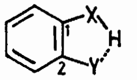
Carbon-13 Nuclear Magnetic Resonance Studies of Aromatic Compounds: Comparison of Hydrogen Bonding Effects in Phenols, Anilides, and Anilines

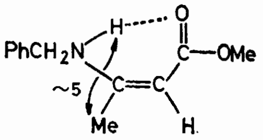
By **Alan E. Sopchik** and **Charles A. Kingsbury,*** Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, U.S.A.

Two- and three-bond ^{13}C n.m.r. coupling constants to ^1H are reported for ring-substituted phenols, anilides, and anilines, plus limited data for thiophenols. The magnitude of the three-bond coupling constants to the phenolic hydroxy were rather insensitive to structural variations designed to alter the geometry of the coupled nuclei and raises the question of the exact geometric dependence of ^3J on geometry. For acetanilides, the difference in magnitude between $^3J_{anti}$ and $^3J_{syn}$ is small. For anilines, the data are not suggestive of a geometric relationship. Thiophenols are similar to phenols. The influence of substitution on coupling constants between ring carbons and hydrogens is discussed briefly. Chemical shifts are reported for 16-*ortho*-substituted aromatic compounds.

INTRAMOLECULAR hydrogen bonding has been extensively studied by i.r. techniques, and by ^1H n.m.r. spectroscopy.[1,2] In other work, ^{17}O and ^{15}N n.m.r. have proved to be very informative with regard to charge densities at donor and acceptor sites.[3,4] With regard to ^{13}C n.m.r. studies of hydrogen bonding, Maciel *et al.*[5] and Lauterbur[6] found that carbonyl resonances were shifted by 3—7 p.p.m. to lower field in *o*-hydroxybenzoates, acetophenones, and benzophenones. More recently Wehrli noted that coupling constants between phenolic OH groups and *ortho*-carbons were observable in 5-hydroxyflavones and flavanones.[7] Chang extended



	X	Y	Other substituents
(1)	O	OCH_3	
(2)	O	OCH_3	(4,5-Br_2)
(3)	O	Cl	
(4)	O	NO_2	
(5)	O	NO_2	(4,6-Br_2)
(6)	O	$COCH_3$	
(7)	O	CHO	
(8)	O	CO_2CH_3	
(9)	S	NO_2	
(10)	S	CO_2CH_3	
(11)	NAc	Cl	
(12)	NAc	NO_2	
(13)	NAc	CO_2CH_3	
(14)	NAc	$SOCH_3$	
(15)	NCHO	Br	(4,6-Br_2)
(16)	NH	NO_2	
(17)	NH	NO_2	(4,6-Br_2)
(18)	NH	Br	(4,6-Br_2)
(19)	NEt	Cl	
(20)	O	SCH_3	
(21)	O	$SOCH_3$	
(22)	NH	CO_2CH_3	



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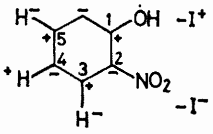

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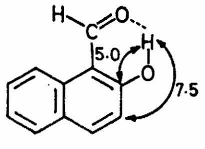

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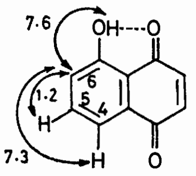

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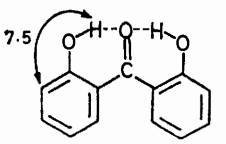

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these observations and suggested revised values for *syn*- and *anti*-geometries of the coupled nuclei, *i.e.* $^3J_{\mathrm{C-C-O-H}}$ *ca.* 2 and 7 Hz respectively.[8,9]

TABLE 1

^{13}C–^{1}H Coupling constants and i.r. Δν values for XH • • • Y hydrogen bonding

