Building with Cubane-1,4-diyl. Synthesis of Aryl-Substituted Cubanes, *p*-[*n*]Cubyls, and Cubane-Separated Bis(arenes)[1]

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Abstract: On treatment with an organolithium 1,4-diiodocubane generates cubane-1,4-diyl, a highly reactive species, shown here to be a versatile precursor to numerous aryl substituted cubanes, available now for the first time in high yield. The diyl is demonstrated to provide a good route to bicubyl and its derivatives. A kind of "living polymerization" of the diyl is developed to give the *p*-[n]cubyls. These oligomers are rigid rods made up of cubanes linked together at the 1 and 4 positions, each cubane adding ~4.15 Å to the length. The properties of these rods, some more than 15 Å long, are discussed, as are methods for modifying their solubility. X-ray crystallographic analyses of some of these compounds are presented, with emphasis on packing parameters.

Background. In 1990 Eaton and Tsanaktsidis reported that reaction of 1,4-diiodocubane (**1**) with phenyllithium in diethyl ether at room temperature gave a good yield of 4-phenylcubyl iodide (**5**).[2] The reaction path, as outlined in Scheme 1, involves rapid iodine−metal exchange between **1** and phenyllithium to give (at equilibrium) a small concentration of 4-iodocubyl lithium (**2**). Loss of lithium iodide therefrom gives a halogen-free intermediate, demonstrated to be symmetric,[2] and dubbed 1,4-dehydrocubane (**3**). Addition of phenyllithium produces 4-phenylcubyl lithium (**4**). Finally, reverse lithium-for-iodine exchange with the iodobenzene generated in the initial step forms the observed product.

Both the initial and final iodine/lithium exchanges in Scheme 1 are equilibrium reactions that can be expected to favor phenyllithium over the cubyllithium. The former is better stabilized as there is higher s character in an exocyclic aromatic orbital (33%) than in an exocyclic cubane orbital (31%).[3,4] Benzene has been shown to be ~1000 times more acidic than cubane kinetically,[5] and probably a similar difference pertains thermodynamically. In accord, we have found experimentally that there is little "net" reaction between equimolar amounts of cubyl iodide and phenyllithium; only a trace amount of cubane is found when the mixture is quenched with water. On the other hand, and appropriately, equimolar amounts of cubyllithium and phenyl iodide react to give cubyl iodide in high yield.

The critical intermediate **3** in Scheme 1, 1,4-dehydrocubane, is very reactive and cannot be isolated and characterized in the usual sense. Its structure, therefore, cannot be taken as fully established.[2] Nonetheless, detailed ab initio calculations by the

Scheme 1

1,4-dehydrocubane
aka cubane-1,4-diyl
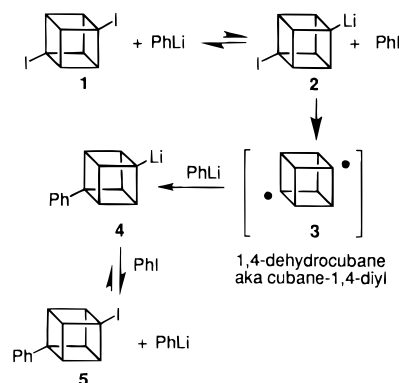
Michl[6] and Borden[7] groups on a number of possible candidate structures have led to the postulate that 1,4-dehydrocubane is cubane-1,4-diyl singlet. Michl's matrix isolation infrared spectroscopic studies are in accord with this theory.[6] The calculations place the singlet state of the diyl below the triplet by more than 10 kcal/mol, suggesting substantial through-bond interaction of the nonbonded electrons.

1,4-Diiodocubane, the precursor of cubanediyl, can be prepared easily from cubane-1,4-diacid, the now well-known entry compound into the cubane system.[3,8,9] Full details have been published already of our application of Barton iodinative decarboxylation of the diacid via its *N*-hydroxypyridine-2-thione (PTOC) ester.[10] Moriarty's more direct procedure, in which the diacid itself is reacted with phenyliodonium diacetate and iodine, has proven to be much easier,[11] and provides the 1,4-diiodide

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(1) Some of this paper is taken from the Ph.D. Thesis of Todd Emrick, The University of Chicago, 1997.

(2) Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* **1990**, *112*, 876.

(3) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962.

(4) Della, E. W.; Hine, P. T.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940.

(5) Dixon, R. E.; Streitwieser, A.; Williams, P. G.; Eaton, P. E. *J. Am. Chem. Soc.* **1991**, *113*, 357.

(6) Hassenrück, H.-D.; Radziszewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, J-D.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 873.

(7) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 875.

(8) (a) Eaton, P. E. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1421. (b) Chapman, N. B.; Key, J. M.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 3860. (c) Luh, T.-Y.; Stock, L. M. *J. Org.Chem.* **1972**, *37*, 338.

(9) The 1,4-dimethyl ester is available commercially from Aldrich Chemical and from SynQuest, Ltd.

(10) Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1989**, *30*, 6967.

(11) (a) Moriarty, R. M., private communication. (b) Moriarty, R. M.; Khosrowshahi, J. S.; Dalecki, T. M. *J. Chem. Soc., Chem. Commun.* **1987**, *9*, 675. (c) Concepción, J. I.; Francisco, C. G.; Freire, R.; Hernández, R.; Salazar, J. A.; Suárez, E. *J. Org. Chem.* **1986**, *51*, 402.

reproducibly on a multigram scale in 85+% yield. Details of our version are given in the Experimental Section.

Synthesis of 4-Arylcubyl Iodides. The generation of cubane-1,4-diyl from **1** under conditions that permit its effective use in synthetic schemes depends critically on experimental conditions and on the organolithium employed. In this section we focus on the use of aryllithiums. Later, we will consider the use of cubyllithiums.

1,4-Diiodocubane is very poorly soluble in diethyl ether, the solvent that routinely gave the cleanest overall results in these reactions.[12] Thus, we could do little more experimentally, on the small scale we were working, than to add the diiodide as a well-powdered solid to the aryllithium already in solution. It was apparent from color changes that reaction of the diiodide occurred (rapidly) as it dissolved (slowly). Thus, the aryllithium was always present and available in excess.

When phenyllithium was used, the yield of 4-phenylcubyl iodide (**5**), isolated pure, was 80−90%. Similar yields of the
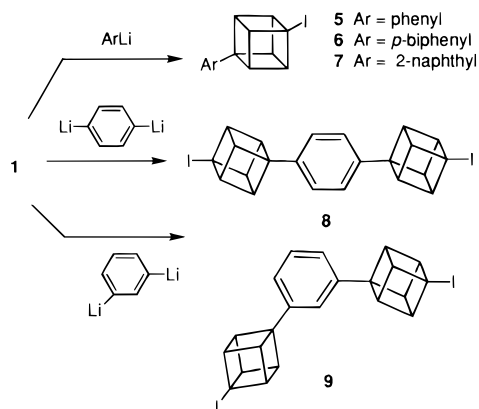
corresponding 4-arylcubyl iodides were achieved when *p*-biphenyllithium (→ **6**) and 2-naphthyllithium (→ **7**) were employed. Use of the doubly lithiated aromatic 1,4-dilithioben-zene, prepared by halogen−metal exchange between *p*-dibro-mobenzene and excess *t*-BuLi,[13] gave *p*-bis(4-iodocubyl)benzene (**8**) in 70% isolated yield. Similarly, reaction of diiodocubane with 1,3-dilithiobenzene[13] gave the meta isomer **9**.

Synthesis of Arylcubanes. In all these cases, the iodine substituents on the cubane skeleton are the result of iodine-for-lithium exchange equilibria as shown in Scheme 1. Initially each of the 4-arylcubyl iodides **5**−**9** is formed as the corresponding arylcubyllithium. It is simple enough to remake these by reaction of **5**−**9** with at least 2 equiv of *t*-BuLi. Under this condition, the cubyllithiums are certainly favored. Not only is the negative charge put in an orbital far more s-rich than that of *tert*-butyl anion, but the equilibrium is "pulled" entirely to the right by *t*-BuLi-induced elimination of HI from *t*-BuI.
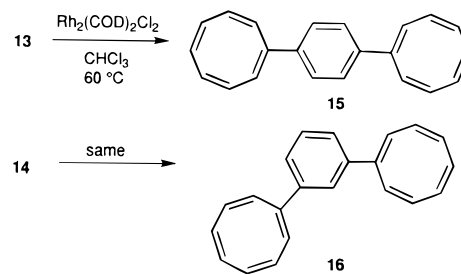
Cubyllithiums appear to be somewhat less reactive than common tertiary alkyllithiums. Perhaps this is related to the increased s character in the exocyclic carbon orbital already referred to. Qualitatively, cubyllithium lasts longer in ether and THF than does *t*-BuLi. Cubyllithiums readily undergo the usual reactions of organolithiums. This is convenient and provides, for example, easy methodology for taking cubyliodides to the corresponding hydrocarbons. Thus, **5**−**9** were converted by protonation of their lithium derivatives to phenylcubane (**10**),

(12) THF is a better solvent for 1,4-diiodocubane, but it is too reactive toward the intermediate cubyllithiums.

(13) (a) Honrath, U.; Shu-Tang, L.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 132. (b) Trepka, W. J.; Sonnenfeld, R. J. *J. Organomet. Chem.* **1969**, *16*, 317.

(*p*-biphenyl)cubane (**11**), (2-naphthyl)cubane (**12**), *p*-(dicubyl)-benzene (**13**), and *m*-(dicubyl)benzene (**14**), respectively.

Aryl Cyclooctatetraenes (COTs) from Arylcubanes. One use of these compounds is the preparation of novel COTs. Research in this Laboratory with Cassar and Halpern years ago showed that rhodium(I) catalysts trigger ring opening of cubane to *syn*-tricyclooctadiene, which in turn undergoes ready (un-catalyzed by the metal) Cope ring opening at 60 °C to cyclooctatetraene.[14] The same holds true for many substituted cubanes. This offers a novel approach to substituted COTs; for example, treatment of *p*-(dicubyl)benzene (**13**) and *m*-(dicubyl)-

benzene (**14**) with Rh$_2$(1,5-cyclooctadiene)$_2$Cl$_2$ provides *p*-(dicyclooctatetraenyl)benzene (**15**) and *m*-(dicyclooctatetraenyl)-benzene (**16**), respectively, each in better than 85% yield. This approach is entirely different from previous modes of access to these compounds.[15]

Cubane Couplings. 4,4′-Diiodobicubyl (**18**)[16a] was always observed as a byproduct (∼5%) of the reactions of aryllithiums with 1,4-diiodocubane. It is formed as shown in Scheme 2 by the unavoidable in situ combination of the intermediates **2** and
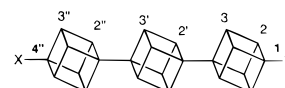
Scheme 2
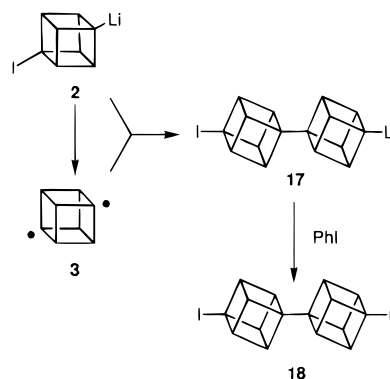
(14) (a) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515. (b) Eaton, P. E.; Galoppini, E.; Gilardi, R. *J. Am. Chem. Soc.* **1994**, *116*, 7588.

(15) (a) Siesel, D. A.; Staley, S. W. *J. Org. Chem.* **1993**, *58*, 7870. (b) Grimm, R. A. Ph.D. Thesis, Carnegie Mellon University, 1997. Prof. S. Staley has informed us privately that the spectroscopic properties of our materials compare reasonably to his considering that different solvents were employed.

(16) (a) This nomenclature is taken from that of the biphenyls and is convenient for simple, symmetric bicubyls. It is not useful for more complex molecules. (b) The *p*(*ara*)-[*n*]cubyls are rigid rods made of *n* cubanes attached directly to one another at opposite corners. The designation 4* is used generically to refer to the most distant cubyl position from a substituent on C1 of a *p*-[*n*]cubyl. The numbering of a specific *p*-[*n*]cubyl follows by extension from the following example.


1-Y, 4″-X- *p*- [3]cubyl;
when X and/or Y = H, it is not specified

3 (cf. Scheme 1) to give **17**, followed by lithium-for-iodine exchange with iodobenzene.

