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Synthesis, structure, and photoreactions of fluorinated 2,11-diaza[3_2]paracyclophane: Photochemical formation of cage-diene type benzene dimer

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Abstract

An octafluorinated 2,11-diaza[3_2]paracyclophane derivative **12** was prepared, and its photochemical reaction was investigated. Upon irradiation at 300 nm, the fluorinated azacyclophane **12** underwent efficient photodimerization of the benzene cores to afford the corresponding photoisomer **13**, which possessed cage diene benzene dimer structure (pentacyclo[6.4.0.0.^{2,7}0.^{3,12}0^{6,9}]dodeca-4,10-diene skeleton). The cage diene structure was established by single-crystal X-ray diffraction analysis. The cage diene **13** thermally isomerized to a *syn-o,o′*-dibenzene isomer **22**. The activation parameters for the thermal isomerization were determined to be E_a = 121 kJ mol^{-1}, $\Delta H^{\neq}$ = 118 kJ mol^{-1}, $\Delta S^{\neq}_{(293\ K)}$ = 22 J mol^{-1} K^{-1}, and $\Delta G^{\neq}_{(293\ K)}$ = 111 kJ mol^{-1}. It was revealed that, by photoirradiation at 300 nm, the *syn-o,o′*-dibenzene isomer **22** underwent facile intramolecular [π4s + π4s] cycloaddition to reproduce the cage diene isomer **13**.

KEYWORDS

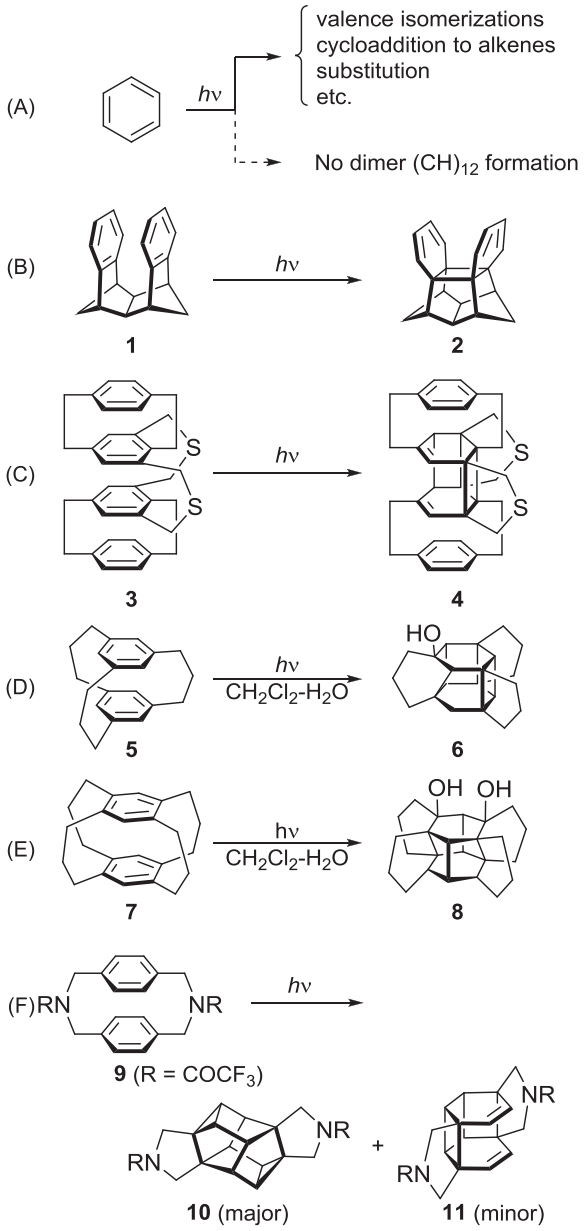
azacyclophane, benzene dimer, cage compound, cyclophane, photocycloaddition

1 | INTRODUCTION

Benzene dimers, $(CH)_{12}$ hydrocarbons, have attracted much attention because they have highly strained and fascinating molecular structures and are generally unstable and difficult to access through conventional thermal or catalytic reactions.[1,2] It has been established that benzenes display variety of photoreaction pathways such as valence isomerizations, cycloadditions with alkenes, and substitution reactions (Scheme 1A). However, they rarely undergo photochemical dimerization.[3] Only a few dimerizations of benzenes have been reported for photolysis of structurally restricted cyclophane systems in which the 2 benzene cores are fixed in a close and specific orientation.[4]

Two pioneering studies on benzene photodimerization in cyclophane systems are the [6 + 6] photocycloaddition of orthocyclophane **1** by Prinzbach (Scheme 1B)[5,6] and the cage diene **4** formation of 4-layered cyclophane **3** by Misumi and Higuchi (Scheme 1C).[7,8] One of the present authors has investigated photoreactions of carbon-bridged [3_3]- and [3_4] cyclophanes (**5**, **7**) and revealed that benzene dimers (**6**, **8**) were obtained through complex rearrangements (Scheme 1D,E).[9–11] The present authors reported that photolysis of a diaza[3_2]paracyclophane **9** produced octahedrane

This paper is dedicated to Professor Waldemar Adam on the occasion of his 80th birthday.



