Monomeric Diphenylketiminodiphenylborane, a Boron–Nitrogen Analogue of an Allene

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AN interesting feature of compounds containing nitrogen attached to three-co-ordinate boron is the extent of $B \mathrel{\overset{\leftharpoonup}{-}} N$ π-bonding in them. If the nitrogen is three-co-ordinate, a structural consequence of such π-bonding is a trigonal planar arrangement of atoms about nitrogen, as in borazines $(R^1BNR^2)_3$[1] or the triborylamine $(C_6H_4O_2B)_3N$.[2] If the nitrogen is two-co-ordinate, as in monomeric iminoboranes $R^1_2B \mathrel{\overset{\leftharpoonup}{-}} N{=}CR^2R^3$, a linear configuration (I) allows maximum π-bonding [*cf.* isoelectronic allenes $R^1_2C:C:CR^2R^3$ and the linear $B \mathrel{\overset{\leftharpoonup}{-}} N{=}C{=}S$ unit in $(Bu^tNBNCS)_4$[3]]. We here describe a compound $Ph_2BN:CPh_2$ which we believe is the first to have such a linear skeleton in gas, solution and crystal phases.

All previously reported imino-derivatives of boron $(R^1_2B{\cdot}N:CR^2R^3)_n$ (R^2 = alkyl or aryl; R^3 = H,[4,5] SR,[6] allyl,[7] or aryl[8]) whose states of association in solution were measured were dimeric ($n = 2$), with appropriate $\nu(C:N)$ at 1580—1680 cm.$^{-1}$ for both solutions and mulls. Their structures are typified by (II),[5] determined by *X*-ray crystallography.[9] However, i.r. absorptions at *ca.* 1820 cm.$^{-1}$ by hot chloroform solutions

TABLE

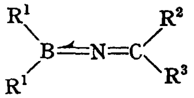
Skeletal stretching frequencies [$\nu(C{=}N)$ *or* $\nu(B\overset{\leftarrow}{=}N{=}C)$; *cm.*$^{-1}$] *of some diphenylketiminoboranes*

$(Br_2BN{:}CPh_2)_2$	1585	$Ph_2BN{:}CPh_2$	1786	$(Me_2BN{:}CPh_2)_2$	1662
$(Cl_2BN{:}CPh_2)_2$	1590	$PhB(N{:}CPh_2)_2$	1672	$^{b}(Et_2BN{:}CPh_2)_n$	1793
$^{a}(PhClBN{:}CPh_2)_n$	1612	$B(N{:}CPh_2)_3$	1650	$(Me_3C_6H_2)_2BN{:}CPh_2$	1792

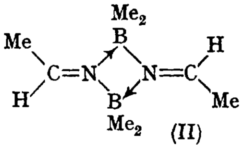
[a, b] *n* not measured; probably 2 and 1, respectively.

of derivatives $(R^1{}_2B{\cdot}N{:}CR^2{\cdot}SR^3)_2$[6] were taken to reflect their partial dissociation into monomers $R^1{}_2B\overset{\leftarrow}{=}N{=}CR^2{\cdot}SR^3$, with linear skeletons as in (I) rather than angular structures (III), and the mass spectrum of $(Me_2B{\cdot}N{:}CPh_2)_2$ had no fragments larger than monomers.[8] Dorokhov and Lappert[10] have now established that gaseous $Bu^n{}_2BN{:}CHBu^t$ is monomeric with a characteristic i.r. absorption $\nu(B\overset{\leftarrow}{=}N{=}C)$ at 1840—1850 cm.$^{-1}$.

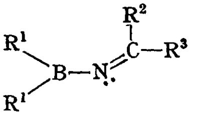
We have obtained diphenylketiminodiphenylborane $Ph_2BN{:}CPh_2$, m.p. 143—144° from Ph_2BCl and either $Ph_2C{:}NLi$ or $2Ph_2C{:}NH$ or[11] $Ph_2C{:}NSiMe_3$. It sublimes at 140°/10^{-3} mm., is monomeric in benzene (by cryoscopy) and in the gas phase (by mass spectroscopy). Its Nujol mull and toluene, tetrahydrofuran, or pyridine solutions absorb at 1785—1795 cm.$^{-1}$ [$\nu(B\overset{\leftarrow}{=}N{=}C)$; dimers like (II) or monomers (III) would have $\nu(C{=}N)$ near 1600 cm.$^{-1}$]. The ready hydrolysis of $Ph_2BN{:}CPh_2$ on exposure to air is consistent with a monomeric structure with three-co-ordinate boron.



(I)



(II)



(III)

Using variations on the preparative procedures already mentioned, we have prepared several other diphenylketiminoboranes. Significant spectroscopic and molecular-weight data are summarised in the Table.

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