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CARBON-13 CHEMICAL SHIFTS OF α,β-UNSATURATED ACIDS

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Abstract—Carbon-13 spectra of 59 α,β-unsaturated carboxylic acids have been measured. Large differential shieldings of ethylenic carbons in the *cis* and *trans* isomers of acrylic acid derivatives were found (altogether 15 isomeric *Z*- and *E*-pairs of acids were investigated). The origin of differential shieldings is complex and both molecular ground states as well as changes in excited states appear to be involved. All measured ^{13}C chemical shifts can be described by additive parameters that provide a straightforward new technique by which structural assignments can be made for a wide variety of isomeric mono-, di- and tri- substituted α,β-unsaturated acids.

INTRODUCTION

DIFFERENTIAL shieldings in proton magnetic resonance spectra of a series of *cis–trans* geometric isomers have been reported by Jackman and Wiley.[1] These differential shieldings were explained in terms of long-range effects on the protons arising from magnetic anisotropies of the C—X bonds. The relationship in substituted ethylenes between proton shifts, substituent groups and molecular geometry is characterized by good additivity of substituent increments.[2,3] Savitsky and Namikawa have shown that ^{13}C chemical shifts of ethylenic carbon atoms in isomeric 1,2-disubstituted ethylene derivatives with identical substituents likewise depend upon the geometrical configuration of these molecules.[4] In the case of ^{13}C shifts, it is no longer possible to explain them in terms of long-range anisotropy effects by assuming a planar geometry for both isomers. The distance of both α- and β-substituents from the ethylenic carbon as well as the angles are similar in geometrical isomers. Small differences in angles[5] (up to 3°) can account for only a small part (<1 ppm) of the total differential shielding.[4] Since the magnetic anisotropy effect could not be the cause of differential shieldings, Savitsky and Namikawa assumed that the inhibition by bulky substituents of resonance forms with negative (for donor substituent groups) or positive (for acceptor substituent groups) charges on ethylenic carbons was a plausible explanation for the observed differences in the ^{13}C shifts of the corresponding isomeric pairs.[4] Later, however, the study of geometrical isomers of an unsymmetrical type showed the very general nature of ^{13}C differential shieldings in *cis–trans* isomeric pairs and led to the assumption by the same authors[6] that repulsive forces which may exist between the substituent groups in *cis* isomers may lead to a weakening of the π bond between the ethylenic carbons and to an enhanced charge separation in this bond. The original assumption was thus effectively reversed, since bulky *cis* substituents in this case lead to increased charges on the carbon atoms of the double bond.

The chemical shifts of ethylenic and α-methylene protons in unsaturated hydrocarbons without polar substituents are also susceptible to geometrical isomerism,[7,8] but the shift differences are small, only 0·04 to 0·10 ppm. The smallness of proton shift differences in *cis–trans* pairs serves as a good illustration of the relative unimportance of magnetic effects as a cause of differential shieldings. The ^{13}C chemical shifts of isomeric octenes were investigated by Lippmaa, Rang, Eisen and Pehk.[9] In all cases the shift of ethylenic carbon atoms in *trans* isomers was smaller (paramagnetic differential shielding) by 1 to 2 ppm, but the differential shielding for adjacent methylene or methyl groups was much larger (5·7 ± 1 ppm) and of the same sign. This trend is a very general one and had been noted earlier for ethylenic carbons in 3-hexene,[10] 2-butene[11] and in the methylene groups of cyclooctene.[12] Since far ultraviolet spectra of unsaturated compounds also show a correlation with molecular geometry, changes in ΔE were suggested[9] as a probable explanation for the analytically very useful diamagnetic differential shift in all *cis* isomers. The investigation of dodecenes,[13] dimethylcyclohexanes,[14,15] decalines and dihydroxycyclohexanes[15] showed that in all cases the chemical shifts of sterically interacting carbon atoms are larger in *cis* isomers.[16] Similar effects in the carbon spectra of methylbenzenes[17] which also reflect conformational features existing between adjacent methyl groups were attributed to bond polarization under the influence of sterically induced strain.[18]

It follows from this short literature survey that differential shieldings in carbon spectra of isomeric molecules are widespread and analytically useful, but the underlying mechanism is as yet little understood, since all possible explanations have been advanced.

