

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/222126976>

# Correlated ground-state ab initio calculations of polymethineimine

ARTICLE *in* CHEMICAL PHYSICS · JULY 2000

Impact Factor: 1.65 · DOI: 10.1016/S0301-0104(00)00156-7

---

CITATIONS

16

---

READS

39

3 AUTHORS, INCLUDING:



[Ayjamal Abdurahman](#)

Université Paris Sorbonne Abu Dhabi

13 PUBLICATIONS 440 CITATIONS

[SEE PROFILE](#)



[Alok Shukla](#)

Indian Institute of Technology Bombay

84 PUBLICATIONS 1,040 CITATIONS

[SEE PROFILE](#)

# Correlated ground-state ab initio calculations of polymethineimine

Ayjamal Abdurahman, Alok Shukla<sup>1</sup>, Michael Dolg<sup>\*,2</sup>

Max-Planck Institut für Physik Komplexer Systeme, Nöthnitzer Str. 38, D-01187 Dresden, Germany

Received 16 March 2000

## Abstract

Ab initio restricted Hartree–Fock and various types of correlated calculations were performed on all three isomers of polymethineimine  $[\text{CHN}]_{\infty}$  using 6-31G\*\* basis sets. Starting from the Bloch-orbital-based Hartree–Fock results, the electron correlation contributions to the ground state energies were calculated by considering finite clusters of increasing size modelling the infinite system. Correlation methods such as Møller–Plesset second-order perturbation theory and coupled-cluster theory with singles and doubles, including a perturbative estimate of triples, were employed. At all levels of theory, and in contrast to the isoelectronic polyacetylene, the *cis-transoid* form of polymethineimine is found to be the lowest in energy. A Wannier-orbital-based and a Bloch-orbital-based Hartree–Fock approach have been tested for the equidistant *all-trans* form and the convergence of subsequent correlation calculations depending on the bond alternation and cluster size has been investigated. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Polymers; Polymethineimine; Polycarbonitrile; Electron correlations

## 1. Introduction

The covalently bonded polymer of hydrocyanic acid or hydrogen cyanide  $[\text{CHN}]_{\infty}$ , also called polymethineimine (PMI), is, at first glance, isoelectronic to polyacetylene (PA)  $[\text{C}_2\text{H}_2]_{\infty}$ . It is the prototype system of polynitriles  $[\text{RCN}]_{\infty}$ , where R denotes some organic rest. PMI is related to PA by the formal replacement of every second CH unit in

PA by a single N atom. This modification causes a doubling of the size of the elementary cell, i.e., whereas PA has an elementary cell CH with an odd number of electrons and is subject to the Peierls distortion [1] causing a bond alternation, PMI has an even number of electrons in the CHN elementary cell.

Experimentally PMI was first synthesized in the early seventies by Wöhrle [2] via a thermally induced ring-opening at 200°C of 1,3,5-triazine complexed by zinc dichloride, i.e.,  $\text{C}_3\text{N}_3\text{H}_3 \times \text{ZnCl}_2$ . Three characteristic IR bands were reported [2] and conductivity measurements indicated that the system is a semiconductor [3]. The presence of a C=N double bond and therefore bond alternation along the chain has been experimentally confirmed [3]. The thermal internal

\* Corresponding author. Tel.: +49-228-73-3839; fax: +49-228-73-9066.

E-mail address: dolg@thch.uni-bonn.de (M. Dolg).

<sup>1</sup> Present address: Department of Physics, Indian Institute of Technology, Powai, Mumbai 400 076, India.

<sup>2</sup> Permanent address: Institut für Physikalische und Theoretische Chemie, Wegelerstr. 12, D-53115 Bonn, Germany.

polymerisation of polyacrylnitrile  $[\text{CH}_2\text{C}(\text{CN})\text{H}]_\infty$  above  $160^\circ\text{C}$  and subsequent dehydration yields a ladder-type polymer of condensed six-rings, formally containing PA and PMI as the two parallel polymeric chains, which are connected by C–C bonds replacing the C–H bonds between every second C in PA and every C in PMI [4]. The resulting polymers and their derivatives are of technical interest as fire-proof clothings. The simplest model for this intra-polymer reaction is the formation of PMI from free HCN, which is of course not observed in this form experimentally.

Theoretically, the PMI system has been investigated at different levels of theory. The first ab initio Hartree–Fock (HF) self-consistent field (SCF) study of *all-trans* PMI by Karpfen [5] 1979 already confirmed the experimentally observed bond alternation. Geometry optimizations [5–7] and a normal mode vibrational frequency analysis have been carried out at the HF [7] and more recently at the second-order many-body perturbation theory (MBPT(2)) [6] levels. Corresponding density functional theory (DFT) results have also been published [8]. Valence effective Hamiltonian (VEH) [9], ab initio HF [5,10], MBPT(2) [6], and linear muffin-tin orbital (LMTO) DFT [11] band structures were also obtained. The frequency-dependent polarizability was studied within coupled-HF theory at the double-zeta basis set level by Gu et al. [12]. Finally, a theoretical investigation of polaron-type defects on the electronic properties has been presented by Del Nero et al. [13].

In this work, the structure and thermodynamic stability of *all-trans* PMI in its ground state is investigated by applying ab initio HF, MBPT(2) and CC (coupled-cluster) theory. For the equidistant structure, all the geometries are optimized applying a Wannier-function-based HF approach. This scheme is expected to be advantageous for the subsequent treatment of electron correlation effects in infinite systems, also those with complex unit cells, by conventional quantum-chemical methods using localized orbitals. Therefore, the numerical accuracy of the WANNIER code [14–17], which was developed in our group, is also demonstrated by comparison to results obtained with the standard Bloch-orbital-based HF approach using the CRYSTAL code of the Turino group [18].

