Formation and X-Ray Analysis of the Supramolecular System Obtained by the Complexation of (*E*)-9,10-Diphenyl-2,5,8,11,14,17-hexaoxaoctadec-9-ene with Sodium Thiocyanate. A New Coordination Type for SCN^-

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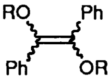
The synthesis and X-ray structure of (*E*)-9,10-diphenyl-2,5,8,11,14,17-hexaoxaoctadec-9-ene **1** and that of its complex with sodium thiocyanate are described. The free ligand is centrosymmetric with the phenyl ring twisted out of the ethylenic plane by 39° and a rather extended conformation of the polyether chain. The complex of **1** with NaSCN has been obtained; its solid state structure is quite unique. There are two (**1A** and **1B**) independent supramolecular systems $\mathbf{1}\cdot 2NaSCN\cdot 2H_2O$ with similar geometries in the asymmetric part of the unit cell. Each system is arranged in infinite independent chains with 'organic' and 'inorganic' parts that alternate. In one of these systems (**1B**), disorder of the C=C double bond is observed. In each complex unit, the polyether side arms in the *trans* position are coordinated each to a different Na^+. The conformation of the polyether chain is $(ag^{\pm}a)(g^{\mp}g^{\mp}a)$ in three cases but the same as in the free ligand $(ag^{\pm}a)(ag^{\pm}g^{\pm})$ in the fourth. Both Na^+ cations have a sixfold octahedral coordination: two O of the polyether, three N of the SCN^- and one O of a water molecule are the ligating atoms of Na(1) while one N of an anion is replaced by a second water molecule for Na(2). In this complex, one observes a bridging of one SCN^- between two cations and even between three cations for the second SCN^-; this last kind of threefold bridging has never been reported before for the thiocyanate anion.

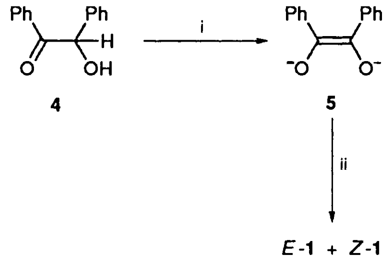
After natural or synthetic oxygenated macrocycles were discovered to be powerful ligands, numerous molecular associations of the host–guest type were studied while the coordination chemistry of alkaline and other cations was developed.[1] With the aim of studying their complexing properties, some α,α′-disubstituted by oxygenated side chains stilbene derivatives have been synthesized **1–3**. The interest in the molecules studied here arises from their potential photoreversible complexation[2] and ionophoric properties.[3]



E,Z-**1** R = $[CH_2CH_2O]_2CH_3$
E,Z-**2** R = $CH_2CH_2OCH_3$
E,Z-**3** R = OCH_3

The synthesis and the solid state structure of (*Z*)-α,α′-di(2-methoxyethoxy)stilbene **2** and that of its complex with sodium thiocyanate have been described.[4] A 1 : 1 complex was observed; the cation was hexa-coordinated to the four ether oxygens, to the anion through N, and to a water molecule forming a distorted octahedron. The X-ray structure of (*Z*)-α,β-dimethoxystilbene **3** has also been reported.[5]

We report here the synthesis and the cation binding properties of (*E*)-9,10-diphenyl-2,5,8,11,14,17-hexaoxaoctadec-9-ene **1**. In our synthesis, **1** is obtained together with its *Z* isomer by bis-*O*-alkylation of benzoin **4** with tosylate of 2-(methoxyethoxy)ethanol **6**. The solvent is 1,4-dioxane. The stilbenediol dianion **5** is generated with sodium hydroxide in the presence of a phase-transfer catalyst *e.g.* benzyltriethylammonium chloride (BTACl).[6] The dianion **5** is dialkylated easily by various alkylating agents.[7] *E*-**1** and *Z*-**1** are obtained in a 6 : 4 mixture which was separated by column chromatography (Scheme 1).



Scheme 1 *Reagents:* i, $2OH^-$, BTACl; ii, **6**

The complexing ability of the *E*-**1** was demonstrated by the isolation of the complex formed between this compound and sodium thiocyanate. The complex of the *Z*-**1** with sodium thiocyanate was not obtained. Both new structures of the free ligand *E*-**1** and of its complex with sodium thiocyanate $\mathbf{1}\cdot 2NaSCN\cdot 2H_2O$ are characterized by ^1H and ^{13}C NMR, FT-IR and mass spectrometry, and they are proven by X-ray analysis as described in the following discussion.

