camera with Cu$K\alpha$-radiation and $Pb(NO_3)_2$ as a standard. The unit cell parameters were refined by a least squares treatment minimizing $\sum w(\sin^2\theta_o - \sin^2\theta_c)^2$ with weights $w = 1/\sin^2 2\theta_o$. The following cell dimensions with estimated standard deviations were obtained:

a = 9.097 ± 0.005 Å; β = 111.38 ± 0.01°;
b = 5.307 ± 0.001 Å; V = 732.0 ± 0.5 Å^3;
c = 16.284 ± 0.003 Å;

Even if the values of a and c are somewhat higher than those published by Clearfield and Smith[4] there are no great difference between the two sets of lattice parameters. The observed and calculated values of $\sin^2\theta$ are listed in Table 1. The X-ray diffraction pattern of crystalline zirconium phosphate is shown in Fig. 1. Both the new and earlier indices of the strongest reflexions are given.

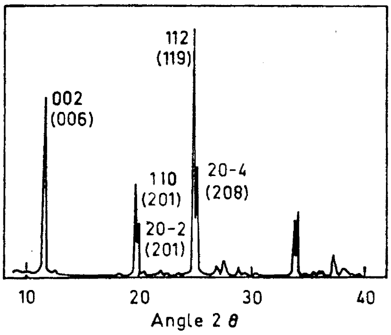

Fig. 1. X-Ray diffraction pattern of crystalline $Zr(HPO_4)_2 \cdot H_2O$. The indices used in Refs. 1 and 2 are put within brackets.

The (wrong) structure of $Zr(HPO_4)_2 \cdot H_2O$ referred to in the preceding papers[1,2] had a hexagonal unit-cell with $a = b =$ 10.5 Å and $c = 45.6$ Å. The zirconium atoms were assumed to occupy the positions (0,0,0; 1/3,2/3,2/3; 2/3,1/3,1/3) in a rhombohedral centered pseudocell of half the cell dimensions. However, Clearfield and Smith[4] have pointed out that in their finally obtained monoclinic structure the zirconium atoms occupy positions very close to (0,0,0; 1/3,2/3,1/3; 2/3,1/3,2/3) in a pseudo-hexagonal cell which is related to the true unit cell as follows: $a_h = a_m/\sqrt{3} = 5.25$ Å, $b_h = b_m = 5.31$ Å, $c_h = (3c_m \cos 21.4°)/2 = 22.74$ Å; c_h is parallel to c_m^*. The conclusions reached in Refs. 1 and 2 are thus correct in their essential parts even if they to some extent are based upon a wrong hexagonal crystal structure for zirconium phosphate.

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The Use of Carbon-13 Shifts in the Structural Determination of α,β-Unsaturated Acids

CHRISTOFFER RAPPE,* ENDEL LIPPMAA,** TÕNIS PEHK,** and KURT ANDERSSON*

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden
and
Estonian Academy of Sciences, Institute of Cybernetics, Tallinn, U.S.S.R.

This paper describes a straightforward ^{13}C-NMR technique by which geometric assignments can be made for a wide variety of di- and trisubstituted α,β-unsaturated acids. The only information required is the ^{13}C chemical shifts for the olefinic carbons of the compound under study. 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 ^1H-NMR spectra,[1] and it is also a complement to the method

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* Uppsala University.
** Estonian Academy.

Table 1. ^{13}C-Shifts for the acids under study.

Compound	δ_β			δ_α		
	Expt.	Calc.	Δ^a	Expt.	Calc.	Δ^a
Z-3-Chloroacrylic acid	60.9	61	−0.1	70.3	70	0.3
E-3-Chloroacrylic acid	56.2	56	0.2	67.5	68	−0.5
Z-3-Bromoacrylic acid	67.6	73	−5.4	71.9	69	2.9
E-3-Bromoacrylic acid	66.1	61	5.1	62.5	63	−0.5
Z-3-Iodoacrylic acid	96.6	99	−2.4	62.2	62	0.2
E-3-Iodoacrylic acid	91.6	95	−3.4	55.1	53	2.0
Z-2,3-Dibromoacrylic acid	65.6	69	−3.4	68.3	71	−2.7
E-2,3-Dibromoacrylic acid	81.8	81	0.8	79.4	77	2.4
Z-3-Bromomethacrylic acid	85.0	79	6.0	58.9	62	−3.1
E-3-Bromomethacrylic acid	70.7	67	3.7	58.8	56	2.8
Z-3-Chloro-2-butenoic acid	47.4	51	−3.6	74.9	74	0.9
E-3-Chloro-2-butenoic acid	40.5	44	−3.5	72.7	74	−1.3
Z-2,3-Dichloro-2-butenoic acid	48.2	52	−3.8	71.5	72	−0.5
E-2,3-Dichloro-2-butenoic acid	59.3	59	0.3	72.9	72	0.9
Z-2,3-Dibromo-2-butenoic acid	55.0	57	−2.0	77.2	77	0.2
E-2,3-Dibromo-2-butenoic acid	72.7	71	1.7	83.3	81	2.3
Z-2-Butenoic acid [b]	44.5	48	−3.5	71.8	70	1.8
E-2-Butenoic acid [b]	46.1	50	−3.9	70.8	68	2.8
Z-2-Pentenoic acid	38.5	39	−0.5	74.0	73	1.0
E-2-Pentenoic acid	40.0	41	−1.0	73.0	72	1.0

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

[b] The data of Savitsky *et al.*[7]

Table 2. Increments for the substituents under study.