This paper describes the results of the investigation of 59 α,β-unsaturated carboxylic acids and gives a straightforward ^{13}C-NMR technique by which geometrical assignments can be made for a wide variety of such acids. The only information required is the ^{13}C chemical shifts for the olefinic carbons of the compound under study. For a structural determination of α,β-unsaturated acids the ^{13}C-NMR method has the advantage that the determination could be based on the shifts of both α- and β-carbon atoms. Moreover, this method does not suffer from the restriction that the compound must contain one or more vinyl protons. The technique complements existing methods for assigning structures to monosubstituted acrylic acids and *cis* and *trans* disubstituted ethylenes based on the magnitude of coupling constants in ^{1}H-NMR spectra,[19] and it is also a complement to the method for assigning structures to higher substituted ethylenes via the additivity of substituent shielding on vinyl proton shifts.[2,3,20]

Additive parameters for ^{13}C-NMR spectra of hydrocarbons have been suggested by Grant and Paul,[21] and by Savitsky and Namikawa,[22] and today the increments are known for important substituents in saturated and unsaturated systems. These parameters do not take into account the geometric situation of the molecule: thus these ^{13}C-increments cannot be used for structural determination of geometric isomers.

METHOD

^{13}C-NMR spectroscopy has been shown to be a useful complement to ^{1}H-NMR spectroscopy. The double resonance spectra can be recorded without any spin-spin splittings: one singlet for each carbon atom, and also with a large range in the signals for closely related carbon atoms, but low natural abundance makes the registration of ^{13}C spectra quite difficult. The absorption signal is about four orders of magnitude less than the corresponding signal from the same number of hydrogen nuclei. Use of adiabatic rapid passage with the registration of the dispersion signal leads to about a sixfold increase of sensitivity. This technique has been successful in the study of relatively simple molecules, but rapid sweep rates and the necessarily strong measuring rf field γH_1 limit spectral resolution so that saturated parts of more complicated molecules give no useful spectra.[16,23] No chemical shifts can be measured from such featureless humps and one has to use double resonance methods for spectrum simplification. Irradiation of hydrogen atoms near their resonance frequencies with a strong perturbing rf field γH_2 decouples the hydrogen and ^{13}C nuclear spins and allows one to obtain spectra with just one single unsplit line for each carbon atom. If

$$|\gamma|\, H_2 \gg |\Delta\omega_2|, \qquad 2\pi\, |J(^{13}C^{1}H)|,$$

then the residual splitting is[24]

$$J_R \cong \frac{J\, \Delta\omega_2}{\gamma H_2}$$

where $\Delta\omega_2$ is the deviation of the perturbing frequency from exact resonance. If a strong enough rf field is used then the residual splitting can be made less than the apparatus linewidth, even if only one setting of the perturbing frequency ω_2 is used for the entire ^{13}C spectrum. Actually the perturbing frequency was changed once in each experiment and was adjusted for optimum decoupling of either all the saturated or ethylenic hydrogen atoms. Although field sweep[25] can also be used, frequency sweep[23,26,27] leads to important simplification of experimental procedure, and was used throughout this work.

Multiplet collapse is accompanied by a corresponding two- or threefold increase of peak values, and an additional increase in line intensity (and the peak value) is possible as a result of the nuclear Overhauser effect.[28] In the case of predominantly dipole-dipole relaxation of ^{13}C nuclei, up to a threefold increase in line intensities is possible. In benzene an increase of the peak value up to 5·5 times has been achieved,[23] but this is not always the case since other relaxation processes may interfere.[29] The Overhauser effect does not depend on scalar spin-spin coupling between ^{13}C and hydrogen nuclei and some line intensity enhancement is achieved for fully substituted unsaturated carbon atoms of the double bond as well as for carboxyl carbons in acids if the methyl protons are saturated. Double resonance was used in all cases and the spectra of carboxylic acids with long saturated chains were registered in the absorption mode. Rapid passage spectra were used in the case of weaker spectra of halogenated acids and the mean shift value for both sweep directions calculated. The last technique is simple and allows one to work much faster with good sensitivity. The precision is less, only about ±0·5 ppm and line forms and relative intensities are distorted, but the mean values for both sweep directions are unaffected. The spectrometer[23] was a universal apparatus designed to allow all nuclei that resonate between 1·5 and 26 MHz to be investigated. The magnetic field strength was 14·1 kG and the perturbing frequency close to 60 MHz. All ^{13}C spectra were registered at 15·1 MHz with frequency sweep and the line positions were measured with an electronic counter. The necessary stability of the line positions was provided by spin stabilization, and a sideband spin generator or a passive stabilizer with a separate probe was used for this purpose. Standard 15 mm test tubes and about 1·5 ml of sample, mostly as neat liquid were used. Resolution was $3\,.\,10^{-7}$ (5 Hz) without rotation. Sample temperature (about 50°C) was higher than room temperature because of dielectric losses. In all cases time sharing was used with high pulse repetition rate (4 to 10 kHz).[30] If the pulse repetition rate is considerably higher than $1/T_2{}^*$, then all double resonance effects are displayed normally, but base-line stability is greatly improved, particularly at low or high sample temperatures.[31] The stability of conventional rf bridges or crossed coils is not high enough if a very strong decoupling field is used. Spectrum accumulation in a multichannel pulse analyser (Nokia LP 4050) was used for the study of single resonance spectra of acrylic acid and for the measurement of weak spectra of some carboxylic acid salts.

