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## Synthesis and Chemistry of 1,3,5,7-Tetranitrocubane Including Measurement of Its Acidity, Formation of *o*-Nitro Anions, and the First Preparations of Pentanitrocubane and Hexanitrocubane<sup>1</sup>

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**Abstract:** Nitro groups on alternate corners of cubane enhance the acidity of cubyl hydrogen ( $pK_a \sim 21$ ) and provide sufficient activation for ready anion formation. The sodium salt of 1,3,5,7-tetranitrocubane reacts easily with electrophiles and leads thereby to yet more highly substituted cubanes, like carbomethoxy- and (trimethylsilyl)tetranitrocubane. Anions from these species are also easily formed and are useful for further substitution on the cubane nucleus. Dinitrogen tetroxide reacts with the anion of tetranitrocubane to give 1,2,3,5,7-pentanitrocubane, the first cubane to contain vicinal nitro groups. The reaction probably involves oxidation of the anion to the corresponding radical. Similarly, the anion of pentanitrocubane is used to prepare 1,2,3,4,5,7-hexanitrocubane, the most highly nitrated cubane made to date. Single-crystal X-ray structural information is given for both penta- and hexanitrocubane.

### Introduction

The “effectiveness” of an explosive is dependent on many things. The energetics of the decomposition reaction and the number of moles and molecular weight of the gaseous products are among the critical factors.<sup>2</sup> Density is also crucial. The more moles of an explosive that can be packed into the limited volume of a shell the better. Less obvious, but more important, the velocity of the propagation wave through an explosive, i.e., the rate of energy release, is proportional to its density squared.

Cubane is a kinetically stable compound (decomposition only

above 220 °C), but a thermodynamic powerhouse ( $\Delta H_f \sim 150$  kcal/mol).<sup>3</sup> It is one of the most dense hydrocarbons known (1.29 g/cm<sup>3</sup>).<sup>4</sup> As molecular volume is (very roughly)<sup>5</sup> a group additive property,<sup>6</sup> highly nitrated cubanes can be predicted to be very dense,<sup>6</sup> and hence they are expected to be very powerful explosives. Octanitrocubane (**1**) is calculated to be 15–30%

(3) (a) Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626. (b) Kirklin, D. R.; Churney, K. L.; Domalski, E. S. *J. Chem. Thermodynam.* **1989**, *21*, 1105.

(4) Fleischer, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3889. For comparison: the density of adamantane is approximately 1.09 g cm<sup>-3</sup>.

(5) A good discussion can be found in: Marchand, A. P.; Zope, A.; Zaragoza, F.; Bott, S. G.; Ammon, H. L.; Z. Du, *Tetrahedron* **1994**, *50*, 1687.

(6) For example: Stine, J. R. *Prediction of Crystal Densities by Group Additivity*, Report LA-8920; Los Alamos National Laboratory: Albuquerque, NM, 1981.

(7) (a) Gilbert, E. E. Private communication, 1979. (b) Alster, J.; Sandus, O.; Genter, R.; Slagg, N.; Ritchie, J. P.; Dewar, M. J. S. Working Group Meeting on High-Energy Molecules, Hilton Head, SC, 28–29 April, 1981.

<sup>†</sup> The University of Chicago.

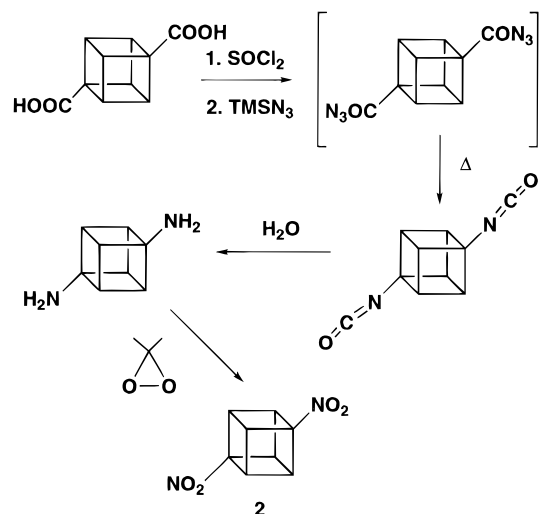
<sup>‡</sup> The Naval Research Laboratory.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1997.

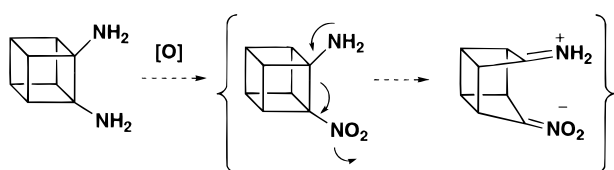
(1) Part of this work was communicated previously: Lukin, K. A.; Li, J.; Gilardi, R.; Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 864.

(2) (a) Kamlet, M. J.; Jacobs, S. J. *J. Chem. Phys.* **1968**, *48*, 23. See also the overviews in: (b) Marchand, A. P. *Tetrahedron* **1988**, *44*, 2377 and (c) Bottaro, J. C. *Chem. Ind.* **1996**, *7*, 249.

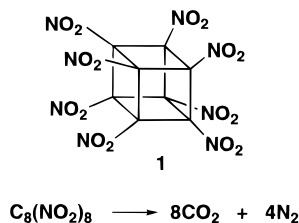
## Scheme 1



## Scheme 2



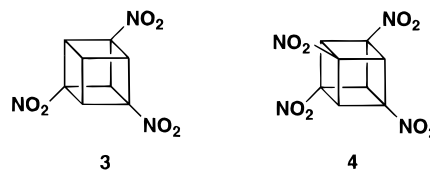
better than HMX,<sup>7</sup> an important explosive produced and used in large quantity.



The introduction of a few nitro groups onto the cubane nucleus is straightforward in certain cases. It can be accomplished by functional group transformation of cubanecarboxylic acids to the corresponding amines via Curtius rearrangement followed by oxidation, as shown, for example, in Scheme 1 for 1,4-dinitrocubane (**2**).<sup>8</sup> The method fails however for cubanes with adjacent carboxylic acid groups. Although the corresponding vicinal diamines can be made and are relatively stable compounds, ring cleavage reactions intervene during attempted oxidation to a 1,2-dinitrocubane. The cubane system is destroyed entirely, probably by a push-pull mechanism something like that shown in Scheme 2. This sort of skeletal cleavage in the cubane systems always happens when attempts are made to place an electron-donating group on a cubane carbon adjacent to one bearing an electron-withdrawing substituent. For example, all attempts at making 2-aminocubanecarboxylic acid have failed.

Cage cleavage via the push-pull mechanism limits the methodology of Scheme 1 to the preparation of nitrocubanes without vicinal nitro groups. It has been applied successfully to the preparation of 1,3,5-trinitrocubane (**3**) and 1,3,5,7-tetranitrocubane (**4**),<sup>9</sup> but as all more highly nitrated cubanes

necessarily have nitro groups on adjacent carbons none can be made without development of a new methodology. We present such methodology in this paper.



## The Precursors

In 1993 we reported the first synthesis of cubane-1,3,5,7-tetracarboxylic acid.<sup>9</sup> For this we utilized techniques for ortho metalation of amide-activated cubanes developed specially for the purpose.<sup>10</sup> The approach was novel, but long and complex. Once 1,3,5,7-tetranitrocubane (**4**) was obtained from the tetraacid (cf., Scheme 1) and was found to be very dense,<sup>9</sup> shock insensitive, and a powerful explosive exceeding expectation,<sup>11</sup> it was clear that a better synthesis would be required. In 1993 Bashir-Hashemi provided just that with his brilliant application<sup>12</sup> of photochemically induced chlorocarbonylation (the Kharasch-Brown reaction<sup>13</sup>) to functionalization of the cubane system. He showed that irradiation of cubane carboxylic acid chloride **5** in excess oxalyl chloride led to substantial formation of cubane-1,3,5,7-tetracarboxylic acid chloride (**12**)—the key intermediate in our original synthesis of tetranitrocubane **4**—presumably by one or more of the paths in Scheme 3.

The product distribution (ratio of positional isomers) from this photochlorocarbonylation is exceedingly dependent on reaction conditions, some evident and others less so. Bashir-Hashemi initially reported the use of tungsten lamp radiation for the chlorocarbonylation. In our hands this proved useful for introduction of one or two chlorocarbonyl groups but impractical for production of the desired tetraacid chloride due to long reaction times (several days). Use of a Rayonet photoreactor (254 nm, quartz cell) at its ambient temperature (40 °C), later recommended,<sup>12b</sup> gave us a mixture of tetraacid chlorides **12**, **13**, and **14** in about a 53:12:35 ratio,<sup>12c</sup> but still required long periods of irradiation. We switched to a higher flux system—a Hanovia, 450-watt, medium pressure Hg arc—and followed the extent of chlorocarbonylation and its stereospecificity by <sup>1</sup>H NMR analysis of aliquots. Our initial experiments were carried out using a Pyrex photoreactor. Under our conditions (see Experimental Section) the first chlorocarbonylation was not as selective as initially described;<sup>12a,14</sup> in addition to the 1,3- and 1,4-diacid chlorides **6** and **7**, cubane-1,2-dicarboxylic acid chloride (**8**) was produced in substantial amount. The ratio of ortho to meta to para disubstituted products,<sup>15</sup> **8** to **6** to **7**, determined before much triacid chloride had formed, was about 6:10:1. This ratio is approximate as the NMR signal for the 1,4-diacid overlaps one of those of the 1,2. Still, it is substantially different from the simple statistical expectation of 3:3:1. Hrovat and Borden's *ab initio* calculations

(10) (a) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724–726. (b) For a review, see: Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.

(11) Army Research, Development and Engineering Center, Picatinny, NJ. Private communication.

(12) (a) Bashir-Hashemi, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 612. (b) Bashir-Hashemi, A.; Li, J.; Gelber, N.; Ammon, H. *J. Org. Chem.* **1995**, *60*, 698. (c) We and Bashir-Hashemi (private communication) have noted that the reaction is somewhat cleaner at 0 °C.

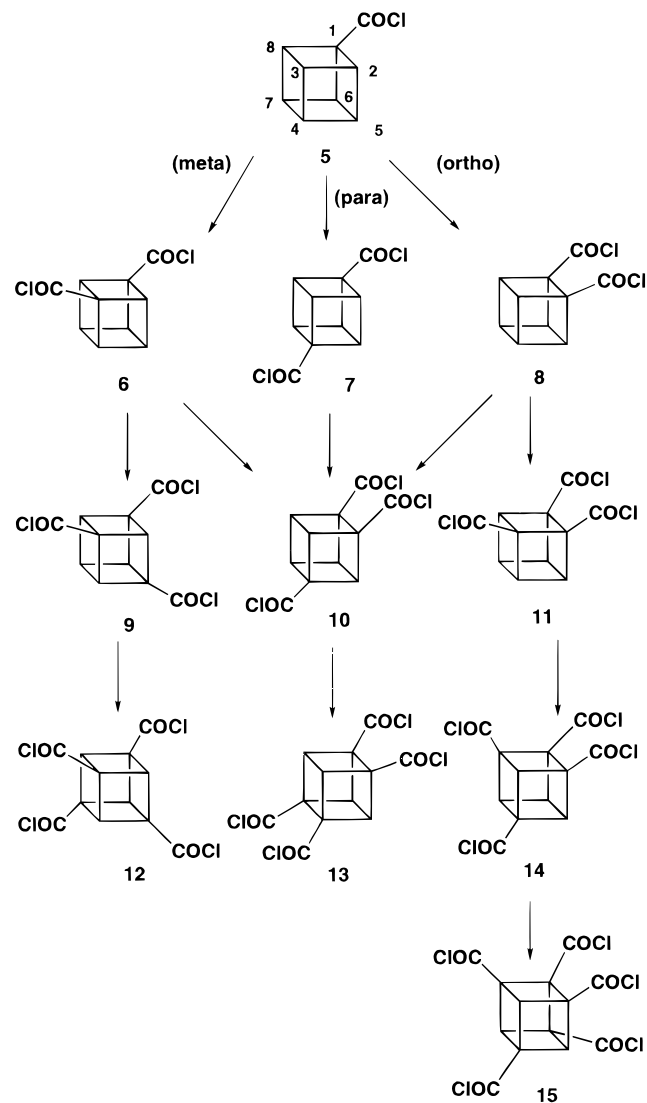
(13) (a) Kharasch, M. S.; Brown, H. C. *J. Am. Chem. Soc.* **1940**, *62*, 454. (b) *Ibid.* **1942**, *64*, 329.

