and its outcomes may be also used to constraint the generation of more reliable structural models. The method has been applied to a large number of protein test structures, showing a good discriminant power with respect to the complexity of the structure, the space group symmetry and the presence of additional beta domains. The accuracy in the determination of the direction of the alpha helix depends on its length, and only helices greater than ten residues may be found with a reliable precision. The automatic procedure has been tested in Matlab and will be included in the software package ILMILIONE, devoted to protein crystal structure solution [3].

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**Keywords: alpha-helix, patterson map, pattern recognition**

## MS58.P22

**Structural and computational analysis of 3,6-dioctyloxiphenyl-2,5-dimethyl-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione**

Betül Şen,[a] Resul Sevinçek,[a] Seçil Çelik,[b] Muhittin Aygün,[a] Serap Alp,[c] *[a]Physics Department, Science Faculty, Dokuz Eylül University, İzmir (Turkey). [b]Chemistry Department, Science&Art Faculty, Celal Bayar University, Manisa. [c]Chemistry Department, Science Faculty, Dokuz Eylül University, İzmir, (Turkey).* E-mail: betul.sen@deu.edu.tr

Diketodiphenylpyrrolopyrroles are industrially important red pigments[1]. The success of these compounds as pigments relies, in part, on their high light fastness and very low solubility in most common solvents.

The title compound was synthesized, structural and spectroscopic properties were investigated. Molecular and crystal structure of 3,6-dioctyloxiphenyl-2,5-dimethyl-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione, $C_{36}H_{48}N_2O_4$, have been determined by single crystal X-ray diffraction study. The title compound is triclinic, with $a$=6.2419(6) Å, $b$= 9.5847 (9) Å, $c$=13.4568 (8) Å, $\alpha$=106.573(7) °, $\beta$=94.244(6)°, $\gamma$=93.154(8)°; Z=1, $D_x$=1.24 g/cm³, $\mu(CuK_\alpha)$=0.08 mm⁻¹, and space group is P-1. The structure was solved by direct methods and refined to a final R=0.055 for 3214 reflections with I>2σ(I). The structure is devoid of classical hydrogen bonds. However, there are two intra-molecular weak interactions between C9-H9···O2 and its inversion counterpart C9[i]-H9[i]···O2[i] (Symmetry code i: 4-x, 1-y, 1-z), with the geometrical parameters: D-A=3.06 Å, H···A= 2.18 Å, D-H···A=158 °.

Optimized geometry and NMR spectra of the title compound were investigated and analyzed using DFT at B3LYP functional by 6-31g(d) basis set. Experimental and computational NMR spectra were determined and compared.

Computational and crystallographic results, NMR spectra and molecular geometry, are in good agreement. RMSD (Root Mean Square Distance) value between crystallographic result and optimized geometry is 9,507·10⁻³Å. The geometry of diketopyrrolopyyrole ring is in agreement with previous study [2, 3].

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**Keywords: diketopyrrolopyrroles, crystal structure, dye-pigment.**

## MS58.P23

**Automatic structure determination for small molecule crystallography**

Hiroyuki Kanda, Tsuneyuki Higashi, Masataka Maeyama, *Rigaku Corporation, Tokyo, (Japan).* E-mail: kanda@rigaku.co.jp

When the automatic structure determination algorithm was proposed over two decades ago [1], it had some technical problems. For example, it took more than a half day to solve a structure because of the limited capability of computers at that time. Recently, the situation has dramatically been changed. We can solve the structure of a small molecule several tens of seconds or sometimes in a few seconds. We have developed a software, AutoSolve, for small molecule crystallography to determine structures automatically.

AutoSolve was designed for organic and metal-organic compounds. This software uses SIR [2] as a direct method and SHELXL[3] as a refinement tool. In addition, we have incorporated a feature to switch among direct methods, SIR, SHELXS and Superflip[4] when a method does not give an initial structure.

In the initial step, AutoSolve assumes all atoms as carbons except heavy atoms and executes refinement by using SHELXL. After that, AutoSolve assigns atoms by taking temperature factors (Biso/Beq), bond distances, and chemical valencies into account. AutoSolve decides when to convert temperature factors to anisotropic and when to add hydrogen atoms by checking the R1 value in every refinement cycle. Finally, the hydrogen atoms are generated by using the SHELXL's HFIX command. Our algorithm follows the conventional structure determination procedure but it gives good results.

In order to evaluate the performance, we picked up 50 samples from Acta Cryst. C and ran AutoSolve. We did not get good results for inorganic compounds. However, AutoSolve gave structures close to final structures for organic compounds with success rate of about 100% and 60% for organic and metal-organic compounds, respectively.

