

Basicity of the Carbonyl Group. Part 13.¹ 4-Substituted Camphors as Models for Transmission of Polar Effects. A Calorimetric, Infra-red and ¹H NMR Study

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In a series of 4-substituted camphors, in which the substituent, X, varies from ethyl through hydrogen to nitro, we have shown that the enthalpies of complexation, with BF₃ in dichloromethane, which cover a range of 14.5 kJ mol⁻¹ correlate well with $r > 0.99$ with polar substituent constants with the sensitivity ρ^* ca. 8.

IR spectroscopy of the free ketones and the more polar BF₃ complexes indicates that the latter are ca. 1.44 times more sensitive to substituent variation.

Complexation occurs at both sites when X = OAc and only at the ketone when X = CO₂Me.

We rationalise the smaller sensitivity of the protons to substituent-induced ¹H shift displacement when in the *E*-complexed form to the electron-attracting effect of complexation that leads to diminished electronic screening. The ⁴J_{H₃exo-H₅exo} coupling is diminished by complexation which enhances hyperconjugation between the C(3)-H_σ and the carbonyl p orbitals to the detriment of back lobe C(3)-H_{3exo}-C(5)-H_{5exo} σ-σ overlap. A number of chemical shift and coupling correlations are reported.

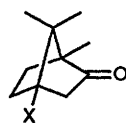
Bicyclic compounds have played an important role in the development of the theory of substituent effects within the field of linear free energy relationships (LFER).² The rigidity of the hydrocarbon framework maintains a constant structural relationship between the substituent and the reaction centre; this allows efficient analysis of transmission models of substituent influences by field/inductive effects.

By means of 4-substituted bicyclo[2.2.2]octanecarboxylic acids Roberts and Moreland³ established a series of purely 'polar' σ' constants,²⁻⁴ free from steric and resonance effects. A number of other ring systems have been investigated, and in order to obtain a greater sensitivity to polar effects the groups of Grob⁵ and Palacek⁶ have measured the pK_a or reactivities of 4-substituted quinuclidines; these have formed the basis for a new set of 'polar' effect constants σ_f⁷. Comparison of the basicity of quinuclidines and the corresponding pyridines enables a measure to be made of the effects of resonance in these systems.⁷ Recently a comprehensive listing of substituent parameters in diverse environments and their interpretation has appeared.⁸

In the present work we have examined the effect of substituents on the Lewis basicity of the carbonyl group by means of a study of the enthalpy of complexation of a selected number of 4-substituted camphors with boron trifluoride. We also

enables one to maintain the distance between substituent and carbonyl about as small as possible compatible with the absence of a direct steric interaction. In previous studies⁹ we have determined the sensitivity of the carbonyl basicity ρ* to 'polar' effects as measured by σ*.¹⁰ The presence of two σ bonds between the carbonyl and the substituent enables one to predict, with the aid of a coefficient of attenuation of 2.8,¹⁰ an effect sufficiently great to be measured with precision. We have previously made a detailed study of the effect of complexation on the carbonyl stretching vibration of the 4-substituted camphors.¹¹ In companion studies we have recently measured enthalpies of complexation of boron trifluoride¹² with nitriles,¹³ aminocyclohexenone derivatives¹⁴ and we have also analysed basicity scales of non-protogenic solvents in terms of interaction with *inter alia* boron trifluoride.¹⁵

Since one of the aims of the present work is a study of correlations of 'polar' effect constants and physicochemical properties of camphors, we have considered our analysis in terms of four different scales of substituent effects. These are (a) σ', the first scale based on a bicyclic system and despite supplementation, still incomplete;^{3,4} (b) σ*, defined by Taft,¹⁰ in order to compare our earlier results;⁹ in the present work substituent variation takes place on an sp³-hybridised carbon (we have also used the values relative to -CH₂X groups); (c) σ₁, defined originally by Taft¹⁶ and refined by Exner,^{17a} Taft¹⁸ and Charton;¹⁹ (d) σ_f⁷ due to Grob⁵ and based on pK_a values of quinuclidines; this scale deviates significantly from σ₁. The values used are given in Table 1.



- 1; X = C₂H₅
- 2; X = CH₃
- 3; X = H
- 4; X = C≡CH
- 5; X = OCOCH₃
- 6; X = CO₂CH₃
- 7; X = Br
- 8; X = Cl
- 9; X = NO₂

report on the IR and ¹H NMR spectra of the free and complexed ketones. The inherent rigidity of the bicyclic skeleton

Experimental

Dichloromethane, a good inert solvent of ketone-BF₃ complexes used in the calorimetric and spectroscopic studies, was purified by the usual method.²⁰

IR spectra of both free and complexed ketones were recorded as moderately dilute solutions in dichloromethane using a Perkin-Elmer 457 spectrophotometer. The spectrometer was purged with dry nitrogen in order to remove irregularities in the 1800-1600 cm⁻¹ region of the absorption bands on account of

