distillation followed by ether extraction, drying, and evaporation operations furnished a residue, which was purified by preparative GC [Chromosorb PNAW 60, 10% CW + 2% KOH (column length 1.8 m, 150 °C)]: yield, 1.06 g (57.4%); IR (neat) ν 2800 cm^{-1} (N-CH$_2$); ^{1}H NMR (C$_6$D$_6$) δ 2.44 (t, 4 H, CH$_2$), 1.80–1.40 (m, 10 H, CH$_2$), 0.97 (s, 9 H, CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 54.4 (s), 47.9 (t), 30.2 (t), 28.5 (t), 26.8 (q), 26.4 (t); MS, *m/e* 169 (M$^+$).

Anal. Calcd for C$_{11}$H$_{23}$N: C, 78.03; H, 13.69; N, 8.27. Found: C, 78.43; H, 13.67; N, 7.90.

Picrate (from ethanol): mp 159 °C.

Anal. Calcd for C$_{17}$H$_{26}$N$_4$O$_7$: C, 51.25; H, 6.58; N, 14.06. Found: C, 51.22; H, 6.56; N, 13.99.

X-ray Structure Analysis. Crystal Data: C$_{11}$H$_{21}$NO; M = 183.29; triclinic; a = 5.966 (3) Å, b = 7.737 (3) Å, c = 12.492 (5) Å; α = 101.83 (3)°, β = 93.34 (4)°, γ = 102.81 (4)°; V = 547.14 (4) Å^3 (at −155 °C, by least-squares refinement on diffractometer angles for 25 automatically centered reflections with $21° \leq 2\theta \leq 25°$, λ = 0.71069 Å); space group $P\bar{1}$ (No. 2); Z = 2; D_x = 1.1129 g cm^{-3}; crystal dimensions; 0.28 × 0.18 × 0.15 mm; μ(Mo Kα) = 0.65 cm^{-1}.

Data Collection and Processing: Syntex R3 four-circle diffractometer, ω scan mode, $2\theta_{max}$ = 70°, ω scan speed 2.0–20.0° min^{-1}, graphite-monochromated Mo Kα radiation; T = −155 ± 0.5 °C; 6091 reflections measured, merging to 4833 independent reflections (R_{merg} = 0.024), giving 3910 unique observed reflections, $F_o \geq 3.5\sigma(F)$.

Structure Analysis and Refinement. The coordinates of all non-hydrogen atoms were determined by direct methods and refined by using the SHELXTL program system[25] with the incorporated scattering factors on a NOVA 3/12 (Data General) computer. The positions of the hydrogen atoms were calculated on ideal geometry and refined as rigid groups (C–H distance, 96 pm; H–C–H angle, 109.5°). Their isotropic temperature factors were given the 1.2 fold of the U_{ij} tensor of the corresponding C atom. The refinement of 145 parameters converged to R = 0.051, R_w = 0.057, weighting scheme $w^{-1} = \sigma^2(F) + (8.3 \times 10^{-4})F^2$: residual maximum electron density 0.403 e/Å^3 between C(2) and C(3), residual minimum electron density 0.24 e/Å^3.

Acknowledgment. We are indebted to Mr. R. Poppek for excellent assistance with the recording of the PE spectra and to Mr. H. Henning for the measurements of IR spectra.

Registry No. **1**, 71512-38-4; **2**, 37727-90-5; **3**, 108696-09-9; **4**, 108696-10-2; **5**, 19719-81-4; **6**, 73676-23-0; **7**, 108696-11-3; **8**, 108696-12-4; cyclooctanone, 502-49-8.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and anisotropic temperature factors and a figure showing the packing of the molecules (6 pages); observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Experimental Evidence of Deviations from a Karplus-Like Relationship of Vicinal Carbon–Proton Coupling Constants in Some Conformationally Rigid Carbohydrate Derivatives

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The values of vicinal carbon–proton coupling constants for the conformationally rigid carbohydrate derivatives *N*-acetyl-3,4-di-*O*-acetyl-1,2-dideoxy-β-D-hexo(pento)pyranosyl[1,2-*d*]oxazolidin-2′-ones (**1–4**), 2,4-di-*O*-acetyl-1-acetamido-1-deoxy-1-*N*,3-*O*-carbonyl-α-L-arabinopyranose (**5**), and 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-hexopyranoses (**6–12**) are reported. $^3J_{C,H}$ values were determined by the selective 2D heteronuclear *J*-resolved method proposed by Bax and Freeman. The values found were used as input parameters for simulating the coupled carbon spectra. From the final best values it may be concluded that both the number and relative orientation of substituents in a complex organic molecule may substantially modify the general shape of the existing Karplus-like relationship between $^3J_{C,H}$ and the corresponding dihedral angle. The crystal structures of *N*-acetyl-3,4-di-*O*-acetyl-1,2-dideoxy-β-D-gluco- and -xylopyranosyl[1,2-*d*]oxazolidin-2′-ones (**1** and **3**) and compound **5** have also been studied in order to determine the geometry of these molecules in the solid state.

