Table 3.

Comparison of intensities used in the determination of absolute configuration.
The ratio q = I(hkl)/I(h̄k̄l̄) is given as observed with standard deviations x 100 in parentheses and as calculated. All together 49 q-ratios were measured. None of those left out was in contradiction to the results listed.

hkl	q(obs)	q(calc)	hkl	q(obs)	q(calc)
111	0.77 (1)	0.72	231	1.11 (3)	1.26
113	0.69 (2)	0.63	23̄1̄	1.14 (2)	1.26
11̄3̄	0.88 (3)	0.69	234	1.40 (4)	1.66
11̄5̄	1.47 (6)	1.34	2̄3̄4	1.23 (3)	1.66
123	0.82 (2)	0.91	332	0.90 (3)	0.91
1̄2̄3	0.91 (2)	0.91	33̄2̄	0.84 (3)	0.91
131	0.61 (1)	0.50	343	0.64 (12)	0.62
13̄1̄	0.59 (1)	0.50	34̄3̄	0.71 (14)	0.62
141	1.16 (5)	1.10	361	1.38 (6)	1.42
1̄4̄1̄	1.15 (5)	1.10	36̄1̄	1.26 (6)	1.42
211	0.81 (1)	0.72	415	0.58 (2)	0.69
223	0.57 (1)	0.48	324	0.76 (2)	0.72
2̄2̄3	0.65 (1)	0.48	32̄4̄	0.87 (3)	0.72

L-(+)-Aspartic acid has the *S*-configuration according to the Cahn-Ingold notation. As (−)-chlorosuccinic acid [2] and (−)-malic acid [3] also have the *S*-configuration, no inversion takes place in the reactions leading from aspartic acid to these two compounds. The structural results are in accordance with those of Doyne et al.[4] When our structural work was completed, we became aware of a subsequent refinement of the data reported in Ref. 4. Doyne reports refined parameters for Zn(II)-aspartate trihydrate in *Advan. Protein Chem.*[12] These data are probably less accurate than those reported here, but on the average there is a good agreement between the two sets of results.

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The Effect of Oxygen Lone Pairs on $^1J(^{13}CH)$ Values in 1,3-Dioxanes

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Recently we have shown that $^1J(^{13}CH)$ values can be used to determine the anomeric configuration in carbohydrate derivatives since the carbon-hydrogen coupling constant is *ca.* 10 Hz larger when the proton is equatorially oriented than when it is axial.[1,2]

We have now studied a number of 1,3-dioxane derivatives and have found that the $^1J(^{13}CH)$ values are dependent on the orientation of the protons relative to the ring oxygens.

The assignments of the ^{13}C-chemical shifts are based mainly on published values as shown in Table 1. Undecoupled spectra were obtained using gated decoupling technique.[3]

The $^1J(^{13}C-H2)$ value of *trans*-2-methyl-5-*t*-butyl-1,3-dioxane (*2*), or of the corresponding 2-phenyl derivative (*3*), was 158

Table 1. ^{13}C-Chemical shifts (ppm)[a] and observed 1 st. order one-bond coupling constants (Hz)[b].

1,3-Dioxane	C-2	C-4	C-5	C-6	5-Cα	5-Cβ	2-Cα	4-Cα	6-Cα	Reference
	93.15	68.22	43.76	68.22	30.36	27.19				
1. 5-*t*-Bu	158									4,9
	166	142.5	127.5	142.5		125				
2. *trans*-2-Me-	98.19	68.09	42.91	68.09	30.03	27.12	20.71			
5-*t*-Bu	158	141.3	127.5	141.3		125	125			4,9
3. *trans*-2-Ph-	100.85	68.87	43.30	68.87	30.23	27.32				
5-*t*-Bu	158	142.5	127.5	142.5		125				4,9
4. *cis*-Paraldehyde	97.78						20.11			4
	159						126.6			
5. *cis*-4,6-di-Me	93.02	72.30	40.98	72.30				21.56	21.56	
	157.5									4,10
	166.5	137	127.5	137				125	125	
6. *trans*-4,6-di-	86.38	67.19	37.38	67.19				19.13	19.13	
Me	161	142.5	127.5	142.5				125	125	4,10
7. 2-*cis*-4-*cis*-6-	97.81	71.79	40.00	71.79			20.97	21.36	21.36	
-tri-Me			123.5							4
	158	138	127.5	138			126.5	125.9	125.9	
8. 2-*trans*-4-*trans*-	93.11	63.76	40.13	63.76			16.70	21.62	21.62	
6-tri-Me	165	140	126	140			126	125.3	125.3	4
9. 2-*cis*-4-*trans*-6-	90.36	66.54	36.18	67.13			20.97	21.43	16.77	
tri-Me	158.5	137	126.5	150			125.8	126.5	125	4,10
10. *trans*-2-*O*-Me-	111.14	65.64	42.62	65.64	30.36	27.45	51.62			
5-*t*-Bu	186	142.5	127.5	142.5		125	144.2			11
11. *cis*-2-*O*-Me-5-	107.78	60.04	42.85	60.04	30.52	27.28	52.14			
t-Bu	193	142.5	127.5	142.5		125	142.5			11

[a] Measured at 22.63 MHz on a Bruker WH-90 instrument, *ca.* 25 % solutions in CDCl$_3$, used as internal reference = 76.90 ppm. [b] ±0.7 Hz using pulsed decoupling technique.