SCHEME 1 Photoreactions of cyclophanes affording benzene dimers

10 and cage diene **11** as the major and minor products, respectively (Scheme 1F).[12] As the corresponding carbon-bridged [3_2]paracyclophane was essentially inert against photoirradiation, the nitrogen-containing bridges have been considered to play a critical role in modifying photoreactivity of the paracyclophane system.[12]

Currently, little information is available concerning effects of aromatic-core substituents on the photochemical behavior of the [3_2]paracyclophane system, namely, that of the nitrogen-bridged cyclophanes.[4] Thus, it would be of interest to reveal the substituent effects on the photochemical behavior. It has been reported that introduction of fluorine atoms into aromatic cores of [3_3]cyclophanes significantly affected the electronic features of the carbon-bridged cyclophane, thus, electronic absorption band of hexafluoro[3_3](1,3,5) cyclophane remarkably blue shifted compared to that of nonsubstituted parent cyclophane.[13] Fluorination on the side chains may modify photochemical properties of a cyclophane system. Upon photolysis, [2_2](1,4)anthracenoparacyclophane having fluorinated side chains underwent unusual intermolecular [π2s + π2s] dimerization.[14,15]

These facts motivated us to investigate the photoreaction of a fluorine-substituted azacyclophane. Fluorinated azacyclophanes would display different photochemical properties compared with the previously reported photoreactive cyclophanes by virtue of both the nitrogen-containing bridging and fluorine substituent effects. Furthermore, it has been expected that the introduction of fluorine atoms stabilizes a photochemically formed strained product structure(s)[16] and enables us to isolate the hitherto unknown photoproduct. Herein, we report the synthesis of novel fluorinated azacyclophane **12** and its photoreaction affording cage diene **13** (Chart 1). Structural analysis, as well as the photo- and thermal behavior of cage diene **13**, are also described.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and structure of fluorinated azacyclophane 12

The synthetic route to fluorinated azacyclophane **12** is shown in Scheme 2. Coupling between the components **14** and **15** in the presence of NaH afforded azacyclophane **16**. As

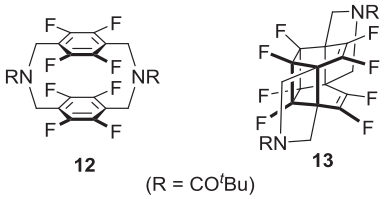
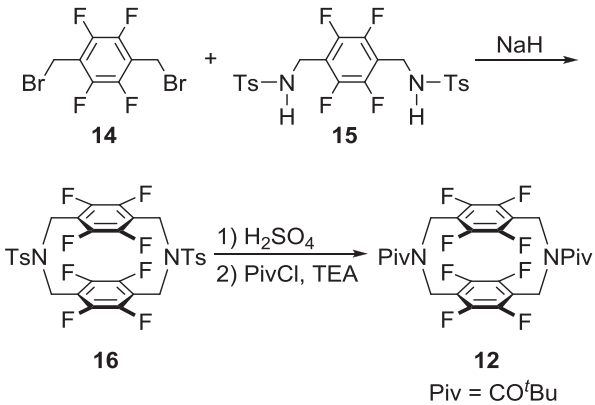


CHART 1 Structures of fluorinated azacyclophane **12** and photoproduct **13**



SCHEME 2 Synthetic route to azacyclophane **12**

tosylamide **16** was hardly soluble in common organic solvents, it was used in the following reaction without purification. Detosylation of **16** was achieved by heating in concentrated sulfuric acid and subsequent reprotection on the amino moiety with pivaloyl chloride afforded the desired azacyclophane **12** in 39% overall yield from **14** and **15**. The pivaloyl amide was selected because of the following 2 reasons: It shows no absorption band in the wavelength region where azacyclophane chromophore displays an absorption band(s) and the amide C–N bond freely rotates at room temperature (rt).[17] The latter makes compounds characterization easy due to negligible contribution of amide rotamers.[12]

