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LAYERED COMPOUNDS XXX.[1] UNUSUAL REACTION OF TRIPLE LAYERED CYCLOPHANES CONTAINING ANTHRACENE NUCLEUS.

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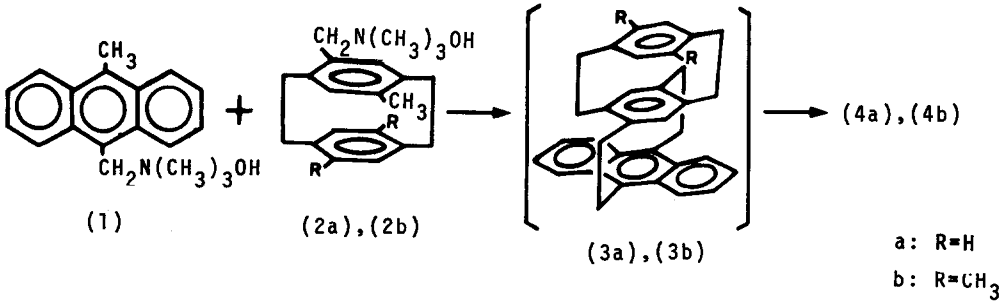
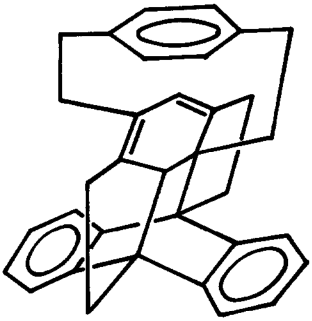
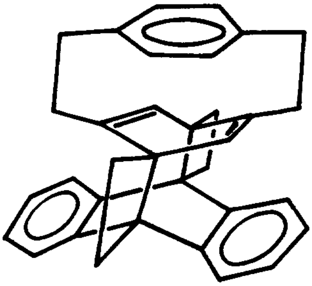
Recently, Korte and his colleagues[2] reported the Diels-Alder reaction of benzene and its derivatives with hexachloropentadiene under high pressure to give 1:2 adducts. This is the first example of dienophilic behavior of benzene. We now wish to describe another example of such an unusual reaction under atmospheric pressure, which was observed in the course of synthetic study of triple-layered anthracenophanes (3a) and (3b) in order to investigate transannular electronic interaction.



Pyrolysis of equimolar mixture of quarternary ammonium hydroxides (1) and (2a) were carried out in boiling xylene in the presence of catalytic amount of phenothiazine. After separation of polymers by filtration the reaction mixture was chromatographed twice on alumina to afford a white solid in a yield of 8.7% (colorless prisms from benzene, mp 238-240.5°C). Although the product gave molecular formula $C_{34}H_{30}$ coinciding with the structure (3a) (by elemental analysis, mass spectrum, and osmometric molecular weight determination), its electronic spectra did not support the structure containing anthracene nucleus.

The spectral data of the product are as follows: Mass spectrum: 438(M^+), 334, 234, 204; UV(THF): 317(1,370), 389 sh(1,830), 268(3,940), 235.5 sh nm(ε 15,700); ^{1}H-NMR($CDCl_3$): δ 1.0-3.0(m, 16H), 4.36(s, 1H), 6.7-7.4 ppm(m, 13H); ^{13}C-NMR ($CDCl_3$, TMS int): 21.03-37.90(methylene, 8 peaks), 51.07-58.53(tertiary and quarternary, 4 peaks), 120.24-139.88 ppm(olefinic and aromatic, 19 peaks). Instead of structure (3a), two possible structures (4a)-I and (4a)-II can be presumed for the product. The latter structure (4a)-II with C_2 symmrtry can be excluded out by the fact that in ^{1}H-NMR spectrum the signal at δ 4.36 ppm corresponds to only one proton absorbtion and in ^{13}C-NMR spectrum there exist thirty-one different signals. Accordingly, (4a)-I remains to be the most reasonable structure for (4a). In order to confirm above assignment, an X-ray crystallographic analysis of (4a) was carried out.


(4a)-I


(4a)-II

Crystal data are: Space group $P2_1/c$; Cell dimensions: a=15.896(3), b=8.937 (2), c=18.575(3) Å and β=120.31(2)°; z=4. A total of 3053 independent reflections was collected on a Rigaku full automatic four-circle diffractometer with Mo-Kα radiation. The structure was solved by a program MULTAN and has been refined by block-diagonal least-square method to an R-factor of 0.085. The resulting molecular structure was confirmed to be (4a)-I as shown in the Figure.

Dimethyl derivative (4b) was also prepared in a similar manner as described for (4a) and showed very similar spectral data and X-ray diffraction pattern[3] ((4b): colorless prisms from benzene, mp 220-235°C, Mass 466(M^+), 334, 262, 204, 132; UV(THF) 316.5 sh(1,460), 295.5(1,870), 275 sh(3,350), 268 sh(3,860), 238 sh nm(ε 12,000); ^{1}H-NMR($CDCl_3$) δ 0.8-3.3(m, 16H), 4.50(s, 1H), 6.4-7.3 ppm(m, 13H)).

