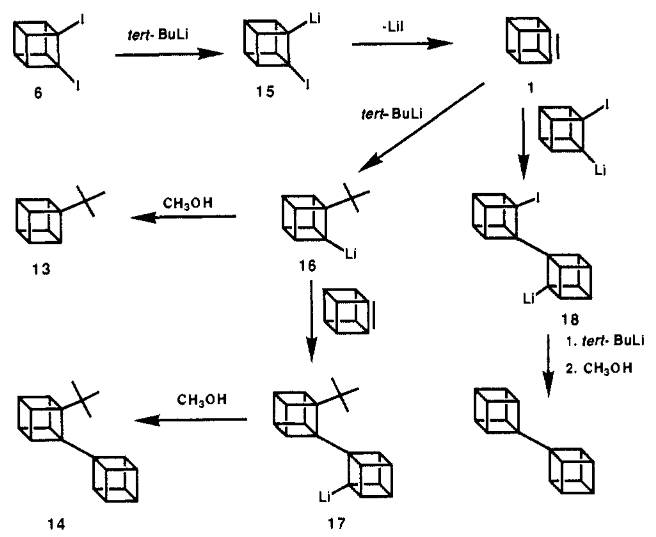
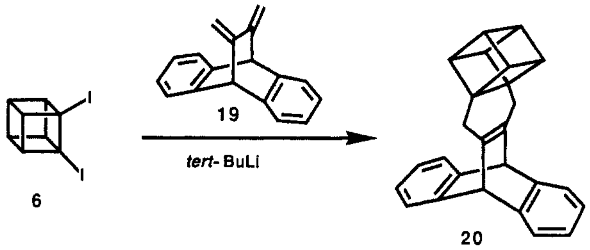
Scheme II



(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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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; $D_{calcd} = 1.24$ 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.

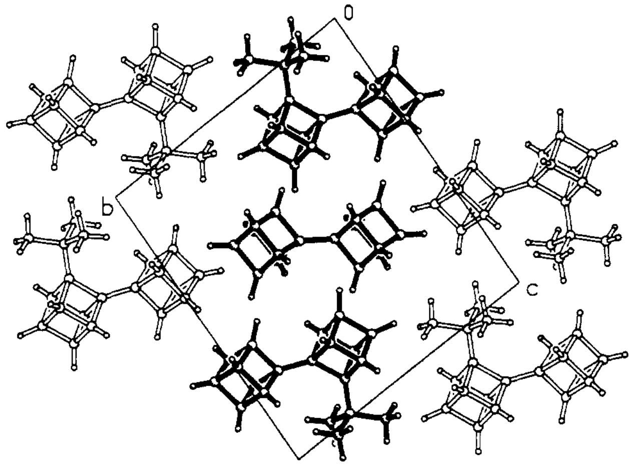

Figure 1. A view of the packing of the cocrystal of the title compounds down the shortest axis (*a*) of the unit cell. The central molecule is cubylcubane; all the surrounding molecules are 2-*tert*-butylcubylcubanes. The three emphasized molecules comprise the "contents" of one unit cell; the centroids of only these three lie inside the cell.

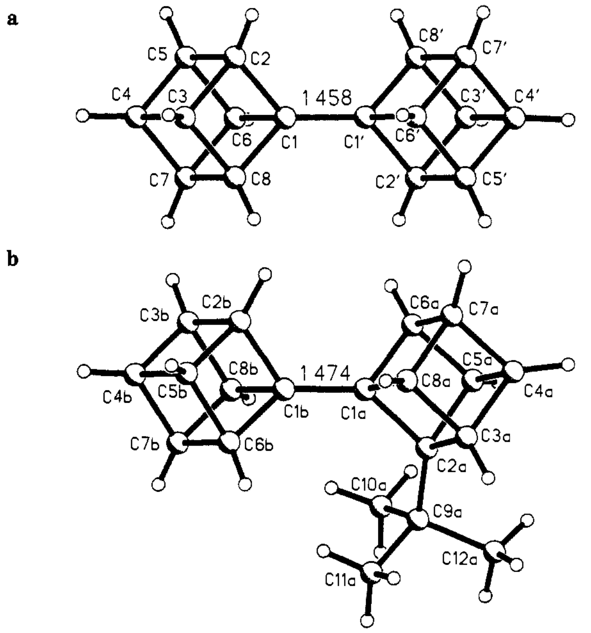

Figure 2. A computer graphic depiction of the X-ray structure of (a) cubylcubane and (b) 2-*tert*-butylcubylcubane. The intercage bond lengths given are in Å.