For polymers with small unit cells, e.g., PMI, a more straightforward finite-cluster approach to electron correlation effects has been found useful [19]. Starting from the Bloch-orbital-based HF data the correlation corrections to the total energy per unit cell were calculated at the MP2, CCSD (CC singles and doubles), and CCSD(T) (CCSD with a perturbative estimate of triples) level using the MOLPRO molecular orbital ab initio program package [20]. The corrected total energies allow the optimization of structural parameters as well as the calculation of the cohesive and polymerization energy of the system. Furthermore, the stability of PMI with respect to its monomer hydrogen cyanide HCN and the small cyclic oligomer 1,3,5-triazine  $\text{C}_3\text{N}_3\text{H}_3$  are also discussed.

The organization of this paper is as follows: In Section 2, the applied methods and computational details are briefly described. The results are then presented and discussed in Section 3. Finally, a summary is given in Section 4.

## 2. Applied methods and computational details

The structure of PMI has not been determined experimentally yet to our knowledge. We have applied a wave-function-based ab initio approach to explore the electronic ground-state properties of the isolated infinite periodic chain. We adopted standard polarized valence double-zeta (6-31G\*\*) basis sets. The polarization functions consisted of a single *p* type exponent of  $0.75 \text{ bohr}^{-2}$  on hydrogen and single *d* type exponents of  $0.6 \text{ bohr}^{-2}$  and  $0.8 \text{ bohr}^{-2}$  on carbon and nitrogen, respectively. Thus, the basis sets are (4s1p)/[2s1p] for hydrogen and (10s4p1d)/[3s2p1d] for carbon and nitrogen. Assuming all C–N bonds of *all-trans* PMI to have the same lengths and the C–H bonds to be perpendicular to the polymer axis, we first optimized the equidistant structure at the HF-SCF level using the WANNIER [14] program. In order to be demonstrate the correctness of our method, the structure has also been optimized by using the Bloch-orbital-based CRYSTAL [18] program. Since basis sets expanded in Gaussian lobe functions and Cartesian–Gaussian functions are used in these programs, the derived results are very similar, but

not identical. The total HF energies obtained with the CRYSTAL program were then taken as an input for a re-optimization at the MP2, CCSD (CC singles and doubles) and CCSD(T) (CCSD with a perturbative estimate of triples) levels. The correlation energy contributions at each geometry have been calculated with the MOLPRO molecular orbital ab initio program package [20] by using a simplified finite-cluster approach outlined below. Although the CCSD(T) approach is one of the most successful and accurate single-reference based methods, nevertheless we include CCSD and MP2 for the purpose of discussion and for comparison to work of other authors. We note here in passing that the results based on WANNIER HF data are virtually identical and that the choice of CRYSTAL HF data plus MOLPRO correlation corrections has merely been made in order to have completely identical basis sets at the HF level and beyond. For the bond-alternating structure of *all-trans* PMI and the *cis-transoid* and *trans-cisoid* forms five independent parameters (lattice constant  $a$ , bond lengths  $r_{\text{C-N}}$ ,  $r_{\text{C=N}}$  and  $r_{\text{C-H}}$ , angle  $\varphi$  of the C–H bond with respect to the polymer axis) were optimized at the HF and the three correlated levels of theory as described above for the equidistant system (Fig. 1). The difference in subsequent bond lengths  $\delta r = r_{\text{C-N}} - r_{\text{C=N}}$  is called the bond alternation in the following. The convergence of our geometrical parameters is better than  $\pm 0.005 \text{ \AA}$  and  $\pm 1^\circ$ .

For polymers with simple unit cells, a straightforward approach for electronic structure calculations beyond the independent-particle level has been proposed recently [19]. In principle, the total energy  $E_{\text{tot}}$  or correlation energy  $E_{\text{cor}}$  per unit cell  $U$  of a polymer  $U_\infty$  can be obtained as the limit:

$$E = \lim_{n \rightarrow \infty} \frac{E(R(U_n)R')}{n}, \quad (1)$$

i.e., by performing calculations for increasingly long oligomers  $R(U_n)R'$ , where the dangling bonds at both ends have been saturated by rest groups  $R$  and  $R'$ , respectively. However, in order to reduce finite-size effects due to the termination of the oligomers by the rests  $R$  and  $R'$ , one should consider instead

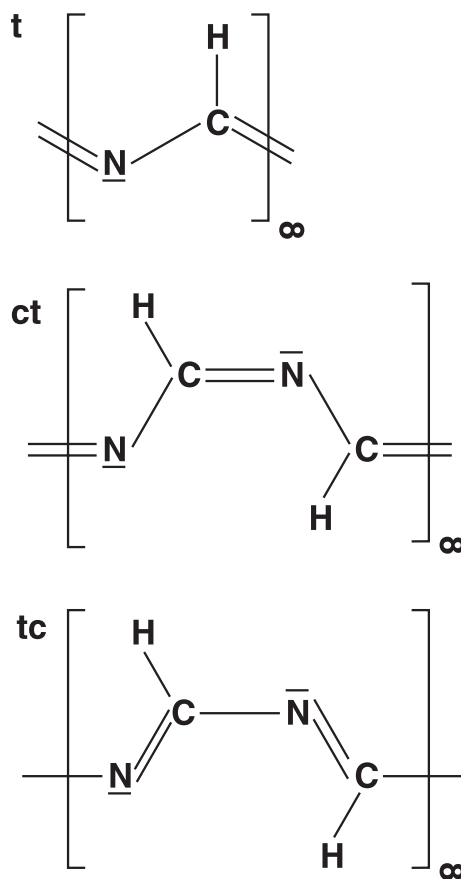


Fig. 1. Structures of *all-trans* (t), *cis-transoid* (ct) and *trans-cisoid* (tc) polymethineimine.

