

# Theoretical Investigations on the Structure of Poly(iminomethylenes) with Aliphatic Side Chains. Conformational Studies and Comparison with Experimental Spectroscopic Data

M. Clericuzio,<sup>\*,†,‡</sup> G. Alagona,<sup>\*,§</sup> C. Ghio,<sup>§</sup> and P. Salvadori<sup>||</sup>

Contribution from CNR, Istituto di Chimica Quantistica ed Energetica Molecolare, Via Risorgimento 35, I-56126 Pisa, Italy, Scuola Normale Superiore, P.zza dei Cavalieri 7, I-56126 Pisa, Italy, and Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

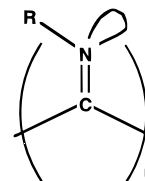
Received May 20, 1996. Revised Manuscript Received October 1, 1996<sup>⊗</sup>

**Abstract:** The ground state energies and structures of octamers of poly(methyl)iminomethylene are investigated ab initio at the 6-31G\* SCF and MP2 levels and compared with those produced by molecular mechanics (MM), using Allinger's MM3 force field. The torsional parameters used in MM3 calculations for the dihedral angle N=C=C=N ( $\phi$ ) have been obtained from ab initio calculations of model diimines ((E,E), (E,Z), and (Z,Z) N,N'-diisopropylethanedimine), in the flexible rotor approximation. At the MM level, bulkier substituents have been considered as well (R = isopropyl, 1-cyclohexylethyl). Both at the ab initio and classical level, conformations close to a  $4_1$  helix are found to be stable, but they never are the absolute minimum. The minimum energy geometry shows a regularly alternating disposition of the substituents on the iminic double bonds (syndio configuration): its backbone conformation (dihedral angles  $\phi$ ) shows dimeric sections which are alternatively trans-planar (E,E sections) and close to  $\pm 90^\circ$  (Z,Z sections). The energy gap between the syndio geometry and the  $4_1$  helix amounts to  $\sim 30$  kcal/mol in the methyl oligomer at the ab initio level vs  $\sim 11$  kcal/mol at the MM3 level. This latter value does not change significantly passing from methyl to isopropyl and 1-cyclohexylethyl. Also, conformations having an inversion of the helical sense along the chain (wormlike chains) are found to be stable according to both calculation methods, and their energies are comparable to those of helical conformers. CD calculations were carried out employing an independent systems approach. The calculated intensities of the CD bands of a model  $4_1$  helix are much higher than what experimentally found, while those calculated for the syndio structure (considered as composed of a series of diiminic units) are comparable to experiment. A negative CD band is predicted to be associated with the  $n-\pi^*$  transition of the iminic chromophore in a  $4_1$  P-helix, as previously found in the literature. The preference for nonhelical conformers could account for various features observed in the UV, CD, and NMR spectra of some poly(iminomethylenes), as reported in literature (absorption at long wavelengths, low intensity of CD bands, chemical shift dispersion of backbone carbons resonances).

## Introduction

Poly(iminomethylenes) (PIM), also named polyisocyanides, are a class of synthetic polymers which has received considerable attention in the recent past. They contain the repeating unit shown in Scheme 1 and are prepared from the corresponding isocyanides mostly by cationic polymerization<sup>1–3</sup> (both protonic and Lewis acids have been used as initiators), or by coordination polymerization employing transition metal compounds, in particular those of Ni(II).<sup>1,4,5</sup> Several PIM bearing

## Scheme 1



different side chains (R) have been synthesized to date (for reviews of synthetic methods see refs 6–9). They have shown some practical use, for instance in nonlinear optical materials<sup>10,11</sup> or as chiral stationary phases in liquid chromatography.<sup>12</sup> Aside from their utilization, their conformational properties are still under debate. In particular it is unclear if there is a secondary

<sup>†</sup> Scuola Normale Superiore.  
<sup>‡</sup> Present address: Dept. of Organic Chemistry 2, Chemical Center, P.O. Box 124, S-22100 Lund (Sweden).  
<sup>§</sup> Istituto di Chimica Quantistica ed Energetica Molecolare.  
<sup>||</sup> Università di Pisa.  
<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1996.  
 (1) Yamamoto, Y.; Takizawa, T.; Hagihara, N. *Nippon Kagaku Zasshi* **1966**, 87, 1355.  
 (2) Saegusa, T.; Taka-Ishi, N.; Ito, Y. *J. Org. Chem.* **1969**, 34, 4040.  
 (3) Millich, F.; Sinclair, R. G., II *J. Polym. Sci., A-1* **1968**, 6, 1417. *Ibid.* Part C **13**, 2150. *J. Polym. Sci., C* **1968**, 22, 33.  
 (4) Nolte, R. J. M.; Stephany, R. W.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1973**, 92, 83. Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1973**, 92, 788.  
 (5) Nolte, R. J. M.; Zwikker, J. W.; Reedijk, J.; Drenth, W. *J. Mol. Catal.* **1978**, 4, 423. Van Beijnen, A. J. M.; Nolte, R. J. M.; Zwikker, J. W.; Drenth, W. *J. Mol. Catal.* **1978**, 4, 427.  
 (6) Millich, F. *Chem. Rev.* **1972**, 72, 101.

(7) Millich, F. *Adv. Polym. Sci.* **1975**, 19, 117.  
 (8) Millich, F. *Macromol. Rev.* **1980**, 15, 207.  
 (9) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, 12, 30.  
 (10) Teerenstra, M. N.; Hagting, J. G.; Oostergetel, G. T.; Schouten, A. J.; Devillers, M. A. C.; Nolte, R. J. M. *Thin Solid Films* **1994**, 248, 110.  
 (11) Kauranen, M.; Verbiest, T.; Meijer, E. W.; Havinga, E. E.; Teerenstra, M. N.; Schouten, A. J.; Nolte, R. J. M.; Persoons, A. *Adv. Mater.* **1995**, 7, 641. Kauranen, M.; Verbiest, T.; Boutton, C.; Teerenstra, M. N.; Clays, K.; Schouten, A. J.; Nolte, R. J. M.; Persoons, A. *Science* **1995**, 270, 966.  
 (12) Yamagishi, A.; Tanaka, I.; Taniguchi, M.; Takahashi, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1113.

structure common to all of them (independent of R) and if this leads to well defined helical conformations.

Poly( $\alpha$ -phenylethyl)iminomethylene was one of the first polymers of this class thoroughly investigated by the school of F. Millich.<sup>3,13,14</sup> On the basis of the examination of space-filling molecular models, the authors proposed that a rational structure of the above polymer could be a tightly coiled helix.<sup>14</sup> Actually, after a series of experimental observations, it was concluded that the secondary structure of that polymer was a  $4_1$  helix, with approximately four residues per turn and a pitch of  $\sim 4.2 \text{ \AA}$ .<sup>7,15</sup> The  $4_1$  helical structure has often been attributed to all poly(iminomethylenes).<sup>16–18</sup> However, lately, experimental evidence for the occurrence of stereo irregularity in the chain of some PIM was reported, as for instance, in poly(*S*)-2,2-dimethyl-1,3-dioxolanyl-4-methyl isocyanide,<sup>19</sup> and in poly(*S*)-1-cyclohexylethyl isocyanide.<sup>20</sup> This was verified both by <sup>13</sup>C NMR in solution and by circular dichroism (CD).

Theoretical calculations on the conformational properties of PIM have been rather scant to date. Huige<sup>21</sup> carried out molecular mechanics calculations of oligoiminomethylenes with various side chains, both aliphatic and aromatic. The author obtained a complete set of force field parameters for the previously neglected iminic functional group. These parameters were obtained from the experimental conformations of a set of model imines and oximes, mostly taken from microwave spectroscopy. The initial data were then fit to the observed vibrational frequencies, in order to obtain an optimized set of parameters for the iminic function.

Also ab initio calculations on model diimines were performed, and the single crystal X-ray structure of *N,N'*-di-*tert*-butyl-ethanediimine at 98 K was solved.<sup>22</sup>

Molecular mechanics calculations were carried out using a program named CFF which exploits the PEF400 force field, developed by the Utrecht Theoretical Group.<sup>23</sup> The results obtained for some aliphatic side chains, in particular *tert*-butyl, seemed to confirm the existence of low energy conformers having rather regular helical conformations, not far from the  $4_1$  helix. These helical conformations appeared to be as the lowest energy ones: nonhelical conformations were found to be higher in energy.

Hoffmann et al.<sup>24</sup> calculated the conformational energy of segments of polyiminomethylenic chains with R = H, CH<sub>3</sub>, *tert*-butyl, using an extended Hückel approach. Interestingly enough, even the all-hydrogen chain does not assume a planar trans conformation, but rather a helical one. An extended trans-planar arrangement is destabilized by the presence of N–N repulsive interactions, mainly due to nitrogen lone pairs. This repulsion (which overrides the conjugation energy) occurs between couples of N atoms which are second nearest neighbor in the chain: it means that such interactions arise when at least three

units are in planar (all-trans) arrangement. This feature will turn out to be important in the light of our results. Anyway, Hoffmann remarks that when substituents bulkier than hydrogen atoms are present, then the driving force to helix formation comes largely from steric reasons.

In the present paper ab initio calculations at the 6-31G\*/SCF and MP2 levels on octamers of poly(methyl)iminomethylene are reported. We believe that eight residues can be a representative segment of polymer, bearing in mind that it would correspond to two turns of the hypothetical  $4_1$  helix.

Moreover octamers of iminomethylenes with larger side chains, viz. isopropyl (*i*-pro) and 1-cyclohexylethyl, are investigated with molecular mechanics calculations, using Allinger's MM3 force field. The parameters for the iminic group are those derived by Huige,<sup>21</sup> but a few of them, of crucial importance, have been obtained by fitting our ab initio results.

With the set of low energy conformers obtained from ab initio and MM3 calculations, we could tentatively explain some features observed in the UV–vis, CD, and <sup>13</sup>C NMR spectra. A theoretical CD calculation, using the approximate independent systems approach, was performed in order to find out the sign of the CD bands of poly(iminomethylenes) in the  $4_1$  conformation, having a definite helical sense (either P or M), and to compare it with experiment.

## Materials and Methods

Ab initio calculations were carried out at the 6-31G\* SCF and MP2 levels making use of Gaussian92<sup>25</sup> on the IBM-RS6000-590 workstations at ICQEM and on the DEC-alpha 2100 at the CNUCE Computing Centre. Full geometry optimizations in vacuo for five different starting structures of the octamers were performed: helical all iso-oriented; helical all iso-oriented but the last unit; no-helical all iso-oriented; no-helical all iso-oriented but the last unit; alternating "up and down" structure. On these optimized structures single point MP2 calculations (about 50 h of CPU time each) have been carried out to evaluate the effect of electron correlation. Additional calculations were carried out on a few dimers in order to study the torsional behavior about the N=C–C=N and the H–C–N=C bonds. Reference to these calculations will be done where appropriate, and their results will be described more extensively when necessary.

Molecular mechanics calculations have been performed using Allinger's MM3(89)<sup>26</sup> force field; initial geometries were prepared with the interactive program PCMODEL.<sup>27</sup> The force field parameters of the iminic functional group are taken from ref 21, except the N=C–C=N and the C=N–C–H torsional ones, which have been derived from our ab initio calculations. The other parameters are those standard of the MM3 force field.

