Structural Versatility of Oxalamide-Based Compounds: A Computational Study on the Isomerization of the Oxalamide Group and the Structural Preferences of the Polyoxalamides

Elaine Armelin, Carlos Alemán, and J. Puiggalí*

Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona E-08028, Spain

puiggali@eq.upc.es

Received January 13, 2001

The conformational properties of the oxalamide group and crystal structure of several polyoxalamides have been investigated by computational methods. First, a detailed quantum mechanical study of the conformational preferences of *N*,*N′*-dimethyloxalamide is reported. Results, which were obtained at the MP2/6-31G(d) level, provide not only the minimum energy conformations but also a description of the energetics and structural changes associated to the isomerization process of the oxalamide group. These quantum mechanical results together with those obtained from additional calculations have been used to develop a set of force-field parameters for the oxalamide group. Molecular mechanics calculations have been performed to test the parameters and to provide new information in terms of energy contributions about the isomerization of the oxalamide group. On the other hand, the new set of parameters has been used to investigate the structural preferences of polyoxalamides (-[NH-CO-CO-NH-$(CH_2)_n$]-) by PCSP calculations. Results indicated that polyoxalamides with an even number of methylene groups adopt a structure with one hydrogen bonding direction, whereas polymers with an odd number of methylene groups prefer a structure with two hydrogen bonding directions. The latter crystal structure is completely different from that observed in conventional polyamides and has been investigated in detail through Monte Carlo simulations.

Introduction

Modified amino acids are of relevant interest in molecular engineering. They have been used to design peptides and peptidomimetics with a controlled fold in the backbone,[1] to prepare bioactive compounds with enhanced stability toward enzymatic degradation,[2,3] and moreover to design new polymeric materials.[4−6]

Among the strategies employed to modify amino acid residues is the alteration of the peptide bond. Thus, the introduction of modified peptide links makes it possible to influence the biological properties of a molecule while retaining the receptor binding ability, which usually depends on the side chains.[7,8] In particular, a very important effort has been devoted to retro-inverso modification, i.e., reversal of the direction of the amide bond, in the past 20 years. In a recent work, Fletcher and Campbell reviewed the development of partially modified retro-inverso peptides covering the most significant advances in their synthesis, biological activity and structure.[3] However, retro-inverso modification has been also of great importance in the material science field. For instance, partially modified retro-inverso glycine has been used to design two families of aliphatic polyamides, i.e., nylons 1,*n*[4] and nylons *n*,3,[5] which present unique structural properties.

Another strategy, which has also become of great interest in recent years, is the replacement of the peptide bond by the oxalamide linkage (-NH-CO-CO-NH-). This substitution is closely related to retromodification since in both cases the hydrogen bonding capabilities are retained. A range of retro-bispeptides having the oxalamide moiety at the center have been prepared as an aid to design enzyme mimics and potential inhibitors.[9] Furthermore, the oxalamide linkage has been successfully used in materials science to design a promising family of polymers, denoted polyoxalamides or nylons *n*,2:[10,11]

$$(\text{-[NH-CO-CO-NH-}(CH_2)_n\text{]-})$$

An important characteristic of these compounds is that some of them[11] adopt a structure different from those

---

[1] (a) Dauber-Osguthorpe, P.; Campbell, M. M.; Osguthorpe, D. J. *Int. J. Pept. Protein Res.* **1991**, *38*, 357. (b) Balaram, P. *Curr. Opin. Struct. Biol.* **1992**, *2*, 845. (c) Benedetti, E. *Biopolymers* **1996**, *40*, 3. (d) Alemán, C. *Proteins* **1997**, *29*, 575.

[2] (a) Verdini, A. S.; Silvestri, S.; Becherucci, C.; Longobardi, M. G.; Parente, L.; Peppoloni, S.; Perretti, M.; Pileri, P.; Pironi, M.; Viscomi, A.; Nencioni, L. *J. Med. Chem.* **1991**, *31*, 3372. (b) Chorev, M.; Goodman, M. *Trends Biotechnol.* **1995**, *13*, 438. (c) Nishikawa, N.; Komazawa, H.; Orisaka, A.; Yoshikane, M.; Yamaguchi, J.; Kojima, M.; Ono, M.; Itoh, I.; Azuma, I.; Fujii, H.; Murata, J.; Saiki, I. *Bioorg. Med. Chem.* **1996**, *6*, 2725.

[3] Fletcher, M. D.; Campbell, M. M. *Chem. Rev.* **1998**, *98*, 763.

[4] (a) Franco, L.; Navarro, E.; Subirana, J. A.; Puiggalí, J. *Macromolecules* **1994**, *27*, 4284. (b) Alemán, C.; Franco, L.; Puiggalí, J. *Macromolecules* **1994**, *27*, 4298. (c) Alemán, C.; Puiggalí. J. *J. Org. Chem.* **1995**, *60*, 910.

[5] (a) Navarro, E.; Puiggalí, J.; Subirana, J. A. *Macromol. Chem. Phys.* **1995**, *96*, 2361. (b) Puiggalí, J.; Aceituno, J. E.; Campos, J. L.; Subirana, J. A. *Macromolecules* **1996**, *29*, 8170.

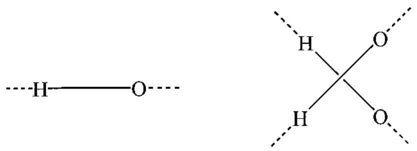
[6] (a) Malcolm, B. R.; Walkinshaw, M. D. *Biopolymers* **1986**, *25*, 607. (b) Zanuy, D.; Alemán, C.; Muñoz-Guerra, S. *Macromol. Theory Simul.* **2000**, *9*, 543. (b) Zanuy, D.; Alemán, C.; Muñoz-Guerra, S. *Int. J. Biol. Macromol.* **1998**, *23*, 175.

[7] Spatola, A. F. In *Chemistry and Biochemistry of Amino Acids, Peptides and Proteins*; Weinstein, B., Ed.; Marcel Dekker: New York, 1983; Vol. 7, pp 267−357.

[8] Marraud, M.; Dupont, V.; Grand, V.; Zerkout, S.; Lecoq, A.; Boussard, G.; Vidal, J.; Collet, A.; Aubry, A. *Biopolymers* **1993**, *33*, 1135.

10.1021/jo010042l CCC: $20.00

Scheme 1. Schematic Projection of a Nylon Chain with One (Left) and Two (Right) Hydrogen Bonding Directions



usually found in conventional nylons that are based on the formations of hydrogen bonds along a single direction (α, β and γ forms).[12] Thus, a structure with two different hydrogen bonding orientations (Scheme 1) is obtained for the polyoxalamides with an odd number of methylene groups.[11] We have postulated this kind of structure for other nylons derived from odd diacids and/or diamines.[13]

Recently,[14] we investigated the minimum energy conformations of *N,N′*-dimethyloxalamide (NdMO), which is the most simple compound involving an oxalamide linkage. They were compared and contrasted with the minima predicted for *N,N′*-diacetylhydrazine with the -CO- groups flanking the -NH- groups, since the hydrazide linkage (-CO-NH-NH-CO-) is the reversal of the oxalamide linkage. However, many other questions about the oxalamide linkage and polyoxalamides remain unanswered. Here we report a rigorous and complete computational study of the oxalamide linkage and both odd and even polyoxalamides. From these calculations we expect to gain vital insight into the different aspects of the oxalamide group and their polymeric derivatives: (i) the energetics and structural changes associated with the isomerization process of the oxalamide group; (ii) the force-field parameters required for the oxalamide group to perform molecular mechanics simulations; (iii) the effect of the number of methylene groups on the structural preferences of polyoxalamides; and (iv) the most relevant features associated with the nonconventional structure of polyoxalamides bearing an odd number of methylene groups.

The outline of the present paper is as follows. In the next section we briefly describe the methods used for the quantum mechanical calculations, force-field parametrization, crystal packing calculations and Monte Carlo (MC) simulations. Next, we present the results on the NdMO and polyoxalamides systems. We also report the minimum energy conformations, the rotational profiles and the main structural trends for NdMO at the MP2/6-31G(d) level. A set of force-field parameters has been explicitly developed for the oxalamide moiety using these quantum mechanical calculations. Furthermore, we analyze the influence of the number of methylene units with regards the structural preferences of polyoxalamides by comparing the packing energies of the different crystal forms observed for these compounds. Finally, the crystal structure displayed by odd polyoxalamides have been the subject of a more detailed study by performing MC simulations of nylon 9,2. The last section presents the conclusions of the work.