Diiodobicubyl **18** is potentially very useful. It is easy enough to imagine reductive couplings (vide infra) providing for the preparation of the rigid rod *p*-[*n*]cubyls.[16b] But its yield by this method is far too low; a better synthesis is necessary. In the combined milieu of Schemes 1 and 2, most of diyl **3** is usually trapped by the aryllithium, present in excess. As the concentration of 4-iodocubyllithium is much lower, it competes poorly. This (now desired) path can be enhanced by employing steric effects to diminish the ability of the aryllithium to add to the diyl. Changing from phenyllithium to *o*-ethylphenyl lithium increased the yield of **18** from 5 to 30%. Use of the yet more hindered mesityllithium increased the yield of **18** to ~50%. Unfortunately, this was not improved when the much more congested 2,4,6-triisopropylphenyl lithium was employed.

Reaction of **18** with *t*-Buli gave 4,4′-dilithiobicubyl (**19**). This is a broadly useful compound as it reacts in standard fashion with simple electrophiles and gives access to a host of bicubyl


21 X = I
22 X = CH₃
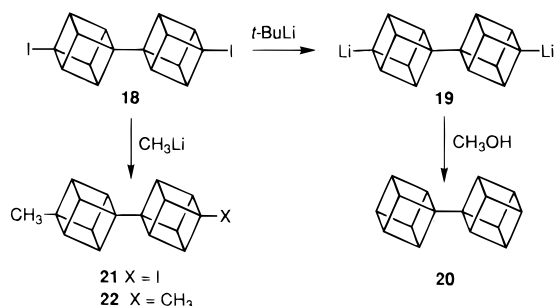
derivatives.[2] Quenching with methanol provides the most convenient access to bicubyl itself (**20**). Treatment of **18** with methyllithium at room temperature gave, in part, 4,4′-dimethylbicubyl (**22**) and the half-methylated compound, 4′-methyl-*p*-[2]cubyl iodide (**21**), both by way of iodine-for-lithium exchange, and then reaction of the cubyllithium so made with connate methyl iodide.

Oligomerization via Cubane-1,4-diyl. The iodobicubyl-lithium **17** in Scheme 2 arises from reaction of a cubyllithium (**2**) with cubane-1,4-diyl (**3**). It too is a cubyllithium, and were conditions of rate and concentration appropriate, it too could react with diyl **3**, thus giving a new cubyllithium, this one with three cubanes in a row. Hypothetically, continuation of this scheme would lead to an oligomerization with cubane-1,4-diyl serving as the "monomer". Indeed, it was clear early on that small amounts of higher molecular weight materials were being formed in these reactions. In practice, the oligomerization does not proceed effectively for the concentration of any cubyllithium formed within this scheme is small, kept that way by rapid iodine-for-lithium exchange with the aryl iodide formed incidentally in the first step of Scheme 1. As noted earlier, these exchanges favor the aryllithium strongly.

Such reasoning led us to use premade 4-phenylcubyl lithium (**4**) *both* to generate *and* to trap cubanediyl. Its precursor, 4-phenylcubyl iodide (**5**), is easily prepared, as already shown in Scheme 1, and it can be isolated pure in 80–85% yield without difficulty. Iodine–metal exchange at −78 °C in diethyl ether using 2 equiv of *t*-BuLi (the "extra" equivalent to destroy *t*-BuI) gave **4** essentially quantitatively.

4-Phenylcubyl lithium is reasonably soluble (~0.10 M) in ether, but 1,4-diiodocubane is not, even at 0 °C where the reaction between the two was best run. The metal–halogen exchange between them is limited therefore by the slow rate of

Scheme 3
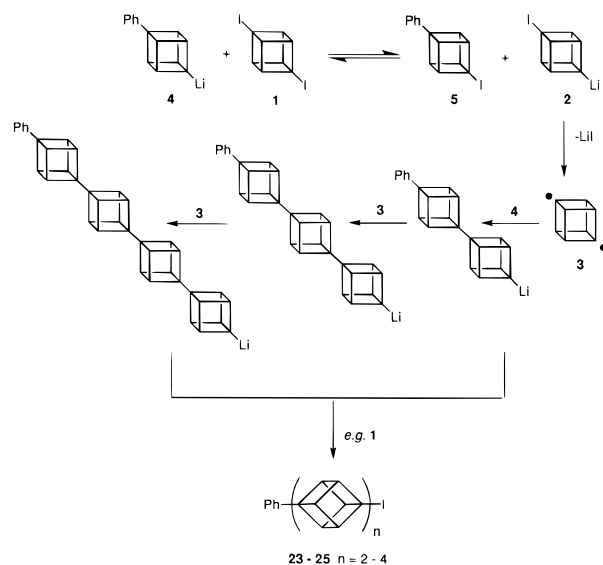
diiodide dissolution. Thus, the concentration of the intermediate 4-iodocubyl lithium is always low, and the diyl as it is formed is trapped, not by 4-iodocubyl lithium but by 4-phenylcubyl lithium or by the growing 4*-phenyl-*p*-[*n*]cubyllithium rod[16b] (Scheme 3).

The process in Scheme 3 is reproducible and reasonably efficient. Most of the 4-phenyliodocubane (the precursor of 4-phenylcubyl lithium) generated can be recovered and reused. About 70% of the 1,4-diiodocubane introduced can be accounted for, mostly incorporated into **23**−**25**, a little is recovered unchanged. The rest must be mostly in higher oligomers, "lost" because of their exceedingly low solubility.

When the ratio of phenylcubyllithium (the initiator) to 1,4-diiodocubane (the monomer precursor) was high (≥4:1), the degree of oligomerization was low; mainly dimers were produced. When the ratio was lowered, somewhat more of each of the higher oligomers **23**−**25** was produced (Table 1). These compounds were separated crudely by trituration and then further purified by column chromatography on silica gel, usually using large amounts of pentane as eluent.

Table 1. *p*-[*n*]Cubyl Oligomer Distribution (% Isolated Yields Based on Incorporated **1**) as a Function of the 4-Phenylcubyllithium (**4**):1,4-Diiodocubane (**1**) Ratio

molar ratio **4:1**	**23** $n = 2$	**24** $n = 3$	**25** $n = 4$
4:1	66	12	
3:1	47	15	
2:1	40	19	3
1:1	38	24	6

Of course, each of the iodides **23**−**25** can be converted to the corresponding lithium derivative by reaction with *t*-BuLi and thence to numerous derivatives. The conversions of **23** and **24** to the parent hydrocarbons 1-phenyl-*p*-[2]cubyl (**26**) and 1-phenyl-*p*-[3]cubyl (**27**), respectively, and of **25** to its car-bomethoxy derivative **28** are given in the Experimental Section as examples.

Arylcubyl iodides other than 4-phenylcubyl iodide, e.g., 4-(*p*-biphenyl)cubyl iodide (**6**) and 4-(2-naphthyl)cubyl iodide (**7**), were used in the process of Scheme 3 with similar results. It is important to have a sense of the utility of this reaction. For example, a run employing 1.528 g of **6** and 1.78 g of 1,4-diiodocubane gave 520 mg of recovered **6**, 930 mg of

1-iodo-4′-(*p*-biphenyl)-*p*-[2]cubyl (**29**), 210 mg of 1-iodo-4″-(*p*-biphenyl)-*p*-[3]cubyl (**30**), and 64 mg of 1-iodo-4‴-(*p*-biphenyl)-*p*-[4]cubyl (**31**).

29

30

31
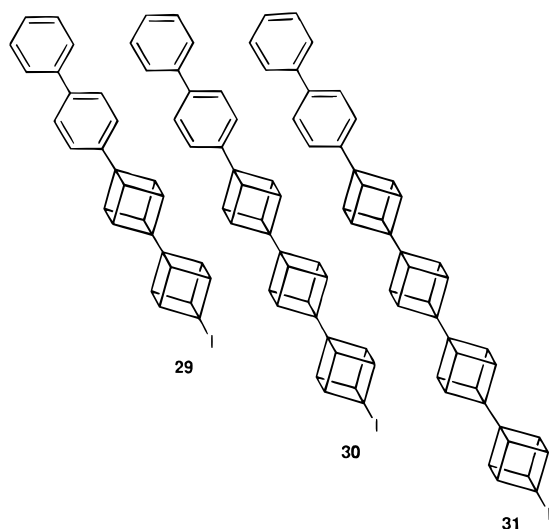
It is useful to know (vide infra) as one inspects these rodlike structures that the distance between the para positions of benzene (∼2.8 Å) and that along the body diagonal between the 1 and 4 positions of cubane (∼2.7 Å) are almost the same. So too are the C−C bond lengths between two phenyl rings (∼1.49 Å), between a phenyl ring and a cubane nucleus (∼1.49 Å), and between two cubanes (∼1.49 Å). Thus, the straight-line, tip-to-tip carbon distance in **31** is almost 20 Å.

Cubyl iodide itself, open at the 4 position, can also be used in Scheme 3, as can 4,4′-diiodobicubyl. This provides access to unsubstituted *p*-[*n*]cubyl rigid rods, the subject of a future paper.[17]

The yields of *p*-[*n*]cubyls with *n* ≥ 3 are not good. There are problems with the dissolution kinetics of 1,4-diiodocubane and with the insolubility of the growing chains. More fundamentally, as careful inspection of Scheme 3 shows, the lithium-for-iodine exchange, which can occur easily among the reaction components, provide a termination mechanism for what otherwise could have been a "living" polymerization.

For the reason above, preparation of higher "cubylogs" is best undertaken by isolating an individual iodo-*p*-[*n*]cubyl from one or another version of Scheme 3 and then using it, now as starting material, for another round. Thus, for example, 1-iodo-4′-phenyl-*p*-[2]cubyl (**23**), formed as shown in Scheme 3 (Table 1, entry 1, 66% isolated yield), was reacted with *t*-BuLi in cold ether. Reaction of an excess (4:1) of the lithio compound so obtained with 1,4-diiodocubane **1** (ratio **23**:**1** = 4:1) gave 1-iodo-4″-phenyl-*p*-[3]cubyl (**24**) in 50% isolated yield.

Solubilized Cubyl Rods. Unelaborated rigid rods of even nominal molecular weight are difficulty soluble, be they

(17) Eaton, P. E.; Virtuani, M.; Xiong, Y.; Pramod, K., in preparation.

(18) (a) Hassenrück, K.; Murthy, G. S.; Lynch, V. M.; Michl, J. *J. Org. Chem.* **1990**, *55*, 1013. (b) Mazal, C.; Paraskos, A. J.; Michl, J. *J. Org. Chem.* **1998**, *63*, 2116 and references therein.

(19) For examples: (a) Percec, V.; Zhao, M.; Bae, J.; Hill, D. H. *Macromolecules* **1996**, *25*, 3727. (b) Baker, K. N.; Fratini, A. V.; Resch, T.; Knachel, H. C.; Adams, W. W.; Socci, E. P.; Farmer, B. L. *Polymer* **1993**, *34*, 1571. (c) John, J. A.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 5011.

(20) Zimmerman, H. E.; King, R. K.; Meinhardt, M. B. *J. Org. Chem.* **1992**, *57*, 5484.

(21) For example: (a) Yang, X.; Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chim. Acta* **1995**, *240*, 371. (b) Müller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.

staffanes,[18] paraphenylenes,[19] rodanes,[20] [*n*]carboranes,[21] or the *p*-[*n*]cubyls of interest here. This presents very frustrating experimental difficulties. Various approaches to alleviating the problem have been tried, here and elsewhere,[22] to more or less effect.

As it is usually the case that less symmetric compounds are more soluble than their symmetric relatives,[22a] Scheme 3 was repeated using 4-(*m*-ethylphenyl)cubyllithium (**32b**) instead of 4-phenylcubyllithium, the idea being to break the full axial symmetry of the developing rod. The starting material, (4-(*m*-ethylphenyl)cubyl iodide (**32a**), was prepared in good yield (70%) by appropriately modifying Scheme 1 (see Experimental Section). As hoped for, the oligomerization triggered by **32b** did give a better ratio (1:2) of the 4″-aryl-*p*-[3]cubyl (**34**, aryl = *m*-ethylphenyl) to 4′-aryl-*p*-[2]cubyl (**33**) than that obtained (1:3) when 4-phenylcubyllithium was used. An isolable amount of the cubylog *p*-[4]cubyl **35** was produced, and for first time we observed (albeit only by mass spectroscopy) the formation of a *p*-[5]cubyl, **36**. The solubilities of the purified (*m*-ethylphenyl)-*p*-[2]cubyl and -*p*-[3]cubyl oligomers are better than those of their desethyl, more symmetrical analogues. The [2]cubyl has reasonable solubility in pentane; the [3]cubyl is somewhat soluble in ether and has good solubility in CH₂Cl₂. Nonetheless, the [4]cubyl **35** is not sufficiently soluble to be useful for elaboration.

