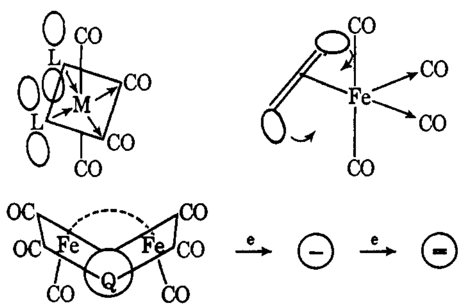

Figure 10.

radical anion are shown in Table VI, in comparison with the neutral material. It is gratifying and totally expected that the changes in direction of isomer shift and magnitude of coupling terms are opposite to those found in the present study. The latter system involves $\pi$ transmission, while the former involves $\sigma$ transmission. It appears, then, that in the octahedral complexes, transmission *to* and *through* the metal atom is *via* the *$\sigma$ framework* as was reported earlier. In the bipyramidal cases, evidence points to a *$\pi$ transmission* to the metal, and in light of the observed changes in carbonyl stretching frequencies, a *$\sigma$ transmission through* the metal atom. In both cases it is not yet known how this effect expresses itself in weaker CO stretching force constants. A pure $\sigma$ argument[52] or one involving $\sigma,\pi$ configuration interaction will equally fit the observed facts.

**Table VI.** Octahedral Mössbauer Parameters (All Measurements Made at −196°)

| Q | Charge | IS,[a,b] mm/sec | QS,[b] mm/sec |
|---|---|---|---|
| $SCH_3$ | ○ | 0.30 | 0.86 |
| | ⊖ | 0.28 | 1.62 |
| $P(CH_3)_2$ | ○ | 0.25 | 0.65 |
| | ⊖ | 0.19 | 1.29 |
| | ⊜ | 0.10 | 1.53 |
| $As(CH_3)_2$ | ○ | 0.28 | 0.81 |
| | ⊖ | 0.18 | 1.86 |

[a] Relative to sodium nitroprusside. [b] Neutral compounds, ±0.005; radical anions and dianion, ±0.02.

**Acknowledgments.** The authors wish to thank the Air Force Office of Scientific Research for support of this work. The trilaminate film was supplied through the courtesy of Mr. E. T. Monigan of Sun Chemical Company and the PDP-8 computer was purchased with a National Science Foundation equipment grant to Virginia Polytechnic Institute. A special note of thanks is due to Dr. Gerald W. Dulaney who provided the software for both the IBM-360 and the Digital Equipment Corporation PDP-8/I.

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(52) *Cf.* G. R. Dobson, *Inorg. Chem.*, **4**, 1673 (1965).

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# $\pi$ Complexation in Ion-Pair Bonding. Tetra(1,4-epoxybutane)disodium(I) Tetramethylbis-1,4-dihydro-1,4-naphthylenedialuminate, $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{10}H_8]_2$, a Novel Organoaluminate Structure[1,2]

**D. J. Brauer and G. D. Stucky**

*Contribution from the Department of Chemistry and Chemical Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.*

*Received November 17, 1969*

**Abstract:** The crystal structure of tetra(1,4-epoxybutane)disodium(I) tetramethylbis-1,4-dihydro-1,4-naphthylenedialuminate, $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{10}H_8]_2$, has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the space group $C_{2h}^5$-$P2_1/c$ with cell dimensions $a = 9.175$ (3) Å, $b = 17.356$ (6) Å, $c = 13.112$ (5) Å, and $\beta = 97.98$ (1)°. The calculated density for two $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{10}H_8]_2$ molecules per unit cell is 1.13 g cm$^{-3}$; unfortunately, no precise measurement of the density of this compound could be made owing to the reactivity of the compound with the liquids used. Three-dimensional least-squares refinement yielded a conventional $R$ factor of 7.5% for 1103 observed reflections. The compound exists as a centrosymmetric, contact ion-pair complex with two $Na(C_4H_8O)_2^+$ cations complexed to the dimeric dianion. Two 1,4-dihydro-1,4-naphthylene groups are fused into the dianion *via* the two dimethylaluminate species. The aluminum–naphthylenic carbon bond distances of 2.056 (10) and 2.074 (10) Å are significantly longer than the aluminum–methyl carbon bond distances of 1.982 (11) and 1.990 (12) Å. The long Al–C bond lengths are interpreted in terms of electron-deficient Al–C bonding due to the partial delocalization of the formal negative charge of the aluminum atoms onto the carbon atoms of the naphthylenic rings.

Lehmkuhl has reported that 2 mol of Na, 1 mol of naphthalene, and 2 mol of triethylaluminum react in tetrahydrofuran (THF) and other low boiling point ethers to yield $Na[C_{10}H_8Al(C_2H_5)_2]\cdot THF$.[3-6] He has

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(1) Previous paper in this series: S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 1150 (1970).

(2) This work was supported by the National Science Foundation and by the Advanced Research Projects Agency under Contract SD-131.

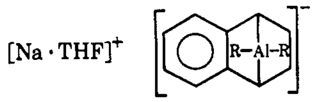
(3) H. Lehmkuhl, *Angew. Chem. Intern. Ed. Engl.*, **4**, 600 (1965).

(4) H. Lehmkuhl, *Tetrahedron Lett.*, **25**, 2811(1966).

(5) H. Lehmkuhl, *ibid.*, **25**, 2817 (1966).

(6) H. Lehmkuhl, *Ann. Chem.*, **719**, 20 (1968).

noted that similar compounds could be formed with either Li or K, and that Al $(CH_3)_3$ could also be used in the reaction. Based upon his conductivity, nuclear magnetic resonance, and chemical evidence, Lehmkuhl has proposed that the compounds exist as slightly dissociated ion pairs, the anion of which was an unusual aluminate complex because, in addition to being bonded to two alkyl groups (R), the aluminum atom was bonded to the 1 and 4 positions of the naphthalene ring.[5] The objective of this investigation was to rigorously establish the coordination at the aluminum atom and to investigate the nature of the ion-pair interaction by carrying out a complete X-ray crystal structural analysis of the above material with R = methyl. This research is part of a more extensive program designed to investigate in detail the structural and electronic properties of organometallic complexes formed with unsaturated organic moieties and main group metals.[1]



## Experimental Section

The compound $[Na(THF)_2]_2[Al(CH_3)_2C_{10}H_8]_2$ was prepared in the inert atmosphere of a glove box by mixing 0.02 mol of $Al(CH_3)_3$, 0.02 mol of Na, and 0.01 mol of $C_{10}H_8$ in 30 ml of THF. The solution was concentrated, and a yellow solid was forced from solution with cyclohexane. The compound was then recrystallized from a mixture of THF, toluene, and cyclohexane.

A small amount of the material was redissolved in THF, and the solution was sealed in a standard Varian nmr tube. The proton nmr spectrum was measured on a Varian A-60A nuclear magnetic resonance spectrometer. The peak positions and relative intensities corresponded well with the reported values for this compound in THF.[5]

## Collection and Reduction of the X-Ray Data

Since $[Na(THF)_2]_2[Al(CH_3)_2C_{10}H_8]_2$ is very sensitive to oxygen and water vapor, the single crystals used in this analysis were mounted in thin-walled glass capillaries. The systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) determined from precession photographs uniquely determined the space group as $C_{2h}{}^5$ - $P2_1/c$.[7] The lattice constants (22°, λ 0.71069 Å) obtained by a least-squares procedure defined below are: $a = 9.175$ (3),[8] $b = 17.356$ (6), $c = 13.112$ (5) Å, $\beta = 97.98$ (1)°. The calculated density for two of the above molecules per unit cell is 1.13 g $cm^{-3}$; unfortunately, the instability of the compound in several organic liquids prevented a precise density determination.

Intensity data were measured on an automated Picker four-circle X-ray diffractometer. The diffractometer was equipped with a highly oriented graphite single-crystal monochromator, and Mo K$\alpha$ radiation was used. The crystal, a block of dimensions 0.39 mm × 0.35 mm × 0.35 mm, was aligned on the diffractometer in such a way that the $a^*$ direction of the crystal and the $\phi$ axis of the diffractometer were coincident. Since $a^*$ is not a symmetry axis, such an alignment does not optimize the conditions for multiple diffraction.[9] The crystal-to-source and crystal-to-detector distances were 21 and 29 cm, respectively, and the detector was equipped with a 9 mm × 9 mm aperture. A take-off angle of 1.0° was used and was found to provide 80% 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, 0.12 (2)°, 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.[10]

The data were measured by the $\theta$–$2\theta$ scan technique. A symmetrical scan of −0.80° from the Mo K$\alpha_1$ peak (λ 0.70930 Å) to 0.80° from the Mo K$\alpha_2$ peak (λ 0.71359 Å) was made at a rate of 1.0° $min^{-1}$. Stationary-crystal–stationary-counter background counts of 10 sec were taken at the beginning and end of each scan. Counter fatigue was minimized by the insertion of copper foil attenuators when the counting rate exceeded 10,000 counts/sec. As a check on the stability of the diffractometer and the crystal, two standard reflections were monitored for every 40 reflections collected. No significant variation in these standard reflections was noticed during data collection. Two spherical forms of data were measured. One form ($hkl$ and $hk\bar{l}$) was measured out to $2\theta = 50°$; but, since less than 10% of the data with $2\theta > 40°$ exceeded three times their standard deviations and were thus considered observed reflections, the second form ($h\bar{k}l$, $\bar{h}kl$) was measured out to $2\theta = 40°$. A total of 6434 reflections were measured of which 3728 were unique.

The data correction was carried out as described previously[11] except that the following polarization correction $\rho$ was used

$$\rho = (\cos^2 2\theta_M + \cos^2 2\theta)/(1 + \cos^2 \theta_M)$$

where $\theta_M$ and $\theta$ are the Bragg angles for the monochromator and the crystal specimen, respectively. No absorption correction was applied ($\mu = 1.34$ $cm^{-1}$) since the transmission factors varied between 0.925 and 0.870. All of the equivalent data were averaged to yield 1103 unique, observed reflections. Only these reflections were used in the least-squares refinement.

## Solution and Refinement of the Structure

An examination of the intensity weighted reciprocal lattice revealed that reflections with $k + l \neq 2n$ were consistently of much lower intensity than those reflections with $k + l = 2n$. In the space group $P2_1/c$ such a phenomenon indicates either that a heavy atom is located at the center of inversion or that a number of atoms lie near $y = 0$ and $y = 1/2$. Only the latter effect could explain the observed intensity distribution since the compound does not contain a heavy atom. Although the detection of this phenomenon did not aid in the structural solution, it helped to explain our rather low ratio of observed intensities to unobserved intensities.

The structure was solved by the symbolic addition procedure.[12] A set of $|E(hkl)|$'s were generated from the data with $2\theta < 40°$ by means of a K-curve.[13]

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[7] "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962, p 99.

[8] Numbers in parentheses here and in succeeding discussions are estimated standard deviations in the least significant digit.

[9] W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

[10] W. R. Busing and H. A. Levy, *ibid.*, **22**, 457 (1967).

[11] D. J. Brauer and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 5462 (1969).

[12] J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

With the aid of several computer programs, the signs of 227 of the 289 $|E(hkl)|$'s $\geq 1.50$ were assigned (of which 225 signs were found to be correct). An E-map calculated with these signed $|E(hkl)|$'s clearly revealed the naphthylenic carbon atoms and the aluminum and sodium atoms. An electron density map calculated from the above model indicated the positions of the methyl carbon atoms on the aluminum atom, both of the THF oxygen atoms, and the four methylene carbon atoms associated with the O(1) THF molecule. An electron density map calculated from this 20-atom model revealed the positions of the four remaining nonhydrogen atoms (C(17), C(18), C(19), C(20)).

The structure was refined by full-matrix least-squares and difference Fourier techniques.[14] The function minimized was $w\Delta^2$, $\Delta = ||F_o| - |F_c||$, 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 modified Hughes's weighting scheme was used in the final stages.[15,16]

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

$$\sigma(|F_o|) = 4|F_{\min}|/|F_o| \text{ for } |F_o| \leq 4|F_{\min}|$$

$$\sigma(|F_o|) = |F_o|/4|F_{\min}| \text{ for } |F_o| > 4|F_{\min}|$$

The value of $|F_{\min}|$ was 7.00. The scattering factor tables for $Al^0$, $Na^0$, O, and C were those calculated by Hanson;[17] the hydrogen form factors were the best spherical scattering factors as calculated by Stewart, Davidson, and Simpson.[18] No attempts were made to correct for anomalous dispersion in this centric, light atom structure. The reliability indices, $R_1$ and $R_2$, are defined as follows.

