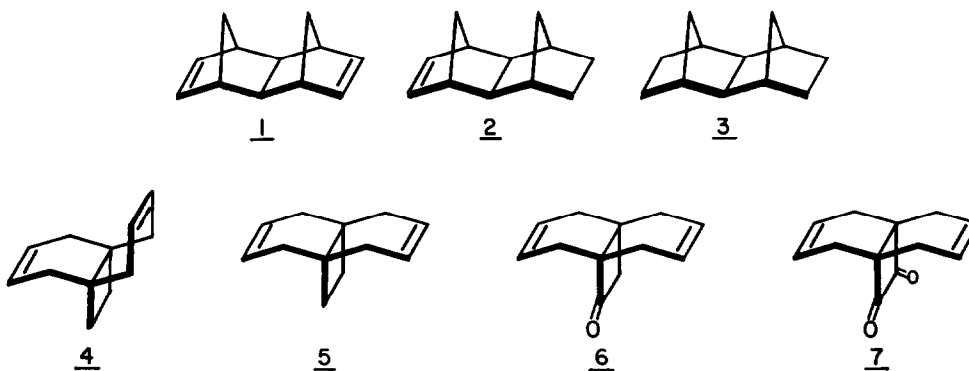


CONFORMATIONAL PREFERENCE OF [4.4.2]-PROPELLA-3,8-DIENES DERIVED FROM  
SINGLE-CRYSTAL X-RAY ANALYSIS AND MOLECULAR MECHANICS CALCULATIONS.

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Summary. The crystal structure of [4.4.2]-propella-3,8-diene-11-one (6) and -11,12-dione (7) coupled with molecular mechanics calculations strongly suggest that [4.4.2]-propella-3,8-diene (5) exists predominantly in the E,E-conformation.

In a recent publication, Paddon-Row *et al.*<sup>1</sup> proposed an alternative model of orbital interactions through bonds. The photoelectron spectra of 1-3 led these authors to derive "a simple general model of OIT-B." From their model it was concluded that [4.4.2]-propella-3,8-diene should exist in the E,Z-conformation (4) rather than the E,E-conformation (5), as previously proposed.<sup>2</sup> We herein demonstrate that the ketone derivative 6, the closest structural crystalline relative to 5, exists in the crystal state in the E,E-orientation and that molecular mechanics calculations on this propelladiene family (5-7) further support this orientation.



Ketone 6 (mp 78-80°C) was previously prepared<sup>2</sup> by the reduction of 12-hydroxy-[4.4.2]-propella-3,8-dien-11-one. Recrystallization of 6 from hexane gave crystals suitable for X-ray analysis. Crystal Data for 6: Crystals of C<sub>12</sub>H<sub>14</sub>O are monoclinic, space group P2<sub>1</sub>/m, a=6.751(1),

$b=9.238(1)$ ,  $c=7.977(2)$  Å;  $\beta=102.99(2)^\circ$ ,  $Z=2$ . Data were collected using MoK $\alpha$  radiation ( $\lambda=0.71073$  Å) on an Enraf-Nonius CAD4 diffractometer to  $\theta=30^\circ$ . The crystal was sealed in a thin-walled glass capillary in order to prevent sublimation during data collection. The structure was solved by direct methods (MULTAN 78)<sup>3</sup> and refined by full-matrix least squares to  $R=0.038$  for 717 observed data. Hydrogen atoms were located from difference maps and refined isotropically. The molecule has exact  $C_s$  symmetry in the crystal. Figure 1 (top view) and especially Figure 2 confirm that ketone 6 possesses the E,E-orientation at least in the crystal.

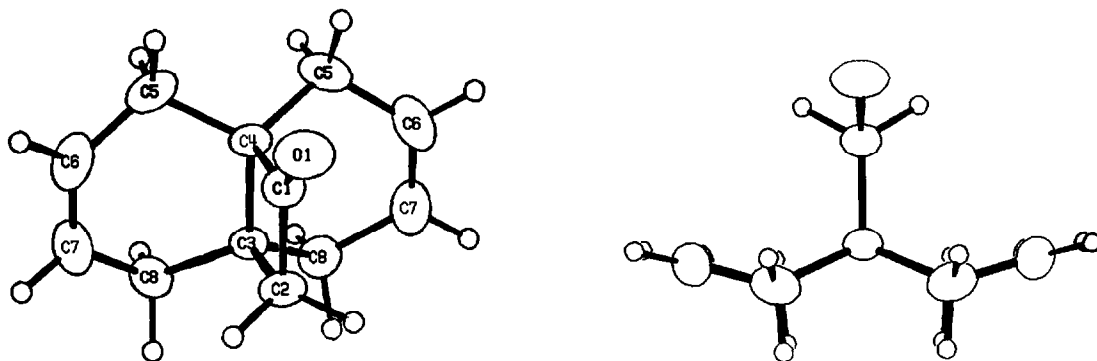


Figure 1. Ketone 6 (top view). Figure 2. Ketone 6 (side view). Selected distances and angles<sup>4</sup> are: C1-O1, 1.199Å; C1-C2, 1.502Å; C1-C4, 1.526Å; C2-C3, 1.561Å; C3-C4, 1.575Å; C3-C8, 1.524Å; C4-C5, 1.533Å; C5-C6, 1.486Å; C6-C7, 1.307Å; C7-C8, 1.495Å; C1-C2-C3, 89.0°; C2-C3-C4, 89.7°; C3-C4-C1, 87.6°; C2-C1-C4, 93.8°. Standard deviations are 0.002Å and 0.1°. The torsion angle C7-C8-C3-C8' is -168.4°.

Molecular mechanics calculations were undertaken to ascertain the energy differences between the E,E-, E,Z-, and Z,Z-conformations of propelladienes 5-7. Using the PROPHEIT<sup>5</sup> system and crystal structure data for 6, Cartesian coordinates were generated for each geometry. The computations were performed using the force field program MM2<sup>6</sup> for 5 and 6, and due to  $\pi$ -conjugation, MMP1<sup>7</sup> for 7. The steric energies are shown in the Table.

Steric energies for 6 show that the E,E-orientation is the predominant conformer, in agreement with the derived crystal structure. The calculated bond lengths and angles for E,E-6 compare favorably with those derived from the x-ray crystal data. Furthermore, the E,E-conformation is the lowest energy conformer throughout the propella-3,8-diene series (5-7) by ca. 2.75 kcal/mol and 6.25 kcal/mol lower than the E,Z- and Z,Z-conformers, respectively.

Table.

<u>Compound</u>	<u>Conformational</u>	<u>E<sub>steric</sub></u> <u>(kcal/mol)</u>	<u>ΔE(kcal/mol)</u>
<u>5<sup>a</sup></u>	E,E	41.34	
	E,Z	43.90	2.56
	Z,Z	47.07	5.73
<u>6<sup>a</sup></u>	E,E	26.07	
	E,Z	28.98	2.91
	Z,Z	32.37	6.30
<u>7<sup>b</sup></u>	E,E	31.58	
	E,Z	34.34	2.76
	Z,Z	38.26	6.68

<sup>a</sup>Calculated by MM2 program<sup>6</sup>. <sup>b</sup>Calculated by MMPI program<sup>7</sup>.

Thus, from the crystal data for 6, the known molecular structure of [4.4.2]-propella-3,8-diene-11,12-dione<sup>8</sup>, and the computational correlations, the suggestion by Paddon-Row et al.<sup>7</sup>, as based on his simple general model of OIT-B, that 5 exists in the E,Z-conformation is not likely to be correct.

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