The effect on solubilities induced by a "floppy" substituent[22b] in the para position of the phenyl group of the 4*-phenyl-*p*-[*n*]-cubyls was investigated briefly. 4-(*p*-Octylphenyl)cubyl iodide was prepared via Scheme 1 by employing 4-octylphenyllithium. Lithiation followed by reaction with 1,4-diiodocubane afforded a set of 1-iodo-4*-(*p*-octylphenyl)-*p*-[*n*]cubyls with *n* = 2−4. Although these were certainly more soluble than their unsubstituted analogues, no substantial improvement in solubility over the *m*-ethyl compounds **33**−**35** was obseved.

In another approach to solubilization,[22c] substituents are distributed along the rigid rod. To this end, we prepared the diyl precursors **38** and **39** (Scheme 4) taking advantage of our earlier discoveries relating to systematic substitution on the cubane nucleus by way of ortho-metalation,[23] in this case ortho-magnesiation of amide **37**.[23c]

Scheme 4

A = C(O)N(*t*-Bu)CH₃

37

TMP = 2,2,6,6-tetramethylpiperidyl

38

39
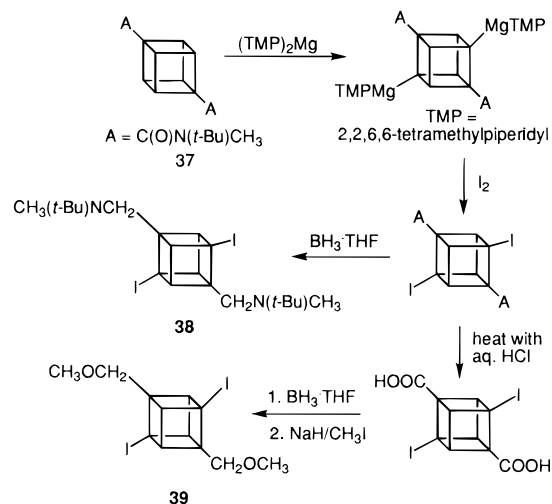
Diiodides **38** and **39** are quite soluble in ether, unlike 1,4-diiodocubane itself. Reaction of each with excess phenyllithium

(22) (a) For example: Lassale, I.; Schmidt, M.; Schlüter, A. D. *Acta Polym.* **1994**, *45*, 389. (b) For example: Tour, J. M. *Adv. Mater.* **1994**, *6*, 190. (c) For example: Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *91*, 1991.

proceeds along the path outlined in Scheme 1 via the intermediate diyls. The product 2,7-disubstituted 4-phenylcubyl iodides **40** and **41**, respectively, are formed in reasonable yields.[24] Nonetheless, we were not able to obtain oligomerization by approaches such as that in Scheme 3. We suspect that the heteroatoms (N or O) in the substituents so alter the properties of the intermediate cubyllithiums that suitable concentrations of the required intermediates cannot be obtained (cf. footnote 24), or perhaps such cubyllithiums are incapable of adding to a cubane diyl.

Solubilization of rigid rods can sometimes be achieved by having flexible alkyl chains along the rod.[23c] As alkyl groups would be expected to be relatively innocuous chemically, this seemed an attractive choice. To this end, we prepared 1,4-diiodo-2,7-dihexylcubane (**42**, Scheme 5, 40% overall), a compound with quite good solubility in both hydrocarbon and ethereal solvents.

Scheme 5

A = C(O)N(*t*-Bu)CH₃
37

42
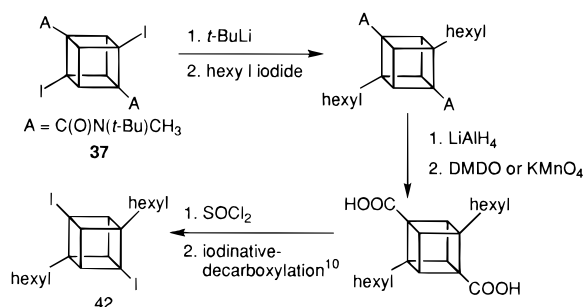
The successful use of **42** in the preparation of high-molecular-weight *p*-[*n*]cubyl rigid rods solubilized by floppy hexyl chain "fur" all along their substantial length will be reported in a later paper. Here we are interested in whether alkyl chain substitution effectively solubilizes 4*-aryl-*p*-[*n*]cubyls. Using the methods already outlined, now through the intermediacy of 2,7-dihexyl-cubane-1,4-diyl, we have prepared and characterized **43**−**46**.

43a X = I
43b X = H

44a X = I
44b X = H

45

46
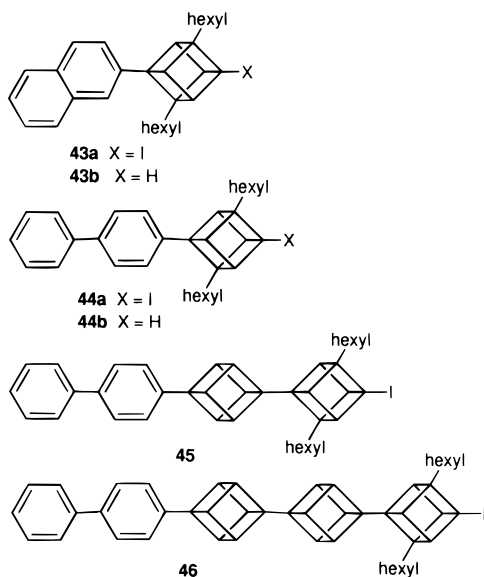
These are all compounds that can be eluted fairly readily from silica gel chromatography columns with pentane. As desired, they are all hydrocarbon soluble, viscous oils at room temperature, quite unlike their counterparts without the hexyl substituents.

Cubane-Separated Biaryls. The rate of electron transfer between donor and acceptor as a function (for example) of the energy differences between their respective radical anions and the distance separating them is an area of considerable interest.[25] The most studied electron donor−acceptor pairs are aromatics, whose oxidation−reduction potentials are well-established, for example, biphenyl and naphthyl. We have already reported on the use of *p*-[*n*]cubyls as well-defined "spacers" between such electroactive groups.[26] The syntheses of these compounds are described in the present paper. Each cubane unit adds 4.15 Å to the rod length. There is easy free rotation about each cubane-to-cubane bond, as the closest approach of hydrogens on adjacent cubes is ∼2.7 Å. Even 2-*tert*-butylcubylcubane is freely rotating at room temperature on the NMR time scale.[2] Rotation about the cubane-to-cubane bond does not change rod length. Bending at this bond does change rod length, but such bending is energetically difficult. About 8 kcal/mol is required for the first 10° excursion; this increases steeply thereafter. Thus, the *p*-[*n*]cubyl oligomers behave as rigid rods of fairly much exactly calculable length.

How can cubyl rods be made with different aryl groups at either end? As shown above, addition of an aryllithium to cubane-1,4-diyl easily puts an aryl group on one end of a developing rod; examples of phenyl-, biphenyl-, and 2-naphthyl-substituted rods of various lengths have been given. The problem is the introduction of a second (and different) aryl group on the opposite end of the rod. We have found that it is possible to couple aryl-substituted cubyl iodide, e.g., the synthesis of 4,4′-biphenylbicubyl (**47**), by oxidation of a cuprate. However, such reactions have proven to be irreproducible and low-yielding. Hence, cross-coupling variants are bound to be both inelegant and unrewarding.

If metal-mediated cross coupling between a cubyl-Y (e.g., cubyl cuprate, stannate, triflate, etc.) and Ar-X (e.g., aryl halide, boronate, etc.) could be brought about, the problem of making cubane-separated mixed biaryls would be simple. However, after much effort we have been forced to conclude that such reactions are inoperable (or nearly so) in the cubane series.[27]

We have developed instead effective protocols, widely extensible, for introduction of aromatic units, viz., *p*-biphenyl, 2-naphthyl, and 9-phenanthryl, built on the reactions of appropriate electrophiles with organolithiums, here aryl[*n*]cubyllithiums. For example, the biphenyl subunit in 1-phenyl-4-(*p*-biphenyl)cubane (**48**) can be introduced smoothly by reaction of 4-phenylcubyllithium (**4**) with 4-phenylcyclohexane-1,2-epoxide, followed by POCl₃/pyridine-induced dehydration and DDQ dehydrogenation. As numerous variants on **4** are easily available (e.g., from **6**−**9**, **23**−**25**, and **43a**−**46a**), this scheme provides for the synthesis of many arylbiphenyl[*n*]cubyls.

(23) (a) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. (b) Bashir-Hashemi, A. *J. Am. Chem. Soc.* **1988**, *110*, 7234. (c) Eaton, P. E.; Lee, C.-H.; Xiong, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8016.

(24) Interestingly, the diiodo−diamido precursor of **38** did not form a diyl on reaction with excess phenyllithium. Apparently, the adjacent amide group so stabilizes[23a] the cubyllithium formed on iodine-for-metal exchange that elimination of LiI does not occur competitively with the second exchange.

(25) For example: (a) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R.; *J. Phys. Chem.* **1986**, *90*, 3673. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18.

(26) Paulson, B.; Pramod, K.; Eaton, P. E.; Closs, G.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 13042.

(27) This seems to us to mean that the very successful couplings of "standard" systems (aromatic, vinyl, allyl) really require participation of the π-unit. However, see: Charette, A. B.; Giroux, A. *J. Org. Chem.* **1996**, *61*, 8718.

(28) (a) Gilman, H.; Gorisch, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 2625. (b) Caple, R.; Chen, G. M.-S.; Nelson, J. D. *J. Org. Chem.* **1971**, *36*, 2874.
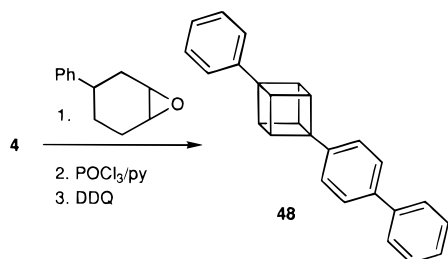
The oxide bridge in naphthalene-1,4-oxide is strained and labile. We expected, considering the literature,[28] that Lewis acid-catalyzed reaction with a cubyllithium would open the oxa ring and lead ultimately to introduction of a β-naphthyl substituent. As it turned out, no catalyst was required. As shown in Scheme 6, for example, the cubyllithiums derived from 1-iodo-4-(*p*-biphenyl)cubyl (**6**) and 1-iodo-4′-(*p*-biphenyl)-*p*-[2]cubyl (**29**) with naphthalene-1,4-oxide in THF at −70 °C to room temperature gave good yields of the corresponding dihydronaphthols **49** and **50**. These were dehydrated nearly quantitatively to 1-(*p*-
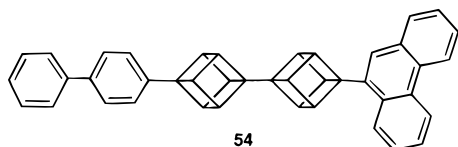
Scheme 6
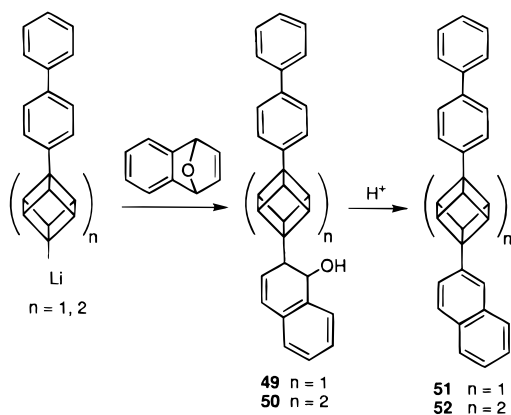
biphenyl)-4-(2-naphthyl)cubane (**51**) and 1-(*p*-biphenyl)-4′-(2-naphthyl)-*p*-[2]cubyl (**52**), respectively, on treatment with a bit of methanesulfonic acid. Again, numerous variations are possible, including the use of alkyl-substituted cubanes to make rods of greater length, but still with reasonable solubility, e.g., the tricubyl **53**, 4″-(*p*-biphenyl)-1-(2-naphthyl)-2,7-dihexyl-*p*-[3]cubyl.
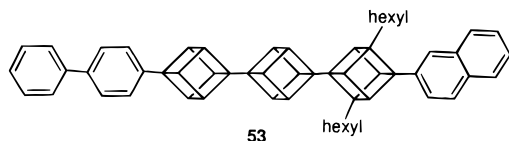
Cubyl-separated biaryls in which one aryl group is 9-phenanthrene, the best electron acceptor of the aromatics considered here, were made via reaction of various arylcubyllithiums with phenanthrene-9,10-epoxide instead of the naphthalene oxide (cf. Scheme 6). For example, **54**, 1-(*p*-biphenyl)-4′-(9-phenanthryl)-

p-[2]cubyl, was prepared in 70% overall isolated yield.