(14) A later report of Bashir-Hashemi *et al.*<sup>12b</sup> includes the formation of cubane-1,2-dicarboxylic acid chloride (see footnote 9 therein).

(8) (a) Eaton, P. E.; Shankar, B. K. R.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (b) Eaton, P. E.; Wicks, E. *J. Org. Chem.* **1988**, *53*, 5353.

(9) Eaton, P. E.; Xiong, Y.; Gilardi, R. *J. Am. Chem. Soc.* **1993**, *115*, 10195.

## Scheme 3



of the charge distribution over the cubane nucleus in the transition state pertaining to cubyl radical formation shows that the least positive charge develops at the positions meta to the site of radical formation.<sup>16</sup> Thus, preference for meta over ortho/para substitution is in agreement with the electron-withdrawing properties of a chlorocarbonyl group and the radical mechanism of the reaction.<sup>17</sup> On the other hand, it is not clear why the observed ratio of ortho to para substitution is ~6:1. Although statistics favors ortho substitution (3:1), the inductive effect must work against this.<sup>18</sup>

When the irradiation was carried further the major products were the 1,3,5-, 1,2,4-, and 1,2,3-cubanetricarboxylic acid chlorides **9**, **10**, and **11** in approximately a 6:4:2 ratio. The first two were identified by comparison to samples prepared from known cubane diacids.<sup>19</sup> The identification of **11**, derived from the previously unknown 1,2,3-triacid, was based on multiplets in its <sup>1</sup>H NMR spectrum at  $\delta$  4.08 and 4.45 ppm

(15) The formal Baeyer system numbering of the cubane skeleton is shown for compound **5** in Scheme 3. Ortho, meta, para designations, as commonly understood, are more easily visualized.

(16) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6459.  
(17) Pryor, W. A.; Davis, W. H., Jr.; Stanley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4754.

(18) Steric effects between ortho substituents on a cubane nucleus are very small.

(19) Eaton, P. E.; Lee, C. H.; Xiong, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8016 and references therein.

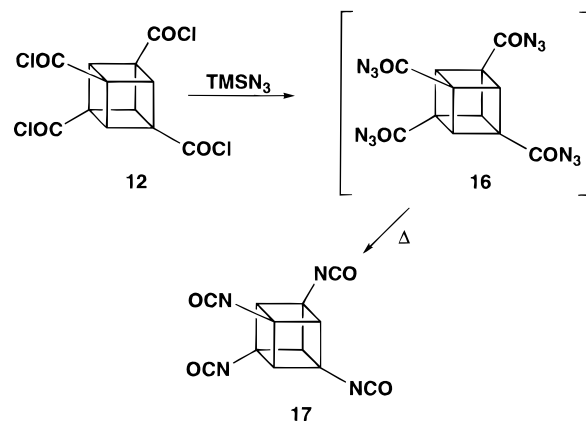
attributable to protons at C<sub>7</sub> and C<sub>4,6</sub>, respectively. A control chlorocarbonylation of pure cubane-1,2-dicarboxylic acid chloride (**8**) gave **10** and **11** in a 2:1 ratio.

Further chlorocarbonylation of compounds **9–11** in a Pyrex photoreactor was slow; we switched to a quartz apparatus. Optimum results were obtained when the temperature of the reaction mixture was kept below 15 °C (see Experimental Section). Under these conditions the first and second chlorocarbonylations were remarkably quick and were over in less than 15 min. Further chlorocarbonylation was quite selective, controlled apparently by the fact that many potential sites are deactivated by two ortho chlorocarbonyl groups (positions 2, 4, 6, 8 in **9**; 3, 5 in **10**; 8 in **11**). Thus, the favored products are the tetraacid chlorides **12**, **13** and **14**.<sup>19</sup> Further reaction of **12** and **13** is made unlikely by the combined deactivation effects, but an additional chlorocarbonylation was observed on **14** ( $\rightarrow$  **15**); position 6 thereof being still sufficiently reactive.

On a preparative scale (10 mmol) irradiation of a 0.1 M solution of cubanecarboxylic acid chloride **5** in oxalyl chloride gave after 3 h roughly a 70:8:22 mixture of the tetrasubstituted cubanes **12–14**, from which the desired 1,3,5,7 isomer **12** could be precipitated in 95% purity by addition of diethyl ether. From most runs we were usually able to obtain about a 30% yield of **12** overall from cubane monoacid. However, we do not wish to leave the impression that the chlorocarbonylation reaction is truly "under control". The variables are many in this complex free-radical reaction and even subtle changes (such as whether the light source is new or aged) affect the yield significantly. In spite of this caveat, the reaction is very useful and provides a convenient preparation of an extraordinarily versatile intermediate.<sup>20</sup>

In previous work the tetraacid chloride **12** had been converted via quadruple Curtius rearrangement of the tetraacyl azide **16** to the corresponding tetraisocyanate **17** (Scheme 4).<sup>19</sup> Acyl

## Scheme 4



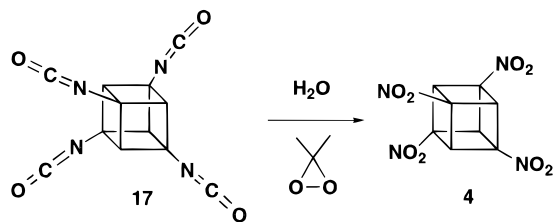
azides are often shock sensitive, dangerous compounds. We have learned (fortunately without serious incident) that cubane acyl azides are primary explosives, worthy of the greatest respect. Such compounds *cannot* be worked with safely unless *always* in dilute solution. This presents experimental difficulties for the uncatalyzed reaction of cubyl acid chlorides with trimethylsilyl azide (TMSN<sub>3</sub>) is very slow in solutions dilute enough to keep the product acyl azide in solution. If excess TMSN<sub>3</sub> be used to enhance the rate, then before thermal rearrangement of the acyl azide can be accomplished in good yield: (1) the excess must be removed (a treacherous procedure); or (2) the solution must be diluted substantially to reduce the

(20) For example, Carell, T.; Wintner, E. A.; Bashir-Hashemi, A.; Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2059.

reaction of  $\text{TMSN}_3$  with the isocyanate.<sup>21</sup> The problem is better resolved by using a catalyst to accelerate acyl azide formation.

Tertiary amines and pyridines are familiar catalysts for transformations of acid chlorides. However, these have not been used as catalysts in "one-pot" azidation/Curtius rearrangements,<sup>22</sup> probably because they can also catalyze oligomerization of the isocyanate.<sup>23</sup> Hertzler,<sup>24</sup> working here, found that triethylamine or pyridine nicely accelerated the conversion of 1,2,4,7-cubane tetraacid chloride (**13**) to the tetraacyl azide, but its rearrangement to isocyanate in the presence of these amines was accompanied by the formation of higher molecular weight material. The much more hindered amine 2,6-di-*tert*-butylpyridine (10 equiv %) catalyzed azidation as well, but did not interfere with the isocyanate. This was mildly puzzling: if the hindered amine were capable of "classic" catalysis of the reactions of the acid chloride, it should also have initiated isocyanate oligomerization.<sup>23</sup> Ultimately it became clear that the real catalyst in the Hertzler work was the pyridinium hydrochloride, formed adventitiously. When a small amount (0.11 equiv %) of 2,6-di-*tert*-butylpyridine dihydrochloride<sup>25</sup> was purposely added to a dilute solution of acid chloride and  $\text{TMSN}_3$  formation of the tetraacyl azide was complete within an hour. The catalytic action of the salt is probably simple, providing free chloride ion to displace azide anion from  $\text{TMSN}_3$ . The resulting pyridinium azide is highly ionized, and thus azide ion becomes available at a good concentration. Hydrogen chloride by itself proved useless as a catalyst for it reacts with  $\text{TMSN}_3$  to give  $\text{TMSCl}$  and hydrazoic acid, which itself is very little ionized ( $\text{p}K_a \sim 4.7$ ). The rearrangement of the tetraacyl azide was carried out in reasonably dilute solution to suppress secondary reactions. The tetraisocyanate **17** was isolated in >80% yield, pure enough to be used directly in the next conversions. In passing, we note that this tetraisocyanate, which has tetrahedral symmetry, is an excellent candidate as a core molecule for polyurethane dendrimers.

To our knowledge, there is still<sup>8b</sup> no way to effect oxidative cleavage of the carbon–nitrogen double bond of an isocyanate. We have, however, demonstrated that dimethyldioxirane (DMDO) in wet acetone efficiently converts isocyanates into nitro compounds via hydration of the isocyanate groups to the carbamic acids, their immediate decarboxylation, and rapid DMDO oxidation of the amines so generated.<sup>8b,26</sup> Pure 1,3,5,7-tetranitrocubane (**4**) was isolated in 45% yield overall from tetraacid chloride **12**—a remarkable feat considering that at least five distinct transformations must occur at *each* of four sites.



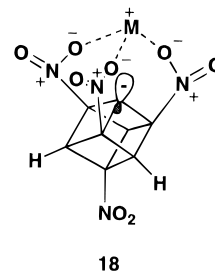
**The Acidity of 1,3,5,7-Tetranitrocubane.** The physical properties, crystal structure, and thermal behavior of 1,3,5,7-

(21) See for example: Gilardi, R.; George, C.; Karle, J.; Eaton, P. E.; Rao, M. *J. Heterocyc. Chem.* **1993**, 1389.

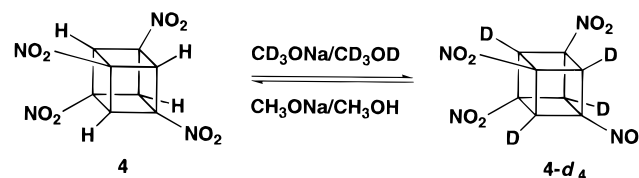
(22) Potassium azide complex with 18-crown-6 in benzene (Warren, J. D.; Press, J. B. *Synth. Commun.* **1980**, 10, 107) and zinc iodide (Farooq, O.; Wang, Q.; Wu, A.; Olah, G. A. *J. Org. Chem.* **1990**, 55, 4282) have been reported to be good catalysts for azidation of acid chlorides with  $\text{TMSN}_3$ . The latter proved unsatisfactory for the case at hand. We did not investigate the other.

