

## An Electron Diffraction Investigation of the Molecular Structure of *anti*- and *syn*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane in the Vapour Phase

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Electron-diffraction studies of gaseous *anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane have been carried out. The parameter values were obtained by least squares refinement on the intensity data assuming harmonic vibrations. The molecules have  $C_2$ -symmetry. In each molecule the deviation from planarity of the carbon skeleton of each individual four-membered ring is the same. The values obtained for the molecular parameters are: in *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane  $(C-C)_{av}$  1.557 (0.002) Å,  $\angle C_1C_2C_3$  111.9 (0.5)° and  $\beta$  (defined as in cyclobutane) 8.0 (2.5)°, in *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane  $(C-C)_{av}$  1.566 (0.003) Å,  $\angle C_1C_2C_3$  119.0 (0.3)° and  $\beta$  9.0 (2.6)°.

*Anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane were prepared by Avram *et al.*<sup>1</sup> in 1960. The structure investigation of these compounds was started in order to study the conformations and bond lengths of adjoining four-membered rings. It is established by several investigators<sup>2-4</sup> that the carbon skeleton of cyclobutane itself deviates from planarity. The investigations by Bastiansen and Skancke<sup>3</sup> using electron diffraction, and Meibom and Snyder<sup>4</sup> using proton nuclear magnetic resonance, both give a dihedral angle of 35°. The angle ( $\beta$ ) is defined as the angle between the planes through the atoms  $C_4C_1C_2$  and  $C_2C_3C_4$ . Bastiansen and de Meijere<sup>5</sup> reported  $\beta$  to be 33° in dicyclobutyl. The C—C bond length was reported to be 1.548 Å in both compounds.

Furasaki,<sup>6</sup> using X-ray crystallographic technique, has studied perchloro-(3,4,7,8-tetramethylene-tricyclo(4.2.0.0<sup>2,5</sup>)octane),  $C_{12}Cl_{12}$ , and reports that the symmetry requires a planar middle ring. The outer rings were determined to be almost planar.

### EXPERIMENTAL

The samples of *anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane were obtained from Prof. C. D. Nenitzescu, Bucuresti. The diffraction diagrams were taken at the Oslo apparatus<sup>7</sup> by Cand. real. A. Almenningen. A rotating sector with an angular opening approximately proportional to  $s^3$  was used. The same two nozzle-to-plate distances were used for both

compounds, namely 480,41 mm and 193,41 mm. The temperature at the nozzle was about 40°C and 65°C during exposures at the long and short distances, respectively. The electron wave length was 0.06459 Å at all recordings.

The experimental data for the two compounds were treated in the same manner. Four plates at each distance were selected for analysis. The photometer traces of each plate were read of at intervals  $\Delta s = 0.25$  Å, and the data were treated according to the procedure which has been described previously.<sup>8</sup> Experimental backgrounds were subtracted from the total scattered intensities and the overlap regions of the obtained molecular intensity functions for each nozzle-to-plate distance were averaged. The experimental backgrounds were later adjusted by comparing experimental and theoretical intensity curves. The experimental intensities were multiplied by  $s/(Z_C - F_C)^2$ . The scattering factors have been calculated by Hanson *et al.*<sup>9</sup>

The final experimental molecular intensity function covered the  $s$ -range 1.25–44.75 Å<sup>-1</sup> and 1.50–45.00 Å<sup>-1</sup> for *anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane, respectively.

