Abstract

\[ \text{[Na(C}_\text{12}H_{18}O_4)_2\text{]C}_\text{12}H_{10\text{,}} \quad \text{(C}_\text{16}H_{36}\text{NaO}_2\text{)}^+\text{C}_\text{12}H_{10\text{,}} \quad M_r = 533\cdot7, \quad \text{monoclinic, } P2_1, \quad a = 11\cdot721(2), \quad b = 13\cdot425(2), \quad c = 9\cdot555(2) \text{ Å, } \beta = 103\cdot08(4) ^\circ \text{[λ(Mo } K\alpha) = 0\cdot71069 Å], } \quad V = 1464\cdot5 \text{ Å}^3, \quad D_x (150 \text{ K}) = 1\cdot21 \text{ Mg m}^{-3}, \quad Z = 2. \] The structure was solved by MULTAN and refined to \( R(F_0) = 0\cdot032 \) and \( R_w(F_0) = 0\cdot041 \) for 2059 reflections measured with graphite-mono-
chromated 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.

Experimental

A solution of the NaBp salt in Tg [Bp = biphenyl; Tg = CH\text{3}O(CH\text{2}CH\text{2}O)\text{3}CH\text{3}] was prepared under high vacuum using standard techniques (Caneters, 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 (0k0 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 three alkali–biphenyl systems in the solid state (Mooij, 1976; de Boer, Klaassen, Mooij & Noordik, 1978), the structure of NaBp. 2Tg [Tg = triglyme, CH\text{3}O(CH\text{2}CH\text{2}O)\text{3}CH\text{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, K Bp. 2Ttg and NaBp. 2Tg.

Table 1. Crystal data

| \( a \) | 11.721(2) Å | \( a = 11\cdot721(2) \) | Z = 2 |
| \( b \) | 13.425(2) | \( b = 13\cdot425(2) \) | \( D_x = 1\cdot21 \) Mg m\(^{-3}\) |
| \( c \) | 9.555(2) | \( c = 9\cdot555(2) \) | \( M_r = 533\cdot7 \) |
| \( \beta \) | 103.08(4) | \( \beta = 103\cdot08(4) ^\circ \) | (cell dimensions at 150 K) |
| \( V \) | 1464.5 Å\(^3\) | \( V = 1464\cdot5 \) Å\(^3\) | |

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data set at 150 K could be obtained. The room-
temperature data were limited in $\theta$ since the maximum
$2\theta$ 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 Na
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, sym-
metry-related intensities were averaged. After Lorentz
and polarization correction, and assigning zero weight
to 642 reflections with a net count less than 3.0o(1) [where
the shape of the crystal could not be accurately deter-
mined. [$\mu$(Mo K\alpha) = 0.107 mm$^{-1}$; maximum cal-
culated 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 deter-
mind 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 $\sum w|F_o -$
$K F_e|^2$, using 2059 observed reflections; $w^{-1} = \sigma^2 (F_o)$ +
0-00075$F_o^2$, where $\sigma^2 (F_o)$ 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.

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 parame-
ters are given in Table 2.*

Discussion

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

Table 2. Positional parameters ($\times 10^4$) for the non-
hydrogen atoms

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>5487 (1)</td>
<td>6716 (1)</td>
<td>7556 (1)</td>
</tr>
</tbody>
</table>

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) 4820 (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) 5550 (3)

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 (3) 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)

* 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.
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.2Ttg (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 tetramethylethylene diamine 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 $D_{2h}$ 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 $120^\circ$ (see Table 3) and significantly smaller than the already reduced value of $117.9^\circ$ in neutral biphenyl.

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

<table>
<thead>
<tr>
<th></th>
<th>NaBp.2Tg(1)</th>
<th>RbBp.2Tg(2)</th>
<th>KBp.2Tg(3)</th>
<th>Bp(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond distances</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–C (Å)</td>
<td>1.381 (2)</td>
<td>1.385 (3)</td>
<td>1.380 (1)</td>
<td>1.388</td>
</tr>
<tr>
<td>C–O (Å)</td>
<td>1.435 (6)</td>
<td>1.441 (8)</td>
<td>1.436 (3)</td>
<td>1.496</td>
</tr>
<tr>
<td>C–O–C (°)</td>
<td>114.7(1)</td>
<td>115.3(3)</td>
<td>115.2(2)</td>
<td>117.9</td>
</tr>
<tr>
<td>O–C–C (°)</td>
<td>122.2 (1)</td>
<td>122.1 (3)</td>
<td>121.9 (1)</td>
<td>121.0</td>
</tr>
</tbody>
</table>

(1) At 150 K, (2) at 100 K, (3) at 120 K, (4) at 110 K.
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 (D₂) 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 (C₂) 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.2Ttg show the effect of the radius of the alkali ions on the packing of similar building units in the solid state. Crystals of NaBp.2Ttg 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.2Ttg 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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References