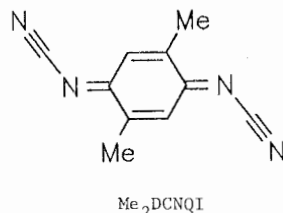


## 06-Crystallography of Organic Compounds

**PS-06.02.03** STRUCTURAL AND MAGNETIC CHARACTERISATION OF ORGANOMETALLIC SALTS OF TCNQ AND DCNQI. By R. Büchner, J.S. Field\* and R.J. Haines, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, South Africa

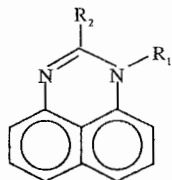
The dinuclear electron-rich thiolato-bridged donor  $[\text{Fe}_2\text{Cp}_2^*(\text{CO})_2(\mu\text{-SET})_2]$  ( $\text{Cp}^*$  = pentamethylcyclopentadienide) reacts with TCNQ (7,7,8,8-tetracyanoquinodimethane) to afford the 1:1 charge-transfer salt  $[\text{Fe}_2\text{Cp}_2^*(\text{CO})_2(\mu\text{-SET})_2](\text{TCNQ})$ . X-ray diffraction studies reveal that the donor cations ( $\text{D}^+$ ) and acceptor anions ( $\text{A}^-$ ) stack in the crystal in the sequence  $\dots\text{D}^+\text{A}^-\text{D}^+\text{A}^-\dots$  with the anions present as diamagnetic pairs  $(\text{TCNQ})_2^{2-}$ . The room temperature magnetic susceptibility confirms a  $S = \frac{1}{2}$  system. The stacking sequence in the analogous 1:1 salt of 2,5-dimethyl-N,N'-dicyanoquinodimethane ( $\text{Me}_2\text{DCNQI}$ ) is different, containing alternating donor cations and acceptor anions  $\dots\text{D}^+\text{A}^-\text{D}^+\text{A}^-\dots$ , and with the planes of the acceptor and adjacent  $\text{Cp}^*$  rings being nearly parallel. The 2-300 K magnetic susceptibility of  $[\text{Fe}_2\text{Cp}_2^*(\text{CO})_2(\mu\text{-SET})_2](\text{Me}_2\text{DCNQI})$  may be fitted by the Curie-Weiss expression with  $\theta = 0$  indicating the absence of cooperative magnetic interactions; this salt is a well-behaved  $S = 1$  system. Details of the above and related work will be presented.



**PS-06.02.04** STRUCTURAL AND SEMIEMPIRICAL STUDIES OF 2-ARYLPERIMIDINE DERIVATIVES.

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Perimidine ( $\text{R}_1=\text{R}_2=\text{H}$ ) is one of the most curious heterocyclic systems, since it is the simplest way to have an heteroaromatic six-membered ring presenting annular tautomerism (Elguero, J., Marzin, C., Katritzky, A.R. & Linda, P. "The tautomerism of heterocycles", Academic Press, New York, 1976). The crystal structures of the following 2-arylperimidine derivatives were undertaken to study the influence of the hydrogen bonds on the overall conformation. The effect of the  $\text{R}_2$  substituent on the perimidine moiety could not be established since, up to now, no suitable crystals of perimidine could be obtained.



Comp	$\text{R}_1$	$\text{R}_2$
I	H	<i>o</i> -HOPh
II	H	9-anthryl
III	Me	Ph
IV	Me	<i>o</i> -MeOPh
V	H	<i>o</i> -MeOPh
VI	H	<i>o</i> -MeOPh

Crystal data:

Formula	a	b	c	$\beta$	S. G.
I $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}$	13.1392(10)	7.6778(3)	13.4780(7)	116.447(4)	$\text{P2}_1/\text{c}$
II $\text{C}_{25}\text{H}_{16}\text{N}_2$	20.8101(5)	20.8101(5)	16.8186(7)		$\text{I4}/\text{a}$
III $\text{C}_{18}\text{H}_{14}\text{N}_2$	17.6446(14)	9.2154(4)	8.3780(3)	102.862(5)	$\text{P2}_1/\text{n}$
IV $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}$	11.4275(6)	16.8070(13)	7.9243(3)	99.830(4)	$\text{P2}_1/\text{c}$
V $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$	8.6719(4)	18.4770(14)	8.4966(4)	95.025(3)	$\text{P2}_1/\text{n}$
VI $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O} \cdot \frac{1}{2}\text{H}_2\text{O}$	15.9820(8)	7.3221(2)	24.9091(15)	106.858(4)	$\text{C2}/\text{c}$

