Conformational solitons in chain molecules; infra-red spectra and *'ab initio'* calculations

M. Del Zoppo and G. Zerbi
Dipartimento di Chimica Industriale, Politecnico, Piazza L. Da Vinci 32, Milano, Italy
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In the search for experimental evidence for conformational solitons or twistons in polymethylene chains, results from *'ab initio'* calculations are presented which suggest that just slight distortions from *trans* planarity of the carbon skeleton of these systems introduce sizeable perturbations in the electronic and dynamical properties of the CH_2 groups. The vibrations of these occur at frequencies slightly higher than those of the transplanar structure and overlap with the absorption of the pinned, classical conformational defects such as *GG*, *GTG'*, end-*TG*, etc. The experimental observations on selectively deuterated stearic acid are presented and discussed.

(Keywords: conformational solitons; infra-red spectra; deuterated stearic acid)

INTRODUCTION

The existence of conformational solitons or 'twistons' has been recently postulated[1] for the explanation of the structural phenomena associated with phase transitions, optical[2,3] and transport properties[4,5] in polymethylene chains such as n-alkanes and fatty acids. The concept of a long, gentle, conformational twist (Utah-twist)[6] thermally activated which may exist in solid orthorhombic n-alkanes and polyethylene has been reformulated in terms of a conformational soliton by Mansfield[7] and Skinner and Wolynes[8]. Such conformational 'excitation' is a collective phenomenon which is the result of an interplay between non-linear intra- and intermolecular forces, extends over approximately 20 CH_2 units[6] and moves along the chain with an estimated velocity of $\approx 10^5$ cm s^{-1} (ref. 7).

The idea of the existence of 'structural' solitons as the origin of various physical properties is not new and has been often discussed by theoretical physicists without strong experimental evidence[9,10]. Recently the existence of solitons in simple hydrogen-bonded organic molecules, as revealed by the infra-red (i.r.) spectrum, has been the subject of an animated debate[11].

In studying the mechanism of 'surface melting' and premelting phenomena, as observed from the vibrational i.r. and Raman spectra of n-alkanes[2] and fatty acids[3], we have used the vibrational i.r. and Raman spectra as a source of experimental data. The data collected do not support the models previously proposed for the understanding of phase transition and melting in these systems[12]; the idea of the existence of conformational 'twistons' seems to be a way to describe the elementary molecular processes associated with some phase transitions in these systems[2,3].

RESULTS AND DISCUSSION

Our first approach was to consider a long polymethylene chain containing a 'twiston' pinned at a given site whose atoms were performing classical small amplitude harmonic oscillations. We calculated both the dipole unweighted density of vibrational states $g(\omega)$ and the i.r. spectrum (frequencies and intensities) and compared the results with the experimental spectrum of n-nonadecane in the pseudorotatory or 'α' phase, which should be the phase where such twistons may exist. A few vibrational transitions were located possibly associated with 'twistons'[1].

The rationale behind our decision of using vibrational spectroscopy as a tool for studying solitonic excitations is the following. Based on the study of temperature-dependent Raman line widths[13], it has been shown that collective librorotational motions of the alkane chains cannot be the origin of longitudinal diffusion and premelting phenomena[12]. Let us then consider a crystallite or a lamella of n-alkane which contains thermally activated twistons, the relative concentration of which depends on their formation energy. For the sake of discussion let us first assume that twistons are pinned within the chain. The vibrational modes topologically localized within the pinned twiston can be calculated in the harmonic approximation and may be matched with the experiments. The dynamical parameters which enter the calculations should change in going from the transplanar to the twiston structure. Basically we have to estimate the conformationally dependent force field (*F* matrix, ref. 14) entering the dynamical calculations. The conformationally dependent kinetic terms are automatically included in the calculation of the so-called *G* matrix[14]. The only way to do this is to carry out *'ab initio'* calculations on model molecules constrained in conformations slightly distorted from the transplanar one and similar to those of the Utah-twist[6].

Vibrational spectra

In the search for conformationally dependent normal modes as spectroscopic markers of twistons, we focused on the absorptions in the i.r. spectra of C–H (C–D) stretchings which generally appear as bands with large intrinsic absorption coefficients and show temperature-dependent frequencies, band shapes and band width[13].

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The frequencies of these modes are known to be conformationally dependent[15,16] for *trans* and *gauche* conformations (or combinations of these).

