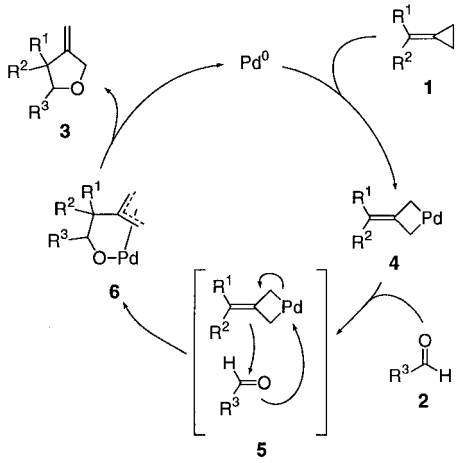

Scheme 3. A plausible mechanism for the palladium-catalyzed [3+2] cycloaddition of alkylidenecyclopropanes **1** with aldehydes **2**.

In conclusion, we are now in a position to synthesize various types of *exo*-methylene–tetrahydrofuran derivatives through the palladium-catalyzed [3+2] cycloaddition between methylenecyclopropanes and aldehydes. The present atom-economical reaction may be potentially useful for constructing biologically important tetrahydrofuran skeletons.

Experimental Section

3a: Compounds **2a** (1.5 mmol) and **1a** (0.5 mmol) were added to a mixture of $[Pd(PPh_3)_4]$ (11.5 mg, 0.01 mmol) and tributylphosphane oxide (4.4 mg, 0.02 mmol) under argon in a pressure vial. The reaction mixture was heated at 120 °C for 5 h, and then filtered through a silica-gel column using ethyl acetate as an eluent. The product was isolated by passing it through a silica-gel column, and purified by medium-pressure liquid column chromatography (silica gel) to afford the cycloadduct **3a**. IR (neat): $\tilde{\nu}$ = 2957–2870, 1663, 1468, 1379, 1148, 1053, 1011, 980, 885, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.79 (t, J = 7.5 Hz, 3H), 0.89–1.33 (m, 12H), 1.45 (td, J = 13.8, 4.0 Hz, 1H), 1.58 (t, J = 8.5 Hz, 2H), 4.45 (td, J = 13.0, 2.5 Hz, 1H), 4.60 (td, J = 13.5, 2.5 Hz, 1H), 4.78–4.79 (m, 2H), 5.02 (t, J = 2.0 Hz, 1H), 6.22 (d, J = 3.5 Hz, 1H), 6.32 (dd, J = 3.2, 2.0 Hz, 1H), 7.35 (dd, J = 2.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.86, 14.00, 23.28, 23.33, 25.78, 26.06, 32.52, 34.40, 51.79, 71.06, 82.82, 103.97, 107.61, 110.00, 141.56, 152.95, 153.45; HR-MS (EI): calcd for $C_{17}H_{26}O_2$: $[M]^+$ 262.1932, found 262.1932.

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A Seven-Membered Carbon-Ring-Fused Phthalocyanine Analogue in which the π System Changes during Dehydrogenation/Hydrogenation Cycles**

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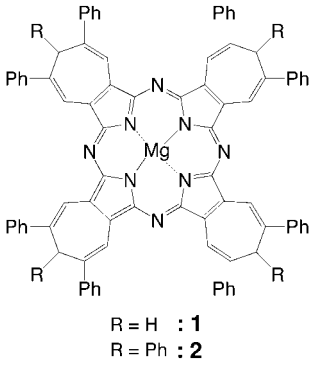
Phthalocyanines (Pcs) have been the subject of intensive study in a variety of academic and commercial fields. For example, they have industrial applications as dyes and pigments, photoconducting reagents in photocopiers, catalysts for removing sulfur from crude oil, deodorants, in the photodynamic therapy of cancer, and as germicides.[1] However, Pc analogues which contain seven-membered carbon rings instead of benzene rings have so far not been reported.[2] Herein we report the first example of this kind of Pc analogue, namely, compound **1**. This compound contains four fused cycloheptatriene (CHT) rings on the periphery of the parent tetraazaporphyrin skeleton. Cycloheptatriene is well known for being able to convert between nonaromatic CHT and the aromatic tropylium cation through a redox reaction during the elimination/recombination of a hydride ion (H^-).[3] Accordingly, we considered that it might be possible to adjust the size of the π-conjugation system in **1** by dehydrogenation/hydrogenation of the CHT



