



A theoretical approach to the influence of the macrocycle conformation on the molecular electronic structure in Mg-porphyrins

L.A. Poveda^a, V.R. Ferro^{a,b}, J.M. García de la Vega^b & R.H. González-Jonte^b

^aCentro de Investigaciones de Energía Solar, Santiago de Cuba 90800, Cuba; ^bDepartamento de Química Física Aplicada, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Received 8 December 1999; Accepted 15 September 2000

Key words: distortion energies, nonplanar distortion modes, porphyrin macrocycle, semiempirical calculations, UV-visible spectra

Summary

Nonplanar saddled (*sad*) ruffled (*ruf*) and domed (*dom*) conformations of the Mg-porphyrin (MgP) macrocycle in several degrees of deformation have been computed. These symmetrical distortion modes were induced in unsubstituted macrocycle using molecular definitions for calculations which permits us to achieve a systematical variation of the nonplanarity varying only a convenient geometrical parameter of the molecule. Series of nonplanar macrocycles like those synthesized in previous works employing peripheral substitutions are obtained. The procedure here used to induce deformations gives the possibility of investigating the modulator role of the out-of-plane distortions on the geometry and electronic properties of the porphyrin avoiding additional influences due to the substituents or the surrounding protein scaffolding.

Introduction

Crystallographic studies on the photosynthetic antenna and reaction centers as well as on heme proteins reveal that the natural porphyrin macrocycle exists in nonplanar forms which are strongly modulated by the steric constraints imposed by the protein matrix [1, 2]. The named ‘conformational effects’ expressed in changes in optical transitions, redox potentials, axial ligand affinity, Raman frequencies, photophysical properties, etc., are increasingly being investigated to determine whether these nonplanar porphyrin distortions of the protein have any significance in the ‘in vivo’ dynamical functional properties of the tetrapyrrole cofactors [1–20].

The complexity of the interactions present in biological systems gives rise to the macrocycle distortions in several ways. A useful procedure for characterizing and quantifying a natural tetrapyrrolic deformation consists in simulating this more complicated out-of-plane structure as an special linear combination of simple symmetrical distortion modes [1, 12]. This method, named normal-coordinate structural decom-

position (NSD), simplifies the description of these geometrical complex structures by means of the characterization of some elementary deformations which resemble, in static form, the out-of-plane normal vibrations of the macrocycle [1, 12].

Synthetic efforts during the last decade have established an exact methodology for obtaining such symmetrical distortion modes of the macrocycle using a new concept: ‘conformational designed’ porphyrins, whereby the introduction of multiple substituents on the porphyrin periphery induces large deformations of the macrocycle [1–20]. The degree and type of deformation can be modulated by the type, size and orientation of the substituents located in β and *meso* sites of the macrocycle. The nonplanar modes most commonly reported in the literature are those named *sad* (B_{2u} vibrational mode) and *ruf* (B_{1u} vibrational mode). In *sad* conformation the pyrrole rings are alternately tilted above and below the average plane through the 24 atoms of the porphyrin core while the *meso* atoms lie approximately in that plane. This distortion appears when the macrocycle is sterically crowded at the periphery as occurs

in dodecaphenylporphyrin [4, 14–16] and octaethyl-tetraphenylporphyrin [3–20]. In *ruf* form, alternate pyrrole rings are twisted clockwise and anticlockwise around the center-nitrogen axis while the *meso* carbon atoms sit alternately above and below the average porphyrin plane. Large deviations from planarity in *ruf* mode are observed in tetra-substituted porphyrins when the substituents are sufficiently bulky as occurs in tetraterbutylporphyrin [9]. Another important deformation named *dom* identifies the pyramidal form adopted by the macrocycle when an axial substituent is ligated through the central metal.

The most common consequence of the macrocycle distortion refers to a red shift in Q and B bands of the UV-visible absorption spectra if compared to what occurs in more planar molecules. INDO/S calculations and cyclic voltammetry measurements attribute this effect to a migration of the frontier orbital in the sense of a smaller gap between HOMO and LUMO [3–5, 7, 10, 17]. An expanding body of optical data confirms that the spectral shift follows a nonlinear behavior when nonplanarity increases and the Q bands appear more shifted than the B ones [3–5, 7, 10, 17]. On the other hand, recent studies employing time-resolved spectroscopy reveal that the ability of the macrocycles to transverse multiple conformational surfaces in the excited states is the principal cause of the abnormal photophysical behavior observed in distorted porphyrins [21, 22]. Conformational excursion induced under excitation is possibly due to the low energetic barrier among the different conformer of the macrocycle resulting in a mixture of the simple symmetrical distortion modes.

The experimental characterization of nonplanar porphyrins deals with an essential difficulty in the study of conformational effects: the changes in geometry and electronic properties of the macrocycle are determined by the substituents as well as by the molecular environment. The electron-withdrawing-donating capacities of the substituents may cause energetic shifts of the frontier orbital and absorption bands. On the other hand, the steric repulsion between near substituents of the macrocycle periphery may alter the typical bond distances and angles of the tetrapyrrole ring in an irregular manner. The study of the unsubstituted distorted macrocycle does not have sense in experimental samples, but it can be approached employing theoretical frameworks which permit the investigation of isolated molecular systems in several conformations.

In the present paper we calculate some models of the unsubstituted porphyrin macrocycle which is distorted in several degrees of *sad* (saddle), *ruf* (ruffled) and *dom* (domed) distortions. By means of an appropriate definition of the internal coordinates of the 25 atoms of the unsubstituted Mg-porphyrin we may induce a systematical out of plane distortion of that macrocycle, thus varying only a convenient geometrical parameter. These models permit the evaluation of the variation of the geometry and electronic properties which are exclusively determined by the nonplanar distortion of the tetrapyrrole ring.

Models and method

In a previous work we demonstrated the capability of the PM3 method for predicting the nonplanar distortion modes for highly peripheral substituted porphyrins [23]. In that theoretical study *sad* and *ruf* distortions were investigated as caused by peripheral substitutions and varying the size and electronic configuration of the metal located into the macrocycle cavity. In the present paper we take advantage of the facilities that the theoretical modeling offers and adopt a different methodology for causing the macrocycle distortions. By means of appropriate definitions of the internal coordinates of the unsubstituted MgP molecule we achieve exact symmetrical distortions, *sad*, *ruf* or *dom* varying systematically only one geometric parameter which is characteristic of each distortion mode (see Figure 1). Once this parameter is frozen, a distorted macrocycle was obtained in several degrees of *sad*, *ruf* and *dom* deformations while all the others parameters were optimized.