(23) (a) Frish, K. C.; Rumao, L. P. *J. Macromol. Sci.* **1970**, C5, 103. (b) However, hindered amines do not react with isocyanates: Knölker, H.-J.; Braxmeier, T. *Tetrahedron Lett.* **1996**, 37, 5861.

tetranitrocubane have been presented previously.<sup>9</sup> Here we are concerned with the wet chemistry of the compound. The symmetry of the molecule (pseudo-tetrahedral) is such that each of the four identical hydrogens is surrounded by three nitro groups, one on each  $\beta$  carbon. The inductive/field<sup>27</sup> electron-withdrawing effect of the nitro group is stronger than that of any other uncharged functionality.<sup>28,29</sup> This, added to the already enhanced acidity of a cubyl C–H group over a typical hydrocarbon,<sup>30</sup> might make it relatively easy to generate the anion of 1,3,5,7-tetranitrocubane. Coordination of the electron-rich oxygen of one or more of the nitro groups with the gegenion could also offer particular stabilization (illustrated in the extreme) to a salt such as **18**. One can also speculate that the highly polarized nitro group(s) might aid the approach of a base and the kinetic deprotonation of the CH group.<sup>31</sup>



Regardless of the intimate details, the acidity of the cubane hydrogens is indeed so enhanced by the nitro groups in 1,3,5,7-tetranitrocubane that their exchange can be effected rapidly even with bases as mild as sodium methoxide in methanol. Reaction of **4** with 0.125 molar  $\text{CD}_3\text{ONa}$  in  $\text{CD}_3\text{OD}$  for 45 min at room temperature followed by quenching with hydrochloric acid and extraction with EtOAc gave in 87% yield **4-d<sub>4</sub>**. The reverse experiment, reaction of **4-d<sub>4</sub>** with  $\text{CH}_3\text{ONa}$  in  $\text{CH}_3\text{OH}$ , returned **4**.



(24) Hertzler, R. L.; Eaton, P. E. *Abstracts of Papers*; 205th National Meeting of the American Chemical Society, Denver, CO, Spring 1993; American Chemical Society: Washington, DC, 1993; Paper 128.

(25) (a) Hopkins, H. P., Jr.; Ali, S. Z. *J. Am. Chem. Soc.* **1977**, 99, 2069.

(b) Arnett, E. M.; Chawla, B. *J. Am. Chem. Soc.* **1978**, 100, 214.

(26) Murray, R. W.; Jeyaraman, R.; Mohan, L. *Tetrahedron Lett.* **1986**, 27, 2335.

(27) Sacher, E. *Tetrahedron Lett.* **1986**, 27, 4683.

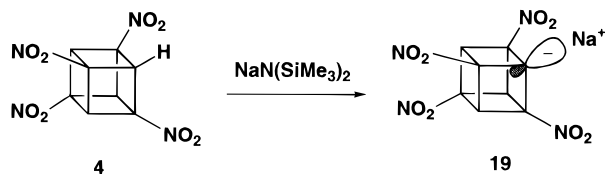
(28) Ceppi, E.; Eckhardt, W.; Grob, C. A. *Tetrahedron Lett.* **1973**, 3627.

(29) Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, 49, 959.

(30) Cubane is approximately 60 000 times more acidic than cyclohexane (Dixon, R. E.; Streitwieser, A.; Williams, P. G.; Eaton, P. E. *J. Am. Chem. Soc.* **1991**, 113, 357), a function of the increased s character in the exocyclic orbitals. Yet this is still quite insufficient to permit significant equilibrium metalation with even powerful amide bases like  $\text{LiTMP}$ .<sup>10</sup>

(31) We can find no definitive evidence in the literature for metalation e.g.,  $\text{CH} \rightarrow \text{CLi}$ ) assisted by an ortho nitro group. Ortho metalation of aromatic nitro compounds is usually unsuccessful; electron transfer is the dominant process instead (Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, 33, 8). However, ortho-lithiated nitrobenzenes (thermally unstable) have been generated by metal–halogen exchange at temperatures below  $-100^\circ\text{C}$  (Köbrich, G.; Buck, P. *Chem. Ber.* **1970**, 103, 1412; **1970**, 103, 1420). When deprotonation  $\beta$  to a nitro group does occur (e.g., in  $\beta$ -nitro ketones because of the carbonyl group) elimination of nitrite and olefin formation follows immediately (Ono, N. In *Nitro Compounds. Recent Advances in Synthesis and Chemistry*, Feuer, H., Nielsen, A. T., Eds.; VCH Publishers Inc., 1990, p 86).

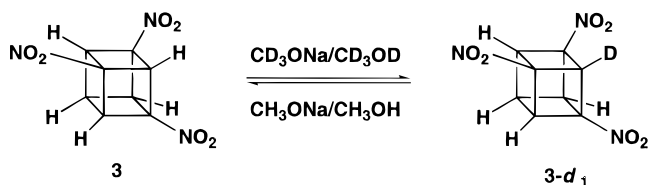
None of the salts which must intervene in these exchanges could be detected in  $\text{CH}_3\text{OD}/\text{CH}_3\text{ONa}$  by NMR. Their concentration must be quite low. We could, however, approximate the  $\text{p}K_a$  of tetranitrocubane **4** from low-temperature proton NMR measurements on equilibrium mixtures with various bases. Reaction of **4** with sodium bis(trimethylsilyl)amide in THF- $d_8$  at  $-75^\circ\text{C}$  showed clearly the formation of tetranitrocubyl sodium **19**. The NMR resonance of three residual protons is a sharp singlet at  $\delta$  5.54 ppm, 0.53 ppm higher field than that of the neutral parent under the same conditions.



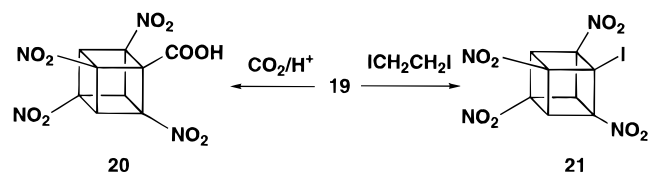
Almost complete ( $\geq 99\%$ ) salt formation occurs in THF on treatment of **4** with one equivalent of sodium bis(trimethylsilyl)amide, but none ( $\leq 1\%$ ) with  $\alpha$ -lithiobenzyl cyanide. As the  $\text{p}K_a$  in THF of bis(trimethylsilyl)amine is 25.8<sup>32</sup> and that of benzyliocyanide is 18.7,<sup>33</sup> the  $\text{p}K_a$  of **4** must be between about 20 and 24. We have been able to narrow this range to 20.5–22.5 by noting that **4** is partially converted to its anion by 1.5 equiv of potassium *tert*-butoxide (the  $\text{p}K_a$  of *tert*-butyl alcohol in THF is given as 21.6).<sup>34</sup> However, this cannot be used to pinpoint the  $\text{p}K_a$  of **4** as the alcohol and alcoholate give only one averaged NMR signal due to rapid proton exchange.

How many nitro groups on cubane are necessary to achieve a measurable and/or synthetically useful acidity? Early experiments with mono- and 1,4-dinitrocubane designed to look for substituent-enhanced acidity were frustrating; complete destruction with strong bases and lack of reactivity with weaker bases were all that could be found.<sup>35</sup> Not even the simplest exchange reaction could be achieved. Clearly, activation by one nitro group is insufficient for  $\beta$ -anion formation, if it occurs at all, instead of what are probably single-electron transfer reactions that somehow unravel the cubane nucleus.

A brief study of 1,3,5-trinitrocubane (**3**),<sup>9</sup> which possesses three hydrogens each with two adjacent nitro groups and one hydrogen surrounded by three nitro groups, showed that only the latter hydrogen underwent D-for-H exchange with  $\text{CD}_3\text{OD}$  in the presence of  $\text{CD}_3\text{ONa}$ . Clearly this demonstrates that the remote fourth nitro group in **4** is not essential for anion formation. But, all three nitro groups about a single CH do seem necessary for successful ortho anion formation with methoxide as the base. We have not yet looked to see if two nitro groups ortho to the same cubyl CH would suffice were stronger bases used, but we suspect this will prove to be the case.

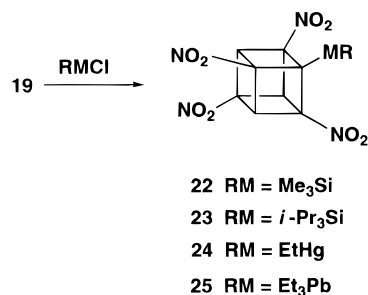


**The Chemistry of 1,3,5,7-Tetranitrocubylsodium.** Tetranitrocubylsodium (**19**), formed directly on treatment of **4** with sodium bis(trimethylsilyl)amide in THF at  $-75^\circ\text{C}$ , is stable for hours at that temperature, but it decomposes rapidly above  $-50^\circ\text{C}$ . Its reactions with electrophiles provide a useful and convenient way to achieve further functionalization of the cubane nucleus. For example, reaction of **19** in THF at  $-75^\circ\text{C}$  with carbon dioxide followed by neutralization gave the tetranitrocubane carboxylic acid **20** in 85% isolated yield. This was characterized as its methyl ester **20a**. Similarly, iodination of **19** using 1,2-diiodoethane as the iodinating agent gave iodo-tetranitrocubane **21** in 70% yield. These compounds are colorless, stable crystalline materials.



1,3,5,7-Tetranitrocubylsodium can also be used conveniently for the preparation of various more covalently bound and more stable metal/metalloid derivatives of tetranitrocubane. (Trimethylsilyl)tetranitrocubane (**22**) was obtained in 80% yield by quenching **19** with chlorotrimethylsilane. Although the compound is air stable, the TMS group is lost on silica gel chromatography, returning tetranitrocubane **4**. Such sensitivity is unusual for carbon–silicon bonds. (Trimethylsilyl)cubane,<sup>36</sup> without nitro groups, is completely stable under such conditions. The easy loss of the TMS group from **22** must trace to the stabilization available to a tetranitrocubyl anion. Nonetheless, the much more hindered silyl derivative (triisopropylsilyl)tetranitrocubane **23** produced in 80% yield when **19** was quenched with triisopropylsilyl chloride (TIPSCl) fully survived purification by chromatography.

Heavy metal derivatives of **4** could be formed with similar ease. Quenching **19** with ethylmercury chloride gave the mercuriated tetranitrocubane **24** in 65% isolated yield. Reaction of **19** with triethyllead chloride gave the plumblynitrocubane **25** in 67% yield. All these metallic derivatives of tetranitrocubane are air-stable solids, soluble in common organic solvents like chloroform or acetone. We anticipate numerous synthetic applications.<sup>37</sup>



The  $^1\text{H}$  NMR spectrum of each of the cubanes prepared in this series of derivatives of 1,3,5,7-tetranitrocubane shows only a single sharp line, reflecting the high molecular symmetry. The  $^{13}\text{C}$  NMR is more revealing, identifying the three identical C– $\text{NO}_2$  groups, the three identical C–H groups, the singular C– $\text{NO}_2$  group remote from the newly introduced substituent, and the carbon bearing this substituent. The introduction of electron-withdrawing substituents on **4** caused only slight

(32) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.

(33) Fraser, R. R.; Mansour, T. S.; Savard, S. *Can. J. Chem.* **1985**, *63*, 3505.

(34) Brown, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 680.

(35) We are grateful to Drs. Ravi Shankar and Gene Wicks for these experiments.

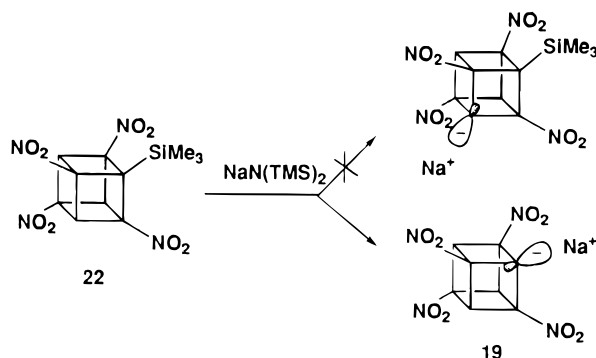
(36) From cubyllithium and  $\text{TMSCl}$ : Emrick, T., this Laboratory.

