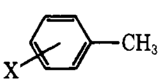
Linear C^{13}—H Coupling Constant–Hammett Sigma-Constant Relationships in Substituted Benzaldehydes

CLAUDE H. YODER and CHARLES D. SCHAEFFER, JR.
Department of Chemistry, Franklin and Marshall College, Lancaster, PA 17604

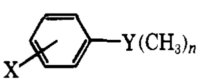
RONALD E. HESS[1]
Department of Chemistry, Ursinus College, Collegeville, PA 19426

The C^{13}—H coupling constants of the aldehydic protons in a series of meta- and para-substituted benzaldehydes have been determined in seven different solvents and linearly related to the Hammett σ-constant of the substituent group. These results suggest a direct dependence of the J-σ slope on the dielectric constant of the solvent.

We have recently reported linear methyl C^{13}—H coupling constant-Hammett σ-constant relationships in aromatic compounds of types I and II, where $Y = C(n = 3)$, $N(n = 2)$, and $O(n = 1)$ (*1*). We have now extended this work to the benzaldehydes, measuring the C^{13}—H coupling constant of the aldehydic proton. As expected, the greater ability of the trigonal carbon atom to transmit the electronic effects of substituent *X* to this proton is reflected in the much greater sensitivity of the C^{13}—H coupling constant to the electronic nature of *X*. Again excellent linear *J*-σ relationships were found, with slopes several times greater in magnitude than those of compound types I and II and with the correlation coefficients of the least-squares lines usually greater than 0.99, regardless of solvent.



I



II

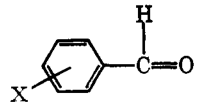
Both factors—the excellent correlation and sizable slope—make this an ideal system for a study of the effects of solvents on *J*-σ relationships. Accordingly, coupling constants were measured in seven solvents and are recorded in Table I. Table II presents the least-square parameters for the *J*-σ lines for all compounds measured in each solvent as well as the parameters for *J*-σ lines based on the seven compounds common to all seven solvents.

For a given benzaldehyde, the coupling constant is highest in dimethylsulfoxide (DMSO), second highest in CH_3OH, while the lowest constants are observed in either benzene or triethylamine. In terms of *J*-σ slopes, the solvents appear to fall into three groups; triethylamine, chloroform, and benzene ($\rho = 7 \pm 0.5$); tetrahydrofuran, methanol, and nitrobenzene ($\rho = 8.7 \pm 0.5$); and dimethylsulfoxide ($\rho > 10$). It is difficult to relate these trends to specific solvent characteristics, but the three groupings certainly suggest a dependence on dielectric constant [although on this basis the THF slope would appear anomalous ($\epsilon_{THF} = 7$) (*3*)]. Further speculation upon the solvent dependence of C^{13}—H coupling constants and *J*-σ relationships we believe to be unwarranted.

EXPERIMENTAL SECTION

Compounds studied were all commercial samples, containing no spurious pmr signals.

Table I. Benzaldehyde CHO C^{13}—H Coupling Constants ($\pm$0.3 Hz)[a,b]



X	$CHCl_3$	C_6H_6	N-$(C_2H_5)_3$	C_4H_8O	C_6H_5-NO_2	CH_3OH	$(CH_3)_2$-SO
p-$N(CH_3)_2$	169.0	168.1		168.4			169.2
p-OCH_3	172.5	172.3	172.4	172.5	172.6	172.7	173.2
p-OC_2H_5	172.2	171.9	172.1	172.0	172.0	172.5	172.9
p-CH_3	173.0	172.8	173.5	173.3	173.2	173.6	174.1
m-CH_3	173.7	173.5	173.3	173.7	173.9	174.2	175.3
p-H	174.9	174.2	174.4	174.7	175.6	175.1	175.6
p-F	175.5	175.3	175.5	176.1			176.6
p-Cl	175.8	175.5	175.4	176.6	176.3	176.8	178.4
p-Br	176.2	175.9		176.6	177.7	177.2	178.5
m-Br	177.3	177.1	177.0	177.9	177.9	178.3	179.9
p-CN	179.4	178.9		179.9	179.7		181.6
p-CO_2H							179.0
p-NO_2	179.8						183.1
m-NO_2	180.2	180.4					

[a] 0.8-gram solute/1.0 ml solvent or 0.8 ml solute/1.0 ml solvent.
[b] Each coupling constant which is omitted was not determined owing to the insolubility of the given compound in the particular solvent. The *p*-COOH derivatives were, of course, not analyzed in the basic solvents.

Table II. *J*-σ Regression Analysis Parameters[a]

	C_6H_6	N-$(C_2H_5)_3$	$CHCl_3$	C_6H_5-NO_2	C_4H_8O	CH_3OH	$(CH_3)_2$-SO
ρ	8.55	7.02	7.89	8.39	9.16	8.80	10.1
C	174.0	174.3	174.3	174.5	174.5	174.9	175.8
r	0.991	0.963	0.993	0.996	0.990	0.997	0.995
S	0.473	0.492	0.416	0.236	0.473	0.188	0.389
n	12	8	13	9	11	8	13
				Common Cases			
ρ	7.46	6.84	7.49	8.43	8.69	8.65	10.6
C	174.0	174.2	174.3	174.5	174.6	174.9	175.8
r	0.994	0.980	0.990	0.994	0.994	0.997	0.997
S	0.221	0.378	0.313	0.257	0.270	0.175	0.225
n	7	7	7	7	7	7	7

[a] ρ and *C* are parameters of the equation: $J = \sigma\rho + C$; *r* is correlation coefficient; *S* is standard deviation of residuals; and *n* is number of compounds. σ-Constants are those reported by Jaffé (*2*).

