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### AB-INITIO STUDIES OF ANOMERIC EFFECT IN THIOSUGARS

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It is well known that anomeric effect<sup>1</sup> plays an important role in carbohydrate chemistry. This effect influences the conformational equilibria in solution and the preferred conformation is solid state. This phenomenon has been well characterized for oxygen systems both theoretically and experimentally. However, recently it has been reported that the replacement of 0-5 and 0-1 oxygens by sulfur in pyranose sugars affect the conformational equilibria in solution<sup>2</sup> and the observed conformations in the solid state<sup>3</sup>. This has been attributed to the reduced anomeric effect in sulfur systems<sup>2-4</sup>. In this note we report the *ab-initio* quantum chemical studies on  $X-C-X$  system when  $X = O$  or  $S$ , and discuss the anomeric effect in sulfur-containing systems.

The Hartree-Fock theory<sup>5</sup> at STO-3G level<sup>6</sup> is used in this study. The calculations were carried out using GAUSSIAN 74 programme, which was adopted to DEC-10 computer. The studies are done using standard bond lengths and angles<sup>7</sup> for methanediol and the geometry given in reference 8 is used for methanedithiol. The conformational energies were computed as functions of two dihedral angles  $\theta$  and  $\phi$  (Fig. 1). The calculated relative energies plotted as a function of the dihedral angle  $\theta$ , for  $\phi = 180^\circ$  or  $-60^\circ$  are shown in Fig. 2 and in Table I. The noteworthy features between the methanediol and the methanedithiol systems are (1) the energy difference,  $\Delta E_1$  between  $(-60^\circ, -60^\circ)$  and  $(180^\circ, -60^\circ)$  conformations is very much reduced in case of methanedithiol, (2) the energy difference,  $\Delta E_2$ , between  $(180^\circ, -60^\circ)$  and  $(180^\circ, 180^\circ)$  conformations is also reduced considerably in the  $S-C-S$  system and finally (3) the  $(180^\circ, 180^\circ)$  conformation which has the maximum potential energy in methanediol becomes one of the local minima in methanedithiol. The same features are

reproduced at 4-31G level and after geometry optimization at STO-3G level<sup>11</sup>.

The above results bring out a few interesting points. The second and third features mentioned in the previous paragraph explain the observed conformation corresponding to  $(ap, ap)$  in 1,5, dithio- $\alpha$ -D-ribo-pyranoside<sup>3</sup> for the fragment  $C-S-C-S-C$ , a confor-

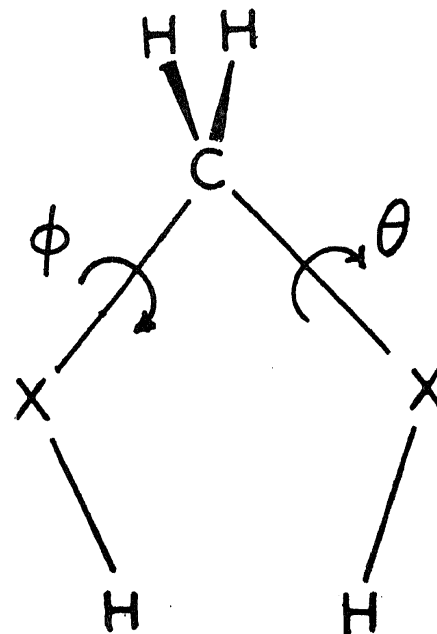


FIG. 1. Schematic representation of the dihedral angles  $\phi$  and  $\theta$  in  $X-C-X$  systems.  $X$  is oxygen in methanediol and sulfur in methanedithiol ( $\theta = \phi = 0^\circ$ ).

