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INFRARED INTENSITIES AS A QUANTITATIVE MEASURE OF INTRAMOLECULAR INTERACTIONS—XVII[1]

PHENYL AND VINYL ALKYL ETHERS AND SULPHIDES

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Abstract—IR frequencies and integrated intensities are reported for the $\nu C{=}C$ mode of vinyl ethers and sulphides and for the 1600 cm^{-1} ring modes of phenyl ethers and sulphides. The electronic interactions between substituents and π-systems are interpreted in terms of conformation and steric hindrance to overlap.

PREVIOUS work has shown that IR intensities of the υ_{16} bands of monosubstituted benzenes afford a measure of the resonance interaction between substituent and ring (Eq. 1).[2] IR intensities of the $\nu C{=}C$ of monosubstituted ethylenes[3] show further that the resonance interaction between substituent and ethylene π-system is of similar type (Eq. 2).

$$A_{\text{mono}} = 17{,}600(\sigma_R^0)^2 + 100 \qquad (1)$$

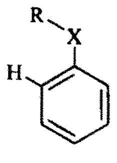
$$A_{\text{ethy}} = 27{,}100(\sigma_R^0)^2 + 80 \qquad (2)$$

Whereas in a monosubstituted benzene only one stable conformation (*cf* **1**) is found, monosubstituted ethylenes with unsymmetrical substituents possess s-*cis* (**2**) and s-*trans* conformers (**3**).

The question arises whether the conjugation in an ethylene capable of s-*cis*/s-*trans* rotational isomerism varies from conformation **2** to **3**. The previous paper[3] indicated that this might be so for s-*cis* and s-*trans* vinyl ketones, and this is discussed in detail in the following paper.[5] Such a behaviour for acyl groups is in agreement with the large differences in ν_{16} intensity calculated for s-*cis* (**5**) and s-*trans* conformers (**6**) of, e.g., *meta*-substituted benzaldehydes.[4] The small difference in ν_{16} intensity calculated for the corresponding conformers of *meta*-substituted anisoles,[4] and the small asymmetry correction for the OMe group[6] indicate that the conjugation between $C{=}C$ and substituent in s-*cis* and s-*trans* vinyl ethers should be effectively constant. Further, unpublished work indicates that the same is true of the SMe group.

It follows that any dependence of the interaction of OR or SR groups with π-systems on the steric requirements of the alkyl group R should be explicable in terms of steric inhibition of resonance, without the added complication of variable conjugation with conformation in the ethylenic compounds. This paper records results which suggest that this does indeed apply.

Phenyl ethers and phenyl sulphides. IR data are shown in Table 1. For the ethers, σ_R^0 is sensibly constant at $-0{\cdot}43$ for OMe, OEt, OBu^n and OPr^i, but the value drops to $-0{\cdot}34$ for OBu^t. This is interpreted as indicating that additional steric hindrance to planarity for OEt and OPr^i over that for OMe is small and is offset by additional electron release. However, for t-butoxybenzene, the additional steric hindrance clearly dominates. This conclusion agrees with the earlier work of Baddeley *et al.*[7] concerning reactivity and UV data and with more recent work on cyclic ethers.[9, 10]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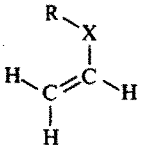
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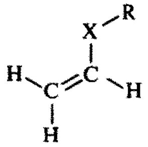
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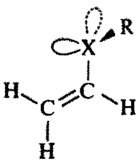
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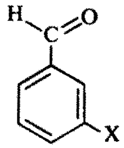
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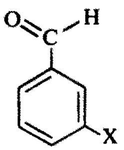
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For the sulphides, σ_R^0 is considerably more sensitive to the size of the alkyl group, falling steadily from $-0{\cdot}25$ to $-0{\cdot}07$ for SMe to SBu^t. The CSC bond angle is significantly smaller than ∠COC and despite the greater S—C bond length, steric effects should be more important in the sulphides than for the ethers. However, as is shown in Figs 1 and 2, steric effects should be small for the phenyl and both the s-*cis* and s-*trans* vinyl derivatives except for R = t-butyl, and another explanation must be sought for the large variation in apparent conjugative power of the SR groups.