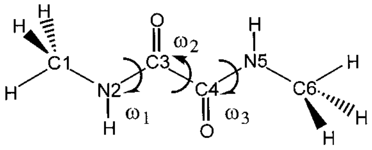


Figure 1. Atom numbering for *N,N′*-dimethyloxalamide (NdMO). The dihedral angles are defined as follows: $\omega_1 = \angle$C1−N2−C3−C4, $\omega_2 = \angle$N2−C3−C4−N5, and $\omega_3 = \angle$C3−C4−N5−C6.

Methods

Quantum Mechanical Calculations. The rotational profiles for NdMO were computed spanning the dihedral angles ω_1 and ω_2 (Figure 1) in steps of 30°. A flexible rotor approximation was used in all cases. Thus, the molecular geometry of each point of the rotational profiles was completely optimized with the obvious exception of the fixed geometrical parameter (ω_1 or ω_2). To evaluate the rotational profile of each torsion, a *trans* conformation was used as starting point for the other dihedral. Eight minima may be anticipated for NdMO by considering the *trans* and *cis* conformations of ω_1, ω_2, and ω_3.[14] However, this number decreases to six as a result of the chemical symmetry of the molecule. Complete geometry optimizations using such structures as starting points led to three different minimum energy conformations. These conformations were characterized as minima by calculating and diagonalizing the Hessian matrix and ensuring that they do not have any negative value.

Geometry optimizations of the minimum energy conformations and all of the points along the curves describing the torsional potentials were performed at the MP2/6-31G(d) level.[15,16] Furthermore, the rotational profiles computed at the MP2/6-31G(d)//MP2/6-31G(d) were compared with those obtained at the HF/6-31G(d)//MP2/6-31G(d) level in order to investigate the effects of electron correlation in the energetics of the oxalamide linkage isomerization.

All quantum mechanical calculations were carried out using the Gaussian-98 suite of programs.[17]

Force-Field Parametrization. Force-field energies ($E_{\rm ff}$) have been computed using the analytical potential function implemented in the PCSP[18] (Prediction of the Crystal Structure of Polymers) and MCDP[19] (Monte Carlo of Dense Systems) computer programs. In detail it presents the following functional form:

$$E_{\rm ff} = \Sigma_{\rm dihedrals}\, V_n/2\; [1 + \cos(n\varphi - \gamma)] + \Sigma_{\rm nonbonded} q_i q_j/\epsilon r_{ij} + \Sigma_{\rm nonbonded}[A_{ij}/r_{ij}^{\;12} - B_{ij}/r_{ij}^{\;6}] \quad (1)$$

---

(9) (a) Ranganathan, D.; Vaish, N. K.; Shah, K.; Roy, R.; Madhusudanan, K. P. *J. Chem. Soc., Chem. Commun.* **1993**, 92. (b) Karle, I.; Rangahathan, D.; Shah, K.; Vaish, N. K. *Int. J. Pept. Protein Res.* **1994**, *43*, 160. (c) Karle, I. L.; Rangahathan, D. *Int. J. Pept. Protein Res.* **1995**, *46*, 18. (d) Karle, I. L.; Ranganathan, D. *Biopolymers* **1995**, *36*, 323.

(10) (a) Shalaby, S. W.; Pearce, E. M.; Fredericks, R. J.; Turi, E. A. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1. (b) Chatani, Y.; Ueda, Y.; Tadokoro, H.; Deits, W.; Vogl, O. *Macromolecules* **1978**, *11*, 636. (c) Gaymans, R. J.; Venkatraman, Schüijer, S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1373.

(11) Franco, L.; Subirana, J. A.; Puiggalí, J. *Macromolecules* **1998**, *31*, 3912.

(12) Xenopoulus, A.; Clark, E. S. In *Nylon Plastics Handbook*; Kohan, M. I., Ed.; Hanser Publishers: Munich, Germany, 1995; Chapter 5.

(13) (a) Puiggalí, J.; Franco, L.; Alemán, C.; Subirana, J. A. *Macromolecules* **1998**, *31*, 8540. (b) Navarro, E.; Alemán, C.; Subirana, J. A.; Puiggalí, J. A. *Macromolecules* **1996**, *29*, 5406.

(14) Alemán, C.; Puiggalí, J. *J. Org. Chem.* **1999**, *64*, 351.

(15) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

(16) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(17) *Gaussian 98*, Revision A.7; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1998.

In the above equation the first term represents dihedral interactions, while the last two terms describes the electrostatic and van der Waals nonbonded interactions, respectively. The nonbonded interactions separated by exactly three bonds (1−4 interactions) are reduced by the application of a scale factor $\xi = 2$. The A_{ij} and B_{ij} parameters included in eq 1 are computed according to

$$A_{ij} = \epsilon_{ij}(R_{ij})^{12} \tag{2}$$

$$B_{ij} = 2\epsilon_{ij}(R_{ij})^{6} \tag{3}$$

where the values used in eqs 2 and 3 for an interaction of atom i and j are $R_{ij} = R_i + R_j$ and $\epsilon_{ij} = (\epsilon_i\epsilon_j)^{1/2}$, R_i and ϵ_i being the van der Waals parameters of atom i.

Energy calculations require a complete set of torsional (V_n and γ) and nonbonding (q_i, q_j, A_{ij}, and B_{ij}) parameters for the oxalamide moiety. On the other hand, bond lengths and angles were kept fixed in both PCSP and MCDP simulations, but precise values for these geometric parameters are required to build the molecular system.

Equilibrium values for the bond lengths and angles were taken from the minimum energy conformations. The torsional term was parametrized using the rotational profiles computed at the MP2/6-31G(d) for the dihedral angles ω_1 and ω_2. The torsional parameters were obtained using the PAPQMD strategy.[4c,20] According to this method, the determination of these parameters was carried out by means a rigorous fitting between the quantum mechanical (ΔE^{qm}) and the molecular mechanical (ΔE^{ff}) energy variations arising from the rotation around a given bond:

$$(\Delta E^{qm} - \Delta E^{ff})^2 = \text{minimum} \tag{4}$$

Moreover, PAPQMD performs the fitting considering all the perturbations that the modification of one torsion angle causes in all the other geometrical variables. Thus, during the variation of one torsion angle, both the bonded and nonbonded distances change markedly. This implies variations in the nonbonded (electrostatic and van der Waals) and bonded (stretching and bending) terms. Accordingly, ΔE^{ff} is expressed as the addition of two energy contributions: (i) the energy directly related to the variation of the torsion angle (ΔE^{tor}) and (ii) the perturbational energy related to all the other variations in the molecular geometry (ΔE^{per}):

$$\Delta E^{ff} = \Delta E^{tor} + \Delta E^{per} \tag{5}$$

Considering eq 5, eq 4 can be rewrittem as

$$(\Delta E^{qm} - \Delta E^{tor} - \Delta E^{per})^2 = \text{minimum} \tag{6}$$

For every value of the rotational profile, the program computes the corresponding perturbation term according to the force-field equations mentioned above and subtracts it from the quantum mechanical energy. The torsional parameters are obtained from the fitting between the corrected quantum mechanical and the ΔE^{tor} energies.

The partial atomic charges were derived by fitting the rigorously defined quantum mechanical Molecular Electrostatic Potential (MEP), which was computed at the HF/6-31G(d) level,[15] to the Coulombic electrostatic potential. This level of theory was used for two reasons. First, previous studies have demonstrated that in general the HF/6-31G(d) level provides reliable quantitative measures of the electrostatic properties.[21] The second reason is that HF/6-31G(d) electrostatic parameters have been included in the libraries of the second generation force fields.[22]

van der Waals atomic parameters are quite transferable[23] and depend mainly on the atomic number and degree of hybridization. Accordingly, the parameters required for the oxalamide moiety were initially extracted from the libraries of standard force fields.[22,24,25] Such parameters were tested by comparing force-field and quantum mechanical calculations. The parameters were varied until the optimum agreement between quantum mechanical and force-field energies was achieved.

