

$\pi$ -GROUPS IN ION-PAIR BONDING. THE MOLECULAR STRUCTURE OF BIS(TETRAHYDROFURAN)SODIUM (9,10-DIHYDRO-9,10-ANTHRYLENE)DIMETHYLALUMINATE  $[\text{Na}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$ , A SODIUM/TRIMETHYLALUMINUM REDUCTION PRODUCT OF ANTHRACENE

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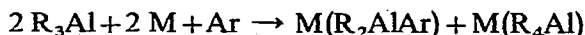
SUMMARY

The structure of  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$  has been determined by three-dimensional X-ray crystallographic techniques. The compound crystallizes in the monoclinic space group  $B2_1/c$ , and the unit cell dimensions are  $a=22.610(18)$ ,  $b=11.256(10)$ ,  $c=17.589(15)$  Å, and  $\beta=93.27(5)^\circ$ . The calculated density for eight  $[\text{Na}(\text{THF})_2][\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]$  monomeric units is  $1.196 \text{ g/cm}^3$ . The structure has been refined by least-squares to a conventional weighted  $R$  value of 0.08. The compound exists as a centrosymmetric, contact ion-pair complex with two  $\text{Na}(\text{THF})_2^+$  cations complexed to the dimeric dianion. Two 1,4-dihydro-1,4-anthrylene groups are fused into the dianion via the two dimethylaluminum species. The average Al-C(anthrylene) bond distance of  $2.060(8)$  Å is significantly longer than the average Al-C(methyl) bond distance of  $2.002(9)$  Å. A discussion of the relative importance of steric and electronic effects is given. The importance of steric effects in ion-pairing is also considered.

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INTRODUCTION

Trialkylaluminum compounds ( $\text{R}_3\text{Al}$ ) are known to react in the presence of alkali metals (M) and olefinic and aromatic hydrocarbons (Ar) according to the following equation:



The scope of these reactions has recently been summarized along with detailed reaction mechanisms<sup>1</sup>. In most cases the structure assigned to the  $(\text{R}_2\text{AlAr})^-$  species was that of a 1,4-addition product, the aluminum atom bonding to two carbon atoms of the aromatic moiety.

We became interested in these compounds for two reasons. First, since the geometries of the proposed anions were quite novel, a detailed investigation of their structure and bonding in the solid state was deemed appropriate. Second, since the

cations are known to be specifically solvated in the solid state, the compounds offer a rather unique opportunity to find out how the cations and anions interact stereochemically in the formation of organic, alkali ion-pairs. Conductivity studies of such ion-pairs in solution have indicated that steric interactions may be important as far as the equilibrium between solvent separated and contact ion-pairs is concerned<sup>2-4</sup>, but little is known in detail of the nature of these interactions.

Recently we have published the results of the first of these studies, the crystal structure of  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$ <sup>5</sup>. This compound was found to contain a dimeric dianion with the aluminum atoms bridging the 1,4' and 4,1' positions of the symmetry related 1,4-dihydronaphthylene rings. The most remarkable feature of the dianion was the presence of Al-C(naphthylene) bonds which were 0.07 Å longer than the Al-C(methyl) bonds. While the geometry of this dianion shows definite signs of steric strain, we ascribed the bond lengthening phenomenon to a delocalization of charge from the aluminum atoms onto the naphthylene rings; thus the Al-C(naphthylene) bonds were thought to possess partial electron-deficient character. In order to investigate further the steric and electronic factors which contribute to the geometry of the anion, the determination of the structure of the anthrylene analogue was commenced. Results from <sup>1</sup>H NMR studies and chemical investigations had previously indicated that the aluminum atoms were bonded at the 9 and 10 positions of the anthrylene ring<sup>6</sup>, and by analogy to the naphthylene compound, a dimeric dianion was expected<sup>5</sup>. Since the counter ion was presumed to consist of a THF coordinated  $\text{Na}^+$ , a comparison of the ion-pairing geometries of the anthrylene and naphthylene compounds should show the importance of steric factors in organosodium ion-pairing.

#### EXPERIMENTAL

Crystals of the compound  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$  were grown by the slow evaporation of a 3/2 mixture of benzene/THF in which the corresponding etherate, prepared as described by Lehmkuhl<sup>6</sup>, had been dissolved. The need for a benzene/THF mixture was the result of the instability of the compound (decomposing in one to three hours to yield a blue solution) in THF. In the benzene/THF mixture, the compound showed no signs of decomposition for up to 36 h. All manipulations of the solids were carried out in a glove box.

Crystals of  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$  were found to be pyrophoric and water sensitive. Accordingly, the crystals were sealed in glass capillaries under an inert atmosphere before the X-ray studies were initiated. The systematic absences ( $0k0$ ,  $k=2n+1$ ;  $h0l$ ,  $l=2n+1$ ) determined by precession and Weissenberg photographs uniquely determined the space group as  $C_{2h}^5-P2_1/c$ . The lattice constants ( $t$  20°,  $\lambda$  0.71069 Å) obtained by a least-squares procedure defined below are:  $a = 13.928(17)^*$ ,  $b = 11.248(15)$ ,  $c = 17.595(23)$  Å,  $\beta = 125.83(6)^\circ$ . Due to the small supply of the crystals, the density could not be measured. The calculated density based upon 4  $[\text{Na}(\text{THF})_2][\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]$  monomers per unit cell is 1.196 g/cm<sup>3</sup>, which is reasonably close to the calculated density of 1.131 g/cm<sup>3</sup> for  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$ <sup>5</sup>. In order to carry out the least-squares refinement of the structure,

\* Numbers in parentheses here and in succeeding discussions are estimated standard deviations in the least significant digit.

it was convenient (*vide infra*) to transform the  $P2_1/c$  unit cell to a  $B2_1/c$  unit cell<sup>7</sup>. The lattice constants for this unit cell obtained by a least-squares procedure similar to that referred to above are:  $a=22.610(18)$ ,  $b=11.256(10)$ ,  $c=17.589(15)$  Å,  $\beta=93.27(5)^\circ$ . All of the results are tabulated with respect to this unit cell choice.

