Tetrahedron Vol. 42, No. 9, pp. 2555 to 2558, 1986
Printed in Great Britain.

0040-4020/86 \$3.00+.00
Pergamon Journals Ltd.

PROPELLANES. PART LXXXVI[†]. THE STRUCTURES OF THE THREE ISOMERIC [4.3.3]PROPELLANE-8,11-DIOLS

MOSHE KAPON, PNINA ASHKENAZI, AND DAVID GINSBURG

Department of Chemistry
Technion - Israel Institute of Technology
Haifa, Israel

(*Received in UK* 18 *February* 1986)

Abstract.- The structures of the title diols have been determined by NMR and X-ray crystallography.

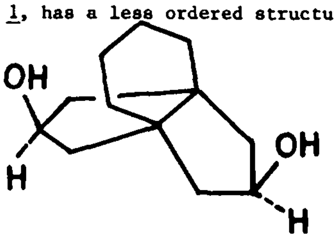
INTRODUCTION

Both Askani[2] and ourselves[3] have prepared the three title compounds by reduction of the corresponding 8,11-dione.

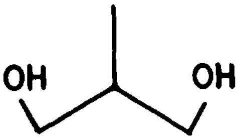
We wished to determine, by comparison with previous work on the structures of aza[4] and thiapropellanes[5] whether the conformations of these rings in the title compounds are similar or different.

RESULTS

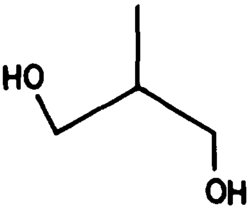
Two of the isomers.are shown in their ORTEP projections. Both the syn, anti- 2 and the anti, anti-diol 3 have their conformations determined mainly by the chair form of the six-membered ring. The five-membered rings in 2 are not envelopes but have C_2 symmetry. Those in 3 remarkably exist in different conformations although the six-membered ring is a chair. One five-membered ring adopts the C_2 conformation and the other the C_s conformation. The third isomer, the syn, syn-diol 1, has a less ordered structure.



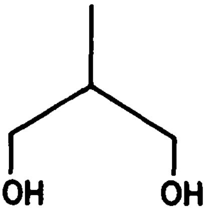
1



1



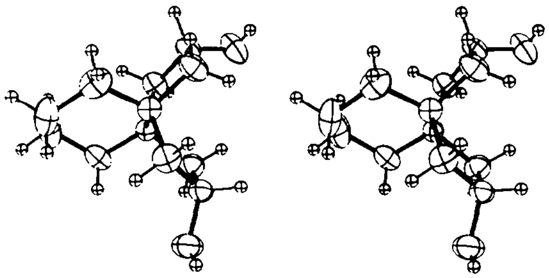
2



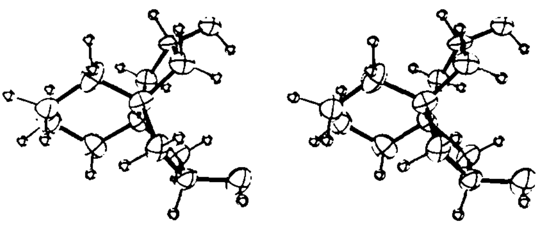
3

It is nevertheless apparent that it crystallizes with 24 molecules in the unit cell. It contains three molecules per asymmetric unit, one of which has C_2 symmetry, the second is of the C_s-type with the third not as defined since the structure refinement reached only 18%. Nevertheless one can discern three different molecular structures which thus cannot be much different in energy. Force field calculations for forms A and B of the syn, syn-diol indeed provide energies of 31.21 kcal/mol, and 31.74 kcal/mol, respectively. The energies for the syn, anti-diol and the anti, anti-diol are 32.27 kcal/mol, and 32.66 kcal/mol, respectively[6].

[†] Part LXXXV: Ref. 1.