Discussion

A stereoscopic view of the free ligand **1**, showing the numbering of the atoms is presented in Fig. 1.[8] Selected bond distances and angles are compared for the free ligand and the complex in Table 1, the torsion angles in the polyether are listed in Table 2.

The molecule of the free ligand **1** is centrosymmetric and the centre of symmetry coincides with a crystallographic centre (at 000) of the unit cell, so that there is only one half molecule in the asymmetric unit. The C=C bond length of 1.333(2) Å is in agreement with the values of 1.328(3) Å observed in (*Z*)-α,β-dimethoxystilbene **3**[5] and that of 1.343(3) Å in (*Z*)-α,α′-di(2-methoxyethoxy)stilbene **2**.[4b] The phenyl ring is twisted out the ethylenic bond plane by 39°. By comparison, in the *Z*

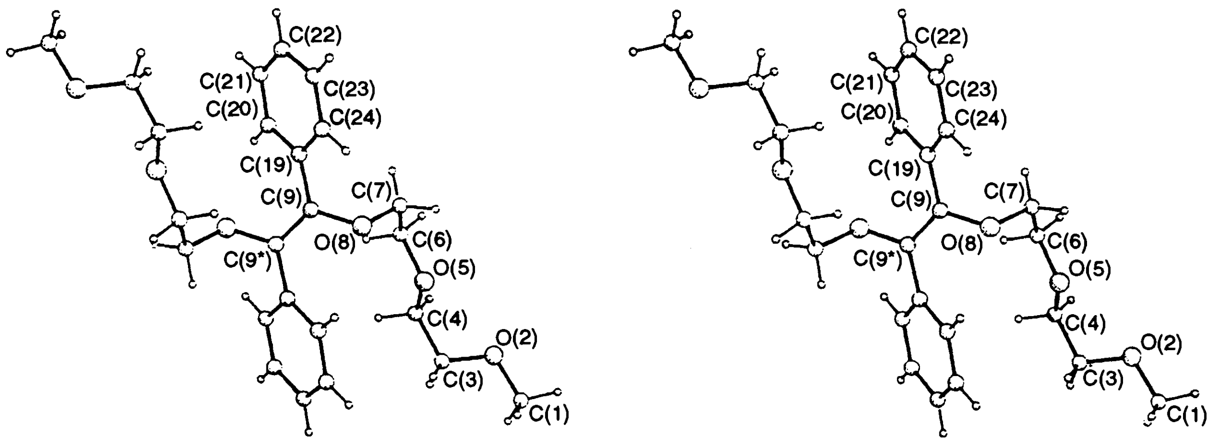


Fig. 1 Stereoscopic view of the free ligand[8]

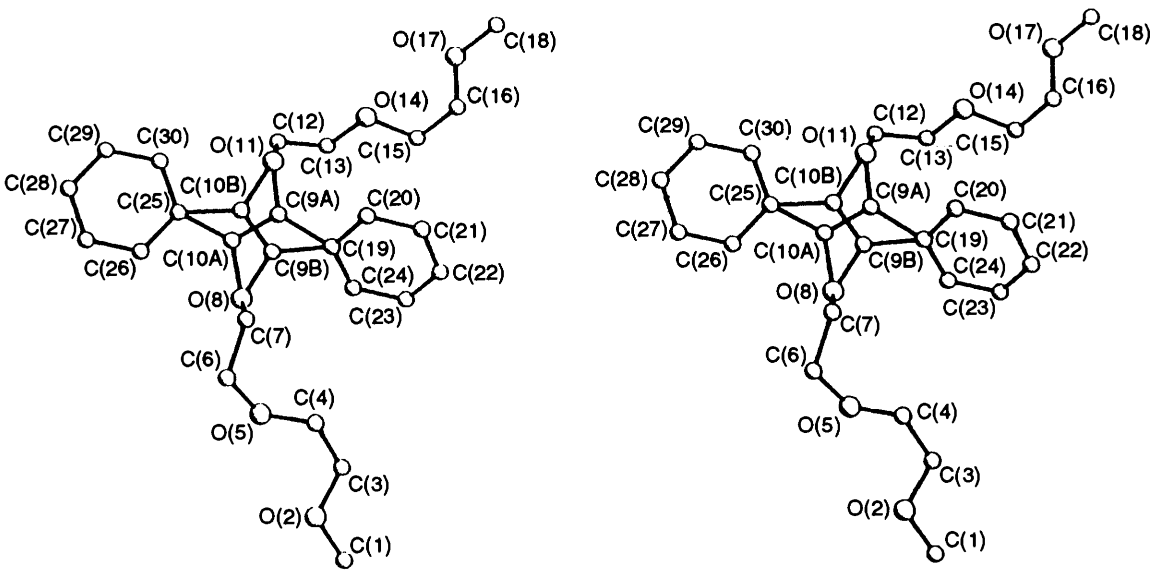


Fig. 2 Stereoscopic view of the disorder C(9)=C(10) atoms in the complex **1B**[8]