The electrostatic term was calculated according to the dipole–dipole formalism, giving a value of 1.1 D to the dipole moment of the N-substituted iminic function, in order to satisfactorily reproduce the permanent dipole moment (1.50 D) observed in *N*-methylethylideneimine by microwave spectroscopy.<sup>28</sup> The dielectric constant was set at 2.0. The  $\pi$  atom routine was used throughout our MM3 calculations, at least to scale the  $V_2$  torsional constants. The dihedral drive option was employed in order to obtain potential energy surfaces in the MM framework (used in the derivation of torsional parameters). Convergence limits were set at a value 10 times lower than the default one.

(25) *Gaussian 92/DFT, Revision G.2*, Frish, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian Inc., Pittsburgh, PA, 1993.

(26) MM3(89), Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.

(27) PCMODEL (Version 2.0), program of Gilbert, K. E., Gajewski, J. J., available from Serena Software, Bloomington, IN.

(28) Meier, J.; Bauder, A.; Gunthard, Hs. H. *J. Chem. Phys.* **1972**, *57*, 1219.

(13) Millich, F.; Sinclair, R. G., II. *Polym. Prepr.* **1965**, *6*, 736.

(14) Millich, F.; Baker, G. K. *Macromolecules* **1969**, *2*, 122.

(15) Huang, S. Y.; Hellmuth, E. W. *Polym. Prepr.* **1974**, *15*, 499.

(16) Van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679.

(17) Harada, T.; Cleij, M. C.; Nolte, R. J. M.; Hezemans, A. M. F.; Drenth, W. *J. Chem. Soc., Chem. Commun.* **1984**, 726.

(18) King, R. B.; Greene, M. J. *J. Polym. Sci. (Polym. Chem.)* **1987**, *25*, 907.

(19) Green, M. M.; Gross, R. A.; Schilling, F.; Zero, K.; Crosby, C., III. *Macromolecules* **1988**, *21*, 1839.

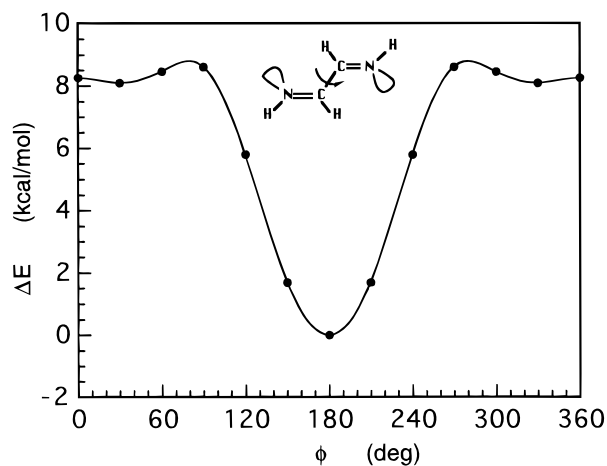
(20) Pini, D.; Iuliano, A.; Salvadori, P. *Macromolecules* **1992**, *25*, 6059.

(21) Huige, C. J. M. *Determination of the conformations of some poly(iminomethylenes) by means of Molecular Mechanics and Circular Dichroism*; Ph.D. thesis, University of Utrecht, The Netherlands, 1985.

(22) Huige, C. J. M.; Spek, A. L.; De Boer, J. L. *Acta Crystallogr.* **1985**, *C41*, 113.

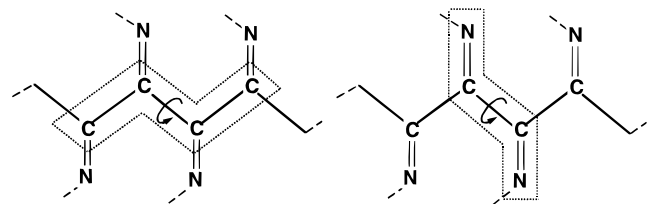
(23) Melberg, S.; Rasmussen, K. *J. Mol. Struct.* **1979**, *57*, 215.

(24) Kollmar, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230.



**Figure 1.** Potential energy profile for the rotation about the C–C bond (angle  $\phi$ ) in (*E,E*)-ethanediimine, as calculated ab initio (SCF/6-31G\* level) in the flexible rotor approximation. The  $\phi = 180^\circ$  (trans) conformer is displayed in the figure.

#### Scheme 2



As far as the CD calculations are concerned, details of the De Voe theory, and of its application to organic molecules, can be found in previous papers.<sup>29–31</sup> About theory and applications of the dynamical ( $\mu$ - $m$ ) method, see refs 32 and 33. For the position of transition charges we followed ref 34: the data of the C=O chromophore were applied to the similar C=N functional group.

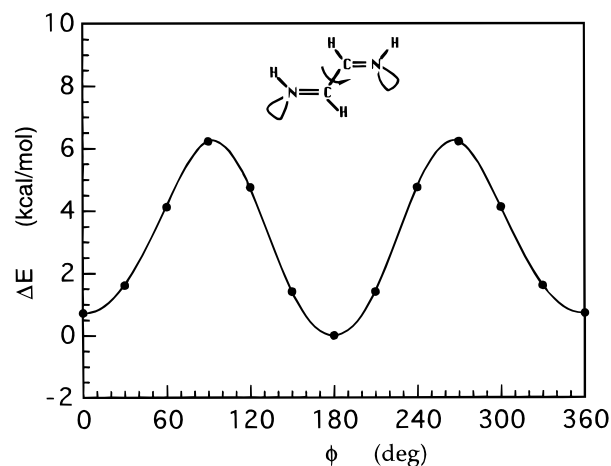
## Results and Discussion

### 1. Geometrical Features of PIM and of Model Diimines.

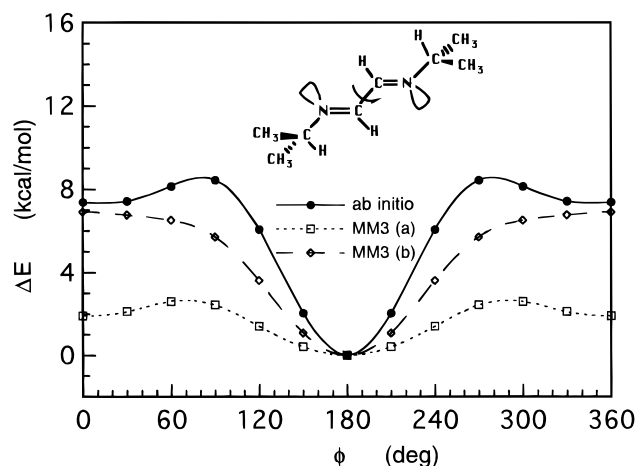
**i.** The backbone conformation is equivalently described either by the dihedral angle C–C–C–C or N=C–C=N (angle  $\phi$ ), as shown in Scheme 2, the central bond being the same in both cases. The latter representation has the advantage to express the angle between iminic moieties and thus is the degree of conjugation among them. Only if this angle is  $90^\circ$  is no conjugation possible, while conjugation increases as this angle tends either to  $0^\circ$  or to  $180^\circ$ . This is important when comparing theoretical structures to the experimental data obtained from optical spectroscopies, which are very sensitive to electronic conjugation among chromophores.

In order to shed some light on the preferred conformations of PIM, we have calculated ab initio the potential energy for rotation around the diiminic central bond  $\phi$  in five model diimines.

The results obtained for (*E,E*)-ethanediimine (Figure 1) show a large energy difference between the cis and trans rotamers ( $\sim 8.3$  kcal/mol), which are separated by a barrier of  $\sim 8.7$  kcal/mol, at  $90^\circ$ , while a shallow secondary minimum ( $\sim 0.6$  kcal/mol deep) occurs about  $\sim 30^\circ$ . The strong destabilization



**Figure 2.** Potential energy profile for the rotation about the C–C bond in (*E,Z*)-ethanediimine, as calculated ab initio (SCF/6-31G\* level) in the flexible rotor approximation. The trans conformer is displayed.



**Figure 3.** Potential energy profiles for the rotation about the C–C bond in (*E,E*)-*N,N'*-diisopropylethanediimine in the flexible rotor approximation. ab initio: SCF/6-31G\* calculations. MM3 (a): in the absence of the torsional term. MM3 (b): with the torsional term  $V_1 = 4.5$ ,  $V_2 = 4.0$ ,  $V_3 = 0.5$  kcal/mol. The trans conformer is displayed.

observed for the *s-cis* form is generally ascribed to the repulsion between nitrogen lone pairs.<sup>35</sup> This potential energy profile was calculated ab initio by Huige<sup>21</sup> using a minimal basis set, in the rigid rotor approximation. Huige found a slightly lower *cis*–*trans* energy gap ( $\sim 7.5$  kcal/mol) and a secondary gauche minimum near  $60^\circ$ ,  $\sim 1.2$  kcal/mol deep. In contrast to the author's opinion, the use of a larger basis set (passing from his minimal to our extended basis set with polarization functions added (6-31G\*)) increases the *cis*–*trans* energy barrier.

In the corresponding (*E,Z*) stereoisomer (Figure 2) the rotational barrier (at  $90^\circ$ ) is just slightly lower ( $\sim 6.3$  kcal/mol), but the *cis*–*trans* difference drops to a mere  $\sim 0.7$  kcal/mol, because the nitrogen lone pairs are far from each other even in the *s-cis* conformer.

The potential energy profile for (*E,E*)-*N,N'*-diisopropylethanediimine (reported in Figure 3) does not change much if compared to its hydrogen equivalent (Figure 1): the *cis*–*trans* gap is  $\sim 7.4$  kcal/mol, the barrier at  $90^\circ$  is  $\sim 8.5$  kcal/mol, while the secondary minimum is slightly deeper ( $\sim 1.1$  kcal/mol) and closer to  $\sim 0^\circ$ .

(29) De Voe, H. *J. Chem. Phys.* **1964**, *41*, 393. *Ibid.* **1965**, *43*, 3199.

(30) Hug, W.; Ciardelli, F.; Tinoco, I., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3407.

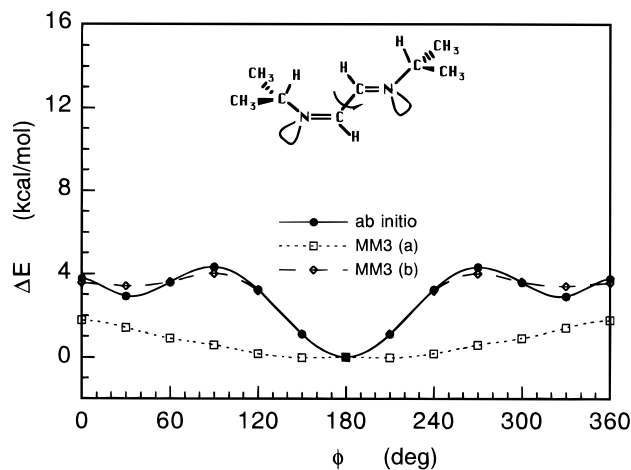
(31) Rosini, C.; Zandomenighi, M.; Salvadori, P. *Tetrahedron Asymm.* **1993**, *4*, 545.

(32) Tinoco, I., Jr. *Adv. Chem. Phys.* **1962**, *4*, 113.

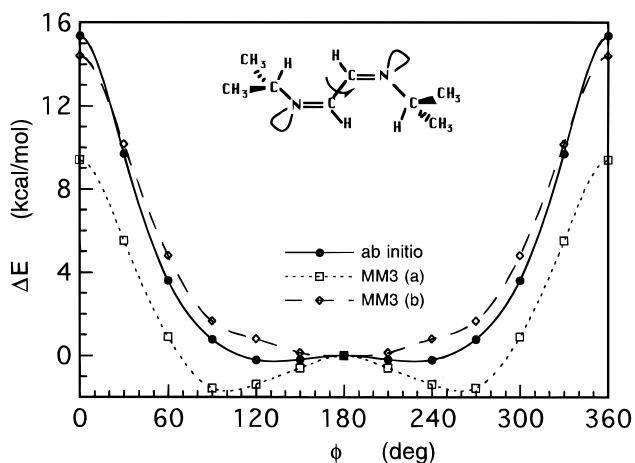
(33) Schellman, J. A.; Nielsen, E. B. *J. Phys. Chem.* **1967**, *71*, 3914.

