Paramagnetic Alkali-Aromatic Ion-Pair Structures.
The Crystal Structure of Bis[1,2-bis(2-methoxyethoxy)ethane]sodium Biphenylide

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Abstract

$[Na(C_8H_{18}O_4)_2]C_{12}H_{10}$, $(C_{16}H_{36}NaO_8)^+C_{12}H_{10}^-$, $M_r = 533 \cdot 7$, monoclinic, $P2_1$, $a = 11 \cdot 721$ (2), $b = 13 \cdot 425$ (2), $c = 9 \cdot 555$ (2) Å, $\beta = 103 \cdot 08$ (4)° $[\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å], $V = 1464 \cdot 5$ Å^3, D_x (150 K) $= 1 \cdot 21$ Mg m^{-3}, $Z = 2$. The structure was solved by *MULTAN* and refined to $R(F_o) = 0 \cdot 032$ and $R_w(F_o) = 0 \cdot 041$ for 2059 reflections measured with graphite-monochromated Mo $K\alpha$ radiation. The complex belongs to the category of solvent-separated ion-pair structures. The biphenyl anion is significantly non-planar. The local symmetry of the sodium–triglyme part of the structure is close to twofold and nearly 222.

Introduction

Szwarc and his co-workers (Szwarc, 1972) have shown that ion-pairs may exist in solution as solvent-separated and contact ion-pairs. After the successful preparation of single crystals of alkali–biphenyl ion-pairs (Canters, Klaassen & de Boer, 1970), X-ray crystal structure determinations have shown that the structures of aromatic ion-pair containing complexes in the solid state can also be characterized as belonging to the solvent-separated or the contact ion-pair category (Brooks & Stucky, 1972; Brooks, Rhine & Stucky, 1972*a,b*; Noordik, van den Hark, Mooij & Klaassen, 1974; Noordik, Degens & Mooij, 1975; Goldberg, Raymond, Harmon & Templeton, 1974; Mooij, Klaassen, de Boer, Degens, van den Hark & Noordik, 1976; Noordik, Schreurs, Gould, Mooij & de Boer, 1978). The structures of the paramagnetic complexes rubidium and potassium biphenyl, crystallized from tetraglyme [CH$_3$O(CH$_2$CH$_2$O)$_4$CH$_3$] and having the composition RbBp.2Ttg and KBp.2Ttg (Bp = biphenyl; Ttg = tetraglyme), may be considered to be built up from solvent-separated ion-pairs. The alkali cations are completely surrounded by two Ttg molecules and are coordinated to the Ttg's through the ten oxygen atoms. To complete the series of alkali biphenyl/glyme crystal structures and to provide the data necessary for the interpretation of magnetic measurements on these

three alkali–biphenyl systems in the solid state (Mooij, 1976; de Boer, Klaassen, Mooij & Noordik, 1978), the structure of NaBp.2Tg [Tg = triglyme, CH$_3$O(CH$_2$CH$_2$O)$_3$CH$_3$] was solved.

The present report is concerned with this structure determination and with a discussion of structural parameters provided by the structure determinations of RbBp.2Ttg, KBp.2Ttg and NaBp.2Tg.

Experimental

A solution of the NaBp salt in Tg [Bp = biphenyl; Tg = CH$_3$O(CH$_2$CH$_2$O)$_3$CH$_3$] was prepared under high vacuum using standard techniques (Canters, Klaassen & de Boer, 1970). Single crystals were obtained by cooling the solution at a rate of 1 K h^{-1} to about 283 K. Since the crystals are very sensitive to air and moisture, they were mounted in thin glass capillaries in a He atmosphere in a glove box. These manipulations were carried out at a temperature of about 253 K in view of the low melting point (about 313 K) of the NaBp.2Tg crystals.

Weissenberg photographs revealed a monoclinic lattice symmetry. Diffractometer measurements showed systematic absences (0*k*0 reflections with *k* odd) consistent with the space group $P2_1$. Crystal data are given in Table 1.

Unit-cell dimensions were determined by least-squares analysis of the setting angles of 25 reflections measured on a CAD-4 diffractometer (Mo $K\alpha$ radiation).

