

## 9-Phenacyl- and 9-(*p*-Methylphenacyl)-3-phenylbenzimidazo[2,1-*b*]thiazole Bromides

BY W. SCHUCKMANN\* AND H. FUESS

Institut für Kristallographie und Mineralogie der Johann-Wolfgang-Goethe-Universität, Senckenberg-Anlage 30, D-6000 Frankfurt am Main, Federal Republic of Germany

AND S. W. PARK† AND W. RIED

Institut für Organische Chemie der Johann-Wolfgang-Goethe-Universität, Theodor-Stern-Kai 7, D-6000 Frankfurt am Main, Federal Republic of Germany

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### Abstract

Benzimidazothiazole reacts with phenacyl bromide to give acylated quaternary salts. The structures of 9-phenacyl- and 9-(*p*-methylphenacyl)-3-phenylbenzimidazo[2,1-*b*]thiazole bromides ( $C_{23}H_{17}BrN_2OS$  and  $C_{24}H_{19}BrN_2OS$ ) have been determined by X-ray methods. Both structures are monoclinic and crystallize in space group  $P2_1/c$ . Lattice constants for 9-phenacyl-3-phenylbenzimidazo[2,1-*b*]thiazole bromide are  $a = 15.888$  (5),  $b = 6.559$  (2),  $c = 27.287$  (8) Å,  $\beta = 135.93$  (5)°; for the *p*-methyl derivative  $a = 10.821$  (3),  $b = 9.419$  (3),  $c = 21.847$  (5),  $\beta = 112.44$  (5)°. The final  $R(F) = 0.039$  and  $0.040$  respectively. The benzimidazothiazole ring system is planar and corresponding distances are similar in both compounds.

### Introduction

The synthesis of benzimidazothiazoles from mercury(II) benzimidazole-2-thiolates and mercury bis(phenylacetyl)ide and aryl isothiocyanates has been described (Ried, Merkel, Park & Dräger, 1975; Park, Ried & Schuckmann, 1977). The crystal structure of 2,8-dibromo-6,7-dimethyl-3-phenylbenzimidazo[2,1-*b*]thiazole has been reported (Park, Ried & Schuckmann, 1977). The reaction of aliphatic imidazothiazoles with aryl isocyanates, aryl isothiocyanates or  $CS_2$  gives dipolar ionic compounds. A similar reaction with benzimidazothiazoles did not occur (Ried *et al.*, 1975). They react, however, with *p*- or *m*-substituted phenacyl bromides and corresponding quaternary salts are obtained. The reaction was performed with ten different *p* and *m* substituents which were characterized by their melting point, IR, NMR and mass spectra (Park, 1975). We describe here the crystal structures of the *p*-methyl and the unsubstituted derivatives.

\* Present address: Núcleo de Geociências da Universidade Federal do Pará, 66 000 Belém-Pará, Brazil.

† Present address: Department of Chemistry, Korea Institute of Science & Technology, 39-1 Hawolgok-dong, Sunbuk-ku, Seoul, Korea.

### Experimental

The reaction of (1) with substituted phenacyl bromides (2) is achieved in solvents such as acetone or ethanol at room temperature or after brief boiling. The products were obtained in 70–90% yield, and gave colourless crystals which sometimes formed needles on recrystallization from methanol or ethanol. Space group and cell dimensions of the unsubstituted (3a) and the *p*-methyl (3b) derivative were determined from precession photographs. Intensities were collected on a Hilger & Watts four-circle computer-controlled diffractometer with a  $\theta/2\theta$  scan technique, a scintillation counter and Ni-filtered  $Cu K\alpha$  radiation. Cell dimensions (Table 1) were refined from the setting angles of 25 reflexions. The background correction was performed by a line profile analysis on the step-scan data (Bartl & Schuckmann, 1966). Lorentz–polarization corrections were applied.

