

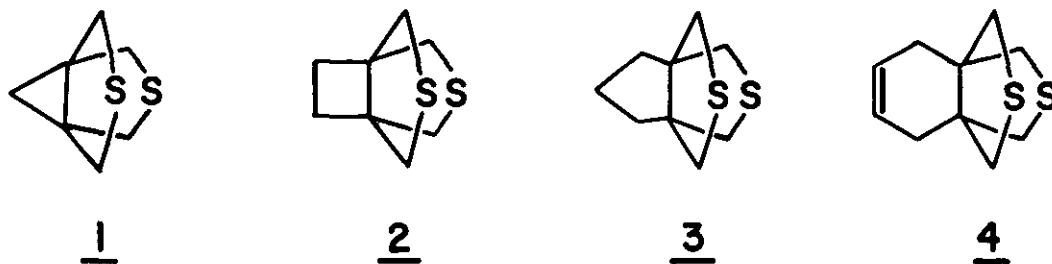
PROPELLANES. LXIII. DITHIA[3.3.n]PROPELLANES AND THEIR HgCl_2 COMPLEXES^{*,†}

Ishai Sataty, Moshe Kapon, Menahem Kaftory and David Ginsburg

Department of Chemistry, Israel Institute of Technology, Haifa

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 thio-phan 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



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 ($^\circ$)
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.

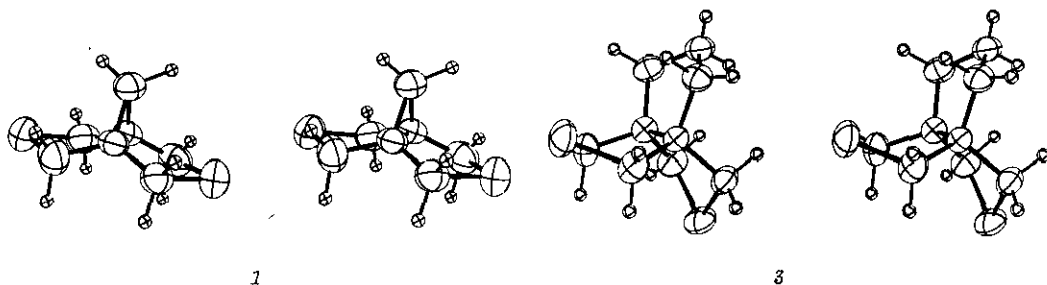
1: M.p. $216-218^\circ$ (dec). (Found: C, 19.76; H, 2.74. $\text{C}_7\text{H}_{10}\text{S}_2\text{Cl}_2\text{Hg}$ requires C, 19.56; H, 2.35%). IR(KBr): 1440, 1180, 940 cm^{-1} .

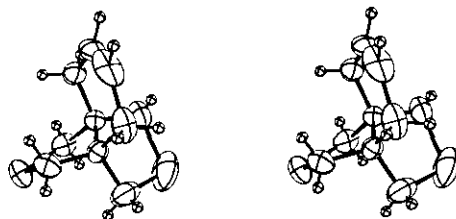
2: M.p. $203-204^\circ$. (Found: C, 21.59; H, 2.98. $\text{C}_8\text{H}_{12}\text{S}_2\text{Cl}_2\text{Hg}$ requires C, 21.65; H, 2.73%). IR(KBr): 1420, 1240, 738 cm^{-1} .

3: M.p. $167-190^\circ$. (Found: C, 23.50; H, 3.18. $\text{C}_9\text{H}_{14}\text{S}_2\text{Cl}_2\text{Hg}$ requires C, 23.61; H, 3.08%). IR(KBr): 1425, 1205, 745 cm^{-1} .

4: M.p. $186-187^\circ$. (Found: C, 25.51; H, 3.52; S, 13.66. $\text{C}_{10}\text{H}_{14}\text{S}_2\text{Cl}_2\text{Hg}$ 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





4

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 $-\text{CH}=\text{CH}-$ 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).

Received, 11th August, 1981