Several crystals were tried, both at room temperature and at about 150 K, before we succeeded in mounting a crystal from which a complete and reliable intensity

Table 1. *Crystal data*

C$_{28}$H$_{46}$NaO$_8$	Monoclinic, $P2_1$
$a = 11 \cdot 721$ (2) Å	$Z = 2$
$b = 13 \cdot 425$ (2)	$D_x = 1 \cdot 21$ Mg m^{-3}
$c = 9 \cdot 555$ (2)	$M_r = 533 \cdot 7$
$\beta = 103 \cdot 08$ (4)°	(cell dimensions at 150 K)
$V = 1464 \cdot 5$ Å^3	

data set at 150 K could be obtained. The room-temperature data were limited in θ since the maximum 2θ at which reflections could be observed was only 30°. The initial data collected at low temperature were incomplete because of crystal mounting problems. The crystal used for successful data collection was fixed in a conical glass capillary by slight melting of the crystal surface, followed by rapid cooling, thus attaching the crystal to the capillary wall by a thin film of frozen glyme. These intensity data were collected on a CAD-4 diffractometer, equipped with a graphite mono-chromator, using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The data were measured at 150 ± 3 K (stream of cold N_2 gas), to the limit $2\theta = 50°$ with the $\omega/2\theta$ scan mode and a scan width of 0.9°. All possible reflections with $l \geq 0$ were measured. The standard reflections, scanned after every 30 min of X-ray exposure time, suffered no significant loss of intensity during data collection. Ignoring the anomalous scattering of sodium, symmetry-related intensities were averaged. After Lorentz and polarization correction, and assigning zero weight to 642 reflections with a net count less than $3 \cdot 0\sigma(I)$ [where $\sigma(I)$ is the standard deviation estimated from counting statistics], 2059 independent structure amplitudes remained and were used in the structure refinement. Absorption corrections were not applied since the shape of the crystal could not be accurately determined. [μ(Mo $K\alpha$) = 0.107 mm^{-1}; maximum calculated effect is less than 3% in the intensity.]

The structure was solved with direct methods utilizing *MULTAN* (Germain, Main & Woolfson, 1971). The E map, calculated with the phases as determined by the *MULTAN* solution with the highest combined figure of merit (out of 64 phase sets), revealed the 37 non-hydrogen atoms of the structure among the 42 highest peaks. Failure to obtain a structure solution from the low-resolution room-temperature data, despite numerous trials, suggests that these data are subject to extensive Patterson overlap.

The refinement was by full-matrix least squares (in three blocks; Tg1, Tg2, Bp/Na) minimizing $\sum w|F_o - KF_c|^2$, using 2059 observed reflections; $w^{-1} = \sigma_c^2(F_o) + 0.00075F_o^2$, where $\sigma_c^2(F_o)$ is from counting statistics. Refinement of the overall scale factor and positional and anisotropic thermal parameters for the non-hydrogen atoms converged at an R value of 0.077. Hydrogen atom positions were calculated and could clearly be located in a subsequent difference synthesis. Introduction of the hydrogen atoms with $B = 4.0$ Å^2, followed by four additional cycles of anisotropic refinement of the non-hydrogen atoms and fixed H-atom parameters, yielded a final $R = \sum |F_o - KF_c|/\sum F_o$ of 0.032 and an $R_w = (\sum w|F_o - KF_c|^2/\sum w|F_o|^2)^{1/2}$ of 0.041. The final parameter shifts were all less than their estimated standard deviations.

The atomic scattering factors for Na, O and C were those of Cromer & Mann (1968) and for H those of

Stewart, Davidson & Simpson (1965). We used the XRAY (1972) system of programs and the *ORTEP* program (Johnson, 1965). The final positional parameters are given in Table 2.*

Discussion

The crystal structure of NaBp.2Tg is built up of biphenyl anions and Na$^+$(2Tg) cations (Na$^+$, coordinated by two triglyme molecules). In Fig. 1 a stereo-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34096 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
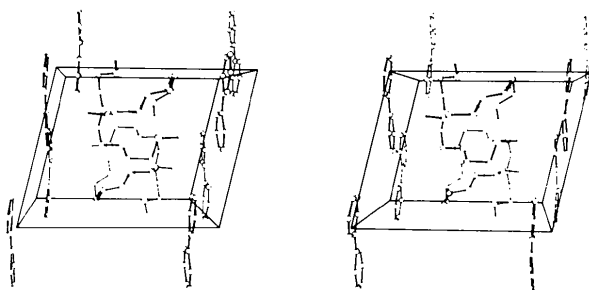
Table 2. *Positional parameters ($\times 10^4$) for the non-hydrogen atoms*

Standard deviations are given in parentheses.

