

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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References

- GRAAFF, R. A. G. DE (1973). *Acta Cryst.* **A29**, 298–301.
 GROTH, P. (1919). *Chemische Kristallographie*. Vol. 5, p. 378. Leipzig: Engelmann.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
 KLEINMAN, D. A. (1972). *Laser Handbook*. Vol. 2, edited by F. T. ARRECHI & E. O. SCHULZ-DUBOIS. Amsterdam: North-Holland.
 KORTÜM, G. & GREINER, G. (1973). *Ber. Bunsenges. Phys. Chem.* **77**, 459–465.
 MARE, P. B. D. DE LA & SUZUKI, H. (1968). *J. Chem. Soc. C*, p. 651.
 SCHEIBE, G. & FEICHTMAYR, F. (1962). *J. Phys. Chem.* **66**, 2449–2455.
 VEENVLIET, H. & MIGCHELSEN, R. (1971). *Z. Kristallogr.* **134**, 291–304.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
 ZWEEGERS, F. P. A. & VARMA, C. A. G. O. (1976). *Chem. Phys.* **12**, 231–235.
 ZWEEGERS, F. P. A. & VARMA, C. A. G. O. (1979). *J. Phys. Chem.* To be published.
 ZWEEGERS, F. P. A., VARMA, C. A. G. O. & DE GRAAFF, R. A. F. (1979). *Acta Cryst.* **B35**, 104–109.

Acta Cryst. (1979). **B35**, 104–109

Solid-State Photochemistry and Crystal Structures of Two Non-Photochromic High-Temperature Modifications of 2,3,4-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 $a = 11.79$ (1), $b = 9.98$ (1), $c = 9.49$ (1) Å, $\beta = 104.04$ (5)°, $Z = 4$ and space group $P2_1/c$. The other has an orthorhombic unit cell with $a = 22.755$ (6), $b = 6.785$ (6), $c = 13.973$ (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 $R_w = 8.4\%$ 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

irradiation of the new crystal modifications at 77 K. Arguments are presented against attributing the visible absorption band induced by UV radiation in the photochromic β -TKN crystal to the 2,3,4-trichloro-1-naphthoxy radical.

Introduction

The reversible photochemical transformation of β -TKN in the crystalline state, into a coloured species, constitutes one of the first examples of photochromism to be investigated (Marckwald, 1899).

Irradiation of the photochromic crystals with UV light causes a change in their colour from colourless to purple. The reverse process proceeds in the dark and can be accelerated by excitation in the visible absorption band of the coloured species at 530 nm (Weigert, 1918). The thermal fading of the colour is a rather slow process which follows first-order kinetics with $t_{1/e} = 323$ min at 295 K and an activation energy of 113 kJ mol^{-1} (Kortüm & Greiner, 1973). Scheibe & Feichtmayr (1962) discovered that a similar photochemical behaviour can also be observed in low-temperature glasses and in solutions in carbon tetrachloride at room temperature. In the latter case, the lifetime of the coloured species is limited to only a few minutes. These authors explained their results in terms of a photochemical cleavage of one of the C(4)-Cl bonds, leaving a free Cl atom and a 2,3,4-trichloro-1-naphthoxy radical, which they assumed to be coloured.

This explanation agrees with the fact that the isomer 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthalene (α -TKN) shows the same reaction in CCl_4 (Fig. 1).