In order to evaluate the degree of distortion we have taken the average atomic deviations of the 25 atoms of the metal-macrocycle with respect to the mean plane of the molecule (δ). This magnitude was defined as: $\delta = 1/25 \sum d_i$; where d_i is the distance of the *i*-atom with respect to the main plane of the molecule. A similar magnitude, the root-mean-square out-of-plane (RMS OOP) distances, has been used by other authors for measuring the degree of nonplanar distortion of the macrocycle as a whole with a reliable description of the deformations regardless of the specific type of distortion [24].

The distorted MgP molecules were optimized using the PM3 [25] hamiltonian included in MOPAC program (6.0 version) [26]. The EF (Eigenvector Following) routine [27] for minimum search was used

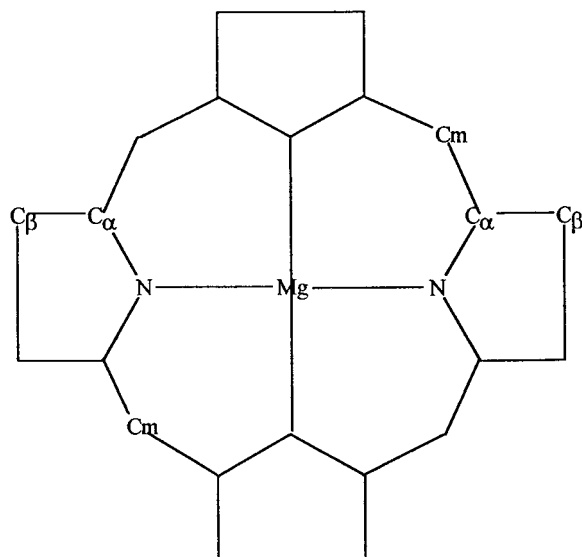


Figure 1. Notation used for defining and controlling the different conformations studied in this work. In *sad*, *ruf* and *dom* conformers were fixed the non-bonding distances $C\beta \dots C\beta$, the non-bonding angles $Cm \dots Mg \dots Cm$ and the bond angles $N-Mg-N$, respectively. The atoms in the molecules were adequately labeled in order to achieve the desirable geometrical control during the optimization.

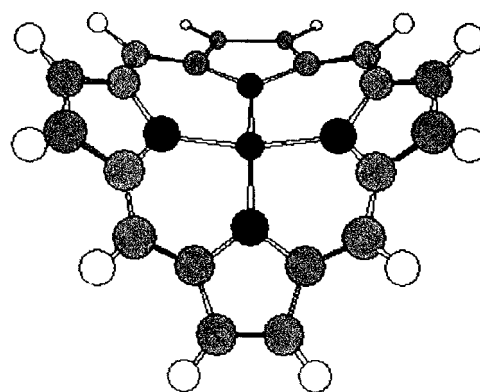
with a maximum step size of 0.02 (Å or radians). Whenever it was possible, the bond lengths and bond angles of the macrocycle were optimized using D_{4h} symmetry restriction. The optimization threshold for the value of gradient norm was fixed to 0.01 kcal/mol/(Å or radians). CNDO/S [28] semiempirical method (implemented in the NDOL, TC-HAVANA package [29]) was used to obtain the UV-visible absorption spectra in CI calculations with 50 occupied and 50 unoccupied orbitals for making single excited configurations.

Results and discussion

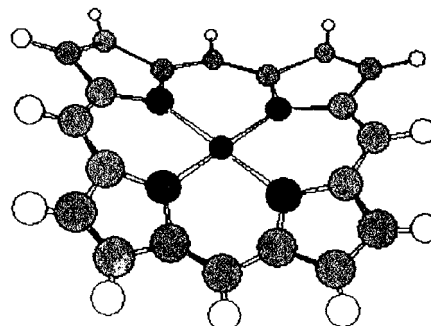
Geometry of the distorted macrocycle

As an example, Figure 2 shows the optimized structures of the unsubstituted MgP molecule in *sad*, *ruf* and *dom* distorted modes. The geometrical and energetic information of the corresponding conformers was reported in order to facilitate the reproduction of our calculations.

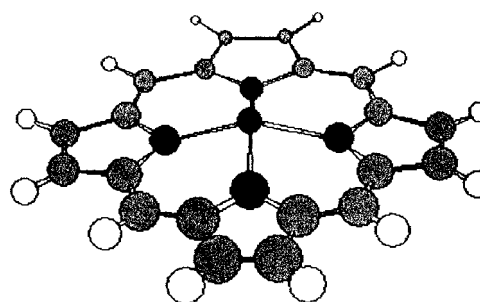
For each symmetrical nonplanar mode we have obtained a set of eight well-defined deformations. The displacements of β -carbons in *sad*-shaped macrocycles reach values between 0.482 and 1.294 Å, and



sad
($\Delta H_f = 203.7 \text{ kcal.mol}^{-1}$) ($\delta = 0.789$) ($d_{C\beta \dots C\beta} = 7.500 \text{ Å}$)



ruf
($\Delta H_f = 189.2 \text{ kcal.mol}^{-1}$) ($\delta = 0.313$) ($a_{Cm \dots Mg \dots Cm} = 160.0^\circ$)



dom
($\Delta H_f = 207.7 \text{ kcal.mol}^{-1}$) ($\delta = 0.107$) ($a_{N-Mg-N} = 150.0^\circ$)

Figure 2. Molecular structure of unsubstituted Mg-porphyrin in *sad*, *ruf* and *dom* distortion modes. ΔH_f is the corresponding heat of formation. Geometrical parameters are defined in the text.

the average atomic deviations of the core atoms from the porphyrin mean plane vary in the interval 0.293–0.753 Å. The pyrrole tilt angles show differences between 7.7° and 25.1° with respect to the porphyrin mean plane. They correspond to a wide range of reported *sad*-shaped porphyrins which have been obtained varying the bulkiness and size of the peripheral substituents [3–20]. In well-defined *ruf* modes here calculated, the *meso* carbons appear deviated from the mean plane and take values in the interval of 0.591–0.970 Å, with an average displacement of the 24 atoms of the macrocycle from 0.313 Å to 0.504 Å. The pyrrole rings exhibit twisted angles which vary in the range of 21.2° to 31.1°. The named ruffling dihedral angle defined by dihedral angle $C\alpha-N...N-C\alpha$ for opposite pyrroles reach values between 32.5° and 57.3°. A similar set of *ruf* distortions have been obtained in *meso*-tetrasubstituted Ni-porphyrins for which the substituents vary in size when the steric crowding at the periphery is increased [9]. The calculated *dom* structures present a systematical variation of the metal deviation from the mean plane (0.304 Å to 0.608 Å) simulating different axial substitutions.

