The equatorial Sn–Cl distances range from 2.884 (7) to 3.291 (7) Å, and the axial Sn–Cl distance is 2.766 (7) Å. These are somewhat long compared to the covalent radii sum of 2.39 Å,[8] but are real covalent interactions since the sum of the van der Waals radii is 4 Å.[8] The Cl(equatorial)–Sn–Cl(equatorial) angles vary between 73° and 81° with individual esd's of ±0.60° (regular pentagon = 72°). The Sn is displaced 0.6 Å from the least-squares plane defined by the five equatorial halogens toward the benzene ring. We view this displacement as arising from a combination of steric constraints imposed by the chelated $AlCl_4^-$ groups and van der Waals repulsion between C and Cl. The Sn–C distances are not significantly different from the 3.08-Å average, and the Sn to center of ring distance is 2.74 (3) Å. The benzene carbon–carbon distances are indistinguishable from free benzene. The Cl(axial)–Sn–center of benzene ring angle is 180° within experimental error. These metal–carbon distances are also quite long compared to, *e.g.*, ruthenocene[9] [Ru–C = 2.21 (2) Å], but again are much shorter than the 4 Å[8] expected from van der Waals radii. These "long" metal–carbon distances are compatible with our views of the bonding; *vide infra.*

There has been considerable recent activity in higher coordination number metal complexes as demonstrated by a symposium[10] and a review.[11] Most seven-coordinate pentagonal bipyramid complexes (few have been definitely established) involve uranium, zirconium, and molybdenum.[12a] However, Hoard[12b] has reported a pentagonal bipyramid structure for tristropolonotin(IV) chloride and hydroxide. We believe our results are the first report of a pentagonal bipyramid seven-coordinate Sn(II) entity.

The nature of the bonding in this pentagonal bipyramid complex is particularly interesting. A reasonable energy level diagram can be constructed using benzene π orbitals, considering only σ bonds between Cl and Sn, assuming C_{5v} symmetry[13] and with the energy level diagram of dibenzenechromium[14] as a reference. The a_1, e_2, e_1 halogen orbitals would lie approximately halfway between aromatic e_1 and e_2, whereas the 5s Sn(II) a_1 might lie close to aromatic e_2 but considerably below the b_2. The e_1 and a_1 5p orbitals might be about 5–7 eV above the 5s, and the 5d about 7 eV above the 5p.[15] It seems energetically unfavorable to make much use of the 5d. The filled MO's of the pentagonal bipyramid complex would then be, in order of increasing energy: $(a_1)^2(e_1)^4(a_1')^2(e_1')^4(a_1'')^2(e_2)^4(a_1''')^2$. This corresponds to a closed shell configuration with moderate separation between a_1''' and the lowest empty MO of e_2' symmetry which would be principally nonbonding aromatic. The lowest a_1 and e_1 MO's would be mostly aromatic. The e_1', a_1', a_1'', and e_2 MO's would be chiefly chlorine σ in character, with a_1' being the axial interaction. If the 5d Sn(II) orbitals play a significant role in this complex, it would be in the lowering of the energy of e_2 and e_2'. The e_2 lowering would correspond to increasing the bond order of the equatorial Sn–Cl bonds, and e_2' lowering would be equivalent to "back-bonding" from metal to aromatic. It is to be noted that the bonding between Sn and the halogens involves five equatorial bonds but only six bonding electrons $[(e_1')^4$ and $(a_1'')^2]$, and the Sn–Cl bonds are long as expected. Nevertheless, it must be borne in mind that there is some aromatic mixing in these orbitals, but this is probably small. It is gratifying to see that the highest filled level is $(a_1''')^2$, which is mostly metal in character, since the Mössbauer spectrum shows that the 5s orbitals are almost fully occupied.[16] The principal bonding between metal and aromatic is in the a_1 and e_1 levels which involve metal 5s and 5p, and may be viewed as charge transfer of π electrons into the empty 5p orbitals of Sn(II). When viewed in this way the bonding can also be described in terms of Mulliken's charge-transfer theory.[17]

Presumably, $(C_6H_6)Pb(AlCl_4)_2 \cdot C_6H_6$ is similar to the above in both geometry and bonding. The Tl complexes are different in stoichiometry and probably geometry due to the contrasting requirements of the Tl(I) ion.

Acknowledgment. Financial support was received from the National Science Foundation under Grant No. GP-12282.

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[8] L. Pauling, "Nature of the Chemical Bond," 3rd ed, The Cornell University Press, Ithaca, N. Y., 1960, pp 246, 260.

[9] E. L. Hardgrove and D. H. Templeton, *Acta Cryst.*, **12**, 28 (1959).