ESR experiments with irradiated solid photochromic β -TKN at low temperature (Wiersma & Nieuwpoort, 1968; Zweegers & Varma, 1976) indicate that radical pairs are formed from nearest-neighbour molecules in the crystal. These investigations provoke

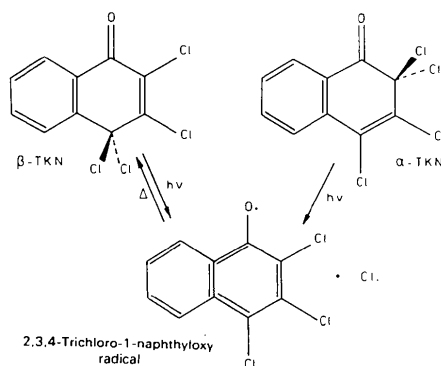


Fig. 1. Photochemical reaction of α - and β -TKN in CCl_4 according to Scheibe & Feichtmayr (1962).

the idea that at least one of the geminate radicals is indeed a 2,3,4-trichloro-1-naphthoxy radical. The α -TKN isomer does not show photochromism in the solid state but, nevertheless, free radicals in irradiated crystals are observed by ESR. An examination of the crystal structure of α -TKN (Zweegers, Varma & de Graaff, 1979) has shown that there are no steric restrictions in the crystal with respect to the formation of the same radical mentioned above. Thus the attribution of the visible absorption band, induced in the photochromic β -TKN crystal, to the trichloro-1-naphthoxy radical becomes doubtful.

As already noticed by Marckwald, non-photochromic crystals of β -TKN may be obtained by heating solid photochromic β -TKN at 373 K. We have succeeded in preparing single crystals of two different crystalline species of β -TKN from solutions at 373 K. These are metastable at room temperature and do not show any photochromic effect. It is to be expected that a detailed knowledge of the several crystal structures of β -TKN should disclose the geometric requirements for its photochromism in the solid state. This paper presents the crystal structures of two high-temperature modifications of β -TKN, thus enabling a comparison with the structure of the photochromic crystal (Veen-vliet & Migchelsen, 1971) to be made. The investigation by ESR of the photochemical behaviour of the non-photochromic crystals is also reported.

Experimental

β -TKN has been prepared according to Marckwald. The two non-photochromic crystal modifications of β -TKN were obtained from solutions in *o*-xylene. A solution of 2 g β -TKN in 10 ml *o*-xylene was carefully kept at a temperature of 373 K. The rate of evaporation of the solvent was controlled by the size of an opening in the container. Evaporation at a rate of 0.5 g *o*-xylene h^{-1} yielded large yellow crystals [hereafter referred to as type (I)]. When the rate of evaporation is reduced by a factor of 5, a different type of yellow crystals are formed from the melt which remain after all the solvent has disappeared. These are prismatic and are referred to as type (II). Both forms are metastable at room temperature, but traces of solid photochromic β -TKN initiate the transformation to the photochromic modification. The infrared spectra taken from (I), (II) and photochromic β -TKN are identical.

The dimensions of the unit cells of both (I) and (II) (Table 1) have been determined on a computer-controlled automatic three-circle diffractometer, using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). For the structure determination of (I), 3014 reflection intensities were measured with the same instrument, varying the glancing angle between 4 and 25° . 1852 reflections are independent, including 170 with counts less than twice

the experimental standard deviations. In the subsequent analysis, the latter were labelled not significant. Systematic absences of the reflections $0k0$ with $k = 2n + 1$ and $h0l$ with $l = 2n + 1$ restrict the space group of (I) to $P2_1/c$. The unit cell has a volume approximately equal to that of the unit cell of photochromic β -TKN, which has been shown to contain four molecules (Veenvliet & Migchelsen, 1971). Since the densities of both crystals are nearly equal, the unit cell of (I) must also contain four molecules.

The structure determination of (II) was based on 2853 reflection intensities, measured with the automatic diffractometer. In this case θ values ranged from 4 to 24°. There are 1738 independent reflections, of which 87 were considered not significant. From the systematic absences of the reflections $0kl$ with $k + l = 2n + 1$ and $hk0$ with $h = 2n + 1$, it follows that the space group must be either $Pmna$ or $Pn2_1a$. The unit cells of (II) and photochromic β -TKN are both orthorhombic and have practically the same values for the lattice constants b

and c . However, the value for the lattice constant a in (II) is about twice as large as in the photochromic case. The densities of (II) and photochromic β -TKN are roughly equal, so (II) must contain eight molecules per unit cell.