Compound	Temp (°C)	Δν/ cm^{-1}	$^3J_{\mathrm{C(6)-XH}}$/ Hz	$^3J_{\mathrm{C(2)-XH}}$/ Hz	$^2J_{\mathrm{C(1)-XH}}$/ Hz
(1)	−10	52	7.4	m	m
(2)	−10	52	8.0	3.4	3.1
(3)	*a*	61	8.0	m	3.8
(4)		346	7.2	m	m
(5)	−28	170	~9	m	2?
(6)			7.5	3.5	m
(7) [b]		475	7.5	m	m
(8) [b]		390	7.5	4.0	2.5
(9)			5	m	m
(10)		75	7.1	3.5	m
(11)	−28	190	~4.5	~2.5	*c*
(12)			4.9	m	*c*
(13)		180	5.4	2.6	*c*
(14)			3.7	m	*c*
(15) [d]			2.8	2.8	*c*
(16)		30	6.8	m	*c*
(17) [d]			6.4	m	
(18) [d]			6.1	6.1	m
(19)	−30		6 [e]		

[a] Observable at normal probe temperature, but difficult to reproduce. [b] First reported by Chang.[8a] Our data are listed, however. [c] Couplings through nitrogen appeared to be near zero, in most cases. [d] [^{2}H$_6$]DMSO solution; all others, CDCl$_3$ solution. [e] *o*-Chloroaniline shows a similar coupling in DMSO.

In acyclic systems, $^3J_{\mathrm{H-C-O-H}}$ coupling constants are observable where strongly hydrogen bonding solvents such as DMSO or acetone slow intermolecular exchange.[10,11] However, *intra*molecular hydrogen bonding does not readily permit $^3J_{\mathrm{H-C-O-H}}$ to be observed even in cases where a powerful hydrogen bond acceptor such as SO is present.[12] In view of this previous work, it was perhaps surprising to find that $^3J_{\mathrm{C-C-O-H}}$ coupling constants can be observed in *ortho*-substituted phenols having weak hydrogen bond acceptors present, using a common commercial grade of CDCl$_3$ as solvent, and a rather high solute concentration. In investigation of acetanilides, $^3J_{\mathrm{C-C-N-H}}$ is easily observed, as N–H exchange is seldom rapid. However, in anilines, the coupling constants between NH and ring carbons were observed with difficulty, although some data were obtained. The coupling constants of interest are listed in Table 1, and chemical shifts are given in Table 2.

The relative ease with which $^3J_{\mathrm{C-C-O(N)-H}}$ are observed in aromatic molecules is in marked contrast to the difficulties in acyclic molecules. Compound (23) remains the only acyclic compound in which we have successfully observed $^3J_{\mathrm{CH}}$. Both (23) and the aromatic molecules (1)—(15) possess considerable rigidity, which enhances the probability of maintaining the hydrogen bond through the observation period.[12,13]

An inventory of other coupling constants involving ring ^{13}C nuclei is given in Table 3 for phenols (2), (4), and (5), and for anilides (12) and (15). These data are typical of the whole, and in general agreement with the findings of Tarpley and Goldstein,[14] and with Weigert and Roberts.[15] Thus, $^3J_{\mathrm{CH}}$ is substantially larger than $^2J_{\mathrm{CH}}$, whereas $^4J_{\mathrm{CH}}$ is variable. In our hands, splittings that could be explicitly assigned to ^4J and to ^2J were often not observable. This observation was common for carbons distant from electronegative groups [*cf.* $^2J_{\mathrm{C(5)-H(4)}}$ for (4)].

With regard to the three-bond coupling constants, carbons lying close to a substituent (*e.g.* NO$_2$) show *smaller* ^3J values than distant carbons.[14] Thus in (4), $^3J_{\mathrm{C(3)-H(5)}} = 8.1$ Hz, whereas $^3J_{\mathrm{C(5)-H(3)}} = 9.9$ Hz. The phenomenon is particularly apparent for compounds with electronegative substituents. Hydroxy is electron withdrawing with respect to the σ bond framework, which is the most probable path for transmission of spin

