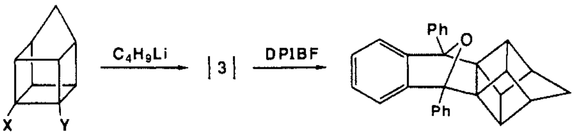
ab initio molecular orbital calculations of the olefin strain energies (OSE) of these and several other pyramidalized alkenes.[4] The calculations predict that cubene (**2**) should have only a slightly larger OSE than **1**, $n = 1$, which led us to conjecture that **2** should be preparable by the same type reaction that we used to generate **1**, $n = 1$.[4] In the following communications Eaton and Maggini report experiments that confirm this prediction.[5] In this communication we report our successful generation of homocub-4(5)-ene (**3**) by an analogous route.

Our choice of **3** as a molecule with which to test our prediction was based on the existence of a published route to a promising precursor (**4**),[6] coupled with the expectation that the additional methylene bridge in homocubene would not substantially decrease the OSE from that computed for cubene. This surmise was tested by ab initio calculations on **3** and its hydrogenation product, homocubane. At the 6-31G* TCSCF level of theory the hydrogenation energy of **3** was actually computed to exceed that of **2**[4] by 7.4 kcal/mol.[7]



8

4, X=Br, Y=CO_2H
5, X=Y=Br
6, X=Br, Y=I
7, X=C_4H_9, Y=I

In order to prepare a vicinal dihalide for dehalogenation to **3**, bromoacid **4** was subjected to a modified Hunsdiecker reaction.[8] Irradiation of 107 mg of **4** in 2.5 mL of CH_2Cl_2 containing 60 mg of HgO, 49 mg of $MgSO_4$, and 96 mg of Br_2 with a 60-W incandescent lamp afforded dibromide **5**[9] in 50% yield. However, attempts to dehalogenate **5** by reaction with *n*-butyllithium in THF at −78 °C[1] led only to recovered starting material.

In order to prepare a dihalide that might prove more reactive toward dehalogenation, the modified Hunsdiecker reaction was repeated, but with iodine in place of bromine. Bromoiodide **6**[9] was obtained in 90% yield and subjected to dehalogenation with 1.1 equiv of *n*-butyllithium in THF at −78 °C in the presence of diphenylisobenzofuran (DPIBF). After warming the reaction mixture to room temperature and adding water, a CH_2Cl_2 solution of maleic anhydride was added to quench the unreacted DPIBF. The DPIBF adduct of maleic anhydride and unreacted maleic anhydride were precipitated from the solution by addition of pentane,[10] and the pentane soluble fraction was evaporated to afford an adduct of **3** with DPIBF in 50% yield.

The crude adduct was purified by recrystallization from pentane at −30 °C to give white crystals, mp 157–8 °C. The exact mass (calcd for $C_{29}H_{22}O$ 386.1671, found 386.1669), ^1H NMR ($CDCl_3$) [δ 1.54 (d, 1 H, J = 11.0 Hz), 1.63 (d, 1 H, J = 11.0 Hz), 2.59 (m, 2 H), 3.15 (m, 2 H), 3.48 (m, 2 H), 6.86 (m, 2 H), 7.13 (m, 2 H), 7.38 (m, 2 H), 7.45 (m, 4 H), 7.59 (m, 4 H)], and proton decoupled ^{13}C NMR ($CDCl_3$) [δ 40.58, 41.46, 41.54, 42.19, 50.56, 91.00, 119.72, 126.72, 127.61, 127.92, 128.30, 136.50, 144.62] of the adduct were wholly consistent with the formulation of its structure as **8**.

When DPIBF was omitted from the reaction mixture and **6** was treated with excess *n*-butyllithium, the product **7**[9] of formal replacement of the bromine in **6** with an *n*-butyl group was the major product. The same product **7** was formed, but in smaller amounts, when DPIBF was present to trap homocub-4(5)-ene (**3**).

