Compounds of Germanium and Tin, 18[◇]

Cleavage Reactions of Hexa-*tert*-butylcyclotrigermane: Racemate versus Conglomerate Crystallization[☆]

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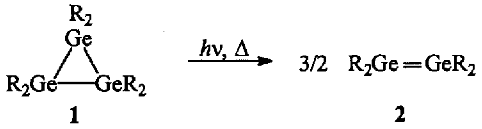
Treatment of hexa-*tert*-butylcyclotrigermane (**3**) with CCl_4, Br_2, and I_2 furnishes the correspondingly substituted 1,3-dichloro- (**4**), 1,3-dibromo- (**5**), and 1,3-diiodotrigermanes (**6**). The symmetries of the molecules of **5** and **6** are very similar (point group C_1) revealing *gauche-anti* conformations and different Ge–Ge bond lengths. However, while **5** crystallizes as a racemate, **6** forms a conglomerate of enantiomerically pure crystals. The X-ray structure analysis of the 1,3-dimethyltrigermane (**7**) derivative, derived from **6** by a sequence of metalation and methylation reactions, reveals more symmetrical molecules of the point group C_2 which also crystallize as a racemate. Irradiation of **3** leads to tetra-*tert*-butyldigermene (**8**) and di-*tert*-butylgermylene (**9**) which could be trapped by addition and cycloaddition reactions with selenium, tellurium, and 3,5-di-*tert*-butyl-1,2-benzoquinone.

The hexaarylcyclotrigermanes **1**, which are known since 1982, can be converted to tetraaryldigermenes photochemically and thermally[2]. These, in turn, undergo a large variety of addition and cycloaddition reactions[8], for example with chalcogens[3–7], alkynes[5,7], and azides[5,7].

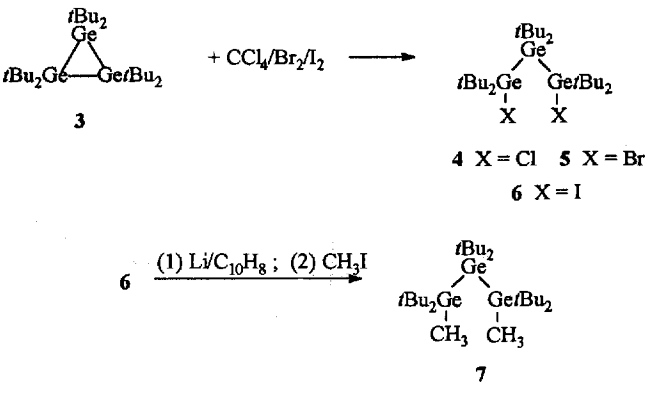
Scheme 1. R = 2,6-$Et_2C_6H_3$, 2,6-$iPr_2C_6H_3$ etc.



Hexa-*tert*-butylcyclotrigermane (**3**)[9], the only known hexaalkylcyclotrigermane[2] to date, behaves rather differently, reacting with the heavier chalcogens by cleavage of just one Ge–Ge bond to give the ring-expanded thia-, selena-[10], and telluratrigermetanes[11]. Very recently, we reported in a short communication[12] that the reaction of **3** with iodine also occurs with cleavage of one Ge–Ge bond and results in the formation of the acyclic hexa-*tert*-butyl-1,3-diiodotrigermane (**6**). According to the crystal structure analysis, **6** assumes the *gauche-trans* conformation and shows different Ge–Ge bond lengths. Surprisingly, **6** crystallizes as a conglomerate of enantiomerically pure crystals.

Although several hundred conglomerates have been described since their initial discovery by Pasteur[13], the enantiomers isolated from them almost all owe their chirality to the presence of stereogenic centers[14]. In contrast, the chirality of **6** is based on a helical arrangement of the germanium and iodine atoms, in which the conformers form either a right-handed or a left-handed helix. This is the first case known to us in which a simple molecular compound containing the heavier elements of group 14 undergoes spontaneous enantiomeric resolution upon crystallization.

Scheme 2



In order to determine whether the surprising formation of a conglomerate is limited to **6** or whether other, structurally related trigermanes crystallize in enantiomerically pure form, we prepared two further 1,3-dihalotrigermanes as well as the 1,3-dimethyl compound **7** (Scheme 2) and elucidated the structures of **5** and **7** by X-ray crystallography.

