

Solid-state Photochemistry. Part 1. Nature of the Stereocontrol in the Photodimerisation of Dibenzylideneacetone by UO_2^{2+} Ion: Crystal and Molecular Structure of *trans*-Dichlorobis(*trans,trans*-dibenzylideneacetone)dioxouranium(vi) and of its Acetic Acid Solvate

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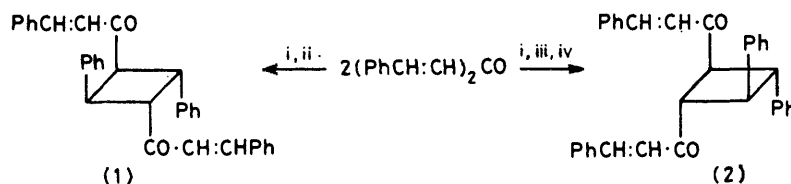
In order to define the orientation of the ligand *trans,trans*-dibenzylideneacetone (dba) before photodimerisation, two complexes, $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2]$ (3) and $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2]\cdot 2\text{CH}_3\text{CO}_2\text{H}$ (4), were prepared and their crystal structures determined from three-dimensional X-ray data by Patterson and Fourier methods. Crystals of (3) are monoclinic, space group $C2/c$, with $Z = 4$ in a cell of dimensions (at 20 °C) $a = 12.397(5)$, $b = 11.587(3)$, $c = 21.950(5)$ Å, and $\beta = 97.89(2)^\circ$; least-squares refinement for 1 697 independent reflections reached R 0.025. Crystals of (4) are triclinic, space group $P\bar{1}$, with $Z = 1$ in a cell of dimensions (at -155 °C) $a = 11.851(2)$, $b = 10.023(3)$, $c = 11.668(3)$ Å, $\alpha = 103.57(2)$, $\beta = 129.20(2)$, and $\gamma = 103.48(2)^\circ$; least-squares refinement for 3 023 reflections reached R 0.035. The solvated form (4) is very much more sensitive to light than the unsolvated form (3). In (4), two pairs of ethylenic bonds in adjacent molecules are 3.50(1) and 3.51(1) Å apart, and the parallelograms formed by these bonds have angles of 97.7(4) and 104.4(5)°. In (3), only one C=C bond is adjacent to another in a neighbouring molecule, with $\text{C}\cdots\text{C}$ 4.09(1) Å and $\text{C}=\text{C}\cdots\text{C}$ angle 123.3(4)°. The intermolecular geometry found for (4) is evidently more favourable for dimerisation than that in (3) and explains their different photosensitivities.

THE photodimerisation of *trans,trans*-dibenzylideneacetone $[(\text{PhCH}:\text{CH})_2\text{CO}]$, dba was discovered by Praetorius and Korn,¹ who observed that in the presence of uranyl chloride, either in acetic acid solution or as solid material, a colourless 'truxillic' type dimer (1) was formed (see Scheme). The same dimer was later obtained by Stobbe and Färber² in the presence of SnCl_4 , implying that the role of the uranyl ion is not that of a sensitiser.³ The structure of (1) has recently been confirmed by ^1H n.m.r.⁴

Ciamician and Silber⁵ found that irradiation of free

other dba (0.2 mol, prepared according to the method of ref. 8), were mixed in a dark room. A yellow-orange precipitate formed rapidly, which was washed and dried. Plate-like crystals (4) $\text{UO}_2\text{Cl}_2(\text{dba})_2\cdot 2\text{CH}_3\text{CO}_2\text{H}$ were obtained by dissolving a few mg of the precipitate in acetic acid (2–3 ml) at 80 °C and cooling the solution. Prismatic crystals of (3) $\text{UO}_2\text{Cl}_2(\text{dba})_2$ were obtained by warming a similar acetic acid solution near to its boiling point and keeping it warm until crystallisation occurred.

Previous Crystallographic Results.—In a preliminary note,⁴ the solvated form (4) was reported to crystallise in space group $C2/m$, with one of the two independent molecules dis-



SCHEME Reagents: i, $h\nu$; ii, UO_2^{2+} or SnCl_4 ; iii, C_6H_6 ; iv, N_2

dba with sunlight in ethanol gives a different dimer which was shown to have a 'truxinic' structure (2) by Rechtenwald *et al.*⁶ Shoppee *et al.*⁷ found recently that irradiation of dba in benzene under nitrogen gives a complex mixture of cyclic compounds, and isolated five of these. The major product is (2) and the four others are trimers. They also confirmed the original report of Praetorius.¹

