68	8.13	1.13	0.46	7.48	1.67	7.71
Br	7.53	7.22	7.30	7.38	8.06	1.12	0.40	7.43	1.75	7.68
	7.60	7.42	7.49	7.66	8.07	1.07	0.41	7.48	1.73	7.72
I	7.86	7.05	7.34	7.67	7.93	1.15	0.44	7.37	1.82	7.68
	7.97	7.23	7.51	7.66	7.88	1.15	0.40	7.48	1.63	7.68
NO_2	7.96	7.55	7.66	7.39	8.25	1.15	0.47	7.46	1.46	7.67
	8.09	7.76	7.86	7.80	8.07	1.22	0.50	7.50	1.38	7.68

[a] Coupling constants are in Hz. The first entry for each compound is for carbon tetrachloride; the second is for DMSO. Values for the constants to fluorine in carbon tetrachloride and DMSO respectively in Hz are J_{3F} = 11.15, 11.56; J_{4F} = 5.02, 5.10; J_{5F} = 0.12, 0.15; and J_{6F} = 7.48, 7.66. The chemical shift of fluorine is 3.61 ppm downfield from TCTFB.

In no case was the acetyl methyl found to couple with the ring protons in the acetophenones. However, a strikingly large coupling constant (5.1 Hz) was observed between the acetyl methyl and fluorine in *o*-fluoroacetophenone. This coupling was found to be temperature sensitive, varying from 6.2 Hz at −63° to 4.1 Hz at 150°. However, the lack of any coupling between the acetophenone methyl protons in the *m*- and *p*-fluoro compounds and in the *o*-trifluoromethylacetophenone suggests the operation of a "through space" coupling for *o*-fluoroacetophenone.

Further decoupling experiments revealed that methyl groups on the ring couple to all ring protons, while methoxy protons and phenolic protons selectively couple with H-3 and H-4, respectively.

While the 1,4-disubstituted naphthalenes should be considered as six spin systems, the couplings between the two isolated protons and the four in the unsubstituted ring are so weak that the spectra approximate very well an AB system imposed upon an independent ABCD system. In general, it was possible to readily identify the AB quartet. Arguing from the spectrum of the 1,4-dimethoxynaphthalene and from various methoxybenzenes, it is reasonable to assign the upfield proton in the AB system to the position adjacent to the methoxy group. Similarly, protons 5 and 8 will be the least shielded protons of the ABCD portion of the spectrum. However, further evidence was required to make specific assignments to H-5 and H-8 as well as H-6 and H-7.

Specific deuteration at H-8 *via* two different schemes for 1-bromo-4-methoxynaphthalene allowed an unequivocal assignment of the lines for H-5 and H-8 in this molecule. The assignments of the chemical shifts for H-6 and H-7 then follow from the magnitudes of the coupling constants required to fit the spectrum, *i.e.*, $J_{56} \cong J_{78} \cong 8.5$ Hz and $J_{67} \cong 6.9$ Hz.

Investigation of the long-range coupling between the protons in the two ring systems using spin tickling techniques now showed H-3 to be coupled to H-7 by *ca.* 0.2 Hz and H-2 to H-6 by the same amount. This result, in contrast to the expectations of the usual zigzag pathway for long-range couplings, provided a convenient method for assigning chemical shifts in the other compounds of this study.[20] In this fashion it was possible to ascertain and assign the parameters to the 1-X-4-methoxynaphthalenes in Tables III and IV.

Finally, the intensities of the H-8 and H-2 protons were observed while saturating the acetyl methyl protons in 4-methoxy-1-acetylnaphthalene with a second oscillator. A peak enhancement of 14% was observed

---

[20] These observations were presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970. At approximately the same time, R. W. Crecely, S. L. Baughcum, K. R. Long, and J. H. Goldstein, *J. Magn. Resonance*, 3, 103 (1970), reported equivalent long-range couplings in some 1,2,4-trisubstituted naphthalenes.

