

whereas both *N*-methyl-2-pyrrolidone molecules are significantly nonplanar. A projection of the structure along the *c* axis is given in Fig. 2. The molecules of adenine form, *via* H-bonds, (see Table 2) dimers related by a centre of symmetry (see Fig. 3). The perpendicular separation of planes formed by adenines in the dimer is 0.049 (4) Å and that of the other pair of adenines related by a centre of symmetry is 3.141 (4) Å. There is an overlap of adenine with *N*-methyl-2-pyrrolidone; distances of atoms of *N*-methyl-2-pyrrolidone from the adenine mean plane are in the range 3.281 (7) to 3.590 (6) Å. There is no overlap between adenine and *N*-methyl-2-pyrrolidone molecules themselves.

A comparison of the bond distances and angles for adenine with those in similar structures (Langer & Huml, 1978*a, b*; Langer, Huml & Lessinger, 1978; Langer, Huml & Zachová, 1979) shows significant differences in geometry, mainly in distances C(6)–N(1), N(1)–C(2), C(2)–N(3), N(3)–C(4), C(6)–N(6) and angles C(6)–N(1)–C(2), N(1)–C(2)–N(3) in the pyrimidine ring [mean weighted values for the above structures are 1.369 (4), 1.359 (3), 1.305 (4), 1.362 (2), 1.303 (2) Å and 123.6 (2), 125.7 (3)°]. These changes occur because in the present case the adenine molecule is neutral; this is supported by the mean values for the neutral molecule as given by Voet & Rich (1970), *i.e.* 1.35 (3), 1.33 (2), 1.315 (8), 1.35 (1), 1.34 (2) Å and 119 (1), 129 (2)°. The slight difference in the distance C(8)–N(9) is possibly due to

different crystal packing. The same explanation holds for a difference in bond lengths C(13)–C(14) and C(23)–C(24) for the two symmetrically independent molecules of *N*-methyl-2-pyrrolidone, although from a statistical point of view both molecules as a whole do not significantly differ.

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Structure of (Di-*tert*-butylmethyleneamino)diphenylborane, C₂₁H₂₈BN*

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Abstract. $M_r = 305.3$, orthorhombic, *Pbca*, $a = 11.534$ (1), $b = 14.875$ (1), $c = 22.909$ (3) Å, $V = 3930.5$ Å³, $Z = 8$, $D_x = 1.032$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.54$ cm⁻¹, $F(000) = 132$, $T = 291$ K, $R = 0.077$ for 1638 observed reflections. The allene-like molecule has a dihedral angle of 94.4° between the

C₂BN and NCC₂ planes. B–N and N–C bond lengths of 1.366 (6) and 1.244 (5) Å, together with a B–N–C angle of 178.2 (4)° indicate substantial π -contribution to both bonds.

Introduction. Compounds in which a methyleneamino (ketimino) group R₂C=N– is bonded to a metal or metalloid atom *M* are of interest because of the question of π -bonding between the N and *M* atoms. Such

* Azomethine derivatives. 21. Part 20: Clegg, Snaith, Shearer, Wade & Whitehead (1983).

π -bonding, evidenced by high ($>1700\text{ cm}^{-1}$) C=N vibrational frequencies, has been conclusively demonstrated by crystal-structure determination for compounds with $M = \text{B}$ (Bullen & Wade, 1971; Bullen, 1973), Al (Shearer, Snaith, Sowerby & Wade, 1971), and Be (Hall, Farmer, Shearer, Sowerby & Wade, 1979). In the series $M(\text{NCPH}_2)_4$ with $M = \text{Si}$, Ge, or Sn, the degree of π -bonding decreases from 'substantial' ($M = \text{Si}$) to 'absent or very slight' ($M = \text{Sn}$) (Alcock, Pierce-Butler, Willey & Wade, 1975). In the case of methylenaminoboranes, $(R_2\text{CNBR}'_2)_n$, associated species are generally found ($n = 2$ or possibly more), unless the substituents R and R' are sufficiently bulky (Collier, Lappert, Snaith & Wade, 1972). For monomeric species, significant B-N π -bonding should give an allene-like structure with linear $\text{B}=\text{N}=\text{C}$, as has been observed for $(\text{mesityl})_2\text{BNCPh}_2$ (Bullen, 1973). We report here the structure of $\text{Ph}_2\text{BNCBu}_2$ (Bu = *tert*-butyl): Bu groups are particularly effective at preventing molecular association (Collier *et al.*, 1972). This compound has $\nu(\text{C}=\text{N})$ 1818 cm^{-1} (KBr disc), suggestive of a linear $\text{B}=\text{N}=\text{C}$ skeleton.