(37) For example: (a) Lukin, K. A.; Li, J.; Gilardi, R.; Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 866. (b) Lukin, K. A.; Li, J.; Gilardi, R.; Eaton, P. E. *J. Org. Chem.*, in press.

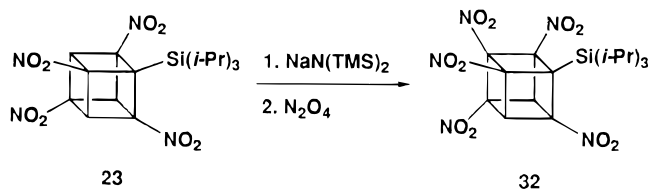


ently dependent on the reaction occurring at the melting interface between  $N_2O_4$  and the frozen solution of the anion.<sup>41</sup>

The relatively high ratio of hydrogen abstraction ( $\rightarrow 4$ ) to nitration ( $\rightarrow 29$ ) in the reaction of tetranitrocubylsodium (**19**) with  $N_2O_4$  (cf., Scheme 5) might be accounted for by a mismatch between tetranitrocubyl radical (**31**) and  $NO_2$  radical, both of which are quite electrophilic. Therefore, placing an electron-donating substituent on the cubane might be helpful. Earlier work in this Laboratory on cubyl cation<sup>42</sup> suggested  $\sigma$ -donors like trimethylsilyl. Attempted metalation/nitration of the trimethylsilyl-substituted tetranitrocubane **22** gave, unexpectedly, a mixture of penta- (**29**) and tetranitrocubanes (**4**), both *without* a TMS substituent. Control experiments showed that metalation



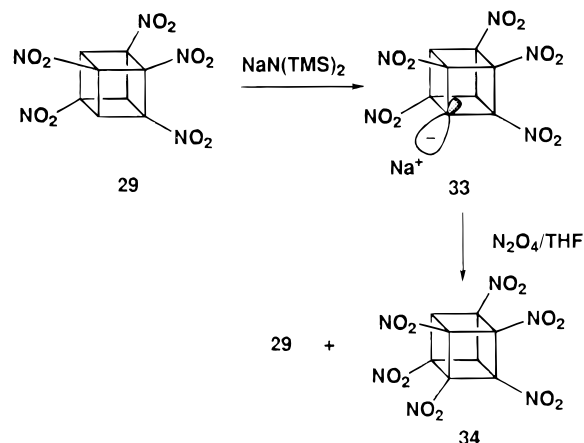
of **22** with  $(TMS)_2NNa$  is more difficult than the corresponding metalation of **4** (reasonable considering the electron donating effects of the silyl substituent); desilylation ( $\rightarrow 19$ ) occurs instead. This probably proceeds by nucleophilic substitution at silicon, a process that would be hindered by bulkier substituents on the silicon atom. Metalation of (triisopropyl)silyltetranitrocubane **23** with  $(TMS)_2NNa$  proceeded without competition from desilylation. Nitration of the resulting anion with  $N_2O_4$  gave a mixture of the TIPS-substituted penta- and tetranitrocubanes **32** and **23**.  $^1H$  NMR analysis of the crude gave a 82:18 ratio for nitration vs hydrogen abstraction, much improved over the 60:40 ratio obtained from nitration of the unsilylated tetranitrocubane. The TIPS-substituted pentanitrocubane **32** was isolated in 70% yield by column chromatography. This material turned out to be very useful in the preparation of hexanitrocubane.



**Hexanitrocubane.** It was not at all surprising, knowing the reactions of the tetranitrocubane, to find that pentanitrocubane **29** was metalated readily by  $(TMS)_2NNa$  in THF to give the sodium salt **33**. However, it soon became clear that such salts are less stable than those of tetranitrocubane. The recovery of skeletally intact cubanes from sequences involving formation of **33** and quenching it with various electrophiles (e.g.,  $TIPSCl \rightarrow 32$ ) was significantly lower than that from comparable reactions involving **19**. Nonetheless, the methodology for nitration of **4** via its sodium salt could be extended to nitration of pentanitrocubane **29** via its salt **33**. Reaction of **29** with  $(TMS)_2NNa$  in THF at  $-78^\circ C$  followed by reaction with  $N_2O_4$  at a melting interface in the manner described previously gave

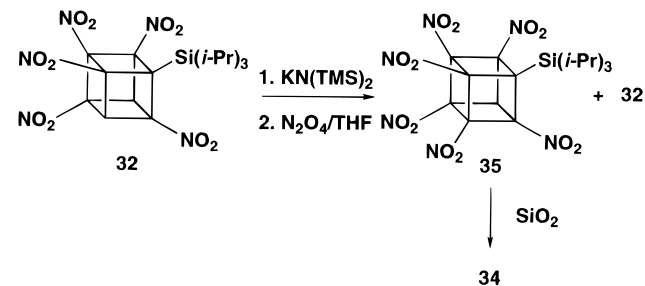
a 30:70 mixture of 1,2,3,4,5,7-hexanitrocubane (**34**) and pentanitrocubane **29** (Scheme 6). The yield was not good. The separation of the two polynitrocubanes was quite difficult, aggravated by the fact that hexanitrocubane, although stable in acetone and acetonitrile, is not stable in alcohols.

### Scheme 6



Metalation/nitration of the TIPS-substituted pentanitrocubane **32**—available either by silylation of **33** or, better, by  $N_2O_4$  nitration of the anion from **23**—provided for a much improved preparation of hexanitrocubane. Formation of an anion from **32** was slow when sodium bis(trimethylsilyl)amide was employed; the analogous potassium base,  $K(TMSN)_2$ , proved to be much more reactive and generated the necessary anion easily at  $-105^\circ C$  in THF. Interfacial nitration with  $N_2O_4$  gave a mixture of (triisopropyl)hexa- and (triisopropyl)pentanitrocubanes, **35** and **32**, in a 60:40 ratio by  $^1H$  NMR analysis. Surprising perhaps, but clearly related to our earlier observation on the behavior of (trimethylsilyl)tetranitrocubane **22**, column chromatography on silica gel of the mixture of **35** and **32** selectively removed the TIPS group from **35**. The liberated hexanitrocubane **34** was then easily separated on the column from the still silylated (triisopropylsilyl)pentanitrocubane, itself quite stable under these conditions. A 30% isolated yield of each compound *pure* was obtained (Scheme 7).

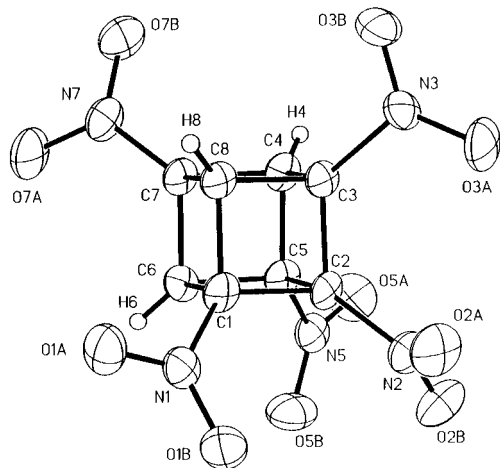
### Scheme 7



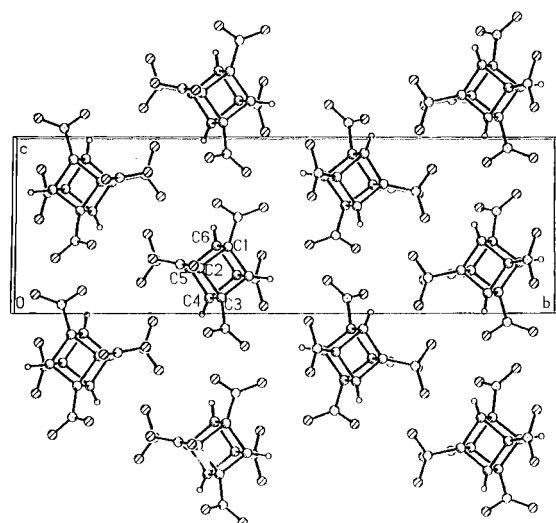
The structure of 1,2,3,4,5,7-hexanitrocubane (**34**) was proven by NMR and X-ray analysis (*vide infra*). The compound forms nicely crystalline, stable solvates with some nonprotic polar solvents. The bis-acetonitrile solvate was used for the X-ray analysis.

**Spectral Comparisons.** The introduction of additional nitro groups onto tetranitrocubane **4** causes substantial downfield shifts of the remaining cubyl protons: **4** (tetranitro),  $\delta = 6.085$ ; **29** (penta-nitro), 6.43; **34** (hexanitro), 6.72 ppm. The effects of variously positioned nitro groups on the  $^{13}C$  chemical shift of a cubyl carbon are roughly constant, as noted previously for lesser nitrated cubanes.<sup>9</sup> At that time, when no vicinal dinitrocubanes were available, the best approximation for predicting

(41) Tani, K.; Lukin, K. A.; Eaton, P. E. *J. Am. Chem. Soc.* **1997**, *119*, 1476.



**Figure 1.** The molecular structure and numbering scheme for 1,2,3,5,7-pentanitrocubane (**29**). Anisotropic thermal envelopes are shown at the 25% population level.



**Figure 2.** A schematic drawing of the full contents of the unit cell of 1,2,3,5,7-pentanitrocubane (**29**) in projection down the *a* axis. Four vertical layers of molecules are shown; each represents a two-dimensional layer of molecules in the crystal. The two layers on the left, related to one another by the glide plane, interlock to form a closely packed double layer. The same applies to the two layers on the right. There are 26 sub-van der Waals contacts across the two layers on the left and, separately, the two on the right. All of the close contacts occur within symmetry-related pairs. The shortest of these is C6...O2A (2.80 Å), more than 0.4 Å less than the 3.22 Å vdW contact. There are only three sub-van der Waals contacts across the boundary between these pairs of layers.

the chemical shift of any particular cubyl carbon in a nitrocubane was  $\delta$  (ppm) = 49.5 + 38*i* + 5.9*o* + 0.7*p* - 4.9*m*, where *i*, *o*, *p*, *m* are, respectively, the number of ipso, ortho, para, and meta nitrated carbons. Now, with data for more highly nitrated cubanes available, the approximation can be refined to  $\delta$  (ppm) = 49.5 + (38 - 4*o*)*i* + 5.9*o* + 0.7*p* - (4.9 - *o*)*m*. This should prove useful identifying the numerous nitrocubanes still sought, but yet to be made, particularly those of reduced symmetry.