carbon–carbon bond lengths are *significantly shorter* than any recorded to date between carbons fully substituted by other carbon atoms. This phenomenon can be understood by considering a simple bonding picture for cubanes. The cage geometry is better accommodated by endocyclic orbitals richer in p character than the sp^3 hybrid of typical tetracoordinated carbon compounds. (Consider that pure p orbitals, like the internuclear connections in cubane, are orthogonal to one another.)' Correspondingly, the exocyclic orbitals on cubane are richer in s character[5] and form shorter, tighter bonds to substituents than would their sp^3 counterparts.[6] Put another way, the carbons of cubanes are pyramidalized past tetrahedral geometry and "pulled back" away from the substituent. There is less steric crowding in cubylcubane than would be found in a hexasubstituted ethane. In 1-adamantyladamantane, for example, the intercage bond is formed from pure (or nearly pure) sp^3-hybridized carbons and is 1.578 (2) Å long,[6a] 0.12 Å longer than in cubylcubane.

Recently Ermer and Lex reported the X-ray structure of cubane-1,4-dicarboxylic acid and specifically discussed the shortening of exocyclic cubane bonds and correlations between bond lengths and angle distortions in saturated organic molecules in a similar way.[7] They predicted that the central bond of cubylcubane would be shortened by 0.08 Å from the expected $C(sp^3)-C(sp^3)$ value. What would be the expected length for a *crystallographically determined* sp^3–sp^3 bond? Allen obtained 1.538 (1) Å from a set of 1798 crystal structure determinations of various types of compounds chosen to exclude errors due to heavy atoms.[8] However, the "normal" distance between two carbons that have no hydrogen substituents might well be longer. We searched the Cambridge Crystallographic Database[9] for all bond lengths between two connected carbons each substituted by three other carbons. This gave a sample of 138 distances: $\langle R \rangle = 1.572$ (35) Å. This compares well with the measured intercage distance in 1-adamantyladamantane. The intercage bond length in cubylcubane is 0.114 Å shorter, rather more than predicted.

The determination of the structures of cubylcubane and 2-*tert*-butylcubylcubane provides many new independent values for cubane bond lengths. If we assume that substituents only affect the length of adjacent cubane bonds, then the cubane edges which are hydrogen-substituted at each end should tend to be equal in length, with a certain random variation due to crystal packing forces and experimental errors. The values from all available X-ray CH–CH edge distances in cubane structures are

a	cubane[4]	1.551 (3) Å	$N = 2$
b	cubylcubane	1.553 (8) Å	$N = 9$
c	2-*tert*-butylcubylcubane	1.556 (6) Å	$N = 16$
d	1,4-dinitrocubane[10]	1.564 (2) Å	$N = 3$
e	1,3-dinitrocubane[11]	1.556 (5) Å	$N = 6$
f	1,4-dicarboxycubane[5]	1.560 (4) Å	$N = 6$

The estimated standard deviations given in parentheses are derived from the variation in each sample, not from the X-ray refinements. "N" gives the number of independently determined bond lengths in each structure. The three cubanes, d, e, and f, substituted with electron-withdrawing substituents have the slightly longer bond lengths, $\langle R \rangle = 1.559$ (1) Å with $N = 15$. When the values from cubanes a, b, and c are pooled, $\langle R \rangle = 1.555$ (1) Å with $N = 27$. If the CH–CH edges from all the structures are pooled together, they form a normal distribution with $\langle R \rangle = 1.556$ Å, $N = 42$, a sample esd of 0.006 Å, and an esd of the mean of 0.0010 Å. The oft-quoted X-ray value for cubane, 1.551 Å,[4] is lower than that found in any derivative, but it is not significantly different from the global mean.

Since the cubane structure was available at the time the MM2 molecule force field was set up, the stretch-bend parameters therein were chosen to reproduce its geometry fairly well (1.551 versus 1.557 Å).[12] It is informative to compare the structures of the new molecules reported here with MM2 predictions. Geometry optimizations of 2-*tert*-butylcubylcubane and cubylcubane, starting from the crystal coordinates, gave intercage bond lengths of 1.489 Å (0.025 Å longer than observed) and 1.486 Å (0.028 Å longer than observed), respectively. The average MM2 bond length predicted for the 16 CH–CH distances in 2-*tert*-butylcubylcubane is 1.558 (2) Å and the same for the 18 such bonds in cubylcubane. These values compare well with the observed 1.556 (6) Å in 2-*tert*-butylcubylcubane and 1.553 (8) Å in cubylcubane. A slight difference between predicted and observed values is apparent for

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[5] $J_{^{13}C-H}$ in cubane is 155 Hz, corresponding to ca. 31% s character, see: (a) Cole, T. W., Jr. Ph.D. Dissertation, The University of Chicago, 1966. (b) Della, E. W.; Hine, T. W.; Patney *J. Org. Chem.* **1977**, *42*, 2940.

