

The ^{13}C -NMR Assignment of Some Spirocyclopropane-attached
Derivatives of the Dicyclopentadiene by the Epoxidation Shift

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The ^{13}C -NMR assignment of dispiro[cyclopropane-1,3'-tricyclo[5.2.1.0^{2,6}]-
deca-4',8'-diene-10',1"-cyclopropane] and its derivatives was given by the
comparison of the magnitudes of the residual coupling in the off-resonance
spectra and by the chemical shift differences induced by the epoxidation of
a double bonds. This was in accord with the former assignment for the di-
cyclopentadiene by Nakagawa *et al.*

The ^{13}C -NMR spectroscopy is a powerful mean of organic structure analysis, but the
assignment of the spectra is often difficult in complicated systems. During the
photooxidations of dispiro[cyclopropane-1,3'-tricyclo[5.2.1.0^{2,6}]-deca-4',8'-diene-
10',1"-cyclopropane] (1),¹⁾ the Diels-Alder dimer of spiroheptadiene (A), we have
measured a number of the ^{13}C -NMR spectra of derivatives. Since they are rigid cage
compounds, the full analysis of the spectra should provide an intimate information
for analyzing ^{13}C -NMR spectra of similar alicyclic derivatives. Indeed, this was
the case when the assignment of the spectra of 1 and its derivatives, obtained by
mutual comparison, made a selection of the previous NMR assignments^{2,3)} for some
derivatives of the *endo*-dimer (27) of cyclopentadiene (B), a basic cage compound.

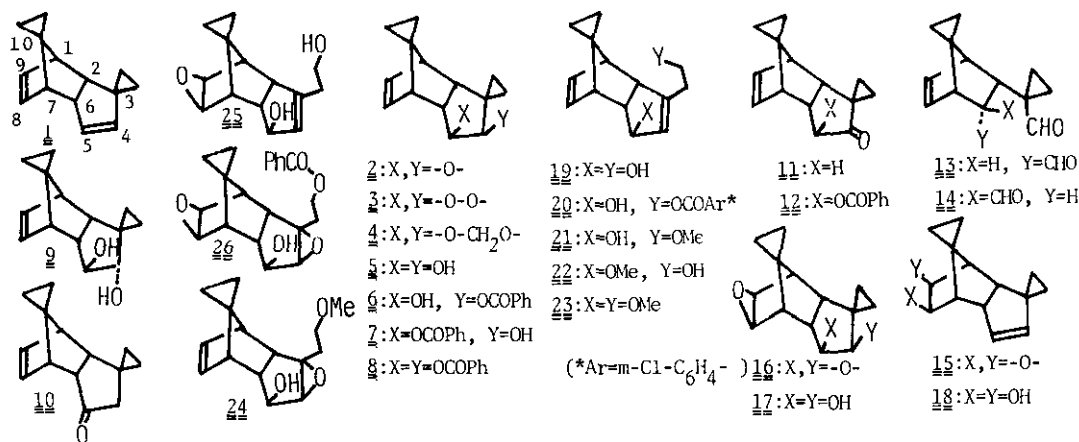


Table 1: The ^{13}C -NMR Spectra of 1 and its Derivatives (in CDCl_3).

