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AZULENOPHANES V

SYNTHESIS AND PHYSICAL PROPERTIES OF [2](5,7)AZULENO[2]PARA- AND METACYCLOPHANES

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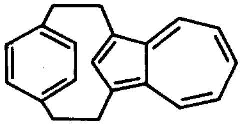
Abstract The title compounds 3 and 4 were synthesized by the usual dithia[3.3]phane coupling and photodesulfurization route. Investigation of their physical properties established their molecular dimension and conformation. Transannular interaction disclosed by their electronic spectra was explained by MO calculations.

In our previous paper[1] we have reported the synthesis and physical properties of [2](1,3)azuleno[2]-paracyclophane (1), in which the five-membered ring of dipolar azulene faces close to the para-bridged benzene ring. No sizable change could be detected in its electronic spectrum when compared with its reference compounds, suggesting that the transannular interaction between benzene and azulene is not so significant in this geometry. The same is true for meta-bridged azulenocyclophane 2 synthesized by Murata[2]. In order to clarify the geometrical effect of these two aromatic rings on the transannular interaction, we have investigated azulenocyclophanes in which benzene ring is facing close to seven-membered ring of azulene. Thus, synthesis and physical properties of [2](5,7)azuleno[2]para- and metacyclophanes (3 and 4) are described herein[3].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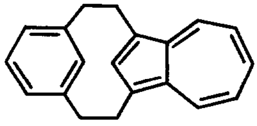
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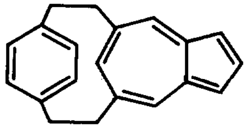
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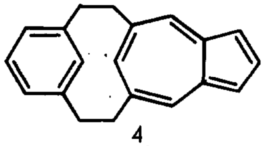
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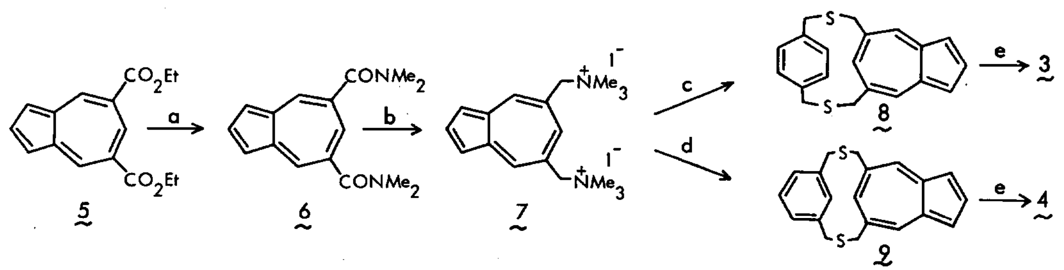
Synthesis They were synthesized by the usual coupling and desulfurization method starting from Jutz's



a: i) KOH, ii) HMPT/HMPA, 91% yield; b: i) $Et_3O^+BF_4^-$, ii) $NaBH_4$, iii) MeI, 59%;
c: p-bis(mercaptomethyl)benzene, NaOMe/MeOH high dilution, 13%; d: m-bis(mercaptomethyl)benzene, NaOMe/MeOH high dilution, 38%; e: hν, $(MeO)_3P$, 0°, 40% for 3, 16% for 4

diethyl 5,7-azulenedicarboxylate (5)5) as shown in scheme. Reduction of 6 by borane-dimethyl sulfide complex gave the diamine in poor yield (3%), but Borch's method6) afforded it in a reasonable yield. Physical constants of 4 and dithia[3.3]azulenocyclophanes 8 and 9 are listed in Table7). Compounds 8 and 9 show some rapid dynamic process in their PMR spectra at room temperature, as is indicated by two singlet nature of methylene signals in both cases and equivalence of benzene protons in 8. Detailed discussion of the process will be presented elsewhere.

X ray Analysis of 3 The crystal of 3 belongs to orthorhombic system of space group Pbca with 8 molecules in a unit cell of dimensions a=12.470(2), b=26.013(3), c=8.779(1)Å. The structure was solved by the MULTAN78 using a total of 1496 unique reflections collected by graphite monochromated Cu Ka radiation and refined by block-diagonal least-squares calculations. The final R value was 6.7%8).

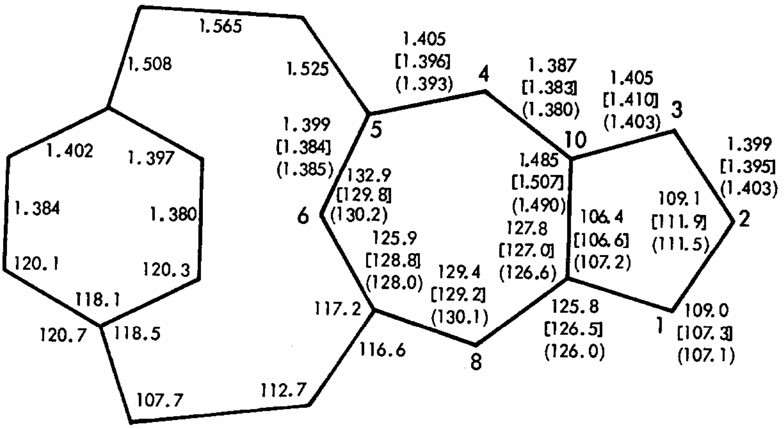


Fig. 1 Averaged bond lengths and angles in 3; [ ]: values for 1, ( ): values for 10
Averaged standard deviation of C-C bond and ∠C-C-C are 0.007Å and 0.4°, respectively.

