PS-06.02.03 STRUCTURAL AND MAGNETIC CHARACTERISATION OF ORGANOMETALLIC SALTS OF TCNQ AND DCQ.  By P.  Schwerer, J.S.  Field and R.J.  Baines, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, South Africa

The dinuclear electron-rich trisolate-bridged donor [Fe₂(C₆)₃(CO)₄] (C₆ = p-toluylcyclopenta- dienide) reacts with TCNQ (7,7,8,8-tetracyanoquinodimethane) to afford the 1:1 charge-transfer salt [Fe₂(C₆)₃(CO)₄](0.5·TCNQ).  X-ray diffraction studies reveal that the donor cations (D•⁻) and acceptor anions (A•⁻) stack in the crystal sequence ...D•⁻-A•⁻-D•⁻..., with the axes present at diamagnetic pairs (TCNQ)²⁻.  The room temperature magnetic susceptibility confirms a S = ½ system.  The stacking sequence in the analogous 1:1 salt of 2,5-dimethyl-N,N-dicyanomethylenimine (Me₂DCNQI) is different, containing alternating donor cations and acceptor anions ...D•⁻-A•⁻-D•⁻..., with the planes of the acceptor and adjacent C≡N rings being nearly parallel.  The 300 K magnetic susceptibility of [Fe₂(C₆)₃(CO)₄](0.5·Me₂DCNQI) may be fitted by the Curie-Weiss expression with θ = 0, indicating the absence of cooperative magnetic interactions; this salt is a well-behaved ½-½ system.  Details of the above and related work will be presented.

PS-06.02.04 STRUCTURAL AND SEMIEMPIRICAL STUDIES OF 2-ARYLPERIMIDINE DERIVATIVES.

By 2,3-Dimethyl-4-phenyl-1H-pyrazole, CSIC, Serrano 119, E-28006 Madrid, Spain.

Perimidine (R = R₂ = H) is one of the most useful heterocyclic systems, since it is the simplest way to have a heterocyclic six-membered ring presenting aminal tautomerism (Elguero, J., Marín, J.C., Katritzky, A.R. & Linda, P. “The tautomorphism of heterocycles”, Academic Press, New York (1976). The crystal structures of the following 2-arylperimidines derivatives were undertaken to study the influence of the hydrophobic effects on the overall conformation. The effect of the R₂ substituent on the perimidine moiety could not be established since, up to now, no suitable crystals of perimidine could be obtained.  

Crystal data:

<table>
<thead>
<tr>
<th>Comp</th>
<th>R₁</th>
<th>R₂</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C₈H₈N₂O₂</td>
<td>13.139(2)</td>
<td>6.7787(3)</td>
<td>13.479(7)</td>
<td>116.44(4)</td>
<td>P₁/c</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>C₈H₈N₂</td>
<td>20.810(1)</td>
<td>20.810(1)</td>
<td>16.818(7)</td>
<td>14/β</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>C₁₀H₈N₂</td>
<td>17.646(1)</td>
<td>9.2154(4)</td>
<td>8.378(3)</td>
<td>102.86(5)</td>
<td>P₂₁/n</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>C₁₀H₈N₂</td>
<td>14.756(1)</td>
<td>13.087(1)</td>
<td>7.954(3)</td>
<td>90.69(4)</td>
<td>P₂₁/c</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>C₁₀H₈N₂</td>
<td>8.879(4)</td>
<td>16.470(4)</td>
<td>8.496(4)</td>
<td>92.03(3)</td>
<td>P₂₁/n</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>C₁₀H₈N₂H₂O₄</td>
<td>15.9820(1)</td>
<td>7.32(2)</td>
<td>24.909(1)</td>
<td>106.83(8)</td>
<td>C2/c</td>
<td></td>
</tr>
</tbody>
</table>

The crystal structures consist of isolated molecules (III, IV, V), pairs of molecules connected through the water molecule by hydrogen bonds (VI) and infinite chains of molecules (I, II).  Moreover, “T-shaped” and stacking interactions between aromatic rings are also present.  The difference in color between compound V and its hemihydrate, VI, can be partially due to the differences in crystal packing.  The total packing coefficients are 0.72, 0.66, 0.69, 0.67, 0.70 and 0.71 respectively.  The water molecule in VI is included within an almost spherical hole of approximate surface and volume of 43.3 Å² and 22.5 Å³ (Carno, P.M. & Martinez-Ripoll, J.M. (1992) J. Mol. Struct. Theor. 258, 139-158).  The high local packing coefficient, 0.80, reveals the significance of the hydrogen bonds.  The X-ray results have been supplemented with a theoretical conformational analysis.  The computational results using semiempirical quantum chemical calculations at AM1 level (MOPAC6.0, Stewart, J.J.P. Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840 USA, 1990) indicate that the molecules adopt a similar conformation (II, IV, VI) to that in the solid state when no strong intermolecular hydrogen bond occurs.  The experimental and calculated dihedral angles between the substituent and the perimidine moiety are:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>3.5(4)</td>
<td>77.8(2)</td>
<td>77.7(2)</td>
<td>64.7(2)</td>
<td>0.5(3)</td>
<td>36.5(4)</td>
</tr>
<tr>
<td>Calc.</td>
<td>54.5</td>
<td>90.0</td>
<td>69.2</td>
<td>70.6</td>
<td>48.0</td>
<td>48.0</td>
</tr>
</tbody>
</table>

The lack of planarity displayed by all the perimidine skeletons, and mainly by their heterocyclic rings, is only supported by the theoretical calculations for compounds IV-VI.