derivatives **2** and **3** the dihedral angles between the aromatic and ethylenic mean planes are 34, 50° and 38, 46°, respectively. The open chain polyether adopts a (ag$^{\pm}$a)(ag$^{\mp}$g$^{\mp}$) conformation from the methyl group towards the C=C central bond (Table 2).[*,9]

The torsion of −81° around C(7)–O(8) allows the chain to take a direction approximately parallel to the plane of the phenyl ring (Fig. 1). This conformation is retained for one of the chains in the complex entity **1B** (see following discussion).

The supramolecular system obtained by the complexation of **1** with NaSCN presents very unique features.

First of all, there are four molecules of **1**·2NaSCN·2H_2O in the unit cell with space group $P\bar{1}$ so that there are two independent complex entities in the asymmetric part; they are labelled in the following complex **1A** and complex **1B**. As it can be seen from Tables 1 and 2 the geometry of **1A** and **1B** is very similar. The main difference is that one of these entities **1B** is disordered in the central part of the organic ligand: the atoms C(9) and C(10) of the ethylenic bond occupy two distinct positions. Fig. 2 shows the organic ligand part of complex **1B** with the two positions of the central bond. At the end of the refinement the occupation factors of these two positions converge to 0.41 and 0.59, respectively. This kind of disorder is not uncommon in stilbene derivatives; by example the same has been observed in the *trans* stilbene structure.[10]

Because of the *E* configuration of the oxygenated side chains of the ligand, it is impossible to obtain a 1 : 1 complex like that observed with *Z*-**2** and NaSCN.[4b] Here, each polyether chain is linked by its two most outside oxygen atoms [O(2), O(5)][O(14), O(17)] to one Na$^+$. Both cations Na$^+$ have a six-fold coordination. In the case of Na(1), in addition to O(2) and O(5), three N atoms of the anions and one O of a water molecule are coordinated; in the case of the other cation [Na(2)], one N of a SCN is replaced by a second water molecule. In each case, the figure of coordination is a quite regular octahedron. The greatest distortions are at the edges occupied by the polyether oxygens: the angles O(2)–Na(1)–O(5) are 69.6(1); 70.5°(2) and O(14)–Na(2)–O(17) 72.4(1), 69.3° (2) for **1A** and **1B**, respectively. When the crystallographic centre of symmetry between them is considered, the surrounding of the Na is like that represented at Fig. 3.

From the sum of the van der Waals radii (1.4 Å for O, 1.5 Å for N)[11] and the effective ionic radii (1.02 Å for Na$^+$ with coordination 6,[12] one may expect distances Na$^+$ ··· O of 2.42 Å and Na$^+$ ··· N of 2.52 Å. The mean values for the four ether oxygens Na$^+$ distances is 2.423 Å, for the ten N ··· Na$^+$ it is 2.541 Å, and for the six Na$^+$ ··· O(water) 2.421 Å. All these average distances are in perfect agreement with predicted values. However, discrepancies from these average values are

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[*] a = *anti* (±120, ±180°), g = *gauche*, g$^+$ (0, 120°); g$^-$ (0, −120°).

Table 1 Selected bond lengths (Å) and angles (°)