Energy Calculations and Monte Carlo Simulations. Energy calculations of polyoxalamides were performed with the new set of force-field parameters developed for the oxalamide moiety and using the PCSP computer program.[18] It is able to generate the atomic coordinates of a polymer in a given crystal lattice, which dimensions are usually determined by diffraction analysis, and to evaluate the energy of the resulting structure. Specifically, the program explores the relative stability of the different arrangements that result when either the molecular conformation or the arrangement of the molecules within the unit cell is varied. By this method the most favorable three-dimensional arrangement, which corresponds to the lowest packing energy of the chains in the crystal lattice, may be ascertained. The PCSP method has been demonstrated to give very good results for polyamides using both conventional and nonconventional structures.[18,26]

The structure of the polyoxalamide with nine methylene units (nylon 9,2) was investigated in some detail using MC simulations. For this purpose the MCDP computer program[19] was used since it is specially designed to simulate polymers with ordered structures. Several MC algorithms have been incorporated in this program that can be used alone or in combination depending on the requirements of the simulation. For the present work we chose the Metropolis algorithm,[27] which is the simplest MC scheme. The following parameters were considered as degrees of freedom in the simulation of *NPT* type: (a) the setting orientation angles of the helices, i.e., for each helix the angle measured between the *a* axis of the simulation box and the vector constituted by the *ab* projections of the helix center and a representative atom of the chain; and (b) the dimensions of the simulation box *a*, *b*, and *c*. All of these parameters are efficiently sampled by the Metropolis algorithm.[19]

The PCSP and MCDP computer programs evaluate the energy using eq 1, i.e., assuming fixed bond lengths and angles. The MC simulation was run at 298 K for 2 ×10^6 steps. Structures were saved and analyzed every 1 × 10^4 steps, resulting in 200 structures. It should be mentioned that the MCDP method has been successfully used to simulate dynamical aspects of the crystal structure of different polyamides.[28] No special treatment was applied for the long-range electrostatic interactions.

---

(18) León, S.; Navas, J. J.; Alemán, C. *Polymer* **1999**, *40*, 7351.

(19) León, S.; Alemán, C.; Escalé, F.; Laso, M. *J. Comput. Chem.* **2001**, *22*, 162.

(20) (a) Alemán, C.; Canela, E. I.; Franco, R.; Orozco, M. *J. Comput. Chem.* **1991**, *12*, 664. (b) Alemán, C.; Orozco, M. *J. Comput.-Aided Mol. Des.* **1992**, *6*, 331. (c) Namba, A. M.; León, S.; da Silva, G. V. J.; Alemán, C. *J. Comput.-Aided Mol. Des.* **2001**, *15*, 235.

(21) (a) Williams, D. E. *Biopolymers* **1990**, *29*, 1367. (b) Bayly, C.; Cieplack, P.; Cornell, W.; Kollman, P. A. *J. Phys. Chem.* **1993**, *97*, 10269. (c) Orozco, M.; Luque, F. J. *J. Comput. Chem.* **1990**, *11*, 909. (d) Alhambra, C.; Luque, F. J.; Orozco, M. *J. Comput. Chem.* **1994**, *15*, 12.

(22) Cornell, W. D.; Cieplak, P.; Bayli, C. L.; Gould, I. R.; Merz, K. M.; Ferguson, D. C.; Spellmeyer, T.; Fox, J. W.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.

(23) (a) Orozco, M.; Alemán, C.; Luque, F. J. *Models Chem.* **1993**, *130*, 695. (b) O'Donnel, T. J.; Rao, S. N.; Koechler, K.; Martin, Y. C.; Eccler, B. J. *J. Comput. Chem.* **1991**, *12*, 209.

(24) Weiner, S. J.; Kollman, P. A.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230.

(25) Nilsson, L.; Karplus, M. *J. Comput. Chem.* **1986**, *7*, 591.

(26) (a) Bermúdez, M.; León, S.; Alemán, C.; Muñoz-Guerra, S. *Macromol. Chem. Phys.* **1999**, *200*, 2065. (b) Bermúdez, M.; León, S.; Alemán, C.; Muñoz-Guerra, S. *Polymer* **2000**, *41*, 8961.

(27) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.

(28) (a) León, S.; Alemán, C.; Muñoz-Guerra, S. *Macromolecules* **2000**, *33*, 5754. (b) León, S.; Alemán, C.; Bermúdez, M.; Muñoz-Guerra, S. *Macromolecules* **2000**, *33*, 8756.

Table 1. Minimum Energy Conformations[a] and Relative Energies of *N,N′*-Dimethyloxalamide (NdMO) Obtained at the MP2/6-31G(d) Level of Theory

	ttt	ctt	csc
ω_1	180.0	0.1	1.8
ω_2	180.0	180.0	144.8
ω_3	180.0	180.0	1.9
ΔE	0.0	6.6	13.3

[a] t,c, and s refer to *trans*, *cis*, and *skew*, respectively. Dihedral angles ω_1, ω_2, and ω_3 are in degrees. Relative energy is in kcal/mol.

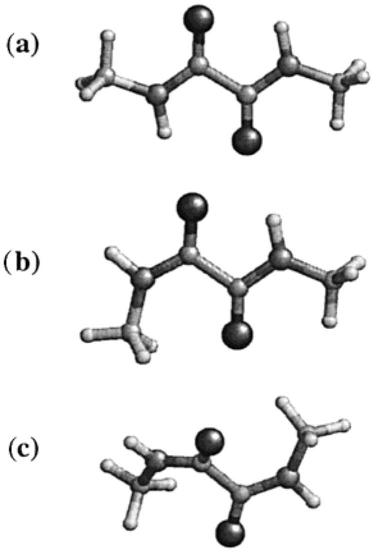


Figure 2. Minimum energy conformations computed at the MP2/6-31G(d) level for *N,N′*-dimethyloxalamide (NdMO): (a) **ttt**, (b) **ctt**, and (c) **csc**.

Periodic boundary conditions were applied in both energy calculations and MC simulation. More specifically, the cell was replicated several times in PCSP calculations, whereas for MCDP calculations translational symmetry was applied in the *a*, *b*, and *c* axes. A cutoff limit of 10 Å was chosen, implying that all atoms of one residue interact with all atoms of another residue if at least one pair of atoms is within the limit. This means that, in practice, many interactions beyond the cutoff limit are taken into account as well.

Results and Discussion

Conformational Properties of the Oxalamide Moiety. The minimum energy conformations of NdMO were reported in our previous work.[14] However, we have included a brief description of them in this work for sake of completeness. The dihedral angles ω_1, ω_2, and ω_3 of three minima predicted at the MP2/6-31G(d) level are shown in Table 1. The lowest energy minimum, denoted **ttt**, exhibits a *trans* (t) conformation in the three dihedral angles. Two other minima were characterized: the **ctt** and **csc**, both of them having a symmetrical counterpart. The **ctt** minimum, in which the dihedral angle ω_1 presents a *cis* (c) conformation, is 6.6 kcal/mol less stable than the **ttt** conformation. In the **csc** structure, which is destabilized by 13.3 kcal/mol, the dihedral angle ω_2 is in *skew* (s) conformation. The three energy minima are displayed in Figure 2.

To obtain a better understanding of the conformational properties of the oxalamide moiety, we have computed the rotational profiles for the dihedral angles ω_1 and ω_2. For this purpose, geometry optimization of all points along the curves describing the torsional potentials was performed at the MP2/6-31G(d) level; the **ttt** was used as starting conformation for such calculations.