$$E = \lim_{n \rightarrow \infty} \Delta E_n = \lim_{n \rightarrow \infty} [E(R(U_{n+1})R') - E(R(U_n)R')], \quad (2)$$

i.e., the energy changes between two oligomers differing just by a single unit cell. This approach has previously been used successfully in calculations for the three isomers of polyacetylene (*all-trans*, *cis-transoid* and *trans-cisoid*) [19], and the two boron-nitrogen systems polyaminoborane and polyiminoborane [21].

Usually, the finite model cluster is simply constructed by saturating the dangling bonds at both ends of a chain of several unit cells length by hydrogen atoms. A unit cell in the middle of such

an oligomer is assumed to be virtually in the same environment as a corresponding unit cell in a polymer of infinite length, especially when only the rather short-range electron correlation effects have to be evaluated. However, in case of PMI without bond alternation such a  $\text{H}[\text{CHN}]_n\text{H}$  model ( $U = \text{CHN}$ ,  $R = R' = \text{H}$ ) does not have the correct symmetry, i.e., the terminal C–H and N–H groups strongly bias the system to yield localized  $\pi$ -bonds. Therefore, we applied symmetric oligomers of the form  $h[\text{CHN}]_n\text{CH}h$ , where  $h$  denotes a nuclear charge of 0.5, at which a full hydrogen basis set is located. Since a symmetric oligomer has to have an odd and even number of C–H groups and N atoms, respectively (or vice versa), one has to add two identical terminal groups with an odd number of electrons to come to a closed-shell model system. The choice of the finite cluster model will be discussed further in Section 3.

As it will be outlined in more detail later, the convergence of  $\Delta E_n$  with respect to  $n$  is much faster for the dynamical correlation energy than for the HF energy, reflecting essentially the local character of electron correlations in contrast to the long-range character of the mean-field interactions. Having at hand HF programs to account accurately for the latter effect (e.g., CRYSTAL, WANNIER) it is tempting to use Eq. (2) only for the correlation energy per unit cell. The calculations for the individual oligomers can be carried out using standard quantum chemical program packages, e.g., MOLPRO [20]. The full symmetry may be exploited when a basis of canonical molecular orbitals is used. Alternatively, one might also use local correlation methods [22,23], which become even more efficient for larger oligomers due to the linear scaling properties. In our case, the correlation energies per unit cell of PMI have been derived from the difference of the correlation energies of  $\text{C}_6\text{N}_5\text{H}_8$  and  $\text{C}_5\text{N}_4\text{H}_7$ . Based on a comparison to a corresponding difference of  $\text{C}_5\text{N}_4\text{H}_7$  and  $\text{C}_4\text{N}_3\text{H}_6$ , we estimate the correlation energy to be converged to better than  $10^{-4}$  a.u. for geometries near the equilibrium structure.

It is interesting to see how the simple finite cluster approach is related to the so-called incremental scheme devised for 3D solids [24,25] and

later also applied to polymers [19]. For this purpose, let us assume that we work in terms of localized orbitals, which can be attributed to specific cells in the polymer. If the reference cell in a polymer is labelled by index 0, and the neighboring cells according to their position with respect to the reference cell are denoted by indices  $\pm 1$ ,  $\pm 2$ , etc., one may write the correlation energy per unit cell as a sum of increments:

$$E_{\text{cor}} = \epsilon_0 + \sum_{i>0} \Delta\epsilon_{0i} + \sum_{j>i>0} \Delta\epsilon_{0ij} + \dots \quad (3)$$

Here,  $\epsilon_0 = \Delta\epsilon_0$  denotes the correlation energy of the electrons in the reference unit cell and the two-body increments  $\Delta\epsilon_{0i}$  are calculated from the correlation energy  $\epsilon_{0i}$  of the reference cell and the cell at position  $i$  by subtracting the one-body terms  $\epsilon_0 = \epsilon_i$ , i.e.,

$$\Delta\epsilon_{0i} = \epsilon_{0i} - 2\epsilon_0. \quad (4)$$

Note that, e.g., the increments  $\Delta\epsilon_{0i}$  and  $\Delta\epsilon_{0,-i}$  are identical and each contributes to both cells 0 and  $i$ , respectively  $-i$ , i.e., the summation can be restricted to positive values of  $i$ . The three-body corrections  $\Delta\epsilon_{0ij}$  are constructed accordingly, i.e., with  $\Delta\epsilon_{0(j-i)} = \Delta\epsilon_{ij}$ :

$$\Delta\epsilon_{0ij} = \epsilon_{0ij} - 3\epsilon_0 - \Delta\epsilon_{0i} - \Delta\epsilon_{0j} - \Delta\epsilon_{0(j-i)}. \quad (5)$$

