The resulting amber-colored viscous liquid was purified by column chromatography, using silica gel (EM 60) and eluting with hexane, chloroform–hexane mixtures, chloroform, and methanol. Fractions eluting with 50–70% chloroform–hexane contained **32**: IR (neat) 3150–3650 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum.[11] A few minor impurities were noted in the spectra. Attempts to recrystallize **32** failed. The estimated yield was 65%.

Methylation of Adducts. Adducts **13**, **14**, **28**, **29**, and **32** were methylated with dimethyl sulfate[25] and analyzed by GC/MS. The products were principally the dimethylated derivatives, contaminated by small amounts of decomposition byproducts resulting from the alkali and THF used in the derivatization procedure.[11] An exception was adduct **28**, which was nearly totally destroyed by the derivatization procedure. The mass spectra are discussed elsewhere.[11]

10-Hydroxy-10-benzyl-9(10*H*)-anthracenone (37). Benzyl chloride was reacted with AHQ^{2-} under the standard conditions; the product **37**, not being a phenol, was precipitated along with the AQ. The precipitate was washed several times with ether to solubilize **37** and leave behind AQ, which is relatively insoluble in ether. The combined ether washings were dried (Na_2SO_4) and evaporated to afford (59% yield) a pale-yellow solid (**37**), which turned pink upon standing in air: mp 144–146 °C, (hexane/toluene); IR (mull) 3200–3500 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(3-oxobutyl)-9(10*H*)-anthracenone (40A). A procedure identical with that used to prepare **37** was employed, the only exception was that the alkylating agent was methyl vinyl ketone (**38**). The crude product was purified by column chromatography, employing silica gel (EM 60) and eluting with hexane, 50:50 hexane–chloroform, chloroform, 50:50 chloroform–THF, and dioxane. The major portion of the product (54% yield) was eluted with the 50:50 chloroform–THF solvent mixture; **40A** was a colorless solid: mp 99–102 °C (methanol–water); IR (mull) 3150–3800 (OH), 1710, 1660 cm^{-1} (carbonyls); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(1-phenyl-3-oxopropyl)-9(10*H*)-anthracenone Hemiacetal (41B). Freshly distilled cinnamaldehyde (**39**) was reacted with AHQ^{2-} under the standard conditions. The workup, however, involved quenching the cool reaction mixture with dilute hydrochloric acid, under nitrogen, filtering in air, and separating the product from AQ by exhaustive extraction with ether, using a Soxhlet extractor. The ether solution was dried (Na_2SO_4) and evaporated to give **41B** in 38% yield: mp 201–205 °C (methanol); IR (mull) 3100–1800 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

Quinonemethide Transfer from 29 to AHQ^{2-}. A mixture of 1.5 g of 10,10-bis(4-hydroxybenzyl)-9(10*H*)-anthracenone (**29**) and 4 equiv of AHQ^{2-} was stirred at 60 °C for 4 h, cooled, exposed to air (until the red color disappeared), and filtered to remove the excess AQ. The filtrate was acidified and the precipitate collected by filtration. Analysis of the product mixture by ^1H NMR and GC/MS (after derivatization)[11] showed that the major components were starting material **29**, adduct **13**, and AQ; there was no evidence for the presence of monoalkylated anthrone adduct **28**.

Registry No. **1**, 39720-27-9; **2**, 60998-35-8; **3**, 45952-61-2; **4**, 5355-17-9; **7**, 79817-03-1; **8**, 22002-17-1; **12**, 79817-04-2; **13**, 79769-65-6; **14**, 79769-67-8; **15**, 79769-66-7; **16**, 79769-68-9; **17**, 79769-69-0; **19**, 623-05-2; **20**, 498-00-0; **22**, 79827-27-3; **23**, 79827-28-4; **24**, 79769-76-9; **25**, 79769-73-6; **27**, 90-44-8; **28**, 79769-71-4; **29**, 79769-72-5; **30**, 79769-70-3; **31**, 69544-83-8; **32** (R = Me), 79769-77-0; **37**, 78787-97-0; **38**, 78-94-4; **39**, 104-55-2; **40A**, 79769-74-7; **41B**, 79769-75-8; α-methylvanillyl alcohol, 2480-86-6; 1-(4-hydroxy-3-methoxyphenyl)-1-propanol, 6997-34-8; AHQ, 4981-66-2; AQ, 84-65-1; AHQ^{2-}, 35339-92-5.

