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THE CRYSTAL STRUCTURE OF TRIMETHYL(QUINUCLIDINE)ALUMINUM

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SUMMARY

The crystal structure of $(CH_3)_3Al\cdot NC_7H_{13}$ has been determined from single-crystal X-ray diffraction data collected by film techniques. The unit cell is monoclinic with $a=8.94\pm0.02$ Å, $b=10.66\pm0.02$ Å, $c=6.84\pm0.02$ Å, $\beta=106°\ 19'\pm10'$, and contains two formula units of the monomeric compound. The space group is $P2_1/m$. Approximately tetrahedral coordination is found about the aluminum atom, and the aluminum–nitrogen bond length is 2.06 Å. Viewed along the aluminum–nitrogen bond, the methyl groups appear in a staggered configuration with respect to the methylene groups of the quinuclidine molecule.

INTRODUCTION

Trimethylaluminum complexes of nitrogen-containing Lewis bases have been the subject of a number of investigations. In solution four-coordinate aluminum is common[1,2], but evidence has been put forward for the existence of five-coordinate aluminum[3,4] under certain circumstances. In the solid state there is no possibility of forming a neutral addition complex of trimethylaluminum with two molecules of an amine as bulky as quinuclidine. However, trimethyl(quinuclidine)aluminum was of interest because of the questions recently raised by the structures of dimethylbis(quinuclidine)magnesium[5] and dimethylbis(quinuclidine)beryllium[6]. For $(CH_3)_2$-$Mg\cdot 2NC_7H_{13}$ the methyl carbon–magnesium–methyl carbon bond angle is 129°, whereas the nitrogen–magnesium–nitrogen bond angle is 108°. In the beryllium analogue the methyl carbon–beryllium–methyl carbon angle is 118°, and the nitrogen–beryllium–nitrogen angle, 111°. The unusually large carbon–metal–carbon bond angle has been explained in terms of steric interactions, electronic effects, and lattice distortions[5,6]. The determination of the crystal structure of trimethyl(quinuclidine)aluminum was undertaken to aid in the assessment of the relative importance of steric and electronic effects in the related beryllium and magnesium compounds.

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TRIMETHYL(QUINUCLIDINE)ALUMINUM