	C-1+C-7	C-2	C-6	C-8+C-9	C-4	C-5	C-3	C-10	C-3 α + β	C-10 σ + α		
<u>1</u> ^{a)}	<u>50.6</u> ^{b)}	<u>51.6</u>	<u>49.8</u>	<u>55.4</u>	<u>134.2</u>	<u>133.3</u>	<u>140.4</u>	<u>129.1</u>	<u>29.7</u>	<u>45.4</u>	<u>11.5</u> , <u>15.4</u>	<u>5.7</u> , <u>7.5</u>
<u>2</u>	<u>51.1</u> ^{c)}	<u>52.0</u> *	<u>52.4</u> *	<u>49.7</u>	<u>136.0</u>	<u>133.2</u>	<u>69.0</u> ^{d)}	<u>61.1</u>	<u>25.1</u>	<u>46.1</u>	<u>10.5</u> , <u>11.2</u>	<u>5.4</u> , <u>7.6</u>
<u>3</u>	<u>49.9</u>	<u>51.9</u>	<u>57.2</u> *	<u>58.1</u> *	<u>138.3</u>	<u>133.2</u>	<u>98.4</u>	<u>90.0</u>	<u>30.0</u>	<u>46.4</u>	<u>11.3</u> , <u>15.3</u>	<u>5.9</u> , <u>7.9</u>
<u>4</u>	<u>50.8</u>	<u>52.3</u> *	<u>51.8</u> *	<u>56.9</u> *	<u>137.9</u>	<u>134.2</u>	<u>87.2</u>	<u>83.3</u>	<u>25.3</u>	<u>45.5</u>	<u>11.7</u> , <u>12.9</u>	<u>5.7</u> , <u>7.8</u>
<u>5</u>	<u>50.8</u> *	<u>52.5</u>	<u>50.2</u> *	<u>53.9</u>	<u>137.5</u>	<u>135.1</u>	<u>79.8</u>	<u>74.7</u>	<u>25.8</u>	<u>47.2</u>	<u>8.9</u> , <u>9.9</u>	<u>5.8</u> , <u>8.0</u>
<u>6</u>	<u>49.9</u>	<u>51.9</u> *	<u>50.4</u> *	<u>54.4</u>	<u>137.1</u>	<u>135.4</u>	<u>84.7</u>	<u>74.1</u>	<u>24.6</u>	<u>47.8</u>	<u>10.2</u> , <u>10.2</u>	<u>5.8</u> , <u>7.9</u>
<u>7</u>	<u>50.2</u>	<u>51.6</u> *	<u>50.6</u> *	<u>52.2</u>	<u>137.4</u>	<u>135.4</u>	<u>78.1</u>	<u>79.2</u>	<u>26.3</u>	<u>47.4</u>	<u>9.3</u> , <u>9.3</u>	<u>5.8</u> , <u>7.9</u>
<u>8</u>	<u>50.1</u> *	<u>52.1</u> *	<u>50.1</u> *	<u>52.3</u> *	<u>137.0</u>	<u>135.8</u>	<u>83.0</u>	<u>75.8</u>	<u>24.9</u>	<u>47.9</u>	<u>9.8</u> , <u>11.1</u>	<u>5.9</u> , <u>8.0</u>
<u>9</u>	<u>48.9</u> *	<u>49.0</u> *	<u>49.8</u> *	<u>49.9</u> *	<u>136.9</u>	<u>135.3</u>	<u>80.6</u>	<u>78.9</u>	<u>23.7</u>	<u>47.7</u>	<u>8.0</u> *, <u>8.9</u>	<u>5.9</u> , <u>7.8</u> *
<u>10</u>	<u>50.7</u>	<u>51.7</u> *	<u>52.6</u> *	<u>57.5</u>	<u>136.0</u>	<u>134.4</u>	<u>51.5</u>	<u>220.2</u>	<u>18.4</u>	<u>46.8</u>	<u>10.4</u> , <u>19.1</u>	<u>6.0</u> , <u>8.0</u>
<u>11</u>	<u>50.4</u>	<u>52.1</u> *	<u>51.6</u> *	<u>38.3</u>	<u>137.1</u>	<u>134.4</u>	<u>219.8</u>	<u>40.3</u>	<u>31.4</u>	<u>44.7</u>	<u>15.9</u> , <u>23.6</u>	<u>5.4</u> , <u>7.4</u>
<u>12</u>	<u>50.0</u> *	<u>51.0</u> *	<u>51.0</u> *	<u>48.0</u>	<u>137.2</u>	<u>135.5</u>	<u>215.0</u>	<u>77.2</u>	<u>31.5</u>	<u>45.8</u>	<u>19.6</u> , <u>23.3</u>	<u>5.7</u> , <u>7.6</u>
<u>13</u>	<u>41.8</u>	<u>49.8</u>	<u>50.7</u>	<u>57.3</u>	<u>137.2</u>	<u>133.5</u>	<u>204.2</u>	<u>201.6</u>	<u>33.3</u>	<u>45.9</u>	<u>11.2</u> , <u>12.5</u>	<u>6.3</u> , <u>8.3</u>