That formation of **7** does not occur simply by exchange of the bromine in **6** with *n*-butyllithium is indicated by the unreactivity of dibromide **5** toward *n*-butyllithium, the expectation that the iodine would be more reactive than the bromine in **6** toward this reagent, and the isolation of **8** when DPIBF is present in the reaction mixture as an olefin-trapping reagent. The route by which **7** is generated presumably involves formation of homocub-4(5)-ene (**3**), addition of *n*-butyllithium to the pyramidalized double bond in **3**, and reaction of the resulting tertiary alkyllithium with either the *n*-butyliodide produced in the first step of the reaction sequence or with unreacted **6**. A similar mechanism has been invoked by Wiberg in order to explain the formation of 1-bromo-4-*n*-butylbicyclo[2.2.0]hexane from the reaction of 1-bromo-4-chlorobicyclo[2.2.0]hexane with *n*-butyllithium.[11] Alkyllithium addition to the double bond of **2** also accounts for the products observed by Eaton and Maggini.[5,12]

The results reported herein provide confirmation of the theoretical prediction that, as in the case of **1**, $n = 1$,[1] a highly pyramidalized double bond can be introduced into the (homo)cubane skeleton by dehalogenation of a vicinal dihalide with *n*-butyllithium. Like bicyclo[2.2.0]hex-1(4)-ene,[11] both cubene (**2**)[5] and homocub-4(5)-ene (**3**) react with alkyllithium reagents, and these alkenes can be trapped as Diels–Alder adducts with dienes. Additional chemistry of **3** and its direct spectroscopic observation are both under investigation.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. 3, 116531-30-7; **4**, 106684-70-2; **5**, 116503-52-7; **6**, 116503-53-8; **7**, 116503-54-9; **8**, 116503-55-0; DPIBF, 5471-63-6.

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(4) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

(5) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, following communications in this issue. We thank Professor Eaton for informing us of his results and for agreeing to simultaneous publication.

(6) Klunder, A. J. H.; Ariaans, G. J. A.; v. d. Loop, A. A. R. M.; Zwanenberg, B. *Tetrahedron* **1986**, *42*, 1903.

(7) The 6-31G* TCSCF energy calculated for homocubene and the SCF energy for homocubane at their 3-21G SCF optimized geometries were, respectively, −345.2380 and −346.5021 hartrees.

(8) Cristol, S. J.; Firth, W. C., Jr. *J. Org. Chem.* **1961**, *26*, 280. Meyers, A. I.; Fleming, M. P. *J. Org. Chem.* **1979**, *44*, 3405.

(9) All new compounds gave spectroscopic and analytical data that were consistent with the assigned structures.

(10) We found that the adduct rearranged on attempted chromatographic separation of it from this mixture.

(11) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E.; Dailey, W. P.; Burgmaier, G. J.; Bailey, W. F.; Warner, P. *Tetrahedron* **1986**, *42*, 1895.

(12) The difference between the type of addition product obtained by Eaton and Maggini[5] and that (**7**) isolated by us is attributable to their use of excess *tert*-butyllithium for generating **2**. Under these reaction conditions, iodocubane derivatives, analogous to **7**, would not be expected to be formed.

Cubene (1,2-Dehydrocubane)

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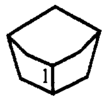
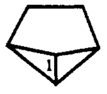
Received June 3, 1988

In recent years we have developed excellent methodology for the synthesis of variously substituted cubanes.[1] This allows us to start with the cubane system, already an extraordinary structure[2] and move outward in our continuing exploration of the limits of bonding in organic compounds.[3] We report now on the synthesis and trapping of 1,2-dehydrocubane (**1**), colloquially "cubene", the most highly pyramidalized olefin yet known.[4]

1



2



3

4

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(1) (a) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. (b) Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *Ibid.* **1987**, *109*, 948. (c) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055. (d) Eaton, P. E.; Cunkle, G. T. *Ibid.* **1986**, *27*, 6055.

(2) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

(3) Eaton, P. E.; Hormann, R. E. *J. Am. Chem. Soc.* **1987**, *109*, 1268. (b) Eaton, P. E.; Hoffmann, K.-L. *Ibid.* **1987**, *109*, 5285.

(4) Pyramidalization is a deviation from planarity. For an olefinic carbon the pyramidalization angle is that between the plane defined by that carbon and its two substituents with the line passing through both olefinic carbons.

