which means a better discriminating power between diastereomers.

Conclusion

In our view, the results reported indicate the possibility of a complete stereochemical elucidation of any aldose from the NMR spectrum of its PAAN derivative. Fulfilment of this possibility depends on two factors: (i) complete and correct analysis of experimental NMR spectra; (ii) correct predictive sets of calculated J values. Increasing accessibility to higher field spectrometers and to a wide range of complementary programs and pulse sequences (LAOCOON-3, homonuclear correlation proton-proton, heteronuclear correlation carbon-proton, ...) makes us feel optimistic on the subject of point i; and, in relation to point ii, the self-improving capabilities of the procedure should be emphasized: in fact, each new correct structural assignation affords a new set of experimental J values that could be used for further sharpening of the P_i parameters set used in the 3JHH program.

Computational Methods

All MM2 calculations were carried out with a local IBM/CMS version of MM2(77).[11] KEONE program was run on a VAX-8800 computer.

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Conformational Study of Peracetylated Aldononitriles

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A conformational study of the tetrose, pentose, hexose, and heptose diastereomeric peracetylated aldononitrile derivatives (PAAN) based on force-field calculations is described.

The study of the structure of flexible organic molecules is a challenging problem of current interest. In the present paper, a detailed molecular mechanics[1] conformational study of the tetrose, pentose, hexose, and heptose (D series) diastereomeric peracetylated aldononitrile derivatives (PAAN) (Figure 1) is presented. This study is closely related to that which led to the setting up of a direct and simple procedure for the stereochemical elucidation of aldoses.[2]

We will use the conformational symbolism proposed by J. A. Mills[3] throughout, but differentiating O//C from C//C interactions by using primed letters for the former (Figure 2).

Selection of Starting Geometries. The importance of a correct selection of starting geometries cannot be overemphasized because in all the computational methods available to date[4] only local energy minima are identified.

Using a very large number of correctly selected starting geometries and (energetically) minimizing them to the nearest local minimum, practically all parts of the conformational space are sampled and the lowest local minimum can be taken as the "global minimum", i.e. the lowest energy state overall. Staggered bond conformations (180: G, G', A. 60: U, U', P. -60: K, K', M; Figure 3) have been taken as starting points in the MM2 energy optimization processes. Combination of these conformations leads to nine possible conformers for each two tetrose PAAN, 27 for each four pentose PAAN, 81 for each eight hexose PAAN, and 243 for each 16 heptose PAAN.

Several approximations have been carried out to reduce the number of conformers to be considered, thus shortening the required computational time.

(a) Conformational considerations concerning C-C-C-C-C, O-C-C-C-C, and O-C-C-C-O fragments. As a rule, in the absence of hydrogen bonding and/or other modifying factors, heavy atom//heavy atom 1,3 interactions (the symbol // will be used to denote 1,3 interactions) destabilize conformers in which they are present.[5] The point to discuss here is the relative extent of destabilizing effect of the three types of 1,3 interactions possible in PAAN derivatives: C//C, C//O, and O//O.

Until recently, the accepted view[6-11] was that C//O interactions were stronger than O//O interactions: typical accepted values in aqueous solution are 2.5-2.6 kcal/mol and 1.9 kcal/mol, respectively.[12-14] Many authors[3,5,15-21]

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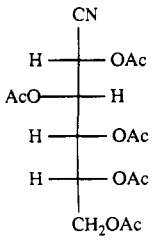

Figure 1. PAAN-glucose.

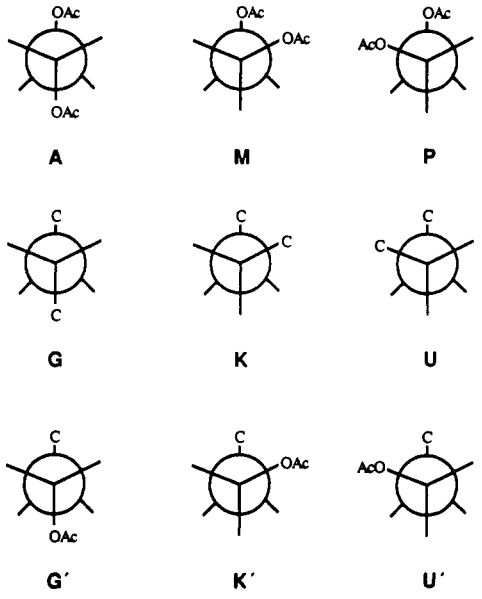

Figure 2. Conformational symbolism proposed by J. A. Mills.

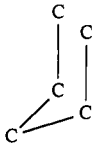

Figure 3. Highly unstable conformation of a chain of five sp^3 carbon atoms.

have admitted, explicitly or implicitly, that the high energy content of conformers with C//O interactions led to very low populations of them in the corresponding conformational equilibria; in other words, those conformers need not be considered.

In a rather recent X-ray study of D-*glycero*-L-*alo*-heptitol, Angyal[22] has shown the presence of a C//O interaction in the conformation adopted by this compound. Starting from this observation, Angyal now accepts that heptitols can exist in solution equilibria as conformers with C//O 1,3-interactions. Furthermore, he consideres that conformers with O//O interactions have a higher energy content than those with C//O. In agreement with the new views, some of our own preliminary MM2 calculations showed a significant high-energy content in PAAN conformers exhibiting O//O interactions.

As a consequence of the above discussion, the conformers with one or more O//O interactions were not considered (population equal to zero) in the conformational analysis of PAAN compounds. It is worth pointing out that the longer the carbon chain the larger the number of O-substituents and the larger the relative number of conformers which are not taken into account.

Chain conformation sequences which lead to O//O interactions are collected in Table I; these sequences depend on the configurations of carbons n and $n + 2$, but not of carbon $n + 1$.

Up to the $n/2$th or $(n + 1)/2$th carbon atom (even or odd carbon chains), the R/S descriptors of a PAAN de-

Table I. Chair Conformation Sequences Which Lead to O//O Interactions

configurations[a]	sequences
nC(R), (n + 2)C(R)	nG, (n + 1)G
	nU, (n + 1)K[b]
nC(R), (n + 2)C(S)	nG, (n + 1)U
	nU, (n + 1)G
nC(S), (n + 2)C(R)	nG, (n + 1)K
	nK, (n + 1)G
nC(S), (n + 2)C(S)	nG, (n + 1)G
	nK, (n + 1)U[b]

[a] Aldose descriptors. [b] This sequence gives rise also to C//C interaction.