[10] Symposium on Unusual Coordination Polyhedra, Abstracts, Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[11] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

[12] (a) M. Elder, *Inorg. Chem.*, 8, 2103 (1969); (b) J. L. Hoard, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, paper O3.

[13] Obviously the true symmetry of the complex is not C_6 but much lower. However, this difference would not materially affect the arguments.

[14] E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **128**, 1234 (1959).

[15] C. E. Moore, "Atomic Energy Levels," Vol. III, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1958, p 82.

[16] L. Cathey, University of South Carolina, private communication, 1968.

[17] R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).

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Mechanistic and Exploratory Organic Photochemistry. XLIX.[1] Excited-State Aromaticity and Energy Localization. The Di-π-methane Rearrangement of Naphthobarrelenes

Sir:

In our recent study of the di-π-methane rearrangement of benzobarrelene (**1**) to form benzosemibullvalene (**2**), we encountered an intriguing preference for vinyl–vinyl bridging over benzo–vinyl bonding.[2] Energetic arguments were advanced to rationalize this selectivity.[2] Our hypothesis suggested that by lowering the triplet excitation energy of the aromatic moiety of the molecule, one might enforce an aromatic–vinyl bridging process.

For this study 2,3-naphthobarrelene (**6**) and 1,2-naphthobarrelene (**7**) were synthesized by reaction of 2,3-naphthyne (**8**) and 1,2-naphthyne (**9**) with benzene.[3]

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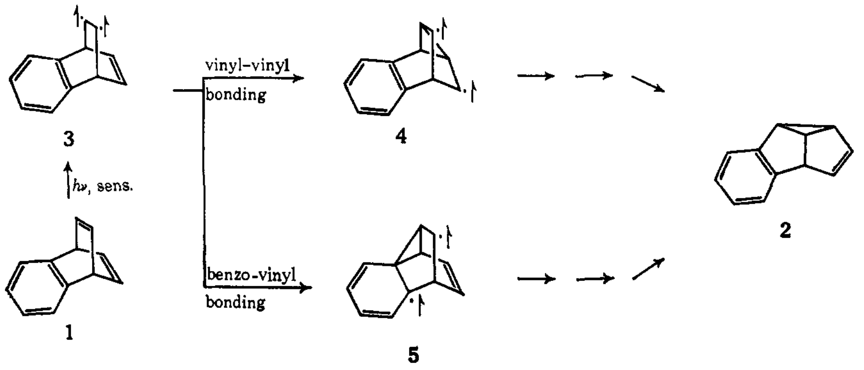
[1] For paper XLVIII of the series see H. E. Zimmerman and S. S. Hixson, *J. Am. Chem. Soc.*, in press.

[2] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

[3] (a) All compounds analyzed properly. (b) Full experimental details are given in our complete paper. (c) Irradiations were mainly with solution filters and a GEAH6 lamp. (d) Deuterations were *ca.*



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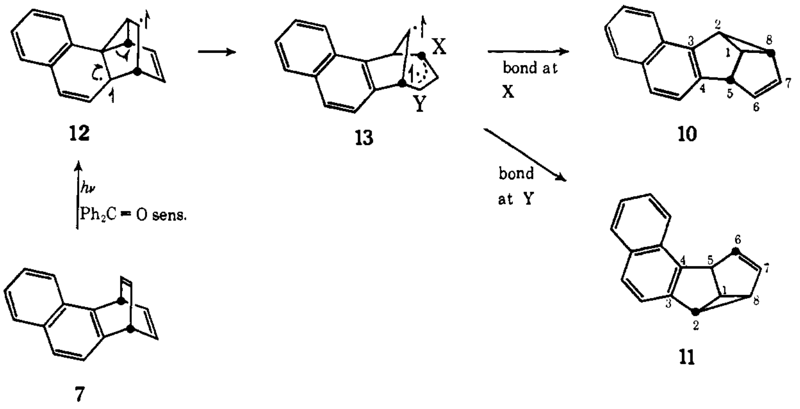

(2)

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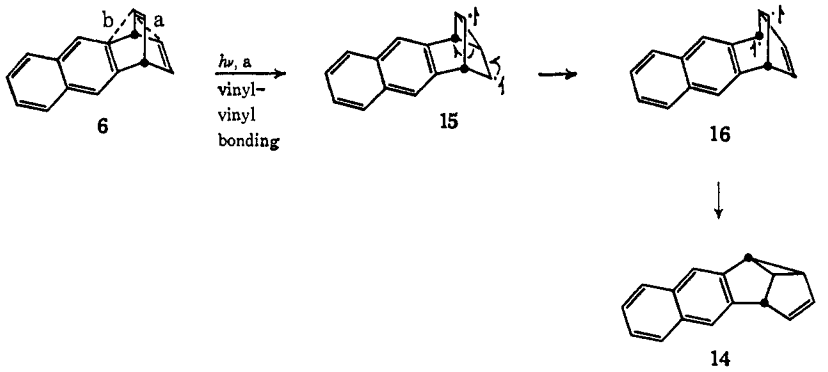

