X-Ray Molecular Structure of 3-Oxa-7,9-dithia- and 9-Oxa-3,7-dithia-bicyclo[3,3,1]nonanes

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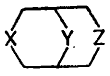
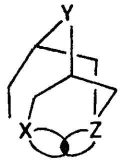
Summary *X*-Ray crystal structure analysis shows that 3-oxa-7,9-dithiabicyclo[3,3,1]nonane (I) exists in the double-chair conformation, but that 9-oxa-3,7-dithiabicyclo[3,3,1]nonane exists in the boat–chair conformation; this phenomenon is discussed in term of lone pair repulsions.

Bicyclo[3,3,1]nonane and its derivatives may exist in double-chair, boat–chair, and double-boat conformations, but double-chair conformations usually predominate both in the solid state[1,2] and in solution.[3–5] Relative stabilisation of the boat–chair conformation is usually associated with introduction of 3-*endo*-substituents on the bicyclo-

[3,3,1]nonane framework.[6,7] However, we supposed that the double-chair conformation could also be destabilized by lone-pair repulsion, structure (III).[8]†



(I) X = O, Y = Z = S
(II) X = Z = S, Y = O



(III)

We tested this assumption by studying the molecular structures of the two isomeric $C_6H_{10}OS_2$ compounds: (I) and (II). *Crystal data*, compound (I): orthorhombic, space group P_{nma}, $a = 12{\cdot}78$, $b = 6{\cdot}72$, $c = 8{\cdot}32$ Å, $D_m = 1{\cdot}49$, $D_c = 1{\cdot}50$ g cm^{-3}, unfiltered Cu-K radiation; compound (II): monoclinic, space group $P2_1/b$, $a = 8{\cdot}71$, $b = 10{\cdot}21$, $c = 8{\cdot}98$ Å, $\gamma = 105°2'$, $Z = 4$, $D_m = 1{\cdot}42$, $D_c = 1{\cdot}40$ g cm^{-3}, unfiltered Mo-K_α radiation. Intensities of 400 and 680 independent reflections for (I) and (II) respectively were estimated visually from multiple-film Weissenberg photographs and were corrected for Lorentz and polarization effects. The structures were solved by Patterson and Fourier techniques and refined by least-square to R 0·147 and 0·140 respectively.

Molecules of (I) adopt the double-chair conformation with a symmetry plane through O(3), S(7), and S(9). The strong repulsion between O(3) and S(7) is clearly reflected in the increase of the O(3) · · · S(7) distance to 3·12 Å (the ideal double-chair value is *ca.* 2·52 Å [2]). Molecules of (II), however, adopt the boat–chair conformation, with S(3) · · · S(7) and S(3) · · · O(9) distances of 4·24 and 2·84 Å, respectively.

Thus compound (I) exists in the double-chair conformation, but compound (II) adopts the boat-chair one. If (II) existed in the double-chair conformation, the S(3)–S(7) distance would be *ca.* 4·6 Å. The sum of the van der Waals radii of two sulphur atoms is 3·6—3·7 Å,[9] and literature data show S · · · S non-bonded contacts in the range 3·6—4·0 Å.[10] Thus, pure steric repulsion seems not to be responsible for the strong destabilization of the double-chair conformation of (II), and we believe that orbital repulsion as in structure (III) is responsible.

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† This repulsion should be greater with increasing atomic number[8] *i.e.* O · · · O < O · · · S < S · · · S. For dipole–dipole repulsion the order should be opposite.

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