SYNTHESIS AND PHYSICAL PROPERTIES OF [2](1,3)AZULENO[2]PARACYCLOPHANE

AND 2,13-DITHIA[3](1,3)AZULENO[3]PARACYCLOPHANE

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The [m.n]phanes represent an interesting class of strained organic compounds having a transannular π-electron interaction between the two facing aromatic rings[1] as was witnessed by several interesting examples[2]. With the expectation of modified interaction caused by the incorporation of dipolar azulene ring in a phane system, [2.2](2,6)azulenophane has recently been synthesized[3]. We describe here synthesis and physical properties of a [2.2]phane with 1,3-bridged azulene and parabridged benzene rings[4].

Synthesis   Azulene-1,3-bis(methyltrimethylammonium) diiodide derived from azulene in 77% yield by Anderson's method[5] was coupled with 1,4-bis(mercaptomethyl) benzene with a base utilizing the high dilution technique to give 2,13-dithia[3](1,3)azuleno[3]paracyclophane (1) in 40% yield. 1: blue needles, m.p. 168°C (dec.); m/e 322 (M$^+$), 185, 155 (b.p.); ν^{KBr} 2881, 1573, 1427, 1221, 887, 743 cm^{-1}; λ^{MeOH}_{max}(logε) 242 (4.24), 295 (4.55), 363 (3.64), 381 (3.81), 578 (sh 2.32), 627 (2.43), 672 (sh 2.33), 755 (sh 1.90); δ^{CS_2} 3.78 (4H, s), 3.93 (4H, s), 6.25 (1H, s), 6.60 (4H, s), 6.91 (2H, t, J=9), 7.37 (1H, t, J=9), 8.06 (2H, d, J=9).

Photodesulfurization of 1 in trimethylphosphite at 0°C gave [2](1,3)azuleno[2]paracyclophane (2) in 70% yield. 2: blue needles, m.p. 139-141°C; m/e 258 (M$^+$), 154 (b.p.); ν^{KBr} 3020, 1573, 904, 744, 725, 582, 555 cm^{-1}; λ^{MeOH}_{max} (log ε) 288 (4.63), 342 (sh 3.44), 348 (sh 3.47), 356 (3.60), 374 (3.39), 574 (2.21), 600 (2.28), 626 (2.33), 670 (2.22), 750 (1.62); $\delta^{C_4Cl_6}$ 2.88 (8H, ABCD type), 5.20 (2H, d, J=1), 6.08 (1H, s), 6.98 (2H, d, J=1), 6.84 (2H, t, J=9), 7.30 (1H, t, J=9), 7.87 (2H, d, J=9).

PMR Spectra   Spectra of 1 and 2 show a common feature: All the aromatic proton signals shift upfield compared with those of the non-bridged reference compounds, in accord with the layered structure. Furthermore, although the shift is generally larger in 2 than in 1, the protons on benzene[6] and the H2 of azulene in each compound show more pronounced effect than the seven-membered ring protons. However, an important difference is revealed in these spectra: In 1 each signal due to the benzene protons (δ 6.60) and the bridge protons (δ 3.93 and 3.78) appear as three singlets suggesting the flipping of azulene ring, while in 2 the former appear as two doublets (δ 5.20 and 6.98) and the latter as an
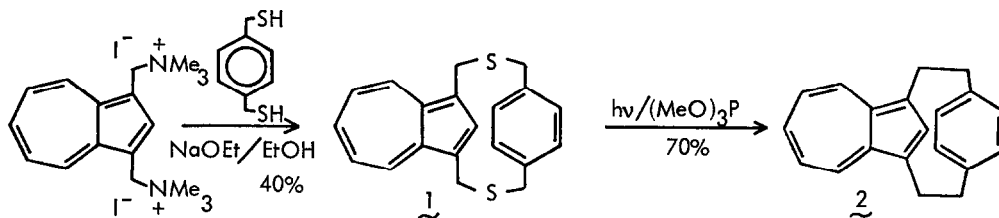
unsymmetrical ABCD pattern, showing a frozen conformation at room temperature. The low-temperature

spectra of $\underset{\sim}{1}$[7] measured in CD_2Cl_2-$CF_3C_2Cl_3$ disclosed coalescence of the benzene ring protons at $-125°C$

and appearance of two broad signals ($\delta \sim 6.4$ and ~ 7.2) at $-135°C$. From these figures, the free energy

of activation ($\Delta G^{\ddagger}$) for the azulene ring flipping was estimated to be around 7 kcal/mol at $-125°C$.[8]