TABLE 2

^{13}C Chemical shifts

Compound [a,b]	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Other
(2)	145.3	146.3	115.2 [c]	115 [c]	113.6 [c]	119.0	56.3 (OCH$_3$)
(5)	151.3	134.4	126.6	111.4	142.8	114.4	
(6)	161.3	118.7	129.8	117.9	135.4	117.3	204.4 (CO) 25.7 (CH$_3$)
(9)	133.2	144.8	125.8 [c]	125.5 [c]	133.5	131.7	
(10)	137.1	124.8	130.6 [c]	123.5	131.4 [c]	129.8	166.8 (CO) 51.9 (CH$_3$)
(12)	134.2	135.9	125.1	122.7	135.2	121.6	168.5 (CO) 25.0 (CH$_3$)
(13)	141.3	114.5	130.4	122.0	134.2	119.9	168 (both CO) 52.0 (CH$_3$), 25.2 (CH$_3$)
(14)	138.7	129.0	131.9 [c]	123.7	125.0 [c]	122.8	168.5 (CO), 40.8 (CH$_3$) 24.3 (CH$_3$)
(15) [d]	134.2	124.3	134.2	120.9	134.2	124.3	159.2 (CO)
(17) [d]	141.1	132.8	127.9	106.7	140.6	112.6	
(18) [d]	143.2	108.7	134.1	107.2	134.1	108.7	
(19)	143.9	118.7	128.8	116.7	127.6	110.9	38.1 (CH$_2$) 14.7 (CH$_3$)
(20)	155.1	120.2	129.5 [c]	119.9	133.4 [c]	114.0	18.8 (CH$_3$)
(21)	155.2	126.4	124.0 [c]	119.9	132.3 [c]	117.0	40.7 (CH$_3$)
(22) [c]	150.2	110.4	130.9	115.8	133.7	116.3	168.2 (CO) 51.2 (CH$_3$)

[a] For (7) and (8) see ref. 8. [b] For compounds (1), (3), (4), (11), (16), and (23), see Sadtler Standard C-13 NMR Spectra Indices, Sadtler Research Laboratories, Philadelphia. We disagree with line assignments in certain cases. [c] Line assignments uncertain; the inverse assignment is also possible. [d] [^{2}H$_6$]DMSO solutions.

information.[16] The effect of hydroxy in (4) diminishes $^3J_{C(6)-H(4)}$ (7.9 Hz) relative to $^3J_{C(4)-H(6)}$ (8.8 Hz), although the effect is smaller than for nitro.[14]

In many other compounds of this study, *i.e.* (3), (7), (8), (13), (14), (16), (17), (22), and (27), similar observations were apparent. However, the simple line separations (LS) were used rather than the computed ^3J values. The LS values usually are sufficiently close to ^3J values to mirror the major trends. In certain compounds lacking electronegative groups Y [(20)—(22)], equivalent splittings were found for certain corresponding pairs of nuclei, e.g. C(3)-H(5), and C(5)-H(3).

In the more highly substituted molecule, 4,6-dibromo-2-nitrophenol (5), $^3J_{C(3)-H(5)}$ (6.0 Hz) is again smaller than $^3J_{C(5)-H(3)}$ (7.0 Hz). However, both coupling constants are small compared to analogous values from (4). The electronegative atom at C(4) reduces ^3J. With this observation in mind, as well as literature data,[14] the $^3J_{C(1)-H(3)}$ and $^3J_{C(1)-H(5)}$ values for (4) were assigned as 6.3 and *ca.* 11.0 Hz respectively. The 2-NO$_2$ group reduces $^3J_{C(1)-H(3)}$. Coupling through C-(SCH$_3$), on the other hand, has but a small effect.

