Substituent effects on the chemical shifts of the bridge protons of benzonorbornenes

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The substituent effects on the chemical shifts of the C_9 bridge protons in a series of 6-substituted benzonorbornees and benzonorbornadienes, and on those of the C_2 protons in 5-substituted 2-indanols, were investigated. They were linearly correlated with the modified Hammett relationship $\tau_{\rm R} - \tau_{\rm H} = \rho(\sigma_{\rm m} + \sigma_{\rm p})/2$. The ρ values obtained from the *anti*- C_9 protons in the bornenes and bornadienes were slightly but significantly larger than those from the corresponding sym protons, whereas no significant difference was observed between the ρ values obtained from sym-9-benzonorbornenols and the indanols. The larger ρ_{anti} values were explained in terms of a stereospecific electronic interaction between the π -electron system of the benzene ring and the orbital system of the bridge carbon. In addition, it was shown that the above modified Hammett relationship gives generally a good agreement with the substituent effects on the aliphatic constituents of benzocyclenes and analogous compounds.

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INTRODUCTION

Williamson and his co-workers (1) reported that the chemical shifts of the methyl protons in p-substituted ethylbenzenes (I) and the protons H_A and H_B in p-substituted phenylhexachlorobicyclo-(2.2.1) heptenes (II) were correlated with the Hammett relationship $\tau_{\rm R} - \tau_{\rm H} = \rho \sigma$, and that all the ρ values obtained were of the same order of magnitude. No compounds of unusual character were found in the bicyclo(2.2.1) heptene series. On the other hand, some remarkable features have been reported in the nuclear magnetic resonance (n.m.r.) spectra of the bridge protons of norbornenyl and norbornadienyl derivatives and their benzo analogues (2-6).



¹All correspondence concerning this paper should be addressed to this author. First is the stereospecific long-range spin coupling between the bridge proton and the ring *endo*-ethano or vinyl protons *anti* to it (2, 3, 5).² Secondly, in norbornene and benzonorbornene, the *anti* bridge proton signal appears at a higher field than does the *syn* proton signal (6). To comprehend these results, a stereospecific orbital interaction between the π -electron system of the ring carbons and the orbital system of the bridge carbon has been discussed with reference to its pronounced participation in the solvolysis reactions of 7-norbornenyl derivatives (3).

Recently, we investigated the acetolysis reactions of *anti*- and *syn*-6-substituted 9benzonorbornenyl p-bromobenzenesulfonates (9, 10)³ and found a significantly large difference in the substituent effects for the two series.

The range of reactivity from 6-methoxy to 6-nitro $(k_{\rm OCH_3}/k_{\rm NO_2})$ in the *anti* series was as great as 386 000 at 77.6°, and the substituent effects were correlated with

²A similar phenomenon was observed in the bicyclo(3.2.1)octene-2 system (7). For a review of long-range spin couplings, see ref. 8.

³The numbering system used in this paper for benzonorbornene is shown in Fig. 1.

good precision by the modified Hammett relationship log $(k_{\rm R}/k_{\rm H}) = \rho_{anti}(\sigma_m^+ + \sigma_p^+)/2$, where ρ_{anti} is -5.10. The implications of the correlation have been discussed in terms of the solvolysis involving the simultaneous participation by the *m* and *p* positions of the aromatic ring (homobenzylic conjugation), so that both σ_m^+ and σ_p^+ contribute to the stability of the transition state, as shown below (9). On the other hand, the corresponding rate range for the *syn* series was only 43. This indicates the absence of such participation in this series.



This paper deals with the substituent effects on the chemical shifts of the C₉ protons of 6-substituted benzonorbornene derivatives. The purpose of this study was to gain insight into the electronic nature of the ground state of compounds of this type, which exhibits very great π -participation.

RESULTS AND DISCUSSION

The following series of benzonorbornenyl derivatives were investigated: benzonorbornenes (III), benzonorbornadienes (IV), *anti-9-benzonorbornenols* (V), and *syn-9-benzonorbornenols* (VI).