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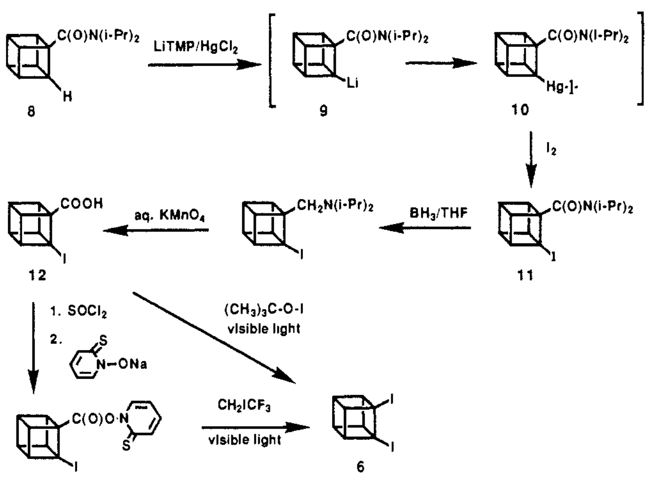
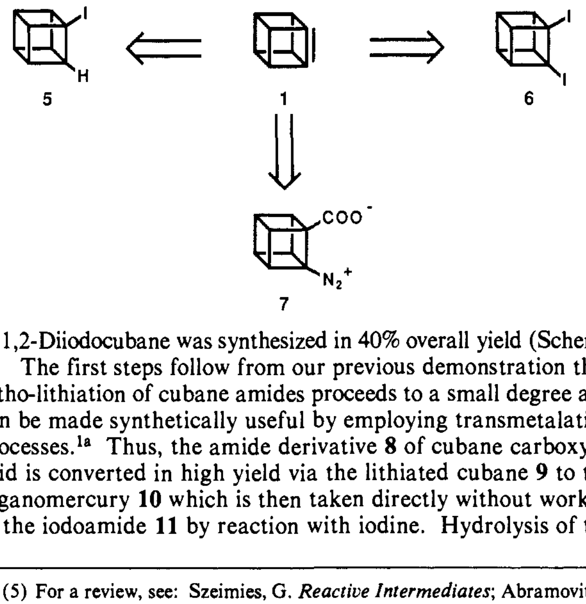
Scheme I



Highly pyramidalized olefins are a special class of compounds.[5] Much of the classical π bonding between parallel p orbitals of adjacent sp^2 hybridized carbons is lost. The rehybridization necessary to accommodate the geometric demands of the skeletons of such systems equates to the introduction of substantial s character into the olefin "bond". Amongst particularly important symmetric examples are the bridged bicyclooctenes (e.g., **2**),[6] the bridged bicyclobutenes (e.g., **3**),[7] and homocub-4(5)-ene (**4**), reported in the preceding communication by Hrovat and Borden.[8] Ab initio calculations at the 6-31G* TCSCF level by Hrovat and Borden give a pyramidalization angle[4] of approximately 53° in **2**, 48° in **3**, and 84° in cubene.[9] The departure of cubene from an "eyeballed" pyramidalization angle of 90° arises in forced flattening of the rigid cubane skeleton.

Potential precursors for cubene include iodocubane (**5**), 1,2-diiodocubane (**6**), and the cubane diazonium carboxylate **7**. We leave consideration of **7** and its amino acid precursor to a later paper. In this communication we present the preparation and behavior of the iodocubanes.



1,2-Diiodocubane was synthesized in 40% overall yield (Scheme I). The first steps follow from our previous demonstration that ortho-lithiation of cubane amides proceeds to a small degree and can be made synthetically useful by employing transmetalation processes.[1a] Thus, the amide derivative **8** of cubane carboxylic acid is converted in high yield via the lithiated cubane **9** to the organomercury **10** which is then taken directly without workup to the iodoamide **11** by reaction with iodine. Hydrolysis of the *N*,*N*-diisopropylcarboxamido group in **11**, as in other cases, is exceedingly difficult and cannot be achieved under even very strong basic conditions. Although the cubane system is remarkably stable to acid, the conditions for effecting acid hydrolysis of the amide are too strenuous and destroy the skeleton. Fortunately, in what should prove a general procedure, we have found that reduction of **11** with $BH_3\cdot THF$ followed by oxidation of the resulting amine with potassium permanganate in aqueous base provides for its "hydrolysis" to the carboxylic acid **12**.