Azacyclophane **12** was characterized by spectroscopic as well as elemental analyses. Furthermore, the structure of azacyclophane **12** was studied by an X-ray crystallographic analysis (Figure 1). An X-ray structure of azacyclophane **9** having no substituent on the benzene cores is also shown to reveal the effects of fluorine atoms on the azacyclophane structure. Selected structural parameters are summarized in Table 1. In the solid state, the side bridges of azacyclophanes **9** and **12** adopted a chair conformation (Figure 1A,E) with the 2 amide parts in an *anti* orientation (Figure 1B,F). For fluorinated derivative **12**, the distance between the mean planes of the benzene rings d_1 is 2.942 Å, which is shorter than that of nonsubstituted one **9** (3.189 Å). Two benzene rings in **12** are tilted by $d_4 = 0.928$ Å from full overlap while those in **9** almost fully overlapped ($d_4 = 0.080$ Å). It is considered that the fluorinated benzene rings in azacyclophane **12** deviated from full overlap conformation to reduce repulsive interaction of polarized $C^{\delta+}$–$F^{\delta-}$ bonds between the 2 benzene rings resulting in the parallel-displacement conformation.[18,19] The benzene rings of the azacyclophanes **9**

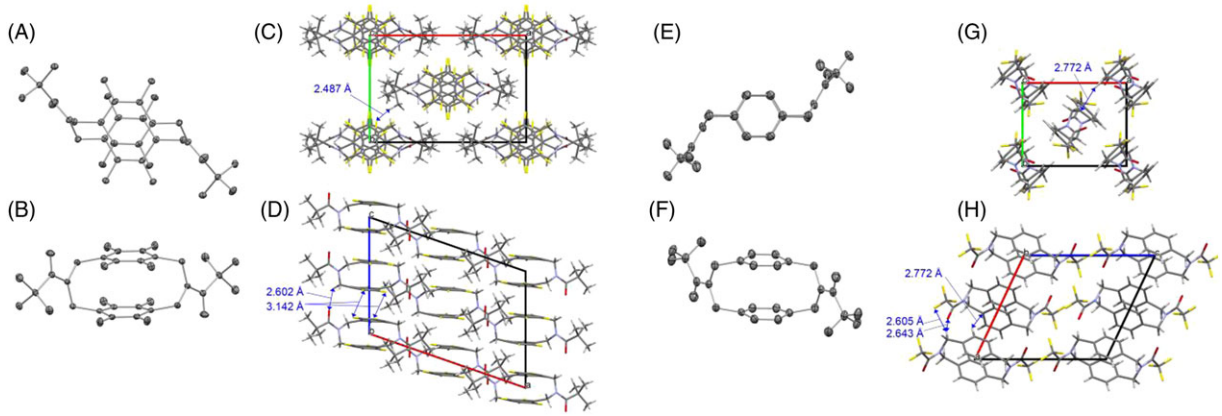
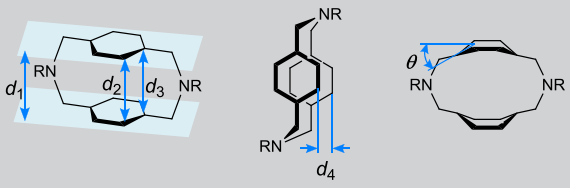


FIGURE 1 X-ray structures of azacyclophanes **9** and **12**. A and B, Molecular structure of **12** top and front views, respectively. C and D, Crystal packing of **12** viewed from *ab* and *ac* planes, respectively. Hydrogen atoms are omitted for clarity. E and F, Molecular structure of **9** top and front views, respectively. Hydrogen atoms are omitted for clarity. G and H, Crystal packing of **9** viewed from *ab* and *ac* planes, respectively

TABLE 1 Structural parameters of azacyclophanes **9** and **12**



Compound	**12**	**9**
d_1 (Å)[a]	2.942	3.189
d_2 (Å)[b]	3.148, 3.130	3.250, 3.237
d_3 (Å)[c]	3.007	3.091
d_4 (Å)[d]	0.928	0.080
θ (°)[e]	5.61, 5.05	6.46, 5.90

[a]Distance between mean planes of the benzene rings.

[b]Nonbonding distance between the bridging carbon atoms.

[c]Nonbonding distance between the nonbridging carbon atoms.

[d]Tilting of the 2 benzene rings.

[e]Folding angle of the benzene rings.

and **12** distorted slightly from planarity with folding angle $\theta = 5.05–6.46°$ (Table 1).

In crystalline, fluorinated molecules of **12** stacked in a face-to-face manner to form one-dimensional column along with *b* axis by an attractive intermolecular C•••F contact (3.142 Å, Figure 1D). In contrast, for nonfluorinated derivative **9**, molecules aligned in an edge-to-face manner (Figure 1 G). The neighboring molecules of **9** contacted through an interaction between the aromatic hydrogen and carbon atoms (Figure 1G). Therefore, the fluorine substitution modifies crystal structure of the azacyclophane system. Such effects of fluorine substitution on crystal structures have also been reported for [3_3]cyclophane system.[13]