Table II. Number of Significative Conformers in the PAAN Derivatives

		Number of conformers		
N[a]	configuration	$3n$[b]	$3n - A$[c]	$3n - B$[d]
4	erythrose	9	9	7
4	threose	9	9	7
5	ribose	27	27	16
5	arabinose	27	27	16
5	xylose	27	27	17
5	lyxose	27	27	17
6	allose	81	63	32
6	altrose	81	63	31
6	glucose	81	63	27
6	mannose	81	63	26
6	gulose	81	63	33
6	idose	81	63	33
6	galactose	81	63	27
6	talose	81	63	27
7	"G"-D-*alo*-heptose[e]	243	153	65
7	"G"-D-*altro*-heptose	243	153	65
7	"G"-D-*gluco*-heptose	243	153	55
7	"G"-D-*manno*-heptose	243	153	55
7	"G"-D-*gulo*-heptose	243	153	51
7	"G"-D-*ido*-heptose	243	153	55
7	"G"-D-*galo*-heptose	243	153	42
7	"G"-D-*talo*-heptose	243	153	44
7	"G"-L-*galo*-heptose	243	153	51
7	"G"-L-*talo*-heptose	243	153	56
7	"G"-L-*gulo*-heptose	243	153	66
7	"G"-L-*ido*-heptose	243	153	66
7	"G"-L-*gluco*-heptose	243	153	45
7	"G"-L-*manno*-heptose	243	153	53
7	"G"-L-*alo*-heptose	243	153	55
7	"G"-L-*altro*-heptose	243	153	55

[a] Number of carbon atoms in the main chain. [b] n is the number of assymetric carbon atoms in the main chain. [c] A = number of conformations which show 1,3 C//C interactions. [d] B = number of conformations which show 1,3 C//C and/or 1,3 O//O interactions. [e] "G" symbolizes "D-*glycero*".

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Table III. Percentage of Population of the Significative Conformers of 4C-, 5C-, 6C-, and 7C-PAAN