All calculations were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall,

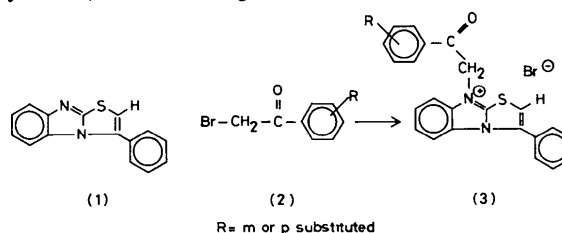


Table 1. General information

	(3a)	(3b)
Space group	$P2_1/c$	$P2_1/c$
$a$ (Å)	15.888 (5)	10.821 (3)
$b$ (Å)	6.559 (2)	9.419 (3)
$c$ (Å)	27.287 (8)	21.847 (7)
$\beta$ (°)	135.93 (5)	112.44 (5)
Number of observed reflexions	2389	2488
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.525	0.525
$Z$	4	4
$V$ (Å <sup>3</sup> )	1978	2058
$D_c$ (Mg m <sup>-3</sup> )	1.51	1.50
$R(F)$	0.039	0.040

Table 2. Atomic coordinates and *e.s.d.*'s

	(3a)			(3b)		
	x	y	z	x	y	z
C(1)	0.6957 (3)	0.5173 (5)	0.0905 (2)	0.8471 (3)	0.2057 (3)	0.3406 (1)
C(2)	0.7589 (3)	0.8024 (5)	0.1518 (2)	1.0179 (3)	0.3032 (3)	0.4215 (1)
C(3)	0.8216 (3)	0.7833 (5)	0.1337 (2)	1.0552 (3)	0.2863 (3)	0.3674 (1)
C(4)	0.9084 (3)	0.9236 (5)	0.1556 (2)	1.1796 (3)	0.3295 (3)	0.3696 (1)
C(5)	0.9285 (3)	1.0836 (6)	0.1956 (2)	1.2660 (3)	0.3861 (3)	0.4291 (2)
C(6)	0.8652 (3)	1.1047 (6)	0.2131 (2)	1.2302 (3)	0.3985 (3)	0.4838 (2)
C(7)	0.7789 (3)	0.9647 (6)	0.1912 (2)	1.1058 (3)	0.3588 (3)	0.4809 (1)
C(8)	0.7996 (3)	0.4868 (6)	0.0610 (2)	0.9101 (3)	0.1745 (3)	0.2519 (1)
C(9)	0.7276 (3)	0.3189 (6)	0.0302 (2)	0.7854 (3)	0.1246 (4)	0.2288 (1)
C(10)	0.8898 (3)	0.5525 (6)	0.0620 (2)	1.0050 (3)	0.1834 (3)	0.2185 (1)
C(11)	1.0017 (4)	0.4600 (7)	0.1071 (2)	1.1183 (4)	0.0977 (4)	0.2385 (2)
C(12)	1.0871 (4)	0.5252 (9)	0.1094 (3)	1.2080 (4)	0.1071 (6)	0.2073 (2)
C(13)	1.0605 (5)	0.6808 (9)	0.0666 (3)	1.1840 (4)	0.2029 (6)	0.1566 (2)
C(14)	0.9492 (5)	0.7698 (8)	0.0211 (3)	1.0733 (5)	0.2868 (5)	0.1366 (2)
C(15)	0.8646 (4)	0.7079 (7)	0.0196 (3)	0.9819 (4)	0.2774 (4)	0.1669 (2)
C(16)	0.6062 (3)	0.5951 (5)	0.1353 (2)	0.8047 (3)	0.2606 (3)	0.4426 (1)
C(17)	0.6820 (3)	0.5475 (5)	0.2121 (2)	0.7902 (3)	0.1167 (3)	0.4704 (1)
C(18)	0.6168 (3)	0.5381 (6)	0.2320 (2)	0.7128 (3)	0.1139 (3)	0.5140 (1)
C(19)	0.4912 (4)	0.5338 (6)	0.1820 (2)	0.6500 (3)	0.2351 (3)	0.5253 (2)
C(20)	0.4351 (4)	0.5311 (7)	0.2040 (3)	0.5823 (3)	0.2278 (3)	0.5675 (2)
C(21)	0.5016 (6)	0.5329 (7)	0.2742 (3)	0.5738 (3)	0.1030 (4)	0.5986 (2)
C(22)	0.6257 (5)	0.5331 (7)	0.3238 (3)	0.6338 (3)	-0.0183 (4)	0.5857 (2)
C(23)	0.6833 (4)	0.5353 (6)	0.3033 (2)	0.7033 (3)	-0.0118 (3)	0.5440 (2)
C(24)				0.4975 (4)	0.0957 (5)	0.6435 (2)
N(1)	0.6814 (2)	0.6346 (4)	0.1242 (1)	0.8868 (2)	0.2545 (3)	0.4029 (1)
N(2)	0.7799 (2)	0.5990 (4)	0.0954 (1)	0.9455 (2)	0.2219 (2)	0.3179 (1)
O	0.7915 (2)	0.5259 (5)	0.2548 (1)	0.8383 (3)	0.0123 (2)	0.4567 (1)
S	0.6351 (1)	0.2948 (1)	0.0432 (1)	0.7055 (1)	0.1307 (1)	0.2847 (1)
Br	0.4462 (1)	0.1104 (1)	0.0630 (1)	0.5116 (1)	0.4401 (1)	0.3441 (1)

