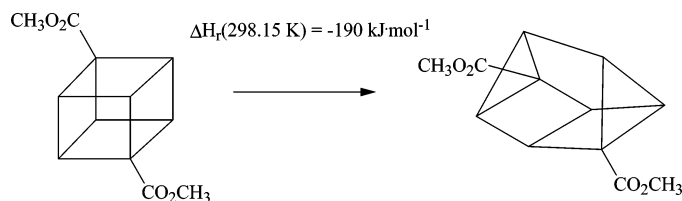


## Cubane, Cuneane, and Their Carboxylates: A Calorimetric, Crystallographic, Computational, and Conceptual Coinvestigation

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This study is a multinational, multidisciplinary contribution to the thermochemistry of dimethyl 1,4-cubanededicarboxylate and the corresponding isomeric, cuneane derivative and provides both structural and thermochemical information regarding the rearrangement of dimethyl 1,4-cubanededicarboxylate to dimethyl 2,6-cuneanededicarboxylate. The enthalpies of formation in the condensed phase at  $T = 298.15$  K of dimethyl 1,4-cubanededicarboxylate (dimethyl pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane-1,4-dicarboxylate) and dimethyl 2,6-cuneanededicarboxylate (dimethyl pentacyclo[3.3.0.0<sup>2,4</sup>.0<sup>3,7</sup>.0<sup>6,8</sup>]octane-2,6-dicarboxylate) have been determined by combustion calorimetry,  $\Delta_f H_m^{\circ}(\text{cr})/\text{kJ}\cdot\text{mol}^{-1} = -232.62 \pm 5.84$  and  $-413.02 \pm 5.16$ , respectively. The enthalpies of sublimation have been evaluated by combining vaporization enthalpies evaluated by correlation-gas chromatography and fusion enthalpies measured by differential scanning calorimetry and adjusted to  $T = 298.15$  K,  $\Delta_{\text{cr}}^{\circ} H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = 117.2 \pm 3.9$  and  $106.8 \pm 3.0$ , respectively. Combination of these two enthalpies resulted in  $\Delta_f H_m^{\circ}(\text{g}, 298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$  of  $-115.4 \pm 7.0$  for dimethyl 1,4-cubanededicarboxylate and  $-306.2 \pm 6.0$  for dimethyl 2,6-cuneanededicarboxylate. These measurements, accompanied by quantum chemical calculations, resulted in values of  $\Delta_f H_m(\text{g}, 298.15 \text{ K}) = 613.0 \pm 9.5$   $\text{kJ}\cdot\text{mol}^{-1}$  for cubane and  $436.4 \pm 8.8$   $\text{kJ}\cdot\text{mol}^{-1}$  for cuneane. From these enthalpies of formation, strain enthalpies of  $681.0 \pm 9.8$  and  $504.4 \pm 9.1$   $\text{kJ}\cdot\text{mol}^{-1}$  were calculated for cubane and cuneane by means of isodesmic reactions, respectively. Crystals of dimethyl 2,6-cuneanededicarboxylate are disordered; the substitution pattern and structure have been confirmed by determination of the X-ray crystal structure of the corresponding diacid.

### Introduction

This is the 40th anniversary of the first successful synthesis of the polycyclic hydrocarbon cubane.<sup>1,2</sup> As

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befits the symmetry and accompanying esthetics, large strain energy and eight tertiary carbons all capable of possible functionalization, the chemistry of this seemingly simple eight-carbon hydrocarbon ( $\text{C}_8\text{H}_8$ ) and its derivatives has blossomed.<sup>3</sup> Soon after the first synthesis of cubane, there were measurements of the enthalpies of combustion and of sublimation.<sup>4</sup> The values of both measurements have been questioned.<sup>5-7</sup> Cuneane is a valence isomer of cubane of considerably lower symmetry. That cuneanes arise from cubanes by  $\text{Ag}^+$ -catalyzed rearrangement suggests that the cuneanes are more (enthalpically) stable than the corresponding cubanes.

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

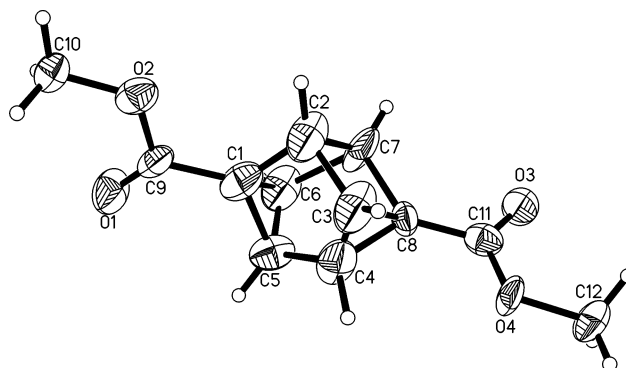
(2) For almost contemporaneous alternative approaches to the synthesis of cubane, see: (a) Barborak, J. C.; Watts, L.; Pettit, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 1328. (b) Chin, C. G.; Cuts, W. H.; Masamune, S. *J. Chem. Soc. Chem. Commun.* **1966**, 880.

This study is a combined experimental and theoretical contribution to the thermochemistry of dimethyl 1,4-cubanedicarboxylate and the corresponding cuneane derivative and provides structural and thermochemical information regarding the rearrangement of dimethyl 1,4-cubanedicarboxylate to dimethyl 2,6-cuneanedicarboxylate. The thermochemical data is also augmented by theoretical calculations on the relative stabilities of the two title compounds as well as on the parent compounds and other related derivatives.

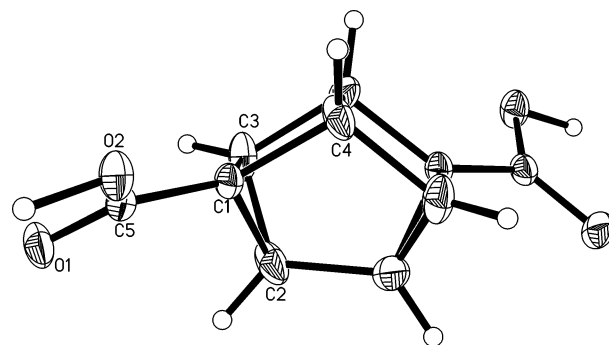
The enthalpies of formation in the condensed phase at  $T = 298.15$  K of dimethyl 1,4-cubanedicarboxylate (dimethyl pentacyclo[4.2.0.0.2<sup>5</sup>0.3<sup>8</sup>0<sup>4,7</sup>]octane-1,4-dicarboxylate) and dimethyl 2,6-cuneanedicarboxylate (dimethyl pentacyclo[3.3.0.0.2<sup>4</sup>0.3<sup>7</sup>0<sup>6,8</sup>]octane-2,6-dicarboxylate) have been determined by combustion calorimetry. The enthalpies of sublimation have been evaluated by combining vaporization enthalpies evaluated by correlation gas chromatography and fusion enthalpies measured by differential scanning calorimetry. Values of  $\Delta_f H^\circ_m(g, 298.15 \text{ K})$  were calculated from these measurements. The structure of dimethyl pentacyclo[3.3.0.0.2<sup>4</sup>0.3<sup>7</sup>0<sup>6,8</sup>]octane-2,6-dicarboxylate obtained from the rearrangement of dimethyl 1,4-cubanedicarboxylate has been determined by an X-ray crystal structure of the corresponding diacid. Some details on the X-ray-determined, crystallographically disordered structure of dimethyl 2,6-cuneanedicarboxylate are also given.

## Results

**A. X-ray Crystallography.** The structure of dimethyl 2,6-cuneanedicarboxylate and 2,6-cuneanedicarboxylic acid as solved by X-ray crystallography is illustrated in Figures 1 and 2. Table 1 contains a comparison of some bond distances between 2,6-cuneanedicarboxylic acid and octamethylcuneane,<sup>8</sup> the only other compound in the Cambridge Data Base with this ring structure. The latter contains two crystallographically unique molecules in the asymmetric unit cell. The bond lengths in Table 1 are displayed by imposing the  $C_2$  molecular axis of symmetry present in 2,6-cuneanedicarboxylic acid on both molecules while maintaining the numbering system shown in



**FIGURE 1.** Projection view of dimethyl 2,6-cuneanedicarboxylate.



**FIGURE 2.** Projection view of 2,6-cuneanedicarboxylic acid with 25% thermal ellipsoids.

**TABLE 1. Comparison of Bond Lengths between 2,6-Cuneanedicarboxylic Acid and Octamethylcuneane**

| bond                     | bond lengths (Å)             |                                |
|--------------------------|------------------------------|--------------------------------|
|                          | 2,6-cuneanedicarboxylic acid | octamethylcuneane <sup>a</sup> |
| C(1)–C(2); C(1)#1–C(2)#1 | 1.518(4)                     | 1.520(2)                       |
| C(1)–C(4); C(1)#1–C(4)#1 | 1.524(4)                     | 1.551(3)                       |
| C(1)–C(3); C(1)#1–C(3)#1 | 1.528(4)                     | 1.535(7)                       |
| C(2)–C(3); C(2)#1–C(3)#1 | 1.458(5)                     | 1.520(2)                       |
| C(2)–C(2)#1              | 1.492(6)                     | 1.532(1)                       |
| C(3)–C(4)#1; C(4)–C(3)#1 | 1.524(4)                     | 1.551(3)                       |
| C(4)–C(4)#1              | 1.585(6)                     | 1.572(2)                       |

