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Diiodotetrasupersilylcyclotetrasilene $(tBu_3Si)_4Si_4I_2$—A Molecule Containing an Unsaturated Si_4 Ring[**]

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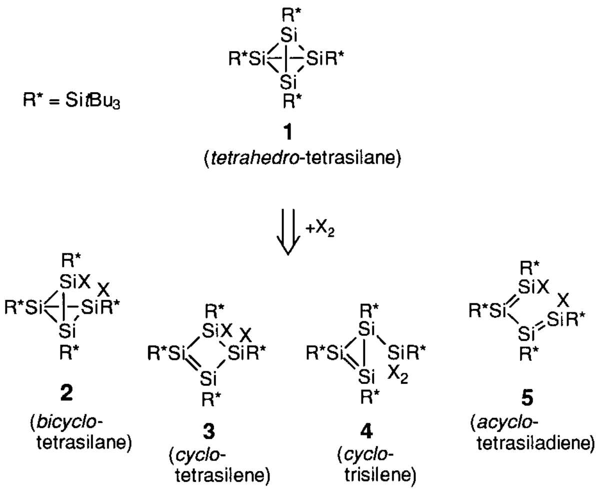
A few years ago we were able to synthesize the first molecular silicon compound containing a Si_4 tetrahedron, the orange tetrasupersilyl-*tetrahedro*-tetrasilane $R^{*}_{4}Si_4$ (**1**; R^{*} = tri-*tert*-butylsilyl, Si*t*Bu$_3$, supersilyl).[1] We noted at the time that **1** is very stable towards water, air, light, and high temperatures and cannot be reduced by sodium even in the presence of [18]crown-6 in benzene under standard conditions. Compound **1** turned out to be more susceptible towards oxidizing agents; initially, however, the tetrahedrane could only be oxidized to complex product mixtures. We have now found that upon reaction with iodine in equimolar amounts at room temperature, **1** quantitatively yields a compound with the molecular formula $R^{*}_{4}Si_4I_2$, whose structure, reactivity, and synthesis are described here.

As long as migrations of the supersilyl groups during the iodination of $R^{*}_{4}Si_4$ are excluded, the four isomeric structures **2**–**5** (X = I) are possible for $R^{*}_{4}Si_4I_2$ (Scheme 1). A *bicyclo*-tetrasilane of type **2** was first proven by Masamune et al. in the form of the pale yellow species $tBu_2(2,6\text{-}Et_2C_6H_3)_4Si_4$ (the *t*Bu groups are located on the central Si atoms of the "Si_4 butterfly").[2] We prepared a further species of type **2**, colorless $R^{*}_{4}H_2Si_4$ (X = H in **2**).[3] The deep orange, air-sensitive $(tBuMe_2Si)_6Si_4$ obtained by Kira et al. in low yields represents a *cyclo*-tetrasilene of type **3**.[4] Upon irradiation, it is supposed to rearrange to a red-brown *bicyclo*-tetrasilane isomer **2**, which in the dark slowly reverts to **3**. The red-brown species $(2,4,6\text{-}iPr_3C_6H_2)_6Si_4$, recently synthesized by Weidenbruch et al.,[5] represents a tetrasiladiene of type **5**. A *cyclo*-trisilene of type **4** has so far only been obtained as the homologous germanium compound $R^{*}_{4}Ge_3$ (Ge instead of Si and R* instead of SiX_2R^{*} in **4**).[6]



Scheme 1. Possible structural isomers for the molecular formula $R^{*}_{4}Si_4X_2$.

$R^{*}_{4}Si_4I_2$ crystallizes from benzene at room temperature in the form of red-orange, light- and moisture-sensitive platelets which are stable in air. They melt with decomposition at 128–130 °C. The structure of this compound is presented in Figure 1. It was obtained by an X-ray structure analysis of a crystal (monoclinic, space group $P2_1/c$) that also contained one molecule of benzene per molecule of $R^{*}_{4}Si_4I_2$.[7] According to the analysis, $R^{*}_{4}Si_4I_2$ exhibits the structure **3** (X = I) and can be termed 1,2-diiodo-1,2,3,4-tetrasupersilylcyclotetrasil-3-ene. The central structural element, which has not been observed before, is a bent unsaturated Si_4 ring with iodine substituents (angle between the planes Si1-Si2-Si3/Si3-Si4-Si1 27.8° and Si2-Si3-Si4/Si4-Si1-Si2 28.1°). The Si=Si distance is 2.257(2) Å and is therefore similar to that in the disilene $(iPr_3Si)_4Si_2$ (2.251(1) Å), which carries very bulky substitu-

