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The Relation between Solid-State Photochemistry and Crystal Structure of 2,2,3,4-Tetrachloro-1-oxo-1,2-dihydronaphthalene (α-TKN)

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Abstract

Crystals of α-TKN are monoclinic prisms with a unit cell containing two molecules. The dimensions of the unit cell are: a = 8·866 (9), b = 6·915 (7), c = 8·688 (9) Å and β = 91·50 (5)°. The crystal symmetry is described by the space group $P2_1$. The crystal structure has been determined from a Patterson map with 1645 independent X-ray reflections. The final refinement by the method of least squares yielded a weighted reliability factor R_w of 5·3%. The short intermolecular O—Cl distance observed in the crystal structure of the isomer 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthalene (β-TKN) is absent in the present case. Irradiation of an α-TKN crystal by UV light at 77 K produces an intense ESR signal at g = 2. It is concluded that identification of the light-induced coloured species in crystalline β-TKN with the 2,3,4-trichloro-1-naphthyloxy radical is very doubtful.

Introduction

α-TKN is an isomer of 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthalene (β-TKN). Scheibe & Feichtmayr (1962) observed that the compounds show similar photochemical behaviours in carbon tetrachloride solution and suggested the explanation sketched in Fig. 1.

A broad structured absorption band appears in the visible wavelength region after irradiation with UV light. The new absorption is centred on 480 nm. At room temperature the lifetime of the coloured photoproduct in liquid solution is only a few minutes (Kortüm & Greiner, 1973). In contrast, the same product has a lifetime $t_{1/e}$ = 323 min at 295 K, when it has been formed in crystalline β-TKN. In the latter case the light-induced colour is accompanied by the formation of radical pairs. A previous publication presents a study of the spin coupling between these radical pairs in single crystals of β-TKN (Zweegers & Varma, 1976). Scheibe & Feichtmayr attributed the photochromism of β-TKN to its dissociation into atomic chlorine and the 2,3,4-trichloro-1-naphthyloxy radical and argued that the latter ought to have a visible absorption band. A number of our experiments, which will be reported separately (Zweegers & Varma, 1979), show that this point of view cannot be justified.

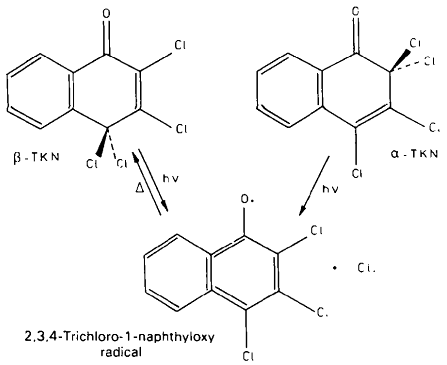

Fig. 1. The photodissociation of α- and β-TKN according to Scheibe.

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Although α-TKN resembles β-TKN in its photoreactions in liquid solution, it does not show photochromism in the solid state. Therefore, the geometrical arrangement of α-TKN molecules in the crystal must inhibit the formation of the photochromic species.

In this paper the crystal structure of α-TKN is described and compared to that of β-TKN which has already been solved (Veenvliet & Migchelsen, 1971). In addition, the effects of UV radiation upon crystalline α-TKN have been determined by ESR. Recently we have prepared two different non-photochromic crystal modifications of β-TKN. The following paper describes the crystal structures and the photochemical behaviour of these modifications (Zweegers, Varma & de Graaff, 1979).

Experimental

α-TKN has been prepared by chlorination of 2,3,4-trichloro-1-naphthol in chloroform solution (de la Mare & Suzuki, 1968). Single crystals grown from benzene solution by slow evaporation of the solvent are diamond-shaped. Their morphology is shown in Fig. 2.

It has already been shown that the unit cell is monoclinic (Groth, 1919). Its dimensions (Table 1) have now been determined on a computer-controlled automatic three-circle diffractometer at room temperature, using monochromated Mo *Kα* radiation ($\lambda = 0\cdot71069$ Å). The volume of the unit cell of α-TKN is approximately half that of the β-TKN cell, which has been shown to contain four molecules. Since the densities of both α- and β-TKN are roughly the same, the unit cell of α-TKN must contain two molecules.