To make a correction for X-ray absorption, the dimensions of both crystals have been measured with a binocular microscope. Experimental reflection intensities have been reduced to structure factors in the usual way by dividing by Lorentz-polarization and absorption factors. The latter factors have been calculated using a Monte Carlo method (de Graaff, 1973).

ESR experiments have been carried out on an X-band spectrometer. The cooled samples were irradiated directly in the cavity with a 1000 W super-high-pressure mercury lamp. Glass filters have been used to limit wavelengths of excitation between 260 and 400 nm.

Structure determination of (I)

Table 1. Crystallographic data of the non-photochromic crystal modifications (I) and (II) of 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthalene (β -TKN)

Standard deviations are given in parentheses.

$C_{10}H_4Cl_4O$, $M_r = 282.0$, $\mu(\text{Mo } K\alpha) = 1.078 \text{ mm}^{-1}$

(I)	(II)
Monoclinic $P2_1/c$	Orthorhombic $Pnma$ or $Pn2_1a$
$a = 11.79$ (1) Å	$a = 22.755$ (6) Å
$b = 9.98$ (1)	$b = 6.785$ (6)
$c = 9.49$ (1)	$c = 13.973$ (6)
$\beta = 104.04$ (5)°	$Z = 8$
$Z = 4$	$U = 2157$ (2) Å ³
$U = 1083$ (2) Å ³	$d_x = 1.749$ (4) Mg m ⁻³
$d_x = 1.742$ (4) Mg m ⁻³	

Table 2. Fractional coordinates and standard deviations ($\times 10^4$) of the non-hydrogen atoms in the monoclinic high-temperature crystal form of β -TKN

	x	y	z
C(1)	8864 (3)	1063 (4)	5663 (4)
C(2)	8382 (3)	2270 (4)	4817 (4)
C(3)	7384 (3)	2258 (3)	3794 (3)
C(4)	6659 (3)	1008 (3)	3406 (3)
C(5)	6579 (3)	-1455 (3)	3868 (4)
C(6)	7010 (4)	-2605 (4)	4622 (4)
C(7)	8029 (4)	-2559 (4)	5719 (5)
C(8)	8623 (3)	-1377 (4)	6042 (4)
C(9)	8202 (3)	-198 (3)	5285 (3)
C(10)	7171 (2)	-240 (3)	4202 (3)
Cl(1)	9172 (1)	3713 (1)	5280 (1)
Cl(2)	6829 (1)	3685 (1)	2874 (1)
Cl(3)	5268 (1)	1340 (1)	3829 (1)
Cl(4)	6377 (1)	748 (1)	1487 (1)
O	9761 (3)	1120 (3)	6616 (3)

From the Patterson synthesis the positions of Cl(1) and Cl(4) could be deduced. The coordinates of the remaining heavy atoms follow from the minimum function calculated from the Patterson synthesis, using the positions of Cl(1) and Cl(4). Least-squares refinement with isotropic temperature parameters resulted in a weighted reliability factor of 13.1%. The positions of the H atoms have been calculated by introducing a C-H bond length of 0.95 Å and sp^2 hybridization of the aromatic C atoms. Full-matrix refinement with anisotropic parameters for all heavy atoms gives an unweighted reliability factor R of 4.8% and an R_w of 5.4%.* An extinction correction according to Zachariasen (1967) has been applied without obtaining further reductions of R and R_w . The final atomic coordinates are listed in Table 2.

Structure determination of (II)

The Patterson synthesis shows a very large number of peaks in the planes $y = 0$ and $y = 0.5$ and a relatively small number of peaks in between these planes. This observation suggests that the molecules are planar and that they lie in planes perpendicular to the b axis, separated by $\frac{1}{2}b$. The choice of space group $Pnma$ means that there have to be two independent molecules, occupying special positions with symmetry m .