Table 3. Calculated coordinates of H atoms

	(3a)			(3b)		
	x	y	z	x	y	z
H(4)	0.954	0.910	0.143	1.205	0.320	0.331
H(5)	0.991	1.187	0.213	1.356	0.419	0.433
H(6)	0.883	1.224	0.242	1.297	0.437	0.526
H(7)	0.733	0.981	0.203	1.079	0.370	0.520
H(9)	0.728	0.219	0.003	0.741	0.087	0.183
H(11)	1.021	0.346	0.138	1.135	0.029	0.276
H(12)	1.168	0.461	0.142	1.289	0.046	0.221
H(13)	1.122	0.729	0.068	1.249	0.211	0.135
H(14)	0.929	0.880	-0.011	1.058	0.356	0.100
H(15)	0.784	0.777	-0.012	0.900	0.339	0.152
H(16)	0.556	0.718	0.121	0.848	0.327	0.480
H(17)	0.553	0.476	0.106	0.714	0.296	0.414
H(19)	0.441	0.533	0.131	0.654	0.327	0.503
H(20)	0.345	0.528	0.168	0.539	0.315	0.576
H(21)	0.459	0.534	0.289			
H(22)	0.674	0.532	0.375	0.627	-0.110	0.607
H(23)	0.774	0.534	0.340	0.747	-0.099	0.536
H(24)				0.539	0.164	0.681
H(25)				0.402	0.122	0.618
H(26)				0.503	-0.003	0.661

1972). The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic temperature factors. All H atoms were located in difference maps. The methyl H atoms indicated a fixed position for the CH<sub>3</sub> group. The H atoms were included at fixed positions assuming

C—H 1.0 Å, with the isotropic thermal parameters of the corresponding C atom. Form factors were those included in the XRAY system and an anomalous dispersion correction (S:  $f' = 0.3$ ,  $f'' = 0.6$ ; Br:  $f' = -0.9$ ,  $f'' = 1.5$ ) was applied. The *R* factors (including all reflections) and the number of observations are given in Table 1.

### Results and discussion

The coordinates of the heavy atoms are given in Table 2.\* The calculated H positions are shown in Table 3. The molecular structures are shown in Figs. 1 and 2 and interatomic distances and angles in Table 4.

The central system of three rings is almost planar in both compounds with maximum deviations of 0.03 (3a) and 0.04 (3b) Å respectively. A separate calculation for the three planes of the ring is given in Table 5 and reveals small angles of about 1° between the normals to the plane. The overall planarity is further confirmed by a calculation of the torsion angles (Table 6).

The shortening of C(1)—N(1) and C(1)—N(2) compared to a single bond is about the same and

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33887 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Interatomic distances (Å) and angles (°)*