RESULTS

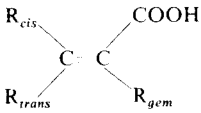
In the present investigation we have made a systematic study of α,β-unsaturated carboxylic acids, among them 15 *Z*- and *E*-pairs, see Tables 1, 2 and 3. The *Z*- and *E*-nomenclature refers to *Z*usammen (together) and *E*ntgegen (opposite) for the groups of priority according to the sequence rules of Cahn, Ingold and Prelog;[32] see also Blackwood *et al.*[33]

The values for the ^{13}C-shifts in ppm from carbon disulfide can be predicted from the two formulae†

$$\delta_\alpha = -\left(64 - \sum_i Z_i^\alpha\right) \quad \text{(ppm)}$$

$$\delta_\beta = -\left(60 - \sum_i Z_i^\beta\right) \quad \text{(ppm)}$$

where the increments of the first carboxylic group is included in the constants 64 and 60 ppm (from the shifts of acrylic acid).[34] We observed that the increments of the various substituents varied with the geometrical position of the substituents. $\sum_i Z_i$ is the sum of the increments for the substituents R_{gem}, R_{cis} and R_{trans}, where *gem*, *cis* and *trans* are relative to the carboxylic group (**1**)



(**1**)

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† Editorial decision: shifts to lower frequency (high field) of reference are designated as negative values.

The increments are given in Table 4. This means that ^{13}C-NMR spectroscopy can be used for structural determination of α,β-unsaturated acids even where ^{1}H-NMR spectroscopy cannot be used.

Among the acids we have studied are the isomeric *Z*- and *E*-2,3-dichloro- and 2,3-dibromo-2-butenoic acids, which do not contain any vinyl protons. Large differences were observed here for the shifts of the β-carbon atoms in the *Z*- and *E*-isomers.

The ^{13}C-NMR chemical shifts showed good additivity; the difference between observed and predicted values are small, even though the substituents studied include the bulky *tert*-butyl group and iodine. Errors usually do not exceed 4 ppm, see Table 1, which is equivalent to $\frac{4}{30}$ = 0·13 ppm in ^{1}H-NMR spectroscopy. For the vinyl proton shifts Matter *et al.* state that three-quarters of their values are within 0·17 ppm of those predicted.[2] We found that 95% of the corresponding ^{13}C-shifts are within 4 ppm of the calculated values. Regarding corresponding shifts (α-C and β-C) for one *Z*- and *E*-pair, the observed and predicted ^{13}C-shifts are always in the same order.

The reason for the existence of additive increments is not clear. Indeed, there is more justification for a pairwise additivity[35] and we have used this approach by introducing one additional increment for crowded halogen atoms. Also, if the molecule under study contains more than one carboxylic group, then the less crowded one must be used as the reference for the increments.