Table 1 Polar substituent parameters used in this study

Substituent	σ^a	σ^{*c}	σ_1^f	$\sigma_1^{g,h}$
C ₂ H ₅	-0.020	-0.115	-0.01	0.03
CH ₃	-0.013	-0.100	-0.01	0.11
H	0	0	0	0
C≡CH	—	0.774 ^d	0.29	1.64
OCOCH ₃	—	0.700 ^e	0.38	2.12
COOCH ₃	0.473 ^b	0.758 ^d	0.32	1.70
Br	0.736	1.000	0.47	2.65
Cl	0.739	1.050	0.47	2.51
NO ₂	1.058	1.69 ^d	0.67	3.48

^a Reference 4. ^b Value for CO₂Et group. ^c Value for CH₂X group; reference 12 unless otherwise stated. ^d I. Koppel, M. Karelson and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, 1973, **10**, 497. ^e J. P. Soumillon and A. Bruylants, *Bull. Soc. Chim. Belg.*, 1969, **78**, 169. ^f M. Charton, *Prog. Phys. Org. Chem.*, 1981, **13**, 119. ^g Reference 5.

Table 2 Stoichiometry of complexes between boron trifluoride and 4-substituted camphors

4-Substituent	Moles BF ₃ /moles base ^a
C ₂ H ₅	1.00
CH ₃	0.99
H	0.99
C≡CH	0.98
OCOCH ₃	1.85 ^b
CO ₂ CH ₃	1.01
Br	0.99
Cl	0.99
NO ₂	0.95

^a Moles of gas absorbed by a 0.6 mol dm⁻³ solution of base (298.15 K, 1 atm). ^b Precipitation occurs at a ratio ~ 0.9–1.0 (insolubility of the 2:1 complex); this prevents a more complete saturation.

water vapour. After complete recording (4000–250 cm⁻¹) of the spectrum under standard conditions (± 5 cm⁻¹), the 1800–1600 cm⁻¹ region was examined in detail as follows: (a) the optical path length was adjusted to obtain a transmission of 30–50%; (b) the abscissa scale was expanded to 5 cm⁻¹ cm⁻¹; (c) a slow scan speed, of 50 cm⁻¹ min⁻¹; (d) the size of spectral slit was adjusted to 2 cm⁻¹; (e) calibration of this region was carried out with the aid of water absorption bands.²¹

The wavelength was measured at both the absorption maximum and at the centre of the band at half optical density. As the ketonic absorption band is practically symmetric the two wavenumbers correspond to better than 0.2 cm⁻¹ (some spectra recorded on more dilute solutions, 0.2 mol dm⁻³, show no detectable differences, except for compound **5**). For this keto-acetate, superposition of the keto and ester absorptions gives a single, broad, asymmetric band. The keto-ester **6** gives two close maxima. We have separated the two bands considering them symmetric, in order to correct the small displacement of the maxima toward each other on account of the superposition. After complexation the carbonyl bands of **5** and **6** were sufficiently separated that no interference occurs. On account of the uncertainties of reading and of the standards we estimate the precision of the complexed carbonyl band measurements to be ± 0.5 cm⁻¹ (except for **5**).

Results and Discussion

Calorimetry and Characterisation of the Complexes.—Both the apparatus used and the method of measurement have been described elsewhere in detail.²² More concentrated solutions (0.6 mol dm⁻³) have, however, been used because complexes of weaker bases tend to dissociate close to the saturation point for

solutions that are 0.3 mol dm⁻³ in base. The Lewis acid is injected into 3 cm³ of solution in 8–12 increments. Reaction is total and the enthalpy of complexation is calculated for each injection by means of the formula given, eqn. (1), where Q

$$\Delta H^\circ = \frac{Q}{n} \quad (1)$$

represents the quantity of heat evolved in the complexation and n is the number of moles of BF₃ injected into the measurement cell.

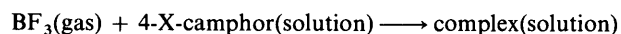
The stoichiometry of the complexes (Table 2) is obtained by saturation of the solution contained in the calorimeter. The total number of moles of BF₃ introduced is corrected for the gas in excess with that which has not reacted.

We have also measured the number of moles of BF₃ absorbed by each base by observation of a break in the slope of the graph, i.e. the heat of reaction vs. number of moles of added BF₃.²³ By these two methods the uncertainty in the stoichiometry varies between 2–5% according to the tendency of the complex to dissociate; this depends on the strength of the base and its concentration. The values given in Table 2 are the mean of 2–4 determinations. The complexes formed are of the type 1:1 except for the acetate **5**, where a 2:1 complex is apparently formed, although precipitation, (which starts at a ratio of ca. 0.9:1 BF₃ to 4-acetylcampor) hinders complete saturation of the solution. In the case of the keto-ester **6**, steric hindrance undoubtedly prevents complexation of the ester function.