(25) R. L. Whistler and M. L. Wolfrom, Ed., "Methods in Carbohydrate Chemistry", Vol. 2, Academic Press, New York, 1963, p 148.

Spectral Evidence of π–π Sandwiching of Aromatic Rings in 10-Benzylanthrones

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A detailed analysis of the ^1H and ^{13}C NMR spectra of several 10-benzylanthrones has shown that the benzyl substituent lies, at least to some extent, over the plane of the anthrone ring. This intramolecular sandwiching of π systems also occurs with selected C_{10}-allyl, alkyl ketone, condensed ring structures. Supporting evidence for sandwiching comes from UV, mass spectral, and X-ray studies.

Alkylation of anthrone and anthrahydroquinone affords C_{10}-substituted anthrones.[1] The latter were characterized by elemental analysis, preparation of derivatives, and spectral means. A portion of the spectral characterization involved nuclear magnetic resonance (NMR). The NMR data is presented here as confirming structural data and as evidence of an unusual conformational preference for the C_{10} substituents.

Results and Discussion

^1H NMR. Table I and II present the ^1H NMR spectral data for some selected anthrone derivatives. In Me_2SO solvent C_{10}-hydroxyl protons appeared at δ 6.3–6.5, indicative of dibenzyl alcohol structures,[2] and phenolic hydroxyl protons came at δ 8.5–9.8; both types exchanged with D_2O addition.

The diacetate derivative of **1**, namely **5**, displayed both aliphatic and aromatic acetate signals; an infrared spectrum also supported this conclusion. The diacetate **5** was one of only a few compounds in which the C_1 and C_8 protons were observed (downfield doublet) separate from the other anthrone aromatic protons.

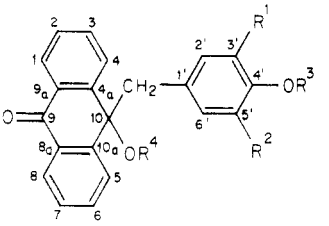
An interesting feature of the ^1H NMR spectra of 10-(*p*-hydroxybenzyl)anthrones was the peculiar upfield shifts observed for the C_{10}-aryl protons. Ordinarily, phenols show

(1) D. R. Dimmel and D. Shepard, accompanying article in this issue.

(2) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 4th ed., Wiley, New York, 1974, pp 181–278.

0022-3263/82/1947-0029$01.25/0

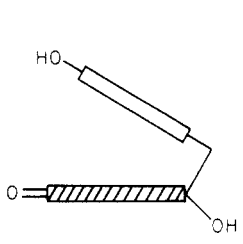
Table I. ^{1}H NMR Spectral Assignments for Some Quinonemethide–Anthrahydroquinone Addition Products[a,b]



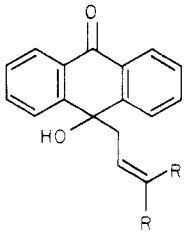
compd no.	1	2	3		4	5
solvent	Me_2SO	Me_2SO	Me_2SO	$CDCl_3$	$CDCl_3$	$CDCl_3$
R^1	H	Cl	OCH_3		H	H
R^2	H	Cl	H		H	H
R^3	H	H	H		Ac	Ac
R^4	H	H	H		H	Ac
phenolic OH	9.00_1^s	9.70_1^s	8.54_1^s	5.44_1^s		
aliphatic OH	6.40_1^s	6.52_1^s	6.46_1^s	2.98_1^s	3.00_1^s	
C_1-C_8 protons	7.4-8.1_8^m	7.4-8.1_8^m	7.4-8.1_8^m	7.2-7.9_8^m	7.2-8.1_8^m	7.2-7.6_8^m, $8.12_2^{d,J=8Hz}$
C_2' proton	$6.16_2^{d,J=9Hz}$	5.90_2^s	5.32_1^m	$5.42_1^{d,J=1Hz}$	$6.58_2^{d,J=9Hz}$	$6.63_2^{d,J=9Hz}$
C_6' proton			$6.18_1^{d,J=9Hz}$	$6.40_1^{d,J=9Hz}$		
C_3' proton	$5.68_2^{d,J=9Hz}$				$6.13_2^{d,J=9Hz}$	$6.15_2^{d,J=9Hz}$
C_5' proton			5.32_1^m	$5.66_1^{d\ of\ d}$		
$-CH_2-$	3.06_2^s	3.08_2^s	3.08_2^s	3.09_2^s	3.12_2^s	3.34_2^s
other			3.20_3^s	3.34_3^s	2.16_3^s	2.16_3^s, 2.19_3^s

[a] Superscript on the assignments refers to splitting pattern, s = singlet, d = double, t = triplet, q = quartet, m = multiplet; the subscript on the assignments refers to relative integrated area of the signal; the J value refers to the coupling constant. [b] All signals are reported in parts per million (δ) units, relative to Me_4Si.