TABLE 3

Compound	^1J/Hz		^2J/Hz		^3J/Hz		^4J/Hz	
(4)	C(3)-H(3)	167.5	C(1)-H(6)	2.6	C(1)-H(3)	~6.3	C(3)-H(6)	~1
	C(4)-H(4)	166.7	C(3)-H(4)	3.7 [b]	C(1)-H(5)	~11	C(1)-H(4)	~1.3
	C(2)-H(5)	161.8	C(4)-H(5)(3)	<1	C(3)-H(5)	8.1		
	C(6)-H(6)	165.5	C(5)-H(6)(4)	<1	C(4)-H(6)	8.8		
			C(6)-H(5)	<1	C(5)-H(3)	9.9		
					C(6)-H(4)	7.9		
(12)	C(3)-H(5)	166.9	C(3)-H(4)	3.5 [b]	C(1)-H(3)	6.3	C(3)-H(6)	1.2
	C(4)-H(4)	166.1	C(4)-H(3)	<1	C(1)-H(5)	8.9		
	C(5)-H(5)	161.3	C(4)-H(5)	<1	C(3)-H(5)	8.3		
	C(6)-H(6)	169.0	C(5)-H(4)	<1	C(4)-H(6)	8.9		
			C(5)-H(6)	<1	C(5)-H(3)	8.6		
			C(6)-H(5)	2.3 [b]	C(6)-H(4)	7.6		
(5)	C(3)-H(3)	174.4	C(4)-H(3)(5)	{4.5 5.2	C(1)-H(3)	6.3	C(6)-H(3)	~1.5
	C(5)-H(5)	172.9	C(6)-H(5)	4.5	C(1)-H(5)	7.9		
					C(3)-H(5)	6.0		
					C(5)-H(3)	~7.0		
(15)	C(3)-H(3)	175.1	C(2)-H(3)	~2.8	C(1)-H(3)	~7.2		
			C(4)-H(3)	4.1	C(3)-H(5)	6.0		
					C(1)-H(3)	~7.2		
					C(2)-N*H*	~2.8		
(2) [a]	C(3)-H(5)	164.4	C(1)-H(6)	4.6	C(1)-H(3)	8.1	C(6)-H(3)	1.1
	C(6)-H(6)	166.5	C(4)-H(3)	4.4	C(4)-H(6)	9.3	C(3)-H(6)	1.1
			C(5)-H(6)	5.2	C(5)-H(3)	9.6		

[a] Line assignments for C(4) and C(5) are not certain. [b] These values resulted from a computer simulation using a negative coupling constant; simulation with a positive coupling constant gave an equally good root mean square error, although the magnitude was different.

In contrast, electronegative substituents attached to the carbon atom at which ^3J originates increase the magnitude of ^3J.[16] Thus, in (2), $^3J_{C(4)-H(6)}$ and $^3J_{C(5)-H(3)}$ (*ca.* 9.5 Hz) are among the largest coupling constants of this study, despite the diminishing effect of 5-Br. Similarly, two-bond coupling constants originating at brominated carbons are large in magnitude; *e.g.* in (2), $^2J_{C(5)-H(6)}$ *ca.* 5 Hz, and $^2J_{C(4)-H(3)}$ *ca.* 4.4 Hz, compared to values of <1 Hz in (4). These ^2J values are quite likely negative in sign,[14] although it is still not entirely clear when negative *versus* positive signs are to be expected.

Couplings originating at brominated carbons are very likely large in magnitude because of enhanced *p* character in the C-Br bond, and therefore enhanced *s* character in the C(Br)-C extending toward ^{1}H.[14,17] The enhanced *s* character improves nuclear-electron spin recognition.[1]

The most difficult data to explain are the effects of adjacent electronegative groups. Thus, the 2-Y group diminishes $^3J_{C(3)-H(5)}$ (relative to $^3J_{C(5)-H(3)}$), but increases $^2J_{C(3)-H(4)}$ (relative to $^2J_{C(4)-H(3)}$) in a great number of cases.[14] An electron withdrawal or a hybridization change due to X should probably affect ^2J and ^3J similarly (in absolute magnitude). Perhaps an explanation may be sought in the polarization of σ electrons by the substituents OH and NO$_2$ as shown in structure (24).[18] Polarization of the σ electrons by both substituents leads to enhanced electron density at C(4), which may permit more efficient transmission of spin information between the attached nuclei C(3) and H(4) compared with the C(4)-H(3) path. Electron withdrawal by NO$_2$, as opposed to a polarization of electrons, may explain the rather low $^3J_{C(3)-H(5)}$ values. However, more detailed studies are obviously needed to pinpoint the exact causes of the changes in coupling constants.