<sup>a</sup> Octamethylcuneane contains two crystallographically unique molecules in the asymmetric unit; values cited are average values.<sup>8</sup>

(3) For some recent reviews, see: (a) Griffin, G. W.; Marchand, A. P. *Chem. Rev.* **1989**, *89*, 997. (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421. (c) Higuchi, H.; Ueda, I. In *Carbocyclic Cage Compounds: Chemistry and Applications*; Osawa, E. J., Yonemitsu, O., Eds.; VCH: New York, 1992; p 217. (d) Bashir-Hashemi, A.; Iyer, S. Alster, J.; Slagg, N. *Chem. Ind.* **1995**, *14*, 551. (e) Tsanaktsidis, J. *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Inc.: Greenwich, CT, 1997; Vol. 6, p 67. (f) Bashir-Hashemi, A. *Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks, Advances in Strained and Interesting Organic Molecules*; Laali, K., Ed.; JAI Press Inc.: Stamford, CT, 1999; p 1. (g) Bashir-Hashemi, A.; Higuchi, H. In *The Chemistry of Cyclobutanes*; Rappoport, Z., Liebman, J. F., Eds.; Wiley: Chichester, 2005; p 873. (h) Quintanilla, E.; Dávalos, J. Z.; Abboud, J. L. M.; Alkorta, I. In *The Chemistry of Cyclobutanes*; Rappoport, Z., Liebman, J. F., Eds.; Wiley: Chichester, 2005; p 177.

(4) Kybett, B. D.; S. Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

(5) Diky, V. V.; Frenkel, M.; Karpushenkava, L. S. *Thermochim. Acta* **2003**, *408*, 115.

(6) Bashir-Hashemi, A.; Chickos, J. S.; Hanshaw, W.; Zhao, H.; Farivar, B. S.; Liebman, J. F. *Thermochim. Acta* **2004**, *424*, 91.

(7) Kirklin, D. R.; Churney, K. L.; Domalski, E. S. *J. Chem. Thermodyn.* **1989**, *21*, 1105.

(8) Imgartinger, H.; Strack, S.; Gleiter, R.; Brand, S.; *Acta Crystallogr. C Cryst. Struct. Commun.* **1997**, *53*, 1145.

Figure 1. The bond lengths for the octamethylcuneane are averages of the distances as reported for the two molecules.<sup>8</sup> With the exception of the C4–C4#1 bond length, all others appear shorter in the diacid. The eclipsed methyl interactions that are present in octamethylcuneane are likely to contribute to the longer bond lengths observed.

**B. Thermochemistry.** The standard enthalpies of combustion and formation of dimethyl 1,4-cubane-dicarboxylate and dimethyl 2,6-cuneanedicarboxylate in the condensed phase at  $T = 298.15$  K are given in the last two columns of Table 2. The energy of combustion of dimethyl 1,4-cubanedicarboxylate was previously determined by Kirklin *et al.*<sup>7</sup> and by Avdonin *et al.*<sup>9</sup> Comparison of the results obtained by these authors with the ones

(9) Avdonin, V. V.; Kirpichev, E. I.; Rubtsov, Y. I.; Romanova, L. E.; Ivanova, M. E.; Eremenko, L. T. *Russ. Chem. Bull.* **1996**, *45*, 2342.

**TABLE 2.** Standard Molar Energy, Enthalpy of Combustion, and Enthalpy of Formation at  $T = 298.15$  K and  $p^0 = 101.325$  kPa

| compound                          | $\Delta U_m^{\circ}(\text{cr})/$<br>$\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_c H_m^{\circ}(\text{cr})/$<br>$\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^{\circ}(\text{cr})/$<br>$\text{kJ}\cdot\text{mol}^{-1}$ |
|-----------------------------------|---|---|---|
| dimethyl 1,4-cubanedicarboxylate  | $-6201.94 \pm 5.63$   | $-6204.48 \pm 5.63$   | $-232.62 \pm 5.84$  |
| dimethyl 2,6-cuneanedicarboxylate | $-6021.55 \pm 4.91$   | $-6024.08 \pm 4.91$   | $-413.02 \pm 5.16$  |

**TABLE 3.** Comparison of the Available Standard Energies and Enthalpies of Combustion and Formation of 1,4-Dimethyl Cubanedicarboxylate at  $T = 298.15$  K

| entry | purity/<br>mol % | char            | method           | no. of<br>expts | aux subst    | amt<br>react          | $\Delta_c u^{\circ}(\text{cr})/$<br>$\text{J}\cdot\text{g}^{-1}$ | $\Delta_c H_m^{\circ}(\text{cr})/$<br>$\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_f H_m^{\circ}(\text{cr})/$<br>$\text{kJ}\cdot\text{mol}^{-1}$ | ref                  |
|-------|------------------|-----------------|------------------|-----------------|--------------|-----------------------|--|---|---|----------------------|
| 1     | >99.7            | DSC             | SBC <sup>a</sup> | 7               | benzoic acid | $m^a \approx 0.131$ g | $-28220.22 \pm 1.95$   | $-6218.09 \pm 1.42$   | $-218.99 \pm 2.12$  | Kirklin <sup>7</sup> |
| 2     | 99.9             | CO <sub>2</sub> | SBC <sup>a</sup> | na <sup>c</sup> | no           | $m \approx 0.180$ g   | $-28187.3$   | $-6205.9$   | $-231.2 \pm 2.5$  | Avdonin <sup>9</sup> |
| 3     | 99.9             | DSC             | SMC <sup>b</sup> | 6               | benzoic acid | $m \approx 0.035$ g   | $-28162.3 \pm 9.3$   | $-6204.48 \pm 5.63$   | $-232.62 \pm 5.84$  | This work            |

<sup>a</sup> SBC: macro bomb combustion calorimeter. <sup>b</sup> SMC: semimicro bomb combustion calorimeter. <sup>c</sup> na: not available.

**TABLE 4.** Summary of Vaporization Enthalpies (Enthalpies in  $\text{kJ}\cdot\text{mol}^{-1}$ )

|                               | $\Delta_f H_m^{\circ}$ (298.15K) (lit.) | mix 1          | mix 2          | mix 3          | mix 4          | $\Delta_f H_m^{\circ}$ (298.15 K) mean <sup>a</sup> |
|-------------------------------|---|----------------|----------------|----------------|----------------|---|
| diethyl malonate              | 65.03                                   |                |                | 63.8           |                | $64.7 \pm 2.0$                                      |
| dimethyl phthalate            | 77.1                                    | 77.9           | 78.0           | 78.1           | 77.9           | $78.0 \pm 2.2$                                      |
| diethyl phthalate             | 85.6                                    | 84.8           | 84.7           | 85.1           | 84.7           | $84.8 \pm 2.2$                                      |
| dimethyl cubanedicarboxylate  |   | $87.8 \pm 2.0$ | $89.2 \pm 2.4$ |                |                | $88.5 \pm 2.2$                                      |
| dimethyl cuneanedicarboxylate |   |                |                | $90.2 \pm 2.0$ | $89.2 \pm 2.2$ | $89.7 \pm 2.1$                                      |
| dibutyl phthalate             | 101.5                                   | 101.7          | 101.5          |                | 101.7          | $101.6 \pm 2.2$                                     |

<sup>a</sup> The uncertainty represents 2 standard deviations in the mean uncertainty associated with the intercept of the equations derived from the correlations.

obtained in our work is given in Table 3. Avdonin *et al.*<sup>9</sup> report complete combustion without the use of an auxiliary substance. Kirklin *et al.*<sup>7</sup> sandwiched layers of the cubane diester with benzoic acid. Small quantities of carbon deposits were observed on the crucible walls. We experienced soot formation in the absence of an auxiliary substance and in a few experiments using benzoic acid. Complete combustion was generally observed when benzoic acid was layered with the cubane diester as described by Kirklin *et al.*<sup>7</sup> and only the results of these experiments are reported. The results obtained in this study, however, are in best agreement with the work of Avdonin *et al.*<sup>9</sup> Combustion of dimethyl 2,6-cuneanedicarboxylate, which was also conducted in the presence of the auxiliary, benzoic acid, does not appear to have been studied previously, nor has that of any other cuneane derivative. No soot formation was observed in these experiments as well.