R = H : **1**
R = Ph : **2**

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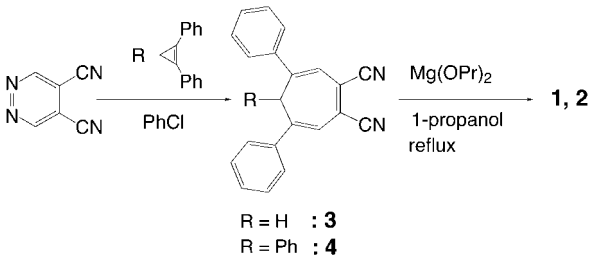
moiety. Compound **1** is, therefore, not only new but can also vary the size and shape of the π-conjugation system. As will be described below, the addition of dehydrogenation/hydrogenation reagents has succeeded in repeatedly and reversibly producing electronic absorption spectra which are indicative of expansion/reduction of the π system.[4] Compound **2**, which has a similar structure to **1**, has also been prepared and studied.

The starting aromatic *ortho*-dinitriles for compounds **1** and **2**, namely, 1,6-diphenyl-3,4-dicyanocycloheptatriene (**3**) and 1,6,7-triphenyl-3,4-dicyanocycloheptatriene (**4**), respectively, were synthesized by treating an equimolar amount of 4,5-dicyanopyridazine[5] and 1,2-diphenylcyclopropene[6, 7] or 1,2,3-triphenylcyclopropene[6, 7] in chlorobenzene at 80 °C for 5 h or at 120 °C overnight, respectively (Scheme 1). Compounds **3** and **4** were isolated as yellow needles after chromatographic separation on silica gel using a mixture of hexane/ethyl acetate (5/1) as eluent, and recrystalization from mixtures of these two solvents. Compounds **1** and **2** were obtained by tetramerization of **3** and **4** in the presence of magnesium in propanol at 140–150 °C for 12–15 h.[4] Purification was performed by silica gel (CH_2Cl_2/MeOH 100/1), alumina (Act. V, $CHCl_3$), and gel-permeation (Bio-beads SX-2, $CHCl_3$) column chromatography, followed by preparative chromatography on alumina ($CHCl_3$/MeOH 100/1). Satisfactory spectroscopic data were obtained for **1** and **2**,[8] with the most interesting data being the FAB-MS data of **1** and **2**. Compound **2** showed a parent ion peak [M^+] at the expected m/z 1505, and the isotropic distribution pattern agreed well with the theoretical pattern, while the high-resolution mass spectral pattern of **1** appears to be a superimposition of the species [M^+] and [$M^+ - H$]. Since compounds having good anionic leaving groups produce cationic fragments after elimination of this kind of group, the above mass spectra of **1** may be an indication that H^- is prone to be liberated from **1**.



Scheme 1. Synthesis of **1** and **2**.

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1** in $CHCl_3$. Although the Q band position is at a relatively long wavelength relative to those of normal Pcs, the absorption spectrum has characteristics of tetraazaporphyrins (TAPs) with approximate D_{4h} symmetry.[9] The red-shifted Q band arises from the expansion of the π system by the fused CHT units and the substituent effect of the phenyl groups, while the Soret band is sharper than found for Pcs. A broad, weak band lying between the Q and Soret bands is similar to a band often seen in the spectra of TAPs, and may be assigned as a n (aza or pyrrole nitrogen) →π* electronic transition.[10] One and three Faraday

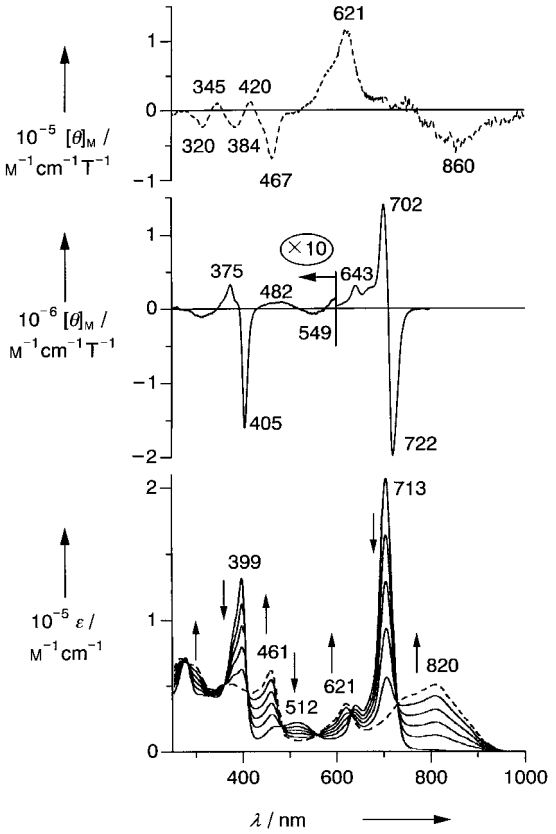


Figure 1. Development of the electronic spectra of **1** by the addition of DDQ (bottom), and its MCD spectra before (middle) and after (top) addition of DDQ in chloroform. The dashed lines denote the spectra at [DDQ]:[**1**] = 1:1.

