Tetrahedron Letters No.52, pp. 5265-5270, 1967. Pergamon Press Ltd. Printed in Great Britain.

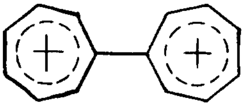
THE DITROPYLIUM DICATION

I.S. Akhrem, E.I. Fedin, B.A. Kvasov, and M.E. Vol'pin
Institute of Organo-Element Compounds, Academy of Sciences, Moscow, USSR

(Received in UK 26 July 1967)

In recent years the synthesis and properties of di- and polycarbonium ions have been the subject of many investigations [I-I2]. The di- and tri-tropylium cations with the seven-membered rings separated by a benzene ring have recently been obtained by Murray and Caplan [4,5].

We now report the synthesis of the ditropylium dication (I) in which the two positively charged rings are directly bonded together.

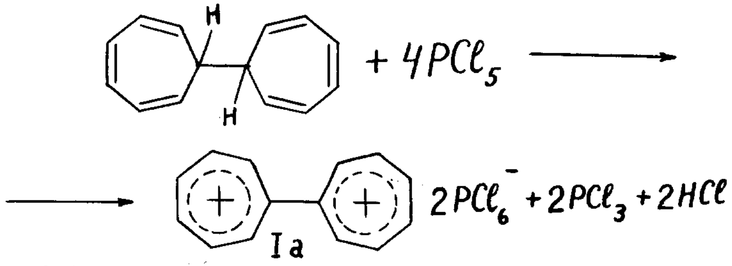

I .

A salt of dication I was obtained by heating ditropyl with a four-fold excess of phosphorus pentachloride in dry carbon tetrachloride for 30 min. at 50°C. A red[x] solid was formed which was extremely sensitive to air, but stabler in dry argon. When carefully washed with CCl_4 under dry argon and vacuum-dried the compound has the composition of the dication salt with two PCl_6^- anions (Ia). Found: C, 24.96, 25.II; H, 2.II, I.90; P, 9.I7, 9.37. $C_{I4}H_{I2}P_2Cl_{I2}$ requires: C, 25.I8; H, I.8I; P, 9.29 %. Thus phosphorus pentachloride had abstracted two hydride ions from ditropyl to form ditropylium hexachlorophosphate.[xx]

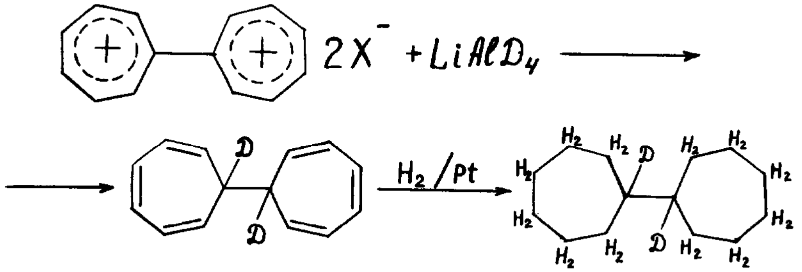
---

[x] The red colour of the solid inconsistent with its UV-spectrum (see below) is probably due to some minor impurities.

[xx] It has been reported [I3] that ditropyl reacts with $(C_6H_5)_3C^+SbCl_6^-$ to form cycloheptatrienyltropylium salt which is rapidly converted into benzylcycloheptatriene. However, we failed to find a similar reaction with PCl_5.

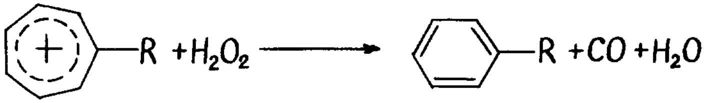


Reduction of Ia with excess of $LiAlH_4$ in ether followed by hydrogenation (on Pt black) yielded dicycloheptyl. With $LiAlD_4$ as reducing agent hydrogenation led to dideuteriodicycloheptyl (weight incsrease of combustion water: found 7000–7200 γ; calc. for $C_{14}H_{24}D_2$: 7629 γ). Thus the reduction scheme may be written as follows (the position of deuterium being indicated tentatively):

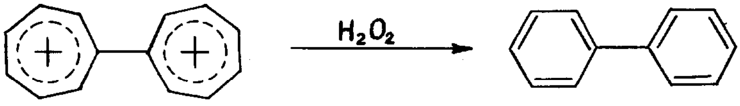


Thus Ia contains two seven-membered rings directly bonded to each other, and the addition of two deuterium atoms confirms the existence of two positive charges.

The structure was also substantiated by the characteristic reaction of tropylium salts with hydrogen peroxide [15]:



It was thereby found that the action of H_2O_2 on Ia in H_2SO_4 yielded diphenyl (Ia was dissolved in 80% H_2SO_4 and treated with 3-fold excess of 15% H_2O_2):



An NQR investigation of a suspension of Ia in CCl_4 revealed no covalent C-Cl bonds.