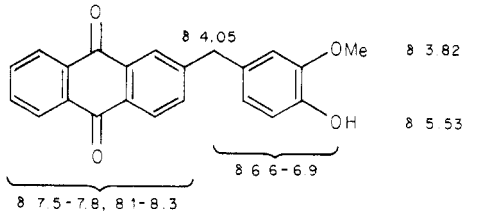
aryl protons in the δ 6.6-7.0 region;[2] however, most of the phenols reported in Tables I and II have phenolic aryl signals in the δ 5.3-6.6 region. These strong upfield shifts suggest that C_{10}-hydroxybenzyl units spend a portion of their time in magnetically shielded regions of the anthrone ring, i.e., sandwich structure **16**. Aryl methoxyl groups which were attached to the phenolic ring also showed upfield shifts (normally δ 3.9,[2] observed at δ 3.2–3.4).



16



17, R = H
18, R = Me

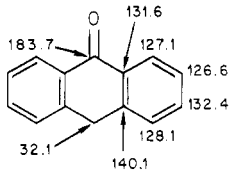


19

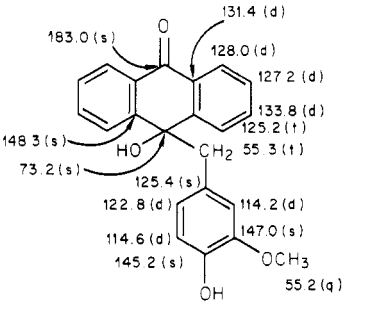
Nonphenolic C_{10} substituents, such as benzyl (**13**), alkyl ketone (**11**), and condensed structure **12**, also showed unusual upfield shifts in their ^{1}H NMR spectra. Deshpande[3] notes that allyl derivative **17** displayed vinyl signals in the δ 4.2–5.2 region, while the dimethyl analogue **18** had methyl signals as δ 0.79 and 1.34, instead of the expected δ 1.8 value.[2] Thus, the occurrence of sandwich conformations must be due to something more than hydrogen bonding between a phenolic hydroxyl group and the anthrone carbonyl group.

Structures which are geometrically forbidden from "sandwiching" because of angle strain would not be expected to show unusual upfield signals in their ^{1}H NMR spectra. This is the case for quinonemethide **10** and 2-vanillylanthraquinone **19**.[4]

^{13}C NMR. Table III and IV present the ^{13}C NMR data for several alkylated anthrones and anthrahydroquinones. The assignments presented in the tables were based on a comparison to the published spectra of anthraquinone[5-7] and anthrone **20**[5,8] and the observed shifts which occurred upon acylation of the C_{10}-hydroxyl group. A direct comparison of anthrone signals to those of structure **3** is given.



20



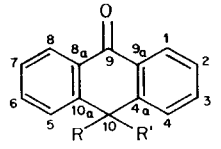
3

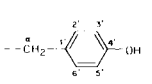
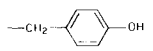
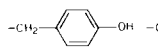
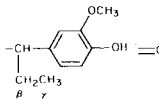
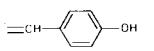
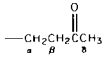
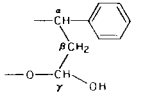
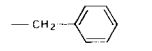
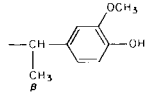
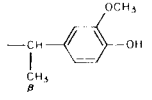
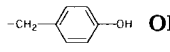
One would not expect substitution at C_{10} to have much effect on the chemical shift positions of the upper part of the anthrone skeleton. Indeed, all the alkylated products showed C_9 at 182.5 ± 1.0 (s), C_{8a}/C_{9a} at 131.0 ± 1.5 (s), C_1/C_8 at 128.0 ± 1.0 (d), C_2/C_7 at 126.7 ± 0.5 (d), and C_3/C_6 at 133.2 ± 1.0 ppm (d); these values correspond well

(3) R. J. Deshpande, *Indian J. Chem.*, **16B**, 389 (1978).