Vaporization enthalpies were obtained by correlation gas chromatography.<sup>6,10</sup> The results of these studies are summarized in Table 4. Also included in Table 4 is a summary of how well the vaporization enthalpy of the standards were reproduced. Since the retention times of dimethyl 1,4-cubane and 2,6-cuneanedicarboxylates were very similar, their vaporization enthalpies were evaluated in separate experiments; the values of both are very similar. As noted above, the literature values are averages of several determinations; details are available in the Supporting Information.

The fusion enthalpies of both the cubane and cuneane diesters are listed in Table 5. The fusion enthalpy of

**TABLE 5.** Fusion Enthalpies of Dimethyl 1,4-Cubanedicarboxylate and Dimethyl 2,6-Cuneanedicarboxylate (Enthalpies in  $\text{kJ}\cdot\text{mol}^{-1}$ )

| run                               | $m/\text{mg}$ | $J/\text{g}$ | onset/ $^{\circ}\text{C}$ | $\Delta_{\text{cr}(1)} H_m^{\circ}(T_{\text{fus}})$ | $T_{\text{fus}}/\text{K}$ |
|-----------------------------------|---------------|--------------|---------------------------|---|---------------------------|
| Dimethyl 1,4-Cubanedicarboxylate  |               |              |                           |   |                           |
| 1 <sup>a</sup>                    | 8.66          | 176.4        | 167.1                     | 38.8  |                           |
| 2 <sup>a</sup>                    | 6.17          | 175.6        | 164.5                     | 38.6  |                           |
| 3 <sup>a</sup>                    | 6.90          | 178.8        | 163.5                     | 39.3  |                           |
| 4 <sup>b</sup>                    | 1.02          |              | 164.5                     | 35.7  |                           |
| average                           |               |              |                           | $38.1 \pm 1.6$                                      | $438.2 \pm 1.5$           |
| lit. <sup>c</sup>                 |               |              |                           | $41.0 \pm 3.0$                                      | $437.8 \pm 0.5$           |
| Dimethyl 2,6-cuneanedicarboxylate |               |              |                           |   |                           |
| 1 <sup>a</sup>                    | 6.47          | 104.6        | 119.4                     | 23.0  |                           |
| 2 <sup>a</sup>                    | 5.89          | 107.6        | 119.3                     | 23.7  |                           |
| 3 <sup>a</sup>                    | 5.54          | 111.6        | 119.2                     | 24.5  |                           |
| 4 <sup>b</sup>                    | 1.10          |              |                           | 22.2  |                           |
| average                           |               |              |                           | $23.4 \pm 1$  | $392.7 \pm 0.1$           |

<sup>a</sup> St. Louis. <sup>b</sup> Madrid. <sup>c</sup> Reference 7.

dimethyl cubanedicarboxylate were also measured previously. The values measured compare within the experimental uncertainty with those reported earlier by Kirklin *et al.*<sup>7</sup> No additional phase transitions were observed for either diester between  $T = 298$  K and  $T = T_{\text{fus}}$ . An average value of  $38.1 \pm 1.6$   $\text{kJ}\cdot\text{mol}^{-1}$  was used in all subsequent calculations. Although the fusion entropies of these two valence isomers might be expected to be similar in magnitude, the smaller fusion entropy of the dimethyl cuneanedicarboxylate is consistent with the fact that the crystal for this material is disordered and that it exists as a racemic material. Furthermore, the low temperature thermal behavior of this material was not investigated.

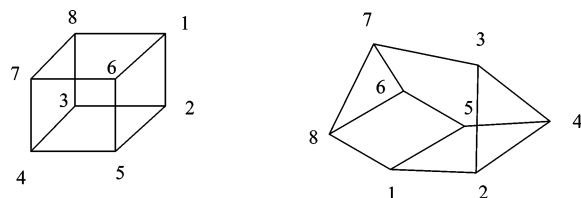
The sublimation enthalpy of both diesters can be obtained by combining the vaporization enthalpy available at  $T = 298.15$  K with the fusion enthalpy once

(10) For a description of the technique see: Chickos, J. S.; Hosseini, S.; Hesse, D. G. *Thermochim. Acta* **1995**, *249*, 41. Chickos, J. S.; Hesse, D. G.; Hosseini, S.; Nichols, G.; Webb, P. *Thermochim. Acta* **1998**, *313*, 101.

**TABLE 6. Sublimation Enthalpies of Dimethyl 1,4-Cubanedicarboxylate and Dimethyl 2,6-Cuneanedicarboxylate (Enthalpies in kJ·mol<sup>-1</sup>)**

|                                   | $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$ | $T_{\text{fus}}/\text{K}$ | $\Delta C_p \Delta T^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$ | $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298\text{ K})^b$ | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298\text{ K})$ | $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298\text{ K})$ |
|-----------------------------------|---|---------------------------|---|---|--|---|
| dimethyl 1,4-cubanedicarboxylate  | $38.1 \pm 1.6$  | 438.2                     | $-9.4 \pm 2.8$  | $28.7 \pm 3.2$  | $88.5 \pm 2.2$   | $117.2 \pm 3.9$   |
| dimethyl 2,6-cuneanedicarboxylate | $23.4 \pm 1.0$  | 392.7                     | $-6.3 \pm 1.9$  | $17.1 \pm 2.1$  | $89.7 \pm 2.1$   | $106.8 \pm 3.0$   |

<sup>a</sup> Heat capacities of the crystal and liquid phase were estimated. Dimethyl 1,4-cubanedicarboxylate, dimethyl 2,6-cuneanedicarboxylate:  $C_p(\text{cr}) = 236.2$ ;  $C_p(\text{l}) = 355.8\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , respectively; <sup>b</sup> Uncertainty ( $\pm 2\sigma$ ) assumed to be 0.3 of the magnitude of the temperature adjustment. at  $T = 298.15\text{ K}$  with the condensed phase enthalpy of formation of dimethyl 1,4-cubane-dicarboxylate and dimethyl 2,6-cuneanedicarboxylate results in the enthalpies of formation in the gas phase given in Table 7.

**FIGURE 3.** Numbering of the positions in cubane and cuneane rings.

adjusted to from  $T = T_{\text{fus}}$  to  $T = 298.15\text{ K}$ . A protocol for doing so using eq 1 has been described previously.<sup>11</sup>

$$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}}/\text{K}) + [0.15C_p(\text{cr}) - 0.26C_p(\text{l}) - 9.83][T_{\text{fus}} - 298.15]/1000 \quad (1)$$

Molar heat capacities of the crystal ( $C_p(\text{cr})$ ) and liquid phase ( $C_p(\text{l})$ ) were estimated; the following values were used for both dimethyl 1,4-cubane-dicarboxylate and dimethyl 2,6-cuneanedicarboxylate:  $C_p(\text{cr}) = 236.2$ ;  $C_p(\text{l}) = 355.8\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The results of the temperature adjustment to the fusion enthalpies are given in Table 6. Combining the sublimation enthalpies at  $T = 298.15\text{ K}$  with the condensed-phase enthalpy of formation of dimethyl 1,4-cubanedicarboxylate and dimethyl 2,6-cuneanedicarboxylate results in the enthalpies of formation in the gas phase given in Table 7.

**C. Theoretical Calculations.** The results from the theoretical calculation for cubane, methyl cubanecarboxylate, the three isomers of dimethyl cubanedicarboxylate, cuneane, the three methyl cuneanecarboxylates, the 10 dimethyl cuneanedicarboxylates, and the reference compounds used in the calculations are available in the Supporting Information. Numbering of the positions in cubane and cuneane rings is shown in Figure 3. It is worth noting that isomers generally have very similar values of zero-point vibrational energies and thermal corrections, when comparing cubane with cuneane, methyl cubanecarboxylate with the methyl cuneanecarboxylates, and the dimethyl cubanedicarboxylates with the dimethyl cuneanedicarboxylates.

Choosing dimethyl 1,4-benzenedicarboxylate as the reference compound, Table 8 compares the relative enthalpies of formation of dimethyl benzenedicarboxylates in gas phase at  $T = 298.15$  as calculated by theory and measured experimentally.

The size of the methyl and dimethyl carboxylates studied in this work does not permit calculations at very high levels, because of their computational cost. However,

(11) Chickos, J. S.; Hanshaw, W. *J. Chem. Eng. Data* **2004**, *49*, 77. Bashir-Hashemi, A.; Chickos, J. S.; Hanshaw, W.; Zhao, H.; Farivar, B. S.; Liebman, J. F. *Thermochim. Acta* **2004**, *424*, 91.