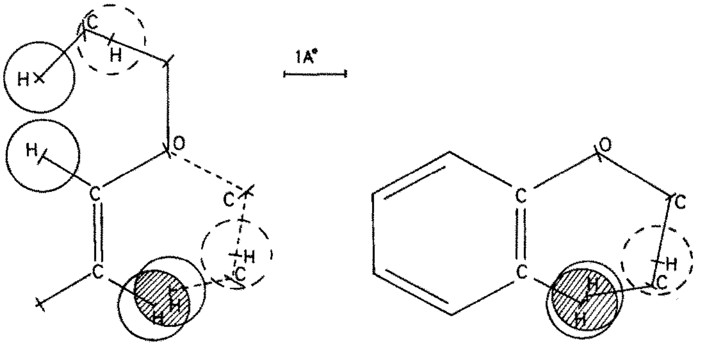

FIG 1. Molecular models of: (a) Planar forms of t-butyl vinyl ether, s-*cis* and s-*trans* conformers. Bond lengths and angles are taken from Ref. 11; (b) Planar forms of t-butyl phenyl ether. Bond lengths and angle are taken from Ref. 10. The rings in dotted line correspond to the methyl derivatives. Interaction radius of hydrogen atom from Ref. 12

TABLE 1. IR AND UV DATA OF ALKYL PHENYL ETHERS AND SULPHIDES

R	PhOR						PhSR					
	IR				UV		IR				UV	
	ν cm^{-1}	ε_A	A^a	σ_R^{0b}	λ^c_{max}	ε^d_{max}	ν cm^{-1}	ε_A	A^a	σ_R^{0b}	λ^c_{max}	ε^e_{max}
Me	1603 1590	208 96	3330	−0·428^f	271	1579	1585	62	1190	−0·249^f	254	10100
Et	1603 1598	233 124	3500	−0·440	271	1938	1587	46	750	−0·192	256	7750
Bu^n	1602 1588	190 97	3280	−0·425	—	—	—	—	—	—	—	—
Cyclohexyl	—	—	—	—	—	—	1582 1572	45 17	650	−0·177	—	—
Pr^i	1606 1589	174 169	3330	−0·428	273	1920	1584 1573	49 14	570	−0·163	257	5770
Ph	1592 1596	114 168	2420	−0·363	—	—	—	—	—	—	—	—
Bu^t	1593 1586	141 69	2160	−0·342	270	454	1582 1572	12 9	200	−0·075	268	1290

[a] Value measured in CCl_4. [b] Value calculated from eq. $[(A - 100)/17600]^{\frac{1}{2}}$. [c] λ_{max} in nm. [d] Values taken from Ref. 7 [e] Values taken from Ref. 8. [f] Although σ_R° values are quoted to three decimal places, uncertainty regarding the overtone correction in equation (1) leads to error of 0·002 for a σ_R° of 0·4, and an error of 0·008 for a σ_R° of 0·2.

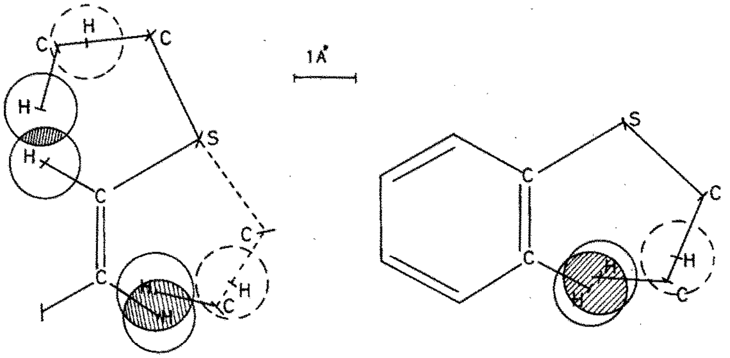

FIG 2. Molecular models of: (a) Planar forms of t-butyl vinyl sulphide, s-*cis* and s-*trans* conformers. Bond lengths and angles are taken from Ref. 13; (b) Planar forms of t-butyl phenyl sulphide. The rings in dotted line correspond to the methyl derivatives. Interaction radius of hydrogen atom from Ref. 12

Whereas for the ethers the only mesomeric interaction from the substituent is electron donation by the oxygen p-orbitals, for the sulphides electron acceptance also occurs into the sulphur d-orbitals and the observed σ_R^0 is the algebraic sum of these two electron displacements. As the SR group is twisted out of the plane of the ring, the π p-overlap is rapidly diminished, but the π d-overlap is unaffected because the overlap of the d(xz) orbital with the p-orbital of the ring is replaced progressively by the overlap of the d(yz) orbital, as shown in Fig 3. NMR studies[14, 15] have shown that there is no, or little, angle dependence for the d-orbital acceptor effect of the sulphur atom. As a consequence, the energy loss on twisting an SR group is expected to be much less that that for twisting an OR group. Hence increasing the size of R in SR is accompanied by more twisting than occurs for OR and this explains the greater sensitivity of the observed σ_R^0 for SR to the size of R. The value of σ_R^0 correlates well with reported[8] ε_{max} for the UV spectra of phenyl sulphides (Fig 4).

