MESO-TETRAKIS[2.2]PARACYCLOPHANYLPORPHYRIN: UNUSUAL STEREOISOMERISM OF A PORPHYRIN DERIVATIVE

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Abstract —— The hindered rotation about four direct bonds between the [2.2]paracyclophanyl substituents and the meso carbon centers of porphyrin in the title compound results in the appearance of many stereoisomers, some of them representing the type of stereoisomerism which had never been encountered before in porphyrin chemistry.

INTRODUCTION

Successful synthesis in our laboratory of meso-tetrakis[2.2]paracyclophanylporphyrin[1], T(PCP)P, as a representative of the novel class of compounds containing the direct link(s) between the paracyclophane and porphine systems drew our attention to the problem of atropoisomers formed[2]. Although some atropoisomers have been separated so far, the whole phenomenon of stereoisomerism of porphyrins substituted by the chiral units of [2.2]paracyclophane, PCP, appeared to us as deserving particular consideration[3].

The experimental difficulties in obtaining suitable crystals for X-ray examination led us to examine the structure of T(PCP)P by theoretical methods. The application of geometry optimization procedure has determined the relative positioning of the planes of porphine and paracyclophane unit(s) and enabled further theoretical treatment concerning the energy barriers between the stereoisomers.

CONFORMATIONAL ANALYSIS

The difficulty in estimating the structure of T(PCP)P by experimental methods gives particular importance to the calculations concerning its conformational states. The conformational analysis had to be performed with the use of the geometry optimization by the semiempirical force field method[4]. The MINDO/3 method[5] was exclusively applied to this molecule containing 158 atoms with a basis set of 422 atomic orbitals. All calculations were performed on a CRAY supercomputer. The program in FORTRAN was used, written by one of the authors (AKW). The Householder-QR-Inverse-Iteration method[6] was modified[7], and applied to matrix diagonalization. This program made possible

calculations for systems containing up to 200 atoms and 500 AOs as the functional base. As the authors' earlier conformational analysis of meso-[2.2]paracyclophanyltriphenylporphyrin, PCPP, showed[8], identical results were achieved by MINDO/3 and CNDO/2 methods. In all calculations, the porphine structure of D_{2h} symmetry[9] was considered based on X-ray diffraction studies[10], see Figure 1. Similarly, for the paracyclophane structural fragment, the geometry chosen was based on crystallographical data of [2.2]paracyclophane[11].

RESULTS AND DISCUSSION

Finding the stable conformers of T(PCP)P represents a task much more complicated than in the case of PCPP[8]. The following factors are responsible for this: (i) greater number of PCP substituents, (ii) two ways of substituting each meso-hydrogen atom of porphyrin by PCP which represent either the R or S configuration[12], see Figure 1, and (iii) the existence of two energetically stable conformers for each way of substitution[8].

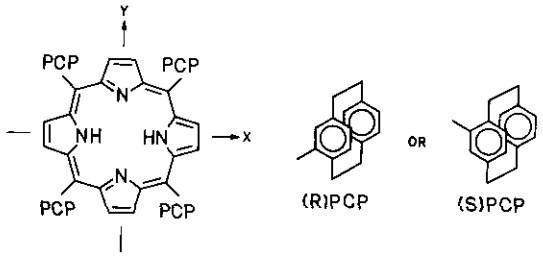

Figure 1. Meso-tetrakis[2.2]paracyclophanylporphyrin, T(PCP)P

The factor (i) of the quantitative character will be considered later. The attention will be first focussed on the two remaining steric factors applied to the mono-PCP substituted porphine. The consequence of factor (ii) are two modes of linking the porphine with PCP, denoted, respectively, as R and S. The S mode of joining the single PCP substituent with the porphine of D_{2h} symmetry is shown in Figure 2.

