for $Pr_2(DPM)_6$ and $Eu_2(DPM)_6$, respectively, very strongly suggests that there is magnetic coupling between the lanthanide ions of the binuclear clusters. The fact that $T_{\text{crit.}} \approx |\theta|$ shows that essentially one exchange interaction is operative in both cases.

The above results are fully consistent with the recent theory of Bleaney[9] for NMR shifts in solutions containing lanthanide chelate reagents. It should be emphasized, however, that this theory is based on the anisotropy in the susceptibility of the *mononuclear*, paramagnetic complex which prevails in solution. Hence, the present study (which was started before Bleaney's paper came to hand) does not provide a critical test of the theory. Experimental confirmation of some of the more fundamental predictions of Bleaney's theory has, very recently, been published by Grotens *et al.*[10]

1. von Ammon, R. and Fischer, R. D. *Angew. Chem.* **84** (1971) 737.
2. Hinckley, C. C. *J. Am. Chem. Soc.* **91** (1969) 5160.
3. Kristiansen, P. and Ledaal, T. *Tetrahedron Letters* **1971** 2817.
4. Kristiansen, P. and Ledaal, T. *Tetrahedron Letters* **1971** 4457.
5. Weissman, S. I. *J. Am. Chem. Soc.* **93** (1971) 4928.
6. Eisentraut, K. J. and Sievers, R. E. *J. Am. Chem. Soc.* **87** (1965) 5254.
7. Erasmus, C. S. and Boeyens, J. C. A. *Acta Cryst.* **B 26** (1970) 1843.
8. Earnshaw, A. *Introduction to Magnetochemistry*, Academic, London, New York 1968.
9. Bleaney, B. *J. Magn. Resonance* **8** (1972) 91.
10. Grotens, A. M., Backus, J. J. M. and de Boer, E. *Tetrahedron Letters* **1973** 1465.

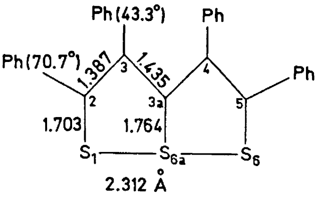
Received June 28, 1973.

The Structure of 2,3,4,5-Tetraphenyl-6a-thiathiophthene

ODDLEIV HJELLUM and
ASBJØRN HORDVIK

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

So far structure studies on 2-phenyl-, 2,4- and 3,4-diphenyl-, and 2,3,4-triphenyl-6a-thiathiophthene have been reported.[1–4]



(I)

The present structure study of 2,3,4,5-tetraphenyl-6a-thiathiophthene (I) has been carried out in order to obtain further information about the degree to which phenyl substituents affect the S – S bonding in 6a-thiathiopthenes; the preliminary results are presented here.

The S(6a) – C(3a) bond in I lies along a crystallographic two-fold axis, and the two halves of the molecule are therefore exactly equal. The bond lengths in the 6a-thiathiophthene system of I are, S(1) – S(6a) = 2.312(2) Å, S(1) – C(2) = 1.703(7) Å, S(6a) – C(3a) = 1.764(10) Å, C(2) – C(3) = 1.387(10) Å, and C(3) – C(3a) = 1.435(8) Å. The phenyl groups in 2 and 3 positions are twisted 70.7° and 43.3° about the respective connecting bonds.

A sample of I was generously supplied by M. Stavaux.[5] The crystals are dark purple and belong to the monoclinic space group $Ic/2$. The cell dimensions are, $a = 20.6370(20)$ Å, $b = 9.7541(8)$ Å, $c = 11.3520(22)$ Å, and $\beta = 92.90(2)°$. There are four molecules per unit cell; density, calculated 1.352 g/cm^3, found 1.36 g/cm^3.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using Mo$K\alpha$ radiation. 1952 reflections were observed within $\theta = 28°$.

The structure was solved by the heavy atom (S) method and refined by full matrix least squares. The *R* factor is 0.04.