aldose	%[a]	conformation[b]	aldose	%	conformation
erythrose	29.0	2K(−64.05)3G′(−180.00)	threose	19.7	2G(−173.41)3K′(−60.50)
	18.7	2G(176.94)3U′(62.67)		18.6	2K(−70.33)3G′(−178.84)
	17.1	2K(−67.50)3U′(62.11)		17.4	2U(58.84)3G′(179.27)
	16.5	2K(−62.78)3K′(−63.67)		14.7	2G(179.96)3G′(179.77)
	12.9	2G(−176.96)3G′(−178.42)		11.0	2K(−72.13)3U′(63.68)
	3.5	2U(64.42)3G′(178.46)		10.8	2U(62.54)3K′(−63.18)
	2.3	2U(67.14)3K′(−63.73)		7.8	2U(57.86)3U′(61.41)
ribose	27.3	2K(−63.88)3G(178.78)4U′(58.65)	arabinose	20.7	2G(−175.39)3G(−174.04)4G′(178.26)
	23.1	2K(−63.41)3G(−178.43)4G′(178.58)		19.9	2U(73.13)3G(176.21)4U′(58.71)
	13.5	2K(−63.34)3K(−56.81)4K′(−58.28)		18.9	2G(−176.40)3G(−176.47)4U′(59.79)
	9.7	2K(−63.68)3K(−56.61)4G′(−176.70)		15.2	2U(74.91)3G(179.31)4G′(178.33)
	4.6	2K(−60.13)3K(−60.40)4U′(72.42)		4.8	2K(−51.82)3K(−59.07)4K′(−54.10)
	4.0	2G(170.37)3U(58.95)4G′(176.24)		3.6	2K(−49.67)3K(−58.83)4U′(78.29)
	3.0	2U(70.03)3G(177.84)4U′(58.92)		2.9	2U(66.47)3U(63.07)4G′(176.25)
xylose	11.3	2K(−69.10)3G(−177.86)4K′(−59.41)	lyxose	18.5	2G(−172.05)3G(−173.40)4K′(−58.66)
	9.6	2G(175.07)3U(62.44)4G′(175.09)		16.9	2U(67.87)3G(178.68)4K′(−59.36)
	9.3	2U(48.74)3U(62.09)4K′(−78.32)		12.9	2G(−172.13)3G(−174.61)4G′(−178.55)
	9.1	2U(49.54)3U(59.79)4U′(53.61)		12.9	2U(61.77)3U(64.11)4G′(175.48)
	9.0	2U(64.71)3G(178.78)4K′(−59.68)		12.9	2U(69.48)3G(176.46)4G′(−179.32)
	9.0	2G(175.61)3U(60.49)4U′(55.73)		7.3	2U(58.25)3U(60.33)4K′(−72.89)
	8.2	2K(−68.02)3G(179.90)4G′(−179.27)		6.2	2U(60.70)3U(59.76)4U′(55.36)
allose	17.2	2K(−63.13)3K(−57.53)4G(−176.40)5U′(59.45)	altrose	14.1	2K(−50.78)3K(−57.38)4G(−175.01)5U′(61.04)
	14.7	2K(−64.34)3K(−60.11)4G(−174.76)5G′(178.60)		10.4	2K(−52.60)3K(−62.37)4K(−52.71)5K′(−56.70)
	11.3	2K(−61.97)3K(−58.58)4K(−52.73)5K′(−55.71)		10.4	2K(−52.27)3K(−60.99)4K(−54.21)5G′(−179.17)
	10.6	2K(−63.04)3K(−59.70)4K(−56.93)5U′(71.00)		7.7	2K(−49.87)3K(−60.97)4G(−173.80)5G′(−179.87)
	7.1	2K(−65.42)3G(173.11)4U(59.87)5G′(176.43)		7.2	2G(−175.01)3G(−174.28)4U(65.84)5G′(175.97)
	5.1	2K(−61.69)3K(−59.38)4K(−54.24)5G′(−176.02)		6.8	2U(74.34)3G(176.91)4U(62.93)5G′(175.75)
	3.8	2K(−66.10)3G(174.88)4U(64.83)5K′(−73.24)		4.9	2K(−52.38)3K(−65.46)4K(−60.27)5U′(68.49)
glucose	13.7	2U(68.67)3G(−178.91)4G(−178.84)5U′(58.31)	mannose	19.7	2G(−171.42)3G(−172.18)4G(−176.86)5U′(58.75)
	13.5	2K(−67.40)3G(−176.44)4G(−176.60)5U′(59.43)		16.0	2G(−171.01)3G(−169.62)4G(−173.89)5G′(178.63)
	12.5	2K(−68.30)3G(−175.76)4G(−174.93)5G′(178.18)		12.3	2U(72.61)3G(−176.41)4G(−174.37)5G′(178.47)
	11.3	2U(68.39)3G(−177.35)4G(−175.33)5G′(178.51)		12.1	2U(70.80)3G(−178.39)4G(−176.39)5U′(59.33)
	10.8	2U(47.49)3U(60.60)4G(161.36)5U′(56.63)		11.0	2U(58.07)3U(70.95)4G(172.34)5G′(179.46)
	5.5	2G(173.77)3U(58.85)4U(58.09)5G′(176.27)		9.2	2U(57.18)3U(70.07)4G(174.73)5U′(61.86)
	4.6	2U(52.26)3U(60.60)4U(58.82)5G′(179.18)		6.4	2U(62.79)3U(57.91)4U(60.73)5K′(−70.93)
gulose	18.6	2K(−60.13)3K(−60.83)4G(−174.21)5K′(−58.94)	idose	14.7	2K(−64.89)3G(−176.10)4U(63.03)5U′(52.12)
	18.3	2G(173.10)3G(176.37)4U(63.88)5U′(55.21)		14.0	2K(−48.39)3K(−60.32)4G(−172.81)5K′(−57.46)
	9.7	2K(−60.11)3K(−60.35)4G(−176.40)5G′(−178.54)		11.3	2G(−172.68)3K(−57.25)4G(−171.82)5K′(−58.16)
	9.5	2G(172.99)3G(174.85)4U(65.31)5G′(175.72)		9.0	2U(68.83)3G(−179.93)4U(62.56)5U′(54.22)
	8.3	2K(−69.48)3G(179.96)4U(61.11)5U′(55.08)		5.1	2U(68.16)3G(179.30)4U(65.47)5G′(174.76)
	7.4	2K(−70.28)3G(179.86)4U(63.13)5G′(174.50)		4.8	2K(−71.10)3G(174.08)4U(62.22)5K′(−73.85)
	4.8	2G(171.14)3G(174.01)4U(68.76)5K′(−72.59)		4.4	2K(−65.77)3G(178.50)4U(65.51)5G′(174.36)
galactose	22.3	2G(177.12)3G(−179.81)4G(−175.87)5K′(−58.53)	talose	27.6	2U(63.57)3G(−175.45)4G(−174.43)5K′(−58.72)
	15.4	2K(−73.85)3G(−172.99)4G(−173.39)5K′(−58.51)		15.3	2U(64.98)3G(−173.39)4G(−176.12)5G′(−178.49)
	12.4	2G(177.09)3G(−179.61)4G(−176.82)5G′(−178.39)		8.6	2U(66.21)3U(57.47)4U(60.50)5K′(−72.44)
	10.6	2K(−75.35)3G(−172.58)4G(−175.92)5G′(−178.20)		5.9	2U(63.51)3U(56.80)4U(57.93)5U′(54.90)
	5.3	2U(56.05)3U(59.02)4U(60.11)5G′(177.91)		5.2	2U(61.44)3G(166.99)4U(65.05)5G′(172.23)
	4.2	2G(175.36)3G(164.40)4U(63.74)5U′(52.39)		5.1	2U(61.47)3G(164.79)4U(62.72)5U′(52.12)
	4.0	2G(175.84)3G(166.84)4U(66.39)5G′(172.18)		5.0	2G(173.61)3U(61.21)4U(60.14)5G′(176.73)
"G"-D-allo[c]	9.4	2K(−61.45)3K(−57.90)4K(−54.08)5G(−175.80)6U′(59.44)	"G"-D-altro	18.9	2K(−52.78)3K(−61.17)4K(−53.33)5G(−178.12)6U′(58.96)
	9.1	2K(−62.29)3K(−59.99)4K(−53.62)5G(−173.83)6G′(179.06)		17.9	2K(−52.18)3K(−62.37)4K(−52.96)5G(−175.83)6G′(179.22)
	6.4	2G(170.71)3U(51.31)4U(63.88)5G(162.41)6U′(55.65)		9.2	2U(68.95)3G(168.02)4U(54.11)5U(63.72)6K′(−78.06)
	6.4	2K(−62.64)3K(−60.18)4K(−57.38)5K(−59.65)6U′(71.70)		5.2	2G(−176.85)3G(−177.93)4U(71.57)5G(168.47)6U′(56.48)
	6.3	2K(−64.10)3G(177.63)4U(53.71)5U(61.95)6K′(−77.48)		4.0	2G(−175.52)3G(−172.36)4K(−77.19)5G(−177.28)6G′(179.04)
	4.6	2K(−62.34)3G(−171.05)4K(−67.89)5G(−175.41)6U′(60.19)		4.0	2G(−177.08)3G(−173.36)4K(−74.91)5G(−177.35)6U′(59.24)
	4.2	2K(−63.45)3G(−173.20)4K(−73.37)5G(−174.88)6G′(179.38)		4.0	2U(72.82)3G(171.78)4U(52.53)5U(61.81)6G′(174.60)
"G"-D-gluco	34.9	2U(54.46)3U(64.06)4U(64.26)5G(171.14)6U′(57.24)	"G"-D-manno	11.9	2G(−171.82)3G(−172.25)4G(−173.82)5U(66.07)6G′(176.34)
	11.2	2G(173.94)3U(58.66)4U(63.11)5G(169.08)6U′(56.35)		8.0	2U(72.71)3G(−176.69)4G(−177.88)5U(66.22)6G′(176.31)
	6.5	2U(53.48)3U(62.67)4U(65.80)5G(173.99)6G′(178.10)		6.9	2U(62.49)3U(61.54)4U(52.53)5U(63.87)6K′(−76.98)
	4.2	2G(173.86)3U(58.34)4U(65.24)5G(170.98)6G′(177.65)		6.4	2G(177.88)3U(71.78)4U(52.35)5U(64.18)6K′(−76.51)
	3.5	2U(54.03)3U(64.05)4U(52.41)5U(64.51)6K′(−77.08)		6.0	2U(59.34)3U(58.26)4G(162.24)5U(60.71)6G′(178.06)
	2.7	2U(69.06)3G(−176.19)4G(−176.34)5U(65.38)6G′(176.57)		5.0	2G(−175.43)3G(−173.26)4G(−177.24)5U(71.58)6K′(−73.01)
	2.6	2K(−67.91)3G(−176.76)4G(−175.29)5U(65.50)6G′(176.07)		4.8	2U(61.78)3U(67.53)4U(83.30)5G(−179.85)6U′(60.69)
"G"-D-gulo	30.8	2G(170.41)3G(173.71)4U(62.24)5U(57.99)6K′(−81.89)	"G"-D-ido	20.9	2G(−170.12)3K(−56.43)4G(−173.71)5G(−172.65)6U′(60.96)
	17.6	2K(−60.15)3K(−63.64)4G(−176.82)5G(−179.01)6U′(58.47)		12.9	2G(−172.19)3K(57.44)4G(−172.35)5G(−174.55)6G′(178.31)
	14.2	2K(−61.77)3K(−64.30)4G(−176.03)5G(−176.06)6G′(177.84)		8.3	2G(171.47)3U(57.62)4U(68.80)5G(162.92)6U′(81.58)
	6.3	2G(171.94)3G(175.62)4U(74.43)5G(169.85)6U′(57.14)		6.1	2K(−71.09)3G(176.34)4U(64.24)5G(162.51)6U′(56.61)
	4.0	2K(−72.23)3G(179.37)4U(69.68)5G(166.02)6U′(56.84)		4.9	2K(−73.96)3G(172.44)4U(59.70)5U(59.35)6K′(−81.98)
	3.2	2G(−177.48)3K(−74.35)4G(−174.97)5G(−174.35)6G′-(177.88)		4.7	2U(64.39)3G(170.56)4U(58.90)5U(63.71)6K′(−70.96)
	3.0	2G(−175.26)3K(−73.65)4G(−174.05)5G(−174.91)6U′(61.85)		4.7	2U(68.40)3G(179.70)4U(72.49)5G(165.97)6U′(56.41)