Methodology for the conversion of **12** to diiodocubane takes its cue from preparations of the monoiodo compound. Iodocubane was first prepared satisfactorily by Della and Abeywickrema from cubane carboxylic acid by irradiation with *tert*-butyl hypoiodite.[10] In our laboratory, Tsanaktsidis has found that it can be made more cleanly and in better yield (80%) by radical-induced decomposition of the thiopyridone *N*-oxide ester of the acid in excess 2-iodo-1,1,1-trifluoroethane.[11] Both of these Barton[12] procedures for iodinative decarboxylation work likewise for the preparation of 1,2-diiodocubane either from the iodo-acid **12** (see Scheme I) or directly from cubane-1,2-dicarboxylic acid, available as we shall report subsequently in 95% yield from **8** by a combination of metalation–transmetalation strategies. As cubane-1,4-dicarboxylic acid, the starting material for all these syntheses, is easily obtained,[13] there is no problem accumulating gram quantities of iodocubane and 1,2-diiodocubane.

Reaction of iodocubane with *n*-butyllithium in THF followed by quenching with methanol gives cubane along with some *n*-butylcubane, the latter formed presumably by alkylation of cubyllithium by connatal *n*-butyl iodide. Similarly, iodocubane undergoes primarily, perhaps exclusively, halogen–metal exchange on treatment with *tert*-butyllithium. Quenching the reaction mixture with methanol gives only cubane in significant amount; there is no alkylation product. Thus, there is no evidence to invoke the formation of cubene from iodocubane under these conditions. Apparently, the kinetic acidity of a cubyl hydrogen is insufficient for the conversion cubyl-H → cubyl-Li to compete with cubyl-I → cubyl-Li. Indeed, this was not unexpected; cubane itself does not react with alkyllithiums.[14]

Treatment of 1,2-diiodocubane with excess *tert*-butyllithium takes quite a different course. Reaction in THF at −70 °C followed by quenching with methanol produces *tert*-butylcubane (**13**) and 2-*tert*-butylcubylcubane (**14**), in a ratio of about 1:2, along with a trace of cubylcubane.[15] The structures of the first two of these products follow convincingly from NMR and mass spectral data. The familiar pattern of a monosubstituted cubane is apparent in the 500 MHz PMR spectrum of **13**: δ 0.80 (s, 9 H, *t*-Bu), 3.76 (m, 6 H), 4.00 ppm (m, 1 H). Appropriately, in the 100 MHz CMR spectrum of this molecule with C_{3v} symmetry there are only resonances for four different kinds of cubyl carbons [δ 42.9 (d, 154 Hz, 3 C), 45.6 (d, 153 Hz, 3 C), 48.8 (d, 155 Hz, 1 C), 66.6 ppm (s, 1 C)] along with the two expected for the *tert*-butyl group. The NMR spectra of **14** are more complex than those of **13** but still can be analyzed. The cubane region is a conglomerate of absorptions due to a monosubstituted cubane and a 1,2-disubstituted cubane. The requisite ten different cubane carbon signals are apparent in the carbon spectrum. Absolute confirmation of the structure of **14** was obtained by X-ray crystallographic analysis at the Naval Research Laboratory

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(5) For a review, see: Szeimies, G. *Reactive Intermediates*; Abramovitch, R., Ed.; 1983; Vol. 3, p 299.

(6) Yin, T.-K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544.

(7) (a) Szeimies, G.; Harnisch, J.; Baumgärtel, O. *J. Am. Chem. Soc.* **1977**, *99*, 5183. (b) Szeimies-Seebach, U.; Harnisch, J.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 848.

(8) Hrovat, D. A.; Borden, W. S. *J. Am. Chem. Soc.*, preceding paper in this issue. We thank Professor Borden for informing us of his work and agreeing to simultaneous publication.

(9) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710. See, also: Schubert, W.; Yoshimine, M.; Pacansky *J. Phys. Chem.* **1981**, *85*, 1340.

(10) Abeywickrema, R. S.; Della, E. E. *J. Org. Chem.* **1980**, *45*, 4226.

(11) Tsanaktsidis, J.; Eaton, P. E., to be submitted for publication.