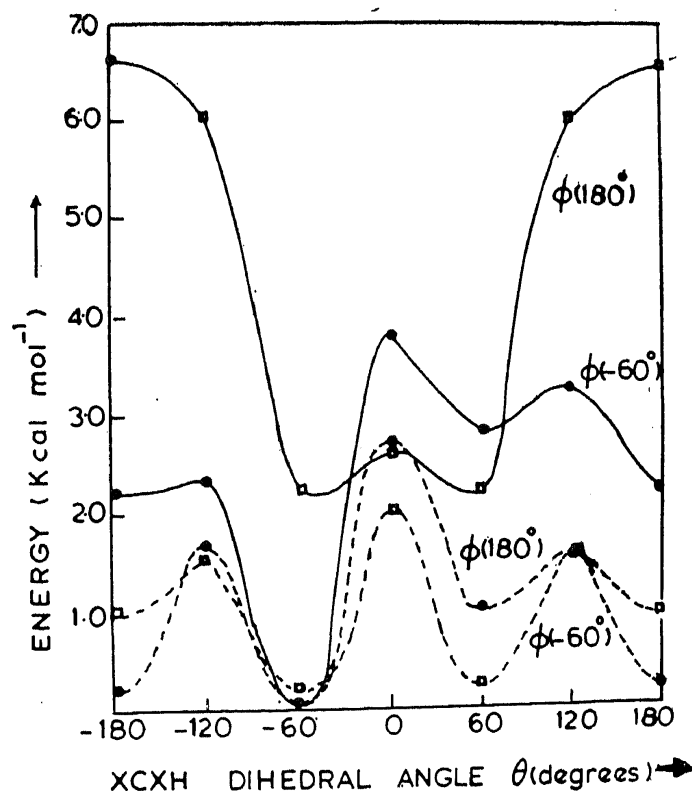


FIG. 2. Sections,  $V(\theta)$  of the potential surface for internal rotation in  $X-C-X$  systems for fixed values of  $\phi$ . The solid lines refer to methanediol and the dotted lines are for methanedithiol.

TABLE I

STO-3G energy differences for various conformations in methanediol and methanedithiol (in Kcal mol<sup>-1</sup>) using standard bond lengths and bond angles

Conformation	Methanediol <sup>a</sup>	Methanedithiol
(sc, sc)	0 <sup>b</sup>	0 <sup>c</sup>
(sc ap)	2.24	0.18
(ap, ap)	6.60	0.97

<sup>a</sup> 4-31G and 6-31G\* calculations on methanediol are reported in reference 9 and reference 10 respectively. STO-3G calculations on methanediol were done in this study, to carry out the comparison of methanediol and methanedithiol at the same level of approximation.

<sup>b</sup> Total energy for this conformation is -187.38249 a.u.

<sup>c</sup> Total energy is -834.223984 a.u.

mation which is never observed and is known to be least favoured due to exoanomeric effect in the oxygen systems.

The results can also be applied to the preferences of ring conformations. Though the ring conformation depends on the environment<sup>12,13</sup> and the nature of hydrogen bonds involved<sup>14</sup>, some features are apparent from the present study. In  $\beta$ -D-ribofuranosides, the <sup>4</sup>C<sub>1</sub> conformation has only one axially oriented OH group (at C3) and <sup>1</sup>C<sub>4</sub> conformation has three axially oriented hydroxyl groups (two of the hydroxyl groups are involved in 1-3 diaxial interactions). Hence non-bonded interaction energies favour <sup>4</sup>C<sub>1</sub> conformation for  $\beta$ -D-pyranoside<sup>15</sup>. However, because of predominance of anomeric effect ( $\Delta E_1$ ), <sup>1</sup>C<sub>4</sub> conformation becomes more favoured for  $\beta$ -D-ribofuranoside. This is in agreement with the observed conformation of  $\beta$ -D-ribofuranoside both in solution<sup>2</sup> and solid state<sup>3</sup>. The present calculation suggests that the anomeric energy ( $\Delta E_1$ ) is reduced considerably in S-C-S system and hence the resulting ring conformation in  $\beta$ -1,5 dithio-D-ribofuranoside may be decided mainly by non-bonded interactions. This explains the existence of this molecules in <sup>4</sup>C<sub>1</sub>(D) conformation in solid state and its predominance in solution.

In the case of  $\alpha$ -D-ribofuranosides, <sup>1</sup>C<sub>4</sub> conformation is slightly more favoured from non-bonded energy calculations. Since the anomeric effect ( $\Delta E_1$ ) is small for S-C-S system, theory predicts that  $\alpha$ -1,5 (d) dithioribofuranoside exist in <sup>4</sup>C<sub>1</sub>  $\rightleftharpoons$  <sup>1</sup>C<sub>4</sub> equilibrium in solution and either of them in solid state depending on the lattice energy. This is in agreement with the experimental studies in solution<sup>2</sup> and solid state<sup>3</sup>.

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## EMBRYOLOGY OF ACANTHOSPERMUM HISPIDUM DC

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ALTHOUGH considerable literature is available on the embryology of the tribe Heliantheae of the family Compositae (see Pullaiah<sup>1</sup>), information on the genus *Acanthospermum* is inadequate. Vaidya<sup>2</sup> studied a few aspects of embryology of *Acanthospermum hispidum*, but no detailed information is available regarding fertilisation, endosperm and embryo development. The present investigation on *Acanthospermum hispidum* DC was undertaken to bridge the gap in our present knowledge of the embryology of the genus.

Pollen grains in *Acanthospermum hispidum* at the time of shedding are three-celled with thick spinous