In order to gain a more detailed comprehension of the deformation process we split the δ magnitude in its components corresponding to the average atomic deviation of the different kinds of atoms of the macrocycle. We consider $\delta\beta$, $\delta\alpha$, δ_N , δ_m and δ_{Mg} as the average atomic deviations of the C β , C α , N, C m and Mg atoms, respectively. Figure 3 shows the variation of some of these magnitudes for calculated *sad*, *ruf* and *dom* distortion modes as a function of the degree of deformation.

A characteristic deviation pattern for each non-planar mode is evident. In *sad* form the β , α and N positions are displaced from the mean plane to different degrees as the deformation increases. The β -carbons are deviated notably from the plane, $\delta\beta$ showing an slight nonlinear behavior, indicating that such positions are more deviated as the molecule is more distorted. On the other hand, the α -carbons and nitrogens appear less deviated in all deformation intervals and δ_N shows a saturate behaviour as the distortion increases. This suggests a rigidity of the central region of the macrocycle with respect to that mode which may be due to the presence of the metal into the cavity. In *ruf* distortion mode the *meso*, α and β positions are displaced almost in the same way for all the deformed macrocycles (the slopes of the linear fits are practically equal) suggesting a more collective character of the *ruf* mode if compared to the *sad* form.

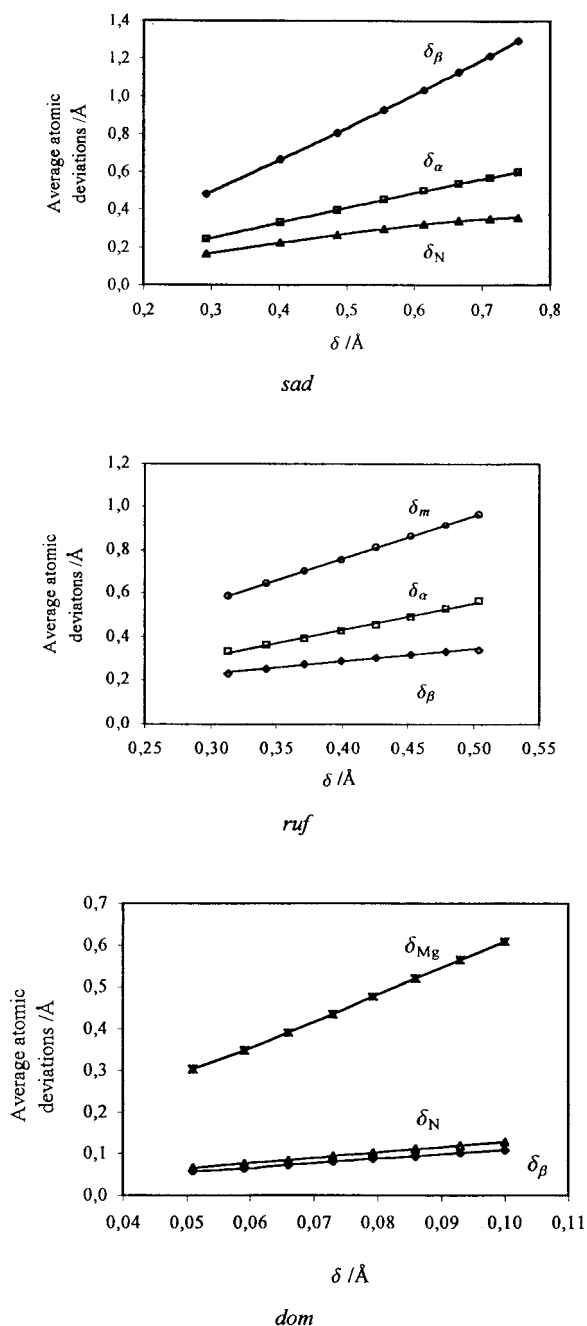


Figure 3. Variation of $\delta\beta$, $\delta\alpha$, δ_N , δ_m and δ_{Mg} with respect to the degree of the macrocycle distortion for *sad*, *ruf* and *dom* distortions.

In *dom* distortion the metal can be significantly deviated from the plane while a negligible distortion of all the other atoms of the macrocycle is observed. This indicates how difficult is to deform the 24 atoms of the tetrapyrrole ring at the expense of deviating the central metal. In other words, the axial displacement of the metal is severely limited by the collective action of all the other atoms of the macrocycle.

The differences between *sad* and *ruf* distortions suggest that the out-of-plane deviations which occur in *sad* mode remove the peripheral steric strain more efficiently than that required to relieve the strain with the *ruf* distortion. In fact, *sad* distortion is most commonly observed when the macrocycle is dodecasubstituted, having sp^2 -bonded groups in the four *meso* positions. Taking into account that in both cases the *meso* carbons remain in the porphyrin plane and the β -carbons can be displaced significantly from the plane, we can obtain a severe *sad* deformation with a minimal steric interaction. On the other hand, in *ruf* distortion the *meso* carbon deviations caused by sp^3 -bonded substituents at the *meso* positions also deviate from the plane the other adjacent pyrrole sites.

In Figure 3, we can appreciate that the points over $\delta\beta$, $\delta\alpha$ and δ_N curves in *sad* form appear spaced for small distortions, but tend to join each other as the deformation increases. The points over δ_m , $\delta\alpha$ and $\delta\beta$ curves in *ruf* mode keep a constant distance in the all deformation interval. This suggests that *sad* mode is easy to induce for small distortions and becomes more difficult as the deformation increase, while the *ruf* distortion exhibits the same degree of difficulty through all the deformation interval.

The nonplanar deformations may induce significant variations in some bond distances and angles of the macrocycle. The Me-N bond lengths which are shortened when deformation increases are a good proof that the macrocycle exists in *sad* and *ruf* modes. This fact has been used to diagnose nonplanar modes in solution which have been previously found in crystal samples [4]. In the models here calculated the Mg-N bonds distances decrease for greater *sad* and *ruf* distortions so that they take values in the intervals of 1.925–1.856 Å and 1.912–1.874 Å, respectively.

Figure 4 shows how some selected parameters of the macrocycle vary as a function of the degree of deformation for *sad* and *ruf* distortion modes.