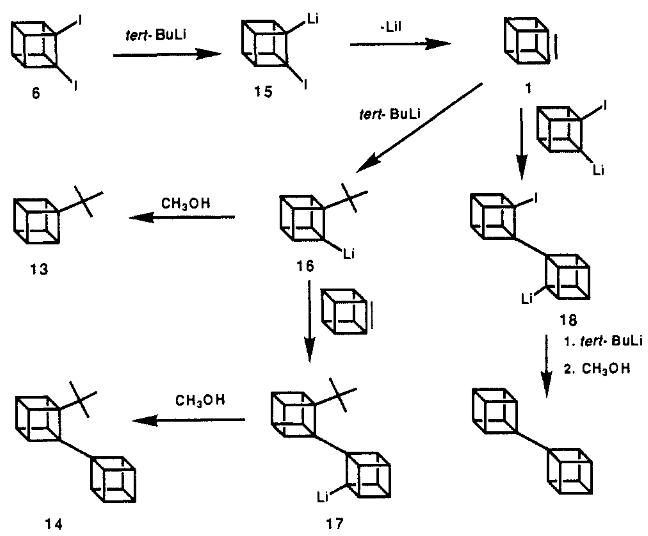
(12) (a) Barton, D. H. R.; Faro, H. P.; Serebryakov, E. P.; Woolsey, N. F. *J. Chem. Soc.* **1965**, 2438. (b) Barton, D. H. R.; Lacher, B.; Zard, S. Z. *Tetrahedron* **1987**, *43*, 4321 and references therein.

(13) (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc. 1* **1964**, *86*, 962, 3157. (b) Chapman, N. B.; Key, J. M.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 3860. (c) Luh, T.-Y.; Stock, L. M. *Ibid.* **1972**, *37*, 338.

(14) The reaction between cubane and *tert*-butyllithium should give cubyllithium, but it does not under any conditions tried to date. This is surely a problem with the kinetics of reaction. Many strained hydrocarbons show the same behavior. To our knowledge, amongst strained hydrocarbons only bicyclobutanes react readily with alkyllithiums to give the metal derivative.

(15) The GC/MS trace for the reaction mixture shows also a component with *m*/*e* of 204. This *m*/*e* may be due to a ion fragment from cubyl cubane or a dimer of cubene. The matter is under investigation.

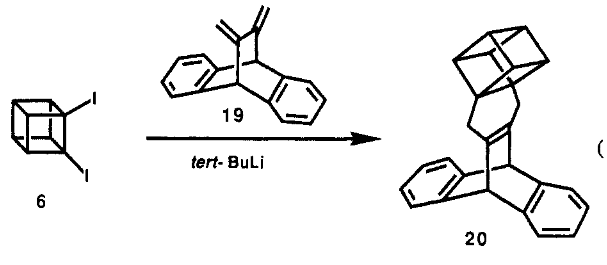
Scheme II



(Washington) as reported in the following communication along with the identification of cubylcubane.[16]

In light of the halogen–metal exchange which occurs on treatment of iodocubane with *tert*-butyllithium, we propose that the reaction of 1,2-diiodocubane with *tert*-butyllithium is initiated by formation of 2-lithioiodocubane (**15**, Scheme II). On loss of lithium iodide this forms cubene (**1**). Addition of *tert*-butyllithium, present in excess in the solution, to this very strained olefin gives the cubyllithium **16**, the precursor of the *tert*-butylcubane isolated. (Note that iodocubane does not give **13** under these conditions.) Addition of **16** to cubene gives **17**, the precursor of 2-*tert*-butylcubylcubane. Finally, the lithium compound **15** could add to cubene to give **18**, which on halogen–metal interchange would give a possible precursor for cubylcubane. All of these reactions proceed by anionic additions to the strained olefin bond. Szeimies and co-workers have already demonstrated abundantly that organolithiums add rapidly to other highly pyramidalized olefins such as the dehydroquadricyclanes[17] and the bridged bicyclobutenes.[6]

Reaction of 1,2-diiodocubane at room temperature with *tert*-butyllithium in benzene containing 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene (**19**)[18] gives the Diels–Alder adduct **20**, mp 204–205 °C, in 64% isolated yield (eq 1).[19] The symmetry