While the spectrum in the C–H stretching range near 3000 cm^{-1} of an hydrocarbon is overcrowded by many lines which are unresolved and not easily assigned, the C–D stretching range (near 2000 cm^{-1}) of an isolated CD_2 group is simpler. We then studied the spectrum of stearic acid molecules selectively labelled in positions 6 or 13. As shown in *Figure 1*, the antisymmetric and symmetric CD_2 stretching motions (d^- and d^+) of the CD_2 group with *trans* conformation on either sides absorb, respectively, near 2167 and 2090 cm^{-1}. Starting from room temperature the two i.r. lines d^- and d^+ show a noticeable asymmetry on the high frequency side which we label (x) and $(x)'$. While the intensity of $(x)'$ does not increase with increasing temperature, the intensity of (x) noticeably increases starting approximately 3–4°C below melting. Moreover the intensities of d^- and d^+ weaken. The fact that the intensity of $(x)'$ is temperature independent suggests that this absorption arises from one overtone or combination whose identification is impossible because of the complexity of the system. We take instead the absorption (x) as arising from a d^- mode of a new structure generated upon heating while still in the solid. In the melt the broad absorptions peaked at frequencies higher than d^- and d^+ dominate and are the convolution of the pairs $(x)/(d^-)$ and $(x)'/(d^+)$. We had hoped to obtain additional data from the analysis of the temperature-dependent spectra in the CH stretching region of a molecule of n-$C_{36}D_{74}$ which contains, as isotopic impurities, CH and CH_2 groups. The spectra turn out to be very complex and the assignment uncertain.

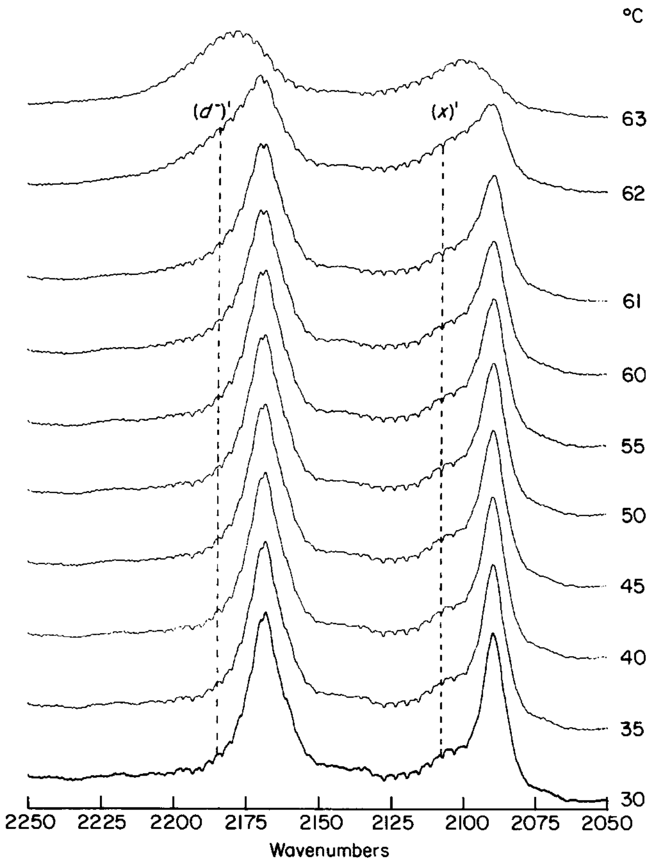


Figure 1 Temperature-dependent i.r. spectra of stearic acid selectively labelled in position 6 in the C–D stretching frequency range

The assignment of the new absorptions and the identification of the new state are the key issue in a search for markers of twistons.

Conformationally dependent electronic properties and vibrational frequencies of CH_2 groups; 'ab initio' *calculations*

From many experimental studies on conformationally distorted polymethylenic chains it is known that in going from *trans* (T, $\tau = 180°C$) to *gauche* (G, $\tau = +/-120°$) conformations and by forming pinned defects of the type GTG', GG, end-TG, etc., the d^+ and d^- modes shift approximately 4–8 cm^{-1} to higher frequencies[13,15,16]. These experiments have been explained in terms of changes of the electronic properties of the C–H bonds as shown by the '*ab initio*' calculations by Schäfer *et al.*[16] and Snyder *et al.*[15].

