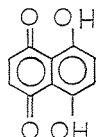


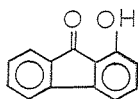
04.4-02 EVIDENCE FOR PROTON TRANSFERS IN THE SOLID STATE. By R. B. Wilson, D. Y. Curtin, and I. C. Paul, School of Chemical Sciences, University of Illinois, Urbana, IL 61801, USA.

Recent investigations of compounds with relatively short intramolecular oxygen-oxygen separations such as β -diketones and β -hydroxyketones have suggested the occurrence of dynamic hydrogen exchange between these oxygen atoms in the solid state. Evidence for this phenomenon is provided by the results of solid state nuclear magnetic resonance, nuclear quadrupole resonance, and X-ray diffraction experiments. Structural and spectroscopic data point out the role of both intra- and intermolecular interactions in influencing this phenomenon.

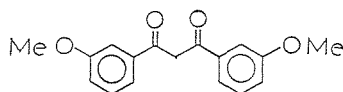
The three forms of naphthazarin, (5,8-dihydroxy-1,4-naphthaquinone (I)), are being studied crystallographically and by solid state ^{13}C NMR spectroscopy (W-I. Shiau, E. N. Duesler, I. C. Paul, D. Y. Curtin, W. G. Blann, and C. A. Fyfe, *J. Amer. Chem. Soc.* (1980) **102**, 4546); the structure of 1-hydroxy-9-fluorenone (II) has been determined in connection with both ^2H and ^{17}O nuclear quadrupole spectroscopy and the solid state behavior of 1,3-bis-(3-methoxyphenyl)-1,3-propanedione (III) and 1-(9-anthranyl)-3-phenyl-1,3-propanedione (IV) are being characterized in light of their recently determined structures. Recent results of these investigations will be described.



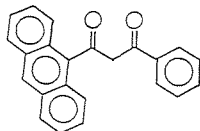
I



II



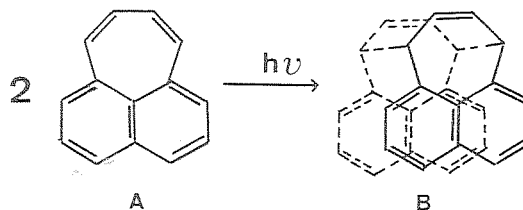
III



IV

04.4-03 THE PHOTO-DIMERIZATION OF CYCLOHEPTA[d,e]-NAPHTHALENE. A SOLID STATE REACTION. By A.C. Hazell (a) and J. Wirz (b), (a) Chemistry Department, Aarhus University, DK-8000 Aarhus C, Denmark, (b) Physikalisches Institut der Universität Basel, Switzerland.

When cyclohepta[d,e]naphthalene (A) (trivial name pleiadene) is irradiated with visible light the bright red crystals become white due to the formation of a dimer. A structure determination showed the dimer to be the 4 + 4 syn adduct (B).



The cell dimensions of the two compounds, A at 100 K, are closely related.

	a	b	c	β
<u>A</u>	8.220(5)	10.687(6)	11.067(7)	104.92(4)
<u>B</u>	16.483(3)	10.479(2)	10.586(2)	98.27(2)

In pleiadene (A. Hazell, R.G. Hazell, and F. Krebs Larsen (1979) 5th European Crystallogr. Meeting, Copenhagen) at 78 K the molecules are stacked in pairs in a head-to-tail arrangement. As the temperature is raised the structure becomes disordered and already at 100 K some 10% are arranged head-to-head. Thus they are in the correct orientation and distance for dimerization to the syn dimer.

04.4-04 A CRYSTALLOGRAPHIC STUDY OF THE SOLID STATE PHOTODIMERIZATION OF 7-METHOXY COUMARIN. By N. Ramasubbu, T.N. Guru Row, V. Ramamurthy, and K. Venkatesan, Department of Organic Chemistry; C.N.R.Rao, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore - 560012, India.

Of the many coumarins investigated by us, only 7-methoxy and 8-methoxy coumarin undergo photodimerization in the solid state. Thus 7-methoxy coumarin gives a cis-anti dimer in 65% yield. In order to investigate whether the molecular packing in the crystal was favourable, providing proper parallel alignment of the potential double bonds, an X-ray crystallographic study was undertaken. 7-Methoxy coumarin crystallizes from benzene in $P\bar{1}$ with $a=6.834(3)$, $b=10.672(4)$, $c=12.600(7)\text{\AA}$, $\alpha=108.2(3)$, $\beta=95.2(4)^\circ$ and $\gamma=95.2(3)^\circ$; $Z=4$. The direct method programme MULTAN-80 was used for the structure determination. Karle recycling and "POSITIONED" in MULTAN-80 yielded the structure. The mutual disposition of the potential double bonds are not favourable for topochemical dimerization. To achieve the cis-anti dimer photoproduct, a rotation of 115.2° for one of the molecules in the asymmetric unit is necessary. We propose that such a rotation is provided by a screw dislocation $(022)\langle 100 \rangle$ rather than orientational point defects or edge dislocation.