

Fig. 3. Stereoscopic view of the unit-cell packing in  $(\eta^{5}-C_{9}H_{7})Cr(CO)_{2}(NO)$ .

five-membered ring than to the plane of the entire ligand.

A stereoscopic view of the unit-cell contents is shown in Fig. 3. No unusually close intermolecular contacts are observed, but it is interesting to note that the indenyl ligands on adjacent molecules are neighbors, while the  $(XO)_3$  (where X = N or C) tripods are stacked in an interlocking fashion. This same packing mode was observed for  $(\eta^5-C_{13}H_9)Cr(CO)_2(NO)$  (Atwood *et al.*, 1979).

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# Structures of the Sodium-*p*-Terphenyl Ion Pairs: Disodium Terphenylide-Tetrahydrofuran (1/6) and Disodium Diterphenylide Terphenyl-1,2-Dimethoxyethane (1/6)

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## Abstract

The crystal structures of  $2Na^+$ .  $C_{18}H_{14}^{2-}$ .  $6C_4H_8O$ [ $Na_2tp.(H_4furan)_6$ ] and  $2Na^+.2C_{18}H_{14}^-.C_{18}H_{14}.6C_4^ H_{10}O_2$  ( $Na_2tp_3.dme_6$ ) have been determined by X-ray diffraction at room temperature and 130 K respectively.  $Na_2tp.(H_4furan)_6$ :  $M_r = 708.6$ , monoclinic,  $P2_1/c$ , a = 11.508 (6), b = 16.531 (4), c = 11.200 (3) Å,  $\beta = 95.13$  (3)°,  $\lambda$ (Cu Ka) = 1.5418 Å, V = 2122.1 Å<sup>3</sup>,  $D_x$  (293 K) = 1.109 Mg m<sup>-3</sup>, Z = 2,  $\mu$ (Cu Ka) = 0.757 mm<sup>-1</sup> (cell dimensions at 293 K). Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub>:  $M_r = 1277.6$ , triclinic,  $P\overline{1}$ , a = 12.204 (4), b = 15.836 (20), c = 12.119 (5) Å, a = 114.04 (5),  $\beta = 114.64$  (3),  $\gamma = 62.39$  (3)°,  $\lambda$ (Cu  $K\alpha$ ) = 1.5418 Å, V = 1818.6 Å<sup>3</sup>,  $D_x$  (130 K) = 1.167 Mg m<sup>-3</sup>, Z = 1,  $\mu$ (Cu  $K\alpha$ ) = 0.726 mm<sup>-1</sup> (cell dimensions at 130 K). The structure of Na<sub>2</sub>tp. (H<sub>4</sub>furan)<sub>6</sub> was refined to  $R(F_o) = 0.125$  for 808 reflections. The complex belongs to the contaction-pair structures. The structure of Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub> was refined to  $R(F_o) = 0.205$  for 1305 reflections. This complex is a member of the class of the solventseparated ion-pair structures.

### Introduction

Optical, NMR, ESR and conductance studies have yielded a wealth of indirect information about the structures of alkali-aromatic ion pairs in solution (Szwarc, 1972). Single-crystal X-ray diffraction studies confirmed similar structures of these ion pairs in the solid state (Mooij, Klaassen, de Boer, Degens, van den Hark & Noordik, 1976; Noordik, van den Hark, Mooij & Klaassen, 1974; Noordik, Degens & Mooij, 1975; Noordik, Schreurs, Gould, Mooij & de Boer, 1978; Brooks & Stucky, 1972; Brooks, Rhine & Stucky, 1972a,b). With solvents of high solvating power (e.g. tri- or tetraglyme), crystals of loose or solventseparated ion pairs are produced. The positive alkali ions and the negative ions are separated from each other by a cage of solvent molecules around the alkali ions. Solvents with less solvating power give rise to crystals with a tight or contact-ion-pair structure in which the positive ions are situated at van der Waals distances from the negative ions.

This study reports the first solid-state structures of two alkali *p*-terphenyl ion pairs; one with a divalent negative *p*-terphenyl ion and  $H_4$  furan (tetrahydro-furan) as solvent, and one with a univalent negative *p*-terphenyl ion, a neutral *p*-terphenyl molecule and dme (1,2-dimethoxyethane) as solvent.

