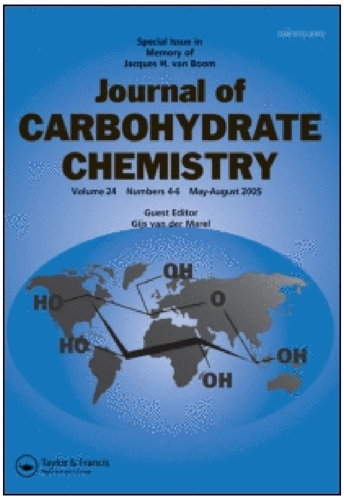

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Application of a Model Building Approach to Molecular Mechanics (MM3) for Calculating Low-Energy Conformations of Tetra-*O*-Acyl-*N,N'*-Dialkyl-D-Glucaramides

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To cite this Article Zhang, Jinsong and Kiely, Donald E.(2006) 'Application of a Model Building Approach to Molecular Mechanics (MM3) for Calculating Low-Energy Conformations of Tetra-*O*-Acyl-*N,N'*-Dialkyl-D-Glucaramides', Journal of Carbohydrate Chemistry, 25: 8, 697 — 711

To link to this Article: DOI: 10.1080/07328300601039385

URL: http://dx.doi.org/10.1080/07328300601039385

Journal of Carbohydrate Chemistry, 25:697–711, 2006
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ISSN: 0732-8303 print 1532-2327 online
DOI: 10.1080/07328300601039385

Application of a Model Building Approach to Molecular Mechanics (MM3) for Calculating Low-Energy Conformations of Tetra-*O*-Acyl-*N,N*′-Dialkyl-D-Glucaramides

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A model building approach was used in conjunction with the MM3 molecular mechanics program to find the low-energy conformations of three tetra-*O*-acyl-*N,N*′-dimethyl-D-glucaramide molecules: tetra-*O*-propanoyl-(**2**), 2-methylpropanoyl-(**3**) and 2,2-dimethyl-propanoyl-*N,N*′-dimethyl-D-glucaramide (**4**), and tetra-*O*-acetyl-*N,N*′-dihexyl-D-glucaramide (**5**). A set of models was chosen for calculation of the low-energy conformations of parent tetra-*O*-acetyl-*N,N*′-dimethyl-D-glucaramide (**1**), with additional models required to simulate conformationally more complex diamides **2**–**5**. The dominant low-energy conformations of **2** and **3** were very similar to that from **1**, whereas very sterically constrained **4**, with four bulky pendant *O*-2,2-dimethylpropanoyl groups, and **5**, with terminal *n*-hexyl groups, adopted different conformations. Stereoregular alternating *head tail–tail head* and repeating *head tail*–poly(hexamethylene 2,3,4,5-tetra-*O*-acetyl-D-glucaramide) oligomers were graphically generated to provide some

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Received May 8, 2006; accepted August 25, 2006.

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insight into the possible conformations of the actual acylated polyamides in nonpolar solution.

Keywords Molecular mechanics, MM3, Tetra-*O*-acyl-*N*,*N*′-dimethyl D-glucaramide, Polyamides

INTRODUCTION

In the preceding paper,[1] a "model building" approach[2–4] was used to calculate low-energy conformations of 2,3,4,5-tetra-*O*-acetyl-*N*,*N*′-dimethyl-D-glucaramide (**1**) using the molecular mechanics program MM3. Application of this approach was driven by the large number of starting conformations (>14,000,000, 3^{15}) possible from the 15 variable torsion angles of **1** (Fig. 1), the parent molecule for this study. The ^{1}H NMR spectrum of **1** showed a large coupling (7.11 Hz) for vicinal H16–H17, indicative of an *anti* relationship between these protons with a dihedral angle of *ca.* 180°.[5] In contrast, the terminal vicinal coupling constants from H15–H16 (3.24 Hz) and H17–H18 (3.89 Hz) were in the range of a *gauche* arrangement for these protons (dihedral angle of *ca.* ±60°[5]). Consequently, in the initial models, the H16-C3-C4-H17 angle was set at 180° with the terminal H15-C2-C3-H16 and H18-C4-C3-H17 dihedral angles set to ±60°.

Based upon these angular restrictions, four initial starting rotamers 1–4 [1] (Fig. 2) were generated and four different "building block" models were used to establish the conformational preferences of different parts of **1**: 1) the End C Model, *N*-methylacetamide, to define the low energy O9-Cl-N7-H19 and O14-C6-N8-H22 dihedral angles; 2) the C1–C2 and C5–C6 Models, 2*R* and

