addition of $NaBPh_4$, correpondingly colored needles precipitated, which regained an orange color under an N_2 atmosphere.

[9] A solution of $[FeBr_2(depe)_2]$ (0.35 g, 0.56 mmol) in MeOH (40 mL) was stirred at room temperature under N_2 overnight. After the addition of $NaBPh_4$ (0.28 g, 0.84 mmol) in MeOH (10 mL), orange prisms of **2** precipitated slowly and were collected by filtration under nitrogen. Yield: 0.45g (90%); ^1H NMR (200 MHz, CD_3OD, 303 K): $\delta = 1.19$ (m, CH_3), 1.98 (m, CH_2), 7.15 (m, Ph); ^{31}P NMR (400 MHz, CD_3OD, 233 K): $\delta = 63.8$ (s); IR (CsI): $\tilde{\nu}_{NN} = 2091\ cm^{-1}$; UV/Vis: $\lambda_{max}(\varepsilon) = 284$ (8666), 328 (sh; 4000), 394 nm (1818 $L\,mol^{-1}cm^{-1}$); elemental analysis calcd for $C_{44}H_{68}BBrN_2P_4Fe$ (895.45): C 59.0, H 7.7, N 3.1; found: C 56.3, H 7.4, N 1.6.

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[11] $\delta = 0.26\ mm\,s^{-1}$ and $\Delta E_Q = 1.42\ mm\,s^{-1}$ at 77 K; see ref. [5].

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[13] X-ray structure analysis of **1**: An orange cube was mounted on a glass fiber by standard inert-gas techniques and cooled immediately. Crystal data for **1**: triclinic, $P\bar{1}$ ($\equiv$no. 2), $a = 13.425(3)$, $b = 17.399(5)$, $c = 19.937(5)$ Å, $\alpha = 102.02(2)$, $\beta = 91.16(1)$, $\gamma = 95.7(3)^\circ$, $V = 4528(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.248\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 0.566\ mm^{-1}$. The data were collected on a Siemens P4 diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, $T = 203$ K) in the range $4 < 2\theta < 50^\circ$; 16528 (15785 symmetry independent) reflections were measured. The phase problem was solved by direct methods (SIR92), from which the heavy atoms were located. The other non-hydrogen atoms were found in subsequent cycles of refinements (SHELXL93) and difference Fourier maps. The hydrogen atoms were taken into account at idealized sites and with isotropic thermal parameters in the final cycle of refinement; 494 parameters, semiempirical absorption correction (ψ scan) $R1 = 0.077$ (3108 reflections with $F_o > 4\sigma(F_o)$), $wR2 = 0.202$ (all data). The unit cell contains two symmetrically independent cations. One of these cations shows some disorder of the chlorine and dinitrogen ligands. This disorder over the two *trans* positions (N_2, Cl) was modeled by partial occupation of these positions with Cl^- and N_2 with a fixed N–N bond length of 1.10 Å. The occupation ratio Cl^-:N_2 of the two positions was refined to 56:44 and 44:56, respectively. Anisotropic thermal parameters were refined for the heavy atoms (Fe, P, Cl); C and N atoms were refined isotropically. In the discussion of the molecular geometry, we exclusively describe the cation which is not disordered. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407743.

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[17] Preliminary crystal data of **2**: triclinic, P1 (no. 1), $a = 11.5727(3)$, $b = 13.3353(4)$, $c = 16.6220(3)$ Å, $\alpha = 108.23(1)$, $\beta = 101.235(2)$, $\gamma = 104.545(2)^\circ$, $V = 2251(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.321\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 1.40\ mm^{-1}$.