PMR spectrum* of the salt Ia dissolved in 100% H_2SO_4 or $BF_3{\cdot}H_2O$ was a narrow singlet, δ 9.55 ppm from TMS, shifted by 0.25-0.3 ppm downfield with respect to tropylium bromide. The singlet of the ditropylium dication was broader (~7 cps) than the singlet of tropylium monocation, but the signal was not split at 100 Mc/s. That the signal at δ =9.55 arises from aromatic protons attached to sp^2-C atom was confirmed by the ^{13}C-H satellites (in $D_2O.BF_3$ solution)**. These are broad unresolved multiplets with complex structure ($J_{^{13}C-H}$ ~ 130-190 cps) and with a centre about 170 cps (for tropylium cation $J_{^{13}C-H}$ = 172 cps [17]). The greater width and complex structure seems to be due to the increase in the number of positions and interactions of ^{13}C atoms with protons in the more complex molecule of dication***.

The UV and PMR spectra of Ia in various solvents indicate that the ditropylium dication is stable only in strongly acidic media. The solutions in concentrated sulfuric, phosphoric, or trifluoroacetic acids reveal a UV absorption maximum at 311-313 mμ, i.e. the ditropylium dication absorption is shifted by 40 mμ towards the long-wave region as compared with unsubstituted tropylium. Solutions of Ia in weaker acids (acetic acid or sulfuric acid below 60%) show a strong irreversible bathochromic shift (λ_{max} = 345-360 mμ) which may be attributed to irreversible reaction of the dication with nucleophiles. The disappearance of the 311-313 mμ band is accompanied by changes in the PMR spectrum: the narrow singlet of the dication at δ 9.55 ppm changes to a broad multiplet shifted upfield indicating that the positive charge on the carbon atoms is decreased.

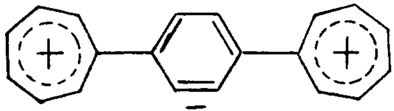
---

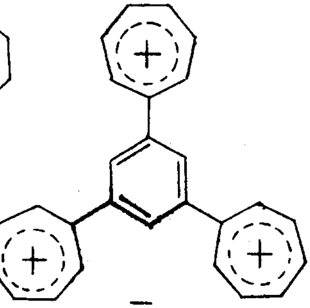
* PMR spectra were taken on Hitachi H-60 spectrometer.

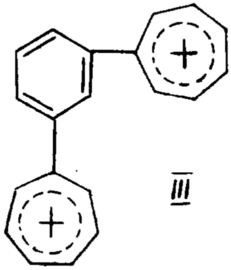
** ^{13}C-H satellites were investigated using a sample with a natural ^{13}C content (1.1%). The spectra were recorded on a spectrum accumulator based on a multichannel analyzer LP 4000 of Finnish Cable Works [16].

*** We have found the same effect in diphenyl and benzene, the broadening of the sidebands being almost twofold.

The fact that the dication exists only in strongly acidic media is confirmed by chemical evidence. The yield of diphenyl from the dication subjected to an action of H_2O_2 in concentrated sulfuric acid is three times that obtained in trifluoroacetic acid solution, and in 20% sulfuric acid or in methyl cyanide only traces of diphenyl are formed. Thus the ditropylium dication can exist only in strong acidic media ($H_0 \geqslant -4.5$), whereas tropylium ion is stable in aqueous acids and in polar organic solvents. Hence the electrophilicity of the ditropylium dication is much greater as compared with that of the monocation. The stability of the dication I is also much lower than that of polycations (II-IV) [4,5] with the tropylium rings separated by a benzene ring:


II

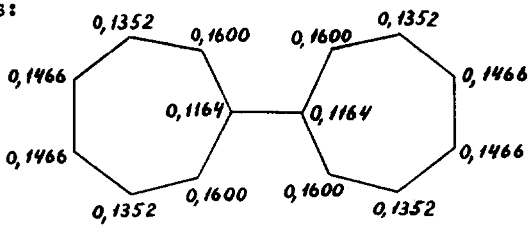

IV


III

Increased electrophilicity of the dication I is in agreement with the fact that the PMR signal of tropylium protons of I is to lower field (δ = 9.55 ppm) than the tropylium signals of II (δ = 8.69), III (δ =8.68) and IV (δ = 8.77).