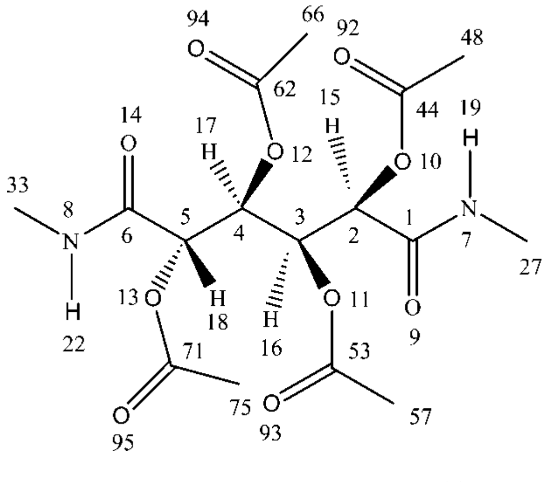
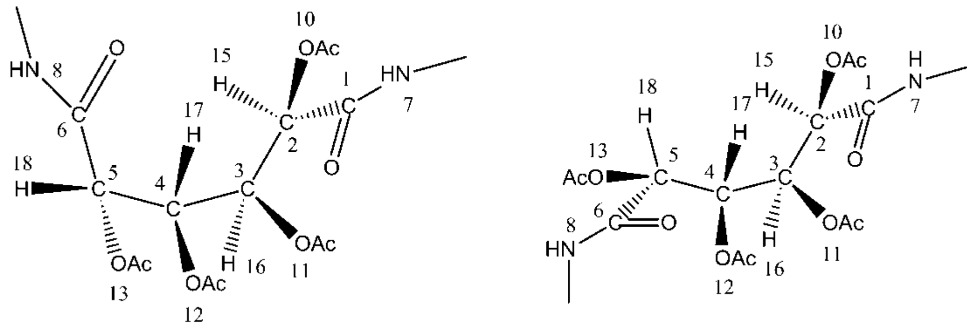
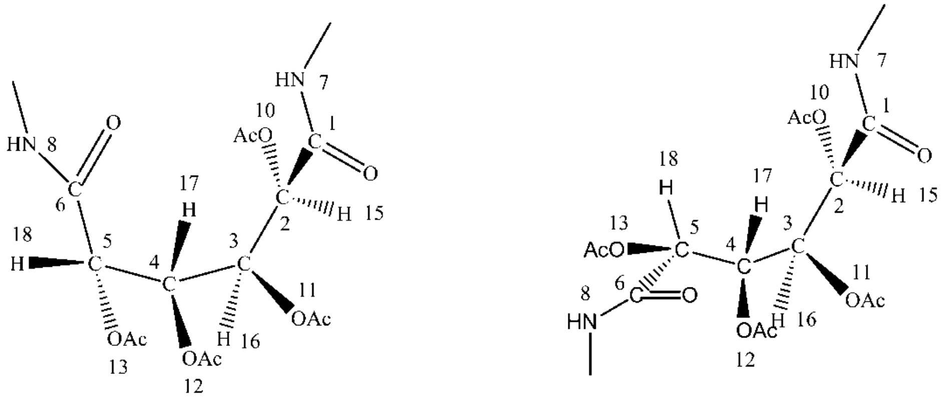


Figure 1: 2,3,4,5-Tetra-*O*-acetyl-*N*,*N*′-dimethyl-D-glucaramide (**1**) with atom numbers generated by the molecular modeling program.



1, Rotamer 1 ($_3G^+{}_4G^-$)

1, Rotamer 2 ($_3G^+{}_4G^+$)



1, Rotamer 3 ($_2G^+{}_3G^+{}_4G^-$)

1, Rotamer 4 ($_2G^+{}_3G^+{}_4G^+$)

R= C(O)CH_3

Figure 2: Four starting rotamers of **1** generated from vicinal H15-H16, H16-H17, and H17-H18 ^1H NMR coupling constant information.[1]

2*S*-*N*-methyl-2-acetoxylpropanamide, to determine the preferred conformational relationship between the terminal acetoxy group on a chiral carbon and the amide carbonyl functions, that is., the O9-C1-C2-O10 and O13-C5-C6-O14 dihedral angles; 3) the Acyloxy Rotamer Model, methyl acetate, to determine the orientation of the carbonyl oxygen of each acetoxy group to the corresponding *O*-alkyl carbon, that is., the dihedral angles C-O-C=O (carbonyl) formed by each of the four acetoxy groups (e.g., C2-O10-C44=O92); and 4) five Vicinal Acyloxy Models from (2*S*,3*S*), (2*S*,3*R*) and (2*R*,3*R*)-2,3-diacetoxybutanes, to mimic the rotameric preferences of two vicinal acetoxy groups on carbons of different chirality and conformational (*gauche* or *anti*) disposition to set the dihedral angle range of H-C-O-C (carbonyl, e.g., H15-C2-O10-C44) before minimization. The calculated torsion

Table 1: Calculated torsion angles (ω, °) of building blocks for **1**.

	Model	Torsion angle	ω (°)	Building blocks
Model 1	End C model	O=C-N-H	180.0	*N*-Methylacetamide
Model 2	C1C2 and C5C6 model	O-C-C=O	± 125.8	*N*-Methyl-2-acetoxylpropanamide
Model 3	Acyloxy rotamer model	C-O-C=O	0.0	Methyl acetate
Model 4	Vicinal acyloxy model	H-C-O-C	$\sim \pm 40.0$	2,3-Diacetoxybutane

angles (ω, °) for the optimized model building block compounds of **1** are shown in Table 1. Rules governing assignment of rotamer labels (e.g., $_3G_4^+G^+$, etc.) are given in reference 6.