DISCUSSION

A first short account of this work has appeared earlier.[36] This short communication did not contain complete data about the acids studied and had as its main objective only the presentation of the increment system for structural analysis of α,β-unsaturated acids. Since the amount of numerical data in Tables 1 and 3 is much larger than in Refs. 4 and 6, it is tempting to check the current interpretations given to the differential shieldings of the ethylenic carbons. The shift differences in isomeric pairs are of the order of 1 to 18 ppm. While this is certainly much more than is common for proton spectra, the mean differential does not exceed significantly the maximum probable error between experimental and calculated shift values. Because of this, and since the liquid acids were measured neat but the crystalline ones in dimethyl sulfoxide solution, a check of possible solvent effects was necessary. Acrylic acid was used for this purpose because single resonance spectra allow the chemical shifts of α- and β-ethylenic carbon atoms to be assigned unequivocally. Some results are given in Table 5. It is immediately clear that solvent effects can be large (1·5 ppm and 1·8 ppm for ethylenic carbons of acrylic acid in dimethyl sulfoxide) and so the maximum error Δ between experimental and calculated shift values cannot be much less than 2 ppm. The solvent effect is even larger for the carbon atom of the carboxylic group, but is less important since this shift is not used for structural analysis. The relationship between this shift and molecular structure is less apparent and difficult to interpret. If the shift differences were caused by deviations from planarity in the *cis* isomer, one could expect to find some parallelism between differential shieldings of the ethylenic carbons and the carboxyl carbon atom, as was found for α,β-unsaturated carbonyl compounds (ketones and aldehydes).[29] Such is indeed the case, but

TABLE 1. ^{13}C CHEMICAL SHIFTS OF THE UNSATURATED ACIDS UNDER STUDY. ($\delta_{CS_2} = 0$)

Compound	δ_{COOH}	δ_α			δ_β			δ_{CH_3}			Sample
		Expt.	Calc.	Δ	Expt.	Calc.	Δ	*gem*[a]	*cis*[a]	*trans*[a]	
Acrylic acid	−22·1	−65·3	−64	−1·3	−60·6	−60	−0·6				neat
Methacrylic acid	−20·6	−57·3	−57	−0·3	−66·2	−66	−0·2	−176·0			neat
Methacrylic acid[c]	−27·3	−56·7	−57	+0·3	−68·5	−66	−2·5	−175·4			neat
3,3-Dimethylacrylic acid	−23·5	−76·9	−74	−2·9	−35·6	−38	+2·4		−173·4	−166·4	neat
Tiglic acid	−23·6	−64·1	−61	−3·1	−56·2	−56	−0·2	−181·0		−179·0	neat
Z-2-Butenoic acid[d]		−71·8	−70	−1·8	−44·5	−48	+3·5				neat
E-2-Butenoic acid[d]		−70·8	−68	−2·8	−46·1	−50	+3·9				neat
E-2-Butenoic acid (crotonic acid)[c]	−28·1	−70·5	−68	−2·5	−48·9	−50	+1·1	−175·7			neat
Z-2-Pentenoic acid[44]	−21·0	−74·0	−73	−1·0	−38·5	−39	+0·5				neat
E-2-Pentenoic acid[44]	−20·6	−73·0	−72	−1·0	−40·0	−41	+1·0				neat
Z-2-Hexenoic acid[44]	−21·0	−73·8	−73	−0·8	−40·5	−39	+1·5				neat
E-2-Hexenoic acid[44]	−20·7	−72·0	−72	0	−41·2	−41	+0·2				neat
Z-4-Methyl-2-pentenoic acid[44]	−21·1	−76·1	−74	−2·1	−34·2	−34	−0·2				neat
E-4-Methyl-2-pentenoic acid[44]	−20·9	−74·8	−73	−1·8	−35·5	−36	+0·5				neat
Z-2-Heptenoic acid[44]	−21·0	−73·7	−73	−0·7	−40·2	−39	−1·2				neat
E-2-Heptenoic acid[d 44]	−20·8	−72·0	−72	0	−41·0	−41	0				neat
E-4,4-Dimethyl-2-pentenoic acid[44]	−24·4	−75·0	−73	−2·0	−34·3	−36	+1·7				[e]
Z-2-Octenoic acid[44]	−19·4	−72·4	−73	+0·6	−38·9	−39	+0·1				neat
E-2-Nonenoic acid[44]	−21·0	−71·8	−72	+0·2	−41·4	−41	−0·4				neat
E-2-Bromo-3-tert.butylacrylic acid[45]	−27·6	−77·8	−82	+4·2	−38·5	−42	+3·5				[e]
Z-3-Chloroacrylic acid[46]	−27·8	−70·3	−70	−0·3	−60·9	−61	+0·1				[e]
E-3-Chloroacrylic acid[46]	−27·8	−67·5	−68	+0·5	−56·2	−56	−0·2				[e]
Z-3-Bromoacrylic acid[46]	−27·4	−71·9	−69	−2·9	−67·6	−73	+5·4				[e]
E-3-Bromoacrylic acid[46]	−27·4	−62·5	−63	+0·5	−66·1	−61	−5·1				[e]
Z-3-Iodoacrylic acid[47]	−26·8	−62·2	−62	−0·2	−96·6	−99	+2·4				[e]
E-3-Iodoacrylic acid[48]	−27·4	−55·1	−53	−2·1	−91·6	−95	+3·4				[e]
Z-2,3-Dichloroacrylic acid[49]	−31·0	−64·4	−66	+1·6	−61·1	−64	+2·9				[e]
Z-2,3-Dibromoacrylic acid[50]	−30·7	−68·3	−71	+2·7	−65·6	−69	+3·4				[e]
E-2,3-Dibromoacrylic acid[50]	−29·8	−79·4	−77	−2·4	−81·8	−81	−0·8				[e]
E-2,3-Diiodoacrylic acid[51]	−26·6	−103·4	−100	−3·4	−106·0	−108	+2·0				[e]