2.2 | Absorption and fluorescence spectra of azacyclophane 12

To obtain an insight into electronic features of azacyclophane **12**, electronic spectra were observed in MeCN at rt. Azacyclophane **12** showed a small absorption band at 270 nm, and the absorption edge showed tailing over 310 nm (Figure 2, blue line). Very weak fluorescence emission band was detected with an emission maximum at 363 nm (Figure 2, red line). As the excitation spectrum of the 363-nm emission band was identical with the absorption profile (Figure 2, dotted line), the fluorescence emission band was unambiguously assigned to azacyclophane **12**. The Stokes shift was estimated to be *ca.* 7500 cm^{-1} suggesting that the 2 benzene chromophores strongly interacted in the excited state to form intramolecular excimer. Such a large Stokes shift was also observed for nonsubstituted azacyclophane **9** (*ca.* 7000 cm^{-1}).[12]

Figure 3 shows frontier orbitals of azacyclophane **12** calculated at the B3LYP/6-31+G(d) theory. In the lowest unoccupied molecular orbital (LUMO), p orbitals of the 2 benzene rings overlap through space in an in-phase manner (π-π interaction). It is notable that the aromatic π orbitals apparently conjugated with the C–N σ bonds and the CH_2

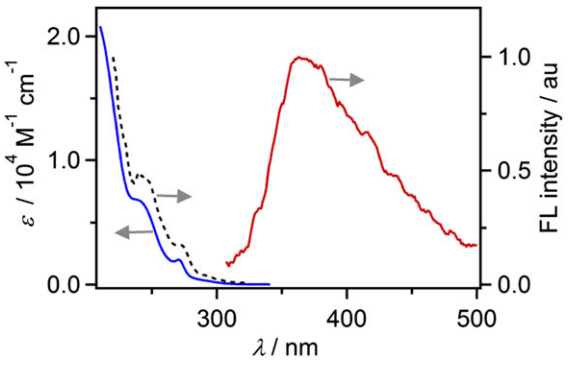


FIGURE 2 Electronic spectra of azacyclophane **12** (MeCN): Absorption (blue line), fluorescence emission (red line), and excitation (dotted line)

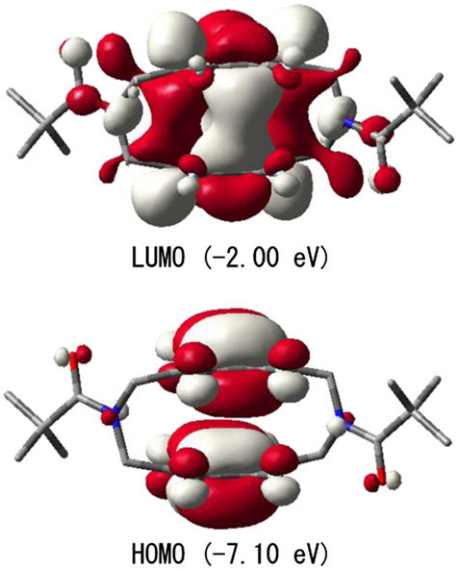


FIGURE 3 Frontier molecular orbitals of azacyclophane **12** (B3LYP/6-31+G(d))

moieties of the side bridges (σ-π interaction). Due to both the π-π and σ-π interactions, 2 benzene rings are considered to strongly interact in the excited state.[12] These theoretical calculation results are consistent with the experimentally observed intramolecular excimer-like fluorescence behavior of azacyclophane **12**.

2.3 | Photochemical reaction of azacyclophane 12

Upon irradiation at 300 nm in $CDCl_3$, azacyclophane **12** underwent an efficient reaction, and formation of a single product was observed by ^{1}H-NMR time-course spectra (Figure 4). The starting azacyclophane **12** was completely consumed after 90 minutes of irradiation, and the photoproduct was observed in 85% yield (Figure 4, inset). The photoproduct was isolated, and, based on spectral analysis, the structure was assigned as a cage diene **13**, which had a pentacyclo[6.4.0.0.^{2,7}0.^{3,12}0^{6,9}]dodeca-4,10-diene skeleton (Scheme 3) and further confirmed by an X-ray crystallographic analysis (*vide infra*). For a preparative photoreaction, the isolation yield of cage diene **13** was 70%. As seen from the inset in Figure 4, the photoproduct **13** was durable under the investigated photolysis conditions. For the photoreaction of nonfluorinated derivative **9**, octahedrane formation is known to be the main photochemical process.[12] In contrast, corresponding octahedrane **17** was not detected for the photoreaction of azacyclophane **12**. Therefore, the fluorine atoms modified the photochemical behavior of the azacyclophane system. Currently, the reason why octahedrane formation is suppressed by the fluorination is not clear, and experimental and theoretical investigations to reveal the substituent effects are underway.