(1)

of the adduct is apparent in its high field NMR spectra: there are only two different kinds of cubyl hydrogen in the compound [δ 3.55 (m, 4 H), 3.84 ppm (m, 2 H)] and three different kinds of cubyl carbon [δ 44.8 (d, 153 Hz, 2 C), 49.8 (d, 153 Hz, 4 C), 50.7 ppm (s, 2 C)], exactly as the assigned structure requires. The remote possibility that the cubane subsection had instead a cuneane skeleton was eliminated by measurement of the ^{13}C–H coupling constants. In the adduct none is higher than 155 Hz; if a cuneane had been present, ^{13}C–H coupling constants in excess of 170 Hz would have been found.[20] *Formal* Alder–Rickert cleavage to the diene and cubene is apparent in the mass spectrum of **20**. Whether or not this can be replicated in flash pyrolysis experiment remains to be seen. We shall report on this, on the metal complexes of cubene, and on its characterization as more information becomes available.

Acknowledgment. This work was supported by the National Institutes of Health (GM 36436). The NSF and the NIH, the latter through The University of Chicago Cancer Research Center (CA 14599), contributed substantially to the departmental instrument facility essential to this work. We are grateful to Professor Borden for prepublication access to his calculations on pyramidalized olefins and to Dr. Bashir-Hashemi for calling our attention to diene **19** and providing a sample.

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[16] Gilardi, R.; Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.*, following paper in this issue.

[17] Harnisch, J.; Baumgärtel, O.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 3370.

[18] Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641 and references therein.

[19] We have also trapped **1** in a Diels–Alder adduct with anthracene. The reaction is not as clean as with **19** as anthracene and *tert*-butyllithium react with one another.

[20] Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6366.

X-ray Structures of Cubylcubane and 2-*tert*-Butylcubylcubane: Short Cage–Cage Bonds[1]

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Received June 13, 1988

As described in the preceding communication about cubene,[2] the major isolable products from the reaction of 1,2-diiodocubane with *tert*-butyllithium are *tert*-butylcubane, a liquid at room temperature, and 2-*tert*-butylcubylcubane. While attempting to recrystallize the latter by slow evaporation of an *n*-octane solution we fortuitously obtained some crystals in which 2-*tert*-butylcubylcubane and cubylcubane had cocrystallized. Apparently, there was a small amount of cubylcubane formed in the reaction, and this was focused in the recrystallization procedure. The centric triclinic unit cell (Figure 1) contains three molecules:[3] two molecules of 2-*tert*-butylcubylcubane (related by a center of symmetry) and one molecule of cubylcubane, it being on a center of symmetry located at the midpoint of the bond linking the two cubane cages.

To within experimental error, the cubylcubane molecule displays (noncrystallographic) D_{3d} symmetry (Figure 2a). The cage bond lengths and angles in the two perfectly staggered cubyl portions are not significantly different from the values in cubane itself.[4] In 2-*tert*-butylcubylcubane (Figure 2b), although the substituent is nearly perfectly staggered relative to the cage, there are still distortions about it due to crowding, most notably lengthening of the C1a–C2a cubane edge to 1.606 (6) Å and opening of the C1b–C1a–C2a angle to 133° (cf. 1.551 Å and 125° in cubane). More interesting are the intercage bond lengths: 1.458 (8) Å in cubylcubane and 1.464 (5) Å in the *tert*-butyl derivative. These

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[1] This work was supported by the Office of Naval Research.

[2] Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.*, submitted for publication.

[3] Space group $P\bar{1}$, $a = 6.3110\ (7)$ Å, $b = 11.772\ (1)$ Å, $c = 13.341\ (1)$ Å, $\alpha = 85.61°$, $\beta = 81.18\ (1)°$, $\gamma = 87.71\ (1)°$. Formula unit, $[C_{20}H_{22}\cdot{}^{1}/_{2}C_{16}H_{14}]$; FW = 365.57; $Z = 2$; volume = 982.8 (2) Å^3; $D_{\text{calcd}} = 1.24$ mg mm^{-3}. Cu Kα X-rays, 2908 reflections observed, $T = 20$ °C, $R = 0.068$.

[4] Fleischer, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3889.

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