Table III (Continued)

aldose	%[a]	conformation[b]	aldose	%	conformation
"G"-D-galacto	26.1	2U(60.48)3U(64.01)4U(63.26)5G(168.29)6U'(57.31)	"G"-D-talo	22.1	2U(64.40)3G(−174.52)4G(−173.28)5G(−175.86)6U'(59.08)
	18.1	2G(177.82)3G(−177.64)4G(−174.95)5G(−176.02)6U'(58.80)		17.8	2U(64.61)3G(−172.94)4G(−171.97)5G(−174.26)6G'(172.24)
	13.8	2G(177.95)3G(−178.91)4G(−172.32)5G(−175.20)6G'(178.32)		16.9	2G(176.68)3U(68.62)4U(59.69)5G(163.68)6U'(56.10)
	12.5	2K(−75.01)3G(−174.26)4G(−173.46)5G(−177.80)6U'(58.49)		10.1	2U(64.95)3U(59.03)4U(61.52)5G(163.82)6U'(56.10)
	10.3	2K(−76.42)3G(−174.36)4G(−171.50)5G(−174.93)6G'(178.68)		4.9	2U(64.95)3U(58.30)4U(63.19)5G(167.75)6G'(177.68)
	7.2	2G(−179.21)3G(−171.43)4U(108.61)5G(−170.65)6U'(64.28)		3.5	2U(61.79)3G(164.46)4U(62.06)5U(67.19)6K'(−66.55)
	4.2	2U(59.77)3U(63.51)4U(63.90)5G(170.05)6G'(177.77)		2.1	2U(64.88)3U(59.50)4U(58.50)5U(63.79)6K'(−70.25)
"G"-L-talo	23.5	2K(−64.11)3G(174.82)4G(176.05)5U(59.94)6U'(52.91)	"G"-L-galacto	25.1	2G(179.71)3G(175.18)4G(178.14)5U(60.70)6U'(52.93)
	12.5	2K(−64.18)3G(173.85)4G(174.81)5U(63.64)6G'(175.17)		19.9	2K(−56.03)3K(−61.55)4K(−58.50)5G(−171.77)6K'(−56.96)
	11.8	2K(−63.35)3K(−57.09)4K(−60.81)5G(−173.85)6K'(−58.86)		12.9	2U(74.70)3G(174.82)4G(177.31)5U(62.45)6U'(55.11)
	8.4	2K(−62.35)3G(173.32)4G(175.88)5U(70,19)6K'(−70.99)		7.0	2G(177.26)3G(177.62)4G(178.16)5U(72.09)6K'(−71.92)
	6.0	2U(70.86)3G(173.15)4G(177.83)5U(60.32)6U'(52.32)		6.3	2G(−178.15)3G(177.64)4G(175.86)5U(64.71)6G'(175.74)
	6.0	2K(−62.82)3G(−172.10)4K(−71.78)5G(−171.97)6K'(−57.74)		5.1	2U(76.35)3G(173.97)4G(175.29)5U(65.73)6G'(175.98)
	5.0	2K(−65.32)3K(−59.91)4K(−60.85)5G(−175.20)6G'(−179.08)		4.2	2K(−57.30)3K(−61.35)4K(−56.75)5G(−175.83)6G'(−178.17)
"G"-L-ido	27.6	2G(178.91)3U(66.26)4G(174.16)5U(65.08)6U'(58.68)	"G"-L-gulo	29.3	2G(−174.90)3G(−179.61)4K(−69.24)5G(177.74)6K'(−62.75)
	9.5	2G(175.06)3U(64.29)4G(−178.82)5U(72.66)6K'(−71.92)		12.5	2G(176.56)3U(73.95)4G(177.20)5U(61.48)6U'(59.43)
	9.4	2K(−68.51)3G(178.80)4K(−67.26)5G(−177.64)6K'(−61.08)		12.0	2U(59.64)3U(61.79)4G(176.64)5U(61.99)6U'(53.18)
	8.4	2G(−162.13)3K(−52.27)4K(−65.90)5G(−173.18)6K'(−55.31)		10.4	2U(68.14)3G(176.60)4K(−69.08)5G(178.23)6K'(−61.93)
	6.1	2U(54.56)3U(75.50)4G(−179.35)5U(60.24)6U'(50.14)		5.9	2G(−174.90)3G(−179.61)4K(−69.24)5G(177.74)6K'(−62.75)
	6.0	2U(61.93)3G(172.96)4K(−68.84)5G(−177.67)6G'(−178.90)		3.9	2U(59.18)3U(62.55)4G(178.41)5U(65.47)6G'(174.56)
	4.5	2U(62.16)3G(−173.68)4K(−69.72)5G(−178.09)6K'(61.72)		2.9	2U(59.12)3U(60.45)4G(175.14)5U(69.52)6K'(−71.58)
"G"-L-manno	28.4	2G(−172.02)3G(−174.20)4G(179.01)5G(−176.89)6K'(−58.90)	"G"-L-gluco	20.8	2K(−69.64)3G(178.52)4G(−179.65)5G(−175.13)6K'(58.42)
	20.5	2K(−71.86)3G(178.58)4G(179.37)5G(−176.22)6K'(−58.88)		19.2	2U(67.75)3G(178.13)4G(179.37)5G(−175.40)6K'(−58.61)
	16.9	2G(172.16)3G(172.56)4G(180.00)5G(−178.12)6G'(−177.67)		11.3	2U(67.96)3G(177.63)4G(179.83)5G(−177.17)6G'(−178.10)
	11.7	2K(−72.43)3G(176.72)4G(−179.44)5G(−177.42)6G'(−178.00)		11.0	2K(−68.68)3G(177.13)4G(−178.77)5G(−177.17)6G'(−178.10)
	4.8	2K(−64.97)3K(−62.29)4K(−56.38)5K(−58.50)6U'(77.70)		2.7	2U(67.65)3G(178.23)4G(163.52)5U(64.51)6U'(52.14)
	3.1	2G(174.00)3G(175.11)4G(166.69)5U(66.64)6U'(51.16)		2.7	2U(67.98)3G(178.24)4G(165.00)5U(65.71)6G'(172.20)
	2.9	2G(173.83)3G(173.98)4G(169.54)5U(71.11)6G'(171.90)		2.7	2G(−174.17)3K(−70.67)4G(−164.20)5G(−174.66)6K'(−58.74)
"G"-L-altro	24.9	2G(174.32)3G(169.84)4U(68.01)5U(61.33)6K'(−80.04)	"G"-L-allo	15.3	2U(65.47)3U(63.88)4G(−177.44)5G(−173.85)6K'(−58.20)
	7.8	2U(51.69)3U(62.37)4U(52.75)5U(64.77)6K'(−70.33)		9.1	2U(61.22)3U(58.47)4U(53.41)5U(68.11)6K'(−70.82)
	6.7	2G(175.10)3G(166.32)4U(62.15)5U(60.74)6G'(176.96)		7.4	2U(61.07)3U(59.83)4U(59.74)5G(168.59)6G'(−179.58)
	6.7	2K(−76.50)3G(173.95)4U(66.61)5U(60.47)6K'(−72.25)		6.4	2U(63.36)3U(57.32)4G(164.22)5U(63.39)6U'(50.72)
	6.6	2G(175.34)3G(170.80)4U(66.19)5U(55.27)6U'(53.69)		6.1	2U(61.16)3U(57.90)4U(53.29)5U(58.77)6U'(55.79)
	6.1	2U(52.22)3U(61.64)4U(52.85)5U(59.46)6U'(55.61)		6.0	2U(58.98)3G(169.30)4U(68.39)5U(59.48)6K'(−83.92)
	5.8	2K(−75.86)3G(168.78)4U(61.68)5U(60.61)6G'(176.98)		5.7	2G(−172.89)3U(79.41)4G(168.26)5U(61.02)6U'(49.06)

[a] Expressed in percentage of total population. [b] In parentheses the corresponding dihedral angle. [c] "G" means D-glycero.

rivative are reversed from those of its parent aldose; this introduces an additional complication which has been avoided here by using the corresponding aldose descriptors throughout.