We have attempted to form a BF₃ complex of *tert*-butyl acetate, a structural analogue of **5**; we were unable to obtain a complex on account of decomposition of the substrate into acetic acid accompanied also by the evolution of a gas, presumably isobutene. In addition, an attempt to form a complex from methyl pivalate, considered as an analogue of **6**, led neither to any detectable heat of complexation nor to any other reaction. This is entirely in accord with the proposal of a unique complexation site, the keto group, in **6**.

¹H NMR spectra were recorded on a Varian A60 spectrometer, with the solvent as an internal reference; substrates were 0.6 mol dm⁻³ in CH₂Cl₂ at 35 °C. Chemical shifts were transferred to the δ (TMS = 0) scale, taking the δ value of CH₂Cl₂ = 5.30 ppm. In previous studies^{9,20} we have shown that the error so introduced is less than the general reproducibility of the instrument (ca. 1 Hz).

Enthalpies of Complexation by Boron Trifluoride.—The enthalpies of complexation ΔH° given in Table 3 correspond to the reaction:



The substituent effects on ΔH° were relatively weaker than in our earlier studies; accordingly, the number of measurements has been increased in order to reduce the confidence limit. The range of $\Delta\Delta H^\circ$ embraces ca. 15 kJ mol⁻¹ (Table 3) with a 95% confidence limit of 0.23 kJ mol⁻¹ on average.

We have examined linear relationships between the enthalpies of complexation and four scales of 'polar' effects, using eqn. (2), where ΔH_x° and ΔH_x° represent enthalpies of complex-

$$\Delta H_x^\circ = \rho^i \sigma^i + \Delta H^\circ \quad (2)$$

ation for camphor itself and the various 4-substituted derivatives. We correlate the enthalpies of complexation with σ scales (which are free-energy derived) in the entirely reasonable belief that any entropy changes are constant throughout the series. A referee has commented that the calorimetric enthalpies involve an endothermic desolvation and an exothermic complexation.

Table 3 Enthalpy of complexation formation between 4-substituted camphors and boron trifluoride^a

4-Substituent	$-\Delta H^\circ/\text{kJ mol}^{-1b}$	n^c
C ₂ H ₅	78.19 ± 0.20	19
CH ₃	77.48 ± 0.19	19
H	77.23 ± 0.20	25
C≡CH	71.96 ± 0.32	11
OCOCH ₃	71.17 ± 0.28	14
CO ₂ CH ₃	71.71 ± 0.25	15
Br	67.73 ± 0.13	14
Cl	68.20 ± 0.29	11
NO ₂	63.65 ± 0.22	14

^a Measurements carried out at 298.15 K on 0.60 mol dm⁻³ solutions of 4-substituted camphors in dichloromethane. ^b Uncertainties are at the 95% confidence level. ^c Number of measurements.

Table 4 Correlations between enthalpies of complexation and polar substituent constants

σ^i	ρ^{ia}	$-\Delta H^\circ_b$	r^c	s.d. ^d	n^e
σ'	13.00 ± 0.31	77.55	0.9986	0.33	7
σ^{*f}	8.11 ± 0.44	77.11	0.9900	0.75	9
σ_1	20.18 ± 0.86	77.71	0.9936	0.60	9
σ_1^\dagger	3.88 ± 0.20	78.06	0.9911	0.71	9

^a Slope with standard deviation. ^b Intercept. ^c Correlation coefficient. ^d Standard deviation of fit. ^e Number of data points. ^f Values for CH₂X groups were used.

We agree and feel that complexation effects are overwhelming. Differential solvation effects (free *vs.* complexed base) have been shown to be small and nearly constant;¹² studies in two different solvents, dichloromethane and nitrobenzene, and comparisons with gas-phase data give very similar trends. Results of the correlations are shown in Table 4. As in the IR study (*vide infra*) good linearity is obtained; σ' constants lead to better correlations and standard deviations. Some linear relationships between the enthalpy of complexation of carbonyl compounds and SbCl₅ with σ^* and σ_1 have been reported by Olofsson.²⁴ However, the intervention of resonance and steric effects limits the generality of these results.

Our previous studies enable us to calculate the sensitivity of the 'polar' effect ρ^* to the enthalpy of complexation of ketones CH₃COR by BF₃.^{9a} We have obtained $\rho^* = 15.65 \pm 0.92$ kJ mol⁻¹ taking into account only ketones CH₃COCH₂X that possess groups CH₂X with neighbouring steric hindrance ($E_s = 0.34 \pm 0.15$). Transmission of the 'polar' effect in camphors, indicated by $\rho^* = 8.11$, is diminished by a factor of *ca.* 1.83 compared to straight chain ketones.