In finite cluster calculations, the sums in Eq. (3) are terminated, and additional contributions due to the terminal rests  $R$  and  $R'$  arise. Disregarding the end groups for the moment and assuming that the ideal oligomer (starting at cell 0 and ending at cell  $n$ ) can be considered to be a part of the polymer, one obtains as an approximation to the correlation energy per unit cell,  $E_{\text{cor}}$ ,

$$E_{\text{cor}}(n+1) - E_{\text{cor}}(n) = \epsilon_0 + \sum_{i>0}^{n+1} \Delta\epsilon_{0i} + \sum_{j>i>0}^{n+1} \Delta\epsilon_{0ij} + \dots + \Delta\epsilon_{012\dots(n+1)}. \quad (6)$$

For a convergent incremental expansion, the error in the correlation energy per unit cell therefore should be smaller than  $\Delta\epsilon_{0n+1}$ , which decays as

$1/(n+1)^6$  for large  $n$  due to van der Waals type correlation contributions. The contributions of the terminal groups  $R$  and  $R'$  also cancel out when building the difference in Eq. (6), except for those terms which refer to one rest and the cell most remote to it in the oligomer, as well as difference in the  $R-R'$  two-body increments for oligomers of length  $n+1$  and  $n$ . Due to the larger distances involved all these corrections should be smaller than  $\Delta\epsilon_{0n+1}$ , at least as long as the rests bear no net charges. It is essential to use only finite model clusters which have as small as possible charge separation in the direction of the polymer axis. In practical calculations, the convergence can be easily checked by comparing results obtained from finite clusters of length  $n-1$ ,  $n$  and  $n+1$ . The advantage of the outlined finite cluster approach is that it can readily be applied to any correlation treatment working in canonical orbitals, its disadvantage is that it becomes impracticable for large unit cells or in the 3D case.

We have also calculated the cohesive energy per unit cell at the HF and correlated level. The atomic HF-SCF, MP2, CCSD and CCSD(T) reference energies (C:  $-37.6769$ ,  $-37.7026$ ,  $-37.7148$ , and  $-37.7151$  a.u.; N:  $-54.3821$ ,  $-54.4149$ ,  $-54.4188$ , and  $-54.4189$  a.u.; and H:  $-0.4982$  a.u.) were obtained with the same basis sets as used in the polymer. In addition to the cohesive energy, we have also evaluated the polymerization energy and the energy difference per CHN unit with respect to the benzene analogue trimer 1,3,5-triazine  $C_3N_3H_3$ . The geometries of the HCN monomer and trimer were optimized at the HF-SCF, MP2, CCSD, and CCSD(T) levels employing the MOLPRO program package [20].

### 3. Results and discussion

Our results for the optimized geometry, the total energy, cohesive energy, and polymerization energy per CHN unit cell of equidistant PMI obtained with the 6-31G\*\* basis set at the HF, MP2, CCSD, and CCSD(T) levels of theory are presented in Table 1. The polymerization energies refer to the fully optimized structure of the HCN monomer for each method. The geometrical parameters obtained with the WANNIER and CRYSTAL program systems are virtually identical, whereas the total energy per CHN unit is 1.4 mHartree lower for the CRYSTAL compared to the WANNIER code. One possible technical reason for this slight deviation is the use of Gaussian lobe and cartesian Gaussian functions in WANNIER and CRYSTAL, respectively. Nevertheless, the difference in the total HF energy of 1.4 mHartree is still within the range of 1 mHartree per atom in the unit cell, which is believed to be the accuracy of the calculations performed with the CRYSTAL program. Large quantities as the cohesive energy differ by less than 1% (8.79 vs. 8.83 eV), but very small values as the polymerization energy by as much as almost 30% (0.13 vs. 0.17 eV). Since the atomic and molecular calculations have been performed with cartesian Gaussian functions using the MOLPRO program package, we refer in the remainder of the paper all energies to the CRYSTAL HF energies.

Electron correlations slightly lengthen both the C–N (0.02 Å) and C–H (0.01 Å) bonds as well as the lattice constant (0.01 Å). Little changes of a few hundredths of an electron volt are observed for the polymerization energy. This indicates that

Table 1

C–N and C–H bond lengths (Å), lattice constant  $a$  (Å), total energy  $E_{\text{tot}}$  (Hartree), cohesive energy  $\Delta E_{\text{coh}}$  and polymerization energy  $\Delta E_{\text{pol}}$  (eV) per CHN unit of the equidistant structure of *all-trans* polymethineimine

Method	$r_{\text{C-N}}$	$r_{\text{C-H}}$	$a$	$E_{\text{tot}}$	$\Delta E_{\text{coh}}$	$\Delta E_{\text{pol}}$
WANNIER HF	1.314	1.099	2.261	−92.8803	8.792	0.131
CRYSTAL HF	1.313	1.099	2.260	−92.8817	8.830	0.169
MP2 <sup>a</sup>	1.335	1.112	2.269	−93.1666	14.99	0.155
CCSD <sup>a</sup>	1.332	1.111	2.268	−93.1735	14.74	0.122
CCSD(T) <sup>a</sup>	1.337	1.114	2.270	−93.1877	15.12	0.174

<sup>a</sup> Correlation contributions added to CRYSTAL HF-SCF data.

the number of bonds in the polymer unit cell and the monomer is essentially the same, i.e., the triple bond of the HCN monomer is converted into two bonds in the polymer unit cell, both having a bond order close to the ideal value of 1.5. A bond order close to 1.5 is supported by the fact that the C–N bond distance is intermediate between the distances of the single and double bonds in the bond-alternating structure, cf. below. Our results range from 0.12 to 0.17 eV and are in reasonable agreement with an empirical estimate of 0.32 eV, based on the standard bond enthalpies of carbon–nitrogen single (3.16 eV), double (6.37 eV) and triple (9.21 eV) bonds [26]. However, due to the formation of new chemical bonds significant changes induced by electron correlation are present in the cohesive energy per unit cell. The correlation contributions are 6.16, 5.91 and 6.29 eV at the MP2, CCSD and CCSD(T) level, respectively, i.e., electron correlation accounts for 40–42% of the cohesive energy at all three levels of theory.