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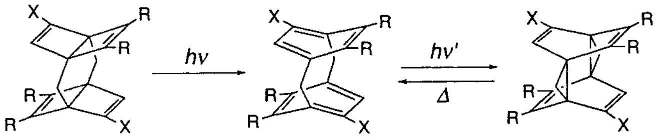
A Kinetically Stabilized [1.1]Paracyclophane: Isolation and X-Ray Structural Analysis[**]

Hidetoshi Kawai, Takanori Suzuki, Masakazu Ohkita, and Takashi Tsuji[*]

In 1993 we reported preparation of the first [1.1]paracyclophane, the bis(methoxycarbonyl) derivative **2b**.[1] The low thermal stability of **2b** and of the subsequently synthesized **2a**[2]—both persistent only below −20 °C in dilute solution—virtually precluded exploration of their physical and chemical properties. The lability of [1.1]paracyclophanes seems to arise from susceptibility of the bridgehead carbon atoms toward addition of numerous reagents, upon which the steric strain inherent in the system is largely relieved. In other words, it seems plausible that the [1.1]paracyclophane skeleton might be kinetically stabilized by the introduction of substituents that sterically shield all four bridgehead sites. Although fulfillment of such a requirement appears formidable at first, examination of molecular models suggests that kinetic stabilization of the [1.1]paracyclophane system might be achieved through **2c**, for which the appropriate precursor **1** should also be accessible. Here we report the isolation and X-ray structural analysis of **2c** as well as its interconversion with the corresponding transannular addition product **3c**.



1 **2** **3**

a: R = X = H **b**: R = H, X = CO_2Me **c**: R = CH_2SiMe_3, X = $CONMe_2$

The synthesis of precursor **1c** is outlined in Scheme 1. Although addition of **5**[3] to **6** was significantly slower than that of **5** to **4**,[2] *anti*-bis-adduct **7** was obtained after prolonged irradiation of **6** in a saturated solution of **5** in CH_2Cl_2. The conversion of **7** into **10** via **8**[4] and **9** proceeded uneventfully, and **10** was transformed into diamide **13** by addition of $LiNMe_2$ followed by hydrolysis. However, the carbon atoms adjacent to the amide groups in **13** are already so sterically hindered that initial attempts to prepare **11** (e.g. by reaction of **12**[5] with PhSeBr, and of **13** with $KH/PhSe_2$[6]) proved fruitless. Taking a hint from the reaction of (phenylselenyl)-amines with unsaturated carbonyl compounds,[7] we obtained **11** by the reaction of **10** with $PhSeNMe_2$.[8] Oxidation of **11** to the selenoxide and subsequent elimination of PhSeOH proceeded smoothly to afford **1c**.

Irradiation of **1c** in degassed *n*-decane with a low-pressure mercury lamp at −20 °C led to formation of the corresponding

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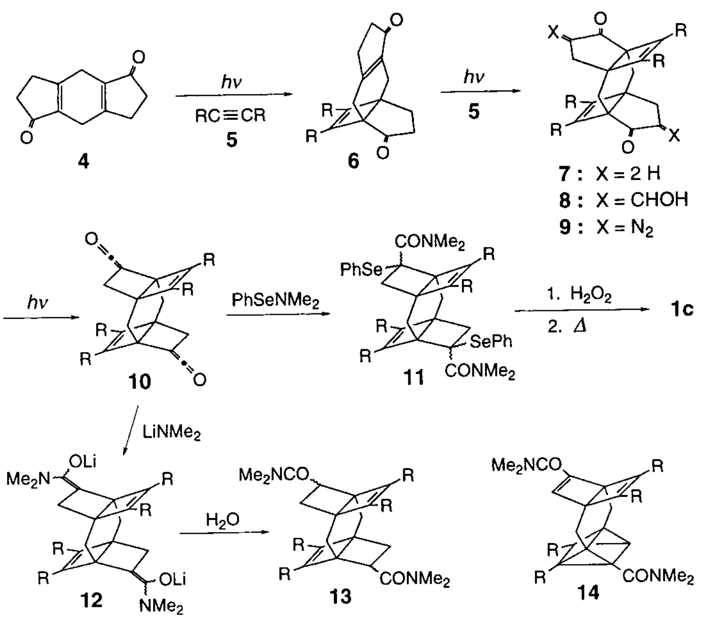

Scheme 1. Preparation of **1c** ($R = CH_2Si(CH_3)_3$).