H	L	OBS	CAL	H	L	OBS	CAL	H	L	OBS	CAL	H	L	OBS	CAL	H	L	OBS	CAL	H	L	OBS	CAL	H	L	OBS	CAL
****	K = 0		****	8	-1	5.4	5.2	8	-2	5.5	5.4	-2	5	6.5	7.3	4	2	7.9	8.1	4	-6	2.2	2.3	3	3	7.5	7.5
1	0	19.8	23.5	9	-1	2.6	3.1	9	-2	3.7	3.3	1	6	6.4	6.6	5	2	12.0	12.4	5	-6	2.0	1.6	4	3	4.6	4.8
2	0	28.6	36.2	0	2	12.2	14.0	10	-2	2.0	2.4	2	6	3.2	3.5	7	2	3.1	4.3	7	-6	1.0	1.2	6	3	1.9	2.7
3	0	34.4	34.6	1	2	18.9	17.2	0	3	21.1	22.8	-2	6	5.4	4.4	8	2	2.6	3.1	3	-7	1.8	1.9	-1	3	9.1	9.7
4	0	41.5	42.8	2	2	4.5	2.8	1	3	3.8	3.5	-3	6	5.2	5.3	-1	2	4.8	5.2	4	-7	1.7	1.9	3	-3	4.3	4.4
5	0	6.1	5.8	3	2	10.9	10.7	2	3	13.0	11.5	6	-6	2.2	2.1	2	-2	2.4	2.6					4	-3	4.2	4.8
7	0	4.1	2.6	4	2	15.2	15.1	3	3	14.8	14.1	7	-6	2.6	2.8	3	-2	1.9	2.6	****	K = 7		****	5	-3	4.2	4.1
8	0	2.4	2.7	5	2	8.3	7.6	4	3	12.5	12.0	-1	7	2.0	2.0	6	-2	2.5	1.9	1	0	6.1	5.8	7	-3	2.4	3.0
0	1	3.4	3.5	6	2	3.5	3.5	6	3	6.4	6.4	-2	7	2.1	1.8	1	3	6.8	6.7	2	0	10.2	11.0	1	4	2.0	2.1
1	1	6.2	2.3	7	2	3.7	4.1	7	3	3.0	2.9					2	3	9.6	9.2	3	0	1.9	1.5	-3	4	3.9	4.7
2	1	8.9	8.9	8	2	3.6	4.1	8	3	1.9	3.0	****	K = 4		****	3	3	4.1	4.2	4	0	5.8	5.8	4	-4	3.3	3.3
3	1	24.3	28.8	-1	2	3.2	7.8	-1	3	21.1	20.7	1	0	15.4	13.6	4	3	4.7	4.9	5	0	2.7	2.4	6	-4	1.8	2.3
4	1	4.8	3.6	-2	2	14.3	15.0	3	-3	10.0	10.6	2	0	9.7	10.0	-1	3	13.1	14.3	0	1	16.3	17.8	7	-4	3.1	3.1
6	1	3.5	3.1	-3	2	1.8	0.5	4	-3	6.7	8.2	4	0	14.4	14.3	2	-3	10.8	10.1	2	1	8.6	7.8	8	-4	0.7	1.1
7	1	2.4	2.3	-4	2	3.3	3.5	5	-3	6.9	5.8	5	0	10.6	10.7	3	-3	3.8	4.1	3	1	12.2	11.5	1	5	2.4	2.5
-1	1	27.5	44.9	-5	2	6.4	5.8	6	-3	3.0	3.5	6	0	3.1	2.6	4	-3	3.0	3.5	4	1	5.7	5.5	2	5	3.4	3.3
-2	1	17.7	19.5	6	-2	6.5	6.5	7	-3	2.8	2.9	7	0	7.6	8.0	5	-3	7.2	7.7	5	1	2.3	2.5	3	5	1.6	2.1
3	-1	1.4	1.0	10	-2	2.0	2.5	0	4	7.0	7.1	8	0	3.7	4.5	6	-3	5.4	4.6	6	1	2.2	2.5	1	-5	3.1	2.8
5	-1	7.8	7.5	0	3	11.3	11.8	1	4	3.3	4.0	0	1	5.6	6.6	1	4	4.5	4.4	7	1	1.9	1.7	-2	5	3.2	3.8
6	-1	7.6	7.6	1	3	4.1	3.0	2	-4	4.7	6.3	1	1	18.5	17.2	2	4	9.5	9.1	-1	1	16.6	16.8	-3	5	3.0	2.2
7	-1	4.1	4.8	2	3	10.5	11.6	3	-4	8.7	9.0	5	1	14.5	14.3	3	4	4.2	4.8	2	-1	1.7	2.5	5	-5	1.7	1.9
10	-1	2.1	2.7	3	3	3.3	2.4	4	-4	5.7	4.9	6	1	4.0	3.4	4	4	4.0	0.2	3	-1	4.4	4.6	6	-5	1.9	1.8
0	2	36.8	39.4	6	3	5.0	5.8	5	-4	5.0	4.7	7	1	3.1	3.3	6	4	1.6	1.9	4	-1	9.4	9.6	7	-5	0.8	0.8
1	2	14.4	13.9	-1	3	7.3	6.5	6	-4	5.1	5.9	8	1	2.7	2.8	-1	4	8.3	9.1	5	-1	6.8	7.4	1	-6	2.3	2.1
2	2	13.2	12.8	-2	3	2.0	0.8	7	-4	5.0	4.2	9	1	3.0	2.7	2	-4	15.3	14.8	8	-1	1.8	2.5	3	-6	1.5	1.9
3	2	20.4	20.6	-3	3	11.5	12.4	1	5	6.4	6.3	-1	1	3.1	1.0	3	-4	3.1	2.4	9	-1	1.3	2.3	4	-6	1.4	1.6