From each of the four starting rotamers, 16 (2^4) conformations were generated and then minimized with the MM3 program applying the "block diagonal then full matrix minimization" protocol at a dielectric constant of 2.0. Of the four low-energy "sickle" conformations generated, the one derived from Rotamer 2 was dominant and accounted for *ca.* 56% of the conformation population.

In the present study, this "model building" approach has been applied to more complex D-glucaramide ester derivatives, that is, tetra-*O*-propanoyl, methylpropanoyl, and dimethylpropanoyl-*N,N'*-dimethyl-D-glucaramide (**2**, **3**, and **4**), and tetra-*O*-acetyl-*N,N'*-dihexyl-D-glucaramide (**5**).[1]

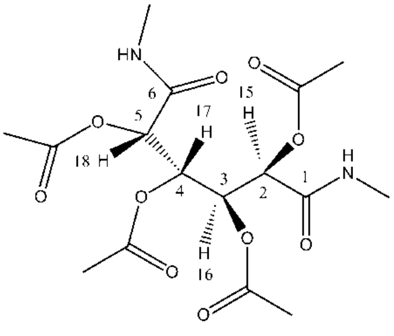
From ^{1}H NMR data reported in the previous paper,[1] as the pendant acyl group becomes bulkier (i.e., acetyl → propanoyl → methylpropanoyl → dimethylpropanoyl), a general increase in H16–H17 coupling is observed, corresponding to a likely increase in the dihedral angle between these two protons and a decrease in conformational flexibility in the middle of these molecules (Fig. 3).

The "model building" approach has now been applied to compounds **2**–**4**[1] but with some modifications to account for the added rotameric possibilities from the pendant propanoyl and 2-methypropanoyl groups of **2** and **3**, respectively. The 2,2-dimethylpropanoyl groups of **4** were considered conformationally equivalent on average, and did not require special consideration. An additional model was generated to mimic the amide hexyl groups of **5** and will be described.

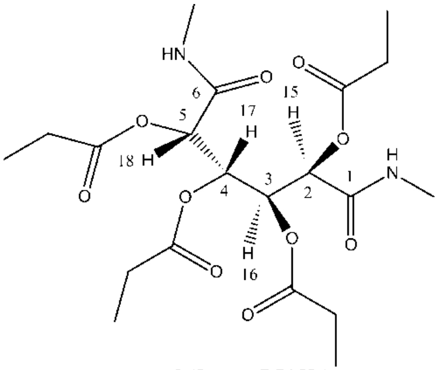
Building Blocks for Conformational Studies of 2–5

Methyl Propanoate Model for 2

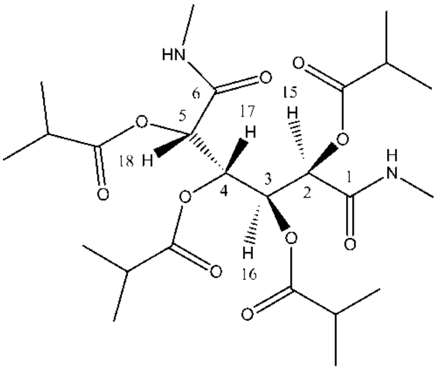
One additional "building block" model was required for 2,3,4,5-tetra-*O*-propanoyl-*N,N'*-dimethyl-D-glucaramide (**2**) to help define the location of the



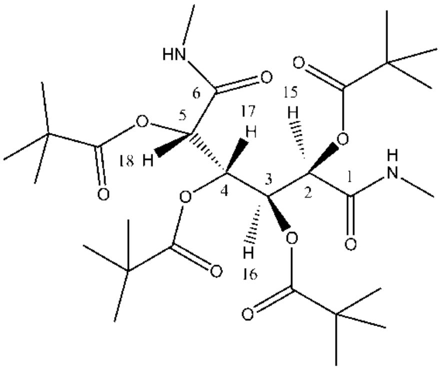
1 ($J_{16,17}$ = 7.11 Hz)



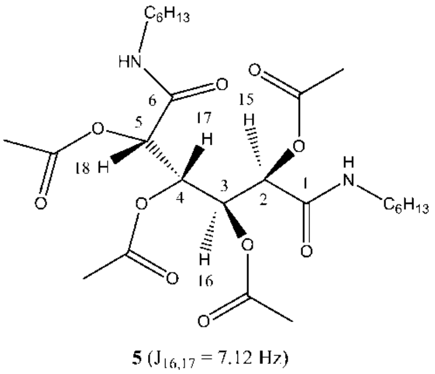
2 ($J_{16,17}$ = 7.76 Hz)



3 ($J_{16,17}$ = 8.41 Hz)



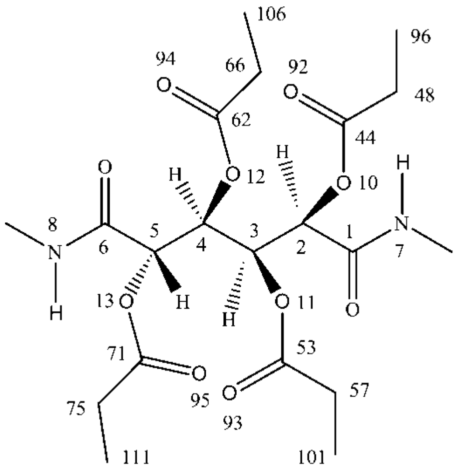
4 ($J_{16,17}$ = 8.61 Hz)