With regard to the coupling constants involving OH, $^3J_{C-C-O-H}$ values were observed in almost every case in which the i.r. data ($\Delta\nu$; Table 1) indicate the existence of a strong hydrogen bond. The magnitude of these ^3J values for (4)—(8) and for (25)—(27) (Table 3) is *ca.* 7 Hz, in agreement with Chang.[8] The *J* values for *syn*-nuclei are somewhat variable, probably due to the effect of the different groups X. The $^3J_{C(2)-OH}$ values were difficult to obtain because of low peak intensity, and insufficient resolution of the rather complex splitting pattern, and thus not many values are available.

In the case of (2) (Table 3), C(6) appears as a simple 2 × 2 pattern at normal probe temperature, 32°, with no observable splitting by OH. At −10°, splitting by OH was observable, with $^3J_{C(6)-OH}$ 8.0 Hz. The i.r.

spectrum indicates a weak intramolecular hydrogen bond, which is consistent with the difficulty in observing a ^3J coupling. Despite the weakness of the hydrogen bond, the magnitude of the coupling suggests that conformational averaging is small. Similarly in the case of (3; X = *o*-Cl), a large value for $^3J_{C(6)-OH}$ was observed (8.0 Hz). This observation was difficult to reproduce because of the weakness of the hydrogen bond.[19] Weak hydrogen bonds have relatively short O–H bond distances, and long (OH)–X distances. The n.m.r. coupling constant should be larger for these short bonds.[20] On the other hand, $^3J_{C(2)-OH}$ is not unusually high in (2).

In 4,6-dibromo-2-nitrophenol (5), competition between hydrogen bonding to Br or to NO_2 is present. The very large $^3J_{C(6)-OH}$ (8 Hz) is consistent with *anti*-geometry, and thus with hydrogen bonding to NO_2, the stronger acceptor. In the case of 4,5,6-tribromo-2-methylthiophenol, hydrogen bonding to Br or to S may occur. The $^3J_{C(6)-OH}$ value (6 Hz) is smaller than usual, but again suggests preferential bonding to S. In *o*-bromophenol, $^3J_{C(6)-OH}$ was not observed even at low temperature.

The presence of a strong hydrogen bond does not always ensure that $^3J_{C(6)-OH}$ can be observed.[21] In the case of 2-methylsulphinylphenol (21), $\Delta\nu$ is *ca.* 200 cm^{-1}, suggestive of a strong hydrogen bond. However, repeated attempts to observe coupling to hydroxy under various conditions were unsuccessful. Insolubility prevented low temperature determinations. The intramolecular SO · · · HO hydrogen bond possesses a rather unfavourable geometry,[12,22,23] and the main attractive force may be electrostatic in nature. The geometry is unfavourable because HO approaches the side of the SO bond.[12] In this case, intermolecular hydrogen bonding may compete favorably with intramolecular bonding, thus facilitating exchange. In the amide analogue (14), NH exchange is slow for other reasons, and $^3J_{C(6)-NH}$ is observed, although the magnitude of this coupling constant is rather small.

In 2-hydroxy-1-naphthaldehyde (25) and juglone (26), the effects of non-rigid *versus* rigid geometry may be tested. However, i.r. and n.m.r. data are not in agreement on the strengths of the hydrogen bonds in question. In (25), the chemical shift of CO is 193 p.p.m. compared with 192 p.p.m. in naphthaldehyde.[24] Hydrogen bonding, which usually causes a downfield shift of CO, is little in evidence in (25) [by comparison, salicylaldehyde (7) CO, 197 p.p.m.; benzaldehyde, 192 p.p.m.[24]]. $\Delta\nu$ is smaller for (25) (*ca.* 360 cm^{-1}) than for salicylaldehyde (*ca.* 475 cm^{-1}). Comparing (25) and (26), the i.r. data suggests that the hydrogen bond is stronger for (25), despite steric hindrance to coplanarity,[25] than for the rigid molecule (26) ($\Delta\nu$ *ca.* 300 cm^{-1}). However, the n.m.r. chemical shift of the hydrogen bonded CO in (26) is 6 p.p.m. downfield from the non-bonded CO, as expected. In any case, the $^3J_{C(6)-OH}$ values for (25)—(27) are very similar, *ca.* 7.5 Hz.