* Lists of structure factors and anisotropic thermal parameters for both (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33876 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The location of the Cl atoms could not be found from the Patterson map in a straightforward manner, because of the large overlap of the peaks. A Patterson-search program (Braun, Hornstra & Leenhouts, 1969) has therefore been employed to find the orientation of a β -TKN molecule with respect to the cell axes. In this method the molecular geometry of β -TKN (Veenvliet & Migchelsen, 1971) and the space group $Pnma$ are introduced as input and the orientation of a molecule is varied to fit the Patterson map. The orientations giving the 28 lower values for the 'measure of fit' have been calculated. The selection of the correct orientation follows after a Fourier synthesis based on structure factor amplitudes from the reflection intensities and use of the phase factors derived from the coordinates which have been obtained from the Patterson search. For the orientation which gives the second-best 'measure of fit', a Fourier synthesis properly generated the second independent molecule in the unit cell. However, when starting with the orientation corresponding to the lowest 'measure of fit' the second independent molecule in the cell could not be generated by the Fourier synthesis.

Full-matrix refinement with isotropic temperature parameters for all 30 heavy atoms resulted in an R_w value of 15.6%. The positions of the H atoms have been calculated assuming a C—H bond length of 0.95 Å and sp^2 hybridization of the aromatic C atoms. Subsequent block-diagonal refinement with anisotropic temperature parameters for all heavy atoms yielded a conventional R value of 7.1% and a weighted reliability factor R_w of 12.0%. The difference Fourier map ($F_o - F_c$) showed no peaks larger than twice the statistical value.

Table 3. Fractional coordinates and standard deviations ($\times 10^4$) of the non-hydrogen atoms in the orthorhombic high-temperature modification of β -TKN

All atoms of molecule (1) have $y = 0.25$, except Cl(3) for which $y = 0.4652$ (3). The atoms of molecule (2) have $y = 0.75$, except Cl(3) which has $y = 0.9652$ (3).

Molecule (1)			Molecule (2)		
	x	z	x	z	
C(1)	3406 (4)	2195 (7)	C(1)	3755 (4)	1887 (6)
C(2)	2893 (4)	1590 (6)	C(2)	3858 (4)	2952 (6)
C(3)	2338 (4)	1917 (6)	C(3)	4396 (4)	3297 (6)
C(4)	2224 (4)	2990 (6)	C(4)	4930 (4)	2706 (6)
C(5)	2683 (4)	4604 (6)	C(5)	5322 (5)	1071 (7)
C(6)	3168 (5)	5184 (7)	C(6)	5242 (5)	32 (7)
C(7)	3719 (5)	4859 (8)	C(7)	4676 (6)	-282 (7)
C(8)	3803 (4)	3843 (7)	C(8)	4206 (5)	290 (7)
C(9)	3322 (4)	3247 (6)	C(9)	4278 (4)	1266 (6)
C(10)	2751 (4)	3625 (6)	C(10)	4849 (4)	1659 (6)
Cl(1)	3014 (2)	376 (2)	Cl(1)	3240 (1)	3636 (2)
Cl(2)	1738 (1)	1199 (2)	Cl(2)	4500 (1)	4532 (2)
Cl(3)	1784 (1)	3240 (2)	Cl(3)	5361 (1)	3030 (2)
O	3901 (3)	1862 (5)	O	3254 (3)	1586 (5)

The coordinates obtained after this refinement are listed in Table 3.*

The rather high value for R_w forced an investigation of the possibility of the noncentrosymmetric space group $Pn2_1a$.

Isotropic refinement in this space group gives an R_w value of about 13%. The refinement with anisotropic temperature parameters has been performed by dividing the least-squares matrix into two blocks. Each block contains the parameters of one molecule. In this way the values of R and R_w have been reduced to about 5.6 and 8.4% respectively. But owing to very large correlations between the Cl parameters (>0.9), the convergence of the least-squares procedure is inadequate in this case. At the same time, the tetrahedral C—Cl bond lengths of the same molecule become unequal by an amount of 0.08 Å. This difference in bond length cannot be realistic.