On the contrary, spectrum of $\underset{\sim}{2}$ showed no change up to $190°C$. $\Delta G^{\ddagger}$ for the flipping in $\underset{\sim}{2}$, estimated to

be larger than 22.0 kcal/mol, is considerably higher than that (20.6 kcal/mol) determined for [2.2]meta-

paracyclophane $(\underset{\sim}{3})$.[9]

   X ray Analysis   The crystal of $\underset{\sim}{2}$ (recrystallized from n-hexane) belongs to monoclinic system with

4 molecules in the unit cell of dimensions $\underline{a}=9.023(1)$ Å, $\underline{b}=19.980(2)$, $\underline{c}=8.259(1)$ and $\beta=109.02(1)°$.

The space group is $P2_1/a$. The structure was solved by the direct method using a total of 1907 unique

reflections collected by CuKα radiation and refined by block-diagonal least-squares calculations. The final

R value was 6.8%.

   Since the molecule has a conformation with two-fold symmetry, averaged values of chemically equiva-

lent bonds and angles are shown in Fig. 1 together with those of azulene-1,3-dipropionic acid $(\underset{\sim}{4})$[10] and

of [2.2]paracyclophane $(\underset{\sim}{5})$.[11] The bond lengths and angles in azulene ring are in good agreement with

those of the strain free analog except for longer transannular bond. Bond lengths and bond angles in

ethano bridge as well as data for benzene ring are very similar with those in $\underset{\sim}{5}$.

   The major distortion of the molecules is clearly seen in side view (Fig. 2). The bending angles of

the benzene ring ($13.8°$, $14.4°$) and that of exocyclic bond of the azulene ring ($13.3°$) are quite similar

with those of $\underset{\sim}{3}$ ($14°$, $14°$, $13°$, respectively).[12]

   Though hydrogens attached to the benzene ring all lie inward, the outside hydrogens bent more than

the inside ones, suggesting repulsion between the inside hydrogens and the π-electron cloud of the azulene

ring. Since there is no short intermolecular contact which give rise to the distortion of the molecule, all

of these distortions should be due to intramolecular factors.

   Based on the geometry of $\underset{\sim}{2}$ thus obtained, the distance between the H2 of azulene and the plane of

the bent benzene ring in the orthogonal orientation of the two aromatic rings (a model of flipping transi-

tion state) was calculated in order to rationalize the large $\Delta G^{\ddagger}$ described above. The distance is around

1.2 Å which is 0.3 Å shorter than the corresponding value of $\underset{\sim}{3}$. The difference in $\Delta G^{\ddagger}$ for the ring

flipping between these two compounds would thus be mainly due to that in repulsion in their rotational

transition states,[13] even if the dipolar structure of azulene ring is considered.[9b]

