

idally. As shown by the C–N–C angle (ca. 140°) of the Newman projection, the molecule as a whole is only slightly flattened. The torsional angle of the orbitals of the two lone pairs is 64° . The structure of **1** corresponds to a propellane skeleton in which a bridge is replaced by two vicinal lone pairs (Fig. 1).

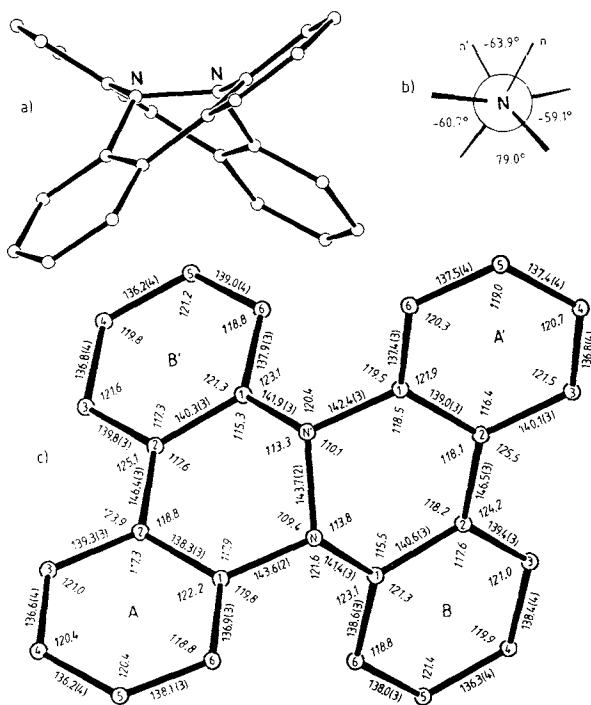


Fig. 1. a) Molecular structure of **1** in the crystal (*M* representation); b) Newman projection (*M*) with torsional angles; c) bond lengths [pm] and angles [$^\circ$].

In dioxane, the enantiomers gave molar optical rotation values of $[\Phi]_D^{20}$ 2130 ± 60 and $[\Phi]_{405}^{20}$ 24700 ± 400 [enantiomer **A**: (+); enantiomer **B**: (-); concentrations 2×10^{-5} to 14×10^{-5} g mL $^{-1}$]. Figure 2 shows the respective CD spectra and the electronic spectrum. A definite assignment of the absolute configuration of the enantiomers could not be carried out, even after determination of several Cu-data sets, since the small dispersion effect of the nitrogen with Cu $\kappa\alpha$ radiation was too small compared to the error of measurement.

The rate constants for the racemization were determined by measurement of the optical rotations in decane; *T* [K] ($k \times 10^4$ [min $^{-1}$]): 370 (642), 360 (233), 350 (75.6), 340 (24.7), 330 (7.34), 320 (2.01). The thermal racemization requires an activation energy of $27.1(\pm 1)$ kcal mol $^{-1}$ [$113(\pm 4)$ kJ mol $^{-1}$]; pre-exponential factor $A = 6.52 \times 10^{14}$. Compound **1** can racemize both by rotation about the N–N axis as well as by double nitrogen-inversion. In both cases, a greater degree of planarization of the molecule is to be expected for the transition state. A comparable planarization can also be achieved by one-electron oxidation, which transforms the destabilizing interaction of the vicinal lone pairs into a bonding three-electron interaction, re-

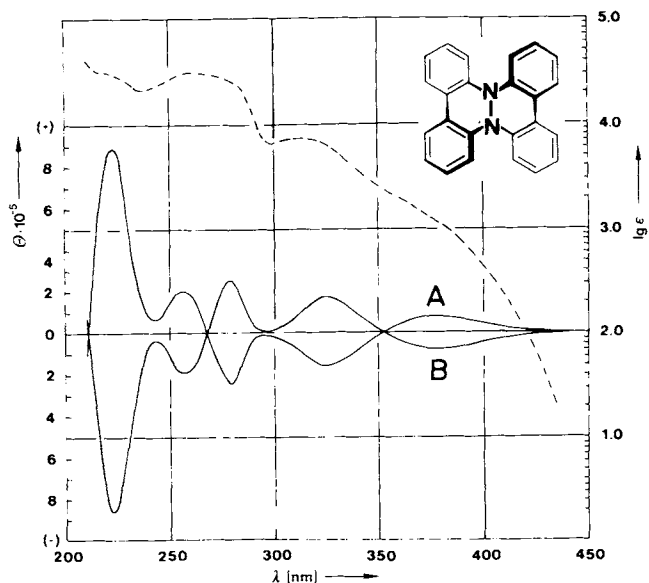


Fig. 2. Electronic spectrum (---) and CD spectra (---) (θ [grad cm 2 dmol $^{-1}$]) of **1** in dioxane (enantiomer **A**: $c = 2 \times 10^{-5}$ g mL $^{-1}$; enantiomer **B**: $c = 1.4 \times 10^{-4}$ g mL $^{-1}$; JASCO J 500).