AutoSolve can reach nearly a complete structure in a few seconds or several tens of seconds, except for inorganic compounds.

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**Keywords: software, automatic, structure**

## MS58.P24

**Partial observations, partial models and partial residuals in least squares refinement**

A. David Rae, *Research School of Chemistry, the Australian National University, Canberra, ACT 0200, (Australia).* E-mail: rae@rsc.anu.edu.au

Certain features of the standard use of least squares methods should cause concern as they are the result of a number of misconceptions. In particular one has to seriously question the use of a global scale, $K$, to assess errors in variables by creating a variance-covariance matrix **M** as $K$ times the inverse of the matrix used to describe the least squares equations. There is also the oversight of not calculating variances for components of the model of the observations, the failure to take sufficient notice of how information is distributed in the observations and how easy it is to make mistakes in the description of twins, powders and pseudo symmetric structures that will not self correct during refinement. Ideas have been developed using partial observations, partial models and partial residuals that suggest how to better identify

**P.MS.58**

systematic errors and how to correct the problems with the way least squares refinement is currently undertaken.

An initial model is used to partition the information in an observation $|\mathbf{Y}(\mathbf{h})|^2 = \Sigma_{m=1,M}|F(\mathbf{h})_m|^2$ where the background is $|F(\mathbf{h})_M|^2$. $\mathbf{Y}(\mathbf{h})$ can be regarded as a vector in an $M$ dimensional space with components $F(\mathbf{h})_m$ $\mathbf{i}_m$. The assumption that there is a direction of interest in Y-space for the description of $\mathbf{Y}\mathrm{obs}(\mathbf{h})$ - $\mathbf{Y}\mathrm{calc}(\mathbf{h})$ is a constraint that creates a partial observation and a partial residual should the directions of $\mathbf{Y}\mathrm{obs}(\mathbf{h})$ and $\mathbf{Y}\mathrm{calc}(\mathbf{h})$ not coincide, eg the back-ground is not refined. This constraint creates residuals $\Delta_{\mathbf{h}m} = |F\mathrm{obs}(\mathbf{h})_m - F\mathrm{calc}(\mathbf{h})_m|$ for a minor component of $\mathbf{Y}\mathrm{obs}(\mathbf{h})$ that are much smaller than the variance based estimates using an estimate of the variance-covariance matrix. This should be interpreted as the refinement of $\Sigma_{\mathbf{h}}f_{\mathbf{h}}w_{\mathbf{h}}\Delta_{\mathbf{h}}^2$ rather than $\Sigma_{\mathbf{h}}w_{\mathbf{h}}'\Delta_{\mathbf{h}}^2$ with $\Sigma_{\mathbf{h}}f_{\mathbf{h}}$ the effective number of observations associated with the refined parameters and $\Sigma_{\mathbf{h}}(1-f_{\mathbf{h}})w_{\mathbf{h}}\Delta_{\mathbf{h}}^2$ is the unrefined component of $\Sigma_{\mathbf{h}}w_{\mathbf{h}}\Delta_{\mathbf{h}}^2$. Both $f_{\mathbf{h}}$ and $w_{\mathbf{h}}$ can change each refinement cycle.

The concept can be extended so that $f_{\mathbf{h}} = \Sigma_j f_{\mathbf{h}j} = \Sigma_m f_{\mathbf{h}m}$ where $f_{\mathbf{h}j}$ is the fraction of the residual assigned to the jth variable and $f_{\mathbf{h}m}$ is the fraction assigned to the mth component. This allows the scaling of the variance-covariance matrix one variable at a time and the evaluation of the effective number of observations associated with a particular component of the structure factors, a particular variable, or a particular set of variables.

For pseudo symmetric structures one can create symmetrized components of the structure factors and one needs to isolate classes of reflections and differences between pseudo symmetric reflections in these classes to check on the reliability of the minor components that may have errors in their relative phases, imposed symmetry and choice of initial model as well as intrinsic problems involving stacking faults and twinning. Differences between pseudo equivalent reflections are unavailable from powder data as these reflections now coincide and this makes the relative phases of symmetrized components unconfirmable and uncorrectable.

**Keywords: partial observations, least squares, refinement**

## MS59.P01

**Polyiodide salts of thioamides**

Anita Owczarzak,[a] Sotiris K. Hadjikakou[b] & Maciej Kubicki[a] *[a]Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6,60-780 Poznań, (Poland). [a]Section of Inorganic and Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, (Greece).* E-mail: aniow@amu.edu.pl

Structural properties of (poly)iodide salts of 2-mercaptopyrimidine (PMT) and its non-aromatic analogue, 3,4,5,6-tetrahydropyrymidinthione (tHPMT) have been studied by means of middle- and high-resolution X-ray diffraction.