4	2	9.8	8.9	-4	3	1.8	1.7	2	5	7.1	6.8	2	-1	3.1	3.0	4	-4	3.8	3.8	0	2	4.9	4.5				
5	2	4.1	3.6	5	-3	4.8	4.7	3	5	2.4	2.1	3	-1	10.0	9.3	5	-4	6.5	7.3	1	2	9.9	8.9	****	K = 9		****
6	2	8.3	8.3	6	-3	9.8	4.8	-1	5	3.0	2.3	4	-1	3.1	2.8	6	-4	6.1	6.4	3	2	5.1	5.3	1	0	3.5	2.8
7	2	3.7	3.7	9	-3	3.6	4.0	2	-5	9.9	9.2	5	-1	8.9	8.9	8	-4	2.4	3.0	4	2	7.9	7.7	2	0	4.0	3.6
-1	2	4.1	6.4	10	-3	2.4	2.4	3	-5	7.6	7.6	6	-1	4.3	3.4	4	5	1.9	2.5	5	2	4.4	4.6	3	0	2.4	2.0
-2	2	15.6	13.5	0	4	4.1	3.7	5	-5	3.8	3.0	9	-1	2.5	2.9	-2	5	2.5	1.9	7	2	1.6	2.6	6	0	3.6	4.1
-4	2	8.0	7.1	2	4	12.2	11.3	6	-5	5.2	5.0	0	2	12.6	12.8	4	-5	2.5	2.1	-1	2	2.3	1.6	0	1	8.4	7.8
3	-2	2.2	3.6	1	4	6.0	6.2	7	-5	3.4	3.4	1	2	4.0	3.5	1	6	4.2	4.6	3	-2	1.6	1.6	2	1	2.6	2.1
6	-2	5.3	5.7	3	4	11.9	10.5	0	6	3.5	3.7	2	2	3.1	3.9	2	6	2.4	2.8	5	-2	4.2	3.6	3	1	6.0	4.8
7	-2	10.0	10.0	4	4	3.0	2.6	3	6	3.3	4.7	3	2	11.3	11.3	2	-6	4.6	4.4	7	-2	1.7	2.8	4	1	5.7	5.7
9	-2	4.3	4.2	5	4	4.9	5.5	-1	6	4.1	3.7	4	2	5.2	4.6	3	-6	4.3	4.7	8	-2	1.4	1.9	7	1	1.6	2.1
10	-2	2.5	3.1	6	4	2.8	3.2	3	-6	2.6	3.2	7	2	4.5	5.3	4	-6	2.3	1.5	0	3	4.9	4.2	-1	1	8.8	8.0
0	3	25.4	24.7	7	4	2.0	2.5	0	7	1.9	2.6	-1	2	20.8	22.0	6	-6	3.3	2.8	1	3	2.9	3.6	2	-1	4.8	4.9
1	3	9.0	9.4	-1	4	14.9	15.0	3	-7	2.9	2.9	-2	2	26.1	26.1	7	-6	1.9	2.0	2	3	8.2	7.8	4	-1	6.8	7.8
2	3	8.1	6.9	-2	4	15.3	15.8	4	-7	2.6	2.7	3	-2	6.9	7.0	5	-7	1.5	1.6	3	3	4.0	3.5	5	-1	5.8	6.1
3	3	21.7	22.5	-4	4	2.1	2.3	7	-7	1.8	1.8	4	-2	8.4	8.9					5	3	1.6	2.8	0	2	7.1	6.8
4	3	17.5	17.4	-5	4	9.6	9.7					5	-2	16.3	15.7	****	K = 6		****	6	3	2.4	2.6	1	2	2.4	1.8
5	3	4.1	4.7	6	-4	6.3	6.2	****	K = 3		****	6	-2	12.6	11.9	1	0	20.2	13.4	-1	3	6.2	6.6	2	2	2.8	2.0
6	3	7.9	8.4	9	-4	2.4	2.3	1	0	2.9	2.7	8	-2	5.6	5.9	2	0	6.9	5.6	-2	3	1.9	2.5	3	2	3.2	3.4
7	3	3.5	3.8	0	5	2.2	1.0	2	0	10.0	9.6	9	-2	2.2	2.3	3	0	16.7	14.9	-3	3	3.4	3.6	4	2	3.1	3.1
8	3	1.9	3.0	-4	5	4.7	4.4	3	0	5.5	4.6	10	-2	1.3	1.9	4	0	12.3	12.0	5	-3	3.0	3.1	5	2	1.8	1.6
-1	3	22.5	23.8	-5	5	3.0	1.4	6	0	7.7	7.0	0	3	11.9	12.8	5	0	3.0	2.9	7	-3	3.8	3.8	-1	2	6.6	7.1
-2	3	9.9	9.1	7	-5	4.4	3.8	5	0	11.5	11.2	1	3	4.0	3.8	6	0	1.9	2.1	9	-3	1.0	2.1	3	-2	4.5	5.2
-3	3	10.1	10.0	9	-5	9.6	0.6	8	0	2.4	2.7	2	3	11.3	11.1	7	0	3.7	3.8	1	4	2.3	2.8	6	-2	3.4	4.0
-5	3	10.2	10.5	0	6	2.3	2.4	9	0	3.5	4.2	3	3	8.0	7.8	0	1	1.4	1.4	2	4	5.5	5.8	4	-2	4.7	5.6
7	-3	3.6	4.2	1	6	5.6	5.2	0	1	16.1	13.0	4	3	8.3	7.5	1	1	19.1	15.7	3	4	5.6	5.6	7	-2	1.6	2.4
9	-3	2.1	2.3	-2	6	3.0	3.3	1	1	19.2	17.1	5	3	2.5	2.2	2	1	8.1	7.1	-1	4	8.2	7.9	1	3	3.2	3.5
0	4	2.7	1.7	-3	6	6.8	6.2	2	1	7.6	6.1	6	3	4.1	4.9	3	1	6.7	6.0	-2	4	8.2	8.3	2	3	3.2	2.8