IR Spectroscopy.—IR spectroscopy offers both a good means of characterisation of the type of complex formed, and a method for the study of electronic effects of substituents.^{17b,25} The results obtained for the carbonyl stretching vibration (wavenumber and widths at half-height) as well as the bands that appear as the result of complexation are given in Table 5. Results of an IR study of a number of 4-substituted camphors in a variety of solvents and in the gas phase are available in the literature.¹¹

The decrease in the wave number of the carbonyl stretching vibration as a consequence of complexation provides direct information for the location of BF₃ on the carbonyl oxygen.²⁶ For the complexes of **5** and **6**, we also note a slight increase in ν_{CO} of the ester function; this confirms the keto group as the site of complexation. The spectrum of the 2:1 complex of the acetate **5** (see Experimental section), which is insoluble in CH₂Cl₂, has

not been recorded. The solution of the complex of **5**, prepared with exactly 1 mole BF₃ per mole of base (4-acetylcampfor) yields a white precipitate which is already present as the acid:base ratio approaches *ca.* 0.9. We interpret this result in terms of an equilibrium between the 1:1 and 2:1 complexes as the acid:base ratio approaches unity, with precipitation of the slightly soluble 2:1 complex.

The width at half-height of the carbonyl absorption bands, which are virtually independent of substituent pattern, confirms our assignments. The bands, ν_{CO} , of the free ketones have a width of 12 ± 1 cm⁻¹ whereas those of the 1:1 complex, ν_{COBF_3} , are 17 ± 1 cm⁻¹, except for **3**. The corresponding absorptions of the esters are rather broader.

The studies of Forel *et al.*²⁷ on the acetone-BF₃ complex enables identification of the new bands that appear as a result of complexation. The broad intense band, sometimes a multiplet, observed at *ca.* 1200 cm⁻¹ corresponds to ν_{BF_3} of the complex Me₂CO·BF₃, which appears at 1212(¹⁰B) and 1163(¹¹B) respectively. In a similar manner, the two frequencies located near 860 and 840 cm⁻¹ are assigned to ν_{OBF_3} by analogy with the values 878(¹⁰B) and 858(¹¹B) cm⁻¹. We also observe two bands in the regions 620–655 and 610–625 cm⁻¹ that arise from coupling between the bicyclic skeleton and BF₃; the corresponding bands are situated at 694 and 623 cm⁻¹ in the complex of Forel *et al.*²⁷

In Table 5 we note a marked variation in carbonyl stretching frequency of both the free ketone, ν_{CO} , and the complex, ν_{COBF_3} , as well as in their difference. We have calculated the linear regression parameters, eqn. (3), where σ^i refers to the polar

$$\nu^x = \nu^0 + \rho^i \sigma^i \quad (3)$$

effect constant, ρ^i (the sensitivity of the vibrator), ν^x the wavenumber of the substituted compound and ν^0 the ordinate with respect to the calculated origin. We characterise the quality of the regression by both the correlation coefficient and its standard deviation. In Table 6 are the results obtained with four polar effect scales and the relevant frequencies ν_{CO} and ν_{COBF_3} .

The precision of the correlation obtained demonstrated that the polar effect alone acts to influence ν_{CO} and ν_{COBF_3} , to the exclusion of other effects. For ν_{CO} the standard deviation of the correlation is of the same order of magnitude as the precision of the spectrometer, whereas it is a little larger for ν_{COBF_3} on account of the broader absorption band.

Brownlee and Topsom²⁵ have remarked on the paucity of reliable literature data for correlations of IR frequencies and σ^i constants for an aliphatic series.* Our data suggests that pertinent results will be produced from studies in bicyclic systems where 'purely spectroscopic' substituent effects are highlighted; rotational isomerism and non-bonded interactions are minimised and there is only a weak mass effect because the rigid structure already has an important mass.

We have shown that the frequency ν_{COBF_3} is more sensitive than ν_{CO} to substitution at C(4) by a factor of 1.44, whatever the scale employed.† This we attribute to the greater polarity of the complexed carbonyl with respect to the free carbonyl.²⁸ This interpretation invokes dipole-dipole interactions with the substituent and relates to electric field effects; it may also be couched in terms of a greater electron demand of the $>\text{C}=\overset{\oplus}{\text{O}}-\text{BF}_3$ group.

The results in Table 4 permit recalculation of the spectro-

* In response to a referee we do not feel that ν_{CO} has any differential entropy component in the present series 1–9.

† An exception exists for the correlations with σ_1 which give a factor of 1.37.