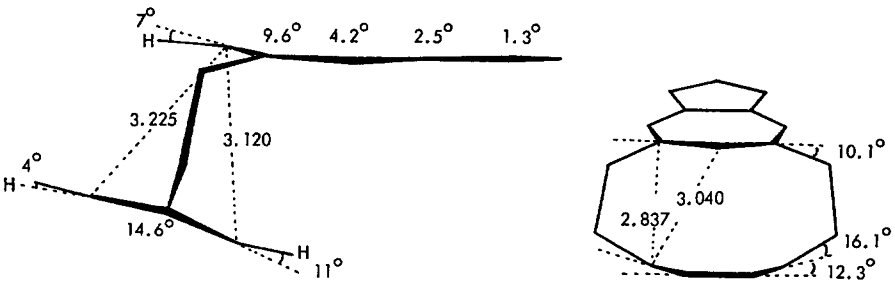


Fig. 2 Side view of 3 with dihedral angles and interplanar atomic distances

Averaged values of chemically equivalent bonds and angles are shown in Fig. 1 together with those of 1 1) (azulene part only) and strain free azulene-1,3-dipropionic acid (10)9). The bond lengths and angles of 3 are generally in good agreement with those of 10. However, some distortion is clear in the vicinity of the bridges suggesting a mechanism of strain release: C_4-C_5 (azulene numbering) and C_5-C_6 bonds are longer, $\angle C_4C_5C_6$ is smaller and $\angle C_5C_6C_7$ larger than those of 10. It is interesting that similar elongation of C_9-C_{10} bond but not angular change was observed in 1. The major distortion of the molecules is clearly shown in a side view (Fig. 2). The azulene ring stays planar except outward bending (9.6°) at C_6. The mean plane of bent benzene inclines 16.3° with respect to that of azulene. The bending angles of boat benzene ring (12.3°) and inward bending of bridge carbons (16.1°) are very similar with those of 1 and [2.2]metaparacyclophane[10]. Hydrogens attached to C_6 azulene carbon and to benzene ring all lie inward.

Since there is no short intermolecular contact which gives rise to the molecular distortion, all of the distortions should be due to intramolecular factors.

PMR Spectra of 4 (Table) Unsymmetrical ABCD pattern of the bridge methylene signals reveals that the flipping of aromatic rings are negligible at room temperature. The up-field shift of inner aromatic protons ($\Delta\delta H_6^{Az}$ 2.46 ppm from 5,7-dimethylazulene (11)[11] and $\Delta\delta H_{2'}^{Bz}$ 1.75 ppm from m-xylene) suggests the stepped (anti) conformation. This was further supported by down-field shift of all outer aromatic protons.

Electronic Spectra The electronic spectra of 3 and 4 are shown in Fig. 3 together with that of 11. Although both the 'Lb and 'La bands of 3 and 4 show no sizable shift and broadening when compared with that of 11, a large bathochromic shift (~2000 cm^{-1}) of 'Bb band is observed in meta-bridged 4. The similar shift of 'Bb was also observed in 2 but not in 1[1,2]. These characteristic shifts can be explained qualitatively by extended Hückel calculations (Fig. 4). Although occupied orbitals (HOMO and NHOMO)[12] of both azulene and benzene can interact with each other, the geometry of 3 does not allow as much efficient mixing of NHOMO orbitals as in 4 where strong interaction is expected because of efficient overlap of large atomic orbitals of inner aryl carbons. The resulted S_2 orbital in 4 is thus higher than that in 3, and causes larger bathochromic shift of 'Bb band[13]. Although both 'Bb and 'La bands of azulene are originated from the combination of two excitations[14], HOMO-NLUMO and NHOMO-LUMO, the large bathochromic shift found only in 'Bb band of 2 and 4 suggests the larger contribution of the latter excitation in 'Bb transition of azulene than the former and *vice versa* in 'La transition.