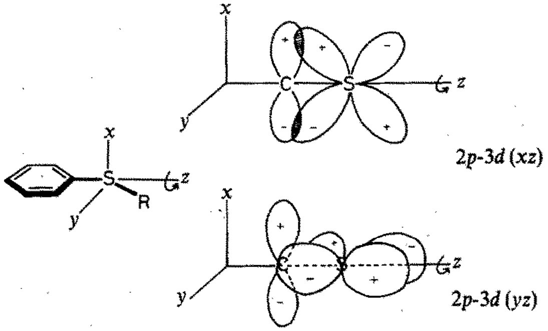

FIG 3. d-π Overlap in alkyl phenyl sulphides

Vinyl ethers. Owen and Sheppard have shown that methyl vinyl ether[16] and ethyl vinyl ether[11] exist as mixtures of two conformers of which the planar cis forms **2** are the more stable with ΔH° 1·15 ± 0·25 kcal mole^{-1} (vapour) or 0·66 ± 0·2

(1,1,2-trichloroethane solvent) for the methyl and 0·8 ± 0·2 kcal mole^{-1} (1,1,2-trichloroethene solvent) for the ethyl ether. The minor conformer was tentatively assigned the non-planar gauche (4) rather than the the *trans*-configuration (3). The micro-wave spectrum confirms the planar *cis* form[17] but was inconclusive regarding the other conformer. NMR evidence which is stated[18] to exclude the planar *trans* form is equivocal because it assumes no difference in anisotropic shielding between the *cis* and (*gauche* or *trans*) forms: a treatment[19] in terms of dipole moment and Kerr constants (*cf* also Ref 20) is inconclusive because the mesomeric moment is assumed to be equal in the two conformers and yet the non-*cis* conformer is concluded to be considerably twisted. In the absence of clear evidence to the contrary, we believe the *trans* conformation to be more likely than the *gauche*.

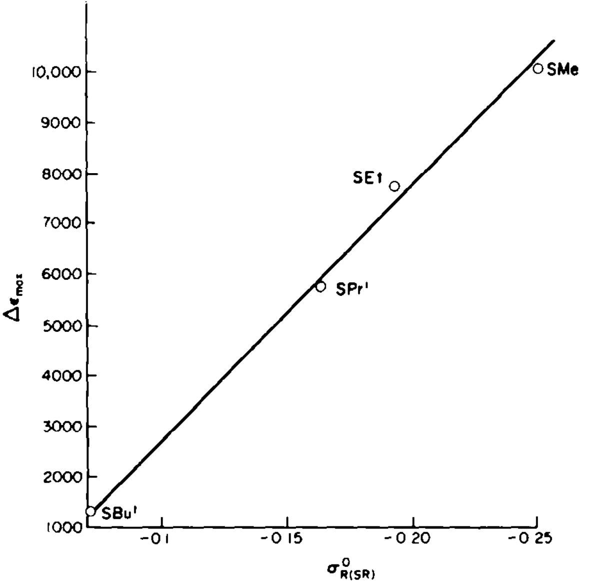

FIG 4. Plots of UV extinction coefficients against σ^0_R(SR) for alkyl phenyl sulphides

Evidence that the proportion of s-*trans* conformer increases markedly for the i-propyl and becomes dominant for the t-butyl vinyl ethers comes from equilibrium data for propenyl ethers.[21] The effectively constant σ^0_R value for OR in vinyl ethers (Table 2) confirms the previously discussed concept of equal conjugation in s-*cis* and s-*trans* forms. This would not hold for the s-*cis* t-butyl ether (*cf* Fig. 1), however this conformer is probably present in only minor amounts in the equilibrium. Ledwith and Woods[22] have recently concluded that variation in steric effects determines the reactivity sequence of alkyl vinyl ethers.