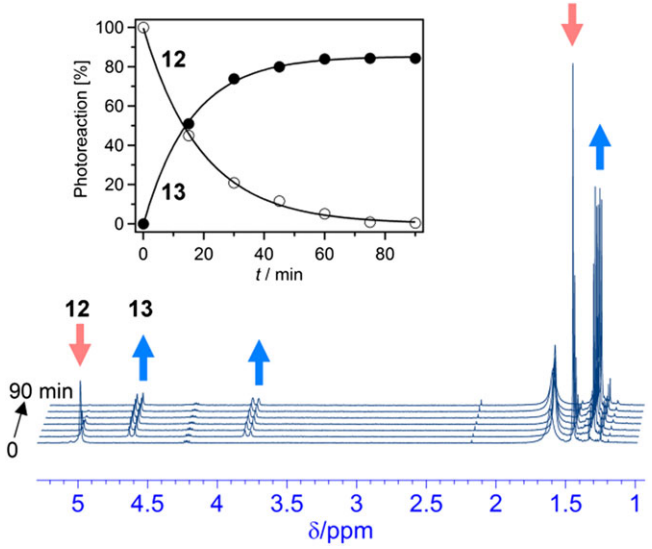
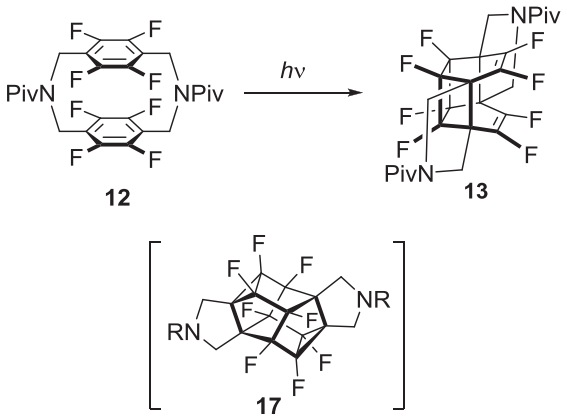


FIGURE 4 ^{1}H NMR spectra of azacyclophane **12** during 300-nm irradiation (in $CDCl_3$). The inset displays time profile for the photolysis (○: **12**, ●: **13**)



SCHEME 3 Photochemical reaction of azacyclophane **12**

2.4 | Structure of cage diene 13

The cage diene structure **13**, *i.e.* pentacyclo[6.4.0.0.^{2,7}0.^{3,12}0^{6,9}]dodeca-4,10-diene skeleton, has been of research interest as highly strained $(CH)_{12}$ class of benzene dimers. Detailed structural features of the parent compound have yet to be elucidated due to its thermal instability undergoing facile dissociation into 2 benzenes.[20,21]

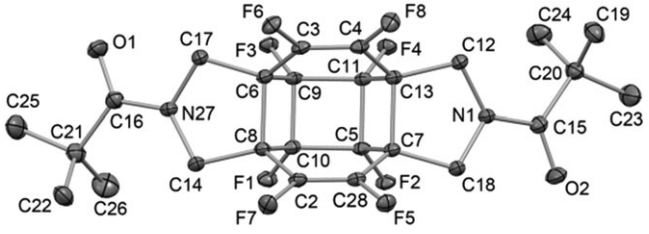


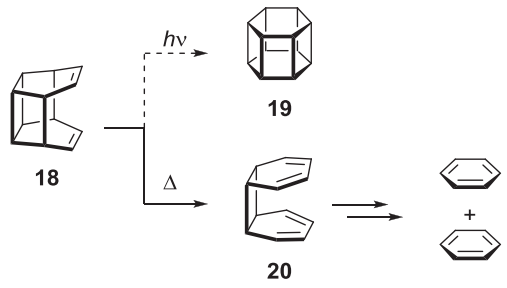
FIGURE 5 X-ray structure of cage diene **13**. Hydrogens are omitted for clarity

Figure 5 shows an X-ray structure of cage diene **13**. The bond distances of the C6–C8 and C7–C13 pillars were 1.624 and 1.626 Å, respectively, which were significantly longer than that of normal C–C single bond in cyclobutane (*ca.* 1.55 Å).[22] The bond distances of C9–C10 and C5–C11 pillars were, respectively, 1.550 and 1.557 Å showing no significant distortion compared to that of normal cyclobutane. The olefinic carbon atoms are placed in proximal positions; nonbonding C–C distances are 2.990 Å for C2–C3 and 2.983 Å for C4–C28.

2.5 | Photo- and thermal reactions of cage diene 13

Chemical reactivity, namely, photoreactivity, of the cage diene framework **18** has been of great interest because it has been expected as a precursor to hexaprismane skeleton **19**.[23,24] We have previously reported that cage diene **11** (see structure in Scheme 1) reverted to azacyclophane **9** upon 300-nm photolysis.[12] We expected that the fluorination might affect the photoreaction of the cage diene system. Additionally, the parent cage diene **18** is known to thermally revert to 2 benzenes through *syn-o,o′*-dibenzene **20** (Scheme 4).[20,21] Therefore, we investigated photochemical (direct and sensitized) and thermal reactions of cage diene **13**.