-2	4	6.1	6.1
-3	4	6.2	6.6
-4	4	9.0	9.4
-6	4	3.4	4.1
6	-4	6.1	6.4
7	-4	8.9	8.2
9	-4	2.0	3.0
10	-4	1.9	2.2
1	5	4.1	3.6
2	5	5.2	5.4
3	5	4.0	4.0
5	5	2.4	2.5
-2	5	6.6	8.3
-3	5	8.8	8.4
-4	5	4.3	3.8
-5	5	4.1	4.3
-6	5	7.4	7.1
7	-5	4.0	3.2
9	-5	2.2	2.2
3	6	3.3	4.4
-1	6	5.6	4.8
-3	6	3.4	2.9
-4	6	3.2	3.8
5	-6	2.4	1.6
7	-6	2.1	2.5
0	7	3.3	3.1
-3	7	3.8	3.6
-4	7	4.0	3.8
**** K = 1 ****			
1	0	23.3	27.7
2	0	34.2	30.2
3	0	19.6	17.2
4	0	7.7	7.4
5	0	4.6	4.0
6	0	7.6	7.0
9	0	1.9	2.1
1	1	13.7	11.8
2	1	12.3	11.2
3	1	27.2	25.9
4	1	18.7	18.1
5	1	8.9	7.5
6	1	6.5	5.4
7	1	3.9	3.7
8	1	2.1	2.1
-1	1	23.1	41.3
-2	1	3.1	3.3
3	-1	5.3	5.3
4	-1	25.1	25.3
5	-1	11.1	10.7
-4	6	4.4	3.7
6	-6	3.6	3.4
7	-6	3.6	3.0
8	-6	1.6	1.4
-1	7	2.5	3.0
-2	7	3.5	3.5
-4	7	2.0	1.8
-5	7	1.9	1.9
**** K = 2 ****			
1	0	17.3	15.9
2	0	12.4	2.3
3	0	19.6	17.1
4	0	29.2	27.1
5	0	5.9	6.2
6	0	4.0	3.2
7	0	6.2	6.3
8	0	3.8	4.5
0	1	4.1	4.1
1	1	2.4	6.6
2	1	7.6	3.8
3	1	10.1	8.8
4	1	3.1	2.8
5	1	8.3	7.4
6	1	4.5	4.9
7	1	3.1	1.7
8	1	2.2	2.8
-1	1	25.4	23.0
-9	1	2.7	3.1
2	-1	2.3	0.9
3	-1	11.8	11.6
4	-1	7.1	7.1
5	-1	3.2	3.3
6	-1	7.6	8.3
7	-1	3.1	3.3
9	-1	2.7	3.4
10	-1	1.5	2.0
0	2	2.8	2.5
1	2	4.3	3.1
2	2	6.6	5.9
3	2	12.3	11.8
6	2	3.1	3.4
7	2	4.7	5.1
-1	2	8.3	11.3
2	-2	17.3	19.3
3	-2	11.4	10.8
4	-2	8.4	7.7
5	-2	10.1	10.2
6	-2	11.8	11.8
7	-2	4.2	3.7
3	1	12.7	11.2
4	1	3.4	2.9
6	1	4.1	3.0
7	1	6.5	6.5
8	1	2.9	3.0
-1	1	27.4	36.6
-2	1	31.8	35.5
-3	1	6.8	6.5
4	-1	15.9	16.5
5	-1	21.4	24.0
6	-1	11.3	11.3
7	-1	7.1	7.3
8	-1	8.1	8.0
9	-1	2.1	2.5
0	2	5.3	6.1
1	2	13.2	13.0
2	2	7.5	7.0
4	2	7.6	6.5
5	2	13.9	13.8
7	2	3.0	3.5
8	2	3.1	4.1
-2	2	4.4	4.3
-3	2	4.8	4.4
-4	2	8.0	9.2
6	-2	5.0	4.8
0	3	10.0	10.3
1	3	9.0	10.3
2	3	8.5	8.4
4	3	6.8	5.8
-1	3	11.3	11.3
-2	3	18.2	21.7
-3	3	12.2	13.1
-4	3	7.8	6.0
5	-3	12.0	12.1
6	-3	8.0	8.4
8	-3	3.1	2.8
9	-3	2.1	1.9
0	4	2.2	3.0
1	4	8.5	9.0
2	4	12.8	12.9
3	4	5.7	5.1
5	4	3.0	2.9
-1	4	13.4	14.1
-2	4	17.3	17.6
-5	4	7.4	6.8
-6	4	4.4	4.0
4	-4	8.0	7.5
0	5	5.7	4.7
2	5	3.5	2.5
4	5	3.6	3.5
7	3	2.3	2.7
-1	3	10.3	12.7
2	-3	7.0	7.0
3	-3	5.9	6.4
4	-3	6.6	7.7
5	-3	3.8	4.2