# Experimental

A solution of Na<sub>2</sub>tp (tp = p-terphenyl) in H<sub>4</sub> furan was prepared under high vacuum using standard techniques (Canters, Klaassen & de Boer, 1970). From this solution single crystals of Na<sub>2</sub>tp. (H<sub>4</sub>furan)<sub>6</sub> were obtained by slow cooling to about 283 K. Single crystals of Na<sub>2</sub>tp<sub>3</sub>. dme<sub>6</sub> were obtained by adding a solution of an equimolar amount of neutral tp in dme to a solution of Na.bp (bp = biphenyl) in dme and cooling to about 283 K (de Boer, Stange & Klaassen, 1981). The crystals are very sensitive to air and moisture and for the X-ray measurement they were mounted in thin glass capillaries in a He atmosphere in a glove box. Because of the low melting point of the crystals, these manipulations were carried out at a temperature of about 253 K. Diffractometer measurements revealed a monoclinic lattice symmetry for Na<sub>2</sub>tp. (H<sub>4</sub>furan)<sub>6</sub>, with systematic absences  $0k0 \ k$  odd and  $h0l \ l$  odd, consistent with space group  $P2_1/c$ . Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub> is triclinic. Unit-cell dimensions were determined by least-squares fitting to the setting angles of 25 reflections measured on a CAD-4 diffractometer (Cu Ka radiation,  $\lambda = 1.5418$  Å).

## $Na_2tp.(H_4furan)_6$

Intensity data for  $2\theta < 96^{\circ}$  (Cu Ka radiation; graphite-crystal monochromator) were collected on a CAD-4 diffractometer at room temperature. Only 808 (out of 1987) independent reflections had significant intensities. [Low-temperature measurements (150 K) did not improve the data.] Absorption correction was not applied. The structure was solved by direct methods (MULTAN 78). The 'best' solution gave 19 non-H atoms. The other six non-H atoms were found from a weighted difference synthesis. H atoms were placed at calculated positions and not refined. Atomic coordinates, anisotropic thermal parameters for Na and the C atoms of the tp ion, and isotropic thermal parameters for the remaining non-H atoms were refined by full-matrix least-squares methods, minimizing  $\sum w(|F_o|)$  $(k|F_c|)^2$ , using 808 reflections;  $w = [\sigma_c^2(F_o) + 0.004F_o^2]^{-1}$ , with  $\sigma_c^2(F_o)$  from counting statistics. The refinement converged to an R value of 0.125, with mean and maximum parameter shifts of 0.08 and 0.54 of their e.s.d.'s. Atomic parameters are given in Table 1.\* Scattering factors were those of Cromer & Mann (1968) for Na<sup>+</sup>, C, O, and of Stewart, Davidson & Simpson (1965) for H.

## Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub>

Intensity data for  $2\theta < 80^{\circ}$  (Cu Ka radiation; graphite-crystal monochromator) were collected on a CAD-4 diffractometer at 130 K. After averaging of symmetry-equivalent reflections, a set of 2204 reflections [1305 reflections with  $I > 3\sigma(I)$ ] was reduced to  $|F_o|$  values. The phase problem was solved by *MULTAN* 78 combined with a translation search based on direct methods (Doesburg & Beurskens, 1980). One of the *MULTAN* solutions gave a recognizable fragment consisting of two partial *p*terphenyl molecules in the same orientation shifted with respect to each other by about half a C-C distance. Starting with one of these fragments a translation search was performed and application of the shift

<sup>\*</sup> Lists of structure factors and anisotropic thermal parameters for Na and the C atoms of the tp ions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35952 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Na<sub>2</sub>tp. $(H_4$ furan)<sub>6</sub>: fractional atomic coordinates and equivalent isotropic thermal parameters  $(\times 10^2)$  for the non-H atoms with e.s.d.'s in parentheses