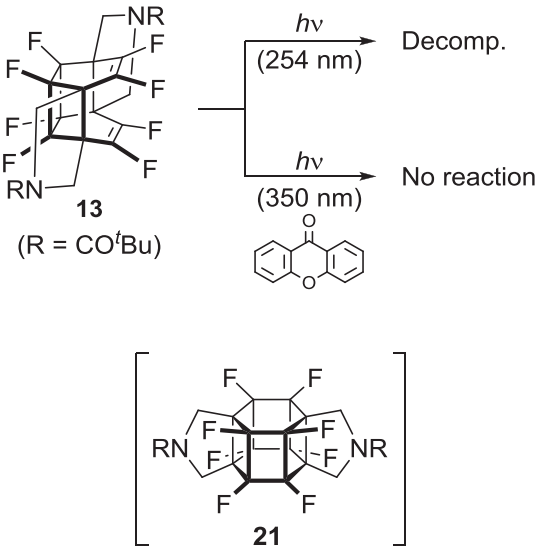
When cage diene **13** was irradiated at 254 nm in nitrogen-purged CD_3CN, it was gradually consumed (Figure S1A). Although, in ^{1}H NMR spectrum of the photolysate, some very small signals evolved after 2.5 hours, no appreciable photoproduct was assigned. Thus, cage diene **13** decomposed to unidentified compounds. Then, xanthone-sensitized photolysis was conducted. We selected xanthone as the triplet sensitizer because it has been reported that xanthone-sensitized photolysis effectively promotes intramolecular [π2s + π2s] cycloaddition of [4 + 4]-type benzene-naphthalene cross-dimers.[25,26] When a 1:1.3 mixture of cage diene **13** and xanthone in degassed acetone-d_6 was irradiated at 350 nm, almost no change in its ^{1}H NMR profile was observed after 1 hour (Figure S1B). From these results, we conclude that cage diene **13** was photolabile to decompose in the excited singlet state while inert in the triplet



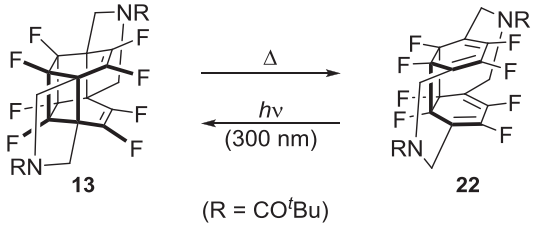
SCHEME 4 Desired photochemical process and reported thermal reversion of cage diene **18**

state. Therefore, the desired hexaprismane **21** is currently not accessible by the photoreaction of cage diene **13** (Scheme 5).

Thermally, cage diene **13** was found to undergo a rearrangement affording *syn-o,o′*-dibenzene **22** (Scheme 6), as in the case reported for the parent compound **18**.[20] To isolate dibenzene **22**, a 1,1,2,2-tetrachloroethane solution of azacyclophane **12** was irradiated at 300 nm for 1.5 hours subsequently heated at 100°C for 0.5 hour. After removal of the solvent, the residue was washed with EtOH to afford dibenzene **22** in 48% isolation yield from **12**. The *syn-o,o′*-dibenzene structure was assigned by NMR spectroscopy as well as high-resolution mass spectrometry. Figure 6 compares the ^{13}C NMR spectra between cage diene **13** and dibenzene **22**. The signal of the bridged carbon atom (C^b) of cage diene **13** resonated at 59.5 ppm (Figure 6, lower); by contrast, that of dibenzene **18** resonated at 111.4 ppm (Figure 6, upper). These results provide an evidence that the bridge carbon atoms C^b are olefinic in the dibenzene structure **22**. Parent *syn-o,o′*-dibenzene **20** has been known to be an unstable compound because it thermally isomerizes to *anti-o,o′*-dibenzene, which finally reverted to 2 benzenes.[20,21] Dibenzene **22** was durable at 100°C for several hours (data not shown). It is presumably because that dibenzene **22** could not isomerize to the corresponding