**Structural Features.** The structure of pentanitrocubane (Figure 1) was obtained by single-crystal X-ray analysis. As only small crystals were available, the precision of the atom positions is low. Nonetheless, it is abundantly clear from the X-ray analysis that the fifth nitro group, although surrounded by three others, enters without the need for notable distortion in the cubane framework. The bond angles and lengths (Table 1) are essentially the same as those corresponding in 1,3,5,7-

**Table 1.** Bond Lengths (Å) and Angles (deg) for 1,2,3,5,7-Pentanitrocubane (**29**)

C(1)–C(2)	1.535(13)	C(1)–C(8)	1.553(14)
C(1)–C(6)	1.574(13)	C(2)–C(93)	1.558(13)
C(2)–C(5)	1.563(12)	C(3)–C(8)	1.523(14)
C(3)–C(4)	1.558(12)	C(4)–C(5)	1.531(14)
C(4)–C(7)	1.549(14)	C(5)–C(6)	1.526(14)
C(6)–C(7)	1.535(14)	C(7)–C(8)	1.569(13)
C(1)–N(1)	1.482(13)	C(2)–N(2)	1.457(12)
C(3)–N(3)	1.510(12)	C(5)–N(5)	1.490(13)
C(7)–N(7)	1.452(13)	N(1)–O(1A)	1.198(11)
N(1)–O(1B)	1.217(11)	N(2)–O(2B)	1.202(11)
N(2)–O(2A)	1.217(11)	N(3)–O(3B)	1.183(10)
N(3)–O(3A)	1.198(10)	N(5)–O(5A)	1.199(11)
N(5)–O(5B)	1.209(10)	N(7)–O(7A)	1.199(11)
N(7)–O(7B)	1.217(11)		
C(2)–C(1)–C(8)	92.7(8)	C(2)–C(1)–C(6)	90.4(7)
C(8)–C(1)–C(6)	90.8(7)	C(1)–C(2)–C(3)	86.8(7)
C(1)–C(2)–C(5)	89.2(6)	C(3)–C(2)–C(5)	88.0(7)
C(8)–C(3)–C(4)	92.0(7)	C(8)–C(3)–C(2)	93.0(7)
C(4)–C(3)–C(2)	91.0(7)	C(5)–C(4)–C(7)	88.8(8)
C(5)–C(4)–C(3)	89.2(7)	C(7)–C(4)–C(3)	88.5(7)
C(6)–C(5)–C(4)	91.3(8)	C(6)–C(5)–C(2)	91.2(7)
C(4)–C(5)–C(2)	91.8(7)	C(5)–C(6)–C(7)	89.5(8)
C(5)–C(6)–C(1)	89.1(7)	C(7)–C(6)–C(1)	89.0(7)
C(6)–C(7)–C(4)	90.3(8)	C(6)–C(7)–C(8)	91.7(7)
C(4)–C(7)–C(8)	90.5(7)	C(3)–C(8)–C(1)	87.4(8)
C(3)–C(8)–C(7)	89.0(7)	C(1)–C(8)–C(7)	88.5(7)
N(1)–C(1)–C(2)	125.0(8)	N(1)–C(1)–C(8)	126.6(9)
N(1)–C(1)–C(6)	121.2(8)	N(2)–C(2)–C(1)	125.8(8)
N(2)–C(2)–C(3)	125.9(8)	N(2)–C(2)–C(5)	128.2(9)
N(3)–C(3)–C(8)	121.7(8)	N(3)–C(3)–C(4)	122.2(8)
N(3)–C(3)–C(2)	127.5(8)	N(5)–C(5)–C(6)	121.2(8)
N(5)–C(5)–C(4)	129.2(8)	N(5)–C(5)–C(2)	122.1(8)
N(7)–C(7)–C(6)	123.8(9)	N(7)–C(7)–C(4)	123.7(8)
N(7)–C(7)–C(8)	126.5(8)	O(1A)–N(1)–C(1)	119.1(10)
O(1B)–N(1)–C(1)	115.8(10)	O(2B)–N(2)–C(2)	119.1(9)
O(2A)–N(2)–C(2)	116.2(10)	O(3B)–N(3)–C(3)	115.5(9)
O(3A)–N(3)–C(3)	118.0(9)	O(5A)–N(5)–C(5)	118.0(10)
O(5B)–N(5)–C(5)	116.6(10)	O(7A)–N(7)–C(7)	119.9(11)
O(7B)–N(7)–C(7)	117.3(10)	O(1A)–N(1)–O(1B)	125.0(10)
O(2B)–N(2)–O(2A)	124.7(10)	O(3B)–N(3)–O(3A)	126.5(9)
O(5A)–N(5)–O(5B)	125.4(11)	O(7A)–N(7)–O(7B)	122.8(10)

tetranitrocubane (**4**).<sup>9</sup> The average interior CCC angle is 88.6° at the even-numbered carbons in **29** and 91.4° at the odd-numbered, nitro-bearing carbons; this pattern and magnitude of angular distortion is found as well in **4**. Although the connection may be tenuous, pentanitrocubane, as noted earlier, has thermal and shock stability similar to those of lesser nitrated cubanes.<sup>9</sup>

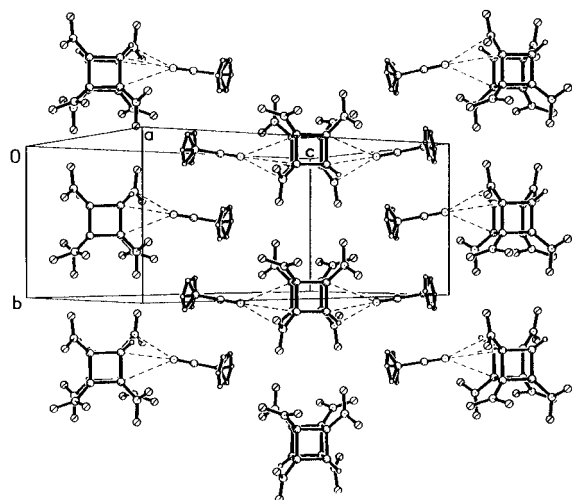
Molecules of **29** are arranged in an interesting way within the crystal polymorph examined. The packing consists of close-packed layers of molecules in the *ac* plane, perpendicular to the 2-fold *b* axis; these layers are seen edge-on in Figure 2. Each of these layers is paired with another that is related by a glide plane (e.g., *x*, 0.5 - *y*, 0.5 + *z*), with which it closely interlocks. A single molecule of **29** has 29 nonbonded O...O and O...C contacts at less than van der Waals contact distances;<sup>42</sup> the shortest are 2.748 Å (O...O) and 2.801 Å (O...C). Only three of these contacts are across the boundary between the interlocked layers.

The distances seen between molecules of **29** are surprisingly short in the interlocked double layers shown in Figure 2. A

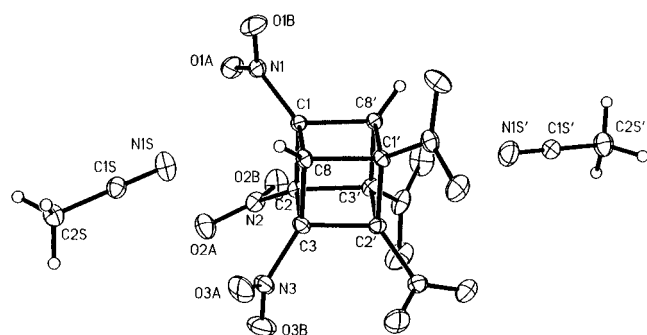
(42) Eaton, P. E.; Zhou, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 3118.

(43) We examined the literature, briefly, to see if more recent results might have rendered obsolete traditional values for van der Waals radii, particularly the value for aliphatic carbon. A recent, massive review (Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384) examined close contacts in 28 000 suitable crystal structures. The analysis pointed out inaccuracies in a few of the still-used 1948 Pauling vdW values (Pauling, L. *The Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1948; pp 187–193) but generally supported the 1964 tabulation of Bondi (Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441). This gives a carbon van der Waals radius of 1.7 Å and an oxygen radius of 1.52 Å.





**Figure 3.** A view of the unit cell and observed packing assembly in a crystal of the bis-acetonitrile solvate of 1,2,3,4,5,7-hexanitrocubane (**34**). The acetonitrile methyl group is disordered. All molecules are more or less in the plane of the paper. The next layer is shifted laterally. Solvent coordination is indicated (see Figure 4).



**Figure 4.** The molecular structure and numbering scheme for the bis-acetonitrile solvate of 1,2,3,4,5,7-hexanitrocubane (**34**). Anisotropic thermal envelopes are shown at the 25% population level. The left and right sides of the molecule are related by a vertical 2-fold axis of symmetry. There are numerous sub-van der Waals close contacts between the solvent nitrogen atom (N1S) and components of the cubane: N1S...N1, 2.963 Å; N1S...C8, 2.867 Å; N1S...C1, 2.976 Å; M1S...C3 3.031 Å.

few distances less than accepted van der Waals contacts<sup>43</sup> are seen in most crystal structures. These are closely scrutinized by crystallographers for sometimes they indicate a local electrostatic or covalent bonding attractive enough to overcome the “Lennard-Jones repulsion” energy that is rapidly rising at the van der Waals contact distance. Otherwise, close (compressed) contacts are the result of a global packing-energy compromise made to produce a better fit overall. The non-bonded O...O contacts in **29** fit this latter pattern, but the nitro oxygen to cubane carbon contacts near the N2 and N5 nitro groups are so short that an unusual attraction must be present if “accepted” van der Waals radii values are correct.<sup>43</sup>

Eight pairs of C...O approaches seen in **29** in the range (2.80–3.06 Å) are considerably below the 3.22 Å Bondi vdW contact distance. Such short distances are not unprecedented, but have heretofore been seen only between polar moieties and trigonal carbons. For example, in chloranil there is a 2.85 Å C=O...C close contact between near neighbors in the crystal.<sup>44</sup> This indicates a strong electrostatic interaction that dominates

**Table 2.** Bond Lengths (Å) and Angles (deg) for 1,2,3,4,5,7-Hexanitrocubane (**34**) Bis-acetonitrile Solvate<sup>a</sup>

C(1)–N(1)	1.466(3)	C(1)–C(8)	1.550(3)
C(2)–N(2)	1.475(3)	C(1)–C(2)	1.561(3)
C(3)–N(3)	1.471(3)	C(1)–C(8)*	1.572(3)
N(1)–O(1A)	1.213(3)	C(2)–C(3)*	1.565(3)
N(1)–O(1B)	1.214(3)	C(2)–C(3)	1.559(3)
N(2)–O(2A)	1.203(3)	C(3)–C(8)	1.548(3)
N(2)–O(2B)	1.220(3)	C(3)–C(2)*	1.565(3)
N(3)–O(3A)	1.212(3)	C(8)–C(1)*	1.572(3)
N(3)–O(3B)	1.220(3)	C(1S)–N(1S)	1.137(3)
C(1S)–C(2S)	1.444(4)		
C(8)–C(1)–C(2)	91.5(2)	C(3)–C(2)–C(1)	88.0(2)
C(8)–C(1)–C(8)*	91.1(2)	C(3)–C(2)–C(3)*	90.2(2)
C(2)–C(1)–C(8)*	90.7(2)	C(1)–C(2)–C(3)*	88.9(2)
C(8)–C(3)–C(2)	91.6(2)	C(3)–C(8)–C(1)	88.8(2)
C(8)–C(3)–C(2)*	91.4(2)	C(3)–C(8)–C(1)*	89.1(2)
C(2)–C(3)–C(2)*	89.8(2)	C(1)–C(8)–C(1)*	88.8(2)
N(1)–C(1)–C(8)	124.6(2)	O(1A)–N(1)–O(1B)	126.7(2)
N(1)–C(1)–C(2)	125.3(2)	O(2A)–N(2)–O(2B)	126.6(2)
N(1)–C(1)–C(8)*	123.5(2)	O(3A)–N(3)–O(3B)	126.8(2)
N(2)–C(2)–C(3)	130.0(2)	O(1A)–N(1)–C(1)	117.4(2)
N(2)–C(2)–C(1)	125.1(2)	O(1B)–N(1)–C(1)	115.9(2)
N(2)–C(2)–C(3)*	122.6(2)	O(2A)–N(2)–C(2)	118.5(2)
N(3)–C(3)–C(8)	126.4(2)	O(2B)–N(2)–C(2)	114.9(2)
N(3)–C(3)–C(2)	125.8(2)	O(3A)–N(3)–C(3)	117.8(2)
N(3)–C(3)–C(2)*	121.4(2)	O(3B)–N(3)–C(3)	115.3(2)
N(1S)–C(1S)–C(2S)	179.1(3)		

<sup>a</sup> The following symmetry transformations are used to generate equivalent atoms:  $1 - x, y, 1.5 - z$ . (Entries are indicated with asterisks.)

the supramolecular assembly. We suggest that similarly strong dipolar forces are acting in the polynitrocubanes. Obviously, there are large dipoles in these molecules, for nitro groups are known for their electron-withdrawing nature. The negative, oxygen poles of the nitro groups are exposed and, as seen in **29**, can approach closely the hindered, electron-deficient faces of the cubane skeleton. In the double layers seen in Figure 2, the nitro group on C5 manages to approach the trinitrosubstituted face (C2C3C4C5) of a neighboring molecule to less than 3 Å; similarly, the nitro group on C2 approaches the dinitrosubstituted face (C4C5C6C7) to 2.8 Å.