Physical and Spectroscopic Properties. Although highly strained and energy-rich, cubane, the arylcubanes, and the *p*-[n]-

cubyls introduced in this paper are all quite stable kinetically. None has ever shown shock sensitivity under usual laboratory conditions. Thermal decomposition does not set in until above 200 °C. Air, light, and moisture, as well as most common reagents, are without effect. Melting points quickly increase with increasing rod length: cubane, 130−131 °C; *p*-[2]cubyl, 169−171 °C; *p*-[3]cubyl, ∼200 °C (dec). Phenylcubane, although essentially the same length as bicubyl, is a liquid at room temperature. The more rodlike 4′-phenyl-*p*-[2]cubyl melts at 163−164 °C. In the 1-iodo-4*-phenyl-*p*-[n]cubyl series, the melting points of *n* = 1−4 are, respectively, 85−86, 144−146, 215−217 (dec), and 225−228 °C (dec). As expected (cf. the [n]staffanes[18a] and the *p*-[n]phenyls[19b]), the solubility of these compounds falls off rapidly with increasing rod length. Cubane is miscible with pentane; the solubility of [2]cubyl is ∼10 mg/mL, but *p*-[3]cubyl is essentially insoluble. The solubility of most 4*-phenyl-*p*-[n]cubyls is very similar to that of the corresponding desphenyl-*p*-[n]cubyl. The phenyl group, unlike an additional cubane, lengthens the rod without lowering its solubility.

NMR Comparisons. The ¹H NMR spectrum of cubane in deuteriochloroform is a single, very sharp resonance at δ 4.03 ppm. The spectra of the *p*-[n]cubyls are far more complex, but a clear trend is apparent. The resonance for the protons at each end of the rod (H1 and H4*) becomes a multiplet spread symmetrically over ∼4.00−4.08 ppm (typical cubane coupling constants are roughly $J_{ortho} \sim 5$ Hz, $J_{meta} \sim 3$ Hz, $J_{para} \sim 1$ Hz).[29] The resonance for the other cubyl protons are shifted upfield significantly. In bicubyl, these produce a broad multiplet extending over $\delta \sim 3.81−3.91$ ppm (400 MHz). In *p*-[3]cubyl, the six identical protons on the central, internal cubane give rise to a new upfield, slightly broadened singlet at δ 3.68 ppm, while the chemical shift spread of the nonterminal protons of the outer cubanes is quite similar to that in bicubyl. The appearance of new upfield resonances ends with *p*-[4]cubyl. The 12 protons on its two inner cubanes appear as a somewhat broadened singlet at δ 3.68 ppm, just as in tricubyl. It is this signal that would likely continue to grow in weight with increasing rod length. However, due to solubility difficulties, the ¹H NMR spectrum of a [5]cubyl has not yet been recorded.
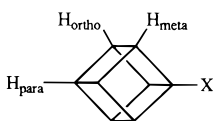
Alkyl substituents on a cubane, like a cubyl substituent, shift the ortho and meta hydrogen resonances upfield from that of cubane itself.[30] Most other substituents result in downfield shifts for the ortho hydrogen resonance. For example, in cubyl iodide the ortho proton resonance is at δ 4.32 ppm; in phenylcubane it is at δ 4.17 ppm. The meta shifts due to these substituents are smaller, but not necessarily downfield. In cubyl iodide, the resonance for the protons meta to the substituent is at δ 4.18 ppm; in phenylcubane, at δ 4.01 ppm.

In 1-iodo-*p*-[2]cubyl, the resonance for protons ortho to iodine is at δ 4.17 ppm, an upfield shift of 0.15 ppm from the ortho protons in iodocubane. This is the result of the meta effect of the additional cubane. Substitution in the 4′ (para) position of this cubyl substituent does not change this; the resonance remains at δ 4.17 ppm in 1-iodo-*p*-[3]cubyl, 1-iodo-4′-phenyl-*p*-[2]cubyl, and 4,4′-diiodobicubyl.
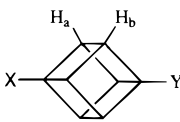
Table 2 shows the observed difference in chemical shift (Δδ) in ppm from cubane (4.03 ppm) for the ortho, meta, and para protons in the X-substituted cubanes central to the work reported here.

(29) Edward, J. T.; Farrell, P. G.; Langford, G. E. *J. Am. Chem. Soc.* **1976**, *98*, 3075.

(30) The ortho, meta, and para Δδ effects on the chemical shift of cubyl hydrogens in methylcubane are, respectively, −0.39, −0.19, and +0.02 ppm. See: Eaton, P. E.; Li, J.; Upadhyaya, S. P. *J. Org. Chem.* **1995**, *60*, 966.

Table 2. Chemical Shift Difference ($\Delta\delta$ ppm) from Cubane for Substituted Cubanes[a]

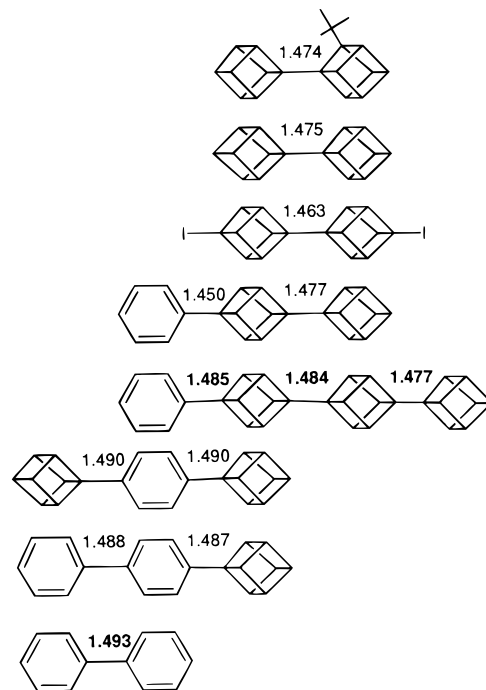| X	H_{ortho}	H_{meta}	H_{para}
iodine	+0.29	+0.15	+0.17
phenyl	+0.14	−0.02	+0.09
cubyl	−0.15	−0.15	+0.02

[a] Downfield shifts are given as positive.

Table 3. Calculated vs Experimental ^{1}H NMR Chemical Shifts (ppm) of Some 1,4-Disubstituted Cubanes

X	Y	H_a(calc)	H_a(exp)	H_b(calc)	H_b(exp)
iodine	phenyl	4.30	4.32	4.32	4.32
phenyl	cubyl	4.02	4.05	3.86	3.88
cubyl	cubyl	3.73	3.68	3.73	3.68
iodine	cubyl	4.17	4.17	4.03	4.03
iodine	iodine	4.47	4.40	4.47	4.40

Substituent effects on ^{1}H NMR chemical shifts of cubyl hydrogens are additive, as first shown by Farrell and co-workers.[29] This observation can now be extended to include cubyl, phenyl, and iodo substituents. So, for example, the chemical shifts of the 1,4-disubstituted cubanes in Table 3 can be calculated successfully from the values in Table 2. 4-Phenylcubyl iodide provides an interesting example. The combination of the ortho effect of iodine with the meta effect of the phenyl substituent results in a predicted chemical shift of [4.03 + (0.29 − 0.02)] = 4.30 ppm for one set of equivalent protons (H_a). The combination of the ortho effect of the phenyl substituent and the meta effect of iodine predicts [4.03 + (0.14 + 0.15)] = 4.32 ppm for the other set (H_b). What is seen is a singlet ($W_{h/2}$ = 0.6 Hz) at 4.32 ppm. This is in contrast to nearly all other unsymmetrical 1,4-disubstituted cubanes, where the two sets of ortho protons give rise to separate multiplets.

Crystal Structures. Growing crystals of *p*-[*n*]cubyls suitable for X-ray analysis has proved to be very difficult. Most form powders or glasses from solution rather than providing well-formed single crystals. Nonetheless, we have obtained good data for the *p*-[*n*]cubyls and the phenyl-*p*-[*n*]cubyls shown in Figure 1. Sufficient data are now available to make some general comments.

In general, when one cubane is attached to another by one bond, the cage units are perfectly staggered, or very nearly so. Both carbons making the cubane-to-cubane bond are fully substituted; nonetheless, the bond is short (~1.48 Å) relative to the "standard" C−C bond length of 1.54 Å and even shorter than that between typical tetrasubstituted carbons, e.g., 1.578 Å in 1,1′-bis(adamantyl).[31] This is as expected[32] for the exocyclic bonding orbital of a cubyl carbon is s rich (31%).[33] For similar reasons, the bond between a phenyl group and a cubane unit is short. So, of course, is the bond between two

(31) Alden, R. A.; Kraut, J.; Traylor, T. G. *J. Am. Chem. Soc.* **1968**, *90*, 74.

(32) (a) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232. (b) Ermer, O.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 447.

(33) (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157. (b) Della, E. W.; Hine, T. W.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940.

Figure 1. Some cubyl−cubyl, cubyl−phenyl, and phenyl−phenyl bond lengths (Å) from X-ray crystallographic analyses. When there is more than one molecule in the unit cell, the length given is the average.

phenyl units as in biphenyl. The hybridization of the exocyclic phenyl orbital is 33% s. Figure 1 gives the cubyl−cubyl and cubyl−phenyl bond lengths now available.[34]

The average distance along the body diagonal in a cubane nucleus is 2.70. The "rod" formed by linking two or more cubanes together at opposite corners, i.e., in the *p*-[*n*]cubyls, is lengthened by ~4.2 Å for each cubane nucleus added. As the 2.8-Å distance between the para positions of a benzene in a biphenyl (average of 480 biphenyls listed in the Cambridge Database) is almost the same as that between C1 and C4 in cubane and the length of phenyl-to-cubyl and phenyl-to-phenyl bonds are much like those of cubyl-to-cubyl bonds, appropriate substitution of a benzene nucleus for a cubane unit into or onto a cubyl rod does not much change its length. Thus, the calculated length, carbon tip to carbon tip, of *p*-[4]cubyl is 15.3 Å and that of 4″-phenyl-*p*-[3]cubyl is 15.4 Å. The actual experimental value (single-crystal X-ray analysis) for the latter is 15.3 Å.

Within a few standard deviations, most of the cubyl and phenyl−cubyl rods we have been able to crystallize and analyze are linear. Save in one case, the maximum departure from a straight line through any three sequential carbons on the long axis of the rod is less than 4° and usually less than 2°. In no instance do we see a coordinated accumulation of deviations. In 4″-phenyl-*p*-[3]cubyl, there is perhaps a more significant deviation from linearity; the phenyl group is cocked ~7° in one molecule of the unit cell and 8.7° in the other. However the precision of the data in this case is less than that in all the others because the best crystal that could be obtained was too thin to scatter strongly.