<u>14</u>	<u>39.6</u>	<u>50.6</u>	<u>51.5</u>	<u>56.6</u>	<u>135.8</u>	<u>135.8</u>	<u>203.3</u>	<u>201.4</u>	<u>33.3</u>	<u>44.7</u>	<u>9.9</u> , <u>10.4</u>	<u>5.5</u> , <u>8.9</u>
<u>15</u>	<u>46.4</u>	<u>45.8</u>	<u>50.0</u>	<u>53.3</u>	<u>52.6</u>	<u>51.4</u>	<u>140.0</u>	<u>127.6</u>	<u>27.6</u> *	<u>27.9</u> *	<u>12.0</u> , <u>15.6</u>	<u>0.5</u> , <u>8.8</u>
<u>16</u>	<u>46.7</u>	<u>46.0</u>	<u>52.2</u>	<u>48.7</u>	<u>51.1</u>	<u>50.4</u>	<u>68.2</u>	<u>59.6</u>	<u>22.7</u>	<u>27.6</u>	<u>10.9</u> , <u>11.6</u>	<u>0.5</u> , <u>9.0</u>
<u>17</u>	<u>45.8</u> *	<u>46.6</u> *	<u>50.0</u>	<u>52.4</u>	<u>52.0</u>	<u>50.8</u>	<u>77.2</u>	<u>73.2</u>	<u>23.6</u>	<u>27.1</u>	<u>7.1</u> , <u>11.0</u>	<u>0.6</u> , <u>9.2</u>
<u>18</u>	<u>52.0</u> *	<u>51.1</u> *	<u>48.1</u>	<u>52.2</u> *	<u>72.9</u>	<u>72.2</u>	<u>138.7</u>	<u>128.7</u>	<u>28.0</u>	<u>33.0</u>	<u>10.8</u> , <u>15.2</u>	<u>0.2</u> , <u>6.3</u>
<u>19</u>	<u>49.2</u>	<u>49.9</u> *	<u>56.1</u>	<u>54.0</u>	<u>133.1</u> *	<u>134.4</u> *	<u>130.8</u>	<u>77.8</u>	<u>147.0</u>	<u>47.0</u>	<u>33.3</u> , <u>59.8</u>	<u>5.8</u> , <u>7.6</u>
<u>20</u>	<u>49.2</u> *	<u>49.9</u> *	<u>56.7</u>	<u>54.1</u>	<u>132.9</u> *	<u>134.3</u> *	<u>130.4</u>	<u>77.9</u>	<u>146.2</u>	<u>47.0</u>	<u>29.5</u> , <u>63.3</u>	<u>5.8</u> , <u>7.5</u>
<u>21</u>	<u>49.3</u> *	<u>49.9</u> *	<u>56.6</u>	<u>54.1</u>	<u>133.1</u> *	<u>134.4</u> *	<u>130.0</u>	<u>77.7</u>	<u>146.8</u>	<u>46.9</u>	<u>30.4</u> , <u>70.6</u>	<u>5.8</u> , <u>7.5</u>
<u>22</u>	<u>49.2</u> *	<u>50.2</u> *	<u>56.7</u>	<u>50.4</u>	<u>133.1</u> *	<u>134.6</u> *	<u>127.4</u>	<u>87.1</u>	<u>148.2</u>	<u>47.2</u>	<u>33.6</u> , <u>60.1</u>	<u>5.8</u> , <u>7.6</u>
<u>23</u>	<u>49.38</u>	<u>50.4</u> *	<u>57.1</u>	<u>50.4</u>	<u>133.2</u> *	<u>134.6</u> *	<u>126.8</u>	<u>87.1</u>	<u>148.3</u>	<u>47.1</u>	<u>30.6</u> , <u>70.8</u>	<u>5.8</u> , <u>7.6</u>
<u>24</u>	<u>49.8</u> *	<u>50.1</u> *	<u>53.6</u> *	<u>54.4</u> *	<u>134.7</u> *	<u>135.5</u> *	<u>69.2</u>	<u>74.5</u>	<u>69.7</u>	<u>47.1</u>	<u>30.4</u> , <u>68.6</u>	<u>5.6</u> , <u>7.7</u>
<u>25</u>	<u>43.4</u> *	<u>45.3</u> *	<u>54.3</u> *	<u>53.4</u> *	<u>50.5</u> *	<u>51.4</u> *	<u>130.8</u>	<u>75.3</u>	<u>145.4</u>	<u>28.4</u>	<u>33.6</u> , <u>59.6</u>	<u>0.5</u> , <u>9.2</u>
<u>26</u>	<u>45.5</u> *	<u>45.7</u> *	<u>51.0</u>	<u>53.9</u>	<u>50.6</u> *	<u>49.9</u> *	<u>69.8</u>	<u>70.9</u>	<u>68.0</u>	<u>28.2</u>	<u>30.1</u> , <u>61.5</u>	<u>0.6</u> , <u>9.4</u>