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1433-7851/98/3720-2869 $ 17.50+.50/0

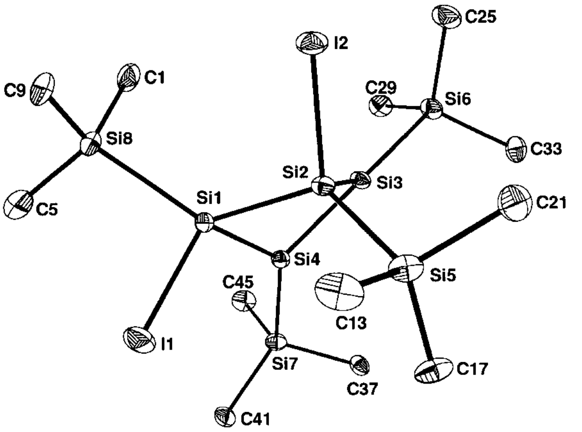
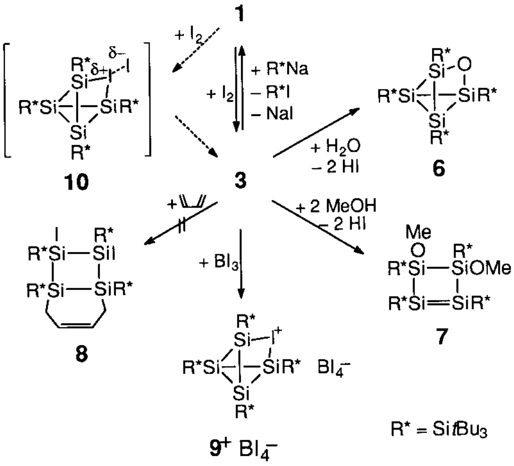


Figure 1. Crystal structure of $\mathbf{3}\cdot C_6H_6$ showing the atom labeling scheme (ORTEP plot, 25% thermal probability ellipsoids; for clarity, methyl groups are not shown). Selected interatomic distances [Å] and angles [°]: Si1−Si2 2.406(2), Si2−Si3 2.379(2), Si3−Si4 2.257(2), Si1−Si4 2.377(2), Si1−Si8 2.527(2), Si2−Si5 2.544(2), Si3−Si6 2.505(2), Si4−Si7 2.504(2), Si1−I1 2.544(2), Si2−I2 2.554(1), Si−C (av) 1.95; Si2-Si1-Si4 84.77(8), Si2-Si1-Si8 126.41(8), Si4-Si1-Si8 124.82(9), Si1-Si2-Si3 84.96(7), Si1-Si2-Si5 125.17(8), Si3-Si2-Si5 122.61(9), Si2-Si3-Si4 88.10(8), Si2-Si3-Si6 135.06(8), Si4-Si3-Si6 136.04(8), Si1-Si4-Si3 88.40(7), Si1-Si4-Si7 135.02(9), Si3-Si4-Si7 136.14(9), Si2-Si1-I1 108.63(7), Si4-Si1-I1 111.55(7), Si8-Si1-I1 100.26(7), Si1-Si2-I2 110.27(7), Si3-Si2-I2 111.64(6), Si5-Si2-I2 101.88(6), C-Si-C (av) 110.8; Si1-Si4-Si3-Si6 142.3, Si6-Si3-Si4-Si7 44.9, Si7-Si4-Si3-Si2 144.7, Si2-Si3-Si4-Si1 28.1, Si4-Si1-Si2-Si3 26.4, Si3-Si2-Si1-Si8 103.8, Si8-Si1-Si2-I2 7.5, I2-Si2-Si1-I1 111.4, I1-Si1-Si2-Si5 10.6, Si5-Si2-Si1-Si4 100.4, Si4-Si1-Si2-Si3 26.4. Crystal structure of $\mathbf{7}\cdot C_6D_6$ (not shown; OMe instead of I in Figure 1). Only the Si and O layers can be described with sufficient accuracy. Selected interatomic distances [Å] and angles [°]: Si1−Si2 2.427, Si1−Si4/Si2−Si3 2.387, Si3−Si4 2.258, Si1−Si8/Si2−Si5 2.465, Si3−Si6/Si4−Si7 2.473, Si1−01/Si2−O2 1.632; Si2-Si1-Si4/Si1-Si2-Si3 85.9, Si2-Si3-Si4/Si1-Si4-Si3 85.93, sum of angles for Si3/Si4 358.9.