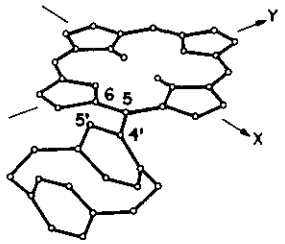

Figure 2. Definition of the dihedral angle

The single C5-C4' bond joins both structural fragments, and the dihedral angle C6-C5-C4'-C5' defines the rotational angle θ between them. The angle $\theta = 0^{\circ}$ when the benzene ring of PCP which is

directly linked to porphine is coplanar with porphine and the second benzene ring, bound by ethane bridges with the first one, is situated below. The value of θ increases as the result of the clockwise rotation (when looking from C5 to C4', i.e. from porphine to PCP). The "down" conformation is assumed for $0^{\circ} < \theta < 90^{\circ}$ and $270^{\circ} < \theta < 360^{\circ}$, while the "up" conformation for $90^{\circ} < \theta < 270^{\circ}$. The alternate mode R, not shown in Figure 2, links porphine with PCP via the C5-C5' bond; the rotation is described again by the dihedral angle C6-C5-C5'-C4', viewed as previously. However, in the latter case for $\theta = 0^{\circ}$, the benzene ring of PCP not bonded directly with porphine is situated above, and the rotation takes place in the anti-clockwise fashion. For the R mode, the θ ranges described above correspond respectively to the "up" and "down" locations. This results in the fact that for the same value of θ considered for R and S modes of bonding, the structures emerge as enantiomers. Factor (iii), based on the conformational analysis performed for PCPP[8], points to the existence of two pairs of these structures. The conformational analysis informs us that the system can assume two energetically stable positions, one for the PCP rotation angle in which $\theta_1 = 141.8^{\circ}$, and another for $\theta_2 = 321.8^{\circ}$. According to the definition of θ for PCP of R configuration there appear the "up" and "down" conformations while for the S configuration of PCP the "down" and "up" conformations come to existence. The calculations point, however, to (1) the energetic equivalence of the "up" and "down" conformations and (2) the high rotation barrier which makes the interconversion of conformers impossible. All this, together with the fact that $\theta_2 - \theta_1 = 180^{\circ}$ leads to the conclusion that the "up" and "down" conformations are identical. Therefore the presence of four structures for PCPP is only imaginary; in reality only one pair of enantiomers exists for this compound. The conformation of the PCP substituents gains, however, importance during the attachment of every other PCP substituent because of the lack of interconversion between the "up" and "down" conformations. As a consequence, a variety of structures of T(PCP)P emerges.

The substitution of porphyrin by four PCP units shows a similarity to the well described substitution resulting in the formation of "picket fence porphyrins"[13,14]. The latter meso-tetrakis(ortho-substituted phenyl)porphyrins can exist as four atropoisomers: αααα, ααaβ, ααββ and αβαβ where α and β denote the location of the ortho-substituent, respectively above and below the porphine plane. The same problem was encountered in mesotetraferrocenylporphyrins[15]. For the latter compounds the quantitative factor (i) had to be considered together with the steric reasons. However, in the case of T(PCP)P, the additional factors (ii) and (iii) gain significance. The reasons why they are responsible for a great increase of the number of atropoisomers are discussed below. Instead of four atropoisomers αααα, ααaβ, ααββ and αβαβ there appear four groups of isomers which will be denoted as UUUU, UUUD, UUDD and UDUD. In this case U denotes the conformation of the PCP substituent in the "up" position while D points to the "down" position, see Figure 3.