As mentioned earlier, density is of critical importance to the performance of an explosive. The overall packing in **29** described above leads to a density of 1.96 g/cm<sup>3</sup> at 21 °C, a value exceeded by very few other CHNO compounds. Even so, it is not idle to speculate on the existence of a yet more dense arrangement. All of the aforementioned close contacts involve just two of the five nitro groups of **29**, those on C2 and C5; the other nitro groups are relatively uncrowded. Thus, an all-around closer (higher density) packing assembly might be achieved in some other polymorph of 1,2,3,5,7-pentanitrocubane or in one of its two positional isomers.

We were unable to obtain a single crystal of 1,2,3,4,5,7-hexanitrocubane free of solvent. The packing in the multimolecule unit cell of the bis-acetonitrile solvate is shown in Figure 3. Note the “channels” of solvent molecules which themselves approach the hexanitrocubane molecules very closely (indeed much less than van der Waals contact distances; see Figure 4). In **34**, each acetonitrile “guest” approaches a trinitrosubstituted face of the cubane frame. The shortest CN...C distance, 2.87 Å, is well below the Bondi<sup>43</sup> van der Waals close contact distance of 3.25 Å and closer than any intermolecular CN...C seen in the Cambridge Structural Database, other than the CN...C contact of 2.76 Å seen between acetonitrile molecules in the solvent cavity of a cyclophane clathrate.<sup>45</sup>

The numerical results for bond lengths and angles in **34** (Table 2) are quite precise; the average distance esd is only 0.003 Å.

(44) Chu, S. C.; Jeffrey, G. A.; Sakurai, T. *Acta Crystallogr.* **1962**, *15*, 661.

(45) Hirotsu, K.; Kamitori, S.; Higuchi, T.; Tabushi, I.; Yamamura, K.; Nonoguchi, H. *J. Inclusion Phenom.* **1984**, *2*, 215.

As this is far better than we were able to do for pentanitrocubane, it is reassuring that detailed comparisons with other cubane and nitrocubane structures reveal again that there are no particular distortions due to steric forces engendered by the numerous adjacent nitro groups. The six (NO<sub>2</sub>)C–C(NO<sub>2</sub>) cube edge lengths average 1.562 Å, not significantly longer than the average of 1.557 Å for the six HC–C–C(NO<sub>2</sub>) edges. The longest C–C bonds in the molecule, 1.572 Å between C(1) and C(8) and the same between the symmetry mates, are of the latter group. Their elongation might be due to an interaction with the solvent. The two solvent molecules closest to **34** in the crystal are nearest the disubstituted face of the molecule and the electronegative ends of the strong acetonitrile dipoles approach most closely (2.867 Å) the two CH corners thereof (Figure 4). It should be mentioned, however, that this effect, although interesting and probably real, is still quite small and probably does not indicate a weakening in the carbon bonding within the cubane framework. Cubane carbon–carbon bond distances have been observed in stable cubanes all the way from 1.522 Å to 1.607 Å.

## Conclusion

In summary, we have demonstrated for the first time direct ortho metalation of saturated nitro compounds, and we have shown that the resulting *o*-nitro carbanions are valuable synthetic intermediates useful for introduction of various substituents. We have developed direct nitration of *o*-nitro carbanions with dinitrogen tetraoxide and have used this method for preparation of the first vicinal nitrocubanes, pentanitrocubane and hexanitrocubane, both of which have been characterized.

## Experimental Section

**General.** Unless otherwise specified, NMR spectra were run in acetone-*d*<sub>6</sub>: <sup>1</sup>H NMR spectra at 400 MHz and referenced to the central line of acetone-*d*<sub>5</sub> (δ 2.05 ppm); <sup>13</sup>C NMR spectra at 100.6 MHz and referenced to the central line of acetone-*d*<sub>6</sub> (δ 29.8 ppm). Proton chemical shifts are ±0.01 ppm. Carbon chemical shifts are ±0.1 ppm. Observed <sup>13</sup>C–<sup>207</sup>Pb couplings are given as *J*<sub>C–Pb</sub>. Merck silica gel 60 (230–400 mesh) was used for column chromatography. The eluting solvent is given parenthetically in the individual procedures. THF was distilled from sodium benzophenone ketyl. THF-*d*<sub>8</sub> was dried over activated 4 Å molecular sieves. All metalations were carried out under argon in oven-dried glassware. "Removal of solvent *in vacuo*" and similar phrases generally refer to rotary evaporation at ~50 Torr. The evaporator bath was not heated above room temperature. Oxalyl chloride and trimethylsilyl azide were purchased from Aldrich and distilled before use. Dimethyldioxirane was prepared as described earlier.<sup>8b</sup> Dinitrogen tetraoxide was purchased from Matheson.

**CAUTION.** Most cubane compounds are quite stable kinetically. Nonetheless, as they are high-energy materials it is prudent to run all reactions thereof behind safety shields. Great care should be taken to assure that crude reaction products are not concentrated at elevated temperature, particularly in the presence of acidic or metallic contaminants. Nitrating agents were always handled in a good hood, behind safety shields.

**Photochemical Chlorocarbonylation of Cubanecarboxylic Acid Chloride with Oxalyl Chloride.** Cubanecarboxylic acid<sup>46</sup> (1.48 g, 10 mmol) was added in four portions to oxalyl chloride (100 mL) well stirred at room temperature. Immediate, vigorous gas evolution was observed. The resulting solution of cubanecarboxylic acid chloride [**5**, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.02 (m, 1 H), 4.06 (m, 3 H), 4.44 ppm (m, 3 H)] was transferred into a Pyrex photoreactor and cooled to –5 °C by pumping through the reactor jacket a 40:60 ethylene glycol/water mixture precooled to –12 °C in an external cooling bath. The cold solution was irradiated using a Hanovia, medium-pressure, 450-watt, mercury arc lamp. <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>) of a sample taken from

the reaction mixture after 15 min irradiation showed that nearly all of **5** had been converted to the diacid chlorides **6**, **7**, and **8** in very approximately a 6:10:1 ratio.

**Cubane-1,3-dicarboxylic acid chloride (6):** δ 4.09 (m, 2 H), 4.43 (m, 2 H), 4.81 ppm (m, 2 H).

**Cubane-1,4-dicarboxylic acid chloride (7):** δ 4.47 ppm (s).

**Cubane-1,2-dicarboxylic acid chloride (8):** δ 4.05 (m, 2 H), 4.47 ppm (pseudo t, *J* = 3.5 Hz, 4 H).

After 50 min of irradiation, a similar <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>) indicated that most of the cubane diacid chlorides had been converted into a mixture of the 1,3,5-, 1,2,4- and 1,2,3-triacid chlorides **9–11** in roughly a 6:4:2 ratio.

**Cubane-1,3,5-tricarboxylic acid chloride (9):** δ 4.15 (dq, *J* = 0.8, 5.2 Hz, 1 H), 4.80 (dd, *J* = 2.8, 5.2 Hz, 3 H), 5.16 ppm (dq, *J* = 0.8, 2.8 Hz, 1 H).

**Cubane-1,2,4-tricarboxylic acid chloride (10):** δ 4.47 (m, 1 H), 4.51 (m, 2 H), 4.86 ppm (m, 2 H).

**Cubane-1,2,3-tricarboxylic acid chloride (11):** δ 4.08 (m, 1 H), 4.40–4.60 ppm (m, 4 H).

In a separate experiment the solution of cubanecarboxylic acid chloride **5** in oxalyl chloride was irradiated for 2.75 h using the same lamp but in a quartz photoreactor. During this time the temperature of the reaction mixture rose slowly to about +12 °C. Evaporation of the excess oxalyl chloride left a mixture composed mainly of the tetraacid chlorides **12–14** in 70:8:22 ratio as determined by <sup>1</sup>H NMR (CDCl<sub>3</sub>).

**Cubane-1,3,5,7-tetracarboxylic acid chloride (12):** δ 5.14 ppm (s).

**Cubane-1,2,4,7-tetracarboxylic acid chloride (13):** δ 4.88 ppm (s).

**Cubane-1,2,3,7-tetracarboxylic acid chloride (14):** δ 4.51 (dt, *J* = 0.8, 5.2 Hz, 1 H), 4.80 (dd, *J* = 2.4, 5.2 Hz, 2 H), 5.17 ppm (dt, *J* = 0.8, 2.4 Hz, 1 H).

The mixture was treated with dry ether (10 mL) and put in a freezer overnight. The resulting precipitate was collected and washed with a small amount of cold ether to give **12** as a white solid (1.1 g, 31%, >95% purity). This material was used without further purification.

**Cubane-1,3,5,7-tetraisocyanate (17).** As this procedure involves as an intermediate a highly explosive acyl azide (**16**) it must be done behind a safety shield. A face mask and heavy gloves should be worn. The acyl azide must be kept in solution at all times.

**Procedure A.** Cubanetetracarboxylic acid chloride **14** (0.7 g, 2 mmol) and 2,6-di-*tert*-butylpyridine (0.2 g, 1 mmol, 15 equiv %) were mixed in dry, alcohol-free chloroform (60 mL) and stirred under nitrogen until the mixture became homogeneous (~25 min). A solution of trimethylsilyl azide (0.97 g, 8 mmol) in chloroform (alcohol free, 5 mL) was added dropwise over 5 min at room temperature. The reaction mixture was stirred for 1.5 h at room temperature (→ tetraacyl azide **16**) taking care that none of the solution splashed up into the necks. An additional 200 mL of dry, alcohol-free chloroform was added and the solution heated at full reflux for 1 h. The solution was cooled and the solvent removed at room temperature *in vacuo* leaving crude tetraisocyanate **17** containing di-*tert*-butylpyridine, etc. This material was used in the next step without further purification.