In an attempt to clarify the role of ligand orientation in the photochemical formation of (1), we have determined the structures of the two complexes (3), $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2]$ and (4), $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2]\cdot 2\text{CH}_3\text{CO}_2\text{H}$ by X-ray single-crystal methods. A preliminary account of some of this work has appeared.⁴

EXPERIMENTAL

Syntheses.—Two solutions in glacial acetic acid (50 ml), one containing uranyl chloride hydrate (0.02 mol) and the

ordered, and the unsolvated form (3) in space group $C2$. Nevertheless, none of these two structures refined in an entirely satisfactory manner, and a complete reinvestigation was begun. It was subsequently found that the solvated form had a pseudo $C2/m$ symmetry in an unreduced cell, the true space group being $P\bar{1}$. It was also found that the unsolvated form belongs to space group $C2/c$ instead of $C2$, the presence of intense reflections of the type $h0l$, $l = 2n + 1$, excluding a c -glide plane, being due to the perfect twinning of all crystals. A detailed discussion of the pseudo-symmetry and twinning encountered in these two structures will be reported elsewhere. Hereafter, only the results of the new investigation are given.

Crystal Data.—*Solvated form* (4). $\text{C}_{34}\text{H}_{26}\text{Cl}_2\text{O}_4\text{U}\cdot 2\text{CH}_3\text{CO}_2\text{H}$, Triclinic, $M = 929$. At -155 °C, $a = 11.851(2)$, $b = 10.023(3)$, $c = 11.668(3)$ Å, $\alpha = 103.57(2)$, $\beta = 129.20(2)$, and $\gamma = 103.48(2)^\circ$, $U = 900.4$ Å³, $Z = 1$, $D_c = 1.714$ g cm^{-3} . Mo- K_α radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 44.7$ cm^{-1} . Space group $P\bar{1}$.

Unsolvated form (3). $\text{C}_{34}\text{H}_{26}\text{O}_4\text{Cl}_2\text{U}$, Monoclinic, $M =$

809. At 20 °C, $a = 12.397(5)$, $b = 11.587(3)$, $c = 21.950(5)$ Å, and $\beta = 97.89(2)^\circ$, $U = 3\ 123.0$ Å³, $Z = 4$, $D_c = 1.726$ g cm⁻³. $\mu(\text{Mo-K}\alpha) = 51.4$ cm⁻¹. Space group $C2/c$.

Data Collection.—Since the solvated form (4) is extremely sensitive to light, only the minimum amount of light necessary to carry out the experiments was used. A plate-like broken fragment of size *ca.* 0.28 × 0.17 × 0.33 mm was mounted on a Syntex $P2_1$ diffractometer (which was used throughout this work) and its temperature lowered to -155 °C with the L-T₁ attachment, to minimise the effect of the undesired photochemical process. By use of Mo-K α radiation and a graphite monochromator, data were collected to 2 θ 50° (0–2 θ scan technique) at a scan rate varying between 1.5 and 29.3 min⁻¹, the peaks being scanned from 1.2° (in 2 θ) above $K_{\alpha 2}$ to -1.2° below $K_{\alpha 1}$. The ratio, total background to scan time, was 0.5. Three standard reflections measured periodically throughout data collection showed no significant decline. Data were corrected for Lorentz polarisation effects and for absorption (for the crystal chosen, the transmission coefficients on F ranged from 0.713 to 0.936). Only the 3 023 data having $I > 3\sigma(I)$ were used in the subsequent structure analysis and refinement.

For form (3), which is much less sensitive to daylight, at least under the conditions of our experiments, it was not felt useful to collect data at low temperatures. A triangular prism, obtained by cleavage, and of size *ca.* 0.32 × 0.22 × 0.07 mm was mounted on the diffractometer. Data were collected as before, but at 20 °C, to 2 θ 50° with a scan range in 2 θ from -0.85 below $K_{\alpha 1}$ to 0.85 above $K_{\alpha 2}$. The scan time was twice the total background time. The data were corrected as before for (4) (transmission coefficients on F from 0.647 to 0.853) and 1 697 independent observed reflections were used in the solution and refinement of the structure. For both forms accurate unit-cell dimensions were obtained by a least-squares fit of the diffractometric angles of 15 reflections.