---

[1] To whom correspondence should be addressed.

Coupling constants were determined by standard side-banding techniques on a Varian A-60D nmr spectrometer with a Hewlett-Packard Model 200CD audio-oscillator and Model 522B electronic counter. The probe temperature was 38 ± 2°C. Recorded values are averages of at least five traces at a 50-cps sweep width (500 sec sweep time) and are believed accurate to within ±0.2 Hz. Solution concentrations were 30% (vol:vol or wt:vol) in all cases.

Solvents used were spectroquality $CHCl_3$ (shaken three times with alumina to remove ethanol), chemical grade C_6H_6 (dried over calcium hydride and distilled), chemical grade THF and $N(C_2H_5)_3$ (distilled and stored over molecular sieve), chemical grade $C_6H_5NO_2$ (stored over molecular sieve), and chemical grade CH_3OH and DMSO (dried over $CaSO_4$ and distilled).

LITERATURE CITED

(1) Carvajal, C., Tölle, K. J., Smid, J., Szwarc, M., *J. Amer. Chem. Soc.*, **87**, 5548 (1965).
(2) Jaffé, H. H., *Chem. Rev.*, **53**, 191 (1953).
(3) Yoder, C. H., Tuck, R. H., Hess, R. E., *J. Amer. Chem. Soc.*, **91**, 539 (1969).

Received for review July 23, 1971. Accepted April 13, 1972.

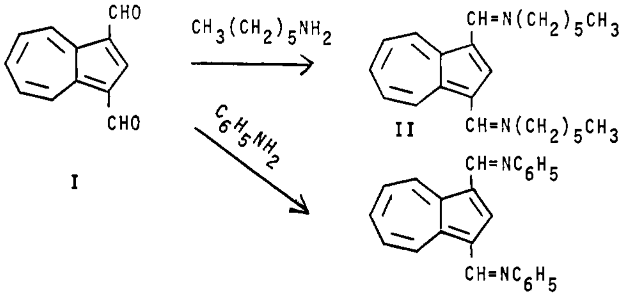
Synthesis of 1,3-Disubstituted Azulenes

G. R. SACCO
Polymer Research Branch, Picatinny Arsenal, Dover, NJ 07801

The syntheses and characterization of several 1,3-disubstituted azulene derivatives are described. Yields, melting points, elemental analysis, and infrared data are reported.

In a previous paper (*4*), we reported the preparation and thermal stabilities of poly-Schiff bases containing azulene. In connection with our investigation of azulene polymers, we now wish to report the syntheses of 1,3-substituted azulenes.

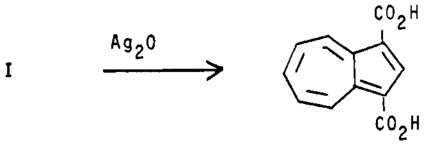
The imines II and III were prepared by the condensation of 1,3-azulenedicarboxaldehyde, I, with hexylamine and aniline, respectively. These derivatives have not been reported.



I II

III

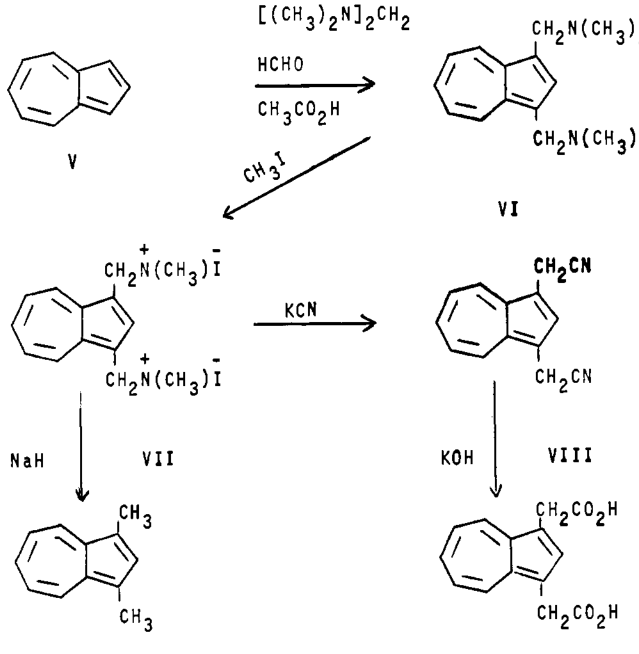
Muhlstadt and co-workers (*3*) reported a 30% yield of 1,3-azulenedicarboxylic acid, IV, by the permanganate oxidation of 1,3-azulenedicarboxaldehyde. The poor yield prompted us to investigate alternate oxidation procedures. When I was oxidized with silver oxide it gave a 90% yield of product:



IV

Azulene, V, was aminomethylated to 1,3-bis(dimethylaminomethyl)azulene, VI. The reaction was effected in glacial acetic acid with paraformaldehyde and *N,N,N,N*-tetramethyldiaminomethane. Treatment of the tertiary amine, VI, with excess methyl iodide gave 1,3-bis(methyltrimethylammonium iodide), VII.

The compounds 1,3-azulenediacetonitrile, VIII, and 1,3-dimethylazulene, X, were prepared by the reaction of VII with potassium cyanide and sodium hydride, respectively. Alkaline hydrolysis of VIII gave 1,3-azulenediacetic acid, IX. The azulene derivatives VIII and IX are reported for the first time.



V VI VII VIII X IX