In 2,2′-dihydroxybenzophenone (27), molecular models clearly indicate that the two benzene rings cannot be coplanar. The chemical shift of CO is *ca.* 6 p.p.m. downfield from benzophenone, similar to singly hydrogen bonded CO groups. The i.r. spectrum of OH is diffuse, and a unique $\Delta\nu$ value cannot be discerned. The broad OH absorption at *ca.* 3 400—3 200 cm^{-1} is suggestive of varying modes of hydrogen bonding.[26]

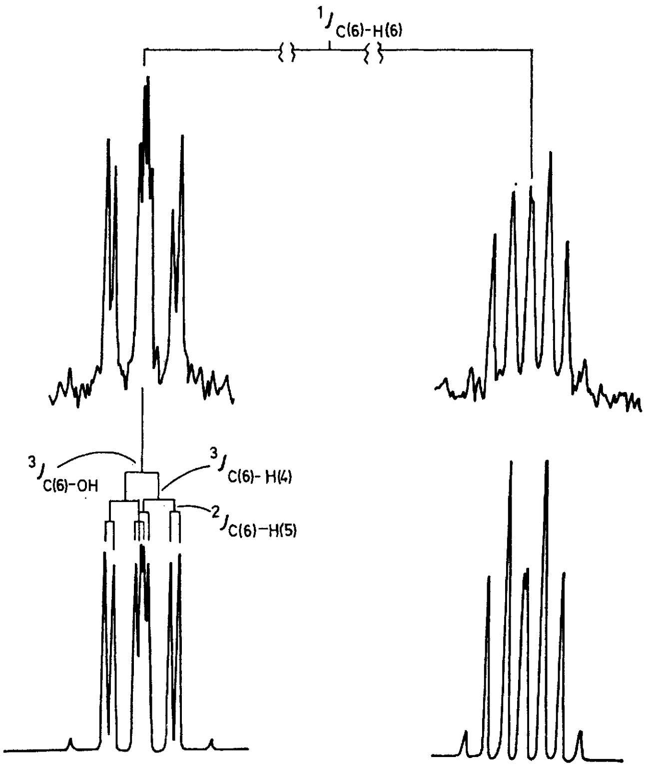
Simultaneous hydrogen bonds from two OH groups to a single acceptor have been postulated, but it seems likely that the capacity of CO to accept the first of two hydrogen bonds is greater than the second.[26] Molecular models show that both OH groups may approach CO within bonding distance despite the tilt of the benzene rings. No ' free ' OH was observable in the i.r. spectrum. $^3J_{C(6)-OH}$ was observed with some difficulty at low temperature. This value (7.5 Hz for both hydroxys) is suggestive of *anti*-geometry, as if each OH were fully hydrogen bonded, and not two alternating single OH · · · OC interactions, in which the other OH is free to occupy a variety of conformations. The large value for $^3J_{C(6)-OH}$ is noteworthy in view of the non-planar geometry, and raises the question of the sensitivity of ^3J to exact geometry.