The stability of *all-trans* PMI without bond-length alternation with respect to small oligomer ring systems was also investigated. 1,3,5-triazine  $C_3N_3H_3$  is isoelectronic to benzene  $C_6H_6$  and was calculated to be 0.469 eV per CHN unit more stable than PMI at the HF level. Again, for the isodesmic reaction from 1,3,5-triazine to PMI, the correlation contributions are small: 1,3,5-triazine is 0.433 and 0.417 eV per CHN unit more stable than equidistant PMI at the MP2 and CCSD(T) level, respectively.

The results of corresponding calculations on the bond-alternating structure of *all-trans* PMI are listed in Table 2. Bond alternation stabilizes PMI

with respect to its equidistant form only very slightly, i.e., the energy lowerings per CHN unit are 0.024 (HF), 0.005 (MP2), 0.033 (CCSD) and 0.019 eV (CCSD(T)). The C–N bond distances for the equidistant structures agree within 0.01 Å with the mean values of the short and long distances in the alternant case, whereas the bond alternation defined as the difference between the bond lengths of C–N single and C=N double bonds amounts to about 0.1 Å at all levels of theory. Due to the absence of experimental structural data, we can compare our results only to other theoretical work. To the best of our knowledge, only Sun and Bartlett [6] have performed a full geometry optimization for PMI at the correlated level within MP2 theory, also using 6-31G\*\* basis sets. Their HF and MP2 results are basically in agreement with ours. We observe, however, that their bond lengths and their lattice constants are typically 0.003 to 0.018 Å smaller than our values. Since Sun and Bartlett did not give a total HF energy, we cannot judge which numbers should be closer to the HF limit. Our value for the bond alternation is reduced from 0.104 Å at the HF level to 0.072 Å at the MP2 level, which is in satisfactory agreement with the corresponding values of 0.100 and 0.086 Å obtained by Sun and Bartlett. At our best level of theory, i.e., CCSD(T), we observe a 0.017 Å longer C–N single bond, a 0.005 Å shorter C=N double bond, essentially no change in the C–H bond distance and a 0.009 Å larger lattice constant than at the MP2 level. It is noteworthy that the calculated CCSD(T) bond alternation of 0.094 Å is only 0.01 Å smaller than the original HF value, and the CCSD bond alter-

Table 2

As in Table 1, but for the bond alternating structure of *all-trans* polymethineimine.  $\varphi$  denotes the N=C–H bond angle and  $\Delta E_{\text{rel}}$  is the relative energy (in eV) per CNH unit with respect to the equidistant structure of *all-trans* polymethineimine

Method	$r_{\text{C-N}}$	$r_{\text{C=N}}$	$r_{\text{C-H}}$	$\varphi$	$a$	$E_{\text{tot}}$	$\Delta E_{\text{rel}}$
CRYSTAL HF	1.372	1.268	1.097	121.4	2.275	–92.8826	–0.025
HF <sup>a</sup>	1.362	1.262	1.094	–	2.269	–	–
MP2 <sup>b</sup>	1.376	1.304	1.112	122.4	2.287	–93.1668	–0.005
MP2 <sup>a</sup>	1.372	1.286	1.102	–	2.281	–	–
CCSD <sup>b</sup>	1.398	1.286	1.110	122.5	2.293	–93.1747	–0.033
CCSD(T) <sup>b</sup>	1.393	1.299	1.113	122.5	2.296	–93.1884	–0.019

<sup>a</sup> Ref. [6].

<sup>b</sup> Correlation contributions added to CRYSTAL HF-SCF data.

Table 3

As in Table 2, but for *cis-transoid* (upper half of the table) and *trans-cisoid* (lower half of the table) polymethineimine.  $\phi$  denotes the N=C–H and N–C–H bond angles. No local minimum has been found at the HF level for the *trans-cisoid* case

Method	$r_{\text{C-N}}$	$r_{\text{C=N}}$	$r_{\text{C-H}}$	$\phi$	$a$	$E_{\text{tot}}$	$\Delta E_{\text{rel}}$
CRYSTAL HF	1.374	1.277	1.080	117.7	4.004	−92.8875	−0.158
MP2 <sup>a</sup>	1.382	1.308	1.093	118.9	3.993	−93.1718	−0.142
CCSD(T) <sup>a</sup>	1.362	1.336	1.096	117.0	4.065	−93.1948	−0.193
MP2 <sup>a</sup>	1.391	1.299	1.095	115.7	4.124	−93.1675	−0.024
CCSD(T) <sup>a</sup>	1.393	1.312	1.097	115.6	4.125	−93.1910	−0.090

<sup>a</sup> Correlation contributions added to CRYSTAL HF-SCF data.

nation of 0.112 Å is even somewhat larger. In case of *all-trans* PA, it is generally found that electron correlation decreases the bond alternation, but for PMI the situation has not necessarily to be the same. However, a possible reason might be that CCSD can break single, but not double bonds, i.e., the C–N and C=N bonds in PMI are treated in an unbalanced way. The perturbative triples in CCSD(T) at least partially correct this deficiency of CCSD. On the other hand, MP2(D) will neither describe the breaking of the C–N nor the C=N bond and an error compensation may occur.