**TABLE 7. Standard Molar Enthalpies of Sublimation  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$  and Formation  $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}$  of the Solid and  $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}$  of the Gas at  $T = 298.15\text{ K}$  and  $p^{\circ} = 101.325\text{ KPa}$  for Dimethyl 1,4-cubanedicarboxylate and Dimethyl 2,6-cuneanedicarboxylate; Enthalpies in kJ·mol<sup>-1</sup>**

| compound                           | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\text{cr})$ | $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$ | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\text{g})$ |
|------------------------------------|---|---|--|
| dimethyl 1,4-cubane-dicarboxylate  | $-232.6 \pm 5.8$  | $117.2 \pm 3.9$                                     | $-115.4 \pm 7.0$   |
| dimethyl 2,6-cuneane-dicarboxylate | $-413.0 \pm 5.2$  | $106.8 \pm 3.0$                                     | $-306.2 \pm 6.0$   |

**TABLE 8. Comparison of the Calculated Relative Enthalpies of Formation of Dimethyl Benzenedicarboxylates with Experiment (Enthalpies in kJ·mol<sup>-1</sup>)**

| compound                          | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\text{g})_{\text{expt}}$ | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\text{g})_{\text{expt}}$ | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\text{g})_{\text{calcd}}$ |
|-----------------------------------|--|--|---|
| dimethyl 1,2-benzenedicarboxylate | $-606.1 \pm 2.7^a$   | 21.9   | 18.2  |
|                                   | $-606.2 \pm 2.6^b$   | 21.2   |   |
| dimethyl 1,3-benzenedicarboxylate | $-629.2 \pm 2.0^a$   | -1.2   | 1.8   |
|                                   | $-627.1 \pm 1.1^b$   | 0.3  |   |
| dimethyl 1,4-benzenedicarboxylate | $-628.0 \pm 1.0^a$   | 0.0  | 0.0   |
|                                   | $-627.4 \pm 1.1^b$   | 0.0  |   |

<sup>a</sup> Value taken from ref 40a. <sup>b</sup> Value taken from ref 40b.

**TABLE 9. Energies at 0 K and Enthalpies at 298 K for Cubane and Cuneane Obtained at Different Gaussian-n Levels<sup>a</sup>**

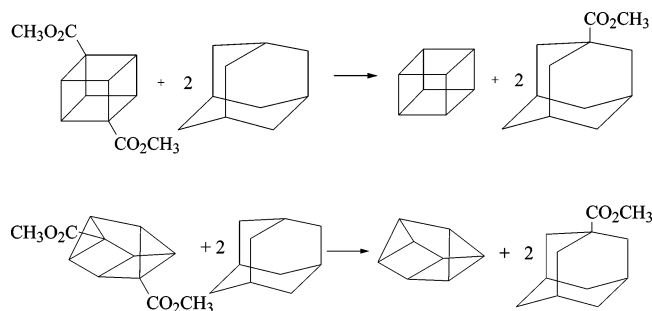
| compound | level     | $E_0$          | $H_{298}$      | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\text{g})$ |
|----------|-----------|----------------|----------------|--|
| cubane   | G2(MP2)   | $-308.84760^a$ | $-308.84201^a$ | 599.5  |
|          | G2        | $-308.85324^a$ | $-308.84765^a$ | 595.5  |
|          | G3//B3LYP | -309.21009     | -309.20450     | 607.1  |
|          | G3        | -309.21826     | -309.21259     | 608.7  |
| cuneane  | G2(MP2)   | $-308.90883$   | $-308.90311$   | 439.1  |
|          | G2        | $-308.91438$   | $-308.90866$   | 435.3  |
|          | G3//B3LYP | -309.27245     | -309.26673     | 445.0  |
|          | G3        | -309.28016     | -309.27435     | 445.3  |

<sup>a</sup> All values in hartrees (1 hartree = 2625.5 kJ·mol<sup>-1</sup>). <sup>a</sup> In last column, enthalpies of formation, in kJ·mol<sup>-1</sup>, calculated using bond separation reactions. <sup>a</sup> Value taken from ref 41.

in the case of the parent compounds, cubane and cuneane, is possible to carry out such type of calculations, to obtain more reliable enthalpies of formation, as it is discussed in the next Section. Calculations have been performed at different Gaussian-n levels. The results obtained are collected in Table 9.

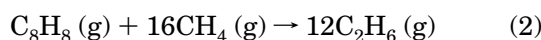
## Discussion

One of the more interesting and perhaps elusive properties of cubane and its derivatives, is its strain energy, i.e., the enthalpy difference between the enthalpy of formation of the cubane and that of an unstrained reference material. We have chosen to use as our refer-



**FIGURE 4.** Homodesmotic reaction for the calculation of the enthalpy of formation of cubane and cuneane using  $\Delta_f H_m^\circ(\text{g})$  of adamantane and methyl 1-adamantanecarboxylate as reference.

ence material for an unstrained quaternary carbon atom bearing a carbomethoxy group ( $\text{C}-\text{CO}_2\text{CH}_3$ ), the difference in the experimental enthalpies of formation of methyl 1-adamantanecarboxylate and adamantane, Figure 4. Also included in Figure 4 is the homodesmotic reaction relating dimethyl cuneanedicarboxylate to cuneane. The theoretical calculations indicate that both reactions are not exactly thermoneutral, resulting in enthalpies of reaction 6.8 and 21.0  $\text{kJ}\cdot\text{mol}^{-1}$ , in the case of cubane and cuneane, respectively. An uncertainty of  $\pm 4 \text{ kJ}\cdot\text{mol}^{-1}$  in the calculated enthalpies of reaction has been assumed. Combining these results with the experimental enthalpies of formation given in Table 10 results in enthalpies of formation,  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K}) = 613.0 \pm 9.5$  and  $436.4 \pm 8.8 \text{ kJ}\cdot\text{mol}^{-1}$ , for cubane and cuneane, respectively. As has been indicated above, we have carried out calculations on cubane and cuneane at different high Gn levels. Applying the bond separation reaction method<sup>12,13</sup> and using the following bond separation reaction



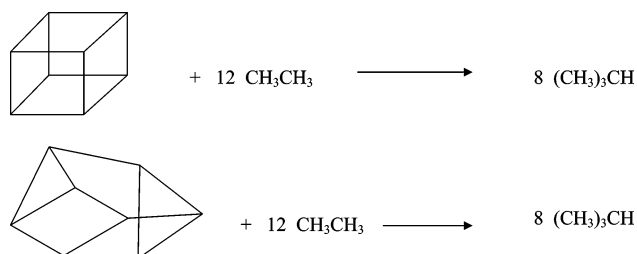
enthalpies of formation,  $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K}) = 602.7 \pm 7.3$  and  $441.2 \pm 7.3 \text{ kJ}\cdot\text{mol}^{-1}$  are calculated for cubane and cuneane, respectively, as average of the values calculated at the different Gaussian-n levels (see Table 9). Values of 597.5<sup>14</sup> and 610.9<sup>15</sup>  $\text{kJ}\cdot\text{mol}^{-1}$  have been previously calculated for cubane at the G2(MP2,SVP) and G3(MP2) levels. A value of 460  $\text{kJ}\cdot\text{mol}^{-1}$  had been estimated for cuneane using group additivity.<sup>16</sup>

Using the isodesmotic reactions and the stoichiometry of Figure 5, strain enthalpies of  $681.0 \pm 9.8$  and  $504.4 \pm 9.1 \text{ kJ}\cdot\text{mol}^{-1}$  are calculated for cubane and cuneane, respectively, using their enthalpies of formation derived from reactions in Figure 4, whereas strain enthalpies of  $670.7 \pm 9.4$  and  $509.2 \pm 9.4 \text{ kJ}\cdot\text{mol}^{-1}$  are calculated using their enthalpies of formation derived from Gaussian-n