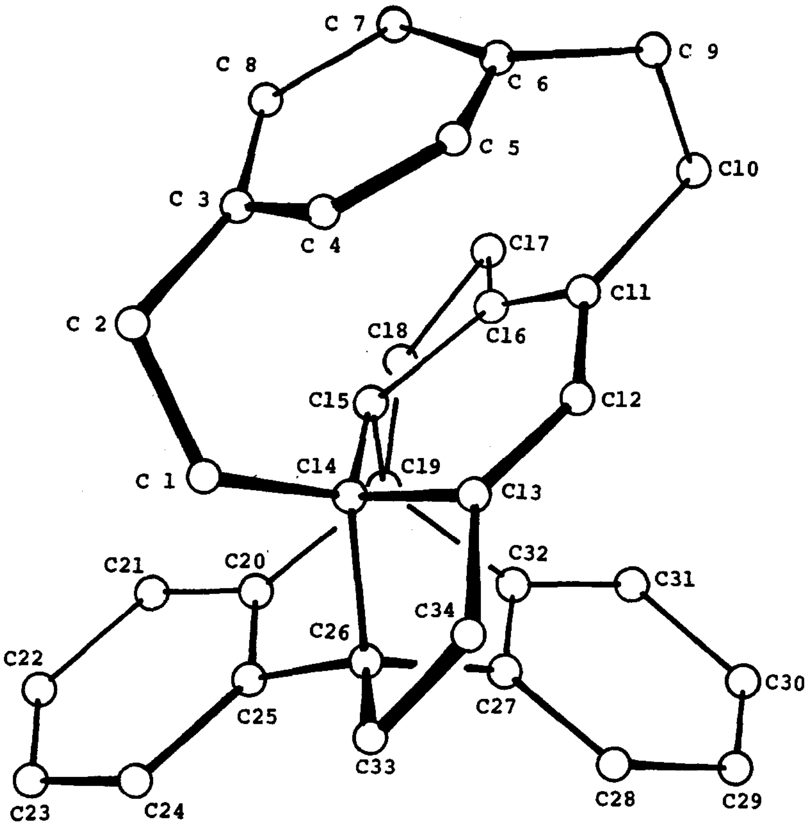
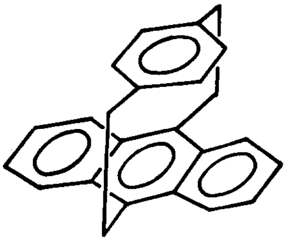


Figure Projection of (4a) along b-axis.

Table Bond lengths in Å.

C 1 --- C 2	1.566	C 1 --- C14	1.571	C 2 --- C 3	1.514
C 3 --- C 4	1.373	C 3 --- C 8	1.393	C 4 --- C 5	1.393
C 5 --- C 6	1.380	C 6 --- C 7	1.388	C 6 --- C 9	1.515
C 7 --- C 8	1.384	C 9 --- C10	1.587	C10 --- C11	1.519
C11 --- C12	1.484	C11 --- C16	1.335	C12 --- C13	1.327
C13 --- C14	1.503	C13 --- C34	1.543	C14 --- C15	1.509
C14 --- C26	1.599	C15 --- C16	1.483	C15 --- C19	1.569
C16 --- C17	1.523	C17 --- C18	1.581	C18 --- C19	1.532
C19 --- C20	1.523	C19 --- C32	1.513	C20 --- C21	1.395
C20 --- C25	1.405	C21 --- C22	1.393	C22 --- C23	1.358
C23 --- C24	1.397	C24 --- C25	1.395	C25 --- C26	1.513
C26 --- C27	1.526	C26 --- C33	1.539	C27 --- C28	1.396
C27 --- C32	1.389	C28 --- C29	1.374	C29 --- C30	1.355
C30 --- C31	1.417	C31 --- C32	1.387	C33 --- C34	1.576

Therefore, it is concluded that (4b) has the same framework as (4a). The formation of the structure (4a)-I clearly indicates that the inner benzene nucleus reacts intramolecularly as a dienophile with closely faced anthracene nucleus. On the other hand double-layered anthracenophane (5)[4] does not undergo such an intramolecular [$\pi 4s + \pi 2s$] cycloaddition as do triple-layered ones. This diffrent reactivity between (3) and (5) may mainly be attributed to a marked strain of the inner benzene nucleus in (3).



(5)

References

1) Part XXIX: T. Umemoto, S. Satani, Y. Sakata, and S. Misumi, to be submitted.

2) W. Jarre, D. Bieniek, and F. Korte, *Angew. Chem.*, 87, 201 (1975).

3) Crystals of (4b) belong to the same space group ($P2_1/C$) and have cell constants similar to those of (4a).

4) A. Iwama, T. Toyoda, T. Otsubo, and S. Misumi, *Chemistry Lett.*, 1973, 587.