E-2-Iodo-3-chloroacrylic acid[47]	−28·0	−105·1	−108	+2·9	−66·3	−70	+3·9			e
Z-3-Iodo-3-bromoacrylic acid[51]	−27·9	−57·8	−61	+3·2	−122·3	−122	−0·3			e
3,3-Dichloroacrylic acid[52]	−29·5	−71·0	−74	+3·0	−57·5	−57	−0·5			e
3,3-Dibromoacrylic acid[h50]	−28·5	−62·8	−68	+5·2	−88·7	−96	+7·3			e
3,3-Dibromomethacrylic acid[50]	−25·0	−54·8	−61	−6·2	−100·1	−102	+1·9	−170·9			e
3,3-Dibromo-2-ethylacrylic acid[50]	−25·1	−49·1	−52	+2·9	−102·0	−102	0			e
3,3-Dibromo-2-propylacrylic acid[50]	−24·1	−49·1	−52	+2·9	−100·8	−102	+1·2			e
3,3-Dibromo-2-isopropylacrylic acid[50]	−24·9	−43·9	−44	+0·1	−104·3	−102	−2·3			e
3,3-Dibromo-2-hydroxymethyl acrylic acid[53]	−25·9	−49·7	−50	+0·3	−100·3	−100	−0·3	−129·1[f]			e
3,3-Dibromo-2-bromomethyl acrylic acid[53]	−27·2	−55·1	−55	−0·1	−89·5	−90	+0·5	−160·0[g]			e
3,3-Diiodoacrylic acid[51]	−26·9	−51·0	−51	0	−160·2	−156	−4·2			e
2,3,3-Trichloroacrylic acid[h62]	−31·5	−69·4	−72	+2·6	−67·7	−65	+0·3			e
3,3-Diiodoacrylic acid[51]	−26·9	−51·0	−51	0	−160·2	−156	−4·2			e
2,3,3-Triiodoacrylic acid[51]	−23·9	−86·9	−89	+2·1	−163·9	−165	+1·1			e
E-3-Chloromethacrylic acid[54]	−25·4	−61·2	−61	−0·2	−61·2	−62	+0·8	−180·3			e
Z-3-Bromomethacrylic acid[55]	−26·0	−58·9	−62	+3·1	−85·0	−79	−6·0	−173·3			e
E-3-Bromomethacrylic acid[55]	−26·9	−58·8	−56	−2·8	−70·7	−67	−3·7	−177·9			e
E-2-Bromocrotonic acid[56]	−30·4	−77·9	−78	+0·1	−51·9	−56	+4·1		−176·1		e
2-Bromo-3-methylcrotonic acid[45]	−27·4	−82·8	−82	−0·8	−46·0	−46	0		−170·0	−165·9	e
Z-3-Chlorocrotonic acid[57]	−27·4	−74·9	−74	−0·9	−47·4	−51	+3·6			−164·7	e
E-3-Chlorocrotonic acid[57]	−26·4	−72·7	−74	+1·3	−40·5	−44	+3·5		−169·3		e
Z-2,3-Dichlorocrotonic acid[58]	−30·2	−71·5	−72	+0·5	−48·2	−52	+3·8		−168·7		e
E-2,3-Dichlorocrotonic acid[58]	−30·0	−72·9	−72	−0·9	−59·3	−59	−0·3			−167·9	e
Z-2,3-Dibromocrotonic acid[50]	−28·9	−77·2	−77	−0·2	−55·0	−57	+2·0		−165·0		e
E-2,3-Dibromocrotonic acid[50]	−27·7	−83·3	−81	−2·3	−72·7	−71	−1·7			−164·7	e
E-2,3-Diiodocrotonic acid[59]	−25·3	−104·5	−104	+0·5	−97·3	−98	+0·7			−154·7	e