SCHEME 5 Photoreactions of cage diene **13**



SCHEME 6 Thermal ring opening and photo ring closure of the cage diene system

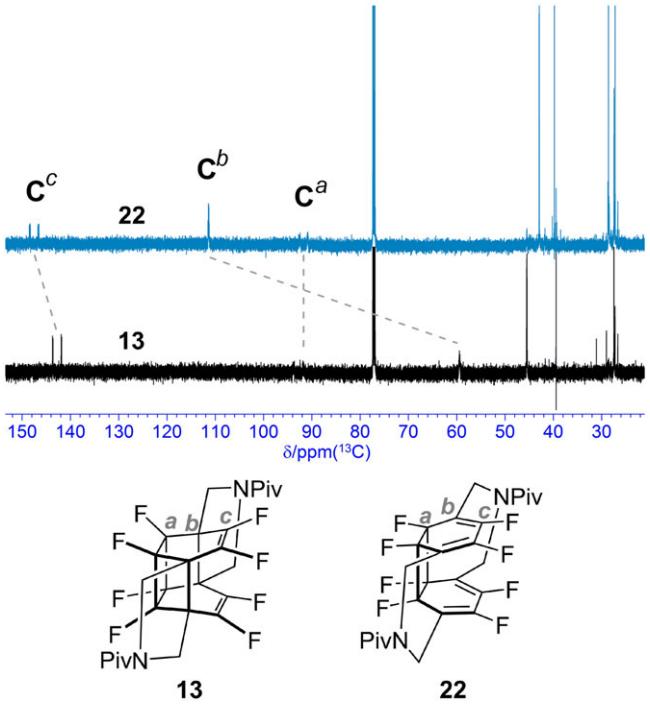


FIGURE 6 ^{13}C NMR spectra of cage diene **13** (lower) and dibenzene **22** (upper) in $CDCl_3$ (150 MHz)

anti-o,o′-dibenzene isomer due to the structural restriction by the side bridges.

The thermolysis process was monitored by ^1H NMR spectroscopy in 1,1,2,2-tetrachloroethane-d_2 to understand the thermal features of cage diene **13**. The thermolysis of cage diene **13** followed first-order kinetics as shown in Figure 7 A. Arrhenius plots for the thermolysis displayed a linear correlation to provide an activation energy, E_a = 121 kJ mol^{-1} (Figure 7). According to the transition state theory, activation parameters for the thermal isomerization were evaluated to be $\Delta H^{\neq}$ = 118 kJ mol^{-1}, $\Delta S^{\neq}_{(293\ K)}$ = 22 J mol^{-1} K^{-1}, and $\Delta G^{\neq}_{(293\ K)}$ = 111 kJ mol^{-1}.

Photochemical behavior of dibenzene **22** was also investigated. Upon 300-nm irradiation for 5 minutes, dibenzene **22** quantitatively reproduced cage diene **13** through an intramolecular [π4s + π4s] cycloaddition (Scheme 6 and Figure S2). To the best of our knowledge, the photoconversion of *syn-o,o′*-dibenzene to cage diene was first observed.

3 | SUMMARY

Fluorinated azacyclophane **12** was synthesized to reveal the effects of fluorine atoms on the structural and electronic features as well as those on the photoreactivity of the azacyclophane system. The X-ray structure of azacyclophane **12** indicated that the molecular structure and crystal packing were modulated by the fluorination on the benzene rings (Figure 1 and Table 1). Upon photoreaction, azacyclophane

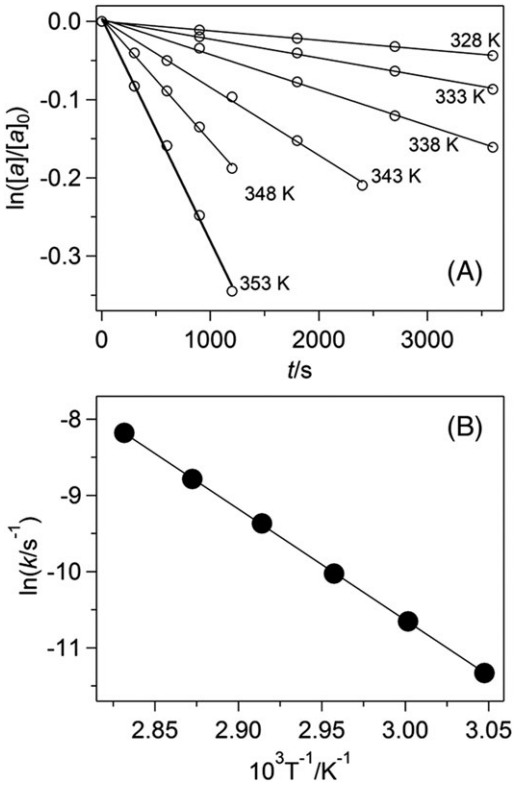


FIGURE 7 A, First-order plots and B, Arrhenius plots for thermal isomerization from cage diene **13** to dibenzene **22** in 1,1,2,2-tetrachloroethane-d_2

12 efficiently produced cage diene **13** as the sole product (Scheme 3). These results show clear contrast to photoreactivity of nonsubstituted analogue **9**, which photochemically produced octahedrane **10** as the major product. It was found that the fluorination on the aromatic rings drastically modified the photoreaction modes of the azacyclophane system. The present results suggest that, by appropriately altering the aromatic substituents, one would control the benzene-benzene photodimerization modes of the azacyclophane system. Currently, theoretical and experimental studies to clarify the substituent effects that modify photoreactivities of the azacyclophane system are underway. The structure of the cage diene **13** was successfully established by an X-ray crystallographic analysis. The bond distances of the C6–C8 and C7–C13 pillars are very long as C–C single bond (approximately 1.624 Å, see Figure 5), which suggests the thermal instability of the cage diene structure.