Intensity data were measured on an automated Picker four-cycle X-ray diffractometer. The diffractometer was equipped with a highly oriented graphite single crystal monochromator, and Mo- $K_\alpha$  radiation was used. The crystal, which might be described roughly as a tabular block of dimensions  $0.46 \times 0.31 \times 0.16$  mm, was aligned on the diffractometer in such a way that the  $[1, -1, 1]$  and the  $\phi$  axis of the diffractometer were coincident. Since the  $[1, -1, 1]$  is not a symmetry axis, such an alignment does not optimize the conditions for multiple diffraction<sup>8</sup>. The crystal-to-source and the crystal-to-detector distances were 21 and 27 cm, respectively, and the detector was equipped with a  $4 \times 4$  mm aperture. A take-off angle was chosen which provided 83% of the intensity of a typical, large peak. The lower level and upper level discriminators of the pulse height analyzer were adjusted to obtain a 95% window centered on the Mo- $K_\alpha$  peak. The full peak width at half-height,  $0.11(2)^\circ$ , as measured by an  $\omega$ -scan technique on several strong reflections, indicated that the mosaicity was satisfactorily low. The lattice constants were obtained by a least-squares refinement on the setting angles of 12 carefully centered reflections<sup>9</sup>.

The data were measured by the  $\theta$ - $2\theta$  scan technique. A symmetrical scan of  $-0.75^\circ$  from the Mo- $K_{\alpha_1}$  peak ( $\lambda=0.70930$  Å) to  $0.75^\circ$  from the Mo- $K_{\alpha_2}$  peak ( $\lambda=0.71359$  Å) was made at the rate of  $1.0^\circ/\text{min}$ . Stationary-crystal/stationary-counter background counts of 10 sec were taken at the beginning and end of each scan. Coincident losses were minimized by the insertion of copper foil attenuators when the counting rate exceeded 10000 counts/sec. As a check on the stability of the diffractometer and the crystal, two standard reflections were monitored for every 100 reflections gathered. No significant variation in the intensities of these standard reflections was noticed during data collection. One form of data was measured out to  $2\theta=45^\circ$ , and it contained 3255 unique reflections.

The data correction was carried out as described previously<sup>5,10</sup>. No absorption correction was applied ( $\mu=1.33 \text{ cm}^{-1}$ ) since the maximum variation in the transmission factors would be less than 5%. The 1269 reflections that had intensities greater than two times their own standard deviation were considered to be observed. Only these reflections were used in the refinement of the structure.

#### SOLUTION AND REFINEMENT

The crystal structure was solved by the symbolic addition procedure<sup>11</sup>. The highest 300  $|E(hkl)|$ 's were generated, and after the symbolic signs of 41 large  $|E(hkl)|$ 's were determined by hand (using three origin reflections and six symbols), the signs of 255  $|E(hkl)|$ 's were determined by computer\*. For the second most likely com-

\* In addition to R. B. K. Dewar, A. L. Stone, and E. B. Fleischer's FAME-MAGIC-LINK-SYMP used in applying the symbolic addition algorithm, other computer calculations were performed with standard programs. W. R. Busing, K. O. Martin, and H. A. Levey's ORFLS and ORFFE were used for least-squares refinement and molecular geometry calculations, respectively. J. Gvildy's ARGONNE FOURIER was used for electron density calculations. Best plane calculations were performed with M. E. Pippy and F. R. Ahmed's MEAN PLANE. Structural illustrations were prepared with the aid of C. K. Johnson's ORTEP.

combination of signs for the six symbols, a total of 267  $|E(hkl)|$ 's were unambiguously given signs. Only nine of these signs were shown to be incorrect. The  $E$ -map generated with these signed  $|E(hkl)|$ 's revealed the positions of the nonhydrogen atoms in the  $\text{Na}[(\text{CH}_3)_2\text{AlC}_{14}\text{H}_{10}]$  fragment. An electron density map based on the signs calculated from this model revealed the positions of all of the remaining nonhydrogen atoms.

The structure was refined by full-matrix least-squares and difference Fourier techniques. The function minimized was  $w \cdot \Delta^2$ ,  $\Delta = ||F_o| - |F_c||$ , where  $w$  is the weight and  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes, respectively. Unit weights were used in the initial stages of refinement, but the following empirical weighting scheme, formulated by a procedure described below, was used in the final stages:

$$w = 1/\sigma(|F_o|)^2$$

$$\sigma(|F_o|) = 2.0 + (28.6 - |F_o|)/23.8 \text{ for } |F_o| \leq 28.6$$

$$\sigma(|F_o|) = 2.0 + (|F_o| - 28.6)/61.0 \text{ for } |F_o| > 28.6$$

The scattering factor tables used for  $\text{Al}^0$ ,  $\text{Na}^0$ ,  $\text{O}^0$ , and  $\text{C}^0$  were those calculated by Hanson<sup>12</sup>; the hydrogen form factors were the best spherical scattering factors as calculated by Stewart, Davidson, and Simpson<sup>13</sup>. No attempts were made to account for anomalous dispersion in this centric light atom structure. The reliability indices,  $R_1$  and  $R_2$ , are defined as follows:

$$R_1 = \Sigma \Delta / \Sigma |F_o|$$

$$R_2 = [\Sigma w \cdot \Delta^2 / \Sigma (w \cdot |F_o|^2)]^{1/2}$$

The initial values of  $R_1$  and  $R_2$  with all nonhydrogen atoms included in the calculation and unit weights were 0.278 and 0.269, respectively. Five cycles of least-squares on the positional and isotropic thermal parameters reduced  $R_1$  to 0.172 and  $R_2$  to 0.166. During isotropic refinement the values of the correlation coefficients between the  $x$  and  $z$  parameters of each atom ranged from 0.56 to 0.61. Correlation between parameters of such magnitudes is known to slow convergence of the least-squares refinement, and in this case the correlation problem could be eliminated by a transformation to a unit cell which possessed a  $\beta$  angle closer to  $90^\circ$ . Accordingly, the unit cell and atom parameters in  $P2_1/c$  were transformed to the centered cell  $B2_1/c$ , in which all further calculations were performed. A difference Fourier was calculated, and it revealed peaks ranging from  $-0.77 \text{ e}/\text{\AA}^3$  to  $0.63 \text{ e}/\text{\AA}^3$  with a background density of  $\pm 0.2 \text{ e}/\text{\AA}^3$ . The largest peaks were in the vicinity of the Al, Na, and THF atoms. The height of a typical anthrylene carbon atom in this structure was  $5.06 \text{ e}/\text{\AA}^3$ . In addition peaks ( $0.30\text{--}0.51 \text{ e}/\text{\AA}^3$ ) in the region of the anthrylenic and methyl carbon atoms were in reasonable positions for all of the expected hydrogen atoms. In order to better account for the difference density features, anisotropic refinement of all of the nonhydrogen atoms was carried out while the constant contribution of all of the hydrogen atoms was added to the calculated structure factors. The positions of the hydrogen atoms were idealized (C-H distances of  $1.02 \text{ \AA}$ ,  $sp^2$  or  $sp^3$  hybridization), and the isotropic temperature factors of the associated carbon atoms were given to the respective hydrogen atoms. Before the first anisotropic refinement cycle, the empirical weighting scheme was derived from a plot of the distribution of  $w \cdot \Delta^2$  with both  $|F_o|$

and  $\sin \theta/\lambda$ . After four cycles of anisotropic refinement, the values of  $R_1$  and  $R_2$  for all of the observed reflections were 0.079 and 0.080, respectively\*. On the final cycle the maximum value of the ratio (shift/standard deviation) was 0.11. The estimated standard deviation of an observation of unit weight was 0.91. The relative validity of the weighting scheme, as judged by the variation of the average of  $w \cdot \Delta^2$  with  $\sin \theta/\lambda$  and  $|F_o|$ , was satisfactory. A careful examination of the strong, low angle reflections indicated that an extinction correction was not needed. A final difference Fourier was calculated, and it contained only residual density ranging from 0.28 to  $-0.30 \text{ e}/\text{\AA}^3$  in a background of  $\pm 0.15 \text{ e}/\text{\AA}^3$ .