The issue we are addressing is whether the upward shift of the CD_2 oscillators occurs only when the molecular distortion is T or G or whether only a slight distortion of the carbon skeleton from transplanarity is capable of introducing sizeable electronic perturbations of the C–H group such as to generate an appreciable shift of the stretching frequencies. If this is the case either *gauche* defects or twistons may be the origin of the observed spectra.

We have carried out '*ab initio*' calculations on the simple molecule of butane. All the calculations: geometry optimization and frequency determination were carried out with the 4–31 G basis set, with the GAUSSIAN-82 programs at the Hartree-Fock level. Geometries have been optimized using Berny's gradient method and frequencies have been computed analytically.

Initially we carried out full geometry optimization of the whole molecule, which turned out to be transplanar, and derived geometry, quadratic valence force field, vibrational frequencies and displacements. Many other conformations have been studied. The conformation particularly relevant for this study is the one in which each torsional angle is distorted 15° in sequence from the starting *trans* structure (later we refer to this as the twisted conformation). A small segment of a long helix is thus generated. The geometry of the molecule is then once again fully optimized but for the backbone torsion constrained in such a distorted conformation.

In this paper we report the results most relevant to the purpose of this study, i.e. obtaining data from '*ab initio*' calculations useful in the search for twistons.

Table 1 gives the calculated force constants for first and second neighbour interactions for the butane molecule in the all *trans* conformation.

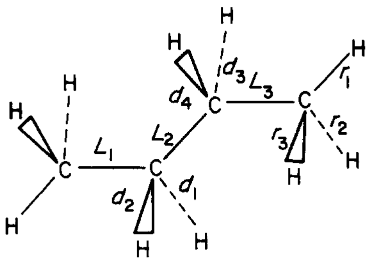
Table 2 gives the first neighbour interactions for the same molecule in three states: transplanar; $\tau = 120°$; and twisted conformation.

We limit our present analysis to the force constants of C–C and C–H bonds.

From *Tables 1* and *2* one can notice that while the interaction between C–C bonds is limited to the first neighbours the interactions between CH_2 groups extend at least to the second neighbours.

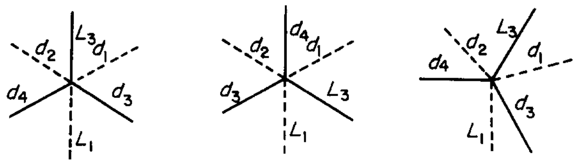
Trans and *gauche* interactions between C–H bonds are consistent in either the transplanar or $\tau = 120°$ cases being negative for $f^{T}_{C\text{-}H/C\text{-}H}$ and positive for $f^{G}_{C\text{-}H/C\text{-}H}$.

Table 1 Force constants (Mdyn Å^{-1}) for first and second neighbour interactions for butane in the *trans* conformation



First neighbour interaction	Second neighbour interaction
$d_1d_4 = d_2d_3 = -0.013$	$d_1r_2 = d_2r_3 = 0.015$
$d_1d_3 = d_2d_4 = 0.015$	$d_1r_3 = d_2r_2 = -0.001$
	$d_1r_1 = d_2r_1 = -0.002$

Table 2 First neighbour interactions for butane



Trans	$\tau = 120°$	Twist
$d_1d_4^T = d_2d_3^T = -0.013$	$d_1d_4^G = 0.017$	$d_1d_4 = -0.010$
	$d_2d_3^G = 0.017$	$d_2d_3 = -0.010$
$d_1d_3^G = d_2d_4^G = 0.015$	$d_1d_3^T = -0.014$	$d_1d_3 = 0.059$
	$d_2d_4^G = 0.018$	$d_2d_4 = 0.007$
$L_1L_1 = L_3L_3 = 4.839$	$L_1L_1 = L_3L_3 = 4.803$	$L_1L_1 = L_3L_3 = 4.831$
$L_2L_2 = 4.785$	$L_2L_2 = 4.779$	$L_2L_2 = 4.578$
$L_1L_2 = L_2L_3 = 0.125$	$L_1L_2 = L_2L_3 = 0.160$	$L_1L_2 = L_2L_3 = 0.107$
$L_1L_3^T = -0.001$	$L_1L_3^G = 0.031$	$L_1L_3 = 0.000$

Table 3 C–H stretching frequencies (cm^{-1})

Trans	Twist	$\tau = 120°$
3162	3110	3162
3169	3147	3162
3175	3174	3178
3178	3175	3180
3181	3223	3200
3204	3227	3201
3237	3236	3238
3242	3240	3240
3243	3250	3252
3246	3251	3265

For the twisted molecule the values of $f_{\text{C–H/C–H}}$ are intermediate.