Carbon–proton coupling constants are not yet routinely used in the conformational analysis of organic molecules due to experimental difficulties involved in their measurement by classical ^{1}H-coupled ^{13}C NMR spectroscopy and to the scarcity of reliable published data.[1] However, it has been shown that vicinal $^3J_{C,H}$ coupling constants are related to the torsion angle C–X–Y–H by a Karplus-like relationship[2] and, therefore, could give interesting conformational information in solution on molecules whose conformations cannot be investigated by ^{1}H NMR spectroscopy, such as those containing five-membered rings, peptides, oligosaccharides (conformation of the glycosidic bonds), etc. Theoretical studies have also demonstrated that there exists a general Karplus plot relating $^3J_{C,H}$ with torsion angle for propane[3] and substituted propanes,[4] al-

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Table I. ^1H NMR Spectral Parameters (δ) and J (Hertz) of 1–5

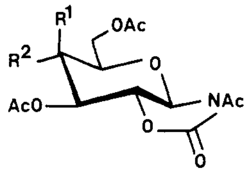
parameter	compound 1^a	2^b	3^b	4^b	5^b
H-1	4.41	5.08	5.08	5.47	6.03
H-2	3.54	4.41	4.01	4.06	5.17
H-3	5.22	5.37	5.45	5.96	4.85
H-4	5.48	5.57	5.12	5.12	5.25
$H-5_{eq}$			4.35	4.08	4.01
$H-5_{ax}$	3.67	4.2	3.66	3.84	3.55
H-6	4.30	4.2			
H-6′	4.13	4.2			
$J_{1,2}$	9.1	9.2	9.2	9.4	2.1
$J_{1,3}$	...	...	...	...	2.1
$J_{2,3}$	11.0	11.3	11.0	2.0	5.0
$J_{3,4}$	8.7	3.6	8.1	3.1	2.5
$J_{4,5_{eq}}$			6.3	6.0	6.4
$J_{4,5_{ax}}$	8.0	1.0	10.0	11.1	11.0
$J_{5_{eq},5_{ax}}$			−12.0	−11.4	−11.9
$J_{5,6}$	4.4	...			
$J_{5,6'}$	2.2	...			
$J_{6,6'}$	−12.8	...			

[a] In C_6D_6. [b] In $CDCl_3$.

though the importance of nonbonded interactions in the value of $^3J_{C,H}$ has been emphasized as well.[5]

As a part of our studies on the conformation of some bicyclic carbohydrate derivatives,[6] we are interested in the conformation of dioxolane-type acetals of carbohydrates, and we have determined carbon–proton coupling constants for a variety of these and related compounds.[7,8] We now report our results on a series of conformationally rigid bicyclic carbohydrate derivatives having five-membered rings in a relatively fixed conformation and pyranoid rings in both the $^4C_1$ and $^1C_4$ conformations. This study has been carried out in an attempt to obtain reliable values of $^3J_{C,H}$ in order to evaluate the extent that a Karplus-like relationship holds for these types of molecules. The values of $^3J_{C,H}$ have been determined by using the selective 2D heteronuclear J-resolved experimental method developed by Bax and Freeman[9] and, in some cases, by simulation of the coupled carbon spectra. This bidimensional method, which uses a selective proton π pulse and permits the observation of long-range couplings between the carbon atoms and the irradiated proton in the F_1 dimension, greatly facilitates the measurements, although some artifacts may appear in the spectra when the irradiated proton is strongly coupled or not sufficiently isolated. In these cases, the simulation of the coupled spectra, when possible, may give good results. We have found that, in our conformationally rigid molecules, the relative position of the substituents along the coupling path greatly influences the $^3J_{C,H}$ values, which results in important deviations from a Karplus-like dependence.

As model compounds having a rigid dioxolane ring and a pyranoid ring with a rigid $^1C_4$ conformation, we have studied the whole series of tri-*O*-acetyl-1,6-anhydro-β-D-hexopyranoses **6–12** with the exception of the D-idose derivative. Also, with a pyranoid ring fixed in the $^1C_4$ conformation, the cyclic carbamate **5** has been examined. The model compounds possessing a pyranoid ring in a fixed $^4C_1$ conformation have been the peracetylated pyranosylamines (1,2-cyclic carbamates) **1–4**.