Solution and Refinement of the Structures.—The crystal structure calculations system X-RAY 76⁹ was used in the solution and refinement of the structures. Calculations were carried out on a Burroughs B 6700 computer. The function minimised in least-squares was $\Sigma w(F_o - F_c)^2$. Atomic scattering factors were from ref. 10, the effects of anomalous dispersion for U and Cl being included in the calculations of F_c , with values of $\Delta f'$ and $\Delta f''$ from ref. 11. The two structures were solved by standard Patterson and difference-Fourier methods. Since in both structures the uranium atoms are located in special positions at the origin, most of the non-hydrogen atoms could be located directly from Patterson maps. All hydrogen atoms in the two structures could be found on difference-Fourier maps, after anisotropic refinement of the non-hydrogen atoms. In the final refinement of the solvated form (4) all non-hydrogen atoms were refined anisotropically, the hydrogen atoms with B values set at 4.0 Å² were not varied, and a weight $w = X \cdot Y$ was applied. In this weighting scheme, $X = \sin \theta/0.215$ or $0.345/\sin \theta$ for $\sin \theta \leq 0.215$ or $\sin \theta \geq 0.345$ respectively, and $Y = F/26.0$ or $50.0/F$ for $F \leq 26.0$ or $F \geq 50.0$ respectively. This refinement gave the values of R 0.035 and R' 0.040. In the last cycle of least-squares refinement, no parameter underwent a shift of $>0.26\sigma$. In the final refinement of the unsolvated form (3), all non-hydrogen atoms were refined anisotropically; hydrogen atoms with B values set at 4.5 Å² were not varied and a weight $w = X \cdot Y$ was applied where $X = \sin \theta/0.190$ or

$0.300/\sin \theta$ for $\sin \theta \leq 0.190$ or $\sin \theta \geq 0.300$ respectively, and $Y = F/90.0$ or $350.0/F$ for $F \leq 90.0$ or $F \geq 350.0$ respectively. The final agreement factors are R 0.025 and R' 0.026. In the last cycle of least-squares refinement, no parameter shifted by $>0.73\sigma$. For both structures, the final values of F_o and F_c suggested that no correction for secondary extinction was necessary. Atom fractional coordinates are given in Tables 1 and 2. Tables of thermal parameters, and listings of observed and calculated structure factors are deposited as Supplementary Publication No. SUP 22478 (41 pp.).*

TABLE 1

Fractional atomic co-ordinates for complex (4) [(UO₂)Cl₂(dba)₂]·2CH₃CO₂H; for non-H atoms × 10⁴ and for H atoms × 10³

	X	Y	Z
U	0	0	0
Cl	601(2)	1 565(2)	2 690(2)
O(1)	1 151(5)	-1 442(5)	1 152(5)
O(2)	1 957(5)	1 444(5)	1 028(6)
C(1)	1 907(7)	-2 130(7)	1 874(7)
C(2)	1 815(7)	-3 448(7)	915(7)
C(3)	953(8)	-3 983(7)	-726(8)
C(4)	757(7)	-5 318(7)	-1 799(7)
C(5)	1 424(8)	-6 276(7)	-1 235(8)
C(6)	1 227(9)	-7 500(8)	-2 317(9)
C(7)	393(9)	-7 771(8)	-3 946(10)
C(8)	-250(9)	-6 817(8)	-4 501(9)
C(9)	-91(9)	-5 615(8)	-3 450(8)
C(10)	2 916(7)	-1 593(7)	3 656(7)
C(11)	3 065(7)	-369(7)	4 616(7)
C(12)	4 050(7)	289(7)	6 425(7)
C(13)	4 011(8)	1 558(8)	7 179(8)
C(14)	4 919(9)	2 229(8)	8 891(9)
C(15)	5 869(9)	1 623(8)	9 868(8)
C(16)	5 936(8)	374(8)	9 129(8)
C(17)	5 018(8)	-300(7)	7 423(8)
C(18)	5 462(8)	4 678(7)	3 710(8)
C(19)	5 809(11)	4 394(10)	2 674(10)
O(3)	4 635(6)	5 371(6)	3 463(6)
O(4)	6 023(6)	4 210(6)	4 787(6)
H(1)	240	-397	148
H(2)	42	-346	-132
H(3)	203	-607	9
H(4)	165	-818	-195
H(5)	11	-879	-488
H(6)	-85	-702	-566
H(7)	-55	-482	-397
H(8)	349	-213	418
H(9)	244	11	403
H(10)	314	200	638
H(11)	506	339	959
H(12)	678	232	1 124
H(13)	658	-18	988
H(14)	500	-125	676
H(15)	444	553	441
H(16)	580	342	236
H(17)	680	517	344
H(18)	512	449	168

DISCUSSION

Intramolecular Bond Distances and Angles.—A view of the centrosymmetric complex (3) (the unsolvated crystal) is shown in Figure 1. The main bond lengths and angles are presented in Table 3 which shows that corresponding intramolecular bond distances are virtually identical in both structures, so that one may simply consider the average of each individual bond over the

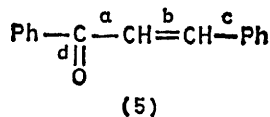
* For details, see Notices to Authors No. 7, in *J.C.S. Perkin II*, 1978, Index issue.

