^{13}C and 220 MHz Analysis of Camphor and Thiocamphor. Anisotropy and Solvent Effects of the C=S Bond

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Summary Comparative investigation of the ^{13}C and ^{1}H (220 MHz) n.m.r. spectra of camphor and thiocamphor provides information regarding the electronic nature of the C=S bond.

MAGNETIC ANISOTROPY,[1] electric-field effects,[2] and the phenomenon of aromatic solvent induced shifts (ASIS)[3] are intrinsically related to the electronic structure of a functional group, and can provide useful information regarding its state of hybridization and approximate polarity. ^{13}C n.m.r. spectroscopy can also be useful in this respect, since ^{13}C chemical-shift values also reflect the electronic environment at a given carbon atom.[4] We report the assignment of the ^{13}C and ^{1}H (at 220 MHz) n.m.r. spectra of camphor (I) and thiocamphor (II) and data concerning the electronic nature of the C=S bond.

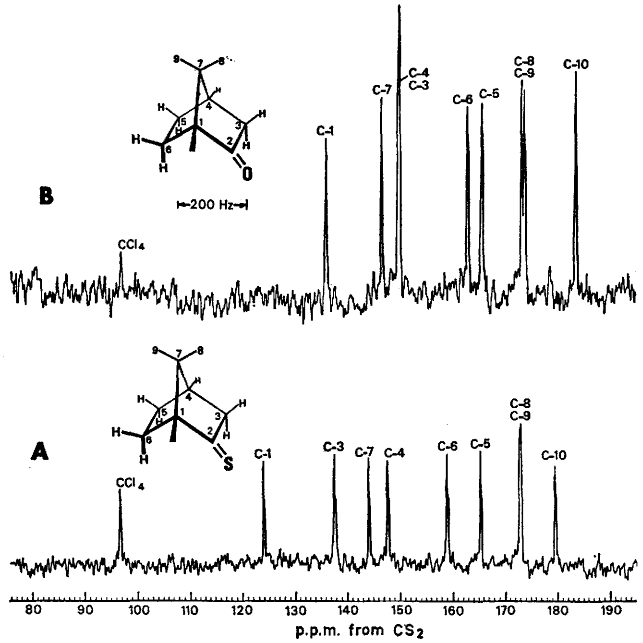

FIGURE 1. *Natural-abundance ^{13}C n.m.r. spectra of saturated solutions of thiocamphor* (A) *and camphor* (B) *in carbon tetrachloride. The spectra shown are the result of approximately* 50 *scans run at* 250 *sec. scan-time.*

Figure 1 shows the ^{13}C n.m.r. spectra of (I) and (II). Assignments for the different carbon atoms are summarized in Table 1. Quaternary carbon signals arising from C-1 and C-7 were assigned unequivocally on the basis of off-resonance noise decoupling experiments,[5] the lower-field signal of the two being assigned to C-1 because of its proximity to the functionalized C-2. Since removal of electronic charge from a carbon nucleus results in orbital contraction with concomitant shift to lower-field values,[4] the lowest-field signal (not shown in Figure 1) in the spectrum of (I) (−22·2 p.p.m.) and (II) (−75·6 p.p.m.) is assigned to C-2. The higher-field resonance position for C-2 in the former case is difficult to rationalize in light of the relative electronegativities of oxygen and sulphur and the experimentally determined[7] similarity of the dipole moments of the C=O (μ = *ca.* 2·98D) and C=S (μ *ca.* 2·89D) bonds. An explanation for this discrepancy can be found from consideration of factors contributing to the paramagnetic screening term σ_p.[4,8] Since σ_p is not only directly related to charge density at a given carbon but also inversely proportional to the mean excitation energy, ΔE (of magnetically allowed transitions), it appears that ΔE is considerably smaller for the C=S bond than for the C=O bond, resulting in the observed greater shielding for C-2 in (I). This is supported by the fact that (II) is highly coloured (orange) and that the $n \rightarrow \pi^*$ transition for the thiocarbonyl group occurs at longer wavelength than that of the carbonyl group. As variation in the heteroatom bonded to C-2 should have little or no effect on the chemical-shift position of distant carbon atoms, the remaining signals, except those originating from C-3, were assigned on the basis of an intensive

TABLE 1

^{13}C *Chemical shift assignments*[a] *for camphor* (I) *and thiocamphor* (II)

Compound[b]	Resonance C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
(I)	+135·5	−22.2	+149·3	+149·3	+165·1	+162·4	+145·9	+173·0	+172·5	+182·8
(II)	+124·0	−75·6	+137·3	+147·0	+165·1	+158·8	+143·9	+172·6	+172·6	+179·2

[a] In p.p.m. from external $^{13}CS_2$; positive and negative values indicate shifts to the high- and low-field side of $^{13}CS_2$, respectively.
[b] Spectra were recorded in CCl_4 solutions.