The final values of the positional and thermal parameters are listed in Tables 1, 2, and 3. Bonded and selected nonbonded interatomic distances for the nonhydrogen atoms are listed in Table 4. Bond angles are tabulated in Table 5. The root-mean-square displacements of the nonhydrogen atoms appear in Table 6. The results of the least-squares best plane calculations are included in Table 7.

## DISCUSSION

The structure of  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$  is illustrated in Fig. 1. As expected, this compound was found to exist as a contact ion-pair which contains a dimeric dianion. The dianion was formed by the linking of two anthracene molecules via two dimethylaluminum species across the 9,10' and 9',10 carbon atoms in the symmetry related rings. Two  $\text{Na}(\text{THF})_2^+$  units serve as the counter-ions. The similarities of the structures of the anthrylene and the naphthylene compounds invites a detailed comparison of the two structures. A comparison should show the importance of such features as nonbonded contacts between the ring atoms and the dimethylaluminum groups and electronic effects such as delocalization of the formal  $-1$  charge of the aluminum atoms into the aromatic rings.

The  $[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2^{2-}$  species, the inner portion of which is illustrated in Fig. 2, deviates only slightly from  $D_{2h}$  symmetry. Accordingly, the following discussion of the dianion will be in terms of the average interatomic distances and angles. The aluminum atom, with its approximate *mm* point symmetry, forms bonds of 2.002(9) Å to two methyl carbon atoms C(15) and C(16) and of 2.060(8) Å to two anthrylene carbon atoms C(9) and C(10'). Neither of these average values differs significantly from those found respectively for similar bonds in the naphthylene compound, 1.986(8) Å and 2.065(8) Å. The angle formed by the methyl groups and the aluminum atom is  $110.9(5)^\circ$ , a value quite close to the value of  $110.1(5)^\circ$  found in the naphthylene compound for the corresponding angle. The bond angle formed by the ring carbon atoms C(9) and C(10') and the aluminum atom of  $120.2(4)^\circ$  is somewhat larger than that found for the corresponding angle in the naphthylene compound,  $116.5(4)^\circ$ . If one assumes that the aluminum atom uses only 3s and 3p orbitals in forming hybrid orbitals to bond to the carbon atoms, then at least two of these four aluminum-carbon bonds must be bent, and the bonds should be more bent in the anthrylene compound than they are in the naphthylene compound.

\* A list of the observed and calculated structure factor amplitudes is contained in the Ph.D. thesis of D. J. Brauer which was submitted to the Graduate College of the University of Illinois and which can be obtained through *Dissertation Abstracts*.

While no crystallographic symmetry is imposed on the anthrylene ring, the actual symmetry realized is nearly  $C_{2v}$ . The carbon atoms in the two xylylene groups deviate slightly but significantly from planarity (Table 7). However the two phenylene rings (planes 3 and 4) are not significantly nonplanar. A systematic study of the non-

TABLE 1

POSITIONAL PARAMETERS FOR THE NONHYDROGEN ATOMS IN  
 $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$

Atom	x	y	z
Al	0.3164(1)	-0.1745(4)	0.2465(2)
Na	0.1424(2)	-0.1868(5)	0.3392(2)
O(1)	0.1310(4)	-0.3853(8)	0.3732(5)
O(2)	0.0486(4)	-0.156(1)	0.3907(5)
C(1)	0.3127(5)	-0.036(1)	0.0565(6)
C(2)	0.3222(5)	0.060(1)	0.0111(6)
C(3)	0.2885(6)	0.160(1)	0.0152(7)
C(4)	0.2422(5)	0.159(1)	0.0666(6)
C(5)	0.0952(5)	-0.080(1)	0.1800(6)
C(6)	0.0725(5)	-0.193(1)	0.1868(7)
C(7)	0.1090(6)	-0.289(1)	0.1847(7)
C(8)	0.1696(6)	-0.273(1)	0.1762(6)
C(9)	0.2569(4)	-0.1423(9)	0.1554(5)
C(10)	0.1793(4)	0.062(1)	0.1613(5)
C(11)	0.1563(5)	-0.061(1)	0.1723(5)
C(12)	0.1931(5)	-0.161(1)	0.1695(5)
C(13)	0.2684(4)	-0.037(1)	0.1088(5)
C(14)	0.2322(5)	0.062(1)	0.1130(5)
C(15)	0.3974(5)	-0.171(1)	0.2049(6)
C(16)	0.2979(5)	-0.336(1)	0.2849(6)
C(17)	0.1647(6)	-0.463(2)	0.4204(9)
C(18)	0.1247(7)	-0.547(1)	0.4537(8)
C(19)	0.0667(7)	-0.532(1)	0.4125(8)
C(20)	0.0806(6)	-0.453(1)	0.3478(9)
C(21)	0.0361(7)	-0.197(2)	0.4651(9)
C(22)	-0.0280(9)	-0.201(2)	0.465(1)
C(23)	-0.0521(7)	-0.127(2)	0.406(1)
C(24)	-0.0013(8)	-0.096(2)	0.3612(9)

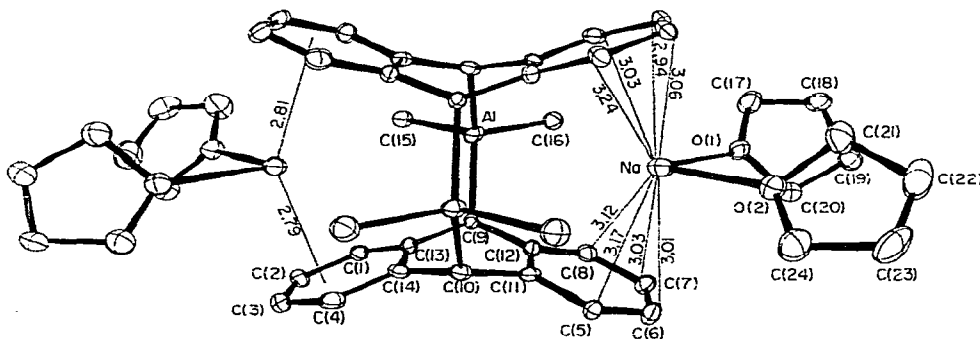


Fig. 1. A perspective drawing of the ion-pair  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$ .

