A Comparison of the Results of PCILO and *ab initio* SCF Calculations for the Molecules Glycine, Cysteine and N–Acetyl–Glycine

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Conformational energy maps for glycine, cysteine and N-acetyl-glycine obtained using PCILO and *ab initio* SCF calculations are compared.

Key words: Conformation – Amino acids.

1. Introduction and Procedure

Conformational energy maps have been produced using two different quantum mechanical methods. The methods used were an *ab initio* SCF procedure using a modified version of the Gaussian 70 program [1] with a minimal (STO-3G) basis set, and the Perturbative Configuration Interaction procedure using Localised Orbitals (PCILO) [2] using a modified version of the program obtained from Prof. A. Pullman [3].

The maps were constructed as described previously [4]. Energies are quoted in kcal mole^{-1} and in general the iso-energy contours are limited to 6 kcal mole^{-1} above the global minimum; in some cases 7 and 8 kcal lines are included in order to illustrate overall trends.

Standard values [5, 6] were used for bond lengths and angles. Torsional angles are defined in Figs. 1 and 2.

2. Results

The glycine molecule has been studied by several authors using various methods [7–12]. Our results parallel those of Ref. [10] and the maps are not reproduced
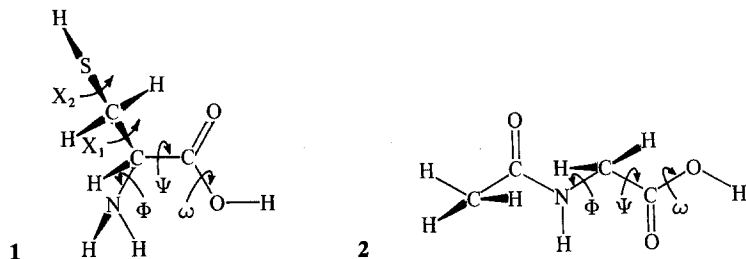
Fig. 1. Cysteine: conformation corresponding to $\phi = \psi = \omega = 0°$; $\chi_1 = 60°$, $\chi_2 = 180°$

Fig. 2. N-acetyl-glycine: conformation corresponding to $\phi = \psi = 180°$, $\omega = 0°$

here. For this molecule both methods agree in favouring planar arrangements and in indicating certain conformations to be of low energy. However, they disagree as to the relative ordering of energy minima and PCILO indicates a number of minima which do not appear at all on the STO-3G maps.

For cysteine the side chain angles χ_1 and χ_2 were fixed at their preferred values of 60° and 180° respectively (both methods agree in favouring these values although other staggered arrangements are also possible); ω was fixed at 0°. The maps are presented in Fig. 3. There is only one minimum, that at $\phi = -60°$, $\psi = 180°$, which does not appear on both maps. However the PCILO map is considerably flatter, indicating a greater number of "accessible" conformations.

For N-acetyl-glycine two values of ω were considered: 0° and 180°, previous calculations having shown these to be the only important values for this angle. The PCILO maps have been presented in an earlier paper [4] which also contains illustrations of C_5, C_7 and "M" conformations. Both methods indicate the C_5 ($\phi = \psi = 180°$, $\omega = 0°$ or 180°) and C_7 ($\omega = 180°$, $\phi = \pm 60°$, $\psi = \mp 60°$) arrangements to be stable. The main contrast is the emphasis PCILO gives to "M"
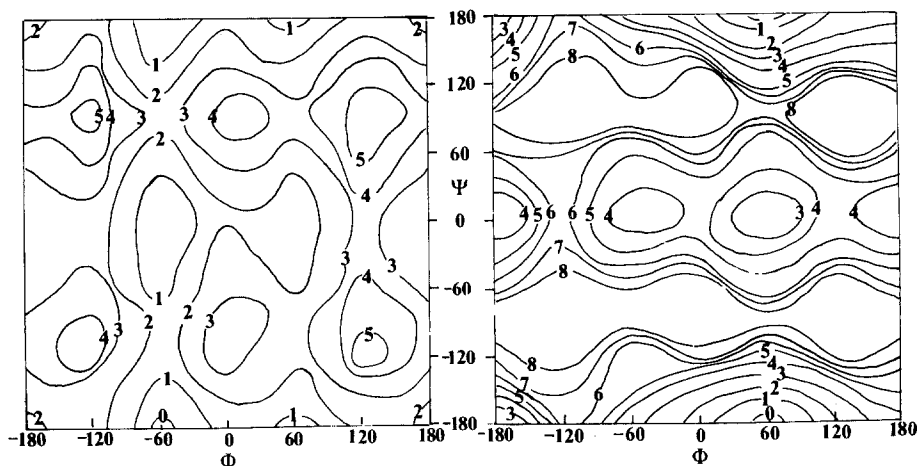