Hz, whereas C-2 in the unsubstituted derivative (*1*) showed up as a double doublet with coupling constants of 158 and 166 Hz. It is known from previously published work [4] that the methyl or phenyl group is equatorially oriented and we therefore conclude that $^1J(^{13}C\text{-}H2_{ax})$ is 158 Hz and $^1J(^{13}C\text{-}H2_{eq})$ is 166 Hz. This is in accordance with the results found in the carbohydrate derivatives mentioned above.

Paraldehyde (*4*) gives a $^1J(^{13}CH)$ value of 159 Hz, consistent with an equatorial methyl group and an axial proton.[4]

cis-4,6-Dimethyl-1,3-dioxane (*5*) exhibits the same $^1J(^{13}C\text{-}H2)$ value as (*1*) (see Table 1). The *trans* isomer (*6*), on the other hand, gives a value of 161 Hz, but it is known from proton NMR spectroscopy that this compound is conformationally unstable [4] and a coupling constant of 158 − 166 Hz would therefore be expected. Substitution of one of the protons at C-2 in (*5*) with a methyl group as in 2-*cis*-4-*cis*-6-trimethyl-1,3-dioxane (*7*) or in 2-*trans*-4-*trans*-6-trimethyl-1,3-dioxane (*8*),

confirms the assignments of the $^1J(^{13}C\text{-}H2)$ values in (*5*) (see Table 1).

Several authors have discussed the effect of electron lone pairs on ^{13}CH coupling constants, and the available evidence indicates that directly bonded ^{13}CH coupling constants are increased when neighbouring lone pairs are present at a position close to the proton.[5-8] This effect may explain the difference in $^1J(^{13}C\text{-}H2)$ values in 1,3-dioxanes since equatorial protons, which are close to the lone pairs of the ring oxygens have larger coupling constants than axial protons.

Both oxygen atoms do not necessarily have to be within the ring with fixed orientation of the lone pairs. This is seen in the carbohydrate derivatives mentioned above, where only one oxygen atom is in the pyranose ring. But also 1,3-dioxane derivatives with an OR-substituent at C-2 exhibit different coupling constants to an axial and to an equatotial proton. Thus 2-*O*-methyl-5-*t*-butyl-1,3-dioxane gives a $^1J(^{13}C\text{-}H2)$ value of 186 Hz for the *trans* isomer (*10*) with an axial proton at C-2

whereas the *cis* isomer (*11*) gives a coupling constants of 193 Hz.

2-*cis*-4-*trans*-6-Trimethyl-1,3-dioxane (*9*) exists mainly in the conformation with the methyl substituent at C-2 equatorial, as shown by Eliel and Knoeber from proton NMR spectra,[4] and we have in accordance herewith found that $^1J(^{13}C$-H2) is 159 Hz. In this compound the coupling constants to H-4 and H-6 are 138 Hz and 150 Hz, respectively. The assignment of these coupling constants is based on the value of $^1J(^{13}C$-H4) $=138$ Hz in (*5*) and (*7*), where H-4 must be axially oriented. We here see that the lone pairs from only one oxygen atom can have a large influence on ^{13}CH coupling constants. This effect has also been found in methyl-pento-pyranosides.[2]

We conclude from these results that the difference in directly bonded ^{13}CH coupling constants to axial and equatorial protons is due to the effect of lone pairs on neighbouring oxygen atoms.

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Structure of Bis-(1-ethynylcyclohexanol)-bis-(triphenylphosphine)platinum

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Crystals of $Pt(P(C_6H_5)_3)_2(C_8H_{12}O)_2$ were kindly supplied by Dr. H. B. Jonassen of Tulane University, New Orleans. The complex has been subject to IR and NMR spectroscopic investigations by Roundhill and Jonassen.[1] Two kinds of crystals were found in the sample: a triclinic modification not yet extensively investigated and the monoclinic form reported here. The monoclinic crystals appear to be the more numerous.

Experimental. A plate-shaped crystal $0.3 \times 0.22 \times 0.51$ mm was mounted along *c*. Cell dimensions and systematic absences were obtained from Weissenberg and precession photographs and were confirmed by diffractometer measurements. The conditions limiting possible reflections were: $0k0$: $k=2n$, $h0l$: $h+l=2n$. hkl: no conditions. The crystals are monoclinic, space group $P2_1/n$, $Z=2$, F.W.= 966.0, $a=8.992$, $b=23.012$, $c=11.585$ Å, $\beta= 105.35°$, $V=2311$ Å³, $D_m=1.43$, $D_c=1.39$ g cm⁻³, $\lambda(MoK\alpha)=0.7107$ Å, $\mu(MoK\alpha)=33.0$ cm⁻¹.

The density was measured by flotation in a mixture of heptane and carbon tetrachloride. Intensities were measured on an Arndt-Phillips linear diffractometer. MoKα radiation was selected by a graphite monochromator. The counting chain included a scintillation counter and a pulse height analyzer. 6288 reflections with $l=0$ to 14 were measured to a sin θ/λ limit of 0.64 Å⁻¹. Symmetry related reflections were averaged. 2898 independent reflections had intensities above two standard deviations as derived by counting statistics and were employed in subsequent computations. Lorentz and polarization factors were applied, assuming the graphite monochromator to behave as an ideal mosaic crystal. An absorption correction was applied, the correction factors ranging from 1.60 to 2.70.

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