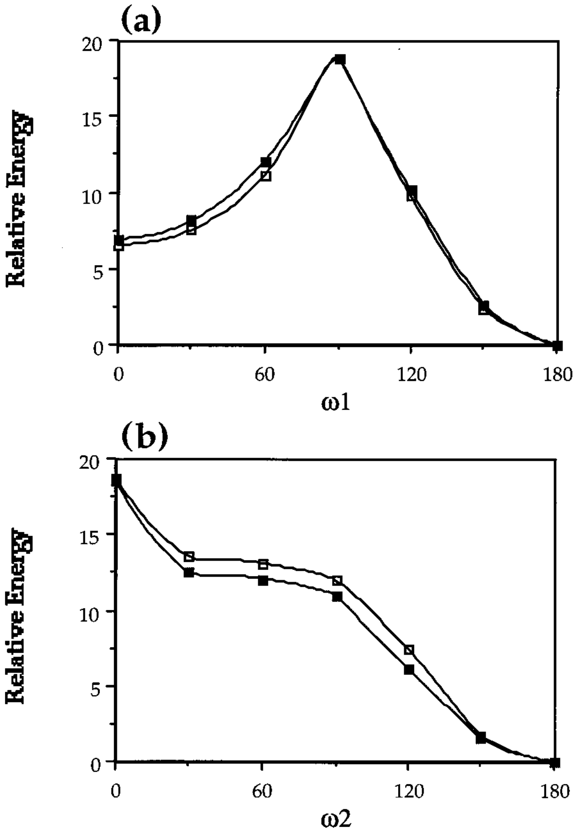


Figure 3. Evolution of the HF/6-31G(d) (■) and MP2/6-31G(d) (□) relative energies (in kcal/mol) for the *N,N′*-dimethyloxalamide (NdMO) as a function of the dihedral angles (in degrees) ω_1 (a) and ω_2 (b).

The evolution of the HF/6-31G(d) and MP2/6-31G(d) energies as a function of the dihedral angle ω_1 is displayed in Figure 3a. The results obtained at the HF level are in quantitative agreement with the MP2 data, the largest difference being 0.9 kcal/mol. The most stable arrangement corresponds to the *trans* and a second minimum arises when the torsional angle ω_1 is 0°. This *cis* conformation is 6.6 kcal/mol less favored than the *trans*. It should be mentioned that such energy difference is about 4 kcal/mol larger than that predicted for the amide bond of *N*-methylacetamide at the same level of theory. On the other hand, the energy barrier for the *cis*-to-*trans* isomerism is 12.3 kcal/mol, whereas barrier for the *trans*-to-*cis* interconversion is 18.9 kcal/mol. These values are close to those found for a typical amide bond. Thus, the energy barrier predicted at the MP2/6-31G(d) level for the *trans*-to-*cis* isomerism of *N*-methylacetamide is 17.7 kcal/mol,[29] while the value provided by NMR is 18.0 kcal/mol.[30]

The rotational profiles obtained for ω_2 from quantum mechanical calculations are displayed in Figure 3b. In this case the largest difference between HF and MP2 results is 2 kcal/mol. The *trans* is the minimum energy conformation, and the *cis* corresponds to an energy barrier of 18.7 kcal/mol. These conformational prefer-

---

[29] Luque, F. J.; Orozco, M. *J. Org. Chem.* **1993**, *58*, 6397.

[30] Drakenberg, J. T.; Forsen, S. *J. Chem. Soc., Chem. Commun.* **1971**, 3683.

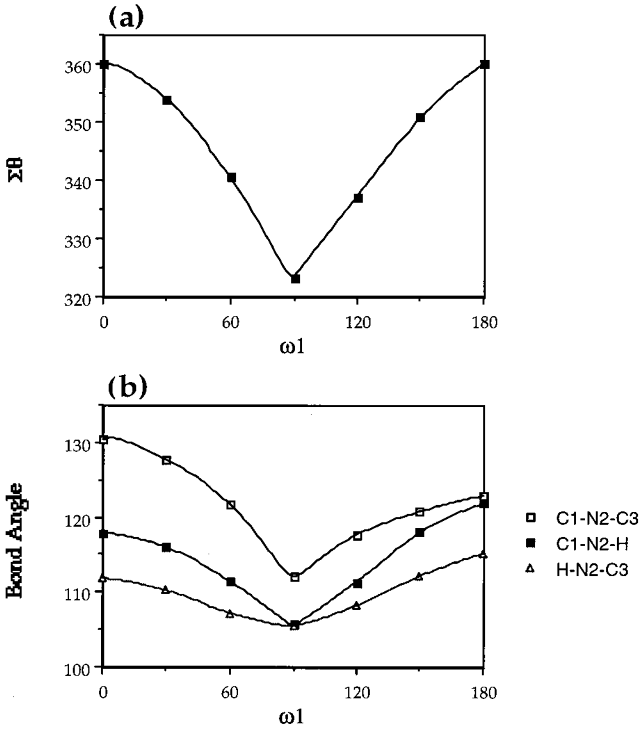


Figure 4. (a) Evolution of $\Sigma\theta$, which corresponds to the sum of the $\angle$C1−N2−C3, $\angle$C1−N2−H, and $\angle$H−N2−C3 bond angles, as a function of the dihedral angle ω_1. (b) Evolution of the $\angle$C1−N2−C3, $\angle$C1−N2−H, and $\angle$H−N2−C3 bond angles as a function of the dihedral angle ω_1. All angles are in degrees.

ences are probably due to the strong repulsive interactions originated by the confronted carbonyl groups. This was confirmed by using the energy partition scheme implemented in MOPAC (ENPART), which provides a qualitative estimation of the intensity of intramolecular interactions. With this partition scheme, we found that the electrostatic contribution is much less favorable for $\omega_2 = 0°$ than for $\omega_2 = 180°$ (see next section). Another interesting feature of the rotational profiles displayed in Figure 3b is the presence of a plateau region at ω_2 values ranging from 90° to 30°, while a sharp increase appears when ω_2 changes from 30° to 0°. The energy partition analysis suggests that such increase is due to the one-center energy terms, which become less favorable in the *cis* planar arrangement.

The planar or pyramidal geometry of the nitrogen atoms has been investigated for all of the structures involved in the rotational profiles of Figure 3. This has been represented by the sum of the $\angle$C1−N2−C3, $\angle$C1−N2−H, and $\angle$H−N2−C3 bond angles, which is denoted $\Sigma\theta$. The value of $\Sigma\theta$ for the **ttt**, **ctt**, and **csc** minima is 360° indicating that the nitrogen atoms retain a planar geometry in these arrangements. Figure 4a shows the dependence between $\Sigma\theta$ and the dihedral angle ω_1. It is worth noting that $\Sigma\theta$ is lower than 360° for all the conformations with exception of the planar ones. The largest degree of pyramidality is achieved in the perpendicular arrangement ($\Sigma\theta = 323.3°$). Indeed, inspection of the evolution of bond angles (Figure 4b) indicates a change from sp^2 to sp^3 hybridization at $\omega_1 = 90°$. Regarding ω_2, the situation appears to be completely different. Thus, the maximum deviation of the parameter $\Sigma\theta$ is 4° ($\Sigma\theta = 356°$ at $\omega_2 = 90°$), the planarity of the nitrogen atoms being almost unaltered by the rotation around the C(O)−C(O) bond.

Table 2. Geometric[a] ($d°$ and $\theta°$ in Å and deg, respectively), Torsional[b] (V_n and γ in kcal/mol and deg, respectively), Electrostatic[c] (q_i in electron units), and van der Waals[d] (R in Å, ϵ in kcal/mol) Parameters

Distances and Angles[a]

distance	d°	angle	θ°
N−C(O)	1.346	N−C(O)−C(O)	111.6
C(O)-C(O)	1.533	H−N−C(O)	115.2
N−H	1.015	O=C−C(O)	121.8
C=O	1.240	O=C−N	126.6

Torsions[b]

dihedral	V_n	γ	n
X−N−C(O)−X	10.0	180	2
X−C(O)−C(O)−X	1.3	180	2

Electrostatic[c] and van der Waals[d]

atom	q_i	R	ϵ
C (methyl)	0.1753	2.00	0.0150
N	−0.3533	1.824	0.1700
H(N)	0.2358	0.600	0.0157
C(O)	0.4460	1.908	0.0860
O	−0.5038	1.661	0.2100

[a] Equilibrium geometric parameters were obtained from geometry optimizations of NdMO at the MP2/6-31G(d) level. [b] Torsional parameters were obtained using the PAPQMD procedure and the torsional profiles computed at the MP2/6-31G(d) level. [c] Atomic charges were derived from the molecular electrostatic potential computed at the HF/6-31G(d) level. [d] van der Waals parameters were taken from the last parametrization of the Amber force field. ref 22.

