(d, 3, $J = 7$ Hz); IR (neat) 1720, 1625 cm^{-1}. The data correspond well to those previously reported for the ethyl ester.[10]

Methyl (1α,2α,5β)-2-Methyl-5-(1-methylethenyl)cyclohexanecarboxylate (8). Ester 7 (32 mg, 0.16 mmol) was dissolved in 1 mL of methylene chloride in a flame-dried flask under nitrogen. $EtAlCl_2$ (0.1 mL of 1.5 M in heptane, 0.15 mmol) was added and the reaction mixture was refluxed for 5 days. Ether and water were added. The organic layer was dried ($MgSO_4$) and evaporated to give 28 mg of crude 8. Flash chromatography on silica gel (99:1 pentane–ether) gave 26 mg (82%) of pure 8: NMR (CCl_4) δ 4.63 (s, 2), 3.62 (s, 3), 2.63 (br, 1), 1.1–2.4 (m, 8), 1.70 (br s, 3), 0.97 (d, 3, $J = 6$ Hz); ^{13}C NMR ($CDCl_3$) δ 139.1 (C=), 108.4 (=CH_2), 50.9 (OCH_3), 44.9 (C_1), 39.2 (C_5), 33.8 (C_2*), 33.5 (C_6*), 31.2 (C_4), 29.7 (C_3), 21.1 (CH_3), 19.5 (CH_3); IR (neat) 3090, 2930, 1735, 1645, 1160, 890, 760 cm^{-1}; GC (10 ft × $^1/_4$ in., 10% Carbowax 20 M, 150 °C) t_R 13 min. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.47; H, 10.27. Found: C, 73.25; H, 10.30.

Methyl (1β,2α,5β)-2-Methyl-5-(1-methylethenyl)cyclohexanecarboxylate (9). Ester 8 (50 mg, 0.26 mmol) was dissolved in 3 mL of 0.5 M sodium methoxide in methanol and heated at reflux for 5 days. The solution was acidified with 1 M hydrochloric acid and extracted with ether. The organic layer was dried (Na_2SO_4) and evaporated to give 77 mg of a mixture of acid and ester. The crude product was treated with diazomethane at 0 °C in ether until the yellow color persisted. The solvent was removed in vacuo to give 45 mg of crude 9. Medium pressure chromatography on silica gel (99:1 pentane–ether) gave 14 mg (28%) of pure 9: NMR ($CDCl_3$) δ (4.63 (br s, 2), 3.67 (s, 3), 1.1–2.3 (m, 9), 1.70 (br s, 3), 0.87 (d, 3, $J = 7$ Hz): ^{13}C NMR ($CDCl_3$) δ 176.3 (C=O), 149.4 (C=), 108.8 (C=CH_2), 51.3 (OCH_3 and C_1), 44.4 (C_5), 34.8 (C_2*), 34.4 (C_3*), 34.2 (C_6*), 31.2 (C_4), 20.8 (CH_3), 20.4 (CH_3); IR (neat) 3090, 2930, 1740, 1650, 890 cm^{-1}; GC (10 ft × $^1/_4$ in. 10% Carbowax 20 M, 150 °C) t_R 15 min.

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Registry No. 5, 2270-60-2; 6, 87803-48-3; 7, 87803-49-4; 8, 87803-50-7; 9, 87803-51-8; dimethylmethyleneammonium iodide, 33797-51-2.