(34) Texter, J.; Stevens, E. S. *J. Chem. Phys.* **1978**, *69*, 1680.

(35) Benedix, R.; Birner, P.; Birnstock, F.; Hennig, H.; Hofmann, H. *J. Mol. Struct.* **1979**, *51*, 99. The authors apply an NDDO semiempirical MO-SCF method to (*E,E*)-ethanediimine and demonstrate that inclusion of the directed interaction of N lone pairs is essential to have a correct *cis*/*trans* energy separation.



**Figure 4.** Potential energy profiles for the rotation about the C–C bond in (*E,Z*)-*N,N'*-diisopropylethanediiimine in the flexible rotor approximation. ab initio: SCF/6-31G\* calculations. MM3 (a): in the absence of the torsional term. MM3 (b): with the torsional term  $V_1 = 1.0$ ,  $V_2 = 14.0$ ,  $V_3 = 0.8$  kcal/mol. The trans conformer is displayed.



**Figure 5.** Potential energy profiles for the rotation about the C–C bond in (*Z,Z*)-*N,N'*-diisopropylethanediiimine in the flexible rotor approximation. ab initio: SCF/6-31G\* calculations. MM3 (a): in the absence of the torsional term. MM3 (b): with the torsional term  $V_1 = 4.5$ ,  $V_2 = 4.0$ ,  $V_3 = 0.5$  kcal/mol. The trans conformer is displayed.

On the other hand, the (*E,Z*) *i*-pro substituted isomer (Figure 4) differs significantly from the (*E,Z*) hydrogen substituted one. The cis–trans separation is  $\sim 3.7$  kcal/mol, the barrier at  $90^\circ$  is 4.5 kcal/mol, and a secondary minimum  $\sim 1.4$  kcal/mol deep appears at  $\sim 30^\circ$ . It is likely that the bulkier isopropyl tends to destabilize the *s*-cis form for steric reasons.

In the (*Z,Z*) isopropyl dimer (Figure 5) a shallow minimum exists between  $90^\circ$  and  $180^\circ$  (the absolute minimum is at  $\sim 120^\circ$ ). A severe steric hindrance in the *s*-cis conformer is probably responsible for the high cis–trans energy gap ( $\sim 16$  kcal/mol).

From an experimental point of view, an *s*-trans planar conformation was observed in *N,N'*-di-*tert*-butyl ethanediiimine (*E,E* configuration) by X-ray diffraction from single crystals at 98 K<sup>22</sup> and at 320 K.<sup>21</sup> However, for the same compound an approximate 80% *gauche* ( $\phi = 65^\circ$ ) and 20% *s*-trans conformation were found by electron diffraction in the gas phase at 353 K.<sup>36</sup> Moreover for several diimines in solution, among which the aliphatic *N,N'*-dibutyl and *N,N'*-diisobutyl, a non-zero dipole moment is observed.<sup>37</sup> This excludes the presence of the *s*-trans

conformer, at least as the only conformer present in solution (at rt). From all these data it might be inferred that as the *N*-substituents become bulkier, there is a stabilization of the *gauche* conformer, depending also on the substituents arrangement.

At this point we tried to reproduce the ab initio energy barrier of diimines with molecular mechanics, using the standard potential energy function of MM3:

$$E_T = V_1/2 (1 + \cos \phi) + V_2/2 (1 - \cos 2\phi) + V_3/2 (1 + \cos 3\phi)$$

and focusing our attention to the *i*-pro substituted diimine, as a model for the dimeric sections of poly(isopropyl)iminomethylene. The procedure we have followed consists of first setting  $V_1$ ,  $V_2$ , and  $V_3$  to 0 kcal/mol and then of checking the energy profile in the absence of the torsional term (results indicated as MM3 (a) in Figures 3–5). A torsional “correction” is eventually introduced to take into account effects which are electronic in nature (thus not accounted for by the other terms of the MM3 energy).

The results for the (*E,E*) isomer are shown in Figure 3. In the absence of the torsional term (MM3 (a)), both the cis–trans energy separation and the  $90^\circ$  barrier are strongly underestimated, if compared to the ab initio results. For a reason which will become evident in the following, we have to find a common set of torsional parameters to be used for both the (*E,E*) and the (*Z,Z*) isomers. Setting  $V_1 = 4.5$ ,  $V_2 = 4.0$ , and  $V_3 = 0.5$  kcal/mol, we obtain the energy profile of Figure 3 (MM3 (b)). The cis–trans separation moves to  $\sim 7$  kcal/mol, while the  $90^\circ$  barrier remains rather low. Note that MM3 calculates the  $\pi$  bond orders and, as a function of them, scales the  $V_2$  torsional parameters to a lower  $V_2$ , which is just 0.72 kcal/mol at  $90^\circ$  in the present case.

In the (*E,Z*) isomer, when  $E_T$  is set to 0 (MM3 (a), Figure 4), a flat curve is obtained, where only a small cis–trans energy separation is found. A pronounced  $90^\circ$  barrier is therefore necessary. Adopting the values  $V_1 = 1.0$ ,  $V_2 = 14.0$ , and  $V_3 = 0.8$  kcal/mol (MM3 (b), Figure 4), a fairly good agreement with the ab initio curve is obtained. At  $90^\circ$   $V_2$  is 2.5 kcal/mol.

Adopting for the (*Z,Z*) isomer the torsional parameters  $V_1 = 4.5$ ,  $V_2 = 4.0$ , and  $V_3 = 0.5$  kcal/mol (MM3 (b), Figure 5) the energy of the *s*-cis conformer is well reproduced, while in the region  $60$ – $150^\circ$  MM3 slightly overestimates the potential energy.

**ii.** The *E,Z* geometrical isomerism around  $N=C$  double bonds plays an important role, as already shown in the case of dimers.

In more extended polymers we considered two configurations:

(a) “Isotactic” when the substituents at nitrogen atoms are all iso-oriented along the chain,<sup>38</sup> i.e. they all point toward the same direction of the growing chain or, equivalently, they all point to the direction opposite to that of the growing chain (iso A, see Scheme 3).

A variant of this configuration (iso B) occurs when the substituent on the last (or first) unit is rotated opposite to all the others. This is a typical end effect, which should have little weight in an extended polymeric chain, but turns out to be significant in rather short oligomers.

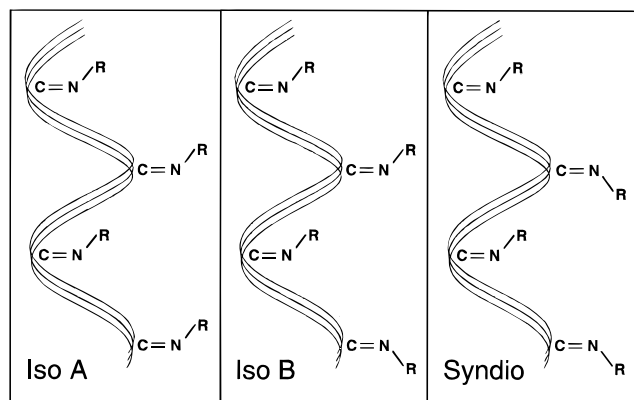
In the isotactic polymer the dimeric sections correspond to a (*E,Z*) diimine, where in the *s*-cis conformer one N lone pair and one N substituent are on the same side. So we used  $V_1 =$

(36) Hargittai, I.; Seip, R. *Acta Chem. Scand.* **1976**, A30, 540.

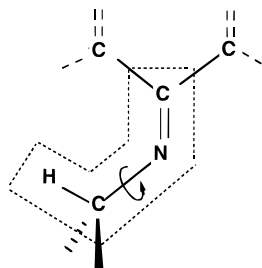
(37) Exner, O.; Kliegman, J. M. *J. Org. Chem.* **1971**, 36, 2015.

(38) Strictly speaking, the terms isotactic and syndiotactic could not be employed in this case, as they refer to the stereochemistry of (pseudo)-asymmetric carbon atoms. We use them as labels to facilitate comprehension of the physical situation.

## Scheme 3



## Scheme 4



1.0,  $V_2 = 14.0$ ,  $V_3 = 0.8$  kcal/mol, as torsional parameters for the  $\phi$  angles in isotactic structures (iso B included).

(b) "Syndiotactic" (also reported in Scheme 3), when the substituents are on opposite sides along the chain, i.e. alternatively up and down with respect to the helical axis. In the syndio polymer the dimeric sections are alternatively (*E,E*) and (*Z,Z*). The previously found values  $V_1 = 4.5$ ,  $V_2 = 4.0$ , and  $V_3 = 0.5$  kcal/mol have been employed to describe the torsional behavior around  $\phi$  angles in the syndio structure.

After the inspection of molecular models, Millich<sup>6,7</sup> excluded that configurations other than "isotactic" could occur, i.e. he denied any configurational freedom based on geometrical isomerism. However, in more recent times, Green et al.<sup>19</sup> proposed that the chemical shift dispersion observed in some <sup>13</sup>C NMR resonances of various PIM in solution could be explained by invoking the occurrence of syn-anti isomerism about C=N double bonds. An analogous possibility was postulated by Drenth et al.,<sup>39</sup> again on the basis of high field NMR in solution. Interestingly, the authors found a distinct splitting of some <sup>1</sup>H NMR signals (and sometimes <sup>13</sup>C too) in most aromatic PIM, but never in aliphatic PIM. The occurrence of random syn-anti isomerism in one (helical) stack was proposed to explain the observed splitting of resonances.

iii. The conformation of side chains is described by the torsional angle C=N-C-H (angle  $\gamma$ ) as shown in Scheme 4. It is widely accepted that methyls (and alkylic substituents in general) eclipse C=N double bonds. Angles  $\gamma$  close to 0° were experimentally found in *N*-methylmethyleimine,<sup>40</sup> and in *N*-methylethylideneimine,<sup>28</sup> by microwave spectroscopy; in (*E,E*)-*N,N'*-di-*tert*-butylethanediiimine, both by electron diffraction in the gas phase,<sup>36</sup> and by X-ray diffraction in the solid state.<sup>22</sup>

Ab initio calculations for the rotation around angle  $\gamma$  in (*E,E*)-*N*-methylethanediiimine find a minimum at 0° and a barrier 2.07

kcal/mol high at 60°, in good agreement with the experimental values obtained by microwave spectroscopy ( $2.10 \pm 0.09$  for *N*-methylethylideneimine<sup>28</sup> and  $1.97 \pm 0.03$  for *N*-methylmethyleimine<sup>40</sup>). The ab initio energy profile is fairly well reproduced with molecular mechanics by assigning  $V_1 = 0$ ,  $V_2 = 0$ , and  $V_3 = -1.5$  kcal/mol to angle  $\gamma$ .

iv. **The Possibility of Optical Isomerism.** If the side chains are achiral, then two helices are possible, assuming the conformational equivalence among residues in the chain: a right handed helix (P-helicity) is generated by regularly repeating positive backbone dihedral angles and, analogously, a left handed helix (M-helicity) by negative backbone angles. These two helices are mirror images of each other, and hence degenerate.

