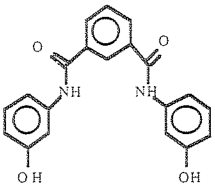
pyrrole NH, and bioactivity (including bioaffinity for some of them, Klaembt, 1996). The 3D structure of the receptor has not been characterized yet. However, systematic analysis of a large number of substrates and inhibitors can provide information about the protein active site.

PS11.01.11 π-π STACKING IN MODEL DYE HOSTS. C.M. Murray, J.F. Malone, R. Docherty, A.J. Lavery, G. Stewart.

Weak hydrogen bonds e.g. C-H...O and weak interactions e.g. π-π stacking and T-bonding have been shown to have a role within crystal structure[1]. The π-π stacking interaction, though weak, is significant in the structure of 1,3 Bis(((3-hydroxyphenyl)amino)carbonyl)benzene which is reported.



This interaction has been quantified using the HABIT program[2]. Semi-empirical calculations of the heat of formation show agreement between the preferred conformation in the gas phase and the single crystal X-Ray diffraction structure. Similar structures retrieved from the Cambridge Structural Database confirm the importance of the π-π interaction for not only single molecule asymmetric units of this type but also asymmetric units which contain hydrated species or co-crystals. Quantification of the values is reported and the conformational preference is also investigated.

1 G.R. Desiriaju *Acc. Chem. Res.* **1991**, 24, 290-296. A.D. Hamilton et al *J. Am. Chem. Soc.* **1988**, 110, 6561-6562. D.R. Boyd et al *J. Am. Chem. Soc.* **1996** in press.

2 G. Clydesdale, R. Docherty, K.J. Roberts *Computer Physics Communications* 64 (**1991**) 311-328.

PS11.01.12 STRUCTURE OF THE LEAD PICRATE COMPLEXES WITH 18-MEMBERED CROWN ETHERS IN THE CRYSTAL STATE AND IN ORGANIC SOLVENTS. N. K. Dalley[1], J. D. Lamb[1], A. Y. Nazarenko[2], E. B. Rusanov[3]. [1]Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, USA, [2]Analytical Chemistry Department, Taras Shevchenko University, Kiev 252033, Ukraine, [3]Institute of Organic Chemistry, NAS of Ukraine, Kiev, Ukraine

Despite the wide use of metal picrates for ion recognition studies, no structural data concerning lead picrate complexes with crown ethers have yet been published. Here we report molecular structures of Pb(18-crown-6)Picr$_2$ x CH_2Cl_2 (I) and Pb(cis-syn-cis-dicyclohexano-18-crown-6)Picr$_2$ (II). In both complexes Pb^{2+} is coordinated six O atoms of macrocycle, which has a distorted D_{3d} geometry (Pb...O separations are 2.64-2.84 Å). Both picrate anions in (I) and only one in (II) are monodentate with Pb...O = 2.47-2.48 Å, while the second one in (II) is bidentate (Pb...O = 2.56 and 2.88 Å). This correlates with the existence of different types of picrate - Pb^{2+} ion pairs in organic solvents in the presence of crown ethers, observed from spectral studies. The structural data together with our previously obtained structures of lead macrocyclic complexes enable us to discuss the features of ion recognition of Pb^{2+} by crown ethers.

Chemical Crystallography of the Future
Open Commission

MS11.02.01 BEYOND ROUTINE STRUCTURE DETERMINATION - THE RENAISSANCE OF SMALL MOIETY CRYSTALLOGRAPHY. A. Alan Pinkerton, Department of Chemistry, University of Toledo, Toledo, OH 43606, USA

The introduction of area detectors, especially the CCD detector, into small moiety crystallography coupled with the availability of powerful, low cost workstations will have as large an impact on the discipline as that made by the introduction of automated diffractometers a quarter of a century ago. In the short term this will lead to a quantum jump in the number of routine structures determined each year. In the long term, crystallographers will devise new experiments and directions to take advantage of this technological advance. A number of potential new directions will be presented. This discussion will be based in part on experiences in my own laboratory and in part by gazing into a crystal ball (pun intended).