(4) T. J. Fullerton and B. I. Fleming, *Sven. Papperstidn.*, **83**, 396 (1980).
(5) O. R. Gottlieb et al., *Phytochemistry*, **16**, 735 (1977).
(6) Y. Berger and A. Castonguay, *Org. Magn. Reson.*, **11** 375 (1978).
(7) A. Arnone, G. Fronza, R. Modelli, and J. St. Pyrek, *J. Magn. Reson.*, **28**, 69 (1977).
(8) J. L. Marshall, A. M. Ihrig, and D. E. Miller, *J. Magn. Reson.*, **16**, 439 (1974).

Table II. ^{1}H NMR Assignments for Selected Anthrahydroquinone and Anthrone Addition Products[a]



compd no.	6	7	8	9	10	11	12	13	14	15
R										
R'	OCH_3	H		OH		OH		OH	OH	H
positions (ppm)							g	e		
C_1, C_8	7.5–8.0 (m)	7.95 (d)	8.29 (d)	7.4–8.0	7.4–8.3 (m)	7.4–8.1 (m)	8.2 (m)	7.2–8.0 (m)	7.3–8.3 (m)	7.2–8.1 (m)
C_2, C_7		7.4–7.6 (m)	7.84 (t)				7.3–7.8 (m)			
C_3, C_6			7.42 (t)							
C_4, C_5			7.88 (d)							
C_{10}		4.72 (t)[b]								4.58 (d)
C-α	3.05 (s)	3.12 (d)[b]	3.67 (s)	f	7.4–8.3 (m)	2.0 (m)	2.29 (d of d)	3.16 (s)	3.06 (q)	f
C-β				1.10 (m)			2.74 (d of t)		1.17 (d)	1.09 (d)
C-γ				0.55 (t)			3.80 (d of d)			
C-δ						1.82 (s)	6.34 (d)			
C_2'	6.18 (d)	6.28 (d)	6.13 (d)	5.34 (s)	7.24 (d)		6.1 (d)	6.08 (d)	5.42 (s)	5.81 (d)[c]
C_6'				6.19 (d)					6.20 (d)	6.43 (d)
C_3'	5.74 (d)	5.98 (d)	6.00 (d)		6.75 (d)		6.9 (m)	6.8–7.0 (m)	5.40 (d)	5.71 (d of d)[d]
C_5'				5.34 (d)						
C_4'									8.56 (s)	8.70 (s)
aryl OH	9.00 (s)	9.03 (s)	9.03 (s)	8.55 (s)	9.77 (s)				6.30 (s)	
aliph OH				6.34 (s)		6.34 (s)		2.62 (s)		
methoxy	3.36 (s)			3.24 (s)					3.33 (s)	3.40 (s)

[a] Values are in δ units relative to Me_4Si = 0; the J values for split signals are in the 7–9-Hz range unless noted otherwise; Me_2SO-d_6 solvent. [b] J = 5 Hz. [c] J = 1 Hz. [d] J = 1 and 8 Hz. [e] Run with $CDCl_3$ as the solvent. [f] Unable to locate this signal; it may be under a strong signal. [g] The α, β, and γ protons comprise a ABB'C system with apparent coupling constants for the major isomer of: AB = 13 Hz, AB' = 7 Hz, BB' = 13 Hz, BC = 6 Hz, and B'C = 0 Hz. The relationships and peak assignments for these protons and for the C_2', C_6' ortho aromatic protons were arrived at by decoupling techniques. The OH proton was not seen; there was a large amount of water in our Me_2SO solvent which may have masked the signal. A spectrum in $CDCl_3$ also did not pinpoint the OH signal. An IR spectrum clearly shows no CHO and the existence of an alcohol.

Table III. ^{13}C NMR Spectral Assignment for Some Quinonemethide-Anthrahydroquinone Addition Products[a]