Fig. 1   Averaged bond lengths and angles in 2

( ) values for azulene-1,3-dipropionic acid (4)
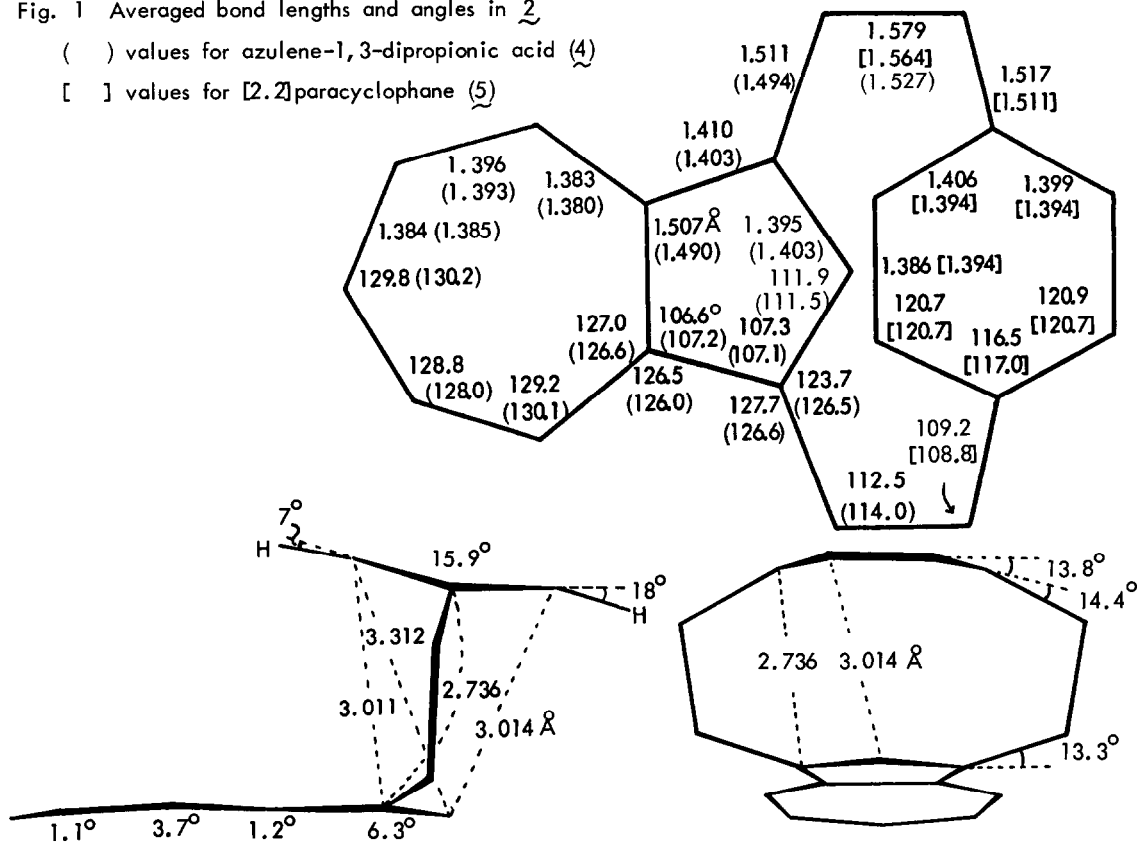
[ ] values for [2.2]paracyclophane (5)

1.579
[1.564]
(1.527)

1.511
(1.494)

1.517
[1.511]

1.396
(1.393)

1.383
(1.380)

1.410
(1.403)

1.406
[1.394]

1.399
[1.394]

1.384 (1.385)

1.507Å
(1.490)

1.395
(1.403)

1.386 [1.394]

129.8 (130.2)

111.9
(111.5)

120.7
[120.7]

120.9
[120.7]

106.6°
(107.2)

107.3
(107.1)

116.5
[117.0]

128.8
(128.0)

127.0
(126.6)

129.2
(130.1)

126.5
(126.0)

123.7
(126.5)

127.7
(126.6)

109.2
[108.8]

112.5
(114.0)

Fig. 2 Side view of the molecule of 2 with the bending angles and interplanar atomic distances

7°

H

15.9°

18°

H

3.312

3.011

2.736

3.014 Å

1.1°   3.7°   1.2°   6.3°

13.8°

14.4°

2.736   3.014 Å

13.3°

Electronic Spectra   Although the spectrum of 1 has little difference, that of 2 in MeOH shows some change, when compared with those of 1,3-dimethyl-azulene (Fig.3); Lb band being blue-shifted by 10-20 nm and La and Bb bands red-shifted by 5-8 nm. However, vibrational fine structure is still visible even for 2 suggesting no appreciable transannular interaction. In acidic solution, an intense absorption is observed at 400 nm with a shoulder at 470 nm. Comparing with 1,3-dimethylazulenium ion, this band is concluded to contain an extra absorption, probably due to the intramolecular charge-transfer interaction. 2 can be recovered unchanged from the acidic solution on dilution with water and extraction.
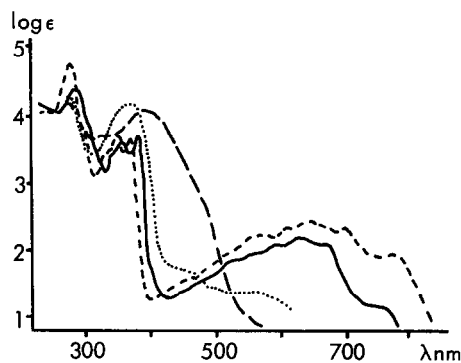

logε

300   500   700   λnm

Fig.3   Electronic spectra of 2
in MeOH and in CF$_3$CO$_2$H
(——)   (— —)
and 1,3-dimethylazulene
in MeOH and in CF$_3$CO$_2$H
(- - - - -)   (·········)