Synthesis of 1,4-Dinitrocubane

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In continuation of a program on the synthesis of energetic compounds with good thermal stability and high density,[1] we undertook the synthesis and characterization of 1,4-dinitrocubane. So far as we are aware, nitrocubanes have not been reported previously. The compound nearest to this class is a nitroperchlorohomocubane, a substance of much less strain energy, prepared by Scherer and Lunt.[2]

Eaton and Cole first entered the cubane series in 1964 with the synthesis of the 1,4-diacid.[3] This compound is available in substantial quantities; several pounds have been made at the University of Chicago over the years. An early attempt to prepare diaminocubane via Curtius rearrangement of the diacyl azide was abandoned when the first sample of the crystalline azide exploded violently. After Yamada's method using diphenylphosphoryl azide for the direct conversion of carboxylic acids to carbamates became available,[4] the project was reopened successfully. Thus, treatment of cubane-1,4-dicarboxylic acid with diphenylphosphoryl azide and triethylamine in *tert*-butyl alcohol at reflux gives 1,4-bis[(*tert*-butoxycarbonyl)amino]cubane in nearly quantitative yield (Chart I). This method avoids completely the sensitive diacyl azide. Hydrolysis and decarboxylation of the carbamate gives 1,4-diaminocubane dihydrochloride, a stable, high-melting, white solid. The corresponding free amine is less stable, decomposing on standing overnight. The crude amine is thus best oxidized directly. After trying many reagents we settled on *m*-chloroperbenzoic acid, stabilized by 4,4′-thiobis(2-*tert*-butyl-6-methylphenol), in refluxing dichloroethane. This gave 1,4-dinitrocubane in 40% yield, sufficient for our purposes.

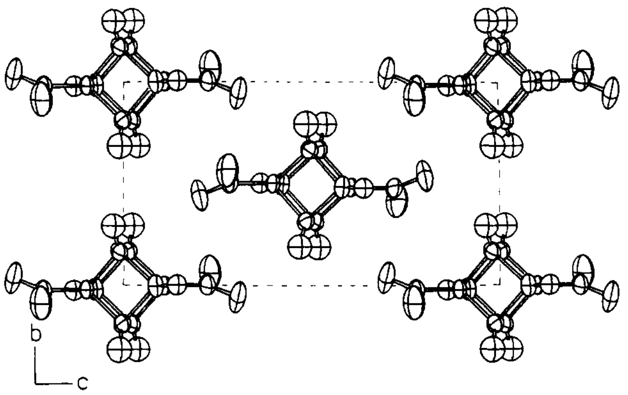
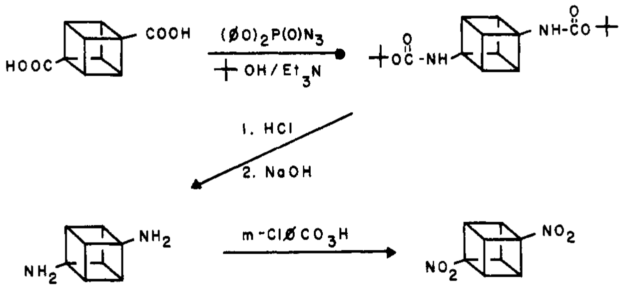


Figure 1. The approximately hexagonally packed [100] sheet of 1,4-dinitrocubane. The dashed lines define the unit cell.

Chart I



Differential scanning calorimetry showed that there was no obvious decomposition of dinitrocubane below its 260 °C melting point.[5] As cubane itself decomposes slowly at temperatures above 200 °C,[6] the strongly electron withdrawing nitro groups seem to stabilize the cubane system, althouth obviously this is a difficult comparison to quantify experimentally. Minimum energy reaction path calculations of the activation energy for ring opening in cubane and several nitro derivatives of cubane via Dewar's UMINDO/3 method indicate that nitro-group sub-

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[1] G. P. Sollott and E. E. Gilbert, *J. Org. Chem.*, **45**, 5405 (1980).

[2] K. V. Scherer, Jr., and R. S. Lunt III, *J. Am. Chem. Soc.*, **88**, 2860 (1966).

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

[4] T. Shioiri, K. Ninomiya, and S. Yamada, *J. Am. Chem. Soc.*, **94**, 6203 (1972).

[5] We are indebted to D. Anderson, ARRADCOM, Dover, NJ, for this measurement.

[6] This decomposition is strongly surface dependent: P. E. Eaton and B. K. Ravi Shankar, unpublished results.