Experimental. Compound prepared from LiNCBu_2 and Ph_2BCl as reported previously (Collier *et al.*, 1972), crystals obtained from pentane by cooling to 238 K, sealed in capillaries, $0.46 \times 0.42 \times 0.18\text{ mm}$. Stoe-Siemens AED diffractometer. Cell parameters from 2θ values of 36 reflections centred at $\pm\omega$ ($20 < 2\theta < 25^\circ$). 4815 reflections with $2\theta < 50^\circ$, h 0–13, k 0–17, l –27–27. On-line profile analysis (Clegg, 1981). No significant intensity variation for three standard reflections. No absorption corrections. 2576 unique data ($R_{\text{int}} = 0.021$), 1638 with $F > 4\sigma(F)$. Multisolution direct methods. Blocked-cascade refinement on F . $w^{-1} = \sigma^2(F) + 0.00184F^2$. H atoms constrained to give C–H = 0.96 \AA , aromatic H on external bisectors of ring angles, methyl H–C–H = 109.5° , $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Anisotropic U_{ij} for non-H atoms. Extinction $x = 2.2(7) \times 10^{-6}$ [$F'_c = F_c/(1 + xF_c^2/\sin^2\theta)^{1/4}$]. Scattering factors from *International Tables for X-ray Crystallography* (1974). 209 parameters, $R = 0.077$, $wR = 0.100$, slope of normal probability plot 1.44. Max. $\Delta/\sigma = 0.016$, mean = 0.003 . Max. peak in final difference map 0.47 e \AA^{-3} , max. hole -0.24 e \AA^{-3} . Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.* Fig. 1 shows the molecular structure.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and the remaining bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39697 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure is similar to that of $(\text{mesityl})_2\text{BNCPh}_2$ (Bullen, 1973). In both structures, thermal motion is high for some of the substituent atoms, limiting the overall precision. The present structure is less severely affected, and is more precisely determined by the larger number of observed data. The Bu groups show large-amplitude torsional vibration about the bonds to C(1).

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
B	4383 (4)	2948 (3)	1476 (2)	53 (2)
N	3301 (3)	3096 (2)	1253 (2)	57 (1)
C(1)	2310 (4)	3205 (3)	1051 (2)	51 (1)
C(2)	1941 (4)	2618 (3)	535 (2)	67 (2)
C(3)	2806 (8)	1875 (6)	454 (4)	197 (5)
C(4)	807 (7)	2207 (7)	604 (4)	216 (5)
C(5)	2074 (9)	3097 (6)	–30 (2)	189 (5)
C(6)	1526 (3)	3912 (3)	1350 (2)	62 (2)
C(7)	2259 (5)	4533 (4)	1726 (3)	111 (2)
C(8)	650 (4)	3458 (4)	1750 (3)	95 (2)
C(9)	865 (5)	4507 (4)	922 (3)	118 (3)
C(11)	5412 (3)	3574 (3)	1266 (2)	51 (1)
C(12)	6487 (3)	3572 (3)	1535 (2)	63 (2)
C(13)	7359 (4)	4162 (3)	1376 (2)	78 (2)
C(14)	7180 (4)	4769 (4)	945 (2)	78 (2)
C(15)	6123 (4)	4800 (4)	671 (2)	80 (2)
C(16)	5252 (4)	4215 (3)	831 (2)	65 (2)
C(21)	4540 (3)	2188 (3)	1947 (2)	52 (1)
C(22)	5480 (4)	1595 (3)	1941 (2)	68 (2)
C(23)	5632 (5)	939 (3)	2355 (3)	81 (2)
C(24)	4836 (4)	857 (3)	2800 (3)	83 (2)
C(25)	3894 (4)	1418 (4)	2823 (2)	79 (2)
C(26)	3751 (3)	2069 (3)	2393 (2)	67 (2)

$$U_{\text{eq}} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

B–N	1.366 (6)	B–C(11)	1.583 (6)
B–C(21)	1.575 (6)	N–C(1)	1.244 (5)
C(1)–C(2)	1.530 (6)	C(1)–C(6)	1.546 (6)
N–B–C(11)	118.5 (4)	N–B–C(21)	118.5 (4)
C(11)–B–C(21)	123.0 (4)	B–N–C(1)	178.2 (4)
N–C(1)–C(2)	117.9 (4)	N–C(1)–C(6)	117.5 (4)
C(2)–C(1)–C(6)	124.6 (3)		