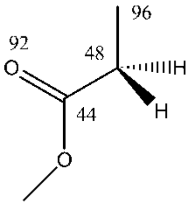
5 ($J_{16,17}$ = 7.12 Hz)

Figure 3: **1**$^{(1)}$–**5** drawn in the same conformation and shown with their respective H16–H17 coupling constants.

terminal methyl unit of the propanoyl group relative to the ester carbonyl oxygen, (i.e. the C-C-C=O dihedral angle). A suitable model compound for this determination is methyl propanoate (Fig. 4). Starting with an extended conformation of methyl propanoate, rotation around the C44–C48 bond from



Tetra-*O*-propanoyl-*N*,*N*′-dimethyl-D-glucaramide (**2**)



Methyl propanoate low energy conformation **A**

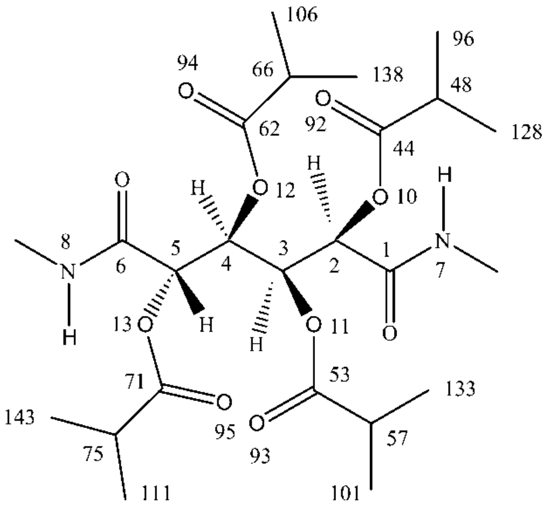
Figure 4: Tetra-*O*-propanoyl-*N*,*N*′-dimethyl-D-glucaramide (**2**) and methyl propanoate low-energy conformation (**A**).

0° to 300° in 60° increments followed by MM3 minimization at a dielectric constant of 2.0 generated three different conformations, the lowest-energy conformation **A** (Fig. 4) with the carbonyl oxygen and methyl carbon eclipsed. The energy difference between **A** and the next higher energy conformation is 2.35 kcal/mol.

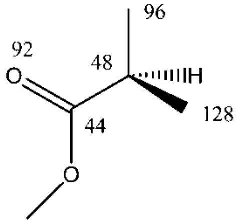
Klimkowski et al.[7] carried out *ab initio* calculations of methyl propanoate and determined that the conformational energy minimum is at a torsional angle of 0° for C-C-C=O, while Moravie et al.[8,9] reported IR and Raman spectra of methyl propanoate in both liquid and crystal states and suggested this same low-energy "*cis* conformation." Based upon the preferred conformation of methyl propanoate, the four O=C-C-C dihedral angles of **2** (O92=C44-C48-C96, O93=C53-C57-C101, O94=C62-C66-C106, and O95=C71-C75-C111) were set at 0.0°.

Methyl 2-Methylpropanoate (B) Model for **3**

Methyl 2-methylpropanoate (**B**, Fig. 5) was chosen to model the pendant *O*-2-methylpropanoyl groups of 2,3,4,5-tetra-*O*-methylpropanoyl-*N*,*N*′-dimethyl-D-glucaramide (**3**) in order to probe the rotation about the C44–C48, C53–C57, C62–C66, and C71–C75 bonds. The ester was minimized by rotating the carbonyl carbon–α carbon bond (e.g., C44–C48) in 60° increments, to generate two enantiomeric low-energy conformers with a $\pm 2.0°$ dihedral angle for the O=C-C-C linkage: **B1**, O92=C44-C48-C96 and **B2**,



Tetra-*O*-methylpropanoyl-*N*,*N*′-dimethyl-D-glucaramide (**3**)



Low energy methyl 2-methylpropanoate conformation (**B**1)