The anti- (H_a) and syn-C₉ protons (H_s) in the n.m.r. spectra of the parent compounds III and IV (R = H) were assigned by proton spin-decoupling and deuteration methods (6). Similar assignments can be made for their 6-substituted derivatives. The



spectra of the 6-methoxy derivatives of III and IV are shown in Figs. 1 and 2, respectively, as representative examples. The signal of H_a (a doublet of triplets) in III appears at a higher field than that of H_s (a doublet of quintets), whereas the signal of H_s (a doublet of triplets, broader) in IV appears at a higher field than that of H_a (a doublet of triplets, narrower). The protons H_s and H_a in the V and VI series are easily assigned (6, 9a, 9b), but the signals of H_a in VI generally become broader because of spin couplings to the hydroxyl protons. The chemical shifts of H_s and H_a in these series of compounds, along with the geminal coupling constants $J_{\mathbf{H}_{s},\mathbf{H}_{a}}$ for III and IV, are summarized in Tables I and II.

The n.m.r. study of 2-indanol was recently reported (11). If the strained bond angles in V and VI are not considered,



5-substituted 2-indanols (VII) are one of the most suitable reference compounds

TABLE I

Chemical shif	ts (at	infinite	dilution)	and	coupling	constants	(c.p.s.)	of the	C ₉ proto	ns in
benzon	orborr	ienes (II	I) and be	enzon	orbornadi	enes (IV)	in carbo	n tetrac	chloride	

		III			IV	
R	$ au_{\mathrm{H}_{s}}$	$ au_{\mathrm{H}a}$	$J_{\mathrm{H}_{s},\mathrm{H}_{a}}$	$ au_{\mathrm{H}s}$	$ au_{\mathrm{H}a}$	$J_{\mathrm{H}_{s},\mathrm{H}_{a}}$
CH ₃ O	8.310	8.560	8.4	7.86_{0}	7.78_{5}	6.9
CH ₃	8.33_{0}	8.57_{0}	8.4	7.86_{0}	7.79_{0}	7.0
Н	8.28_{5}	8.54_{5}	8.5	7.81_{0}	7.75_{0}	7.0
Cl	8.281	8.52_{9}	8.8	7.81_{2}	7.73_{8}	7.0
Br	8.28	8.53_{8}	8.8	7.80_{7}	7.75_{1}	7.0
CH ₃ CO	8.265	8.47_{5}	8.7			
CN	8.25_{3}	8.467	9.0	7.78_{7}	7.67_{5}	7.1
NO_2	8.20_{5}	8.42_{5}	9.0			· · · · · · · · · · · · · · · · · · ·

INAMOTO ET AL.: SUBSTITUENT EFFECTS



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1187

TABLE II Chemical shifts (at infinite dilution) of the C_9 protons in *anti*- and *syn*-9benzonorbornenols (V and VI) in carbon tetrachloride

R	$\boldsymbol{\tau}_{\mathrm{H}_{\mathcal{B}}}~(\mathrm{V})$	$ au_{\mathrm{H}_a}$ (VI)
CH₃O	6.28	6.00
CH₃ H	$6.31 \\ 6.26$	$\begin{array}{c} 6.01 \\ 5.97 \end{array}$
Cl	6.25	5.94
NO_2	6.18	5.84

among the non-bridged benzocyclenes for the study of the significant nature of benzonorbornene systems. Various derivatives of VII were synthesized and the chemical shifts of their C_2 protons (H_i) were determined (Table III).