ents.[8] The Si−Si single bonds (2.38 – 2.54 Å) are longer than expected (2.34 Å).[9] The ring atoms Si3 and Si4 are surrounded in an approximately planar fashion by one double-bonded and two single-bonded Si atoms (sum of angles around Si3 359.2, around Si4 359.6°; the planes Si2-Si3-Si6 and Si1-Si4-Si7 form an angle of 2.9 and 2.2°, respectively, with the line along Si3−Si4; for comparison: $(t\text{BuMe}_2\text{Si})_6\text{Si}_4$:[4] 13.3 and 13.2°). The angle between the middle planes Si3-Si2-Si6-Si4 and Si4-Si1-Si7-Si3 (Si=Si torsion angle or Si−Si=Si−Si dihedral angle) is 30.8° (in fact, Si3 and Si4 are displaced by 0.87 and 0.12 Å, respectively, above the planes Si2-Si6-Si4 and Si1-Si7-Si3, respectively). The ring atoms Si1 and Si2 are each surrounded in a distorted tetrahedral fashion by one I and three Si atoms. The substituents on Si1 and Si2 are arranged in a staggered conformation, with the I atoms in a *gauche* position to each other (if the Si_4 ring were flattened, the I atoms would be in a *trans* configuration).

The cyclotetrasilene **3**, which can be prepared from **1** and I_2, can be converted back into **1** by reaction with supersilylsodium. The unsaturated Si atoms as well as the Si atoms bonded to iodine within the Si_4 ring of **3** act as reactive centers (Scheme 2). The unsaturated character of the Si−Si double bond, observed for other disilenes, is not strong owing to the steric shielding by the rather bulky substituents.[10] This can be seen, for example, in the fact that the compound is thermally stable up to over 100°C. The double bond also reacts relatively slowly with iodine, which can also be determined from the possibility of a synthesis of **3** (X = I) from **1** and I_2 (in fact, I_2 does react with **3**—albeit more slowly than with **1**—to form R*I and $R^*_3Si_4I_5$).[11] Contrary to expectations, water and methanol do not attack the disilene moiety, but rather substitute the silicon-bound iodine atom with formation of the light yellow species **6**, which exhibits the *bicyclo*-tetrasilane structure **2** (X/X = O; cf. Fig. 2), or the orange compound **7**, which has the *cyclo*-tetrasilene structure **3** (X/X = OMe/OMe; see Figure 1; Scheme 2). Finally, under standard conditions, **3** (X = I) is inert towards butadiene (the Diels – Alder adduct **8** is not formed) and oxygen. However, the rearrangement of the *cyclo*-tetrasilene framework into the *bicyclo*-tetrasilane structure, which is required for the hydrolysis of **3** to yield **6**, cannot take place without participation of the Si−Si double bond. This indicates that the double bond reacts slowly only in intermolecular, but not in intramolecular reactions (see the formation of $\mathbf{9}^+$ from **3**).



Scheme 2. Reactivity and synthesis of $R^*_4Si_4X_2$.

The fact that **3** converts comparatively readily at room temperature into **6** and **7** is surprising, as substitutions at Si centers usually proceed by associative activation (S_N2 mechanism) and are therefore drastically slowed down by bulky, nonreactive groups at the substitution site, such as in **3** (X = I).[9] As such bulky, nonreactive groups tend to facilitate substitutions proceeding by dissociative activation (S_N1 mechanism), one possible explanation for the rapid conversion of **3** into **6** and **7** is that the intermediate $\mathbf{9}^+$ is formed.[12] An observation in favor of this mechanism is that **3** (X = I) reacts with equimolar amounts of BI_3 in dichloromethane at room temperature to yield a colorless compound. Based on its ^{11}B NMR spectrum, this species contains only BI_4^- as a boron-containing group, and its ^1H, ^{13}C, and ^{29}Si NMR spectra are consistent with the structure of the cation $\mathbf{9}^+$ shown in Scheme 2 (see the Experimental Section). Furthermore, addition of H_2O or MeOH to a solution of this species results in the formation of **6** and **7**. The very small, colorless needles obtained from dichloromethane at −25°C proved unsuitable for a crystal structure analysis.