0022-3263/84/1949-0185$01.50/0

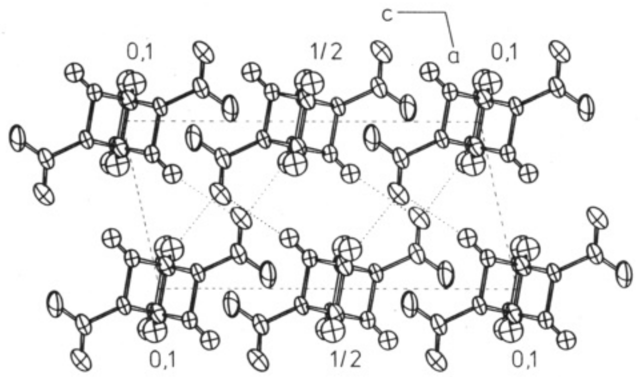

Figure 2. Projection of the unit cell down [010] showing the packing of successive sheets of 1,4-dinitrocubane.

stituents should stabilize the carbon–carbon bonds in cubane.[7]

The density of dinitrocubane was predicted following Kitaigorodsky's approach[8] but with use of improved data.[9a] Thus, the molar volume of dinitrocubane was obtained by taking the molar volume of cubane itself (80.86 cm^3/mol, calculated from X-ray diffraction data[10]), subtracting twice the atomic volume of hydrogen (3.60 cm^3/mol), and adding twice the estimated nitro-group volume (21.61 cm^3/mol).[9b] Division of the molecular weight of dinitrocubane by the molar volume so obtained gave an estimated density for dinitrocubane of 1.66 g/cm^3. This approach is necessarily insensitive to substitution pattern.

The X-ray crystal structure of 1,4-dinitrocubane was determined. The methodology, fully refined results, labeling, selected inter-and intramolecular distances, and angles are available as supplementary material. There are two molecules per unit cell, placed about centers of symmetry and related by glide planes. All atoms lie on general equivalent sites. Calculation from the cell size and content gives a density of 1.66 g/cm^3, in accord with that obtained by the flotation method (1.66(5) g/cm^3 in aqueous KI) and in remarkably good agreement with that obtained from group additivity rules.

The packing generated by the $P2_1/c$ symmetry is a severe distortion of the rhombohedral packing found in cubane.[10] The dinitrocubane structure consists of approximately hexagonally packed molecular sheets on [100], with the distance between molecular centers ranging between 6.26 and 6.58 Å (Figure 1). The closest molecular approach within these sheets is 2.93 Å between the O_2 and H_4 atoms on molecules with centers related by a $[0\,{}^1/{}_2\,{}^1/{}_2]$ displacement. Successive sheets (Figure 2), packed on [100], have closest intermolecular approaches of 2.53 and 2.66 Å, approximating van der Waals spacings, between O_1 and the H_3 and H_2 atoms on molecules with centers displaced by $[1{}^1/{}_2{}^1/{}_2]$ and [100], respectively. The crystal structure of dinitrocubane then seems describable simply in terms of Kitaigorodsky's general observations on molecular crystals,[8] namely, the structure adopted is that which produces the closest molecular packing; projections of one molecule are inserted into hollows of others. The approximate close packing on [100] in dinitrocubane seems to be the most efficient planar packing available; similarly the packing of successive sheets follows the "lock and key" principle outlined by Kitaigorodsky.

Experimental Section

1,4-Bis[(*tert*-butoxycarbonyl)amino]cubane. A solution of cubane-1,4-dicarboxylic acid (2.5 g, 13 mmol), triethylamine (2.72 g, 26 mmol), and diphenylphosphoryl azide (7.1 g, 26 mmol) in *tert*-butyl alcohol (40 mL) was refluxed for 12 h, cooled, and then poured into saturated, aqueous sodium bicarbonate solution (150 mL). The precipitate (4.1 g, 94%) was filtered, washed well with water, and air-dried: mp > 220 °C; IR (KBr) 3300, 1690 cm^{-1}. Anal. Calcd for $C_{18}H_{26}N_2O_4$: C, 64.65; h, 7.84; N, 8.38. Found: C, 63.88; 64.02; H, 7.25, 7.32; N, 8.65, 9.01. Further attempts at purification only raised the nitrogen content (9.63) presumably because of hydrolysis and decarboxylation.

