WEIGHTS FROM GOOD ESTIMATE OF STANDARD UNCERTAINTIES OF THE INTENSITIES

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Spagna & Camalli (J. Appl. Cryst. (1999) **32**, 934-942) presented an analysis of weighting schemes currently used by crystallographers to refine small or medium sized crystal structures by least squares method. These schemes are empirical functions to calculate the weights based on the observed quantities or on the standard uncertainty of the observations, derived by counting statistics. The first recommendation in the paper of Schwarzenbach et al. (Acta Cryst. (1989) A**45**, 63-75) states 'All reflections to be used in the refinement process should be measured more than once...', according the theory of least squares where the weights should be the inverse of the variance - covariance matrix of the observations. To follow this recommendation, we have chosen a solved structure and using the same crystal well stable under X-rays, we carried out a data collection where each reflection was measured six times. 31157 reflections (resolution 0.80 Å) were collected and processed to yield 4820 unique reflections (merging R factor = 0.015). 4121 observed ($I > 3\sigma(I)$) reflections were used in subsequent calculations. The structure was refined using various strategies and the results are compared against the standard experiment.

Keywords: COMPUTING REFINEMENT

EXPERIMENTAL VS. THEORETICAL GEOMETRIES IN MANGANESE COMPLEXES

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The experimental geometry obtained from single-crystal X-ray diffraction for a couple of binuclear S-bridged manganese complexes(1) is compared to the results of theoretical calculations made at the *ab initio* level by using Density Functional Theory methods.
Diffraction data for $[(CO)_4Mn\{(PPh_2)_2CSC(PPh_2)_2\}Mn(CO)_4].½(CH_2Cl_2)$ [1] and
$[(CO)_4Mn\{(PPh_2)_2CHSSCH(PPh_2)_2\}Mn(CO)_4][ClO_4]_2.CH_2Cl_2.HClO_4.5H_2O$ [2] have been collected using standard procedures. Experimental geometries are in good agreement with results reported for similar compounds. For instance, the C-S-C angle in compound [1] has been found to be 113(1)° and the S-S bond distance in [2] is 2.056(4) Å.
Theoretical geometry optimizations for both main compounds have been made using the method B3LYP with the basis set 6-31G. In order to achieve convergence in a reasonable time, phenyl groups were replaced by methyl groups in a first instance and by hydrogen atoms in a second run (which was also useful to test the validity of the replacements), leading to similar results in both cases. The optimized geometries obtained were somewhat relaxed when compared to the experimental ones, with nearly equal bond and torsion angles but longer bond lengths. For instance, the C-S-C angle found for compound [1] was 110(1)° for both the hydrogen and the methyl substituted derivatives, whereas the S-S bond distance found in compound [2] was 2.275(5) Å. Further (and better) results have been obtained by enlarging the basis set used.
References
(1) Ruiz, J., Ceroni, M., Quinzani, O. V., Riera, V., Vivanco, M., Garcia-Granda, S., Van der Maelen, J. F., Lanfranchi, M., and Tiripicchio, A., Chem. Eur. J., (2001), 7: 4422-4430.

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THE STRUCTURE AND THERMAL MOTION OF B800-850 LH2 COMPLEX FROM *RPS. ACIDOPHILA* AT 2.0 Å: FUNCTIONALLY RELEVANT MOTION

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Light Harvesting Complex II (LH2) traps solar energy, which is transferred to the Reaction Centre where chemical photosynthesis begins. The energy trapping efficiency depends on optimal orientations of several bacteriochlorophyll and carotenoid molecules whose interactions are modified by dynamic motions or static disorder through coupling with the protein and membrane environments. This effects the degree of energy localization and relaxation times. An understanding of this requires an accurate atomic model as well as thermal properties. To this end the B800-850 LH2 from *Rps acidophila* has been refined using TLS tensor refinement implemented in REMAC5. The much improved electron density has revealed, for each repeating unit, a second carotenoid molecule and the remaining 5 residues of the α-chain. We show that the additional benefits of TLS refinement are: an insight into possible dynamic modes and disorder in the structure. The TLS model provides an alternative to the stochastic models used for interpreting spectroscopic experiments by giving information on amplitudes and directions of collective modes of motion. The observed displacements may have a significant effect on pigment-pigment energy interactions and transfer.

Keywords: **LIGHT HARVESTING TLS REFINEMENT ENERGY TRANSFER**

LIPID-PROTEIN INTERACTIONS IN MEMBRANES: A MOLECULAR MODELLING STUDY

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Numerous recent experimental results contradict a commonly held belief that the lipid bilayer matrix of biomembranes is a passive and structureless 'solvent' for the membrane proteins. In fact, it appears that the membrane lipids play active roles in the membrane proteins functioning both by providing an interface with the fluid membrane environment and interacting specifically with integral or peripheral proteins. Unfortunately, neither atomic level details nor time scales of lipid–protein interactions are known. In the presented study, a molecular dynamics (MD) simulation method is applied to study these properties in a hydrated bilayer. The method is well suited for this purpose, the time and length resolutions being superior to those provided by experimental methods. The vasopressin receptor (V2R) was embedded in a palmitoyloleoylphosphatidylcholine bilayer and simulated using AMBER 5.0 for 3 ns. The initial V2R model was obtained using a rule-based automated method for G protein-coupled receptors (GPCR) modelling, implementing both the crystal structure of bovine rhodopsin from X-ray diffraction at 2.5 Å and the sequence analysis over the GPCR superfamily. The model was refined using constrained simulated annealing in vacuum. Analyses of the 2-ns trajectory provided the number of the receptor boundary lipids, detailed description of their interactions with the receptor, and the rate of exchange between boundary and bulk lipids. Enabled also the comparison of conformation and isomerization of chains of boundary and bulk lipids.
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