0	4	8.8	8.3
1	4	4.9	5.2
-1	4	5.2	4.8
4	4	3.1	2.8
2	-4	8.7	8.5
3	-4	5.5	5.3
4	-4	3.0	1.9
5	-4	5.6	5.1
6	-4	4.4	4.5
1	5	5.2	6.2
3	5	5.1	0.6
2	-5	11.4	11.5
3	-5	7.1	6.6
5	-5	3.0	2.7
6	-5	5.7	5.1
7	-5	2.2	2.9
0	6	3.0	3.0
3	6	2.5	3.3
1	-6	3.4	2.1
0	7	1.7	2.0
3	-7	2.2	2.3
**** K = 5 ****			
1	0	18.1	16.3
2	0	15.5	14.6
4	0	7.3	8.3
5	0	10.4	10.6
6	0	2.5	1.6
9	0	1.9	2.4
0	1	9.4	6.8
1	1	7.7	7.1
2	1	2.2	3.1
3	1	14.9	14.9
4	1	3.7	2.4
7	1	3.5	4.5
-1	1	30.9	30.7
2	-1	16.6	16.2
3	-1	3.0	3.1
4	-1	13.7	13.2
5	-1	15.6	16.1
6	-1	6.8	7.0
7	-1	5.4	5.5
8	-1	5.1	5.5
1	2	18.5	16.4
4	1	6.2	6.4
5	1	7.6	7.7
7	1	2.2	2.9
1	-1	3.7	3.7
2	-1	4.6	6.0
4	-1	2.1	3.3
5	-1	1.8	2.2
0	2	8.2	8.6
2	2	9.3	9.4
3	2	13.5	13.2
5	2	2.3	3.2
6	2	2.7	2.8
-1	2	14.7	17.2
-2	2	5.8	5.7
4	-2	4.5	5.0
5	-2	6.4	7.1
6	-2	5.2	5.2
9	-2	2.3	2.6
0	3	7.6	7.5
1	3	5.3	5.5
2	3	5.2	4.7
3	3	8.4	9.1
4	3	5.6	8.0
6	3	3.7	4.5
7	3	1.7	2.8
-1	3	7.1	7.3
-2	3	2.6	3.6
4	-3	1.8	2.3
5	-3	6.1	6.0
6	-3	3.6	3.2
8	-3	2.1	2.6
1	4	3.4	1.8
2	4	1.9	1.7
5	4	2.2	2.2
-1	4	3.1	3.4
-4	4	4.7	4.3
3	-4	2.2	1.8
6	-4	2.4	2.0
7	-4	2.9	3.1
8	-4	2.4	2.3
1	5	3.1	3.1
2	5	4.1	4.5
3	5	1.6	1.9
-1	5	4.1	1.5
-2	5	7.1	7.7
-3	5	5.9	5.3
5	-5	2.3	1.3
6	-5	5.2	5.2
-1	6	1.9	2.0
7	-6	1.7	1.1
4	-4	1.8	2.4
5	-4	5.6	6.2
6	-4	4.8	3.8
4	-5	4.0	3.4
7	-5	2.1	2.3
-4	6	1.8	1.7
2	-6	1.9	2.3
6	-6	1.6	1.7
1	-7	0.8	1.5
2	-7	1.5	2.2
**** K = 8 ****			
1	0	8.2	7.5
2	0	4.2	3.3
3	0	8.5	7.8
4	0	10.6	10.5
5	0	2.7	2.6
6	0	2.8	2.6
7	0	2.2	2.2
8	0	1.4	1.9
0	1	3.1	3.8
1	1	3.8	3.0
2	1	2.7	1.8
3	1	4.2	4.0
4	1	2.3	2.3
5	1	2.0	1.5
6	1	1.9	1.9
-1	1	5.3	6.2
2	-1	3.5	3.4
3	-1	4.7	5.2
4	-1	2.6	3.4
5	-1	1.6	1.0
6	-1	3.3	3.9
7	-1	2.5	3.4
0	2	6.4	5.9
2	2	5.7	5.5
3	2	7.5	5.9
4	2	2.7	2.4
6	2	2.3	2.6
7	2	1.1	1.6
-1	2	6.6	6.6
-2	2	4.1	4.4
3	-2	2.7	2.8
4	-2	3.8	3.4
5	-2	4.2	4.7
6	-2	3.3	3.5
7	-2	2.3	2.2
8	-2	1.4	1.4
0	3	8.7	8.5
2	3	5.3	4.7
-1	3	2.4	1.7
-2	3	4.9	5.3
3	-3	5.0	5.8
5	-3	3.4	3.4
6	-3	2.5	3.0
7	-3	2.0	2.4
0	4	3.5	3.0
1	4	3.1	3.0
2	4	5.8	4.9
3	4	3.4	3.6
-1	4	7.3	7.1
-2	4	4.4	4.2
4	-4	2.7	2.7
5	-4	2.5	2.7
0	5	3.0	2.0
3	-5	2.4	2.4
3	-6	1.1	1.6