	(3a)	(3b)		(3a)	(3b)
C(1)–N(1)	1.339 (7)	1.343 (4)	N(1)–C(1)–N(2)	110.3 (3)	110.1 (2)
C(1)–N(2)	1.354 (6)	1.344 (4)	N(1)–C(1)–S	136.5 (4)	136.1 (3)
C(1)–S	1.713 (3)	1.706 (3)	N(2)–C(1)–S	113.2 (4)	113.9 (2)
C(2)–C(3)	1.401 (8)	1.396 (5)	C(3)–C(2)–C(7)	121.5 (4)	121.2 (3)
C(2)–C(7)	1.379 (6)	1.386 (4)	C(3)–C(2)–N(1)	108.3 (4)	107.9 (2)
C(2)–N(1)	1.401 (5)	1.396 (4)	C(7)–C(2)–N(1)	130.3 (5)	130.9 (3)
C(3)–C(4)	1.386 (6)	1.389 (5)	C(2)–C(3)–C(4)	121.8 (4)	121.8 (2)
C(3)–N(2)	1.412 (4)	1.403 (3)	C(2)–C(3)–N(2)	105.2 (3)	105.6 (3)
C(4)–C(5)	1.376 (6)	1.386 (4)	C(4)–C(3)–N(2)	133.0 (5)	132.6 (3)
C(5)–C(6)	1.397 (9)	1.394 (5)	C(3)–C(4)–C(5)	116.2 (5)	116.3 (3)
C(6)–C(7)	1.380 (6)	1.375 (5)	C(4)–C(5)–C(6)	122.2 (4)	121.8 (3)
C(8)–C(9)	1.380 (6)	1.333 (4)	C(5)–C(6)–C(7)	121.5 (4)	121.7 (3)
C(8)–C(10)	1.478 (8)	1.471 (5)	C(2)–C(7)–C(6)	116.8 (5)	117.1 (3)
C(8)–N(2)	1.395 (7)	1.416 (4)	C(9)–C(8)–C(10)	128.5 (5)	129.1 (3)
C(9)–S	1.748 (6)	1.745 (4)	C(9)–C(8)–N(2)	110.3 (5)	109.7 (3)
C(9)–Br'	3.454 (4)	3.461 (3)	C(10)–C(8)–N(2)	121.2 (3)	121.2 (2)
C(10)–C(11)	1.378 (6)	1.392 (5)	C(8)–C(10)–C(11)	120.0 (4)	120.6 (3)
C(10)–C(15)	1.369 (7)	1.379 (5)	C(8)–C(10)–C(15)	120.7 (4)	119.9 (3)
C(11)–C(12)	1.381 (11)	1.387 (7)	C(17)–C(16)–N(1)	111.6 (3)	112.5 (3)
C(12)–C(13)	1.368 (10)	1.374 (7)	C(16)–C(17)–C(18)	116.4 (3)	116.2 (3)
C(13)–C(14)	1.363 (8)	1.361 (7)	C(16)–C(17)–O	120.8 (5)	120.7 (3)
C(14)–C(15)	1.374 (12)	1.387 (7)	C(18)–C(17)–O	122.7 (4)	123.1 (3)
C(16)–C(17)	1.520 (6)	1.517 (4)	C(17)–C(18)–C(19)	122.1 (5)	121.9 (3)
C(16)–N(1)	1.452 (7)	1.460 (5)	C(17)–C(18)–C(23)	118.9 (4)	118.9 (3)
C(16)–Br'	3.641 (4)	3.513 (3)	C(1)–N(1)–C(2)	107.6 (4)	107.6 (3)
C(17)–C(18)	1.478 (10)	1.489 (5)	C(1)–N(1)–C(16)	127.8 (3)	125.7 (2)
C(17)–O	1.221 (5)	1.203 (4)	C(2)–N(1)–C(16)	124.5 (4)	126.6 (2)
C(18)–C(19)	1.389 (6)	1.398 (5)	C(1)–N(2)–C(3)	108.6 (4)	108.8 (2)
C(18)–C(23)	1.394 (7)	1.376 (4)	C(1)–N(2)–C(8)	114.0 (3)	113.3 (2)
C(19)–C(20)	1.387 (12)	1.381 (6)	C(3)–N(2)–C(8)	137.3 (4)	137.9 (3)
C(20)–C(21)	1.370 (11)	1.378 (5)	C(1)–S–C(9)	88.6 (2)	88.0 (2)
C(21)–C(22)	1.373 (9)	1.395 (5)	C(20)–C(21)–C(24)		121.1 (3)
C(22)–C(23)	1.374 (13)	1.385 (6)	C(22)–C(21)–C(24)		120.4 (3)
S–Br''	3.428 (1)	3.407 (1)			
C(21)–C(24)		1.507 (6)			