In both *sad* and *ruf* modes the variations in bond distances and angles of the macrocycle follow the same behavior as the nonplanarity increases: both the N-C α bond distance and the C α -C $_m$ -C α angle

decrease, while both the C α -C $_m$ and C β -C β bond distances and the C α -N-C α angle increase. Similar variations in bond distances and angles of the macrocycle have been reported for NiTC $_x$ TPP ($x = 5, 6, 7$) which exhibits increasing *sad* deformation when x increases [17]. In spite of the phenomenological similarities described above (Figure 4), there are differences concerning the structural mechanism through which both kinds of distortion may occur. We can understand such differences taking into account that both distortions occur along different directions. The *sad* mode bends the N-M-N bond directions giving rise to a remarkable variation in C α -N-C α and N-C α geometric parameters, and expands the C β -C β bond distances to a large extent due to the opposite displacement of the adjacent pyrrole rings. The *ruf* form bends the nonbond C $_m$...Mg...C $_m$ directions causing a twisting of the pyrrole rings. As consequence, the *meso* bridge geometric parameter is the most affected (see Figure 4). Thus, the *sad* distortion gives rise to a major strength on the macrocycle geometry than that obtained with the *ruf* mode.

The relationships between selected structural parameters and δ magnitude in several degrees of deformation show differences for *sad* and *ruf* distortions. In *sad* forms the structural parameters which better correlate with δ are the N-C α bond distance ($r = -0.991$), the C α -N-C α bond angle ($r = 0.987$) and the core size (defined as the length of the projection of the metal-nitrogen bond into the average plane of the pyrrole nitrogens) ($r = -0.998$). The variations in such structural parameters as *sad* distortion increases show good correlations with several structural sensitive Raman lines which are shifted toward low frequencies when compared to planar porphyrins [15–17, 20]. The correlation analysis between the structural parameters and δ in *ruf* nonplanar macrocycles shows a more homogeneous behavior than that observed for the *sad* mode. All the structural parameters are highly correlated with the average atomic deviations corresponding to the collective character of *ruf* mode. Therefore, we can argue that the structural marker modes in *ruf* distortion are determined by the total nonplanar distortion rather than by an specific structural parameter of the macrocycle. A similar result was obtained in a previous Resonance Raman study in a series of deformed nitro-octoethylporphyrins which exhibit different conformers (*sad*, *ruf* or mixed) with different degrees of nonplanarity [24].

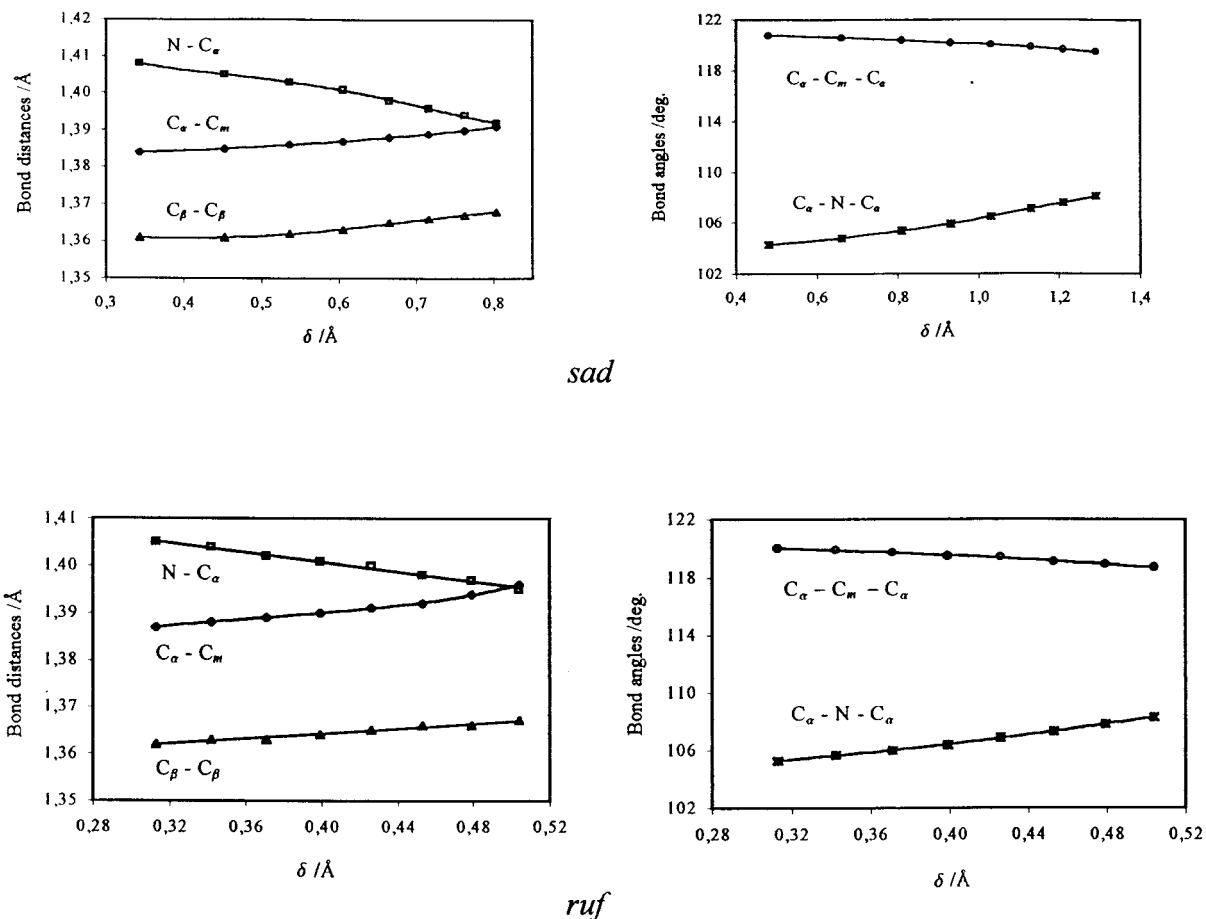


Figure 4. Relationships between the degree of deformation in *sad* (top) and *ruf* (bottom) modes and some structural parameters of the macrocycle. Bond distances (left panels): $N-C_\alpha$, $C_\alpha-C_m$, $C_\beta-C_\beta$; bond angles (right panels): $C_\alpha-C_m-C_\alpha$, $C_\alpha-N-C_\alpha$.

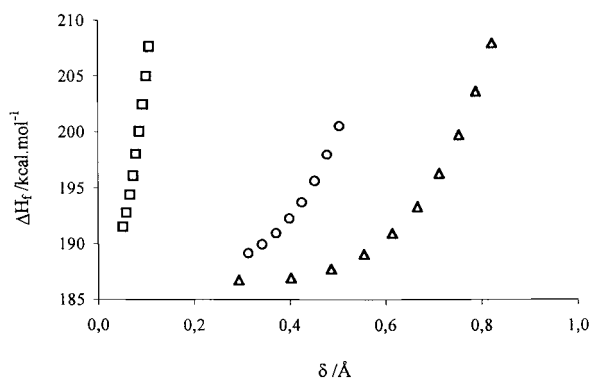


Figure 5. Variation in the heat of formation (ΔH_f) of the MgP when the degree (δ) of *sad* (Δ), *ruf* (\circ) and *dom* (\square) macrocycle distortions varies.