On the other hand, U,K and K,U sequences, within a chain of five consecutive sp^3 carbon atoms, lead to highly unstable conformations with C//C interactions[23] (Figure 3). Conformers with this arrangement would have a population lower than 0.1% and have also been ignored. PAAN carbon 1 is sp hybridized and, consequently, the above type of interaction does not exist in tetrose and pentose derivatives. Table II shows the number of conformers for each PAAN derivative which have to be taken into account after disregarding conformers in which C//C and/or O//O interactions are present.

(b) Statistical analysis[24,25] of X-ray structural data for 118 aliphatic esters (Cambridge Structural Database) demonstrates clear conformational preferences (Figure 4)

Figure 4. Prefered conformations of aliphatic acetates.

which have been taken into account in the present study. As starting points in energy optimization calculations, primary acetoxy groups have been given the C_{sp^2}–O_{sp^3} synperiplanar and O_{sp^3}–C_{sp^3} antiperiplanar conformation and secondary groups the C_{sp^2}–O_{sp^3} synperiplanar and O_{sp^3}–C_{sp^3} anticlinal conformation.[26]

Selection of MM2 Parameters. A local IBM/CMS version of MM2(77) Allinger's molecular mechanics program[1] has been used to which the cyano group parameters recently proposed by ourselves[27] have been added. The primitive ester group parameters have been modified.

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(27) Castells, J.; Jaime, C.; López-Calahorra, F.; Santaló, N.; Velasco, D. *J. Org. Chem.* **1988**, *53*, 5363–5366.

Current MM2(77) ester parameters are derived from taking the ester group as a simple juxtaposition of carbonyl and alkoxy groupings; nonbonding electron pairs on the alkoxy oxygen are dealt with as pseudoatoms. Even the generally accepted resonance description of the ester group makes this approach questionable. Ōsawa[28] has found that MM2(77) current values are clearly unsatisfactory for vicinal alcohol polyesters and proposes a new set based on data reported by Dunitz[25] for 118 aliphatic esters. Furthermore, the nonbonding electron pairs on the alkoxy oxygen should not be considered explicitly, and their effects should be incorporated into other structural parameters.

As a consequence of the above changes, the MM2(77) ester group dipole moments to be employed in the calculation of electrostatic effects have to be modified.

Possible Solvent Effect. In principle, conformational populations may depend on solvent polarity, but, according to the information afforded by NMR studies,[2] in the case of the peracetylated aldononitriles this dependence can be ignored.

Within the framework of a molecular mechanics approach, the role of solvent polarity must be modest because it acts only through its incidence on the dipolar energy component of the steric energy of a molecule[29] and does not modify the other (and very important) energy contributions: stretching, bending, torsion, and van der Waals energy. In any case, the dependence found would have to be rather small.

In the MM2(77) program used in the present study, solvent polarity is dealt with by means of the "effective dielectric constant" parameter, a high value of which corresponds to a high polarity and to a small dipolar energy contribution to the steric energy of the system. Values over 20 practically reduce this contribution to zero. In the present work, the default value in the current program (1.5), which corresponds to a very low polarity, has been used throughout.

PAAN derivatives are much more polar than hydrocarbons and, consequently, solvent effects on favored conformations can differ in both series; however, it is worth mentioning a recent paper[30] in which by applying the di-^{13}C-labeling method, no conformational changes were found in hydrocarbons dissolved in various solvents.

Results and Discussion

No attempt has been made to generate complete energy curves for each PAAN derivative, as a function of the dihedral angle of each C_{sp^3}–C_{sp^3} bond. Instead, the energy optimization processes have been performed starting in the selected conformers (see previous discussion) and imposing no restrictions whatsoever on bond lengths, bond angles, and dihedral angles. It should be pointed out that the dihedral angle which has as axis the C_{n-1}–C_n bond has also bee considered; in this case the G′,U′,K′ symbolism is used (Figure 3).

For each PAAN derivative, computer work affords the conformers whose sequences of bond conformations (dihedral angles) correspond to energy minima together with their relative populations. Relevant data related explicitly to chain conformations (including the terminal primary acetoxy group) are collected in Table III and Figure 5.

It is worth mentioning that due to the sp hybridization of the cyano carbon, at this end of the PAAN molecule, the OC_2–C_3C_4 conformation is perhaps energetically more important than the reported C_1C_2–C_3C_4 conformation. Table IV shows how both conformation types are connected through the configuration of C_2.

C–O/C–O relationships (A,M,P) have not been included in Tables III and IV because they are also determined by the respective bond conformations (G,U,K) and carbon configurations (Table V). Before analyzing the results

Table IV. Relationships between C_2 Configuration and CC_2–C_3C Conformation with OC_2–C_3 Conformation.

C_2 configuration[a]	CC_2–C_3C conformation	OC_2–C_3 conformation
R	G	U′
	U	K′
	K	G′
S	G	K′
	U	G′
	K	U′

Table V. Relationships between C Configurations and CC–CC Conformations with OC–CO Conformations

configuration	C–C_n/C_{n+1}–C conformation	O–C_n/C_{n+1}–O conformation
*n*C(*R*), (*n* + 1)C(*R*)	*n*G	*n*A
	*n*U	*n*P
	*n*K	*n*M
*n*C(R), (*n* + 1)C(*S*)	*n*G	*n*M
	*n*U	*n*A
	*n*K	*n*P
*n*C(*S*), (*n* + 1)C(*R*)	*n*G	*n*P
	*n*U	*n*M
	*n*K	*n*A
*n*C(*S*), (*n* + 1)C(*S*)	*n*G	*n*A
	*n*U	*n*P
	*n*K	*n*M

Table VI. Ratio Majoritary/Total Number of Conformers in 4C-, 5C-, 6C-, and 7C-PAAN

aldose	*A*[a]	*B*[b]	%
erythrose	4	7	57.1
threose	5	7	71.4
ribose	5	16	31.3
arabinose	4	16	25.0
xylose	8	17	47.1
lyxose	5	17	29.4
allose	9	32	28.1
altrose	11	31	35.5
glucose	8	27	29.6
mannose	6	26	23.1
gulose	7	33	21.2
idose	10	33	30.3
galactose	8	27	29.6
talose	8	27	29.6
"G"-D-*allo*-heptose	14	65	21.5
"G"-D-*altro*-heptose	11	65	16.9
"G"-D-*gluco*-heptose	12	55	21.8
"G"-D-*manno*-heptose	15	55	27.3
"G"-D-*gulo*-heptose	6	51	11.8
"G"-D-*ido*-heptose	12	55	21.8
"G"-D-*galacto*-heptose	5	42	11.9
"G"-D-*talo*-heptose	6	44	13.6
"G"-L-*talo*-heptose	8	56	14.3
"G"-L-*galacto*-heptose	6	51	11.8
"G"-L-*ido*-heptose	9	66	13.6
"G"-L-*gulo*-heptose	7	66	10.6
"G"-L-*manno*-heptose	4	53	7.6
"G"-L-*gluco*-heptose	11	45	24.4
"G"-L-*altro*-heptose	10	55	18.2
"G"-L-*allo*-heptose	13	55	23.6

[a] Number of conformers that account for 75% of the total population. [b] Number of possible conformers. "G" symbolizes D-glycero.

