Orientation of Photo-dimerization by Metal Ions: the Crystal Structure of Bis(dibenzylideneacetone)uranyl Dichloride

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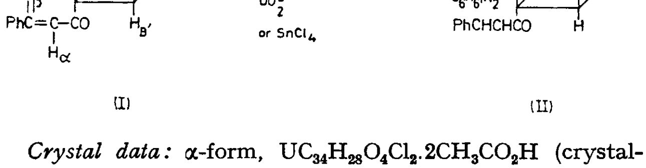
Summary. The crystal structure of bis(dibenzylideneacetone)uranyl dichloride shows that the photo-dimer of dibenzylideneacetone produced in the presence of uranyl salts is formed intermolecularly, and that its stereochemistry results from the presence of the bulky uranyl chloride group.

The photo-dimerization of *trans,trans*-dibenzylideneacetone (DBA) was first reported by Praetorius[1] in 1909, who showed that in the presence of uranyl salts, either in solution or the solid state, a 'truxillic' type dimer(I) was formed; tin chloride was later shown to have the same effect,[2] implying that the role of the uranyl ion is not that of a sensitiser.[3] Recently,[4] the photo-dimerization of the free ketone has been proved to give a 'truxinic' dimer (II).

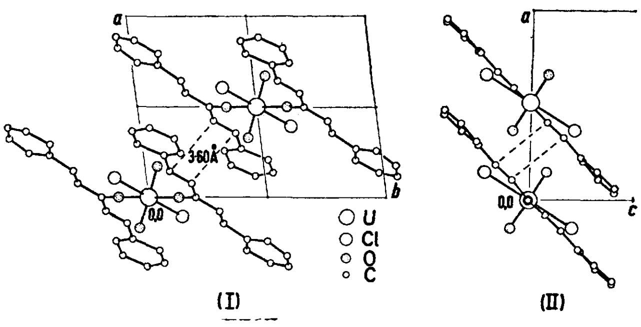
The structure of (I) has now been confirmed by ^1H n.m.r. spectroscopy. The spectrum shows a multiplet for 20 aromatic protons (centred at δ 7·30), a single doublet centred at 6·42 for the two pairs H_α and H_β, with $J_{\alpha\beta}$ 16 Hz so that both pairs must be *trans*-oriented, and a multiplet centred at 4·65 for the two pairs or cyclobutane protons, H_A, $H_{A'}$; H_B, $H_{B'}$, which form a symmetrical *trans*-AA′BB′ pattern.

The crystal structure of the uranyl chloride complex was examined in the hope of explaining the mechanism of orientation.



(I) (II)

Crystal data: α-form, $UC_{34}H_{28}O_4Cl_2.2CH_3CO_2H$ (crystallized from acetic acid), monoclinic, *C*2/*m*, $a = 9{\cdot}671(5)$, $b = 17{\cdot}745(9)$, $c = 21{\cdot}54(2)$ Å, $\beta = 91{\cdot}934(9)°$, $Z = 4$; of the two independent molecules one is severely disordered, and the discussion relates to the ordered molecule (site symmetry $2/m$). 1080 observed reflections were collected rapidly on a Syntex $P2_1$ diffractometer in almost total darkness. The structure was solved by the heavy-atom method and refined to a current R value of 0·121 (U and Cl with anisotropic temperature factors).



Figure

(I) View nearly normal to the a–b face of the unit cell showing two molecules related by the C-centre and the close approach between them.

(II) View down b, showing the relative orientation of the two DBA molecules, (only one shown attached to each uranium atom).

The structure (Figure) shows the UO_2^{2+} group to be *trans*-co-ordinated in a square plane by the two Cl^- ions and the two DBA molecules. These are planar with a fully extended conformation. The interaction that leads to photo-dimerization is revealed as intermolecular, between a molecule with its uranium atom at the origin and one related by C-centring (Figure); and the DBA molecules approach each other head-to-tail eclipsed, as required for the formation of (I). The C–C distance across which a bond forms on irradiation is 3·60Å (*c.f.* 3·6–4·1Å in α-*trans*-cinnamic acid[5]). The acetic acid is present only as solvent of crystallization, but nevertheless plays an important role; crystallization above 80 °C produces an unsolvated β-form, monoclinic, $C2$, a = 12·72(3), b = 11·83(2), c = 22·58(3)Å, β = 97·70(5)°.

The nearest $\begin{matrix}C---C\\ \| \qquad \|\\ C---C\end{matrix}$ approach is again between DBA molecules in complexes related by C-centring, but the change in cell constants leads to C - - - C distances of 5·9 Å and photo-dimerization does not occur.†

The persistence of the orientation effect in solution, and in $SnCl_4$ complexes (doubtless also *trans*-bis-co-ordinated) shows that it is not simply the chance result of the molecular packing. A consideration of the way in which molecules of the uranyl complex could approach each other shows that this is the only possible orientation. Essentially, a $(DBA)UO_2Cl_2$ group is a very bulky object attached to the functional DBA molecule. Two DBA molecules can then only approach each other with both bulky groups away from the point of approach. The further requirement that the double bonds be aligned parallel rather than orthogonal leaves the observed arrangement as the only possible one for dimerization. This contrasts with the much greater freedom of isolated pairs of molecules to take up different orientations.

We would suggest as a general principle that appropriate systems will show similar restrictions on the orientation of photodimerization when bulky groups, and in particular metal ions, are attached.

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† Ref. 1 is incorrect in reporting its occurrence.

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