	x	y	z
Na	5487 (1)	6716 (1)	7556 (1)
Biphenyl anion			
C(17)	9648 (3)	404 (2)	2798 (4)
C(18)	9629 (3)	−665 (3)	2953 (4)
C(19)	9913 (3)	−1122 (3)	4277 (4)
C(20)	10235 (3)	−572 (4)	5543 (4)
C(21)	10237 (3)	463 (3)	5443 (4)
C(22)	9956 (3)	942 (3)	4127 (3)
C(23)	9398 (3)	889 (3)	1425 (3)
C(24)	9195 (3)	356 (3)	92 (3)
C(25)	9031 (3)	835 (3)	−1217 (4)
C(26)	9031 (3)	1867 (4)	−1321 (4)
C(27)	9183 (3)	2417 (3)	−33 (4)
C(28)	9344 (3)	1952 (3)	1283 (3)
Triglyme 1			
C(1)	7202 (4)	7171 (3)	10922 (4)
O(1)	6902 (2)	6370 (2)	9934 (2)
C(2)	7908 (3)	5795 (3)	9860 (3)
C(3)	7606 (3)	5070 (3)	8655 (3)
O(2)	7175 (2)	5623 (2)	7364 (2)
C(4)	7203 (3)	5081 (2)	6081 (3)
C(5)	6781 (3)	5776 (3)	4854 (3)
O(3)	5601 (2)	6038 (2)	4870 (2)
C(6)	5202 (3)	6891 (3)	4022 (3)
C(7)	3924 (3)	7020 (3)	3991 (3)
O(4)	3799 (2)	7157 (2)	5431 (2)
C(8)	2596 (3)	7127 (3)	5503 (4)
Triglyme 2			
C(9)	8072 (3)	7922 (3)	7163 (4)
O(5)	6841 (2)	8067 (2)	7014 (2)
C(10)	6608 (3)	9089 (2)	7262 (3)
C(11)	5340 (3)	9181 (2)	7292 (3)
O(6)	5139 (2)	8574 (2)	8429 (2)
C(12)	4014 (3)	8705 (3)	8711 (4)
C(13)	3837 (3)	7885 (3)	9697 (3)
O(7)	3916 (2)	6975 (2)	8960 (2)
C(14)	3815 (3)	6108 (2)	9787 (3)
C(15)	3513 (3)	5259 (3)	8749 (3)
O(8)	4402 (2)	5165 (2)	7952 (2)
C(16)	4058 (4)	4484 (3)	6803 (4)

Fig. 1. Stereoview of the packing. The *a* axis runs horizontally across the page, the *c* axis runs down the page.

view along the *b* axis is given. The present structure can clearly be characterized as belonging to the category of solvent-separated ion-pair structures. Thereby it is a member of the same category as the crystal structures of RbBp.2Tg (Mooij, Klaassen, de Boer, Degens, van den Hark & Noordik, 1976) and KBp.2Ttg (Noordik, Schreurs, Gould, Mooij & de Boer, 1978). Crystal structures of some diamagnetic aromatic ion-pairs in which tetramethylethylenediamine or bis-quinuclidine are the coordinating molecules (Rhine, Davis & Stucky, 1975; Walczak & Stucky, 1976) and crystal structures of alkali complexes of cyclooctatetraene (Goldberg, Raymond, Harmon & Templeton, 1974; Noordik, Degens & Mooij, 1975) have been reported to belong to the class of contact ion-pair structures. All of these crystal structure determinations firmly underline the existence of two distinct types of ion-pairs in the solid state, demonstrating that the concept of solvent-separated and contact ion-pairs, which descends from spectroscopic experiments in solution, also holds in the solid state.

The biphenyl anion

The atomic numbering and the individual bond distances in the biphenyl anion are given in Fig. 2. In Table 3 bond distances and angles, averaged to 222 (D_2) symmetry, are compared with the corresponding values in RbBp.2Ttg and KBp.2Ttg, and also with those in neutral biphenyl (Charbonneau & Delugeard, 1976). The pattern of a shortened central C—C bond and lengthened 'inner' C—C bonds as compared with neutral biphenyl is found in all three of the anions and corresponds with the calculated bond-order changes on going from the neutral molecule to the anion (Mooij, Klaassen, de Boer, Degens, van den Hark & Noordik, 1976). The increased *ortho*-hydrogen repulsion, in comparison with neutral biphenyl, which is caused by the shortening of the central C—C bond, expresses itself in the values of the bond angles at the carbon atoms of the central C—C bond. These angles are significantly smaller than 120° (see Table 3) and significantly smaller than the already reduced value of 117·9° in neutral biphenyl.

The phenyl rings in the biphenyl anion are nearly planar; the maximum deviation of the least-squares planes is 0·023 Å and the dihedral angle between the two rings is 7·3°. In RbBp.2Ttg this angle was 9·4°. (In KBp.2Ttg it could not be determined because of disorder.) However, the geometry of the biphenyl anion in RbBp.2Ttg and NaBp.2Tg differs significantly: in RbBp.2Ttg the dihedral angle is a torsion angle around the central C—C bond; in the present compound the dihedral angle is composed of torsion around, as well as bending of, the longer molecular axis such that the angle between the lines C(18)···C(22) and C(24)···C(28) is 5·0° and the angle between the lines C(20)···C(17) and C(23)···C(26) is 5·1°. In RbBp.2Ttg these values are 9·0 and 0·1° respectively.