Energetics of the macrocycle distortions

The variations of the heat of formation with respect to δ for *sad*, *ruf* and *dom* deformations are shown in Figure 5.

From the energetic point of view in almost all deformation intervals the nonplanar modes have the following order: *dom* > *ruf* > *sad*. This order is maintained excepting for high distortions in which the *sad* mode becomes more difficult to induce than the *ruf* one. The energetic needs associated with the deformation process of the macrocycle by deviation unit are ca. 300 and 60 kcal mol⁻¹ Å⁻¹ for *dom* and *ruf* distortions, respectively. A particularly interesting case is presented for *sad* distortion of the MgP. In ΔH_f vs. δ behavior two sections are distinguished: the first one belongs to small *sad* distortions of the macrocycle with an energy need of ca. 5.0 kcal mol⁻¹ Å⁻¹, while the second section belongs to high deformations

with $\sim 70 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. This suggests that small *sad* distortions can be induced by very weak strains such as metal-nitrogen attractions if the metal size is relatively small. In fact, the PM3 full optimization of the MgP occurs in *sad* conformation with $\delta \sim 0.3 \text{ \AA}$ and a previous investigation on nonplanar porphyrins has concluded that small sized metals favour the out-of-plane *sad* distortion [15]. On the other hand, the increase in *sad* deformation makes more difficult to induce it. Additional external influences like substitutions or environment constraints will be necessary in that case.

In Figure 6 the variations of the heat of formation with respect to the different component of δ for each distortion mode are shown.

As it can be observed, the β -carbons can be deviated from the plane almost freely for the *sad* mode, while the energetic difficulties of that distortion are related with the nitrogens and α -carbons. The *ruf* mode shows distinct features. In this case the energetic requirements of the deformation are almost equally distributed among the different kinds of atoms which are deviated from the plane. For small deformations a *sad* mode is easier to induce than a *ruf* mode, whereas this situation is inverted as deformation increases. This change is produced because the central region of the macrocycle exhibits a great rigidity when deformation increases. We can understand this considering that a systematical increase of *sad* out-of-plane mode bends the N-M-N bond directions giving rise to a dramatic decrease of the core size. While the systematical twisting of the pyrrole rings for an increased *ruf* deformation originates an stretching of the N-M-N bond directions the core size being, in this case, less diminished. In fact, in the structures here calculated the core size diminishes from 1.918 \AA to 1.825 \AA and from 1.912 \AA to 1.874 \AA when *sad* and *ruf* distortions increase, respectively.

As regards the *dom* mode, the central metal can be displaced from the plane fairly freely due to the weakness of the interactions of this atom with the pyrrole ligands, but this geometry deformation is restricted by the out-of-plane distortion of all the other atoms of the tetrapyrrole ring.

Mix of conformers

Several changes in porphyrins, such as oxidation, coordination state of the central metal or photoexcitation, may influence the relative energies of the low-energy conformers allowing the mix of the symmetrical dis-

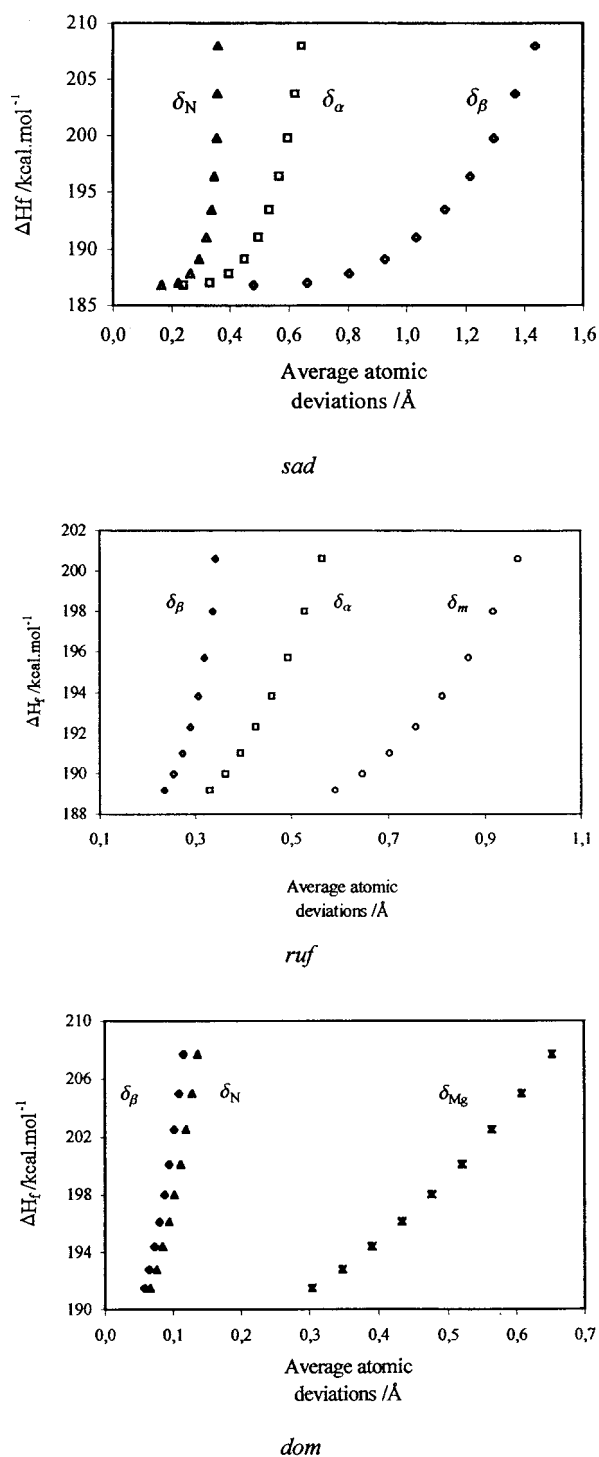
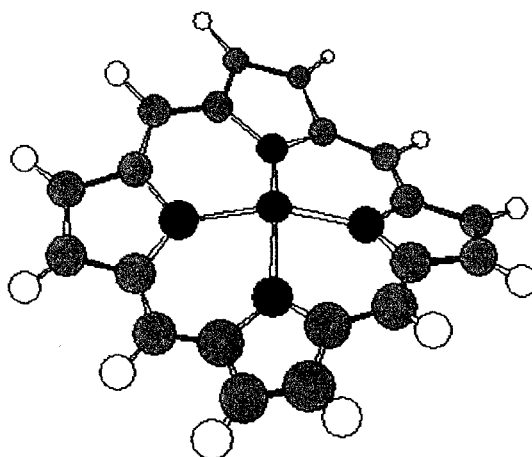
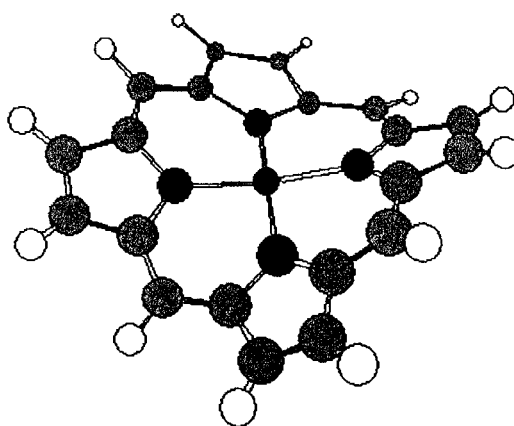