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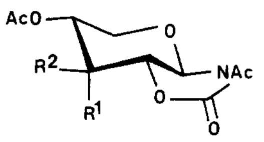
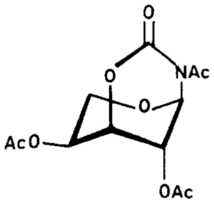
2 $R^1 = OAc$ $R^2 = H$



3 $R^1 = H$ $R^2 = OAc$

4 $R^1 = OAc$ $R^2 = H$



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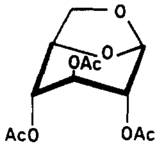

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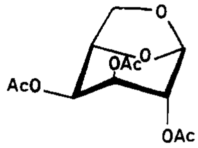

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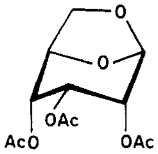

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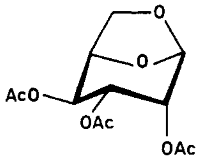

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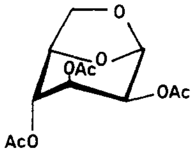

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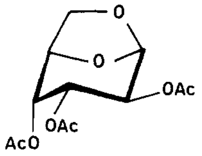

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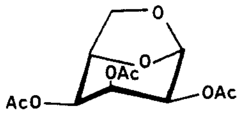

12

Reaction of β-D-xylopyranosyl azide and β-D-ribopyranosyl azide with carbon dioxide and triphenylphosphine in acetone and subsequent acetylation, as previously reported[10] for the preparation of **1** and **2**, gave the corresponding 1,2-cyclic carbamates **3** and **4**, respectively. Similar treatment of α-L-arabinopyranosyl azide gave a product **5**, whose ^1H NMR spectrum (Table I) showed large long-range $J_{1,3}$ (2.1 Hz), small $J_{1,2}$ (2.1 Hz), and large $J_{4,5_{ax}}$ (11.0 Hz) coupling constants, indicative of a $^1C_4$ chair conformation of the pyranoid ring, rather unlike that for a 1,2-trans-fused cyclic carbamate structure. The X-ray crystallographic analysis of this substance indicated the structure to be that of a 1,3-cyclic carbamate **5**.

Since there had been some uncertainty as to the actual configuration of the 1,2-cyclic carbamate derivatives[11] and a very accurate knowledge of the geometry of these compounds, also in the solid state, was needed for our conformational studies on bicyclic carbohydrate derivatives, the X-ray crystallographic analyses of compounds **1** and **3** were also performed. Two unique molecules of **5** were present in the unit cell. It could be concluded from the crystallographic study that compound **5** shows the more even distribution of intracyclic bond angles and different

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Table II. Experimental Torsion Angles (Degrees) for the Six- and Five-Membered Rings in 1, 3, and 5

	compound			
angles	1	3	5	5′
O-5–C-1–C-2–C-3	74.0 (3)	76.9 (3)	–60.3 (4)	–60.6 (4)
C-1–C-2–C-3–C-4	–61.4 (3)	–62.0 (3)	58.8 (4)	58.5 (4)
C-2–C-3–C-4–C-5	55.0 (4)	50.0 (4)	–56.2 (4)	–56.2 (4)
C-3–C-4–C-5–O-5	–54.8 (4)	–50.3 (4)	51.5 (4)	51.7 (4)
C-4–C-5–O-5–C-1	59.0 (3)	57.7 (4)	–54.4 (4)	–54.5 (4)
C-5–O-5–C-1–C-2	–69.7 (3)	–70.1 (3)	60.5 (4)	61.0 (4)
C-2–O-2–C-6/7–N-1	–10.8 (4)	–13.9 (4)		
O-2–C-6/7–N-1–C-1	–12.3 (4)	–12.2 (4)		
C-6/7–N-1–C-1–C-2	28.3 (3)	31.0 (3)		
N-1–C-1–C-2–O-2	–34.1 (3)	–38.2 (3)		
C-1–C-2–O-2–C-6/7	28.7 (4)	33.3 (3)		
N-1–C-1–C-2–C-3			63.8 (3)	63.1 (4)
C-1–C-2–C-3–O-3			–62.1 (3)	–61.5 (4)
C-2–C-3–O-3–C-6			32.3 (4)	32.3 (5)
C-3–O-3–C-6–N-1			–2.3 (5)	–1.9 (5)
O-3–C-6–N-1–C-1			4.5 (4)	2.9 (5)
C-6–N-1–C-1–C-2			–36.1 (4)	–34.6 (4)

Table III. Proton–Proton and Carbon–Proton Torsion Angles (Degrees) from X-ray Analyses of 1, 3, and 5