a) For preparation of 1-26, see Ref. 1.

b) Figures expressed in italic letters were determined by selective decoupling experiments.

c) Asterisked figures may be mutually reversed.

d) Underlined figures were assigned by magnitudes of J_R in the off-resonance experiments.

First of all, among eight methine carbon signals of a bisepoxide(16) appearing in a range of 45 to 70 ppm from internal TMS, the two at δ : 68.2 and 59.6, being deshielded than others, are ascribable to the oxygenated carbons(C-4 and C-5) by comparisons with the 4,5-epoxide of 1(2). The others appearing together in narrow range, 46 to 52 ppm, are difficult to make a clear assignment on the chemical shift ground, but the large residual coupling in the off-resonance spectrum(J_R) for the signals at 50.4 and 51.1 (each 66 Hz)⁴⁾ led to assign them to be C-9 and C-8 from others (ca. 48 Hz). Same is true for 8,9-epoxide(15) of 1: Among six methine carbons appeared between 46 to 53, the epoxy carbon signals were shown to be at 52.6(C-8) and 51.4(C-9) by larger J_R (ca. 60 and 64 Hz), than the others(40

to 43 Hz). Similarly, a diepoxy glycol monoester(26) showed two methine carbons at *ca.* 70 ppm; one at 70.9 is attributable to the hydroxyl carbon, and the other at 69.8 having large J_R to C-4 epoxy signal. The remaining epoxy carbon signals were at 49.9 and 50.6. An epoxy alcohol(25) revealed a similar feature.

Nextly, α -carbons of aldehydes were also assignable; the spectrum of 13 showed such signals, C-3 and C-6, with large $^2J_{CC-H}$ -splittings at 33.3(d, $J_R=14$ Hz) and 57.3 (dd, $J_R=48$, 10 Hz). The whole data are compiled in Table 1.

Based on the above assignment, we have tried a differentiation of previous ^{13}C -NMR assignments^{2,3)} on 27 and its derivatives by comparisons of the $\Delta\delta$ induced by the epoxidation, since we have a series of epoxy derivatives for comparison. Indeed, the 8,9-epoxidation caused a remarkable change in their carbon chemical shifts. As expected, the $\Delta\delta$ for C-8 and C-9 were as large as -80 to -86 ppm, which are similar to that of the epoxidation shift between 29 and its 8,9-epoxy derivative(30), $\Delta\delta(30-29)$, -85.2, but, our $\Delta\delta$ for the C-10 were *ca.* -17 to -20, being smaller than that of $\Delta\delta(30-29)$, -22.7. This must be due to the proximity of the epoxy to spiro-cyclopropane groups. Contrasting figures observed for the epoxidation shifts of C-10a(*ca.* -5) and C-10s(*ca.* +1.5) in these derivatives must be interpreted on the same ground, and constituted a firm evidence for differentiation of C-10 and C-3 methylene carbons. As figured in Table 2, our $\Delta\delta$ of methine carbons were consistent to the data of norbornene series,⁵⁾ and in the same time, the whole $\Delta\delta(30-29)$ data disproved the Kleinpeter's assignment.³⁾

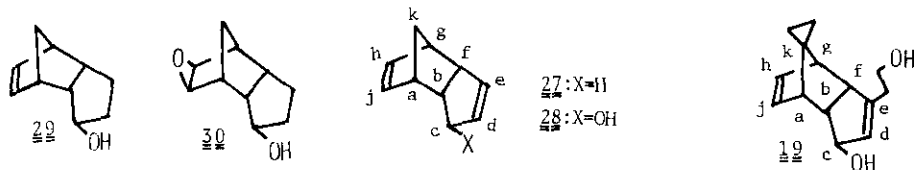
Table 2: The Chemical Shift Differences due to the Epoxidation at C-8 and C-9.