Figure 6. Variation in the heat of formation of the distorted macrocycle through the different components of the average atomic deviations: δ_β (\diamond), δ_α (\square), δ_N (\triangle), δ_m (\circ) and δ_{Mg} (*).

*gab*

($\Delta H_f = 204.3 \text{ kcal.mol}^{-1}$) ($\delta = 0.274$) ($a_{N-Mg-N} = 152.0^\circ$, $a_{Cm \dots Mg \dots Cm} = 177.8$ and 143.0°)

*sadruf*

($\Delta H_f = 187.9 \text{ kcal.mol}^{-1}$) ($\delta = 0.397$) ($d_{C\beta \dots C\beta} = 8.164 \text{ \AA}$, $a_{Cm \dots Mg \dots Cm} = 174.1^\circ$)

Figure 7. Molecular structure of unsubstituted Mg-porphyrin in the mixed conformational modes *gab* and *sadruf*. ΔH_f is the corresponding heat of formation. Geometrical parameters are defined in the text.

tortion modes of the macrocycle [1, 12, 13, 21, 22]. Such structural modifications have been largely investigated due to their functional significance in the charge transfer process and the oxygen transport. A mixture of *dom* and *ruf* modes have been observed in disubstituted nickel-porphyrins [12]. The resulting conformation is called *gab* (*dom* + *ruf*) in which the macrocycle is folded about a line through two opposite bridging *meso* carbons of the porphyrin ring. CuOETPP whose neutral form exists in *sad* conformation, adopts an additional *ruf* conformation when it is oxidized (*sadruf* mixed conformation). Figure 7 shows 3D representations of the optimized geometries in *gab* and *sadruf* mixed conformations. Figure 8 con-

tains a diagram for illustrating the atomic deviations of the 25 atoms of the core for both *gab* and *sadruf* mixed structures here calculated. The results of the Figures 7 and 8 correspond to the same structures.

It is interesting to explain how the *gab* conformation shown in Figure 7 was obtained. In *dom* mode the metal is located above the plane in opposite direction to all the other atoms of the macrocycle, while the *meso* carbons lie on the plane. In order to calculate a pure *dom* structure, it was necessary to restrict the *meso* positions so that they could lie on the mean plane of the macrocycle. On the contrary, the conformation fell into a *gab* mixed distortion, when two opposite *meso* bridges are more deviated than all the

others (see Figure 8). That is, a metal deviation from the plane adds a *ruf* mode to the induced *dom* when *meso* sites are left free to the optimization. This presumably occurs because the *dom* mode which is only induced by metal deviations exists in an unstable conformation which is stabilized when the macrocycle is much more relaxed. We can argue that axial ligated porphyrin which do not have *meso* substitution tend to adopt a *gab* distortion.

Axial coordination and non-*meso* substitutions are found frequently in natural porphyrins such as chlorophyll, cytochromes or heme proteins, and the crystallographic data conclude that the distortions observed in the majority of such porphyrinic protein complexes fall into the *ruf* category [1, 8]. Thus, our results suggest that the conformation of the porphyrin cofactor is strongly determined by the protein micro-environment and that the axial ligation plays an important role in the conformation of the natural macrocycle.

The possibility of transverse multiple conformers in the multiconformational surfaces is due to the low barrier that exists among simple symmetrical nonplanar modes. An energetic diagram of the relative energy among selected macrocycles distorted into a *sad*, *ruf* and *dom* modes, and their corresponding mixed conformers is shown in Figure 9. Each point indicates the heat of formation for each pure or mixed structure as predicted by the PM3 method.

The addition of the *ruf* conformer to the pure *dom* mode gives a *gab* structure which is more stable than the *dom* one in $\sim 1 \text{ kcal.mol}^{-1}$. We select as *dom* macrocycles those with N-Mg-N bond angles of 152° and in which the obtained *gab* conformation has an additional twisting of the pyrrole rings of 30° . The reported *ruf*-deformed molecule in Figure 9 has twisted pyrrole rings of 33° while the *sad* conformer corresponds to the unsubstituted Mg-porphyrin which exists -accordingly with our PM3 calculations- in the *sad*-shaped conformation with pyrroles tilting from the mean plane of the molecule in 22° . The *sadruf* mixed conformation shown in Figure 9 was obtained locating propyle chains in the *meso* sites of Mg-porphyrin thus resulting a more unstable structure ($\sim 1 \text{ kcal mol}^{-1}$) with an additional *ruf* deformation with a slight pyrrole twist of 10° .