TABLE 2

Fractional atomic co-ordinates for complex (3) [(UO₂)Cl₂-(dba)₂]; for non-H atoms × 10⁴ and for H atoms × 10³

	X	Y	Z
U	0	0	5 000
Cl	292.7(18)	-1 239.0(17)	4 009.1(9)
O(1)	726(4)	1 530(4)	4 576(2)
O(2)	1 311(4)	-373(4)	5 358(2)
C(1)	1 285(5)	2 410(6)	4 410(3)
C(2)	1 796(6)	2 327(6)	3 852(3)
C(3)	1 649(6)	1 429(6)	3 472(3)
C(4)	2 108(6)	1 296(6)	2 895(3)
C(5)	1 682(6)	448(7)	2 485(3)
C(6)	2 059(8)	315(7)	1 923(4)
C(7)	2 872(7)	1 009(8)	1 771(3)
C(8)	3 319(7)	1 833(8)	2 175(4)
C(9)	2 951(6)	1 983(7)	2 738(3)
C(10)	1 421(5)	3 461(6)	4 754(3)
C(11)	931(6)	3 640(6)	5 259(3)
C(12)	990(6)	4 662(5)	5 647(3)
C(13)	434(6)	4 635(6)	6 161(4)
C(14)	441(7)	5 582(8)	6 541(4)
C(15)	1 014(7)	6 564(8)	6 421(4)
C(16)	1 568(7)	6 604(7)	5 926(4)
C(17)	1 542(7)	5 656(7)	5 536(4)
H(1)	225	294	375
H(2)	111	75	358
H(3)	103	90	258
H(4)	174	-27	163
H(5)	314	92	139
H(6)	391	233	207
H(7)	319	250	300
H(8)	181	419	457
H(9)	47	309	538
H(10)	40	388	623
H(11)	50	558	686
H(12)	103	721	669
H(13)	196	729	585
H(14)	188	570	517

two forms. The formulae used in averaging¹² are: $d_{av} = \sum_i (d_i/\sigma_i^2) / \sum_i (1/\sigma_i^2)$ and $\sigma^{-1} = \sum_i (1/\sigma_i^2)$, where d_i are the individual bond distances and σ_i the corresponding estimated standard deviations. The uranium atom is octahedrally surrounded by two chlorine atoms, two oxygen atoms of the uranyl group, and two keto oxygen atoms of the dba ligands, at average distances of 2.674(2), 1.752(3), and 2.295(4) Å. For comparison, the seven-coordinate U^{VI} complex UO₂Cl₂(C₁₂H₂₂O₂S)¹³ has mean U-Cl, U-O(uranyl), and U-O(ligand) bond distances of 2.67(1), 1.76(3), and 2.49(2). In another seven-coordinate complex, UO₂(C₃H₇O₂)₂(C₆H₁₁ON)¹⁴ mean U-O(uranyl) distances are 1.794(4) Å and U-O(ligand) are 2.367(2) Å. Whereas the U-O(uranyl) distance is fairly constant in different complexes, the U-O(ligand) distances vary from one complex to another, depending on the uranium co-ordination number and steric interactions. It seems that the U-O(dba) distance [2.295(4) Å] found here is at the short end of the range experimentally observed. The dba moieties in both



structures are in the *trans,trans*-conformation. No direct comparison between bond distances in the ligand and in

TABLE 3

Bond distances (Å) and angles (°) for the solvated (4) and unsolvated (3) complexes