(28) Ōsawa, E., personal communication.
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(30) Menger, F. M.; D'Angelo, L. L.; *J. Am. Chem. Soc.* **1988**, *110*, 8241–8242.

Table VII. Main Conformations for the 16 Heptose PAAN and Their Relation with the Conformations of Lowest Members

"G"-D-alo[a]	2K3K4K5G6U′ (1)	2K3K4K5G6G′ (2)	2G3U4U5G6U′ (3)	2K3K4K5K6U′ (4)	2K3G4U5U6K′ (5)	2K3G4K5G6U′ (6)	2K3G4K5G6G′ (7)
alose	2K3K4G5U′ (1)	2K3K4G5G′ (2)	–	2K3K4K5U′ (4)	–	–	–
ribose	2K3G4U′ (1)	2K3G4G′ (2)	2U3G4U′ (7)	2K3K4U′ (5)	–	2K3G4U′ (1)	2K3G5G′ (2)
erythrose	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)	2K3U′ (3)	2U3K′ (7)	2G3U′ (2)	2G3G′ (5)
"G"-D-altro	2K3K4K5G6U′ (1)	2K3K4K5G6G′ (2)	2U3G4U5U6K′ (3)	2G3G4U5G6U′ (4)	2G3G4K5G6G′ (5)	2G3G4K5G6U′ (6)	2U3G4U5U6G′ (7)
alose	2K3K4G5U′ (1)	2K3K4G5G′ (2)	–	–	–	–	–
ribose	2K3G4U′ (1)	2K3G4G′ (2)	–	2U3G4U′ (7)	2K3G4G′ (2)	2K3G4U′ (1)	–
erythrose	2G3U′ (2)	2G3G′ (5)	2U3K′ (7)	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)	2U3G′ (6)
"G"-D-gluco	2U3U4U5G6U′ (1)	2G3U4U5G6U′ (2)	2U3U4U5G6G′ (3)	2G3U4U5G6G′ (4)	2U3U4U5U6K′ (5)	2U3G4G5U6G′ (6)	2K3G4G5U6G′ (7)
altrose	–	–	–	–	–	2G3G4U5G′ (5)	2G3G4U5G′ (5)
ribose	2U3G4U′ (7)	2G3U4G′ (6)	–	–	–	2G3U4G′ (6)	2G3U4G′ (6)
erythrose	2G3U′ (2)	2G3U′ (2)	2G3G′ (5)	2G3G′ (5)	2U3K′ (7)	2U3G′ (6)	2U3G′ (6)
"G"-D-manno	2G3G4G5U6G′ (1)	2U3G4G5U6G′ (2)	2U3U4U5U6K′ (3)	2G3U4U5U6K′ (4)	2U3U4G5U6G′ (5)	2G3G4G5U6K′ (6)	2U3U4U5G6U′ (7)
altrose	2G3G4U5G′ (5)	2G3G4U5G′ (5)	–	–	2U3G4U5G′ (6)	–	–
ribose	2G3U4G′ (6)	2G3U4G′ (6)	–	–	2G3U4G′ (6)	–	2U3G4U′ (7)
erythrose	2U3G′ (6)	2U3G′ (6)	2U3K′ (7)	2U3K′ (7)	2U3G′ (6)	2U3K′ (7)	2G3U′ (2)
"G"-D-gulo	2G3G4U5U6K′ (1)	2K3K4G5G6U′ (2)	2K3K4G5G6G′ (3)	2G3G4U5G6U′ (4)	2K3G4U5G6U′ (5)	2G3K4G5G6G′ (6)	2G3K4G5G6U′ (7)
glucose	–	3K3G4G5U′ (2)	2K3G4G5G′ (3)	–	–	2K3G4G5G′ (3)	2K3G4G5U′ (2)
arabinose	–	2G3G4U′ (3)	2G3G4G′ (1)	2U3G4U′ (2)	2U3G4U′ (2)	2G3G4G′ (1)	2G3G4U′ (3)
erythrose	2U3K′ (7)	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)
"G"-D-ido	2G3K4G5G6U′ (1)	2G3K4G5G6G′ (2)	2G3U4U5G6U′ (3)	2K3G4U5U6K′ (4)	2U3G4U5U6K′ (5)	2K3G4U5G6U′ (6)	2U3G4U5G6U′ (7)
glucose	2K3G4G5U′ (2)	2K3G4G5G′ (3)	2U3U4G5U′ (5)	–	–	–	–
arabinose	2G3G4U′ (3)	2G3G4G′ (1)	2U3G4U′ (2)	–	–	2U3G4U′ (2)	2U3G4U′ (2)
erythrose	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)	2U3K′ (7)	2U3K′ (7)	2G3U′ (2)	2G3U′ (2)
"G"-D-galacto	2U3U4U5G6U′ (1)	2G3G4G5G6U′ (2)	2G3G4G5G6G′ (3)	2K3G4G5G6U′ (4)	2K3G4G5G6G′ (5)	2G3G4U5G6U′ (6)	2U3U4U5G6G′ (7)
mannose	2U3U4G5U′ (6)	2G3G4G5U′ (1)	2G3G4G5G′ (2)	2G3G4G5U′ (1)	2G3G4G5G′ (2)	–	2U3U4G5G′ (5)
arabinose	2U3G4U′ (2)	2G3G4U′ (3)	2G3G4U′ (3)	2G3G4U′ (3)	2G3G4G′ (1)	2U3G4U′ (2)	2U3G4G′ (4)
erythrose	2G3U′ (2)	2G3U′ (2)	2G3U′ (2)	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)	2G3G′ (5)
"G"-D-talo	2U3G4G5G6U′ (1)	2U3G4G5G6G′ (2)	2G3U4U5G6U′ (3)	2U3U4U5G6U′ (4)	2U3U4U5G6G′ (5)	2U3G4U5U6K′ (6)	2U3U4U5U6K′ (7)
mannose	2G3G4G5U′ (1)	2G3G4G5G′ (2)	2U3U4G5U′ (6)	2U3U4G5U′ (6)	2U3U4G5G′ (5)	–	2U3U4U5K′ (7)
arabinose	2G3G4U′ (3)	2G3G4G′ (1)	2U3G4U′ (2)	2U3G4U′ (2)	2U3G4G′ (4)	–	–
erythrose	2G3U′ (2)	2G3G′ (5)	2G3U′ (2)	2G3U′ (2)	2G3G′ (5)	2U3K′ (7)	2U3K′ (7)
"G"-L-talo	2K3G4G5U6U′ (1)	2K3G4G5U6G′ (2)	2K3K4K5G6K′ (3)	2K3G4G5U6K′ (4)	2U3G4G5U6U′ (5)	2K3G4K5G6K′ (6)	2K3K4K5G6G′ (7)
gulose	2G3G4U5U′ (2)	2G3G4U5G′ (3)	2K3K4G5K′ (1)	2G3G4U5K′ (7)	2G3G4U5U′ (2)	–	2K3K4G5G′ (6)