1,4-Diaminocubane Dihydrochloride. Hydrogen chloride gas was bubbled through a suspension of 1,4-bis[(*tert*-butoxycarbonyl)amino]cubane (3 g) in methanol (30 mL) at –60 °C until the mixture became homogeneous. The solution was then left to warm to room temperature. The methanol was removed in vacuo. The residue was filtered and washed with ice-cold ethanol. 1,4-Diaminocubane dihydrochloride was isolated as a white solid (1.24 g, 67%), which could be purified by crystallization from methanol/acetone: mp > 260 °C; IR (KBr) 3100–2700 cm^{-1} (br); ^1H NMR (CD_3OD) δ 4.21 (s). Anal. Calcd for $C_8H_{12}N_2Cl_2$: C, 46.39; H, 5.84; N, 13.53. Found: C, 46.03; H, 5.43; N, 12.66. There was much variation from sample to sample, a familiar problem with amine hydrochlorides.

1,4-Diaminocubane. A solution of 1,4-diaminocubane dihydrochloride (200 mg, 0.96 mmol) in aqueous sodium hydroxide [80 mg (2 mmol) in 5 mL of water] was extracted with dichloromethane (6 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to leave 1,4-diaminocubane as a yellow solid (92 mg, 71%): ^1H NMR ($CDCl_3$) δ 3.52 (s). This material was unstable and was taken on directly.

1,4-Dinitrocubane. The free diamine was dissolved in dichloroethane (5 mL), and the solution was added dropwise to a refluxing solution of *m*-chloroperbenzoic acid (1.42 g, 8.16 mmol) and 4,4′-thiobis(2-*tert*-butyl-6-methylphenol) (7 mg) in dichloroethane (10 mL). The whole was refluxed for 4 h. The reaction mixture was cooled to room temperature and then worked up by adding methylene chloride until everything had dissolved. The solution was washed with aqueous sodium hydroxide (5%, 3 × 50 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuo. 1,4-Dinitrocubane was isolated as white crystals by preparative silica gel TLC (CH_2Cl_2): 52 mg, 40%; mp 260 °C dec; ^1H NMR ($CDCl_3$) δ 4.66 (s); IR (KBr) 1510, 1370, 1355, 1190, 950, 810 cm^{-1}; MS, *m/e* ($P - NO_2$) calcd 148.0399, found 148.0373. Anal. Calcd for $C_8H_6N_2O_4$: C, 49.49; H, 3.12; N, 14.43. Found: C, 49.37; H, 3.23; N, 14.26.

Acknowledgment. Those in the Department of Chemistry thank the National Science Foundation for partial support of this work (NSF-CHE78-07430).

Registry No. 1,4-Bis[(*tert*-butoxycarbonyl)amino]cubane, 87830-27-1; cubane-1,4-dicarboxylic acid, 32846-66-5; diphenylphosphoryl azide, 26386-88-9; *tert*-butyl alcohol, 75-65-0; 1,4-diaminocubane dihydrochloride, 87830-28-2; 1,4-diaminocubane, 87830-29-3; 1,4-dinitrocubane, 87830-30-6.

Supplementary Material Available: (a) X-ray data collection and structure determination, (b) Labeled ORTEP drawing of 1,4-dinitrocubane, (c) Table I listing refined spatial coordinates and temperature factor parameters (with standard deviations) for atoms in the dinitrocubane asymmetric unit, (d) Table II listing selected crystallographic distances in 1,4-dinitrocubane (in angstroms), (e) Table III listing intramolecular bond angles in degrees in 1,4-dinitrocubane (6 pages). Ordering information is given on any current masthead page.

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