**TABLE 10.** Experimental and Calculated Enthalpies of Formation ( $\text{kJ}\cdot\text{mol}^{-1}$ )<sup>a</sup>

| compound                           | $\Delta_f H_m^\circ(\text{g})_{\text{expt}}$ | $\Delta_f H_m^\circ(\text{g})_{\text{calcd}}$                    | $\Delta_{\text{strain}} H_m(\text{g})$               |
|------------------------------------|--|--|--|
| methane                            | $-74.4 \pm 0.4^b$                            |  |  |
| ethane                             | $-83.8 \pm 0.3^b$                            |  |  |
| propane                            | $-104.7 \pm 0.5^b$                           |  |  |
| isobutane                          | $-134.2 \pm 0.6^b$                           |  |  |
| cyclopropane                       | $53.3 \pm 0.5^b$                             |  |  |
| cyclobutane                        | $27.7 \pm 1.1^b$                             |  |  |
| cyclopentane                       | $-76.4 \pm 0.7^b$                            |  |  |
| benzene                            | $82.9 \pm 0.5^c$                             |  |  |
| methyl benzoate                    | $-276.1 \pm 4.0^d$                           |  |  |
| adamantane                         | $-134.6 \pm 2.2^b$                           |  | 0.0 <sup>e</sup>                                     |
| methyl cyclopropane-carboxylate    | $-309.8 \pm 0.7^f$                           |  |  |
| methyl cyclobutane-carboxylate     | $-327.7 \pm 1.3^f$                           |  |  |
| methyl 1-adamantanecarboxylate     | $-495.4 \pm 2.7^g$                           |  | 0.0 <sup>e</sup>                                     |
| dimethyl 1,4-cubane-dicarboxylate  | $-115.4 \pm 7.0^{h,i}$                       | <i>j</i>   | $674.2 \pm 9.8^h$                                    |
|                                    | $-100.1 \pm 4.4^k$                           |  | $678.5^h$<br>$595.8^k$                               |
| dimethyl 2,6-cuneane-dicarboxylate | $-306.2 \pm 6.0^{h,i}$                       | <i>j</i>   | $483.4 \pm 8.8^h$                                    |
|                                    |  |  | $484.7^h$  |
| cubane                             | $622.2 \pm 3.7^l$                            | <b><math>613.0 \pm 9.5^{h,m}</math></b><br>$602.7 \pm 7.3^{h,n}$ | $681.0 \pm 9.8^{h,o}$<br>$670.7 \pm 9.4^{h,n}$       |
| cuneane                            |  | <b><math>436.4 \pm 8.8^{h,m}</math></b><br>$441.2 \pm 7.3^{h,n}$ | $504.4 \pm 9.1^{h,o}$<br>$509.2 \pm 9.4^{h,n}$       |
| bicyclobutane                      | $217.1 \pm 0.8^b$                            |  | $505.7^{h,p}$<br>$276.0^q$<br>$266.0^r$<br>$260.7^k$ |
| methyl 1-bicyclobutane-carboxylate | $-164.6 \pm 0.7^b$                           |  | $255.1^s$<br>$222.3^k$                               |

<sup>a</sup> Uncertainties represent  $\pm 2\sigma$ ; values in bold are recommended. <sup>b</sup> Value taken from ref 17. <sup>c</sup> Value taken from ref 42. <sup>d</sup> Value taken from ref 43. <sup>e</sup> Used as reference, taken to be strainless. This is, admittedly, somewhat contentious. However, what is more important in the current strain context is the assumption that these species have the same strain energy. <sup>f</sup> Value taken from ref 18. <sup>g</sup> Value taken from ref 44. <sup>h</sup> This work. <sup>i</sup> Experimental value from Table 7. <sup>j</sup> See Table 11. <sup>k</sup> Value taken from ref 7. <sup>l</sup> Value taken from ref 4. <sup>m</sup> Calculated from the homodesmotic reaction of Figure 4. <sup>n</sup> Results from Gaussian-n calculations. <sup>o</sup> Calculated from the isodesmotic reaction of Figure 5. <sup>p</sup> Results from MP2(FULL)/6-31G(d) level. <sup>q</sup> Calculated from  $\Delta_f H_m^\circ(\text{g})_{\text{expt}}$  of bicyclobutane + 5 ethane  $\rightarrow$  2 propane + 2 isobutane. <sup>r</sup> Calculated using Benson's strain free group values (ref 45). <sup>s</sup> Calculated using the strain energy of bicyclobutane and the exothermicity of the following reaction: bicyclobutane + methyl 1-adamantanecarboxylate  $\rightarrow$  methyl 1-bicyclobutanecarboxylate + adamantane.



**FIGURE 5.** Isodesmotic reaction for the calculation of the strain enthalpy of cubane and cuneane; enthalpies in  $\text{kJ}\cdot\text{mol}^{-1}$  using  $\Delta_f H_m^\circ(\text{g})$  of ethane and isobutane as reference.

calculations. The corresponding values obtained directly from the theoretical calculations, at the MP2(FULL)/6-31G(d) level, are 685.3 and 505.7  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. Similar estimations of the strain energy of the dicar-

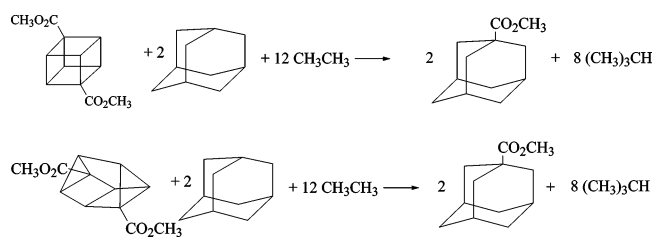
(12) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *J. Chem. Phys.* **1997**, *106*, 6764.

(13) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(14) Wang, H.; Law, C. K. *J. Phys. Chem. B* **1997**, *101*, 3400.

(15) Rogers, D. W. *J. Mol. Struct.* **2000**, *556*, 207. In his paper, the value calculated, 146  $\text{kcal}\cdot\text{mol}^{-1}$  (Table 3), was incorrectly transcribed to section 4.2 as 148.7  $\text{kcal}\cdot\text{mol}^{-1}$  (personal communication with Professor Donald W. Rogers).

(16) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Ber.* **1988**, *121*, 369.



**FIGURE 6.** Isodesmic reaction for the calculation of the strain enthalpy of dimethyl 1,4-cubanedicarboxylate and dimethyl 2,6-cuneanedicarboxylate.

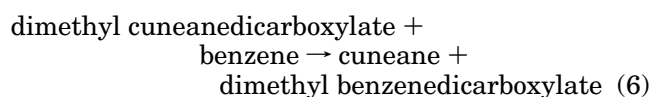
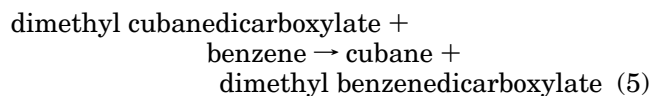
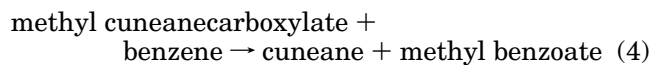
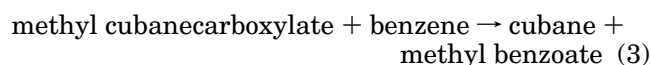
bomethoxy derivatives, Figure 6, results in strain enthalpies of  $674.2 \pm 9.0$  and  $483.4 \pm 8.8$   $\text{kJ}\cdot\text{mol}^{-1}$  for dimethyl 1,4-cubanedicarboxylate and dimethyl 2,6-cuneanedicarboxylate, respectively. The corresponding values obtained directly from the theoretical calculations, at the MP2(FULL)/6-31G(d) level, are 678.5 and 484.7  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively.

Kybett et al.<sup>4</sup> report a strain energy of 657  $\text{kJ}\cdot\text{mol}^{-1}$  for cubane. Their difficulty in obtaining complete combustion has already been noted, and the sublimation enthalpy reported for cubane has also been shown to be in serious error.<sup>5,6</sup> Kirklín et al.<sup>7</sup> using the sublimation enthalpy data of cubane were fortuitously able to estimate the sublimation enthalpy of dimethyl cubanedicarboxylate as 118.9  $\text{kJ}\cdot\text{mol}^{-1}$ ; this number is within the experimental uncertainty of the value obtained in this study. Their enthalpy of formation,  $\Delta_f H^\circ_{\text{m}}(\text{g}, 298.15 \text{ K})$ , of cubane, 665.3  $\text{kJ}\cdot\text{mol}^{-1}$ , was derived from data on the dicarbomethoxy derivative (Table 7, entry 1) using cyclobutane and bicyclobutane and their corresponding carbomethoxy derivatives as reference materials in homodesmic reactions similar to those shown in Figure 6. A strain enthalpy of 674.7  $\text{kJ}\cdot\text{mol}^{-1}$  was calculated using the enthalpy of formation of gaseous cubane and a strain free group increment for a tertiary  $\text{sp}^3$  carbon,  $(\text{C}(\text{C})_3(\text{H})) = -1.17$   $\text{kJ}\cdot\text{mol}^{-1}$ .<sup>7</sup> Despite obvious differences in the numerical values used, the strain energies calculated are identical to the results of this work.

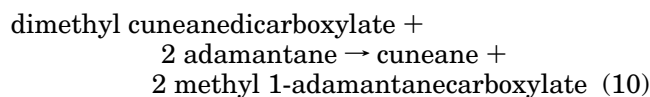
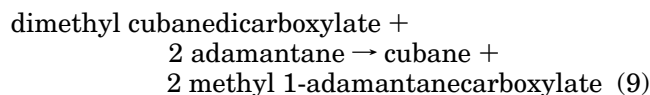
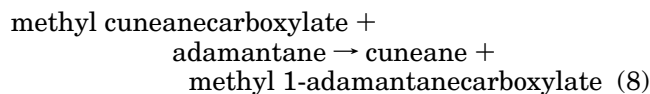
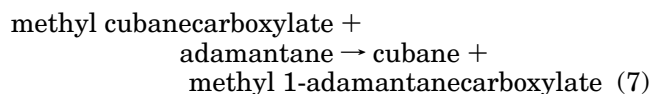
A decrease in strain energy is often observed in going from the parent compound to a substituted derivative. Using similar homodesmic and isodesmic reactions for methyl 1-bicyclobutanecarboxylate and bicyclobutane (Figures 4 and 5, Table 10), Kirklín et al.<sup>7</sup> calculated a difference in strain enthalpy of 38.4  $\text{kJ}\cdot\text{mol}^{-1}$  per carbomethoxy substituent. In this work, the total decrease in strain for cubane and cuneane going to the corresponding 1,4- and 2,6-dicarbomethoxy derivatives is calculated as 6.8 and 21.0  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. This is considerably less than previous estimates.<sup>7</sup>

Theoretical values of the enthalpies of formation for all the methyl and dimethyl cubane- and cuneanecarboxylates studied in this work can be obtained using two sets of isodesmic reactions with benzene/methyl benzenecarboxylates (series I reactions, 3–6) or adamantane/methyl 1-adamantanecarboxylate (series II reactions, 7–10) as references.