EXPERIMENTAL

Sample preparation

$(CH_3)_3Al \cdot NC_7H_{13}$ was prepared by the addition of $(CH_3)_3Al$ to a benzene solution of quinuclidine. After one hour of heating at 50°, the solution was cooled and the clear, colorless, air-sensitive crystalline product was collected. Single crystals for X-ray analysis were isolated by vacuum sublimation and sealed in thin-walled glass capillaries.

Crystal data for $(CH_3)_3Al \cdot NC_7H_{13}$

The compound crystallizes in the monoclinic crystal system. Systematic absences allow the space group to be $P2_1/m$ or $P2_1$. The lattice parameters are: $a = 8.94 \pm 0.02$ Å, $b = 10.66 \pm 0.02$ Å, $c = 6.84 \pm 0.02$ Å, $\beta = 106° \, 19' \pm 10'$, $V = 626$ Å^3, $Z = 2$, $\rho_{calc} = 0.97$ g/cm^3, and $\rho_{obsd} = 1.00$ g/cm^3.

Ten layers of multiple-film equi-inclination Weissenberg data ($h0l$ to $h10l$) were obtained with Ni-filtered Cu-$K\alpha$ radiation. 675 independent reflections were visually estimated by comparison with a calibrated intensity scale. The crystal used was a polyhedron of rather uniform dimensions with a diameter of 0.2 mm. The linear absorption coefficient is 10.5 cm^{-1} for Cu-$K\alpha$ radiation, and absorption corrections were deemed unnecessary. Lorentz, polarization, and spot size corrections were made. The individual layers of data were placed on a common scale by means of precession intensity data.