The rod length of bicubyl, from H-to-H, is 8.7 Å. A view down the *z* axis of the unit cell (Figure 2) shows a sheet of

(34) (a) The value for 2-*tert*-butylbicubyl comes from ref 32a. Note the length quoted in the text differs from that in the illustration; the latter is correct. (b) The cubyl−cubyl bond length for bicubyl is from the analysis reported herein of a pure crystal; another value, 1.45 Å, occurs in a co-crystal with 2-*tert*-butylcubylcubane; see: ref 32a. (c) For biphenyl, see: Charbonneau, G. T.; Delugeard, Y. *Acta Crystallogr.* **1977**, *B33*, 1586.
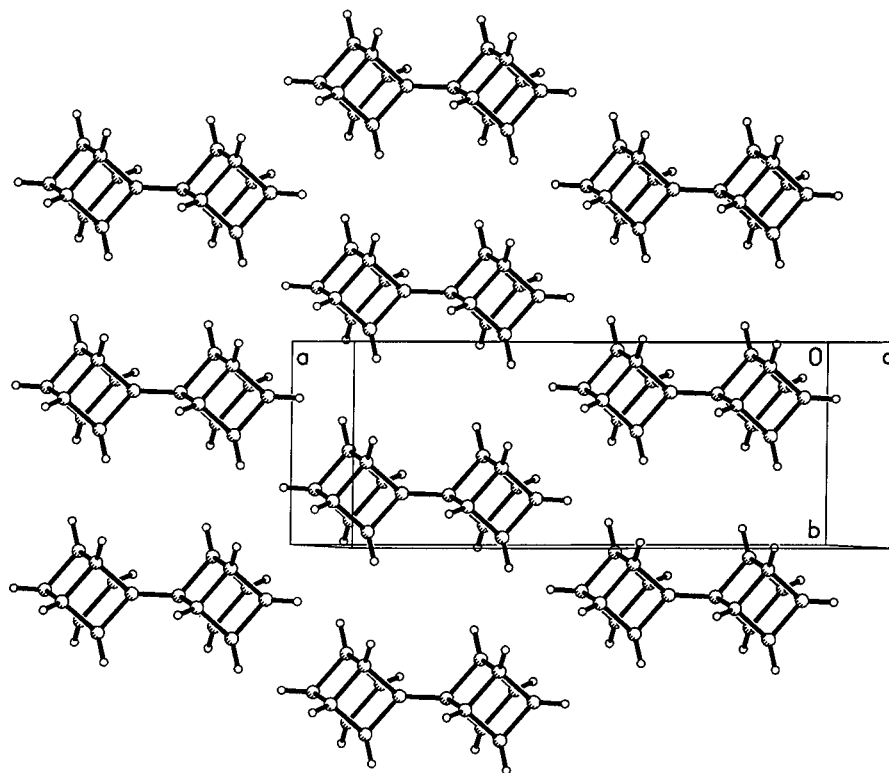
Figure 2. View showing a single layer of bicubyl (**20**) molecules in the *ab* plane with their centers at $z = 0.5$. Individual molecular axes are tipped slightly (16°) out of this plane. Identical layers occur at $z = 0$ and $z = 1$, laterally displaced so that molecules lie over and under the gaps between those in the layer illustrated.
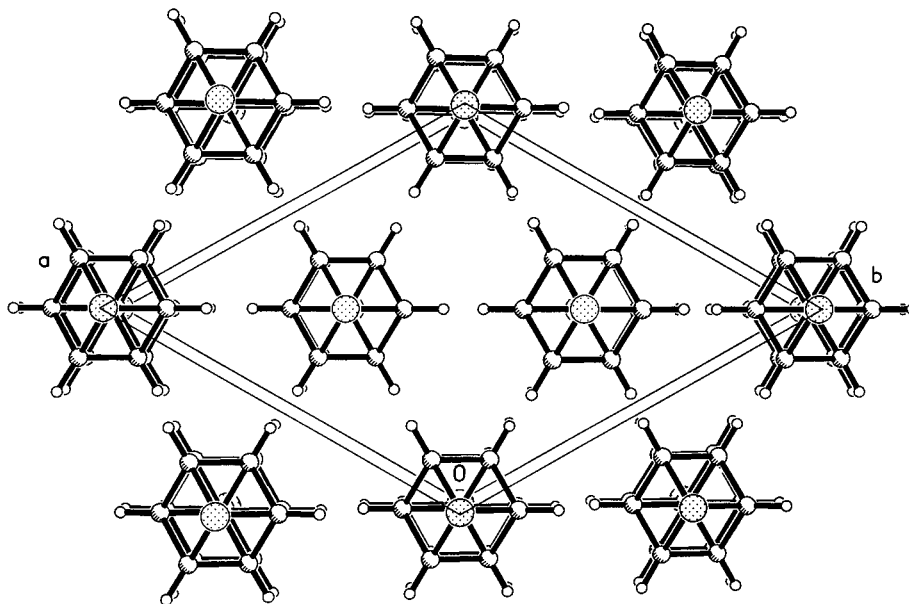
Figure 3. View down the trigonal (*c*) axis of the unit cell showing the stacking in 4,4′-diiodobicubyl (**18**). Each molecule is surrounded by a hexagonal array of close neighbors. These are alternately displaced, relative to the central molecule, by *c*/3 (5.12 Å) toward or away from the viewer; this is about a half-molecule length.

molecules packing in horizontal rows which lie, on average, in the same plane.

4,4′-Diiodobicubyl (**18**) was crystallized from benzene. The molecule is of such high symmetry that only four carbon atoms (C1−4) are unique; the rest can be generated by symmetry transformations. As in bicubyl, the molecules pack in planar sheets; the sheets are packed to give the hexagonal arrangement

of molecules shown in the "end-on" view of Figure 3.

Crystals of *p*-dicubylbenzene (**13**) were grown by slow evaporation from a methylene chloride solution. The rod is 13.16 Å from tip to tip (H to H). The rod is almost straight; the C1′-C2-C1A angle is 178.1°, and C1−C1A−C4A is 178.6°. Molecules of **13** pack in parallel layers, as shown in Figure 4, but the steric bulk of the cubane core prevents the close approaches between phenyl groups seen in *p*-[*n*]phenyls.[36] The

(35) For references and enlightening discussions, see: (a) Brock, C. P. *Acta Crystallogr.* **1980**, *B36*, 968. (b) Brock C. P.; Minton, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 4586.

(36) Baudour, P. J. L.; Delugeard, Y.; Cailleau, H. *Acta Crystallogr.* **1976**, *B32*, 150.
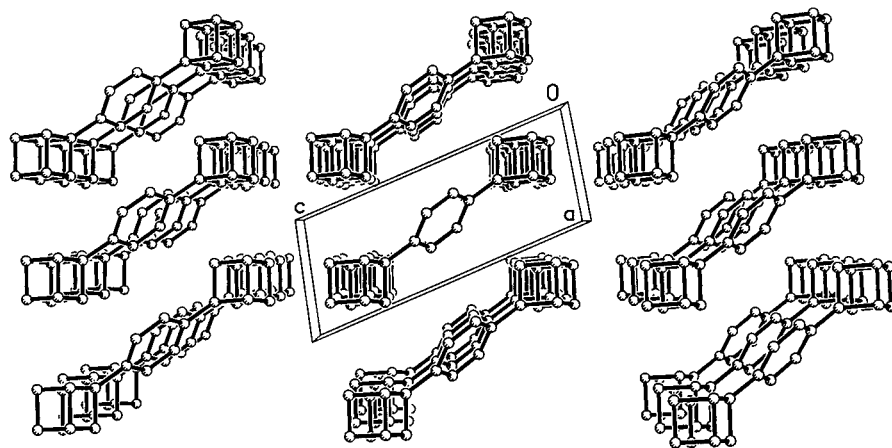
Figure 4. Triclinic crystal packing in *p*-dicubylbenzene (**13**). This low symmetry leads to an arrangement in which all molecular axes are parallel; the central benzene units are well separated from one another, while the cubyl units pack with many close (near vdW) contacts.
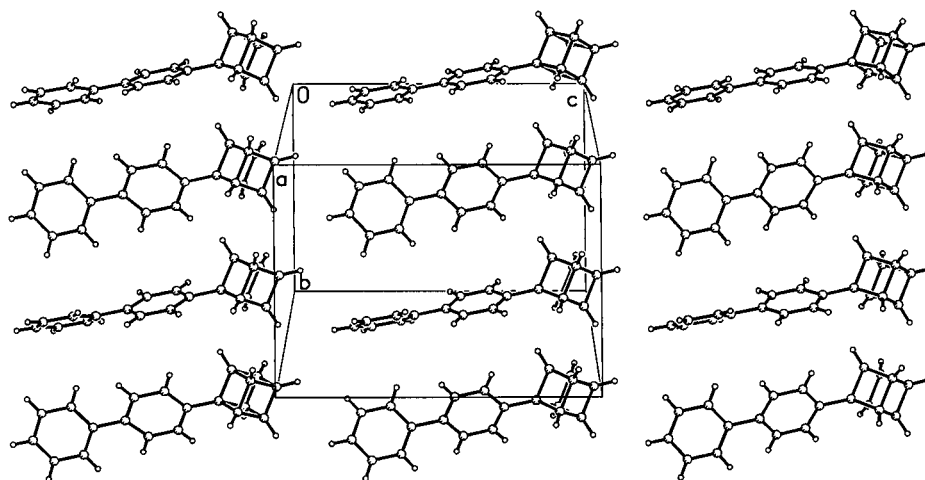
Figure 5. View of one layer of (*p*-biphenyl)cubane (**11**) that lies at the $x = 0.75$ level in the unit cell. Here all of the axes are approximately parallel, but the phenyl groups rotate relative to their phenyl neighbors, to make a perpendicular approach. This is very similar to the type of herringbone packing seen in the polyphenyls.[36]

molecules slide by one another along their long axes so that the bulky cubane portions can avoid one another. This brings a cubyl hydrogen into close contact (2.86 Å) with the center of a benzene ring of an adjacent molecule, perhaps in weak hydrogen-bonding interaction with the π-system. The interaction occurs on both sides of each benzene ring and is repeated along an infinite ladder of molecules through the crystal.

(*p*-Biphenyl)cubane (**11**) was crystallized from hexane at −20 °C. It is a rod 13.21 Å from tip to tip (H to H). The unit cell is composed of two not-quite-identical molecules. The phenyl–phenyl torsional angle in the biphenyl group of each (21° for one, 29° for the other) is quite different from the room-temperature arrangement in crystalline biphenyl, *p*-[3]phenyl, and *p*-[4]phenyl, which (oddly) are flat.[35] However, these molecules in low-temperature crystalline phases are twisted,[35] as are also most substituted biphenyls. Statistically, the average twist is ∼21° (237 structures from the Cambridge Database), similar to what is observed in **11**. The packing (Figure 5) in **11** is such that the molecular axes are approximately parallel, but the molecules undergo cylindrical rotation about their axes so that adjacent phenyl groups are almost perpendicular to each other. This is very similar to the packing in *p*-[3]phenyl.[36]

Crystals of 1-phenyl-*p*-[2]cubyl (**26**) were grown by slow evaporation of a chloroform solution. The molecule is a rod 13.08 Å long. The packing is complicated. There are four molecules in the unit cell (Figure 6). Unlike the *p*-[*n*]phenyls,

the long axis of the cell does not correspond to the long molecular axis of any member of the cell. The packing is such that there are layered pairs of stacks in which the cubyl ends of one stack meet the cubyl ends of another such that their molecular axes are parallel. The phenyl groups, on the other hand, interface in herringbone fashion from stack to stack.

There are two independent molecules in the asymmetric unit of 1-phenyl-*p*-[3]cubyl (**27**). Although the symmetry of the orthorhombic (*Pna*2₁) packing scheme is more complex than in the triclinic packing in **26**, the main features are remarkably similar. The phenyl ends interleave in a herringbone junction with a large change in axis direction, while the cubyl ends abut other cubyl ends with parallel molecular axes. The molecules do not all lie in the same plane. It is tempting to believe that a pattern of this sort is developing as a common feature as the rods lengthen, but until more data become available it is too early to be sure.