It appears that an exact solution of the structure of modification (II) is impossible at this stage. If the space group $Pnma$ is adopted, well established structure parameters are obtained, but the molecule is restricted to a planar configuration.

Allowance, instead, for non-planarity of the molecule by taking the space group $Pn2_1a$ leads to lower values for R and R_w . But then the refinement of the parameters cannot be carried out successfully. From the R and R_w values, it seems probable that the actual structure has space group $Pn2_1a$. However, in the difference Fourier map made in the case of space group $Pnma$, there are no large peaks. Therefore the corre-

* See previous footnote.

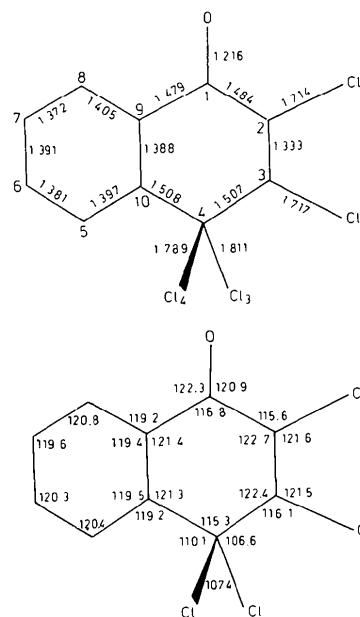


Fig. 2. Bond lengths (Å) and valence angles ($^{\circ}$) of the β -TKN molecule in the monoclinic high-temperature crystal form.

sponding refined structure parameters must adequately describe the actual structure, but small deviations from a planar molecular geometry may be present.

Discussion of the crystal structures and ESR results

The shape of the β -TKN molecule as it appears in the monoclinic high-temperature modification is given in Fig. 2. The standard deviations in the C—C, C—O and C—Cl bond lengths are 0.005, 0.005 and 0.003 Å respectively. The standard deviations in the C—C—C, C—C—O, C—C—Cl and Cl—C—Cl valence angles are 0.3, 0.3, 0.1 and 0.1° respectively. There are no significant differences in bond lengths and only small changes in valence angles compared to the geometry of

the β -TKN molecule in the photochromic crystal (Veenliet & Migchelsen, 1971). In particular, there is a difference of about 2° between corresponding tetrahedral C—Cl valence angles in the two structures. Nevertheless, the β -TKN molecule is still nearly planar in this high-temperature crystal form. Only C(4) is tilted 0.05 Å above the plane of the aromatic ring.

The geometries of the two independent molecules in the orthorhombic high-temperature modification are not determined accurately because the standard deviations in the coordinates are relatively large. On consideration of these standard deviations, there is reasonable agreement between the molecular geometries found in the two non-photochromic crystal structures. Projections of the structures of the photochromic crystal and the orthorhombic high-temperature modification are given in Figs. 3 and 4. Both forms show a layered structure in which the β -TKN molecules are perpendicular to the b axis. The distance between successive layers of molecules is $\frac{1}{2}b$, which is approximately the same value in both cases. A similar structure has also been determined for the α -TKN isomer (Zweegers, Varma & de Graaff, 1979).

It is obvious from Figs. 3 and 4 that the arrangement of β -TKN molecules in the planes $y = 0.25$ and $y = 0.75$ is quite different for both structures. Molecules (1) and (2) in the figures are much closer together in the photochromic crystal than in the high-temperature structure. The distance between the centres of the C(9)—C(10) bonds of (1) and (2) is 4.03 Å in the former and 5.58 Å in the latter. The very short intermolecular O—Cl distance of 2.973 Å observed in the crystal of photochromic β -TKN has disappeared in the orthorhombic high-temperature structure. The latter has a value of 4.17 Å for the shortest intermolecular O—Cl distance between an out-of-plane Cl atom and the nearest O atom.