As it can be derived from Figure 9, the trend of the macrocycle for adopting a more stable conformation leads to greater out-of-plane distortion of the entire tetrapyrrole ring. That is, the mixture of pure nonplanar modes can be an internal mechanism for achieving more stable structures of the macrocycle in spite of the

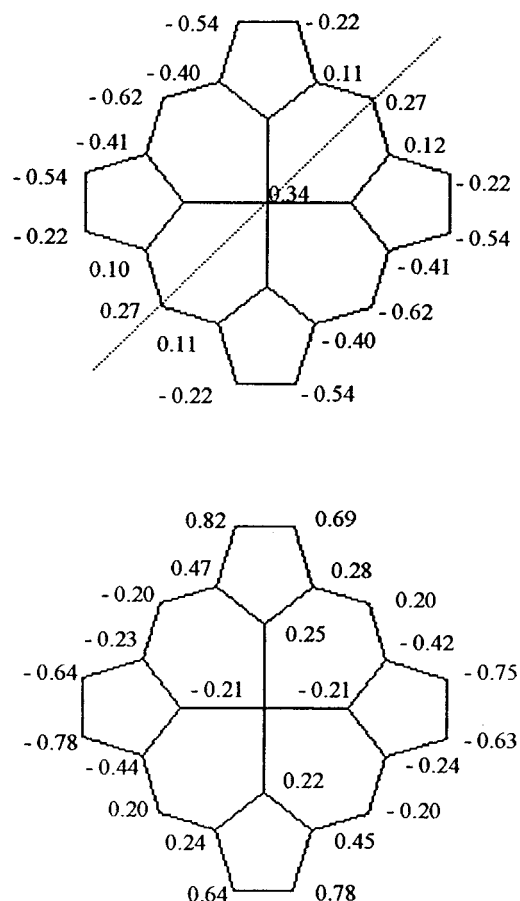


Figure 8. Displacements from the mean plane of the atoms which comprise the porphyrin macrocycle of *gab* (top) and *sadruf* (bottom) structures. The dotted line indicates the direction of the macrocycle folding in the *gab* conformer.

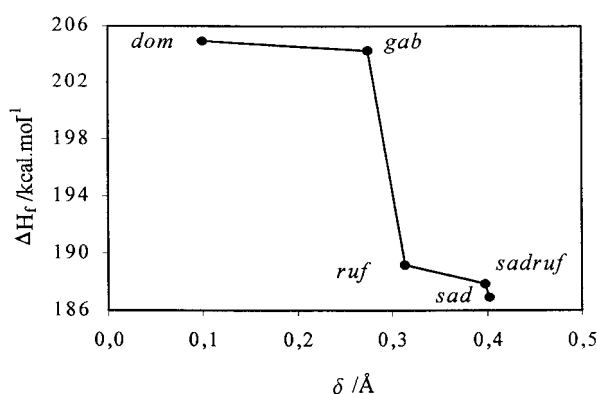


Figure 9. Relative energy of the pure and mixed conformers of the macrocycle. The *sad*, *ruf*, *dom*, *gab* and *sadruf* structures correspond to the conformations depicted in Figures 2 and 7.

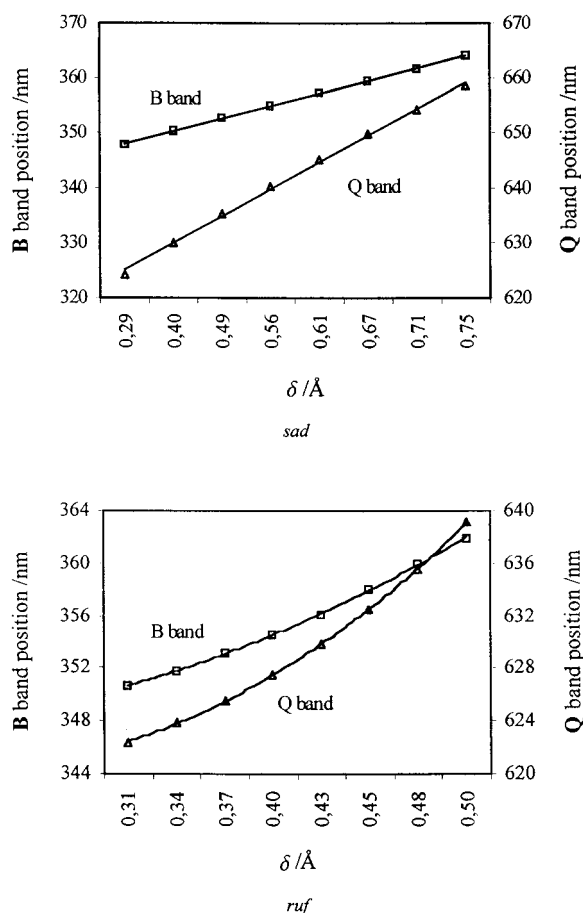


Figure 10. Position of the Q and b absorption maxima as a function of the macrocycle distortion. CNDO/S calculations over the PM3 optimized geometries.

multiple interactions with the molecular environment.

Electronic spectrum

Figure 10 shows the positions of the Q and B bands, predicted by CNDO/S method, when the degree of distortion for *sad* and *ruf* modes vary.

As it can be observed, the loss of macrocycle planarity gives rise to a spectral shift. The Q band is more shifted than the B one. In the present calculations the Q band can be shifted with respect to the planar conformation up to 42 and 22 nm for *sad* and *ruf* modes, respectively. The oscillator strength of the Q band is relatively constant for the three distortion modes; however, the oscillator strength of the B band decreases in *sad* and *ruf* deformations by more than 25% and 20%, respectively. In *dom* mode either the

displacement of the absorption bands or variation in band intensity do not practically take place. This occurs because the tetrapyrrole ring is slightly distorted from the mean plane of the molecule in spite of the large metal deviation.

CNDO/S predicts linear spectral shifts as the *sad* distortion increases. On the contrary, for the *ruf* mode this relationship has a quadratic character for both the Q and B bands (See Figure 10). We obtain an identical behaviour to that shown in Figure 10 using other descriptions of *sad* and *ruf* distortion, such as pyrrole tilting for *sad* and ruffling dihedral angle ($C\alpha-N\dots N-C\alpha$) for *ruf* mode. A previous experimental spectroscopic study in a series of Nickel(II) *meso*-tetrasubstituted macrocycle which undergoes several degrees of *ruf* deformation has concluded that both the Q and B band positions are shifted to low energy following a quadratic least-square fit as a function of ruffling dihedral angle [9]. In that study, the increase in nonplanar distortion is achieved using several alkyl substituents which exhibit approximately the same electronic inductive properties, allowing to neglect the electronic effect on the spectra.

Previous INDO/S calculations and cyclic voltammetric measurements have concluded that the optical red shift exhibited by nonplanar porphyrins is attributed to a smaller gap between HOMOs and LUMOs, the LUMOs migration being less sensitive to the deformation than the HOMOs displacements [3–5, 7–10, 17]. We may expect that the cause of the different features here obtained for the spectral shift of the *sad* and *ruf* deformations (see Figure 10) may be related with a different influence of both classes of macrocycle distortions on the HOMO and HOMO-1 energetic positions. Therefore, the different nodal pattern of these highest occupied orbitals must be taken into account.