Atoms	(4)	(3)
<i>(a) Distances</i>		
U-Cl	2.676(3)	2.673(2)
U-O(1)	2.296(6)	2.294(5)
U-O(2)	1.737(6)	1.759(4)
O(1)-C(1)	1.262(9)	1.267(8)
C(1)-C(2)	1.447(12)	1.458(10)
C(2)-C(3)	1.338(11)	1.331(10)
C(3)-C(4)	1.454(12)	1.465(10)
C(4)-C(5)	1.405(11)	1.385(10)
C(5)-C(6)	1.385(14)	1.388(12)
C(6)-C(7)	1.386(14)	1.365(13)
C(7)-C(8)	1.385(14)	1.367(12)
C(8)-C(9)	1.378(15)	1.387(12)
C(9)-C(4)	1.397(12)	1.394(11)
C(1)-C(10)	1.441(10)	1.431(9)
C(10)-C(11)	1.340(12)	1.351(10)
C(11)-C(12)	1.458(10)	1.454(9)
C(12)-C(13)	1.396(13)	1.402(11)
C(13)-C(14)	1.384(12)	1.377(12)
C(14)-C(15)	1.399(12)	1.386(13)
C(15)-C(16)	1.395(14)	1.363(14)
C(16)-C(17)	1.375(12)	1.392(12)
C(17)-C(12)	1.404(11)	1.378(11)
C(18)-C(19)	1.495(19)	
C(18)-O(3)	1.257(12)	
C(18)-O(4)	1.268(11)	
<i>(b) Angles</i>		
Cl-U-O(1)	90.7(2)	89.6(1)
Cl-U-O(2)	90.6(2)	90.6(2)
O(1)-U-O(2)	90.7(2)	89.3(2)
U-O(1)-C(1)	175.1(4)	169.4(4)
O(1)-C(1)-C(2)	119.6(7)	120.6(6)
C(1)-C(2)-C(3)	122.7(7)	122.8(6)
C(2)-C(3)-C(4)	126.5(7)	126.0(7)
C(3)-C(4)-C(5)	123.2(7)	118.5(6)
C(3)-C(4)-C(9)	117.7(7)	123.1(6)
C(5)-C(4)-C(9)	119.1(8)	118.4(7)
C(4)-C(5)-C(6)	119.8(8)	120.8(7)
C(5)-C(6)-C(7)	120.3(8)	120.0(7)
C(6)-C(7)-C(8)	120.1(1.0)	120.1(8)
C(7)-C(8)-C(9)	120.2(9)	120.7(8)
C(8)-C(9)-C(4)	120.5(8)	119.9(7)
C(2)-C(1)-C(10)	119.0(7)	117.9(6)
O(1)-C(1)-C(10)	121.4(7)	121.6(6)
C(1)-C(10)-C(11)	121.8(7)	122.1(6)
C(10)-C(11)-C(12)	127.0(7)	127.8(7)
C(11)-C(12)-C(13)	117.8(7)	117.5(6)
C(11)-C(12)-C(17)	123.0(8)	124.3(7)
C(13)-C(12)-C(17)	119.2(7)	118.2(6)
C(12)-C(13)-C(14)	120.4(8)	120.4(7)
C(13)-C(14)-C(15)	119.9(8)	120.1(8)
C(14)-C(15)-C(16)	119.9(8)	120.4(9)
C(15)-C(16)-C(17)	120.0(8)	119.5(8)
C(16)-C(17)-C(12)	120.6(8)	121.4(8)
C(19)-C(18)-O(3)	118.0(9)	
C(19)-C(18)-O(4)	118.0(9)	
O(3)-C(18)-O(4)	124.0(1.1)	
<i>(c) Intermolecular contacts</i>		
C(2) ··· C(3)	3.510(14)	> 5.0
C(10) ··· C(11)	3.500(12)	4.091(10)
O(3) ··· O(4)	2.592(13)	
C(3)-C(2) ··· C(3')	104.4(5)	
C(11)-C(10) ··· C(11')	97.7(4)	123.3(4)

free dba is available, but interatomic distances in free chalcone (5) and some of its derivatives are known.¹⁵ In this work, the mean dba bond distances are: a 1.443(5), b 1.340(5), c 1.458(5), and d 1.265(6) Å. The mean distances for chalcone and its derivatives are: a 1.480(8), b 1.328(6), c 1.459(10), and d 1.225(10) Å.

This suggests that the dba bond distances in both complexes are only marginally affected by metal co-ordination. In the palladium(0) complexes, $[\text{Pd}_2(\text{dba})_3]$ (ref. 16) and $[\text{Pd}(\text{dba})_3]$ (ref. 17), where the metal is directly