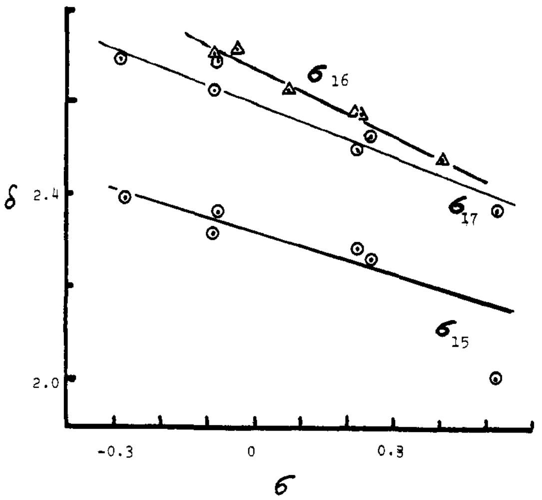


Figure 1. Chemical shifts for H-5, H-6, and H-7 in the 1-X-naphthalenes[24] plotted against the appropriate σ values.

at H-3 due to the nuclear Overhauser effect.[21] No effect was noted at H-8. Similarly, irradiation of the methine proton of the isobutyryl group in the corresponding 4-methoxynaphthalene produced a 6% enhancement of intensity at H-3 and no effect at H-8. No NOE was observed at H-3 or H-8 when the methyl groups of the isobutyryl or pivalyl groups were irradiated.

Table III. Chemical Shifts (ppm from TMS) of a Series of 1-X-4-Methoxynaphthalenes in Carbon Tetrachloride Solution

X	δ_2	δ_3	δ_5	δ_6	δ_7	δ_8
OCH_3	6.46	6.46	8.12	7.38	7.38	8.12
CH_3	7.03	6.50	8.21	7.35	7.39	7.78
Cl	7.30	6.50	8.17	7.41	7.49	8.12
Br	7.49	6.44	8.15	7.39	7.46	8.08
I	7.77	6.34	8.11	7.36	7.45	7.93
CN	7.65	6.68	8.17	7.46	7.57	8.06
NO_2	8.10	6.56	8.13	7.42	7.53	8.61
CHO	7.60	6.62	8.14	7.42	7.55	9.22
$COCH_3$	7.71	6.47	8.16	7.38	7.50	9.01
COC_2H_5	7.67	6.49	8.17	7.38	7.49	8.88
$COCH(CH_3)_2$	7.65	6.55	8.19	7.39	7.48	8.62
$COC(CH_3)_3$	7.16	6.66	8.19	7.37	7.39	7.56

Table IV. Coupling Constants (Hz) for a Series of 1-X-4-Methoxynaphthalenes

Substituent	J_{23}	J_{56}	J_{57}	J_{58}	J_{67}	J_{68}	J_{78}
OCH_3		8.47	1.26	0.73	6.83	1.26	8.47
CH_3	7.74	8.44	1.24	0.71	6.79	1.24	8.59
Cl	8.21	8.48	1.33	0.72	6.88	1.33	8.51
Br	8.16	8.41	1.23	0.61	6.84	1.23	8.56
I	8.13	8.41	1.37	0.68	6.85	1.37	8.51
CN	8.00	8.47	1.30	0.70	6.95	1.30	8.43
NO_2	8.67	8.61	1.37	0.72	6.88	1.37	8.87
CHO	8.00	8.49	1.41	0.73	6.91	1.41	8.65
$COCH_3$	8.20	8.51	1.45	0.67	6.84	1.45	8.82
COC_2H_5	8.20	8.54	1.44	0.71	6.82	1.44	8.76
$COCH(CH_3)_2$	8.15	8.52	1.44	0.75	6.84	1.44	8.79
$COC(CH_3)_3$	7.90	8.50	1.42	0.76	6.85	1.42	8.61

Discussion

Substituent Effects, Chemical Shifts, and *Q*. The parameter *Q* has been shown to correlate chemical shifts for nearby protons, carbons, and fluorines in substituted benzenes[1g] and protons in olefins.[2] Hruska, *et al.*,[2] conceived the mode of operation of the *Q* effect to be a paramagnetic interaction between the substituent and nucleus in question. There is now substantial evidence that the effect operates through the bonds not across space. While there appears to be a geometric factor for groups such as nitro, hydroxy, amino, and methoxy,[3] it is evidently not the same as that usually invoked by magnetic anisotropy.