	Free ligand	Complex **1A**	Complex **1B**		
O(2) ··· C(1)	1.404(3)	1.419(7)	1.428(7)		
C(3) ··· O(2)	1.402(2)	1.407(6)	1.402(7)		
C(4) ··· C(3)	1.485(3)	1.490(7)	1.486(8)		
O(5) ··· C(4)	1.414(2)	1.426(6)	1.437(6)		
C(6) ··· O(5)	1.415(2)	1.431(6)	1.431(6)		
C(7) ··· C(6)	1.484(3)	1.471(7)	1.498(8)		
O(8) ··· C(7)	1.441(2)	1.438(6)	1.417(7)		
C(9) ··· O(8)	1.389(2)	1.377(6)	1.41(3)	··· C(10A)	1.52(2)
C(9) ··· C(10)(9*)	1.333(3)	1.328(7)	1.32(2)		1.32(2)
C(19)–C(9)	1.487(2)	1.487(7)	1.49(2)		1.56(2)
O(11) ··· C(10)		1.419(6)	1.48(2)	··· C(9A)	1.36(3)
C(25) ··· C(10)		1.473(7)	1.55(2)		1.51(2)
C(12) ··· O(11)		1.442(6)	1.446(8)		
C(13) ··· C(12)		1.433(7)	1.400(9)		
O(14) ··· C(13)		1.442(6)	1.394(8)		
C(15) ··· O(14)		1.414(6)	1.437(7)		
C(16) ··· C(15)		1.501(7)	1.452(9)		
O(17) ··· C(16)		1.410(6)	1.409(7)		
C(18) ··· O(17)		1.410(7)	1.384(8)		
Coordination distances/Å		Complex **1A**	Complex **1B**		
Na(1) ··· O(2)		2.373(4)	2.365(4)		
Na(1) ··· O(5)		2.503(4)	2.539(4)		
Na(1) ··· N(36)		2.556(5)	2.603(5)		
Na(1) ··· N(33)[a]		2.528(5)	N33[d] 2.537(5)		
Na(1) ··· N(36)[b]		2.506(5)	N36[e] 2.475(5)		
Na(1) ··· O(91)		2.444(4)	2.441(4)		
Na(2) ··· O(14)		2.346(4)	2.465(5)		
Na(2) ··· O(17)		2.410(4)	2.384(5)		
Na(2) ··· N(33)		2.524(5)	2.516(5)		
Na(2) ··· N(36)[c]		2.589(5)	2.571(5)		
Na(2) ··· O(90)		2.478(5)	2.421(5)		
Na(2) ··· O(91)[c]		2.338(4)	2.404(5)		
Anions					
C(32) ··· S(31)		1.610(7)	1.654(7)		
N(33) ··· C(32)		1.172(6)	1.141(6)		
C(35) ··· S(34)		1.620(6)	1.636(7)		
N(36) ··· C(35)		1.157(6)	1.162(6)		
Angles in the polyether/°	Free ligand	**1A**	**1B**		
C(3)–O(2)–C(1)	113.4(2)	112.6(5)	112.6(5)		
C(4)–C(3)–O(2)	109.9(2)	108.6(5)	110.1(5)		
O(5)–C(4)–C(3)	110.0(2)	108.5(4)	108.9(5)		
C(6)–O(5)–C(4)	113.6(1)	113.2(4)	112.6(4)		
C(7)–C(6)–O(5)	109.7(2)	115.4(4)	114.7(5)		
O(8)–C(7)–C(6)	112.1(1)	108.5(4)	110.7(5)		
C(9)–O(8)–C(7)	113.2(2)	114.3(4)	105.8(6)	C(10A)–C(8)–C(7)	119.2(8)
O(8)–C(9)–C(10)(C9*)	118.4(2)	118.9(5)	112(2)	C(8)–C(10A)–C(9A)	111(2)
C(19)–C(9)–O(8)	115.5(1)	116.6(5)	127.6(12)	C(8)–C(10A)–C(25)	126(1)
C(19)–C(9)–C(10)	126.0(2)	124.2(5)	120.(3)		118(3)
O(11)–C(10)–C(9)		115.0(5)	112(2)		115(2)
C(25)–C(10)–C(9)		131.6(5)	123(3)		122(3)
C(25)–C(10)–O(11)		113.4(5)	124.7(11)	C(19)–C(9A)–C(11)	127(1)
C(12)–O(11)–C(10)		110.1(4)	116.7(8)	C(12)–C(11)–C(9A)	117.4(8)
C(13)–C(12)–O(11)		110.5(5)	116.4(6)		
O(14)–C(13)–C(12)		116.1(5)	113.7(6)		
C(15)–O(14)–C(13)		115.2(4)	111.0(6)		
C(16)–C(15)–O(14)		107.7(4)	108.1(5)		
O(17)–C(16)–C(15)		108.4(4)	108.1(6)		
C(18)–O(17)–C(16)		113.2(4)	110.7(6)		
Anions					
N(33)–C(32)–S(31)	179.2(5)	178.9(6)			
N(36)–C(35)–S(34)	178.9(5)	179.0(5)			
C(33)–C(32)–Na(2)	125.5(4)	131.1(5)			
C(32)–N(33)–Na(1)[a]	129.2(4)	128.7(4)			
C(35)–N(36)–Na(1)[b]	126.1(4)	125.4(5)Na(1)[e]			
C(35)–N(36)–Na(1)	124.2(4)	122.8(4)			
C(35)–N(36)–Na(2)[c]	123.1(4)	124.1(4)			

[a] $-x, -y, 1 - z$. [b] $-x, -y - 1, -z + 1$. [c] $x, y + 1, z$. [d] $-x + 1, -y + 1, -z + 2$. [e] $-x + 1, -y, -z + 2$.