A zeroth-order model for the molecular structure was determined from the radial distribution (RD) function obtained by Fourier inversion of the modified experimental intensity curve.<sup>10</sup> The molecular parameters were refined on the intensity curve by the least squares method.<sup>11–13</sup>

Information about the closely spaced bond distances was obtained from the autocorrelation power spectrum (APS)<sup>14,15</sup> The APS-function is calculated by a cosine Fourier transform of the short interval autocorrelation function  $A(\tau)$ :

$$\text{APS} = 2 \int_0^{\tau_{\max}} A(\tau) \exp[-\alpha\tau] \cos(\tau r) \, d\tau$$

where  $\alpha$  is a constant,  $\tau$  is limited by the  $s$ -range of the experimental data.  $A(\tau)$  is defined as the convolution of the intensity curve:

$$A(\tau) = 2\alpha \int_{s_{\min}}^{s_{\max}} I(s) I(s-\tau) \exp[-2\alpha(s_{\max}-s)] \, ds$$

The numerical calculations were performed on IBM 1620 and Univac 1107 with computer programs written by members of the Oslo electron-diffraction group.<sup>16</sup>

## STRUCTURE ANALYSIS

The experimental molecular intensities for *anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane are shown in Figs. 1 and 2, respectively, where they can be compared to the corresponding theoretical intensities which were calculated using the final parameters in Table 1. The adopted numbering of the atoms in the molecules is given in Fig. 3.

In Figs. 4 and 5 the experimental radial distribution functions are given. The first four peaks on the RD-curves represent analogous distances in the molecules, namely the C–H, C–C, C<sub>1</sub>···C<sub>5</sub>, C<sub>1</sub>···C<sub>3</sub> distances, respectively. The position of the fourth peak is different by about 0.1 Å owing to a larger C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> bond angle in *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane than in *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane. The peak complexes at about 3.0 Å represent the C<sub>1</sub>···C<sub>4</sub> and C<sub>3</sub>···C<sub>6</sub> distances. In *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane the C<sub>3</sub>···C<sub>8</sub> and C<sub>4</sub>···C<sub>8</sub> distances also contribute to this peak complex while the corresponding distances are found at about 4.0 Å and 4.2 Å for *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane.

For both molecules the correspondence is very satisfactory between experimental and theoretical RD-curves for the respective models, where the deviations from planarity of each four-membered ring are the same (Figs. 4

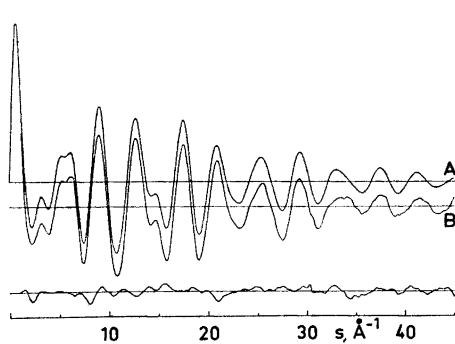


Fig. 1. *anti*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Theoretical (A) and experimental (B) molecular intensity functions.

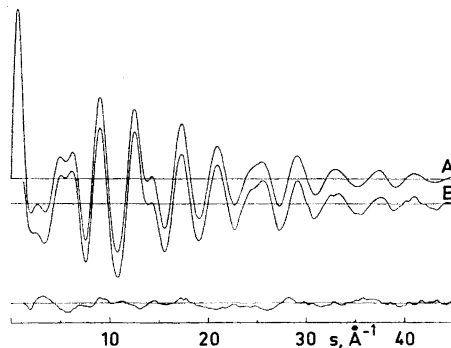


Fig. 2. *syn*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Theoretical (A) and experimental (B) molecular intensity functions.

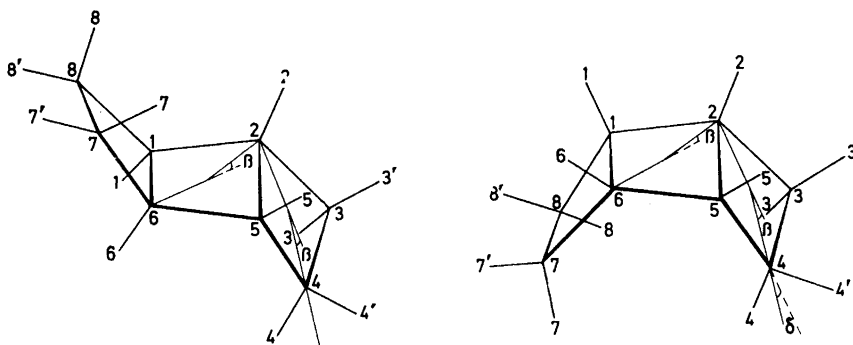


Fig. 3. Numbering of the atoms in *anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane.