**Procedure B (Recommended).** Anhydrous hydrogen chloride, bubbled through concentrated H<sub>2</sub>SO<sub>4</sub>, was introduced slowly for 5 min into a solution of 2,6-di-*tert*-butylpyridine (0.100 g, 0.523 mmol) in 10 mL of dry diethyl ether. A white precipitate formed. The solvent was removed *in vacuo* at room temperature. The residue was pumped at <1 mm for 15 min (no longer!). The white salt so obtained, assumed to be 2,6-di-*tert*-butylpyridine·2HCl,<sup>25</sup> was dissolved in dry, alcohol-free chloroform (4.00 mL). Separately, cubanetetracarboxylic acid chloride **14** (79.6 mg, 0.225 mmol) was refluxed in oxalyl chloride (5 mL) for about 2 h in oxalyl chloride to ensure that any that had been partially hydrolyzed during weighing or storage was reconverted to **14**. After the solution was cooled to room temperature it was clarified by filtration through a fine frit (Schlenk technique), and the oxalyl chloride was removed *in vacuo* at room temperature. The residue was dissolved in dry, alcohol-free chloroform (5.6 mL). A clear solution was obtained. A catalytic amount of the pyridinium salt solution (191 mL, 4.78 mg, 0.0250 mmol) was added. A solution of trimethylsilyl

(46) Eaton, P. E.; Nordari, N.; Tsanaktsidis, J.; Upadhyaya, S. P. *Synthesis* 1995, 501.

azide (94% by  $^1\text{H}$  NMR, 140  $\mu\text{L}$ , 0.114 g contained, 0.991 mmol; the contaminant is hexamethyldisiloxane) in dry, alcohol-free chloroform (1.2 mL) was added dropwise over 5 min. The funnel was rinsed with chloroform (0.5 mL). The mixture was stirred at room temperature for about 4 h after which the  $^1\text{H}$  NMR spectrum of an aliquot showed no cubyl signal at higher field than the strong, sharp singlet at 4.69 ppm corresponding to the tetraacyl azide. Some multiplets at lower field due to partial rearrangement of acyl azide groups to isocyanates were just visible. The solution was diluted with dry, alcohol-free chloroform (28 mL) and heated at reflux for 1 h and then cooled. An aliquot examined by  $^1\text{H}$  NMR examination of an aliquot showed a small amount of material with a multiplet at 4.36 ppm. The desired tetraisocyanate appeared as a strong, sharp singlet at 4.32 ppm (estimated yield by integration > 85–95%). Evaporation of the solvent *in vacuo* furnished the crude tetraisocyanate as a slightly yellow solid.

**1,3,5,7-Tetranitrocubane (4).** A solution of the crude tetraisocyanate **17** (procedure A) in carefully dried acetone (20 mL) was added dropwise over 1.5 h to a stirred solution of dimethyldioxirane (0.06 M) in acetone (660 mL) and water (60 mL) cooled in an iced water bath. After the addition was completed the bath was removed. The reaction mixture was stirred at room temperature overnight. Evaporation of solvents *in vacuo* left crude **4** as a cream-colored solid. This was dissolved in methanol (45 mL) and the solution refluxed with activated charcoal for 15 min. The charcoal was filtered and the solution concentrated to ~15 mL. If it were still brown or dark yellow, the treatment with charcoal was repeated as necessary. Ultimately a pale yellow solution was obtained. It was concentrated to 5 mL and then cooled. The precipitate was tetranitrocubane **4** (0.26 g, 47% overall from **12**) identical spectroscopically to that previously obtained:<sup>9</sup>  $^1\text{H}$  NMR  $\delta$  6.085 ppm (s);  $^{13}\text{C}$  NMR  $\delta$  67.9, 73.2 ppm.

**Proton–Deuterium Exchange on Tetranitrocubane.** Tetranitrocubane (**4**, 10 mg) was dissolved in  $\text{CD}_3\text{OD}$  (2.5 mL) at room temperature. A sodium methoxide solution, prepared earlier by reacting sodium (10 mg) with  $\text{CD}_3\text{OD}$  (1 mL), was added in one portion with stirring. The reaction mixture was stirred at room temperature for 45 min then added dropwise into stirred aqueous hydrochloric acid (1 M, 25 mL). The mixture was extracted with ethyl acetate (3  $\times$  10 mL). The combined organic layer was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the organic solvents left **4-*d*<sub>4</sub>** (8.8 mg, 87%):  $^{13}\text{C}$  NMR  $\delta$  67.6 (t,  $J_{\text{C-D}} = 28.2$  Hz, C-2, C-4, C-6, C-8), 73.0 ppm (C-1, C-3, C-5, C-7).

**2,4,6,8-Tetranitrocubylsodium (19).** Sodium bis(trimethylsilyl)amide (65  $\mu\text{L}$ , 1 M in THF, 0.065 mmol) was added dropwise to a solution under argon of tetranitrocubane **4** (14 mg, 0.05 mmol) in THF (2 mL) cooled to  $-78^\circ\text{C}$ . The resulting yellow solution of **19** [ $^1\text{H}$  NMR  $\delta$ , (THF- $d_6$ ,  $-78^\circ\text{C}$ )  $\delta$  5.54 ppm (s)] was stirred for 5 min at this temperature. The solution was kept at  $-78^\circ\text{C}$  until used. A batch was made for each of the experiments below.

**2,4,6,8-Tetranitrocubancarboxylic Acid Methyl Ester (20a).** Carbon dioxide was bubbled for 10 min through the solution of tetranitrocubylsodium at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature and then the stream of  $\text{CO}_2$  was discontinued. The solvent was evaporated *in vacuo*. The residue was diluted with water (2 mL), acidified to pH 1 with concentrated hydrochloric acid, and then extracted with 1:1 ether–THF (3  $\times$  1 mL). The extract was dried with  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent left crude acid **20** containing 15% of tetranitrocubane **4** by  $^1\text{H}$  NMR. The acid was converted into its methyl ester by treatment with ethereal diazomethane. Crystallization from 95:5 chloroform–acetonitrile gave the pure ester **20a** (13 mg, 75%):  $^1\text{H}$  NMR  $\delta$  3.84 (s, 3 H), 6.22 ppm (s, 3 H);  $^{13}\text{C}$  NMR  $\delta$  54.3 ( $\text{CH}_3$ ), 67.0 (3 C, CH), 72.0, 73.4, 75.2 (3 C), 159.9 ppm (C=O). Anal. Calcd for  $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_{10}$ : C, 35.10; H, 1.76. Found: C, 35.01; H, 1.59.

**1,3,5,7-Tetranitro-2-iodocubane (21).** 1,2-Diiodoethane (28 mg, 0.1 mmol) was added to the THF solution of tetranitrocubylsodium at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature, and then the solvent was evaporated *in vacuo*. The residue was extracted with chloroform (5  $\times$  1 mL). Evaporation of the solvent followed by column chromatography ( $\text{CH}_2\text{Cl}_2$ ) gave **21** (12 mg, 60%):  $^1\text{H}$  NMR  $\delta$  6.19 ppm (s);  $^{13}\text{C}$  NMR  $\delta$  43.9, 67.6 (3 C, CH), 72.1, 75.2 ppm (3C). Anal. Calcd for  $\text{C}_8\text{H}_3\text{I}_2\text{N}_4\text{O}_8$ : C, 23.43; H, 0.74. Found: C, 24.11; H, 0.97.

**1,3,5,7-Tetranitro-2-(trimethylsilyl)cubane (22).** Chlorotrimethylsilane (0.3 mL, excess) was added by syringe to the THF solution of tetranitrocubylsodium at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature, and then the solvent and excess of chlorotrimethylsilane were evaporated *in vacuo*. The residue was extracted with  $\text{CHCl}_3$  (3  $\times$  2 mL). Evaporation of the solvent left **22** (14 mg, 80%) as good quality material:  $^1\text{H}$  NMR  $\delta$  0.16 (s, 9 H), 6.07 ppm (s, 3 H);  $^{13}\text{C}$  NMR  $\delta$   $-3.3$  (3 C,  $\text{CH}_3$ ), 67.8 (3 C, CH), 71.7, 74.4 (3 C), 75.5 ppm. Attempted purification of this material by column chromatography gave tetranitrocubane **4**.

**1,3,5,7-Tetranitro-2-(triisopropylsilyl)cubane (23).** Chloro(triisopropyl)silane (21  $\mu\text{L}$ , 0.10 mmol) was added by syringe in one portion to the solution of tetranitrocubylsodium at  $-78^\circ\text{C}$ . The reaction mixture was stirred at  $-78^\circ\text{C}$  for 5 min and then allowed to warm to room temperature. The solvent was evaporated *in vacuo*. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  3 mL). Evaporation of the solvent followed by column chromatography ( $-78^\circ\text{C}$ ) gave **23** (17 mg, 80%):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 1.04–1.08 (m, 21 H), 5.86 ppm (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  10.7 (3 C, CH–Si), 19.1 (6 C,  $\text{CH}_3$ ), 65.1 (3 C, CH), 69.7, 74.2 (3 C), 85.5 ppm. Anal. Calcd for  $\text{C}_{17}\text{H}_{24}\text{N}_4\text{O}_8\text{Si}$ : C, 46.36; H, 5.49. Found: C, 46.09; H, 5.34.

**1,3,5,7-Tetranitro-2-(ethylmercury)cubane (24).** Ethylmercury chloride (29 mg, 0.11 mmol) was added in one portion to the THF solution of tetranitrocubylsodium at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature, and then the solvent was evaporated *in vacuo*. The residue was extracted with acetone (3  $\times$  2 mL). Evaporation of the solvent followed by column chromatography (85:15  $\text{CH}_2\text{Cl}_2$ /pentane) gave **24** (14 mg, 55%):  $^1\text{H}$  NMR  $\delta$  1.3 (t,  $J = 8$  Hz, 3 H), 1.43 (q,  $J = 8$  Hz, 2 H), 6.08 ppm (s, 3 H);  $^{13}\text{C}$  NMR  $\delta$  13.5 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_2$ ), 69.1 (3 C), 73.7, 75.4 (3 C), 107.0 ppm. Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{HgN}_4\text{O}_8$ : C, 23.42; H, 1.57. Found: C, 23.07; H, 1.61.

**1,3,5,7-Tetranitro-2-(triethylplumbly)cubane (25).** Triethyllead chloride (33 mg, 0.10 mmol) was added in one portion to the solution of tetranitrocubylsodium at  $-78^\circ\text{C}$ . The reaction mixture was stirred at  $-78^\circ\text{C}$  for 5 min then allowed to warm to room temperature. The solvent was evaporated *in vacuo*. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  3 mL). Removal of the solvent followed by column chromatography (80:20  $\text{CH}_2\text{Cl}_2$ /pentane) gave **25** (19 mg, 66%):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 1.49 (t,  $J = 8$  Hz, 9 H), 1.94 (q,  $J = 8$  Hz, 6 H), 5.88 ppm (s, 3 H);  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 13.9 (3 C,  $\text{CH}_3$ ),  $J_{\text{C-Pb}} = 31$  Hz), 17.6 (3 C,  $\text{CH}_2\text{Pb}$ ,  $J_{\text{C-Pb}} = 175$  Hz), 67.5 (3 C, CH), 71.2, 73.6 (3 C), 79.1 ppm ( $J_{\text{C-Pb}} = 538$  Hz). Anal. Calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_8\text{Pb}$ : C, 29.12; H, 3.14. Found: C, 29.27; H, 3.00.

**2,4,6,8-Tetranitrocubane-1,3-dicarboxylic Acid Dimethyl Ester (26a).** Tetranitrocubane **3** (14 mg, 0.05 mmol) was treated with excess (5 equiv) sodium bis(trimethylsilyl)amide in THF at  $-78^\circ\text{C}$ . Quenching with  $\text{CO}_2$  and workup as described above for **20** gave a mixture of tetranitrocubane mono- and dicarboxylic acids (**20** and **26**) in a 70:30 ratio. These were converted into the corresponding mono- and dimethyl esters by treatment with diazomethane. For the diester **26a**:  $^1\text{H}$  NMR  $\delta$  3.90 (s, 6 H), 6.34 ppm (s, 3 H);  $^{13}\text{C}$  NMR  $\delta$  54.5 ( $\text{CH}_3$ ), 66.3 (CH), 72.5, 74.4, 76.5, 159.3 ppm (C=O).

