

SULPHONESTER PODANDS. A NEW CLASS OF CLATHRATES.

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ABSTRACT. The new clathrates based on di- and triethylene glycol ether of phenol sulphonic acid-4 and 1-naphtol-sulphonic acid-4 are presented. The four series of p-substituted phenol esters were obtained /Fig.1/. Generally, only the derivatives of triethylene glycol ether of naphtholsulphonic acid give complexes with benzene or toluene /Tab.I/, but not with smaller molecules of acetonitrile or nitromethane.

INTRODUCTION

The design and synthesis of new classes of compounds able to form clathrates /clathrands/ and also other species complexing uncharged molecules are the subject of many investigations /1-5/.

In our investigations of naphthalene crown-type compounds derivatives of aromatic sulphonic acids we have obtained several cyclic sulphonamides /6,7/.

In this paper we report our results of synthesis and properties of sulphonester clathrands.

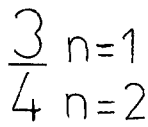
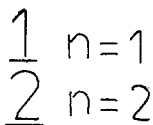
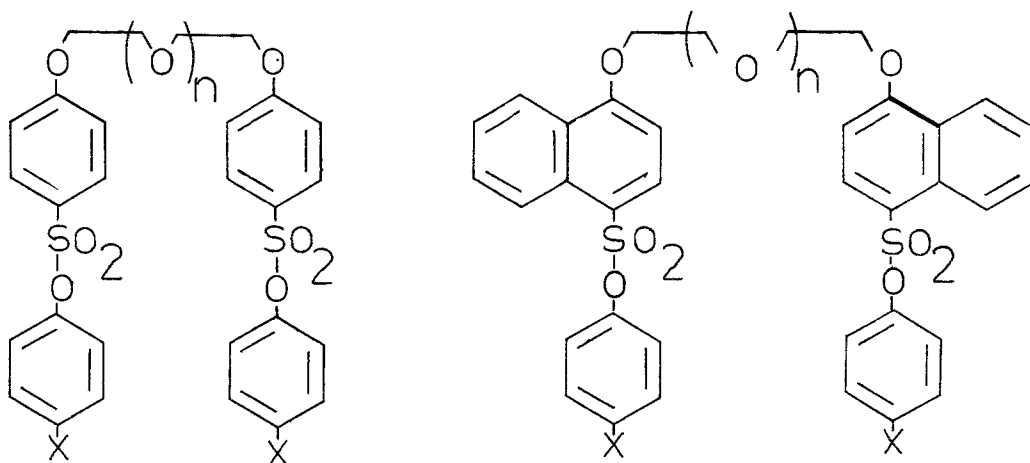
RESULTS AND DISCUSSION

The compounds obtained recently are shown in Fig.1. The compounds were obtained by direct esterification of phenols by bis-sulphochloride using triethylamine as a base. The reaction proceeds smoothly and give good yields. However, the use of chloroform in the naphthol series was necessary to dissolve the chloride. We have observed that some of the sulphonesters are able to form complexes with solvent molecule/s/ by simple recrystallisation from benzene or toluene. The complex formation and stoichiometry was checked by ¹H-NMR spectroscopy.

The results are shown in TAB.I.

TAB.II presents physico-chemical data of non-clathrate compounds.

Almost all of the phenolic ethers are oil substances.



- a X = H b X = CH₃
 c X = OCH₃
 d X = NO₂

FIG.1

In these series only the compound 1d can be obtained in crystalline state. However, triethylene ether 2a forms oil, which slowly changes to glassy solid after a few weeks.

It is very interesting that complex formation can generally be established only in the case of triethylene glycol ethers of naphthol sulphonic acid /compounds 4a-d/. In four series of compounds only two exceptions were found, namely the sulphonesters 1d and 3d. Both compounds bear -NO₂ group in phenol ring.

It seems, that nitro group is responsible for the formation of complexes, although the complex 3d-PhCH₃ is not stable. If it is true, it is not clear, why the sulphonester 2d

does not give a clathrate.

The aliphatic chain in the diethylene analogs is probably too short to enable the formation of the enough large cavity in a crystal lattice. On the other hand our attempts to obtain complexes with smaller molecule/s/ of nitromethane and/or acetonitril failed in all cases.

The stoichiometry of complexes with benzene is 1:2 / the ester 4c gives 1:1/, and those of toluene 1:1. Based on NMR spectra no simple stoichiometry could be detected for the complex 4a-PhCH₃.

The complexes with benzene and toluene are stable for several months.

The syntheses of other examples and crystallographic studies will be published in the future.