Series I:



Series II:



Depending of the values taken for the enthalpies of formation of cubane and cuneane, different values of the enthalpies of formation for all the methyl and dimethyl cubane- and cuneanecarboxylates are obtained. These values are collected in Table 11. As can be observed from the table, the calculated values for dimethyl 1,4-cubanedicarboxylate and dimethyl 2,6-cuneanedicarboxylate are in very good agreement with those values experimentally determined in this work.

The rearrangement of cubanes to the more stable cuneanes confirmed by the thermochemical measurements is also consistent with theory. An isomerization enthalpy calculated by theory at the MP2(FULL)/6-31G(d) level as  $-179.6$   $\text{kJ}\cdot\text{mol}^{-1}$  compares to a value of  $-161.5$   $\text{kJ}\cdot\text{mol}^{-1}$  obtained from Gaussian-n calculations. For the isomerization of dimethyl 1,4-cubanedicarboxylate to dimethyl 2,6-cuneanedicarboxylate, a theoretical isomerization enthalpy of  $-193.9$   $\text{kJ}\cdot\text{mol}^{-1}$  can be compared to the experimental value of  $-190.8 \pm 9.2$   $\text{kJ}\cdot\text{mol}^{-1}$ .

Are these enthalpy of formation and isomerization values plausible? Although cubane is unequivocally a pentacyclic compound, it is still appealing to describe it as composed of six rings or faces, namely six cyclobutanes. Likewise, cuneane is describable as six ring or faces but in this case, two apiece of cyclopropane, cyclobutane, and cyclopentane. Accordingly, the isomerization of cubane to cuneane corresponds to the transformation of four cyclobutanes into two cyclopropanes and two cyclopentanes. Because cubane and cuneane are composed of the same number and types of groups ( $\text{C}(\text{C})_3(\text{H})$ , tertiary  $\text{sp}^3$ ), the isomerization enthalpy corresponds directly to the change in strain energy of the two polycycles. Because cyclopropane, cyclobutane and cyclopentane all have the same groups ( $\text{C}(\text{C})_2(\text{H})_2$ , secondary

**TABLE 11.** Calculated Relative and Absolute Enthalpies of Formation for All the Cubanes and Cuneanes Studied in This Work (Enthalpies in kJ·mol<sup>-1</sup>)

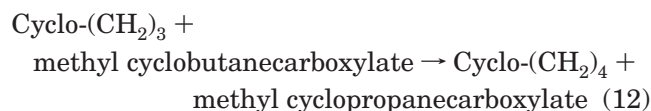
|                                   | $\Delta\Delta_f H_m^\circ(g)_{\text{calcd}}^a$ | $\Delta_f H_m^\circ(g)_{\text{calc}}$ from series I reactions |          | $\Delta_f H_m^\circ(g)_{\text{calc}}$ from series II reactions |          |
|-----------------------------------|--|---|----------|--|----------|
|                                   |  | <i>b</i>  | <i>c</i> | <i>b</i>   | <i>c</i> |
| cubane                            | 179.6  | 613.0   | 602.7    | 613.0  | 602.7    |
| cuneane                           | 0.0  | 436.4   | 441.2    | 436.4  | 441.2    |
| methyl cubanecarboxylate          | 187.0  | 250.9   | 240.6    | 248.0  | 237.7    |
| methyl 1-cuneanecarboxylate       | 11.5   | 78.4  | 83.2     | 75.6   | 80.4     |
| methyl 2-cuneanecarboxylate       | 0.0  | 66.9  | 71.7     | 64.1   | 68.9     |
| methyl 3-cuneanecarboxylate       | 2.8  | 69.7  | 74.5     | 66.9   | 71.7     |
| dimethyl 1,2-cubanedicarboxylate  | 191.4  | -102.5  | -112.8   | -117.9   | -128.2   |
| dimethyl 1,3-cubanedicarboxylate  | 195.6  | -104.9  | -115.2   | -113.7   | -124.0   |
| dimethyl 1,4-cubanedicarboxylate  | 193.9  | -103.7  | -114.0   | -115.4   | -125.7   |
| dimethyl 1,2-cuneanedicarboxylate | 10.0   | -280.8  | -276.0   | -296.2   | -291.4   |
| dimethyl 1,3-cuneanedicarboxylate | 16.4   | -281.1  | -276.3   | -289.9   | -285.1   |
| dimethyl 1,4-cuneanedicarboxylate | 10.7   | -286.8  | -282.0   | -295.6   | -290.8   |
| dimethyl 1,5-cuneanedicarboxylate | 20.6   | -270.3  | -265.5   | -285.7   | -280.9   |
| dimethyl 2,3-cuneanedicarboxylate | 15.2   | -275.6  | -270.8   | -291.1   | -286.3   |
| dimethyl 2,4-cuneanedicarboxylate | 8.3  | -282.6  | -277.8   | -298.0   | -293.2   |
| dimethyl 2,6-cuneanedicarboxylate | 0.0  | -294.5  | -289.7   | -306.3   | -301.5   |
| dimethyl 2,7-cuneanedicarboxylate | 2.8  | -294.7  | -289.9   | -303.4   | -298.6   |
| dimethyl 2,8-cuneanedicarboxylate | 0.0  | -297.5  | -292.7   | -306.2   | -301.4   |
| dimethyl 3,7-cuneanedicarboxylate | 29.5   | -261.4  | -256.6   | -276.8   | -272.0   |

<sup>a</sup> MP2(FULL)/6-31G(d) level. <sup>b</sup> Values calculated using for cubane and cuneane their enthalpies of formation obtained using reactions in Figure 4. <sup>c</sup> Values calculated using for cubane and cuneane using enthalpies of formation obtained from theoretical calculations at several Gn levels. See text.

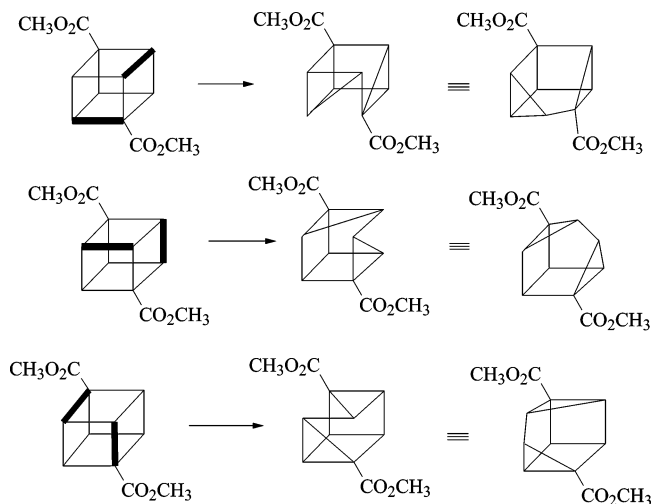
sp<sup>3</sup>) we may equate the enthalpy of the reaction



with the desired strain energy change. From the enthalpies of formation of the three cycloalkanes taken from ref 17, we find an exothermicity or strain lessening of  $-157.0 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$ , a value encouragingly close to the above exothermicity of the cubane to cuneane rearrangement. Consider now the rearrangement of the cubane and cuneane dicarboxylate esters. This process differs from that of the parent hydrocarbons by transforming two esters on four-membered rings into two on three-membered rings. Since the two substituents that compose dimethyl cubane and cuneane dicarboxylate are identical, we may estimate the difference of the rearrangement enthalpy of the esters and hydrocarbons to be twice the exothermicity of the reaction



Accepting the enthalpies of formation of the parent cycloalkanes from ref 17 and that of the methyl carboxylate esters from ref 18, we find a reaction exothermicity of  $-7.7 \pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$ . The strain energy difference between dimethyl 1,4-cubanedicarboxylate and dimethyl 2,6-cuneanedicarboxylate is expected to be  $15.4 \text{ kJ}\cdot\text{mol}^{-1}$  higher than that of the difference between cubane and cuneane. We had earlier derived (in this paper) theoretical values of 6.8 and  $21.0 \text{ kJ}\cdot\text{mol}^{-1}$  for the total decrease in strain for cubane and cuneane going to the corresponding 1,4- and 2,6 dicarbomethoxy derivatives, re-



**FIGURE 7.** Three distinct least motion pathways for the rearrangement of dimethyl 1,4-cubanedicarboxylate involving inversion of configuration of both migrating CHCR (R = H, R =  $-\text{CO}_2\text{CH}_3$ ) centers.

spectively. This difference is  $14.2 \text{ kJ}\cdot\text{mol}^{-1}$ , corroborating theory with our thermochemical experiments and models.