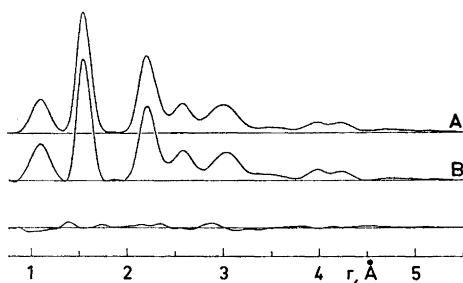


Fig. 4. *anti*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Theoretical (A) and experimental (B) radial distribution functions,  $k=0.0015 \text{ \AA}^2$ .

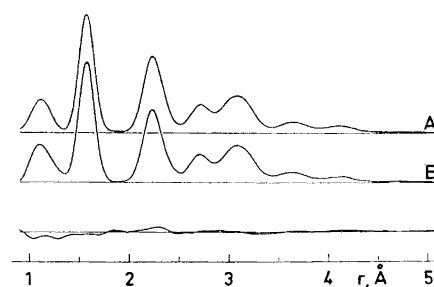


Fig. 5. *syn*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Theoretical (A) and experimental (B) radial distribution functions,  $k=0.0015 \text{ \AA}^2$ .

and 5). The fit is certainly much better than for any models with a planar middle ring which were tested in the earlier stage of the analysis. Therefore only models with equal puckering of all rings, characterized by the independent parameters  $(C-C)_{av}$ ,  $(C-H)_{av}$ ,  $C_1 \cdots C_3$ ,  $C_1 \cdots C_5$ ,  $C_3 \cdots H_3$  (or  $C_5 \cdots H_3'$ )\* and  $\angle C_1C_2H_2$ , were considered for least squares analysis. We assumed the planes through the HCH atoms to be perpendicular on their respective CCC planes bisecting the angles CCC. Also the reciprocal condition that the plane CCC bisects the angle HCH was assumed at the initial stage of the analysis. This condition leads to no additional discrepancies between experimental and theoretical data for *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane, while a better agreement is obtained for *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane by assuming the angle  $\delta$  between the plane CCC and a plane bisecting the plane HCH to be about 5°. (Fig. 3).

Except for the angles  $C_1C_2H_2$  which were assumed, all the independent structure parameters and the  $u$ -values for the bond distances and the non-bonded carbon-carbon distances were refined. The  $u$ -values for the non-bonded carbon-hydrogen distances were assumed from experience with analogous hydrocarbons. The values gave a good agreement between experimental and theoretical RD curves. The contributions from the non-bonded hydrogen-hydrogen distances were treated as constant and adjusted in the final stage of the refinement.

Table 1 lists the final parameters determined by least squares refinement. In each molecule the  $(C-C)_{av}$  distance is the average of four different bond distances. The intensity contribution from closely spaced bond distances is a damped sine curve corresponding to the average distance, times a cosine factor, which has almost the same effect as an additional damping.<sup>10</sup> Thus a good correspondence between experimental and theoretical intensity curves can be obtained both for the average distance and for the separate distances if the  $u$ -values for these distances are adjusted properly. It follows that this also applies to the corresponding RD curves.

However, additional information about the separation of closely spaced bond distances may be obtained by comparing experimental and theoretical APS functions. The position of a peak on the APS curve with contributions from closely spaced bond distances is shifted compared to the peak calculated for the average distance. The shift is ascribed to correlation between closely located peaks.<sup>14</sup> Therefore, if good correspondence between experimental and corresponding theoretical APS functions calculated using the average bond distance, is obtained, the separation must be small. We believe this to be the case in the tricyclo(4.2.0.0<sup>2,5</sup>)octanes, since such correspondence is obtained, Figs. 6 and 7. It is in fact so good for one of the molecules, *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane, that we consider the bond distances to be very close to the average value, determined by the least squares refinement in this molecule. No change was therefore made in the condition which constrained the least squares refinements to molecular models with identical C—C bonds.