Our results for the C–N and C=N bond lengths of 1.393 and 1.299 Å, respectively, are in modest agreement with the DFT values of Springborg [11], i.e., 1.413 and 1.344 Å. The deviations may be due to the fact that the latter results stem from a partially restricted geometry optimization. The agreement with the gradient-corrected DFT results of Hirata and Iwata [8], i.e., 1.373 and 1.300 Å, is somewhat better, although these authors applied only 3-21G basis sets.

Hirata and Iwata found *cis-transoid* PMI to be about 0.16 eV per CNH unit lower in energy than the *all-trans* conformer studied so far. Del Nero and Laks [27] claimed however, that improvement of the basis sets and inclusion of electron correlation by means of DFT finally yields the *all-trans* conformer to be the most stable structure by about 0.08 eV per CNH unit. We finally note that the use of a planar structure of *all-trans* PMI was questioned by Del Nero and Laks, but their evidence was based on finite cluster calculations for the di-, tri- and tetramer H[CHN]<sub>n</sub>H ( $n = 2, 3, 4$ ). Due to this open question, we also investigated the *cis-transoid* and *trans-cisoid* forms of PMI at the HF, MP2 and CCSD(T) level. Our results are summa-

rized in Table 3. We were unable to locate a local minimum corresponding to the *trans-cisoid* form of PMI at the HF level, whereas the *cis-transoid* structure was found to be 0.13 eV more stable than the bond-alternating *all-trans* conformer. At the MP2 level, the bond-alternating *all-trans* and *trans-cisoid* forms are almost degenerate, with the *cis-transoid* PMI being 0.14 eV lower in energy. Finally, the CCSD(T) results show the *cis-transoid* structure to be lower in energy than the bond-alternating *all-trans* conformer by 0.17 eV, whereas the *trans-cisoid* form is 0.07 eV more stable.

At the HF (MP2) level, the bond alternation of *cis-transoid* PMI of 0.097 Å (0.074 Å) is very similar to the one observed for the *all-trans* conformer, i.e., 0.104 Å (0.072 Å). However, at the CCSD(T) level the bond alternation of *cis-transoid* PMI is reduced to 0.026 Å, compared to 0.094 Å for the *all-trans* form.

On the basis of the CCSD(T) results, we estimate *cis-transoid* PMI to be about 0.22 eV per CHN unit less stable than 1,3,5-triazine. The corresponding HF and MP2 results are 0.31 and 0.19 eV, respectively. The pronounced endothermicity of the polymerization reaction might be due to the loss of “resonance energy” when going from 1,3,5-triazine to PMI. Note that the resonance energy of the isoelectronic benzene is estimated to be 1.56 eV, 0.52 eV per C<sub>2</sub>H<sub>2</sub> unit. In fact, based on the data presented for *all-trans*-PA in an earlier publication [19], we estimate this polymer at the CCSD(T) level using correlation-consistent polarized valence triple-zeta basis sets to be by 0.60 eV per C<sub>2</sub>H<sub>2</sub> unit less stable than benzene. The thermal conversion of 1,3,5-triazine to PMI in presence of metal halides like ZnCl<sub>2</sub>, SnCl<sub>4</sub> or TiCl<sub>4</sub> at temperatures between 200°C and 300°C was



observed by Wöhrle [2,3]. The enthalpy of polymerisation was determined from a  $\log K_e$  over  $1/T$  Van't Hoff diagram to be 4 kcal/mol or 0.17 eV [3] (we obtained 0.21 eV when using the original data from Table 2 in Ref. [3]), compared to our best estimate of 0.66 eV (CCSD(T) result for three CNH units, cf. above). In view of the fact that the elementary analysis of the synthesized product did not correspond to pure PMI, but contained between 12% and 34% other elements besides C, N and H, and that the ratio between C and N varied between 0.93 and 1.09, we are confident that the remaining discrepancies would be smaller after a remeasurement with modern experimental techniques, e.g., a systematic exclusion of air to avoid partial oxidation.

Finally, we want to add some comments regarding the use of the incremental scheme or the simpler approach using oligomers for the evaluation of correlation energies of infinite clusters. The basic idea is that the long-range interactions are treated in a HF calculation for the infinite system and the short-range dynamical correlation in a MP2, CCSD, or CCSD(T) calculation for a finite embedded cluster. Problems are encountered when the single-reference approach breaks down due to non-dynamical correlation effects, e.g., when studying the equidistant structure of PMI. One may look at this case to be the transition state between the two possible forms of bond-alternating PMI. When going from one form to the other one C–N  $\pi$ -bond is half-way broken, the other half-way formed. HF calculations for infinite systems produce a symmetric energy profile, whereas this is not the case for finite cluster calculations, if simply the dangling bonds of a section of  $n$  unit cells of PMI are saturated with hydrogen. Such a  $H[CHN]_nH$  model cluster can describe well only one form of bond-alternating PMI and formally corresponds to a Zwitter-ion with positive and negative partial charges on the terminal C and N atoms, respectively, for the other form. The correct state with unpaired electrons on the terminal C and N atoms cannot be described at the HF level. In the subsequent correlation calculations, the missing non-dynamical correlation effects are accounted for and enter the poorly convergent correlation contributions added to the HF energies