TABLE 2

ANISOTROPIC THERMAL PARAMETERS FOR THE NONHYDROGEN ATOMS IN [Na(THF)<sub>2</sub>]<sub>2</sub>[Al(CH<sub>3</sub>)<sub>2</sub>C<sub>14</sub>H<sub>10</sub>]<sub>2</sub>

Atom	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Al	0.0017(1)	0.0017(4)	0.0032(1)	0.0002(1)	0.0002(1)	-0.0004(2)
Na	0.0026(1)	0.0164(7)	0.0040(2)	-0.0002(2)	-0.0000(1)	0.0007(3)
O(1)	0.0029(2)	0.016(1)	0.0059(4)	-0.0008(4)	-0.0003(2)	0.0025(6)
O(2)	0.0024(2)	0.024(2)	0.0062(4)	0.0006(5)	0.0006(3)	0.0007(7)
C(1)	0.0023(3)	0.012(1)	0.0029(4)	-0.0001(5)	0.0002(3)	0.0005(7)
C(2)	0.0027(3)	0.017(2)	0.0025(4)	-0.0007(7)	0.0004(3)	0.0013(3)
C(3)	0.0030(4)	0.015(2)	0.0041(5)	-0.0015(7)	0.0003(4)	0.0027(8)
C(4)	0.0023(3)	0.013(2)	0.0025(4)	0.0001(6)	-0.0005(3)	-0.0003(7)
C(5)	0.0018(3)	0.013(2)	0.0042(5)	-0.0004(6)	0.0002(3)	0.0001(7)
C(6)	0.0020(3)	0.019(2)	0.0045(5)	-0.0025(8)	0.0003(3)	-0.001(1)
C(7)	0.0025(4)	0.019(2)	0.0037(5)	-0.0029(7)	0.0000(4)	-0.0010(9)
C(8)	0.0032(4)	0.011(2)	0.0027(4)	-0.0008(6)	0.0002(3)	-0.0006(6)
C(9)	0.0019(3)	0.009(1)	0.0024(4)	-0.0008(4)	0.0006(2)	-0.0008(6)
C(10)	0.0020(3)	0.010(1)	0.0026(4)	0.0004(5)	-0.0001(3)	0.0002(6)
C(11)	0.0018(3)	0.010(1)	0.0021(4)	0.0005(5)	-0.0004(3)	0.0000(6)
C(12)	0.0022(3)	0.009(1)	0.0025(4)	-0.0013(6)	0.0003(3)	-0.0004(6)
C(13)	0.0015(2)	0.012(1)	0.0026(4)	-0.0009(5)	0.0005(3)	0.0004(7)
C(14)	0.0019(3)	0.011(1)	0.0020(4)	0.0000(5)	-0.0002(3)	0.0002(6)
C(15)	0.0024(3)	0.017(2)	0.0051(5)	0.0015(6)	0.0009(3)	-0.0007(9)
C(16)	0.0034(3)	0.012(2)	0.0049(5)	0.0000(6)	0.0000(3)	0.0004(8)
C(17)	0.0037(5)	0.018(2)	0.0085(9)	-0.0007(8)	-0.0011(5)	0.005(1)
C(18)	0.0046(5)	0.020(2)	0.0066(7)	-0.0024(9)	-0.0023(5)	0.006(1)
C(19)	0.0042(5)	0.016(2)	0.0062(7)	-0.0001(8)	-0.0004(5)	0.002(1)
C(20)	0.0035(4)	0.018(2)	0.0059(7)	-0.0003(8)	-0.0004(4)	0.001(1)
C(21)	0.0041(5)	0.027(3)	0.0074(8)	0.002(1)	0.0018(5)	0.001(1)
C(22)	0.0038(6)	0.035(4)	0.013(1)	-0.003(1)	0.0024(7)	0.004(2)
C(23)	0.0022(4)	0.034(4)	0.013(1)	0.002(1)	0.0008(6)	-0.004(2)
C(24)	0.0034(5)	0.026(3)	0.010(1)	0.002(1)	0.008(6)	0.003(1)

<sup>a</sup> The form of the anisotropic ellipsoid is  $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + \beta_{12} h \cdot k + \beta_{13} h \cdot l + \beta_{23} k \cdot l)]$ .

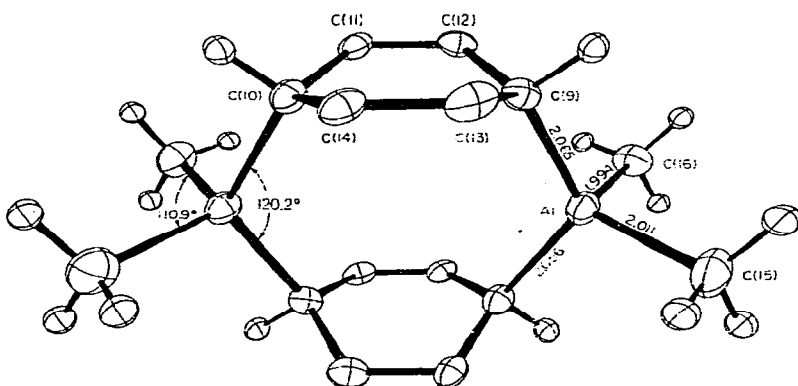


Fig. 2. A view of the inner portion of the dianion in [Na(THF)<sub>2</sub>]<sub>2</sub>[Al(CH<sub>3</sub>)<sub>2</sub>C<sub>14</sub>H<sub>10</sub>]<sub>2</sub>.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS FOR THE HYDROGEN ATOMS IN  
[Na(THF)<sub>2</sub>]<sub>2</sub>[Al(CH<sub>3</sub>)<sub>2</sub>C<sub>14</sub>H<sub>10</sub>]<sub>2</sub>