Substituent R		$Z_i\beta$			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[b,c]		+ 6			−24	
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 $CH(OH)_2$.

for assigning structures to higher substituted ethylenes *via* the additivity of substituent shielding on vinyl proton shifts.[2,3]

^{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. 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.

Additive parameters for ^{13}C-NMR spectra of hydrocarbons have been suggested by Grant and Paul,[4] and by Savitsky and Namikawa,[5] and today the increments are known for important substituents in saturated and unsaturated systems. However, the theoretical background for the additivity does not seem to be completely understood.[6,7] ^{13}C-NMR spectra have previously been recorded for rather many olefinic and alicyclic compounds, and small differences were found between ^{13}C chemical shifts in stereoisomers.[7–13] Although Savitsky *et al.* observed differences in the ^{13}C chemical shifts for the two geometric isomers,[7] their parameters do not take any account of the geometric situation of the molecule: thus these ^{13}C-increments cannot be used for structural determination of geometric isomers.

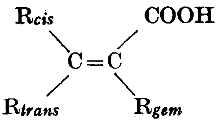
In the present investigation we have made a systematic study of α,β-unsaturated carboxylic acids, among them 14 Z- and E-pairs, see Table 1. The Z- and E-nomenclature refers to *Z*usammen (together) and *E*ntgegen (opposite) for the groups of priority according to the sequence rules of Cahn, Ingold and Prelog;[14] see also Blackwood *et al.*[15]

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

$$\delta_\alpha = 64 + \sum_i Z_i^\alpha \qquad \text{(ppm)}$$

$$\delta_\beta = 60 + \sum_i Z_i^\beta \qquad \text{(ppm)}$$

where the increments of the first carboxylic group is included in the constants 64 and 60 ppm (from the shifts of acrylic acid). Contrary to Savitsky *et al.*[7] we observed that the increments of the various substituents *varied with the geometrical position* of the substituent. $\sum Z_i$ is the sum of the increments for the substituents R_{gem}, R_{cis}, and R_{trans}, where *gem*, *cis*, and *trans* refer to the carboxylic group



The increments are given in Table 2. This means that ^{13}C-NMR spectroscopy can be used for *structural* determination of α,β-unsaturated acids where ^{1}H-NMR spectroscopy cannot be used.

The ^{13}C-NMR chemical shifts showed good additivity; the differences 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 $4/30 = 0.13$ ppm in ^{1}H-NMR spectroscopy. For the vinyl proton shifts Pascual *et al.* state that three-quarters of their values are within 0.15 ppm from the predicted ones.[3] 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 reasons for the existence of additive increments [4–7] is not clear. Indeed, there is more justification for a pairwise additivity [16] 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 reference for the increments.

Liquid compounds are studied neat, crystalline substances in about 50 % DMSO solution.

Agreement can be found between our increments, given in Table 2, and the corresponding increments given by Savitsky.[7] The best agreement was found between $Z_i{}^{\alpha}{}_{gem}$ and $\delta_C{}^x$.

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 Z- and E-isomers.

A detailed description of the ^{13}C-NMR technique used, complete tables for all acids studied and all ^{13}C-shifts, and references for the preparation of the α,β-unsaturated acids will be given elsewhere.

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An Apparatus for Displacement Electrophoresis

STIG FREDRIKSSON

Department of Physical Chemistry, Chalmers Institute of Technology, Gothenburg, Sweden

During the last three years, several papers[1–7] have been published on an electrophoretic technique of separating ions of the same charge-sign but different mobilities. According to this technique, originally suggested by Kendall[8] and later named "displacement electrophoresis" by Martin,[3] a sample of the ions to be separated is placed, in the direction of migration, behind a more mobile ion than any of the same charge-sign in the sample, and in front of a less mobile ion. On passage of current, the ions in the sample will arrange themselves, in the order of decreasing mobility, into a system of consecutive zones, separated by sharp moving boundaries. The length of a zone is proportional to the amount of the ion in the sample. The proportionality constant is a function of the mobility of the sample ion and the concentration and mobility of the fast ion.

At this laboratory, work has been going on since 1964 to develop, according to the principles above, an apparatus for quantitative analysis of fatty acid mixtures. As, among other things, the ways of introducing the sample and detecting the moving boundaries with the apparatus constructed here are quite different from those in the literature cited, a short description of its design and function is given below together with some results obtained with it.

The electrophoresis apparatus consists basically of a U-tube of glass (Fig. 1) with attached electrode vessels (E_1, E_2). The U-tube is surrounded by a cooling mantle of glass. The electrodes are platinum wires, dipping down about 1 cm into the solutions. To facilitate the introduction of the sample, a special valve (V) is inserted between the narrower leg (U_1, ∅ 4 mm) of the U-tube and E_1.

The valve consists of three pieces of Perspex, two of which are fixed (A and B in Fig. 2) and one (C) is movable between two end positions by means of an oblong hole (H) and a screw (S). In each piece,