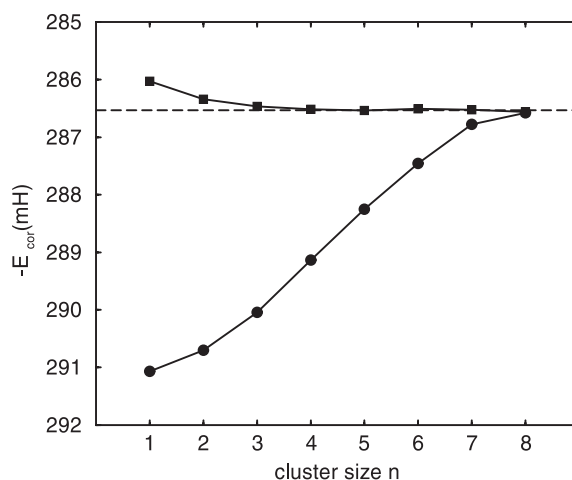


Fig. 2. Correlation energy per unit cell  $E_{cor}$  (mHartree) for the equidistant structure of polymethineimine from MP2 calculations of model clusters  $H[CHN]_nH$  (●) and  $h[CHN]_nCHh$  (■). The cluster size  $n$  on the abscissa denotes that the energy difference of the oligomers with  $n+1$  and  $n$  unit cells has been used to evaluate  $E_{cor}$ . The dashed line denotes the  $h[CHN]_nCHh$  averaged values of  $n=4-8$ .

evaluated for the infinite system. A model cluster much better adapted for the treatment of the equidistant structure of *all-trans* PMI is the system used for the present work, i.e.,  $h[CHN]_nCHh$ . Here both forms of the bond alternation in *all-trans* PMI are described identically well due to the symmetry of the system and artefacts caused by nondynamical correlation are much smaller. The different convergence behavior of the MP2 correlation energies per CHN unit derived from the model clusters  $H[CHN]_nH$  and  $h[CHN]_nCHh$  is depicted in Fig. 2 for the equidistant structure of *all-trans* PMI. A similar behavior is present for CCSD and CCSD(T), but it is not possible to study sufficiently large cluster sizes for the slowly converging case.

Besides the convergence of the correlation energy, it is also interesting to look at the convergence of the total HF and MP2 energy per unit cell (Fig. 3). As “correct” results, we took the HF energy from the Bloch-orbital-based CRYSTAL calculations as well as this energy plus the correlation energy determined from the  $h[CHN]_nCHh$  clusters (dashed zero line). In both cases, the

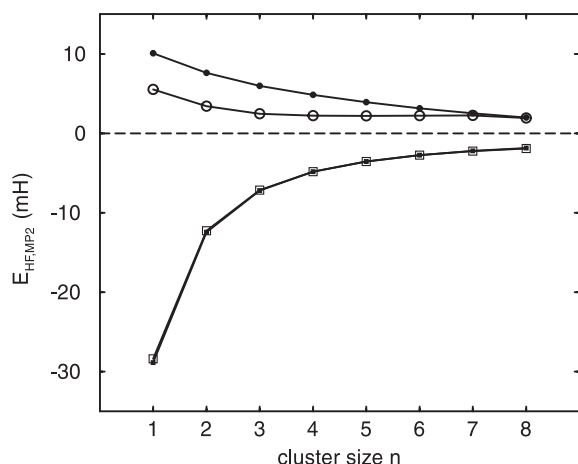


Fig. 3. As in Fig. 2, but for the total Hartree–Fock ( $E_{\text{HF}}$ ; filled symbols) and Möller–Plesset ( $E_{\text{MP2}}$ ; empty symbols) energy per unit cell (mHartree).  $E_{\text{HF}}$  is given relative to the Bloch-orbital-based Hartree–Fock result obtained with the CRYSTAL code,  $E_{\text{MP2}}$  relative to this result plus the correlation contribution from the  $h[\text{CHN}]_n\text{CH}h$  oligomers from Fig. 2.

convergence towards the correct result appears to be much better for the  $\text{H}[\text{CHN}]_n\text{H}$  model cluster, at least for small values of  $n$ . However, whereas the convergence behavior of the HF and MP2 energies is virtually identical for the  $h[\text{CHN}]_n\text{CH}h$  clusters, in case of the  $\text{H}[\text{CHN}]_n\text{H}$  systems, the MP2 energy approaches the limiting value initially faster than the HF energy. We attribute the slower variation of the  $\text{H}[\text{CHN}]_n\text{H}$  energies to the fact that for these clusters, the  $\pi$  bonds are artificially localized. It is also obvious that the convergence for both clusters towards the correct result becomes tediously slow for increasing  $n$  and a mHartree accuracy will be reached far beyond  $n = 10$ , thus making the approach impracticable for accurate total HF or MP2 energies.

Fig. 4 shows the dependence of the correlation energies derived from the  $\text{H}[\text{CHN}]_n\text{H}$  oligomers for different values of the bond alternation. It is seen that the convergence becomes better in the region of the equilibrium structure, but still quite large values of  $n$  have to be chosen to achieve a convergence of 1 mHartree or better.

