

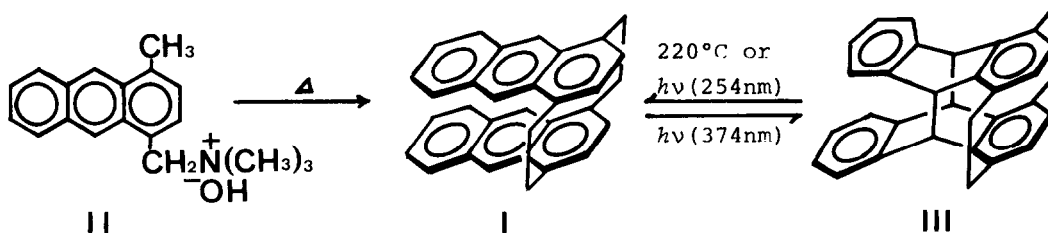
LAYERED COMPOUNDS. LI.<sup>1)</sup> THE CRYSTAL STRUCTURE OF  
 SYN[2.2]ANTHRACENOPHANE

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(Received in Japan 8 February 1978; received in UK for publication 7 March 1978)

In the previous communication of this series, we reported the preparation of syn[2.2](1,4)anthracenophane (I) by pyrolysis of ammonium base II and a photochemical interconversion between the two isomeric cyclophanes I and III.<sup>2)</sup> The compound I shows an excimer fluorescence spectrum with shorter lifetime in longer wavelength region than two isomeric anthracenophanes, anti[2.2](1,4)- and [2.2](1,4)(9,10)-, and anthracene excimer.<sup>3)</sup> On the other hand, [2.2](9,10)anthracenophane shows no fluorescence spectrum. The comparison of these excimer fluorescence spectra distinctly indicates that the non-bonding distance between the active sites of two anthracene moieties, i.e., 9- and 10-positions of the parent anthracene nucleus, is the most important factor to solve a relationship between excimer structure and fluorescence spectrum. We have carried out an X-ray crystallographic analysis of the titled compound I for this purpose as well as a detailed interpretation of the other spectral data.



The crystals are monoclinic with the cell dimensions,  $a=25.539(2)$ ,  $b=8.152(1)$ ,  $c=20.561(3)\text{\AA}$ , and  $\beta=106.03(1)^\circ$  (at  $-149^\circ\text{C}$ );  $z=8$ ; space group  $A_2$ . A total of 4477 observed independent reflections was collected on Rigaku Denki full automatic four-circle diffractometer with Mo-K $\alpha$  radiation monochromized by graphite at  $-149^\circ\text{C}$  using  $\theta$ - $2\theta$  scan technique (scan speed  $2^\circ(2\theta)/\text{min}$ ) and in a dark room to avoid the photochemical cycloaddition above stated.

The deduction of the structure was carried out by translational and rotational operations in the Patterson functions with the idealized molecular structure for the titled compound, which was modelled by reference to the



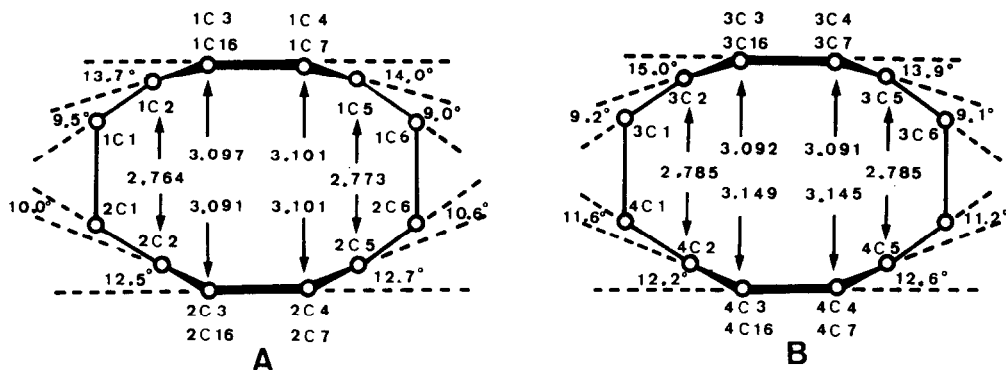


Fig. 3. Side view of [2.2]paracyclophane moiety of the compound I.

structure of a similar compound [2.2](9,10)anthracenophane.<sup>4)</sup> Thus, the position of a molecule (A) of two anthracenophanes involved in an asymmetric unit was deduced by this rigid body motion analysis and then another molecule (B) was determined by the Fourier synthesis using the carbon atoms positional parameters of the molecule A. The structure refinement was done by means of the block-diagonal least-squares method, after the positions of hydrogen atoms were estimated from geometrical consideration. The final residual index R was 0.055 for all the observed reflections.

The bond lengths and bond angles of the two anthracenophane molecules are shown in Fig. 1. There the four bridge Csp<sup>3</sup>-Csp<sup>3</sup> bonds, 1C(1)-2C(1), 1C(6)-2C(6), 3C(1)-4C(1), and 3C(6)-4C(6), are elongated by 0.03-0.04 Å than the corresponding bonds of [2.2]paracyclophane,<sup>5)</sup> and all the C(3)-C(4), C(5)-C(7), C(11)-C(12), and C(2)-C(16) bonds of the four anthracene nuclei are slightly longer than those of the parent anthracene.<sup>7)</sup>

The non-bonding interatomic distances and the mutual displacement between the two anthracene nuclei in each anthracenophane are shown in Fig. 2. It is of great interest that the two anthracene rings in each molecule are closely fixed in nearly parallel, i.e., with the angles 9.5° and 5.1° between the two end benzene rings, against our first expectation of being fairly apart with each other due to steric repulsion. This parallel stacking of the two anthracene rings is clearly attributable to a little bending of C(7)-C(8) and C(15)-C(16) bonds of each anthracene moiety toward the inside of the molecule. Such a bending of the corresponding bonds was generally observed in [n]paracyclophane and [2.2]para- and meta-cyclophane systems<sup>5, 6)</sup> and is theoretically explainable as a deformation for preventing a decrease in the resonance interaction among π-electrons at the carbon atoms, C(2), C(3), C(4), C(5), C(7), and C(16), of each benzene ring bridged with ethylene.<sup>8)</sup>

Severe repulsive interactions are resulted from considerably short non-bonding interatomic distances, 1C(8)...2C(8) and 1C(15)...2C(15), of largely overlapped molecule A, the values of which are shorter than the van der Waals

spacing. On the other hand, another molecule B shows more longer interatomic distances between the corresponding carbon atoms owing to larger mutual displacement of the two anthracene rings along its longer axis. These interatomic repulsions are reflected in the bending angles of the ethylene-bridged benzene, namely [2.2]paracyclophane moiety, as seen in Fig. 3 and in the elongation of the aforesaid bridge Csp<sup>3</sup>-Csp<sup>3</sup> bonds. Thus, all the benzene rings of the two [2.2]paracyclophane moieties are bent with larger bending angles and, in other words, with more severe strain than the parent [2.2]paracyclophane.

The present analysis demonstrates that all the anthracene rings of the titled compound I are in parallel stacking suitable for forming an excimer and that the non-bonding interatomic distances between the two pairs of active sites, C(8) and C(15), are longer than the corresponding one of [2.2](9,10)-anthracenophane<sup>4)</sup> but shorter than that of the anthracene excimer. As a result, the fluorescence spectra of a series of [2.2]anthracenophanes are explained in close connection with their structures.

The authors wish to thank Professors Jiro Tanaka and Noboru Mataga for their helpful discussions.

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