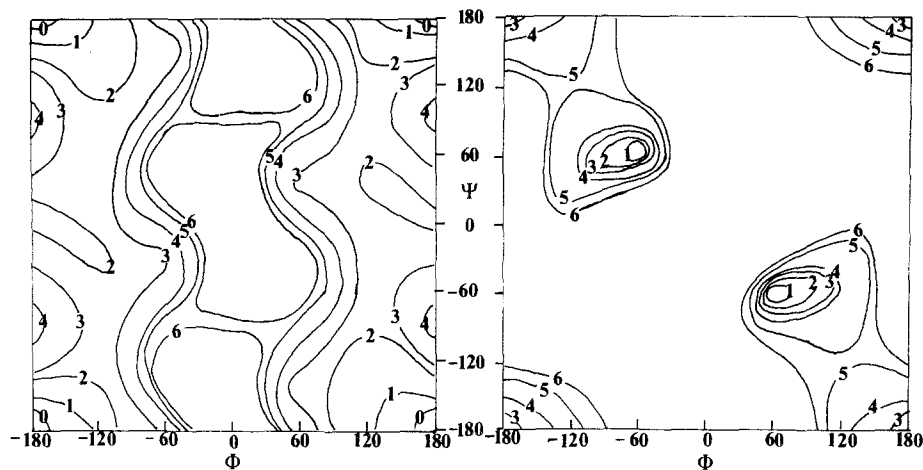**Fig. 3.** Conformational energy maps for cysteine (a) PCILO (b) STO-3G

Fig. 4. STO-3G conformational energy maps for N-acetyl-glycine: (a) $\omega = 0°$ (b) $\omega = 180°$

conformations (these occur for $\phi = 0°$, $\psi = \pm 90°$, $\omega = 0°$ or $180°$). For $\omega = 180°$ they represent stable conformations equivalent in energy to the C_5 arrangement. For $\omega = 0°$ they are ~1 kcal more stable than C_5. On the STO-3G maps (Fig. 4) the "M" conformations occur at saddle points 5.7 and 11 kcal above the global minimum for $\omega = 0°$ and $180°$ respectively.

A limited number of calculations have been performed for this molecule using an extended basis (4-31G) set and the Gaussian 76 program [13]. These calculations are not yet complete but those performed so far indicate the same relative ordering of minima as has been obtained with the STO-3G basis, though with higher barriers to rotation. The "M" conformations still appear as saddle-points but with energies of 14.7 and 26.2 kcal above the minimum for $\omega = 0°$ and $180°$ respectively. It therefore seems unlikely that these conformations are important.

3. Conclusion

From the study of these three molecules it appears that, in comparison with STO-3G basis *ab initio* calculations, PCILO tends to give low values for barrier heights, resulting in conformational energy maps that are rather flat. PCILO also predicts certain conformations to be of low energy which have no corresponding energy minima on the *ab initio* maps. However it should also be noted that there is no minimum on any of the *ab initio* maps which does not have a corresponding minimum on the appropriate PCILO map.

It is perhaps possible to conclude that while PCILO does not reproduce exactly the results of *ab initio* calculations, a preliminary study of a molecule using PCILO may be very useful. A two dimensional conformational energy map can be produced very rapidly using PCILO and the minima shown on such a map could then provide the starting point for more accurate calculations.

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