For groups other than the halogens and hydrogen it has been necessary to develop an experimental method of obtaining *Q* values.[1c,g] Of necessity, these values contain contributions from more conventional electronic effects (*i.e.*, field effects and resonance effects), and no satisfactory separation of these terms has been brought about as yet.

Several years ago Adcock and Dewar[22] examined the effect of substituents on fluorine chemical shifts for a series of substituted fluoronaphthalenes and concluded that for most positions the chemical shifts were largely determined by field and resonance effects. Dewar and coworkers[23] also developed a rather simple method for calculating σ values at various positions of the naphthalene ring.

In order to further examine the effect of varying substituents on proton chemical shifts in aromatic systems, the parameters for a series of 1-X-4-methoxynaphthalenes were determined (Tables III and IV). During the course of these determinations, Emsley, *et al.*,[24] published a similar set of parameters for a series of 1-X-naphthalenes. Chemical shift trends are the same in each series, but a rather larger range of shifts is evidenced in the monosubstituted series, and these data will be used in developing several points of interest.[25]

Examination of the data in Table III and that of Emsley, *et al.*,[24] showed a linear dependence of chemical shifts with σ_{15}, σ_{16}, and σ_{17} (Figure 1). Correlation coefficients were 0.91, 0.97, and 0.99, respectively. On this basis, it would appear that the same determinative factors operate for proton chemical shifts at sites remote from the substituent as for fluorine chemical shifts.

It has been known for some time that substituents at C-1 cause a deshielding effect at the peri proton (H-8) in the naphthalenes,[26] and it would be natural to assume that the time-dependent electric field of the substituent (van der Waals or disperison effect) of the type proposed by Sutcliffe and coworkers[27] might be important here. The deshielding at H-8, however, covers a range of 0.19 ppm in going from 1-chloro to 1-iodo in our series (Table III), while the deshielding at H-2 is 0.47 ppm for the same series with about

(21) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

(22) W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967).

(23) See the various references cited in ref 22.

(24) J. W. Emsley, S. R. Salman, and R. A. Story, *J. Chem. Soc. B*, 1513 (1970).

(25) The data for 1-iodonaphthalene[24] fail to fit any of our correlations, and one must assume that an error occurred at some point in the determination.

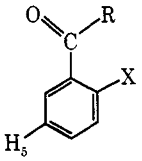
(26) G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).

(27) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964).

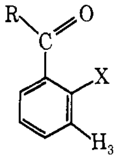
the same overlap of H-2 or H-8 with the substituent. Multiple regression analyses of the data in Table III as well as that of Emsley, *et al.*,[24] using a linear combination of Dewar's field constants[23,28] and Q gave good fits with standard deviations of 0.02 ppm. Since the same type of linear relations hold for H-3 in the naphthalenes and for meta protons, carbons, and fluorines in benzenes where reasonably the van der Waals shift is nil, one is inclined to conclude that field and Q effects are the operable shielding mechanisms at both H-3 and H-8.

Conformations of Carbonyl Group and Q. As noted in Table I, the H-6 chemical shifts for the halobenzaldehydes are insensitive to the nature of the halogen. Thus, it is possible to use the empirical approach previously exploited[1] to determine a $Q(2)$ value of 4.22 for the aldehyde group. This value seems to characterize the proton adjacent to the aldehyde group for several of our other series.

Reasonably, the various benzaldehydes and acetophenones in this study will have carbonyl groups favoring conformations I or II below. From the insensitiveness of the H-6 chemical shifts in the halobenzaldehydes to the size of the ortho halogen it would appear that I is favored. Support for this contention is provided by the observed stereospecific coupling of the aldehyde protons to H-5.[29]



I



II

R = H or alkyl

In contrast, the aldehyde protons of 2-hydroxy- and 2-aminobenzaldehyde in carbon tetrachloride are specifically coupled to H-3 indicating that hydrogen bond formation favors II. It is not surprising, therefore, to find that the H-6 chemical shifts in these compounds do not fall on the appropriate Q plots for the respective phenols and anilines as the aldehyde Q value from the 2-chloro aldehyde characterizes I not II.