TABLE 2

220 *MHz* ^{1}H *n.m.r. data*[a] *for camphor* (I) *and thiocamphor* (II)

Compound	Solvent[b]	Resonance *exo*-3-H	*endo*-3-H	4-H	*exo*-5-H	*endo*-5-H	*exo*-6-H	*endo*-6-H	8-CH$_3$	9-CH$_3$	10-CH$_3$
(I)	CDCl$_3$	2·35	1·84	2·09	1·94	1·41	1·67	1·32	0·83	0·95	0·90
	C$_6$D$_6$	2·09	1·56	1·65	1·59	0·96	1·34	1·18	0·59	0·64	0·87
	Δ	+0·26	+0·28	+0·44	+0·35	+0·45	+0·33	+0·14	+0·24	+0·31	+0·03
(II)	CDCl$_3$	2·78	2·40	2·17	2·00	1·38	1·76	1·27	0·78	1·02	1·09
	C$_6$D$_6$	2·55	2·17	1·69	1·60	0·97	1·40	1·09	0·55	0·69	1·09
	Δ	+0·23	+0·23	+0·48	+0·40	+0·41	+0·36	+0·18	+0·23	+0·33	0·00

[a] In p.p.m. from internal Me_4Si. Assignments were made on the basis of first-order analysis and are in accord with the known coupling constant and chemical-shift behaviour for bicycloheptane systems.[10]
[b] $\Delta = \delta(CDCl_3) - \delta(C_6D_6)$.

study of bornanone derivatives.[6] The remaining unassigned signal in the spectrum of (I) (+149·3 p.p.m.) and (II) (+137·3 p.p.m.) was accordingly attributed to C-3.

Solvent and anisotropy effects associated with the C=S bond provide further evidence of its polarity. ^{1}H n.m.r. data recorded at 220 MHz for (I) and (II) in both deuteriochloroform and perdeuteriobenzene solutions are shown in Table 2. Aromatic systems like benzene preferentially solvate electron-deficient sites within a solute molecule.[11] Thus, protons situated in the vicinity of a polar functional group experience screening effects due to ring current effects in the associated aromatic nucleus,[12] the magnitudes of which are proportional to the dipole moment[13] of the function under study. The similar Δ-values recorded for corresponding protons in (I) and (II) (see Table 2) thus support the previous experimental evidence[7] for the similar magnitudes of the C=O and C=S dipoles. It is further evident from Table 2 that observed Δ-values can best be rationalized in terms of the solvation "complex" depicted in Figure 2a, which is in excellent agreement with (and thus adds further support for) the generalized model for benzene–polar solute associations suggested by Ledaal.[14] The large Δ-values recorded for 4-H, *exo*-5-H, *endo*-5-H, and 9-CH$_3$ in (I) and (II) necessitate that these protons be spatially proximal to the shielding region of the associated benzene nucleus, while *exo*-3-H, *endo*-3-H, *endo*-6-H, and *exo*-6-H having slightly smaller Δ-values must be more distant, and 10-CH$_3$ having a negligible Δ-value must be spatially remote from this area.

Since the dipole moments for the C=O and C=S bonds are similar in magnitude, electric-field screening effects for these bonds will be approximately the same.† Any differences in their nuclear screening characteristics must therefore be attributed to differences in the anisotropy of their magnetic susceptibilities and thus to differences in their electronic structures. For the C=O function which does not possess an axis of symmetry, three susceptibilities X_x, X_y, and X_z, as shown in Figure 2b, are necessary to describe the screening environment around this bond.[15] Based on empirical evidence, [16] it has been shown that, for the C=O bond, X_y is shielding (positive), while X_x and X_z are deshielding (negative).

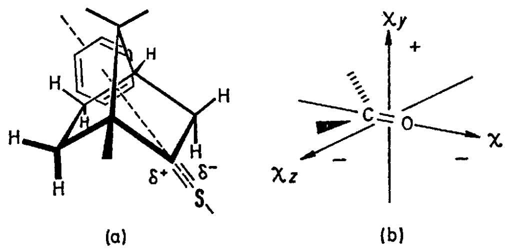

FIGURE 2. (a) *Suggested geometry for the association between thiocamphor* (II) *and benzene as deduced from solvent shifts*; (b) *co-ordinate susceptibilities for* C=O *bond.*

Inspection of shift values recorded for (II) in Table 2 show that the co-ordinate susceptibilities associated with the C=S function are quantitatively different from, but qualitatively similar to, those associated with the C=O function. Thus in (II) relative to (I) X_y is more shielding (*i.e.* more positive) as witnessed by the higher-field value for 8-CH$_3$, X_x is more deshielding as witnessed by the lower-field positions for 4-H and *exo*-5-H, and X_z is also more deshielding as witnessed by the lower-field positions for 10-CH$_3$ and *exo*-2-H and *endo*-2-H. These observations demonstrate that the C=S bond, unlike the sulphoxide bond,‡ is similar to the C=O bond in bond order and

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† The electric field screening coefficient (σ_E) for a polar functional group is given in its simplest form by the expression $\sigma_E = k\mu e_z \times 10^{-12}$, where k is a constant e_z a geometrical quantity, and μ the dipole moment for the bond under consideration. Thus if μ has approximately the same magnitude in the C=O and C=S bonds, their σ_E values likewise will be similar.

therefore permits similar screening "cones" to be drawn for these bonds.

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‡ The sulphoxide bond is drawn often in such a way (*e.g.* S=O) as to implicate electronic similarity to the C=O bond. However, the nuclear screening behaviour of the sulphoxide bond definitely rules out such a comparison. Previous studies by Burg[17] have indicated that because of $d,p-\pi$ overlap the S → O bond approximates electronically a triple bond. This is borne out in recent n.m.r. investigations of sulphoxides[18] which have shown that the screening environment associated with the S → O bond resembles closely that of an acetylenic bond.

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