

Infrared Spectroscopic Evidence of Dative Beryllium–Nitrogen π -Bonding in Bis(ketimino)-derivatives of Beryllium

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THE tendency of the more electropositive first-row elements to form multiple bonds to nitrogen falls markedly in the sequence $C > B > Be$.¹ Whereas $C=N$ compounds seldom tend to associate to oligomers or polymers containing only C–N links, boron–nitrogen compounds $R_2N \rightleftharpoons BX_2$ or $RN \rightleftharpoons BX$ generally oligomerise (thereby exchanging a σ - and a π -bond for two σ -bonds),² and beryllium–nitrogen compounds R_2NBeX always oligomerise unless prevented by the bulk of R and X.³ That beryllium–nitrogen dative π -bonding can nevertheless be strong enough to influence the geometry of a molecule was suggested recently by

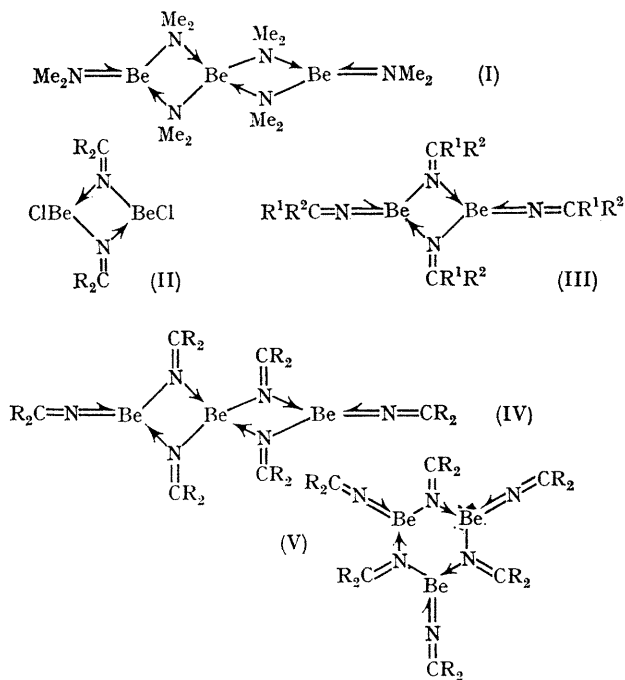
Atwood and Stucky,⁴ who found a trigonal planar coordination about the non-bridging nitrogen atoms of the trimer $[(Me_2N)_2Be]_3$ (I). This shape allows maximum overlap of the vacant beryllium and filled nitrogen $2p$ -orbitals considered to form the π -bonds. As similar $Be \rightleftharpoons N$ π -bonding in ketimino derivatives $(R_2C:N)_2Be$ would involve linear groups $C=N \rightleftharpoons Be$ with distinctive i.r. absorptions, which could moreover, be compared with related $C=N \rightleftharpoons B$ ⁵ and $C=N=C$ ⁶ systems, we prepared some ketiminoberyllium chlorides $(R^1R^2C:NBeCl)_2$, which contain only bridging ketimino-groups (II), and some

† The ¹H n.m.r. spectrum of $[(p\text{-tolyl}_2C:N)_2Be]_3$, in which the aromatic protons of the bridging and terminal ketimino-groups give rise to multiplets at τ 3.0 (intensity 2) and 2.1 (intensity 1), apparently respectively, rules out a six-membered-ring structure (V).

TABLE

Compound	m.p. (°C)	$\nu(\text{C}=\text{N})$ (bridging) (cm^{-1})	$\nu(\text{C}=\text{N}=\text{Be})$ (terminal) (cm^{-1})
$(\text{Ph}_2\text{C}:\text{NBeCl})_2$	120—121	1608	—
$(p\text{-tolyl}_2\text{C}:\text{NBeCl})_2$	268—270	1610	—
$(p\text{-tolylBu}^t\text{C}:\text{NBeCl})_2$	160—165 ^a	1614	—
$[(\text{Ph}_2\text{C}:\text{N})_2\text{Be}]_n^b$	>100	1627	1732
$[(p\text{-tolyl}_2\text{C}:\text{N})_2\text{Be}]_3$	349—351 ^a	1626	1731
$[(p\text{-tolylBu}^t\text{C}:\text{N})_2\text{Be}]_2$	73—75 ^c	1637	1739

^a Decomposes; ^b too low solubility in benzene for recrystallisation or for cryoscopic determination of M , the method used for all the other compounds; ^c softens without melting; decomposes at *ca.* 280°.



bisketimino-derivatives $[(\text{R}^1\text{R}^2\text{C}:\text{N})_2\text{Be}]_n$, which being oligomeric also contain terminal ketimino-groups attached to three-co-ordinate beryllium (III, IV), confirmed their identities by elemental analyses, and recorded their i.r. spectra as Nujol mulls.

The six new compounds listed in the Table were prepared from 1 or 2 $\text{R}^1\text{R}^2\text{C}:\text{NLi} + \text{BeCl}_2$ in ether, and recrystallised from benzene. Their $\text{C}=\text{N}$ stretching absorptions were strong readily identified bands whose frequencies are in the Table. Whereas the colourless dimeric iminoberyllium halides $(\text{R}^1\text{R}^2\text{C}:\text{NBeCl})_2$ have $\nu(\text{C}=\text{N})$ at *ca.* 1610 cm^{-1} , the yellow bisketimino-derivatives $[(\text{R}^1\text{R}^2\text{C}:\text{N})_2\text{Be}]_n$ absorb both near 1630 cm^{-1} [$\nu(\text{C}=\text{N})$ for bridging ketimino-groups] and near 1735 cm^{-1} . This last band is taken as evidence of a linear $\text{C}=\text{N}=\text{Be}$ skeleton for the terminal ketimino-groups in the dimer (III; $\text{R}^1 = p\text{-tolyl}$; $\text{R}^2 = \text{Bu}^t$) and trimer (IV; $\text{R} = p\text{-tolyl}$);[†] *cf.* $\nu(\text{C}=\text{N}=\text{B})$ at 1786 cm^{-1} for $\text{Ph}_2\text{C}=\text{N}=\text{BPh}_2$ ⁵ and $\nu(\text{C}=\text{N}=\text{C})$ at 1845 cm^{-1} for $\text{Ph}_2\text{C}=\text{N}=\text{CPh}_3$.⁶ The decreasing frequency of $\nu(\text{C}=\text{N}=\text{M})$ in the sequence $\text{M}=\text{C} > \text{B} > \text{Be}$ is believed to reflect the decreasing $\text{N}=\text{M}$ bond order in the same sequence.

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² See, *e.g.* K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds", Springer-Verlag, Berlin, 1965.

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⁴ J. L. Atwood and G. D. Stucky, *Chem. Comm.*, 1967, 1169.

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⁶ B. Samuel and K. Wade, *Chem. Comm.*, 1968, 1081.