Table 2 Selected torsion angles (°) (σ = 1°)

	Free ligand	Complex **1A**	Complex **1B**		
C(1)–O(2)–C(3)–C(4)	−178	169	−171		
O(2)–C(3)–C(4)–O(5)	−72	64	−66		
C(3)–C(4)–O(5)–C(6)	179	−168	170		
C(4)–O(5)–C(6)–C(7)	166	−68	68		
O(5)–C(6)–C(7)–O(8)	−72	−67	64		
C(6)–C(7)–O(8)–C(9)	−81	169	−166	··· C(10A)	152
C(7)–O(8)–C(9)–C(10)	113	126	−115	··· C(10A)–C(9A)	81
O(8)–C(9)–C(10)–O(11)	180	174	−178	··· C(10A)–C(9A) ···	−175
C(9)–C(10)–O(11)–C(12)		−88	108	C(10A)–C(9A) ···	−98
C(10)–O(11)–C(12)–C(13)		−171	−109	C(9A) ···	−67
O(11)–C(12)–C(13)–O(14)		−58	−65		
C(12)–C(13)–O(14)–C(15)		−67	157		
C(13)–O(14)–C(15)–C(16)		−178	−177		
O(14)–C(15)–C(16)–O(17)		68	−66		
C(15)–C(16)–O(17)–C(18)		179	−176		

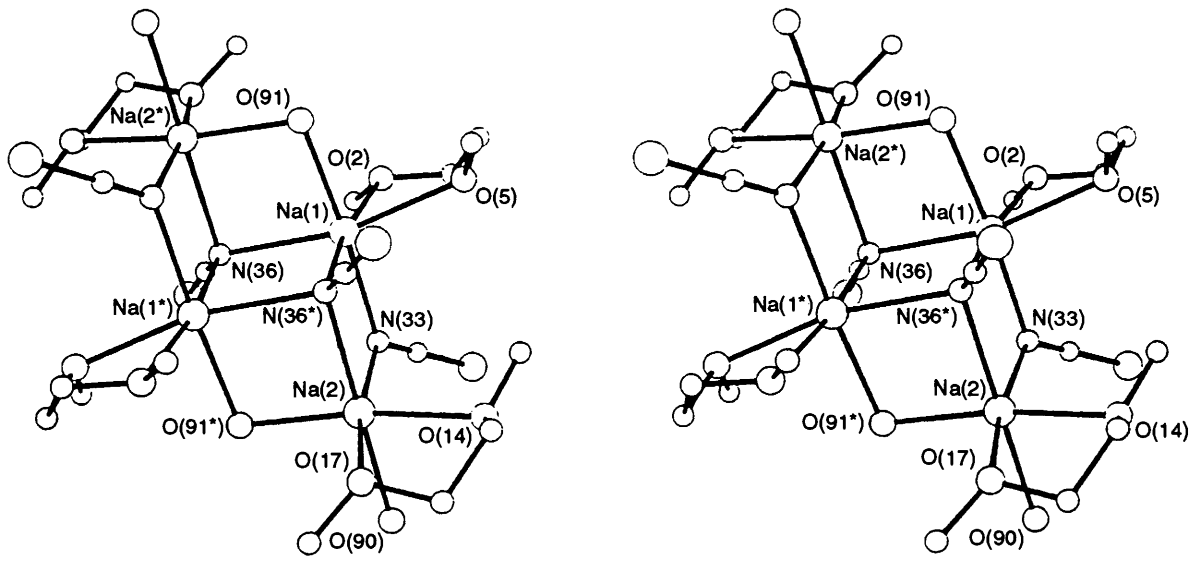

Fig. 3 Stereoscopic view of the surrounding of the cations[8]

observed; for example it seems that one Na$^+$ ··· O(ether) is significantly shorter than the other one in all the four side arms (Table 1). The Na(2) ··· O(91) in **1A** [2.338(4) Å] is also shorter than the other Na$^+$ ··· O(water) distances. Finally, it has to be noted that the Na$^+$ ··· N and Na$^+$ ··· O distances observed here are longer by 0.1 Å than those reported for the complex of (*Z*)-α,α′-di(2-methoxyethoxy)stilbene **2** with NaSCN.[4b]