	x	У	z	$U_{ m eq}({ m \AA}^2)$
Na	0.128 (1)	0.073 (1)	0.877 (1)	9 (1)
C(1)	-0·024 (2)	–0·054 (1)́	0.908 (2)	7 (1)
C(2)	0.070 (2)	-0.069(2)	0.990 (2)	8 (1)
C(3)	0.101 (2)	-0.017(2)	1.087 (2)	6 (1)
C(4)	0.195 (2)	-0.027(2)	1.178 (2)	7 (1)
C(5)	0.274 (2)	0.099 (2)	1.170 (2)	10 (1)
C(6)	0.369 (2)	-0.111(2)	1.259 (3)	11(1)
C(7)	0.383 (3)	-0.064(3)	1.358 (3)	12 (2)
C(8)	0.312(3)	0.002 (2)	1.359 (2)	10(1)
C(9)	0.220(2)	0.023 (2)	1.282 (2)	8 (1)
O(1)	0.237(2)	0.181 (1)	0.950 (2)	12(1)
C(10)	0.276 (2)	0.199 (2)	1.071 (2)	13 (1)
C(11)	0.371(3)	0.264(2)	1.057 (3)	15 (1)
C(12)	0.407 (3)	0.262(2)	0.935 (3)	18 (2)
C(13)	0.302 (4)	0.228(2)	0.866 (3)	20 (2)
O(2)	0.061(2)	0.143(1)	0.705(2)	11(1)
C(14)	0.041(3)	0.098 (2)	0.598 (3)	15 (1)
C(15)	-0.043(3)	0.152(3)	0.526(3)	20 (2)
C(16)	-0.100(3)	0.201 (2)	0.597 (3)	16 (1)
C(17)	-0.030 (3)	0.202 (2)	0.709 (2)	13 (1)
O(3)	0.278 (2)	0.007(1)	0.799 (2)	12 (1)
C(18)	0.269 (4)	<b>−0</b> ·053 (3)	0.705 (3)	22 (2)
C(19)	0.351 (4)	-0.118(3)	0.734 (4)	26 (2)
C(20)	0.418 (4)	-0.086(3)	0.830 (4)	23 (2)
C(21)	0.385 (4)	-0.011(3)	0.866 (3)	20 (2)

indicated by the first peak of the search resulted in the correct positioning of this *p*-terphenyl fragment in the unit cell. The Na<sup>+</sup> ion, a second tp molecule and several ether fragments were found from successive weighted difference Fourier maps. Refinement was by full-matrix least squares where  $\dot{\Sigma} (|F_o| - k|F_c|)^2$  was minimized. Severe disorder in the dme molecules prevented an unambiguous identification and refinement of all atoms of these molecules. The most consistent refinement was obtained in space group P1 and resulted in an R value of 0.205 for 1305 reflections with mean and maximum parameter shifts of 0.37 and 2.76 of their e.s.d.'s. The atomic parameters are given in Table 2.\* Scattering factors used were the same as before. Routine calculations were performed with XRAY 72 and XRAY 76 (Stewart, 1972, 1976).

#### Discussion

The crystal structure of Na<sub>2</sub>tp. (H<sub>4</sub> furan)<sub>6</sub> is built up of *p*-terphenyl anions and [Na(H<sub>4</sub>furan)<sub>3</sub>]<sup>+</sup> cations (Na<sup>+</sup> coordinated by three H<sub>4</sub>furan molecules). Fig. 2 shows a perspective view along the Na<sup>+</sup>...Na<sup>+</sup> direction, and Fig. 1 presents a stereoscopic view of the ionic packing in the unit cell. Both figures clearly show a contaction-pair structure. The Na<sup>+</sup> ions are located above and below the centre of the central ring of the *p*-terphenyl ion at a distance of 2.43 Å, and at one side each of the Na<sup>+</sup> ions is coordinated by three H<sub>4</sub>furan molecules. The O atoms of these three molecules are situated at the corners of an equilateral triangle which is almost parallel to the plane of the *p*-terphenyl ion (Table 3). Hückel calculations (assuming a planar structure) show a charge density of 0.9 e at the central ring and of 0.55 e at the end rings, giving an explanation for the position of the Na<sup>+</sup> ions with respect to the terphenyl

# Table 2. Na<sub>2</sub>tp<sub>3</sub>. dme<sub>6</sub>: fractional atomic coordinates and equivalent isotropic thermal parameters $(\times 10^2)$ for the non-H atoms with e.s.d.'s in parentheses