MS11.02.02 TIME-RESOLVED STRUCTURE ANALYSIS OF CRYSTALLINE-STATE REACTION BY A NEW DIFFRACTOMETER DESIGNED FOR RAPID DATA COLLECTION. Yuji Ohashi, Department of Chemistry, Tokyo Institute of Chemistry, Ookayama, Meguro-ku, Tokyo 152, Japan

The structural change of the reactant molecules can be directly observed by stepwise structure analysis using a new diffractometer in the process of the reaction. Since we found that the chiral cyanoethyl group bonded to the cobalt atom in a cobaloxime complex crystal was racemized by X-ray exposure without degradation of the single crystal form[1], many solid-state reactions with retaining the single crystal form, crystalline-state reaction, have been observed[2]. Recently several crystalline-state reactions which proceeds within ten hours have been found[3]. In order to analyze the structural changes in such reactions, we have designed and constructed a new diffractometer for rapid data collection[4]. The diffractometer, which has two imaging plates as detectors, enables us to collect the three-dimensional intensity data within two hours. Several examples of the direct observation of the structural changes by stepwise crystal structure analyses using the diffractometer will be shown and a new crystal chemistry based on the time-resolved structure analysis will be proposed.

[1] Y. Ohashi and Y. Sasada, Nature, 267, 142 (1977)
[2] "Reactivity in Molecular Crystals", Ed. by Y. Ohashi, VCH (1993)
[3] Y. Ohashi et al., Bull. Chem. Soc. Jpn., 68, 2517 (1995)
[4] Y Ohashi and H. Uekusa. J. Mol. Struc.. (1995) in press.

MS11.02.03 EXPERIMENTAL X-RAY DIFFRACTION EVIDENCE OF THE UNUSUAL BOND BENDING IN SMALL MOLECULES. M. Antipin*, and R. Boese,** Institute of Organoelement Compounds, Moscow, Russia.* Institute of Inorganic Chemistry, University of Essen, Germany**

Molecular structure and geometry are often the only kind of information that many chemists are interesting in as a final result of the X-ray analysis. Meanwhile, much more information may be extracted now from X-ray diffraction data using modern opportunities of this method. Thus, multipole representation of the electron density distributions and its topological analysis allow to describe the nature of some chemical bonds in new terms of the bond paths, critical point positions etc. This approach was found to be very fruitful for description bonding in small cyclic or strained cage molecules, where so called bent bonds are present.

In the deformation electron density (DED) maps the bending evidences as a shift of the DED bond maxima outward the internuclear lines connecting bonded atoms. Modern quantum chemical calculations show however, that bent bonds are much more abundant, some small acyclic and non-strained molecules having atoms with lone pairs (LP), may form bent bonds, but direct experimental evidence for this effect is absent.

In the present work a charge density study based on the high-resolution low temperature X-ray diffraction data was performed for series of crystals (s-tetrazines, ammonia, simplest carborane), where unusual bent bonds may be observed. It was found for s-tetrazines that DED maxima in N-N bonds are shifted to the centers of the 6-membered heterocycles because of repulsion between nitrogen LP's and electron density of the N-N bonds. The similar effect was found for ammonia molecule: DED maxima are shifted from the N-H lines inside the NH3 tetrahedron, and this result is in agreement with the bond critical point positions and quantum calculations. In the structure of the smallest carborane with the C2B3 central frame the bent C-B bonds were found together with the multicenter DED maxima in the middles of the 3-angles faces in this electron-precise molecule. The general conclusion about charge density analysis in molecules studied shows that straight bonds indicated"by lines" between atoms are more the exception than the rule.