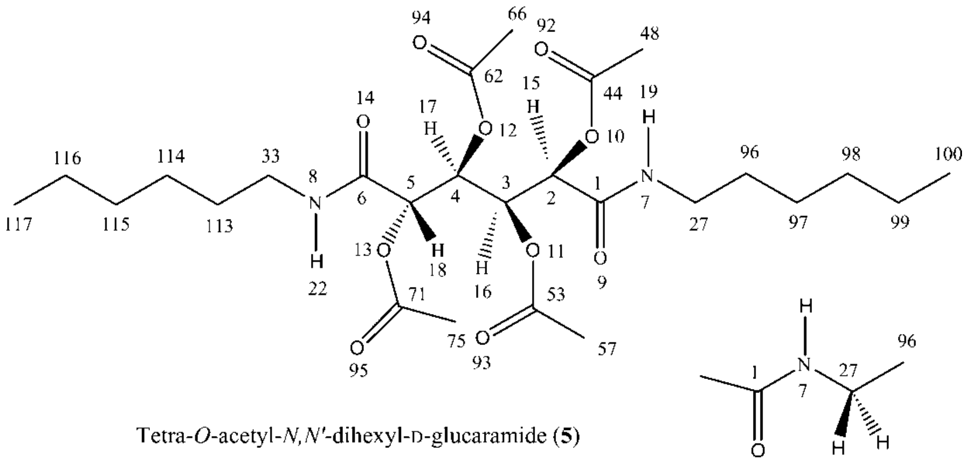
Figure 5: Tetra-*O*-methylpropanoyl-*N*,*N*′-dimethyl-D-glucaramide and low-energy methyl 2-methylpropanoate conformation (**B1**).

O92=C44-C48-C128. The only other unique conformation was 1.43 kcal/mol higher in energy than **B1** or **B2**.

The energy equivalent mirror image conformation **B2**, not shown, puts C-96 behind the O92-C44-C48-C128 plane and would be as likely as **B1**. In keeping with the intent to use reasonable models for the molecular mechanics computations while keeping the system as uncomplicated as possible, the four-pendant 2-methylpropanoyl on **3** was given conformation **B1** (C-128 front) in one set of 64 conformations, and the mirror image conformation **B**2 (C-96 back) in a second set of conformations. Consequently, the four O=C-C-C dihedral angles O92=C44-C48-C128/C96, O93=C53-C57-C133/C101, O94=C62-C66-C138/C106, and O95=C71-C75-C143/C111, were set at 0.0° in the conformational study of **3**.

N-Ethylacetamide (D) Model for **5**

For compound (**5**), 2,3,4,5-tetra-*O*-acetyl-*N*,*N*′-dihexyl-D-glucaramide, a model was required to establish the rotameric preference of the *n*-hexyl group on the amide nitrogens. *N*-ethylacetamide (**D**, Fig. 6) was selected as the simplest model for the *n*-hexylamido group in order to evaluate the carbonyl C-N-C-C dihedral angle (i.e., that between the amide carbonyl carbon and the β-alkyl carbon of any unbranched alkyl chain bound to the amide nitrogen). Rotation around the above bond (C1-N7-C27-C96) in 60.0° increments gave three conformers, **D1**, **D2**, and **D3**. Conformations **D1** and



Tetra-*O*-acetyl-*N*,*N*′-dihexyl-D-glucaramide (**5**)

N-Ethylacetamide (Model **D**)

Figure 6: *N*-Ethylacetamide (**D**) model and 2,3,4,5-tetra-*O*-acetyl-*N*,*N*′-dihexyl-D-glucaramide (**5**).

D2 have almost identical energies and are only 0.20 kcal/mol lower in energy than conformation **D3**. Enantiomeric **D1** and **D2** have the β-carbon close to a *gauche* relationship (±80.4°) with the amide carbonyl carbon, whereas **D3** is seen with the β-carbon *anti* (180.0°) to the carbonyl carbon. The comparable energy values from these conformations indicates that there is no obvious angular preference between the amide carbonyl carbon and the alkyl chain beginning with the β-carbon and so the *anti* conformation of *N*-ethylacetamide (**D**, Fig. 6) was arbitrarily chosen to model the amidohexyl groups of **5** to simulate an extended polymer structure.

Molecular Mechanics Study of Compounds 2–5

Computational Protocols

Applying the molecular mechanics program MM3 in the Alchemy 2000 (Tripos) computing software, compounds **2**–**5** were minimized using the same protocol as described for **1**,[1] block diagonal then full matrix minimization at a dielectric constant of 2.0. In addition, results from the methyl propanoate (**A**) model were applied to the pendant ester groups of **2** and results from the methyl 2-methylpropanoate (**B**) model to the ester groups of **3**. The 2,2-dimethylpropanoyl groups of **4** with three equivalent methyl groups attached to the α-carbon of the ester function were treated in the same way as the acetyl groups in **1**. For **5**, the *N*-ethylacetamide (**D**) model was applied as indicated.

Computational Results

The energy differences and calculated percent populations for the four lowest (of 64) energy conformations for each of the diamides **2**–**4** are presented in Tables 2 to 4, respectively. Percent populations were calculated as previously described.[1] These low-energy conformations are labeled according to their compound number, starting rotamer number followed by **m** (minimum). For example **2-2m** corresponds to the low (minimum) energy conformer from rotamer 2 of compound **2**.

The models applied to diamide **1** were also applied to *N*,*N*′-dihexyl analog **5**. Results from the *N*-ethylacetamide (**D**) model (Fig. 6) as applied to **5** suggested that rotation around the N7–C1 bond and N8–C6 amido-*N*-hexyl groups of **5** would generate three staggered conformations of similar energy and increase the typical set of 64 conformers per diamide to 576 conformers. Given the comparable energies of all of these conformers and in order to simplify the

Table 2: Energy differences and calculated percent populations for the four lowest (of 64) energy conformers of **2, 2-1m** to **2-4m**, based on conformation **A** (Fig. 4).