It was, however, possible to determine the structure of **6**, which is isoelectronic (in terms of valence electrons) to $\mathbf{9}^+$ and which had been identified by mass spectrometry and NMR spectroscopy as $\mathrm{R_4^*Si_4O}$. Crystals of the composition $\mathrm{R_4^*Si_4O \cdot 0.75\,C_6D_6}$ were obtained and a X-ray crystal structure analysis was performed. There was a disorder in the position of the O atom which spans one the six edges in the $\mathrm{R_4^*Si_4}$ tetrahedron in **6**; the O atom is disordered over all six possible positions. The crystallographic characterization can therefore only be taken as proof of the gross structure. The Si–Si distances range from 2.376(2) to 2.434(2) Å, and the Si–O distances from 1.67(3) to 1.73(3) Å. As expected, the longest Si–Si distance (Si1–Si4) is that where the oxygen atom exhibits the highest occupancy factor (0.404). Figure 2 depicts this structure of **6** (the sum of all occupancy factors is 1).[13]

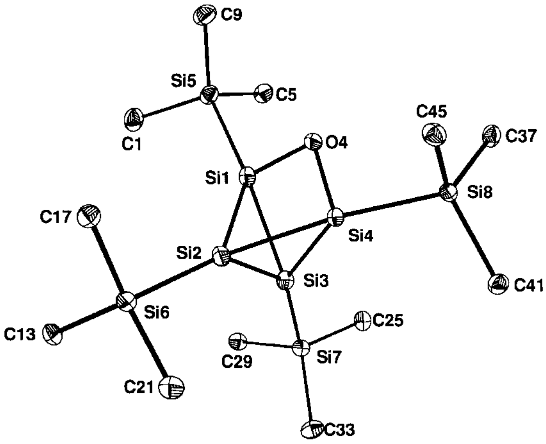


Figure 2. Crystal structure of $\mathbf{6}\cdot 0.75\,\mathrm{C_6D_6}$ showing the atom labeling scheme (ORTEP plot, 25% thermal probability ellipsoids; for clarity, methyl groups are not shown). The O atom is disordered over the six edges of the tetrahedron formed by Si1-Si2-Si3-Si4, but it has the highest occupancy between Si1 and Si4 (0.4039; only the unit with this O position is shown). The interatomic distances [Å] and angles [°] found therefore only approximate the actual values: Si1–Si2 2.386(2), Si1–Si3 2.391(2), Si1–Si4 2.434(2), Si2–Si3 2.398(2), Si2–Si4 2.376(2), Si3–Si4 2.395(1), Si1–Si5 2.376(2), Si2–Si6 2.378(2), Si3–Si7 2.377(1), Si4–Si8 2.370(1); Si–O distances within the Si-O-Si bridges: Si1-O-Si2 1.73(3)/1.68(2), Si1-O-Si3 1.68(2)/1.69(2), Si1-O-Si4 1.676(6)/1.726(8), Si2-O-Si3 1.72(2)/1.74(2), Si2-O-Si4 1.70(3)/1.67(3), Si3-O-Si4 1.66(1)/1.70(1); Si-Si-Si angle in the Si1-Si2-Si3-Si4 tetrahedron: at Si1 60.25(4)/59.04(4)/59.51(4), at Si2 61.49(4)/60.23(4)/59.97(4), at Si3 61.15(4)/59.78(5)/59.43(4), at Si4 60.33(4)/59.46(5)/59.34(4); Si1-O-Si2 89(1), Si1-O-Si3 90(1), Si1-O-Si4 91.4(3), Si2-O-Si3 87.6(8), Si2-O-Si4 90(2), Si3-O-Si4 91.0(7). Structure of $\mathrm{2\,R_4^*Si_4O \cdot R_4^*Si_4O_2 \cdot 4.5\,C_6D_6}$ in the mixed crystal (not shown). As for $\mathbf{6}\cdot 0.75\,\mathrm{C_6D_6}$, the O atoms of the molecules are disordered over the six edges of the central $\mathrm{Si_4}$ tetrahedron. The Si–Si distances range from 2.391(3) to 2.463(3) Å, and the Si–O distances from 1.61(3) to 1.70(3) Å. The longest Si–Si distance is found for those Si atoms above which the O atom position with the highest occupancy factor (0.444) is located (sum of all occupancy factors is 1.31).