On account of the higher reactivity of the lighter halogens in comparison with iodine, the reaction with bromine to furnish **5** must be performed at low temperature and with

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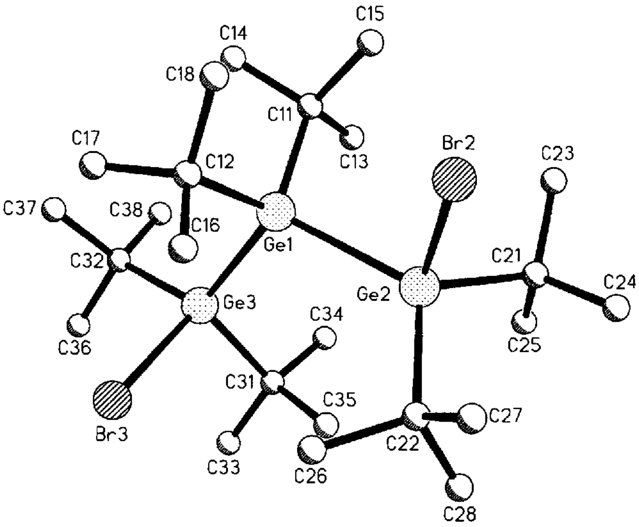
exclusion of light to prevent cleavage of all Ge–Ge bonds in **3**. The synthesis of **4** is realized most simply by the reaction of tetrachloromethane with **3**. The formation of the 1,3-dimethyltrigermane **7** proved to be difficult but was finally achieved by double metalation of **6** with lithium/naphthalene and subsequent methylation with iodomethane.

Figure 1. Molecular structure of **5** in the crystal (hydrogen atoms omitted). Selected bond lengths [pm] and angles [°]: Ge(1)–Ge(2) 262.3(1), Ge(1)–Ge(3) 259.5(1), Ge(2)–Br(2) 237.1(1), Ge(3)–Br(3) 238.5(1), Ge(1)–C(11) 204.2(6), Ge(1)–C(12) 205.4(7), Ge(2)–C(21) 207.1(6), Ge(2)–C(22) 206.2(6), Ge(3)–C(31) 201.8(8), Ge(3)–C(32) 205.3(6); Ge(2)–Ge(1)–Ge(3) 113.5(1). Torsion angles [°]: Ge(2)–Ge(1)–Ge(3)–Br(3) 81.4, Ge(3)–Ge(1)–Ge(2)–Br(2) −166.1

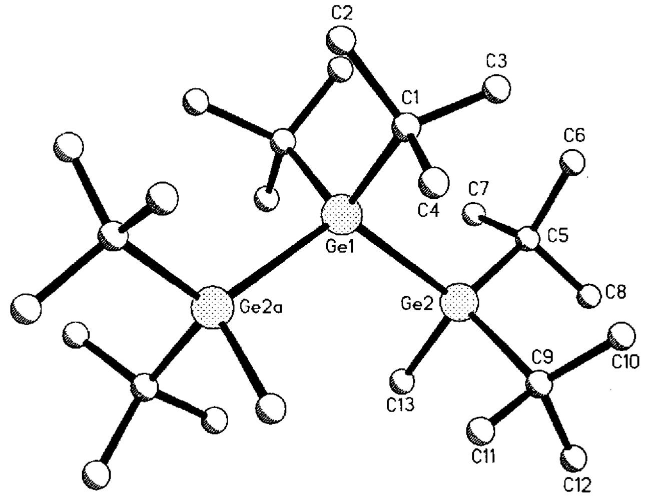


The X-ray crystal structure of the 1,3-dibromo derivative **5** (Figure 1) showed firstly that the structures of the individual molecules of this compound are very similar to that of **6**. Like **6**, compound **5** has a helical arrangement of the germanium and bromine atoms and a *gauche-trans* conformation of the substituents. The different Ge–Ge bond lengths (266.0 and 262.2 pm) observed in **6** are again seen in **5** [262.3(1) and 259.5(1) pm]; these separations are somewhat shorter on account of the lower spatial demands of bromine in comparison with iodine but are still markedly longer than the normal Ge–Ge bond length of 244 pm. In contrast to **6**, however, **5** crystallizes as a racemate in which the two enantiomers occupy the unit cells in pairs.

