06-Crystallography of Organic Compounds

The crystal structures consist of isolated molecules (IV, V, VI), 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 VI is 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 a nearly square planar moiety of approximate surface area and volume of 43.0 Å² and 22.5 Å³ (Caro.J.H. & Martinez-Ripoll,J.1992) J. Mol. Struct. Theor.Obes_588, 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. Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840 USA, 1990) indicate that the molecules adopt a similar conformation (IV, VI) to that in the solid state when no strong intramolecular hydrogen bond occurs. The experimental and calculated dihedral angles between the substituent and the phenylidene moiety are:

<table>
<thead>
<tr>
<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), 77.8(2), 77.2(2), 64.7(2), 0.5(3), 36.5(4)</td>
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<tr>
<td>Calc.</td>
<td>54.5, 90.0, 69.2, 70.6, 48.0, 48.0</td>
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The lack of planarity displayed by all the phenylidene 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 
α-KETOLUMINICINOMIC ACID HYDRATE BY SINGLE CRYSTAL X-RAY DIFFRACTION

By T. lwaeda and S. Kashino® Department of Chemistry, Faculty of Science, Okayama University, Japan

α-Ketoluminomicomic acid has been found to be photodimerizable in the crystals of its hydrate (Ac2) to form a tetrahedral photodimer (ACB4) without a loss of the water molecules during the reaction lwaeda, Kashino and Ishi, Acta Cryst. 1989, 45, 1575-1578]. The crystal structure of ACB4 was closely related to that of AC2. The space group and the mole of hydrogen bonds of ACB4 were the same as those of AC2. On the solid-state photodimerization dynamic single crystal X-ray diffraction studies have been reported on the reaction of 2-benzyl-5-benzylidene-cyclopentanone and its p-bromine derivative (Nakamura, Jones, Thomas, Bartholome and McVickar, J. Phys. Chem. 1981, 85, 336-344). 1 and on phenyl-cyclohexene cycloaddition (Plunger and Settrander, Photochem. Photobiol. 1989, 49, 375-379).

In the present work, the crystal structure of an intermediate stage of the solid-state photodimerization of AC2 has been analyzed at the conversion rate of 12%; C18H18NO, 2H2O, Mr = 241.21, monoclinic, P21/n, a = 18.34(5), b = 8.072(2), c = 11.310(4), β = 105.0(2)°, V = 1211.8(1) Å³, Z = 4, 8, 2.13 M cells m², Cu Kα, λ = 1.54178 Å, μ = 0.89 mm⁻¹, F(000) = 512, T = 296 K, b = 0.10 Å for 16% unique reflections with I(F) > 3σ(F).

The present study revealed the structures of the monomer and photodimeric component at the intermediate stage. The photodimer component viewed along the b axis is shown in Fig. 1 by superimposing the molecules in AC2 and ACB4. As seen from Fig. 1 the atomic movements...