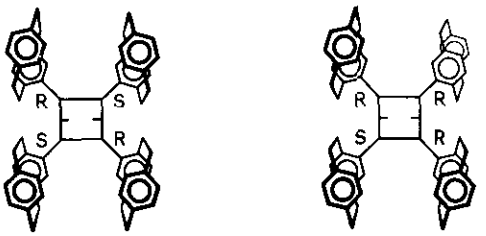

Figure 3. Two stereoisomers of T(PCP)P given as examples of differences between two configurations (RSRS vs RSRR) and two conformations (UUUU) vs UUUD)

The influence of the (ii) factor in the case of T(PCP)P makes possible existence of 16 configurational combinations: RRRR, RRRS, RRSR, RSRR, SRRR, RRSS, RSSR, RSRS, SSSS, SSSR, SSRS, SRSS, RSSS, SSRR, SRRS and SRSR. In general, the structures corresponding to the first eight configurations should be the enantiomers of the eight remaining structures. For example this relation always concerns the structures of the RRRR and SSSS combination. For the remaining combinations such a relation is not so obvious because it depends on the factor (iii). It is known that independently of the R or S configuration of the PCP substituent, each has U and D conformations. Therefore, each out of the first eight combinations can represent one of the four following structures: UUUU, UUUD, UUDD and UDUD. Taking account of the factors (i) and (ii) gives, however, the structures which can be identical for different configurational combinations. In effect, the number of stereoisomers varies depending on the type of the structure, see Figure 4. For UUUU two structures representing the RRRR and RRRS configurations are enantiomers while the structures RRSS and RSRS represent the meso forms; totally 6 stereoisomers appear. For UUUD the eight structures shown are enantiomers that gives 16 stereoisomers. For UUDD four structures of RRSS, RSRS, SRRS and RSSR configurations represent the meso forms while the remaining three structures RRRR, RRRS and RSRR are enantiomers; as a result ten stereoisomers exist. Finally for UDUD three structures of RRRR, RRRS and RRSS configurations are enantiomers and one RSRS configuration represents the meso form which amounts to 7 stereoisomers. Total number of stereoisomers is 39.

Conformational analysis of T(PCP)P confirmed the stereochemical considerations presented above. The analysis was performed for five selected structures of identical topology, see Figure 5: (RSRS)-UUUU, (RSRR)-UUUD, (SRRS)-UUDD, (RSSR)-UUDD and (RRRR)-UDUD, the symbols in brackets denoting the configurations of the PCP substituents. The conformation given for each PCP substituent represents the primary conformation: the rotation angle θ is expressed depending of the configuration of the substituent according to the already described rule (see Figure 2). The simultaneous change of the rotation angle θ assumed in the calculations was identical for all PCP substituents.

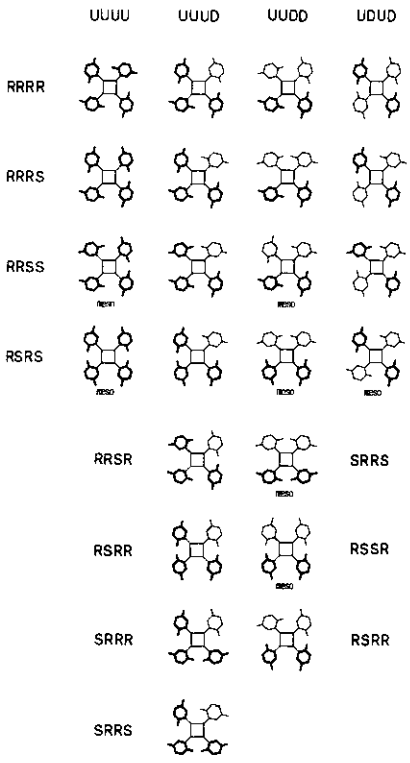

Figure 4. All possible meso forms and representatives of the enantiomeric pairs of T(PCP)P. Those not labelled meso have enantiomeric pairs.

The heavy lines denote the benzene rings of the [2.2]paracyclophanyl substituents not linked directly with porphyrin core which are turned "up". Each benzene ring directly linked to porphyrin core is denoted by a normal line; the second benzene ring is always located below it.

The calculations showed in all cases that stable conformers appear only for two rotation angle values, $\theta_1 = 141.8^{\circ}$ and $\theta_2 = 321.8^{\circ}$, the energy values of both conformers being the same. An identical result has been reached by the authors earlier on meso-[2.2]paracyclophanyltriphenylporphyrin, PCPP[8]. The energies of the five considered conformers are shown in Figure 5.