Table 1. *Crystal data of α-TKN* (2,2,3,4-*tetrachloro*-1-*oxo*-1,2-*dihydronaphthalene*)

$C_{10}H_4Cl_4O$, $M_r = 282\cdot0$, $\mu(\mathrm{Mo}\ K\alpha) = 1\cdot078\ \mathrm{mm}^{-1}$, m.p. 377–378 K.

$a = 8\cdot866\ (9)$ Å $Z = 2$
$b = 6\cdot915\ (7)$ $U = 532 \pm 1$ Å^3
$c = 8\cdot688\ (9)$ $d_x = 1\cdot772\ (3)\ \mathrm{Mg\ m^{-3}}$
$\beta = 91\cdot50\ (5)°$

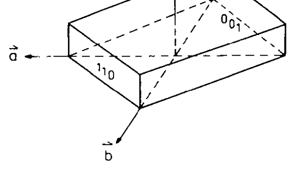

Fig. 2. The morphology of the α-TKN crystal. The *b* axis points along the shortest diagonal of the (001) plane.

The structure has been determined from 2747 reflection intensities which have been measured with the same equipment. The glancing angle has been varied between 4 and 30°. 1645 reflections turned out to be independent. Of these, 102 were considered to be not significant because their intensities were less than twice the experimental standard deviations. The macroscopic dimensions of the crystal have been measured by means of a binocular microscope to enable a correction for X-ray absorption to be made.

For the estimation of the efficiency of second-harmonic generation (SHG) of laser light by crystalline α-TKN relative to α-quartz, we have used the beam from a pulsed Nd^{3+} glass laser for the fundamental frequency. The pulse width is 15 ns FWHM and the energy is around 5 mJ per pulse. The laser output at 1·06 μm has been divided into two beams of equal intensity in a double-beam experiment.

One channel contains a powdered sample of α-quartz as a reference and the other a powdered sample of α-TKN. Prior to detection of SHG the fundamental 1·06 μm light was completely removed by Schott BG 18 filters. Stray light contributions from laser flash lamps have been carefully eliminated. Narrow-band interference filters transmitting only SHG light of 0·53 μm have been inserted in front of the photomultipliers.

ESR experiments have been performed on an X-band spectrometer at 77 K. The samples were irradiated directly in the cavity with a 1000 W super-high-pressure mercury lamp. A glass filter has been inserted to limit the wavelength range between 260 and 400 nm.

Structure determination and refinement

The only reflections which are systematically absent are $0k0$ with $k = 2n + 1$. This observation restricts the space group to $P2_1$ or $P2_1/m$. The experimental intensities have been corrected for X-ray absorption using a Monte Carlo method to calculate the transmission factors (de Graaff, 1973). The Patterson synthesis shows a large number of peaks in the planes $y = 0$ and $y = 0\cdot5$, and a relatively small number of peaks in between these planes. This strongly suggests that the molecules are planar and lie in planes perpendicular to the *b* axis, separated by $\frac{1}{2}b$. The coordinates of Cl(1) and Cl(4) in Fig. 4, which belong to the same molecule, have been established from the Patterson map.

The positions of all heavy atoms could be deduced from the minimum function derived from the Patterson synthesis and the positions of Cl(1) and Cl(4). An isotropic least-squares refinement gave a reliability factor $R = 17\cdot2\%$ when the space group $P2_1$ was adopted. The Fourier synthesis based on the refined parameters yielded the positions of H(5) and H(8).

H(6) and H(7) were located by means of a Fourier synthesis based on the atomic parameters obtained after an anisotropic refinement, keeping C(6) and C(7) isotropic. Full-matrix refinement with anisotropic parameters for all atoms except H gave an R value of 4·6% and a weighted reliability factor R_w of 5·6%. These values have finally been reduced to 3·9 and 5·3%, respectively, by an extinction correction according to Zachariasen (1967).* In Table 2 the atomic coordinates are listed.