Experimental Section

General Information. NMR spectra were run on samples in solution in chloroform-*d* or (when specified) CD₂Cl₂ at ambient probe temperature: ¹H NMR at 400 MHz and referenced to internal tetramethylsilane; ¹³C NMR spectra at 100.6 MHz and referenced to the central line of the solvent. Proton chemical shifts are reported to a precision of ±0.01 ppm, carbon chemical shifts to a precision of ±0.1 ppm, sufficient for the purpose at hand. Infrared spectra were taken of
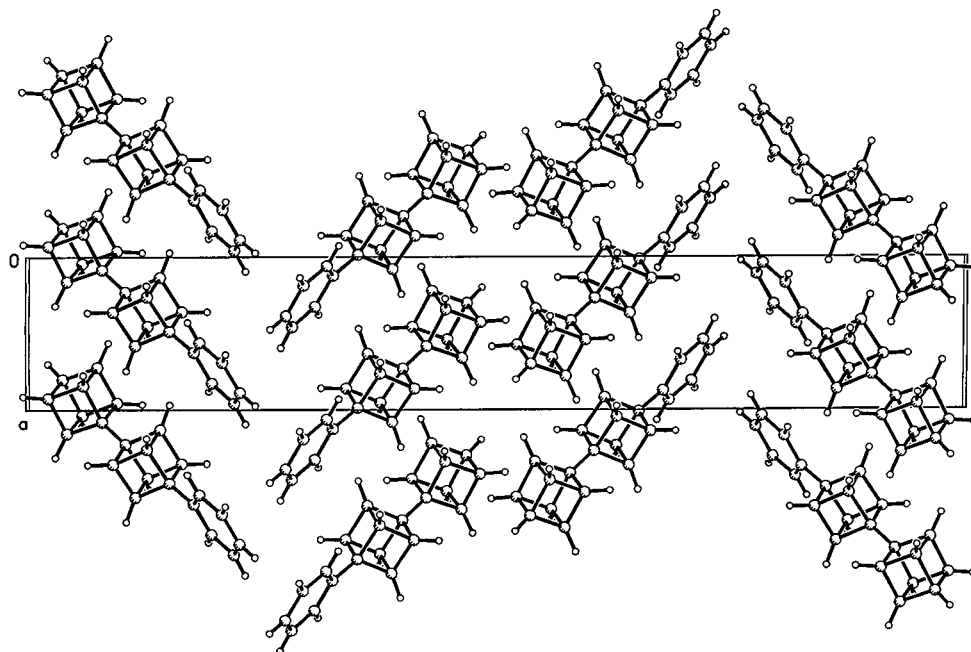
Figure 6. View down the *c* axis of the 1-phenyl-*p*-[2]cubyl (**26**) packing arrangement. There are two independent molecules in the asymmetric unit. The two different types stack in double layers which form a phenyl−herringbone interface where the phenyl end groups meet. There is no change in axis direction when bicubyl units abut those from another layer.

compounds in KBr pellets. Alkyllithium solutions were prepared as needed or obtained from Aldrich and titrated prior to use.[37] The commercial solutions of *t*-BuLi used were generally 1.7 M in pentane. Most reactions, as appropriate, were conducted under argon. Diethyl ether and tetrahydrofuran were freshly distilled from sodium/benzophenone before use. Purifications were normally accomplished by open column chromatography on Merck silica gel 60 (230−400 mesh) eluting patiently (!) with pure pentane unless otherwise specified. The mass spectra are 70-eV electron impact spectra. "Standard workup" means the following: add the mixture to water; extract with the named solvent; wash the extract with water followed by brine; dry over Na_2SO_4 or $MgSO_4$; remove solvent on a rotary evaporator at about 30−50 Torr with the bath held near room temperature. Data collection for single-crystal X-ray diffraction analyses was carried out on an automated Bruker diffractometer equipped with an incident beam monochromator. Space group assignments were based on systematic absences present in the diffraction patterns and were confirmed by structure solution and refinement. All structures were initially determined by direct methods, aided by the program XS, and refined with the full-matrix least-squares program XLS, contained in the SHELXTL collection of computer programs (Sheldrick, G. M. SHELXTL Crystallographic Software Version 5. Bruker Analytical Instruments, Madison, WI, 1994). This refinement program does not omit weaker data and refines only on "observed" data; it uses all data, weighted as to its precision, and refines on F^2, not F values. The weighted F^2 R value, w$R2$, is directly proportional to the minimized sum of squares and is reported. The traditional R values based on F are also reported, but values are somewhat higher when all data are included. In the cases below involving weaker data sets, traditional R's based only on "observed" $[I > 2\sigma(I)]$ data are given for comparison, but here also, all data were used to refine the structures.

Only illustrative procedures/characterizations are given here; the remainder are available in the Supplemental Material.

1,4-Diiodocubane (1). Iodobenzene diacetate (10.0 g, 31.2 mmol) and iodine (8.50 g, 33.5 mmol) were added as solids to a stirred suspension of cubane-1,4-dicarboxylic acid (2.00 g, 10.4 mmol) in dry benzene (200 mL) at room temperature. The purple mixture obtained

was refluxed for 6 h. The solution was cooled and washed with aqueous saturated Na_2SO_3 (2 × 50 mL) to remove iodine and then with water (50 mL) and brine (50 mL). The organic portion was dried over $MgSO_4$, filtered, and the solvent removed to leave a mixture of 1,4-diiodocubane and iodobenzene. Trituration with cold hexane dissolved away the latter and left **1** (3.20 g, 85%) as a white solid: mp 225−226 °C (lit.[38] mp 226−227 °C).

4-Phenylcubyl Iodide (5). A solution of *t*-BuLi in pentane (14.7 mL, 25.0 mmol) was added to a stirred solution of bromobenzene (1.88 g, 12.0 mmol) in ether (60 mL) under argon at −78 °C. (Commercial phenyllithium can be used instead, but its quality must be carefully checked as it is often contaminated with an appreciable amount of biphenyl.) The pale yellow solution was allowed to reach room temperature on its own (∼15 min) and was then cooled to 0 °C. Solid, powdered 1,4-diiodocubane (1.78 g, 5.00 mmol) was added all at once. The cooling bath was removed, and the mixture stirred for 40 min at room temperature. The resulting yellow, homogeneous solution was cooled to −20 °C and quenched with MeOH (1 mL). Standard workup (CH_2Cl_2, 50 mL) and chromatography (hexanes) afforded **5** (1.35 g, 88%) as a white solid: mp 85−86 °C; ^{1}H NMR δ 7.34 (t, 2H), 7.19 (m, 1H), 7.15 (d, 2H), 4.32 ppm (s, 6H); ^{13}C NMR δ 141.5, 128.5, 126.3, 124.7, 60.4 (cubyl, C-phenyl), 54.3 (cubyl, 3C), 51.9 (cubyl, 3C), 39.0 ppm (cubyl, C-I); MS *m/e* 306 (P+, 100), 180 (5), 179 (20), 178 (50), 152 (10), 102 (5) 89 (15). Anal. Calcd for $C_{14}H_{11}I$: C, 54.92; H, 3.61. Found: C, 54.88; H, 3.60.

Phenylcubane (10). A solution of *t*-BuLi in pentane (1.6 mL, 2.7 mmol) was added to a stirred suspension of **5** (366 mg, 1.20 mmol) in ether (15 mL) at −78 °C. A pale yellow, homogeneous solution formed. The dry ice/acetone bath was replaced with an ice/water bath. The mixture was stirred for 15 min and then quenched carefully with MeOH (1 mL). Standard workup (ether, 20 mL) and chromatography (hexanes) afforded **10** (179 mg, 83%) as a colorless liquid: ^{1}H NMR δ 4.01 (m, 3H), 4.12 (m, 1H), 4.17 (m, 3H), 7.20 (m, 3H), 7.38 ppm (t, 2H); ^{13}C NMR δ 44.1 (cubyl, 3C), 48.6 (cubyl, 1C), 51.2 (cubyl, 3C), 59.9 (cubyl, C-phenyl), 124.6, 125.6, 128.3, 143.4 ppm; MS *m/e* 80 (P+, 15), 179 (90), 178 (100), 165 (75), 152 (40), 115 (25), 102 (60). Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71; Found: C, 93.34; H, 6.69.

p-Bis(cyclooctatetraenyl)benzene (15). A solution of *p*-dicubylbenzene (**13**, 282 mg, 1.00 mmol) and [Rh(1,5-cyclooctadiene)Cl]₂ (20 mg, 0.04 mmol) in $CHCl_3$ (10 mL) in a tube with a stopcock was degassed using five freeze−thaw cycles and then heated at 60 °C for 16 h. The crude mixture was filtered through a small column of

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polymer-bound triphenylphosphine to remove the catalyst. The solvent was removed in vacuo, and the residue was chromatographed using 5% Et$_2$O in pentane. Cyclooctatetraene **15** (250 mg, 89%) was obtained as a yellow, crystalline compound:[15a] UV (Et$_2$O) λ_{max} 224 (16 210), 270 (16 500), 320 nm (7060); IR ν 3009, 2996, 1700, 1684, 1652, 863, 806, 739, 667, 640, 563 cm^{-1}; ^{1}H NMR δ 5.88 (br, 6H), 5.96 (br, 2H), 6.07 (br, 4H), 6.24 (br, 2H), 7.24 ppm (s, 4H); ^{13}C NMR δ 126.0, 127.8, 131.5, 131.7, 132.1, 132.2, 132.5, 132.8, 139.2, 141.5 ppm; MS *m/e* 282 (P$^+$, 90), 202 (100), 189 (60), 178 (50), 152 (20), 77 (20). Anal. Calcd for C$_{22}$H$_{18}$: C, 93.58; H, 6.41. Found: C, 93.55; H, 6.38.

4,4′-Diiodobicubyl (18, 1,4′-Diiodo-*p*-[2]cubyl). A solution of *t*-BuLi in pentane (2.6 mL, 4.4 mmol) was added to a stirred solution of mesityl bromide (438 mg, 2.20 mmol) in ether (5 mL) and cooled in a dry ice/acetone bath. The pale yellow reaction mixture was allowed to warm to room temperature and was then transferred by cannula to a cooled (ice/water bath), well-stirred suspension of **1** (356 mg, 1.00 mmol) in ether (10 mL). A yellow suspension formed immediately. The cooling bath was removed; reaction mixture was stirred at room temperature for 1 h. An orange suspension formed. The mixture was cooled (ice/water bath); MeOH (1 mL) was added. Standard workup (CH$_2$Cl$_2$, 25 mL) gave a pale orange semisolid. Trituration with hexanes left **18** (120 mg, 52%) as an off-white powder. It was purified by chromatography to give 112 mg (49%) of white material. A portion was crystallized from hot benzene for X-ray analysis: mp 193−196 °C; ^{1}H NMR δ 4.02 (m, 6H), 4.17 ppm (m, 6H); ^{13}C NMR δ 39.4 (cubyl C-I), 47.4 (cubyl, 6C), 54.4 (cubyl, 6C), 57.9 ppm (cubyl− cubyl). Anal. Calcd for C$_{16}$H$_{12}$I$_2$: C, 41.95; H, 2.64. Found: C, 42.86; H, 2.76. Crystal data: **18** (FW 458.06) crystallizes in the rhombohedral space group *R*(-3)*m*, with $a = 8.9775(3)$ Å, $b = 8.9775(3)$ Å, $c = 15.364(1)$ Å, ($\alpha = \beta = 90°$, $\lambda = 120°$, volume 1072.40(9) Å^3, $Z = 3$; density (X-ray) 2.128 g/cm^3. A clear $0.28 \times 0.22 \times 0.22$ mm crystal, in the shape of an almost-cubic chunk was used, with Mo Kα radiation, $\lambda = 0.710\,73$ Å, at $T = 294(2)$ K. The refinement agreement factors were $R = 0.0313$, w$R2 = 0.0655$ for all 373 unique reflections.

Chromatography (hexanes) of the hexanes-soluble material afforded **4-mesitylcubyl iodide** (21 mg, 10%): mp 127−129 °C; ^{1}H NMR δ 2.22 (s, 3H), 2.27 (s, 6H), 4.35 (m, 3H), 4.51 (m, 3H), 6.75 ppm (s, 2H); ^{13}C NMR δ 20.5, 21.4, 37.3 (cubyl, C-I), 53.8 (cubyl, 3C), 54.5 (cubyl, 3C), 63.7 (cubyl, C-mesityl), 129.9, 134.4, 135.7, 136.0 ppm; MS (*m/e* 348 (P$^+$, 100), 206 (15), 191 (10), 103 (15), 76 (5).