compd no.	1	2	3	4	5
solvent	Me_2SO	Me_2SO	Me_2SO	$CDCl_3$	$CDCl_3$
R^1	H	Cl	OCH_3	H	H
R^2	H	Cl	H	H	H
R^3	H	H	H	Ac	Ac
R^4	H	H	H	H	Ac
C_1, C_8	127.7_l^d	128.0_l^d	128.0_l^d	128.4_l^d	127.7_l^d
C_2, C_7	126.8_l^d	127.0_l^d	127.2_l^d	127.0_l^d	126.8_l^d
C_3, C_6	133.6_l^d	133.6_l^d	133.8_l^d	133.4_l^d	133.1_l^d
C_4, C_5	125.3_l^d	125.6_l^d	125.2_l^d	126.2_l^d	123.8_l^d
C_{8a}, C_{9a}	130.8^s	131.1_m^s	131.4_{w-m}^s	132.6_w^s	130.7_w^s
C_{4a}, C_{10a}	148.0_m^s	(147.8_m^s)	$[148.3_m^s]$	147.2_w^s	143.4_w^s
C_9	182.4_w^s	182.6_w^s	183.0_w^s	183.4_w^s	181.8_w^s
C_{10}	73.0_m^s	72.6_m^s	73.2_m^s	73.8_w^s	79.0_w^s
$-CH_2-$	54.8_{w-m}^t	53.9_m^t	55.3_m^t	54.8_m^t	52.7_m^t
C_1'	125.1_m^s	128.4_m^s	125.4_m^s	131.3_w^s	130.2_w^s
C_2', C_6'	130.8_l^d	130.2_l^d	114.2_m^d, 122.8_m^d	131.4_l^d	131.7_l^d
C_3', C_5'	114.2_l^d	121.2_m^s	$[147.0_{w-m}^s]$, 114.6^d	120.6_l^d	120.3_l^d
C_4'	156.0_{w-m}^s	(147.8_m^s)	$[145.2_{w-m}^s]$	151.0_w^s	149.4_w^s
ester >C=O				169.8_w^s	168.7_w^s, 168.0_w^s
CH_3			55.2_m^q	21.0_{w-m}^q	21.6_m^q, 21.0_m^q

[a] Refer to Table I for the nomenclature and meaning of superscripts; the subscripts in this table refer to intensity of the signal; w = weak, m = moderate, and l = large, parentheses mean only one signal seen for supposedly two carbons, brackets mean assignments could be reversed.

with those of anthrone itself.

Replacement of one of the C_{10} hydrogens of anthrone with a benzyl group, i.e., compounds **7** and **15**, altered the chemical shifts of the lower portion of the anthrone ring in the following way: C_4/C_5 decreased from 128.1 to 125.6, C_{4a}/C_{10a} increased from 140.1 to about 143, and C_{10} increased from 32.1 to about 46 ppm. The downfield shifts can be explained by a positive polar effect exhibited by the substituent. The fact that the downfield shifts were not as large as would be calculated[9] and that C_4/C_5 experienced an upfield shift can be explained by a negative effect due to steric compression[9] as a result to the attached bulky substituent.

Placing both hydroxyl and alkyl substituents at C_{10} caused the following changes in the anthrone chemical shifts: C_4/C_5 decreased from 128.1 to about 125.5, C_{4a}/C_{10a} increased from 140.1 to about 147, and C_{10} increased from 32.1 to about 73 ppm. Acylation of the C_{10} hydroxyl, i.e., **5**, caused even more pronounced shifts, probably due to the acetate's greater withdrawing effect and greater bulk. The C_{10} carbon was shifted considerably upfield in the cyclized product **12**.

If the C_{10} substituent lacked symmetry and a sandwich structure (**16**) is assumed, one would expect that the two side rings of the anthrone skeleton would exhibit different chemical shifts. This was, indeed, observed for the α-substituted benzyl-substituted compounds **9**, **12**, **14**, and **15**, which contained an asymmetric carbon, and the quinonemethide **10**, which has cis/trans geometry. In several of these cases, the aromatic region was to complicated to make assignments, but the C_{4a} and C_{10a} carbons were observed as two distinct signals.

Interestingly, compound **3** showed a simple spectrum even though the C_{10} substituent here is dissymmetrical in a sandwiched conformation. This suggests that the π-complexed phenolic ring must undergo rapid bond rotations around the aryl-benzyl carbon such that the methoxyl group spends equal time over each side ring of the anthrone skeleton.

The chemical shift of the benzyl carbon of the C_{10}-benzyl substituent showed the expected variation[9] as a result of changes in the polar and steric effects of the other C_{10} substituent. The chemical shifts of the other carbons of the C_{10}-benzyl and alkyl substituents agree well with predicted values[9] and models of similar structure.