The Na⁺(2Tg) cation

C—O bond distances in the Tg molecules are 1·415 (5) to 1·432 (5) Å with an average value of 1·425 Å. For the C—C bonds these values are 1·488 (5), 1·501 (5) and 1·495 Å respectively. C—O—C angles are 109·9 (3)° to 113·8 (3)°; average value 112·1°. O—C—C angles are 106·7 (3)° to 109·8 (3)°; average value 107·8°. The Na—O distances range from 2·504 (4) Å to 2·755 (4) Å with an average value of 2·579 Å.

Table 3. *Average geometry of biphenyl ion (molecule) in different compounds*

	NaBp.2Tg[1]	RbBp.2Ttg[2]	KBp.2Ttg[3]	Bp[4]
a	1·435 (6) Å	1·441 (8) Å	1·436 (3) Å	1·496 (3) Å
b	1·436 (3)	1·425 (5)	1·430 (5)	1·397 (3)
c	1·381 (2)	1·385 (3)	1·380 (1)	1·388 (3)
d	1·397 (5)	1·404 (3)	1·391 (1)	1·385 (3)
α	114·7 (1)°	115·3 (3)°	115·2 (2)°	117·9 (2)°
β	122·2 (1)	122·1 (3)	121·9 (1)	121·0 (2)
δ	117·9 (3)	117·3 (3)	118·2 (2)	118·9 (2)
γ	121·6 (2)	121·6 (2)	121·4 (1)	120·7 (2)

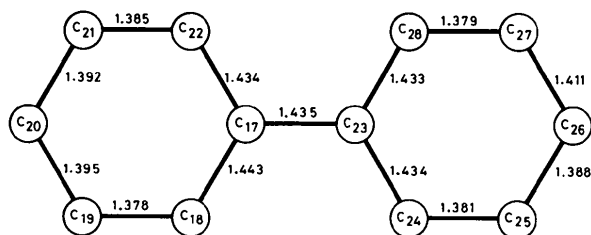(1) At 150 K, (2) at 100 K, (3) at 120 K, (4) at 110 K.

Fig. 2. Atomic numbering and bond lengths in the Bp⁻ ion in NaBp.2Tg. (E.s.d. = 0·006 Å.)

The coordination spheres of the Na^+, K^+ and Rb^+ ions are discussed elsewhere (de Boer, Klaassen, Mooij & Noordik, 1978) and we will limit our present discussion to the overall geometry of the cations.

The $Na^+(2Tg)$ cation shows nearly 222 (D_2) symmetry. To idealize the most pronounced pseudo-twofold axis $(Z$, Table 4) an average atomic shift of only 0·02 Å is required. The other two nearly twofold axes are less pronounced and an average shift of 0·13 Å is required to idealize the twofold symmetry around these directions. The cations in RbBp.2Ttg and KBp.2Ttg exhibit less symmetry and show only one (pseudo) twofold axis [2 (C_2) symmetry] (Noordik, Schreurs, Gould, Mooij & de Boer, 1978). For $Rb^+(2Ttg)$ the required average shift to idealize this axis is 0·13 Å and for $K^+(2Ttg)$ it is 0·14 Å. In Table 4 the direction of the pseudo-twofold axis in the three compounds is given together with the average atomic shift required to idealize the twofold symmetry. These data show that in $K^+(2Ttg)$ the local pseudo-twofold axis nearly coincides with the crystallographic b axis. This 'coincidence' of a local pseudo-twofold axis with a crystallographic twofold axis in the centrosymmetric space group $C2/c$ explains the observed disorder in the KBp.2Ttg structure.

The crystal structure determinations of the three alkali–biphenyl–glyme systems RbBp.2Ttg, KBp.2Ttg and NaBp.2Tg show the effect of the radius of the alkali ions on the packing of similar building units in the solid state. Crystals of NaBp.Ttg could not be prepared; the 'hole' formed by the oxygen atoms of the Ttg molecules is probably too large for Na^+, radius 1·18 Å. However, single crystals of NaBp.2Tg are 'stable' and the cations exhibit local twofold symmetry. A similar local symmetry is shown by the cations in RbBp.2Ttg and KBp.2Ttg, but the local symmetry axes in these compounds have a completely different orientation, apparently resulting from the minor difference of about 0·1 Å in ionic radius (1·53 Å for K^+

vs 1·62 Å for Rb^+), and the packing of the same building units is completely different.

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Table 4. *Local twofold axis through the cations*

Structure	Direction cosines of $Z^{(2)}$ with			$d^{(1)}$
	a	b	c^*	
NaBp.2Tg	0·058	0·699	−0·137	0·02 Å
RbBp.2Ttg	0·915	−0·347	0·206	0·13 Å
KBp.2Ttg	−0·022	0·999	−0·040	0·14 Å

(1) Average atomic shift to achieve ideal twofold symmetry, (2) most pronounced pseudo-twofold axis.