Bicubyl (20) was prepared as described for **10** using **18** in THF (10 mL) and *t*-BuLi in pentane (0.65 mL, 1.5 M, 1.0 mmol). Standard workup (ether) followed by flash chromatography (pentane) afforded **20** (41 mg, 91%) as a white crystalline solid: mp 175 °C; IR ν 2978, 2968, 1210, 865, 833 cm^{-1}; ^{1}H NMR (500 MHz) δ 4.04 (m, 2H) 3.87 ppm (m, 12H); ^{13}C NMR (125 MHz) δ 57.6 (quaternary C), 49.4, 46.4, 44.1 (ppm); MS *m/e* 206 (P$^+$, 70), 205 (100), 191 (90), 178 (70), 101 (40), 89 (55), 77 (55), 63 (50). Bicubyl (fw = 206.27) crystallizes in the monoclinic space group (*C*2/*c*, with $a = 16.240(4)$ Å, $b = 6.216-$ (1) Å, $c = 10.289(2)$ Å, $\beta = 99.23(2)°$, volume 1025.2(4) Å^3, $Z = 4$; density (X-ray) 1.336 g/cm^3. A clear colorless $0.66 \times 0.16 \times 0.06$ mm crystal, a prism, was used, with Mo Kα radiation, $\lambda = 0.710\,73$ Å, at $T = 223(2)$ K. The refinement agreement factors were $R = 0.0675$, w$R2 = 0.1199$ for all 917 unique reflections.

4,4′-Dimethylbicubyl (22). Methyllithium (0.505 mmol) in ether was added dropwise to a suspension of **18** (115 mg, 0.25 mmol) in dry THF at −78 °C. The mixture was allowed to come to room temperature and was stirred for 30 min. It was then cooled to −70 °C; a few drops of methanol were added slowly. Standard workup (CH$_2$Cl$_2$) followed by chromatography (pentane) gave first **22** (20 mg): ^{1}H NMR δ 3.68 (m, 6H), 3.46 (m, 6H), 126 (s, 6H) ppm; ^{13}C NMR δ 58.7, 57.1, 46.4, 42.5, 20.0 ppm; MS *m/e* 219 (P$^+$ − CH$_3$), 203 (50), 178 (70), 165 (40), 141 (40), 115 (100), 91 (50). Anal. calcd for C$_{18}$H$_{18}$: C, 92.26; H, 7.73. Found: C, 92.21; H, 7.71. Further elution gave 32 mg of **4′-methyl-*p*-[2]cubyl iodide (21)**: ^{1}H NMR δ 4.17 (m, 3H), 4.02 (m, 3H), 3.68 (m, 3H), 3.48 (m, 3H), 1.27 (s, 3H); ^{13}C NMR δ 58.6, 57.9, 57.2, 54.6, 47.5, 46.3, 42.4, 40.3, 19.8 ppm; MS *m/e* 219 (P$^+$ − I), 202 (100), 189 (30), 152 (30), 115 (30), 91 (20), 77 (30). Anal. Calcd for C$_{17}$H$_{15}$I: C, 58.98; H, 4.36. Found: C, 59.00, H, 4.33. Further elution gave 20 mg of "unreacted" starting material.

1-Iodo-4′-phenyl-*p*-[2]cubyl (23), 1-Iodo-4″-phenyl-*p*-[3]cubyl (24), and 1-Iodo-4‴-phenyl-*p*-[4]cubyl (25). A homogeneous solution of 4-phenylcubyl iodide (**5**, 612 mg, 2.00 mmol) in stirred diethyl ether (20 mL) was cooled to −77 °C (internal thermocouple). *t*-BuLi in pentane (2.35 mL, 4.00 mmol) was added dropwise; the solution was allowed to warm to −20 °C. The clear, pale yellow solution was cooled to −70 °C. Finely powdered, solid 1,4-diiodocubane (712 mg, 2.00 mmol) was added in one portion. The mixture was stirred at −70 °C for 10 min and then allowed to warm to 0 °C. It was stirred for 30 min and then cooled to −40 °C. Iodine (500 mg) was added. The mixture was allowed to come to room temperature and stirred there for 20 min. The whole was poured into aqueous 5% Na$_2$SO$_3$ (25 mL) sufficient to remove iodine. The reaction flask was rinsed with ether (30 mL). The whole was washed with H$_2$O (25 mL) and then brine (25 mL). The clear, orange ether layer was removed carefully. The remaining ether-insoluble product on top of the aqueous layer and on the sides of the funnel were extracted first into CH$_2$Cl$_2$ (3 × 15 mL) and then into CHCl$_3$ (3 × 15 mL). Separately, the extracts were dried and evaporated and found to contain 450, 321, and 29 mg of crude product, respectively. The residue from the CHCl$_3$ fraction was triturated with ether and then CH$_2$Cl$_2$. It was dried in vacuo to give **25** (24 mg, 6%): mp 225−228 °C (dec); ^{1}H NMR δ 3.74 (m, 6H), 3.84 (m, 6H), 3.97 (m, 6H), 4.06 (m, 3H), 4.18 (m, 3H), 7.16 (t, 1H), 7.20 (d, 2H), 7.33 ppm (t, 2H); ^{13}C NMR, solubility too poor; MS *m/e* 612 (P$^+$, 10), 485 (7), 408 (5), 303 (25), 289 (40), 265 (40), 226 (50), 202 (100), 179 (40), 178 (90), 152 (60), 114 (50). Anal. Calcd for C$_{38}$H$_{29}$I: C, 74.51; H, 4.76. Found C, 74.42; H, 4.70. The residue from the CH$_2$Cl$_2$ extract was triturated several times with ether and then dried in vacuo leaving **24** (124 mg, 24%): mp 215−217 °C (dec); ^{1}H NMR δ 3.73 (m, 6H), 3.86 (m, 3H), 4.00 (m, 3H), 4.05 (m, 3H), 4.18 (m, 3H), 7.15 (t, 1H), 7.20 (d, 2H), 7.34 ppm (t, 2H); ^{13}C NMR δ 40.3, 42.8, 42.9, 43.0, 47.5, 47.7, 54.7, 58.5, 58.68, 58.71, 59.4, 61.3, 124.6, 125.6, 128.3, 143.4 ppm; MS *m/e* 510 (P$^+$, 10), 383 (7), 289 (15), 265 (20), 254 (50), 202 (55), 178 (60), 165 (30), 152 (35), 128 (100). Anal. Calcd for C$_{30}$H$_{23}$I: C, 70.59; H, 4.52. Found C, 70.58; H, 4.50. The residue from the ether layer was subjected to chromatography. Phenylcubane (15 mg) was found in the early fractions; 1-phenyl-*p*-[2]cubyl (**26**, 10 mg) in the later ones. Further elution gave **5** (220 mg), followed by pure **23** (342 mg, 42%): mp 143−145 °C; ^{1}H NMR δ 3.85 (m, 3H), 4.01 (m, 3H), 4.08 (m, 3H), 4.21 (m, 3H), 7.21 (m, 3H), 7.36 ppm (t, 2H); ^{13}C NMR δ 40.0, 42.8, 47.5, 47.6, 54.6, 58.1, 58.4, 61.3, 124.6, 125.7, 128.3, 143.1 ppm; MS *m/e* 408 (P$^+$, 2), 281 (15), 265 (65), 202 (100), 178 (75), 127 (25), 77 (30). Anal. Calcd for C$_{22}$H$_{17}$I: C, 64.72; H, 4.19. Found: C, 64.66; H, 4.17.

1-Phenyl-*p*-[3]cubyl (27). *t*-BuLi solution (0.15 mL, 0.25 mmol) was added dropwise to a suspension of **25** (51 mg, 0.10 mmol) in dry THF (5 mL) at −78 °C. The mixture was allowed to warm to −10 °C over 30 min and was then quenched with methanol. Standard workup (CHCl$_3$, 4 × 15 mL) gave a white solid, which was purified by chromatography to give 36 mg (94%) of the hydrocarbon: IR ν 2970, 1599, 1498, 1444, 1228, 1412, 1189, 1032, 833, 749, 697, 503 cm^{-1}; ^{1}H NMR δ 3.73 (m, 6H), 3.88 (m, 6H), 3.90 (m, 3H), 4.00 (m, 3H), 4.05 (m, 1H), 7.18 (t, 1H), 7.22 (d, 2H), 7.37 ppm (t, 2H); ^{13}C NMR δ 42.9, 44.1, 46.4, 47.7, 49.3, 57.7, 58.8, 59.30, 59.34, 61.3, 124.6, 125.6, 128.3, 143.5 ppm. Anal. Calcd for C$_{30}$H$_{24}$: C, 93.71; H, 6.28. Found: C, 93.74; H, 6.29. Crystal data: **27** (fw 384.49) crystallizes in the orthorhombic space group *Pna*2$_1$, with $a = 10.258(2)$ Å, $b = 6.067(2)$ Å, $c = 62.85(2)$ Å, volume 3911(2) Å^3, $Z = 8$; density (X-ray) 1.306 g/cm^3. A colorless $0.60 \times 0.20 \times 0.01$ mm crystal, a very thin plate, was used, with Cu Kα radiation, $\lambda = 1.541\,78$ Å, at $T = 223(2)$ K. The refinement agreement factors were quite high, primarily because the data were very weak; $R = 0.1793$; w$R2 = 0.3269$ for all 2491 unique reflections, and $R = 0.0900$, w$R2 = 0.2133$ for 1250 reflections with [$I > 2\sigma(I)$].

1,4-Diiodo-2,7-bis(*N*-methyl-*N*-*tert*-butylaminomethyl)cubane (38). A solution of BH$_3$·THF (5.5 mL, 5.5 mmol) was added to a stirred suspension of 1,4-diiodo-2,7-bis(*N*-methyl-*N*-*tert*-butylcarboxamido)-cubane[23c] (**37**, 400 mg, 0.69 mmol) in THF (20 mL) at room temperature. The mixture was heated to reflux for 4 h, then cooled, quenched with MeOH (4 mL), and concentrated, leaving a white solid. This was suspended with stirring in dimethoxyethane (50 mL).

Hydrochloric acid (2 M, 50 mL) was added, and the mixture was heated to reflux for 4 h; a clear, colorless solution was obtained. The mixture was basified using aqueous NaOH, and the product was extracted into CH_2Cl_2 (4 × 25 mL). The extract was washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated to afford **38** (240 mg, 63%): mp 154−156 °C; ^{1}H NMR δ 4.27 (s, 4H), 2.52 (s, 4H), 2.21 (s, 6H), 1.06 (s, 18H); ^{13}C NMR δ 63.9, 57.3, 54.0, 53.6, 40.2, 36.9, 26.2 ppm; HRMS calcd 554.0655, found 554.0625. Anal. Calcd for $C_{20}H_{32}N_2I_2$: C, 43.34; H, 5.82; N, 5.05. Found C, 43.28; H, 5.88; N, 4.98.

1,4-Diiodo-2,7-bis(methoxymethyl)cubane (39). Hydrochloric acid (25 mL, 5 M) was added over 15 min to a stirred suspension of 1,4-diiodo-2,7-bis(*N*-methyl-*N*-*tert*-butylcarboxamido)cubane (750 mg, 1.29 mmol) in dimethoxyethane (30 mL). The mixture was heated to reflux for 24 h. DME was removed in vacuo. The residual aqueous suspension was filtered. The solid was rinsed with cold water and dried to give crude **1,4-diiodo-2,7-bis(hydroxycarbonyl)cubane** (350 mg, 61%): ^{1}H NMR (DMSO-d_6) δ 13.03 (br, 2H), 4.52 ppm (s, 4H). A solution of BH_3·THF (4.5 mL, 4.5 mmol) was added slowly to a stirred suspension of this crude diacid (0.25 g, 0.56 mmol) in THF (15 mL) at 0 °C under nitrogen. The cloudy, white suspension was stirred at room temperature for 8 h. The reaction was then quenched with MeOH (4 mL). The solvent and borates were removed in vacuo to afford **1,4-diiodo-2,7-bis(hydroxymethyl)cubane** (230 mg, 98%): mp 190−195 °C (dec); ^{1}H NMR (DMSO-d_6) δ 4.72 (t, 2H, OH, *J* = 5 Hz), 4.21 (s, 4H), 3.48 ppm (d, 4H, *J* = 5 Hz); ^{13}C NMR (DMSO-d_6) δ 64.3, 62.0, 54.4, 36.7 ppm. Powdered NaH (100 mg, 4.2 mmol) was added in one portion to a stirred solution of this crude diol (150 mg, 0.36 mmol) in DME (12 mL) at room temperature under nitrogen. The gray suspension obtained was stirred for 5 h, CH_3I (0.50 mL, 8.0 mmol) was added, and the suspension was stirred overnight. The mixture was quenched cautiously with H_2O. Standard workup (CH_2Cl_2, 30 mL) afforded the title diether **39** (150 mg, 94%) as a white solid: mp 115−117 °C; ^{1}H NMR δ 4.26 (s, cubyl, 4H), 3.52 (s, 4H), 3.41 ppm (s, 6H); ^{13}C NMR δ 72.9, 62.8, 59.3, 55.1, 36.1 ppm; MS *m/z* 444 (P+, <1), 399 (P+ − CH_2OCH_3, 5), 241 (40), 159 (70), 145 (85), 115 (100). Anal. Calcd for $C_{12}H_{14}I_2O_2$: C, 32.46; H, 3.18. Found: C, 32.54; H, 3.15.