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

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

The initial values of $R_1$ and $R_2$ with all nonhydrogen atoms included in the calculation, unit weights, and only the observed data with $2\theta \leq 40°$ were 0.230 and 0.243, respectively. After incorporation of the Hughes's weighting scheme and after six cycles of least-squares refinement on the positional parameters and the isotropic temperature factors for all of the nonhydrogen atoms, the residuals for all of the observed data were $R_1 = 0.142$ and $R_2 = 0.153$. At this point evidence for disordered carbon atoms in the THF molecules was given by their large root-mean-square amplitudes of vibration, 0.34–0.44 Å. In addition, some of the C–C bond distances in these rings became unusually short (1.46 (2) Å). An examination of a difference Fourier revealed peaks ranging from −0.54 to 0.65 e/Å$^3$ with a background density of ±0.2 e/Å$^3$, the largest peaks being in the region of the Na atom and in the vicinity of the THF rings. At the end of the refinement, a typical naphthylenic carbon atom had an electron density of 5.05 e/Å$^3$, a typical methylene group in the THF ring associated with O(1) had a density of 2.83 e/Å$^3$, and a typical methylene carbon in the other THF ring had a density of 2.15 e/Å$^3$. The distribution of density near the THF carbon atoms was consistent with a model in which each THF carbon atom was alternately puckered out of the plane of the remaining carbon atoms. Evidence for the hydrogen atoms bonded to naphthylenic and methyl carbon atoms was given by peaks of density 0.4–0.6 e/Å$^3$ at reasonable positions with respect to these carbon atoms (0.9–1.2 Å, $sp^2$ and $sp^3$ hybridization). In addition, the distribution of electron density in the region of the naphthylenic carbon atoms suggested anisotropic motion for these atoms. It was felt that on the basis of the observations listed above that a model which gave anisotropic temperature factors to all of the nonhydrogen atoms would more adequately account for the observed electron density distribution. Accordingly, three cycles of least-squares refinement were carried out with all atoms given anisotropic temperature factors. The resulting residuals, $R_1$ and $R_2$, were 0.095 and 0.101, respectively. The decrease in $R_2$ was significant on the 0.995 confidence level.[19] An examination of a subsequent difference Fourier revealed peaks in the range −0.29 to 0.37 e/Å with a background density of approximately 0.15 e/Å$^3$. The larger peaks (0.30–0.37 e/Å$^3$) occurred in the same reasonable hydrogen atom positions mentioned above. It was felt, however, that more reasonable X-ray hydrogen positional parameters could be obtained by calculating their positions on the basis of C–H bond distances of 0.95 Å and bond angles consistent with the appropriate $sp^2$ or $sp^3$ hybridization. Attempts to locate similarly the methylene hydrogen atoms of the THF group were abandoned because peaks did not consistently occur in the difference Fourier in the calculated positions. Each hydrogen atom was assigned an isotropic temperature factor equal to that which the corresponding carbon atom possessed at the end of the isotropic refinement. Three more cycles of least-squares refinement on the 24 nonhydrogen atom parameters were carried out with the hydrogen parameters held constant. Convergence was thus reached with $R_1 = 0.075$ and $R_2 = 0.080$. On the final cycle the maximum value of the ratio (shift/standard deviation) was 0.02. The standard deviation of an observation of unit weight was 1.56, suggesting either that the model is somewhat inadequate (for example, in correcting for the disorder in the THF atom positions, *vide infra*) or that the standard deviations of the observed structure amplitudes have been underestimated. The relative validity of the weighting scheme, as judged by the variation of the average of $w\Delta^2$ with $\sin\theta/\lambda$ and $|F_o|$, was satisfactory. A structure factor calculation for the 2625 unobserved reflections showed that for only seven reflections was the condition $\Delta \leq 4\sigma(|F_o|)$ violated.[11] A careful ex-

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(13) (a) S. P. Patterman, "Program K-CURVE," Department of Chemistry and Chemical Engineering, University of Illinois, 1969; (b) J. Karle and H. Hauptman, *Acta Cryst.*, **6**, 473 (1953).

(14) The local versions of several standard computer programs were used. The symbolic addition procedure was carried out with the aid of R. Dewar and A. Stone's MAGIC·LINK·SYMPL. Fourier series were calculated with J. Gvildys' "Two- and Three-Dimensional Fourier Summation Program." The least-squares program was W. R. Busing, K. O. Martin, and H. A. Levy's ORFLS. Interatomic distances and angles and their corresponding standard deviations were calculated by W. R. Busing, K. O. Martin, and H. A. Levy's ORFFE. C. K. Johnson's ORTEP was used to draw the structural illustrations. Least-squares best planes were calculated by M. E. Pippy and F. R. Ahmed's MEAN PLANE.

(15) E. W. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941).

(16) S. C. Abrahams and J. M. Reddy, *J. Chem. Phys.*, **43**, 2533 (1965).

(17) H. P. Hanson, F. Herman, J. E. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(19) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

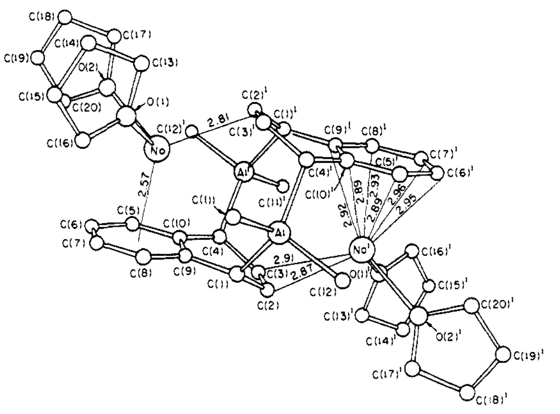

Figure 1. A drawing of the ion pair $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{10}H_8]_2$.

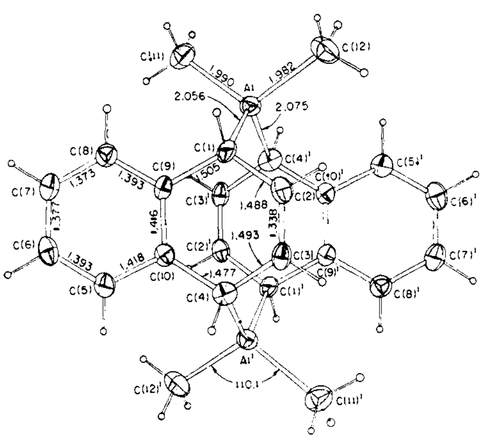

Figure 2. A drawing of the dianion.

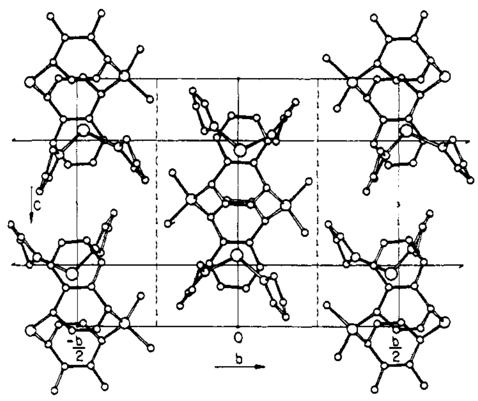

Figure 3. The *bc* projection of the unit cell of $[Na(C_4H_8O)_2]_2$-$[Al(CH_3)_2C_{10}H_8]_2$.

amination of the low angle reflections did not indicate that an extinction correction was needed.

A difference Fourier contained residual electron density of −0.25 to 0.34 e/Å$^3$ in a background of ±0.13 e/Å$^3$. All of the peaks over 0.20 e/Å$^3$ occurred in the vicinity of the THF rings and presumably result from our inability to correct for the disorder in the THF carbon atom positions and to locate the methylene hydrogen atoms.

The final values for the atomic positional and thermal parameters appear in Table I and a listing of the observed and calculated structure factor amplitudes ×10 appear in Table II. Bonded and nonbonded distances appear in Table III while the bond angles appear in Table IV. Our numbering system is shown in Figures 1–3. The root-mean-square amplitudes of vibration along the principle axes for all of the nonhydrogen atoms are included in Table V, and the least-squares best planes are listed in Table VI.[20]

## Description of the Crystal Structure

The structure of $[Na(THF)_2]_2[Al(CH_3)_2C_{10}H_8]_2$ found by this analysis and illustrated in Figure 1 can be described as a contact ion-pair complex in which two naphthalene molecules are incorporated into a centrosymmetric, ten-membered, heterocyclic dianion by the bridging of two dimethylaluminate species across the 1,4′ and 4,1′ positions of the symmetry related rings while two $Na(THF)_2^+$ species serve as the counterions. As such, the basic structure deviates significantly from that proposed by Lehmkuhl only in that a dimeric species was formed. The fact that Lehmkuhl reports one molecule of THF per monomer is not inconsistent with the above formula because he vacuum dried the solid before making the analysis while we made no attempt to dry the crystals used in this analysis.

Another view of the dianion is shown in Figure 2. The aluminum–methyl carbon bond lengths of 1.982 (11) and 1.990 (12) Å compare well with the average single bond Al–C distances of 1.970 (11), 1.98 (1), and 1.944 (7) Å found respectively in $[Al(CH_3)_3]_2$,[21] $[Al(CH_3)_3]_2C_4H_8O_2$,[22] and $[(CH_3)_2AlSCH_3]_n$.[11] The aluminum–naphthylenic carbon bond distances of 2.056 (10) and 2.074 (10) Å lie approximately halfway between the Al–C single bond distances above and the average Al–C electron-deficient bond distances of 2.14 (1) and 2.182 (5) Å in $[Al(CH_3)_3]_2$[21] and $[Al(C_6H_5)_3]_2$,[23] respectively. The long Al–C bond lengths are especially peculiar because if this compound is correctly formulated as an aluminate complex, then to a first approximation the geometry about the aluminum atom should be tetrahedral and, therefore, all Al–C bond distances should be of equal length. Two factors, which may cause a deviation from such a geometry are inter- and intramolecular steric interactions and partial delocalization of the anionic charge onto the unsaturated carbon atoms. These effects will now be discussed.

The major causes of steric strain in the molecule appear to be the close, nonbonded contacts of Al with C(2), C(9), C(3)′, and C(10)′ and the inter-ring repulsions between C(1) and C(4)′ and between C(4) and C(1)′. The distortion in the molecule introduced by the aluminum atom nonbonded repulsions are manifested by the substantial deviations from tetrahedral symmetry at C(1) and C(4); specifically, the angles C(9)–C(1)–Al, C(10)′–C(4)′–Al, C(2)–C(1)–Al, and C(3)′–C(4)′–Al are 119.5 (6), 118.4 (7), 114.0 (6), and 113.6 (7)°, respectively. The net result of the increased Al–C(1) and Al–C(4)′ distances (compared to the average of 1.99 Å for the other Al–C bond distances) and the angular distortion from tetrahedral symmetry at C(1) and C(4) has been to increase the Al–C(9), Al–

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[20] D. M. Blow, *Acta. Cryst.*, **13**, 168 (1960).

[21] R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **89**, 3121 (1967).

[22] J. L. Atwood and G. D. Stucky, *ibid.*, **89**, 5362 (1967).

[23] J. F. Malone and W. S. McDonald, *Chem. Commun.*, 445 (1967).