\* The angle HCH was represented by the distance  $C_3 \cdots H_3$  in *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane and the distance  $C_5 \cdots H_3'$  in *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane.

Table 1. *anti*- and *syn*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Distances ( $r$ ) and root-mean-squares amplitudes of vibration ( $u$ ) in Å. Standard deviations in the refined parameters, given in brackets, are corrected as suggested by Seip *et al.*<sup>17</sup> and for the effect of errors in the electron wave length.<sup>10</sup>

	<i>anti</i> -		<i>syn</i> -	
	$r$	$u$	$r$	$u$
(C—C) <sub>av</sub>	1.557 (0.002)	0.048 (0.001)	1.566 (0.003)	0.054 (0.001)
C <sub>1</sub> —C <sub>3</sub>	2.579 (0.007)	0.068 (0.004)	2.698 (0.007)	0.072 (0.004)
C <sub>1</sub> —C <sub>5</sub>	2.199 (0.003)	0.055 (0.002)	2.211 (0.003)	0.062 (0.002)
(C—H) <sub>av</sub>	1.103 (0.006)	0.075 (0.003)	1.111 (0.007)	0.080 (0.003)
C <sub>1</sub> —H <sub>3'</sub>	2.248	0.080	2.215	0.092
C <sub>1</sub> —H <sub>8</sub>	2.248 (0.009)	0.080 (0.005)	2.294	0.094
C <sub>5</sub> —H <sub>3'</sub>	2.931	0.110	2.862	0.094
C <sub>1</sub> —H <sub>7'</sub>	3.024	0.110	2.862 (0.017)	0.094
C <sub>1</sub> —C <sub>4</sub>	2.933	0.077	3.036	0.087 (0.019)
C <sub>2</sub> —C <sub>7</sub>	2.933	0.077	3.187	0.067
C <sub>3</sub> —C <sub>6</sub>	3.080	0.077 (0.014)	3.187	0.067 (0.012)
C <sub>5</sub> —C <sub>8</sub>	3.080	0.077	3.036	0.087 (0.019)
C <sub>3</sub> —C <sub>8</sub>	3.963	0.085	3.087	0.101 (0.020)
C <sub>3</sub> —C <sub>7</sub>	4.249	0.085 (0.016)	3.649	0.121
C <sub>4</sub> —C <sub>8</sub>	4.249	0.085	3.246	0.100
C <sub>1</sub> —H <sub>2</sub>	2.306	0.095	2.293	0.090
C <sub>5</sub> —H <sub>7</sub>	2.667	0.110	2.946	0.105
C <sub>6</sub> —H <sub>4</sub>	2.667	0.110	2.894	0.105
C <sub>1</sub> —H <sub>3</sub>	2.715	0.110	2.946	0.105
C <sub>2</sub> —H <sub>4</sub>	2.715	0.110	2.894	0.105
C <sub>3</sub> —H <sub>1</sub>	2.782	0.110	3.610	0.105
C <sub>8</sub> —H <sub>2</sub>	2.782	0.110	3.651	0.105
C <sub>4</sub> —H <sub>6</sub>	2.837	0.110	3.651	0.105
C <sub>7</sub> —H <sub>5</sub>	2.837	0.110	3.610	0.105
C <sub>1</sub> —H <sub>7</sub>	2.931	0.110	3.087	0.100
C <sub>2</sub> —H <sub>4</sub>	2.931	0.110	2.992	0.100
C <sub>6</sub> —H <sub>8</sub>	2.931	0.110	2.979	0.094
C <sub>2</sub> —H <sub>4'</sub>	3.024	0.110	2.979	0.094
C <sub>5</sub> —H <sub>3</sub>	3.024	0.110	3.087	0.100
C <sub>6</sub> —H <sub>8</sub>	3.024	0.110	2.992	0.100
C <sub>3</sub> —H <sub>5</sub>	3.025	0.110	2.994	0.094
C <sub>5</sub> —H <sub>1</sub>	3.025	0.110	3.095	0.094
C <sub>1</sub> —H <sub>5</sub>	3.105	0.110	3.095	0.094
C <sub>2</sub> —H <sub>6</sub>	3.105	0.110	2.994	0.094
C <sub>1</sub> —H <sub>4</sub>	3.155	0.120	3.359	0.119
C <sub>2</sub> —H <sub>7</sub>	3.155	0.120	3.699	0.119
C <sub>4</sub> —H <sub>1</sub>	3.295	0.120	4.093	0.127
C <sub>7</sub> —H <sub>2</sub>	3.295	0.120	4.177	0.100
C <sub>5</sub> —H <sub>7</sub>	3.480	0.120	3.359	0.119
C <sub>6</sub> —H <sub>3</sub>	3.480	0.120	3.699	0.119
C <sub>5</sub> —H <sub>7'</sub>	3.503	0.110	3.615	0.110
C <sub>6</sub> —H <sub>4'</sub>	3.503	0.110	3.583	0.110
C <sub>1</sub> —H <sub>3</sub>	3.569	0.110	3.615	0.110
C <sub>2</sub> —H <sub>8</sub>	3.569	0.110	3.583	0.110
C <sub>3</sub> —H <sub>6</sub>	3.609	0.120	4.177	0.100
C <sub>8</sub> —H <sub>5</sub>	3.609	0.120	4.093	0.127
C <sub>1</sub> —H <sub>4'</sub>	3.980	0.120	4.040	0.119
C <sub>2</sub> —H <sub>7'</sub>	3.980	0.120	4.091	0.110
C <sub>5</sub> —H <sub>8</sub>	4.060	0.120	4.040	0.119
C <sub>6</sub> —H <sub>3'</sub>	4.060	0.120	4.091	0.110
C <sub>4</sub> —H <sub>7</sub>	4.205	0.120	2.860	0.110