How to consider the processes by which the cubanes isomerize into the corresponding cuneanes? Figure 7 illustrates three formal pathways by which dimethyl 1,4-cubanedicarboxylate can rearrange to a mixture of dimethyl 1,3- and dimethyl 2,6-cuneanedicarboxylates.<sup>8</sup> The migrating bonds in Figure 7 are shown in bold and the rearrangement requires inversion of configuration of both migrating CHCR (R = H, or  $-\text{CO}_2\text{CH}_3$ ) centers. The role of the metal ion is ignored; therefore these pathways should not be considered in a mechanistic context. That other isomeric dicarbomethoxy isomers are not formed even though the theoretical calculations (Table 11) predict some of them to be as stable as the 1,3 and 2,6 isomers, suggests that the rearrangement is not more extensive than illustrated in this figure. The theoretical

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calculations predict the 1,3-dicarbomethoxy isomer to be approximately  $16 \text{ kJ}\cdot\text{mol}^{-1}$  less stable than the corresponding 2,6- isomer. Only the top pathway produces dimethyl 1,3-cuneanedicarboxylate. On the basis of product analysis (40/900 mg), about 5% of the reaction proceeds through this formal pathway. The formation of the 1,3-isomer suggests that the rearrangement is not governed solely by thermodynamics or by the principle of least motion.

## Experimental Section

**Dimethyl 2,6-Cuneanedicarboxylate.** A mixture of dimethyl 1,4-cubanededicarboxylate [1.0 g,  $^1\text{H NMR}(\text{CDCl}_3)$ ;  $\delta$  4.25 (s, 6H), 3.72 (s, 6H, -OMe) ppm] and silver perbromate (1.0 g) in 50 mL of dry toluene was heated at  $100^\circ\text{C}$  for 12 h. The progress of the reaction was followed by  $^1\text{H NMR}$ . The mixture was concentrated under vacuum and chromatographed on silica gel using methylene chloride/hexane (1/1) as eluent. Approximately 860 mg of pure dimethyl 2,6-cuneanedicarboxylate was obtained (recrystallized from methylene chloride/hexane) [ $^1\text{H NMR}(\text{CDCl}_3)$   $\delta$  3.62 (s, 6H, -OMe), 3.10 (m, 6H) ppm; mp  $118\text{--}119^\circ\text{C}$ , lit.<sup>19</sup> mp  $116\text{--}117^\circ\text{C}$ ] along with dimethyl 1,3-cuneanedicarboxylate (~40 mg:  $^1\text{H NMR}(\text{CDCl}_3)$   $\delta$  3.76 (s, 3H, -OMe), 3.73 (s, 3H, -OMe), 3.23 (m, 4H), 2.56 (m, 2H) ppm; mp  $124\text{--}125^\circ\text{C}$ , lit.<sup>19</sup> mp  $122\text{--}123^\circ\text{C}$ ). The 2,6-cuneane diester was analyzed both by gas chromatography and by DSC to determine purity. Both analyses did not indicate the presence of any other isomer.

**2,6-Cuneanedicarboxylic Acid.** Dimethyl 2,6-cuneanedicarboxylate (32 mg, 0.15 mmol) was stirred in 400  $\mu\text{L}$  of 1 N NaOH and a few microliters of ethanol overnight at room temperature. The next day, the solution was acidified with 6 N HCl and extracted several times with 10 mL portions of ether. The ether layers were combined and allowed to evaporate. A white crystalline residue remained (20 mg) which was dissolved in hot ethanol and allowed to stand. The crystals isolated, mp  $>250^\circ\text{C}$ ;  $\nu_{\text{max}}$  broad absorption from 3300 to 2500, 1659.5, 1432, 886, 734.4  $\text{cm}^{-1}$  (IR spectrum obtained using an ATR accessory), were analyzed by X-ray crystallography.

**X-ray Crystal Structure: Dimethyl 2,6-Cuneanedicarboxylate.** The crystal structure of dimethyl 2,6-cuneanedicarboxylate was disordered. Attempts at solving the crystal structure provided unrealistic bond distances due to disorder. The structure was solved both in  $C2/c$  and in a lower symmetry space groups  $Cc$  to see if a better disorder model can be obtained. The  $Cc$  structure is presented as Figure 1 since this model identifies the relative position of the two carbomethoxy groups and eliminates the possibility of a rearrangement occurring during base-catalyzed hydrolysis of the diester. Additional structural information can be found in the Supporting Information.

**2,6-Cuneanedicarboxylic Acid.** Colorless crystals were grown by slow evaporation from an ethanol solution at ambient temperature. A crystal with dimensions  $0.10 \times 0.07 \times 0.04 \text{ mm}^3$  was mounted on a glass fiber in a random orientation. Preliminary examination and data collection was performed using a single-crystal X-ray diffractometer using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) equipped with a sealed tube X-ray source at  $T = 150 \text{ K}$ . Preliminary unit cell constants were determined with a set of 45 narrow frames ( $0.4^\circ$  in  $\omega$ ) scans. The data set collected consists of 3636 frames with a frame width of  $0.3^\circ$  in  $\omega$  and counting time of 15 s/frame at a crystal to detector distance of 4.900 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages were used for data collection and

data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids of 4034 reflections ( $\theta < 25.97^\circ$ ). Collected data were corrected for systematic errors using SADABS<sup>20</sup> based on the Laue symmetry using equivalent reflections. The integration process yielded 11,712 reflections of which 1592 were independent reflections.

Crystal data and intensity data collection parameters are provided in the Supporting Information. Structure solution and refinement were carried out using the SHELXTL software package.<sup>21</sup> The structure was solved by direct methods and refined successfully in the space group  $C2/c$ . Full matrix least-squares refinement was carried out by minimizing  $\Sigma w(F_o^2 - F_c^2)^2$ . The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding model (AFIX m3). The final residual values were  $R(F) = 4.5\%$  for 1176 observed reflections [ $I > 2\sigma(I)$ ] and  $wR(F^2) = 11.6\%$ ;  $s = 1.0$  for all data. A projection view of the molecule with non-hydrogen atoms represented by 25% probability ellipsoids, and showing the atom labeling is presented in Figure 2. Additional structural information can be found in the Supporting Information.

Complete listings of the atomic coordinates for the non-hydrogen atoms and the geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are deposited with the Cambridge Crystallographic Data Center (CCDC 272994, dimethyl 2,6-cuneanedicarboxylate; CCDC 272995, 2,6-cuneanedicarboxylic acid).

**Combustion Experiments.** The energy of combustion of dimethyl 1,4-cubanededicarboxylate and dimethyl 2,6-cuneanedicarboxylate were determined in Madrid in an isoperibolic static micro-bomb calorimeter developed recently. A detailed description of the calorimetric system can be found in earlier papers.<sup>22,23</sup> The calorimetric temperatures were measured to within  $\pm 1 \times 10^{-4} \text{ K}$  by means of a  $100 \Omega$  platinum resistance thermometer, using a calibrated resistance bridge interfaced to a microcomputer programmed to calculate the adiabatic temperature change. The energy of reaction was always referenced to the final temperature of  $T = 298.15 \text{ K}$ . The energy equivalent of the calorimeter  $\epsilon(\text{calor})$  was determined from the combustion of benzoic acid, NIST standard reference sample 39j. From nine calibration experiments,  $\epsilon(\text{calor}) = (2102.54 \pm 0.56) \text{ J}\cdot\text{K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean. To obtain only  $\text{CO}_2$  as the oxidized carbon product of the combustion reactions of both compounds (i.e., no CO), several methods and auxiliary substances were used. The best results were obtained when benzoic acid NIST 39j was used as an aid in the combustion reaction. The calorimetric standard, SRM 39j, has a certified specific energy of combustion of  $-(26434 \pm 3) \text{ J g}^{-1}$ . This reduces to  $26414.0 \text{ J g}^{-1}$  at  $298.15 \text{ K}$  and standard-state conditions. Three benzoic acid pellets and two pellets of the compound studied were alternatively placed and weighed into the platinum crucible. The method followed was the same previously described by Kirklin, Churney and Domalski.<sup>7</sup> To verify complete combustion at the end of each experiment, the total quantity of gas in the bomb was slowly released ( $0.2 \text{ cm}^3\cdot\text{s}^{-1}$ ) through Dräger tubes. No traces of CO were detected (sensitivity levels were approximately  $1 \times 10^{-6}$  mass fraction). No traces of carbon residue were observed in any of the runs. The massic energies of combustion of both compounds were determined by burning the samples in oxygen, with  $0.05 \text{ cm}^3$  of water added to the bomb. The combustion bomb was flushed and filled with oxygen, previously freed from combustible impurities, at an initial pressure of 3.04 MPa. The

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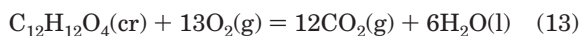
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empirical formula and massic energy of combustion of the cotton-thread fuse used in the experiments with this microbomb,  $C_{1.000}H_{1.740}O_{0.871}$  and  $-(17410 \pm 37) \text{ J}\cdot\text{g}^{-1}$ , respectively, were determined in the Madrid laboratory. All samples were weighed on an ultra-micro balance and corrections of apparent mass to mass were made.