The H-3 chemical shifts of the 2-hydroxy and 2-amino aldehyde confirm the hydrogen bonding in these compounds in yet another way. The Q plot for H-3 in the aldehyde series is shown in Figure 2 where it may be seen that hydroxyl and amino points are best fitted with $Q(2)$ values characteristic of these groups in the hydrogen bonding situation.

The failure of the point for nitrobenzaldehyde to fall on the line in Figure 2 suggests that the nitro group is tipped somewhat out of the plane of the aromatic ring.

Not unexpectedly, the acetyl proves to be more sensitive to steric factors than the formyl group. The variation in chemical shifts for H-6 in the 2-haloacetophenones stands in contrast to the behavior of the aldehydes. Clearly no one Q value characterizes the ortho-substituted acetyl group in the acetophenones. For large ortho substituents a value of *ca.* 2.5 will serve for rough predictive purposes.

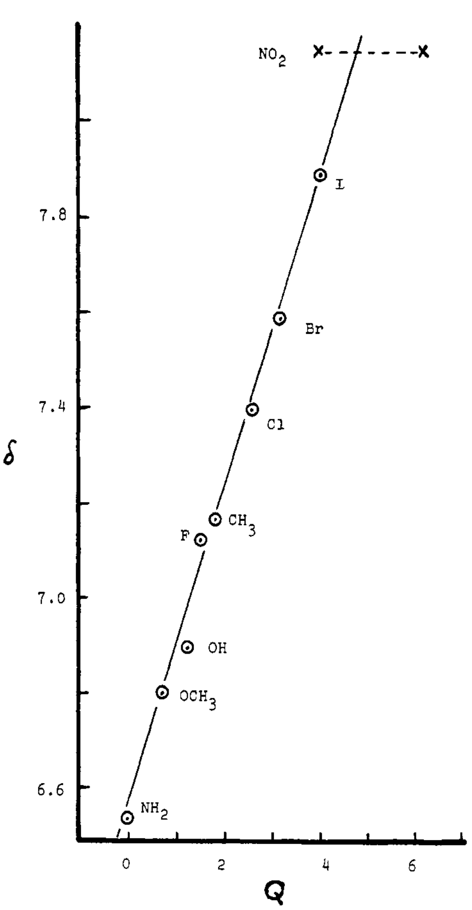


Figure 2. Plot of the H-3 chemical shifts *vs.* Q for a series of 2-X-benzaldehydes.

As derived from the parent dihalobenzene plot,[1] the Q value for acetyl (4.1) in 2-fluoroacetophenone begins to approach the value from acetophenone itself (5.2).[1e] The behavior of the methyl proton coupling to the ortho fluorine parallels the observations of others on postulated "through space" proton to fluorine couplings.[30] Conformations I and II are in equilibrium. The more stable form is I (the "through space" coupling enlarges on going to lower temperatures). Presumably, the dipole-dipole interaction of the C–F and carbonyl group dominates the steric interaction of the methyl group and the fluorine.[31]

The H-3 chemical shifts for the acetophenones *vs.* Q are plotted in Figure 3. In carbon tetrachloride the amino and hydroxyl groups are both hydrogen bonded to their respective carbonyl groups (the $Q(2)$ values of both are required). In DMSO the intramolecular hydrogen bond is broken, and the $Q(1)$ values for the two groups fit the data best.[32]

The conformational preferences of the acetyl group are highly dependent on the adjacent substituents. In carbon tetrachloride, form II clearly predominates

---

[28] By the Dewar method of calculation, σ_{18} is proportional directly to the field constant F for the substituent. Similar fits were obtained using the substituent field contants ($\mathfrak{F}$) of C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

[29] G. J. Karabatsos and F. M. Vane, *ibid.*, **85**, 3887 (1963); S. Forsen and A. Hoffman, *J. Mol. Spectrosc.*, **20**, 168 (1966).

[30] (a) P. C. Myhre, J. W. Edmonds, and D. J. Kruger, *J. Amer. Chem. Soc.*, **88**, 2459 (1966); (b) J. P. N. Brewer, H. Hesney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

[31] Examination of space-filling models shows this to be a more important steric factor than the oxygen–fluorine interaction.

[32] The nitro group appears to be tipped out of the ring plane in both solvents.