It is not yet clear why such similar molecules as **5** and **6** crystallize on the one hand as a racemate and on the other hand as a conglomerate. Possible intermolecular contacts which could conceivably provide a cause for the different crystallization behavior can presumably be discounted. The bromine-bromine separations in the various molecules of **5** are markedly longer (500 pm) than the corresponding iodine-iodine separations in **6** (456 pm), but even the latter distance is probably too long to render weak iodine-iodine interactions between neighboring molecules possible.

In contrast to **5** and **6**, the 1,3-dimethyltrigermane **7**, which is formally related to **5** on account of the similar spatial requirements of the methyl groups and the bromine atoms, exhibits a C_2 axis which passes through the central germanium atom and bisects the Ge–Ge–Ge angle. Although the individual molecules of **7** are chiral, the compound, similar to **5**, crystallizes as a racemate in which a pair of the enantiomers occupies the unit cell. The crystal structures of the two trigermanes investigated in this work clearly reveal that, although crystallization as a conglomerate does indeed occur in the case of the diiodo derivative **6**, this behavior is not transferable to other molecules containing the X–Ge–Ge–Ge structural unit.

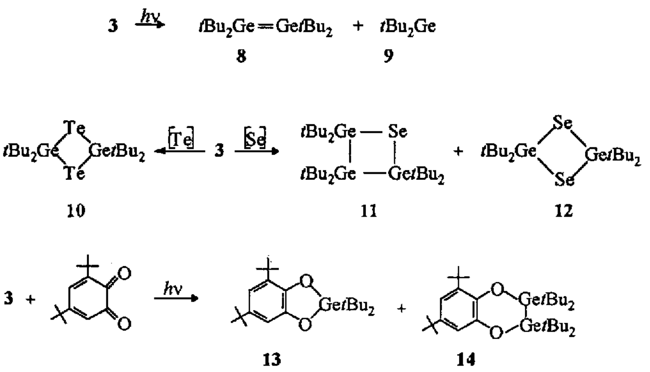
Figure 2. Molecular structure of **7** in the crystal (hydrogen atoms omitted). Selected bond lengths [pm] and angles [°]: Ge(1)–Ge(2) 262.0(1), Ge(1)–C(1) 205.3(4), Ge(2)–C(5) 205.2(6), Ge(2)–C(9) 202.2(4), Ge(2)–C(13) 197.9(4); Ge(2)–Ge(1)–Ge(2a) 118.6(1)



Although compound **3** reacts in the dark and under mild conditions with cleavage of only one Ge–Ge bond to furnish cyclic or acyclic trigermanes, the question as to whether this cyclotrigermane would react under photochemical conditions with simultaneous cleavage of two Ge–Ge bonds to give the digermene **8** together with the germylene **9** was previously not resolved. Although we were recently able to trap the corresponding 1,2-digermacyclobutane by photolysis of **3** in the presence of phenylacetylene, the formation of the adduct presumably follows from a [2 + 2] cycloaddition of the digermene **8** to the alkyne[12]. However, the primary formation of a [2 + 1] cycloadduct from **9** and the alkyne followed by insertion of a further molecule of **9** into one of the strained Ge–C bonds of the three-membered ring cannot be excluded[15]. The only known tetraalkyldigermene $R_2Ge{=}GeR_2$ [R = $CH(SiMe_3)_2$] is stable in the solid state but reacts in solution exclusively as the singlet germylene[16].

We now discovered some reactions which prove that, similar to hexa-*tert*-butylcyclotrisilane[17], **7** reacts under photolytic conditions to furnish **8** and **9** simultaneously and that these species can be trapped individually or also simultaneously. For example, irradiation of **3** in the presence of triethylphosphane telluride affords, presumably by addition of tellurium to **9**, a germanetellurane, and cyclodimerization of this species proceeds by head-to-tail coupling to provide the isolated 1,3,2,4-ditelluradigermetane **10**. The photochemical reaction of **3** in the presence of trimethylphosphane selenide proceeds in part differently since in this case an inseparable mixture of the 1,3,2,4-diselenadigermetane **12** analogously to **10** and the selenatrigermetane **11**[10] results. Thus, in the case of the more reactive selenium as compared to tellurium it seems that both the photochemical ring cleavage furnishing **8** and **9** and the insertion of selenium into the still intact three-membered ring proceed with comparable reaction rates.