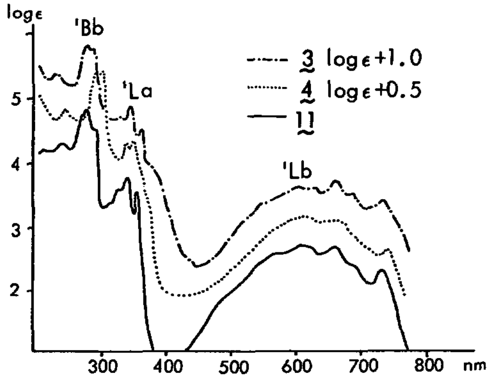


Fig. 3 Electronic spectra of 3, 4 and 11 in cyclohexane

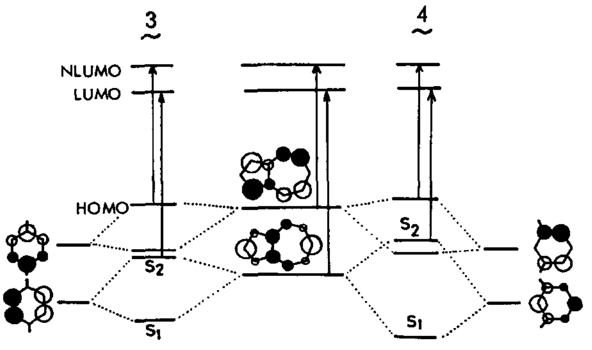


Fig. 4 Schematic representation of MO diagram

TABLE

4: blue prisms, m.p. 224-225°; m/e 258 (M^{+}, b.p.), 243, 230, 215, 202, 153; ν^{KBr} 2920, 2840, 1570, 1445, 1392, 935, 790, 755, 720 cm^{-1}; $\lambda_{max}^{c\text{-}hexane}$ 250 ($\log\epsilon$ 4.16), 295 (4.69), 305 (4.69), 341 (3.65), 356 (3.77), 370 (2.70 sh), 610 (2.51), 660 (2.49), 690 (2.15 sh), 736 nm (2.06); δ^{CDCl_3} 2.12-3.45 (8H, m, ABCD), 4.84 (1H, br.s, H_6^{Az}), 5.21 (1H, br.s, $H_{2'}^{Bz}$), 7.11 (2H, m, $H_{4',6'}^{Bz}$), 7.25 (2H, d, 4.0, $H_{1,3}^{Az}$), 7.37 (1H, m, $H_{5'}^{Bz}$), 7.81 (1H, br.s, H_2^{Az}), 8.25 (2H, d, 1.5, $H_{4,8}^{Az}$).

8: blue needles, m.p. 200-203°(dec.); m/e 322 (M^{+}, b.p.), 217, 185, 155; ν^{KBr} 1570, 1413, 1400, 905, 815, 750, 742 cm^{-1}; $\lambda_{max}^{c\text{-}hexane}$ 286 ($\log\epsilon$ 4.79), 297 (4.71 sh), 340 (3.72 sh), 353 (3.95), 365 (3.67 sh), 370 (4.10), 563 (2.85 sh), 590 (2.60), 612 (2.60), 644 (2.62), 6.70 (2.42), 712 nm (2.39); δ^{CS_2} 3.54 (4H, s), 3.80 (4H, s), 5.69 (1H, t, 1.5 Hz), 6.90 (4H, s), 7.00 (2H, d, 4.0), 7.58 (1H, t, 4.0), 7.89 ppm (2H, d, 1.5).

9: blue needles, m.p. 154.5-155.5°(dec.); m/e 322 (M^{+}, b.p.), 217, 185, 171, 155, 141; ν^{KBr} 2880, 1570, 1485, 1443, 1400, 1215, 1050, 895, 795, 752, 708, 695 cm^{-1}; $\lambda_{max}^{c\text{-}hexane}$ 244 ($\log\epsilon$ 4.18), 289 (4.62 sh), 296 (4.67), 344 (3.60 sh), 355 (3.79), 373 (3.80), 570 (2.44 sh), 595 (2.55), 617 (2.54), 650 (2.61), 675 (2.42), 720 nm (2.32); δ^{CS_2} 3.71 (4H, s), 3.75 (4H, s), 6.66 (1H, t, 1.5), 6.62-6.92 (4H, m), 7.02 (2H, d, 4.0), 7.59 (1H, t, 4.0), 7.97 (2H, t, 1.5).

References and Notes

1) Y. Fukazawa, M. Aoyagi and S. Itô, Tetrahedron Letters, 1067 (1978).

2) Y. Nesumi, T. Nakazawa and I. Murata, Chemistry Letters, 771 (1979).

3) The synthesis of **3** together with that of [2](4,7)azuleno[2]paracyclophane has been performed and some of their physical properties examined by Misumi[4]. We describe the synthesis because our approach is different from theirs.

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7) Physical data of **3** are reported in Ref. 4. We have however found its m.p. 167-168.5°. We have also found the chemical shift of inner azulene proton at 5.81 ppm and that of inner benzene protons at 5.90 ppm, their intensity ratio being 1 : 2.

8) Final crystallographic coordinates have been deposited in the Cambridge Crystallographic Data Center.

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13) The calculations show that the lowering of LUMO is not appreciable in both cases. From the symmetric nature of azulene orbitals, the situation is also very similar in **1** and **2**.

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