TABL	E III
Chemical shif dilution) of th in 2-indano carbon tet	ts (at infinite le C_2 protons ls (VII) in rachloride
R	$ au_{\mathrm{H}_{i}}$
$\begin{array}{c} CH_{3}O\\ C_{2}H_{5}\\ H\\ CH_{3}CO\\ NO_{2} \end{array}$	$5.44 \\ 5.43 \\ 5.40 \\ 5.36 \\ 5.30$

In compounds III-VII, the effect of a substituent would be transmitted concurrently from the substituent to the *m* and pposition, where the aliphatic ring is fused to the benzene ring, and thereupon separately to the C_9 protons through the two aliphatic C-C bonds. Therefore, it seems, a priori, reasonable that the substituent effects on these types of protons are concerned with half the sum of both the *m* and p substituent constants. Thus, Hammett plots of the chemical shifts, $\tau_{\rm R} - \tau_{\rm H}$, versus $(\sigma_m + \sigma_p)/2$ resulted in good linear relationships.⁴ The ρ values obtained and the statistical analyses are summarized in Table IV.

The C_9 protons and H_i correspond, in a classical sense, to the methyl protons in I

and the protons H_A and H_B in II. The chemical shifts of the methyl protons and H_{A} and H_{B} should be correlated with σ^{0} , because it is considered that only the inductive effect acts upon the protons. The ρ values for these protons were very similar to each other: -0.13_3 , -0.12_6 , and -0.13_0 p.p.m., respectively (if the halogen substituents were neglected: -0.14_0 , -0.13_6 , and -0.12_8 p.p.m., respectively), as predicted from the same location of the protons. These ρ values are of the same order of magnitude as those obtained for the series of III-VII (Table IV). This fact also supports the idea that the use of half the sum of both the m and p substituent constants is preferable for benzocyclenes. As further examples, the chemical shifts of the methyl protons in 5- and 6-substituted 2-methylbenzoazoles (VIII) (13, 14) and of the methylene protons in 1-substituted 3,4methylenedioxybenzenes (IX) (15) were



plotted against $(\sigma_m + \sigma_p)/2$, giving a good linear relationship.⁵

The most salient feature of the present results is that all the ρ values for H_a are slightly but definitely larger than those for the corresponding H_s, which are of nearly the same magnitude as the ρ value for H_i, beyond the probable error. Therefore, a similar tendency was observed between the substituent effects on the chemical shifts and the rates of the acetolysis reactions. According to the Kirkwood–Westheimer equation (16), the Hammett ρ values in the same reaction under the same conditions are proportional to $\cos \theta/r^2$ (17, 18), where

⁴The substituent constants were taken from the table of Ritchie and Sager (12).

⁵Although, for VIII, the plots were made against σ in the references (13, 14) cited (*m* and *p* were defined for the nitrogen atom), the deviations were similar to those in the plots made against ($\sigma_m + \sigma_p$)/2. The deviation might be attributed to the different atoms (nitrogen and Y) in the transmission route from the *m* or *p* positions of the substituent to the methyl group.

INAMOTO ET AL.: SUBSTITUENT EFFECTS

TABLE IV

		<i>p</i> valu	es (p.p.m.)			
Compound	Proton	- <i>ρ</i>	r*	s†	n‡	с§
III	H,	$0.123\ , \P$	0.956	0.0104	8	0.024
	-	0.122,**	0.951	0.0109	8	0.021
		0.125, ¶, ††	0.970	0.0111	6	0.021
		0.123¶,**,††	0.970	0.0111	6	0.018
	Ha	0.161,¶	0.946	0.0153	8	0.014
		0.160,**	0.949	0.0155	8	0.010
		$0.165 , \P, \dagger \dagger$	0.992	0.0070	6	0.006
		0.163¶,**,††	0.999	0.0020	6	0.003
IV	H	$0.117 , \P$	0.890	0.0203	6	0.041
		0.121,**	0.914	0.0182	6	0.029
		$0.123 , \P, \dagger \dagger$	0.895	0.0292	4	0.030
		0.130¶,**,††	0.925	0.0254	4	0.027
	Ha	$0.151 \ , \P$	0.916	0.0223	6	0.025
		0.153¶,**	0.920	0.0220	6	0.022
		0.167 , $\P, \dagger \dagger$	0.962	0.0227	4	0.019
		0.176¶,**,††	0.988	0.0130	4	0.014
V	H_s	0.130	0.958	0.0153	5	0.021
		0.128^{**}	0.958	0.0150	5	0.018
		$0.134 , \dagger \dagger$	0.965	0.0134 ·	4	0.019
		0.132**,††	0.966	0.0169	4	0.015
VI	Ha	$0.189\ $	0.982	0.0139	5	0.019
		0.187**	0.989	0.0105	5	0.014
~		$0.193 \ , \dagger \dagger$	0.987	0.0157	4 -	0.017
		0.191**,††	0.995	0.0091	4	0.011
VII	$\mathbf{H}_{\mathbf{i}}$	0.123	0.966	0.0159	5	0.018
-		0.149^{**}	0.979	0.0127	5	0.016