$\Delta\delta$	C-1	C-7	C-2	C-6	C-8	C-9	C-3	C-10	C-10s	C-10a	C-3a	C-3b
(<u>15-1</u>)	-4.2	-5.8	+0.2	-2.1	-81.6	-81.9	-2.1	-17.5	+1.3	-5.2	+0.5	+0.3
(<u>16-2</u>)	-4.4	-6.0	-0.2	-1.0	-84.9	-82.8	-2.4	-18.5	+1.4	-4.9	+0.4	+0.4
(<u>17-5</u>)	-5.0	-5.9	-0.2	-1.5	-85.5	-84.3	-2.3	-20.1	+1.2	-5.2	-1.6	+1.1
(<u>25-19</u>)	-5.8	-4.6	-1.8	-0.6	-82.6	-83.0	-1.6	-18.6	+1.6	-5.3		
(<u>26-24</u>)	-4.3	-4.4	-2.6	-0.5	-84.8	-84.9	-1.7	-18.9	+1.7	-5.0		
(<u>30-29</u>) ^{a)}	-5.4	-5.7	-0.3	-1.5	-85.2	-85.2	-2.2	-22.7				
(<u>30-29</u>) ^{b)}	-0.3	-5.8	-5.7	-1.5	-85.2	-85.2	-2.2	-22.7				

a) Calculated after revision of the data given in Ref. 3.

b) Calculated after assignment of Ref. 3.

On the other hand, the Nakagawa's assignment showed a consistency with our results; using their figures of 27 and 28,²⁾ $\Delta\delta(1-27)$ and $\Delta\delta(19-28)$ were calculated. Relatively large $\Delta\delta(1-27)$ values observed were all explained in terms of the spiro-cyclopropanes; C-a, C-g, C-b and C d showed a down-field shift, while C-c and C-k,



spirocarbons, did a high-field shift. The $\Delta\delta(\underline{1}-\underline{27})$ of C-d and C-e showed same signs and order in magnitudes with the $\Delta\delta(\underline{A}-\underline{B})$ of the α - and β -carbon signals(+7.0 and -3.7). The $\Delta\delta(\underline{19}-\underline{28})$ were also characteristic; especially, by removing one of the spirocyclopropane rings, the down-field shift for C-b and C-d and the high-field shift for C-c disappeared. Large negative $\Delta\delta$, -6.3 for C-d, and positive $\Delta\delta$, +11.8 for C-e, are ascribable to a newly formed β -hydroxyethyl group at C-e; the figures coincide well with those of cyclopentene and its 1-propyl derivative (-6.7 and +13.7)

Table 3. The ^{13}C -NMR Comparisons of $\underline{1}$ and $\underline{19}$ with $\underline{27}$ and $\underline{28}$.

	C-a	C-g	C-b	C-f	C-h	C-j	C-d	C-e	C-c	C-k
$\underline{1}$	50.6	51.6	49.8	55.4	134.2	133.3	140.4	129.1	29.7	45.4
$\underline{27}^a)$	46.3	45.3	41.3	54.8	131.9	132.2	132.1	135.6	34.7	50.3
$\Delta\delta$	+4.3	+6.3	+8.5	+0.6	+2.3	+1.1	+8.3	-6.5	-5.0	-4.9
$\underline{19}$	49.9	49.2	54.0	56.1	134.4	133.1	130.8	147.0	77.8	47.0
$\underline{28}^a)$	44.5	44.5	53.0	54.5	132.2	134.6	137.1	135.2	78.4	51.1
$\Delta\delta$	+5.4	+4.7	+1.0	+1.3	+2.2	-1.5	-6.3	+11.8	-0.6	-4.1

a) Data were taken from Ref. 2.

References and Notes

†) This paper is dedicated to Prof. Tetsuji Kametani, Tohoku University.

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- 4) In the heteronuclear off-resonance spectra, the residual splitting (J_R) is given by Eq. 1:⁶⁾

$$J_R = [(\Delta\nu - J_0/2)^2 + (\gamma_{H_2})^2]^{1/2} - [(\Delta\nu + J_0/2)^2 + (\gamma_{H_2})^2]^{1/2} \dots (\text{Eq. 1})$$

Where $\Delta\nu$ is the difference between the resonance frequencies, and γ_{H_2} is the power of decoupling field. If $\gamma_{H_2} \gg |\Delta\nu|$, Eq. 1 can be simplified to Eq. 2:

$$\Delta\nu = \gamma_{H_2} J_R / J_0 \dots (\text{Eq. 2}).$$

Hence, under certain conditions, if $\Delta\nu$ of some nuclei were nearly equal, the J_R becomes parallel to J_0 , i.e., to s-character.
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