Drenth et al.<sup>41</sup> could (partially) resolve (+) and (-) rotating fractions of poly(*tert*-butyl)iminomethylene by means of HPLC, employing poly((+)-*sec*-butyl)iminomethylene as stationary phase, and assigned the absolute configuration by CD calculations (see section 4). If the side chains are chiral, then we have four different possibilities: *R*-P helix, *R*-M helix, *S*-P helix, *S*-M helix. Given a certain configuration of side chains, say *S*, the two helices, P and M, will now be diastereomeric and in principle not degenerate.

Huige<sup>21</sup> calculated a lower energy for *S* side chains (than for *R* ones) in P helices (for aliphatic substituents, but not for the aromatic  $\alpha$ -phenylethyl), probably due to the preference for eclipsed side chains. The relative stability of the two diastereomers may be of importance when discussing screw sense induction in the polymerization of chiral isocyanides, at least on a thermodynamic ground.<sup>42-44</sup>

**2. Ab Initio Calculations on the Methyl Oligomer.** Full geometry optimizations at the SCF/6-31G\* level have been carried out on five model-built conformers of octa(methyl)iminomethylene. The relevant results are summarized in Table 1, where the geometries are in order of increasing energy.

The syndio configuration (conformation 1 in Table 1) is by far the lowest in energy, being some 30 kcal/mol more stable than the iso ones at the SCF level (26.6 kcal/mol at the MP2 level), and does not correspond to a helical conformation, even though a helical structure (obtained with PCMODEL) was used as the starting arrangement. It is however highly symmetric, as is evident from Figure 6: an overall  $C_2$  rotation axis is present between backbone carbons 4 and 5, and local binary axes are also present inside each tetrameric unit, viz. between C2-C3 and C6-C7. In particular the (*E,E*) dimeric units are trans-planar ( $\phi \approx 180^\circ$ , where a deep minimum is calculated in *E,E* diimines, see Figures 1 and 3), while the (*Z,Z*) ones are rotated at  $\pm 90^\circ$  with respect to the plane formed by the preceding two units. At  $\pm 90^\circ$  no maximum is present in the (*Z,Z*) diisopropyl diimine, as can be inferred from Figure 5. The overall structure of the octamer is thus composed of four (*E,E*) *s*-trans diiminic planes, each normal to the two adjacent ones on both sides, and coplanar with next neighbor ones. As an example, plane no. 2 is normal to planes no. 1 and no. 3 and is coplanar with plane no. 4. The molecule belongs to the  $C_2$  point symmetry group, and this means that the syndio geometry is intrinsically chiral. Notice that trans-planarity is limited to two adjacent units, so that the repulsive N-N interactions predicted by Hoffmann et al.<sup>24</sup> for a trimeric trans-planar unit are prevented in this structure.

(41) Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932. HPLC = high pressure liquid chromatography.

(42) Van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F. *Tetrahedron* **1976**, *32*, 2017.

(43) Van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwicker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679.

(44) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 4400.

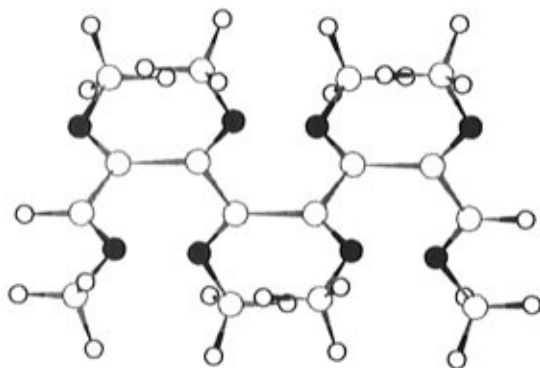
(39) Kamer, P. C. J.; Drenth, W.; Nolte, R. J. M. *Polym. Prepr. (ACS Div. Polym. Chem.)* **1989**, *30*, 418.

(40) Sastry, K. V. L. N.; Curl, R. F., Jr. *J. Chem. Phys.* **1964**, *41*, 77. Yardley, J. T.; Hinze, J.; Curl, R. F., Jr. *J. Chem. Phys.* **1964**, *41*, 2562.

**Table 1.** N=C—C=N ( $\phi_1$ – $\phi_7$ ) Dihedral Angles (see text) for Five SCF/6-31G\*-Optimized Structures of Octa(methyl)iminomethylene, Their Relative Energies with Respect to Conformation 1 at the SCF and MP2 levels (–1056.462118 and –1159.797350 hartrees, respectively), and Dipole Moments

	conformation 1 syndio	conformation 2 iso B (wl) <sup>a</sup>	conformation 3 iso B (he) <sup>b</sup>	conformation 4 iso A (wl) <sup>a</sup>	conformation 5 iso A (he) <sup>b</sup>
$\Delta E_{\text{SCF}}^c$	0.0	30.09	30.97	31.70	32.18
$\Delta E_{\text{MP2}}^c$	0.0	26.59	28.66	28.71	29.21
$\phi_1$	–175.8	–40.6	36.2	38.6	38.4
$\phi_2$	87.1	53.2	46.7	61.9	60.2
$\phi_3$	–179.4	54.7	65.7	71.5	74.9
$\phi_4$	–87.5	61.1	64.9	88.2	82.5
$\phi_5$	–179.4	55.8	99.3	88.4	79.3
$\phi_6$	87.1	–131.0	115.6	–126.9	87.3
$\phi_7$	–175.8	30.6	21.1	29.6	45.2
$\mu^d$	0.11	6.63	8.53	9.23	10.34

<sup>a</sup> Wormlike structure. <sup>b</sup> Helical Structure. <sup>c</sup> kcal/mol. <sup>d</sup> Dipole moment in debyes.

**Figure 6.** Minimum energy conformation of octa(methyl)iminomethylene (conformation 1 syndio in Table 1) obtained from ab initio calculations. Nitrogens drawn in black.**Table 2.** Additional Molecular Parameters for the 6-31G\*/SCF-Optimized Structure of Syndio Octa(methyl)iminomethylene<sup>a</sup>

monomer	$R_{\text{C=N}}$	$\angle\text{C=N-C}$	$\gamma^b$
1	1.249	118.8	–0.8
2	1.251	121.8	3.6
3	1.251	122.3	–2.0
4	1.250	122.1	–4.3
5	1.250	122.1	–4.3
6	1.251	122.3	–2.1
7	1.251	121.8	3.6
8	1.249	118.8	–0.8

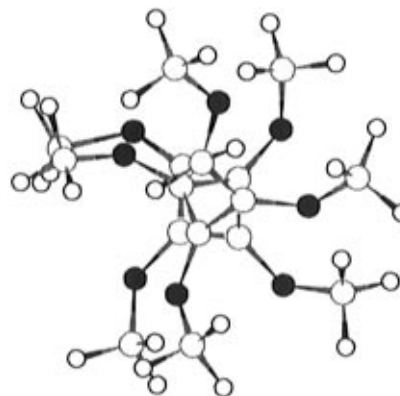
<sup>a</sup> Distances in angstroms, angles in degrees. <sup>b</sup> Dihedral angle C=N–C–H.

Additional geometrical parameters of the syndio structure are reported in Table 2; the iminic C=N bond lengths are somewhat shorter than experimentally found (1.25 Å vs ~1.27 Å by X-ray diffraction,<sup>22</sup> and ~1.28 Å by electron diffraction<sup>36</sup>).

Conformations 2–5, all iso, are very close in energy, lying within a range of ~2 kcal/mol. Configurations iso B (conformations 2 and 3) are slightly more stable than the corresponding iso A (conformations 4 and 5) at the SCF level. As previously stated, this should be only an end effect, due to the limited length of the chain.

A second “end disorder” effect lies in the occurrence of irregular angles at the two ends of the chain, i.e. in  $\phi_1$  and  $\phi_7$ . So we shall discuss the iso geometries focusing on inner backbone angles only, i.e.  $\phi_2$  to  $\phi_6$ .

Out of the four geometries, two are helical (conformations 3 and 5) and two are nonhelical (conformations 2 and 4). We consider as “nonhelical” those conformations where a change of sign occurs in one of the inner backbone dihedral angles. This corresponds to an inversion of helical sense (in this case from P to M), which leads to the so called “wormlike” chains. The occurrence of such structures has been proposed for various

**Figure 7.** A helical conformation of octa(methyl)iminomethylene (conformation 5 iso A in Table 1) obtained from ab initio calculations. Nitrogens in black.**Table 3.** Helical Parameters of the “Best” 4<sub>1</sub> Helices

	R = methyl (ab initio) conformation 5	R = isopropyl conformation 2	R = (S)-1-cyclohexylethyl conformation 4
$\Delta E^a$	32.18	10.3	13.7
$\langle\phi\rangle^b$	76.8	64.5	66.0
$\langle n\rangle^c$	3.7	4.2	4.1
$\langle h\rangle^d$	1.05	0.98	1.00
$\langle p\rangle^e$	3.9	4.1	4.1

<sup>a</sup> kcal/mol. <sup>b</sup> Average value of the N=C–C=N dihedral angle. <sup>c</sup> Average number of residues per turn. <sup>d</sup> Average translation along helical axis of monomer unit (Å). <sup>e</sup> Average pitch (Å). All parameters refer to helical inner sections, i.e., units 2 to 7.

classes of synthetic polymers.<sup>45,46</sup> In our case this helix reversal occurs at  $\phi_6$  in both geometries 2 and 4 (see Table 1).

Passing to helical conformations, we can say that conformation 3 is not a very regular helix, because of a pronounced dispersion of  $\phi$  angles (from ~47° to ~116°), two of them being greater than 90° ( $\phi_5$  and  $\phi_6$ ). Conformation 5 (depicted in Figure 7) has a good degree of regularity, with  $\phi$ 's ranging from ~60° to ~87° (average value 76.8°). For this conformation we calculated the helical parameters<sup>47</sup> reported in Table 3. Considering the average values of  $n$ ,  $h$ , and  $p$  (3.7, 1.05 Å, and 3.9 Å, respectively), it can be inferred that the existence of local minima corresponding to the 4<sub>1</sub> helix is confirmed, but they are not global minima. Moreover according to our ab initio calculations, helical structures are slightly less stable than wormlike chains, at least in the methyl oligomers. The energy gap between helical and wormlike structures increases somewhat

(45) Pino, P.; Luisi, P. L. *J. Chim. Phys.* **1968**, *65*, 130.

(46) Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 8850.

(47) Program based on a least-square algorithm, written by Pelliccioni, A. (CNR, Rome, Italy).

**Table 4.** Conformations of Octa(methyl)iminomethylene, As Obtained from MM3 Calculations, Relative Energies with Respect to Conformation 1, and Dipole Moments. The Main Partial Contributions to the MM3 Energy Are Also Reported<sup>a</sup>

	conformation 1 syndio	conformation 2 iso B (wl) <sup>b</sup>	conformation 3 iso B (he) <sup>c</sup>	conformation 4 iso A (he) <sup>c</sup>	conformation 5 iso A (wl) <sup>b</sup>
$\Delta E^a$	0.0	10.6	10.9	13.9	14.0
$\phi_1$	-179.3	-177.3	-178.5	-150.8	-149.1
$\phi_2$	98.8	61.7	60.4	60.4	59.9
$\phi_3$	179.6	57.0	52.7	51.8	56.5
$\phi_4$	-98.9	64.6	58.0	57.8	63.1
$\phi_5$	179.4	57.9	50.5	50.5	57.0
$\phi_6$	98.8	-136.0	55.9	57.1	-138.2
$\phi_7$	-179.4	41.7	41.8	43.3	42.4
stretching	0.8	0.8	0.8	0.8	0.8
bending	20.7	25.1	25.3	28.2	28.2
VdW <sup>d</sup>	10.0	8.1	8.1	7.2	7.3
torsional	-25.1	-18.8	-19.0	-17.5	-17.3
elect. <sup>e</sup>	2.2	3.9	4.2	3.8	3.4
$\mu^f$	0.16	2.73	4.92	6.07	3.97

<sup>a</sup> kcal/mol. <sup>b</sup> Wormlike structure. <sup>c</sup> Helical structure. <sup>d</sup> Van Der Waals. <sup>e</sup> Electrostatic. <sup>f</sup> Dipole moment in debyes.