Table 5 Characteristic IR frequencies of 4-substituted camphors and their boron trifluoride complexes (ν/cm^{-1} , in CH_2Cl_2)

4-Substituent	$\nu_{\text{CO}} (w_{\text{CO}})^a$	$\nu_{\text{COBF}_3} (w_{\text{COBF}_3})^a$	$\Delta\nu (\Delta w)$	New bands in the complex ^e				
C_2H_5	1737.7(13.0)	1656.5 (18.0)	81.2 (-5)	1200 (s,b)	865 (m)	840 (s)	655 (m)	625 (m)
CH_3	1737.5 (12.0)	1658.0 (17.0)	79.5 (-5)	1215, 1200, 1175 (s,b)	858 (m)	840 (s)	648 (m)	620 (m)
H	1737.1 (11.5)	1656.7 (13.0)	80.4 (-1.5)	1200, 1185 (s,b)	860 (m)	840 (s)	645 (s,b)	600 (w)
$\text{C}\equiv\text{CH}$	1744.9 (12.0)	1666.7 (18.0)	78.2 (-6)	1208 (s,b)	868 (m)	843 (s)	650 (m)	625 (m)
OCOCH_3	$1742.4 \pm 1.5 (19.5)^b$	$1674.4 \pm 1.5 (18.0 \pm 1)^d$ $1744.0 \pm 1.0 (16 \pm 3)$ ester	72 ± 5 -4 ± 5 ester	1210 (s,b)	865 (w)	840 (s)	640 (w,b)	615 (w)
COOCH_3	1744.4 (12.0) ^c 1723.2 (17.0) ester	1666.8 (16.5) 1731.6 (23.5) ester	77.6 (-4.5) $-8.4 (-6.5)$ ester	1205 (s,b)	870 (w)	840 (s)	640 (m,b)	610 (sh)
Br	1747.8 (11.0)	1671.9 (16.5)	75.9 (-5.5)	1205 (s,b)	858 (w)	840 (s)	635 (m,b)	610 (m)
Cl	1748.7 (10.5)	1672.9 (17.0)	75.8 (-6)	1208 (s,b)	860 (m)	840 (s)	640 (m)	613 (m)
NO_2	1754.3 (11.0)	1681.7 (16.0)	72.6 (-5)	1215 (s,b)	863 (w)	835 (s)	620 (sh)	610 (s)

^a ν = wavenumber; w = bandwidth at half of the maximum optical density; ν taken at the maximum and at the centre of the band at half the maximum optical density are within 0.2 cm^{-1} unless otherwise stated, w are reproducible to 0.5 cm^{-1} . ^b Asymmetric band ($\nu_{\text{max}} = 1743.1 \text{ cm}^{-1}$; $\nu_{\text{OD}/2} = 1741.6 \text{ cm}^{-1}$) due to the superposition of the ketone and ester band at *ca.* 1745 and 1740 cm^{-1} , respectively. ^c The true maxima are at 1743.9 and 1724.8 cm^{-1} . True values obtained by separation into two distinct bands. ^d Corresponding to the 1:1 complex in equilibrium with the 2:1 complex. The superposition of the bands accounts for the uncertainties. ^e Study restricted to regions free from solvent and KBr attack by BF_3 .

Table 6 Correlation of the carbonyl frequencies^a with polar substituent constants

	σ^i	$\rho^{i,b}$	$\nu^{\text{O}c}$	r^d	s^e	n^f
ν_{CO}	σ'	15.21 ± 0.56	1737.47	0.9966	0.61	7
	σ^{*g}	9.55 ± 0.42	1738.01	0.9942	0.72	8
	σ_1	23.93 ± 0.97	1737.47	0.9951	0.67	8
	σ_1^{\ddagger}	4.61 ± 0.24	1737.07	0.9923	0.84	8
ν_{COBF_3}	σ'	21.96 ± 1.01	1657.03	0.9948	1.09	7
	σ^{*g}	13.75 ± 0.74	1657.71	0.9914	1.28	8
	σ_1	34.65 ± 1.73	1656.90	0.9926	1.19	8
	σ_1^{\ddagger}	6.64 ± 0.38	1656.34	0.9901	1.37	8

^a The value for compound **5** was omitted (see Text). ^b Slope with standard deviation. ^c Intercept. ^d Correlation coefficient. ^e Standard deviation of the fit. ^f Number of data points. ^g Values for CH_2X groups used.

Table 7 Displacements of proton chemical shifts of 4-substituted camphors brought about by complexation with boron trifluoride

Proton	Chemical shift displacement (ppm)	Position relative to complexed function
$\text{H}_{3\text{exo}}$	0.73 ± 0.05	α
$\text{H}_{3\text{endo}}$	0.77 ± 0.05	α
$\text{C}(10)\text{H}_3$	0.215 ± 0.015	β
$\text{C}(8)\text{H}_3$	0.07 ± 0.02	γ
$\text{C}(9)\text{H}_3$	0.10 ± 0.02	γ

scopic parameters from σ^i constants or *vice versa*. The frequency of the carbonyl could not be accurately determined in the case of **5**. We can now calculate $\nu_{\text{CO}} = 1746.0 \pm 1.1 \text{ cm}^{-1}$ and $\nu_{\text{COBF}_3} = 1669.3 \pm 1.7 \text{ cm}^{-1}$ for this compound.