Vinyl sulphides (Table 3). Temperature dependence of IR absorption has shown[13] that methyl vinyl sulphide exists in two rotational isomers. The s-*cis* isomer is found to be the more stable, with $\Delta H^\circ = 1{\cdot}4$ kcal mole^{-1} (in gas phase). The complete NMR analysis of alkyl vinyl sulphides has been reported recently,[23] and results are interpreted in terms of mesomeric interaction. The σ^0_R value for SR in the vinyl

TABLE 2. IR DATA OF ALKYL VINYL ETHERS ($CH_2:CHOR$)

OR	ν cm^{-1}	ε_A	A_{total}[c]	$\sigma^{\circ}_{R(Eth)}$[d]	$\sigma^{\circ}_{R(Ph)}$[e]
OMe[a]	1652				
	1639[b]	—	—	—	−0·428
	1616				
OEt	1652	159			
	1638[b]	88[b]	5150	−0·433[f]	−0·440
	1612	55			
OBu^n	1652	159			
	1636[b]	89[b]	5260	−0·437	−0·425
	1612	57			
OPr^i	1652	54			
	1636[b]	145[b]	5130	−0·432	−0·428
	1612	84			
OBu^t	1638[b]	169[b]	5150	−0·433	−0·342

[a] Compound of low boiling point (12°C). [b] Data for s-*trans* form (*cf* Refs. 11 and 16). [c] Value measured in CCl_4. [d] Value from $[(A\text{-}80)/27100]^{\frac{1}{2}}$. [e] Value from $[(A\text{-}100)/17600]^{\frac{1}{2}}$. [f] Although σ°_{R} values are quoted to three decimal places, uncertainty regarding the overtone correction in equation (2) leads to an error of 0·001 for σ°_{R} of 0·4.

TABLE 3. IR DATA OF ALKYL VINYL SULPHIDES ($CH_2:CH—SR$)

SR	ν	ε_A	A[a]	$\sigma^{\circ}_{R(Eth)}$[b]	$\sigma^{c}_{R(Ph)}$[c]
SMe	1584	147	1675	−0·243[d]	−0·249
SEt	1585	106	1430	−0·223	−0·192
	1582	116			
SPr^i	1585	123	1270	−0·210	−0·163
	1583	107			
SBu^t	1584	130	1090	−0·193	−0·075

[a] Value measured in CCl_4. [b] Values from $[(A - 80)/27100]^{\frac{1}{2}}$. [c] Values from $[(A - 100)/17600]^{\frac{1}{2}}$. [d] Although σ°_{R} values are quoted to three decimal places, uncertainty regarding the overtone correction in equation (2) leads to an error of 0·004 for a σ°_{R} of 0·2.

sulphides shows a decrease with increasing size of R parallel to, but much smaller than. that found in the phenyl sulphides. We expect that for the s-*cis* conformers of the vinyl sulphides approximately the same interaction between substituent and π-system as for the phenyl sulphides (*cf* Fig 2). However, steric hindrance will be considerably less in the s-*trans* conformer, and hence the existence of a considerable proportion in the s-*trans* form will tend to keep variations of σ^0_R as measured for SR in the vinyl sulphides to a much lower value than that for the phenyl sulphides. Such behaviour is indeed found.

EXPERIMENTAL

The IR spectra have been recorded on a Perkin-Elmer spectrometer 125. The method used for calculations of infrared intensities is the same as described in previous papers on this topic.

The compounds commercially available have been purified by standard procedures. The following compounds were prepared by the literature methods indicated: t-butoxybenzene, b.p. 52°/6 mm (lit[7]

60°/8 mm). Alkyl phenyl sulphides: isopropyl, b.p. 81°/4·5 mm (lit[24] 207·5°/750 mm); cyclohexyl, b.p. 118°/0·5 mm (lit[25] 108/0·1 mm); t-butyl, b.p. 67°/1·5 mm (lit[24] 73°/5 mm). Isopropyl vinyl ether,[26] b.p. 56° (lit[27] 55·5–56·5°), t-butyl vinyl ether,[26] b.p. 82° (lit[27] 80·5–81°). Alkyl vinyl sulphides: methyl, b.p. 70° (lit[28] 69–70°); ethyl, b.p. 92° (lit[29] 92°); isopropyl,[29] b.p. 44°/50 mm (lit[30] 107°); t-butyl,[29] b.p. 46°/90 mm (lit[23] 41°/120 mm).

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