Scheme 3



The trapping reactions of **8** and **9** with 3,5-di-*tert*-butyl-1,2-benzoquinone depend strongly on the ratio of the starting compounds. When **3** is irradiated with the quinone in a molar ratio of 1:1.5, an inseparable mixture of the germylene adduct **13** and the [4 + 2] cycloadduct **14** is obtained. On the other hand, when a larger excess of the quinone is employed only the product **13** can be isolated in the pure state. Thus, it is possible to unambiguously prove the presence of the cycloadduct **14** in the mixture by means of NMR and mass spectrometry. The present observations in combination with earlier results[12] clearly demonstrate that compound **3** – in contradistinction to the hexaarylcyclotrigermanes **1** – furnishes the digermene **8** and the germylene **9** as the primary cleavage products upon irradiation.

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Experimental

All manipulations were performed by using Schlenk techniques under dry nitrogen or argon. Solvents were purified, dried, and distilled under argon. – ^1H and ^{13}C NMR: Bruker AM 300. – MS: Varian MAT 212. – Elemental analyses: Analytische Laboratorien, D-51779 Lindlar, Germany.

The cyclotrigermane **3** was prepared according to the literature procedure[10]. Photolyses were carried out by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

1,1,2,2,3,3-Hexa-tert-butyl-1,3-dichlorotrigermane (**4**): Compound **3** (150 mg, 0.27 mmol) was dissolved in 40 ml of tetrachloromethane. After a few min the reaction was shown to be complete by the disappearance of the pale yellow color of **3** and by TLC analysis. Tetrachloromethane was removed and the residue dissolved in 20 ml of *n*-hexane. Cooling of the solution to –25°C provided 95 mg (56%) of colorless needles of **4**, m.p. 125°C. – ^1H NMR (C_6D_6, 25°C): δ = 1.40 (s, 36H), 1.45 (s, 18H). – ^{13}C NMR (C_6D_6, 25°C): δ = 31.70 (C_p), 33.94 (C_p), 34.46 (C_q), 37.99 (C_q). C_p and C_q refer to primary and quaternary carbon atoms. – MS (CI, isobutane), *m/z* (%): 595 (100) [M^+ – Cl]. – $C_{24}H_{54}Cl_2Ge_3$ (631.4): calcd. C 64.90, H 9.41; found C 64.77, H 9.35.

1,3-Dibromo-1,1,2,2,3,3-hexa-tert-butyltrigermane (**5**): In the dark bromine (50 mg, 0.25 mmol) was added at –78°C to a solution of **3** (100 mg, 0.18 mmol) in 40 ml of petroleum ether (40–60°C). After stirring for 1 h, the solvent and excess bromine were removed by vacuum distillation, and the residue was dissolved in a minimum amount of *n*-hexane. Cooling to –25°C yielded 48 mg (37%) colorless crystals of **5**, m.p. 126°C. – ^1H NMR (C_6D_6, 25°C): δ = 1.46 (s, 36H), 1.52 (s, 18H). – ^{13}C NMR: δ = 32.35 (C_p), 34.06 (C_p), 35.38 (C_q), 37.87 (C_q). – MS (CI, isobutane), *m/z* (%): 641 (100) [M^+ – Br]. – $C_{24}H_{54}Br_2Ge_3$ (720.3): calcd. C 40.02, H 7.56; found C 40.12, H 7.44.