For three of the side arms, the conformation of the polyether chain is (ag$^{\pm}$a)(g$^{\mp}$g$^{\mp}$a) going from the methyl group towards the C=C bond.[9] (See torsion angles at Table 2.) For the fourth oxyethylene unit, that with O(14)O(17) in **1B**, a (ag$^{\pm}$a)(ag$^{\pm}$g$^{\pm}$) conformation is observed. This arrangement is the same as that adopted by the side chains in the free ligand **1**. In all cases, the folding of the chain with a genuine corner with two adjacent gauche bonds (g$^{\pm}$g$^{\pm}$) is observed.

There is only a very slight torsion around the ethylenic bond [O(8)–C(9)=C(10)–O(11) = 174° in **1A**, −178° and −175° for the two positions in **1B**]. This is less than in the complex of *Z*-**2**·NaSCN where a torsion of −11.3(6)° was observed.[4b] The orientation of the phenyl groups is different from that reported in the free ligand or in *Z*-**2**·NaSCN; in both **1A** and **1B** one of the aromatic rings is nearly coplanar with the ethylenic mean plane (dihedral angles between the mean planes = 7° for both **1A** and **1B**) while the second one makes an angle of approximately 50° with the C=C plane (dihedral angles of 53° in **1A** and 45° in **1B**). In *Z*-**2**·NaSCN, the phenyl rings are twisted out the ethylenic plane by 56° and 47° indicating a greater degree of deconjugation.

A stereoscopic representation of the complex **1A** is presented at Fig. 4. Complexes **1A** and **1B** are completely independent in the sense that they do not have any atom in common. Each of them makes an infinite chain along which, the organic and inorganic parts alternate. In the large ring Na(1) ··· [O(2)O(5)O(14)O(17)] ··· Na(2) ··· N(33), N(36) ··· Na(1*) ··· [O(2)O(5)O(14)O(17)]* ··· Na(2*) ··· N(33*), N(36*) Na(1), the C=C double bonds and the aromatic ring of the ligand and its centrosymmetric equivalent are superposed so that the distance between C(9)=C(10) and C(9*)=C(10*) bonds is 4.351 Å in **1A** and 4.364, 4.593 Å in **1B**.

The most unique feature of this structure is certainly the bridging of the SCN anions of a type never reported before. As the coordination and the geometry are similar in **1A** and **1B**, we have to discuss only two SCN anions. In the first one [N(33)–C(32)–S(31)] the N atom is coordinated to two different Na$^+$ cations. This kind of bridging (type 17 in ref. 13) is uncommon, the bridging by both the N and the S atoms (type 14 in ref. 13) being the rule. Only a few cases of such structures are known[13] among which $\mathrm{Re_2(Bu^n{}_4N)_3(NCS)_{10}}$ (ref. 14) and $\mathrm{[K_2C_{24}H_{32}O_8](NCS)_2}$.[15] The second SCN anion [N(36)–C(35)–S(34)] is linked by its N atom to three Na$^+$ cations; this a bridging of a type never observed before. As shown on Table 1, the geometry of both SCN anions is similar and quite normal. They are effectively linear as the angles at the carbon atoms range from 178.9(6) to 179.2(5)°. There are no significant differences between the observed distances and the expected values for C–N and C–S in the two anions. Moreover the mean

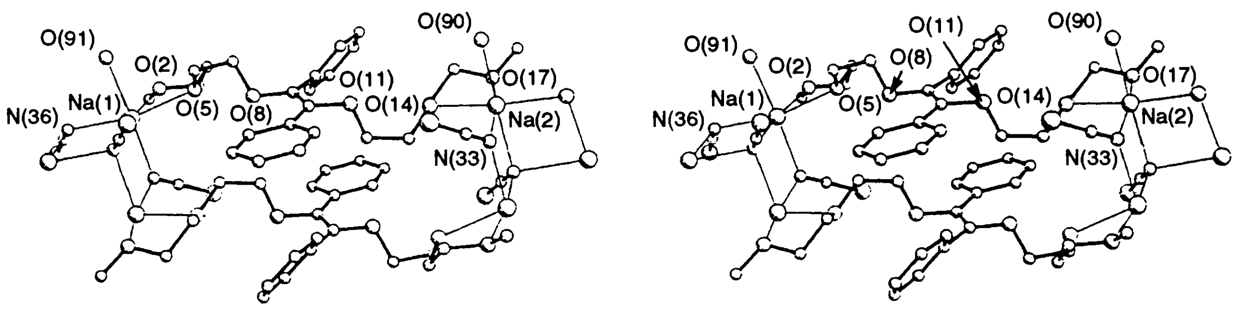

Fig. 4 Stereoscopic view of complex **1A**[8]

values of these bond lengths, respectively 1.158 and 1.630 Å are just the same as the average values reported by Allen *et al.* in their compilation.[16] The angles around N(33) and N(36) range from 123 to 131° (Table 1).