The authors are indebted to Dr. M. Stavaux, Faculté des Sciences de Caen, France, for providing a sample of 2,3,4,5-tetraphenyl-6a-thiathiophthene.

1. Bezzi, S. *Gazz. Chim. Ital.* **92** (1962) 859.
2. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 2001; **23** (1969) 1852.
3. Johnson, P. L. and Paul, I. C. *Chem. Commun.* **1969** 1014.
4. Hordvik, A. *Acta Chem. Scand.* **25** (1971) 1822.
5. Stavaux, M. and Lozac'h, N. *Bull. Soc. Chim. France* **1967** 2082.

Received July 11, 1973.

Addition of Hydrogen Chloride and Deuterium Chloride to 2-*exo*-Methoxy-5-norbornene

ERKKI KANTOLAHTI

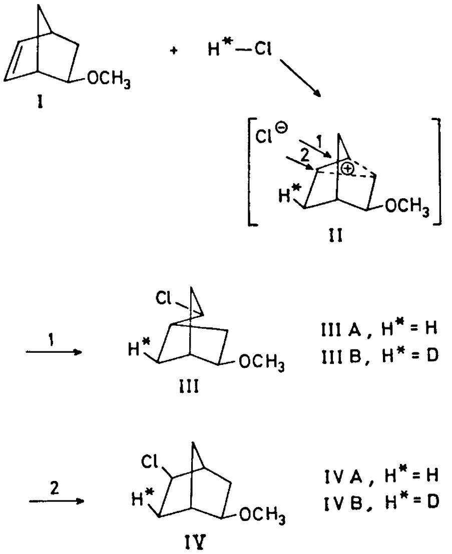
Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland

Additions of hydrogen chloride and deuterium chloride to bicyclic bridge compounds have been very extensively studied.[1-4] In this work the reaction of 2-*exo*-methoxy-5-norbornene (I) with hydrogen chloride in methylene chloride at room temperature has been investigated and found to give two main products, 2-*endo*-methoxy-5-*exo*-chloronorbornane (IIIA) and 2-*exo*-methoxy- 5-*exo*-chloronorbornane (IVA). Addition of deuterium chloride to I under similar reaction conditions also gave two main products, 2-*endo*-methoxy-5-*exo*-chloro-7-*anti*-deuterionorbornane (IIIB) and 2-*exo*-methoxy-5-*exo*-chloro-6-*exo*-deuterionorbornane (IVB). The results were verified by NMR and mass spectroscopy.

Dehydronorbornyl methyl ether (I) was prepared by acid-catalyzed addition of methanol to norbornadiene.[5] The reaction yielded a mixture of I and *exo*-3-methoxynortricyclene (V) in the ratio 1:2. The methyl ethers (I) and (V) were separated by preparative gas chromatography.

exo-Dehydronorbornyl methyl ether (I) was treated with dry, gaseous hydrogen chloride in methylene chloride at room temperature for 24 h. Gas chromatographic analysis showed that the reaction had proceeded almost to completion. The reaction gave a mixture of IIIA and IVA in the ratio 52:48, as measured by the retention times and peak heights. Separation of IIIA and IVA was carried out by preparative gas chromatography.

The reaction of I with deuterium chloride was performed as above, using the labelled, dry gas prepared by the method of Dewar and Fahey.[6] In this case the reaction time was 48 h. The reaction gave a mixture of IIIB and IVB in the ratio 47:53. The stereochemical structure of IIIA, IIIB, IVA, and IVB could be deduced from the NMR spectra of the products of the reactions of I with hydrogen chloride and deuterium chloride. The correspondence of the product ratios reflects the mechanism for the stereochemical course of the additions of hydrogen chloride and deuterium chloride to I. It seems plausible that reaction proceeds *via* the "asymmetrically bridged" cation route:[7-9]



The proton resonance spectrum of 2-*endo*- methoxy-5-*exo*- chloronorbornane