A-term-type curves are observed in the Q and Soret band regions, respectively, in the MCD spectrum, which suggests that there are several orbitally degenerate excited states.[9]

The redox potentials were measured in *o*-dichlorobenzene containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}). The first oxidation, and first and second reductions of **1** were detected at 0.15, −1.39, and −1.73 V versus the ferrocenium/ferrocene (Fc^+/Fc) couple, respectively, while those of **2** were found at 0.26, −1.36, and −1.70 V, respectively; in comparison those for tetra-*tert*-butylated MgPc [Mg{(*t*Bu)$_4$Pc}] appear at −0.02, −1.64, and approximately −2.0 V.[11] The differences in potential between the first oxidation and reduction couples (1.54 and 1.62 V) are similar to those of normal Pcs (approximately 1.5–1.7 V).[12] In addition, all the couples were reversible one-electron processes and therefore could be assigned to ligand oxidation and reduction not involving hydrogen atoms of the CHT moiety. Accordingly, chemical dehydrogenation/hydrogenation was examined using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as the dehydrogenation reagent (Figure 1). The Q band at 713 nm disappeared with an increasing concentration of DDQ at room temperature, and a new peak developed in the red region at 820 nm. The spectral changes became saturated when [DDQ]:[**1**] = 1:1. Further addition of DDQ did not cause any spectroscopic change. In addition, many isosbestic points were detected throughout the whole spectral region during this process, which indicate that these changes are

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occurring between two distinct systems. We were able to detect the $[M^+ - H]$ peak (that is m/z 1200) in the mass spectrum of the solution containing an equimolar amount of **1** and DDQ. To further confirm that the above spectroscopic change is the result of the expansion of the π system (namely removal of H^- from the CHT moiety), the following experiments were carried out: a) EPR measurements on the solution containing an equimolar amount of **1** and DDQ: DDQ has a highly positive reduction potential (0.51 V[13] versus Fc^+/Fc). Accordingly, an electron transfer from **1** to DDQ may occur to produce an electron-oxidized, EPR-detectable species. This possibility appears to be ruled out since the solution was EPR-silent.[14] b) Variation of the quinone molecules: DDQ has cyano groups which can coordinate to the magnesium ions of **1**. In addition, since it is a flat, electron-deficient molecule, it may form a charge-transfer complex with **1** through π–π interactions. In order to rule out these as possible causes of the spectroscopic changes seen in Figure 1, quinones with different structures and reduction potentials were tried instead of DDQ. These were, in order of decreasing oxidation ability: tetrachloro-1,2-benzoquinone (*o*-chloranil, reduction potential = 0.38 V[13] versus Fc^+/Fc), tetrachloro-1,4-benzoquinone (*p*-chloranil, 0.22 V[13]), and 1,4-benzoquinone (−0.05 V[13]). *o*-Chloranil gave similar spectroscopic changes at room temperature as observed when DDQ was used (Figure 1), while a similar change was only observed for *p*-chloranil when the solution was heated or left for a long period (about 12 hours). The use of 1,4-benzoquinone, which has the weakest oxidation strength, did not yield any spectroscopic changes even after lengthy heating. Thus, these experiments using several types of quinone indicate that the changes in Figure 1 are not caused by coordination of the DDQ molecule to the Mg ion in **1** nor by the quinone structure, but are a result of the hydrogen-extraction power. c) Spectroscopic change on addition of DDQ to the metallotetraazaporphyrin (MtTAP): In order to support the conclusion that the spectroscopic changes depicted in Figure 1 are associated with the CHT moiety, a comparative experiment was performed in which DDQ was added to a solution of [Mg{(tBu)$_4$TAP}] in chloroform. Although TAP is a parent molecule of **1**, the addition of DDQ ([DDQ]:[**1**] = 1:1) did not produce any spectroscopic changes, which implies that the changes shown in Figure 1 on addition of DDQ are associated with the CHT moiety of **1**. d) Comparison of compounds **1** and **2** on addition of DDQ: A similar spectroscopic change occurred very slowly (by about two orders of magnitude) when DDQ was added to **2**. This more-difficult dehydrogenation correlates with the structural change from **3** to **4**,[3c] that is, from a CHT structure having two hydrogen atoms to one with one hydrogen atom and one phenyl group at the seventh position. It is known that dehydrogenation of an alkane to an alkene becomes more difficult when bulky substituents are linked to the same carbon atom as that of the leaving hydrogen atom.[3c, 15] Therefore, this experiment further supports the suggestion that the dehydrogenation in **1** occurs at the seventh position of the CHT moiety. e) Determination of the MCD spectra on addition of DDQ: After the addition of DDQ ([DDQ]:[**1**] = 1:1), the MCD spectra changed as shown by the dashed line in Figure 1, with peaks appearing roughly at the positions of the absorption peaks (Faraday *B* terms). This observation indicates that the symmetry of the π-conjugation system of **1** is lowered from D_{4h}, thus agreeing with a chromophore with C_{2v} symmetry when one CHT ring is oxidized.