**Table I.** Positional and Thermal Parameters for $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{10}H_8]_2$

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$[a] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Al | −0.0275 (4) | 0.1465 (2) | 0.5097 (3) | 0.0151 (5) | 0.0029 (1) | 0.0055 (2) | 0.0002 (2) | 0.0004 (3) | −0.0002 (2) |
| Na | 0.1626 (4) | 0.0136 (3) | 0.3036 (3) | 0.0138 (6) | 0.0063 (2) | 0.0067 (3) | −0.0007 (3) | 0.0007 (3) | 0.0002 (2) |
| O(1) | 0.293 (1) | 0.1182 (5) | 0.2510 (7) | 0.020 (2) | 0.0080 (5) | 0.9115 (8) | −0.0021 (7) | 0.002 (1) | 0.0029 (5) |
| O(2) | 0.323 (1) | −0.0628 (5) | 0.2218 (7) | 0.021 (2) | 0.0091 (5) | 0.0094 (7) | 0.0024 (7) | 0.0010 (9) | −0.0010 (5) |
| C(1) | −0.182 (1) | 0.0789 (5) | 0.4233 (7) | 0.015 (2) | 0.0034 (4) | 0.0040 (7) | 0.0003 (7) | −0.001 (1) | 0.0007 (5) |
| C(2) | −0.260 (1) | 0.0247 (7) | 0.4852 (8) | 0.011 (2) | 0.0048 (6) | 0.0059 (8) | 0.0004 (8) | 0.0018 (9) | −0.0005 (5) |
| C(3) | −0.248 (1) | −0.0520 (7) | 0.4805 (7) | 0.011 (2) | 0.0049 (6) | 0.0043 (7) | −0.0016 (8) | 0.0005 (9) | 0.0002 (5) |
| C(4) | −0.153 (1) | −0.0900 (6) | 0.4116 (8) | 0.011 (2) | 0.0037 (4) | 0.0065 (9) | −0.0012 (7) | −0.002 (1) | −0.0003 (5) |
| C(5) | −0.101 (1) | −0.0718 (6) | 0.2295 (8) | 0.014 (2) | 0.0044 (5) | 0.0047 (8) | 0.0003 (7) | −0.0026 (9) | −0.0001 (5) |
| C(6) | −0.085 (1) | −0.0268 (8) | 0.1438 (8) | 0.016 (2) | 0.0063 (7) | 0.0050 (9) | 0.0003 (9) | −0.000 (1) | −0.0010 (6) |
| C(7) | −0.097 (1) | 0.0520 (8) | 0.1514 (8) | 0.016 (2) | 0.0058 (7) | 0.0052 (9) | −0.0006 (9) | 0.000 (1) | 0.0011 (6) |
| C(8) | −0.125 (1) | 0.0857 (6) | 0.2414 (9) | 0.014 (2) | 0.0040 (5) | 0.0063 (9) | 0.0005 (8) | 0.001 (1) | 0.0003 (6) |
| C(9) | −0.145 (1) | 0.0412 (7) | 0.3268 (7) | 0.010 (2) | 0.0040 (6) | 0.0043 (9) | −0.0020 (7) | −0.0005 (9) | 0.0004 (5) |
| C(10) | −0.131 (1) | −0.0399 (7) | 0.3241 (7) | 0.012 (2) | 0.0036 (5) | 0.0042 (9) | −0.0012 (7) | −0.0018 (9) | −0.0004 (5) |
| C(11) | 0.054 (1) | 0.2228 (6) | 0.4191 (9) | 0.023 (2) | 0.0046 (5) | 0.0082 (9) | −0.0016 (9) | −0.001 (1) | 0.0011 (6) |
| C(12) | −0.138 (1) | 0.2003 (7) | 0.6082 (9) | 0.024 (2) | 0.0054 (6) | 0.0086 (9) | 0.002 (1) | 0.001 (1) | −0.0021 (6) |
| C(13) | 0.441 (2) | 0.1383 (9) | 0.295 (1) | 0.019 (3) | 0.0103 (9) | 0.016 (2) | −0.004 (1) | 0.001 (2) | 0.003 (1) |
| C(14) | 0.508 (2) | 0.166 (1) | 0.202 (1) | 0.018 (2) | 0.014 (1) | 0.018 (2) | 0.001 (1) | 0.005 (2) | 0.006 (1) |
| C(15) | 0.380 (2) | 0.198 (1) | 0.125 (1) | 0.019 (2) | 0.012 (1) | 0.015 (1) | 0.003 (1) | 0.006 (2) | 0.006 (1) |
| C(16) | 0.248 (2) | 0.168 (1) | 0.162 (1) | 0.022 (3) | 0.015 (1) | 0.017 (2) | −0.001 (2) | 0.001 (2) | 0.011 (1) |
| C(17) | 0.469 (2) | −0.086 (1) | 0.253 (1) | 0.014 (3) | 0.015 (1) | 0.018 (2) | 0.006 (1) | −0.005 (2) | −0.005 (1) |
| C(18) | 0.525 (2) | −0.111 (2) | 0.154 (2) | 0.020 (3) | 0.023 (2) | 0.020 (2) | 0.001 (2) | 0.002 (2) | −0.009 (2) |
| C(19) | 0.400 (2) | −0.126 (2) | 0.082 (2) | 0.025 (3) | 0.027 (2) | 0.017 (2) | 0.010 (2) | 0.003 (2) | −0.010 (2) |
| C(20) | 0.275 (2) | −0.094 (2) | 0.124 (1) | 0.027 (3) | 0.028 (2) | 0.012 (2) | 0.008 (2) | −0.002 (2) | −0.010 (2) |
| H(1)C(1) | −0.247[b] | 0.120 | 0.395 | 3.6[c] | | | | | |
| H(1)C(2) | −0.326 | 0.045 | 0.531 | 4.1 | | | | | |
| H(1)C(3) | −0.299 | −0.085 | 0.525 | 3.8 | | | | | |
| H(1)C(4) | −0.205 | −0.134 | 0.375 | 4.4 | | | | | |
| H(1)C(5) | −0.090 | −0.128 | 0.226 | 4.2 | | | | | |
| H(1)C(6) | −0.066 | −0.052 | 0.079 | 4.7 | | | | | |
| H(1)C(7) | −0.086 | 0.085 | 0.092 | 4.6 | | | | | |
| H(1)C(8) | −0.131 | 0.142 | 0.247 | 4.3 | | | | | |
| H(1)C(11) | 0.124 | 0.260 | 0.457 | 5.6 | | | | | |
| H(2)C(11) | 0.108 | 0.199 | 0.366 | 5.6 | | | | | |
| H(3)C(11) | −0.024 | 0.255 | 0.378 | 5.6 | | | | | |
| H(1)C(12) | −0.078 | 0.238 | 0.652 | 5.9 | | | | | |
| H(2)C(12) | −0.224 | 0.231 | 0.572 | 5.9 | | | | | |
| H(3)C(12) | −0.182 | 0.165 | 0.655 | 5.9 | | | | | |

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The positional and thermal parameters of the hydrogen atoms were not refined. [c] The hydrogen atoms were given isotropic temperature factors of the form $\exp[-B(\sin^2\theta/\lambda^2)]$.

C(10)′, Al–C(2), and Al–C(3)′ contact distances by 0.23, 0.21, 0.13, and 0.14 Å, respectively. The steric strain introduced into the molecule by the repulsions between C(1), C(4)′ and C(4), C(1)′ is revealed by the large C(1)–Al–C(4)′ angle of 116.5 (4)°. Because of this angular distortion at the aluminum atom and because of the longer Al–C(1) and Al–C(4)′ bond lengths, the nonbonded distance C(1)–C(4)′ has been increased from 3.25 to 3.513 (11) Å. Although it is apparent that the geometry at Al, C(1), and C(4) has been distorted from ideal tetrahedral symmetry by a variety of short, nonbonded contacts, it is not clear that these steric forces alone can account for the unusual Al–C(1) and Al–C(4)′ bond lengths. In fact, it should be mentioned that the average Al–C bond distance, where C is a carbon atom in a terminal phenyl group, in $[Al(C_6H_5)_3]_2$ is normal (1.958 (2) Å) although the average nonbonded distance from the aluminum to the *ortho* carbon atoms in these phenyl groups is 2.95 Å.[23] This observation is consistent with the view, as pointed out by one of the referees, that nonbonded contacts with second nearest neighbors may distort bond angles but do not, in general, cause a large deviation from "normal" bond lengths.

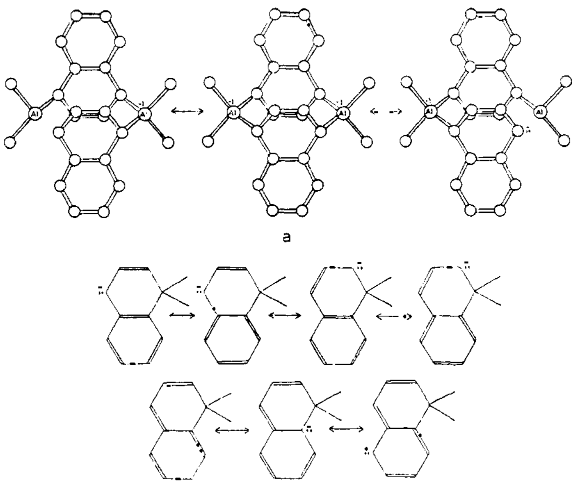

Figure 4. (a) Resonance forms which shift electron density from the aluminum atoms to the α carbon atoms in the naphthylenic moity. (b) Resonance forms which delocalize the negative charge throughout the naphthylenic ring.

An explanation for the long Al–C(1) and Al–C(4)′ bond lengths may be that the observed bonds are hybrids of resonance structures in which the aluminum is bonded to either two or one of the naphthylenic carbons (see Figure 4a). The importance of the one-bond structures can be enhanced by delocalization of the negative charge from the α carbons as is shown in Figure 4b;

Table II. Observed and Calculated Structure Factor Amplitudes in Electrons × 10 ($F(000) = 6960$)