Table 1. Continued.

C <sub>7</sub> -H <sub>4</sub>	4.205	0.120	2.701	0.110
C <sub>5</sub> -H <sub>6</sub>	4.207	0.120	2.701	0.110
C <sub>5</sub> -H <sub>3</sub>	4.207	0.120	2.860	0.110
C <sub>5</sub> -H <sub>7</sub>	4.541	0.130	3.754	0.158
C <sub>5</sub> -H <sub>4</sub>	4.541	0.130	3.043	0.158
C <sub>4</sub> -H <sub>6</sub>	4.710	0.130	3.043	0.158
C <sub>7</sub> -H <sub>5</sub>	4.710	0.130	3.754	0.158
C <sub>4</sub> -H <sub>7</sub> '	4.785	0.120	4.174	0.110
C <sub>5</sub> -H <sub>8</sub> '	4.785	0.120	4.091	0.110
C <sub>4</sub> -H <sub>8</sub> '	5.106	0.130	4.357	0.158
C <sub>7</sub> -H <sub>8</sub> '	5.106	0.130	4.721	0.158
C <sub>5</sub> -H <sub>7</sub> '	5.207	0.130	4.721	0.158
C <sub>5</sub> -H <sub>4</sub> '	5.207	0.130	4.357	0.158

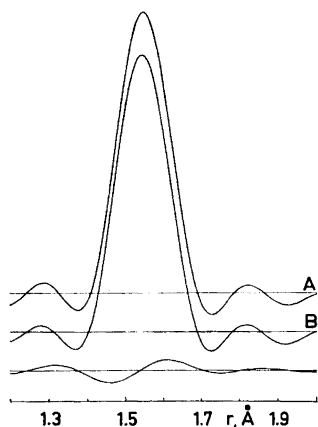


Fig. 6. *anti*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Theoretical (A) and experimental (B) autocorrelation power spectra,  $\alpha=0.03$ ,  $\tau_{\max}=30.00 \text{ \AA}^{-1}$ .