A stereographic projection of the monoclinic high-temperature crystal structure is shown in Fig. 5. Of the three structures it is only in this crystal form that the

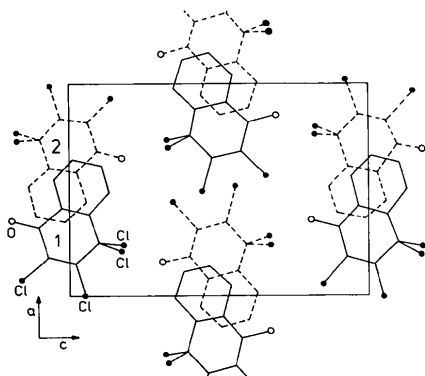


Fig. 3. The crystal structure of photochromic β -TKN viewed along the b axis (Vleenvliet & Migchelsen, 1971). Molecules drawn with full lines are in the plane $y = 0.25$; others lie in the plane $y = -0.25$. Both planes are mirror planes in space group $Pnma$.

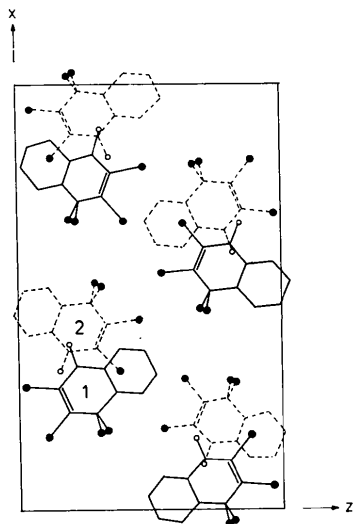


Fig. 4. The crystal structure of the orthorhombic high-temperature modification of β -TKN viewed along the b axis (space group $Pnma$). The two independent molecules (1) and (2) have $y = 0.25$ and $y = -0.25$ respectively.

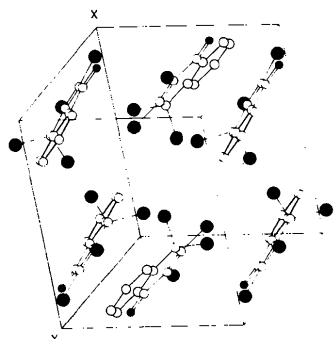


Fig. 5. The crystal structure of the monoclinic high-temperature modification of β -TKN. The short axis of the naphthalene skeleton of the molecules is almost perpendicular to the crystallographic y axis.

molecular planes are not all mutually parallel. The C(9)–C(10) bonds of the molecules are perpendicular to the y axis. The distance between the centres of the C(9)–C(10) bonds in the two neighbours that are parallel is 6.369 Å. For the two neighbours that are not parallel this distance is 6.583 Å. The shortest intermolecular separation between an out-of-plane Cl atom and an O atom is 5.072 Å in this crystal structure.

Another intriguing question is whether or not the thermally induced transformation of solid β -TKN from photochromic to non-photochromic modifications, that occurs at temperatures of about 373 K (Marckwald, 1899), bears any relation to the structures of the single crystals presented here. We have studied the conversion with powder X-ray diffractograms, after heating a polycrystalline photochromic β -TKN sample at 373 K. A comparison of the single-crystal diffraction data with a diffractogram taken after heating a polycrystalline sample for 2 h did not show the presence of (I) in the heated solid. However, by using the lattice constants and reflection intensities of (II), the positions and intensities of all peaks in the powder diffractogram can be matched by calculation. After a further 12 h of heating the positions of the peaks in the diffractogram were still the same, but the intensities had changed considerably. Thus the crystals formed after prolonged heating cannot simply be the modification (II) and it appears that still other non-photochromic crystal modifications of β -TKN exist.