Low-energy conformers	**2-2m**		**2-4m**		**2-1m**		**2-3m**
Energy difference kcal/mol		0.64		0.39		0.27	
Calculated percent population	61.4		21.0		10.8		6.8

Table 3a: Energy differences and calculated percent populations for the four lowest (of 64) energy conformers of **3**, **3-1m** to **3-4m**, based on conformation **B**1 (Fig. 5).

Low-energy conformers	**3-2m**		**3-1m**		**3-4m**		**3-3m**
Energy difference kcal/mol		0.68		0.14		0.86	
Calculated percent population	61.5		19.6		15.3		3.6

Table 3b: Energy differences and calculated percent populations for the four lowest (of 64) energy conformers of **3**, **3-1m** to **3-4m**, based on conformation **B2**.

Low-energy conformers	**3-2m**		**3-1m**		**3-4m**		**3-3m**
Energy difference kcal/mol		1.14		0.19		1.29	
Calculated percent population	79.2		11.5		8.4		0.9

Table 4: Energy differences and calculated percent populations for the four lowest (of 64) energy conformers of **4**, **4-1m** to **4-4m**.

Low-energy conformers	**4-1m**		**4-2m**		**4-4m**		**4-3m**
Energy difference kcal/mol		0.05		1.27		0.73	
Calculated percent population	49.3		45.2		5.3		0.3

computational process, only the fully extended conformation of the terminal amidohexyl groups was calculated. The C1-N7-C27-C96 and C6-N8-C33-C112 dihedral angles were both set to 180.0°, and 64 original conformations were generated. The energy differences and calculated percent populations for the four lowest (of 64) energy conformations of the diamide **5** are presented in Table 5.

Calculated low energy conformations **2-2m**, **3-2m**, **4-1m**, **4-2m**, and **5-3m** from starting compounds **2**–**5** with associated intramolecular hydrogen bonds (Å) are shown in Figure 7. Both **2** and **3**, like parent molecule **1**, have a lowest-energy conformer derived from the corresponding rotamer 2. Conformer **2-2m** has a single intramolecular hydrogen bond (2.00′) N7-H19---92O=C. Hydrogen bonds were only considered at an interatomic distance of 2.10 Δ or less.[10] In contrast, conformer **3-2m**, with bulkier pendant methylpropanoyl groups, has no intramolecular hydrogen bonds and derives its stability from the absence of unfavorable steric interactions A more comprehensive conformation evaluation of **3** based on models **B1** and **B2** would take into account the 16 (4^2) conformational variations of the 64 rotamers, or a total of 1,024 conformations. In this modeling study only the 64 rotamers with the C-128 in front (**B1**) and 64 rotamers with C-96 back (**B**2) were considered, both sets giving similar energy distributions for the final low-energy conformations (Tables 3a and 3b). These comparable results suggest that they are representative of a study that would include all 1,024 conformations.

The low-energy conformation from **4**, the most sterically demanding diamide with pendant diemethylpropanoyl units, has two energetically

Table 5: Energy differences and calculated percent populations for the four lowest (of 64) energy conformers of **5**, **5-1m** to **5-4m**.

Low-energy conformers	**5-3m**		**5-2m**		**5-4m**		**5-1m**
Energy difference kcal/mol		0.96		0.05		0. 15	
Calculated percent population	71.4		21.0		10.8		6.8