| H | L | OBS | CAL |
|---|---|---|---|
| ******** K= 0 ****** | | | |
| 0 | 2 | 1081 | 042 |
| 0 | 4 | 200 | 323 |
| 0 | 6 | 144 | 151 |
| 0 | 8 | 253 | 254 |
| 0 | 10 | 186 | 187 |
| 0 | 12 | 124 | 223 |
| 1 | 1 | 506 | 747 |
| 1 | 2 | 96 | 81 |
| 1 | 3 | 848 | 756 |
| 1 | 5 | 641 | 580 |
| 1 | 6 | 111 | 116 |
| 1 | 8 | 184 | 169 |
| 1 | -10 | 121 | 101 |
| 1 | 11 | 422 | 423 |
| 1 | 12 | 114 | 116 |
| 1 | -13 | 111 | 70 |
| 1 | 14 | 113 | 41 |
| 2 | 6 | 1376 | 1422 |
| 2 | 1 | 147 | 142 |
| 2 | 2 | 656 | 672 |
| 2 | 3 | 506 | 479 |
| 2 | 4 | 441 | 433 |
| 2 | 6 | 287 | 271 |
| 2 | 8 | 107 | 122 |
| 2 | -0 | 118 | 117 |
| 1 | 11 | 171 | 170 |
| 2 | -72 | 00 | 31 |
| 3 | 1 | 84 | 4 |
| 3 | 2 | 523 | 471 |
| 3 | 3 | 571 | 534 |
| 3 | 4 | 341 | 341 |
| 3 | 5 | 364 | 321 |
| 3 | 6 | 86 | 79 |
| 3 | 7 | 180 | 206 |
| 3 | 8 | 103 | 701 |
| 3 | 0 | 226 | 228 |
| 1 | -13 | 133 | 141 |
| 4 | 0 | 868 | 566 |
| 4 | 1 | 647 | 586 |
| 6 | 2 | 133 | 110 |
| 4 | 3 | 106 | 201 |
| 4 | 4 | 466 | 460 |
| 4 | 5 | 07 | 81 |
| 4 | 6 | 331 | 313 |
| 4 | 7 | 100 | 106 |
| 4 | 6 | 371 | 341 |
| 4 | 12 | 117 | 112 |
| 5 | 1 | 194 | 186 |
| 5 | 2 | 388 | 328 |
| 5 | 3 | 287 | 184 |
| 5 | 5 | 286 | 294 |
| 5 | 6 | 207 | 207 |
| 5 | 7 | 109 | 110 |
| 5 | 0 | 102 | 83 |
| 6 | 0 | 354 | 180 |
| 6 | 1 | 111 | 123 |
| 6 | 2 | 171 | 171 |
| 6 | 3 | 363 | 371 |
| 6 | 5 | 196 | 199 |
| 6 | 6 | 314 | 701 |
| 6 | 7 | 111 | 217 |
| 6 | 10 | 206 | 211 |
| 7 | 1 | 111 | 120 |
| 7 | 4 | 126 | 119 |
| 7 | 5 | 701 | 721 |
| 7 | 6 | 06 | 07 |
| 7 | 0 | 157 | 166 |
| 6 | 0 | 166 | 151 |
| 8 | 1 | 106 | 163 |
| 8 | 2 | 06 | 81 |
| 8 | 3 | 100 | 126 |
| 8 | 4 | 146 | 183 |
| 8 | 5 | 120 | 146 |
| 6 | 6 | 100 | 116 |
| 8 | 0 | 128 | 127 |
| 0 | 2 | 238 | 216 |
| 0 | 3 | 307 | 301 |
| 0 | 4 | 187 | 171 |
| 9 | -5 | 00 | 88 |
| 0 | 7 | 251 | 159 |
| 0 | 6 | 123 | 101 |
| 10 | 0 | 253 | 254 |
| 10 | 1 | 181 | 186 |
| 10 | 2 | 222 | 228 |
| 10 | 3 | 176 | 186 |
| 10 | 4 | 201 | 219 |
| 10 | 5 | 141 | 126 |
| 10 | 6 | 408 | 409 |
| 10 | 8 | 101 | 81 |
| 10 | -12 | 121 | 86 |
| 11 | 1 | 181 | 105 |
| 11 | 2 | 101 | 71 |
| 11 | 3 | 114 | 188 |
| 11 | 5 | 141 | 236 |
| 11 | 1 | 123 | 111 |
| 11 | 8 | 143 | 181 |
| 12 | -1 | 111 | 00 |
| 12 | 3 | 161 | 156 |
| 11 | 4 | 111 | 86 |
| 12 | 5 | 151 | 186 |
| 12 | 6 | 151 | 157 |
| 12 | 7 | 111 | 101 |
| 12 | -11 | 117 | 116 |
| 13 | 1 | 157 | 161 |
| 33 | 3 | 181 | 186 |
| 13 | -8 | 153 | 141 |
| 14 | 0 | 171 | 173 |
| 14 | 2 | 127 | 122 |
| 14 | 4 | 142 | 156 |
| 16 | 0 | 123 | 121 |
| 17 | -1 | 141 | 146 |
| 17 | -5 | 107 | 68 |
| ******** K= 1 ****** | | | |
| 0 | 0 | 731 | 1082 |
| 0 | 2 | 88 | 89 |
| 8 | -2 | 1328 | 1074 |
| 0 | 4 | 437 | 301 |
| 0 | -4 | 178 | 158 |
| 0 | 4 | 350 | 373 |
| 0 | -6 | 213 | 111 |
| 0 | -8 | 181 | 178 |
| 0 | 16 | 161 | 178 |
| 0 | 12 | 119 | 106 |
| 0 | -12 | 248 | 241 |
| 0 | -14 | 153 | 133 |
| 1 | 0 | 128 | 86 |
| 1 | 1 | 974 | 818 |
| 1 | -1 | 488 | 468 |
| 1 | 2 | 134 | 136 |
| 1 | -2 | 388 | 317 |
| 1 | 3 | 508 | 516 |
| 1 | -3 | 449 | 446 |
| 1 | -4 | 78 | 91 |
| 1 | 5 | 272 | 267 |
| 1 | -5 | 140 | 179 |
| 1 | 7 | 177 | 147 |
| 1 | -7 | 92 | 86 |
| 1 | -4 | 120 | 133 |
| 1 | -9 | 182 | 181 |
| 1 | -10 | 119 | 114 |
| 1 | 11 | 368 | 368 |
| 1 | -11 | 133 | 117 |
| 1 | -12 | 112 | 86 |
| 1 | 13 | 144 | 142 |
| 1 | -15 | 113 | 01 |
| 2 | 8 | 504 | 482 |
| 2 | -1 | 82 | 56 |
| 2 | 2 | 838 | 806 |
| 2 | -2 | 478 | 454 |
| 2 | 3 | 104 | 181 |
| 2 | 4 | 837 | 414 |
| 2 | -4 | 243 | 231 |
| 2 | 5 | 119 | 103 |
| 2 | 6 | 148 | 179 |
| 2 | -6 | 203 | 201 |
| 2 | -1 | 228 | 221 |
| 1 | 6 | 152 | 187 |
| 2 | -6 | 129 | 131 |
| 2 | 0 | 121 | 111 |
| 2 | 11 | 128 | 121 |
| 2 | -11 | 189 | 183 |
| 2 | 12 | 104 | 78 |
| 2 | 14 | 108 | 06 |
| 3 | 0 | 120 | 287 |
| 3 | 1 | 1377 | 1279 |
| 3 | -1 | 220 | 254 |
| 3 | 2 | 421 | 410 |
| 3 | -2 | 509 | 471 |
| 3 | 3 | 878 | 648 |
| 3 | -3 | 129 | 101 |
| 3 | 4 | 204 | 106 |
| 3 | 5 | 270 | 278 |
| 3 | 7 | 376 | 364 |
| 3 | -7 | 358 | 378 |
| 3 | 8 | 01 | 51 |
| 3 | 0 | 373 | 388 |
| 3 | -0 | 01 | 81 |
| 3 | 13 | 103 | 103 |
| 4 | 0 | 884 | 813 |
| 4 | 1 | 181 | 154 |
| 4 | -1 | 057 | 021 |
| 4 | 2 | 186 | 181 |
| 4 | -2 | 1182 | 1114 |
| 4 | 3 | 163 | 171 |
| 4 | -1 | 426 | 814 |
| 4 | 4 | 381 | 366 |
| 4 | -4 | 511 | 401 |
| 4 | 5 | 93 | 101 |
| 4 | -5 | 144 | 126 |
| 4 | 6 | 111 | 142 |
| 4 | 7 | 136 | 16 |
| 4 | 8 | 401 | 406 |
| 4 | -8 | 137 | 130 |
| 4 | -9 | 167 | 160 |
| 4 | 10 | 141 | 138 |
| 5 | 0 | 231 | 126 |
| 5 | 1 | 381 | 311 |
| 5 | -1 | 276 | 173 |
| 5 | 2 | 77 | 88 |
| 5 | -2 | 486 | 488 |
| 5 | -3 | 577 | 534 |
| 5 | 4 | 111 | 128 |
| 5 | -4 | 138 | 144 |
| 5 | 5 | 128 | 128 |
| 5 | -5 | 103 | 104 |
| 5 | -6 | 254 | 264 |
| 5 | 7 | 161 | 178 |
| 5 | -7 | 126 | 141 |
| 5 | 9 | 117 | 149 |
| 5 | -0 | 287 | 301 |
| 5 | -10 | 138 | 138 |
| 6 | 1 | 167 | 176 |
| 6 | 2 | 404 | 408 |
| 6 | -2 | 117 | 117 |
| 6 | 3 | 86 | 07 |
| 6 | 4 | 186 | 176 |
| 6 | -4 | 247 | 251 |
| 6 | 5 | 64 | 87 |
| 6 | -5 | 359 | 382 |
| 6 | 6 | 841 | 430 |
| 6 | -6 | 207 | 214 |
| 6 | 7 | 130 | 140 |
| 6 | -8 | 164 | 171 |
| 6 | -10 | 114 | 111 |
| 7 | 1 | 439 | 819 |
| 7 | -1 | 118 | 173 |
| 7 | 2 | 146 | 176 |
| 7 | 3 | 157 | 163 |
| 7 | -3 | 328 | 346 |
| 7 | -4 | 186 | 101 |
| 7 | 5 | 490 | 517 |
| 7 | -5 | 330 | 344 |
| 7 | -6 | 106 | 111 |
| 7 | 7 | 286 | 287 |
| 7 | -8 | 151 | 126 |
| 7 | -0 | 160 | 163 |
| 7 | -11 | 101 | 07 |
| 8 | -1 | 184 | 106 |
| 8 | 2 | 331 | 336 |
| 8 | 3 | 106 | 108 |
| 8 | -3 | 208 | 106 |
| 8 | -4 | 308 | 306 |
| 8 | 5 | 175 | 187 |
| 8 | 6 | 107 | 301 |
| 8 | -6 | 126 | 131 |
| 8 | 7 | 00 | 06 |
| 8 | -7 | 171 | 107 |
| 8 | -0 | 101 | 08 |
| 8 | -10 | 121 | 134 |
| 8 | -13 | 126 | 73 |
| 9 | 0 | 153 | 181 |
| 0 | 1 | 253 | 256 |
| 0 | -1 | 146 | 136 |
| 0 | 1 | 308 | 316 |
| 9 | -2 | 198 | 106 |
| 0 | 3 | 181 | 111 |
| 0 | 5 | 131 | 144 |
| 9 | -5 | 174 | 182 |
| 0 | -6 | 208 | 101 |
| 9 | -7 | 188 | 134 |
| 9 | -8 | 137 | 105 |
| 10 | 0 | 108 | 218 |
| 10 | 1 | 01 | 128 |
| 10 | -2 | 284 | 201 |
| 10 | 3 | 164 | 164 |
| 10 | -3 | 101 | 116 |
| 10 | 4 | 283 | 281 |
| 10 | 6 | 198 | 188 |
| 10 | -6 | 331 | 330 |
| 30 | 7 | 119 | 118 |
| 10 | -7 | 107 | 111 |
| 10 | 8 | 111 | 106 |
| 10 | -8 | 158 | 171 |
| 10 | -9 | 138 | 144 |
| 11 | 0 | 141 | 166 |
| 11 | -3 | 101 | 108 |
| 11 | 2 | 251 | 281 |
| 11 | -1 | 121 | 126 |
| 11 | 3 | 183 | 104 |
| 11 | -3 | 122 | 122 |
| 11 | -4 | 108 | 41 |
| 11 | 5 | 304 | 313 |
| 11 | -7 | 144 | 148 |
| 11 | 8 | 117 | 111 |
| 11 | -3 | 120 | 113 |
| 11 | -4 | 263 | 153 |
| 11 | -8 | 181 | 181 |
| 11 | 7 | 118 | 151 |
| 11 | 8 | 114 | 06 |
| 13 | 0 | 304 | 58 |
| 13 | 1 | 148 | 187 |
| 13 | -1 | 181 | 156 |
| 13 | 1 | 126 | 111 |
| 13 | 3 | 181 | 181 |
| 13 | -3 | 160 | 178 |
| 33 | -4 | 130 | 141 |
| 13 | -3 | 143 | 159 |
| 33 | 7 | 101 | 111 |
| 13 | -3 | 108 | 76 |
| 13 | 11 | 108 | 67 |
| 14 | 0 | 154 | 157 |
| 14 | 2 | 181 | 104 |
| 14 | -2 | 128 | 104 |
| 18 | -3 | 113 | 119 |
| 14 | 4 | 111 | 94 |
| 14 | -4 | 118 | 131 |
| 14 | -6 | 111 | 81 |
| 34 | -7 | 118 | 101 |
| 15 | 1 | 108 | 01 |
| 15 | 1 | 133 | 106 |
| 15 | -4 | 141 | 151 |
| 16 | 8 | 128 | 121 |
| 18 | -3 | 121 | 108 |
| 16 | -8 | 111 | 28 |
| 17 | -1 | 177 | 187 |
| 18 | -4 | 108 | 19 |
| ******** K= 2 ****** | | | |
| 0 | 0 | 83 | 132 |
| 0 | 1 | 634 | 840 |
| 0 | -1 | 783 | 686 |
| 0 | 4 | 111 | 137 |
| 0 | -4 | 142 | 156 |
| 0 | 6 | 208 | 181 |
| 0 | -6 | 138 | 116 |
| 0 | -8 | 241 | 144 |
| 0 | 10 | 257 | 286 |
| 0 | -10 | 168 | 283 |
| 0 | -11 | 118 | 119 |
| 1 | 0 | 778 | 286 |
| 1 | 1 | 1877 | 1839 |
| 1 | -1 | 706 | 736 |
| 1 | 1 | 164 | 146 |
| 1 | -2 | 101 | 278 |
| 3 | 3 | 123 | 147 |
| 1 | -4 | 88 | 51 |
| 1 | 5 | 177 | 169 |
| 1 | -3 | 116 | 91 |
| 1 | -6 | 111 | 132 |
| 1 | 7 | 251 | 246 |
| 1 | -7 | 181 | 181 |
| 1 | -8 | 111 | 211 |
| 1 | -0 | 136 | 130 |
| 1 | 10 | 113 | 01 |
| 1 | -10 | 101 | 01 |
| 1 | 11 | 190 | 201 |
| 1 | -11 | 157 | 153 |
| 1 | -13 | 101 | 87 |
| 2 | 0 | 367 | 756 |
| 2 | -1 | 442 | 410 |
| 1 | 2 | 511 | 481 |
| 1 | -2 | 156 | 141 |
| 2 | 3 | 174 | 188 |
| 1 | 4 | 770 | 751 |
| 2 | -4 | 106 | 96 |
| 1 | -5 | 801 | 557 |
| 1 | 6 | 108 | 123 |
| 1 | -6 | 338 | 346 |
| 1 | 7 | 01 | 83 |
| 1 | -8 | 96 | 81 |
| 1 | -0 | 134 | 134 |
| 2 | -10 | 326 | 330 |
| 1 | -12 | 111 | 51 |
| 2 | -13 | 123 | 112 |
| 3 | 0 | 117 | 257 |
| 3 | 1 | 771 | 741 |
| 3 | -1 | 714 | 601 |
| 3 | 2 | 108 | 66 |
| 3 | -2 | 307 | 300 |
| 3 | 3 | 481 | 501 |
| 3 | -4 | 180 | 216 |