TAB. I			PhH	mp.	PhCH ₃	mp.
Comp.	mp of free comp./°C/					
1	a	83-6	-		-	
	b	oil	-		-	
	c	oil	-		-	
	d	oil	-		-	
2	a	oil	-		-	
	b	oil	-		-	
	c	oil	-		-	
	d	64-5	1 : 1	82-3	1 : 1	44-5
3	a	123/clear. 146/	-		-	
	b	147-8	-		-	
	c	181-3	-		-	
	d	105 /clear. 123/	-		1 : 1	110
4	a	120-1	1 : 2	120-2	x	94
	b	117-9	1 : 2	76-7	1 : 1	92
	c	75-6	1 : 1	95-6	1 : 1	160-1
	d	141-2	1 : 2	138-9	1 : 1	130

x - no simple stoichiometry could be detected

EXPERIMENTAL

The NMR spectra were taken on TESLA 80 MHz and JEOL PS-100 /90 MHz/ apparatuses. The melting points were measured in a Buchi SMP-20 apparatus in capillary tube and are not corrected. The IR spectra were measured as a film or

in KBr pellets on SPECORD 78.

All NMR spectra were measured in DMSO- d_6 solution at room temperature with HDMSO as an external standard. DMSO was chosen to avoid overlapping. However, in some cases $/X=OCH_2/$ an increased measurement temperature was necessary to shift H_2O signal.

All compounds were dried by exposure to air for one day and in vacuo at 30° for the next day.

The changes in NMR spectra of free and solvated compounds were not significant / no more than 0.05 ppm/.

The purity of compounds was checked by TLC.

All the compounds were synthesized by one of the following methods:

Method A for compounds 1 and 2:

5 mM of the bis-sulphochloride, 10 mM of the appropriate phenol and 1.4 ml of triethylamine was stirred for 3 hours. in 50 ml of benzene. The amine hydrochloride was filtrated off. The solution was chromatographed on alumina /basic, activity I/ with benzene as eluent. The solvent was distilled of under diminished pressure.

Method B for naphtholsulphonic derivatives 3 and 4:

The amounts of starting materials as in the method A were stirred in 100-150 ml of chloroform for 3 hours.

The solution was washed with water, then with 5% HCl and again with water, dried over $MgSO_4$ and chromatographed silica gel using $CHCl_3$ as eluent.

The complex compounds 3 were obtained by crystallization from benzene or toluene.

TAB. II

Comp.	IR $/ cm^{-1} /$	NMR $/ ppm /$	Analysis		Yield $/ \% /$
			Theor.	Found	
1a	1590, 1450, 1365, 1265, 1205, 1165, 1150, 860, 845	7.95 d, $J=8$ 7.65-7.12 m /12 H/ 4.39 m /4H/ 4.17m 4H	C=58.94 H=4.59 S= 11.24	58.67 4.66 11.30	62
1b	1590, 1500, 1360, 1260, 1190, 1160 1090, 860, 840	7.92d, $J=8Hz$ 4H, 7.33dd, $J=8Hz, 8H, 7.08$ d, $J=8Hz, 4H, 4.41$ m, 4H, 4.05m 4H 2.43 s, 6H	C=60.19 H= 5.05 S= 10.71	59.92 5.35 11.02	65
1c	1590, 1505, 1370, 1265, 1250, 1200, 1170, 1100, 680,	7.92d, $J=9Hz$, 4H, 7.37d, $J=9Hz, 4H, 7.12$	C=57.13 H= 4.79 S= 10.17	57.29 4.54 10.44	60

TAB. II-continued

Comp.	Ir	NMR	Analysis		Yield
			Theor.	Found	
		s, 8H, 4.45m 4H 4.06m, 4H, 3.93 s, 6H			
1d	1595, 1545, 1440 1365, 1350, 1260 1170, 870, 845	8.42d J=9Hz 4H, 7.97d J= 8Hz 4H 7.52 d, J=8Hz 4H 7.36d J=9Hz 4H, 4.43m 4H 4.08m 4H	C=50.91 H= 3.66 S= 9.71 N= 4.24	50.84 3.84 9.60 4.08	70
2a	1595, 1490, 1370 1260, 1200, 1170 1150, 860	7.95d J=8Hz 4H 7.65-7.12 m 12H, 4.37m 4H, 4.18m 4H 3.87s 4H	C=58.62 H= 4.92 S=10.43	58.94 5.45 10.76	74
2b	1590, 1495, 1365 1260, 1190, 1170 1085, 860, 840	7.95d J=8Hz 4H 7.35dd J≈8Hz 8H 7.09d J=8Hz 4H 4.40m 4H 4.0 m 4H 3.83 s 4H 2.30 s 6H	C=59.80 H= 5.33 S= 9.98	58.41 5.61 10.0	79
2c	1595, 1500, 1375 1260, 1250, 1200 1170, 1100, 870 845	7.95d J=9Hz 4H 7.37d J= 9Hz 4H, 7.13 bs 8H, 4.42 m 4H, 3.92m 4H, 3.92 s 6H 3.85 s 4H	C=57.13 H= 5.08 S= 9.53	57.19 5.25 9.78	74
2d	1590, 1540, 1500 1440, 1370, 1350 1260, 1170, 860 840	8.43d J= 10Hz 4H, 7.98d J= 8Hz 4H, 7.50d J=10 Hz 4H, 7.46d J=8Hz 4H, 4.28m 4H 4.00m 4H, 3.82 s 4H	C=51.13 H= 4.00 S= 9.10 N= 3.98	51.17 4.07 9.42 3.68	60
3a	1590, 1580, 1505 1360, 1260, 1250 1190, 1140, 1090 860, 850	8.80d J=8.5Hz 2H, 8.52d J= 8.5Hz 2H, 8.30-7.71m 6H 7.41m 6H 7.07 m 6H 4.52m 4H 4.11m 4H	C=64.46 H=4.51 S= 9.56	64.22 4.80 9.86	77