Atom	<i>x</i> <sup>a</sup>	<i>y</i>	<i>z</i>	<i>B</i> <sup>b</sup>
H(1)C(1)	0.339	-0.110	0.052	4.6
H(1)C(2)	0.355	0.057	-0.026	5.5
H(1)C(3)	0.296	0.233	-0.017	6.1
H(1)C(4)	0.216	0.232	0.069	5.0
H(1)C(5)	0.067	-0.009	0.181	4.8
H(1)C(6)	0.028	-0.205	0.193	5.5
H(1)C(7)	0.092	-0.373	0.189	5.8
H(1)C(8)	0.197	-0.345	0.175	5.3
H(1)C(9)	0.267	-0.211	0.121	3.9
H(1)C(10)	0.146	0.104	0.130	4.2
H(1)C(15)	0.406	-0.087	0.186	6.1
H(2)C(15)	0.428	-0.193	0.247	6.1
H(3)C(15)	0.399	-0.230	0.161	6.1
H(1)C(16)	0.257	-0.336	0.306	6.6
H(2)C(16)	0.299	-0.396	0.241	6.6
H(3)C(16)	0.328	-0.359	0.327	6.6
H(1)C(17)	0.187	-0.416	0.462	8.0
H(2)C(17)	0.194	-0.508	0.389	8.0
H(1)C(18)	0.122	-0.529	0.510	9.1
H(2)C(18)	0.140	-0.632	0.447	9.1
H(1)C(19)	0.037	-0.493	0.446	7.3
H(2)C(19)	0.505	-0.612	0.393	7.3
H(1)C(20)	0.046	-0.399	0.334	7.1
H(2)C(20)	0.090	-0.503	0.302	7.1
H(1)C(21)	0.053	-0.139	0.506	8.2
H(2)C(21)	0.054	-0.279	0.475	8.2
H(1)C(22)	-0.041	-0.171	0.517	11.1
H(2)C(22)	-0.042	-0.286	0.457	11.1
H(1)C(23)	-0.071	-0.053	0.428	10.9
H(2)C(23)	-0.083	-0.173	0.373	10.9
H(1)C(24)	0.006	-0.006	0.364	10.4
H(2)C(24)	-0.010	-0.120	0.306	10.4

<sup>a</sup> The positional and thermal parameters for the hydrogen atoms were not refined.<sup>b</sup> The hydrogen atoms were given isotropic temperature factors of the form  $\exp[-B \cdot (\sin^2 \theta / \lambda^2)]$ .

planarity of the anthrylene moiety indicates that each xylylene group is deformed at the fusion edge of the phenylene rings (planes 3 and 4) and the *cis*-2-butene groups (planes 5 and 6) by 4.7° and 3.7°, respectively. The deformation is such that the phenylene rings are turned away from the nearest Na atom. The dihedral angle between planes 1 and 2 of 144.1° is very close to that found<sup>14</sup> in dihydroanthracene, 145°, but is smaller than that found<sup>15</sup> in the naphthylene compound for the corresponding dihedral angle, 152.0(15)°, and in 1,4-cyclohexadiene, 159.3(7)°. The average value of the twelve phenylenic C-C bond lengths, 1.389(18) Å, is quite similar to that found in benzene<sup>16</sup>; thus the aromatic character of this part of the dianion is confirmed. The substituted methylene carbon-aromatic carbon bond lengths [1.490(18) Å] are the same as those found in naphthylene compound [1.491(12) Å] and are probably



TABLE 4

INTERATOMIC DISTANCES (Å) FOR THE NONHYDROGEN ATOMS<sup>a</sup> IN [Na(THF)<sub>2</sub>]<sub>2</sub>[Al(CH<sub>3</sub>)<sub>2</sub>C<sub>14</sub>H<sub>10</sub>]<sub>2</sub>

<i>Bond distances</i>			
Al-C(9)	2.065(10)	C(5)-C(11)	1.413(14)
Al-C(10) <sup>b</sup>	2.056(11)	C(6)-C(7)	1.362(17)
Al-C(15)	2.011(11)	C(7)-C(8)	1.398(15)
Al-C(16)	1.994(13)	C(8)-C(12)	1.378(14)
Na-O(1)	2.331(11)	C(9)-C(12)	1.491(13)
Na-O(2)	2.377(9)	C(9)-C(13)	1.470(13)
O(1)-C(17)	1.403(15)	C(10)-C(11)	1.497(15)
O(1)-C(20)	1.424(14)	C(10)-C(14)	1.504(13)
O(2)-C(21)	1.430(16)	C(11)-C(12)	1.399(14)
O(2)-C(24)	1.392(16)	C(13)-C(14)	1.391(14)
C(1)-C(2)	1.374(15)	C(17)-C(18)	1.45(2)
C(1)-C(13)	1.398(13)	C(18)-C(19)	1.47(2)
C(2)-C(3)	1.364(16)	C(19)-C(20)	1.49(2)
C(3)-C(4)	1.422(15)	C(21)-C(22)	1.45(2)
C(4)-C(14)	1.392(14)	C(22)-C(23)	1.42(2)
C(5)-C(6)	1.376(16)	C(23)-C(24)	1.47(2)
<i>Selected nonbonded distances</i>			
Al-Na	4.348(6)	Na-C(24)	3.449(18)
Al-Na'	4.455(7)	O(1)-O(2)	3.209(14)
Al-C(11')	3.059(12)	C(9)-C(10')	3.572(13)
Al-C(12)	3.032(11)	C(15)-C(1)	3.493(16)
Al-C(13)	3.022(11)	C(15)-C(5')	3.475(17)
Al-C(14')	3.037(11)	C(15)-C(9)	3.261(15)
Na-C(1')	3.239(12)	C(15)-C(10')	3.242(14)
Na-C(2')	3.059(13)	C(15)-C(11')	3.640(17)
Na-C(3')	2.937(12)	C(15)-C(13)	3.612(16)
Na-C(4')	3.026(10)	C(15)-C(16)	3.298(17)
Na-C(5)	3.174(12)	C(16)-C(4')	3.447(16)
Na-C(6)	3.034(13)	C(16)-C(8)	3.457(17)
Na-C(7)	3.009(12)	C(16)-C(9)	3.252(15)
Na-C(8)	3.121(12)	C(16)-C(10')	3.261(18)
Na-C(11)	3.291(11)	C(16)-C(12)	3.618(16)
Na-C(12)	3.272(10)	C(16)-C(14')	3.654(17)
Na-C(13')	3.324(12)	C(17)-C(3')	3.725(22)
Na-C(14')	3.234(11)	C(19)-C(21)	3.959(24)
Na-C(17)	3.448(17)	C(20)-C(7)	3.502(20)
Na-C(20)	3.316(17)	C(20)-C(21)	3.723(23)
Na-C(21)	3.361(16)	C(21)-C(2)	3.554(21)
		C(24)-C(6)	3.740(22)

<sup>a</sup> Errors in the lattice parameters are included in the estimated standard deviations.<sup>b</sup> The coordinates of the primed atoms are related to those of the asymmetric unit as follows:  $x', y', z' = \frac{1}{2} - x, -y, \frac{1}{2} - z$ .