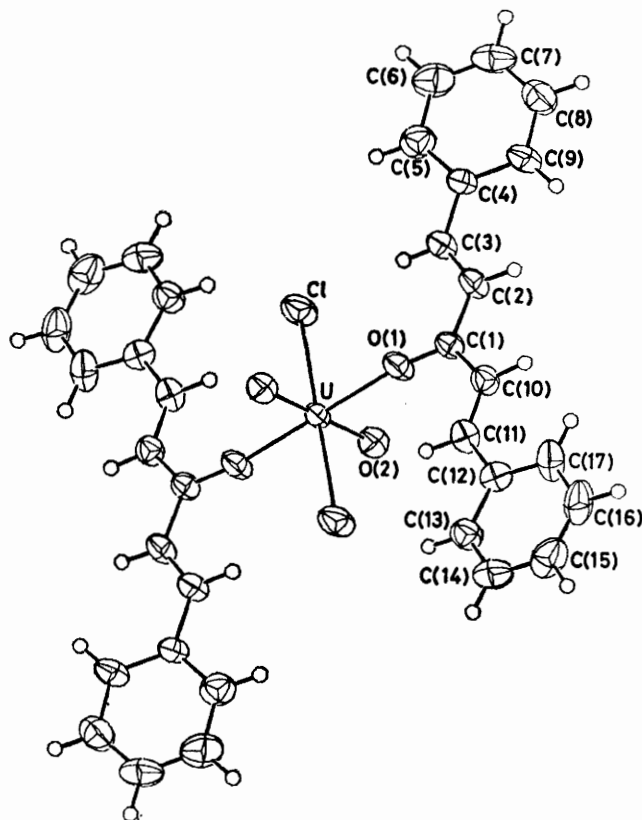


FIGURE 1 $[(\text{UO}_2)\text{Cl}_2(\text{dba})_2]$, compound (3). View of the complex molecule. Thermal ellipsoids of non-hydrogen atoms are scaled at 50% probability. Hydrogen atoms are represented as circles of arbitrary size. The complex molecule in the solvated form (4) is very similar

bonded to one vinyl group of each dba, the bond distances in the ligand vary significantly and cannot be averaged. For $[\text{Pd}_2(\text{dba})_3]$, extreme individual values for bonds are: a 1.44–1.67, b 1.24–1.39, and d 1.18–1.25 Å.

The planarity of different groups of atoms in dba can be estimated from Table 4. A trial least-squares plane calculation over all dba atoms showed a maximum out-of-plane distance of 0.16 Å for the solvated form (4) and 0.45 Å for the unsolvated form (3). For (4), the angles between planes are: (3)–(4) 2.4, (2)–(4) 1.3, and (1)–(3) 4.8°. For the unsolvated form, corresponding angles are 5.4, 2.4, and 14.3°. This last value shows that in (3) one phenyl group [plane (1)] is appreciably tilted relative to the rest of the molecule.

Intermolecular Contacts.—*Unsolvated form.* A pair of neighbouring complex molecules related by a centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$ is shown in Figure 2. The separation between C=C bonds in these adjacent molecules is 4.09(1) Å. In the parallelogram of atoms formed by the pair of bonds, the angle $\text{C}(11)\text{—C}(10)\cdots\text{C}(11')$ is

TABLE 4

Deviations (Å) of atoms from least-squares planes. Those for the solvated (4) form precede those for the unsolvated form (3)

Plane (1): Phenyl ring C(4)–(9)

C(1) 0.001, –0.012; C(5) 0.005, 0.009; C(6) –0.004, 0.000; C(7) –0.003, –0.006; C(8) 0.008, 0.003; C(9) –0.007, 0.003

Plane (2): Phenyl ring C(12)–(17)

C(12) –0.001, 0.002; C(13) 0.002, 0.005; C(14) 0.004, –0.006; C(15) –0.010, –0.001; C(16) 0.011, 0.008

Plane (3): Vinyl group C(1)–(4)

C(1) –0.008, –0.010; C(2) 0.007, 0.009; C(3) 0.009, 0.011; C(4) –0.008, –0.010

Plane (4): Vinyl group C(1), C(10)–(12)

C(1) 0.002, –0.003; C(10) –0.002, 0.002; C(11) –0.002, 0.003; C(12) 0.002, –0.003

Plane (5): Acetic acid in (4)

C(18) –0.001, C(19) 0.000, O(3) 0.000, O(4) 0.000

123.3(4)°. These two facts do not favour the fast formation of a dimer: the angle is far from 90° and the distance of 4.09 Å is greater than many other intermolecular contacts which simply result from the normal packing of the molecules. There are, for example, seven independent interatomic distances <3.5 Å in this structure, four between a carbon (or oxygen) not carrying a hydrogen atom, and a carbon carrying one (minimum distance 3.32 Å), and three between carbons each carrying a hydrogen (minimum distance 3.39 Å). The other vinyl group, C(2)–C(3), is at a distance >5 Å from its centrosymmetrically related pair.