[6] The discussions in (a) Alden, R. A.; Kraut, J.; Traylor, T. G. *J. Am. Chem. Soc.* **1968**, *90*, 74 and in (b) Dewar, M. J. S. *Hyperconjugation*; The Ronald Press Co.: New York, 1962; p 53ff are useful.

[7] Ermer, O.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *25*, 447. One of us (PE) is grateful to Prof. Ermer for interesting discussions on such matters.

[8] Allen, F. H. *Acta Crystallogr.* **1981**, *B37*, 890.

[9] Kennard, O.; Watson, D.; Allen, F.; Motherwell, W.; Town, W.; Rodgers, J. *J. Chem. Brit.* **1975**, *11*, 213.

[10] Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185.

[11] Stevens, E. D. University of New Orleans, private communication.

[12] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Eaton, P. E. *Tetrahedron Lett.* **1983**, *24*, 3697.

the bonds adjacent to the intercage bond; MM2 predicts 1.550 Å for all six of these bonds in cubylcubane, whereas they are observed to be 1.568 (9) Å, slightly longer than the other cube edges. A much larger difference exists between the prediction, 1.551 Å, and the observation, 1.606 (6) Å, for the cube edge between the intercage link and the *tert*-butyl substituent in 2-*tert*-butylcubylcubane. The origin of these differences is not clear; MM2 may treat the nonbonded interactions too softly and/or crystal packing forces may be responsible.

Supplementary Material Available: Data collection parameters and tables of atomic positional parameters, Cartesian coordinates, bond distances, bond angles, torsion angles, and anisotropic thermal parameters for cubylcubane and *tert*-butylcubylcubane (7 pages); table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

New Developments in Cubane Chemistry: Phenylcubanes

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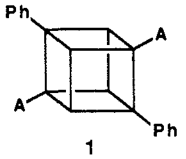
Received June 7, 1988

As part of a program of research directed toward developing novel energetic materials, we have prepared diphenylcubane diamide **1** and bromophenylcubane diamide **2**.



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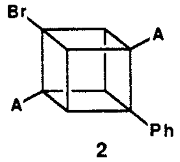
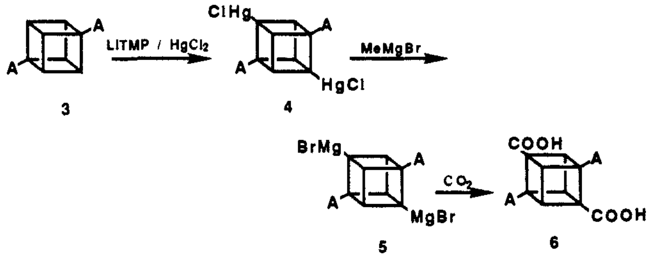


2

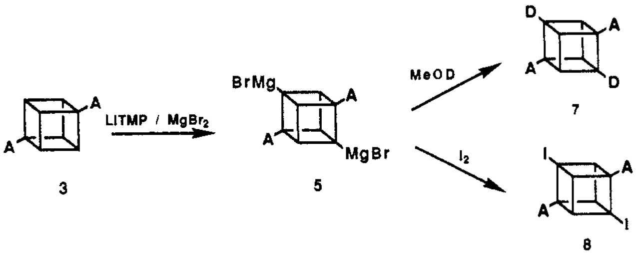
A = C(O)N[CH(CH$_3$)$_2$]$_2$

Since the first synthesis of cubane,[1] there has been a great deal of effort to functionalize the cubane skeleton. Eaton et al. have recently developed a methodology in which amido cubanes can be functionalized through a reverse transmetalation procedure.[2] For example, the reaction of cubane diamide **3** with an excess of lithium tetramethylpiperidide (LiTMP) and mercuric chloride gives compound **4**, which upon reverse transmetalation with CH$_3$MgBr, followed by carboxylation of intermediate **5**, furnishes diacid cubane diamide **6** in a reasonable yield.