	compound			
angles	1	3	5	5′
H-1–C-1–C-2–H-2	–168 (3)	–165 (3)	61 (4)	63 (4)
H-2–C-2–C-3–H-3	174 (3)	177 (3)	–58 (5)	–62 (4)
H-3–C-3–C-4–H-4	173 (3)	162 (3)	–63 (4)	–55 (4)
H-4–C-4–C-5–H-5_{ax}	–176 (4)	–163 (4)	170 (4)	164 (4)
H-4–C-4–C-5–H-5_{eq}		–42 (4)	46 (4)	49 (5)
C-1–C-2–C-3–H-3	61 (2)	57 (3)	–179 (3)	–179 (3)
C-1–O-5–C-5–H-5_{ax}	–58 (3)	–66 (3)	66 (4)	69 (3)
C-1–O-5–C-5–H-5_{eq}		178 (3)	–175 (4)	–176 (3)
C-2–C-3–C-4–H-4	–66 (3)	–78 (2)	63 (3)	69 (3)
C-3–C-2–C-1–H-1	–53 (3)	–44 (2)	–177 (3)	–178 (3)
C-3–C-4–C-5–H-5_{ax}	65 (3)	72 (2)	–68 (3)	–72 (3)
C-3–C-4–C-5–H-5_{eq}		–167 (3)	168 (4)	174 (3)
C-4–C-3–C-2–H-2	52 (2)	58 (2)	–180 (3)	175 (3)
C-5–O-5–C-1–H-1	56 (3)	51 (3)	–178 (4)	–179 (3)
C-5–C-4–C-3–H-3	–66 (2)	–69 (3)	179 (3)	180 (3)
C-6–C-5–C-4–H-4	–57 (3)			

Table IV. Proton Torsion Angles (Degrees) for 1–5 from NMR Data

	compound				
angle	1	2	3	4	5
H-1–C-1–C-2–H-2	180	180	180	180	68
H-2–C-2–C-3–H-3	180	180	180	63	–54
H-3–C-3–C-4–H-4	168	49	164	53	–58
H-4–C-4–C-5–H-5_{ax}	–155	–55	–164	180	180
H-4–C-4–C-5–H-5_{eq}			–53	–54	51

geometry around N-1, which is almost planar in this compound with angles adding around 360.0 (2)° and 359.8 (2)°, while the sum is 352.3 (3)° for 1 and 348.3 (3)° for 3. The pyranoid rings present $^4C_1$ conformation for 1 and 3 and $^1C_4$ conformation for 5; the six-membered cyclic carbamate ring of 5 shows an E_2 conformation; and the five-membered rings of 1 and 3 have $^1T_2$ conformations. Tables II and III show some torsion angles for these compounds, following the numbering scheme indicated in Figures 1–3.

The conformation in solution of the pyranoid ring of the cyclic carbamates 1–5 has been determined by ^1H NMR spectroscopy. Table IV shows the proton–proton torsion angles calculated from the $^3J_{H,H}$ values (Table I) by using the equation proposed by Altona.[12] Comparison of Tables III and IV indicates a similar conformation of the pyranoid ring in the solid state and in solution. Therefore, these compounds, as with the derivatives of 1,6-anhydrȯ-β-D-hexopyranoses,[13] could be good models to study the dependence of the heteronuclear coupling constants on the torsion angles and the orientation of substituents.

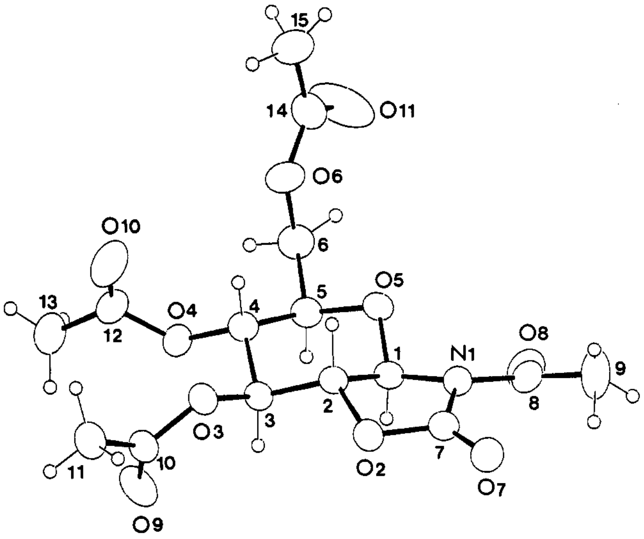

Figure 1. ORTEP view of the molecular structure of 1, showing the atomic numbering.

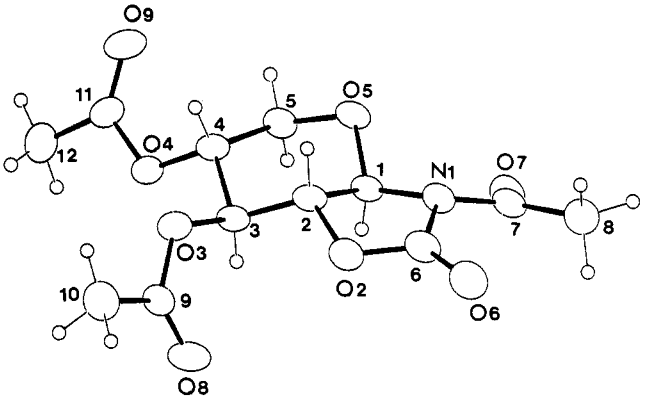

Figure 2. ORTEP view of the molecular structure of 3, showing the atomic numbering.