Particularly interesting is the fact that for the twisted molecule the diagonal force constant for the central C_2–C_3 bond is smaller than for the *trans* or $\tau = 120°$ case indicating that the C–C bond weakens or relaxes upon twisting.

The calculated frequencies are listed in *Table 3* and their behaviour is reported in *Figure 2*.

The assignment of each energy level to the normal modes of the molecule is easy for the *trans* case, when molecular symmetry helps. By changing the torsional angle the symmetry lowers and vibrational coupling occurs throughout the whole molecule. By analysing vibrational amplitudes one can still conclude that some modes are topologically more localized on some of the CH_2 groups. Some modes are even localized on single C–H groups. This localization takes place because of the geometrical distortion of the molecule. The correlation between the vibrational frequencies in the different structures (*Figure 2*) points out that the antisymmetric A_u CH_2 stretching (d^-) shifts upwards in going from the transplanar to the twisted geometry and the B_u CH_2 stretching (d^+) shifts downward. The spectroscopic consequence is a depletion of the absorption intensity due to CH_2 d^- and CH_2 d^+ modes and the generation of new absorptions at higher and lower frequencies, respectively. A temperature-dependent absorption on the high frequency side of d^- is observed (x) while no absorption is observed below d^+. We thus focus our attention on d^-.

CONCLUSIONS

'*Ab initio*' calculations derived from the study of n-butane suggest that: the electronic and vibrational properties of C–H bonds are strongly dependent on the conformation of the C–C skeleton. Let us refer to the electronic interactions between σ bonds as 'σ conjugation'[17]. If the concept of *trans* effect in 'σ conjugated' systems is considered, slight deformation from the *trans* structure modifies 'σ conjugation' and changes the minimum energy structure, force constants and dynamics of the system. This is particularly true when a collective slight distortion of the chain is considered. Also, 'σ conjugation' is shown to extend further than the first neighbour[18], thus indicating the collective character of such an

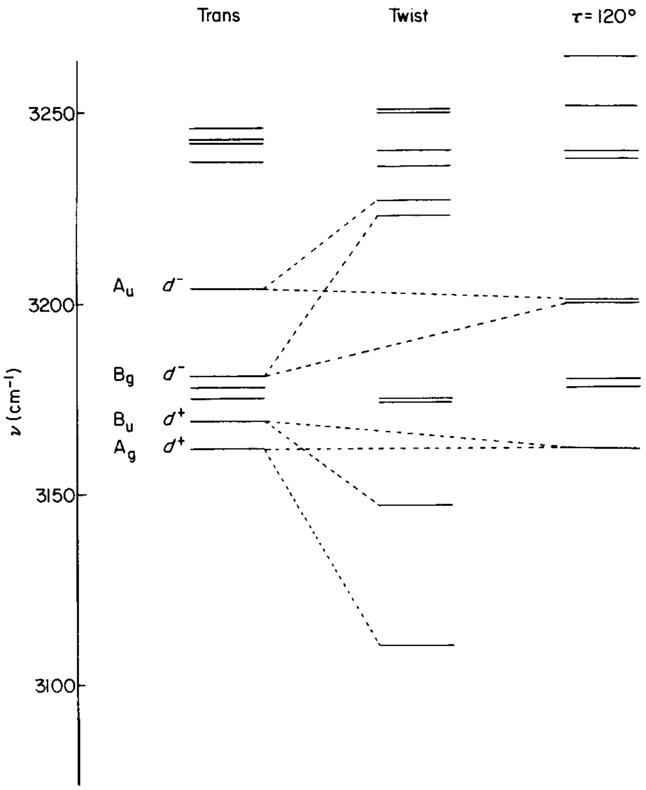


Figure 2 Schematic representation of the calculated frequencies, ν, in the C–H stretching region of the butane molecule constrained in different conformations

electronic effect and of the derived dynamical and spectroscopic phenomena (diagonal force constants etc.).

From the view point of twistons and spectra this study gives the following results.

