Steric Effects on the Carbonyl Stretching Frequencies of Alkyl Styryl Ketones

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Summary Quantitative relationships between the carbonyl stretching frequency and the Taft σ^* and E_S parameters have been found for the *s-cis-* and *s-trans-* conformers of alkyl styryl ketones; estimates of the contribution by the steric parameter to these relationships have been made.

As part of a general investigation of structure–reactivity relationships of $\alpha\beta$-unsaturated ketones, we have observed a novel dependency of the carbonyl stretching frequency on steric effects for alkyl styryl ketones. Linear free energy relationships have been previously reported to exist between the carbonyl stretching frequency of several systems of carbonyl compounds and Taft σ^* values.[1,2] Also, numerous reports have appeared in which interpretations of various stretching frequency data have been made in terms of steric effects.[2,3] However, there does not appear to have been a case reported for which the role of the steric effect has been quantitatively assessed. We now report the observation of a quantitative relationship between the carbonyl stretching frequency and σ^* and E_S for the *s-cis-* and *s-trans*-conformers of a series of alkyl styryl ketones.

TABLE 1

Carbonyl band positions (cm^{-1}*) for* PhCH : CH·CO·CH_2R *in* CCl_4[a]

R	*s-cis*	*s-trans*
H	1697·7	1676·3
Me	1697·2	1674·6
Et	1695·4	1672·5
Pr^n	1695·1	1671·9
Pr^i	1693·7	1669·3

[a] Measurements were made on *ca.* 5% solutions at *ca.* 40 ± 3° using a Beckman IR-12 instrument essentially as described in ref. 7.

TABLE 2

Results from statistical treatments of band position data

	ν *vs.* σ^*				ν *vs.* E_S				ν *vs.* σ^* and E_S					
Isomer	s	ρ	r	i	s	ρ	r	i	a	b	i	e	r	$\%E_S$
s-cis	0·041	0·024	0·754	−41·5	0·135	0·209	0·947	−356·0	7·5±5·2	3·57±0·76	1697·8	0·428	0·982	76±13
s-trans ..	0·037	0·016	0·803	−26·9	0·118	0·131	0·960	−219·4	15·8±2·9	5·55±0·42	1676·4	0·237	0·998	70±4

s = standard deviation. ρ = slope of the line. r = correlation coefficient. i = intercept. a = regression coefficient for σ^* b = regression coefficient for E_S. e = standard error of estimate. $\%E_S$ = contribution of E_S to correlation; see ref. 8.

Charton[4] has recently demonstrated that the Taft steric parameter E_S is a function of the van der Waals radii of the groups. In view of these results, we have limited our investigation to alkyl styryl ketones with alkyl groups of the same type (·CH_2R). Hayes and Timmons[5] have recently reported the carbonyl band assignments for the *s-cis-* and *s-trans-* (or non *s-cis-*) conformers for some alkyl styryl ketones, and we have made band assignments on analogy with their work. Table 1 contains the stretching-frequency data for the two conformers of all the alkyl styryl ketones of the type ·CH_2R, where R is a simple alkyl group for which both σ^* and E_S values are known.[6] Table 2 contains the results of a least-squares and a multiple-regression treatment of the stretching-frequency data by methods we have previously described;[7] the data were treated independently with σ^* and E_S and by a linear combination of σ^* and E_S. Included in Table 2 is the result of a $\%E_S$ calculation, the assessment of the contribution of E_S to the multiple correlation, which is identical with the $\%R$ calculation developed by Swain and Lupton.[8]

As can be seen from Table 2, very poor correlations are obtained using σ^* with data from both conformers. In contrast, reasonable correlations are obtained when the stretching frequency data are treated with E_S. Indeed, the two-parameter approach employing σ^* and E_S gives good correlations for both the *s-cis-* and *s-trans*-conformers ($r = 0{\cdot}982$ and $0{\cdot}998$, respectively). The E_S value of approximately 75% for both the *s-cis-* and *s-trans*-conformers demonstrates the importance of steric effects on the carbonyl stretching frequency in these systems.

We suggest, in this case, that the role of the steric factor on the carbonyl stretching frequency is steric inhibition of resonance. Steric inhibition of resonance and its influence on the carbonyl stretching frequency in this system can be described in terms of the degree of coplanarity of the styryl group with the carbonyl group. The degree of coplanarity should be a function of non-bonding interactions of the alkyl group with the vinyl hydrogen α to the carbonyl group in the *s-cis*-conformer and the interaction between the alkyl group and the vinyl hydrogen β to the carbonyl group in the *s-trans*-conformer.

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