o values (n n m)

Correlation coefficient.

The magnetic anisotropy effects of the H_a proton of III, -0.016 for the H_a proton of IV, and -0.016 for the H_a proton of IV, and -0.016 for the H_a proton of IV, and -0.016 for the H_a proton of IV.

The halogen substituents were neglected in the calculation.

 θ is the angle between the direction of the bond dipole in a substituent and the direction joining the center of the dipole to a reaction center, and r is the distance between the center of the dipole and the reaction center. From a CENCO-Petersen molecular model, it can be seen that the values of $\cos \theta/r^2$ for the syn protons are larger than those for the anti protons; thus, it was expected that ρ_{syn} would be larger than ρ_{anti} . On the contrary, the results showed that the ρ values for H_a were always larger than those for H_s.

One might be inclined to interpret this contradiction on the basis of the variation of the ring-current effect with the substituent. However, an interpretation of this kind can be eliminated as follows. Suppose that H_s is located at or near the border of the shielding-deshielding surface of the adjacent benzene ring and H_a is in the deshielding region, as shown below (the CENCO-Petersen model suggests this).



The ring-current effect on H_s and its substituent effects should be very small. On the other hand, H_a should be less shielded (τ decrease) if an electron-donating group such as a methoxyl group is substituted, which increases the ring-current effect. If an electron-attracting group such as a nitro group, which decreases the ring-current effect, is introduced, H_a should be more shielded (τ increase). Therefore, the ρ value expected for H_a should be smaller than that for H_s on the assumption that, in the absence of the ring-current effect, the Hammett ρ values (a measure of the sensitivity of the substituent effect) for H_a and H_s are equal to each other, and are in turn similar to the ρ value for the methyl protons in ethylbenzenes. Suppose H_a is on the border of the shielding-deshielding surface and H_s is in the shielding region; then H_s is more shielded (τ increase) as electron-donating substituents are introduced, whereas it is less shielded when electron-attracting substituents are introduced (τ decrease). Therefore, in this case also, the ρ value for H_s should be larger than that for H_a . However, the present values showed an opposite tendency.

Consequently, a novel type of electronic transmission to the *anti* protons from the benzene π -orbital system was considered.⁶ The stereospecific, long-range spin coupling between the bridge proton and the vinyl protons *anti* to it, which was observed in the 7-substituted norbornene and related systems, has been accounted for by the assumption that a unique type of conjugation arises from the interaction of both p orbitals of the double bond and the small

backside lobe of the sp³ orbital of the bridge carbon used in the bonding with the *anti* hydrogen (2, 3, 8). The same argument can be used to explain most reasonably the present results. The absence of such a factor in H_s would give a ρ value similar to that in the model compound, H_i.



Although not directly related, the present results do not conflict with the mechanism used for the explanation of the solvolytic behavior of 7-benzonorbornenyl p-bromobenzenesulfonates (9, 19) and with that suggested for the polarographic reduction potential of 7-benzonorbornenones (20). They do, however, demonstrate that a kind of electronic interaction occurs even in the ground state. In the electron spin resonance study of semidiones derived from bicyclo-(2.2.1) heptanes and bicyclo(2.2.2) octanes and related compounds (21), the hyperfine splitting constants of the *anti* protons were larger than those of the corresponding syn protons. This observation might be related to our results.