1,4-Diiodo-2,7-dihexylcubane (42). A solution of *t*-BuLi in pentane (1.9 mL, 3.2 mmol) was added slowly over ∼5 min to a stirred suspension of 1,4-diiodo-2,7-bis(*N*-methyl-*N*-*tert*-butylcarboxamido)-cubane (410 mg, 0.704 mmol) in THF (70 mL) at −77 °C. A yellow suspension formed; the temperature rose to −60 °C. Hexyl iodide (Aldrich, 0.85 mL, 5.6 mmol) was added, and the mixture was allowed to warm to room temperature. Standard workup (CH_2Cl_2) and chromatography (4:1 hexanes/EtOAc) afforded **1,4-bis(*N*-methyl-*N*-*tert*-butylcarboxamido)-2,7-dihexylcubane** (190 mg, 54%) as a pale yellow solid: ^{1}H NMR δ 3.87 (s, 4H), 2.80 (s, 6H), 1.62 (br, 4H), 1.41 (s, 18H), 1.24 (br, 16H), 0.87 ppm (t, 6H). The procedure was repeated to accumulate more material. Part of the crude product (260 mg, 0.520 mmol) was dissolved in stirred THF (20 mL). Lithium aluminum hydride (120 mg, 3.16 mmol) was added in one portion. The mixture was heated to reflux for 4.5 h, cooled to 0 °C, and quenched carefully with water (3 mL). Standard workup (CH_2Cl_2) gave **1,4-bis(*N*-methyl-*N*-*tert*-butylaminomethyl)-2,7-dihexylcubane** (190 mg, 80%) as a yellow oil: ^{1}H NMR δ 3.36 (s, 4H), 2.58 (s, 6H), 1.57 (br, 4H), 1.24 (br, 16H), 1.01 (s, 18H), 0.87 ppm (t, 6H). It was used as it was directly; 220 mg (0.44 mmol) in a little acetone was added to a stirred solution of dimethyldioxirane (125 mL, ∼0.10 M) in acetone at 0 °C. The solution was stirred overnight at room temperature. The solvent was removed in vacuo; trituration of the residue with CH_2Cl_2 left **1,4-bis-(hydroxycarbonyl)-2,7-dihexylcubane** (100 mg, 63%) as a white solid: ^{1}H NMR (acetone-d_6) δ 3.82 (s, 4H), 1.70 (br, 4H), 1.29 (br, 16H), 0.86 ppm (br, 6H). Barton iododecarboxylation[10] using 50 mg (0.14 mmol) of the crude diacid, oxalyl chloride (5 mL), anhydrous sodium salt of 2-thiopyridone N-oxide (52 mg, 0.35 mmol), 4-(*N*,*N*-dimethylamino)pyridine (2 mg), CF_3CH_2I (0.07 mL, 0.7 mmol), and dry benzene (4 mL) gave, after standard workup and chromatography (pentane), **42** (40 mg, 55%) as a white solid: mp 76−77 °C; ^{1}H NMR δ 4.08 (s, 4H), 1.57 (br, 4H), 1.38 (br, 16H), 0.89 ppm (t, 6H); ^{13}C NMR δ 65.9, 56.2, 40.4, 32.9, 31.7, 29.3, 23.0, 22.6, 14.1 ppm; Anal. Calcd for $C_{20}H_{30}I_2$: C, 45.82; H, 5.77. Found C, 45.88; H, 5.82.

4,4′-Diphenylbicubyl (47). Naphthalene (350 mg, 2.73 mmol) was stirred in dry THF (5 mL). Freshly cut lithium metal (20 mg, 2.8 mmol) was added. The mixture was sonicated for 2 h using a cleaning bath. The resulting deep green solution of lithium naphthalenide was cooled to about −100 °C using a methanol/liquid nitrogen slush. A −78 °C solution of CuCN (90 mg, 1.0 mmol) and LiBr (175 mg, 2.02 mmol) in THF (3 mL) was added. A dark red solution of Cu(0) formed.[39] Separately, a solution of **5** (80 mg, 0.26 mmol) in THF (2 mL) was cooled to −40 °C (CH_3CN/dry ice bath) and then transferred by cannula into the Cu(0) solution. The mixture was stirred for 10 min and then the methanol/liquid nitrogen bath was replaced with a dry ice/acetone bath. Nitrobenzene (0.35 mL, 3.4 mmol) was added, and the reaction mixture was allowed to warm to room temperature on its own. Aqueous saturated NH_4Cl (3 mL) was added. Standard workup with ether (3 × 10 mL) gave a dark semisolid. Column chromatography (hexanes) was used to separate the desired product from excess naphthalene and nitrobenzene. A second chromatography (1:1 hexanes/CH_2Cl_2) afforded **47** (9.7 mg, 21%): mp 180−182 °C; ^{1}H NMR δ 3.91 (m, 6H), 4.03 (m, 6H), 7.24 (m, 6H), 7.38 ppm (t, 4H); ^{13}C NMR δ 43.0, 47.8, 58.8, 61.5, 124.7, 125.7, 128.4, 143.4 ppm; MS *m/e* 358 (P+, 2), 341, (15), 265 (40), 239 (50), 202 (100), 154 (50), 102 (40). Anal. Calcd for $C_{28}H_{22}$: C, 93.82; H, 6.17. Found: C, 93.76; H, 6.15.

1-Phenyl-4-(*p*-biphenyl)cubane (48). *t*-BuLi in pentane (2.35 mL, 4.00 mmol) was added dropwise to a homogeneous solution of **5** (612 mg, 2.00 mmol) in dry ether (20 mL) cooled in dry ice/acetone bath. The resulting solution was allowed to warm to 0 °C and was then cooled to −70 °C. 4-Phenyl-1,2-epoxycyclohexane[40] (400 mg, 2.40 mmol) was added dropwise. The mixture was allowed to come to room temperature and then stirred for 4 h. Methanol was added dropwise. Standard workup (CH_2Cl_2, 3 × 10 mL) gave a slightly colored oil that was purifed by chromatography (3:1 pentane/ether). A late fraction (300 mg) was a viscous oil taken to be the expected alcohol (OH in IR). It was dissolved in dry pyridine (3 mL). The solution was cooled to 0 °C. Phosphorus oxychloride (650 μL) was added dropwise. The mixture was stirred at room temperature for 14 h, cooled in an ice bath, and carefully quenched by dropwise addition of water. Standard workup (ether, 3 × 10 mL) gave an oil (320 mg). This was cleaned somewhat by quick passage through a small column of silica gel. The IR spectrum then showed no hydroxyl absorption. The material was dissolved in benzene (5 mL); DDQ (900 mg) was added. The solution was heated at 60 °C for 12 h, then cooled, and added to water. The CH_2Cl_2 (3 × 10 mL) extract was washed twice with dilute aqueous NaOH, water, and brine. Removal of solvent left a yellowish solid. Chromatography (pentane) gave 200 mg of a 92:8 mixture (by NMR) favoring **48**, the desired isomer, contaminated with some of the meta biphenyl isomer. **48**: ^{1}H NMR δ 4.19 (s, 6H), 7.61−7.20 (14H) ppm; ^{13}C NMR δ 47.7, 47.8, 60.6, 60.8, 124.7, 125.2, 125.8, 127.0, 127.0, 127.1, 128.4, 128.7, 138.7, 141.0, 142.1, 143.0 ppm; MS *m/e* 332 (P+), 230 (100), 178 (80), 152 (50), 115, (20), 102 (20), 77 (20). Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.05. Found: C, 93.88; H, 6.06.

1-(*p*-Biphenyl)-4-(2-naphthyl)cubane (51). *t*-BuLi solution (0.59 mL, 1.0 mmol) was added dropwise to a stirred solution of **6** (191 mg, 0.500 mmol) in ether (10 mL) and the resultant mixture was cooled in dry ice/acetone. The mixture was warmed to −10 °C and then cooled to −70 °C. Solid naphthalene-1,4-oxide[28] (75 mg, 0.60 mmol) was added, and the whole stirred at −70 °C for 10 min. The mixture slowly acquired an orange color. The cooling bath was removed, and the mixture was allowed to warm to room temperature. It was cooled to −30 °C and quenched with methanol. Standard workup (Et2O, 3 × 10 mL) and chromatography (10% Et2O in pentane) gave the dihydro-naphthol **49** (176 mg, 88%): ^{1}H NMR δ 2.80 (m, 1H), 3.97 (m, 3H), 4.15 (m, 3H), 4.84 (br, 1H), 5.95 (dd, 1H), 6.54 (dd, 1H), 7.16 (d, 1H), 7.24−7.37 (6H), 7.43 (t, 2H), 7.59 ppm (d, 4H); ^{13}C NMR δ 42.7, 45.0, 48.5, 59.5, 60.3, 70.1, 125.2, 125.8, 126.6, 126.9, 127.1, 127.6, 127.8, 128.0, 128.6, 128.7, 132.5, 136.2, 138.6, 141.1, 142.4 ppm. It was dissolved without further purification in CH_2Cl_2 (10 mL). A drop of methanesulfonic acid was added, and the solution was stirred at room

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temperature for 4 h. Standard workup (including a wash with aqueous NaHCO$_3$) followed by chromatography gave **51** (165 mg, 86% overall) as a white solid. Crystallization from ether/pentane gave white needles: ^{1}H NMR δ 4.26 (m, 6H), 7.37 (m, 3H), 7.45 (m, 5H), 7.62 (m, 5H), 7.82, (d, 2H), 7.86 ppm d, 1H); ^{13}C NMR δ 47.7, 47.8, 60.7, 61.1, 122.8, 123.5, 125.2, 125.3, 126.0, 127.0, 127.1, 127.5, 127.6, 128.2, 128.7, 131.9, 133.5, 138.8, 140.3, 141.1, 142.1 ppm; MS *m/e* 382 (P$^+$, 40), 230 (60), 204 (65), 152 (60), 97 (60), 77 (70). Anal. Calcd for C$_{30}$H$_{22}$: C, 94.20; H, 5.79. Found: C, 94.14; H, 5.77.

1-(*p*-Biphenyl)-4′-(9-phenanthryl)-*p*-[2]cubyl (54) was prepared in a similar way using **29** (242 mg, 0.500 mmol) suspended in ether (20 mL), *t*-BuLi in pentane (0.62 mL, 1.05 mmol), and phenanthrene-9,10-oxide ^{41} (100 mg, 0.600 mmol). The intermediate dihydrophenanthrol was chromatographed (10% ether in pentane) to give a clean sample (233 mg, 80%), which was directly dehydrated. Chromatography (10% ether in pentane) afforded **54** (206 mg, 77% overall) as a pale yellow solid: ^{1}H NMR δ 4.00 (m, 3H)), 4.22 (m, 6H), 4.32 (m, 3H), 7.34− 7.88 (16H), 8.66 (d, 1H), 8.78 ppm (d, 1H); ^{13}C NMR δ 43.0, 43.2, 47.5, 47.9, 57.2, 58.4, 61.2, 62.6, 122.4, 123.2, 123.4, 125.2, 125.6, 126.0, 126.2, 126.3, 126.6, 127.0, 127.1, 128.3, 128.7, 129.5, 130.3, 130.9, 131.7, 136.8, 138.6, 141.1, 142.5 ppm. HRMS calcd for C$_{42}$H$_{30}$: *m/e* 534.2347; found 534.2349.

Supporting Information Available: Drawings of compounds **10**−**14**, **26**−**28**, **32**−**36**, **40**, **41**, and **47**; experimental procedures for **6**−**9**, **11**−**14**, **16**, **26**, **28**−**35**, **40**, **41**, **43**−**46**, **50**, **52**, and **53**; tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and views of the X-ray structures of **11**, **13**, **18**, **20**, **26**, and **27** with numbering systems used and thermal ellipsoids; view of the molecular packing in a crystal of **27** (PDF). This material is available for free on the Internet at http://pubs.acs.org.

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