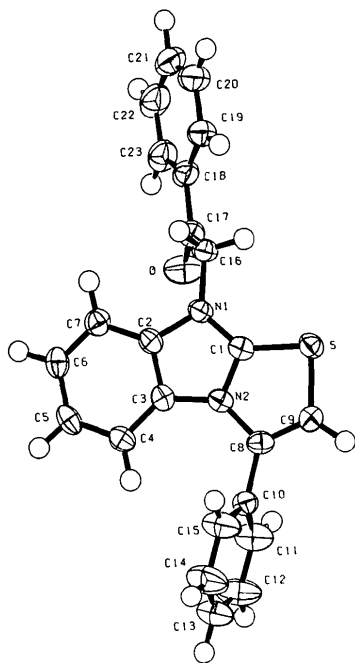
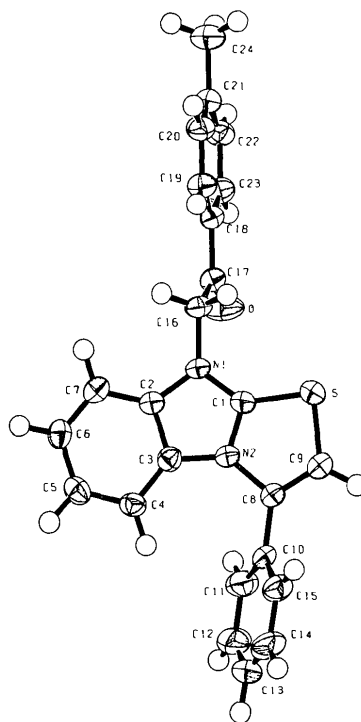
Fig. 1. Molecular structure and numbering scheme for 9-phenacyl-3-phenylbenzimidazo[2,1-*b*]thiazole bromide.Fig. 2. Molecular structure and numbering scheme for 9-(*p*-methylphenacyl)-3-phenylbenzimidazo[2,1-*b*]thiazole bromide.

Table 5. Best planes and deviations (Å)

		(3a)	(3b)
Plane 2, benzene	C(2)	0.008	0.011
	C(3)	-0.005	-0.014
	C(4)	0.000	0.005
	C(5)	0.003	0.008
	C(6)	-0.001	-0.012
	C(7)	-0.004	0.002
Plane 3, imidazole	C(1)	-0.006	0.000
	C(2)	0.002	-0.012
	C(3)	-0.005	0.012
	N(1)	0.002	0.007
	N(2)	0.007	-0.008
Plane 4, thiazole	C(1)	-0.003	0.005
	C(8)	0.001	-0.002
	C(9)	-0.003	0.004
	N(2)	0.001	-0.003
	S	0.003	-0.005
Plane 7	C(16)	0.004	-0.001
	C(17)	-0.013	0.004
	C(18)	0.004	-0.001
	O	0.005	-0.001
Plane 9, phenyl (1)	C(10)	0.001	0.005
	C(11)	-0.005	0.000
	C(12)	0.001	-0.005
	C(13)	0.007	0.003
	C(14)	-0.010	0.003
	C(15)	0.006	-0.007
Plane 8, phenyl (2)	C(18)	0.010	0.009
	C(19)	-0.004	-0.008
	C(20)	-0.005	-0.001
	C(21)	0.009	0.010
	C(22)	-0.003	-0.009
	C(23)	-0.006	-0.005

Angles between normals to planes (°)

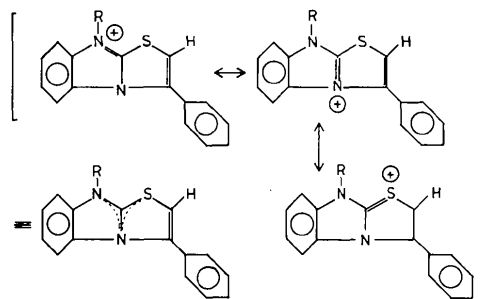
	(3a)	(3b)
1*-2	0.8	1.38
1-3	0.9	0.9
1-4	0.4	0.7
2-3	1.7	2.1
1-3	121.5	101.2
1-9	77.7	69.4
3-4	1.1	0.5

\* Plane 1 is the best plane of the central system of three rings.

indicates delocalization of the  $\pi$  electrons in the N(1)-C(1)-N(2) portion of the imidazole ring. The C(3)-N(2) and C(2)-N(1) distances of about 1.40 Å may, however, preclude complete delocalization.