EXPERIMENTAL⁷

Measurements of Spectra

The n.m.r. spectra of the compounds of series III and IV were determined with a Varian HA-100 spectrometer operating at 100 Mc.p.s. in the frequency-swept and tetramethylsilane-locked mode.

⁷The melting points were measured by capillary and are corrected. The boiling points are uncorrected. All the compounds used in the present study were shown by vapor-phase chromatographic analysis to be homogeneous.

TABLE V 6-Substituted benzonorbornenes

	De 'll' en e inte			Carbon,	%	Hydroge	en, %
Substituent	(mm), °C	$n_{\rm D}$ (°C)	Formula	Calculated	Found	Calculated	Found
Br Cl CH₃ CH₃O CN	$\begin{array}{c} 110 \ (5) \\ 86.5 \ (5) \\ 105{-}106 \ (17) \\ 115{-}116 \ (11) \\ 121 \ (5) \end{array}$	$\begin{array}{c} 1.5894 \ (23) \\ 1.5655 \ (25) \\ 1.5440 \ (26.5) \\ 1.5518 \ (28.5) \\ 1.5687 \ (23) \end{array}$	$\begin{array}{c} C_{11}H_{11}Br\\ C_{11}H_{11}Cl\\ C_{12}H_{14}\\ C_{12}H_{14}\\ C_{12}H_{14}O\\ C_{12}H_{11}N\end{array}$	$59.21 \\73.89 \\91.08 \\82.72 \\85.17$	59.1273.9590.8682.7485.03	$\begin{array}{c} 4.97 \\ 6.21 \\ 8.92 \\ 8.10 \\ 6.55 \end{array}$	$5.12 \\ 6.21 \\ 9.02 \\ 8.15 \\ 6.63$

1190

⁶From the statistical analysis it could not be determined which substituent constant, σ or σ^0 , correlated better with the present data (Table IV). This implies that the electronic transmission proposed here is not so large as to be shown by the substituent constants.

INAMOTO ET AL.: SUBSTITUENT EFFECTS

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		6 Hyc	Found Calculat
		Carbon, 9	Calculated
V I	leir acetates		Formula
IABLE	2-Indanols and th	Recrustallization	solvent*

			i i i		Carbon,	%	Hydrogen	%
5-Substituent	2-Substituent	Melting point, °C	Kecrystallization solvent*	Formula	Calculated	Found	Calculated	Found
CH ₃ CO	НО	71–72	ц	C13H1.03	74.97	74.97	6.86	6 61
CH ₃ CO	0C0CH ₃	64.5 - 65.5	HE	C13H14O3	71.54	71.80	6.47	6.57
C_2H_5	HO	76.5-77.5	Н	C11H140	81.44	81.62	8.70	8.74
CH3C00	0C0CH3	72-73	Э	C ₁₃ H ₁₄ O ₄	66.65	66.84	6.02	6.09
CH ₃ O	HO	72–73	- HE	$C_{10}H_{12}O_{2}$	73.14	73.21	7.37	7.44
NO_2	HO	62-69	M	C ₉ H ₉ O ₃ N	60.33	60.03	5.06	5.32
NO_2	0C0CH ₃	86.5 - 87.5	H	C ₁₁ H ₁₁ O ₄ N	59.72	59.73	5.01	4.94
*E = ether, H = 1	u-hexane, M = methanol	, and HE = a mixture of n -	hexane and ether.	-				

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1191

The calibration was performed by a Hewlett-Packard HP-5212A electronic counter. The spectra of the compounds of series V-VII were recorded on a Varian A-60 spectrometer, the calibration of which was checked by the usual side-band technique with a Hewlett-Packard HP-200CD audio-oscillator and an HP-521C electronic counter.