Table 2. *Fractional coordinates of α-TKN*

The standard deviations in the last digits are given in parentheses.

	x	y	z
C(1)	0·4001 (3)	0·778 (2)	0·2547 (3)
C(2)	0·2375 (4)	0·779 (2)	0·3167 (3)
C(3)	0·1126 (3)	0·786 (2)	0·1987 (3)
C(4)	0·1400 (3)	0·779 (2)	0·0480 (3)
C(5)	0·3158 (4)	0·779 (2)	−0·1719 (3)
C(6)	0·4596 (4)	0·779 (2)	−0·2284 (3)
C(7)	0·5825 (4)	0·787 (2)	−0·1270 (3)
C(8)	0·5617 (3)	0·778 (2)	0·0289 (3)
C(9)	0·4180 (3)	0·780 (1)	0·0864 (3)
C(10)	0·2912 (3)	0·776 (1)	−0·0146 (3)
O	0·5052 (3)	0·783 (1)	0·3445 (3)
Cl(1)	0·2275 (3)	0·569 (1)	0·4352 (2)
Cl(2)	0·2192 (2)	0·990 (1)	0·4331 (2)
Cl(3)	−0·0677 (1)	0·782 (1)	0·2676 (1)
Cl(4)	−0·0097 (1)	0·783 (1)	−0·0825 (1)
H(5)	0·237 (4)	0·76 (1)	−0·235 (4)
H(6)	0·476 (4)	0·75 (1)	−0·345 (4)
H(7)	0·659 (4)	0·75 (1)	−0·159 (4)
H(8)	0·647 (4)	0·76 (1)	0·091 (4)

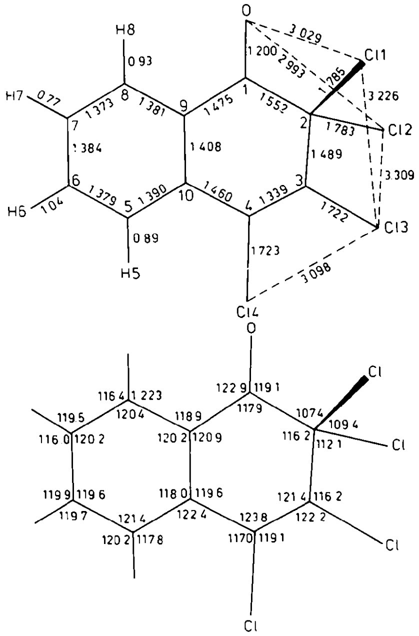

Fig. 3. Bond lengths (Å) and valence angles (°) of the α-TKN molecule.

The space group $P2_1/m$ has been rejected for the following two reasons. (1) Refinement in this centrosymmetric space group gives final values for R and R_w of 4·5 and 6·5% respectively. These reliability factors are significantly higher than in the refinement mentioned earlier. According to the Hamilton (1965) R-test, it can be stated with more than 99·9% certainty that the noncentrosymmetric space group should be regarded as the more appropriate symmetry description. (2) A physical justification for the choice of $P2_1$ has been found from the SHG of laser light in crystalline samples of α-TKN. The process of SHG is strictly forbidden in centrosymmetric crystal structures (Kleinman, 1972). We established that the SHG efficiency in α-TKN is certainly a factor of 5 larger than in α-quartz. Since α-quartz is known to have a noncentrosymmetric structure, the absence of a centre of symmetry in α-TKN must be concluded.

Geometry of the α-TKN molecule

The bond lengths and valence angles of the α-TKN molecule are shown in Fig. 3. The standard deviations calculated from those given in Table 2, taking into account the errors in the cell edges, are listed in Table 3. The relatively large standard deviation of 0·008 Å in the values for the tetrahedral C—Cl bond lengths is entirely due to the large standard deviation of 0·01 Å in the y coordinates of the atoms.

It is a striking feature that α-TKN is a nearly planar molecule. Only C(3) and C(7) are slightly (0·05 Å) above the plane through the remaining C atoms. The planar molecular conformation is not expected from a Dreiding-type model of the α-TKN molecule. In this type of model, considerable strain is introduced into the chlorinated ring and there is a strong tendency for C(2) to be lifted out of the plane of the benzene ring. The

Table 3. *Standard deviations in bond lengths and valence angles of the α-TKN molecule*

	Standard deviation		Standard deviation
C—C	0·005 Å	C—C—C	0·2°
C—O	0·005	C—C—O	
C(sp^2)—Cl	0·003	C—C(sp^2)—Cl	
C(sp^3)—Cl	0·008	C—C(sp^3)—Cl	0·5
		Cl—C(sp^3)—Cl	
		C—C—H	2

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33877 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

planarity is even more surprising since the distance between the non-bonded atom pairs Cl(1)···Cl(3) and Cl(2)···Cl(3), which is less than the sum of the van der Waals radii (3·70 Å), means steric hindrance. However, it must be pointed out that the strain is somewhat less severe than in the case of β-TKN where similar interactions between non-bonded atoms are approximately 0·35 Å shorter.