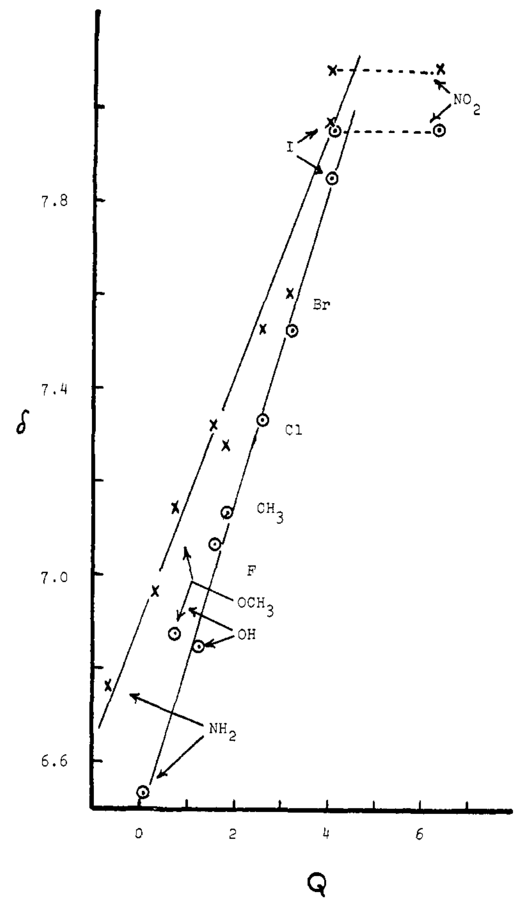


Figure 3. Plot of the H-3 chemical shifts for the 2-X-acetophenones *vs.* *Q*. The lower line is for carbon tetrachloride solutions and the upper is for DMSO.

for the hydroxy and amino compounds, while in the haloacetophenones the populations of I and II vary with the halogen. Yet the *Q* relation holds for the H-3 chemical shifts (Figure 3). Clearly any electronic or magnetic anisotropy effects of the acetyl group which might depend on the geometric relation to H-3 are muted by the intervening substituent, a point which has been made before.[1a,c]

Application of the *Q* relation to the H-2 chemical shifts in the naphthalene series is shown in Figure 4. Not unexpectedly the nitro group appears to require an intermediate value, suggesting that the peri interaction causes it, on the average, to be tilted with respect to the ring plane. Similar effects have been noticed before when sterically small groups such as fluorine[1e] or methyl[1g] are ortho to the nitro group.

Of more interest is the requirement of the aldehyde group. Clearly the *Q* value of 4.22 derived earlier for the aldehyde group does not apply. However, from the plots for the appropriate phenols[1d] and anilines[1g] one concludes that a value of 3.48 characterizes the aldehyde group when hydrogen bonded to an adjacent ortho substituent. Using this value the H-2 chemical shift for 4-methoxy-1-naphthaldehyde fits nicely on the plot in Figure 4.

The implication of this result is that conformation III is favored over IV even though space-filling models show the latter to be the sterically preferred form. Several lines of evidence supporting this postulation are offered below. It goes without saying that some compensating factor such as hydrogen bonding of the carbonyl oxygen to the peri hydrogen must be advanced to explain this observation. A similar rationalization of chemical shift data for some acetonaphthones has been offered by Dudek.[26]

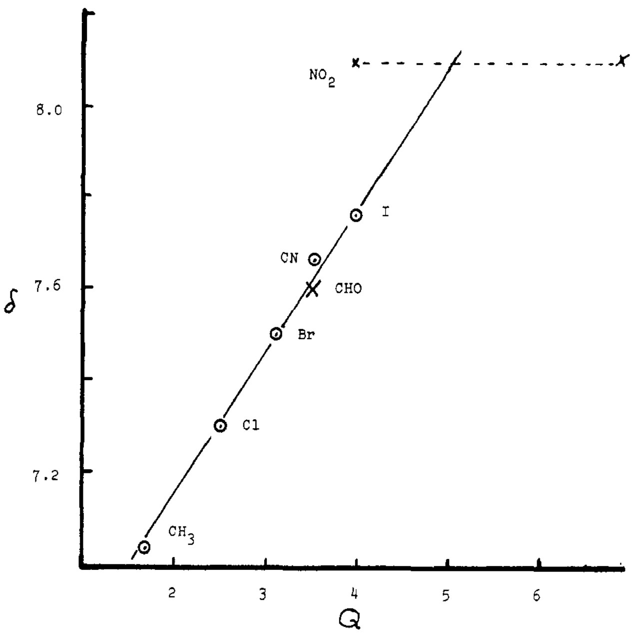
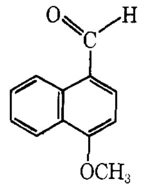
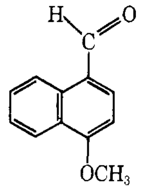