Since the use of cyclohexane as the solvent was inadequate for the present study, the samples were dissolved in carbon tetrachloride (about 5%) containing about 1% tetramethylsilane as an internal reference to measure the respective proton signals at successively diluted concentrations. The reproducibility of the chemical shifts and the coupling constants was about 0.01 p.p.m. and 0.2 c.p.s., respectively. The chemical shifts obtained at several concentrations were extrapolated to infinite dilution. Most of the solutions showed no significant dilution shift in this concentration range, but for the compounds of the series VI a somewhat larger dilution shift (about 0.06 p.p.m.) was observed. The low solubility of the 6-nitro derivative of VI and the 5-nitro derivative of VII in the solvent demanded the use of the chemical shift of a saturated solution only.

Preparation of Benzonorbornadiene and Its Derivatives

Benzonorbornadiene (22) and its 6-substituted derivatives (IV, R = H, CH₃O, CH₃, Cl, or Br) (23) were synthesized. 6-Cyanobenzonorbornadiene, m.p. 65-66°, was obtained by treatment of 6-bromobenzonorbornadiene with cuprous cyanide in boiling dimethylformamide, using a standard procedure.

Anal. Calcd. for $C_{12}H_9N$: C, 86.20; H, 5.43. Found: C, 85.90; H, 5.58.

Benzonorbornene (22) and its 6-acetyl, 6-chloro, and 6-nitro derivatives (III, R = H, $CH_{3}CO$, Cl, or NO₂) (24) were obtained by standard methods. Catalytic reductions of the above benzonorbornadienes gave the other 6-substituted benzonorbornenes used in this study. The properties and analyses of the new benzonorbornenes thus prepared are summarized in Table V. All of the anti- and syn-9benzonorbornenols (V and VI) were prepared by previously reported methods (9a). 6-Methyl-syn-9benzonorbornenol had m.p. 86.5-87.5°.

Anal. Calcd. for C₁₂H₁₄O: C, 82.72; H, 8.10. Found: C. 82.59; H. 8.27.

Preparations of 2-Indanol Derivatives

It is known that Friedel-Crafts acylations of indanes yield predominantly β -substituted compounds without the accompanying isomerization and disproportionation of the cycloalkyl groups (25). Therefore, the preparations of 5-substituted indanols (VII) were carried out by acylation of 2-indanol acetate with acetyl chloride and aluminium chloride in carbon disulfide.8 The positions of the acyl groups that were introduced were confirmed by the

n.m.r. signal patterns of the aromatic protons, which showed two protons as a multiplet representing the AB part of an ABK system, and a proton as a second-order quartet of an ABK system. Vaporphase chromatographic analyses of 5-acetyl-2-indanol acetate, after recrystallization, indicated the presence of less than 0.5% of the 4-substituted isomer. Under our conditions, the retention times of the 5-isomers were considerably longer than those of the 4-isomers. 5-Acetyl-2-indanol was obtained by acidic hydrolysis of purified 5-acetyl-2-indanol acetate.

The Baeyer-Villiger oxidation of 5-acetyl-2-indanol acetate with m-chloroperbenzoic acid in dichloromethane yielded 5-acetoxy-2-indanol acetate, the hydrolysis of which with lithium aluminium hydride followed by methylation of the phenolic hydroxyl group with dimethyl sulfate gave 5methoxy-2-indanol. Wolff-Kishner reaction of 5acetyl-2-indanol acetate gave 5-ethyl-2-indanol (cf. ref. 27).

Treatment of 2-indanol acetate with nitric acid acetic anhydride yielded a mixture of 4- and 5-nitro-2-indanol acetates, which were distinguishable by vapor-phase chromatography. Pure 5-nitro-2-indanol acetate was obtained by subjection of the mixture to a combination of recrystallization and elution chromatography on alumina. Acid hydrolysis of the acetate gave pure 5-nitro-2-indanol.

The properties and analyses of the 2-indanol derivatives prepared here are listed in Table VI.

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⁸For a standard procedure, refer to Brown et al. (26).

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