In both isomers, the non-chlorinated ring has a nearly hexagonal shape. Another common feature is the difference in C—Cl bonds, involving on the one hand the sp^3- and on the other the sp^2-hybridized C atoms. The C—Cl bonds adjacent to the C—C double bond are about 0·06 Å shorter than the C(2)—Cl bonds. Regarding the large standard deviation in the C(2)—Cl bonds for α-TKN, one can say that this difference of 0·06 Å is the same as in the β-TKN molecule, where C(sp^2)—Cl and C(sp^3)—Cl bonds are 1·713 and 1·800 Å respectively.

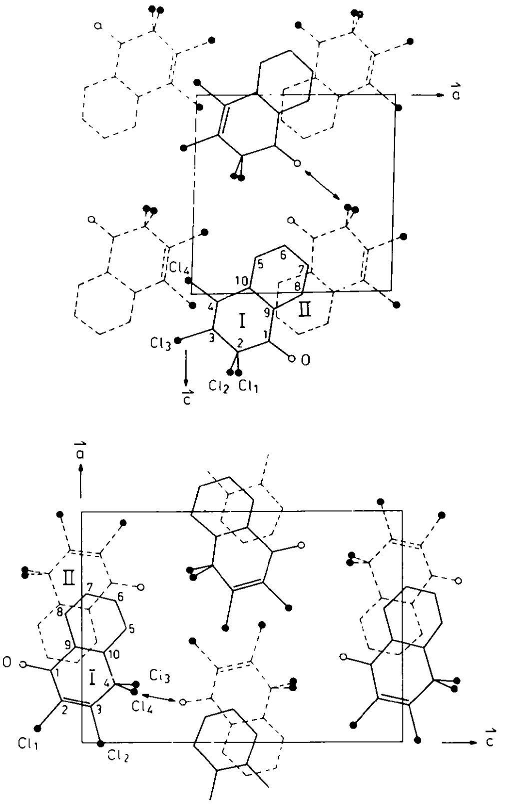

Fig. 4. The crystal structures of α-TKN (top) and β-TKN (bottom) viewed along the crystallographic *b* axis. α-TKN molecules in the plane $y = 0{\cdot}78$ are indicated by thick lines, the broken-line molecules lie in the plane $y = 0{\cdot}28$. In the β-TKN structure, thick-line molecules lie in the plane $y = 0{\cdot}75$ and the broken-line ones have $y = 0{\cdot}25$. In the latter case both planes are mirror planes of the space group *Pnma*. In both structures, the double-headed arrow indicates the shortest intermolecular O—Cl distance.

Crystal structure and ESR results

A projection of the crystal structure of α-TKN on the *ac* plane is presented in Fig. 4 (to enable a comparison with β-TKN, its structure is also depicted).

The distance between two successive layers of molecules is 3·46 Å in the α-TKN lattice. This is nearly equal to the separation of 3·50 Å between layers of molecules in the β-TKN crystal. The Cl atoms adjacent to the C—C double bond play an important role in the packing of molecules in both crystal structures. In both cases, these Cl atoms form an almost close-packed layer with an interatomic distance of 3·88 Å, nearly equal to the sum of the van der Waals radii. In the β-TKN crystal there is a very short distance between an O atom on one molecule and the nearest Cl atom of a neighbouring molecule (Veenvliet & Migchelsen, 1971). This O—Cl distance of 2·973 Å is close to the intramolecular O—Cl(1) and O—Cl(2) distances of, respectively, 3·029 and 2·993 Å in the α-TKN molecule. The shortest intermolecular O—Cl distance in the α-TKN lattice is 3·600 Å.