Other Spectral Data. If the two aromatic systems of the 10-(*p*-hydroxybenzyl)anthrones were acting independently, ultraviolet spectra should show γ_{max} at 270–280 ($\epsilon \approx 1500$) and 257 nm (ϵ 25 000), attributed to the phenolic and anthrone subunits.[10] However, the adducts **1–3** display a single γ_{max} at 272–278 nm (ϵ 12 000–13 000), indicative of phenol/quinone charge-transfer complexes.[11]

Additional evidence for ring sandwiching in the 10-(*p*-hydroxybenzyl)anthrones was provided by mass spectroscopy. The mass spectra showed the expected molecular ions and a prominent fragmentation which generated AHQ and the corresponding quinonemethide. This fragmentation was not observed when the phenolic hydroxyl group was derivatized to a methyl ether. A logical interpretation of this fragmentation is that the phenolic hydroxyl group resides somewhat close to the anthrone carbonyl group (structure **16**) and a hydrogen atom is transferred from the one to the other group during a conserted set of bond breakages. The mass spectra of the adducts and derivatized products are discussed in detail elsewhere.[12]

Fullerton[13] has obtained X-ray crystal structure of 10,10-divanillylanthrone, a methoxy-substituted analogue of **8**. He observes the folding over of vanillyl rings, both above and below the anthrone ring.

Conclusions

Spectral evidence suggests that there exists an attraction between π electrons of the anthrone ring and the π electrons of an attached C_{10}-benzyl or allyl substituent. This

(9) G. C. Levy, R. L. Lichter, and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed., Wiley-Interscience, New York, 1980, Chapters 2–4.

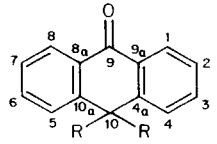
(10) A. Farrington, P. E. Nelson, and N. Vanderhoek, *Appita*, **33**, 248 (1979).

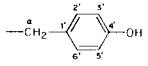
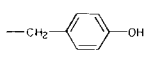
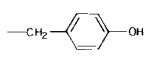
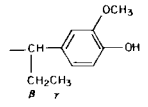
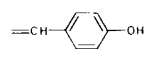
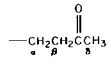
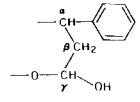
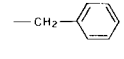
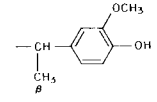
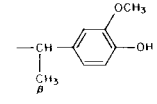
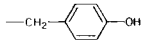
(11) J. March, "Advanced Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1977, pp 79–82, and references cited therein.

(12) D. R. Dimmel and D. Shepard, *J. Wood Chem. Technol.*, in press (1981).

(13) K. L. Brown and T. J. Fullerton, *Acta Crystallogr., Sect. B*, **36**, 3199 (1980).

Table IV. ^{13}C NMR Assignments for Selected Anthrahydroquinone and Anthrone Addition Products[a]



compd no.	6	7	8	9	10	11	12	13	14	15
R										
R′	OCH_3	H		OH		OH		OH	OH	H
positions (ppm)	*b*	*b*		*b*	*b*		*b*	*b,d*	*b*	*b*
C_1, C_8	127.0 (d)	128.4	129.0 (d)			127.4 (d)		127.7		
C_2, C_7	126.2 (d)	126.5	127.2 (d)			126.2 (d)		126.2		
C_3, C_6	132.8 (d)	132.2 (d)	133.7 (d)		{132.6 (d) {134.2 (d)	133.3 (d)		133.0 (d)		
C_4, C_5	124.7 (d)	125.6	126.4 (d)			125.6 (d)		125.7		
C_{8a}, C_{9a}		131.5 (s)	132.3 (s)		{129.3 (s) {131.2 (s)	129.7 (s)		131.0 (s)		
C_{4a}, C_{10a}	147.3 (s)	143.7 (s)	146.8 (s)	{144.5 (s) {144.7 (s)	{139.8 (s) {135.8 (s)	147.7 (s)	{147.6 {143.7	146.3 (s)	144.4 (s)	{143.3 (s) {142.0 (s)
C_9	181.5 (s)	182.6 (s)	183.1 (s)	181.7 (s)	183.0 (s)	182.6 (s)	182.5	182.4	181.2 (s)	182.9 (s)
C_{10}	72.5 (s)	43.3 (d)	50.0 (s)	74.7 (s)		70.5 (s)	87.2, 85.7[c]	73.8 (s)	74.4 (s)	49.6 (d)
C-α	54.4 (t)	46.6 (t)	48.7 (t)	63.0 (d)		{42.5 (t)	59.4, 61.2[c]	55.4 (t)	54.1 (t)	48.3 (d)
C-β				21.6 (t)		{37.7 (t)	37.5		15.4 (q)	17.3 (q)
C-γ				12.6 (q)		206.4 (s)	98.6, 100.0[c]			
C-δ						29.3 (q)				
C_1'		128.3 (s)	127.7 (s)					134.2 (s)		
C_2'	130.3 (d)	129.8	130.5 (d)	114.1 (d)	130.6 (d)			130.0	112.9 (d)	112.5 (d)
C_6'	130.3 (d)	129.8	130.5 (d)		130.6 (d)			130.0	120.8 (d)	120.3 (d)
C_3'	113.6 (d)	113.8 (d)	114.2 (d)	149.2 (s)	115.2 (d)			127.2	148.4 (s)	146.1 (s)
C_5'	113.6 (d)	114.6 (d)	114.2 (d)	114.1 (d)	115.2 (d)			127.2	113.7 (d)	114.3 (d)
C_4'	155.1 (s)	155.1 (s)	155.1 (s)	145.9 (s)	157.3 (s)			126.5	145.4 (s)	144.8 (s)
methoxy	49.3 (q)			55.0 (s)					54.7 (q)	55.5 (q)