The above data indicate that one CHT ring in **1** is aromatized by the action of DDQ (dehydrogenation), which is in agreement with a previous report that DDQ eliminates H^- ions from cycloheptatrienes.[3a] The reverse spectroscopic change was observed repeatedly when $LiAlH_4$, a hydrogenation reagent, was added, which is also in accord with the previous report that a tropylium cation accepts H^- ions to return to cycloheptatriene.[3b] Thus, we have succeeded for the first time in reversibly and repeatedly changing the size and symmetry of the π system of Pc derivatives by a new concept using a dehydrogenation/hydrogenation process.

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[6] **3** is a new compound, but was synthesized in 56% yield using a method similar to that for **4**.[7] M.p. 189.2–190.9 °C; elemental analysis calcd for $C_{21}H_{14}N_2$: C 85.69, H 4.79, N 9.52; found: C 85.64, H 5.07, N 9.45; IR (KBr): $\tilde{\nu}$ = 2361.2, 2218.4, 1558.7, 1444.9, 846.9, 760.0, 692.5 cm^{-1}; EI-MS: m/z: 294 $[M^+]$; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 2H), 6.81 (s, 2H), 7.3–7.5 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.7, 117.1, 120.7, 122.1, 127.7, 129.0, 130.1, 137.2, 140.1. **4** is a known compound,[7] but NMR and mass spectral data were not reported. Our NMR and mass spectral data for **4** are as follows: ^1H NMR (400 MHz, $CDCl_3$): δ = 5.92 (s, 1H), 6.95 (s, 2H), 7.1–7.2 (m, 5H), 7.4–7.6 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.5, 116.7, 119.6, 122.8, 126.3, 127.6, 128.0, 128.3, 129.2, 130.3, 137.2, 139.8, 145.2; EI-MS: m/z: 370 $[M^+]$.

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[8] Representative data. **1**: elemental analysis calcd for $C_{84}H_{56}N_8Mg \cdot 3H_2O$: C 80.34, H 4.98, N 8.92; found: C 80.21, H 4.96, N 9.33; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 713 (20.4), 645 (3.8), 512 (2.5), 399 (13.3), 277 nm (7.4). **2**: elemental analysis calcd for $C_{108}H_{72}N_8Mg \cdot 2H_2O$: C 84.12, H 4.97, N 7.27; found: C 83.77, H 5.30, N 7.10; FAB-MS: m/z: 1505.6 $[M^+]$; UV/Vis ($CHCl_3$): λ_{max} ($\varepsilon \times 10^{-4}$) = 718 (14.3), 651 (2.6), 516 (1.7), 404 (9.4), 277 nm (5.3).

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[14] Indeed a Pc oxidized by DDQ generally shows EPR signals near $g = 2$, which is characteristic of organic radicals. See for example: P. Mu, T. Nakano, M. Handa, K. Kasuga, K. Sogabe, *Bull. Chem. Soc. Jpn*. **1991**, *64*, 3202, and references [11] and [12] therein.

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A Dense and Efficient Clathrate Hydrate Structure with Unusual Cages**

Konstantin A. Udachin, Christopher I. Ratcliffe, and John A. Ripmeester*

Clathrate hydrates, hydrogen-bonded networks of water molecules stabilized by the presence of guest molecules, are found in both natural[1] and industrial settings[2] and hence have considerable potential to affect human welfare.[3] As well, they are seen as ideal models for the hydration of hydrophobic bioorganic materials.[4] The three known hydrate structural families,[5, 6] structure (str.) I, II, and H, have the pentagonal dodecahedron (5^{12} cage) as a common feature. In fact, str. II and str. H are based on the stacking of layers of 5^{12} cages so that other polytypes are likely to exist as well.[7] Herein we report a new, highly complex hydrate structure that does not have 5^{12} polyhedra and contains two unusual cages, one of which has not been reported before. This new structure is denser than the other hydrate structures because of the low number of empty small cavities, and is likely to be a preferred structure for guests of intermediate dimensions at ambient or somewhat elevated pressures.

