

THE CRYSTAL STRUCTURE OF DIMERIC METHYL-1-PROPYNYL-BERYLLIUM-TRIMETHYLAMINE*

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SUMMARY

The crystal and molecular structure of the dimer of methyl-1-propynyl-beryllium-trimethylamine, $[\text{CH}_3\text{BeC}\equiv\text{CCH}_3\cdot\text{N}(\text{CH}_3)_3]_2$, has been determined by least-square refinement ($R=0.049$) of 1156 counter measured X-ray intensities. This compound crystallizes in space group $P2_1/n$ in a cell of dimensions $a_0=13.371$, $b_0=9.290$, $c_0=7.249$ Å and $\beta=101.485^\circ$; with two discrete, dimeric molecules per cell, the calculated density is $0.92\text{ g}\cdot\text{cm}^{-3}$.

In the molecule, two beryllium atoms are joined by two propynyl groups to form a planar four-membered ring with the terminal triple-bonded carbon atoms of the propynyl groups acting as the bridging atoms. The beryllium-carbon distances in the ring are 1.85 Å and 1.89 Å. Additionally a methyl group and a trimethyl amine group are bonded to each beryllium atom. The propynyl groups are almost in a plane defined by the beryllium and bridging carbon atoms with the amine and methyl groups disposed in another plane perpendicular to the first. This is the first published structure study on a compound containing an electron-deficient bridge between light metal atoms formed by *sp* hybridized carbon.

INTRODUCTION

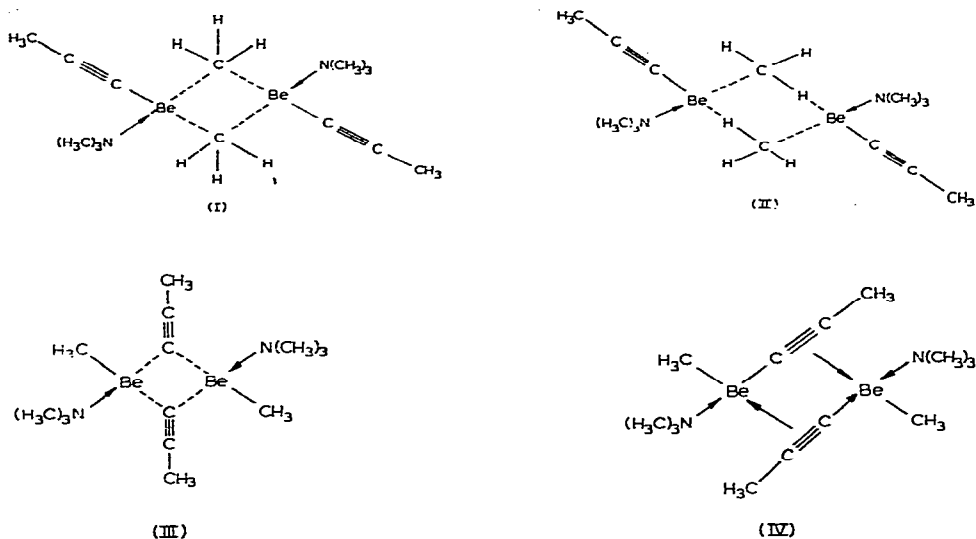
Several organometallic compounds containing acetylenic groups bound to metal atoms are believed to be associated by means of electron-deficient acetylenic bridges. The dimeric aluminum compound, $(\text{Me}_2\text{AlC}\equiv\text{CPh})_2$, is one example¹ and evidence has been obtained from the temperature dependence of the NMR spectrum in favor of the association being due to bridging acetylenic rather than to bridging methyl groups². Similarly, the phenyl groups in $(\text{Me}_2\text{AlPh})_2$ were shown to form the bridges between the aluminum atoms and the presence of bridging phenyl groups was subsequently confirmed by a crystal structure analysis³. There has, however, been no crystallographic confirmation of the presence of acetylenic bridges in $(\text{Me}_2\text{AlC}\equiv\text{CPh})_2$ or its gallium or indium analogues.