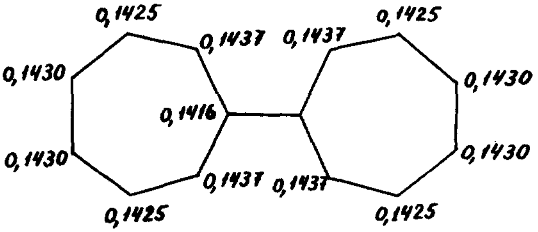
It is to be noted that despite the evident non-equivalence of the hydrogens of I, its PMR spectrum is a distinct singlet unresolved on the 100 Mc instrument. In II-IV complex multiplets were observed from tropylium rings.

Hückel M.O. calculation of a planar model of the ditropylium dication showed significant variation of effective electron charges localized on different carbon atoms:

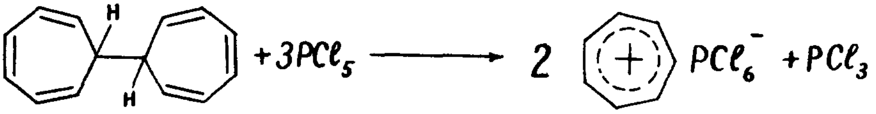


However, mutual repulsion of the ortho-hydrogens would not permit this cation to be planar. The steric repulsion might be expected to be stronger than in the diphenyl (dihedral angle 42°) due to the smaller distance between the ortho-hydrogens and to mutual repulsion of the charged ortho C and H atoms.

Calculation of non-planar models of dication I shows that an increase of the dihedral angle equalizes effective charges, the equalization being almost complete when this angle exceeds 78°. This result suggest a possible explanation for the equivalence of protons in the PMR spectrum[x]. The charge distribution when the dihedral angle equals 78° is as follows:



The action of phosphorus pentachloride on ditropyl leading to the ditropylium dication I is accompanied by an interesting side-reaction, namely the rupture of the ditropyl C–C bond and formation of tropylium hexachlorophesphate:



PMR data showed a 7:I ratio of the di- and mono-cation formed. Besides PCl_5, other electrophilic reagents such as concentrated sulfuric acid, bromine, etc.

---

[x] We have estimated the difference in the shielding of the α-, β- and γ-protons according to G. Fraenkel et al.[I8] This estimation demonstrates either a conformation of the dication with rings normal to one another, or such a hindered rotation whose period is much greater than the lifetime of the planar conformation.

are able to cause rupture of the C–C bond and formation of the tropylium cation. However, only PCl_5 leads to the dication.

Acknowlegments. We wish to thank Mrs. N.P. Gambaryan for her valuable discussion of quantum-mechanical data, A.V. Tootkevich for M.O. calculation and G.K. Semin and Miss T.A. Babushkina for NQR spectra.

REFERENCES

I. H.Hart and J.S.Fleming, Tetrahedron Letters, 983 (I962).

2. H.Hart, J.S.Fleming, and J.L.Dye, J.Am.Chem.Soc., 86, 2079 (I964).

3. H.Volz and M.H.Volz de Lecea, Tetrahedron Letters, I87I (I964); E.C.Kirby and D.H.Reid, J.Chem.Soc., 3579 (I96I).

4. R.W. Murray and M.L.Kaplan, Tetrahedron Letters, 2903 (I965).

5. R.W. Murray and M.L.Kaplan, Tetrahedron Letters, I307 (I967).

6. N.Wiberg and J.W.Buchler, Angew.Chem., 74, 490 (I962).

7. R.Wizinger, Chem.Ber., I377 (I927).

8. R.E.Buckles and N.A.Meinhart, J.Am.Chem.Soc., 74, II7I (I952).

9. R.E.Buckles and W.D.Womer, J.Am.Chem.Soc., 80, 5055 (I958).

IO. R.E. Buckles, R.E.Erickson, J.D.Snyder, and W.B.Person, J.Am.Chem.Soc., 82, 2444 (I960).

II. D.H.Anderson, R.M.Elofson, H.S.Gutowsky, S.Levine, and R.B.Sandin, J.Am.Chem.Soc., 83, 3I57 (I96I).

I2. H.Hart, T.Sulzberg, and R.R. Rafos, J.Am.Chem.Soc., 85, I800 (I963); a reference to unpublished data of H.Hart and H.Tanida.

I3. H.J.Dauben and D.Bertelli, a private communication in the paper published in J.Org.Chem., 28, 262 (I963).

I4. M.E.Vol'pin, D.N.Kursanov, and V.G.Dulova, Tetrahedron, 8, 33 (I960).

I5. J.W.Wilt and D.Piszkiewicz, Chem. and Ind., I76I (I963).

I6. B.A.Kvasov, "Radiospectroscopy", vol. 5, Pierm', I967 (in Russian).

I7. H.Spiesecke and W.G.Schneider, Tetrahedron Letters, 468 (I96I).

I8. G.Fraenkel, R.E.Carter, A.McLachlan, and J.H. Richards, J.Am.Chem.Soc., 82, 5846 (I960).