[1.1]paracyclophane **2c** (which exhibits absorption bands at $\lambda_{max} = 321$, 377, and 464 nm), isomer **3c** resulting from a secondary transannular [4+4] addition within **2c**, and a product to which structure **14** is tentatively assigned.[9] That **2c** has a much greater kinetic stability than **2a** or **2b** was clearly demonstrated when a dilute solution of **2c** was heated in the dark in the absence of air. The intensity of the UV/Vis absorptions due to **2c** remained unchanged for 2 h at 50 °C and decreased only by 8% after the solution was heated at 100 °C for 1.5 h. It should be recalled that **2a**,**b** are stable only below −20 °C in dilute solution. When **2c** was transformed into **3c** by irradiation in solution with light of wavelength greater than 420 nm and the resulting solution was allowed to stand in the dark at room temperature, the characteristic UV/Vis absorption due to **2c** slowly developed. This confirms the ability of **3c** to revert thermally into **2c** at ambient or higher temperatures (Figure 1).[10] Because **2c** is very susceptible to photochemical reaction to give **3c**,[11] and also because its high absorptivity extends to long wavelengths, photolysis of **1c** tends to afford mainly **3c** rather than the primary product **2c** except at very low conversion: Irradiation of **1c** with a high-pressure mercury lamp through Pyrex in benzene produced **2c**, **3c**, and **14** in yields of 5, 66, and 6%, respectively, after 80% conversion. Air-stable **3c** is readily isolated from the mixture as colorless crystals, and it can be converted quantitatively into **2c** upon mild heating as a solution in a deaerated solvent such as benzene or hexane. This facilitates the preparation of the fairly air-sensitive **2c** in pure form. Activation parameters for the cycloreversion are $\Delta H^{\neq} = (21.1 \pm 0.8)$ kcal mol^{-1} and $\Delta S^{\neq} = (-10.5 \pm 2.6)$ cal K^{-1} mol^{-1}, and the half-life of **3c** at 40.0 °C is (191 ± 2) min in *n*-hexane.[12] When a solution of **3c** in degassed benzene was heated at 45 °C for 15 h and then cooled to 5 °C, the resulting **2c** separated from solution in the form of orange-red crystals.

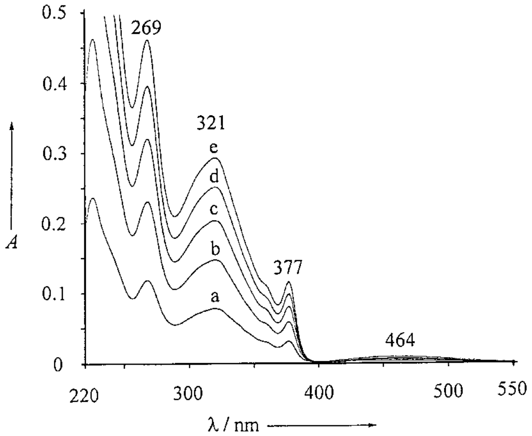

Figure 1. UV/Vis absorption observed upon heating a solution of **3c** in *n*-hexane at 48 °C for a) 30, b) 60, c) 90, d) 120, and e) 150 min. This is regarded as an indicator of the thermal regeneration of **2c**.

Table 1. Selected spectroscopic data for **1c**, **2c**, **3c**, and **14**.

1c: ^{1}H NMR (400 MHz, CD_2Cl_2, TMS): $\delta = -0.002$ (s, 18H), 0.002 (s, 18H), 1.28 (d, $J = 14.7$ Hz, 2H), 1.40 (dd, $J = 14.2$, 1.5 Hz, 2H), 1.47 (d, $J = 14.2$ Hz, 2H), 1.53 (dd, $J = 14.7$, 1.5 Hz, 2H), 2.22 (d, $J = 14.7$ Hz, 2H), 2.46 (d, $J = 14.7$ Hz, 2H), 2.91 (brs, 6H), 3.07 (brs, 6H), 6.69 (s, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, TMS): $\delta = -0.78$, −0.71, 16.74, 16.85, 35.19, 37.81, 51.91, 56.57, 143.97, 144.67, 149.20, 150.41, 164.51; IR (neat): $\tilde{\nu} = 1628$, 1578, 1248, 842 cm^{-1}; UV/Vis (*n*-hexane): $\lambda_{max}(\varepsilon) = 255$ nm (6900); EI-MS: *m/z* 666.3924 (calcd for $C_{36}H_{62}N_2O_2Si_4$: 666.3888).