| 3 | 5 | 118 | 124 |
| 3 | -5 | 736 | 696 |
| 3 | -6 | 108 | 103 |
| 3 | 7 | 316 | 313 |
| 3 | -7 | 241 | 241 |
| 3 | -8 | 111 | 48 |
| 3 | 9 | 134 | 138 |
| 3 | -10 | 123 | 117 |
| 3 | -11 | 191 | 104 |
| 3 | 13 | 121 | 111 |
| 4 | 0 | 353 | 359 |
| 4 | 1 | 103 | 171 |
| 4 | -1 | 131 | 131 |
| 4 | 2 | 101 | 141 |
| 4 | -2 | 683 | 611 |
| 4 | 3 | 02 | 57 |
| 4 | 4 | 576 | 569 |
| 4 | -4 | 406 | 384 |
| 4 | 5 | 91 | 111 |
| 4 | 6 | 350 | 358 |
| 4 | -6 | 468 | 473 |
| 4 | -7 | 187 | 198 |
| 4 | 8 | 130 | 121 |
| 4 | 9 | 102 | 109 |
| 4 | -0 | 107 | 106 |
| 4 | 10 | 133 | 111 |
| 4 | -10 | 208 | 108 |
| 8 | -11 | 157 | 187 |
| 5 | 0 | 478 | 704 |
| 5 | 1 | 861 | 670 |
| 5 | -1 | 731 | 606 |
| 5 | 1 | 109 | 301 |
| 5 | -2 | 158 | 154 |
| 5 | 3 | 108 | 76 |
| 5 | -3 | 106 | 188 |
| 5 | 4 | 104 | 71 |
| 5 | -4 | 574 | 579 |
| 5 | 5 | 154 | 131 |
| 5 | -5 | 731 | 808 |
| 5 | 6 | 83 | 61 |
| 5 | -6 | 100 | 108 |
| 5 | 7 | 240 | 136 |
| 5 | -7 | 114 | 107 |
| 5 | -8 | 131 | 110 |
| 5 | 9 | 106 | 214 |
| 5 | -10 | 108 | 116 |
| 5 | 11 | 100 | 76 |
| 6 | 0 | 171 | 171 |
| 6 | -1 | 268 | 269 |
| 6 | 2 | 888 | 487 |
| 6 | 4 | 187 | 173 |
| 6 | -5 | 361 | 356 |
| 6 | -6 | 94 | 81 |
| 6 | 8 | 119 | 106 |
| 6 | -8 | 111 | 114 |
| 6 | 0 | 121 | 131 |
| 6 | -10 | 118 | 146 |
| 6 | 11 | 133 | 134 |
| 7 | 0 | 158 | 127 |
| 3 | 1 | 716 | 713 |
| 7 | -1 | 111 | 113 |
| 7 | 1 | 136 | 111 |
| 7 | -2 | 309 | 319 |
| 7 | 3 | 167 | 161 |
| 7 | -3 | 556 | 580 |
| 7 | 4 | 124 | 147 |
| 7 | -4 | 261 | 257 |
| 7 | 5 | 114 | 119 |
| 7 | 6 | 107 | 116 |
| 7 | -6 | 91 | 89 |
| 7 | 7 | 261 | 171 |
| 7 | -7 | 138 | 139 |
| 7 | -9 | 122 | 71 |
| 8 | 0 | 128 | 151 |
| 8 | 1 | 106 | 91 |
| 8 | -1 | 151 | 114 |
| 8 | 2 | 163 | 181 |
| 8 | -1 | 181 | 210 |
| 8 | 3 | 00 | 106 |
| 8 | -3 | 104 | 113 |
| 8 | -4 | 88 | 11 |
| 8 | -5 | 00 | 89 |
| 8 | 6 | 101 | 189 |
| 8 | -7 | 188 | 181 |
| 8 | 8 | 108 | 76 |
| 8 | -10 | 178 | 183 |
| 9 | 0 | 121 | 120 |
| 0 | 1 | 288 | 276 |
| 0 | -1 | 197 | 199 |
| 0 | 1 | 02 | 87 |
| 0 | 4 | 136 | 146 |
| 9 | -4 | 148 | 138 |
| 9 | 5 | 171 | 184 |
| 9 | -6 | 111 | 116 |
| 9 | -7 | 141 | 148 |
| 0 | -8 | 133 | 123 |
| 9 | 0 | 117 | 117 |
| 9 | -12 | 131 | 111 |
| 10 | 0 | 111 | 136 |
| 10 | 1 | 118 | 114 |
| 10 | -2 | 201 | 113 |
| 10 | 3 | 151 | 148 |
| 10 | 4 | 170 | 186 |
| 10 | 5 | 00 | 80 |
| 10 | -6 | 131 | 126 |
| 10 | -7 | 129 | 136 |
| 10 | 0 | 107 | 72 |
| 10 | 10 | 128 | 121 |
| 11 | 0 | 113 | 101 |
| 11 | -1 | 284 | 261 |
| 11 | -1 | 308 | 76 |
| 11 | 3 | 207 | 200 |
| 11 | 5 | 118 | 143 |
| 11 | -5 | 340 | 153 |
| 11 | 6 | 114 | 121 |
| 17 | -6 | 104 | 711 |
| 11 | 7 | 150 | 163 |
| 11 | -7 | 146 | 141 |
| 11 | -8 | 104 | 81 |
| 11 | 1 | 166 | 168 |
| 12 | -4 | 201 | 201 |
| 11 | 5 | 138 | 122 |
| 11 | -5 | 146 | 151 |
| 11 | 6 | 141 | 139 |
| 13 | 0 | 126 | 118 |
| 13 | 1 | 176 | 180 |
| 33 | -1 | 114 | 113 |
| 13 | 3 | 319 | 123 |
| 13 | -3 | 140 | 138 |
| 13 | -5 | 106 | 214 |
| 13 | 6 | 113 | 100 |
| 13 | 7 | 236 | 156 |
| 13 | -10 | 107 | 34 |
| 14 | 0 | 149 | 146 |
| 14 | 2 | 181 | 168 |
| 14 | -4 | 237 | 108 |
| 14 | 6 | 151 | 164 |
| 14 | -7 | 117 | 139 |
| 14 | 8 | 118 | 71 |
| 14 | -8 | 131 | 70 |
| 35 | -4 | 111 | 107 |
| 16 | 0 | 104 | 73 |
| 17 | -5 | 108 | 81 |
| ******** K= 3 ****** | | | |
| 0 | 0 | 738 | 701 |
| 0 | 2 | 1411 | 1378 |
| 0 | -1 | 101 | 86 |
| 0 | 4 | 264 | 171 |
| 0 | -4 | 608 | 586 |
| 0 | 6 | 153 | 151 |
| 0 | -6 | 80 | 111 |
| 0 | 8 | 837 | 848 |
| 0 | -8 | 388 | 351 |
| 0 | 10 | 201 | 118 |
| 0 | -10 | 247 | 139 |
| 0 | 14 | 161 | 167 |
| 3 | 0 | 04 | 89 |
| 1 | 1 | 881 | 814 |
| 1 | -1 | 393 | 388 |
| 1 | 1 | 161 | 171 |
| 1 | -1 | 110 | 126 |
| 1 | 3 | 888 | 887 |
| 1 | -3 | 301 | 379 |
| 1 | 4 | 231 | 136 |
| 1 | -4 | 261 | 254 |
| 1 | 5 | 128 | 241 |
| 1 | -5 | 331 | 316 |
| 1 | 6 | 92 | 44 |
| 1 | -6 | 137 | 138 |
| 1 | 7 | 428 | 451 |
| 1 | -7 | 166 | 251 |
| 3 | -8 | 187 | 207 |
| 1 | -9 | 338 | 146 |
| 1 | -11 | 261 | 274 |
| 2 | 0 | 661 | 611 |
| 1 | -1 | 330 | 118 |
| 1 | 1 | 300 | 300 |
| 1 | 3 | 131 | 181 |
| 1 | -3 | 111 | 301 |
| 1 | -5 | 246 | 150 |
| 2 | 6 | 180 | 173 |
| 2 | -6 | 138 | 131 |
| 1 | -7 | 378 | 384 |
| 1 | 8 | 246 | 231 |
| 1 | -8 | 111 | 101 |
| 1 | -0 | 141 | 146 |
| 1 | -10 | 158 | 250 |
| 2 | 11 | 130 | 136 |
| 3 | 0 | 153 | 151 |
| 3 | 1 | 533 | 527 |
| 3 | 1 | 128 | 74 |
| 3 | -1 | 148 | 226 |
| 3 | -3 | 413 | 401 |
| 3 | 4 | 111 | 116 |
| 3 | -4 | 130 | 144 |
| 3 | 5 | 418 | 421 |
| 3 | -5 | 842 | 848 |
| 3 | -8 | 134 | 116 |
| 3 | -10 | 121 | 121 |
| 3 | 11 | 114 | 111 |
| 3 | -11 | 157 | 166 |
| 4 | 0 | 166 | 177 |
| 4 | 1 | 146 | 248 |
| 4 | -1 | 201 | 104 |
| 4 | 3 | 141 | 343 |
| 4 | -4 | 564 | 530 |
| 4 | 6 | 346 | 347 |
| 4 | -6 | 138 | 130 |
| 4 | -7 | 131 | 141 |
| 4 | 10 | 134 | 141 |
| 4 | -10 | 118 | 114 |
| 5 | 0 | 356 | 348 |
| 5 | 1 | 204 | 101 |
| 5 | -1 | 188 | 183 |
| 5 | 1 | 08 | 01 |
| 5 | -2 | 78 | 03 |
| 5 | 3 | 247 | 143 |
| 5 | -3 | 288 | 204 |
| 5 | -4 | 206 | 216 |
| 5 | 5 | 100 | 111 |
| 5 | -5 | 341 | 336 |
| 5 | 7 | 103 | 118 |
| 5 | -8 | 127 | 121 |
| 5 | -10 | 171 | 183 |
| 6 | 0 | 107 | 08 |
| 6 | 1 | 116 | 138 |
| 6 | -1 | 166 | 160 |
| 6 | 2 | 306 | 301 |
| 6 | -1 | 466 | 481 |
| 6 | 3 | 153 | 146 |
| 6 | -3 | 310 | 347 |
| 6 | -4 | 103 | 98 |
| 6 | 5 | 111 | 111 |
| 6 | -5 | 108 | 134 |
| 6 | 8 | 276 | 270 |
| 6 | -11 | 121 | 107 |
| 6 | 11 | 186 | 178 |
| 7 | 1 | 423 | 416 |
| 7 | -1 | 121 | 234 |
| 7 | -2 | 136 | 150 |
| 7 | 3 | 03 | 81 |
| 7 | -3 | 361 | 386 |
| 7 | 4 | 106 | 87 |
| 7 | 5 | 101 | 82 |
| 7 | -6 | 103 | 106 |
| 7 | 7 | 168 | 164 |
| 7 | -7 | 111 | 106 |
| 7 | 13 | 311 | 02 |
| 8 | 0 | 154 | 146 |
| 8 | 1 | 127 | 138 |
| 8 | -1 | 321 | 336 |
| 8 | 2 | 181 | 128 |
| 8 | -2 | 103 | 101 |
| 8 | 3 | 06 | 114 |
| 8 | -3 | 103 | 104 |
| 8 | 8 | 138 | 110 |
| 8 | -11 | 117 | 318 |
| 0 | -1 | 187 | 148 |
| 9 | -1 | 101 | 188 |
| 0 | 4 | 103 | 86 |
| 0 | 5 | 181 | 703 |
| 9 | 6 | 106 | 108 |
| 0 | 0 | 141 | 111 |
| 10 | 0 | 186 | 180 |
| 10 | 2 | 101 | 100 |
| 10 | -1 | 131 | 116 |
| 10 | 4 | 213 | 211 |
| 10 | -4 | 113 | 116 |
| 10 | -7 | 110 | 143 |
| 10 | 6 | 384 | 161 |
| 10 | 10 | 146 | 167 |
| 11 | 0 | 128 | 124 |
| 11 | 1 | 388 | 106 |
| 11 | -1 | 212 | 284 |
| 11 | 2 | 166 | 184 |
| 11 | -2 | 121 | 123 |
| 11 | 3 | 153 | 181 |
| 11 | -3 | 121 | 114 |
| 11 | 4 | 184 | 156 |
| 11 | -4 | 153 | 161 |
| 11 | 5 | 121 | 316 |
| 11 | -5 | 122 | 111 |
| 11 | 6 | 181 | 384 |
| 11 | -6 | 106 | 121 |
| 12 | 0 | 108 | 93 |
| 31 | -1 | 108 | 108 |
| 11 | 3 | 100 | 80 |
| 11 | -1 | 226 | 134 |
| 11 | 4 | 123 | 120 |
| 12 | 5 | 111 | 112 |
| 11 | -5 | 191 | 196 |
| 31 | 6 | 161 | 173 |
| 12 | -0 | 151 | 140 |
| 13 | 0 | 113 | 87 |
| 13 | 1 | 133 | 124 |
| 13 | 2 | 181 | 137 |
| 13 | -2 | 121 | 106 |
| 13 | -4 | 106 | 06 |
| 13 | -5 | 148 | 157 |
| 13 | 6 | 111 | 102 |
| 13 | 7 | 187 | 158 |
| 14 | 0 | 106 | 86 |
| 14 | 1 | 117 | 136 |
| 14 | -6 | 188 | 176 |
| 15 | -6 | 117 | 66 |
| 15 | -10 | 107 | 36 |
| 17 | 5 | 110 | 06 |
| ******** K= 4 ****** | | | |
| 0 | 0 | 173 | 157 |
| 0 | 1 | 686 | 728 |
| 0 | -1 | 344 | 353 |
| 0 | 4 | 837 | 833 |
| 0 | -6 | 460 | 486 |
| 0 | 8 | 336 | 338 |
| 0 | -8 | 311 | 104 |
| 0 | -10 | 156 | 156 |
| 1 | 1 | 106 | 89 |
| 1 | -1 | 271 | 261 |
| 1 | 2 | 211 | 101 |
| 1 | 3 | 649 | 682 |
| 1 | -3 | 462 | 461 |
| 1 | 4 | 109 | 111 |
| 1 | 5 | 136 | 251 |
| 1 | -5 | 07 | 06 |
| 1 | -6 | 503 | 531 |
| 1 | 7 | 100 | 89 |
| 1 | -7 | 303 | 300 |
| 1 | -8 | 117 | 136 |
| 1 | 9 | 106 | 183 |
| 1 | -0 | 181 | 166 |
| 1 | 11 | 120 | 338 |
| 1 | 13 | 143 | 184 |
| 2 | 0 | 316 | 358 |
| 2 | 1 | 171 | 187 |
| 1 | 2 | 471 | 466 |
| 2 | -1 | 441 | 466 |
| 2 | 3 | 184 | 186 |
| 1 | -3 | 124 | 113 |
| 2 | 6 | 133 | 131 |
| 1 | -6 | 114 | 116 |
| 1 | 5 | 181 | 180 |
| 2 | -5 | 140 | 154 |
| 2 | 6 | 278 | 178 |
| 2 | -6 | 106 | 67 |
| 2 | -7 | 146 | 151 |
| 2 | 6 | 248 | 157 |
| 1 | -8 | 103 | 00 |
| 1 | -0 | 256 | 257 |
| 3 | 0 | 181 | 131 |
| 3 | 1 | 284 | 162 |
| 3 | -1 | 141 | 146 |
| 3 | 2 | 108 | 126 |
| 3 | -2 | 07 | 01 |
| 3 | 5 | 148 | 162 |
| 3 | -5 | 118 | 117 |
| 3 | -6 | 126 | 111 |
| 3 | -7 | 132 | 141 |
| 3 | -10 | 157 | 156 |
| 3 | 11 | 126 | 156 |
| 3 | -11 | 108 | 71 |
| 4 | 0 | 454 | 456 |
| 4 | 1 | 248 | 236 |
| 4 | -1 | 136 | 189 |
| 4 | 2 | 109 | 181 |
| 4 | -2 | 116 | 187 |
| 4 | -3 | 06 | 74 |
| 4 | -4 | 111 | 106 |
| 4 | -5 | 151 | 156 |
| 6 | 6 | 413 | 417 |
| 4 | -6 | 347 | 143 |
| 5 | 0 | 98 | 01 |