The preparation of **3** by the action of $\mathrm{I_2}$ on **1** in heptane at 0 °C in the dark leads initially to a heptane-insoluble black solid, which slowly converts into the red species **3** (X = I) when dissolved in benzene at room temperature. The black intermediate could be species **10**, which rearranges into the iodine-containing compound **3** by way of the dissociation products $\mathbf{9}^+$ and $\mathrm{I^-}$ (Scheme 2). This mechanism would also explain why the two iodine atoms in **3** are located on opposite sides of the $\mathrm{Si_4}$ ring.

Experimental Section

3 (X = I): A solution of iodine (0.13 g, 0.51 mmol) in *n*-heptane (50 mL) is slowly added, under exclusion of light, to a solution of **1**[1] (0.45 g, 0.49 mmol) in *n*-heptane (50 mL) at 0 °C; a black suspension forms thereby. After all volatile components have been removed under an oil-pump vacuum, benzene (50 mL) is added to the remaining black residue. The residue dissolves within one hour, forming a red solution. NMR spectra of this solution show **3** (X = I) to be the sole product. The benzene is removed under an oil-pump vacuum. Recrystallization of the red residue in benzene (10 mL) at room temperature yields $\mathbf{3}\cdot\mathrm{C_6H_6}$ (0.35 g, 0.30 mmol, 61%) in the form of red platelets which melt with decomposition at 128–130 °C; ^{1}H NMR ($\mathrm{C_6D_6}$, TMS internal standard): $\delta = 1.39/1.61$ (s/s; 6*t*Bu/6*t*Bu); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, TMS internal standard): $\delta = 26.4/28.0$ (6*C*Me$_3$/6*C*Me$_3$), 33.7/33.9 (6C*Me$_3$*/6C*Me$_3$*); ^{29}Si NMR ($\mathrm{C_6D_6}$, TMS external standard): $\delta = 38.2/49.2$ (2Si*t*Bu$_3$/2Si*t*Bu$_3$), −56.5 (2SiI), 164.4 (2 >Si=).

Preparation of **6** from **3**: An NMR tube is filled with **3** (X = I; 0.08 g, 0.07 mmol) and $\mathrm{C_6D_6}$ (0.5 mL), then sealed, but not completely airtight, and left to stand for one week. The red solution slowly turns light yellow, and light yellow crystals of the composition $\mathbf{6}\cdot 0.75\,\mathrm{C_6D_6}$ are formed (according to NMR spectra, the remaining solution only contains **6**); ^{1}H NMR ($\mathrm{C_6D_6}$, TMS internal standard): $\delta = 1.33/1.42$ (s/s; 6*t*Bu/6*t*Bu); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, TMS internal standard): $\delta = 24.6$ (12*C*Me$_3$), 31.8/32.4 (6C*Me$_3$*/6C*Me$_3$*); ^{29}Si NMR ($\mathrm{C_6D_6}$, TMS external standard): $\delta = 27.8/39.0$ (2Si*t*Bu$_3$/2Si*t*Bu$_3$), −106.4 (SiSi), −7.2 (SiOSi); MS: *m/z* (%): 924.8 (100) [M^+], 908.8 (0.7) [$M^+ - \mathrm{O}$] (the correct isotopic pattern was observed in both cases; in addition, the product with the composition $\mathrm{2\,R_4^*SiO \cdot R_4^*SiO_2 \cdot 4.5\,C_6D_6}$, which was obtained from **1** and excess water-containing $\mathrm{I_2}$, showed a small signal at 940.8 [M^++O]).

7: A solution of **3** (X = I; 0.11 g, 0.09 mmol) in benzene (20 mL) is allowed to react for one hour at room temperature with degassed methanol (2 mL). After all volatile components have been removed under an oil-pump vacuum, the residue is dissolved in $\mathrm{C_6D_6}$ (0.6 mL; heated to 60 °C). Upon cooling and concentration of the solution, 0.03 g (0.03 mmol, 33%) of orange platelets precipitate that exhibit the composition $\mathbf{7}\cdot\mathrm{C_6D_6}$. They melt with decomposition at 160–161 °C; ^{1}H NMR ($\mathrm{C_6D_6}$, TMS internal standard): $\delta = 1.38/1.44$ (s/s; 6*t*Bu/6*t*Bu), 3.55 (s, 2OC*H$_3$*); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, TMS internal standard): $\delta = 25.4/25.6$ (6*C*Me$_3$/6*C*Me$_3$), 33.1/33.3 (6C*Me$_3$*/6C*Me$_3$*), 54.9 (2OCH$_3$); ^{29}Si NMR ($\mathrm{C_6D_6}$, INEPT, TMS external standard): $\delta = 29.9/44.0$ (2Si*t*Bu$_3$/2Si*t*Bu$_3$).