**1,3-Bis(trimethylsilyl)-2,4,6,8-tetranitrocubane (27).** Tetranitrocubane **4** (14 mg, 0.05 mmol) was treated with excess (3 equiv) of sodium bis(trimethylsilyl)amide in THF at  $-78^\circ\text{C}$ . Quenching the reaction mixture with chlorotrimethylsilane and workup as described above gave a mixture of mono- and bis(trimethylsilyl)tetranitrocubanes **22** and **27** in a 20:80 ratio. The bis(trimethylsilyl) compound **27** (13 mg, 60%) was obtained pure by crystallization from 60:40 hexane/chloroform:  $^1\text{H}$  NMR  $\delta$  0.19 (s, 18 H), 6.10 ppm (s, 2 H);  $^{13}\text{C}$  NMR  $\delta$   $-3.2$  (6 C,  $\text{CH}_3$ ), 67.1 (2 C, CH), 72.7 (2 C), 75.4 (2 C), 75.8 ppm (2 C). Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{N}_4\text{O}_8\text{Si}_2$ : C, 39.24; H, 4.70. Found: C, 39.03; H, 4.59.

**1,3-Bis(triisopropylsilyl)-2,4,6,8-tetranitrocubane (28).** Tetranitrocubane **4** (14 mg, 0.05 mmol) was treated with excess (3 equiv) of sodium bis(trimethylsilyl)amide in THF at  $-78^\circ\text{C}$ . Quenching the reaction mixture with excess chlorotriisopropylsilane (4 equiv) and workup as described above gave a mixture of mono- and bis(triisopropylsilyl)tetranitrocubanes **23** and **28** in a 20:80 ratio. Compound **28** (21 mg, 70%) was isolated by column chromatography (50:50  $\text{CH}_2\text{Cl}_2$ /pentane):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 1.07 (d,  $J = 7.5$  Hz, 36 H), 1.25–1.35 (m, 6 H), 5.90 ppm (s, 2 H);  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 12.0 (6

C, CH–Si), 19.8 (12 C, CH<sub>3</sub>), 63.7 (2 C, CH), 72.7 (2 C), 77.6 (2 C), 84.5 ppm (2 C). Anal. Calcd for C<sub>26</sub>H<sub>44</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>2</sub>: C, 52.32; H, 7.43. Found: C, 52.66; H, 7.59.

**1,2,3,5,7-Pentanitrocubane (29).** The solution of tetranitrocubylsodium under a nitrogen atmosphere was frozen into a glass by using a liquid nitrogen bath. Excess N<sub>2</sub>O<sub>4</sub> (~0.4 mL, condensed into a separate tube and then evaporated through a cannula into the reaction flask) was deposited onto this solid at –196 °C. The resulting two-phase mixture was warmed briefly in a room temperature methanol bath with shaking until it had just melted and become homogeneous, then it was stirred and allowed to warm to 10 °C. (The whole warming process took about 5 min.) The solvent and excess N<sub>2</sub>O<sub>4</sub> were evaporated *in vacuo*. The residual solid was extracted with acetone (2 × 1 mL). Evaporation of the extract gave a mixture of penta- and tetranitrocubanes **29** and **4** in a 60:40 ratio as determined by <sup>1</sup>H NMR. It was triturated with 96:4 chloroform/methanol (6 × 2 mL). Evaporation of the extract left a mixture of penta- and tetranitrocubanes in 85:15 ratio. Pentanitrocubane (**29**, 7 mg, 40%) was obtained pure by chromatographic (95:5 dichloromethane–acetonitrile) separation: <sup>1</sup>H NMR δ 6.43 ppm (s, 3 H); <sup>13</sup>C NMR δ 66.5 (3 C, CH), 72.8, 78.8 (3 C), 93.0 ppm. X-ray-quality crystals of **29** were prepared by crystallation from 1-propanol.

**Reaction of Tetranitrocubylsodium with Nitril Chloride.** Nitril chloride (~0.2 mL, excess) was evaporated over 1 min into a solution of tetranitrocubylsodium in THF at –78 °C. The mixture was stirred at –78 °C for 5 min, then allowed to warm to room temperature. The solvent and excess nitril chloride were evaporated *in vacuo*. The solid remaining was identified by <sup>1</sup>H NMR as a mixture of tetranitrocubane **4**, chlorotetranitrocubane **30**, and pentanitrocubane **29** in 75:15:10 ratio.

**1-Chloro-2,4,6,8-tetranitrocubane (30).** A batch of the solution of tetranitrocubylsodium under nitrogen was frozen into a glass using a liquid nitrogen bath. NO<sub>2</sub>Cl (~0.25 mL, excess) was deposited onto the solid at –196 °C. The resulting mixture was warmed briefly with shaking until it had melted and become homogeneous, and then it was stirred and allowed to warm to 10 °C (over ~5 min). The solvent and excess NO<sub>2</sub>Cl were evaporated *in vacuo*. The remaining solid was extracted with acetone (2 × 1 mL). Evaporation of the solvent left a mixture of chlorotetranitrocubane **30**, tetranitrocubane **4**, and pentanitrocubane **29** in 60:33:7 ratio as determined by <sup>1</sup>H NMR. Chloronitrocubane **30** (7 mg, 45%) was obtained by chromatography (95:5 dichloromethane–acetonitrile): <sup>1</sup>H NMR δ 6.22 ppm (s, 3 H); <sup>13</sup>C NMR δ 66.3 (3 C, CH), 72.9, 78.7 (3 C), 79.4 ppm. Anal. Calcd for C<sub>8</sub>H<sub>3</sub>ClN<sub>4</sub>O<sub>8</sub>: C, 30.16; H, 0.94. Found: C, 30.79; H, 1.00.

**1,2,3,5,7-Pentanitro-4-(triisopropylsilyl)cubane (32).** Sodium bis(trimethylsilyl)amide (100 μL, 1 M in THF, 0.1 mmol) was added dropwise to a solution under argon of (triisopropylsilyl)tetranitrocubane **23** (33 mg, 0.075 mmol) in THF (3 mL) at –78 °C. The orange solution was stirred for 5 min at this temperature then frozen and nitrated with N<sub>2</sub>O<sub>4</sub> (~0.4 mL, excess) as described for the preparation of **29**. The solvent and excess N<sub>2</sub>O<sub>4</sub> were removed *in vacuo*. The solid remaining was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 2 mL). Evaporation followed by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) gave **32** (25 mg, 70%, containing 8–10% of **23** by <sup>1</sup>H NMR). Crystallization from CHCl<sub>3</sub> gave pure **32**: <sup>1</sup>H NMR (δ, CD<sub>2</sub>Cl<sub>2</sub>) 1.11 (d, *J* = 7 Hz, 18 H), 1.21–1.32 (m, 6 H) 6.04 ppm (s, 2 H); <sup>13</sup>C NMR (δ, CD<sub>2</sub>Cl<sub>2</sub>) 11.6 (3 C, CH–Si), 19.6 (6 C, CH<sub>3</sub>), 63.1 (3 C, CH), 73.3, 74.6, 79.7, 84.1, 90.9 ppm.

**1,2,3,4,5,7-Hexanitrocubane (34).** **Method A.** Sodium bis(trimethylsilyl)amide (38 μL of 1 M solution in THF, 0.038 mmol) was added

dropwise to a solution of pentanitrocubane **29** (10 mg, 0.03 mmol) in THF (4 mL) cooled to –78 °C under nitrogen. This was frozen under nitrogen with liquid nitrogen and nitrated with N<sub>2</sub>O<sub>4</sub> (~0.4 mL, excess) as described for the preparation of **29**. The solvent and excess N<sub>2</sub>O<sub>4</sub> were removed *in vacuo*. The residual solid was extracted with acetone (2 × 1 mL). Evaporation left a mixture of penta- and hexanitrocubanes **29** and **34** in 70:30 ratio as determined by <sup>1</sup>H NMR.

**Method B.** Potassium bis(trimethylsilyl)amide (100 μL, 0.5 M in toluene, 0.05 mmol) was added dropwise over 1 min to a solution under nitrogen of (triisopropylsilyl)pentanitrocubane **32** (20 mg, 0.04 mmol) in THF (1.75 mL) cooled to –105 °C (isooctane–N<sub>2</sub> bath). The solution of the potassium salt of **32** so made was then immediately frozen with liquid nitrogen and nitrated with N<sub>2</sub>O<sub>4</sub> (~0.4 mL, excess) as described for the preparation of **29**. The solvent and excess N<sub>2</sub>O<sub>4</sub> were evaporated *in vacuo*. The solid remaining was extracted with acetone (2 × 1 mL). Evaporation left a 60:40 mixture (by <sup>1</sup>H NMR) of silylated pentanitrocubane **32** with the two hexanitrocubanes **34** and **35** (their ratio was quite variable). Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) gave first **32** (6 mg, 30%). Further elution (96:4 CH<sub>2</sub>Cl<sub>2</sub>/acetonitrile) gave hexanitrocubane **34** (5 mg, 30%) as a white solid: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 6.73 ppm (s, 2 H); <sup>13</sup>C NMR δ 65.0 (2 C, CH), 78.9 (2 C), 83.1 (2 C), 91.0 ppm. Crystallization from 95:5 chloroform/acetonitrile gave X-ray-quality crystals of the bis-acetonitrile solvate hexanitrocubane.

Sometimes small amounts of (triisopropylsilyl)hexanitrocubane **35** were isolated: <sup>1</sup>H NMR (δ, CD<sub>2</sub>Cl<sub>2</sub>) 1.13 (d, *J* = 7.5 Hz, 18 H), 1.40–1.50 (m, 3 H), 6.23 ppm (s, 1 H).

**Single-Crystal X-ray Analysis of Compounds 29 and 34.** Details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK).

**1,2,3,5,7-Pentanitrocubane (29).** Crystals of **29** belong to monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c* with *a* = 6.637(3), *b* = 23.275(14), *c* = 7.860(5) Å, β = 113.21(5)°, *Z* = 4, *D*<sub>x</sub> = 1.959 g/cm<sup>3</sup>. The thin-plate crystal was quite small (0.01 × 0.35 × 0.40 mm), leading to a somewhat weak set of diffraction intensities, and thus low precision in the numerical results. *R* = 0.0668, *R*<sub>w2</sub> = 0.1647 for 686 unique reflections with *I* > 2σ(*I*). [*R* = 0.1136 for all 1051 data.]

**1,2,3,4,5,7-Hexanitrocubane (34).** Crystals of **34** are monoclinic, space group *C*2/*c*, with *a* = 13.0102(7), *b* = 7.7242(6), *c* = 18.0758(12) Å, β = 95.404(7)°, *Z* = 4, *D*<sub>x</sub> = 1.676 g/cm<sup>3</sup>, all at *T* = –50 °C. The asymmetric unit is comprised of 1/2 of **34**, and one acetonitrile molecule; a crystallographic 2-fold axis passes through the centers of the di- and tetrasubstituted faces of the cube. *R* = 0.0407, *R*<sub>w2</sub> = 0.1062 for all 1241 unique reflections. The indicated precision in the numerical results is ~4 times higher than that for **29**; the appearance of bonding-electron density peaks in the final electron density map indicated above-average diffraction quality.

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