| 5 | 1 | 222 | 123 |
| 5 | -1 | 314 | 306 |
| 5 | 1 | 154 | 153 |
| 5 | -2 | 376 | 372 |
| 5 | 3 | 138 | 131 |
| 5 | -3 | 163 | 166 |
| 5 | -4 | 101 | 107 |
| 5 | 5 | 174 | 183 |
| 5 | -5 | 238 | 236 |
| 5 | -7 | 177 | 178 |
| 6 | 0 | 190 | 204 |
| 6 | 1 | 202 | 221 |
| 6 | -1 | 100 | 116 |
| 6 | 1 | 03 | 101 |
| 6 | -1 | 283 | 188 |
| 6 | 4 | 176 | 186 |
| 6 | -4 | 238 | 236 |
| 6 | -6 | 137 | 151 |
| 6 | 8 | 101 | 106 |
| 6 | -10 | 104 | 121 |
| 6 | -12 | 138 | 100 |
| 7 | 0 | 146 | 146 |
| 7 | -1 | 356 | 383 |
| 7 | 1 | 187 | 171 |
| 7 | 3 | 198 | 177 |
| 7 | -3 | 291 | 301 |
| 7 | 4 | 184 | 151 |
| 7 | -4 | 107 | 83 |
| 7 | 7 | 113 | 111 |
| 7 | -7 | 130 | 121 |
| 7 | 9 | 207 | 208 |
| 7 | 11 | 118 | 111 |
| 7 | -31 | 126 | 186 |
| 8 | 0 | 131 | 138 |
| 8 | 1 | 248 | 181 |
| 8 | -1 | 202 | 113 |
| 8 | 1 | 141 | 121 |
| 8 | -3 | 119 | 111 |
| 8 | -4 | 141 | 123 |
| 8 | -5 | 158 | 187 |
| 8 | -8 | 123 | 311 |
| 8 | 9 | 111 | 81 |
| 8 | -30 | 122 | 03 |
| 8 | -11 | 109 | 107 |
| 0 | 0 | 101 | 212 |
| 0 | 1 | 157 | 187 |
| 0 | -2 | 217 | 224 |
| 0 | -3 | 181 | 153 |
| 9 | 4 | 126 | 113 |
| 9 | -4 | 157 | 171 |
| 0 | -0 | 123 | 146 |
| 10 | 0 | 103 | 106 |
| 10 | 2 | 162 | 284 |
| 10 | -2 | 147 | 154 |
| 10 | -4 | 103 | 203 |
| 10 | 5 | 300 | 186 |
| 10 | 8 | 161 | 176 |
| 30 | 10 | 140 | 112 |
| 11 | 1 | 202 | 214 |
| 11 | -1 | 101 | 116 |
| 11 | -3 | 186 | 170 |
| 11 | -4 | 111 | 116 |
| 11 | -8 | 134 | 126 |
| 12 | -3 | 208 | 228 |
| 31 | -4 | 101 | 211 |
| 12 | -5 | 106 | 74 |
| 11 | 6 | 107 | 311 |
| 12 | -7 | 147 | 141 |
| 13 | 1 | 120 | 117 |
| 11 | -3 | 114 | 111 |
| 13 | 5 | 142 | 123 |
| 13 | -30 | 107 | 18 |
| 14 | 0 | 100 | 76 |
| 14 | -1 | 111 | 84 |
| 14 | -3 | 121 | 131 |
| 14 | 4 | 116 | 86 |
| 14 | 8 | 153 | 121 |
| 14 | -6 | 114 | 01 |
| 15 | -1 | 106 | 36 |
| 15 | 4 | 114 | 06 |
| 17 | 3 | 111 | 07 |
| 17 | -5 | 118 | 48 |
| 18 | -2 | 128 | 31 |
| 18 | 4 | 131 | 37 |
| ******** K= 5 ****** | | | |
| 0 | 0 | 316 | 384 |
| 0 | 1 | 720 | 721 |
| 0 | -2 | 406 | 416 |
| 0 | -4 | 133 | 131 |
| 0 | -6 | 144 | 141 |
| 0 | 8 | 107 | 106 |
| 0 | -4 | 108 | 87 |
| 0 | -10 | 170 | 101 |
| 1 | 0 | 08 | 41 |
| 1 | 1 | 278 | 281 |
| 3 | -1 | 386 | 107 |
| 1 | 1 | 131 | 181 |
| 1 | -1 | 101 | 111 |
| 1 | 3 | 173 | 140 |
| 1 | -3 | 280 | 256 |
| 1 | 5 | 120 | 143 |
| 1 | -5 | 151 | 146 |
| 1 | -6 | 108 | 102 |
| 1 | 7 | 101 | 101 |
| 1 | -8 | 130 | 147 |
| 1 | -10 | 139 | 149 |
| 1 | 11 | 100 | 176 |
| 1 | 0 | 323 | 314 |
| 1 | 1 | 151 | 160 |
| 2 | -1 | 08 | 123 |
| 2 | 2 | 146 | 128 |
| 2 | -2 | 04 | 51 |
| 2 | 3 | 113 | 83 |
| 2 | -5 | 171 | 181 |
| 2 | 6 | 228 | 223 |
| 2 | -6 | 108 | 111 |
| 2 | -8 | 162 | 164 |
| 2 | -9 | 159 | 156 |
| 2 | -10 | 160 | 171 |
| 3 | 1 | 143 | 151 |
| 3 | -1 | 177 | 189 |
| 3 | 2 | 158 | 161 |
| 3 | -1 | 117 | 111 |
| 3 | 3 | 110 | 132 |
| 3 | -3 | 319 | 323 |
| 3 | -6 | 151 | 141 |
| 3 | 5 | 264 | 281 |
| 3 | 7 | 181 | 176 |
| 3 | -10 | 224 | 217 |
| 3 | 11 | 156 | 162 |
| 3 | -31 | 113 | 36 |
| 4 | 1 | 167 | 177 |
| 4 | -1 | 166 | 176 |
| 4 | 2 | 401 | 407 |
| 4 | -2 | 108 | 303 |
| 4 | 3 | 252 | 266 |
| 4 | -3 | 130 | 138 |
| 4 | 4 | 00 | 73 |
| 4 | -5 | 174 | 160 |
| 4 | 6 | 301 | 333 |
| 4 | 7 | 126 | 133 |
| 4 | -7 | 162 | 151 |
| 4 | -8 | 103 | 61 |
| 4 | -9 | 116 | 101 |
| 5 | 0 | 120 | 111 |
| 5 | 1 | 360 | 373 |
| 5 | -1 | 150 | 167 |
| 5 | 1 | 101 | 186 |
| 5 | -2 | 257 | 267 |
| 5 | -4 | 381 | 178 |
| 5 | -5 | 124 | 138 |
| 5 | -6 | 107 | 107 |
| 6 | 0 | 267 | 268 |
| 6 | -1 | 350 | 376 |
| 6 | 2 | 274 | 286 |
| 6 | 3 | 200 | 111 |
| 6 | -3 | 118 | 118 |
| 6 | 4 | 126 | 227 |
| 6 | -4 | 114 | 120 |
| 6 | 5 | 141 | 141 |
| 6 | -6 | 08 | 53 |
| 6 | 7 | 112 | 103 |
| 6 | 8 | 178 | 186 |
| 6 | 10 | 116 | 03 |
| 7 | -1 | 169 | 184 |
| 7 | -6 | 188 | 106 |
| 7 | 5 | 107 | 88 |
| 7 | -5 | 117 | 108 |
| 7 | 7 | 167 | 161 |
| 7 | -7 | 111 | 131 |
| 7 | -8 | 101 | 28 |
| 7 | -9 | 134 | 124 |
| 8 | 0 | 156 | 161 |
| 8 | 1 | 180 | 181 |
| 8 | -1 | 167 | 170 |
| 8 | 1 | 344 | 136 |
| 8 | -3 | 128 | 144 |
| 8 | 4 | 176 | 166 |
| 8 | -5 | 136 | 117 |
| 8 | -7 | 111 | 86 |
| 9 | 0 | 156 | 158 |
| 9 | 1 | 143 | 136 |
| 0 | -1 | 117 | 102 |
| 0 | -4 | 118 | 211 |
| 9 | -5 | 141 | 141 |
| 9 | 6 | 116 | 100 |
| 0 | -6 | 100 | 131 |
| 10 | 1 | 178 | 186 |
| 10 | -6 | 243 | 151 |
| 10 | -5 | 194 | 191 |
| 10 | 6 | 701 | 86 |
| 10 | 8 | 151 | 111 |
| 31 | 1 | 113 | 08 |
| 11 | -3 | 116 | 97 |
| 11 | 7 | 189 | 167 |
| 12 | -1 | 106 | 51 |
| 11 | -3 | 144 | 151 |
| 11 | -4 | 181 | 186 |
| 11 | -7 | 133 | 113 |
| 13 | -1 | 113 | 106 |
| 33 | 3 | 118 | 101 |
| 13 | 5 | 144 | 141 |
| ******** K= 6 ****** | | | |
| 0 | 0 | 171 | 154 |
| 0 | 2 | 183 | 181 |
| 0 | -1 | 118 | 112 |
| 0 | 4 | 111 | 122 |
| 0 | -4 | 171 | 261 |
| 0 | -10 | 181 | 173 |
| 1 | 0 | 98 | 87 |
| 1 | 1 | 221 | 236 |
| 1 | -1 | 110 | 116 |
| 1 | -2 | 110 | 131 |
| 1 | 3 | 108 | 211 |
| 1 | -3 | 333 | 349 |
| 1 | -4 | 236 | 228 |
| 1 | -6 | 118 | 121 |
| 1 | -7 | 134 | 740 |
| 1 | -0 | 117 | 107 |
| 1 | 0 | 106 | 01 |
| 2 | 1 | 141 | 161 |
| 2 | -1 | 218 | 216 |
| 2 | 1 | 161 | 140 |
| 2 | -2 | 348 | 358 |
| 2 | -3 | 110 | 07 |
| 2 | 4 | 108 | 101 |
| 2 | 5 | 116 | 122 |
| 1 | 6 | 156 | 141 |
| 2 | -6 | 231 | 216 |
| 2 | -0 | 131 | 128 |
| 3 | 0 | 151 | 146 |
| 3 | -1 | 158 | 136 |
| 3 | 1 | 141 | 117 |
| 3 | 3 | 304 | 411 |
| 3 | -3 | 240 | 247 |
| 3 | -4 | 103 | 56 |
| 3 | -5 | 117 | 48 |
| 3 | -7 | 146 | 186 |
| 4 | 2 | 103 | 180 |
| 4 | -2 | 312 | 316 |
| 4 | -3 | 188 | 151 |
| 4 | 5 | 118 | 112 |
| 4 | -5 | 128 | 111 |
| 4 | -6 | 113 | 41 |
| 4 | -7 | 136 | 148 |
| 4 | 8 | 161 | 132 |
| 4 | -8 | 111 | 98 |
| 5 | 0 | 231 | 732 |
| 5 | -1 | 118 | 134 |
| 5 | -2 | 206 | 216 |
| 5 | 3 | 182 | 181 |
| 5 | -3 | 184 | 171 |
| 5 | 4 | 200 | 208 |
| 5 | -4 | 104 | 88 |
| 5 | 5 | 120 | 126 |
| 5 | -4 | 183 | 188 |
| 5 | -8 | 122 | 111 |
| 5 | -12 | 131 | 00 |
| 6 | -1 | 141 | 146 |
| 6 | -3 | 111 | 110 |
| 6 | 4 | 110 | 101 |
| 6 | 8 | 138 | 148 |
| 6 | -7 | 126 | 104 |
| 7 | -1 | 111 | 121 |
| 7 | 3 | 112 | 111 |
| 7 | 5 | 164 | 153 |
| 7 | -5 | 100 | 111 |
| 7 | 7 | 128 | 00 |
| 8 | 1 | 148 | 156 |
| 8 | 4 | 112 | 128 |
| 8 | -5 | 154 | 181 |
| 8 | -4 | 148 | 128 |
| 8 | -9 | 131 | 111 |
| 0 | 0 | 176 | 174 |
| 0 | -4 | 172 | 171 |
| 0 | -8 | 158 | 149 |
| 10 | 2 | 108 | 81 |
| 10 | -5 | 138 | 128 |
| 11 | 2 | 121 | 122 |
| 11 | -2 | 111 | 82 |
| 11 | -4 | 111 | 03 |
| 11 | 7 | 153 | 141 |
| 12 | 0 | 121 | 04 |
| 12 | -1 | 127 | 117 |
| 12 | 5 | 142 | 06 |
| 13 | -5 | 111 | 36 |
| 15 | -6 | 122 | 59 |
| ******** K= 7 ****** | | | |
| 0 | 8 | 257 | 281 |
| 0 | -2 | 178 | 173 |
| 0 | -4 | 147 | 158 |
| 0 | 8 | 121 | 134 |
| 0 | -8 | 122 | 121 |
| 1 | 0 | 114 | 126 |
| 1 | 1 | 403 | 471 |
| 1 | -2 | 101 | 81 |
| 1 | 3 | 341 | 357 |
| 1 | -4 | 187 | 191 |
| 1 | 5 | 200 | 216 |
| 2 | 0 | 141 | 154 |
| 2 | 1 | 201 | 287 |
| 2 | -1 | 40 | 01 |
| 2 | -3 | 311 | 327 |
| 2 | -8 | 124 | 128 |
| 3 | 1 | 103 | 181 |
| 3 | -1 | 186 | 171 |
| 3 | 1 | 157 | 134 |
| 3 | 4 | 118 | 06 |
| 3 | -4 | 136 | 130 |
| 3 | -5 | 108 | 127 |
| 4 | 1 | 124 | 113 |
| 4 | 3 | 114 | 118 |
| 4 | -5 | 111 | 111 |
| 4 | 6 | 122 | 141 |
| 4 | 8 | 147 | 138 |
| 4 | 0 | 112 | 48 |
| 4 | -10 | 106 | 73 |
| 5 | 2 | 138 | 146 |
| 5 | -2 | 123 | 121 |
| 5 | -3 | 211 | 212 |
| 5 | -5 | 148 | 123 |
| 5 | -8 | 133 | 128 |
| 5 | 7 | 118 | 88 |
| 5 | -8 | 111 | 119 |
| 6 | 1 | 114 | 93 |
| 6 | 1 | 141 | 128 |
| 6 | -2 | 110 | 189 |
| 6 | -4 | 118 | 112 |
| 6 | 8 | 170 | 161 |
| 7 | -1 | 302 | 71 |
| 7 | -5 | 118 | 110 |
| 8 | -2 | 111 | 119 |
| 8 | 3 | 144 | 139 |
| 8 | -4 | 110 | 131 |
| 8 | -0 | 113 | 01 |
| 0 | 1 | 352 | 141 |
| 11 | 0 | 187 | 147 |
| 11 | 4 | 118 | 102 |
| 11 | 7 | 131 | 78 |
| 13 | 0 | 121 | 04 |
| 15 | -1 | 114 | 58 |
| ******** K= 8 ****** | | | |
| 0 | 0 | 128 | 132 |
| 0 | -2 | 137 | 161 |
| 0 | 6 | 180 | 173 |
| 1 | 1 | 138 | 140 |
| 1 | -2 | 177 | 186 |
| 3 | -3 | 111 | 101 |
| 3 | -8 | 116 | 112 |
| 2 | -1 | 126 | 101 |
| 2 | -3 | 180 | 151 |
| 2 | -8 | 126 | 121 |
| 2 | 5 | 106 | 84 |
| 2 | -5 | 121 | 136 |
| 3 | 1 | 100 | 101 |
| 3 | -5 | 120 | 187 |
| 3 | -4 | 121 | 114 |
| 5 | 0 | 110 | 181 |
| 5 | 2 | 111 | 108 |
| 7 | 6 | 106 | 16 |
| 7 | 7 | 107 | 21 |
| 8 | -1 | 112 | 88 |
| 8 | 3 | 138 | 126 |
| 0 | 1 | 117 | 111 |
| ******** K= 9 ****** | | | |
| 0 | 0 | 116 | 81 |
| 3 | 1 | 113 | 52 |
| 5 | 2 | 117 | 123 |
| 6 | 1 | 111 | 06 |
| ******** K=10 ****** | | | |
| 0 | -2 | 114 | 17 |
| 1 | 3 | 120 | 107 |