not significantly shorter than the commonly accepted C( $sp^2$ )-C( $sp^3$ ) bond length of 1.510(5) Å<sup>17</sup>. The bond angles formed by the substituted methylene carbon atoms and the adjacent aromatic carbon atoms are 112.8(9)<sup>o</sup>, and this average value may be compared with the 111.5(6)<sup>o</sup> value for the corresponding angles in the naphthylene compound. The four aromatic carbon atom-substituted methylene carbon atom-

TABLE 5

BOND ANGLES ( $^{\circ}$ )<sup>a</sup> IN  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$ 

C(9)-Al-C(10')	120.2(4)	C(12)-C(9)-C(13)	114.1(9)
C(9)-Al-C(15)	106.3(4)	Al'-C(10)-C(11)	118.0(7)
C(9)-Al-C(16)	106.4(4)	Al'-C(10)-C(14)	116.3(8)
C(10')-Al-C(15)	105.7(5)	C(11)-C(10)-C(14)	112(1)
C(10')-Al-C(16)	107.2(5)	C(5)-C(11)-C(10)	120(1)
C(15)-Al-C(16)	110.9(5)	C(5)-C(11)-C(12)	118(1)
O(1)-Na-O(2)	85.9(4)	C(10)-C(11)-C(12)	122(1)
Na-O(1)-C(17)	133.4(9)	C(8)-C(12)-C(9)	122(1)
Na-O(1)-C(20)	122.1(9)	C(8)-C(12)-C(11)	120(1)
C(17)-O(1)-C(20)	104(1)	C(9)-C(12)-C(11)	119(1)
Na-O(2)-C(21)	122.0(8)	C(1)-C(13)-C(9)	122(1)
Na-O(2)-C(24)	130.7(9)	C(1)-C(13)-C(14)	118(1)
C(21)-O(2)-C(24)	107(1)	C(9)-C(13)-C(14)	119.5(9)
C(2)-C(1)-C(13)	122(1)	C(4)-C(14)-C(10)	120(1)
C(1)-C(2)-C(3)	121(1)	C(4)-C(14)-C(13)	119(1)
C(2)-C(3)-C(4)	117(1)	C(10)-C(14)-C(13)	121(1)
C(3)-C(4)-C(14)	122(1)	O(1)-C(17)-C(18)	108(1)
C(6)-C(5)-C(11)	121(1)	C(17)-C(18)-C(19)	107(1)
C(5)-C(6)-C(7)	120(1)	C(18)-C(19)-C(20)	103(1)
C(6)-C(7)-C(8)	120(1)	O(1)-C(20)-C(19)	106(1)
C(7)-C(8)-C(12)	121(1)	O(2)-C(21)-C(22)	105(1)
Al-C(9)-C(12)	116.1(6)	C(21)-C(22)-C(23)	109(2)
Al-C(9)-C(13)	116.4(7)	C(22)-C(23)-C(24)	105(1)
		O(2)-C(24)-C(23)	109(1)

<sup>a</sup> See footnotes to Table 4.

aluminum atom bond angles, such as C(12)-C(9)-Al, average 116.7(8) $^{\circ}$ . The corresponding angles in the naphthylene dianion fall into two groups [113.8(5) $^{\circ}$  and 119.0(6) $^{\circ}$ ] reflecting the asymmetry of the dianion at the substituted methylene carbon atoms.

The differences in the structures of the naphthylene and anthrylene dianions, particularly at the aluminum atoms and substituted methylene carbon atoms, can be rationalized best by considering how the monomeric anions  $[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]^-$  and  $[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]^-$  would dimerize. The monomeric anions would have the dimethylaluminum group bonded at the 9 carbon in the anthrylene compound and at the 1 carbon in the naphthylene compound. The group would most likely occupy the axial position on the ring with the ring atoms folded away from it because this position is sterically most favorable in 1,4-cyclohexadiene<sup>15</sup>. As the monomers approach each other with the aluminum atoms oriented to bond to the appropriate ring atoms, the aluminum atoms must move toward the equatorial positions in order to decrease the bond angle formed with the two ring carbon atoms, which might be initially about 170 $^{\circ}$ . During this process steric interactions between the ring carbon atoms [principally C(5), C(5'), C(8), and C(8') in the naphthylene dimer and C(1), C(1'), C(4), C(4'), C(5), C(5'), C(8), C(8') in the anthrylene dimer] and the methyl carbon atoms would tend to keep the rings folded; thus the hydrogen atoms bonded to the substituted methylene groups would be crowded by the other three atoms bonded to the substituted methylene groups. This process would halt when

TABLE 6

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ( $\text{\AA}$ ) ALONG THE PRINCIPLE AXES  $R_i$  FOR  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$ 

Atom	$R_1$	$R_2$	$R_3$
Al	0.207(5)	0.222(4)	0.266(5)
Na	0.246(6)	0.261(6)	0.327(7)
O(1)	0.26(1)	0.27(1)	0.36(1)
O(2)	0.24(1)	0.31(1)	0.39(1)
C(1)	0.21(2)	0.24(2)	0.28(2)
C(2)	0.19(2)	0.26(2)	0.34(2)
C(3)	0.21(2)	0.27(2)	0.35(2)
C(4)	0.18(2)	0.26(2)	0.29(2)
C(5)	0.21(2)	0.26(2)	0.29(2)
C(6)	0.20(2)	0.26(2)	0.37(2)
C(7)	0.21(2)	0.25(2)	0.38(2)
C(8)	0.20(2)	0.25(2)	0.30(2)
C(9)	0.18(2)	0.21(2)	0.26(2)
C(10)	0.20(2)	0.23(2)	0.26(2)
C(11)	0.17(2)	0.22(2)	0.26(2)
C(12)	0.19(2)	0.20(2)	0.28(2)
C(13)	0.17(2)	0.22(2)	0.28(2)
C(14)	0.17(2)	0.23(2)	0.26(2)
C(15)	0.21(2)	0.30(1)	0.34(2)
C(16)	0.27(2)	0.28(2)	0.30(2)
C(17)	0.26(2)	0.30(2)	0.43(2)
C(18)	0.22(2)	0.31(2)	0.47(2)
C(19)	0.28(2)	0.32(2)	0.36(2)
C(20)	0.28(2)	0.31(2)	0.35(2)
C(21)	0.27(2)	0.36(2)	0.43(2)
C(22)	0.26(2)	0.44(2)	0.51(3)
C(23)	0.23(2)	0.42(2)	0.50(3)
C(24)	0.28(2)	0.36(2)	0.45(2)