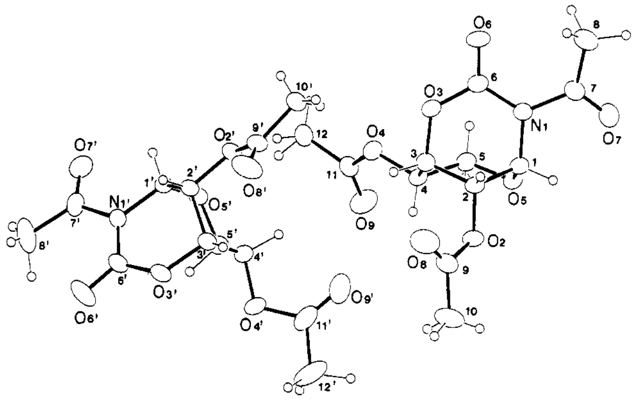

Figure 3. ORTEP view of the molecular structure of 5, showing the atomic numbering and the two independent molecules in the cell unit.

The $^3J_{C,H}$ values for compounds 1–5 and 6–12 are shown in Tables V and VI, respectively. Some small discrepancies (<±10%) among the coupling constants determined by the method of Bax and Freeman and those by spectral simulation are evident. We estimate an error of ±0.15 Hz in

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Table V. $^3J_{C,H}$ Values[a] (Hertz) for Solutions of 1–5

	compound									
	1[b]		2[c]		3[c]		4[c]		5[c]	
$^3J_{C,H}$	a	b	a	b	a	b	a	b	a	b
$J_{C\text{-}1,H\text{-}3}$	2.1	2.2	2.6	2.7	1.9		5.7	5.7	4.5	4.1
$J_{C\text{-}1,H\text{-}5_{ax}}$	2.2	2.2	3.0	2.7	3.0	3.0	2.9	2.7	1.8	1.3
$J_{C\text{-}1,H\text{-}5_{eq}}$					12.2	12.1	11.2	11.2	7.9	8.2
$J_{C\text{-}2,H\text{-}4}$	1.1	1.0	6.1	6.4	1.3	1.3	0	0		
$J_{C\text{-}3,H\text{-}1}$		3.2	4.1			4.0	2.5	3.0	4.3	4.7
$J_{C\text{-}3,H\text{-}5_{ax}}$		0.8	0	0	1.3	0.8	1.4	1.3	2.2	2.2
$J_{C\text{-}3,H\text{-}5_{eq}}$					8.2	8.1	6.9	5.6	3.8	4.5
$J_{C\text{-}4,H\text{-}2}$		1.2	0		1.9	1.9	1.0		4.8	4.3
$J_{C\text{-}5,H\text{-}1}$	2.1		2.0		1.8	1.9	1.9	1.2	7.0	7.0
$J_{C\text{-}5,H\text{-}3}$	1.9		0		0.8	0.1	4.7	4.3	4.2	3.6
$J_{C\text{-}6,H\text{-}4}$	4.1	3.0	0	0						

[a] (a) Obtained by the Bax and Freeman method.[9] (b) Best values from simulated spectra. [b] In C_6D_6. [c] In $CDCl_3$.

Table VI. Vicinal $^3J_{C,H}$ (Hertz) for 6–12 in CD_3COCD_3[a]

	compound													
	6		**7**		**8**		**9**		**10**		**11**		**12**	
$^3J_{C,H}$	a	b	a	b	a	b	a	b	a	b	a	b	a	b
$J_{C\text{-}1,H\text{-}3}$	2.8	2.6	3.7	3.6	0	0	1.4	0	5.2	5.3	0.8	0		5.8
$J_{C\text{-}1,H\text{-}5}$	6.2	6.2	6.2	6.2	6.8	6.7	7.1	6.9	5.8	5.3	7.0	7.0	6.5	5.8
$J_{C\text{-}1,H\text{-}6_{exo}}$	0	0.9	0.8	0.8	0.8	0	0.8	0	1.2	0	1.1	0	1.4	0
$J_{C\text{-}1,H\text{-}6_{endo}}$	3.9	3.6		3.6	3.7	3.6	3.9	3.7	3.7	3.6	4.0	3.8	3.8	3.6
$J_{C\text{-}2,H\text{-}4}$	2.5	2.5	0			4.9	0	0	4.7	4.2		5.3	0	0
$J_{C\text{-}3,H\text{-}1}$	3.7	3.8	4.6	4.8	5.5	4.7	5.6	6.3	4.1		5.0	4.8	4.8	
$J_{C\text{-}3,H\text{-}5}$	4.0	3.8	5.5	4.9	6.8	6.9	6.7	6.3	5.2		7.8	7.2	6.5	
$J_{C\text{-}4,H\text{-}2}$	2.7		4.6		5.3		5.8	6.0	1.3		6.8	0	0	
$J_{C\text{-}4,H\text{-}6_{exo}}$	9.3		6.0		9.3		6.2	6.0	10.1		10.1	9.5	6.5	
$J_{C\text{-}4,H\text{-}6_{endo}}$	4.6		2.7		4.0		3.0	3.0	4.3		4.8	4.6	2.4	
$J_{C\text{-}5,H\text{-}1}$	5.3	5.4	5.3		5.8	5.8	5.8	5.9	5.3	5.1	5.9	5.9	5.2	5.0
$J_{C\text{-}5,H\text{-}3}$	3.0	2.8	1.1		0	0	0	0	4.2	4.3	0	0	5.6	5.0
$J_{C\text{-}6,H\text{-}1}$	5.3	5.2	5.3	5.4	5.3	5.4	5.2	5.0	5.8	5.7	5.8	5.8	5.9	5.8
$J_{C\text{-}6,H\text{-}4}$	1.4	1.3	5.6	5.4		0	5.0	5.0	0.8	0	0	0	5.9	5.8