xylose	2G3U4U′ (6)	2G3U4G′ (2)	2K3G4K′ (1)	–	2G3U4U′ (6)	2K3G4K′ (1)	2K3G4G′ (7)
threose	2U3U′ (7)	2U3G′ (3)	2G3K′ (1)	2U3K′ (6)	2U3U′ (7)	2G3K′ (1)	2G3G′ (4)
"G"-L-galacto	2G3G4G5U6U′ (1)	2K3K4K5G6K′ (2)	2U3G4G5U6U′ (3)	2G3G4G5U6K′ (4)	2G3G4G5U6G′ (5)	2U3G4G5U6G′ (6)	2K3K4K5G6G′ (7)
gulose	2G3G4U5U′ (2)	2K3K4G5K′ (1)	2G3G4U5U′ (2)	2G3G4U5K′ (7)	2G3G4U5G (3)	2G3G4U5G′ (3)	3K4K5G6G′ (6)
xylose	2G3U4U′ (6)	2K3G4K′ (1)	2G3U4U′ (6)	–	2G3U4G′ (2)	2G3U4G′ (2)	2K3G4G′ (7)
threose	2U3U′ (7)	2G3K′ (1)	2U3U′ (7)	2U3K′ (6)	2U3G′ (3)	2U3G′ (3)	2G3G′ (4)
"G"-L-ido	2G3U4G5U6U′ (1)	2G3U4G5U6K′ (2)	2K3G4K5G6K′ (3)	2G3K4K5G6K′ (4)	2U3U4G5U6U′ (5)	2U3G4K5G6G′ (6)	2U3G4K5G6K′ (7)
idose	U3G4U5U′ (4)	–	2G3K4G5K′ (3)	2K3K4G5K′ (2)	2U3G4U5U′ (4)	–	2G3K4G5K′ (3)
xylose	2G3U4U′ (6)	–	2K3G4K′ (1)	2K3G4K′ (1)	2G3U4U′ (6)	2K3G4G′ (7)	2K3G4K′ (1)
threose	2U3U′ (7)	2U3K′ (6)	2G3K′ (1)	2G3K′ (1)	2U3U′ (7)	2G3G′ (4)	2G3K′ (1)
"G"-L-gulo	2G3G4K5G6K′ (1)	2G3U4G5U6U′ (2)	2U3U4G5U6U′ (3)	2U3G4K5G6K′ (4)	2G3G4K5G6K′ (5)	2U3U4G5U6G′ (6)	2U3U4G5U6K′ (7)
idose	2G3K4G5K′ (3)	2U3G4U5U′ (4)	2U3G4U5U′ (4)	2G3K4G5K′ (3)	2G3K4G5K′ (3)	2U3G4U5G′ (5)	–
xylose	2K3G4K′ (1)	2G3U4U′ (6)	2G3U4U′ (6)	2K3G4K′ (1)	2K3G4K′ (1)	2G3U4G′ (2)	–
threose	2G3K′ (1)	2U3U′ (7)	2U3U′ (7)	2G3K′ (1)	2G3K′ (1)	2U3G′ (3)	2U3K′ (6)
"G"-L-manno	2G3G4G5G6K′ (1)	2K3G4G5G6K′ (2)	2G3G4G5G6G′ (3)	2K3G4G5G6G′ (4)	2K3K4K5K6U′ (5)	2G3G4G5U6U′ (6)	2G3G4G5U6G′ (7)
galactose	2G3G4G5K′ (1)	2G3G4G5K′ (1)	2G3G4G5G′ (3)	2G3G4G5G′ (3)	–	2G3G4U5U′ (6)	2G3G4U5G′ (7)
lyxose	2G3G4K′ (1)	2G3G4K′ (1)	2G3G4G′ (3)	2G3G4G′ (3)	–	–	–
threose	2G3K′ (1)	2G3K′ (1)	2G3G′ (4)	2G3G′ (4)	2K3U′ (5)	2U3U′ (7)	2U3G′ (3)
"G"-L-gluco	2K3G4G5G6K′ (1)	2U3G4G5G6K′ (2)	2U3G4G5G6G′ (3)	2K3G4G5G6G′ (4)	2U3G4G5U6U′ (5)	2U3G4G5U6G′ (6)	2G3K4G5G6K′ (7)
galactose	2G3G4G5K′ (1)	2G3G4G5K′ (1)	2G3G4G5G′ (3)	2G3G4G5G′ (3)	2G3G4U5U′ (6)	2G3G4U5G′ (7)	2K3G4G5K′ (2)
lyxose	2G3G4K′ (1)	2G3G4K′ (1)	2G3G4G′ (3)	–	–	–	2G3G4K′ (1)
threose	2G3K′ (1)	2G3K′ (1)	2G3G′ (4)	2G3G′ (4)	2U3U′ (7)	2U3G′ (3)	2G3K′ (1)
"G"-L-altro	2G3G4U5U6K′ (1)	2U3U4U5U6K′ (2)	2G3G4U5U6G′ (3)	2K3G4U5U6K′ (4)	2G3G4U5U6U′ (5)	2U3U4U5U6U′ (6)	2K3G4U5U6G′ (7)
talose	–	2U3U4U5K′ (3)	2G3U4U5G′ (7)	–	–	2U3U4U5U′ (4)	2G3U4U5G′ (7)
lyxose	2U3U4K′ (6)	2U3U4K′ (6)	2U3U4G′ (4)	2U3U4K′ (6)	2U3U4U′ (7)	2U3U4U′ (7)	2U3U4G′ (4)
threose	2U3K′ (6)	2U3K′ (6)	2U3G′ (3)	2U3K′ (6)	2U3U′ (7)	2U3U′ (7)	2U3G′ (3)
"G"-L-alo	2G3U4G5G6K′ (1)	2U3U4U5U6K′ (2)	2U3U4U5G6G′ (3)	2U3U4G5U6U′ (4)	2U3U4U5U6U′ (5)	2U3G4U5U6K′ (6)	2G3U4G5U6U′ (7)
talose	2U3G4G5K′ (1)	2U3U4U5K′ (3)	–	2U3G4U5U′ (6)	2U3U4U5U′ (4)	–	2U3G4U5U′ (6)
lyxose	2G3G4K′ (1)	2U3U4K′ (6)	2U3G4G′ (5)	–	2U3U4U′ (7)	2U3U4K′ (6)	–
threose	2G3K′ (1)	2U3K′ (6)	2G3G′ (4)	2U3U′ (7)	2U3U′ (7)	2U3K′ (6)	2U3U′ (7)

[a] "G" symbolizes D-glycero.

presented in Table III and Figure 5, it should be pointed out that the overall correctness of the calculated dihedral angles and conformer populations is strongly supported by the agreement between the calculated sets of H,H vicinal J values obtained by using these set and the experimental ones.[2]

On the other hand, there are gratifying coincidences between the main conformations deduced in the present molecular mechanics study and the proposals, mostly based on NMR spectral data, of Binkley et al.[31] and Lee and Scanlon[32] for C5- and C6-PAAN and those of Mills,[3] Angyal,[22] and others for alditols and related compounds.