the repulsions between the methyl groups and the ring carbon atoms increase as rapidly as the energy gained through better aluminum–ring carbon overlap. In the case of the naphthylene dianion, some of the repulsions between the methyl groups and the carbon atoms C(5) and C(8) may be reduced by rotating the dimethylaluminum species towards C(2) and C(3). Indeed such a rotation did take place as indicated by the variation in the aromatic carbon, substituted methylene carbon, aluminum bond angles noted previously. Of course, a similar rotation of the dimethylaluminum species in the anthrylene dianion will not be beneficial. Thus the angle C(1)–Al–C(4') can become smaller in the naphthylene dimer than the angle C(9)–Al–C(10') can in the anthrylene dimer. That steric strain is greater in the latter dimer is indicated by the fact that the distances between the methyl carbon atoms and the ring atoms mentioned earlier, 3.47(2)  $\text{\AA}$ , are 0.12(1)  $\text{\AA}$  shorter than the corresponding distances in the former dimer. In both cases the contacts are less than the sum of the Van der Waals radii of the methyl group and an aromatic carbon atom, 3.70  $\text{\AA}$ <sup>18</sup>. These relatively close nonbonded contacts may be in part responsible for the deformation of the xylylene moieties from planarity. It would be tempting to conclude from the constancy of the long Al–C bond lengths in the two structures that the bond leng-

TABLE 7

BEST WEIGHTED LEAST-SQUARES PLANES FOR  $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_{10}]_2$ 

Plane	Atoms in plane	Equation of plane <sup>a,b</sup>
1 <sup>c</sup>	C(1), C(2), C(3), C(4) C(9), C(10), C(13), C(14)	$-0.5715 x - 0.3826 y - 0.7259 z - 4.5977 = 0$
2 <sup>c</sup>	C(5), C(6), C(7), C(8) C(9), C(10), C(11), C(12)	$-0.1221 x - 0.0543 y - 0.9910 z - 3.3350 = 0$
3	C(1), C(2), C(3), C(4) C(13), C(14)	$-0.5964 x - 0.3795 y - 0.7073 z - 4.7379 = 0$
4	C(5), C(6), C(7), C(8) C(11), C(12)	$-0.1014 x - 0.0436 y - 0.9939 z - 3.3104 = 0$
5	C(9), C(10), C(13), C(14)	$-0.5349 x - 0.3699 y - 0.7597 z - 4.4979 = 0$
6	C(9), C(10), C(11), C(12)	$-0.1575 x - 0.0758 y - 0.9846 z - 3.4554 = 0$

## DEVIATION OF ATOMS FROM PLANES (Å)

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
C(1)	0.02(1)		0.01(1)			
C(2)	0.04(1)		0.01(1)			
C(3)	0.00(1)	-0.02(1)				
C(4)	-0.03(1)	0.01(1)				
C(5)		0.01(1)		0.01(1)		
C(6)		0.02(1)		0.00(1)		
C(7)		0.02(1)		0.00(1)		
C(8)		-0.01(1)		0.00(1)		
C(9)	-0.008(9)	0.027(9)			-0.006(9)	-0.001(9)
C(10)	0.050(9)	0.015(9)			0.006(9)	0.001(9)
C(11)		-0.037(9)		-0.008(9)		-0.001(9)
C(12)		-0.029(9)		0.006(9)		0.001(9)
C(13)	-0.036(9)		-0.010(9)		0.013(9)	
C(14)	-0.05(1)		0.01(1)		-0.02(1)	
Na		-2.805(4)		-2.810(4)		
Na'	-2.785(4)		-2.783(4)			
$\chi^2$	93.2	49.0	4.0	1.9	5.4	0.0

<sup>a</sup> The orthogonal unit cell vectors  $x, y, z$  are related to the monoclinic unit cell vectors  $a, b, c$  as follows:  $(x, y, z) = (a + c \cos \beta, b, c \sin \beta)$ .

<sup>b</sup> The weight of each atom was inversely proportional to the mean variance of the positional parameters of that atom perpendicular to the least-squares best plane.

<sup>c</sup> Dihedral angle between Planes 1 and 2 is  $144.1(20)^\circ$ .

thening does not reflect a steric effect; however, our lack of knowledge of the Al-C potential energy surface precludes such a conclusion. Similarly we find it difficult to evaluate the consequence of the steric crowding of H(1)C(9) and H(1)C(10) by the aluminum atoms.

Previously we postulated an electron delocalization scheme in which charge density was removed from the Al-C(naphthylene) bonds and placed upon the naphthylene species via various resonance structures. A logical extension of this argument would predict that the Al-C(anthrylene) bond lengths should be longer because more resonance forms are available to delocalize the charge density. Apparently this scheme is not reliable in predicting changes in Al-C bond lengths. Perhaps it would

be better to consider the longer Al-C bond lengths as simply indicating a reduced basicity of the substituted methylene carbon atoms. It has been postulated that the basicities of such carbon atoms is determined by both inductive and resonance effects<sup>19</sup>. It does not seem obvious that the inductive effect of a phenylene and ethylene group should be much less than that of two phenylene groups. Also, as noted above, the dihedral angle of the anthrylene group is smaller than that of the naphthylene group. Certainly this fact should tend to diminish the difference in resonance delocalization between the anthrylene and naphthylene groups. Thus the similarity of the long Al-C bond lengths in the two structures neither excludes nor confirms the operation of electronic effects in the bond lengthening. It would seem that in order to unravel the electronic and steric influences, the structure of a compound prepared with 1,4-dimethylnaphthalene, trimethylaluminum, and sodium could be helpful if the bridged dimer is formed.

The cations are formed by a Na<sup>+</sup> and two THF molecules. The bond lengths Na-O(1) and Na-O(2) are 2.331(11) Å and 2.377(9) Å, respectively. The average Na-O bond length of 2.354(7) Å is slightly but not significantly longer than the 2.338(6) Å value found in the naphthylene structure. The angle O(1)-Na-O(2) is 85.9(4)°, almost exactly the same as that found in the naphthylene cation, 85.8(3)°. The remainder of the sodium coordination sphere is formed by the anthrylene carbon atoms. The cation is rather symmetrically positioned between the protruding anthrylenic ring planes, the distances from the sodium to the weighted least-squares best planes 1 and 2 being 2.785(4) Å and 2.805(4) Å, respectively. The dihedral angles formed by the plane through atoms Na, O(1), and O(2) and by the anthrylene carbon planes 1 and 2 are 17.8° and 18.7°, respectively; therefore, the plane defined by Na, O(1), and O(2) very nearly bisects the dianion. The shorter sodium, anthrylene carbon contacts range from 2.937(12) Å to 3.324(12) Å. As can be seen in Fig. 1, the sodium atom is displaced from a point over the center of the phenylene rings to one over the outer parts of the rings. Thus the geometry for the Na<sup>+</sup> ring carbon atom interaction differs considerably from that found in the naphthylene case, where the 8 closest Na-C contacts ranged from 2.87 to 2.96 Å with the Na<sup>+</sup> positioned over the middle of the phenylene ring.