4 | EXPERIMENTAL

4.1 | *N,N′*-dipivaloyl-5,6,8,9,14,15,17,18-octafluoro-2,11-diaza[3_2]paracyclophane 2

A mixture of NaH (60% in mineral oil, 0.304 g, 12.7 mmol) and tosylamide **15** (2.02 g, 3.91 mmol) in DMF (70 mL) and a solution of dibromide **14** (1.31 g, 3.91 mmol) in DMF (70 mL) were dropped into DMF (400 mL) at rt under a nitrogen atmosphere during a period of 5.5 hours. The mixture was stirred for additional 37 hours at rt. The resulting mixture was concentrated under reduced pressure and MeOH (20 mL) was added to the residue. The precipitate formed was collected to afford azacyclophane **16** (1.62 g) as colorless crystals. The compound **16** was used in the following reaction without further purification because of its poor solubility in common solvents.

Compound **16** (308 mg, 0.45 mmol) was dissolved in 95% H_2SO_4 (4 mL) and heated at 70°C for 3 hours. After cooling, the solution was cautiously diluted with water and extracted with CH_2Cl_2 (3 × 15 mL). The water phase was basified with 10 % NaOH aq. and extracted with $CHCl_3$ (3 × 15 mL). The solution was dried over anhyd. $MgSO_4$. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (5 mL), and Et_3N (181 μL, 1.30 mmol) was added. To the solution was dropwise added a solution of pivaloyl chloride (159 μL, 1.30 mmol) in CH_2Cl_2 (1 mL) at 0°C under a nitrogen atmosphere. The mixture was then stirred at rt for 3 hours. The solution was extracted with $CHCl_3$ (30 mL), and the extract was dried over anhyd. $MgSO_4$. After removal of the solvent, azacyclophane **12** was obtained as colorless crystals (0.16 g, 39% from **14** and **15**).

Physical data: mp 289–292°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 1.44 (s, 18H), 4.98 (s, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C = 29.0, 40.1, 41.7, 115.5, 145.0 (J_{CF} = 253 Hz), 177.9. ^{19}F NMR (282 MHz, $CDCl_3$). δ_F = −142.0 (s). IR (neat) ν_{max} 1638 cm^{-1} (C=O). Anal. Calcd for $C_{26}H_{26}F_8N_2O_2$: C, 56.73; H, 4.76; N, 5.09. Found: C, 56.67; H, 4.59; N, 5.04. HRMS (FAB) Calcd. for $C_{26}H_{27}F_8N_2O_2$: 551.1946. Found: 551.1919 ([M + H]).

4.2 | Cage diene 13

Five solutions of azacyclophane **12** (5 × 2.0 mg, 5 × 3.6 μmol) in CH_2Cl_2 (5 × 2 mL) was purged with nitrogen and irradiated at 300 nm for 90 minutes at rt in Pyrex NMR tubes. After removal of the solvent under reduced pressure, the residue was washed with EtOH to afford cage diene **13** as colorless crystals (7.0 mg, 70%).

Physical data: mp > 280°C dec. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 1.31 (s, 18H), 3.79 (d, 4H, J = 12.5 Hz), 4.62 (d, 4H, J = 12.5 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C = 27.4, 39.4, 45.5, 59.5, 92.7 (d, J_{CF} = 274 Hz), 142.8 (d, J_{CF} = 269 Hz), 177.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ_F = −191.3 (s, 4F), −142.6 (s, 4F). IR (neat) ν_{max} 1634 cm^{-1} (C=O). HRMS (FAB) Calcd. for $C_{26}H_{27}F_8N_2O_2$: 551.1946. Found: 551.1966 ([M + H]).

4.3 | *o,o′*-dibenzene 22

Five Pyrex tubes, each containing a solutions of azacyclophane **12** (5 × 2.0 mg, 5 × 3.6 μmol) in

$CHCl_2CHCl_2$ (5 × 2 mL, purged with nitrogen), were irradiated at 300 nm for 90 minutes at rt to afford cage diene **13**. The solutions were then heated at 100°C for 0.5 hour. After removal of the solvent under reduced pressure, the residue was washed with EtOH to afford *o*,*o*′-dibenzene **22** as colorless crystals (4.8 mg, 48% from **12**).

Physical data: mp > 300°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 1.33 (s, 18H), 3.92 (d, 4H, J = 16.6 Hz), 5.22 (d, 4H, J = 16.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C = 28.6, 39.8, 42.9, 91.6 (d, J = 249 Hz), 111.4, 147.5 (d, J_{CF} = 271 Hz), 178.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ_F = −181.2 (s, 4F), −127.2 (s, 4F). IR (neat) ν_{max} 1634 cm^{-1} (C═O). HRMS (FAB) Calcd. for $C_{26}H_{27}F_8N_2O_2$: 551.1946. Found: 551.1918 ([M + H]).

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