$\mathbf{9}^+\mathrm{BI_4^-}$: Compound **3** (X = I; 0.031 g, 0.027 mmol) and $\mathrm{BI_3}$ (0.011 g, 0.028 mmol) are dissolved in $\mathrm{CD_2Cl_2}$ (0.6 mL). A new compound is formed exclusively, which, according to NMR spectra and other results, is $\mathbf{9}^+\mathrm{BI_4^-}$. Thus far, only very small colorless needles have been obtained upon cooling, which have proven unsuitable for X-ray crystal structure analysis; ^{1}H NMR ($\mathrm{CD_2Cl_2}$, TMS internal standard): $\delta = 1.34/1.36$ (br/s; 6*t*Bu/6*t*Bu); ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, TMS internal standard): $\delta = 25.5$ (12*C*Me$_3$), 32.4/32.7 (6C*Me$_3$*/6C*Me$_3$*); ^{29}Si NMR ($\mathrm{CD_2Cl_2}$, TMS external standard): $\delta =$ 50.8/51.6 (2Si*t*Bu$_3$/2Si*t*Bu$_3$), −129.7 (two central Si atoms of the $\mathrm{Si_4}$ butterfly; typical high-field signal for $\mathrm{Si_3}$ rings), −29.9 (two outer Si atoms of the $\mathrm{Si_4}$ butterfly; owing to the neighboring positive charge on the I atom these signals are shifted downfield compared to typical signals for $\mathrm{Si_3}$ rings; Si shifts for Si cations or Si atoms in Si=Si groups are expected at δ values above +100[10, 14]); ^{11}B NMR ($\mathrm{CD_2Cl_2}$, $\mathrm{BF_3}$ internal standard): $\delta = -127$ ($\mathrm{BI_4^-}$; this corresponds to the literature value for $\mathrm{BI_4^-}$[15]).

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Expanding the Potential of DNA for Binding and Catalysis: Highly Functionalized dUTP Derivatives That Are Substrates for Thermostable DNA Polymerases**

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Nucleic acid libraries provide tremendous opportunities for the selection of novel ligands and catalysts since the polymerase chain reaction (PCR) allows for the synthesis and selection of libraries containing more than 10^{14} different molecules. There are now many examples of nucleic acids that have been selected to bind proteins and small molecules and to catalyze a limited set of reactions.[1–3] The catalytic and mechanistic scope of nucleic acids is limited since the natural nucleotide monomers possess minimal functionality relative to the repertoire available to nature's dominant catalytic biopolymers, proteins. In recognition of this shortcoming much attention has been focused on the development of functionalized nucleotides suitable for in vitro selection with the hope of increasing the potential of nucleic acids for binding and catalysis.[4] Functionalized nucleotide triphosphates have been shown to be substrates for RNA polymerases,[4d, h] and catalytic RNAs that are dependent on the modified base[5] for their activity have been selected. In a similar manner to RNA, DNA has also been selected to bind proteins and small molecules and more recently to catalyze reactions.[1–3] While DNA possesses enhanced stability relative to RNA, the lack of a 2′-hydroxyl group, which provides for the enhanced stability of this molecule, further reduces the potential for chemical functionalization. In contrast to the success achieved in identifying modified nucleotide triphosphates for RNA libraries, there is but a single example of a deoxynucleotide triphosphate, 5-(1-pentynyl)-2′deoxyuridine triphosphate, which is a good substrate for a thermostable DNA polymerase and has been utilized in an in vitro DNA selection study.[6] Indeed, difficulties in identifying modified deoxynucleotide triphophate substrates for the thermostable polymerases required for PCR have led recently to the development of novel strategies for in vitro selection without enzymatic amplification.[7] Therefore, the major impediment to the creation of novel functionally modified DNA catalysts and binding molecules is the determination of the structures of the substrate that are accepted by the thermostable polymerases. Herein, we provide a solution to this problem through the systematic synthesis and study of deoxyuridine triphosphate derivatives and disclose the discovery of a class

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