sulting in a planarization of the pyramidal arrangement of the substituents. **1** $^{\oplus\oplus}$ should therefore have a very low racemization barrier. This is in fact observed. Oxidation of the enantiomers affords an optically inactive radical cation.^[4]

The above findings indicate that the high racemization barrier of **1** is essentially due to the *gauche* effect^[5] of the vicinal lone pairs. Their interaction with the coupled π -electron system proves to be surprisingly small.

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1, 100992-72-1; *ent-1*, 100992-73-2.

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Strontium and Barium Alkoxostannates(II) – Molecules with S_6 Symmetry**

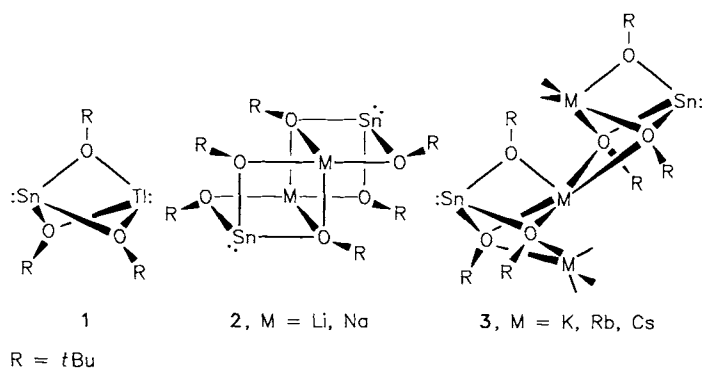
By Michael Veith,* Dieter Käfer, and Volker Huch

Tris(*tert*-butyloxo)stannates of the alkali-metals^[1] and of monovalent thallium^[2] exhibit a remarkable variety of structures. Whereas the stannates of thallium, **1**, as well as

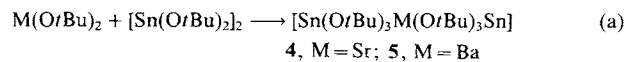
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those of lithium and sodium, **2**, form cage-like, molecular units, those of potassium, rubidium and cesium, **3**, form polymers. The structures are illustrated in formulas 1–3, where the lines between the atoms represent, as usual, electron pairs, either in the sense of a two-center bond or a donor-acceptor bond (formal charges not shown). Our interest now turned to the question of whether these structural principles are preserved when two tris(*tert*-butyl-oxo)stannate ligands are available per "cation", i.e. on going to divalent metal "cations".



To check this we have examined the reaction of *tert*-butoxides of Mg,^[3] Ca,^[4] Sr,^[5] and Ba,^[5] which are insoluble in benzene, with a solution of tin di-*tert*-butoxide^[6] [Eq. (a)]. Mg(*Or*Bu)₂ and Ca(*Or*Bu)₂ do not react, even in boil-



ing benzene (¹H-NMR, quantitative recovery of the starting substances), whereas Sr(*Or*Bu)₂ and Ba(*Or*Bu)₂ undergo complete reaction in accord with Equation (a). The sharp distinction between the *tert*-butoxides of calcium and strontium is also demonstrated in the following experiment: A Ca/Sr alloy was converted into a mixture of the *tert*-butoxides, which was then treated with a benzene solution of [Sn(*Or*Bu)₂]₂ (molar ratio 2 : 1); only the strontium salt was found to react! It dissolved completely, whereas the calcium salt remained undissolved. This procedure can be exploited without difficulty for the quantitative separation of Sr and Ca.

The compounds **4** and **5** are colorless, and crystallize isotypically (decomposition temperatures: 220 and 270°C, respectively). Both show a singlet in the ¹H-NMR spectrum (**4**: δ = 1.44 (1.42), **5**: δ = 1.41 (1.40) in benzene (toluene)), and the elemental analyses and mass spectra are consistent with the formula given in Equation (a). We have determined the structure of **4** by single-crystal X-ray structure analysis (Fig. 1).