Force-Field Parametrization. The MP2/6-31G(d) optimized geometries of NdMO were used to determine equilibrium bond lengths and angles for the oxalamide moiety. More specifically, these geometric parameters (Table 2) were taken from the **ttt** conformation, which is predicted to be the lowest energy minimum.

The torsional term has been parametrized using an approach in which only the nature of the two central atoms is considered. Accordingly, all the torsions $\{A_i\}$−B−C−$\{D_i\}$ associated with the central bond B−C have the same parameters. The torsional energy parameters (V_n), the values of the phase angle (γ), and the periodicity associated with the rotations around the N−C(O) and C(O)−C(O) bonds of the oxalamide moiety were obtained using the rotational profiles computed at the MP2/6-31G(d) level. A Fourier expansion truncated at the third term, i.e., $n = 3$ in the first term of eq 1, was used to describe the torsional energy. Results are listed in Table 2. In all cases the values of V_1 and V_3 were negligible. Thus, for the two rotations the calculation from the corrected quantum mechanical energies (see eq 6) leads to the definition of a profile of periodicity two.

The coefficient of the torsional term V_2 for the rotation of the N−C(O) bond is very similar to that reported in standard force fields for a typical amide group.[22,23] However, the torsional parameters for the rotation of the C(O)−C(O) bond are quite unexpected. Thus, MP2/6-31G(d) calculations lead to a profile of periodicity one (Figure 3b), whereas the application of the corrections introduced by the PAPQMD procedure leads to torsional parameters with periodicity two. This points out the importance of the perturbational energy (eqs 5 and 6) in the strategy used for the parametrization the torsional term. Thus, the profile displayed in Figure 3b includes a considerable number of nonbonding repulsive interactions, which are corrected by eq 6. Furthermore, the torsional potential

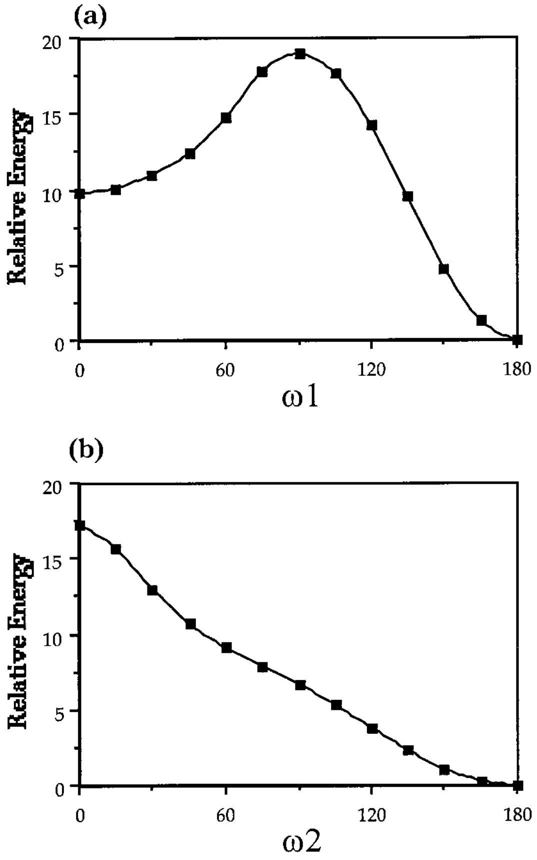


Figure 5. Evolution of the force-field energy as a function of the dihedral angles ω_1 (a) and ω_2 (b).

V_2 is very low with respect to large the energy barrier predicted by MP2/6-31G(d) calculations, indicating that such a barrier is mainly due to nonbonding interactions, i.e., electrostatic and/or van der Waals, rather than to dihedral interactions.

Finally, Table 2 includes the atomic charges (q_i) and the van der Waals parameters (R and ϵ) for NdMO molecule. It should be mentioned that the best agreement between quantum mechanical and classical calculations was obtained using the last parametrization of the Amber force field[22] for the van der Waals energy term.

The energy profiles for the rotation around the N−C(O) and C(O)−C(O) bonds were determined in order to test the precision of the force-field parameters reported in Table 2. The evolution of the force-field energy as a function of the dihedral angle ω_1 is displayed in Figure 5a. It is worth noting that the classical profile correctly reproduces those determined from quantum mechanical calculations. Thus, the *trans*-to-*cis* energy barrier predicted from force-field calculations is 18.9 kcal/mol, the difference with respect to the MP2/6-31G(d) value being only 0.1 kcal/mol. On the other hand, the stability of the *cis* conformation is overestimated by about 3 kcal/mol with respect to the quantum mechanical value. It should be mentioned that the description of the *cis* conformation, when required, can easily be improved by incorporating a torsional term V_1. However, in this case the profile as a whole, mainly at the barrier region, will get worse since this term was negligible in the PAPQMD fitting.

The energy profile determined for the rotation around the C(O)−C(O) bond is represented in Figure 5b. It corresponds to a profile with periodicity one and energy barrier of 17.2 kcal/mol. The comparison between the force-field and the MP2/6-31G(d) (Figure 3b) energy profiles indicates a good agreement, the root-mean-square deviation (rmsd) between the two profiles and the error associated to the energy barrier being of 2.9 kcal/mol and 8%, respectively. However, it should be mentioned that force-field calculations are not able to reproduce the plateau region found by quantum mechanical calculations. This could be attributed to the difficulties of classical methods for representing some electronic effects typical of quantum mechanical methods.

Table 3. Energy Contributions[a] (in kcal/mol) for the Most Representative Conformations Arising from the Rotational Profiles of ω_1 and ω_2 for *N,N′*-Dimethyloxalamide (NdMO)

ω_1/ω_2	E_{tot}	E_{ele}	E_{vdW}	E_{tor}
$\omega_1 = 180^b$	−26.1	−27.8	1.6	0.0
$\omega_1 = 90^b$	−7.2	−25.6	1.4	17.0
$\omega_1 = 0^b$	−16.3	−28.5	12.2	0.0
$\omega_2 = 180^c$	−20.0	−22.2	2.2	0.0
$\omega_2 = 90^c$	−13.3	−14.7	0.1	1.3
$\omega_2 = 0^c$	−2.8	−7.8	5.0	0.0

[a] The different energy terms refer to total energy (E_{tot}), electrostatic energy (E_{ele}), van der Waals energy (E_{vdW}), and torsional energy (E_{tor}). [b] A *trans* conformation was used as starting point for ω_2. [c] A *trans* conformation was used as starting point for ω_1.

Table 3 shows the energy contributions computed for the most representative conformations of the rotational profiles displayed in Figure 5. As can be seen, the van der Waals and torsional terms drive the conformational preferences of ω_1. Thus, the van der Waals contribution is 10.6 kcal/mol less stable for the *cis* conformation than for the *trans*, while the energy barrier mainly arises from the torsional contribution. On the other hand, electrostatic interactions are essential in the rotation around the C(O)−C(O) bond. The electrostatic contribution is less favorable for the conformation with $\omega_2 = 0°$ than for that with $\omega_2 = 180°$ by 14.4 kcal/mol. Thus, this term rapidly increases when the dihedral angle ω_2 decreases. On the other hand, the van der Waals contribution stabilizes the *trans* conformation with respect to the *cis* by only 2.8 kcal/mol, this value being about five times lower than that provided by the electrostatic term.