**Table 5.** Conformations of Octa(isopropyl)iminomethylene, As Obtained from MM3, Relative Energies with Respect to Conformation 1, and Dipole Moments. The Main Partial Contributions to the MM3 Energy Are Also Reported<sup>a</sup>

	conformation 1 syndio	conformation 2 iso B (he) <sup>b</sup>	conformation 3 iso B (wl) <sup>c</sup>	conformation 4 iso B (wl) <sup>c</sup>	conformation 5 iso B (wl) <sup>c</sup>
$\Delta E^a$	0	10.3	10.4	12.5	14.9
$\phi_1$	178.4	176.6	171.8	176.5	-165.7
$\phi_2$	95.0	63.0	57.0	45.4	63.0
$\phi_3$	-177.3	49.0	55.3	61.5	99.6
$\phi_4$	-92.2	81.6	89.7	120.9	-72.9
$\phi_5$	-178.9	52.9	80.6	-73.5	145.5
$\phi_6$	92.4	76.0	-114.3	110.4	116.4
$\phi_7$	-176.5	174.3	-163.6	170.1	159.1
stretching	1.7	1.8	1.8	1.9	1.9
bending	21.9	25.1	25.1	26.8	27.7
VdW <sup>d</sup>	15.5	15.7	14.7	16.1	16.5
torsional	-20.4	-15.3	-14.2	-15.1	-14.2
elect. <sup>e</sup>	2.2	3.9	3.8	3.6	3.8
$\mu^f$	0.05	5.35	5.57	4.91	6.50

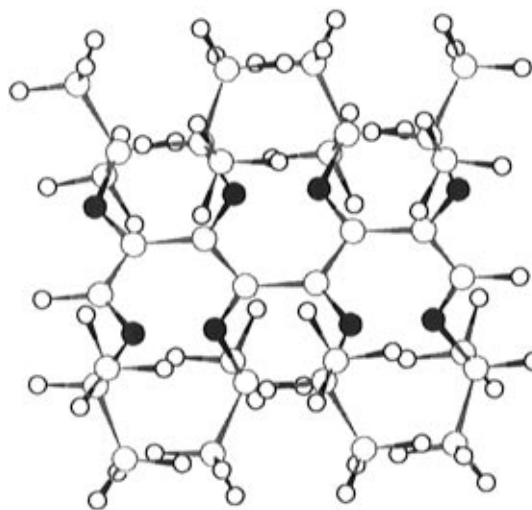
<sup>a</sup> kcal/mol. <sup>b</sup> Helical structure. <sup>c</sup> Wormlike structure. <sup>d</sup> Van der Waals. <sup>e</sup> Electrostatic. <sup>f</sup> Dipole moment in debyes.

including the correlation corrections at the MP2 level, at least for iso B, while the wormlike iso A becomes almost as stable as the helical iso B.

**3. Molecular Mechanics. 3.1. R = Methyl.** The results obtained for the methyl octamer are summarized in Table 4, where the geometries are again in order of increasing energy.

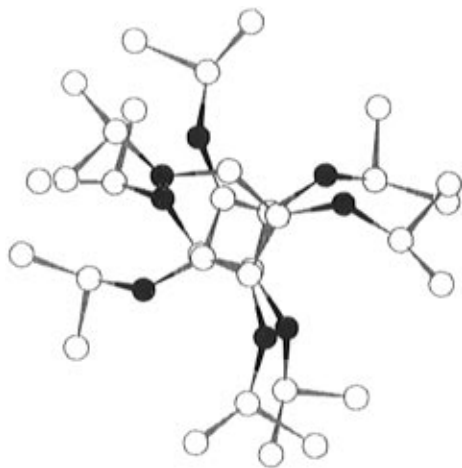
First of all it is worth checking how reliable is MM3 with respect to ab initio results. It is soon evident that molecular mechanics calculations produce a lower energy gap between the syndio geometry (conformation 1) and its next neighbor in energy (conformation 2, wormlike iso B):  $\sim 11$  kcal/mol vs the  $\sim 30$  indicated by ab initio calculations at the SCF level, and  $\sim 27$  at MP2 level. This is rationalized if one looks at the energy partition among the various terms in the bottom part of Table 4: the Van der Waals contribution of conformation 1 is slightly less favorable than that of conformations 2–5, whereas the bending term and, mainly, the torsional one favor conformation 1. Thus, the driving force to conformation 1 is not steric but electronic, and hence MM3 calculations fail to fully reproduce this effect. Moreover the MM3 energy of helical conformations is almost equal to that of the corresponding wormlike chains.

Finally it is interesting to note the values of the permanent dipole moment, which are predicted to be almost zero for the syndio conformation (owing to its symmetry), and rather high for the iso conformations, where wormlike chains dipole moments are a fraction of those of the corresponding helical conformers (2.7 vs 4.9 D and 3.97 vs 6.07 D for iso A and iso B, respectively). This is a common feature observed also at the ab initio level (Table 1) and, at least in part, when dealing with the other two side chains (Tables 5 and 6).

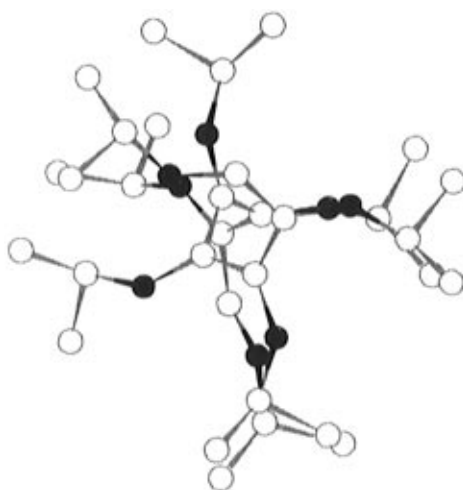
**Figure 8.** Syndio minimum energy conformation of octa(isopropyl)iminomethylene (conformation 1 in Table 5) obtained from MM3 calculations. Nitrogens in black.

Configurations of the iso A type, being constantly higher in energy than the corresponding iso B, will not be further considered in our MM3 calculations.

**3.2. R = Isopropyl.** The syndio geometry is again the lowest energy conformation (Table 5). It still retains its high degree of symmetry, as is evident from Figure 8 and from the value of its dipole moment. The energy difference between the syndio and iso B conformations of the i-pro octamer are comparable with those found for the methyl octamer.



**Figure 9.** Iso B helical conformation of octa(isopropyl)iminomethylene (conformation 2 in Table 5) obtained from MM3 calculations. Nitrogens in black; hydrogens not shown.

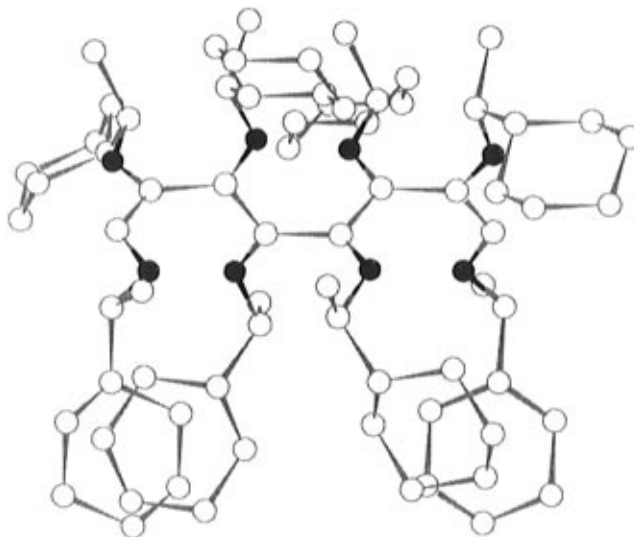


**Figure 10.** A wormlike conformation of octa(isopropyl)iminomethylene (conformation 3 in Table 5) obtained from MM3 calculations. A helix reverse is present between the sixth and the seventh monomer. Nitrogens in black; hydrogens not shown.

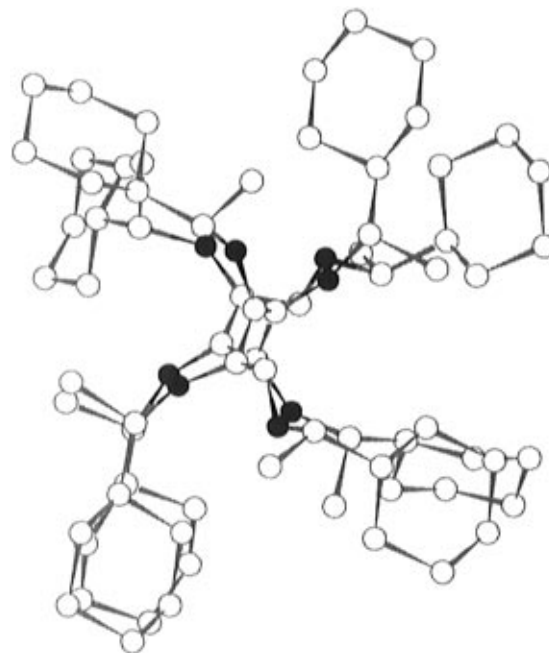
Only the most stable iso conformations are reported in Table 5, because due to the presence of the *i*-pro groups a number of local minima are found, whose energies are not far from one another. For an efficient sampling of the conformational space, several different starting structures have been used. This problem becomes even more dramatic in the case of the 1-cyclohexylethyl derivative.

In the *i*-pro octamer beside helical conformation 2 (Figure 9, hydrogens not displayed) we find three different wormlike chains (conformations 3–5 in Table 5), having inversions of helical sense at  $\phi_6$ ,  $\phi_5$ , or  $\phi_4$ , respectively. The wormlike conformation 3 (Figure 10) is as stable as conformation 2, while conformations 4 and 5 are somewhat higher in energy. The helical parameters of conformation 2 are reported in Table 3: its structure is again very close to a  $4_1$  helix.

**3.3. R = 1-Cyclohexylethyl.** In the case of the 1-cyclohexylethyl derivative the absolute configuration of side chains must be taken into account. We calculated MM3 energies starting from P-helices with both *S* and *R* substituents (Table 6). The lowest energy structure is the syndio alternating geometry bearing the *R* enantiomer. Its diastereomeric partner with *S* side chains lies 2.2 kcal/mol higher in energy. So a small preference for *R* substituents in this enantiomer of the syndio geometry is found, and it is mainly due to the VdW term.



**Figure 11.** Syndio minimum energy conformation of octa(*R*)-(1-cyclohexylethyl)iminomethylene (conformation 1 in Table 6) obtained from MM3 calculations. Nitrogens in black; hydrogens not shown.



**Figure 12.** A helical conformation of octa((*S*)-(1-cyclohexylethyl))-iminomethylene (conformation 4 in Table 6) obtained from MM3 calculations. Nitrogens in black; hydrogens not shown.