In the case of the thiols (9) and (10), the magnitudes of the couplings to hydroxy are approximately the same as for phenols. The i.r. data suggest that thiols are weak hydrogen bond donors.[27] However, despite the rather high acidity of thiols, the exchange reaction is not particularly rapid. Splittings by SH have been observed in non-hydrogen bonded systems in neutral solvents.[28]

The anilides (12)—(15) exhibit somewhat more variable data. Thus, $^3J_{C(6)-NH}$ varies from 3.6 to 5.4 Hz, whereas $^3J_{C(2)-NH}$ is *ca.* 3 Hz in those cases in which this coupling could be observed. In compounds lacking an intramolecular hydrogen bond, *i.e. o*-acetyltoluidide, the C(6) signal was broad, and a coupling constant to NH could not be discerned. For (13), a change in solvent from $CDCl_3$ to [$^2H_6$]DMSO resulted in a change in $^3J_{C(6)-NH}$ from 5.4 to 4.5 Hz, probably the effect of intermolecular hydrogen bonding in the latter solvent.[29,30] The $^3J_{C(6)-NH}$ values for (13) appeared to be roughly insensitive to temperature up to *ca.* 100°.[8] In the case of phenols [*e.g.* (4)] discussed earlier, $^3J_{C(6)-OH}$ could not be observed in [$^2H_6$]DMSO. For (4), the coupling between C(6) and OH persisted to *ca.* 90°. The magnitude of $^3J_{C(6)-OH}$ was not highly temperature dependent.

Certain formanilides were also studied, *e.g. o*-chloroformanilide. In many cases, two signals were observed for a given carbon, probably due to different amide conformations.[31] The ^3J values appeared to be similar to those of the analogous acetanilide. In 2,4,6-tribromoformanilide, however, only a single resonance per carbon was observed. The C(2) and C(6) signals were equivalent, and must reflect an average of various geometries ($^3J_{C(2)(6)-NH}$ is 2.8 Hz, in [$^2H_6$]DMSO). The conformer with CO–NH out-of-plane with respect to the aromatic ring must be a large contributor in view of steric effects and the powerful hydrogen bonding nature of the solvent. The large magnitude of ^3J relative to $^3J_{anti}$ and $^3J_{syn}$ is noteworthy.

With regard to the anilines (16)—(18), C(6) appeared to be equally coupled to both NH_2 protons, with $^3J_{C(6)-NH}$ 6.1—6.8 Hz. These coupling constants must reflect the average of *syn*- and *anti*-geometries (or in [$^2H_6$]DMSO, perhaps other geometries).[29,30] In order to obtain an 'averaged' ^3J value of *ca.* 6 Hz, $^3J_{anti}$ and $^3J_{syn}$ would have to be substantially larger than the values indicated for the closely related anilides. To test the effect of a single NH *versus* the NH_2 group, *o*-chloro-*N*-ethylaniline was studied. At —35° $^3J_{C(6)-NH}$ is *ca.* 6 Hz, similar to the primary anilines.



^{13}C N.m.r. spectrum of C(6) of juglone (26), illustrating the dissimilarity of the two spectral regions

Comments on ^{13}C *Splittings.*—The warning against the rather common assumption of first-order character in ^{13}C splittings by ^1H should be reiterated.[32] First-order character, of course, depends upon the separation of ^1H lines in relation to ^1H coupling constants, and not upon the large separation of ^{13}C from ^1H lines. A case in point is juglone (26), in which the two branches of the C(6) pattern (caused by the large $^1J_{C(6)-H(6)}$) are markedly dissimilar in appearance (Figure). The same ^1J moves one branch of the H(6) pattern near the H(5) and H(4) lines and moves the other branch further away. In the ^{13}C spectrum, one branch of the C(6) pattern, corresponding to H(6) lines perturbed by H(5) and H(4), is complex. The other branch is nearly first-order.[33]

Conclusions.—The effect of geometry on ^3J suggested by Chang is generally supported by the data for the phenols of this study. However, some question remains as to the exact nature of the dependence of ^3J on non-planarity (possibly small) of the interacting nuclei. A complex dependence of ^3J on dihedral angle, as found by Barfield *et al.* in allylic systems, may be present.[34] The anilides show some tendencies for a geometric effect, but the small differences between $^3J_{anti}$ and $^3J_{syn}$ and the variability of the data limit the usefulness of ^3J as an indication of geometry. The limited data presently available for anilines do not suggest a geometric dependence of ^3J.