The crystal lattice of **4** contains molecules of point symmetry S₆(3), packed, internally interlocked, parallel to (001) within the layers and in the [001] direction with the layer sequence A, B, C... (the angle in the rhombohedral unit cell is 52.2°). If we consider only the skeletal atoms, then the polycycle can be built from two trigonal bipyramids connected via a common apex with retention of the threefold axis. This apical position, which at the same time is a center of inversion, is occupied by the Sr atom, which is situated in a distorted octahedral environment (O–Sr–O: 90 ± 24.4(1)°). The Sn atoms are, as in the related compounds 1–3, trigonal-pyramidally coordinated (O–Sn–O:

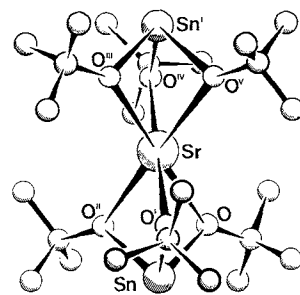
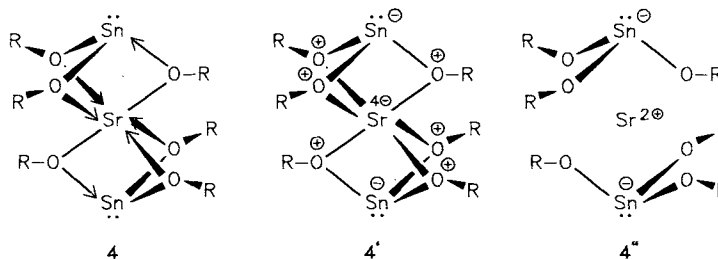


Fig. 1. Structure of **4** in the crystal. The unmarked atoms are C atoms; the H atoms are not shown. The point symmetry of **4** in the crystal is reduced from D_{3d}(3̄m) to S₆(3) by slight rotation of the *tert*-butyl groups. Cell dimensions: a = 1017(1), c = 2986(2) pm, space group: R3̄; Z = 3. Four-circle diffractometer (Siemens) R = 0.033 (all atoms anisotropic) at a reflection-parameter ratio of 15.0 : 1. Some selected bond lengths [pm] and angles [°]: Sn–O 207.8(3), Sr–O 252.3(3), O–C 141.8(6); O–Sr–O' 65.6(1), Sn–O–C 124.9(3), Sr–O–C 142.8(3). Further details of the structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-51786, the names of the authors, and the full citation of the journal.

82.3(1)°). The equatorial apices of the two bipyramids are occupied by the oxygen atoms, which, as expected, are at shorter distances from the Sn atoms than from the Sr atom (cf. Fig. 1). A striking feature is that the O atoms are not, as in **1**^[2], located in a pyramidal, but in a trigonal-planar environment (sum of angles at the O atoms: 359.5°)—perhaps this arises as a result of intramolecular interactions. Actually, the *tert*-butyl groups in the molecule are in unusual close proximity (distance between the centers of the *tert*-butyl groups 511 and 550 pm); they completely shield the metal atom in the center of the molecule. If the central metal atom were to be even smaller than strontium, the *tert*-butyl groups would repel each other extremely strongly. The Ca atom is probably already too small (Ca–O in CaO: 240.5 pm^[6]).

The structure of **4**, like that of **1**–**3**, is very difficult to formulate. Besides the formulation as the donor-acceptor complex **4**, other possible formulations are those with formal charges or ionic substructures **4'** and **4''**, respectively.



In **4''** the two halves of the molecule are held together by electrostatic forces, with striking similarity to strontium oxide: The SrO₆ polyhedron in **4** could be regarded as a section of the SrO structure,^[6] since the Sr–O distances are also very similar (in SrO: 258.0 pm; in **4**: 252.3(3) pm). Compounds such as **4** and **5** are therefore extraordinarily remarkable in that they contain alkaline-earth metal atoms yet nevertheless are molecularly structured. **4** and **5** are soluble in non-polar solvents such as hexane, benzene, and toluene.

Procedure

A solution of freshly sublimed $[\text{Sn}(\text{OrBu})_2]$ [7] (1.2 g, 4.53 mmol) in benzene (25 mL) was added dropwise to a suspension of $\text{M}(\text{OrBu})_2$, $\text{M} = \text{Sr}$, Ba (6 mmol) in benzene (10 mL). The mixture was stirred for 2 h, filtered, and the filtrate evaporated almost to dryness. The product crystallized out as colorless platelets. Yield: 1.59 g (92%) **4** or 1.71 g (93%) **5**.

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4, 101165-23-5; **5**, 101165-24-6.

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Diels–Alder Adducts of Benzene with Arenes and Their [4 + 2] Cycloreversion**

By Achim Bertsch, Wolfram Grimme,* and Gerd Reinhardt

A continuum of reaction pathways exists for the [4 + 2] cycloreversion, from the simultaneous breaking of two single bonds to stepwise bond cleavage. The retrocleavage of Diels–Alder adducts formed from two arenes should most closely resemble the ideal synchronous reaction. Both components lack the two singly occupied p-orbitals necessary to become aromatic, and only simultaneous formation of these two centers enables the transition state to acquire part of this stabilization. Having reported earlier the adduct **4** between benzene and naphthalene,^[1] we now report the Diels–Alder adducts of benzene both with itself and with anthracene and naphthalene.