PS-06.02.05 DIRECT OBSERVATION OF THE SOLID-STATE PHOTOREACTION OF 2-ACETYLMETHINONICAMIDE ACID HYDRATE BY SINGLE CRYSTAL X-RAY DIFFRACTION

By T. Ivanova and S. Kashiho*, Department of Chemistry, Faculty of Science, Okayama University, Japan

2-Acetylmethinonnic acid has been found to be photo-dimerizable in the crystals of its dihydrate (AC2) to form a tetrahedral product (AC2D) without a loss of the water molecules during the reaction in solution.  The X-ray structure determination of 2-acetylmethinonnic acid (AC2) and its dihydrate (AC2D) has been reported recently.  The effects of the different positions of the N(1) atom on the crystal structure of AC2 have been investigated.  In the present work, the crystal structure of an intermediate stage of the solid-state photoconversion of AC2 has been obtained and analyzed at the conversion rate of 12%: C₈H₈N₂O₂ · 2H₂O, Mr = 241.24, monoclinic, P2₁/n, a = 18.34(4) Å, b = 9.072(2) Å, c = 11.310(4) Å, β = 105.0(2)°, V = 1211.1(6) Å³, Z = 4, Dm = 1.33 Me · cm⁻³, Cu Kα, λ = 1.54178 Å, μ = 0.89 mm⁻¹, F(000) = 512, T = 296 K, β = 10.4% for 16 unique reflections with |F| > LARGER than 3σ(|F|).  The present study revealed the structures of the monomer and photodimeric components at the intermediate stage.  The photodimeric component viewed along the b axis is shown in Fig. 1 by superimposing the molecules in AC2 and AC2D.  As seen from Fig. 1 the atomic movements...
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accompanied by the dimerization are smaller than those estimated from the structure of AC4. The water molecules move maintaining their relative distance almost constant to keep the hydrogen bonding between them. The modes of hydrogen bonding at the intermediate stage and the features of the atomic movements are discussed.

Fig. 1. The composite diagram around a center of symmetry of the photodimer components, and the molecules in AC2 and AC4. Open bonds and large circles for AC1. bold bonds and medium circles for the photodimer component, and thin bonds and small circles for AC4.

Table 1. Structural Features of Dianthracenes

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Dihedral Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/B</td>
<td>θ</td>
</tr>
<tr>
<td>1a</td>
<td>1.530(5) 43.2; 41.9; 136.8; 138.8</td>
</tr>
<tr>
<td>1b</td>
<td>1.639(2) 43.2; 43.4; 130.7; 143.0</td>
</tr>
<tr>
<td>1c</td>
<td>1.657(4) 43.2; 43.4; 130.7; 143.0</td>
</tr>
</tbody>
</table>

In 1- and 2-symmetrical dianthracenes 1d and 1e, the difference in spatial demand due to the rotationally blocked 2-hydroxy-2-propyl groups is born out by distinctly different dihedral angles between aromatic rings (see Fig. 1).

Fig. 1. Schematic presentation of stereo-isomeric dianthracenes 1d and 1e.

PS-06.02.06 MOLECULAR STRUCTURES OF DIANTHRACENES


The molecular structures of bridgehead substituted dianthracenes 1a-e, prepared photochemically from 9-methoxy-9-methoxy-10-methyl, and 9-(2-hydroxy-2-propyl)dianthracene, have been established by X-ray diffraction.

La: R²⁺R⁺⁻CMe; R₂⁻R³⁻⁻Me,
lb: R²⁺R⁺⁻CMe; R₂⁻R³⁻⁻Me; R³⁻⁻H
lc: R²⁺R⁺⁻CMe; R₂⁻R³⁻⁻Me; R³⁻⁻H
ld/le: R¹⁺R⁺⁻2-hydroxy-2-propyl; R²⁻R³⁻⁻H

For dianthracenes 1a-c, topological features in terms of lengths of photochemically formed bonds, and dihedral angles between planes of aromatic rings are summarized in Table 1.

PS-06.02.07 CRYSTAL STRUCTURES OF SOME ORGANIC CO-CRYSTALS By Hidehiro UEKUSA*, Yuji OHASHI, Tokyo Institute of Technolgy, Japan, and Fumio TODA, Fuku University, Japan.

Recently, many types of solid-solid organic reactions, such as a coupling of piemuls, Wittig, Fornier reaction and iodol condensation, have been found. Only mixing a powder of some organic compounds, these reactions can easily occur. In the solid-solid reaction, regio and stereo selective reactions are expected. In a course of the study of developing a new reaction field for the solid-solid reaction, the crystal structures of two co-crystals, (1) N, N'-dibenzoyl-urea and N, N'-dicyclohexylurea (1) complex crystal and (2) PhCONMe and PhNHCOCMe 1:1 mixed crystal, have been determined. Especially using a mixed crystal as a reactant or host compound, a new sophisticated reaction field may be obtained.

Crystal | (1) | (2)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>26.013(2)</td>
<td>19.368(3)</td>
</tr>
<tr>
<td>b</td>
<td>9.156(1)</td>
<td>8.089(1)</td>
</tr>
<tr>
<td>c</td>
<td>11.32(2)</td>
<td>9.186(1)</td>
</tr>
<tr>
<td>δ(°)</td>
<td>90.83(3)</td>
<td>90.83(3)</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>2659.1(4)</td>
<td>1484.9(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>Pnca</td>
</tr>
</tbody>
</table>

(1)