ORTEP OF 2

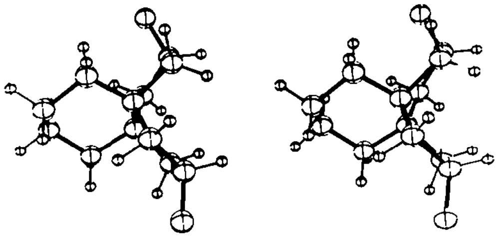


ORTEP OF 3

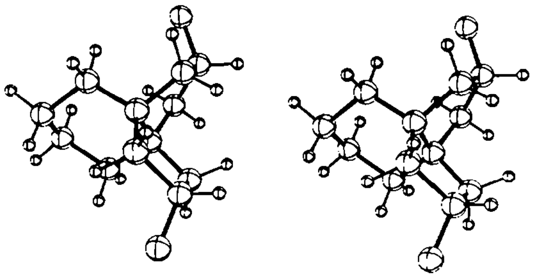
The three molecules in the asymmetric unit of the syn, syn-diol are crystallographically independent of each other. As can be seen from the ORTEP projections of the separate molecules of 1, A and B are more ordered whilst C appears to exist in three different conformations, all occupying the same crystallographic site. Only its major conformation is illustrated in the ORTEP of 1C.

As may be seen in projection 1A, the six-membered ring is a chair. The other rings are best described as envelopes (C_s), the flaps are formed by the two carbons of the conjoining bond of the propellane and the third adjacent to one of these, as is evident from calculation of the torsion angles involved. The unusual folding of the two five-membered rings may be described as head to head.

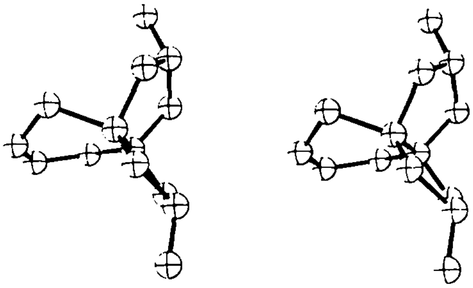
In 1B, however, both five-membered rings exist as half-chairs (C_2), the two-fold axis bisecting the conjoining bond. The six-membered ring is again, as expected, a chair.



ORTEP OF 1A



ORTEP OF 1B

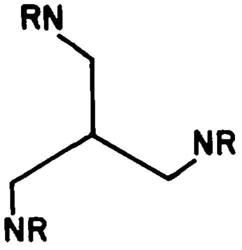


ORTEP OF 1C

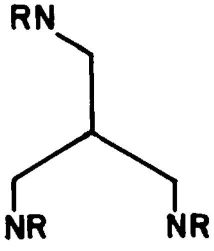
The major conformer of molecule C, shown in projection 1C is unusual. Although the geometry is less accurate due to disorder, it is remarkable to find the six-membered ring as a twist-boat. The five-membered rings are in a flattened C_s conformation with the flaps being formed in each ring by the three atoms excluding those of the conjoining bond. They are arranged head to tail.

DISCUSSION

These structures, containing two cyclopentane rings, are not analogous to those in the 3,7,10-triaza[3.3.3]propellanes carrying various substituents on the nitrogen atoms[4] in which all the five-membered rings have envelope conformations (C_s) in the sense of 4, all the flaps turning in the same direction, rather than in 5. The opposite is true when the carbocyclic compounds are compared to these azapropellanes[4].

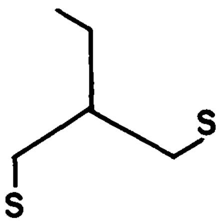


4

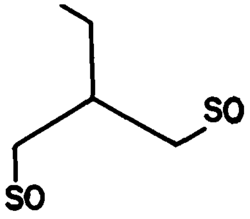


5

Comparison of the three C_2-diols with dithiapropellanes[5] is not as clearcut as in the case of the triazapropellanes. The sulfur-containing compounds sometimes also have C_2 symmetry but the 5-membered rings in 7,10-dithia[3.3.3]propellane 6, 8,11-dithia[4.3.3]propell-3-ene disulfoxide 7 have envelope conformations (C_s) with the flaps pointing in the same direction. It is not clear why the parent of 7, 8,11-dithia[4.3.3.]propell-3-ene itself has C_2 symmetry[5]. The C_s conformations in these cases are, however, different from those of the C_s-diols described herein.



