

# PHOTODIMERIZATION OF INDOLE DERIVATIVES

Tohru Hino\* and Mikio Taniguchi

Faculty of Pharmaceutical Sciences, Chiba University, Chiba-shi 280, Japan

Tadamasa Date

Research Laboratory of Tanabe Pharmaceutical Co, Toda-shi, Saitama-ken

Yoichi Iidaka

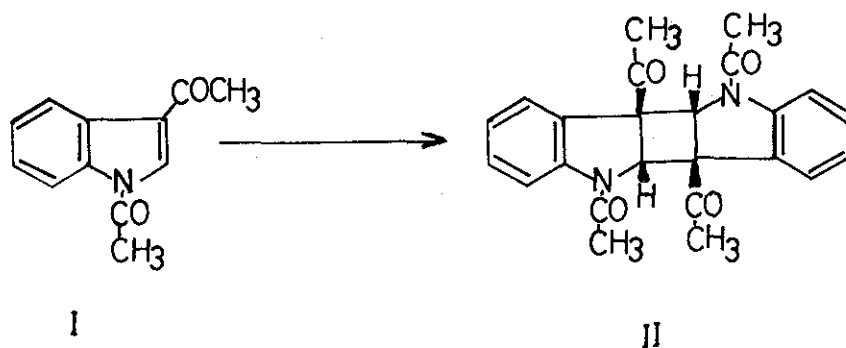
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo

1,3-Diacetylintole(I) gave cyclobutane-dimer(II) by irradiation in various solvents.

The photodimerization of indene, benzofuran, and benzothiophene 1,1-dioxide<sup>1</sup> with or without sensitizer to form cyclobutane derivatives has been reported. While the photocycloaddition of 1-acetylintoles with aromatic ketones or olefins to form cyclobutane derivatives or oxetane derivatives was reported<sup>2</sup>, no example of photodimerization of indole derivatives has been known. We now report photodimerization of 1,3-diacetylintole(I) to cyclobutane derivative(II).

Irradiation of 1,3-diacetylintole(I) in ethanol (33 mM solution with 200 W mercury lamp (Pyrex filter) for 9 hr precipitated the dimer(II), mp 280°(decomp) [ $\lambda_{\max}$  (EtOH) 255 nm;  $\delta$ (DMSO- $d_6$ ) 2.10(s, 6H), 2.44(s, 6H), 5.76(s, 2H), 7.63(q, 2H);  $\nu_{\max}$  (KBr) 1700 and 1675  $\text{cm}^{-1}$ ; m/e 402( $M^+$ ), 201, 160, 145] in 33% yield. Any other isomeric dimers were not isolated by using benzophenone as a sensitizer or changing the solvent to methanol, tert. butanol, benzene, or acetone. The yield of the dimer in ethanol decreased with

lower the concentration of I, partly due to side reactions such as migration of 1-acetyl group.<sup>3</sup> The reaction in tert. butanol( 28 mM solution) gave II in 39% yield as a sole product. 3-Acetyl-, 1-acetyl-, or 1-benzenesulfonylindoles did not give the corresponding dimer under similar conditions. The dimer reverted to I on heating or on treatment with trifluoroacetic acid. By treating with potassium hydroxide in ethanol the dimer decomposed to 3-acetylindole quantitatively. As the spectral data of the dimer could not differentiate four possible structures for cyclobutane dimers ( syn or anti isomers in head-to-head or head-to-tail structures), the dimer was subjected to x-ray analysis. The dimer crystallized into the tetragonal space group  $P4_2c$  with four molecules per unit cell and cell parameters:  $a_0 = 11.369(3)$  Å,  $c_0 = 15.065(8)$  Å. The molecular structure was revealed by the direct method using the program MULTAN<sup>4</sup> and refined by the block-diagonal matrix least-squares method. The final R-factor was 8.4%. The molecule has a two-fold symmetry and a syn head-to-tail structure (Fig 1).



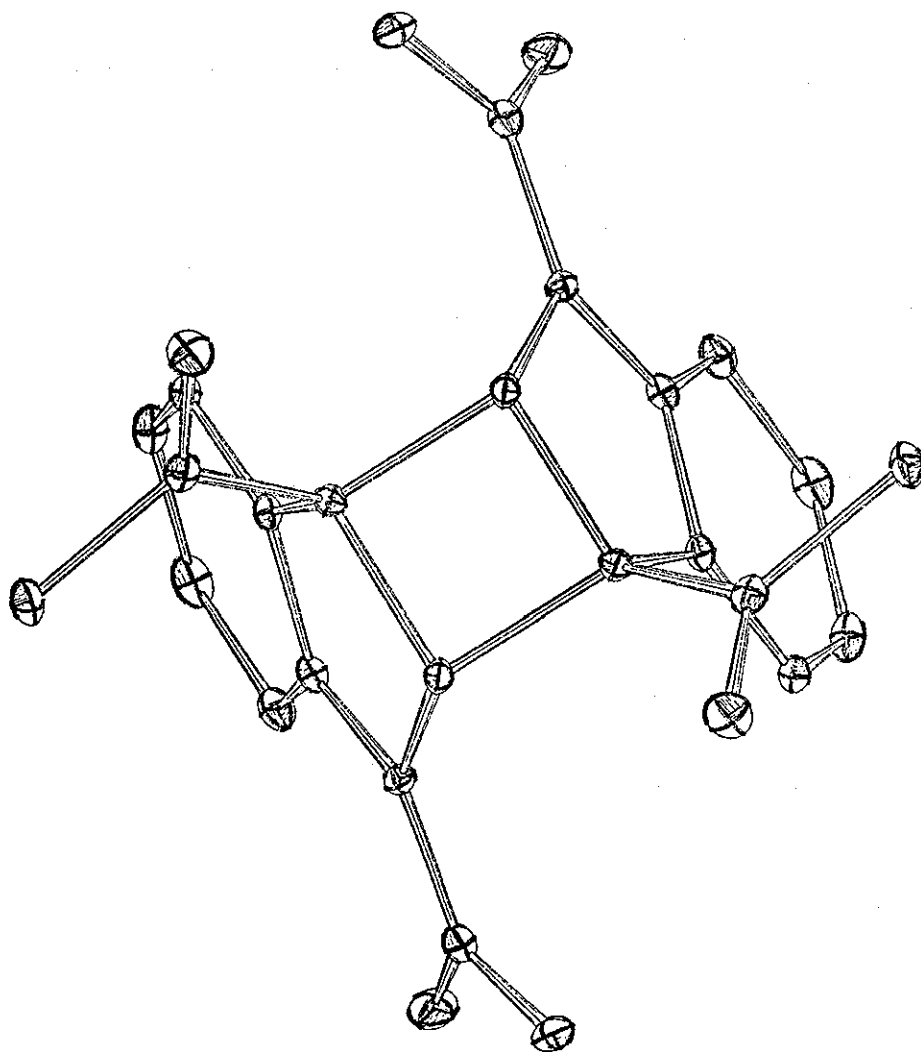


Fig. 1

Other indole derivatives which have electron withdrawing substituents at 1- and 3-positions, such as 1-methoxycarbonyl-3-acetylindole, 1-benzoyl-3-acetylindole, and 1-acetyl-3-indolecarboxaldehyde, did not give the corresponding dimer under similar conditions. However, methyl 1-methoxycarbonyl-3-indolecarboxylate which has the same substituents at 1- and 3-positions, gave a similar type of the dimer, mp 285°, under comparable conditions.

#### REFERENCES

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