Structure of Polyoxalamides: Influence of the Number of Methylene. A number of X-ray studies on polyoxalamides derived from an even diamine has been reported along the last years.[10] Thus, powder patterns have been reported for nylons 10,2,[10a] 8,2,[10a] 6,2[10a] and 4,2,[10c] whereas fiber patterns have only been reported for nylons 6,2[10b] and 12,2.[10a] A fully extended conformation for the polymer chains has been proposed in all cases, with intermolecular hydrogen bonds set between neighboring molecular chains (Figure 6). This structure presents one hydrogen bonding direction and is similar to the characteristic α-form of nylons.[12] On the other hand, only one odd polyoxamide has been investigated.[11] This is nylon 9,2, which was studied using transmission electron microscopy, selected area electron diffraction, and X-ray diffraction. A structure with two hydrogen bonding directions, i.e. each molecule is hydrogen bonded to its four neighbors, was proposed for this polymer (Figure 7). In this structure the molecular chains are slightly contracted with respect to the all-*trans* conformation. Thus, the torsional angles associated to the NH−CH$_2$ bonds deviate 25° from the *trans* conformation in

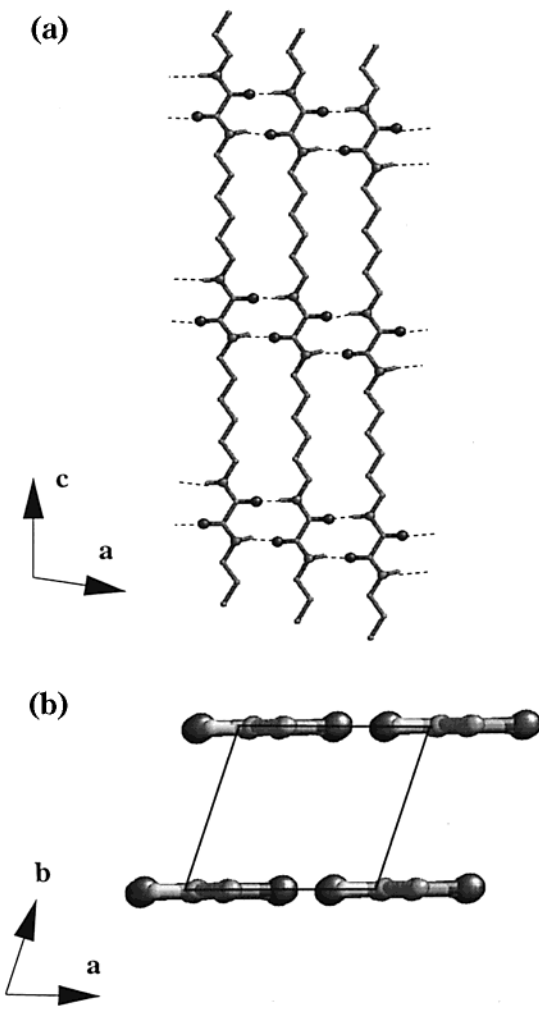


Figure 6. Crystal structure for even polyoxamides (nylons even,2). (a) Hydrogen bonded sheet for nylon 6,2. Dashed lines indicate the N−H···O hydrogen bonds that are formed when the adjacent chains are shifted. (b) Nylon 6,2 unit cell (a = 5.15 Å, b = 7.54 Å, c-fiber axis = 12.39 Å, $\alpha = 32.4°$, $\beta = 73.5°$, and $\gamma = 61.9°$) projected down the c axis.

order to optimize the hydrogen bonds with the neighboring chains.

It is worth noting that the extended conformation found in even polyoxalamides should not be favored for odd polyoxalamides because of hydrogen bonds cannot be well established (Figure 8a). Thus, in odd polyoxalamides with extended conformation only 50% of hydrogen bonds can be formed with neighboring chains because of the opposite relative orientation of consecutive oxalamide groups along the polymer chain. A similar situation appears when the contracted conformation proposed for nylon 9,2 is considered for even polyoxalamides (Figure 8b). However, no energy analysis about the stability of the structures proposed for even and odd polyoxalamides as well as about the influence of the methylene segment on such stability has been reported.

The energy of the structures with one- and two-hydrogen bonding directions proposed for even and odd polyoxalamides, respectively, has been computed using the PCSP computer program. Calculations have been performed for polymers with n methylene groups in the aliphatic segment (nylons n,2), where n ranges from 4 to 11. The cell dimensions used to built the crystal lattices were taken from nylon 6,2[10b] [$a_o = 5.15$ Å, $b_o = 7.54$ Å, $\alpha = 32.4°$, $\beta = 73.5°$ and $\gamma = 61.9°$] and nylon 9,2[11] [a_o = 5.45 Å, b_o = 8.70 Å, $\alpha = \gamma = 90°$ and $\beta = 47.9°$], the fiber period c_o depending on the number methylene groups. According to Franco et al.,[11] the conformation for the structure with two hydrogen bonding directions was built by considering the following criteria based on a $2/c$ molecular symmetry: (i) the torsional angles φ_1 and φ_2 (Figure 9) are equal to 155° ($\varphi_1 = \varphi_2 = 155°$) while the remaining torsional angles are equal to 180°, and (ii) the equivalent torsional angles of consecutive repeat units are equal but with opposite sign. Note that the small deviations of φ_1 and φ_2 with respect to the *trans* conformation (180°) result in a significant rotation (about 45°) of the oxalamide planar groups with respecto to the plane defined by the methylene segment (Figure 7). Molecular conformations were kept fixed during the calculations.

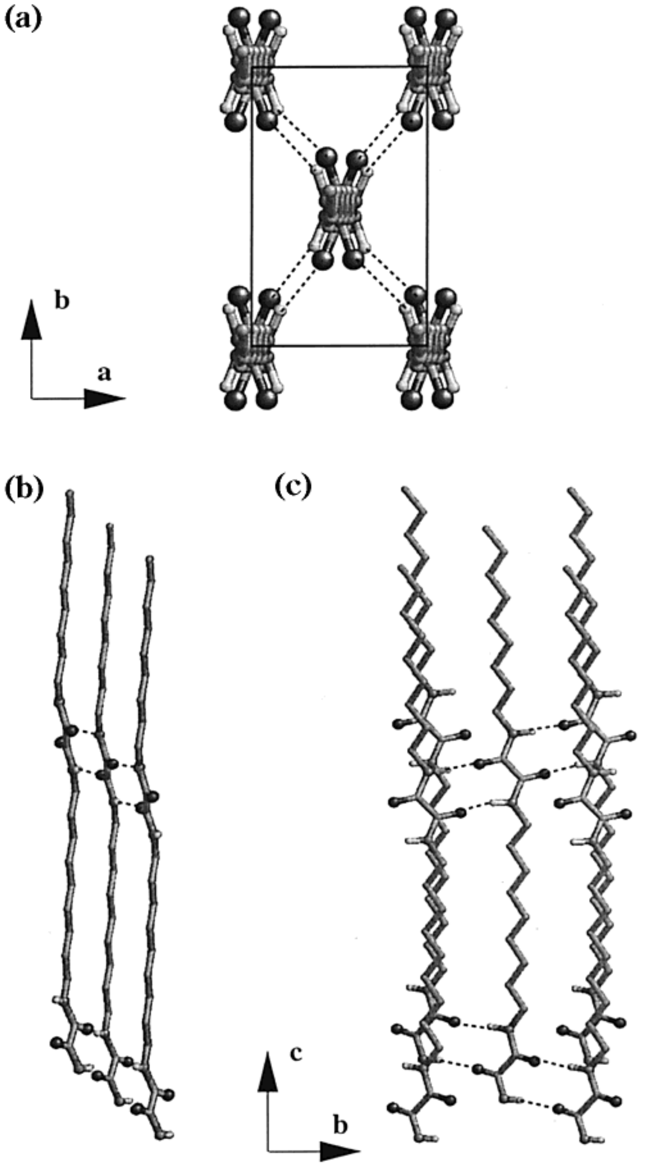


Figure 7. Crystal structure for odd polyoxalamides (nylons odd,2). (a) Nylon 9,2 unit cell (a = 5.45 Å, b = 8.7 Å, c-fiber axis = 31.8 Å and $\beta = 47.9°$) projected down the c axis. It is worth noting that hydrogen bonds (dashed lines) are established along the two diagonals of the unit cell. (b) view along the b axis. (c) bc projection of the unit cell.