This paper describes the crystal structure of dimeric methyl-1-propynyl-beryllium-trimethylamine, $[\text{CH}_3\text{BeC}\equiv\text{CCH}_3\cdot\text{N}(\text{CH}_3)_3]_2$. The structure determina-

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tion of this complex was of interest not only because this is the first compound to be prepared containing two different organic groups bound to beryllium⁴, but also because it would reveal the nature of its association. Thus it could possibly associate by methyl bridges of the commonly postulated type, as in (I) or of the type involving bridging hydrogens, as in (II) as reported for the dimer of trimethylaluminum⁵. It should be noted, however, that a more recent nuclear quadrupole resonance study⁶ has cast doubt on the presence of the hydrogen bond linkage in the trimethylaluminum dimer.



Since the NMR studies on dimethyl(phenylethynyl)aluminum indicated that acetylenic groups form stronger bridges than methyl groups, structures involving bridging acetylenic groups between beryllium atoms also are to be expected. These, however, could be of two types as in (III) and (IV).

EXPERIMENTAL

The complex $[\text{CH}_3\text{BeC}\equiv\text{CCH}_3 \cdot \text{N}(\text{CH}_3)_3]_2$ has a formula weight of 244.4 and crystallizes as colorless prisms. Since the complex reacts readily with air the data crystal was sealed in a Lindeman glass capillary. Precession photographs indicated monoclinic symmetry. The systematic absences of $h + l$ odd for $h0l$ and k odd for $0k0$ were consistent with the space group $P2_1/n$. The unit cell parameters, determined on a Picker diffractometer fitted with an Electronics and Alloys full-circle, have the following values at 20° : $a = 13.371(8) \text{ \AA}$, $b = 9.290(4) \text{ \AA}$, $c = 7.249(8) \text{ \AA}$, $\beta = 101.485(9)^\circ$, $V = 882.42 \text{ \AA}^3$. In these measurements the wave-length of $\text{Mo } K\alpha_1$ radiation was taken as 0.70926 \AA . The crystal density computed for two dimeric units per cell is $0.9201 \text{ g} \cdot \text{cm}^{-3}$; an experimental density was not obtained because of the reactivity of the compound.

The 1156 three-dimensional $\text{Mo } K\alpha$ intensity data were measured with a scintillation counter employing pulse-height discrimination using the θ - 2θ scan technique (scan speed $\frac{1}{2}$ deg/min; width from $2\theta \cdot \lambda_1 - 1.25^\circ$ to $2\theta \cdot \lambda_2 + 1.25^\circ$; back-

ground 20 s count each at beginning and end of scan). Of these data, 430 were measured to be less than 3σ ($\sigma = \sqrt{(N_{SC} + K \cdot N_B)}$, where N_{SC} , N_B , and K are the total scan count, background counts, and ratio of the scan to background time, respectively); and, hence, assigned a value equal to 3σ , and considered to be unobserved in subsequent calculations.

The structure was solved by direct methods, using the symbolic addition procedure of Karle and Karle⁷ as programmed by R. V. Chartain, E. G. Boonstran, and J. M. Stewart in X-RAY 71⁸. A set of 196 normalized structure factors yielded an E map which clearly showed all the positions of the nonhydrogen atoms. A subsequent Fourier map during refinement located the hydrogen positions. Positional and thermal parameters were refined by full-matrix least-squares refinement, with the function $\Sigma \cdot \omega \cdot (F_o - F_c)^2$ minimized, in which weights were assigned from counting statistics or, for unobserved reflections with $|F_o| > |F_c|$, set equal to zero. Isotropic thermal parameters were refined for the hydrogen atoms. Scattering factors from Table 3.3.1A (p. 202) of Vol. 3 of the *International Tables for X-Ray Crystallography* (1962) were used to calculate structure factors. A final reliability index, $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$, is 0.049; the final atomic positional and thermal parameters are given in Table 1. The thermal parameters are of the form $\exp(-2\pi^2 \Sigma \Sigma U_{ij} \cdot h_i \cdot h_j \cdot a_i^* \cdot a_j^*)$. Lists of observed and calculated structure factors may be obtained from the authors or NAPS*. Notation used is shown in Figure 1; hydrogen atoms are labeled H(Xi), where X is the carbon atom to which the hydrogen is attached and i is an index.