 $U_{eq}$  defined according to Hamilton (1959).

	x	у	z	$U_{ m eq}({ m \AA}^2)$
Na+	0.2908 (10)	0.7358 (8)	0.5179 (9)	6.9 (1)
C(1)	0.120(3)	0.764(2)	0.979(2)	7 (2)
$\overline{C(2)}$	0.040(2)	0.865(2)	0.997(2)	6(2)
C(3)	-0.093(2)	0.899(2)	0.987(2)	6(2)
(2)	-0.139(2)	0.826(2)	0.964(2)	5(2)
C(5)	-0.064(2)	0.724(2)	0.949(2)	5(2)
(6)	0.067(2)	0.691(1)	0.954(2)	3(1)
(0)	0.363(2)	0.451(2)	0.930(2)	4(2)
つ(8)	0.280(2)	0.552(2)	0.938(2)	4(1)
~(0)	0.147(2)	0.590(2)	0.943(2)	5(1)
(10)	0.100(2)	0.516(2)	0.936(2)	5(1)
	0.180(2)	0.418(2)	0.934(2)	5(2)
(11)	0.311(2)	0.388(2)	0.927(2)	6(2)
(12)	0.605(3)	0.147(2)	0.913(2)	8 (2)
(13)	0.531(2)	0.245(2)	0.023(2)	6(2)
2(14)	0.306(2)	0.243(2) 0.278(2)	0.915(2)	5(2)
(15)	0.346(2)	0.200(2)	0.916(2)	5(2)
(10)	0.426(2)	0.209(2)	0.000(2)	6(2)
7(18)	0.420(2)	0.075(2)	0.909(2)	7(2)
7(10)	0.056(3)	0.470(2)	0.508(2)	$\frac{7}{10}$
(17)	0.001(3)	0.411(2)	0.408(3)	10(2)
(20)	0.091(3)	0.411(2)	0.496(3)	9(2)
(21)	0.010(3)	0.443(2)	0.370(3)	0(2)
(22)	0.152(4)	0.307(2)	0.470(3)	17(3)
(23)	0.132(4) 0.234(3)	0.223(3)	0.359(4)	17(4) 12(3)
2(24)	0.254(3)	0.062(2)	0.338(3)	12(3) 17(4)
(25)	0.351(4)	0.002(3)	0.433(4)	17(4) 16(3)
2(20)	0.205(4)	0.240(3)	0.582(4)	10(3)
2(27)	0.293(4)	0.249(4)	0.562(3)	7 (2)
J(1)	0.140(4) 0.254(6)	0.893(2)	0.034(3)	20 (6)
J(2) T(20)	0.234(0)	0.001(4)	0.439(0)	20 (0)
(20)	0.140(0)	0.079(3)	0.743(4)	10(3)
(29)	0.240(0)	0.933(0)	0.792(0)	13(0)
(30)	0.219(7)	0.973(3)	0.392(7)	13(7)
2(31)	0.200(1)	0.644(0)	0.338(3)	17(7) 12(4)
D(3) = D(4)	0.502(4)	0.003(3)	0.658(3)	12(4)
-(22)	0.242(4)	0.719(2)	0.038(2)	4 (3) 5 (4)
C(32)	0.242(4) 0.437(6)	0.641(5)	0.030(4)	11 (6)
(33)	0.437(0)	0.041(3)	0.737(3)	5(4)
C(34)	0.517(3)	0.702(4)	0.700(4)	J (4)
$\mathcal{L}(33)$	0.339(3)	0.772(4)	0.073(3)	12 (4)
$\mathcal{J}(3)$	0.373(4)	0.030(3)	0.344(4)	12 (4)
$\mathcal{O}(0)$	0.104(4)	0.122(3)	0.337(3)	10 (4)
C(30)	0.282 (8)	0.333(8)	0.009(/)	18 (8)
C(37)	0.282(0)	0.382(4)	0.300 (8)	8 (S)
C(38)	0.135(1)	0.041(4)	0.239(4)	0(3)
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All atoms of the solvent molecules were assigned a fixed population parameter of 0.50.