Experimental

The spectra were measured under standard conditions on Bruker WM250 and AMX500 spectrometers with ASPECT 2000 and ASPECT 3000 computers using a 5 mm ^1H probe and a 10 mm broadband probe at room temp. (25 °C) $CDCl_3$ solvent was used as an internal deuterium lock signal and as an internal spectral reference (δ 76.9 for ^{13}C).

The reported ^{13}C and ^1H chemical shifts are accurate to *ca.* 0.01 ppm. The following abbreviations are used: s. singlet; d. doublet; t. triplet; q. quartet; m. multiplet; b. broad.

IR and mass spectra were recorded on a Perkin-Elmer 1710 FT-IR and TSQ 70 Finningan Mat apparatus respectively. Melting points were determined using Dr Tottoli's apparatus and are uncorrected.

Preparation of **1**.—To a 500 cm^3 four necked flask equipped with thermometer, nitrogen inlet tube, reflux condenser, dropping funnel and magnetic stirrer were charged successively with stirring the tosylate 25 g (0.090 mol), benzoin 8.8 g (0.040 mol) and sodium hydroxide 6.6 g (0.165 mol). The solvent 1.4 dioxane (100 cm^3 distilled from sodium hydride) and benzyltriethylammonium chloride 0.95 (0.004 mol) was added under the phase-transfer conditions. With nitrogen bubbling, the stirred mixture was heated for 7 h to 80(1) °C by using a temperature-controlled oil bath.

The resultant was cooled to room temp., poured into ice and extracted four times with diethyl ether (100 cm^3). The combined ether extract was washed twice with water (150 cm^3) and dried over magnesium sulfate. Evaporation of the solvent gave a pale yellow, viscous oil. The crude products *E*-**1** and *Z*-**1** obtained were chromatographed over silica gel with ethyl acetate–hexane (6:4) + 1% triethylamine.

Evaporation of the eluent solvent, gave the fraction containing *E*-**1** which was recrystallized at −20 ° from ethyl acetate–hexane (2:8), to yield 46% of colourless crystals: m.p. 46–47 °C.

The fraction containing the *Z*-**1** give colourless viscous oil: yield 54%.

Spectral Properties of E-**1**.—δ_H 3.35 (6 H, s), 3.45 (8 H, s), 3.53 (4 H, bm), 3.65 (4 H, bm), 7.27 (2 H, bm), 7.35 (4 H, bm) and 7.79 (4 H, bm); δ_C 58.71 (q, CH_3), 69.60 (t, CH_2), 69.82 (t, CH_2), 70.10 (t, CH_2) 71.72 (t, CH_2), 127.36 (d, C *para*), 127.60 (d, C *meta*), 128.47 (d, C *ortho*), 134.07 (s, C *ipso*) and 144.09 (s, C olef); ν_{max}(KBr)/cm^{-1} 3062w (CH), 3036w (CH). 2980s (CH), 2883s (CH), 1598m (C=C arom), 1494m (C=C arom), 1252s (=C–O–C as), 1106s (C–O–C), 1030s (=C–O–C sym), 767s and 698s (Ph); *m/z* (EI) 59 (CH_3-O-CH_2-CH_2^+), 77 (Ph^+), 103, 105 (Ph CO^+) and 416 (M^+).

Preparation of the Complex of E-**1** *with* NaSCN.—A solution of *E*-**1** (1 mmol, 0.416 g) and NaSCN (2 mmol, 0.162 g) in 20 cm^3 of dry acetone was prepared.

A colourless powder was obtained by slow evaporation from acetone at 15 °C. Subsequent recrystallization from ethyl acetate–hexane (6:4) at −20 °C afforded 89% colourless needles, m.p. 78–79 °C. The complex **2** is not stable in solution.