DESCRIPTION OF THE STRUCTURE

As shown in Fig. 1 the structure of the methyl-1-propynylberyllium-trimethylamine dimer corresponds to possibility (III) of the Introduction with the terminal triple-bonded carbons of the two propynyl groups serving as a bridging atom between two beryllium atoms. The dimer is centrosymmetric and situated at an inversion center in the space group $P2_1/n$ and, consequently, the four-membered ring formed by the two beryllium atoms and the two bridging carbon atoms is planar. In this four-membered ring, the average value for the electron deficient Be-C bonds is 1.87 Å (Table 2) while the value for the Be-C-Be bond angle is 77°. The only other published structure with electron deficient Be-C-Be bonds is that for polymeric dimethylberyllium⁹; however, that structure determination was based on two dimensional data with standard deviations sufficiently large to negate any conclusions based on a comparison of those bond distances (Be-C of 1.93 Å; C-C contact separations of 3.06, 3.11, and 3.20 Å) and angles (Be-C-Be of 66°; C-Be-C of 114°) with the present values. However, as expected, the distances in this determination for the electron deficient Be-C(5) and Be-C(5') bonds are longer than the bond distance involving beryllium and the carbon in the terminal methyl group [Be-C(4)] which has a value of 1.75 Å. Mootz *et al.*¹⁰ have reported a value of 1.71 Å for the beryllium-carbon bond involving the terminal methyl group of the methyl(trimethylsilanolato)beryllium tetramer and Almenningen *et al.*¹¹ have published a value of 1.698 Å from electron

* The Table of structure factors has been deposited as NAPS Document No. 01312, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting \$2.00 for a microfiche or \$ 5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(continued on p. 12)

TABLE 1

ATOMIC POSITIONS AND THERMAL PARAMETERS FOR $[\text{CH}_3\text{BeC}\equiv\text{CCH}_3\text{-N}(\text{CH}_3)_3]_2$

Atom	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Be	0.4981(3)	0.3750(5)	0.5148(6)	0.054(2)	0.057(2)	0.067(3)	0.000(2)	0.015(2)	0.005(2)
N	0.4318(2)	0.2786(3)	0.3095(4)	0.068(2)	0.062(2)	0.068(2)	-0.001(1)	0.013(1)	-0.003(1)
C(1)	0.5049(4)	0.1787(5)	0.2464(8)	0.099(3)	0.074(3)	0.103(3)	0.004(3)	0.028(3)	-0.018(3)
C(2)	0.3498(4)	0.1894(6)	0.3607(9)	0.090(3)	0.098(4)	0.117(4)	-0.032(3)	0.022(3)	-0.018(3)
C(3)	0.3868(5)	0.3723(6)	0.1505(7)	0.119(4)	0.084(3)	0.071(3)	0.008(3)	-0.010(3)	-0.005(3)
C(4)	0.5459(4)	0.2620(6)	0.7047(7)	0.087(3)	0.076(3)	0.083(3)	0.007(3)	0.018(3)	0.015(2)
C(5)	0.4041(2)	0.5139(4)	0.5663(5)	0.054(2)	0.071(2)	0.063(2)	0.001(2)	0.020(2)	0.002(2)
C(6)	0.3277(3)	0.5120(4)	0.6230(5)	0.067(2)	0.082(3)	0.077(2)	0.017(2)	0.024(2)	0.025(2)
C(7)	0.2304(5)	0.5057(13)	0.6889(13)	0.075(3)	0.242(10)	0.149(6)	0.046(5)	0.063(4)	0.098(7)
H(11)	0.547(3)	0.120(5)	0.360(6)	0.075(14)					
H(12)	0.472(3)	0.117(5)	0.131(6)	0.081(15)					
H(13)	0.560(3)	0.234(5)	0.219(6)	0.067(14)					
H(21)	0.382(4)	0.131(6)	0.483(8)	0.118(22)					
H(22)	0.305(4)	0.145(6)	0.253(7)	0.093(17)					
H(23)	0.301(3)	0.255(5)	0.405(6)	0.084(17)					
H(31)	0.437(3)	0.436(5)	0.128(6)	0.071(15)					
H(32)	0.347(3)	0.316(4)	0.050(4)	0.064(13)					
H(33)	0.337(3)	0.440(5)	0.198(6)	0.082(15)					
H(41)	0.588(4)	0.306(5)	0.813(7)	0.097(19)					
H(42)	0.493(4)	0.212(6)	0.748(7)	0.117(22)					
H(43)	0.582(4)	0.199(5)	0.679(7)	0.096(23)					
H(71)	0.170(6)	0.513(8)	0.618(10)	0.183(36)					
H(72)	0.243(7)	0.600(11)	0.778(13)	0.195(61)					
H(73)	0.234(4)	0.442(6)	0.798(8)	0.116(21)					