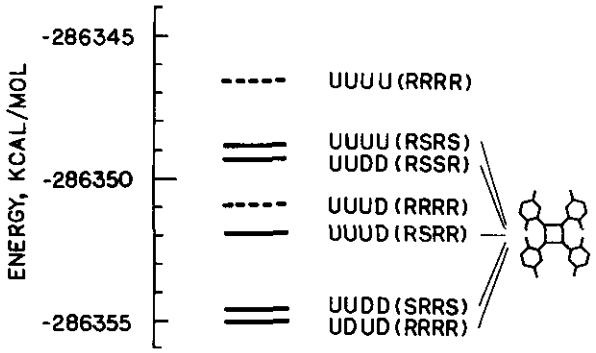

Figure 5. Total energies of some stereoisomers of T(PCP)P. Five stereoisomers represent the same topology shown on the right

The (RRRR)-UDUD conformer has the lowest energy while (RSRS)-UUUU has the highest energy. The difference in energy between these extremes equals 6.2 kcal/mol. Let us notice that conformers similar in structure, (RSSR)-UUDD and (SRRS)-UUDD, show distinctly different energies. In between them the (RSRR)-UUUD conformer is located.

The regarded conformational analysis treatment allowed us to consider only five conformers. Because of the size of the molecule and the number of stereoisoemrs (see Figure 4), it would be very difficult to perform the analysis of all of them. Therefore a question arises concerning the relation between the remaining conformers and those already considered. We focussed attention on the (RRRR)-UUUD and (RRRR)-UUUU conformers which have different topology and are different from the five discussed previously. They both represent the same configurations and can be reached from (RRRR)-UDUD (see its ORTEP drawing in Figure 6) by changing the conformational orientation of the PCP substituents from D ($\theta_2 = 321.8^{\circ}$) to U ($\theta_1 = 141.8^{\circ}$); the change should concern one and two substituents for the first and the second case, respectively. The energies of both conformers are presented by the dashed lines in Figure 5. The relative energies form the following order: $E_{UDUD} < E_{UUUD} < E_{UUUU}$. For the reasons described above, no conformer could be converted into another (high energy barrier) even if only one PCP substituent changes its conformation. The influence of the tautomerism (the inner H atoms located either along the x or the y axis) on the

energies of conformers is insignificant and does not influence the above considerations.

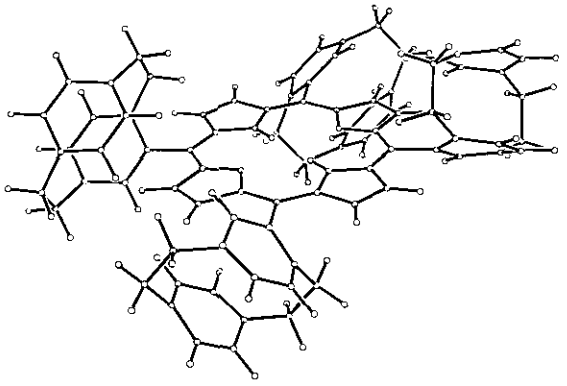

Figure 6. Structure of the T(PCP)P (RRRR)-UDUD stereoisomer according to ORTEP

CONCLUSIONS

As many as 39 stereoisomers of T(PCP)P result from the substitution of porphine in meso position by four PCP substituents in two modes (each in R or S configuration) and two energetically allowed conformations (U and D) appearing for each configuration. Such a number of species and the way they are differentiated are unknown so far for the derivatives of porphyrin. Conformational analysis was performed for five stereoisomers representing the same topology. The greatest difference in energy calculated (by MINDO/3) was 6.2 kcal/mol between the (RRRR-UDUD and (RSRS)-UUUU stereoisomers. Any two stereoisomers are separated by an energy barrier high enough to exclude the possibility of interconversion.

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