The distance from the sodium atom to the center of the dianion, 3.639(4) Å, is 0.450(5) Å longer than the value 3.189(3) Å found for the corresponding distance in the naphthylene compound. It can be shown that if the sodium atom was near a point above the middle of both phenylene rings, the distance of the sodium atom to the midpoints would be 2.69 Å, from the sodium atom to the phenylene carbon atoms would be 3.03 Å, and from the sodium to the center of the dianion would be 3.21 Å. Obviously, the coulombic attraction between the cation and the dianion would be increased by the movement of the cation towards the center of the ring. However, bringing the cation closer to the center of the dianion must increase the steric repulsions between the phenylene carbon atoms and the  $\alpha$ -methylene groups of the THF molecules. In the observed configuration, each of the  $\alpha$ -methylene groups has one nonbonded contact with a phenylene carbon atom of 3.74 Å or less. The shorter distances are C(20)-C(7), 3.502(20) Å, and C(21)-C(2), 3.554(21) Å. That the corresponding nonbonded contacts in the naphthylene structure were found to be only slightly longer than those listed above supports the idea that the steric interactions between the solvent molecules coordinated to the metal ion and the

carbon atoms of the anion ultimately determine the closeness of approach of the metal ion to the anion. Several other features of the cation geometry are pertinent here. Both the THF groups are rotated in the same sense about the Na–O(1) and Na–O(2) bonds. This rotation is witnessed by the similar dihedral angles of 123.4° and 130.6° formed by the Na, O(1), O(2) plane with the least-squares best planes defined by Na, O(1), C(17), C(20) and Na, O(2), C(21), C(24), respectively. The dihedral angle between the latter two planes of 66.2° is evidence for the partial folding over of the THF rings. When these facts are coupled with the O(1)–Na–O(2) angle of 85.9(4)°, it becomes clear that the cation has been streamlined in order to facilitate a close approach to the dianion. It must be noted here that the above interpretation is only qualitative since the presence of several nonbonded contacts between a neighboring dianion and several THF  $\alpha$ -carbon atoms, which are smaller than the van der Waals distance, indicates that crystal packing forces also play a role in these distortions. Still it is apparent that steric interactions do play a rather large role in the stereochemistry of contact ion-pairs. Previous studies by ultraviolet/visible spectroscopy and electric conductivity of ion-pair compounds in solution have indicated that the steric requirements of the solvent can determine the extent of solvation of metal ions<sup>2,3</sup>. The results of conductivity studies on sodium tetraphenylethane and disodium tetraphenylethane have indicated that the steric requirements of the anion may be important in determining the position of the equilibrium between solvent separated and contact ion-pairs<sup>4</sup>.

Roberts and Szwarc have suggested that in THF the sodium ion is coordinated by four solvent molecules<sup>4</sup>. If solid-state packing forces are not very important, it would appear that the combination of the basicity of the naphthylene and anthrylene dianions and the entropy energy gained by desolvation of the sodium ion are sufficient to bring about the displacement of two THF molecules during the formation of these contact ion-pairs. Unfortunately, little is known from solution work of the exact extent of solvation of the metal ions in contact ion-pairs; therefore, it is difficult to comment further on the strength of the ion-pair interaction observed in these studies. The Na–C contacts found in these studies are considerably longer than those observed in sodium acetylide<sup>20</sup>, 2.49(10) Å and 2.71(10) Å, and in ethylsodium<sup>21</sup>, 2.63(10) Å and 2.68(10) Å. The sodium ions in these structures are unsolvated, and, therefore, they should act as stronger acids towards their respective carbanions than the solvated sodium cations observed here should act towards the dianions.

Some of the bond lengths in the THF rings show some signs of either high thermal motion or disorder. However, the average C–O bond length found is 1.412(18) Å, a value which compares favorably to that found in the naphthylene structure, 1.426(30) Å, and to that found in the gas phase for THF, 1.428(1) Å<sup>21</sup>. The C–C bond lengths average 1.46(2) Å, a value much lower than that found in the gas phase, 1.536(1) Å<sup>22</sup>. An inspection of Table 6 indicates that the THF atoms possess relatively large root-mean-square displacements. Similar observations have been reported in a variety of structures containing the THF ligand<sup>5,23</sup> and have been ascribed to either high thermal motion or to a puckering disorder. It might be noted here that THF is known to undergo essentially free pseudo-rotation in the gas phase and that the twisted form of the ligand is slightly more stable than is the bent form<sup>24</sup>. While the conformational behavior of the gas phase THF molecule is undoubtedly different than that of a coordinated THF molecule in the solid state as is shown by the bent

conformation found for both ligands in this analysis, this behavior is consistent with the overall looseness of the ligand as indicated in Table 6. The presence of this looseness is unfortunate because it tends to obscure the instantaneous environmental detail of each of the THF atoms. In particular, the geometric arrangement of atoms about the oxygen atoms is pertinent to a discussion of the mode of bonding of THF to  $\text{Na}^+$ . Since this bond must be predominantly ion-dipole in character, one might wonder if the oxygen atom orients a lone-pair in the direction of the  $\text{Na}^+$  and thus achieves a pyramidal coordination geometry, or if the oxygen atom orients its negative dipole in the direction of the  $\text{Na}^+$  and thus achieves a planar coordination geometry. Least-squares best plane calculations including the appropriate sodium, oxygen, and THF  $\alpha$ -carbon atoms from the naphthylene and anthrylene structures show only slight deviations from planarity. Thus the latter form of sodium-oxygen bonding is favored. But since the positional parameters found in these analyses may not represent the instantaneous environment of the oxygen atoms, the results of the best plane calculations are of questionable significance.

The dimeric rather than the monomeric structures of the anions in the naphthylene and anthrylene compounds are favored by the smaller deviations from tetrahedral angles about the aluminum atoms in the dianions than about the aluminum atom in the hypothetical monoanions. For example, if a monomeric anion contains an aluminum atom bonded at 2.062 Å (the average aluminum-substituted methylene carbon bond length for the two structures) to two carbon atoms separated by 2.923 Å (the average cross ring substituted methylene carbon-substituted methylene carbon distance), the bridge angle at the aluminum atom would be  $90.3^\circ$ . This  $19.2^\circ$  deviation from the tetrahedral angle of  $109.5^\circ$  can be compared with the average deviation of  $8.9^\circ$  from the tetrahedral value observed in the two structures. This argument can be extended quickly to predict dimeric structures for the compounds formed from the benzene derivatives and the 1,3-butadienes. Examination of molecular models indicates that even higher polymers may be formed from ethene and styrene<sup>1</sup>.

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