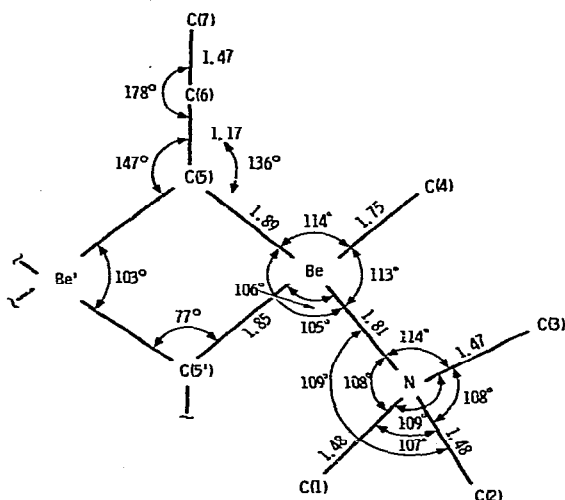


Fig. 1. Labels of atoms used in methyl-1-propynylberyllium-trimethylamine dimer. Only one half of the centrosymmetric molecule is shown.

TABLE 2

INTERATOMIC SEPARATIONS AND ANGLES

A. Intramolecular

Bond distances (Å)

Be-N	1.811(5)	C(2)-H(23)	1.00(5)
Be-C(4)	1.748(7)	C(3)-H(31)	0.94(4)
Be-C(5)	1.890(6)	C(3)-H(32)	0.97(4)
Be-C(5')	1.852(6)	C(3)-H(33)	1.02(5)
N-C(1)	1.484(6)	C(4)-H(41)	0.96(5)
N-C(2)	1.479(7)	C(4)-H(42)	0.95(6)
N-C(3)	1.474(6)	C(4)-H(43)	0.80(5)
C(1)-H(11)	1.05(4)	C(5)-C(6)	1.174(5)
C(1)-H(12)	1.03(4)	C(6)-C(7)	1.473(9)
C(1)-H(13)	0.96(5)	C(7)-H(71)	0.87(7)
C(2)-H(21)	1.05(5)	C(7)-H(72)	1.08(10)
C(2)-H(22)	0.98(5)	C(7)-H(73)	0.98(6)

Bond angles (°)

Be-N-C(3)	114.1(3)	N-Be-C(4)	113.1(3)
C(1)-N-C(2)	107.1(4)	N-Be-C(5)	105.3(2)
C(1)-N-C(3)	108.6(4)	N-Be-C(5')	106.0(3)
C(2)-N-C(3)	108.6(4)	C(4)-Be-C(5)	114.0(3)
Be-C(5)-C(6)	135.9(3)	C(4)-Be-C(5')	114.5(3)
Be-C(5)-Be'	77.2(2)	C(5)-Be-C(5')	102.8(3)
Be'-C(5)-C(6)	146.9(3)	Be-N-C(1)	108.5(3)
C(5)-C(6)-C(7)	178.0(5)	Be-N-C(2)	109.7(3)

Contact interactions (Å)