furthermore, such delocalization would increase the coulombic interaction between the anions and cations since the ring carbon atoms are closer to the sodium ion than the aluminum atoms are. Such one-bond resonance forms are probably less stable energetically than the two-bond form because the energy lost in breaking the Al–C bond and rehybridization of the α carbon is quite likely to be greater than the energy gained by delocalization of the negative charge and by the enhanced coulombic interaction. On the other hand, the electron deficiency predicted by this argument for the Al–C(1) and Al–C(4)′ bonds is supported, but not proved, by their greater sensitivity to alcoholysis compared to that of the Al–C(11) and Al–C(12) bonds,[5,6] a behavior reminiscent of that of the electron-deficient bonds in $[Al(CH_3)_3]_2$.

The carbon–carbon bond distances in the phenylene group do not deviate significantly from their average value of 1.395 (19) Å, which compares favorably with the 1.392 (10) Å value reported for benzene.[24] The average length of the carbon–carbon bonds C(1)–C(2), C(1)–C(9), C(3)–C(4), and C(4)–C(10) is 1.491

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(24) E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc.*, **A247**, 1 (1958).

**Table III.** Interatomic Distances (Å) for the Nonhydrogen Atoms[a] Bonded Distances

| | | | |
|---|---|---|---|
| | Bonded Distances | | |
| Al–C(1) | 2.056 (10) | C(9)–C(10) | 1.416 (12) |
| Al–C(4)′ [b] | 2.074 (10) | C(13)–C(14) | 1.52 (2) |
| Al–C(11) | 1.990 (12) | C(13)–O(1) | 1.44 (1) |
| Al–C(12) | 1.982 (11) | C(14)–C(15) | 1.54 (2) |
| C(1)–C(2) | 1.488 (13) | C(15)–C(16) | 1.47 (2) |
| C(1)–C(9) | 1.505 (13) | C(16)–O(1) | 1.46 (1) |
| C(2)–C(3) | 1.338 (13) | C(17)–C(18) | 1.52 (2) |
| C(3)–C(4) | 1.493 (13) | C(17)–O(2) | 1.40 (1) |
| C(4)–C(10) | 1.477 (13) | C(18)–C(19) | 1.41 (2) |
| C(5)–C(6) | 1.393 (14) | C(19)–C(20) | 1.46 (2) |
| C(5)–C(10) | 1.418 (13) | C(20)–O(2) | 1.40 (2) |
| C(6)–C(7) | 1.377 (15) | Na–O(1) | 2.330 (9) |
| C(7)–C(8) | 1.373 (15) | Na–O(2) | 2.347 (9) |
| C(8)–C(9) | 1.393 (13) | | |
| | Selected Nonbonded Distances | | |
| Al–C(2) | 2.988 (11) | C(4)–C(11)′ | 3.242 (15) |
| Al–C(3)′ | 3.002 (11) | C(4)–C(12)′ | 3.326 (15) |
| Al–C(9) | 3.089 (11) | C(4)–Na | 3.844 (11) |
| Al–C(10)′ | 3.065 (11) | C(4)–Na′ | 3.975 (11) |
| Al–Na | 4.120 (9) | C(5)–Na | 2.888 (11) |
| Al–Na′ | 4.012 (9) | C(6)–C(20) | 3.541 (21) |
| C(1)–C(4)′ | 3.513 (11) | C(6)–Na | 2.953 (11) |
| C(1)–C(11) | 3.309 (14) | C(7)–Na | 2.962 (11) |
| C(1)–C(12) | 3.195 (15) | C(8)–C(11) | 3.565 (16) |
| C(1)–Na | 3.889 (11) | C(8)–Na | 2.931 (11) |
| C(1)–Na′ | 3.905 (10) | C(9)–C(11) | 3.755 (16) |
| C(2)–C(12) | 3.554 (16) | C(9)–Na | 2.920 (10) |
| C(2)–Na′ | 2.867 (11) | C(10)–Na | 2.893 (10) |
| C(3)–C(11)′ | 3.613 (16) | C(11)–C(12) | 3.256 (17) |
| C(3)–Na′ | 2.908 (10) | O(1)–O(2) | 3.182 (13) |