Figure 4. A plot of the chemical shifts of H-2 for a series of 1-X-4-methoxynaphthalenes *vs.* *Q*. The range of values for the nitro group is shown as is the special value for the aldehyde group when in a hydrogen bonding situation.



III



IV

If III is the preferred conformation over IV, one would expect no long-range coupling of the aldehyde proton to H-3, and this expectation was the one experimentally realized.

In order to provide further evidence, a series of 1-acyl-4-methoxynaphthalenes was examined (Table III). In progressing from the aldehyde group to the pivalyl group one finds a progressively more shielded peri hydrogen by *ca.* 1.6 ppm. Calculations using the magnetic anisotropy diagrams of Jackman and Sternhell[33] suggest that in going from III to a conformation with the carbonyl group at right angles to the ring plane the peri hydrogen should become more shielded by about 1.1 ppm.

Finally, the chemical shifts at H-8 and H-2 of 1-acetyl-4-methoxynaphthalene were observed while the acetyl methyl group was subjected to a second irradiating frequency. A definite nuclear Overhauser effect (NOE) was observed at H-2. The peak heights and

---

(33) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 88. For an opposing view of the magnetic anisotropy of the carbonyl group, see G. J. Karabatsos, *et al.*, *J. Amer. Chem. Soc.*, **89**, 5067 (1967). Our dimensions were taken from Dreiding models, and no account was made of the replacement of the hydrogen by a *tert*-butyl group on the carbonyl.

area associated with these transitions were enhanced by 14 and 5%, respectively. No change was noted in the H-8 transitions. A similar effect was noted when the methine proton in the 1-isobutyryl-4-methoxynaphthalene was irradiated although the NOE was smaller (6 and 2%, respectively). No effect was noted on irradiating the *tert*-butyl methyls of the pivalyl compound. These results are consistent with the earlier data for the aldehyde group. For acetyl, III is still preferred, but as the substituent on the carbonyl groups grows larger in size a nonplanar relation develops between the carbonyl group and the ring. No evidence has been found to suggest that conformation IV is of importance in these substances.

Acknowledgment. This work was supported by the Robert A. Welch Foundation. We wish to express our gratitude to the foundation. One of us (A. M. I.) wishes to express his appreciation to the T. C. U. Research Foundation for a postdoctoral fellowship.

Base-Induced Rearrangement of γ-Diketones. II. Demonstration of the Occurrence of Skeletal Rearrangement and of the Reversibility of the Reaction[1,2]

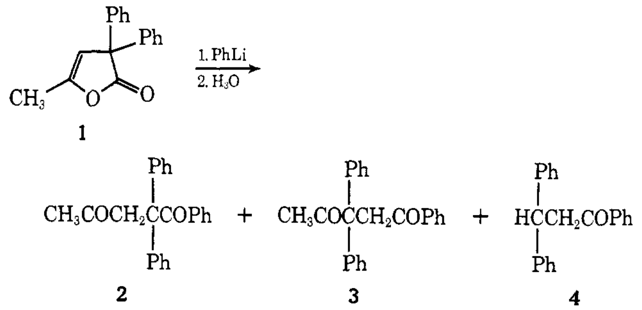
Peter Yates* and Michael J. Betts

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada. *Received August 23, 1971*