¹H NMR Effects.—Complexation-induced changes in the chemical shifts and coupling constants of the rigid 4-substituted camphors are deduced from the data given in Table 7. Of the geminal C(3) protons, $\text{H}_{3\text{exo}}$ is readily distinguished by virtue of its long-range (⁴J) coupling with $\text{H}_{5\text{exo}}$ in an ABX system. The

coupling constants ${}^2J_{\text{H}_{3\text{exo}}-\text{H}_{3\text{endo}}}$ and ${}^4J_{\text{H}_{3\text{exo}}-\text{H}_{5\text{exo}}}$ are generally directly measurable. With one exception $\text{H}_{3\text{exo}}$ absorbs at lower field than $\text{H}_{3\text{endo}}$; in the case of the acetate **5** a preferred rotameric conformation may be responsible for the inversion of chemical shifts. Of the three methyl groups, the sharpest signal is assigned to the C(10) protons and the *anti* C(9) methyl protons are more deshielded than their *syn* C(8) counterparts.²⁹

Chemical shifts of the C(3) protons of the free ketones are mainly influenced by the polar effect of the substituent; however the magnetic³⁰ or field anisotropy³¹ can introduce irregularities, especially for the acetate **5**, in which $\delta_{\text{H}_{3\text{endo}}} > \delta_{\text{H}_{3\text{exo}}}$. The most likely reason for this is a rotamer of the C(4) substituent in which the acetate carbonyl is close to $\text{H}_{3\text{endo}}$.

For the remaining compounds the chemical shifts of the C(3) methylene protons are given by eqns. (4) and (5). The chemical

$$\delta_{\text{H}_{3\text{exo}}} = (1.43 \pm 0.27)\sigma_1 + 2.05 \quad (4)$$

$$r = 0.9098, s = 0.18, n = 8 \text{ (no OAc)}$$

$$\delta_{\text{H}_{3\text{endo}}} = (1.03 \pm 0.14)\sigma_1 + 1.85 \quad (5)$$

$$r = 0.9510, s = 0.09, n = 8 \text{ (no OAc)}$$

shifts of the C(10) methyl protons give a good correlation with polar effects. Here, eqn. (6), a slight deviation exists for the CO_2Me and Br substituents.

$$\delta\text{-C}(10)\text{H}_3 = (0.17 \pm 0.04)\sigma_1 + 0.84 \quad (6)$$

$$r = 0.8487, s = 0.03, n = 8 \text{ (no OAc)}$$

No satisfactory correlation exists for the chemical shifts of the protons $\text{C}(8)\text{H}_3$ and $\text{C}(9)\text{H}_3$. Here the effectively constant $\Delta\delta$ values of 0.10–0.14 ppm for most of the substituents are significantly less than for those with anisotropic character *i.e.* OAc, CO_2Me and NO_2 which can have preferred rotamers.

Complexed ketones. Complexation involves displacement towards low field of all the ¹H NMR signals;²⁶ the effects are essentially constant when X varies, except for the acetate **5**. This anomaly, also observed in the calorimetry and IR experiments, is discussed in these sections.

The ¹H chemical shift displacements, $\Delta\delta$, brought about by

Table 8 ^1H NMR Chemical shifts and coupling constants of 4-substituted camphors and their boron trifluoride complexes in dichloromethane as 0.6 mol dm $^{-3}$ solutions^a

X (BF ₃ complex)	$\delta\text{H}_{3\text{exo}}$	$\delta\text{H}_{3\text{endo}}$	$\delta\text{C}(10)\text{H}_3$	$\delta\text{C}(9)\text{H}_3$	$\delta\text{C}(8)\text{H}_3$	χ	2J	4J
Et	1.92	1.92	0.85	0.80	0.67	<i>a</i>	<i>b</i>	<i>b</i>
Me	2.70	2.73	1.08	0.92	0.75	<i>a</i>	<i>b</i>	<i>b</i>
	1.96	1.83	0.83	0.80	0.67	1.00	19.0	2.2
	2.73	2.63	1.05	0.90	0.75	1.08	21.8	1.1
H	2.30	1.80	0.83	0.92	0.75	<i>a</i>	17.0	2.5 ^c
	3.00	2.54	1.05	1.01	0.87	<i>a</i>	22.0	1.6 ^c
C \equiv CH	2.35	2.13	0.88	0.95	0.85	2.25	18.2	2.7
	3.08	2.92	1.10	1.05	0.90	2.37	21.5	1.6
OAc	2.37	2.76	0.88	0.57	0.76	2.02	18.0	2.9
	2.92	3.27	1.03	1.03	0.87	2.15	20.3	2.5
CO ₂ Me	2.68	2.05	0.85	0.95	0.78	3.70	18.3	3.0
	3.38	2.82	1.07	1.07	0.85	3.75	21.8	3.1
Br	2.63	2.48	0.97	0.97	0.87	—	18.0	3.0
	3.28	3.17	1.17	1.05	0.92	—	21.4	1.9
Cl	2.52	2.38	0.92	0.93	0.83	—	18.0	3.2
	3.19	3.10	1.13	1.05	0.90	—	21.3	2.0
NO ₂	3.17	2.48	0.93	1.07	0.88	—	17.8	3.6
	3.84	3.20	1.13	1.18	0.95	—	21.4	2.8