(3)

• represents H label

The low triplet energy (61 kcal/mol)[3e] of the naphthalene moiety compared to 85 kcal/mol for isolated ethylenic groups promised to concentrate triplet excitation in the naphtho ring of the excited naphthobarrelenes. To determine the bridging processes occurring, perdeuterated 1,2- and 2,3-naphthobarrelene were prepared using lithium N-deuteriocyclohexylamide;[2] vinyl and aryl hydrogens were exchanged leaving bridgehead hydrogens as a label.[2,3]

Indeed, benzophenone-sensitized photolysis of perdeuterated 1,2-naphthobarrelene (**7**) in cyclohexane gave the *syn*- and *anti*-1,2-naphthosemibullvalenes (**10** and **11**) with the label in the *syn* isomer exclusively at C-5 and C-8 and the label in the *anti* product totally at C-2 and C-6. This is consistent with α-naphtho–vinyl bridging initiating the reaction (see eq 2). Application of the same type of mechanistic reasoning but with alternative types of bridging leads to different and unobserved label distributions.[4] Thus, in this case, the end of the molecule most involved in the excitation process is the end which reacts.

In contrast, the direct and sensitized photolyses[3] of perdeuterated 2,3-naphthobarrelene (**6**) gave 2,3-naphthosemibullvalene (**14**) labeled exclusively at the benzylic positions. It is seen that this product arises from vinyl–vinyl bonding; note eq 3. In this case no naphthocyclooctatetraene product was encountered in the direct photolyses.[4] Clearly this reaction is not being

90% complete at vinyl positions and corrections were made for residual vinyl hydrogen. HA100 nmr analysis allowed separate identification of all protons. (e) Triplet energies of 61 kcal/mol were obtained for **6** and **7** by phosphorescence emission measurements.

(4) Direct irradiation of 1,2-naphthobarrelene afforded semibullvalene product which arose primarily (*i.e.*, 58%) by α-naphtho–vinyl bridging but included 42% of *syn* and *anti* product which arose by vinyl–vinyl bridging. The major product was 1,2-naphthocyclooctatetraene labeled β to the naphtho ring. These appear to be singlet products and will be discussed in our full paper.

controlled by localization of excitation energy. Rather it appears that this reaction is being guided by a reluctance of the β position of the naphthalene moiety to involve itself in the bridging process. This can be ascribed to residual aromaticity still present in the triplet, with the result that an excessive electron localization energy is demanded in the excited state paralleling the ground-state situation.

The results and deductions regarding the excited-state reactivity preferences are summarized in Chart I.

Chart I. Summary of and Deductions from the Photochemistry

Reactant and conditions	Bonding[a]
1,2-NB,[b] sensitized	α-Naphtho–vinyl
1,2-NB, direct	α-Naphtho–vinyl (17%), vinyl–vinyl (13%) Naphtho–vinyl cycloaddition (70%)
2,3-NB, sensitized	Vinyl–vinyl
2,3-NB, direct	Vinyl–vinyl
	Order of Preference of Processes
For the triplet	α-Naphtho–vinyl bridging > Vinyl–vinyl bridging > β-Naphtho–vinyl bridging
For the singlet	α-Naphtho–vinyl bridging ≃ Vinyl–vinyl bridging > β-Naphtho–vinyl bridging

[a] All are two-center bridging processes except for the four-center cycloaddition indicated. [b] Naphthobarrelene (NB).

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The Synthesis of the 1-Methoxy-2,8,10-tridehydro[17]annulenyl Anion, an Aromatic 17-Membered Ring Cyclic System[1]

Sir:

The cyclopentadienyl anion (**1**) is a well-known member ($n = 1$) of a series of aromatic monoanions containing ($4n + 2$) out-of-plane π electrons in a single ($4n + 1$)-membered carbocyclic ring.[2] The only higher members known are the cyclononatetraenyl ([9]annulenyl) anion (**2**, $n = 2$)[3] and the 1,5-methano-


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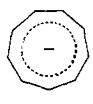
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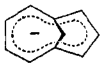
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cyclononatetraenyl anion (**3**, $n = 2$),[4] both of which also proved to be aromatic. It was of interest to investigate the synthesis of macrocyclic members of this series in order to determine whether they would also show aromatic character.[5] We now report the synthesis of the 1-methoxy-2,8,10-tridehydro[17]annulenyl anion (**8**), the first known macrocyclic member ($n = 4$). The anion **8** is isoelectronic with [18]annulene[6] and was found to possess marked aromaticity.