Conclusions

Theoretical frameworks offer the possibility of investigating the multiconformational surfaces of porphyrin macrocycle only determined by the physical interactions of 24 atoms of the ruffled tetrapyrrole ring. By means of an appropriate redefinition of the internal coordinates of the unsubstituted macrocycle we may induce a systematical variation of the degree of deformation in *sad*, *ruf* and *dom* distortion modes. Such nonplanar models permit to study the named conformational effects, thus avoiding other ex-

ternal influences due to substitutions or the molecular environment.

The *sad*, *ruf* and *dom* distortions can be measured by the average atomic deviations of the macrocycle atoms from the mean plane (δ). This magnitude gives a simple and reliable description of the deformations regardless of the specific type of distortion and can be split in its different components ($\delta\beta$, $\delta\alpha$, δ_N , δ_m) making a detailed analysis of the deformation processes possible.

The present study confirms that important changes in the geometry, energy and electronic properties of the porphyrin may occur when the macrocycle trans-verses multiple conformers of the multiconformational surface.

Acknowledgements

This work received financial support from the Dirección General de Investigación Científica of Spain (Grant PB97-0027) and from the Programa Nacional de Ciencia y Tecnología of the Cuban Ministry of Science (Research Project No. 00411203). Victor R. Ferro Fernández gratefully acknowledges the financial support of the Ministerio de Educación y Cultura of Spain (Grant: SAB1998-0165) during his sabbatical leave.

References

- Shelnutt, J.A., Song, X.Z., Ma, J.G., Jia, S.L., Jentzen, W. and Medforth, C.J., *Chem. Soc. Rev.*, 27 (1998) 31.
- Hobbs, J.D. and Shelnutt, J.A., *J. Protein Chem.* B14 (1995) 19, and references therein.
- Barkigia, K.M., Chanturanpong, L., Smith, K.M. and Fajer, J.J., *J. Am. Chem. Soc.* 110 (1988) 7566.
- Barkigia, K.M., Renner, M.W., Furenli, L.R., Medforth, C.J., Smith, K.M. and Fajer, J., *J. Am. Chem. Soc.*, 115 (1993) 3627.
- Barkigia, K.M., Berber, M.D., Fajer, J., Medforth, C.J., Renner, M.W. and Smith, K.M., *J. Am. Chem. Soc.*, 000 (1990) 8851.
- Medforth, C.J., Senge, M.O., Forsyth, T.P., Hobbs, D.J., Shelnutt, J.A. and Smith, K.M., *Inorg. Chem.* 33 (1994) 3865.
- Medforth, C.J., Senge, M.O., Smith, K.M., Sparks, L.D. and Shelnutt, J.A., *J. Am. Chem. Soc.*, 114 (1992) 9859.
- Jentzen, W., Song, X.Z. and Shelnutt, J.A., *J. Phys. Chem.*, B101 (1997) 1684.
- Jentzen, W., Simpson, M.C., Hobbs, J.D., Song, X.Z., Ema, T., Nelson, N.Y., Medforth, C.J., Smith, K.M., Veyrat, M., Mazzanti, M., Ramasseul, R., Marchon, J.C., Takeuchi, T., Goddar, W.A., Shelnutt, J.A., *J. Am. Chem. Soc.*, 117 (1995) 11085.
- Medforth, C.J., Berber, M.D., Smith, K.M. and Shelnutt, J., *Tetrahedron Lett.*, 31 (1990) 3719.
- Senge, M.O., Medforth, C.J., Sparks, L.D., Shelnutt, J.A., Smith, K.M., *Inorg. Chem.*, 32 (1993) 1716.
- Song, X.Z., Jentzen, W., Jia, S.L., Jaquinod, L., Nurco, D.J., Medforth, C.J., Smith, K.M. and Shelnutt, J.A., *J. Am. Chem. Soc.*, 118 (1996) 12975.
- Renner, M.W., Barkigia, K.M., Zhang, Y., Medforth, C.J., Smith, K.M. and Fajer, J., *J. Am. Chem. Soc.*, 116 (1994) 8582.
- Nurco, D.J., Medforth, C.J., Forsyth, T.P., Olmstead, M.M. and Smith, K.M., *J. Am. Chem. Soc.*, 118 (1996) 10918.
- Sparks, L.D., Medforth, C.J., Park, M.S., Chamberlain, J.R., Ondrias, M.R., Senge, M.O., Smith, K.M. and Shelnutt, J.A., *J. Am. Chem. Soc.*, 115 (1993) 581.
- Shelnutt, J.A., Medforth, C.J., Berber, M.D., Barkigia, K.M. and Smith, K.M., *J. Am. Chem. Soc.*, 113 (1991) 4077.
- Sparks, L.D., Anderson, K.K., Medforth, C.J., Smith, K.M. and Shelnutt, J.A., *Inorg. Chem.*, 000 (1994) 2279.
- Piffat, Ch., Melamed, D. and Spiro, Th.G., *J. Phys. Chem.*, 97 (1993) 7441.
- Stichternath, A., Schweitzer-Stenner, R., Dreybridt, W., Mak, R.S.M., Li, X.Y., Sparks, L.D., Shelnutt, J.A., Medforth, C.J. and Smith, K.M., *J. Phys. Chem.*, 97 (1993) 3701.
- Shelnutt, J.A., Majumder, S.A., Sparks, L.D., Hobbs, D.J., Medforth, C.J., Senge, M.O., Smith, K.M., Miura, M., Luo, L. and Quirke, J.M.E., *J. Raman Spect.*, 23 (1992) 523.
- Gentemann, S., Medforth, C.J., Ema, T., Nelson, N.Y., Smith, K.M., Fajer, J. and Holten, D., *Chem. Phys. Lett.*, 245 (1995) 441.
- Drain, Ch.M., Kirmaier, Ch., Medforth, C.J., Nurco, D.J., Smith, K.M. and Holten, D., *J. Phys. Chem.*, 100 (1996) 1184.
- Poveda, L.A., Ferro, V.R., García de la Vega, J.M. and González-Jonte, R.H. *Phys. Chem. Chem. Phys.*, 2 (2000) 4147.
- Hobbs, D.J., Majumder, S.A., Luo, L., Sickelsmith, G.A., Quirke, J. M.E., Medforth, C.J., Smith, K.M. and Shelnutt, J.A., *J. Am. Chem. Soc.*, 116 (1994) 3261.
- Stewart, J.J.P., *J. Comput. Chem.*, 10 (1989) 209.
- Stewart, J.J.P., *Q. C. P. E.*, no. 581 (1990).
- Baker, J., *J. Comput. Chem.*, 7 (1986) 385.
- del Bene, J. and Jaffé, H.H., *J. Chem. Phys.*, 48 (1968) 1807.
- Montero, L.A., NDOL-Programs Package. Version 3.0, La Habana (1995).