^a Chemical shifts are in ppm; coupling constants *J* in Hz (see Experimental section). ^b Non-analysable. ^c Spectrum of deceptive simplicity. ^d ABXY system; the measured couplings are thus apparent couplings.

complexation are given in Table 8. Values of $\Delta\delta$ decrease with increasing proton-carbonyl group separation.²⁶ For $\text{H}_{3\text{exo}}$ and $\text{H}_{3\text{endo}}$ the differences $\Delta\delta$, 0.04 ppm and for $\text{C}(8)\text{H}_3$ and $\text{C}(9)\text{H}_3$, both 0.03 ppm, are attributable to through-space effects, anisotropic or electric field in origin, due to the carbonyl group as a consequence of complexation. The reproducibility of $\Delta\delta$ for each type of methyl is a confirmation of our assignments. The high $\Delta\delta$ value for $\text{C}(10)\text{H}_3$ is due to its proximity to the carbonyl group.

The complexed ketones also show a correlation between the $\text{H}_{3\text{exo}}$ and $\text{H}_{3\text{endo}}$ chemical shifts and polar effect constants. These are given by eqns. (7) and (8). The slopes are smaller than

$$\delta_{\text{H}_{3\text{exo}}} = (1.28 \pm 0.25)\sigma_1 + 2.80 \quad (7)$$

$$r = 0.9001, s = 0.17, n = 8 \text{ (no OAc)}$$

$$\delta_{\text{H}_{3\text{endo}}} = (0.91 \pm 0.14)\sigma_1 + 2.64 \quad (8)$$

$$r = 0.9458, s = 0.09, n = 8 \text{ (no OAc)}$$

for the free ketones, although the standard deviations are too high to be definitive.

For these protons better correlations are observed for the $\text{H}_{3\text{exo}}$ proton chemical shift in the free and complexed ketone, and likewise for the $\text{H}_{3\text{endo}}$ protons. We thus obtain eqns. (9) and (10). Displacement of these protons is thus less sensitive to the

$$\delta_{\text{H}_{3\text{exo}}}(\text{complexed}) = (0.904 \pm 0.066)\delta_{\text{H}_{3\text{exo}}}(\text{free}) + 0.94 \quad (9)$$

$$r = 0.997, s = 0.029, n = 8$$

$$\delta_{\text{H}_{3\text{endo}}}(\text{complexed}) = (0.883 + 0.102)\delta_{\text{H}_{3\text{endo}}}(\text{free}) + 1.00 \quad (10)$$

$$r = 0.993, s = 0.031, n = 8$$

effect of substituents when in the complexed form. This is readily explained in terms of the electron-attracting effect of the complexation; this increases the polarity of the C-H bond, making it less polarisable. In turn this diminishes the electronic screening around the proton and the chemical shifts are less sensitive to the substituent effects.

For the keto-acetate **5** we observed an abnormal sequence of chemical shifts; differences with respect to the free ketone are smaller in this case. The $\Delta\delta$ values (in ppm) in this case are $\text{H}_{3\text{exo}}$, 0.55; $\text{H}_{3\text{endo}}$, 0.51; $\text{C}(10)\text{H}_3$, 0.15; $\text{C}(8)\text{H}_3$, 0.06; $\text{C}(9)\text{H}_3$, 0.11. However, the protons of the acetate methyl undergo a

deshielding of 0.13 ppm whereas those of the methoxycarbonyl group of **6** only experience a deshielding of 0.05 ppm despite the separation from the site of complexation and the nature of the intervening bonds being similar.³²

The deshielding of the protons α to the ketone is less than the mean value observed for the other compounds (*vide supra*); this is due to an exchange, probably rapid, of BF_3 between the two carbonyl groups, as observed in the IR spectrum.

Configuration of the complexes. The chemical shift displacements induced on the methylene protons adjacent to the carbonyl are significantly different according to the structure of the ketone; thus we find 0.73 ppm (mean value) for the 4-substituted camphors compared with literature values of 0.61 to 0.57 ppm for butan-2-one,²⁶ in the case of acetone the value is 0.62–0.56 ppm.^{9a,26} The value is related to the geometry of the complex. Ketones hindered on one side of the carbonyl group only have a much more stable *E*-configuration. Thus, the BF_3 complexation-induced deshielding of the protons α to the carbonyl group is 0.53 ppm for cyclohexanone, but 0.72 ppm for the $\text{C}(6)$ protons of 2,2,3,3,5,5-hexamethylcyclohexanone.³³ For the BF_3 -complexed 2,3,3,5,5-pentamethylcyclohexanone of configuration *E* with respect to the $\text{C}(2)$ methyl, deshieldings of the equatorial and axial $\text{C}(6)$ protons were respectively, 1.04 and 0.35 ppm and a geometry shown in Fig. 1 is envisaged.³³

