

## Bonding in Electron-deficient and Electron-precise $\text{Be}_2\text{C}_2$ Ring Systems: X-Ray Crystal Structure of the Dimeric Dipropynylberyllium-trimethylamine

Norman A. Bell,<sup>\*a</sup> Ian W. Nowell,<sup>a</sup> and (the late) Harrison M. M. Shearer<sup>b</sup>

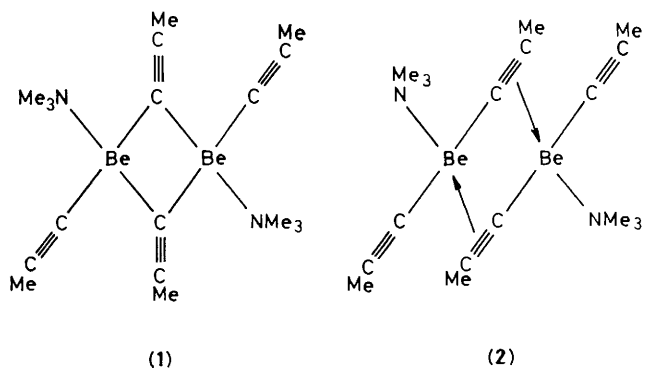
<sup>a</sup> Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, U.K.

<sup>b</sup> Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, U.K.

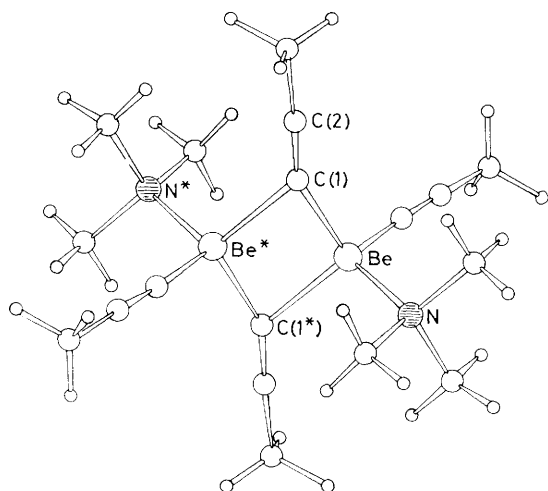
An X-ray crystal structure determination shows that  $[(\text{MeC}\equiv\text{C})_2\text{BeNMe}_3]_2$  contains two independent centrosymmetric dimers in which the  $\mu$ -alkynyl groups exhibit quite different types of interactions with the beryllium atoms.

Reaction of dipropynylberyllium with trimethylamine gives rise to the complex  $(\text{MeC}\equiv\text{C})_2\text{BeNMe}_3$  which has been shown by cryoscopic and i.r. measurements to be dimeric and to contain a  $\text{Be}_2\text{C}_2$  ring system.<sup>1</sup> Two likely structures (1) and (2) may be postulated for the complex.

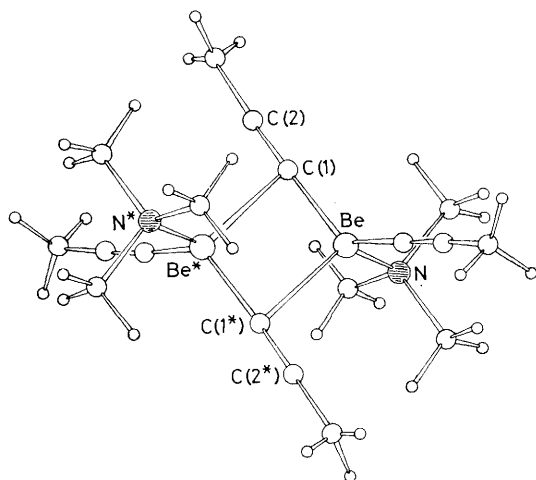
In  $[(\text{MeC}\equiv\text{C})\text{MeBeNMe}_3]_2$  the bridging propynyl group effectively functions as a 2-electron donor [type (1)], although asymmetry of the  $\text{Be}-\text{C}\equiv\text{C}$  angles [135.9(3) and 146.9(3)°] indicates a weak  $\pi$ -interaction between the alkynyl group and beryllium.<sup>2</sup> We now report the crystal structure of  $[(\text{MeC}\equiv\text{C})_2\text{BeNMe}_3]_2$ , one of a limited number of structural studies of organoberyllium compounds containing  $(\text{Be}_2\text{C}_2)_n$  ring systems,<sup>2,3</sup> and the first example of a dialkynyl-beryllium complex. The unit cell is found to contain two independent



dimers which afford an ideal opportunity for comparison of the structural types (1) and (2).