[a] (a) Obtained by the Bax and Freeman method.[9] (b) Best values from simulated spectra.

the values of the couplings. Figure 4 shows an example of comparison of partial experimental and simulated ^{13}C NMR spectra. For trans-type torsion angles, $^3J_{C,H}$ takes values between 3.8 and 12.2 Hz for the cyclic carbamate compounds **1–5** and between 2.5 and 10 Hz for the 1,6-anhydro-β-D-hexopyranose derivatives **6–12**. For gauche-type torsion angles, $^3J_{C,H}$ is always smaller than 4.6 Hz. Thus, the $^3J_{C,H}$ values appear rather scattered, and other factors besides the value of the torsion angles must strongly influence the coupling constant. The largest values are observed for $J_{C\text{-}1,H\text{-}5_{eq}}$ in compounds **3** and **4** (>11 Hz), and these values are more than 3 Hz larger than that for compound **5**, which, according to molecular models, has a similar torsion angle C-1–O-5–C-5–H-5_{eq}. The *N*-acetyl groups are trans-oriented with respect to C-5 in compounds **3** and **4** and gauche-oriented in compound **5**. A similar effect is observed for the value $J_{C\text{-}4,H\text{-}6_{exo}}$ for compounds **6**, **8**, **10**, **11** in which the acetoxy group at C-4 is trans-oriented with respect to C-6, in comparison with compounds **7**, **9**, and **12** in which the acetoxy group at C-4 is gauche-oriented with respect to C-6. Similarly, the value of $J_{C\text{-}3,H\text{-}5_{eq}}$ is larger for compound **3**, in which the acetoxy group at C-3 is trans to C-5, than for compound **4**, in which the acetoxy group at C-3 is gauche to C-5; the values of $J_{C\text{-}3,H\text{-}5}$ in the 1,6-anhydro-β-D-hexopyranose derivatives **6–12** are always larger for those compounds with an equatorially oriented acetoxy group at C-3 trans to C-5. However, in these latter cases, the couplings are smaller than in the previous ones ($J_{C\text{-}1,H\text{-}5_{eq}}$ and $J_{C\text{-}4\text{-}6_{exo}}$). These results are in accord with previous molecular orbital calculations[4] on 1-fluoropropane, which predicted coupling constants 3 and 0.2 Hz larger than those for the unsubstituted molecule when the fluorine atom was trans- or gauche-oriented, respectively, with respect to the carbon bearing the coupled proton and also predicted a decrease of the value of the coupling constant when the number of the electronegative substituents was increased at the γ-carbon atom.[4,5]

A characteristic feature of the spectra of the 1,6-anhydro-β-D-hexopyranose derivatives **6–12** is that the couplings across oxygen atoms, $J_{C\text{-}1,H\text{-}5'}$, $J_{C\text{-}1,H\text{-}6_{endo}}$, $J_{C\text{-}1,H\text{-}6_{exo}}$, $J_{C\text{-}5,H\text{-}1}$, and $J_{C\text{-}6,H\text{-}1}$, are fairly constant, and this seems to indicate that when the coupling path remains the same, the value of $^3J_{C,H}$ does not vary if the torsion angle does not change. However, the values for $J_{C\text{-}1,H\text{-}5}$ are almost 1 Hz larger than those for $J_{C\text{-}5,H\text{-}1}$ and $J_{C\text{-}6,H\text{-}1}$ in compounds **6–12** in spite of the torsion angles being very similar. This result could be accounted for as above by considering that C-1 bears two strongly electronegative substituents while C-5 supports only one, but it could also be explained by the fact that, according to calculations,[4,5] the more electronegative the coupled carbon the larger the value of the coupling constant.