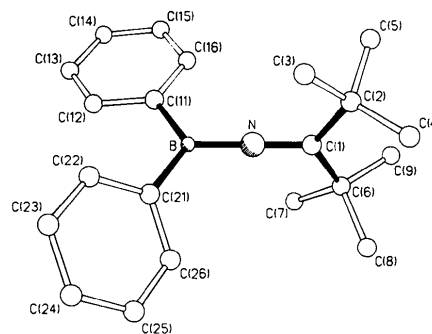


Fig. 1. The molecular structure, without H atoms, showing the atom-labelling scheme.

Coordination of B and of C(1) is essentially planar [r.m.s. $\Delta = 0.008$ (4) Å for C₂BN, 0.004 (4) Å for NCC₂]. These two planes are mutually approximately perpendicular [dihedral angle = 94.4 (4)°]. The molecule thus has an allene-like structure. The short B–N and N–C bonds and virtually linear B–N–C indicate considerable π -bonding in these two bonds, in accordance with this description. Large deviations from linearity for M–N–C linkages in methyleneaminometalloid compounds have been taken to indicate little or no π -bonding when M = Ge or Sn (Alcock *et al.*, 1975), but steric factors can produce deviations of up to 20° from linearity even when π -bonding is considered to be very substantial (Shearer *et al.*, 1971; Hall *et al.*, 1979). In Ph₂BNCBu₂ the deviation is negligible.

Steric effects prevent both Ph groups from being coplanar with the C₂BN unit. Angles subtended by the two rings with this unit are 8.0 (4)° [C(11)–C(16); r.m.s. $\Delta = 0.004$ (3) Å] and 43.6° [C(21)–C(26); r.m.s. $\Delta = 0.007$ (3) Å]. No shortening of the B–C(11) bond relative to B–C(21) as a result of conjugation is, however, observed. The opening up of the C(11)–B–C(21) and C(2)–C(1)–C(6) angles above 120° may also be ascribed to steric interaction of the two Ph and of the two Bu substituents.

The NCBu₂ ligand geometry in Ph₂BNCBu₂ is virtually identical to that reported (Jennings, Snaith, Mahmoud, Wallwork, Bryan, Halfpenny, Petch & Wade, 1983) for the tris(methyleneamino)borane B(NCBu₂)₃, which has a paddle-wheel-shaped struc-

ture, with three allene-like B=N=C units with B–N and N–C distances of 1.39 and 1.23 Å respectively, BNC angles of 166°, mutually perpendicular BN₃ and BNC₂ planes, and $\nu(\text{C}=\text{N})$ (KBr disc) 1735 cm⁻¹.

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4,4,8 α -Trimethyl-8 $\alpha\beta$ -methoxycarbonyl-4 $\alpha\beta$,5,8,8 α -tetrahydro-1(4H)-naphthalenone,* C₁₅H₂₀O₃

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Abstract. $M_r = 248.32$, triclinic, $P\bar{1}$, $a = 8.308$ (3), $b = 11.649$ (4), $c = 8.233$ (3) Å, $\alpha = 98.16$ (3), $\beta = 111.63$ (3), $\gamma = 106.14$ (3)°, $V = 684.4$ (5) Å³, $Z = 2$, $D_x = 1.205$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.77$ cm⁻¹, $F(000) = 268$, $T = 295$ K, final $R = 0.065$ for 1011 observed reflections. The half-chair cyclohexene ring is *cis*-fused to a half-chair cyclohexenone ring. Although the packing arrangement is ideally suited

for [2 + 2] photodimerization, the molecule is photochemically inert in the solid state due to steric compression between the potentially reacting molecules and their stationary lattice neighbours.

Introduction. Irradiation of (1) in solution yields the cage compound resulting from intramolecular [2 + 2] cycloaddition. However, compound (1) is photochemically inert when irradiated in the solid state (Ariel, Askari, Scheffer, Trotter & Walsh, 1984). The present crystallographic study was undertaken to

* IUPAC name: methyl 1,1,5 α -trimethyl-4-oxo-1,4,4a,5,8,8 $\alpha\beta$ -hexahydronaphthalene-4 $\alpha\beta$ -carboxylate.