Conformation 1 (displayed in Figure 11) shows a more distorted binary symmetry than in the two previous cases (Figures 6 and 8), probably owing to the bulkiness of the substituent.

The lowest energy iso geometries are the helical no. 3 (*R* side chains) and no. 4 (*S* side chains): conformation 4 is a very regular  $4_1$  helix (parameters reported in Table 3) with an evident quaternary helical symmetry (Figure 12). They lie, respectively,  $\sim 14$  and  $\sim 11$  kcal/mol higher than the corresponding syndio ones having the same absolute configuration of the side chains. Two more helical geometries are found, viz. no. 5 (*R*) and no. 6 (*S*), lying at a somewhat higher energy.

From our MM3 calculations a definite preference for *S* or *R* side chains in the  $4_1$  helix cannot be found. By comparing conformations 4 and 5 that bear almost the same succession of  $\phi$  dihedral angles, in fact, the P-helix with *S* side chains shows a slightly larger stability (0.6 kcal/mol), as previously found.<sup>21</sup>



Anyway in the two more irregular helices no. 3 and no. 6 (which also have similar dihedrals,  $\phi$ ), the *R* diastereomer is favoured by 1.4 kcal/mol. Moreover, in both cases the *R* diastereomer has a better VdW term. It is difficult to figure out whether this result is due to limitations of the calculation method (connected to an inefficient sampling of the multim minima energy surface), or else whether there are really various terms of the energy which cancel out one another.

Various wormlike chains are found as well (only some of them, namely conformations 7–10, are reported in Table 6), but they are higher in energy than their helical counterparts with side chains in the same absolute configuration. Conformation 7 is displayed in Figure 13.

Therefore according to MM3, passing from methyl to isopropyl and then to 1-cyclohexylethyl, helical conformations become progressively more stable than wormlike chains. They are also more regular, showing a minor dispersion of angles  $\phi$ . Anyway, a word of caution is necessary, as in comparison with ab initio results MM3 somehow overestimates the stability of helical structures.

The energy of the wormlike structure with *R* substituents (conformation 10,  $\phi_4$  rotated) turns out to be significantly higher in energy ( $\sim 9$  kcal/mol) than its *S* corresponding structure (conformation 9). Once again the VdW term favors the *R* diastereomer, while the torsional term is strongly in favor of the *S* one.

**3.4. The Helical–Wormlike Interconversion (helix reversal).** In their statistical thermodynamic study of polyisocyanates, Green et al.<sup>46</sup> address the question of how flexible is the backbone structure of those polymers. In particular such flexibility arises from inversions of helical sense (P–M): these dynamic reversals are characterized by a definite energy barrier ( $E_r$ ) and in principle can occur randomly in the backbone of the polymer chain. The occurrence of such backbone motions can be postulated in the case of PIM too.

From a computational point of view, we can give only partial answers. We have calculated with MM3 the energy barrier for the rotation around an inner  $\phi$  (more exactly  $\phi_5$ ) in the *i*-pro and in the (*S*)-1-cyclohexylethyl octamers (Figure 14). These curves, besides the intrinsic limitations of the method, are obtained *in vacuo* and hence do not take into account solvent effects and thermal motions. So they are just indicative results.

According to MM3, for both molecules  $g^+$  and  $g^-$  minima are present, the former being always lower in energy; maxima are at  $\sim 0^\circ$  in the isopropyl oligomer, and at  $\sim -20^\circ$  in the 1-cyclohexylethyl one. The rotational barrier  $E_r$  amounts to  $\sim 5$  kcal/mol (isopropyl) and increases to  $\sim 20$  kcal/mol (1-cyclohexylethyl). Therefore it seems that such interconversions should be rather easy in the case of a substituent as large as isopropyl, whereas in the case of the bulky 1-cyclohexylethyl substituent the resulting helix should be considerably more rigid.

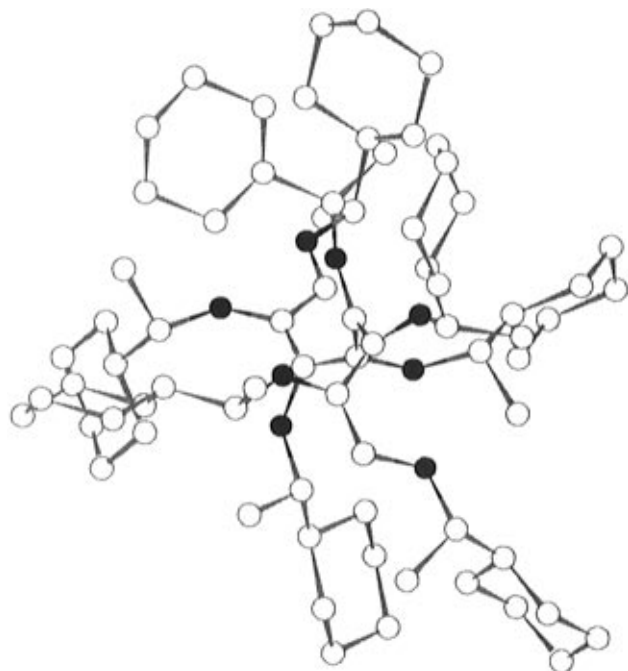
**4. Comparison with Experimental Results and CD Calculations.** Using our set of low energy geometries, we can try to give a tentative explanation of some features experimentally observed in the spectroscopic studies of PIM in solution.

In high resolution  $^{13}\text{C}$  NMR of several PIM, extensive chemical shift dispersion has been observed for some carbon resonances, in particular for those of backbone carbons.<sup>19,20,39</sup> The chemical shift of these nuclei should be the most sensitive one to polymer conformation, so that the above finding is hardly compatible with the idea of regular, stiff helices, which should be characterized by a relatively rigid conformational equivalence among monomer residues. Possible explanations have been given which include *E,Z* (syn–anti) geometrical isomerism about C=N double bonds,<sup>19,39</sup> and helix reversals.<sup>19</sup>

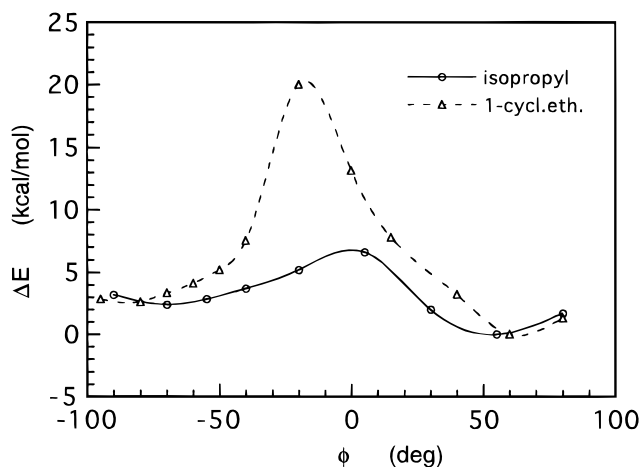
**Table 6.** Conformations of Octa(1-cyclohexylethyl)iminomethylene, As Obtained from MM3, Relative Energies with Respect to Conformation 1, and Dipole Moments. The Main Partial Contributions to the Energy Are Also Reported<sup>a</sup>

	conformation 1		conformation 2		conformation 3		conformation 4		conformation 5		conformation 6		conformation 7		conformation 8		conformation 9		conformation 10		
	<i>R</i> syndio	<i>S</i> syndio	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	<i>R</i> iso B (he) <sup>b</sup>	<i>S</i> iso B (he) <sup>b</sup>	
$\Delta E^a$	0	2.2	13.6	13.7	14.3	14.3	15.0	15.0	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2	16.2
$\phi_1$	179.0	-178.8	-15.4	26.3	30.0	30.0	-28.6	-28.6	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7
$\phi_2$	90.8	101.1	55.9	54.2	57.9	57.9	51.4	51.4	52.1	52.1	52.1	52.1	52.1	52.1	52.1	52.1	52.1	52.1	52.1	52.1	52.1
$\phi_3$	-172.6	178.2	50.7	71.4	67.5	67.5	63.2	63.2	74.5	74.5	74.5	74.5	74.5	74.5	74.5	74.5	74.5	74.5	74.5	74.5	74.5
$\phi_4$	-94.6	-82.6	87.5	66.8	63.8	63.8	78.5	78.5	98.9	98.9	98.9	98.9	98.9	98.9	98.9	98.9	98.9	98.9	98.9	98.9	98.9
$\phi_5$	-168.4	178.3	55.4	59.1	64.5	64.5	58.0	58.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0	-57.0
$\phi_6$	93.2	86.0	79.3	78.5	69.8	69.8	94.5	94.5	92.0	92.0	92.0	92.0	92.0	92.0	92.0	92.0	92.0	92.0	92.0	92.0	92.0
$\phi_7$	164.4	-171.0	173.7	42.5	44.2	44.2	173.8	173.8	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3	-137.3
stretching	6.3	6.3	6.7	6.3	6.3	6.3	6.1	6.1	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
bending	31.2	32.7	33.0	31.7	33.6	33.6	36.9	36.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9	34.9
VdW <sup>d</sup>	52.9	55.1	54.6	54.1	52.1	52.1	55.5	55.5	54.4	54.4	54.4	54.4	54.4	54.4	54.4	54.4	54.4	54.4	54.4	54.4	54.4
torsional	6.7	5.4	14.0	16.2	16.9	16.9	11.6	11.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6	15.6
elect. <sup>e</sup>	2.3	2.2	4.7	4.9	4.9	4.9	4.4	4.4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
$\mu^f$	0.69	0.58	8.55	5.95	6.10	6.10	8.38	8.38	6.02	6.02	6.02	6.02	6.02	6.02	6.02	6.02	6.02	6.02	6.02	6.02	6.02

<sup>a</sup> kcal/mol. <sup>b</sup> Helical structure. <sup>c</sup> Wormlike structure. <sup>d</sup> Van der Waals. <sup>e</sup> Electrostatic. <sup>f</sup> Dipole moment in debyes.



**Figure 13.** A wormlike conformation of octa(*S*)-(1-cyclohexylethyl)iminomethylene (conformation 7 in Table 6) obtained from MM3 calculations. A helix reverse is present between the fifth and the sixth monomer. Nitrogens in black; hydrogens not shown.



**Figure 14.** Potential energy surfaces for the rotation about  $\phi$ ; in octa-(isopropyl)iminomethylene (isopropyl) and in octa(*S*)-(1-cyclohexylethyl)iminomethylene (1-cycl.eth.).

We have demonstrated that syn-anti isomerism is possible in PIM, at least on the basis of thermodynamic (stability) considerations. According to our calculations, the lowest energy syndio configuration shows regular *E,Z* isomerism and is also composed of three different alternating backbone dihedral angles, i.e.  $\sim 180$ ,  $\sim 90$ ,  $\sim -90$ . Irregular syn-anti isomerism, as the one suggested by Drenth et al.,<sup>39</sup> was not considered in our conformational calculations. Moreover wormlike chains, containing helix reversals, are found to be stable as well.