[a] Values are in parts per million relative to $Me_4Si = 0$; Me_2SO-d_6 solvent; off-resonance observed splitting is given in the parentheses. [b] The lack of assignment for the peak position or splitting was due to the complexity of aromatic region, which was either a result of overlapping signals or disymmetry of the molecule or both. [c] This compound is a mixture of stereoisomers; the first value of the two assignments represents the more intense peak. [d] The aromatic assignments are quite tentative in this case.

attraction leads to conformations possessing sandwiched structures.

The observation of intramolecular $\pi-\pi$ complexing in these simple systems lends support to a proposed mechanism of action of anthraquinone during the pulping of wood. This proposal, which was arrived at simultaneously by several investigators, including this author, is that anthraquinone and/or its reduced form may promote pulping by complexing with wood constituents, followed by electron transfer between structures.

Experimental Section

The equipment used, procedures, and source of compounds studied can be found in the previous publication.[1]

Registry No. 1, 79769-65-6; 2, 79769-66-7; 3, 79769-67-8; 4, 79769-68-9; 5, 79769-69-0; 6, 79769-70-3; 7, 79769-71-4; 8, 79769-72-5; 9, 79769-73-6; 10, 69544-83-8; 11, 79769-74-7; 12, 79769-75-8; 13, 78787-97-0; 14, 79769-76-9; 15, 79769-77-0.

The Tertiary Amide as an Effective Director of Ortho Lithiation

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The tertiary amides *N,N*-diethylbenzamide (1) and *N,N*-diisopropylbenzamide (3) give the ortho-lithiated species 2 on treatment with *sec*-BuLi/TMEDA or *n*-BuLi/TMEDA, respectively, at −78 °C. Lithiation of 1 followed by reaction with either methyl iodide, ethyl iodide, benzophenone, acetone, benzaldehyde, or trimethoxyborane–hydrogen peroxide gives the expected ortho substituted product. Intramolecular competition between the diethylamido and chloro, methoxyl, sulfonamido, (dimethylamino)methyl, or oxazolino functions in ortho- and para-substituted benzamides establishes the tertiary amido group to be more effective in directing metalation than any noncarboxamide functional group under the prescribed conditions. Complimentarity of directing effects is observed with the chloro and methoxyl groups in the meta-substituted diethylbenzamides but not with the methyl group. The secondary amide is found to have a directing ability comparable to the tertiary amide with *sec*-BuLi/TMEDA at −78 °C in THF although the yields are low. ^{13}C NMR chemical shifts are particularly useful for the structural assignments which are confirmed chemically by lactonization of some products. A labeling study with *N,N*-diisopropyl-2,6-dideuteriobenzamide suggests that lithiation of the ortho position of 3 is direct and not the result of rearrangement of an initially formed α-aza anion. Control of metalation at the ortho or benzylic position by proper selection of the organolithium base is illustrated for *N,N*-diisopropyl-*p*-toluamide. The value of the tertiary amide for control of ortho lithiations and regiospecific aromatic substitutions is noted.