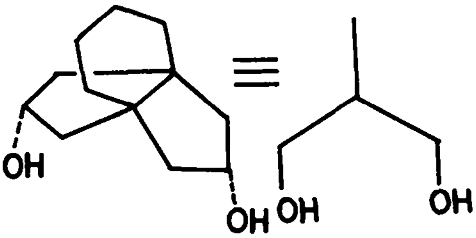
6



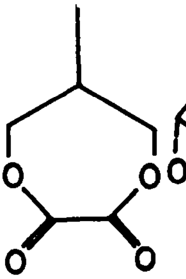
7

Despite the solid state conformation found for each five-membered [4.3.3] diol herein, it is clear that it is not too costly in energy to bring the hydroxyl groups in the anti, anti-diol 8 into a conformation with the OH groups close to each other, since the dilactone 9 is prepared by heating with oxalic acid[3]. The same is true for the anti-anti-diol 10 which gives a cyclic carbonate, 11 albeit under stringent conditions[7].

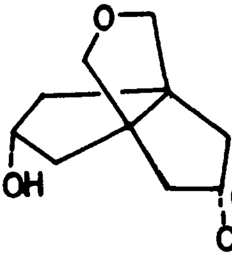
We have calculated from the 400 MHz spectra of the three diols, the coupling constants for the protons in their five-membered rings and the pertinent angles. When the latter solution spectra are compared to the results obtained from the respective crystal structures, we conclude that the five-membered rings are all in the C_s (envelope) conformation as defined above or in the C_2 conformation; it is not possible to distinguish between the two. These results differ from those obtained for bicyclic [3.3.0] compounds where classical C_s envelopes are discerned[8]. Classical C_s envelopes are also found in [3.3.1] propellane derivatives[9].



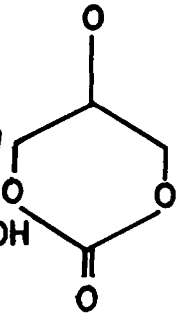
8



9



10



11

The NMR data for 2 and 3 are in accord with the crystallographic data. The NMR spectra of the two isomeric syn- and anti- monoketols corresponding to the above diols have also been measured. We do not have their X-ray structures but the NMR data indicate that each exists either in the C_s conformation as defined for the diols or the C_2 conformation.

In contradistinction to the [4.3.3] diols described herein, the NMR data measured for the [20.3.3] diols[10] indicates the presence of classical C_s envelope conformations for the five-membered rings.

The detailed NMR data may be obtained by writing to the authors.

REFERENCES

1. P. Ashkenazi, M. Kaftory, T. Sayraç, G. Maier, and D. Ginsburg, *Tetrahedron*, XXXX.
2. R. Askani, R. Kirsten, and B. Dugall, *Tetrahedron, 37,* 4437 (1981).
3. S. Bhanumati, P. Ashkenazi, S. Migdal, and D. Ginsburg, *Helv. Chim. Acta, 66,* 2703 (1983).
4. M. Kapon, M. Kaftory, P. Knowles, O. Weinberg, and D. Ginsburg, *Heterocycles,* in press.
5. a) I. Sataty, M. Kapon, M. Kaftory, and D. Ginsburg, *Heterocycles, 17,* 159 (1982).
   b) F.H. Herbstein, P. Askenazi, M. Kaftory, M. Kapon, G.M. Reisner, and D. Ginsburg, *Acta Crystal.,* in press.
6. a) U. Burkert and N.L. Allinger, "Molecular Mechanics", ACS Monograph 177, 1982, American Chemical Society, Washington, D.C. b) Program MM2 (QCPE No. 395).
7. E. Cohen and D. Ginsburg, *Tetrahedron, 40,* 5273 (1984).
8. D. Gardetti, J.-C. Gramain, J. Lhomme, C. Pascard, and T. Prange, *Bull. Soc. Chim. France, II,* 404 (1984).
9. L.W. Jenneskens, L.A.M. Turkenburg, W.H. de Wolf, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas, 104,* 184 (1985).
10. P. Ashkenazi, O. Weinberg, A. Zlota, and D. Ginsburg, *Synthesis,* in press.