The crystal structures consist of isolated molecules (III, IV, V), pairs of molecules connected through the water molecule by hydrogen bonds (VI) and infinite chains of molecules (I, II). Moreover, "T-shaped" and stacking interactions between aromatic rings are also present. The difference in color between compound V and its hemihydrate, VI, can be partially due to the differences in crystal packing. The total packing coefficients are 0.72, 0.66, 0.69, 0.67, 0.70 and 0.71 respectively. The water molecule in VI is included within an almost spherical hole of approximate surface and volume of  $43.0 \text{ \AA}^2$  and  $22.9 \text{ \AA}^3$  (Cano, F.H. & Martinez-Ripoll, M. (1992) J. Mol. Struct. Theochem 258, 139-158). The high local packing coefficient, 0.80, reveals the significance of the hydrogen bonds.

The X-ray results have been supplemented with a theoretical conformational analysis. The computational results using semiempirical quantum chemical calculations at AM1 level (MOPAC6.0, Stewart, J.J.P. Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840 USA, 1990) indicate that the molecules adopt a similar conformation (II-IV, VI) to that in the solid state when no strong intramolecular hydrogen bond occurs. The experimental and calculated dihedral angles between the substituent and the perimidine moiety are:

	I	II	III	IV	V	VI
Obs.	3.5(4)	77.8(2)	77.7(2)	64.7(2)	0.5(3)	36.5(4)
Calc.	54.5	90.0	69.2	70.6	48.0	48.0

The lack of planarity displayed by all the perimidine skeletons, and mainly by their heterocyclic rings, is only supported by the theoretical calculations for compounds IV-VI.

**PS-06.02.05** DIRECT OBSERVATION OF THE SOLID-STATE PHOTOREACTION OF  $\alpha$ -ACETYLAMINOCINNAMIC ACID DIHYDRATE BY SINGLE CRYSTAL X-RAY DIFFRACTION

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$\alpha$ -Acetylaminocinnamic acid has been found to be photodimerizable in the crystals of its dihydrate (AC2) to form a tetrahydrate of the photodimer (ACD4) without a loss of the water molecules during the reaction (Iwamoto, Kashino and Haisa, Acta Cryst., 1989, C45, 1753-1758). The crystal structure of ACD4 was closely related to that of AC2, and the space group and the mode of hydrogen bonds of ACD4 were the same as those of AC2. On the solid-state(2+2) photoaddition dynamic single crystal X-ray diffraction studies have been reported on the reaction of 2-benzyl-5-benzylidene-cyclopentanone and its *p*-bromo derivative (Nakanishi, Jones, Thomas, Hursthouse and Motevalli, J. Phys. Chem., 1981, 85, 3636-3642), and on psoralen-thymine cycloaddition (Pfluger and Ostrander, Photochem. Photobiol., 1989, 49, 375-379).

In the present work, the crystal structure of an intermediate stage of the solid-state photodimerization of AC2 has been analyzed at the conversion rate of 12%:  $\text{C}_{11}\text{H}_{11}\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mr}=241.24$ , monoclinic,  $\text{P2}_1/\text{a}$ ,  $a=18.346(5)$ ,  $b=6.072(2)$ ,  $c=11.310(4)$  Å,  $\beta=105.90(2)^\circ$ ,  $V=1211.8(6)$  Å<sup>3</sup>,  $Z=4$ ,  $D_x=1.323$  Mg m<sup>-3</sup>, Cu K $\alpha$ ,  $\lambda=1.54178$  Å,  $\mu=0.89$  mm<sup>-1</sup>,  $F(000)=512$ ,  $T=295$  K,  $R=0.108$  for 1678 unique reflections with  $|F_o|$  larger than  $\sigma(F_o)$ .

The present study revealed the structures of the monomer and photodimer components at the intermediate stage. The photodimer component viewed along the *b* axis is shown in Fig. 1 by superimposing the molecules in AC2 and ACD4. As seen from Fig. 1 the atomic movements