The formation of regiospecifically ortho metalated aromatics by deprotonation, illustrated for substituted benzenes in Scheme I, is a reaction of synthetic value and mechanistic interest. A classic and seminal case is the reaction of anisole with *n*-butyllithium to give 2-lithioanisole reported by Gilman and by Wittig over 40 years ago.[1] Early developments, initially by Gilman and Hauser with subsequent contributions from many other laboratories, expanded the scope of these metalations to a variety of substituted aromatic and olefinic systems.[1,2]

In a recent, excellent review of this area, Gschwend and Rodriguez suggested a hierarchical order of substituent directing abilities which corresponds to the order shown in Scheme I with the more activating group to the left in the series. This order was defined for coordinatively unsaturated metalating agents and, as Gschwend and Rodriguez point out, the relative ability of a substituent to direct a metalation can generally be interpreted in terms of an interplay of inductive and complexation effects.[2]

Until a few years ago the substituents which were regarded as useful directors for ortho metalations were those which would sensibly be considered to be inert to the strong organometallic bases used for deprotonation. Recently, however, it has been reported that groups which might be thought to be susceptible to nucleophilic addition by the organolithium bases can retain their structural integrity and function as effective ortho directors. Discoveries that oxazolines[3] and tertiary amides[4] are capable of directing lithiation to positions adjacent to these substituents have been reported and quickly adopted for synthetic purposes.[5-7] The oxazoline has been placed between the sulfonamide and secondary carboxamide in the directing order of Gschwend and Rodriguez.[2] Recently we[8] and Meyers and Lutomski[9] have communicated ob-

(1) H. Gilman and R. L. Bebb, *J. Am. Chem. Soc.*, **61**, 109 (1939); H. Gilman and F. J. Webb, *ibid.*, **62**, 987 (1940); G. Wittig and G. Fuhrmann, *Chem. Ber.*, **73**, 1197 (1940); see H. Gilman and J. W. Morton, Jr., *Org. React.*, **8**, 258 (1954), for a review of the early literature.

(2) H. W. Gschwend and H. R. Rodriguez, *Org. React.*, **26**, 1–360 (1979).

(3) H. W. Gschwend and A. Hamdan, *J. Org. Chem.*, **40**, 2008 (1975); A. I. Meyers and E. D. Mihelich, *ibid.*, **40**, 3158 (1975).

(4) P. Beak and R. A. Brown, *J. Org. Chem.*, **42**, 1823 (1977).

(5) For cases involving the oxazoline, see A. Padwa, A. Ku, A. Mazzu, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **98**, 1048 (1976); M. S. Newman and S. Kumar, *J. Org. Chem.*, **43**, 370 (1978); T. D. Harris, B. Neuschwander, and V. Boekelheide, *ibid.*, **43**, 727 (1978); L. D. Vecchia and I. Vlattas, *ibid.*, **42**, 2649 (1977); A. Padwa and A. Ku, *J. Am. Chem. Soc.*, **100**, 2181 (1978); A. I. Meyers and R. A. Gabel, *Tetrahedron Lett.*, 227 (1978); C. R. Ellefson, *J. Org. Chem.*, **44**, 1533 (1979); S. Djuric, T. Sarkar, and P. Magnus, *J. Am. Chem. Soc.*, **102**, 6885 (1980), and references cited therein.

(6) For cases involving the tertiary amide: (a) S. O. deSilva, J. N. Reed, and V. Snieckus, *Tetrahedron Lett.*, 5099 (1978); (b) S. O. deSilva and V. Snieckus, *ibid.*, 5103 (1978); (c) S. O. deSilva, I. Ahmad, and V. Snieckus, *ibid.*, 5107 (1978); (d) S. O. deSilva, M. Watanabe, and V. Snieckus, *J. Org. Chem.*, **44**, 4802 (1979); (e) S. O. deSilva, I. Ahmad, and V. Snieckus, *Can. J. Chem.*, **57**, 1598 (1979); (f) M. Watanabe and V. Snieckus, *J. Am. Chem. Soc.*, **102**, 1457 (1980).

(7) Other groups which might be susceptible to nucleophilic substitution but retain their identity and direct ortho lithiation in the presence of a second activating group include (a) the meta alkoxy substituted imine [F. E. Ziegler and K. W. Fowler, *J. Org. Chem.*, *41*, 1564 (1976)] and (b) *m*-chloro nitrile (ref 2).

(8) P. Beak and R. A. Brown, *J. Org. Chem.*, **44**, 4463 (1979).

(9) A. I. Meyers and K. Lutomski, *J. Org. Chem.*, **44**, 4464 (1979).

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