It has been reported by our group that treatment of **4** in freshly distilled tetrahydrofuran with potassium *t*-butoxide in *t*-butyl alcohol gives rise to two unstable red substances.[7] These substances are best obtained by a modified process,[8] whereby each is formed in *ca.* 10–15% yield. The compound more strongly adsorbed on alumina proved to be the 2,8,10-tridehydro[17]annulenone **5**. It formed unstable dark red crystals which decomposed on attempted melting point determination; mass spectrum (all at 70 eV), *m/e* 230 (M) and 202 (M − CO, base peak); $\lambda_{\max}^{Et_2O}$ 293 nm (ϵ 61,000), 304 (74,000), 463 (1000), *ca.* 500 sh (820), and *ca.* 540 sh (360); $\nu_{\max}^{CHCl_3}$ (cm^{-1}) 2190 ($C\equiv C$) and 1625 ($C=O$). The nmr spectrum ($CDCl_3$, 100 MHz) of **5** consisted of three superimposed quartets (total 3 H) at τ −0.50, −0.26, and −0.10 (H_5, H_{14}, and H_{16}; $J_{5,6} = J_{14,13} = J_{16,15} = 12$ Hz, $J_{5,4} = J_{14,15} = J_{16,17} = 16$ Hz), a multiplet (2 H) at 3.53–3.88 (H_6 and H_{13}), a quartet (1 H) at 4.00 (H_{15}; $J_{15,16} = 12$ Hz, $J_{15,14} = 16$ Hz), a doublet (1 H) at 4.28 (H_{17}; $J_{17,16} = 16$ Hz), a doublet (1 H) at 4.70 (H_4; $J_{4,5} = 16$ Hz), and a doublet (2 H) at 4.84 (H_7 and H_{12}; $J_{7,6} = J_{12,13} = 10$ Hz). Catalytic hydrogenation of **5** in ethanol over 10% palladium–charcoal led to cycloheptadecanone. The data show **5** to be a dehydro[17]annulenone made up of three acetylenic, three *trans*, and two *cis* ethylenic bonds, as well as a carbonyl group. The sequence of these groups, as in **5**,[9] follows from its nmr spectrum and the nmr spectra of the derived substances described below. The low-field position of the inner protons and the high-field position of the outer protons indicate the existence of a paramagnetic ring current, as already found for 2,8,10,16-tetradehydro[17]annulenone.[7]

Reduction of **5** in ether–methanol with an excess of sodium borohydride at room temperature for 25 min gave the alcohol **6** in essentially quantitative yield as unstable yellow crystals, which decomposed on attempted melting point determination; mass spectrum, *m/e* 232 (M) and 202 (M − OH − CH); $\lambda_{\max}^{Et_2O}$ 253 nm (ϵ 15,000), 282 (48,000), 291 (60,000), 408 (4100), and 433 (2900); $\nu_{\max}^{CH_2Cl_2}$ (cm^{-1}) 3680, 3580 (OH), 2200 ($C\equiv C$), and 1605 ($C=C$); nmr spectrum ($CDCl_3$, 100 MHz), broad band (1 H) at τ 8.24 (removed by addition of D_2O) assigned to the hydroxyl group. Oxidation of **6** in ether–cyclohexane with manganese dioxide regenerated **5**, showing that the polyenyne system had been unaffected in the reduction.

Methylation of **6** in ether by shaking with methyl iodide and silver oxide for 5 hr, followed by tlc on

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(1) Unsaturated Macrocyclic Compounds. LXVII. For part LXVI, see D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron*, **25**, 2837 (1969).

(2) See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 10.

(3) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); E. A. La Lancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

(4) W. Grimme, M. Kaufhold, U. Dettmeier, and E. Vogel, *Angew. Chem.*, **78**, 643 (1966).

(5) In the parallel series of dianions made up of a $4n$-membered carbocyclic ring, it has been shown recently that the macrocyclic [16]-annulenyl dianion ($n = 4$) is aromatic (J. F. M. Oth, G. Anthoine, and J. M. Gilles, *Tetrahedron Letters*, 6265 (1968)).

(6) See F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967), and references cited there.

(7) G. W. Brown and F. Sondheimer, *J. Am. Chem. Soc.*, **91**, 760 (1969).

(8) The process involves addition of **4** in tetrahydrofuran to a solution of freshly sublimed potassium *t*-butoxide in tetrahydrofuran at −70° under strictly anhydrous conditions, warming to −40° after 15 min, and then pouring into water. The conditions were found to be critical, small changes leading to inferior results.

(9) A molecular model of **5** indicates that it can exist in a relatively strainless planar conformation.