TAB. II-continued

Comp.	IR	NMR	Analysis		Yield
			Theor.	Found	
3b	1590, 1580, 1500 1360, 1255, 1175 1140, 1080, 860 830	8.82d J=8Hz 2H, 8.53d J=8Hz, 2H 8.20d J= 9Hz 2H, 8.07-7.75m 4H, 7.18d J= 8Hz 6H, 6.91 d J=8Hz 4H 4.58m 4H, 4.25 m4H, 2.32 s 6H	C=65.13	65.33	67
3c	1590, 1575, 1505 1500, 1360, 1265 1250, 1190, 1170 1140, 1095, 865 845	8.82d J=8.5Hz 2H, 8.55d J= 8.5Hz 2H, 8.18 d J=8Hz 2H, 8.05-7.55 m 4H, 7.30-6.95 m 10H 4.50 m 4H, 4.10 m 4H 3.80 s 6H	C=62.45 H= 4.69 S= 8.77	62.00 4.41 9.04	60
3d	1605, 1580, 1510 1360, 1345, 1200 1170, 1130, 1190 860	8.80d J=8Hz 2H 8.55d J=8Hz 2H 8.31d J=9Hz 4H 8.28d J=9Hz 2H 8.15-7.68m 4H 7.37d J=9Hz 4H 7.27d J=9Hz 2H 4.65m 4H 4.30m 4H	C=56.84 H= 3.71 S= 8.43 N= 3.68	56.76 4.08 8.24 3.45	72
4a	1585, 1570, 1505 1375, 1365, 1275 1200, 1190, 1175 1085, 960, 850	8.82d J=8.5Hz 2H, 8.52d J= 8.5Hz 2H, 8.30- 7.71m 6H, 7.41 m 6H, 7.07m 6H 4.52m 4H, 4.11 m 4H, 3.92s 4H	C=63.85 H= 4.79 S= 8.97	63.49 4.62 8.75	89
4b	1590, 1580, 1500 1360, 1250, 1175 1140, 1080, 960 850	8.83d J=9Hz 2H 8.51d J=8Hz 2H 8.17d J=8Hz 2H 8.00-7.75 m 4H 7.21-6.81 m 10 H, 4.45m 4H, 4.17m 4H, 3.88 s 4H 2.25 s 6H	C=64.67 H= 5.16 S= 8.63	64.83 5.24 8.82	79
4c	1590, 1570, 1500 1370, 1270, 1250 1190, 1160, 1140 1090, 960, 860	8.82d J=9Hz 2H 8.55d J=9Hz 2H 8.18dd J=8Hz 2H	C=62.00 H= 4.94 S= 8.28	61.85 5.31 8.22	82

TAB. II-continued

Comp.	IR	NMR	Analysis		Yield
			Theor.	Found	
		8.05-7.55m 4H			
		7.30-6.95m 10H			
		4.50m 4H, 4.10			
		m 4H, 3.91s 4H			
		3.80 s 6H			
4d	1600,1580,1510	8.85d J=8Hz 2H	C=56.71	56.70	62
	1365,1340,1200	8.55d J=8Hz 2H	H= 4.01	4.50	
	1170,1135,1190	8.30d J=9Hz 4H	S= 7.97	7.91	
	865	8.26d J=9Hz 2H	N= 3.48	4.58	
		8.15-7.66m 4H			
		7.37d J=9Hz 4H			
		7.27d J=9Hz 2H			
		4.65m 4H, 4.30			
		m 4H, 3.90s 4H			

ACKNOWLEDGEMENTS

This work was partly supported by Polish Academy of Science

REFERENCES

- 1/ for example D.McNicol, J.J.Kendrick, D.R.Wilson - Chem.Soc.Rev. 1978 7/1/65
- 2/ "Host-guest Complex Chemistry/ F.Vogtle /Eds/
- 3/ F.Vogtle, H.-G.Lohr, H.Puff, W.Schuh - Angew.Chem.Int. Ed. 1983 22/5/ 409
- 4/ W.Rasshofer, F.Vogtle -Tetrahedron Letters 1978 /3/ 309
- 5/ F.Vogtle, W.M.Muller - Chem.Ber. 1980 113 2081
- 6/ L.Prajer-Janczewska, H.Bartosz-Bechowski -Second International Symposium On Clathrate Compounds and Molecular Inclusion Phenomena, Parma 30.08-3.09.82
- 7/ L.Prajer-Janczewska, H.Bartosz-Bechowski - Pol.J.Chem. 1984 in print