<sup>\*</sup> See previous footnote.

ions. Na ··· C(*p*-terphenyl) distances range from 2.78 to 2.86 Å (e.s.d. 0.03 Å). The atomic numbering is shown in Fig. 3. C–C bond distances in the *p*-terphenyl anion range from 1.34 to 1.51 Å (e.s.d. 0.04 Å). The central C–C bond connecting two phenyl rings is shortened with respect to the value in neutral *p*-terphenyl (*e.g.* Lisensky, Johnson & Levy, 1976), thus increasing the *ortho*-hydrogen repulsion. This is also expressed in the values of the bond angles at the C atoms of the central C–C bond which are significantly smaller than 120°. The change in geometry going from neutral tp to  $tp^{2-}$  corresponds to calculated (Hückel) bond-order changes and is similar to the trend observed in biphenyl systems (Mooij *et al.*, 1976). As the *p*-terphenyl ion is situated at an inversion centre, the two end rings are parallel.

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Fig. 1.  $Na_2tp.(H_4 \text{ furan})_6$ : Stereoscopic view of the packing, *a* axis horizontal, *b* axis vertical.



Fig. 2.  $Na_2tp.(H_4 \text{ furan})_6$ : Perspective view along the  $Na^+ \cdots Na^+$  direction.



Fig. 3. Na<sub>2</sub>tp. (H<sub>4</sub> furan)<sub>6</sub>: Atomic numbering, bond distances (Å) and angles (°). The numbering of the remaining two H<sub>4</sub>furan molecules is  $O(2)\cdots C(17)$  and  $O(3)\cdots C(2)$ . Distances and angles given for H<sub>4</sub>furan are average values. E.s.d.'s are 0.04 Å and 3°. Primed atoms are generated by the centre of symmetry (indicated).

The torsion angle around the central C–C bond is  $4\cdot3^{\circ}$ . Since the reflection intensity data were collected at 293 K, the possibility of static disorder (Baudour, Delugeard & Cailleau, 1976) exists. Intensity measurements at 150 K gave evidence of a structural rearrangement, possibly similar to that of neutral *p*-terphenyl at 113 K. Atomic distances in the H<sub>4</sub> furan molecules range from  $1\cdot35$  to  $1\cdot56$  Å (e.s.d.  $0\cdot06$  Å) for C–C bonds and from  $1\cdot41$  to  $1\cdot47$  Å (e.s.d.  $0\cdot05$  Å) for C–O bonds.

Refinement of the Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub> structure is difficult but since the two crystallographically independent p-terphenyl molecules and the Na<sup>+</sup> ion show a stable behaviour during the least-squares refinement, the geometry and conformation of this part of the structure are reasonably well defined. Calculated Fourier and difference Fourier syntheses show the presence of a dense cloud of electron density around the Na<sup>+</sup> ion. A suitable disorder model for the dme molecules could not be developed. The coordinates given for the dme molecules (Table 2) represent small peaks in this density cloud with a chemically acceptable geometry. The electron density represented by these 'atoms' appears to be about 50% of the expected density and the high R value can at least be partially attributed to the fact that 50% of the electrons of the solvent molecules are missing. The structure of Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub> consists of Na<sup>+</sup> ions coordinated by three dme molecules, *p*-terphenyl ions and neutral *p*-terphenyl molecules. The synthesis of the complex (equimolar amounts of tp and bp<sup>-</sup>) and ESR measurements (de Boer et al., 1981; a spectrum with one exchangenarrowed line) point to a paramagnetic structure with tp<sup>-</sup> ions and therefore the *p*-terphenyl molecules at a general position (tp1) have a formal charge -1 and the *p*-terphenyl molecules at the special position 1 (tp2), a formal charge 0. The ions tp1 have an orientation almost parallel to the *ab* plane. The molecules tp2 are located between two symmetry-related ions tp1, resulting in a stacking of ions tp1, separated from each other by neutral molecules tp2, along the c axis. Between these stacks the Na<sup>+</sup> ions coordinated by dme are situated. A stereoscopic view of the structure along the c axis is given in Fig. 4, clearly showing the

Table 3. Dihedral angles (°) and Na<sup>+</sup> contact distances (Å) in Na<sub>2</sub>tp.  $(H_4 \text{ furan})_6$ 