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[a] Referred to the carboxylic group.

[b] $\Delta = \delta_{\text{expt.}} - \delta_{\text{calc.}}$

[c] Allyl ester.

[d] The data of Savitsky *et al.*

[e] Approximately 60% solution in dimethyl sulfoxide.

[f] Hydroxymethyl group.

[g] Bromomethyl group.

[h] Added in proof.

the correlation is very rough and the relative shift in the *cis*, or the sterically more crowded isomer, is not diamagnetic in all cases. It is clear, however, that the carboxylic group is instrumental in the large solvent effects of acrylic acid. Solvent effects of similar magnitude were found for methacryclic acid, but in the case of allyl methacrylate where the free carboxyl group was absent, only fairly uniform (0·4 ppm) paramagnetic shifts were found for all carbon atoms, even for the carbons of the allyl group. It is well known that dimethyl sulfoxide inhibits proton exchange and ionization. In the case of the acrylate ion in water solution the solvent effects were still larger and of a different character, leading to the reversal of ethylenic carbon shifts.

TABLE 2. ^{13}C CHEMICAL SHIFTS OF THE SIDE CHAINS OF THE UNSATURATED ACIDS UNDER STUDY ($\delta_{CS_2} = 0$)

Compound	Carbon atoms of the side chain					
	C_4[a]	C_5	C_6	C_7	C_8	C_9
Z-2-Pentenoic acid	−170·2	−179·8				
E-2-Pentenoic acid	−167·9	−181·4				
Z-2-Hexenoic acid	−162·1	−171·0	−179·9			
E-2-Hexenoic acid	−158·6	−171·7	−179·5			
Z-4-Methyl-2-pentenoic acid	−165·5	−171·3				
E-4-Methyl-2-pentenoic acid	−162·1	−172·3				
Z-2-Heptenoic acid	−164·2	−161·8	−170·7	−179·5		
E-4,4-Dimethyl-2-pentenoic acid	−159·2	−164·0				
Z-2-Octenoic acid	−162·8	−162·8	−160·2	−169·2	−178·0	
E-2-Nonenoic acid	−160·6	−164·7	−164·0	−161·0	−170·4	−179·1

[a] Methylene group adjacent to the double bond.

The solvent shift of the carboxyl group was paramagnetic in this case. Such a paramagnetic shift upon ionization is a regular feature, and was noted in the case of saturated acids as well.[37] In the case of acetic and butyric acids, salt formation leads to relative paramagnetic shifts of carboxyl and α-methylene carbon resonances, by 3 and 5 ppm respectively. These shifts are slightly larger in the case of acrylic acid, but of the same sign. These selective solvent effects are hard to interpret but useful for spectrum assignment. The assignment of the two ethylenic resonance peaks in the spectra of mucochloric and mucobromic acids is difficult (see Table 3). Although these acids are unstable in alkaline medium, the spectra could still be measured. There was a large paramagnetic shift of the high-field line in the ethylenic part of the spectrum of mucochloric acid. This result led to a reversal of the previous assignment and to a corresponding change of increments.[36] It must be noted that the new increments for the hydrated aldehydic group are more in line with other increments.

The total range of solvent shifts in the case of α-ethylenic carbon atom of acrylic acid is 7 ppm and 5·3 ppm for the other end of the double bond. Such shifts are sufficiently large to question whether any discussion of small shift differences (less than 1 ppm) between different compounds is warranted. Nevertheless, some qualitative conclusions are still possible.