STRUCTURE DETERMINATION AND REFINEMENT

Statistical tests based on normalized structure factors clearly indicated the space group to be the centric $P2_1/m$. Structure solution was accomplished by means of the symbolic addition procedure[7]. Isotropic refinement of the thermal and positio-

TABLE 2

FINAL ATOMIC POSITIONAL PARAMETERS FOR TRIMETHYL(QUINUCLIDINE)ALUMINUM

Atom	x/a	y/b	z/c
Al	0.1333(3)	0.2500	−0.1486(5)
N	−0.1060(8)	0.2500	−0.2562(11)
C(1)	−0.1558(14)	0.2500	−0.4828(15)
C(2)	−0.3397(13)	0.2500	−0.5619(19)
C(5)	−0.1741(9)	0.1365(9)	−0.1825(13)
C(6)	−0.3516(9)	0.1331(10)	−0.2580(15)
C(7)	−0.4085(13)	0.2500	−0.3860(21)
C(8)	0.1995(9)	0.0920(8)	−0.2633(12)
C(10)	0.1761(13)	0.2500	0.1549(15)
H1(C(5))	−0.1435	0.1368	−0.0378
H2(C(5))	−0.1345	0.0633	−0.2298
H1(C(6))	−0.3935	0.1318	−0.1448
H2(C(6))	−0.3844	0.0603	−0.3387
H(C(7))	−0.5194	0.2500	−0.4321
H1(C(1))	−0.1165	0.1772	−0.5315
H1(C(2))	−0.3738	0.3228	−0.6421

nal parameters for the nine nonhydrogen atoms in the asymmetric unit afforded an R value of 17.8%. An empirical weighting scheme based on the satisfaction of Cruickshank's criterion[8] was selected. Anisotropic refinement of all nonhydrogen atoms yielded a final $R_1 = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] \times 100 = 11.3\%$, and $R_2 = [\Sigma W(|F_o| - |F_c|)^2/\Sigma W|F_o|^2]^{\frac{1}{2}} \times 100 = 13.4\%$. Unobserved reflections were not included in the refinement. Hydrogen atom coordinates for the quinuclidine molecule were calculated and used but not refined. The hydrogen–carbon distance was 0.95Å and the isotropic

TABLE 3

BOND LENGTHS AND ANGLES FOR TRIMETHYL(QUINUCLIDINE)ALUMINUM

Bond	Distance (Å)	Angle	(°)
Al–N	2.06(1)	C(8)–Al–C(10)	114.3(3)
Al–C(8)	2.02(1)	C(8)–Al–C(9)	113.3(3)
Al–C(10)	2.00(1)	C(8)–Al–N	104.5(3)
N–C(1)	1.49(1)	C(10)–Al–N	104.4(3)
N–C(5)	1.50(1)	Al–N–C(1)	110.4(4)
C(1)–C(2)	1.58(2)	Al–N–C(5)	111.0(4)
C(5)–C(6)	1.52(1)	C(1)–N–C(5)	108.6(5)
C(2)–C(7)	1.50(2)	C(3)–N–C(5)	107.1(5)
C(6)–C(7)	1.52(1)	N–C(5)–C(6)	112.7(4)
Non-bonded distances (Å)			
C(1)–C(5)	2.43(1)	C(1)–C(2)–C(7)	110.3(8)
C(3)–C(5)	2.42(1)	C(5)–C(6)–C(7)	108.8(8)
C(9)–C(8)	3.37(1)	C(2)–C(7)–C(6)	108.4(7)
C(9)–C(10)	3.38(1)	C(4)–C(7)–C(6)	109.5(8)
N–C(7)	2.60(1)		
N–C(2)	2.51(1)		
N–C(6)	2.52(1)		
C(10)–C(5)	3.54(1)		
C(8)–C(1)	3.54(1)		
C(8)–C(5)	3.57(1)		

TABLE 4

ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) FOR TRIMETHYL(QUINUCLIDINE)ALUMINUM

Anisotropic temperature factors are of the form:
$\exp[-(\beta_{11}\cdot h^2 + \beta_{22}\cdot k^2 + \beta_{33}\cdot l^2 + \beta_{12}\cdot h\cdot k + \beta_{13}\cdot h\cdot l + \beta_{23}\cdot k\cdot l)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	156(4)	71(3)	310(8)		38(4)	
N	169(13)	85(10)	282(21)		35(13)	
C(1)	263(22)	175(19)	246(29)		31(20)	
C(2)	197(20)	198(22)	449(42)		59(23)	
C(5)	200(13)	151(13)	619(34)	−22(10)	62(17)	146(17)
C(6)	185(13)	202(16)	726(39)	−48(12)	18(18)	135(21)
C(7)	161(18)	218(23)	575(53)		− 3(25)	
C(8)	240(14)	95(10)	477(28)	37(9)	82(16)	− 6(13)
C(10)	263(22)	161(18)	268(30)		−32(21)	

thermal parameters for the hydrogen atoms were set at 4.6 (the value indicated as the overall thermal parameter by a standard Wilson plot). Hydrogen atoms on the methyl groups were not located. A final difference Fourier showed no peaks larger than 0.7 e/Å^3. The final value for the standard deviation of an observation of unit weight was 0.94. The final observed and calculated structure factor amplitudes are listed in Table 1. Final atomic parameters and standard deviations are tabulated in Table 2. Interatomic distances, angles, and errors are given in Table 3. Anisotropic thermal parameters are shown in Table 4.