Optical spectroscopies, such as UV-vis and CD, are very sensitive to such conformational details as monomer conjugation (if they are absorptive in the near UV); CD is particularly sensitive to the local conformation and hence to the secondary structure of (macro)molecules. A common feature in the UV spectra of aliphatic PIM is the non-zero absorption at rather long wavelength, say in the range 300–400 nm.<sup>19,20</sup> The intensity of these bands is generally very weak, with  $\epsilon$  amounting to few hundreds of  $1 \times \text{mol}^{-1} \times \text{cm}^{-1}$ . It is

**Table 7.** Near-UV Electronic Transitions in (*E,E*)-*N,N'*-Diisopropylethanediimine, As Calculated by CNDO/S-CI. Sixty Configurations Included in CI. Geometry As Minimized by MM3 (s-trans minimum energy conformer)

transition no.	wavelength (nm)	oscillator strength	polarization			wavelength (nm) <sup>a</sup>
			<i>i</i>	<i>j</i>	<i>k</i>	
1	353.0	0.006	0.017	-0.016	0.999	272.8
2	315.9	0.005	-0.028	0.018	-0.999	245.0
3	214.1	1.068	0.740	-0.672	-0.005	208.8
4	189.5	0.009	-0.194	0.203	-0.960	175.5

<sup>a</sup> Wavelengths of transitions when CI is not used.

therefore likely that such bands arise from electric dipole moment forbidden transitions.

In nonconjugated iminic compounds, a weak UV band ( $\epsilon < 500$ ) at  $\sim 240$ – $250$  nm and an intense one ( $\epsilon > 10000$ ) at 170–175 nm are experimentally found.<sup>48</sup> In first approximation, considering only valence shell transitions, they have been assigned to the  $n-\pi^*$  and the  $\pi-\pi^*$  transitions of the iminic chromophore, respectively.<sup>48,49</sup>

For diiminic compounds, in the UV spectrum of (*E,E*)-*N,N'*-di-*tert*-butylethanediimine (in hexane) a band at 286 nm ( $\epsilon \sim 200$ ) and a second one at 203 nm ( $\epsilon \sim 24000$ ) have been reported;<sup>21</sup> in *N,N'*-di-*n*-butylbutane diimine absorption maxima at 206 nm ( $\epsilon = 17000$ ) and at 209 nm ( $\epsilon = 18500$ ) were found.<sup>50</sup> Thus both transitions are significantly red-shifted in diimines, where conjugation occurs, at least in part.

The results of CNDO/S-CI<sup>51</sup> calculations, reported in Table 7, on (*E,E*)-*N,N'*-diisopropylethanediimine (s-trans conformer), the “building block” of the syndio geometry of the *i*-pro octamer, show four transitions in the near UV ( $\lambda > 180$  nm). In particular, transitions no. 1 and 2 have  $n-\pi^*$  character: their moments are normal to the iminic plane and both have small oscillator strengths. The lowest energy one is predicted to occur at 353 nm, that is, at rather lower energies than what is experimentally found (note that it occurs at 273 nm when CI is not performed<sup>52</sup>).

Transition no. 3 can be definitely assimilated to a  $\pi-\pi^*$  one: it has a large dipolar strength, and its moment lies within the diiminic plane. In particular the direction calculated by CNDO/S is collinear with the vector connecting nitrogens 1 and 4. Its predicted frequency ( $\lambda = 214$  nm with CI, or 209 nm without CI) is now in good agreement with experiment ( $\lambda = 203$ – $209$  nm). Note the close resemblance with the butadiene  $\pi-\pi^*$  transition (both molecules have  $C_{2h}$  symmetry).

So the approximate CNDO/S-CI calculation method can reproduce fairly well the red-shift consequent to conjugation which is actually found experimentally. Similar results were obtained, always by means of CNDO/S-CI calculations, by

(48) Bonnett, R. In *Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: New York, 1970.

(49) Smith, H. E.; Chen, F. M. *J. Org. Chem.* **1979**, *44*, 2775.

(50) Nandi, S. D. *Tetrahedron* **1972**, *28*, 845.

(51) CNDO/S, Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807. *Ibid.* **1968**, *49*, 1221. *Ibid.* **1969**, *50*, 1126. Ellis, R. L.; Kuehnlenz, G.; Jaffé, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

(52) The use of configuration interaction in CNDO/S calculations has been subjected to criticisms: see, for instance, Bouman, T. D.; Lightner, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3145. The authors find that inclusion of CI shifts the  $n-\pi^*$  transition of ketones at too low energies, exactly what was found by us in our diimine.

Smith et al.<sup>49</sup> the authors compared the calculated spectrum of conjugated benzylidenimine to that of methylenimine.

Interestingly enough, in our case, two electric-dipole forbidden transitions are calculated at long wavelengths. This suggests that in a conjugate planar dimeric imine, the relatively simple attribution of the  $n-\pi^*$  transition (as generally adopted in the case of monomeric nonconjugated imines) becomes not so straightforward. As previously noted, the experimental UV spectra of PIM show non-zero absorption at wavelengths above 300 nm, often like a more or less unstructured tail extending up to  $\sim 400$  nm.<sup>19,20</sup>

The CD spectra of aliphatic PIM generally show more than one absorption band at wavelengths  $>260$  nm,<sup>19,20,42,43</sup> in correspondence to the above mentioned isotropic absorption bands. When achiral side chains are present,<sup>42</sup> the intensity of these CD bands is very low ( $\Delta\epsilon \sim -0.06$  at 290 nm). This can be partly due to the lack in enantiomeric purity of the sample.

But even when chiral side chains are concerned, the intensity of the CD bands at long wavelengths remains rather low.<sup>19,20,43</sup> In two PIM synthesized from chiral isocyanides,<sup>20</sup> the intensity of the CD band at  $\sim 250$  nm is lower than the corresponding one of the (model) monomer.

Drenth and co-workers<sup>42,43</sup> interpreted the CD bands at long wavelengths as resulting from an exciton couplet centered at  $\sim 280$  nm. This is questionable, since very weak absorption bands are found in the corresponding UV spectra in the same spectral region; moreover the foregoing CD bands often show a nonconservative shape. The same authors could separate optically active fractions of poly(*tert*-butyl)iminomethylene.<sup>41</sup> Since the side chains of this molecule are achiral, its optical activity only lies in the postulated preference for helical structures with a definite helical sense (either P or M). These authors eventually assigned the absolute configuration of this molecule<sup>42</sup> performing CD calculations based on Tinoco's theory of the optical activity of helical polymers.<sup>53</sup> A negative CD band was predicted to be associated with the longest wavelength transition of a PIM P helix. Lately Huijge<sup>21</sup> made an analogous assignment for the CD of oligo(*tert*-butyl)iminomethylenes (as minimized by MM), calculated employing the De Voe coupled oscillators theory.<sup>29</sup>

In both calculations the CD at long wavelengths was considered to be originated by the coupling of  $n-\pi^*$  electric dipole transitions of iminic chromophores. The moment of this transition is polarized perpendicular to the C=N-C plane,<sup>49</sup> and is small in module ( $|\mu|$  (calcd) = 0.6 D;<sup>49</sup>  $\epsilon$  (exp)  $\sim 200$ <sup>48</sup>). No magnetic dipole terms were included in the calculations.

It has been demonstrated that in case of electric-dipole forbidden, magnetic-dipole allowed transitions, as the iminic  $n-\pi^*$  one, the contribution of the coupled oscillators mechanism accounts for only a small part of the observed rotational strength, even if it generally provides the correct sign.<sup>34,54</sup> We verified this in PIM.<sup>55</sup>

In such cases it is important to include magnetic dipole contributions, mainly the dynamic ( $\mu-m$ ) coupling mechanism. The dynamic mechanism allows the interaction of magnetic dipole moments on one group with electric dipole moments on other groups.<sup>32,33</sup> It has been used to predict the optical activity of alcohols,<sup>54</sup> ketones,<sup>56</sup> amino acids,<sup>57</sup> peptides,<sup>58</sup> and so on.

In particular we used the following equation:<sup>32</sup>

$$R = -2 \sum_{i \neq j} \sum_{a \neq b} \frac{\text{Im}[V_{i0a;j0b}(\mu_{j0b} \cdot m_{i0a} \nu_b)]}{h(\nu_b^2 - \nu_a^2)}$$

where  $R$  is the rotatory strength,  $\text{Im}$  denotes that the imaginary part must be taken,  $\mu$  and  $m$  are the electric and the magnetic dipole moments, respectively, of transitions  $0-b$  and  $0-a$ , which are centered at frequencies  $\nu_b$  and  $\nu_a$ .  $V_{i0a;j0b}$  is the electrostatic interaction potential which mixes the transitions  $0-a$ ,  $0-b$ , .... The sum runs over all transitions (to excited states  $a, b, \dots$ ) and all groups  $i, j, \dots$ . The rotatory strengths resulting from this formula were then converted into  $\Delta\epsilon$  assuming a gaussian shape of the absorption band, and a finite bandwidth. In Table 8 the spectroscopic parameters employed in our CD calculations are listed.

We performed CD calculations on our minimized octa((*S*)-1-cyclohexylethyl)iminomethylene as a model for poly((*S*)-1-cyclohexylethyl)iminomethylene, which has been synthesized in our lab, and whose CD spectrum has been recorded.<sup>20</sup> To this purpose the spectrum was divided into two regions: at  $\lambda < 210$  nm we calculated  $\Delta\epsilon$  employing the De Voe coupled oscillators mechanism (coupling of iminic  $\pi-\pi^*$  transitions). Now intense absorption bands ( $\epsilon > 10000$ ) are found in iminic compounds in this spectral region, so that the coupled oscillator term is expected to give a major contribution to the observed rotational strength. At longer wavelengths ( $\lambda > 210$  nm) we applied the dynamic ( $\mu-m$ ) mechanism (coupling of iminic  $n-\pi^*$  and  $\pi-\pi^*$  transitions).

The spectrum, calculated<sup>59</sup> for a helical conformation (conformation 4 from Table 6) close to a  $4_1$  helix, is displayed in Figure 15 together with the experimental one (from ref 20). Aside from the relative signs of the bands (the calculated ones would be nearly reversed in an M helix), a striking difference in intensity is evident: by using both the De Voe method and the dynamic one, an intensity 1 order of magnitude higher is predicted *vs* that found in the experimental CD spectrum. A symmetric, intense exciton couplet, obtained with the De Voe method, is not present in the experiment (even though the comparison with the experimental spectrum cannot be done at  $\lambda < 180$  nm). Moreover no bands are calculated at long wavelengths ( $\lambda > 280$  nm), apart from the tail of the 248 nm centered  $n-\pi^*$  transition: this is evident, as in the present calculation we have used the spectral parameters of nonconjugated imines (see Table 8), so that conjugation, and the relative red-shift of transitions, cannot be taken into account.

Our approximate CD calculations give us one more argument against a regular  $4_1$  helix, both diastereomerically and enantiomerically pure, being the predominant structure of aliphatic PIM in solution.

Anyway we too predict a negative CD band to be associated with the lowest energy  $n-\pi^*$  transition of aliphatic PIM in a regular right handed (P)  $4_1$  helix, thus confirming the absolute configuration assignment made by Drenth and co-workers<sup>42</sup> and by Huijge.<sup>21</sup>

The presence of electronic conjugation found in the syndio conformation prevents the application of methods relying on the independent systems approach (like the De Voe and the dynamic mechanisms of optical activity), if the properties of monomeric imines are to be used in the calculation, as previously done. This difficulty can be circumvented considering the syndio structure as composed of a series of planar (*E,E*)

(53) Tinoco, I., Jr. *J. Chim. Phys.* **1968**, *65*, 91.

(54) Snyder, P. A.; Johnson, W. C., Jr. *J. Chem. Phys.* **1973**, *59*, 2618. Snyder, P. A.; Johnson, W. C., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2939.

(55) Clericuzio, M. Ph.D. thesis, Scuola Normale Superiore, Pisa, 1993.

(56) Höhn, E. G.; Weigang, O. E., Jr. *J. Chem. Phys.* **1968**, *48*, 1127.