1,1,2,2,3,3-Hexa-tert-butyl-1,3-diiodotrigermane (**6**)[12]: A solution of **3** (100 mg, 0.18 mmol) in 50 ml of *n*-hexane was cooled to –78°C, and a solution of iodine (46 mg, 0.18 mmol) in 30 ml of *n*-hexane was added dropwise. The mixture was allowed to warm to room temp. and then concentrated to a volume of 30 ml. Cooling to –25°C furnished 120 mg (83%) of **6** as colorless needles, m.p. (enantiomers) 122°C. – ^1H NMR (C_6D_6, 25°C): δ = 1.44 (s, 36H), 1.57 (s, 18H). – ^{13}C NMR ($CDCl_3$, 25°C): δ = 33.13 (C_p), 34.46 (C_p), 37.02 (C_q), 37.34 (C_q). – MS (CI, isobutane), *m/z* (%): 687 (100%) [M^+ – I]. – $C_{24}H_{54}Ge_3I_2$ (814.3): calcd. C 35.40, H 6.68, I 31.17; found C 35.29, H 6.58, I 31.07.

1,1,2,2,3,3-Hexa-tert-butyl-1,3-dimethyltrigermane (**7**): A solution of **6** (100 mg, 0.123 mmol) in 30 ml of THF was cooled to –78°C, and a suspension of approx. 0.54 mmol of lithium naphthalenide in 30 ml of THF was added dropwise. After stirring for 10 min a solution of iodomethane (100 mg, 0.70 mmol) in 15 ml of petroleum ether (40–60°C) was added dropwise. The mixture was allowed to warm to room temp., and all volatile components were removed in vacuo. The residue was dissolved in a minimum amount of *n*-hexane, lithium iodide was filtered off and the solvent removed. The resultant oil yielded after standing for approx. 4 weeks at room temp. 15 mg (21%) of **7** as colorless crystals, m.p. 164°C. – ^1H NMR (C_6D_6): δ = 0.46 (s, 6H), 1.26 (s, 36H), 1.45 (s, 18H). – ^{13}C NMR (C_6D_6): δ = 14.31 (C_p), 31.47 (C_q), 31.99 (C_q), 32.63 (C_p), 34.35 (C_p). – MS (CI, isobutane), *m/z* (%): 575 (100) [M^+ – CH_3]. – $C_{26}H_{60}Ge_3$ (590.6): calcd. C 52.88, H 10.24; found C 52.62, H 10.04.

2,2,4,4-Tetra-tert-butyl-1,3,2,4-ditelluradigermetane (**10**): A solution of **3** (150 mg, 0.27 mmol) and triethylphosphane telluride (200 mg, 0.81 mmol) in 70 ml of *n*-hexane was irradiated at –25°C until **3** was no longer detectable by TLC (about 2.5 h). Excess Et_3PTe was removed by sublimation and the solution concentrated to a volume of 30 ml. Cooling to 4°C afforded 46 mg (27%) of **10** as yellow crystals, m.p. 261°C (subl.). – ^1H NMR (C_6D_6, 25°C): δ = 1.22 (s). – ^{13}C NMR: δ = 28.66 (C_p), 29.13 (C_q). – MS (CI, isobutane), *m/z* (%): 639 (100) [M^+]. – $C_{16}H_{36}Ge_2Te_2$ (628.9): calcd. C 30.56, H 5.77; found C 30.62, H 5.68.

Photolysis of **3** *in the Presence of Triethylphosphane Selenide:* A solution of **3** (150 mg, 0.27 mmol) and triethylphosphane selenide (160 mg, 0.81 mmol) in 70 ml of *n*-hexane was irradiated at –25°C until **3** was no longer detectable by TLC (about 3 h). Excess Et_3PSe was removed by sublimation and the solution concentrated to a volume of 20 ml. Cooling to –25°C furnished 38 mg of yellow crystals of a mixture of *2,2,3,3,4,4-hexa-tert-butylselenatrigermetane* (**11**)[10] and of *2,2,4,4-tetra-tert-butyl-1,3,2,4-diselenadigermetane* (**12**). This signals of **11** are omitted from the following list. – ^1H NMR (C_6D_6, 25°C): δ = 1.28 (s). – ^{13}C NMR (C_6D_6, 25°C):