DISCUSSION

Trimethyl(quinuclidine)aluminum, shown in Fig. 1, contains a crystallographic mirror plane. The methyl groups and quinuclidine methylene groups viewed down the aluminum–nitrogen bond appear in a staggered configuration. The same orientation has been observed for the related compound trichloro(trimethylamine)aluminum[9]. There are in fact other similarities between $(CH_3)_3Al\cdot NC_7H_{13}$ and $Cl_3Al\cdot N(CH_3)_3$. Both belong to the monoclinic crystal system, crystallize in either $P2_1$ or $P2_1/m$, and exhibit b and c lattice parameters which are the same to within the reported standard deviations. However, Grant *et al.*[9] chose space group $P2_1$ on the basis of a more acceptable least-squares refinement for their structure.

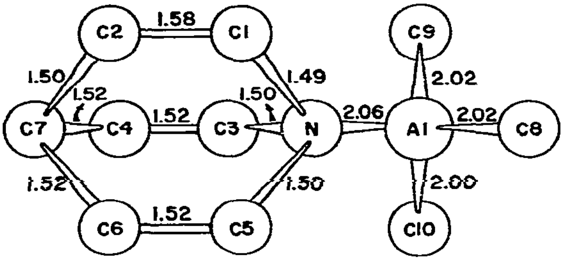

Fig. 1. The molecular structure of trimethyl(quinuclidine)aluminum.

In the present study, the aluminum–nitrogen bond distance of 2.06 Å is significantly longer than the value reported for $Cl_3Al\cdot N(CH_3)_3$ (1.96 Å). The difference may be due in part to the presence of a small frontal steric interaction in $(CH_3)_3Al\cdot NC_7H_{13}$, and in part to the larger positive charge on the aluminum atom in $Cl_3Al\cdot N(CH_3)_3$. The closest methyl–methylene approach in $(CH_3)_3Al\cdot NC_7H_{13}$ of 3.54 Å may be compared to methyl–methylene distances of 3.27 Å in $(CH_3)_2Be\cdot 2NC_7H_{13}$ and 3.58 Å in $(CH_3)_2Mg\cdot 2NC_7H_{13}$. The shortest intermolecular distance is 3.95 Å between methyl and methylene groups.

Eyman *et al.*[2] in calorimetric studies of a number of trimethylaluminum adducts with nitrogen donors found the total solution enthalpy sequence to be $(CH_3)_2NH > CH_3NH_2 \sim (CH_3)_3N > NH_3$. The position of trimethylamine was attributed to frontal strain. They further predicted that the N–Al–C angle would be less than the tetrahedral value on the basis of electron repulsion arguments put forward with the structure of the bis(trimethylaluminum)dioxane adduct[10]. Verification for the idea is seen in the N–Al–C angle of 104.5° in $(CH_3)_3Al\cdot NC_7H_{13}$.

An alternative explanation for the observed bond angles in trimethyl(quinuclidine)aluminum is found in the concept of second-order rehybridization[11]. The hybrid orbitals employed by aluminum to bond the carbon atoms contain more s character than the orbital used to bond the more electronegative nitrogen atom. Thus, the carbon–aluminum–carbon bond angles (113–114°) are larger than the tetrahedral value. The same argument may be applied to dimethylbis(quinuclidine)-magnesium, but a 20° deviation from tetrahedral geometry is observed in the carbon–magnesium–carbon angle. It seems unlikely that the difference in electronegativity between carbon and nitrogen is the sole driving force for a distortion of this magnitude.

The aluminum–carbon bond lengths of 2.00 Å and 2.02 Å agree well with values reported in other organoaluminum compounds[10,12]. The bond distances and angles in the quinuclidine molecule are normal[5,6].

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