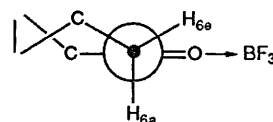


Fig. 1

In the 4-substituted camphors, systematically higher values are observed for $\text{H}_{3\text{endo}}$, 0.77 ppm, with respect to $\text{H}_{3\text{exo}}$, 0.73 ppm. This indicates that the carbonyl group is not completely symmetrical with respect to the $\text{H}_{3\text{exo}}$ and $\text{H}_{3\text{endo}}$ protons. A similar finding has been noted in two X-ray crystal-structure determinations.³⁴ The geometry of the complex is such that boron lies in the plane of the carbonyl group with a C=O-B angle, which although not accurately known is probably much less than 180°; the configuration is almost certainly *E* and indeed there is precedent for this from both camphor oxime³⁵ and *N*,4-dinitrocamphorimine.³⁶

Coupling constants. Complexation leads simultaneously to an increase in the absolute value of the geminal coupling $|^2J_{\text{H}_{3\text{exo}}-\text{H}_{3\text{endo}}}|$ of 3.4 ± 0.2 Hz and to a decrease of the long-range coupling $^4J_{\text{H}_{3\text{exo}}-\text{H}_{5\text{exo}}}$ of 0.9 ± 0.3 Hz; since the geminal coupling is negative both variations correspond to decreases.

In an extension of earlier work,³⁷ we observe, for the above long-range coupling, eqns. (11) and (12), in which the standard

$$^4J = (1.75 \pm 0.22)\sigma_1 + 2.32 \quad (11)$$

$$r = 0.9540, s = 0.14, n = 8 \text{ (no Et)}$$

$$^4J = (1.76 \pm 0.24)\sigma_1 + 2.32 \quad (12)$$

$$r = 0.9574, s = 0.15, n = 7 \text{ (no Et, OAc)}$$

deviation is the same order of precision as the measurements. Complexation decreases both the value of this coupling and also the quality of the correlation which now becomes eqn. (13).

$$^4J = (1.84 \pm 0.47)\sigma_1 + 1.25 \quad (13)$$

$$r = 0.8907, s = 0.29, n = 6 \text{ (no Et, OAc, CO}_2\text{Me)}$$

This so-called W coupling^{38,39} shown here has a significant contribution from overlap of the back lobes of the C-H σ orbitals, as shown in Fig. 2. Throughout the series 1-9 the

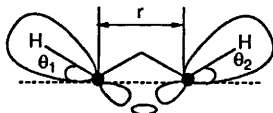


Fig. 2

geometry is taken as constant but electron-withdrawing substituents increase the overlap between the back lobes. However, in going from the free to complexed ketone one notes an inverse effect. This we attribute to hyperconjugation between the C(3) protons and the carbonyl group (Fig. 3).

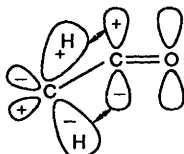


Fig. 3

Overlap between the C-H σ orbitals and the p orbital at the carbonyl carbon reduces the possibility of back lobe $\sigma-\sigma$ overlap (Fig. 2), and this in turn reduces the coupling constant. Complexation of the carbonyl group increases the electronegativity of C(2) and then the hyperconjugation accentuates the decrease in 4J . It is not possible to exclude a geometric explanation in which an increase in the angle θ_2 may arise from an interaction between BF_3 and $\text{H}_{3\text{exo}}$.

Geminal couplings decrease algebraically as a result of complexation. Although such an effect may be associated in principle with a decrease in the angle $\text{H}_{3\text{exo}}-\text{C}(3)-\text{H}_{3\text{endo}}$,⁴⁰ this explanation is untenable because it would correspond to an increase in 4J and would be the opposite of expectations based on a repulsion between the protons concerned and BF_3 . A decrease in the electronegativity of the group bonded to the methylene function can also bring about a diminution, but such is not the case for complexation of BF_3 to the carbonyl. However, hyperconjugation leads to a negative contribution to the coupling⁴¹ which increases as a result of complexation and explains the increase in the absolute value of 2J . This is in accord with the hypothesis proposed for the complexation-induced decrease in these compounds. Also, a deformation brought about by interaction of $\text{H}_{3\text{exo}}$ and BF_3 , as considered in the

analysis of ^1H chemical shifts can also contribute to a decrease in the algebraic value of the geminal coupling $^2J_{\text{H}_{3\text{exo}}-\text{H}_{3\text{endo}}}$ in moving the (complexed) carbonyl group closer to the plane that bisects those formed by $\text{C}(2)\text{C}(3)\text{H}_{3\text{exo}}$ and $\text{C}(2)\text{C}(3)\text{H}_{3\text{endo}}$.⁴²

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