The problems described in the previous sections can be overcome by interfacing highly efficient correlation codes to Wannier-orbital-based poly-

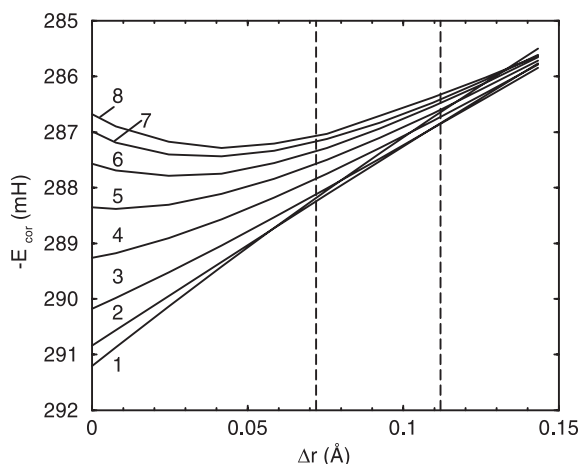


Fig. 4. Correlation energy per unit cell  $E_{\text{cor}}$  (mHartree) of *all-trans* polymethineimine from MP2 calculations of model clusters  $\text{H}[\text{CHN}]_n\text{H}$  in dependence of the bond alternation  $\Delta r$  (Å). The cluster size  $n$  labelling the curves denotes that the energy difference of the oligomers with  $n + 1$  and  $n$  unit cells has been used to evaluate  $E_{\text{cor}}$ . The dashed vertical lines denote the minimum and maximum bond alternation found in the present work.

mer programs. A first step in this direction has been taken as described in a recent paper on the LiH chain [28], but more program development is required to come to a routine approach.

#### 4. Conclusions

A recently developed ab initio Wannier-function-based Hartree–Fock approach was applied to polymethineimine and yields results which are in excellent agreement with those obtained using the more common Bloch-orbital-based method. Various quantities such as the total energy per unit cell, cohesive energy, polymerization energy, and equilibrium geometry parameters were presented at the Hartree–Fock level and different levels of correlation treatment. The bond alternating structure of *all-trans* polymethineimine was found to be slightly more stable than the equidistant structure at all levels of theory. As it is the case for polyacetylene, electron correlations tend to reduce the bond alternation. In contrast to polyacetylene, the *cis-transoid* form of polymethineimine is more

stable than the *all-trans* form by 0.19 eV per CNH unit. We predict C–N and C=N bond lengths of 1.36 and 1.34 Å, respectively, a C–H bond length of 1.10 Å and a lattice constant of 4.07 Å. Further, the heat of polymerisation starting from 1,3,5-triazine is predicted to be 0.22 eV per CHN unit, i.e., the reaction is endothermic in agreement with experimental evidence.

### Acknowledgements

The authors are grateful to Prof. P. Fulde for continuous support and to F. Schautz for helpful discussions and critically reading the paper. Thanks are due to Prof. D. Wöhrle for comments on the early experimental work.

### References

- [1] R. Peierls, Quantum Theory of Solids, Oxford University Press, London, 1955, p. 108.
- [2] D. Wöhrle, Tetrahedron Lett. 22 (1971) 1969.
- [3] D. Wöhrle, Makromol. Chem. 175 (1974) 1751.
- [4] H.R. Christen, F. Vögtle, Organische Chemie, vol. II, Salle and Sauerländer, Frankfurt, 1990, p. 171.
- [5] A. Karpfen, Chem. Phys. Lett. 64 (1979) 299.
- [6] J.Q. Sun, R.J. Bartlett, J. Chem. Phys. 108 (1998) 301.
- [7] H. Teramae, T. Yamabe, J. Chem. Phys. 81 (1984) 3564.
- [8] S. Hirata, S. Iwata, J. Chem. Phys. 107 (1997) 10075.
- [9] J.L. Brédas, B. Thémans, J.M. André, J. Chem. Phys. 78 (1983) 6137.
- [10] D. Jacquemin, B. Champagne, J.M. André, J. Chem. Phys. 108 (1998) 1023.
- [11] M. Springborg, Z. Naturforsch. 48a (1993) 159.
- [12] F.L. Gu, P. Otto, J. Ladik, J. Mol. Model. 3 (1997) 182.
- [13] J. Del Nero, B. Laks, J. Mol. Struct. (Theochem) 394 (1997) 209.
- [14] A. Shukla, M. Dolg, H. Stoll, P. Fulde, Computer Program WANNIER, unpublished.
- [15] A. Shukla, M. Dolg, H. Stoll, P. Fulde, Chem. Phys. Lett. 262 (1996) 213.
- [16] A. Shukla, M. Dolg, P. Fulde, H. Stoll, Phys. Rev. B 57 (1998) 1471.
- [17] A. Shukla, M. Dolg, H. Stoll, Phys. Rev. B 58 (1998) 4325.
- [18] R. Dovesi, V.R. Saunders, C. Roetti, M. Causa, N.M. Harrison, R. Orlando, E. Apra, CRYSTAL95 User's Manual, University of Turin, Italy, 1996.
- [19] M. Yu, S. Kalvoda, M. Dolg, Chem. Phys. 224 (1997) 121.
- [20] H.-J. Werner, P. Knowles, MOLPRO 1994 is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, A. Berning, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, P. Palmieri, K.A. Peterson, R.M. Pitzer, H. Stoll, A.J. Stone, P.R. Taylor.
- [21] A. Abdurahman, M. Albrecht, A. Shukla, M. Dolg, J. Chem. Phys. 110 (1999) 8819.
- [22] P. Pulay, Chem. Phys. Lett. 100 (1983) 151.
- [23] C. Hampel, H.-J. Werner, J. Chem. Phys. 104 (1996) 6286.
- [24] H. Stoll, Phys. Rev. B 46 (1991) 6700.
- [25] H. Stoll, J. Chem. Phys. 97 (1992) 8449.
- [26] H.-G. Elias, Makromoleküle, 5. Auflage, Hüthig and Wepf, Basel, 1990, p. 360.
- [27] J. Del Nero, B. Laks, R. Custodio, Synth. Met. 85 (1997) 1127.
- [28] A. Abdurahman, A. Shukla, M. Dolg, J. Chem. Phys. 112 (2000) 4801.