C(1)-C(4)	3.348(8)	C(2)-C(3)	2.398(9)
C(2)-C(4)	3.308(8)	C(4)-C(3')	3.617(8)
C(2)-C(5)	3.377(6)	C(3)-C(5')	3.297(6)
C(3)-C(5)	3.255(6)	C(3)-C(6')	3.992(6)
C(3)-C(6)	3.888(6)	C(1)-C(5')	3.290(9)
C(4)-C(5)	3.053(7)	C(1)-C(6')	3.650(8)
C(4)-C(6)	3.683(7)	C(4)-C(5')	3.028(7)
C(1)-C(2)	2.383(9)	C(4)-C(6')	3.809(7)
C(1)-C(3)	2.402(9)		
H(11)-H(43)	2.39	H(13)-H(31)	2.50
H(21)-H(42)	2.31	H(22)-H(32)	2.31
H(12)-H(22)	2.57	H(23)-H(33)	2.39
H(11)-H(21)	2.55	H(31)-H(41')	2.47
H(12)-H(32)	2.48	H(33)-H(41')	2.58

 B. Intermolecular^a (Å)

C(4)-C(3) ⁱ	4.330(8)	C(1)-C(7) ^{iv}	3.564(10)
C(7)-C(3) ⁱ	3.784(10)	C(7)-C(2) ^v	4.015(12)
C(5)-C(3) ⁱ	4.484(6)	C(3)-C(2) ^{vi}	4.312(8)
C(4)-C(1) ⁱ	4.144(8)	C(7)-C(2) ^{vi}	4.270(11)
C(6)-C(3) ⁱ	3.966(6)	C(7)-C(1) ^{vi}	4.300(9)
C(2)-C(4) ⁱⁱ	4.474(8)	C(5)-C(2) ^{vi}	4.425(6)
C(4)-C(1) ⁱⁱ	4.176(7)	C(7)-C(3) ^{vi}	4.310(12)
C(4)-C(2) ⁱⁱⁱ	4.021(8)	C(6)-C(2) ^{vi}	4.162(7)

^a ⁱ $x, y, 1+z$
^{iv} $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
ⁱⁱ $1-x, -y, 1-z$
^v $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$
ⁱⁱⁱ $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
^{vi} $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

diffraction measurements on monomeric dimethylberyllium in the vapor state. The Be-N bond distance of 1.81 Å is near that of 1.78 Å reported by Atwood and Stucky¹² for four-coordinate bridging nitrogen in bis(dimethylamino)beryllium.

The carbon-carbon triple bond distance C(5)-C(6) of 1.17 Å is somewhat less than the accepted average value of 1.205 Å, but the single bond carbon-carbon distance C(6)-C(7) of 1.47 Å compares very closely to the accepted average $sp-sp^3$ distance of 1.46 Å. The carbon-nitrogen distances, N-C(1) etc., are also very close to the accepted average value of 1.47 for sp^3 carbon-nitrogen. The value for the C(5)-C(6) bond distance does not significantly lengthen if it is calculated with the assumption of in-phase motion¹³; however, the value for C(6)-C(7) increases to 1.50 Å while those for N-C increase to 1.49 Å.

It is noteworthy that the propynyl group is tilted toward one of the beryllium atoms of the ring, the Be-C(5)-C(6) angle being 136° as compared to 147° for the Be'-C(5)-C(6) angle. It has been suggested¹² that this tilt may result from a bonding interaction between the π bonding electrons of the carbon-carbon triple bond and the beryllium atom (Be) as illustrated in possibility (IV) of the Introduction. This interpretation appears to be reinforced by the fact that the length of the beryllium-carbon bond nearest the carbon-carbon triple bond, Be-C(5) exceeds that of the farther beryllium-carbon bond, Be'-C(5), by 0.038 Å. Intramolecular contact interactions (Table 2A; the prime indicate atoms related to those labeled by the inversion center of the molecule, see Fig. 2; all H-H separations less than 2.8 Å are listed) do not appear to be responsible for the tilt; the shorter C(4)-C(6) distance (3.68 Å) occurs in a direction which would tend to decrease the tilt. However, since an alternate explanation (given below) resulting from packing of the molecules in the crystal structure of the solid can be made, either an electron diffraction study of the vapor phase or other structure studies on beryllium compounds containing an acetylenic group would be necessary to verify this contention.