MS11.02.04 DYEING CRYSTALS

Bart Kahr, Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393

The future of small molecule crystallography is wedded more closely to the past than many of us might suspect. It is our purpose here to demonstrate that many important crystalline materials were studied and abandoned before their time. For example, scientists for 150 years have studied crystals that adsorb and overgrow organic dyes during growth from solution. A wide variety of scientific and technological questions have motivated these researches including: the nature of pleochroism, limitations of the law of isomorphism, photosensitization of silver halides for photography, crystallization of ceramics, colloid stabilization, habit modification, epitaxy, preparation of explosives, and fertilizer identification. While mixed crystals of salts and dyes have not been objects of systematic study for a half century, they will undoubtedly appeal to a new generation of scientists because of their rich stereochemistry, and because crystals of simple ionic salts containing oriented, monodispersed, organic dyes promise spectroscopic and photonic applications. This review assembles previous observations that make up of the history of dyed crystals, while translating the descriptive crystallographic observations of past generations into a language that may be readily applied by the contemporary researcher. Next, we present our recent contributions and those of others according to host counteranion and including the following ions: sulfates, phosphates, carboxylates, carbonates, nitrates, halates, and halides. We show how structural studies of some historical dye inclusions are used in the design of new dye inclusions with prescribed physical properties. Both diastereoselective and enantioselective recognition process are illustrated. Dyed salt crystals are introduced as new solid state lasers and other potential optoelectronic devices. Comparisons with contemporary strategies for the matrix isolation of organic chromophores and biomolecules are presented. Here, we hope to restore a substantial body of chemical research to the contemporary scientific dialogue. We conclude by asking whether diffraction techniques of the future such as intense synchrotron x-ray sources coupled with careful analyses of diffuse scattering can contribute to structural studies of the aforementioned crystals.

MS11.02.05 QUALITY CONTROL AND DEPOSITION IN THE CAMBRIDGE STRUCTURAL DATABASE.

Sam Motherwell, Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge, CB2 1EZ. U.K.

All entries in the Cambridge Structural Database are subjected to an extensive sequence of software tests before archiving. The PreQuest program performs two types of checking (a) internal consistency checks e.g. bonds calculated from coordinates versus those given by authors and (b) chemical/crystallographic checks e.g. formulation, abnormal bond lengths, close contacts between molecules. The program is continually being augmented with new tests, e.g. for mis-assigned space groups. 2D chemical diagrams can be input manually or generated automatically from 3D coordinates using geometrical bond-type criteria. PreQuest has been developed to read CIF input data but also reads other established formats such as SHELX.

Modern diffractometry is generating valuable crystal structures by the thousand. It is unlikely that all of these will reach the public domain through formal publication methods, but it is essential that these indispensable data are recorded for future use. The CCDC is already closely involved in journal deposition schemes, and now wishes to extend its coverage to incorporate direct depositions from experimentalists. The PreQuest program will be made available for on-site data validation if required and, after validation at CCDC, authors would receive a CCDC Deposition Number to identify each individual structure. These Numbers could be cited in any subsequent publication. Lists of private communications will be placed in the public domain and individual data sets will be freely available on request.

MS11.02.06 CONTROLLED CRYSTALLIZATION FROM SOLUTION AND 'IN SITU' BY IR-LASER: THE CIRCUMVENT OF PLASTIC PHASES.

Roland Boese, Markus Nuesse, and Michael Nussbaumer-Universität-GH Essen, Germany

Two systems for crystallization are described: The 'in situ' crystallization device and an apparatus for a controlled cooling crystallization.

The 'in situ' crystallization device applies a focused infrared laser beam at the capillary which is cooled with an open gas stream on the diffractometer. The position of the heated (molten) zone and the intensity of the laser beam are computer controlled. This allows to grow single crystals from samples with very low melting points (e.g. gases at ambient) and to monitor the process with a video camera as well as by the diffraction pattern, ideally with a CCD detector. The device is suited to crystallize and sublime neat material in the capillary but also to crystallize from solution in order to circumvent plastic phases: The low temperature, ordered phase of norbornadiene is presented.

The second device is for the controlled crystallization by cooling of a solution and consists of two parts: A commercial particle counter using the scatter of laser light detects the number and size of the crystal seeds which emerge when cooling the solution. The computer-controlled warm-up and stopping of a stirring process then allows to observe the growing of the crystals at the bottom of a cuvette my means of a video camera. A series of pictures of a growing crystal while cooling slowly (e.g. 1° C per day) is assembled for a movie for observation of the process.