Dimethyl ether (DME) is one of a few guests[8, 9] that forms two distinct hydrates.[10] A phase diagram (not illustrated) shows a hydrate of composition $DME \cdot 17\,H_2O$ melting incongruently at $-20\,^{\circ}C$ (this hydrate was shown to be a str. II hydrate) and a lower hydrate of composition $DME \cdot 7\,H_2O$ melting incongruently at $-28\,^{\circ}C$. Evidence from dielectric and NMR spectroscopic measurements[11] suggested a highly anisotropic environment for the DME guest in the lower hydrate and this led to the supposition that the structure might be the same as that of the tetragonal bromine hydrate.[12] Below, we present the actual structure of the DME hydrate, which although it does have a number of cages in common with bromine hydrate, is unique and has several unusual cages.

The structure[13] of this hydrate is trigonal, space group $P321$, $a = 34.995$, $c = 12.368$ Å, and can be described as $12\,P \cdot 12\,T \cdot 24\,T' \cdot 12\,U \cdot 348\,H_2O$, where P is the $5^{12}6^3$ cage, also known from bromine hydrate, T is the well-known $5^{12}6^2$ cage from str. I hydrate, T′ is a previously unobserved cage designated as $4^15^{10}6^3$, and U is a small cage designated as $4^25^86^1$. The latter has been observed in the structure of one of the hydrates of propylamine.[5] The DME molecules reside in all three types of large cages in the structure, giving an overall composition of $DME \cdot 7.25\,H_2O$. There is no interaction between guest and host other than the van der Waals' contacts usual for the true clathrate hydrates. The T′ cage has not been recorded in either the hydrate[5] or clathrasil[14] literature, and thus this structure represents a new way[5] of filling three-dimensional space by stacking a novel combination of cages. The new hydrate falls outside the structural numbering scheme proposed by Jeffrey,[5] and we propose that the structure be known as structure T (from trigonal) hydrate.

The overall structure is shown in Figure 1, the constituent cages in Figure 2. The packing motifs resulting in the trigonal structure derive from several units with three-fold symmetry: clusters of three cages, where pairs of cages share a face so that the three have one common edge, or clusters of four where three cages are attached to a central cage by sharing a face. The guest positions in the three cages are disordered but quite well defined: a single position can be seen for each DME methyl group, whereas multiple positions are observed for the oxygen centers. As in previous work on hydrates,[15] ^2H NMR spectroscopy has shown the disorder to be dynamic. For samples corresponding to the str. II composition, the lineshape in the ^2H NMR spectrum is isotropic, as expected for DME undergoing rapid reorientation in the large pseudospherical $5^{12}6^4$ cage. Str. T shows an anisotropic lineshape

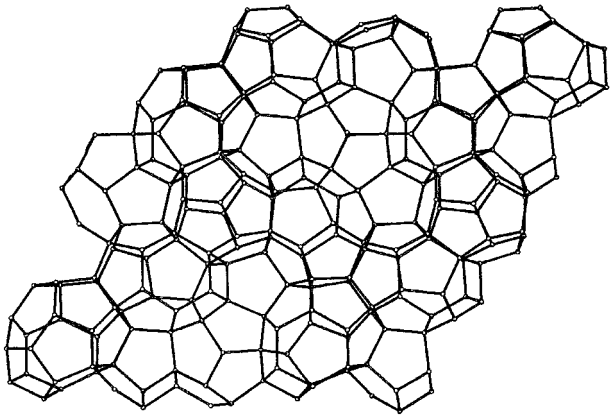

Figure 1. General view of the str. T hydrate as determined by single crystal X-ray diffraction.

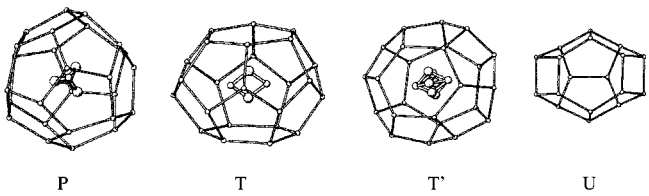

Figure 2. View of the cages in the str. T hydrate; the large cages show the location of the disordered DME guest.

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