**Figure 1.**  $[(\text{MeC}\equiv\text{C})_2\text{BeNMe}_3]_2$ ; molecule 1. Selected bond distances (Å) and angles ( $^\circ$ ): Be–C(1\*), 1.904; Be–C<sub>2</sub>Me, 1.719; Be–C(1), 1.836; Be–C(1)–C(2), 154.9; Be–C(1)–Be\*, 76.6; Be\*–C(1)–C(2), 128.5; C(1)–Be–C(1)\*, 103.4; e.s.d.s ca. 0.006 Å and 0.4 $^\circ$ .



**Figure 2.**  $[(\text{MeC}\equiv\text{C})_2\text{BeNMe}_3]_2$ ; molecule 2. Selected bond distances and angles: Be–C(1), 1.763; Be–C<sub>2</sub>Me, 1.735; Be–C(1\*), 2.042; Be–C(2\*), 2.538; Be–C(1)–C(2), 168.6; Be–C(1)–Be\*, 83.8; Be\*–C(1)–C(2), 100.2; C(1)–Be–C(1\*), 96.2; C(1)–C(2)–Be\*, 52.4; e.s.d.s ca. 0.006 Å and 0.4 $^\circ$ .

*Crystal data:* Crystals of  $(\text{MeC}\equiv\text{C})_2\text{BeNMe}_3$  are triclinic, with  $a = 9.115(1)$ ,  $b = 13.519(1)$ ,  $c = 8.384(1)$  Å,  $\alpha = 102.8(1)$ ,  $\beta = 99.0(1)$ ,  $\gamma = 94.8(1)^\circ$ , space group  $P\bar{1}$ ,  $Z = 4$  (two independent dimers),  $R = 0.076$  for 1493 independent reflections having  $I/\sigma(I) > 3.0$ .†

The beryllium atoms are in approximately tetrahedral environments in the two independent centrosymmetric dimers (Figures 1 and 2) and, while both  $\text{Be}_2\text{C}_2$  rings are crystallographically required to be planar, the four-membered rings have quite different geometries. Molecule 1 (Figure 1) is tending towards structural type (1), with the  $\mu$ -propynyl groups functioning as 2e donors. There is, however, some asymmetry in the Be–C(1)–C(2) angles [154.9(4) and 128.5(4) $^\circ$ ] which indicates limited  $\pi$ -interaction between the C(1)≡C(2) bond and Be\*. In contrast, the  $\mu$ -propynyl groups in molecule 2 (Figure 2), which tends towards type (2), function as 3e donors, being involved in  $\sigma$ - and  $\pi$ -type interactions to the two beryllium atoms. The differing bonding of the  $\mu$ -propynyl groups in the two molecules results in one  $\text{Be}_2\text{C}_2$  ring being predominantly electron-deficient (molecule 1) while the other ring is effectively electron-precise (molecule 2). In support of this we find the Be–Be\* distance in molecule 1 to be considerably smaller than in molecule 2 [2.319(6) and 2.549(6) Å], indicating cross-ring metal–metal bonding to be more important in molecule 1. Additionally the Be–C(1) distance in molecule 2 is similar to the Be–C (terminal) distance whereas the Be\*–C(1) distance is much longer and also the beryllium-alkynyl carbon atoms approach colinearity. The presence of greater Be $\cdots$ Be interaction in molecule 1 is accompanied by an opening of the C(1)–Be–C(1\*) angle from 96.2(4) to 103.4(4) $^\circ$ .

Differences in the geometry of the two  $\text{Be}_2\text{C}_2$  ring systems cannot be attributed to distortions arising from inter- or intra-molecular contacts; rather the co-existence of the different bonding modes in the two rings [ $\mu$ -propynyl(2e donor) + Be $\cdots$ Be interaction vs.  $\mu$ -propynyl(3e donor)] indicates the overall energies to be very similar.

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## References

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.