The comparison of data in Table 1 shows that it is difficult to account for the stereochemical effects only through changes in the ground state wave functions and

TABLE 3. ^{13}C CHEMICAL SHIFTS OF DICARBOXYLIC AND ALDEHYDO ACIDS ($\delta_{CS_2} = 0$)

		δ_α			δ_β					
Compound	δ_{COO}[a]	Expt.	Calc.	Δ[b]	Expt.	Calc.	Δ[b]	δ_{COO}	δ_{COH}[c]	δ_{CH_3}
Maleic acid	−25·4	−62·0	−62	0	−62·0	−62	0	−25·4		
Fumaric acid	−25·9	−58·3	−58	−0·3	−58·3	−58	−0·3	−25·9		
Bromocitraconic acid[d] [55]	−26·1	−54·3	−54	−0·3	−71·0	−69	−2·0	−27·9		−172·4
Bromocitraconic anhydride[55]	−28·8	−46·8	. .	. .	−66·6	. .	. .	−31·7		−181·4
Mesaconic acid[e]	−24·3	−65·7	−64	−1·7	−49·7	−46	−3·7	−25·5		−178·8
Bromomesaconic acid[55]	−23·5	−51·2	−56	+4·8	−82·6	−77	−5·6	−28·0		−174·2
Z-Mucochloric acid[60]	−29·2	−70·3	−70	−0·3	−42·8	−42	−0·8	. .	−95·4	
Z-Mucobromic acid[61]	−27·9	−75·5	−75	−0·5	−45·5	−47	+1·5	. .	−92·8	

[a] Less crowded carboxylic group, adjacent to C_α.

[b] $\Delta = \delta_{expt.} - \delta_{calc.}$.

[c] Most probably the hydrated form $CH(OH)_2$.

[d] Dimethyl ester.

[e] Methylfumaric acid.

TABLE 4. INCREMENTS FOR THE SUBSTITUENTS UNDER STUDY

Substituent R	Z_i^{β}			Z_i^{α}		
	gem	*cis*	*trans*	*gem*	*cis*	*trans*
H	0	0	0	0	0	0
Cl	−8	−1	+4	+2	−6	−4
Br[a]	−8	−13[a]	−1[a]	−8	−5	+1
I[a]	−9	−39[a]	−35[a]	−38	+2	+11
CH_3	−6	+12	+10	+7	−6	−4
n-C_2, C_3, . . .	−6	+21	+19	+16	−9	−8
α-Branched C_3, C_4, . . .	−6	+26	+24	+24	−10	−9
CH_2OH[b]	−4			+18		
CH_2Br[b]	+6			+13		
CHO[bc]		+22			−4	
COOH ($COOOCH_3$)[b]		−2	+2		+2	+6

[a] Additional increment −22 ppm for $=CBr_2$, $=CBrI$ and $=CI_2$ groups.

[b] A very limited number of compounds was studied.

[c] Most probably the hydrated form $CH(OH)_2$.

charges on the carbon atoms.[4,6] The theory of Savitsky leaves open the mechanism of formation of such charges and does not allow one to interpret the differential shieldings in symmetrically substituted ethylenes. Moreover, if repulsive forces between substituents were the dominant cause for differential shieldings, one would expect the increments of *tert*-butyl and *iso*propyl groups to be very different from those for other alkyl groups; however, this is not the case. At the same time it is interesting to note that agreement can be found between our increments, given in Table 4, and the corresponding increments reported by Savitsky.[6] The best agreement was found between $Z_i^{\alpha}{}_{gem}$ and $\delta_{C^{\alpha}}$, but also between $\frac{1}{2}(Z_i^{\alpha}{}_{cis} + Z_i^{\alpha}{}_{trans})$ and $\delta_{C^{\alpha}}$ as well as between $\frac{1}{2}(Z_i^{\beta}{}_{cis} + Z_i^{\beta}{}_{trans})$ and $\delta_{C^{\beta}}$. It is possible that such empirical increments have a more general applicability for the structural analysis of ethylenic compounds.