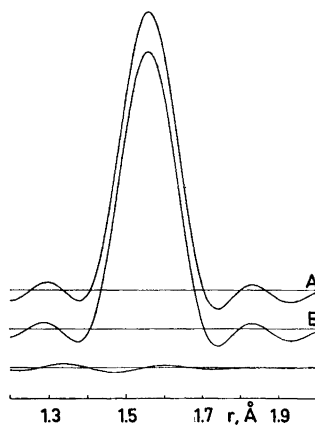


Fig. 7. *syn*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane. Theoretical (A) and experimental (B) autocorrelation power spectra,  $\alpha=0.03$ ,  $\tau_{\max}=30.00 \text{ \AA}^{-1}$ .

## DISCUSSION

*anti*- and *syn*-Tricyclo(4.2.0.0<sup>2,5</sup>)octane have  $C_2$ -symmetry. In the first compound the two-fold axis of symmetry bisects the C<sub>1</sub>-C<sub>2</sub> and C<sub>5</sub>-C<sub>6</sub> bonds, in the latter compound it is perpendicular to a plane through the middle of the bonds in the central ring. The carbon skeleton of each four-membered ring deviates from planarity and within each molecule the deviations are essentially the same. The structure parameters determined in this investigation are presented in Table 2. Fluctuations in the electron beam wave length are included in the error estimates even though the data were recorded in a short period of time to avoid changes in the experimental conditions.

The difference between the (C-C)<sub>av</sub> distances in the two molecules is determined to be more than twice the value of the standard deviation. The

Table 2. Structure parameters for *anti*- and *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane, distances given in Å and angles in degrees. Standard deviations, given in brackets, are corrected as suggested by Seip *et al.*<sup>17</sup> and for the effect of errors in the electron wave length.<sup>10</sup>

	<i>anti</i> -	<i>syn</i> -
(C—C) <sub>av</sub>	1.557 (0.002)	1.566 (0.003)
(C—H) <sub>av</sub>	1.103 (0.006)	1.111 (0.007)
∠C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	111.9 (0.5)	119.0 (0.3)
β <sup>a</sup>	8.0 (2.5)	9.0 (2.6)
∠H <sub>3</sub> C <sub>3</sub> H <sub>3</sub> '	109.0 (1.4)	110.9 (1.4)
δ <sup>b</sup>	0	5

<sup>a</sup> The deviation from planarity of the carbon skeleton in the four-membered rings, defined as in cyclobutane.

<sup>b</sup> Estimated from the RD curve, not refined.

separation of bond distances within each molecule is shown to be small, it is therefore not probable that the observed difference is due to one individual type of bond. Of course if this deviation is real it is easily rationalized by the extra strain that occurs in *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane. In this compound the angle C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> was also found to be significantly larger (119.0°) than in *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane (111.9°). There is also a difference in δ which is the angle between the CCC angle bisector and the respective HCH plane. In *syn*-tricyclo(4.2.0.0<sup>2,5</sup>)octane the greater repulsion between the hydrogens in the CH<sub>2</sub>-groups is overcome by pushing these groups away from each other, increasing the shortest hydrogen-hydrogen distance to about 2.13 Å.

The puckering parameter, β, is not significantly different in the two compounds. It is small compared to cyclobutane itself (35°<sup>3,4</sup>). In a crystal structure determination of a derivative of *anti*-tricyclo(4.2.0.0<sup>2,5</sup>)octane — perchloro-(3,4,7,8-tetramethylene-tricyclo(4.2.0.0<sup>2,5</sup>)octane) — the middle ring was found to be planar (symmetry requirement) and the outer rings to be almost planar.<sup>6</sup> Small differences in β between the middle and the outer rings would not be observable for the tricyclo(4.2.0.0<sup>2,5</sup>)octanes reported here. However, it is verified that neither models with all rings planar nor models with a planar middle ring and puckered peripheral rings are consistent with the experimental data. Models with a puckered middle ring and planar outer rings seem very unlikely. For cyclobutane itself it has also been observed that derivatives can be planar in the crystalline state.<sup>18</sup>

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