Irradiation of the photochromic β -TKN crystal at 77 K with UV light causes the formation of radical pairs. The analysis of the dipolar coupling between the two unpaired electron spins by ESR has shown that the radicals are formed from neighbouring molecules in the crystal, e.g. molecules (1) and (2) in Fig. 3. The nature of these radicals could not be established definitely from the ESR results, but it seems very probable that at least one of the geminate radicals is the 2,3,4-trichloro-1-naphthoxy radical, formed by homolytic cleavage of a C(4)–Cl bond. According to Scheibe this radical should also be responsible for the photo-induced absorption in the visible wavelength region.

The two non-photochromic crystal modifications of β -TKN behave photochemically in the same way and similarly to α -TKN. Irradiation with UV light ($260 < \lambda < 400\text{nm}$) at 77 K gives a doublet signal in the ESR spectrum with a linewidth of 15×10^{-4} T, which again might originate from the naphthoxy radical. This signal is persistent at 77 K, but disappears when the sample is quickly brought to room temperature and cooled again to 77 K. Neither at room temperature nor at 77 K can any coloration of the irradiated samples be detected.

In the condensed phase there is in general a large probability for recombination of the trichloro-1-naphthoxy radical and the Cl atom formed by dissociation of a C(4)–Cl bond. Obviously, this is what

happens in the non-photochromic crystals. Only at low temperature is the released Cl atom prevented from returning to its original site. Since at 77 K no triplet ESR signals are observed in the irradiated samples of the high-temperature modifications, the radicals produced must be further apart than in the photochromic crystal. This conclusion is confirmed by the absence of relatively short distances between nearest-neighbour molecules in the non-photochromic crystals. The radical formed by reaction of the free Cl atom with a neighbouring molecule will be too remote to couple with the precursor to a triplet spin state.

Contrasting the very short lifetime of the radicals which are produced photochemically in the non-photochromic crystals of β -TKN, radical pairs in irradiated photochromic β -TKN are much more stable. ESR experiments (Zweegers & Varma, 1979) have shown that these radical pairs decay at 295 K following first-order kinetics with $t_{1/e} = 17.5$ min. The relative stability may be explained by the short intermolecular O–Cl distance in photochromic β -TKN. On its return to the sterically unfavourable original position, the released Cl atom has to surmount an energy barrier which is not present in the high-temperature crystal forms.

A very important conclusion from the lifetime measurements of the triplet states in photochromic β -TKN is that the radical pairs and the coloured photo-product cannot be identical. The coloured species lives about twenty times longer than the radical pairs.

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References

- BRAUN, P. B., HORNSTRA, J. & LEENHOUTS, J. I. (1969). *Philips Res. Rep.* **42**, 85–118.
 GRAAFF, R. A. G. DE (1973). *Acta Cryst.* **A29**, 298–301.
 KORTÜM, G. & GREINER, G. (1973). *Ber. Bunsenges. Phys. Chem.* **77**, 459–465.
 MARCKWALD, W. (1899). *Z. Phys. Chem.* **30**, 140–145.
 SCHEIBE, G. & FEICHTMAYR, F. (1962). *J. Phys. Chem.* **66**, 2449–2455.
 VEENVLIET, H. & MIGCHELSEN, T. (1971). *Z. Kristallogr.* **134**, 291–304.
 WEIGERT, F. (1918). *Z. Elektrochem.* **24**, 222.
 WIERSMA, D. A. & NIEUWPOORT, W. C. (1968). *Chem. Phys. Lett.* **2**, 637–639.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
 ZWEEGERS, F. P. A. & VARMA, C. A. G. O. (1976). *Chem. Phys.* **12**, 231–235.
 ZWEEGERS, F. P. A. & VARMA, C. A. G. O. (1979). *J. Phys. Chem.* To be published.
 ZWEEGERS, F. P. A., VARMA, C. A. G. O. & DE GRAAFF, R. A. G. (1979). *Acta Cryst.* **B35**, 100–104.