Fig. 2 illustrates the packing of the molecules in the structure. The contact between molecules involves only weak van der Waals forces; although two carbon-carbon separations are less than 4.0 Å (Table 2B) considered to be the contact distance between methyl groups, the hydrogen atoms associated with these methyl groups are positioned to yield acceptable interhydrogen contact values. A reasonable radius for hydrogen is ~ 1.2 Å; the closest two hydrogen-hydrogen separations involving C(3) and C(7)^I are: (a) H(32)-H(73)^I at 2.43 Å and (b) H(33)-H(73)^I at 2.95 Å and involving C(1) and C(7)^{IV} are (c) H(11)-H(73)^{IV} at 2.69 Å and (d) H(13)-H(73)^{IV} at 2.80 Å. Two other short, intermolecular hydrogen-hydrogen contact separations involve C(7)-C(1)^{VI} with (e) H(71)-H(12)^{VI} at 2.54 Å and C(7)-C(2)^V with (f) H(72)-H(21)^V at 2.65 Å. Separation (a) and (b) as well as the separation C(6)-C(3)^I, which is a reasonable separation for an acetylenic π cloud interacting with a methyl group, result from molecules stacked along *c* (for example, using the center molecule in Fig. 2a and considering the molecules which superimpose on this molecule along the *c* direction) and, hence, are in directions with components which counter or prevent the tilt from being larger; separations (c) and (d) act in a similar manner (interaction with the upper right molecule in Fig. 2a as well as other symmetry related interactions with the remaining molecules at the three corners tend to "push" in a counterclockwise direction). Interactions (e) and (f) as well as the slightly longer contacts between C(7)-C(2)^{VI} and C(7)-C(3)^{VI} are along directions which tend to produce the tilt. Should be angle of tilt

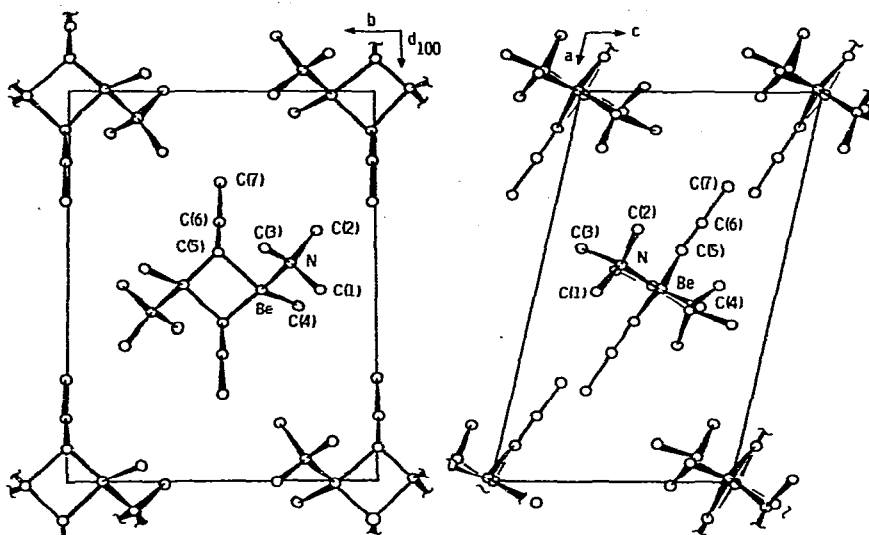


Fig. 2. (a) Projection along the c axis. Note the alignment of the major portion of the molecule is such as to introduce additional pseudosymmetry for this projection. (b) Projection along the two-fold axis.

decrease from the observed 5.5° by about 1° , the shortest of the above mentioned separations, (a), would increase and become equal to that for (e); any larger decrease would result in exceptionally short, probably impossible hydrogen-hydrogen interactions. The latter argument assumes there would be no reorientation of the methyl groups.

Nevertheless, these contact separations are sufficiently large to permit relatively large thermal motion. In particular the propynyl groups undergo large vibrations along the b axis in the plane described by the cyclic carbons and the beryllium atoms.

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