Solvated form. For this form, both alkene groups C(2)–C(3) and C(10)–C(11), belonging to the complex molecule centred at the origin, interact with alkene groups in neighbouring molecules through centres of symmetry at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$. This is shown in Figure 3; Figure 4 shows the complete packing of one unit cell. The distance $\text{C}(2)\cdots\text{C}(3')$ and $\text{C}(10)\cdots\text{C}(11')$ are

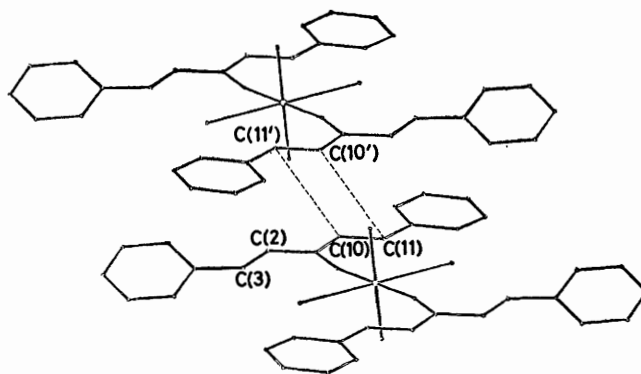


FIGURE 2 View of two neighbouring molecules of (3) related by a centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$

3.51(1) and 3.50(1) Å; angles $\text{C}(3)\text{—C}(2)\cdots\text{C}(3')$ and $\text{C}(11)\text{—C}(10)\cdots\text{C}(11')$ are 97.7(4) and 104.5(5)°. Excluding the distance between oxygen atoms in pairs of acetic acid molecules, there are 13 independent

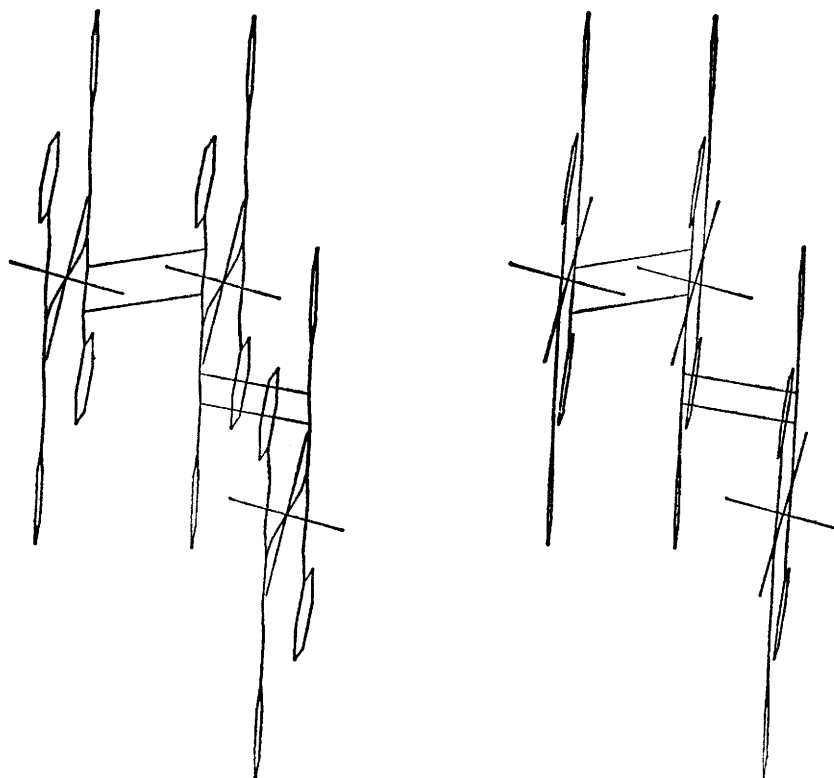


FIGURE 3 $[(UO_2)Cl_2(dba)_2] \cdot 2CH_3CO_2H$, compound (4). A stereoscopic pair of drawings showing three complex molecules. Two alkene bonds belonging to one dba ligand interact with two bonds in neighbouring molecules

intermolecular distances $< 3.5 \text{ \AA}$, the shortest being $O(2) \cdots C(18)$ of $3.176(7) \text{ \AA}$. There are only two distances $< 4.0 \text{ \AA}$ involving the acetic acid molecules, and both involve an unsaturated C atom, $O(3) \cdots C(2)$ $3.514(9)$ and $O(4) \cdots C(10)$ $3.56(1) \text{ \AA}$. The angle between the least-squares plane calculated through all

dba atoms and the plane of the acetic acid molecule is 34.8° . Several pairs of acetic acid molecules have also been included in Figure 4, so as to demonstrate the packing of all molecules in this conformation. The acetic acid molecules form pairs related by centres of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The distance $O(3) \cdots O(4')$ [$2.59(1) \text{ \AA}$] suggests the existence of a strong hydrogen bond.

The presence of solvent is not required for the photodimerisation process: irradiation of the unsolvated form also produces the dimer, though very slowly. Its role is probably therefore one of 'space-filling', allowing the complexes to align themselves with better intermolecular contacts; the face-to-face π - π interactions are probably the most important forces involved.

