

## Direct Observation of the Effect of Transannular Interaction on the Single Bond Lengths of Tricyclo[2.1.0.0<sup>2,5</sup>]pentane Derivatives

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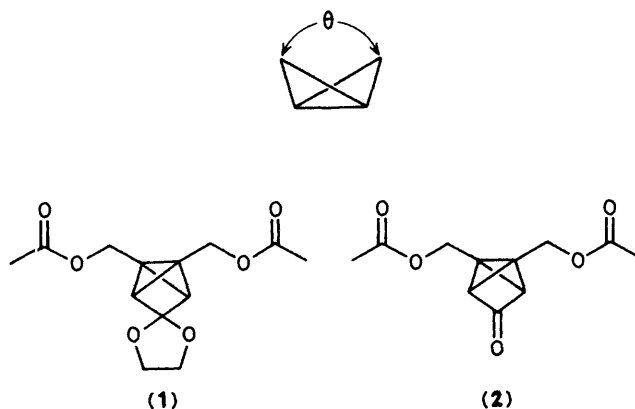
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X-Ray structure analysis of 1',5'-bis(acetoxymethyl)spiro(1,3-dioxolane-2,3'-tricyclo[2.1.0.0<sup>2,5</sup>]pentane) (**1**) reveals that the bond distance (1.455 Å) between the bridgehead carbon atoms is elongated in comparison with the same bond in the ketone 1,5-bis(acetoxymethyl)tricyclo[2.1.0.0<sup>2,5</sup>]pentan-3-one (**2**), thereby providing direct evidence of an unusual transannular interaction between the carbonyl group and the bridging bond.

The bond distance between the bridgehead carbons in bicyclobutane derivatives is a linear function of the folding angle  $\theta$ .<sup>1,2</sup> We now identify transannular interaction with a bridging carbonyl group as an additional factor which influences the unusual bonding in tricyclo[2.1.0.0<sup>2,5</sup>]pentane derivatives.

We have determined the crystal structure of the tricyclo[2.1.0.0<sup>2,5</sup>]pentane derivative 1',5'-bis(acetoxymethyl)spiro(1,3-dioxolane-2,3'-tricyclo[2.1.0.0<sup>2,5</sup>]pentane), (**1**),<sup>†</sup>

<sup>†</sup> Crystal data: C<sub>13</sub>H<sub>16</sub>O<sub>6</sub>, triclinic, space group  $P\bar{1}$ ;  $a = 8.291(1)$ ,  $b = 9.613(1)$ ,  $c = 10.473(2)$  Å;  $\alpha = 114.30(1)$ ,  $\beta = 109.89(1)$ ,  $\gamma = 96.92(1)^\circ$ ;  $Z = 2$ ; 1931 reflections with  $I > 2.5 \sigma(I)$  out of 3325 measured;  $R = 0.051$ . The cell dimensions were determined by a least squares method from 25 high-order reflections ( $2\theta > 42^\circ$ ). The intensities were collected on a diffractometer (Mo- $K_\alpha$  radiation, graphite monochromator,  $\omega$ - $2\theta$  scan). Lorentz and polarization corrections were applied, and absorption effects were neglected. The crystal structure was solved by direct methods with the program Multan.<sup>5</sup> The positions of the hydrogen atoms were calculated according to stereochemical requirements or were found by a difference Fourier synthesis. In a full-matrix procedure the hydrogen atoms were refined isotropically and the carbon atoms anisotropically. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citations for this communication.



for comparison with that<sup>1b</sup> of the corresponding ketone (**2**).

The molecular structure of (**1**) with the bond lengths is shown in Figure 1. In the ketone (**2**)<sup>1b</sup> the carbonyl group produces a significant shortening of the bridging C(1)–C(2) bond (see Figure 1 for numbering). The C(1)–C(2) bond length is 1.416 Å in (**2**), while it is 1.455 Å in (**1**). A carbonyl group attached to a cyclopropane ring in the bisected orientation<sup>3</sup> leads to a shortening of the distal bond by 0.026 Å. The dihedral angles of 96.8° and 95.7° for (**1**) and

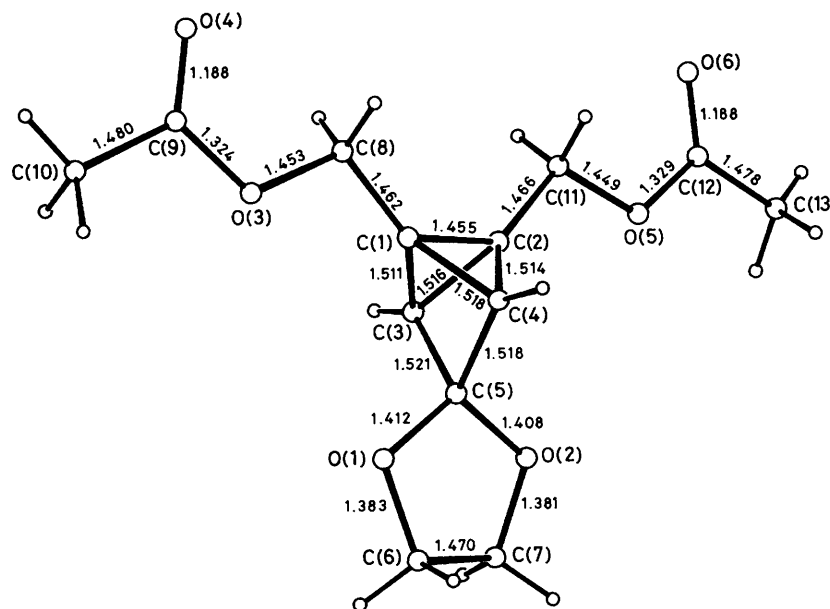


Figure 1. Structure of compound (1) with bond distances in Å. The estimated standard deviations are 0.002–0.004 Å.

(2),<sup>1</sup> are sufficiently close in magnitude that the crucial folding angles  $\theta$  are essentially identical in both compounds.

Photoelectron spectroscopy and MINDO/3 calculations on tricyclo[2.1.0.0<sup>2,5</sup>]pentane compounds predict a reduction of antibonding contributions in the C(1)–C(2) bond because of the electron acceptor properties of the ketone carbonyl group.<sup>4</sup> The calculations compare the ketone and the corresponding olefin (C=CH<sub>2</sub> in place of C=O) and the predicted effect is small. Within these limits, the measurements reported here provide direct confirmation of these ideas.

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