Force-field calculations of nylons n,2 were performed using the torsional and van der Waals parameters

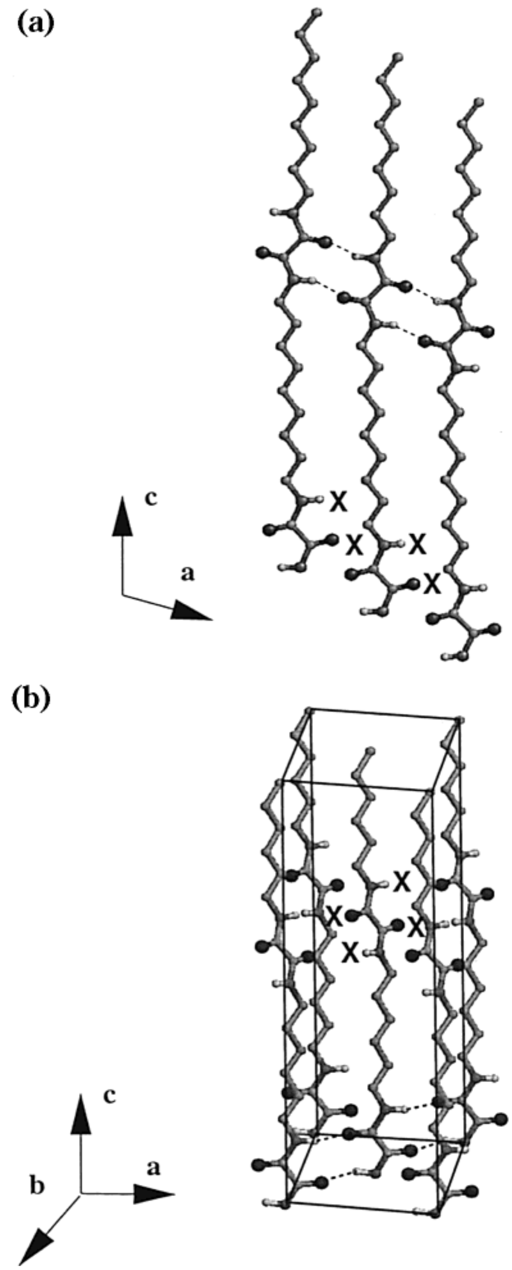


Figure 8. (a) Nylon 9,2 with the extended conformation proposed for even polyoxalamides. (b) Nylon 6,2 with the contracted conformation proposed for odd polyoxalamides. In both cases only 50% of hydrogen bonds (dashed lines) can be established between neighboring chains. The crosses indicate the positions that are not able to form the hydrogen bonds.

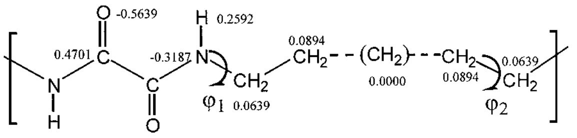


Figure 9. Torsional angles and atomic charges for polyoxalamides.

displayed in Table 2 for the oxalamide moiety. For computational efficiency reasons, the aliphatic segment was represented using a united atom approach for the CH_2 groups. van der Waals parameters for the CH_2 pseudoatom were taken from the united atom parametrization of the Amber force field ($R = 1.924$ Å and $\epsilon = 0.12$ kcal/mol).[24] Partial atomic charges were computed for the chemical repetitive unit of nylons n,2 with n ranging from 4 to 11. The results suggested a unique set of electrostatic parameters for all these compounds, which is displayed in Figure 9.

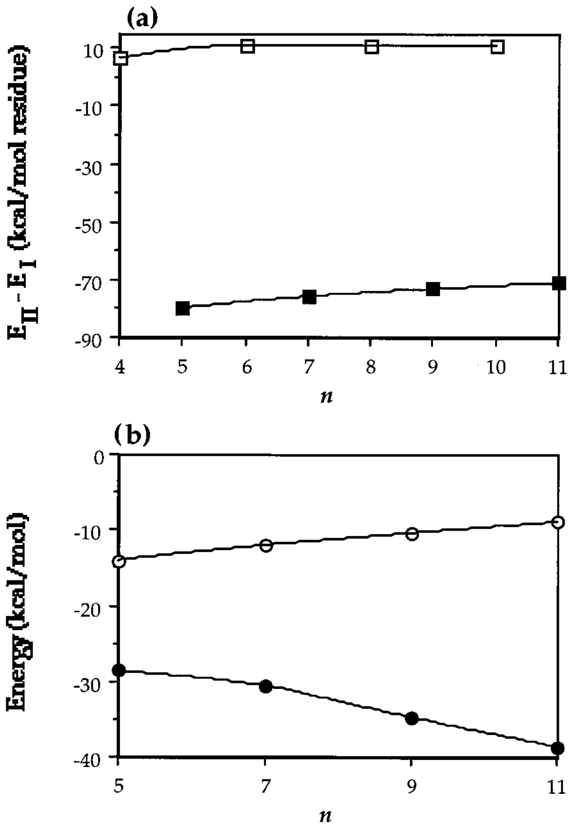


Figure 10. (a) Variation of the relative energy between the two- (E_{II}) and one-directions (E_I) structures versus the number of methylene groups for even (white square) and odd (black square) polyoxamides. (b) Variation of the electrostatic (white circle) and van der Waals (black circle) contributions for the structure with two hydrogen bonding directions of odd polyoxalamides.

Energy results are shown in Figure 10, where the energy difference between the structures with one and two hydrogen bonding directions is represented. As it can be seen the structure with hydrogen bonds along a single direction is the most stable for all the even polyoxalamides. The energy difference between the two structures increases from 6.5 to 11.0 kcal/mol·residue when the number of methylene groups increases from 4 to 6. As can be seen in Table 4, which shows the energy contributions obtained for the two structures of nylons 4,2 and 6,2, this extra stabilization is mainly due to the electrostatic contribution. Thus, the electrostatic interactions, which favor the structure with a single hydrogen bonding direction in all cases, are more attractive in nylon 6,2 than in nylon 4,2. On the other hand, for nylons 8,2 and 10,2 the energy difference is about 11 kcal/mol·residue, similar to that of nylon 6,2. Furthermore, no significant trend was found in the relative energy contributions of nylons n,2 with $n > 6$ with respect to those of nylon 6,2.

It should be mentioned that for all the systems investigated the cell parameters, with exception of the fiber period c, of the of the one- and two-direction structures were kept fixed at the values experimentally measured for nylon 6,2 and 9,2, respectively. The fiber period depends on the size of the aliphatic segment and

Table 4. Energy Contributions[a] (in kcal/mol·residue) Obtained from the PCSP Calculations for the Structures with One and Two Hydrogen Bonding Directions of Nylons 4,2 and 6,2

	structure	E_{tot}	E_{intra}	E_{el}	E_{vdW}
nylon 4,2	one-direction	−49.5	−18.2	−15.3	−16.0
	two-directions	−43.0	−19.3	−3.3	−20.4
nylon 6,2	one-direction	−58.1	−19.0	−18.5	−20.5
	two-directions	−47.1	−20.5	−2.4	−24.2
nylon 8,2	one-direction	−61.9	−18.9	−18.5	−24.4
	two-directions	−50.7	−20.3	−2.3	−28.1
nylon 10,2	one-direction	−65.0	−18.7	−18.3	−28.1
	two-directions	−53.5	−20.0	−2.1	−31.3

[a] The different energy terms refer to one residue, where E_{tot} = total energy, E_{intra} = intraresidue energy, E_{el} = interresidue electrostatic energy, and E_{vdW} = interresidue van der Waals energy.

Table 5. Energy Contributions[a] (in kcal/mol·residue) Obtained from the PCSP Calculations for the Structures with One and Two Hydrogen Bonding Directions of Nylons 5,2 and 11,2

	structure	E_{tot}	E_{intra}	E_{el}	E_{vdW}
nylon 5,2	one-direction	10.2	−20.6	12.9	17.7
	two-directions	−65.4	−22.8	−14.0	−28.6
nylon 7,2	one-direction	8.1	−21.7	1.8	19.0
	two-directions	−65.1	−22.4	−12.2	−30.5
nylon 9,2	one-direction	5.6	−22.4	1.2	21.9
	two-directions	−67.5	−22.4	−10.4	−34.7
nylon 11,2	one-direction	0.8	−22.3	1.2	22.0
	two-directions	−70.2	−22.6	−8.9	−38.6

[a] The different energy terms refer to one residue, where E_{tot} = total energy, E_{intra} = intraresidue energy, E_{el} = interresidue electrostatic energy, and E_{vdW} = interresidue van der Waals energy.

the conformation, being therefore different in each case. However, this parameters was neither allowed to vary during PCSP calculations. Thus, it should be noted that our aim is to compare the stability of two well-known structures, i.e., the structures with one and two hydrogen bonding directions, and not investigate the distortions that the repulsive interactions induce in the less favored structure. To check the sensitivity of our energy calculations to small variations in the dimensions of the lattice, we carried out complementary calculations considering a variation of ±0.1 Å in the cell parameters, which is the widest margin of error experimentally acceptable. The resulting plots (data not shown) are similar to those displayed in Figure 10a, indicating that the relative stability for the different models is not qualitatively affected.