EXPERIMENTAL

I.r. spectra were run on a Perkin-Elmer 621 instrument, using 1 mm NaCl solution cells. The solvent, $CHCl_3$, was dried over P_2O_5 and distilled immediately prior to use. The approximate concentration for the i.r. determinations was 10 mg ml^{-1} (further dilutions were made to observe spectral changes, if any). Other i.r. data were taken from the literature: (1), (3), (4), (6)—(8),[35] (12),[36] (16), (22).[37]

Noise-decoupled ^{13}C spectra (Table 2) and coupled spectra (Tables 1 and 3) were taken on a Varian XL-100 instrument operating at 25.2 MHz, and at normal probe temperature (*ca.* 32°) unless otherwise specified. The gated mode of decoupler operation was used for coupled spectra.[38] Usually 3—10 K of transients were collected using the maximum data points available for the spectral width (computer calculated error, ± 0.38 Hz in line position for 1.5 K spectral width for the data in Tables 1 and 3; ± 1.25 Hz for the data in Table 2). The approximate tipping angle was 55°. Solutions were made up to *ca.* 160 mg ml^{-1} solvent. The solvents were $CDCl_3$ or [$^2H_6$]DMSO were common commercial grades (usually Thompson, Packard, Inc.): $CDCl_3$ was treated by passage through activated alumina to remove vestiges of water; [$^2H_6$]DMSO was allowed to dry by standing over CaH_2, and filtered directly into a dried n.m.r. tube. For (21), a carefully purified and dried sample was used, and the n.m.r. solvent, $CDCl_3$, was freed from DCl, and distilled into a dried container under nitrogen with precautions about moisture, acid, *etc.* taken in the spectral run.

The identity of the couplings to OH, *etc.* was verified by treatment of the sample with trifluoroacetic acid (TFA), D_2O, or less frequently, DMSO, to see which line separations varied or were eliminated. The standard for the spectra was the centre line of the $CDCl_3$ pattern, taken as 76.9 p.p.m. from tetramethylsilane.[24] Low temperature calibration of the instrument were done using the ^1H line separations of methanol, and extrapolated to ^{13}C spectra using the same instrument settings (estimated accuracy $\pm 4°$).

Simulations of the spectra of juglone (26), and the C(6) or 2-XH couplings were done with the LAOCON3 program.[39] For the data in Table 3, the root mean square error was less than 0.15 for the iterations.[40] The computer generated plot of the simulated spectrum was superimposable on the original (± 0.1 Hz) well within the error in line position (± 0.38 Hz). The iterations were made leading the computer to approach solutions with signs of coupling constants similar to those found by Tarpley and Goldstein.[14]

Compounds (1), (3), (4), (7)—(9), (16), (23), and (26) were commercial products that were either distilled or recrystallized before use. Other compounds of this study were prepared by literature syntheses: (2), m.p. 92—93° (lit.,[41] 94—95°); (5), m.p. 116—117° (lit.,[42] 117°); (6), b.p. 94—99° at 15 mmHg (lit.,[43] 105—106° at 20 mmHg); (10), b.p. 134—136° at 15 mmHg (lit.,[44] 262—263° at 728 mmHg); (11), m.p. 85—87° (lit.,[45] 86.7°); (12), m.p. 90—91° (lit.,[46] 94°); (13), m.p. 96—98° (lit.,[47] 98—99°); (15), 217—220° (lit.,[48] 221°); (17), m.p. 127—128° (lit.,[49] 124—125°); (18), m.p. 116—118° (lit.,[50] 119—120°); (20), b.p. 104—105° at 22 mmHg (lit.,[51] 105° at 22 mmHg); (21), m.p. 127—128° (lit.,[52] 127—128°); (23) was prepared *in situ* by adding benzylamine to ethyl acetoacetate, drying over molecular sieve, and running the spectrum directly; (25), m.p. 78—80° (lit.,[53] 80—81°); (27), m.p. 60—62° (lit.,[54] 62—63°).

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