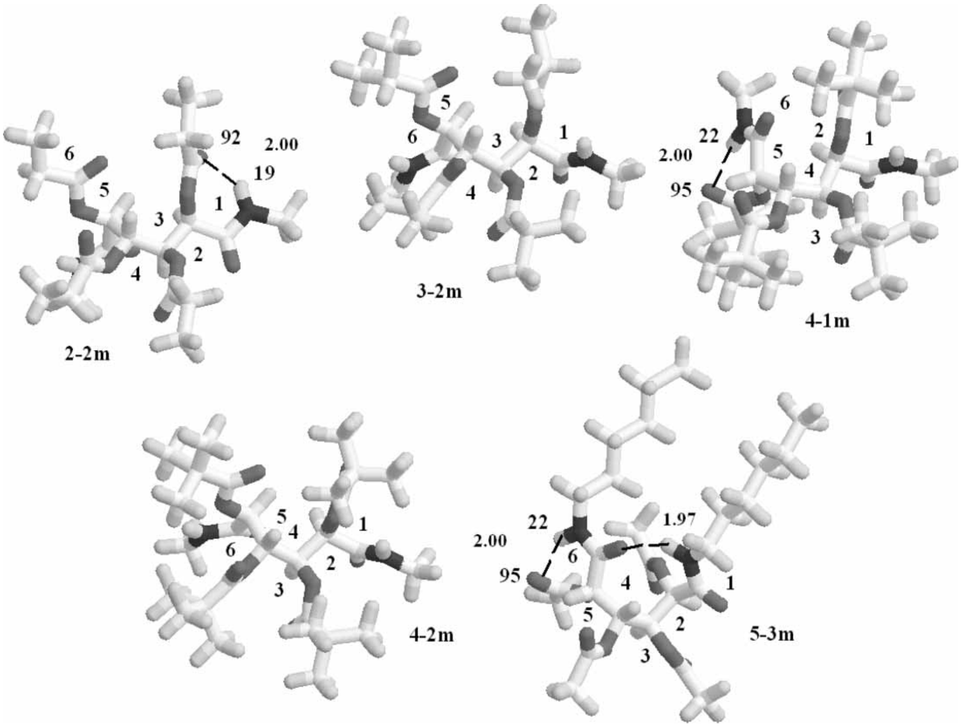


Figure 7: Calculated low-energy conformations **2-2m**, **3-2m**, **4-1m, 4-2m**, and **5-3m** from starting compounds **2**–**5** with associated intramolecular hydrogen bonds (Å). The 1.97′ hydrogen bond in **5-3m** is between unlabeled O14 and N19.

comparable low-energy conformers, **4-1m** at 49% and **4-2m** at 45%. Conformation **4-2m**, like conformation **3-2m**, exhibits no intramolecular hydrogen bonding and derives its stability from the absence of unfavorable steric interactions. In contrast, conformation **4-1m** is characterized by an intramolecular hydrogen bond (2.00 Å) N8-H22---95O=C71 at the C-6 end of the glucaryl unit.

Conformation **5-3m**, derived from corresponding rotamer 3, represents a relatively high 71% of the low-energy conformations for *N,N′*-dihexyl diamide (**5**) and is conformationally more compact than the other low-energy conformations described. An intramolecular hydrogen bond (1.97′) N7-H19---140=C6 links the two ends of **5** and brings the two hexyl units relatively close together. A second hydrogen bond (2.00 Å) N8-H22---95O=C71 also adds to the stability of this conformer. Compounds **5** and **1** both have pendant *O*-acetyl groups and differ only in the terminal alkyl groups being *n*-hexyl or methyl, respectively. However, there is free rotation in these diamides around the C1–N7 and C6–N8 bonds,[1] which allows the hexyl groups to be oriented as seen in **5-3m**, an overall conformational preference for **5** notably different than that observed for **1**. To get some further insight into how the length of the *N*-alkyl groups might impact the conformational distribution of additional acetylated diamides derived from **1**, the terminal *N*-methyl groups of the four low-energy conformations of parent diamide **1** were successively replaced with ethyl, *n*-propyl, and *n*-butyl groups, respectively, and then each conformation minimized as described. The low-energy conformation from parent compound **1**[1] and the diethyl analog was a **2m** conformation, but was a **4m** conformation for the *n*-propyl analog and a **3m** conformation for the *n*-butyl analog and, as noted, the *n*-hexyl analog (**5**). Consequently, these results suggest that the different *N,N′*-dialkyl diamides described are conformationally driven to some extent by the length of the pendant alkyl groups, but the specific steric and/or electrostatic origins of these conformational preferences are not obvious at this point.

Vicinal Proton Dihedral Angles for 2–5

The MM3 generated dihedral angles (ω, °) and calculated ^{1}H NMR vicinal coupling constants (J, Hz) for low-energy conformations of **2**–**5** are given in Table 6. The corresponding coupling constants were calculated with a modified Karplus/Altona equation[5] and compared with experimental ^{1}H NMR values (Table 7).

The trends in the calculated $J_{15,16}$ and $J_{17,18}$ values for **2**–**5** are in keeping with dihedral angles of *ca.* 60° but are notably lower than the observed couplings. In contrast, the calculated coupling constants for *anti* protons H16–H17 are on the order of 10 Hz, which is a little larger than the average (*ca.* 8 Hz) couplings observed. As previously noted, many of the conformations derived from **2**–**5** form intramolecular hydrogen bonds involving NH22 at the C6 end of these molecules. These hydrogen bonds tend to make the H17-C3-C4-H18 angle 75° or higher and lower the overall H17–H18 coupling constant. Consequently, in evaluating the relative importance of computationally derived conformations from diamides of the type described in this report, and independent of the MM3 computational protocol that generates such conformations, it is important to keep in mind that varying degrees of intramolecular hydrogen bonding can bias the calculated conformational populations. Clearly, the above results and comparisons are derived from a small population of conformers that while based on steric factors and modeling results, still most likely exclude the contributions of many secondary forms.

Conformations of Stereoregular Poly(hexamethylene 2,3,4,5-tetra-*O*-acetyl-D-glucaramides)—Some Possibilities

Copolymerization of (2*R*, 3*S*, 4*S*, 5*S*)-D-glucaric acid with alkylenediamines can be carried out to give either stereoregular repeating *head, tail*[11]–or

Table 6: MM3 generated dihedral angles (ω, °) and calculated ^{1}H NMR vicinal coupling constants (J, Hz) for low-energy conformations of **2**–**5**.