2c: ^{1}H NMR (CD_2Cl_2): $\delta = -0.14$ (s, 18H), 0.00 (s, 18H), 2.08 (d, $J = 15.1$ Hz, 2H), 2.25 (d, $J = 15.1$ Hz, 2H), 2.41 (d, $J = 15.1$ Hz, 2H), 2.74 (d, $J = 15.1$ Hz, 2H), 3.07 (brs, 6H), 3.16 (brs, 6H), 3.61 (d, $J = 12.7$ Hz, 2H), 3.67 (d, $J = 12.7$ Hz, 2H), 7.67 (s 2H).

3c: ^{1}H NMR (CD_2Cl_2): $\delta = 0.00$ (s, 18H), 0.03 (s, 18H), 1.09 (dd, $J = 14.7$, 1.5 Hz, 2H), 1.43 (dd, $J = 14.7$, 1.5 Hz, 2H), 1.54 (d, $J = 6.8$ Hz, 2H), 1.55 (d, $J = 14.7$ Hz, 2H), 1.58 (d, $J = 14.7$ Hz, 2H), 2.12 (d, $J = 6.8$ Hz, 2H), 2.91 (s, 12H), 6.07 (s, 2H).

14: ^{1}H NMR ($CDCl_3$): $\delta = -0.01$ (s, 9H), 0.02 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.75 (d, $J = 15.1$ Hz, 1H), 0.90 (d, $J = 15.1$ Hz, 1H), 0.92 (d, $J = 15.1$ Hz, 1H), 1.07 (d, $J = 15.1$ Hz, 1H), 1.16 (d, $J = 12.7$ Hz, 1H), 1.20 (d, $J = 12.7$ Hz, 1H), 1.25–1.30 (m, 3H), 1.48 (d, $J = 14.1$ Hz, 1H), 2.09 (d, $J = 12.7$ Hz, 1H), 2.22 (d, $J = 12.7$ Hz, 1H), 2.87 (s, 3H), 2.97 (brs, 3H), 3.06 (s, 3H), 3.10 (s, 1H), 3.16 (brs, 3H), 6.38 (s, 1H).

The X-ray structural analysis reveals that **2c** has C_i symmetry in the crystalline state, and the [1.1]paracyclophane core is slightly distorted from ideal D_{2h} symmetry (Figure 2).[13] The transannular interatomic distance between the opposing bridgehead carbon atoms C2 and C12 is 2.376(5) Å (almost 1.0 Å less than the sum of the van der Waals radii), and the corresponding distances between nonbridgehead carbon atoms (C6–C10 and C7–C11) are 3.025(5) and 2.996(5) Å, respectively. The dihedral angle α between the mean plane of the four nonbridgehead aromatic carbon atoms and the plane of the adjoining flap is 25.6° on the side bearing the amide group and 24.3° on the other. The extent of out-of-plane bending of the bridging carbon atom, β, is 26.8° on the side nearer to the amide group and 22.9° on the far side.[14] Thus, the average total bending angle ($\alpha + \beta$) is 49.8°, the largest value ever reported for a paracyclophane and only slightly less than that calculated for [5]paracyclophane.[15, 16] As expected from an examination of molecular models, each of the nearly planar amide groups is slightly twisted from coplanarity with the adjoining aromatic ring, which places one