The study shows that photodimerisation occurs when adjacent molecules are correctly oriented, with alkene groups in neighbouring molecules facing each other and parallel, and the uranyl groups turned away. The production of the 'truxillic' dimer follows directly from this, because the two uranyl groups must be on the far sides of the molecules from the point of contact. Clearly, this orientation effect will occur both in the solid state, and in solution. It will also be expected if some other bulky group is attached to each dba, and thus explains the formation of the 'truxillic' dimer in the presence of $SnCl_4$. The structure of (4) also suggests the potential formation of a trimer, since two vinyl bonds in the same dba ligand are involved in almost the same geometry. This is of interest because, in other conditions, the dimer may not be the only product of the

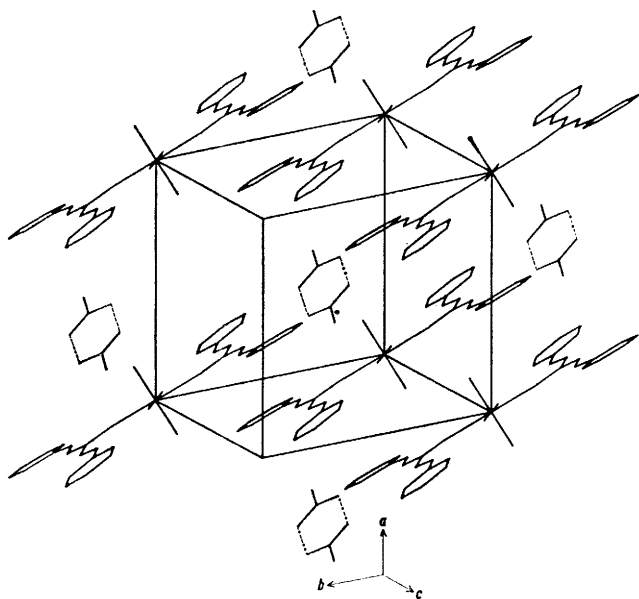


FIGURE 4 One unit cell of complex (4) showing the packing of the complex and the acetic acid molecules. The molecules on two corners are omitted for clarity

photoreaction, and the formation of a trimer may occur. This is in fact what happens^{5,7} when free dba is irradiated in different conditions.

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REFERENCES

- ¹ P. Praetorius, Thesis, Halle, 1909; P. Praetorius and F. Korn, *Ber.*, 1910, **43**, 2744.
- ² H. Stobbe and E. Färber, *Ber.*, 1925, **58**, 1548.
- ³ R. Matsushima and S. Sakaraba, *Chem. Letters*, 1973, 1077.
- ⁴ N. W. Alcock, N. Herron, T. J. Kemp, and C. W. Shoppee, *J.C.S. Chem. Comm.*, 1975, 785.
- ⁵ G. Ciamician and P. Silber, *Ber.*, 1909, **42**, 1386.
- ⁶ G. W. Rechtenwald, T. N. Pitts, and R. L. Letsinger, *J. Amer. Chem. Soc.*, 1953, **75**, 3028.
- ⁷ C. W. Shoppee, Y. Wang, S. Sternhell, and G. C. Brophy, *J.C.S. Perkin I*, 1976, 1880.
- ⁸ C. R. Conard and M. A. Doliver, *Org. Synth.*, 1959, **2**, 167.
- ⁹ J. M. Stewart, Report TR 446, 1976, Computer Science Center, University of Maryland, College Park, Maryland, U.S.A.
- ¹⁰ D. T. Cromer and T. Mann, *Acta Cryst.*, 1968, **A24**, 321.
- ¹¹ D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
- ¹² A. Chiesi Villa, A. Gaetani Manfredotti, C. Guastini, and M. Nardelis, *Acta Cryst.*, 1974, **B30**, 2788.
- ¹³ L. Baracco, G. Bombieri, S. Degetto, E. Forsellini, G. Marangoni, G. Paolucci, and R. Graziani, *J.C.S. Dalton*, 1975, 2161.
- ¹⁴ J. M. Haigh, L. R. Nassimbeni, R. A. Pauptit, A. L. Rogers, and G. M. Sheldrick, *Acta Cryst.*, 1976, **B32**, 1398.
- ¹⁵ D. Rabinovich and Z. Shakked, *Acta Cryst.*, 1974, **B30**, 2829.
- ¹⁶ C. G. Pierpont and M. C. Mazza, *Inorg. Chem.*, 1974, **13**, 1891.
- ¹⁷ M. C. Mazza and C. G. Pierpont, *Inorg. Chem.*, 1973, **12**, 2955.