1. The experimental observation of the temperature-dependent i.r. absorption in the d^- CD_2 stretching region is not unequivocal evidence for the formation of classical pinned defects of the type *GG*, *GTG'* and end-*TG* as so far traditionally believed. As a matter of fact, by using the frequency of the CD_2 rocking mode as a marker for the *T*/*G* conformational distortions[2,19], it has already been concluded that at either side of the CD_2 group the conformation is mainly transplanar[3]. Instead, the existence of slightly twisted chains such as the twistons might account for these absorptions.
2. The fact that solitons or twistons are not pinned but may be mobile along the chain does not hinder the proposed interpretation. As already discussed in reference 1, the band width is inversely proportional to the vibrational lifetime of each normal mode. If the velocity of the twiston is small the vibrational lifetime is long enough to give rise to an observable i.r. band. If the twiston moves along the chain very rapidly the vibrational lifetimes are too short and the band broadens and flattens in a broad continuum. The fact that a band with a width at half maximum of $\approx 20\ \mathrm{cm}^{-1}$ is experimentally observed sets an upper limit to the velocity of the twiston estimated at $10^4\ \mathrm{cm\ s}^{-1}$, in acceptable agreement with the theoretical value[1].
3. This work presents a possible model which seems to account for the observed spectroscopic and diffusion phenomena for polymethylene chains in the solid orthorhombic lattice. The aim of the calculations presented was to find additional information which may support or refute the existence of conformational twistons. The evidence collected is neither compelling nor completely negative. The model needs to be supported or dismissed by other physical techniques such as solid state nuclear magnetic resonance or neutron scattering.

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REFERENCES

1 Zerbi, G. and Longhi, G. *Polymer* 1988, **29**, 1827

2 Zerbi, G., Magni, R., Gussoni, M., Holland Moritz, K., Bigotto, A. B. and Dirlikov, S. *J. Chem. Phys.* 1981, **75**, 3175

3 Del Zoppo, M. and Zerbi, G. *Polymer* 1989, **30**, 658

4 Ungar, G. and Keller, A. *Colloid Polym. Sci.* 1979, **90**, 257

5 Piazza, R. and Zerbi, G. *Polymer* 1982, **23**, 1921

6 Mansfield, M. and Boyd, R. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 1227

7 Mansfield, M. *Chem. Phys. Lett.* 1980, **69**, 383

8 Skinner, J. L. and Wolynes, P. G. *J. Chem. Phys.* 1980, **73** (8), 4015; Skinner, J. L. and Wolynes, P. G. *J. Chem. Phys.* 1980, **73** (8), 4022

9 Davydov, S. A. in 'Solitons in Molecular Systems' (Ed. D. Reidel), Dordrecht, Amsterdam, 1985

10 Takeno, S. (Ed.) 'Dynamical Problems in Soliton Systems', Springer Verlag, Berlin, 1985

11 Scott, A. C. in 'Dynamical Problems in Soliton Systems' (Ed. S. Takeno), Springer Verlag, Berlin, 1985, p. 224; Careri, G., Buontempo, U., Galluzzi, F., Scott, A. C., Gratton, E. and Shyamsunder, E. *Phys. Rev. B, Condens. Matter* 1984, **30** (8), 4689; Dellepiane, G., Abbate, S., Bosi, P. and Zerbi, G. *J. Chem. Phys.* 1980, **73**, 1040

12 Del Zoppo, M. and Zerbi, G. to be published

13 Zerbi, G., Roncone, P., Longhi, G. and Wunder, S. *J. Chem. Phys.* 1987, **89**, 166

14 Wilson, E. B., Decius, J. L. and Cross, P. C. 'Molecular Vibrations', McGraw Hill, New York, 1955

15 Aljibury, A. L., Snyder, R. G., Strauss, H. L. and Raghavachari, K. *J. Chem. Phys.* 1986, **84** (12), 6872

16 McKean, D. C. *Chem. Soc. Rev.* 1978, **7**, 399; Schäfer, L., Siam, K., Ewbank, J. D. and Osawa, E. *J. Mol. Str. (Theochem.)* 1986, **139**, 125

17 Dewar, M. J. S. *J. Am. Chem. Soc.* 1984, **106**, 669

18 Ricard, L., Abbate, S. and Zerbi, G. *J. Phys. Chem.* 1985, **89**, 4793

19 Snyder, R. G. and Poore, M. W. *Macromolecules* 1973, **6**, 709