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

**Table IV.** Bond Angles (deg)[a]

| | | | |
|---|---|---|---|
| C(1)–Al–C(4)′ | 116.5 (4) | C(8)–C(9)–C(10) | 121 (1) |
| C(1)–Al–C(11) | 109.7 (5) | C(4)–C(10)–C(5) | 121 (1) |
| C(1)–Al–C(12) | 104.6 (5) | C(4)–C(10)–C(9) | 123 (1) |
| C(4)′–Al–C(11) | 105.8 (5) | C(5)–C(10)–C(9) | 116 (1) |
| C(4)′–Al–C(12) | 110.1 (5) | C(14)–C(13)–O(1) | 103 (1) |
| C(11)–Al–C(12) | 110.1 (5) | C(15)–C(14)–C(13) | 107 (1) |
| Al–C(1)–C(2) | 114.0 (6) | C(16)–C(15)–C(14) | 104 (1) |
| Al–C(1)–C(9) | 119.5 (7) | C(15)–C(16)–O(1) | 109 (1) |
| C(2)–C(1)–C(9) | 111.5 (8) | C(18)–C(17)–O(2) | 105 (1) |
| C(1)–C(2)–C(3) | 123.7 (9) | C(17)–C(18)–C(19) | 107 (1) |
| C(2)–C(3)–C(4) | 122 (1) | C(18)–C(19)–C(20) | 106 (2) |
| Al′–C(4)–C(3) | 113.6 (7) | C(19)–C(20)–O(2) | 109 (1) |
| Al′–C(4)–C(10) | 118.4 (7) | C(13)–O(1)–C(16) | 109 (1) |
| C(3)–C(4)–C(10) | 111.5 (8) | C(13)–O(1)–Na | 124.4 (8) |
| C(6)–C(5)–C(10) | 123 (1) | C(16)–O(1)–Na | 126.5 (9) |
| C(5)–C(6)–C(7) | 119 (1) | C(17)–O(2)–C(20) | 109 (1) |
| C(6)–C(7)–C(8) | 121 (1) | C(17)–O(2)–Na | 132 (1) |
| C(7)–C(8)–C(9) | 121 (1) | C(20)–O(2)–Na | 120 (1) |
| C(1)–C(9)–C(8) | 120 (1) | O(1)–Na–O(2) | 85.8 (3) |
| C(1)–C(9)–C(10) | 119 (1) | | |

[a] See footnotes in Table II.

**Table V.** Root-Mean-Square Amplitudes of Vibration (Å) along the Principal Axes *R*

| Atom | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| Al | 0.207 (5) | 0.218 (5) | 0.257 (4) |
| Na | 0.232 (5) | 0.247 (5) | 0.311 (6) |
| O(1) | 0.26 (1) | 0.30 (1) | 0.39 (1) |
| O(2) | 0.28 (1) | 0.29 (1) | 0.39 (1) |
| C(1) | 0.17 (2) | 0.24 (1) | 0.26 (1) |
| C(2) | 0.20 (2) | 0.23 (2) | 0.27 (2) |
| C(3) | 0.19 (2) | 0.21 (2) | 0.28 (2) |
| C(4) | 0.18 (2) | 0.24 (2) | 0.27 1) |
| C(5) | 0.17 (2) | 0.26 (1) | 0.28 (1) |
| C(6) | 0.20 (2) | 0.26 (2) | 0.32 (2) |
| C(7) | 0.20 (2) | 0.26 (2) | 0.31 (2) |
| C(8) | 0.23 (2) | 0.24 (2) | 0.26 (2) |
| C(9) | 0.17 (2) | 0.20 (2) | 0.27 (2) |
| C(10) | 0.16 (2) | 0.23 (2) | 0.26 (1) |
| C(11) | 0.24 (2) | 0.26 (2) | 0.34 (1) |
| C(12) | 0.23 (2) | 0.29 (2) | 0.35 (2) |
| C(13) | 0.26 (2) | 0.34 (2) | 0.44 (2) |
| C(14) | 0.26 (2) | 0.33 (2) | 0.51 (2) |
| C(15) | 0.27 (2) | 0.28 (2) | 0.48 (2) |
| C(16) | 0.23 (2) | 0.31 (2) | 0.57 (2) |
| C(17) | 0.21 (2) | 0.35 (2) | 0.53 (2) |
| C(18) | 0.28 (2) | 0.35 (2) | 0.63 (3) |
| C(19) | 0.25 (3) | 0.35 (3) | 0.69 (3) |
| C(20) | 0.25 (2) | 0.31 (2) | 0.70 (3) |

**Table VI.** Best Weighted Least-Squares Planes

| Plane | Atoms in plane | Equation of plane[a,b] |
|---|---|---|
| 1 | C(1), C(4), C(5), C(6), C(7), C(8), C(9), C(10) | $-0.9416X - 0.0712Y - 0.3291Z - 0.3745 = 0$ |
| 2 | C(5), C(6), C(7), C(8), C(9), C(10) | $-0.9463X - 0.0687Y - 0.3159Z - 0.4158 = 0$ |
| 3 | C(1), C(4), C(9), C(10) | $-0.9332X - 0.0743Y - 0.3517Z - 0.2454 = 0$ |
| 4 | C(1), C(2), C(3), C(4) | $-0.6792X - 0.0279Y - 0.7335Z + 2.4120 = 0$ |

Deviation of Atoms from Planes (Å)

| Atom | Plane 1 | Plane 2 | Plane 3 | Plane 4 |
|---|---|---|---|---|
| C(1) | 0.02 (1) | | 0.00 (1) | 0.00 (1) |
| C(2) | | | | 0.00 (1) |
| C(3) | | | | 0.001 (9) |
| C(4) | 0.008 (9) | | 0.001 (9) | 0.00 (1) |
| C(5) | 0.00 (1) | 0.00 (1) | | |
| C(6) | 0.02 (1) | 0.01 (1) | | |
| C(7) | 0.01 (1) | 0.00 (1) | | |
| C(8) | −0.02 (1) | −0.01 (1) | | |
| C(9) | −0.009 (9) | 0.014 (9) | 0.006 (9) | |
| C(10) | −0.027 (9) | −0.009 (9) | −0.01 (1) | |
| Na | −2.573 (4) | −2.568 (4) | | |

Dihedral Angles between Planes

| Plane A | Plane B | Dihedral angle (deg) |
|---|---|---|
| 1 | 4 | 152.0 (15)[c] |
| 2 | 4 | 151.2 (15) |
| 3 | 4 | 153.4 (15) |

[a] The orthogonal unit cell vectors $X$, $Y$, $Z$ are related to the monoclinic vectors $a$, $b$, $c$ as follows: $(X, Y, Z) = (a + c \cos \beta, b, c \sin \beta)$. [b] The weight of each atom was inversely proportional to the mean variance of the positional parameters of that atom. [c] These standard deviations are projected from values obtained from ORFFE calculations.

(12) Å, which does not deviate significantly from the average value 1.510 (5) Å reported for $C(sp^2)$–$C(sp^3)$ bond distances.[25] As is shown in Table VI, the atoms C(1), C(4), C(5), C(6), C(7), C(8), C(9), and C(10) deviate only slighly from their least-squares best plane. The C(2)–C(3) bond length of 1.338 (13) Å compares well with the well-known value of 1.34 Å for carbon–carbon double bonds. The carbon atoms C(1), C(2), C(3), and C(4) are planar within experimental error (Table VI), and the dihedral angle between the above planes is 152.0 (15)°. For completeness, other planes through various sets of naphthylenic carbon atoms are listed in Table VI, but those planes described above appear to be the most structurally significant.

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(25) "Tables of Interatomic Distances and Configuration in Molecules and Ions; Supplement 1956–1959," Special Publication No. 18, The Chemical Society, London, 1965, p S15s.

The contact ion-pair nature of this compound can best be seen by examining the placement and coordination of the sodium ion. The cation lies 2.573 (4) Å above the least-squares best plane defined by the atoms C(1), C(4), C(5), C(6), C(7), C(8), C(9), and C(10), and the distance from the sodium to a line joining atoms C(2)′ and C(3)′ is 2.807 (11) Å. The eight closest sodium–carbon contacts vary from 2.867 (10) to 2.962 (11) Å, values which are somewhat larger than the sum of the ionic radius of $Na^+$ and the van der Waals radius of $sp^2$ carbons, 2.70 Å.[26] The position occupied by the cation is consistent with its desire to be as close as possible to the formal centers of negative charge, the aluminum atoms, and does not appear to resolve the question of the relative basicities of the $AlR_4^-$ group *vs.* that of the organic $\pi$ cloud toward $Na^+$. The coordination about the sodium ion is completed by two molecules of THF. The average Na–O distance of 2.338 (9) Å is somewhat larger than the sum of the respective covalent radii, 2.26 Å, but is approximately equal to the sum of the ionic radius of $Na^+$ and the van der Waals radii of oxygen, 2.35 Å.[26] The O(1)–Na–O(2) angle is small, 85.7 (3)°, but since there are no unusually short nonbonded contacts between the THF ring atoms and the other atoms, this angle does not appear to be closed by steric crowding.

The THF carbon atoms are obviously disordered; therefore, we place little faith in either their positional or thermal parameters. Accordingly, the corresponding bond distances and angles should not be taken seriously.

The nature of ion-pair complexes in solution has received much recent interest, and it seems appropriate to discuss this crystal structure in terms of contact and solvent separated ion pairs. Two obvious driving forces have made this compound a contact ion pair in the solid state. First, the high charge on the dianion coupled with the ability of the cation to move close to the centers of charge makes possible a strong coulombic interaction if a contact ion pair is formed. Second, the complex found in this analysis has a rather compact shape and thus is able to pack well in the unit cell; the coordination of more solvent about the cation, therefore, should lead to a less efficient molecular packing. The relative importance of the two driving forces could best be evaluated if the dominant species in THF solution at room temperature were known; however, the necessary conductivity or molecular weight studies have not been made. However, since such complexes as sodium naphthalene and sodium biphenyl have been shown to exist mainly as contact ion pairs at 25° in THF solution,[27] it might be predicted that $[Na(THF)_2]_2[Al(CH_3)_2C_{10}H_8]_2$ exists predominantly as a contact ion pair under similar conditions.

Lehmkuhl has proposed two mechanisms for the formation of the $Na[AlR_2C_{10}H_8]$ species. The final step in both mechanisms is the reduction by sodium of a 1-dialkylaluminum-1-hydronaphthyl radical which is formed either by the reaction of the dialkylaluminum cation with a naphthalene radical (mechanism one) or by the reaction of the dialkylaluminum radial with naphthalene. In order to form the dimer, however, the dialkylaluminum species would not bridge the 1 and 4 positions on the naphthalene but rather would remain coordinated only to the $\alpha$ carbon. Two such carbanions polymerize in a head-to-tail fashion to form the dimer. Thus, the above represents a 1,4 addition to a conjugated system and may be applicable to the reaction of 1,3-butadiene with sodium and trimethylaluminum. A product has been isolated from such a reaction and has been postulated to be a monomeric species.[28] Also, a similar reaction with anthracene has been reported.[6] It appears that dimeric or high polymers are possible products of these reactions, and further investigations are being made in the solid and solution phase in order to better define their stereochemistries.

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[26] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

[27] P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

[28] H. Lehmkuhl, *Angew. Chem. Intern. Ed. Engl.*, 5, 663 (1966).