The "numerical shift" in going from an aldose family to the next should be kept in mind in discussing results: carbon 4 in a tetrose becomes carbon 5 in a pentose, carbon 6 in an hexose, and so on.

General Trends. An important feature that emerges from Table III and Figure 5 is the diminishing percentage of populationally significant conformers with increasing chain length. In Table VI this fact is concretized by giving (for each PAAN derivative) the percentage of conformers

(31) Binkley, W. W.; Diehl, D. R.; Binkley, R. W. *Carbohydr. Res.* **1971**, *18*, 459–465.

(32) Lee, J. B.; Scanlon, B. F. *Tetrahedron* **1969**, *25*, 3413–3428.

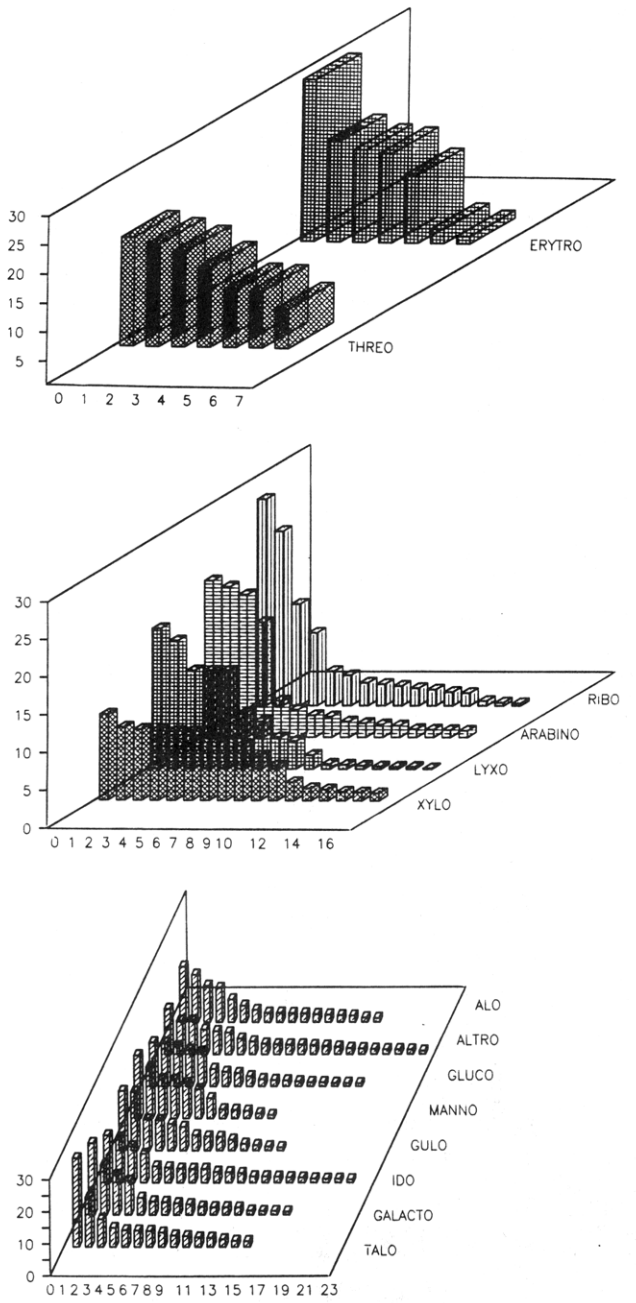

Figure 5. Conformational populations of 4C-, 5C-, and 6C-PAAN derivatives. *x* axis, number of conformers; *y* axis, percentage.

which together account for about 75% of the total population. It can be concluded that with increasing chain length the number of destabilizing interactions increases faster than the number of carbon atoms and, as a consequence, the relative number of populationally significant conformers is reduced. The observed progressive rigidity points to a single dominant conformation in the case of a very long carbon chain. Tetrose and pentose PAAN conformers deserve some further comments. The populations of the seven possible conformers in threose PAAN are of such a magnitude that they should all be taken into account; in fact, the highest population (19.7%, 2G3K conformer) differs only by a factor of 2.5 from the lowest (7.8%, 2U3U conformer). In erythrose PAAN the situation is better defined: one conformer (2K3G) has a clearly higher population (29.0%) than the others, and two conformers (2U3G and 2U3K) have populations (3.5 and 2.3%, respectively) that are nearly insignificant.

Ribose and arabinose (the two epimers of erythrose) PAAN have 16 conformers each and in both derivatives 4 conformers account for 75% of the total population. Ribose PAAN shows a steep decreasing in populations (27.3, 23.1, 13.5, 9.9%) whereas the 4 conformer populations are rather similar in the arabinose derivative (20.7, 19.9, 18.9, 15.2%). Lyxose and xylose (the two epimers of threose) PAAN have 17 conformers each. It can be observed that 75% of the total populatioin is accounted for by 5 conformers in the former and by 8 in the latter. In both cases, but particularly in the xylose derivative, there is a flat distribution of populations: 18.5, 16.9, 12.9, 12.9, 12.9% and 11.3, 9.6, 9.3, 9.1, 9.0, 9.0, 8.2, 7.8% (followed by 7.3, 5.9, ...%), respectively, which is similar to that of threose PAAN.

Before leaving the present heading, a rather obvious conclusion should be emphasized: there is little point in discussing conformational problems in terms of one or two "favored" conformations, as it has been done up to now; instead, the usual situation appears to be the existence of a complex equilibrium in which several conformers have a population which cannot be ignored.

Main Conformations. An interesting question is the possible existence of conformational relationships between the homomorphic members[20] of the C4, C5, C6, ... families; their existence would have predictive value for families of higher order. In the carbohydrate literature the situation, mostly discussed on the basis of NMR spectral correlations, is far from clear.[16,20,22]

In an effort to clarify this question within the PAAN families, in Table VII the 16 heptose PAAN are shown together with the homomorphically related hexose, pentose, and tetrose PAAN. The seven main (most abundant) conformations of each heptose PAAN are given as well as the 336 related conformations of the homomorphic compounds (numbers 1,2,3, ... in parenthesis show the priority of each conformation in the corresponding population table). It can be observed that 51 out of a total of 336 conformations occupy the first place in the corresponding populational table; 56, the second; 36, the third; 19, the fourth; 24, the fifth; 43, the sixth; and 44, the seventh place. It is thus clear that the conformation sequences present in the most populated C4 conformers are also present in the main C5 conformers and that the sequences present in these C5 conformers are also present in the main C6 conformers, and so on.

In conclusion, it can be affirmed that some conformation sequences are energetically favored whatever the length of the carbon chain but, surprisingly enough, neither the most populated conformation of erythrose nor those of altrose, glucose, and idose are found among the 448 (336 + 112) conformational sequences reported in Table VII.

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