References and Footnotes

1) B.H. Smith, "Bridged Aromatic Compounds", Academic Press, N.Y. (1964), D.J. Cram and J.M. Cram, Accounts Chem. Res., 4, 204 (1971), F. Vögtle and P. Neumann, Angew. Chem. Intern. Ed., 11, 73 (1972), G.R. Newkome, J.D. Sauer, J.M. Roper and D.C. Hager, Chem. Rev., 77, 513 (1977).

2) e.g. D.J. Cram and A.C. Day, J. Org. Chem., 31, 1227 (1966), W. Rebafka and H.A. Staab, Angew. Chem. Intern. Ed., 13, 203 (1974).

3) R. Luhowy and P.M. Keehn, Tetrahedron Letters, 1043 (1976), J. Am. Chem. Soc., 99, 3797 (1977), N. Kato, Y. Fukazawa and S. Itô, Tetrahedron Letters, 2045 (1976).

4) The synthesis of [2](4,7)azuleno[2]paracyclophane has recently been reported. T. Kawashima, T. Otsubo, Y. Sakata and S. Misumi, "10th Symposium on Nonbenzenoid Aromatic Compounds", Abstract, p.80, Matsuyama, Japan (1977). Cf. Preceding paper.

5) A.G. Anderson, Jr., R.G. Anderson and T.S. Fujita, J. Org. Chem., 27, 4535 (1962).

6) As is described, benzene ring protons in 2 appear as two doublets, so that mean value is compared with the singlet in 1.

7) We wish to express our gratitude to Professor S. Masamune, University of Alberta, for the PMR measurements at low temperatures.

8) During these measurements, the signals due to the azulene ring protons were found to broaden at around -130°C, revealing the presence of another dynamic process in addition to the ring flipping. This broadening is probably due to the inversion of the bridge system (Fig.), since the $\Delta G^{\ddagger}$ of bridge inversion in structurally related [3.3]paracyclophane is known to be 11.7 kcal/mol (F.A.L. Anet and M.A. Brown, J. Am. Chem. Soc., 91, 2389 (1969)) and the substitution of methylenes by sulfur atoms reduces the $\Delta G^{\ddagger}$ of the inversion by several kcal/mol (J.R. Fletcher and I.O. Sutherland, Chem. Commun., 1504 (1969), F. Vögtle and A.H. Effler, Chem. Ber., 102, 3071 (1969)).
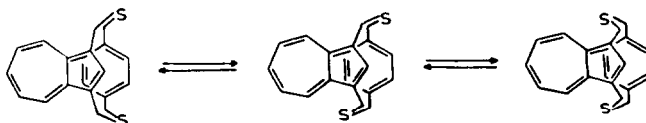
9) a) D.T. Hefelfinger and D.J. Cram, J. Am. Chem. Soc., 92, 1073 (1970), ibid., 93, 4767 (1971), F. Vögtle, Chem. Ber., 102, 3077 (1969), S. Akabori, S. Hayashi, M. Nawa and K. Shiomi, Tetrahedron Letters, 3727 (1969), b) S.A. Sherrod, R.L. da Costa, R.A. Barnes and V. Boekelheide, J. Am. Chem. Soc., 96, 1565 (1974).

10) H.L. Ammon and M. Sundaralingam, J. Am. Chem. Soc., 88, 4794 (1966).

11) H. Hope, J. Bernstein and K.N. Trueblood, Acta Cryst., B28, 1733 (1972).

12) D.T. Hefelfinger and D.J. Cram, J. Am. Chem. Soc., 93, 4754 (1971).

13) H···C repulsive energy calculated using Hendrickson's parameters (J. Am. Chem. Soc., 89, 7036 (1967)) is 9 kcal/mol more than that of 3.