For the correction of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and corrections to the standard state, we have used the values of density  $\rho$ , massic heat capacity  $c_p$ , and  $(\delta V/\delta T)_p$  and  $(\delta V/\delta T)_p$  (see Table S9, Supporting Information). The density and heat capacity at  $T = 298.15 \text{ K}$  for dimethyl 2,6-cuneanedicarboxylate were determined in this work by X-ray and DSC, respectively.

Standard-state corrections were made according to Hubbard et al.<sup>24</sup> The atomic weights of the elements used are those recommended by IUPAC in 1999.<sup>25</sup> The results of the combustion experiments are given in Table 2 (and Table S10, Supporting Information). The symbols in these tables have the same meaning as those in ref 26 and the experimental values have been derived, similarly. The massic energy of combustion of the compound is referenced to the final temperature of the experiments,  $T = 298.15 \text{ K}$ . The uncertainties in the standard molar energy and enthalpy of combustion are twice the final overall standard deviation of the mean and were estimated as outlined by Olofsson.<sup>27</sup> The standard molar energy and enthalpy of combustion reference to the following combustion reaction:



The standard molar energy of combustion and standard molar enthalpies of combustion and formation of dimethyl 1,4-cubanedecarboxylate and dimethyl 2,6-cuneanedicarboxylate in solid phase were determined from the results reported in Table S10, Supporting Information. The values for the standard molar enthalpies of formation of  $H_2O(\text{l})$  and  $CO_2(\text{g})$  at  $T = 298.15 \text{ K}$  are respectively:  $-(285.830 \pm 0.042)$  and  $-(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$ ; values were taken from CODATA.<sup>28</sup>

**Thermochemical Analysis: Fusion Enthalpies.** A differential scanning calorimeter equipped with an intracooler unit was used in Madrid and a standard DSC was used in St. Louis to determine the purities, melting temperatures, heat capacities and enthalpies of fusion of dimethyl 1,4-cubanedecarboxylate and dimethyl 2,6-cuneanedicarboxylate. The instrument's temperature scale was calibrated by measuring the melting temperature of the recommended high-purity reference materials: benzoic acid,<sup>29</sup> tin, and indium.<sup>30,31</sup> The power scale was calibrated with high-purity indium (mass fraction:  $>0.99999$ ) as reference material.<sup>31</sup> Thermograms of samples hermetically sealed in aluminum pans were recorded in a nitrogen atmosphere. All the pans were weighed before and after the experiments in order to confirm that no product had volatilized. The samples were weighed on microbalances with a sensitivity of  $1 \times 10^{-6} \text{ g}$  (Madrid) and  $1 \times 10^{-5} \text{ g}$  (St. Louis), respectively. For determination of the purities, temperatures and enthalpies of transitions, a heating rate of  $0.04 \text{ K s}^{-1}$  was

used. For each compound, a fresh sample was used for each run. After calibration, several runs with high-purity benzoic acid and indium were performed under the same conditions as the experimental measurements; results for accuracy in temperatures and enthalpy determinations were 0.2 and 1.6%, respectively. Details are given in ref 32.

**Vaporization Enthalpies.** The vaporization enthalpies of dimethyl 1,4-cubane and 2,6-cuneanedicarboxylates were measured by correlation-gas chromatography. All gas chromatographic standards were commercial samples and were used without any further purification. The vaporization enthalpies of the standards were obtained from the literature. Most of the values of the standards reported in the literature have been measured under different experimental conditions. The available literature values are summarized in the Supporting Information along with a summary of how each value was chosen. Entries for each standard were adjusted from the mean temperature of measurement to  $T = 298.15 \text{ K}$  using eq 14 where  $C_{p1}$  refers to the molar heat capacity of each liquid standard which was estimated and  $T_m$  refers to the mean temperature of measurement.<sup>33</sup>

$$\Delta_1^{\text{g}}H_m(298.15 \text{ K})/\text{J mol}^{-1} = \Delta_1^{\text{g}}H_m(T_m) + (10.58 + 0.26 C_{p1})(T_m - 298.15) \quad (14)$$

Each standard was analyzed by gas chromatography and found to be at least 99 mol % pure. Correlation gas chromatography experiments were performed on an instrument equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of approximately 100/1. Retention times were recorded to three significant figures following the decimal point; they are provided in the Supporting Information. The instrument was run isothermally using either a 15 (mixtures 1, 3, and 4) or 30 m (mixture 4) phenylmethyl silicone capillary column. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent,  $\text{CH}_2\text{Cl}_2$ , which increased with increasing temperature, was used to determine the dead volume of the column. Adjusted retention times,  $t_a$ , were calculated by subtracting the measured retention time of the solvent from the retention time of each analyte as a function of temperature, usually over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently. Temperature was maintained constant by the gas chromatograph to  $\pm 0.1 \text{ K}$ .

A plot of  $\ln(1/t_a)$  against  $1/T(\text{K})$  resulted in straight lines characterized by the parameters available in the Supporting Information. Correlation of the enthalpy of transfer from the column to the gas phase at the mean temperature of measurement,  $\Delta_{\text{sln}}^{\text{v}}H_m(T_m)$ , against the vaporization enthalpies of the standards,  $\Delta_1^{\text{g}}H_m(298.15 \text{ K})$ , resulted in the correlation equations (15–18). These equations were used to calculate the vaporization enthalpy of the cubane and cuneane diesters.

$$\Delta_1^{\text{g}}H_m(298 \text{ K}) = (1.3562 \pm 0.078) \Delta_{\text{sln}}^{\text{v}}H_m(457 \text{ K}) + (11.68 \pm 1.0)r^2 = 0.9967 \quad (15)$$

$$\Delta_1^{\text{g}}H_m(298 \text{ K}) = (1.3406 \pm 0.090) \Delta_{\text{sln}}^{\text{v}}H_m(457 \text{ K}) + (13.48 \pm 1.2)r^2 = 0.9954 \quad (16)$$

$$\Delta_1^{\text{g}}H_m(298 \text{ K}) = (1.379 \pm 0.084) \Delta_{\text{sln}}^{\text{v}}H_m(412 \text{ K}) + (6.79 \pm 0.93)r^2 = 0.9963 \quad (17)$$

$$\Delta_1^{\text{g}}H_m(298 \text{ K}) = (1.395 \pm 0.088) \Delta_{\text{sln}}^{\text{v}}H_m(458 \text{ K}) + (7.794 \pm 1.10)r^2 = 0.9960 \quad (18)$$

**Computational Details.** Standard ab initio molecular orbital calculations<sup>13</sup> were performed with the Gaussian03

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series of programs.<sup>34</sup> For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level. The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to minima of the potential energy surface and to evaluate the corresponding zero-point vibrational energies, ZPE, and the thermal corrections at 298 K. ZPE values were scaled by the empirical factor 0.9135.<sup>35</sup> All the minima found at the HF/6-31G(d) level were again fully re-optimized at the MP2(FULL)/6-31G(d) level. Electronic energies, zero-point vibrational energies, and thermal correction to enthalpies for all the cubanes and cuneanes studied in this work, and other compounds used as references, are collected in Table S13, Supporting Information. In the case of parent compounds, cubane and cuneane, and because of their smaller size, we have carried out calculations at several Gaussian-n levels: G2(MP2),<sup>36</sup> G2,<sup>37</sup> G3/B3LYP,<sup>38</sup> and G3,<sup>39</sup> the values being collected in Table 9.

### Summary

Through a combined calorimetric, crystallographic, and computational effort, the first definitive determinations

of the structure and energetics of a pair of cubane and cuneane isomers have been made. It is found that dimethyl cuneane-2,6-dicarboxylate is thermodynamically some 190 kJ·mol<sup>-1</sup> more stable than its synthetic precursor, the more symmetric, dimethyl cubane-1,4-dicarboxylate.

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**Supporting Information Available:** Experimental details as well as X-ray crystallographic data (CIF), retention times, details on the theoretical calculations, and references to literature data used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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