(57) Snyder, P. A.; Johnson, W. C., Jr. *Biopolymers* **1973**, *12*, 975.

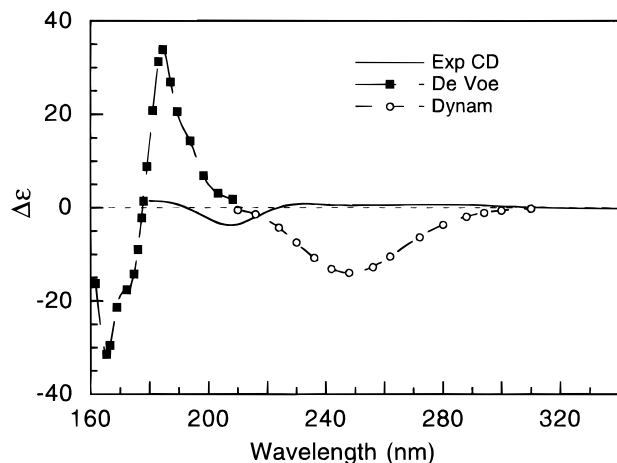
(58) Woody, R. W.; Tinoco, I., Jr. *J. Chem. Phys.* **1967**, *46*, 4927.

(59) In De Voe calculations only the transitions of the iminic chromophore were taken into account. In dynamic ones the contribution of side chains (C-C and C-H bonds) were considered, too. However, in the present case the optical activity due to side chains is small compared to that of the iminic backbone.

**Table 8.** Spectroscopic Parameters Employed in CD Calculations

transition	
$n-\pi^*$ of the iminic chromophore	dynamic
position	on the nitrogen atom (pure $p_y \rightarrow p_x$ )
direction of the magnetic dipole	parallel to the C=N bond
module	1.0 BM
frequency	40.32 kK (248 nm)
half bandwidth	4.0 kK
transition charges	quadrupole
position of transition charges	at the corners of a square centered on nitrogen and perpendicular to the C=N bond
$\pi-\pi^*$ of the iminic chromophore	De Voe + dynamic
position	in the middle of the C=N bond
direction of the electric dipole	parallel to the C=N bond
module	2.8 D
frequency	57.1 kK (175 nm)
half bandwidth	3.0 kK
transition charges	dipole <sup>a</sup>
position of transition charges	along the bond, spaced of 0.1 Å
$\sigma-\sigma^*$ of C-C bonds	dynamic
position	in the middle of the C-C bond
direction	parallel to the C-C bond
module	1.1 D
frequency	75.0 kK (133 nm)
transition charges	dipole <sup>a</sup>
position of transition charges	along the bond, spaced of 0.1 Å
$\sigma-\sigma^*$ of C-H bonds	dynamic
position	in the middle of the C-H bond
direction	parallel to the C-H bond
module	0.9 D
frequency	99.0 kK (101 nm)
transition charges	dipole <sup>a</sup>
position of transition charges	along the bond, spaced of 0.1 Å
$\pi-\pi^*$ of the diiminic chromophore	De Voe
position	between iminic carbons 2 and 3 <sup>b</sup>
direction of the electric dipole	from nitrogen 1 to nitrogen 4 <sup>b</sup>
module	4.2 D
frequency	47.85 kK (210 nm)
half bandwidth	3.0 kK

<sup>a</sup> The mixing potential  $V_{ij}$  is calculated according to a Coulombic charge-charge formalism in dynamic and according to a dipole-dipole formalism in De Voe. <sup>b</sup> See the structure sketched in Table 7.



**Figure 15.** Comparison of the experimental CD spectrum (exp CD) of poly((*S*)-1-cyclohexylethyl)iminomethylene (from ref 20, in hexane) and the calculated CD spectra of octa((*S*)-1-cyclohexylethyl)iminomethylene (conformation 4 in Table 6). De Voe: results obtained from the De Voe coupled oscillator method. Dynam: results obtained from the ( $\mu-m$ ) dynamic method. All  $\Delta\epsilon$  (in  $1 \times 10^4 \text{ mol}^{-1} \times \text{cm}^{-1}$ ) are reported per monomer unit.

diimines with no conjugation among them (their planes being normal to each other). We performed a calculation employing the De Voe method, allowing the interaction of four diiminic  $\pi-\pi^*$  transitions directed as predicted by CNDO/S (the

parameters employed are listed in Table 8).<sup>60</sup> We used the most symmetric syndio geometry obtained from the ab initio calculations, namely the methyl octamer one (see Table 1).

The results are shown in Figure 16: this time CD bands comparable in intensity with the experimental ones are calculated. Anyway, again the symmetric exciton couplet centered at 210 nm, as predicted by the De Voe method, is not experimentally observed.

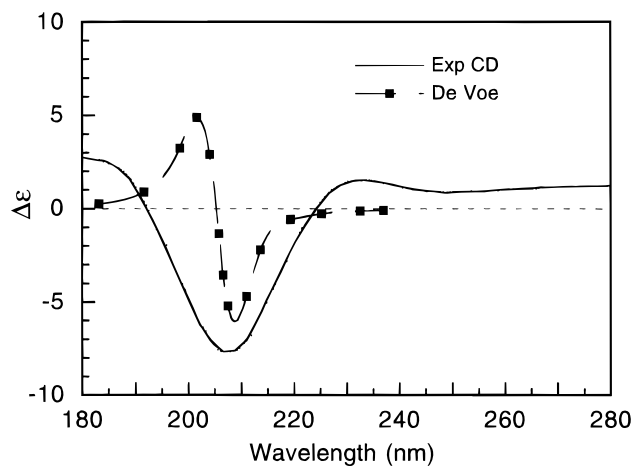
In poly((*S*)-1-cyclohexylethyl)iminomethylene two more contributions to optical activity should be considered: (i) the backbone structure is now predicted to be considerably distorted (see Table 6 and Figure 12); (ii) the optical activity of side chains has to be taken into account. In particular, when distortion from planarity occurs in the diiminic backbone, then a completely different mechanism of optical activity arises, i.e. the one due to the intrinsically dissymmetric chromophore.<sup>61</sup>

## Conclusions

A number of different geometries are possible in poly(iminomethylenes), PIM, according to our ab initio and molecular mechanics simulations. However one geometry ("syndio"), at least within the limited set of initial conformations explored, is by far the most stable one with both calculation methods.

(60) An analogous calculation using the dynamic method would be complicated by (i) the predicted presence of two " $n-\pi^*$ " transitions; (ii) the nonobvious localization of the transitions themselves and of the relative quadrupolar transition charges.

(61) Bystricky, S.; Koos, M.; Repas, M. *Chem. Zvest.* **1981**, 35, 679.



**Figure 16.** Comparison of the experimental CD spectrum (exp CD) of poly((*S*)-1-cyclohexylethyl)iminomethylene (from ref 20, modified) and the calculated CD spectra of the syndio geometry of octa(methyl)iminomethylene (conformation 1 in Table 1), obtained employing the De Voe coupled oscillator method (De Voe).  $\Delta\epsilon$  (in  $1 \times \text{mol}^{-1} \times \text{cm}^{-1}$ ) per monomer unit. Note that in this case the monomer unit corresponds to a diimine (see text).

This geometry, definitely a nonhelical but a highly symmetric one, has a regularly alternating configuration of side chains on C=N double bonds, and an alternating  $180^\circ \pm 90^\circ$  conformation of the backbone N=C–C=N dihedral angles. This has been verified for octa(methyl)iminomethylene, as calculated *ab initio* with a 6-31G\* basis set, and for octa(methyl), (*i*-pro), (*S*)- and (*R*)-(1-cyclohexylethyl)iminomethylene, as calculated with Allinger's MM3 molecular mechanics force field, using a set of parameters optimized for the iminic functional group. Part of the driving force to this conformation seems to lie in the large preference for *E,E* trans-planar diiminic units: the rotation around the N=C–C=N central bond in *E,E* ethanediimine (as calculated *ab initio*) shows a *cis*–*trans* energy difference of  $\sim 8$  kcal/mol in the flexible rotor approximation.

If the substituents around N=C bonds are all iso-oriented ("iso" structures), then we find two types of backbone conformations, which correspond to the  $4_1$  helix and to wormlike chains (where a sign inversion in the backbone angles occurs). These two conformations are close in energy, with a slight preference for the latter at the *ab initio* level. MM3 calculations show the opposite, at least for the bulkier substituents. MM3 also indicates that there is a somewhat higher tendency to form regular  $4_1$  helices as the size of the substituent increases.

The energy barrier for helix reversal is predicted to be small ( $\sim 5$  kcal/mol) in the *i*-pro octamer and significantly larger ( $\sim 20$  kcal/mol) in the 1-cyclohexylethyl octamer.

There is no clear-cut preference for *R* or *S* side chains in the  $4_1$  P-helix. In fact, nearly degenerate diastereomeric structures have been obtained with MM3, where the various terms of the energy tend to cancel out reciprocally.

If we compare either the *ab initio* or MM low energy structures to spectroscopic experimental results, we find that several features do not support the predominance of the  $4_1$  helix.

The absorption at long wavelengths, which is constantly observed in the UV–vis spectra of PIM, is very likely due to chromophore conjugation. This has been partly demonstrated by us performing CNDO/S-CI calculations on a model planar diimine, where a considerable red-shift of transitions over nonconjugate imines is found. As the above planar diimine is the repeating unit of the syndio structure, we can say that the occurrence of such a geometry can at least partially account for the absorption at long wavelengths.

As far as CD is concerned, the most striking feature of the experimental spectra is the small intensity of the bands. We performed approximate CD calculations using the independent system method. For a right handed (*P*)  $4_1$  helix, a strong negative CD band is calculated at 248 nm. This confirms the absolute configuration assignment reported in literature, but contrasts with the low value experimentally found.

Our CD calculations for the syndio geometry show that the intensity of its predicted bands is now not very far from the experiment, even though their shape and frequency position poorly match the experimental data.

Note that the  $4_1$  helix is often quoted as the characteristic secondary structure of poly(iminomethylenes). According to our calculations, and on the basis of mere thermodynamic considerations, the syndio geometry seems to be much more favorable. Our results, however, do not claim that PIM are all in the syndio geometry. In fact both the syndio structure and the  $4_1$  helix are stereo regular geometries, while NMR and CD data suggest that some of the structures assumed by PIM in solution are either configurationally or conformationally disordered or both. Among such structures we have only calculated the energy of wormlike chains (characterized by random breaks in the helical sense), but a number of other stereochemical breaks are possible. Also the presence of different geometries in solution is probable.

In the present study we have on purpose not taken into account PIM bearing aromatic side chains. Poly( $\alpha$ -phenylethyl)iminomethylene seems to be the one for which a larger body of evidence for at least a partial occurrence of a rigid helical structure has been given. Moreover different high resolution NMR spectra in solution have been observed in aromatic *vs* aliphatic PIM. The stacking tendency of aromatic rings, however, might play a role in driving the final conformations.

**Acknowledgment.** A grant of computer time from the CNUCE Computing Centre is gratefully acknowledged. We are deeply indebted to Dr. A. Pelliccioni (CNR Rome, Italy) for making available to us the program which calculates helical parameters. We are grateful to Prof. R. J. M. Nolte (Univ. of Nijmegen, The Netherlands) providing us with C. J. M. Huige's thesis. We are also thankful to Dr. A. Iuliano (Univ. of Pisa, Italy) for the fruitful exchange of data and suggestions about the experimental properties of poly(iminomethylenes), and to Prof. C. Rosini (Univ. of Basilicata, Potenza, Italy) for valuable discussions.

JA961692N