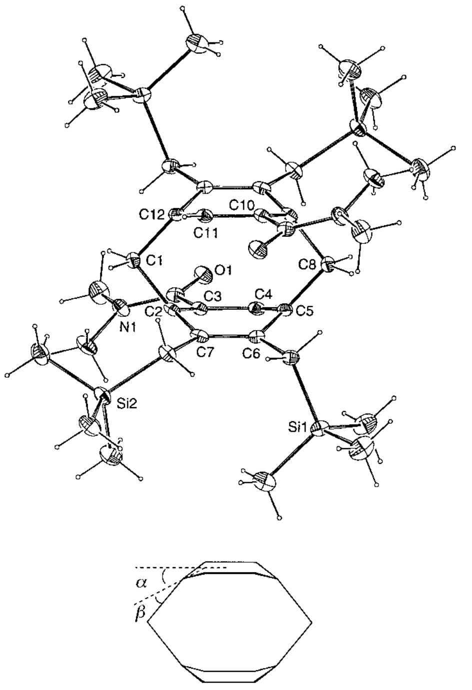

Figure 2. Crystal structure of **2c**. Selected bond lengths [Å] and angles [°]: C1–C2 1.560(6), C1–C12 1.551(6), C2–C3 1.421(6), C2–C7 1.422(6), C3–C4 1.400(6), C4–C5 1.386(6), C5–C6 1.443(6), C6–C7 1.396(6), C2–C12 2.376(5), C6–C10 3.025(5), C7–C11 2.996(5); C1-C2-C3 118.0(4), C1-C2-C7 117.9(4), C2-C1-C12 99.6(3), C3-C2-C7 116.5(4), C4-C5-C6 115.4(4), C4-C5-C8 118.2(4), C6-C5-C8 120.9(4).

of the N-methyl groups above the adjacent bridgehead carbon atom. Preferential adoption of a similar conformation in solution is supported by the observation of a positive NOE between protons of the methylene bridge and the N-methyl protons.[17] The trimethylsilyl groups preferentially occupy the space near the neighboring bridgehead carbon atoms, thereby minimizing repulsive steric interactions: mutual, transannular, and with the methylene bridges. Thus, the aromatic substituents of **2c** effectively shield the bridgehead carbon atoms from access by attacking reagents; this is certainly the reason for the remarkable stability of **2c**.

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[8] To our knowledge, the preparation of α-selenylated carboxamides through the reaction of ketene with selenylamines was previously unknown.

[9] As with **1a** and **1b**, a product resulting from the aromatization of only one of the Dewar-benzene moieties of **1c** was not detected in the photolysate.

[10] According to theoretical calculations, **2a** is more stable than **3a** by 26.2 kcal mol^{-1} at the B3LYP/6-31G* level and by 20.0 kcal mol^{-1} at the MP2/6-31G*//RHF/6-31G* level.[2]

[11] The photochemical transformation of **2** into **3** represents the first direct preparation of a *p,p'*-benzene dimer. To our knowledge, [2.2]paracyclophanes do not undergo such a transannular [4+4] addition under irradiation. Apparently, the photochemical reactivity of **2** is dictated by the geometrical constraint imposed upon it: the face-to-face arrangement of two bent benzene rings in close proximity. For photoadditions of aromatic compounds, see J. J. McCullough, *Chem. Rev.* **1987**, *87*, 811.

[12] The rate of this cycloreversion is comparable to those for known *p,p'*-benzene dimers: N. C. Yang, M. Chen, P. Chen, *J. Am. Chem. Soc.* **1984**, *106*, 7310; H. Gan, J. L. King, N. C. Yang, *Tetrahedron Lett.* **1989**, *30*, 1205.

[13] Crystal data for [1.1]paracyclophane **2c**·benzene: $C_{36}H_{62}N_2O_2Si_4\cdot C_6H_6$, $M = 745.36$, $0.40 \times 0.40 \times 0.10$ mm^3, triclinic, $P\bar{1}$, $a = 9.564(3)$, $b = 10.156(5)$, $c = 12.299(5)$ Å, $\alpha = 98.86(4)$, $\beta = 108.85(3)$, $\gamma = 98.51(4)^\circ$, $V = 1092(1)$ Å^3, ($Z = 1$), $\rho_{calcd} = 1.134$ g cm^{-1}. A total of 3640 independent reflections ($2\theta_{max} = 52^\circ$) were measured at $T = 203$ K (ω-2θ scan mode, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). No absorption correction was applied ($\mu = 1.097$ cm^{-1}). The structure was solved by direct methods (Crystan). Hydrogen atoms are located at the calculated positions. Refinement by the full-matrix least-squares method on F gave a final R value of 0.078 ($wR = 0.112$) for 3022 reflections with $I > 3\sigma(I)$ and 260 parameters. Residual electron density is 0.37 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100696. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] There exists some ambiguity concerning the bending angles α and β since the nonbridgehead aromatic carbon atoms are displaced from the mean plane by 0.004–0.011 Å and the plane of the methylene bridge is not exactly orthogonal to that formed by the bridgehead and the adjacent aromatic carbon atoms.

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[17] A weak NOE was also observed between the N-methyl and the aromatic protons. Therefore, the amide groups seem to flip-flop more or less freely in solution with respect to the aromatic rings.