PROPELLANES. LXIII. DITHIA[3.3.n]PROPELLANES AND THEIR $HgCl_2$ COMPLEXES*,†

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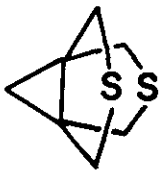
Abstract - Complexes of dithia[3.3.1], dithia[3.3.2], dithia[3.3.3]propellane and of dithia[4.3.3]propellene with $HgCl_2$ have been prepared. X-ray structures have been determined of most of the complexes and of the uncomplexed substrates.

It has been claimed that a "Klammer" effect would be expected in propellanes, with respect to the angle between the planes of two rings common throughout the series and dependent upon the size of the third ring.[1] In the system we have chosen to test this hypothesis two thiophan rings exist. The third ring is either a cyclopropane (*in 1*),[2] a cyclobutane (*in 2*),[2] a cyclopentane (*in 3*)[2] and a cyclohexene (*in 4*).[3] We shall report elsewhere details on the oxidation of some of these and of related chemistry but we wish to report herein the angles found between the



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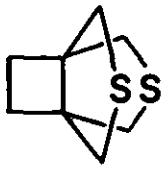

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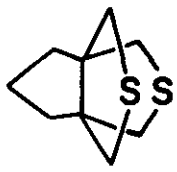

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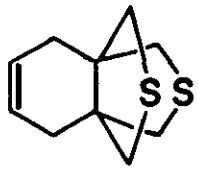

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planes of the 5-membered thioether rings in those compounds whose X-ray structures could be determined.

Unfortunately we have not been able to obtain crystals of *2* suitable for X-ray structural determination; nor were suitable those of its complexes with $HgCl_2$, $HgBr_2$ or $CdCl_2$. Thus we must omit *2* from the comparison, weakening the breadth of the homologous series being compared. Nevertheless, the Table shows that the expected "Klammer" effect does indeed occur in this series, *i.e.* the angle between the two thioether rings decreases with increasing size of the third ring. In other words, lowering the size of the third ring is equivalent to pinching a clamp and the angle

* Dedicated to Professor Kyosuke Tsuda on the occasion of his 75th birthday.

† Part 62. P. Ashkenazi, M. Kaftory, D. Arad, Y. Apeloig and D. Ginsburg, *Helv. Chim. Acta, 64,* 579 (1981).

between the thioether rings increases. The angle for *2* and its $HgCl_2$complex would thus be expected to be *ca* 130° but crystals of *2* are too plastic to give results whilst those of the complex are also unfortunately unsuitable.

Table

Substrate	Angle between thioether rings (°)
1	Molecule A, 138.5; Molecule B, 137.7
3	120.0
4	106.5
1·$HgCl_2$	141.1
3·$HgCl_2$	120.1
4·$HgCl_2$	108.4
4·$CdCl_2$	Molecule A, 105.8; Molecule B, 109.9

Preparation of $HgCl_2$ complexes. - Equimolar solutions of substrate (*1-3*) and $HgCl_2$ (0.33 mmol) in absolute EtOH (*4* in MeOH) were mixed with stirring and were warmed when necessary to clarify the solution. After standing for a few days, crystals which had formed were collected, dried and analyzed.

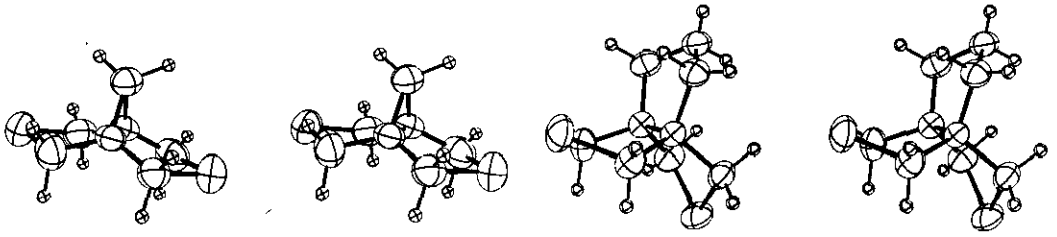
1: M.p. 216-218°(dec). (Found: C, 19.76: H, 2.74. $C_7H_{10}S_2Cl_2Hg$ requires C, 19.56; H, 2.35%). IR(KBr): 1440, 1180, 940 cm^{-1}.

2: M.p. 203-204°. (Found: C, 21.59; H, 2.98. $C_8H_{12}S_2Cl_2Hg$ requires C, 21.65; H, 2.73%). IR(KBr): 1420, 1240, 738 cm^{-1}.

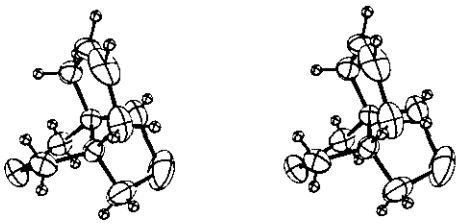
3: M.p. 167-190°. (Found: C, 23.50; H, 3.18. $C_9H_{14}S_2Cl_2Hg$ requires C, 23.61; H, 3.08%). IR(KBr): 1425, 1205, 745 cm^{-1}.

4: M.p. 186-187°. (Found: C, 25.51; H, 3.52; S, 13.66. $C_{10}H_{14}S_2Cl_2Hg$ requires C, 25.56; H, 3.00; S, 13.65%). IR(KBr); 1440, 1225, 710 cm^{-1}.

The ORTEP representations of *1*, *3*, *4* are shown below. The X-ray structural data will be published elsewhere.[4]



1 *3*



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It is of interest to note that the cyclohexene ring in *4* assumes the half-chair conformation albeit in other propellane molecules containing cyclohexene rings these may assume the boat conformations.[5] [4.4.4]Propella-3,8,12-triene has all three cyclohexene rings in the half-chair conformation.[6] The result for *4* is therefore not surprising as this affords another case of analogy between the carbocyclic compound and one in which a -CH=CH- entity is replaced by S.

References

1. We do not find the reference for this term but it is not our original idea. Perhaps we remember the word Klammer from a conversation, possibly with Prof. H.-D. Martin. *Cf.* "Propellan-effekt", H.-D. Martin and M. Hekman, *Chimia, 28,* 12 (1974).
2. We thank Prof. Dr. K. Weinges, Heidelberg, for samples of these compounds.
3. J. Altman, E. Babad, J. Pucknat, N. Reshef and D. Ginsburg, *Tetrahedron, 24,* 975 (1968).
4. By M. Kapon (*1, 3*) and M. Kaftory (*4*).
5. E.g. M. Kaftory and J.D. Dunitz, *Acta Cryst., B32,* 617 (1976). M. Kaftory, J.D. Dunitz and O.S. Mills, *Ibid., B32,* 619 (1976).
6. O. Ermer, R. Gerdil and J.D. Dunitz, *Helv. Chim. Acta, 54,* 2476 (1971).

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