The data of Tables V and VI also seem to reflect an important influence of the orientation of the β substituent on the values of $^3J_{C,H}$ in spite of the fact that molecular orbital calculations predicted strong contributions only for those β substituents trans-oriented to the coupled proton. This contribution and that of the δ substituent should also be considered.[4,5]

It could be concluded from these results that the relative orientation of substituents in a complex organic molecule does substantially modify the general shape of the existing Karplus-like relationship between the values of $^3J_{C,H}$ and the torsion angles and that, at the present moment, it is not possible to obtain a satisfactory simple trigonometric

Table VII. Crystal Analysis Parameters at Room Temperature

		Crystal Data	
formula	$C_{12}H_{14}N_8$	$C_{12}H_{14}N_8$	$C_{15}H_{19}N_{10}$
crystal habit	cubic, transparent, colorless	plate, transparent, colorless	prismatic, transparent, colorless
crystal size (mm)	0.5	0.17 × 0.47 × 0.05	0.33 × 0.50 × 0.17
symmetry	triclinic, $P1$	monoclinic, $P2_1$	orthorhombic, $P2_12_12_1$
unit cell determination	least-squares fit from 80 reflections ($\theta < 45°$)	least-squares fit from 80 reflections ($\theta < 45°$)	least-squares fit from 90 reflections ($\theta < 45°$)
unit cell dimensions			
a, b, c (Å)	9.6223 (3), 10.4581 (3), 7.9109 (2)	11.2450 (3), 7.2125 (1), 8.6653 (2)	20.2876 (13), 15.6078 (7), 5.5628 (1)
α, β, γ (deg)	105.224 (3), 90.415 (2), 64.832 (2)	90, 81.046 (2), 80	
packing V (Å^3), Z	690.84 (4), 2	702.68 (31), 2	1761.41 (14), 4
d_{calcd} (g·cm^{-3}), M_r, $F(000)$	1.443, 300.25, 314	1.419, 300.25, 314	1.408, 373.32, 784
		Experimental Data	
technique	four-circle diffractometer, Philips PW1100; bisecting geometry; graphite-oriented monochromator, Cu Kα; $\omega/2\theta$ scans, scan width 1.5°; detector apertures 1 × 1°, θ_{max} 65°; 1 min/reflex		
number of reflections			
independent	2328	1306	1768
observed	2285 [$3\sigma(I)$ criterion]	1130 [$3\sigma(I)$ criterion]	1531 [$3\sigma(I)$ criterion]
standard reflections	2 reflections every 80 min, no variation		
		Solution and Refinement	
solution	direct methods		
refinement	least-squares on F_o with 2 blocks	least-squares on F_o with 1 block	least-squares on F_o with 1 block
parameters			
number of variables	496	249	311
degrees of freedom	1789	881	1220
ratio of freedom	4.6	4.5	4.9
H atoms	difference synthesis		
final shift/error	0.40	0.11	0.19
w scheme	empirical as to give no trends in $\langle w\Delta^2F\rangle$ vs. $\langle \lvert F_o\rvert\rangle$ and $\langle(\sin)\theta)/\lambda\rangle$		
max thermal value	U_{33}(O9′) = 0.215 (6) Å^2	U_{33}(O9) = 0.092 (2) Å^2	U_{22}(O11) = 0.229 (7) Å^2
final ΔF peaks	0.21 e Å^{-3}	0.15 e Å^{-3}	0.23 e Å^{-3}
final R and R_w	0.042, 0.044	0.034, 0.038	0.043, 0.048
computer and programs	Vax 11/750, X-RAY 76,[17] MULTAN 80,[16] and ref 18		

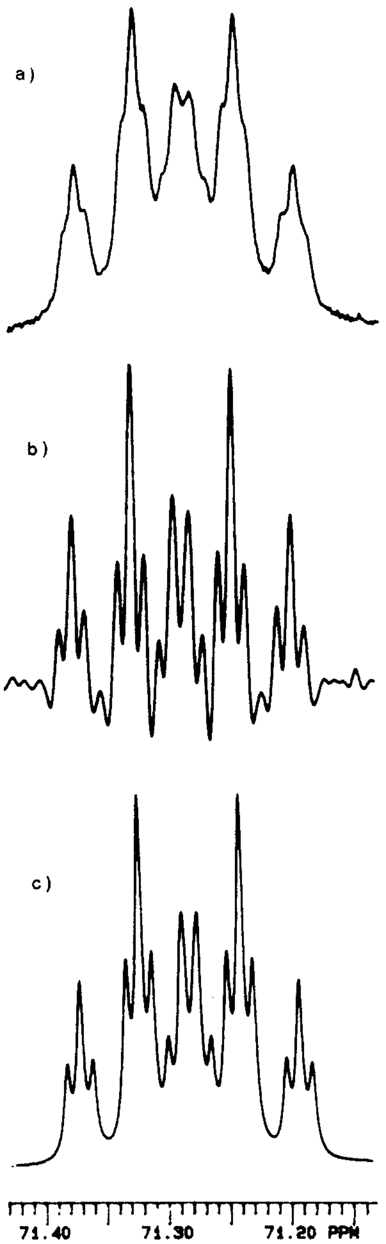

Figure 4. Experimental (a), resolution enhanced (b), and simulated (c) ^{13}C NMR spectra of C-1 of compound 7. Only a branch is shown for simplicity.

relationship similar to that found for vicinal proton–proton couplings.[12] An important number of reliable $^3J_{C,H}$ values in a variety of conformationally rigid structures should be determined before these coupling constants can be safely used in conformational analysis.[14] Therefore, much care should be taken when determining angles from $^3J_{C,H}$ values using some of the published equations or plots, because a configurational change of any of the atoms involved in the coupling path can drastically influence the value of the coupling constant.