Conformations	H15-C2-C3-H16 (ω, °)	H16-C3-C4-H17 (ω, °)	H17-C4-C518 (ω, °)	$J_{15,16}$ (Hz) Calcd	$J_{16,17}$ (Hz) Calcd	$J_{17,18}$ (Hz) Calcd
2-1m	59.2	175.1	−76.2	1.03	9.76	0.97
2-2m	57.0	174.0	61.7	1.24	9.66	2.21
2-3m	−54.7	−176.7	−82.7	4.66	10.27	0.72
2-4m	−59.8	−174.8	77.2	3.90	10.34	0.92
3-1m^a	64.8	176.1	−76.6	0.59	9.84	0.95
3-2m^a	58.5	178.0	59.7	1.09	9.98	2.45
3-3m^a	−55.5	−172.0	−78.6	4.53	10.40	0.85
3-4m^a	−62.7	−174.9	76.3	3.48	10.34	0.96
4-1m	66.7	175.1	−76.7	0.47	9.75	0.94
4-2m	59.4	172.9	64.4	1.01	9.56	1.92
4-3m	−58.2	−171.6	−79.6	4.13	10.40	0.81
4-4m	−62.7	−175.1	75.2	3.46	10.33	1.03
5-1m	62.9	−175.4	−68.4	0.72	10.32	1.53
5-2m	57.1	174.2	60.3	1.23	9.68	2.38
5-3m	−63.6	−178.2	−96.2	3.40	10.21	0.90
5-4m	−59.9	175.4	78.9	3.88	10.32	0.84

^{a}Based on model **B1**.

alternating *head, tail–tail, head* poly(alkylene-D-glucaramides).[12] As the long-term objective of these computational studies is to try to better understand the conformations of polyhydoxypolyamides and their *O*-acyl derivatives, conformational representations of *O*-acylated stereoregular, repeating *head tail–* and stereoregular, alternating *head tail–tail head*-poly(hexamethylene 2,3,4,5-tetra-*O*-acetyl-D-glucaramide) oligomers (Fig. 8) were built, based on the structure of the low energy conformation of **5** (**5-3m**), and then minimized. The repeating oligomers (composed of two *O*-acetylated glucaryl units, one repeating hexamethylene unit, and *N*-propyl terminal groups) represent segments of stereoregular, repeating *head tail–* and alternating *head tail–tail head*-poly(hexamethylene 2,3,4,5-tetra-*O*-acetyl-D-glucaramide). The

Table 7: Calculated average vicinal coupling constant values (J, Hz) from the low-energy conformations of **2**–**5** and the observed coupling constant values.

Compound	$J_{15,16}$ (Calcd)	$J_{16,17}$ (Calcd)	$J_{17,18}$ (Calcd)	$J_{15,16}$ (Obs)	$J_{16,17}$ (Obs)	$J_{17,18}$ (Obs)
2	2.01	9.86	1.70	3.23	7.76	3.88
3^a	1.00	10.02	1.87	2.59	8.41	3.24
4	0.88	9.70	1.39	1.83	8.61	2.75
5	3.11	10.15	1.11	3.17	7.62	3.81

^{a}Based on model **B1**.

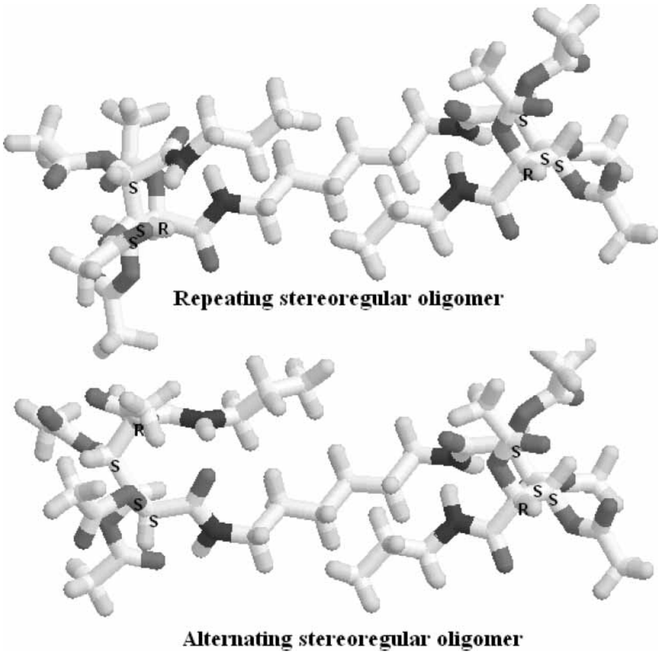


Figure 8: Computationally generated and minimized repeating and alternating stereoregular oligomers of poly(hexamethylene 2,3,4,5-tetra-*O*-acetyl-D-glucaramides).

highly bent conformation of the D-glucaryl units in both oligomers brings the hydrophilic alkylene units relatively close together, suggesting that a similar orientation of groups in the corresponding polymer may exist in suitable nonpolar solvents (e.g., chloroform). Terminal *n*-hexyl units were not included in these models as the Alchemy program limited the size of the molecule that could be minimized.

ACKNOWLEDGEMENTS

This work was funded by grants from the USDA Cooperative State Research, Education and Extension Services, awards 2002-34463-11929 and 2003-34463-13003. J. Zhang also thanks the Shafizadeh Center for additional support as a graduate student while at the University of Montana.

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