A pronounced localization had been observed, however, for the free base (Park *et al.*, 1977) where C(1)-N(1) with a length of 1.303 Å shows almost double-bond character. The shortening of C(1)-N(2) (0.036-0.045 Å) and the lengthening of C(1)-N(1) (0.036-0.038 Å) compared to the free base suggest that the partial double-bond character is a function of the molecular environment. C(1)-S lengths are about the same for the free base and for the two derivatives. The double-bond character is less pronounced (bond

shortening of 0.017-0.023 Å compared to a single bond) than for C-N. The following resonance structures may therefore be formulated.



An expectation value of 3.62 Å for a C-H...Br hydrogen bond was calculated by Power, Pletcher & Sax (1970) based on a hydrogen bond radius of CH of 1.64 and an acceptor radius for Br of 1.98 Å. These authors found C...Br- distances of 3.542 and 3.631 Å in *N*-benzyl-4-methylthiazolium bromide which are very similar to those found by us (3.513 and 3.641 Å). The C(16)-H(17)...Br- angle is about 160° in both compounds and the H...Br distances about 2.70 for (3a) and 2.53 Å for (3b). The favourable orientation of the C-H...Br- bond together with the distances makes it reasonable to classify this interaction as a

Table 6. Torsion angles (°)

	(3a)	(3b)
O-C(17)-C(18)-C(23)	10	5
C(17)-C(16)-N(1)-C(1)	70	74
N(1)-C(16)-C(17)-O	7	3
N(1)-C(1)-S-C(9)	0	1
N(1)-C(1)-N(2)-C(8)	0	1
S-C(1)-N(2)-C(3)	1	1
C(2)-C(3)-N(2)-C(8)	2	0
C(8)-C(9)-S-C(1)	0	0
N(2)-C(8)-C(9)-S	0	0
N(9)-C(8)-N(2)-C(1)	0	0
S-C(1)-N(2)-C(8)	0	0

weak hydrogen bond. This argument is further supported by the shift of the paramagnetic resonance signal of the CH<sub>2</sub> group (Park, 1975), which suggests a loosening of the C-H bonds.

Both phenyl rings are planar in the two compounds. They form angles of 58 and 78° (3a) and 79 and 69° (3b) with the heterocyclic plane.

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*Acta Cryst.* (1979). **B35**, 100–104

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

BY F. P. A. ZWEEGERS, C. A. G. O. VARMA AND R. A. G. DE GRAAFF

*Department of Chemistry, State University, Gorlaeus Laboratories, PO Box 9502, 2300 RA Leiden, The Netherlands*

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### Abstract

Crystals of  $\alpha$ -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  $\beta = 91.50$  (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 ( $\beta$ -TKN) is absent in the present case. Irradiation of an  $\alpha$ -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  $\beta$ -TKN with the 2,3,4-trichloro-1-naphthoxy radical is very doubtful.

### Introduction

$\alpha$ -TKN is an isomer of 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthalene ( $\beta$ -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 photo-product 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  $\beta$ -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  $\beta$ -TKN (Zweegers & Varma, 1976). Scheibe & Feichtmayr attributed the photochromism of  $\beta$ -TKN to its dissociation into atomic chlorine and the 2,3,4-trichloro-1-naphthoxy 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.

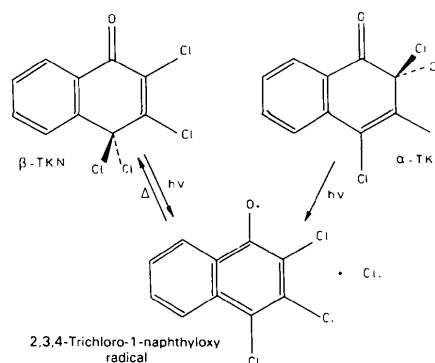


Fig. 1. The photodissociation of  $\alpha$ - and  $\beta$ -TKN according to Scheibe.