Spectral Properties of the Complex of E-**1** *with* NaSCN.—ν_{max}(KBr)/cm^{-1} 3052w (CH), 3036w (CH), 2983s (CH), 2883s. (CH), 2067s (N=C=S asym), 1598m (Arom), 1495m (Arom), 1252s (=C–O–C asym) 1106s (C–O–C), 1030s (=C–O–C sym), 833w (NCS sym), 767s and 699s (Ph); *m/z* (FAB) 1251 [M + Na]$^+$, 1179 (1251 − $4H_2O$), 1098 [1179 − NaSCN], 1017 [1098 − NaSCN], 615 [M/2 + 1]$^{++}$, 601 [1017 − $C_{24}H_{32}O_6$], 520 [601 − NaSCN], 439 [520 − NaSCN], 416 [$C_{24}H_{32}O_6$], 233 [benzil + Na]$^+$, 103 [(–CH_2–$CH_2O)_2$–CH_3]$^+$ and 59[CH_3O–CH_2–CH_2–]$^+$.

X-Ray Analysis of 1 *and* 1·2NaSCN·2H$_2$O

Crystal measurement and refinement data are summarized in Table 3. The lattice parameters were refined using 15 reflections for **1** and 17 reflections for **1**·2NaSCN·$2H_2O$ in the range 5° ⩽ 2θ ⩽ 50°. For **1**, a Syntex $P2_1$ four circle diffractometer with graphite monochromatized MoKα was used for the data collection; for **1**·2NaSCN·$2H_2O$, a Huber four circle diffractometer and RU200 rotating anode generator equipped with a monochromatized CuKα radiation was used. For both measurements, one standard reflection was checked every 50 reflections and no significant deviation was observed. Both structures were solved by SHELXS86.[17] For **1**, all H atoms were localized from a difference Fourier synthesis; for **1**·2NaSCN·$2H_2O$, only the H of the water molecules were localized, all the others were calculated with AFIX of SHELXL93.[18] For **1**, anisotropic least squares refinement with SHELX76[19] using *F*; for **1**·2NaSCN·$2H_2O$, with SHELXL93[18] using F^2. The H atoms were refined isotropically with a common refined temperature factor. In the complex, the region around the C(9)=C(10) double bond of entity B was disordered (see Fig. 2). Two positions for each carbon atom were refined (labelled A and B). Restraints on the C(9)=C(10) bond lengths (target value 1.33 Å, σ 0.03 Å) and on non-bonded 1–3 distances (target: same value, σ 0.03 Å) were applied. At the end of the refinement, the occupation factors converge to 0.41 for position A and 0.59 for position B. Atomic scattering factors from International Tables for X-ray Crystallography, vol. IV, 1974.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Instructions for Authors, 1994.

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Table 3 Data collection and refinement parameters

	1	**2**
Formula	$C_{24}H_{32}O_6$	$C_{24}H_{32}O_6 \cdot 2NaSCN \cdot 2H_2O$
M_r	416.51	614.69
System	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	9.743(2)	8.961(4)
b/Å	12.147(2)	16.183(9)
c/Å	9.800(2)	23.507(10)
α/°		106.37(5)
β/°	101.56(2)	91.85(4)
γ/°		104.10(5)
V/Å^3	1136.3(4)	3153(3)
Z	2	4
D_x/g cm^{-3}	1.22	1.30
λ/Å	0.710 69	1.54178
F(000)	448	1296
μ/cm^{-1}	0.93	21.6
Approximate crystal size/mm	0.30 × 0.20 × 0.15	0.20 × 0.16 × 0.06
Collection range $(\sin \theta/\lambda)_{\max}$/Å^{-1}	0.59	0.50
Range of *hkl*	$0 \leq h \leq 11$ $0 \leq k \leq 14$ $-11 \leq l \leq 11$	$0 \leq h \leq 8$ $-16 \leq k \leq 15$ $-23 \leq l \leq 23$
Indices of standard refl.	3 −4 1	0 3 −1
No. of measured refl.	2009	6472
No. of observed refl. $[I \leq 2.5\sigma(I)]$	1523	5243
No. of parameters	185	765
No. of restraints	0	22
Refinement	SHELX76	SHELXL93
R	0.035	$(I \geq 2\sigma I)$0.060 (all data) 0.079
R_w	0.039	(R_{w2}) 0.15
Weight	$1/(\sigma^2 + 0.000\,25F^2)$	$1/[\sigma^2 F_o{}^2 + 0.0753P^2 + 3.10P]$
S	1.76	(on F^2) 1.045
(Δ/σ)	0.02	0.04
ρ (max, min)/e Å^{-3}	0.14–0.13	0.34–0.19

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