Experimental Section

General Methods. Melting points were determined in capillary tubes and are uncorrected. TLC was performed on silica gel GF254 (Merck) with detection by charring with sulfuric acid. Flash column chromatography was performed on Macherey Nogel (230–400-mesh) silica gel. Optical rotations were determined with a Perkin-Elmer polarimeter.

Materials. Compounds 1, 2,[10] and 6–12[13] were prepared as reported previously.

***N*-Acetyl-3,4-di-*O*-acetyl-1,2-dideoxy-β-D-xylopyranosyl-[1,2-*d*]oxazolidin-2′-one (3).** 3 was prepared from 1-deoxy-β-D-xylopyranosyl 1-azide as described for 1 and 2.[10] Recrystallization from ethanol gave 3 (68%): mp 190–192 °C; $[\alpha]_D$ −25° (*c* 1, chloroform). Anal. Calcd for $C_{12}H_{15}NO_8$: C, 47.87; H, 5.02; N, 4.65. Found: C, 48.07; H, 5.24; N, 4.56.

***N*-Acetyl-3,4-di-*O*-acetyl-1,2-dideoxy-β-D-ribopyranosyl-1-deoxy[1,1-*d*]oxazolidin-2′-one (4).** 4 was prepared from 1-deoxy-β-D-ribopyranosyl 1-azide as described for 1 and 2.[10] Recrystallization from ethanol gave 4 (57%): mp 185–186 °C; $[\alpha]_D$ +27° (*c* 1, chloroform). Anal. Calcd for $C_{12}H_{15}NO_8$: C, 47.87; H 5.02; N, 4.65. Found: C, 47.59; H, 5.15; N, 4.78.

2,4-Di-*O*-acetyl-1-acetamido-1-deoxy-1-*N*,3-*O*-carbonyl-α-L-arabinopyranose (5). Attempted preparation of the corresponding 1,2-dideoxy-α-L-arabinopyranosyl derivative as above, from 1-deoxy-α-L-arabinopyranosyl azide, failed. Instead, recrystallization of the resulting product from ethanol gave 5 (39%): mp 133–135 °C; $[\alpha]_D$ −13° (*c* 0, 5, chloroform). Anal. Calcd for $C_{12}H_{15}NO_8$: C, 47.87; H, 5.02; N, 4.65. Found: C, 48.07; H, 5.24; N, 4.56.

NMR Data. The ^1H NMR spectra ($CDCl_3$ or C_6D_6, internal Me_4Si) were recorded on a Varian XL-300 spectrometer.

The ^{13}C NMR spectra (75 MHz) were recorded on the same spectrometer. Long-range carbon–proton coupling constants were measured according to Bax and Freeman.[9] The pulse sequence contained a preparation period for establishment of NOE (5 s) followed by a variable evolution period incremented in 32 steps, giving a spectral width in the F_1 dimension of ±7.5 Hz. The proton-flip technique was used with decoupler pulse intensity $\gamma B_2/2\pi = 25$ Hz and π pulse of 20 ms. The measured geminal and vicinal coupling constants were used as input for simulating the coupled carbon spectra. The experimental and calculated spectra matched satisfactorily. Some discrepancies were found between observed and calculated couplings, particularly in those cases in which the irradiated proton was not far enough from its neighbors or was strongly coupled to others. Artifacts at $F_1 = 0$ also appeared in some cases, probably due to pulse imperfections.[9]

X-ray Data. Crystal and experimental data and refinement parameters are given in Table VII.

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Registry No. 1, 95266-86-7; 2, 100759-73-7; 3, 108696-06-6; 4, 108741-34-0; 5, 108741-35-1; 6, 13242-55-2; 7, 4132-24-5; 8, 14661-09-7; 9, 14661-13-3; 10, 13242-48-3; 11, 14661-10-0; 12, 14661-16-6; 1-deoxy-β-D-xylopyranosyl 1-azide, 51368-20-8; 1-deoxy-β-D-ribopyranosyl 1-azide, 85219-76-7.

Supplementary Material Available: Tables of final atomic coordinates for the non-hydrogen atoms, bond distances and angles, final hydrogen coordinates, and thermal parameters for 1, 3, and 5 (12 pages); observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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