Abstract: 5,5-Dimethyl-1,3,3-triphenyl-1,4-hexanedione-*2*-^{13}C, prepared by the reaction of 2-diazoacetophenone-*2*-^{13}C with diphenylketene to give 4-hydroxy-2,2,4-triphenyl-3-butenoic-*3*-^{13}C acid lactone followed by treatment of the lactone with *tert*-butyllithium, gave 5,5-dimethyl-1,2,2-triphenyl-1,4-hexanedione-*3*-^{13}C on treatment in ether with sodium methoxide. The occurrence of skeletal rearrangement is thus demonstrated, and it is concluded that the base-induced interconversion of γ-diketones involves the intermediacy of homoenolate ions rather than 1,2 phenyl migrations. The rearrangement reaction has been shown to be reversible in the cases of 1-(1-naphthyl)-2,2,4-triphenyl-1,4-butanedione and 2,2,4-triphenyl-1-(*p*-tolyl)-1,4-butanedione.

It has recently been reported from these laboratories[1] that treatment of the lactone **1** with phenyllithium followed by aqueous work-up gives 1,2,2-triphenyl-1,4-pentanedione (**2**), 1,3,3-triphenyl-1,4-pentanedione (**3**), and 3,3-diphenylpropiophenone (**4**) (Scheme I). It was concluded that the formation of the γ-diketone **3** involved the rearrangement of an enolate ion of the γ-diketone **2** since the yield of **3** relative to **2** increased with longer reaction time. This conclusion was confirmed by the observation that treatment of **2** with sodium methoxide in ether gave a mixture of the cyclopentenones **5** and **6** (Scheme II); under these conditions the cyclopentenones themselves are not interconverted, and thus **2** must have undergone partial base-induced conversion to **3**, which then gave **6**.

Scheme I

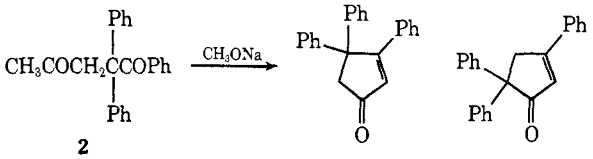


1

$\mathrm{CH_3COCH_2\overset{Ph}{\underset{Ph}{C}}COPh}$ + $\mathrm{CH_3CO\overset{Ph}{\underset{Ph}{C}}CH_2COPh}$ + $\mathrm{H\overset{Ph}{\underset{Ph}{C}}CH_2COPh}$

2 3 4

Scheme II

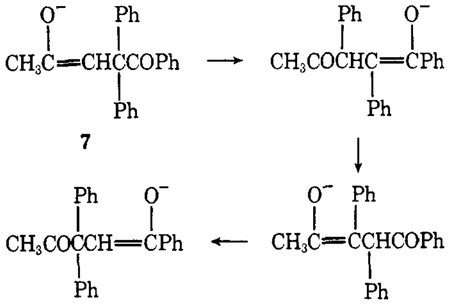


$\mathrm{CH_3COCH_2\overset{Ph}{\underset{Ph}{C}}COPh \xrightarrow{CH_3ONa}}$

2 5 6

Two general types of pathway were considered in accounting for the rearrangement. In one (Scheme III), the anion **7** derived from **2** is converted to the anion **8** corresponding to **3** by two 1,2 migrations of the phenyl groups with an intermediate 1,2 migration of hydrogen. In the other (Scheme IV), the anion **7** is converted to the anion **8** *via* two homoenolate ions. On both theoretical and experimental grounds the mechanism depicted in

Scheme III



$\mathrm{CH_3\overset{O^-}{C}{=}CH\overset{Ph}{\underset{Ph}{C}}COPh \longrightarrow CH_3CO\overset{Ph}{C}H\underset{Ph}{C}{=}\overset{O^-}{C}Ph}$

7

$\mathrm{CH_3CO\overset{Ph}{\underset{Ph}{C}}CH{=}\overset{O^-}{C}Ph \longleftarrow CH_3\overset{O^-}{C}{=}\overset{Ph}{C}\underset{Ph}{C}HCOPh}$

8

---

[1] Paper I: P. Yates, G. D. Abrams, M. J. Betts, and S. Goldstein, *Can. J. Chem.*, 49, 2850 (1971).

[2] A preliminary report on part of this work has appeared: M. J. Betts and P. Yates, *J. Amer. Chem. Soc.*, 92, 6982 (1970).