A detailed analysis of the different energy contributions listed in Table 4 allows to explain the structural preferences of nylons even,2. The intraresidue energy term, which accounts for the nonbonding interactions (electrostatic and van der Waals) between atoms of the same residue, is predicted to be more stable for the structure with two hydrogen bonding directions than for the structure with a single hydrogen bonding direction. Thus, the contracted conformation of the former is favored by about 1.1−1.5 kcal/mol·residue with respect to the fully extended conformation of the latter. On the other hand, data of Table 4 reveals how much more favorable is the electrostatic term for the structure with a single hydrogen bonding direction (about 11.9−16.2 kcal/mol·residue). This is due to the unfavorable geometry of the structure with two hydrogen bonding directions (Figure 8b), which provides a strong repulsive contribution rather than an attractive one. Finally, van der Waals energies are invariably lower for the structure with two hydrogen bonding directions (about 3.2−4.4 kcal/mol·residue). However, such stabilization is not enough to counterbalance the unfavorable hydrogen bonding geometry.

Inspection to the results obtained for odd polyoxamides indicates that the structure with two hydrogen bonding directions is much more favored (about 70−80 kcal/mol·residue) that the structure with a single hydrogen bonding direction. Thus, in all cases the latter structure presents a strong repulsive van der Waals and electrostatic contributions because the carbonyl groups are confronted (Figure 8a). This is clearly reflected in Table 5, which shows the energy contributions obtained for the two structures of nylons odd,2. Pilot calculations allowing the variation of dihedral angles were performed for these polymers assuming the structure with a single hydrogen bonding direction. An evolution toward unreliable nonperiodic structures was obtained as a result of the minimization of the unfavorable interactions.

On the other hand, the variation of the electrostatic and van der Waals contributions versus the number of methylene groups for the structure with two hydrogen bonding directions of nylons odd,2 is displayed in Figure 10b. It is worth noting that the van der Waals term becomes more stable when the number of methylene groups increases. This feature reveals that the indicated structure not only allows the formation of all the hydrogen bonds between oxalamide groups but also an efficient packing of the methylene groups is achieved. Thus, in this structure the relationship between the methylene units belonging to the nearest chains along the *a* axis is closer to an eclipsed (uncrossed) arrangement than to an alternated (crossed) one, the former situation being the most favorable for nonorthogonal systems.[28a] On the other hand, the electrostatic contribution increases when the distance between the oxalamide groups of two consecutive chemical repeating units belonging to different chains increases.

To improve our knowledge about the structure with two hydrogen bonding directions of odd polyoxalamides, a MC simulation of an infinite crystal of nylon 9,2 was performed for 2.1 × 10^6 steps using as starting geometry the structure proposed by Franco et al.[11] (Figure 7). The box used in the simulation consists of seven explicit chains of two residues, the dimensions being $a = 2a_o$, $b = 2b_o$, and $c = 2c_o$, where a_o, b_o, and c_o are the unit cell dimensions for nylon 92. The degrees of freedom in the simulation were the setting angle and the length of the *a* and *b* edges of the simulation box. The backbone dihedral angles were kept fixed at the values previously described, which is consistent with experimental data, i.e., the unit repeat length and the angle between the oxalamide planar groups and the plane defined by the aliphatic segment. Three-dimensional periodic boundary conditions were applied.

Inspection of the energy as function of the number of MC steps indicates that the system was equilibrated after as few as 1 × 10^4 steps (data not shown). Figure 11a shows the evolution of the setting angle as a function of the number of steps for the last 2 × 10^6 steps. As can be seen, the setting angle is about −58° during all the simulation, this value being very close to the starting one (−60°). This means that the intermolecular hydrogen bonds remain formed during the simulation, no disrup-

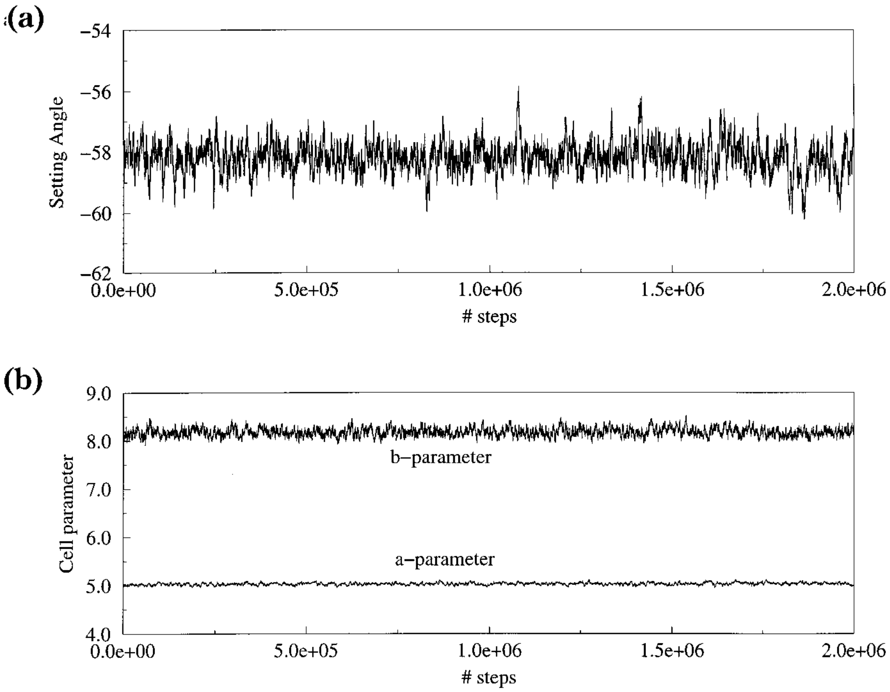


Figure 11. Setting angle (a) and cell parameters (b) of nylon 9,2 as a function of the number of steps.

tion being observed. This result points out that the model with two hydrogen bonding directions is a very stable structure. It should be mentioned that a recent study of nylon 46 lamellar crystals using molecular dynamics simulations indicated that in conventional structures the hydrogen bonds are frequently disrupted and formed again.[28b]

Figure 11b presents the values of the cell parameters a_o and b_o obtained from the MC simulation. It is worth noting that the converged values ($a_o = 5.01$ Å and $b_o = 8.23$ Å) are shorter than the experimental data ($a_o = 5.45$ Å, $b_o = 8.70$ Å). However, the agreement with experimental data is good and indicates that the simulation indeed captures the most essential trends of the structure of odd polyoxalamides. The Amber force field is at least partially responsible of the deviation between theoretical and experimental values; the van der Waals parameters used to describe the methylene groups probably allow an excessive approximation between the neighbor chains.

Conclusions

We investigated in detail several aspects of the oxalamide group. First, we studied the isomerization process of the oxalamide group in NdMO by using ab initio calculations at the MP2/6-31G(d) level. After this a set of force-field parameters able to reproduce with reasonable accuracy quantum mechanical data of NdMO was developed. The parameters developed for simple compounds containing one oxalamide group have been extended to polyoxalamides, and predictions have been made. Among these the most stricking may be the effect of the number of methylene groups in the relative stability of the structures with one and two hydrogen bonding directions proposed for polyoxalamides.

Acknowledgment. Authors are indebted to Dr. Glenford Wrigth for grammatical assistance and to the Centre de Supercomputació de Catalunya (CESCA) for computational facilities. This research has been supported by a grant from CICYT (MAT2000-0995).

Supporting Information Available: Atomic coordinates of the minimum energy conformations and the most relevant structures of the rotational profiles of NdMO obtained at the MP2/6-31G(d) level. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010042L