Plane I		Plane 2		
C(1), C(2), C(3), C(1' C(1), C(2), C(3), C(1' C(4), C(5), C(6), C(7)	), C(2'), C(3') ), C(2'), C(3') , C(8), C(9)	/ C(4), C(5), C(6), C(7), / O(1), O(2), O(3) / O(1), O(2), O(3)	C(8), C(9)	4·3 3·2 5·9
NaO(1) Na-O(2) Na O(3) Na-C(1) Na-C(2)	2·29 (2) 2·31 (2) 2·29 (2) 2·78 (2) 2·79 (3)	Na-C(3) Na-C(1') Na C(2') Na-C(3')	2.83 (2) 2.80 (2) 2.84 (3) 2.86 (2)	

Primed atoms are related to the unprimed ones via 1 at (001).

solvent-separated ion-pair structure. The distances from the Na<sup>+</sup> ion to *p*-terphenyl C atoms range from 4.6 to 6.0 Å. The contacts of the Na<sup>+</sup> ion with the O atoms of the dme molecules are summarized in Table 5 and are similar to those between the Na ion and the O atoms in Na<sub>2</sub>tp. (H<sub>4</sub> furan)<sub>6</sub>. Bond distances and angles in Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub> are summarized in Table 4. The phenyl rings in the *p*-terphenyl molecules tp1 are planar (maximum deviation from least-squares planes 1.5



Fig. 4.  $Na_2tp_3$ . dme<sub>6</sub>: Stereoscopic view of the packing along the c axis; a axis horizontal, b axis vertical.

# Table 4. Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub>: bond distances (Å) and angles (°) for the two terphenyl units with e.s.d.'s in parentheses

Primed atoms are generated by inversion at  $(0, \frac{1}{2}, \frac{1}{2})$ . Atomic numbering is shown below.

		tpi		tpz	
C(1)-C(2) C(2)-C(3) C(3)-C(4) C(4)-C(5) C(5)-C(6) C(6)-C(1) C(6)-C(9) C(7)-C(8) C(7)-C(9)	1.42 (3) 1.43 (4) 1.39 (5) 1.41 (3) 1.41 (3) 1.45 (5) 1.42 (3) 1.43 (3)	$\begin{array}{c} C(10)-C(11)\\ C(11)-C(12)\\ C(12)-C(7)\\ C(12)-C(15)\\ C(13)-C(14)\\ C(14)-C(15)\\ C(15)-C(16)\\ C(16)-C(17)\\ \end{array}$	1.39 (3) 1.48 (4) 1.39 (5) 1.55 (3) 1.39 (3) 1.45 (4) 1.48 (5) 1.40 (3)	$\begin{array}{c} C(19)-C(20)\\ C(19)-C(21')\\ C(20)-C(21)\\ C(20)-C(22)\\ C(22)-C(23)\\ C(22)-C(27)\\ C(23)-C(24)\\ C(24)-C(25)\\ C(24)-C(25)\\ \end{array}$	1.38 (4) 1.23 (4) 1.52 (4) 1.52 (4) 1.50 (5) 1.73 (5) 1.55 (5) 1.46 (5)
C(8) - C(9) C(9) - C(10)	1·46 (4) 1·49 (5)	C(17)-C(18) C(18)-C(13)	1·47 (4) 1·45 (5)	C(25)–C(26) C(26)–C(27)	1·54 (6) 1·53 (7)



Table 5. Na–O contact distances (Å) in Na<sub>2</sub>tp<sub>3</sub>.dme<sub>6</sub>

Na–O(1)	2.54 (3)	Na-O(4)	2.40 (3)
Na-O(2)	2.57 (8)	Na-O(5)	2.36 (5)
Na-O(3)	2.31 (5)	Na-O(6)	2.34 (4)

e.s.d.). The dihedral angles between the middle and end rings in the *p*-terphenyl ion tp1 are 8.9(5) and  $1.7(5)^\circ$ ; in tp2 the angle is 28(2)°, a value different from the values resulting from low-temperature studies of neutral *p*-terphenyls where angles of 11 and 12° have been found (Lisensky *et al.*, 1976; Baudour, Cailleau & Yelon, 1977).

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