The Diels–Alder trimer **1** of benzene decomposes at 100°C to benzene without evidence for the formation of the intermediate *o,p'*-dibenzene **2**.^[2,8] The retrocleavage of **1** also takes place upon irradiation with a high-pressure mercury lamp through quartz. If the reaction is carried out at –90°C in CD_2Cl_2 in an NMR tube and followed by

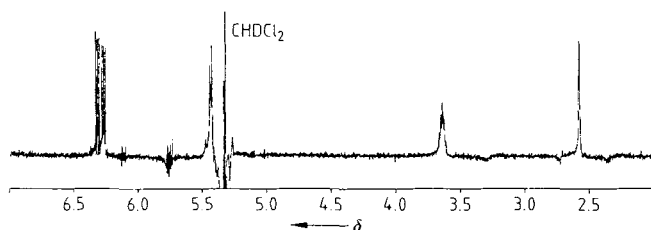
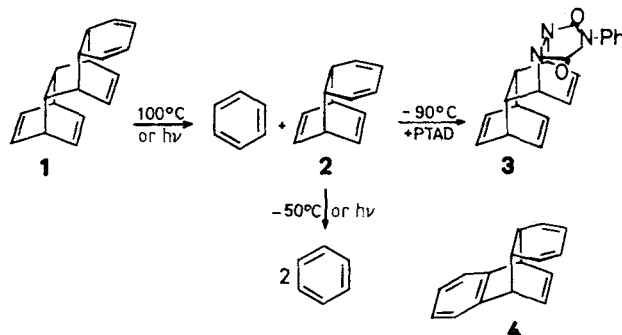


Fig. 1. 300-MHz ^1H -NMR spectrum of *o,p'*-dibenzene **2** in CD_2Cl_2 at –90°C. The CHDCl_2 signal has been truncated.

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recording the ^1H -NMR spectrum, signals other than that of benzene are observed, which first build up and then decrease during the course of the reaction. These signals correspond to those expected for *o,p'*-dibenzene (Fig. 1): upon heating of the sample to room temperature, they disappear in favor of the benzene signal. At –90°C, the intermediate photoproduct reacts with 4-phenyl-1,2,4-triazolodione (PTAD) to form the adduct **3**, the structure of which also confirms the presence of **2**.



The kinetics of the [4 + 2] cycloreversion of *o,p'*-dibenzene **2** was determined by flash photolysis.^[3] A solution of the tribenzene **1** in isoctane (8×10^{-5} M) was irradiated in a quartz cuvette ($l = 10$ cm) with a flash from a capacitor discharge and the transient UV absorption of the dibenzene formed, **2**, was recorded at 280 nm. The lifetime of **2** is ca. 0.5 s at room temperature; the kinetic parameters of the decomposition were derived from nine rate constants in the temperature range 20–55°C (see Table 2).

In order to synthesize the more stable adducts **5–7**, anthracene and naphthalene were allowed to react with *p*-benzoquinone. With anthracene, **5a** was the sole product, whereas with naphthalene a 1:1 mixture of the stereoisomers **6a** and **7a** was obtained. By hydrogenation with zinc in acetic acid, **5b** and a mixture of **6b** and **7b** were obtained; these compounds were then converted into the bistosylhydrazones **5c–7c**. Reaction with *n*-butyllithium in tetrahydrofuran/*n*-hexane at 0°C afforded the anthracene adduct **5[4]** and a 1:1 mixture of the isomeric naphthalene adducts **6** and **7**, respectively.

The adduct **10**, involving the outer ring of anthracene, was obtained from 4a,9,9a,10-tetrahydroanthracene **8**.^[5] Cycloaddition of *p*-benzoquinone afforded the adduct **9a**, which, as described above, was converted into the hydrocarbon **9** via the intermediates **9b** and **9c**. Before dehydrogenation of the tetralin moiety in **9**, the cyclohexadiene ring must be protected by addition of 4-ethyl-1,2,4-triazolodione to give adduct **9d**. After formation of the naphthalene system in **10d** by heating with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in tetrachloroethane, the protecting group is removed by basic hydrolysis and oxidation with copper(II) chloride.

The adducts so obtained (Table 1) decompose cleanly into their aromatic components between 0 and 100°C; the nonseparated isomeric naphthalene adducts **6** and **7** have the same lifetime. In order to measure the rates of cycloreversion, a degassed solution of the compound in dodecane (10^{-5} M) was added to a thermostated polarimeter cuvette ($l = 5$ cm); the formation of naphthalene, anthracene, and naphthalene was followed by continuous re-