Irradiation of a β-TKN crystal at low temperature produces radical pairs in a triplet ground state (Zweegers & Varma, 1976). Analysis of the ESR spectra has shown that a radical pair is generated from two neighbouring β-TKN molecules in the crystal, *e.g.* molecules (I) and (II) in Fig. 4. Although the nature of the radicals could not be established definitely, it seems very likely that at least one of the two radicals constituting the pair is a trichloro-1-naphthyloxy radical (Fig. 1). According to Scheibe, the latter should cause colouration of the irradiated crystal. When an α-TKN crystal is irradiated with UV light at liquid-nitrogen temperature, no triplet ESR signals can be observed. Instead a strong doublet signal ($g = 2$) appears with a linewidth of some 15 $\times 10^{-4}$ T. The signal is stable at 77 K. When the sample is quickly brought to room temperature and cooled again to liquid-nitrogen temperature, only a small doublet ESR absorption remains. Neither at room temperature nor at 77 K can visible absorption by photoproducts from the irradiation of α-TKN be detected.

When it is assumed that the primary photochemical step is photodissociation of a C(2)—Cl bond, resulting in a Cl atom and a trichloro-1-naphthyloxy radical, it must be concluded that the liberated Cl atom does not attack the neighbouring molecule in the α-TKN lattice. If this were the case, two radicals would be formed from nearest-neighbour molecules in the α-TKN crystal, *e.g.* molecules (I) and (II) (Fig. 4). Such a radical pair would have practically the same characteristics as the radical pairs formed in β-TKN crystals. Although the distance between the centres of the C(9)—C(10) bonds of molecules (I) and (II) ion the α-TKN crystal (4·39 Å) is a little longer than that in the β-TKN crystal (4·03 Å), the dipolar coupling between the unpaired electron spins would still be sufficiently large to produce a triplet ESR spectrum. The positions of the out-of-plane Cl atoms in α-TKN are such that attack on the neighbouring molecule is less probable than in the crystal of β-TKN. In the former case it seems likely that the released Cl atom is trapped in the crystal at low temperature, some distance away from the remaining trichloro-1-naphthyloxy radical. Fast recombination occurs when the temperature is raised. No colour is generated in the α-TKN crystal upon irradiation although formation of the trichloro-1-naphthyloxy radical seems very probable.

In view of these facts, assignment of the photochromic behaviour of crystalline β-TKN to the trichloro-1-naphthyloxy radical is very questionable.

Evidence against the theory of Scheibe, derived from the investigation of the photochemical behaviour of α-TKN and β-TKN in solution and from ESR spectroscopy of the 2,3,4-trichloro-1-naphthyloxy radical in solution, will be presented elsewhere (Zweegers & Varma, 1979).

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Solid-State Photochemistry and Crystal Structures of Two Non-Photochromic High-Temperature Modifications of 2,3,4,4-Tetrachloro-1-oxo-1,4-dihydronaphthalene (β-TKN)

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Abstract

Two different non-photochromic crystal modifications of β-TKN have been grown from *o*-xylene solutions at 373 K. One has a monoclinic unit cell with $a = 11{\cdot}79\,(1)$, $b = 9{\cdot}98\,(1)$, $c = 9{\cdot}49\,(1)$ Å, $\beta = 104{\cdot}04\,(5)^\circ$, $Z = 4$ and space group $P2_1/c$. The other has an orthorhombic unit cell with $a = 22{\cdot}755\,(6)$, $b = 6{\cdot}785\,(6)$, $c = 13{\cdot}973\,(6)$ Å, $Z = 8$ and space group $Pnma$ or $Pn2_1a$. The former structure has been determined directly from the Patterson function; the latter has been obtained by a vector-search method. A final weighted reliability factor R_w of 5·4% has been reached for the monoclinic structure. The orthorhombic structure was refined to $R_w = 12\%$ for $Pnma$ and to $R_w = 8{\cdot}4\%$ for $Pn2_1a$. However, in the latter case the least-squares refinement did not yield satisfactory results, owing to large correlations between the chlorine parameters. The very short intermolecular O—Cl distance of 2·973 Å found in the photochromic crystal is not present in the non-photochromic modifications. The formation of isolated radicals upon irradiation of both high-temperature crystal forms with UV light has been investigated by ESR. Unlike the case of the photochemistry of photochromic β-TKN crystals, no coloured species or radical pairs are observed after

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