TABLE 5. SOLVENT EFFECTS

Compound	Solution	^{13}C chemical shifts[a]				
		CH_2	CH	C	CH_3	COO
Acrylic acid	neat	−60·6	−65·3			−22·1
	50 per cent in water	−60·3	−64·8			−23·1
	50 per cent in dimethyl sulfoxide	−62·1	−63·5			−25·3
	50 per cent of potassium acrylate in water	−65·9	−58·3			−18·1
Methacrylic acid	neat	−66·2		−57·3	−176·0	−20·6
	50 per cent in dimethyl sulfoxide	−67·6		−56·3	−175·3	−23·7
Allyl methacrylate[b]	neat	−68·5		−56·7	−175·4	−27·3
	50 per cent in dimethyl sulfoxide	−67·8		−56·7	−175·1	−26·9

[a] Measured at 50°C temperature.

[b] Acid moiety only.

There is certainly a definite parallelism between the differential shieldings and both dynamic and static[38] polarizabilities of the relevant bonds.[18] If this approach is correct, then it should not be confined to the C—H bond only. Of course, the agreement can only be of qualitative nature, since the molecular polarizability tensor is only formally divisible into bond increments which are, in general, not additive. Good additivity is only possible for the mean value of polarizability[39] and not for the longitudinal components.

It seems that, in addition to differences between molecular ground state wave functions, the excited states may be involved as well. Changes in ΔE have attracted undeservedly little attention as a cause for the differential shielding in pairs of stereoisomers.[9] It is well known that the spectra of ethylenic compounds in the far ultraviolet are susceptible to the geometric configuration. *Cis* isomers absorb at 176·5 ± 1·5 and *trans* isomers at 179 ± 1 nm.[40] Likewise *cis* cinnamic acid has an absorption peak at 264 nm ($\varepsilon = 9500$) and the *trans* acid at 273 nm ($\varepsilon = 20{,}000$).[41] The longer-wavelength part of the far ultraviolet spectrum of butane contains strong lines which correspond to $\sigma \rightarrow \sigma^*$ transitions. The broad line at 142 nm corresponds to the transoid conformation, but the line at 133·5 nm to the *gauche* conformation,[42] where the molecular conformation of n-butane is close to the ethylenic *cis* configuration with some interaction between the substituent groups. If the paramagnetic part of the screening constant in substituted ethylenes is not very different from the value for ethylene, one could expect to have a relationship between the relative displacement of ultraviolet peaks and differential shieldings, equal to 1·8 ppm/nm. The experimental values are less than this, as was the case for cyclic ketones where the same interpretation of ^{13}C chemical shifts was used.[43]

Practically no data about ultraviolet spectra of acrylic acids have been published. Preliminary experiments with *E*- and *Z*-pairs of iodoacrylic, 2,3-dibromoacrylic and 2,3-dibromocrotonic acids showed that the ultraviolet spectra of the isomeric acids are very different. The more crowded isomers, in which the halogen atom and carboxylic group were in *cis* positions had stronger absorption at shorter wavelengths. The sum total of chemical shifts of ethylenic carbons was larger (more diamagnetic) for these acids, as could be expected for larger mean excitation energies ΔE. Of course, the more crowded isomer is *Z*-isomer in the case of monosubstituted acids and *E*-isomer for 2,3-dibromo acids. The difference in ultraviolet spectra is largest for the pair of isomeric 2,3-dibromoacrylic acids, where the differential shielding of ethylenic carbons is also largest.

The carbon chemical shifts of unsubstituted α,β-unsaturated acids (see Table 2) behave in a regular manner. The differential shieldings of both ethylenic and side chain methylene carbons in pairs of isomeric acids are very close to the values found for octenes.[9] Clearly, these shifts and particularly the chemical shift of the methylene group, adjacent to the double bond, may be used for geometrical assignments. It is important to note that the chemical shift of the carboxylic carbon atom in the same acids is much less susceptible to geometrical isomerism than is the shift of the last-mentioned methylene carbon, even though the polarizability of C═O bond is much higher than the polarizability of C—H bond in the methylene group.[38] The shifts of methyl groups are just as characteristic of molecular structure as the methylene shifts. In addition to this, these shifts provide some additional information about the position of halogen atoms or other methyl groups in the molecule. *Gem*-substitution leads to a significant 10 ppm paramagnetic downfield shift of the methyl carbon resonance. *Trans*-substitution leads to a smaller (5 ppm) paramagnetic shift while the effect of *cis* substitution is in general diamagnetic. Substituent effects are remarkably independent of the substituent character (halogen or methyl) and follow the general pattern established for unsaturated hydrocarbons.

EXPERIMENTAL

References to the preparation of the acids under study are given in Tables 1 and 3.

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