Table 1. Crystallographic data of **5** and **7**

	5	**7**
Formula	$C_{24}H_{54}Br_2Ge_3$	$C_{26}H_{60}Ge_3$
Mol. mass	723.28	590.53
Cryst. size [mm]	0.25 x 0.40 x 1.15	0.15 x 0.30 x 1.15
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a [pm]	1076.4(3)	2484.2(4)
b [pm]	1864.8(3)	890.8(2)
c [pm]	1638.0(3)	1694.6(2)
β [°]	108.10(1)	124.71(1)
V [x 10^6 pm^3]	3125(1)	3083(1)
Z	4	4
$d_{calcd.}$ [g cm^{-3}]	1.537	1.272
Diffractometer	Siemens P4	Siemens P4
Radiation (graphite-monochromated) [pm]	Mo-K_α 71.073	Mo-K_α 71.073
T [K]	296(2)	296(2)
μ [mm^{-1}]	5.34	2.92
Scan method	ω	ω
2θ (max) [°]	55	55
Total no. of reflections	7779	3861
No. of unique reflections	7164	3547
No of observed reflections [$F > 3\sigma(F)$]	5268	2955
Data-to-parameter ratio	20.0	22.2
R, Rw	0.054, 0.049	0.064, 0.066
Residual electron density [e nm^{-3}]	112, -65	92, -98

δ = 28.95 (C_p), 29.28 (C_q). – MS (CI, isobutane), m/z (%): 533 (11) [M^+].

2,2,4,6-Tetra-tert-butyl-1,3,2-benzodioxagermole (**13**) *and 2,2,3,3,5,7-Hexa-tert-butyl-2,3-dihydro-1,4,2,3-benzodioxadigermine* (**14**). – a) A solution of **3** (150 mg, 0.27 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (88 mg, 0.40 mmol) in 70 ml of *n*-hexane was irradiated at −25°C until **3** was no longer detectable by TLC (about 70 min). During the photolysis the color of the solution changed from green to yellow. Concentration of the solution to a volume of 20 ml and cooling to −25°C yielded 130 mg of pale yellow crystals of an inseparable 1:1 mixture of **13** and **14**. – **14** [The signals of **13** (see below) are omitted from the following list]: ^{1}H NMR (C_6D_6, 25°C): δ = 1.22 (s, 18H), 1.28 (s, 18H), 1.33 (s, 9H), 1.69 (s, 9H), 7.17–7.23 (2H). – ^{13}C NMR (C_6D_6, 25°C): δ = 29.46 (C_p), 30.03 (C_p), 30.87 (C_p), 31.97 (C_p), 32.68 (C_q), 33.02 (C_q), 34.27 (C_q), 35.99 (C_q), 115.37 (CH), 118.26 (CH), 129.27 (C_q), 139.20 (C_q), 141.12 (C_q), 150.00 (C_q). – MS (CI, isobutane), m/z (%): 594 (14) [M^+].

b) The reaction was carried out as described above, but using **3** (100 mg, 0.18 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (118 mg, 0.54 mmol) in a molar ratio of 1:3. After irradiation for 2 h, 38 mg (52% related to **9**) of **13** was obtained as pure pale yellow crystals, m.p. 93°C. – ^{1}H NMR (C_6D_6, 25°C): δ = 1.05 (s, 18H), 1.33 (s, 9H), 1.69 (s, 9H), 7.06–7.32 (2H). – ^{13}C NMR (C_6D_6, 25°C): δ = 26.78 (C_p), 29.85 (C_p), 32.05 (C_p), 32.86 (C_q), 34.64 (C_q), 35.16 (C_q), 109.78 (CH), 113.81 (CH), 134.58 (C_q), 141.88 (C_q), 147.53 (C_q), 151.99 (C_q). – MS (CI, isobutane), m/z (%): 408 (100) [MH^+]. – $C_{22}H_{38}GeO_2$ (407.2): calcd. C 64.90, H 9.41; found C 64.77, H 9.35.

X-ray Structural Analyses of Compounds **5** *and* **7**: Single crystals were grown from saturated solutions in *n*-hexane. The structures were solved by direct phase determination using the SHELXTL PLUS program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically. Crystal data and numerical data of the structure determinations are given in Table 1[18].

☆ Dedicated to Professor *Marianne Baudler* on the occasion of her 75th birthday.

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[18] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-404482 (**5**) and CSD-404483 (**7**), the names of the authors, and the journal citation.

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