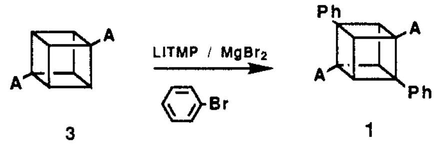


However, because of the high toxicity of organomercury compounds, scale-up of this method was limited. Therefore, it was desirable to undertake an alternate procedure in which the use of mercury compounds would be avoided. We now report the direct and successful synthesis of **5** and its application to the synthesis of phenylcubanes.

In our hands, the reaction of cubane diamide **3** with an excess of LiTMP/MgBr$_2$ in THF at 0 °C, followed by quenching the reaction mixture with CH$_3$OD or I$_2$ gave dideuteriated cubane diamide **7** and diiodocubane diamide **8** in 80% and 72% yields, respectively.



Perhaps the greatest significance of this procedure is that it presents a potential route for the synthesis of phenylcubanes. The synthesis of phenylcubanes has been the target of intensive studies over the last 30 years.[3] To the best of our knowledge, no conclusive evidence for introducing a phenyl group to the cubane skeleton has yet been reported. In our initial attempts, cross-coupling reactions of **4** with bromobenzene[4] or reaction of **8** with phenylboric acid[5] using palladium catalysts were not successful. However, the reaction of cubane diamide **3** with 10 equiv of LiTMP and 4.0 equivalents of MgBr$_2$·etherate in THF at 0 °C, followed by the addition of 10.0 equiv of bromobenzene, gave diphenylcubane diamide **1** in 53% yield.



The structure of **1** was clear from its ^{1}H NMR and mass spectra.[6] The 300 MHz ^{1}H NMR spectrum had six resonances at δ 0.60 (d, J = 6 Hz, 12 H), 1.28 (d, J = 6 Hz, 12 H), 3.06 and 3.20 (septets, J = 6 Hz, 2 H each), 4.45 (s, 4 H), 7.20–7.40 (m, 10 H). The EI mass spectrum shows a molecular ion at 510 with fragmentations at 467, 411, 382, 283, 252 (100), 128, and 100. Carbon-13 NMR and elemental analysis data were in agreement with the structure **1**.[7]

A reasonable mechanism for the formation of **1** is presented in Scheme I. In this postulated mechanism, a benzyne intermediate was formed in situ from the reaction of excess of LiTMP with bromobenzene.[8] Benzyne subsequently reacts with di-Grignard **5** to give intermediate **9**. When the reaction mixture was quenched with I$_2$, compound **10** was isolated in 25% yield.

[†] Mailing address: Geo-Centers, Inc., 762 Route 15 South, Lake Hopatcong, NJ 07849

(1) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

(2) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 948. Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055.

(3) For a review of earlier work, see: Barborak, J. C. Ph.D. Thesis: The University of Texas at Austin, 1968. Freedman, H. H. *J. Am. Chem. Soc.* **1961**, *83*, 2195. Büchi, G.; Perry, C. W.; Rob, E. W. *J. Org. Chem.* **1962**, *27*, 4106. Tsutsui, M. *Chem. Ind. (London)* **1962**, 780. Cookson, R. C.; Jones, D. W. *Proc. Chem. Soc.* **1963**, 115. Pawley G. S.; Lipscomb, W. N.; Freedman, H. H. *J. Am. Chem. Soc.* **1964**, *86*, 4725. Throndsen, H. P.; Wheatley, P. J.; Zeiss, H. *Proc. Chem. Soc.* **1964**, 357. Slobodin, Ya. M.; Khitrov, A. P. *Zh. Org. Khim.* **1970**, *6*, 1751. Slobodin, Ya. M.; Aleksandrov, I. V.; Khitrov, A. P. *Zh. Org. Khim.* **1977**, *13*, 1377.

(4) For cross-coupling reactions of mercury compounds, see: Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer Verlag: New York, 1985.

(5) For palladium-catalyzed cross-coupling of arylboronic acids with aryl halides, see: Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237. Sharp, M. J.; Snieckus, V. *Tetrahedron Lett.* **1985**, *26*, 5997.

(6) I am indebted to Dr. T.-H. Chen, ARDEC, for the mass spectra and to Dr. T. Axenrod, CCNY, for the NMR spectra.

(7) The X-ray structure of the reduction product of **1**, 1,4-bis(*N*,*N*-diisopropylaminomethylene)-2,7-diphenylcubane, shows an unusually short bond length of 1.484 Å for the phenyl–cubane C–C bond. Details of the X-ray structure will be published elsewhere.

(8) For the chemistry of benzyne, see: Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.

0002-7863/88/1510-7234$01.50/0