The reaction of PMT with hydroiodic acid in a molar ratio of 1:1 produced the mixture of $PMT^+I^-$ (**1**) and $PMT^+(I_4^{2-})_{0.5}$ (**2**), while tHPMT reacts with diiodine in the presence of HI and (in 1:1:1 molar ratio) forms the ionic complex $[(tHPMT)_2I^-(I_4^{2-})_{0.5}]$ (**3**). On the other hand this latter compound in the presence of HCl reacts with diiodine and, depending on the molar ratio, forms either $[(((tHPMT)_2)^{2+})_3(Cl^-)_{1.5}(I^-)_2(I^{3-})_{2.5}]$ (**4**) for a molar ratio 1:1:1 or $[((tHPMT)_2)^{2+}(I_3^-)(I_3^-)_{0.5}(Cl^-)_{0.5}]$ (**5**) for 1:1:2.

The crystal structures of all these compounds have been determined by standard X-ray diffraction method; for (**2**) also high resolution data are collected and preliminary results of the deformation electron density analysis are promising. Additionally, some of the compounds were also spectroscopically studied.

In the salts we have observed the rare forms of polyiodides i.e. tetra- and hexaiodides and the huge variety of different intermolecular interactions including strong and weak hydrogen bonds, halogen bonds, sulfur···halogen and coulombic interactions. Some examples of the interactions found are shown below:
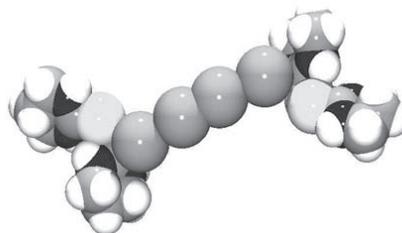


Figure 1. A view of the tetraiodide interacting with the disulfide bridge.

**Keywords: polyiodides, thioamides, intermolecular interactions**

## MS59.P02

**Anion···π, lone pair···π, and F···F interactions in nucleobase derivatives**

Elies Molins,[a] Ignasi Mata,[a] Angel García-Raso,[b] Miquel Barceló-Oliver,[b] Francisca M. Albertí,[b] Juan J. Fiol,[b] Yolanda Lagos,[b] Marta Torres,[b] Angel Terrón,[b] Carolina Estarellas,[b] Antonio Frontera,[b] David Quiñonero[b] and Pere M. Deyà,[b] *[a]Institut de Ciència de Materials de Barcelona ICMAB-CSIC, Bellaterra, (Spain). [b]Universitat de les Illes Balears (UIB), Palma de Mallorca, (Spain).* E-mail: elies.molins@icmab.es

Hydrophobic interactions in nucleobase derivatives substituted with long aliphatic chains favors the formation of layers of nucleobases and, in the case of salts, anions separated by the aliphatic chains, giving rise to crystal packings that reminds of lipid bilayers (Figure). Although the strongest intermolecular interaction inside the nucleobase layer is hydrogen bonding, other interactions such as π···π stacking, anion···π, lone pair···π and fluorine···fluorine play a fundamental role in determining the conformation of the nucleobases inside the layers. The complex interplay between these interactions gives rise to features that have been analyzed by theoretical calculations, such as the formation of anion···π / π···π / π···anion assemblies [1], the stabilization of planar layers of fluorinated molecules by F···F interactions [2], or the favoring of lp···π over π···π interactions when electron-withdrawing substituents are present [3]. Results stresses the importance of these interactions, that should be taken into account in crystal engineering and crystal structure prediction efforts with nucleobases and other N-substituted heterocycles.
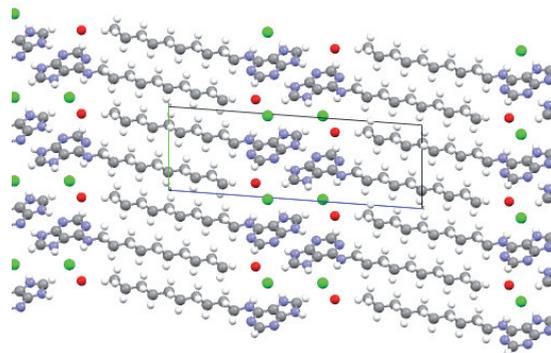


Crystal structure of N⁶-decyladenine·HCl hydrate