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Di-*tert*-butyl ketone hydrazone and di-*tert*-butyl ketone triphenylphosphoranylidenehydrazone

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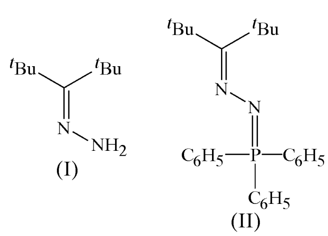
Reaction of di-*tert*-butyl ketone with hydrazine hydrate gives di-*tert*-butyl ketone hydrazone, $C_9H_{20}N_2$, which is dimerized by double hydrogen bonding in the solid state. Further reaction of this compound with dibromotriphenylphosphorane gives di-*tert*-butyl ketone triphenylphosphoranylidenehydrazone, $C_{27}H_{33}N_2P$, in the structure of which double chains parallel to the *c* axis are formed through weak C—H$\cdots\pi$ and π–π stacking interactions. The hydrazone group is nearly planar in both cases. In the second compound, one of the aromatic rings is nearly coplanar with the hydrazone moiety, indicating possible π-conjugation.

Comment

To date, the highly sterically crowded alkene tetra-*tert*-butylethylene has not been synthesized, in spite of many attempts using various methods, such as the McMurry coupling reaction (Ephritikhine & Villiers, 2004), Barton's extrusion process (Barton *et al.*, 1974) and reactions exploiting other possible pathways (Sulzbach *et al.*, 1996). During our investigations into the McMurry reaction, we have particularly studied the carbonyl coupling of benzophenone and di-*tert*-butyl ketone with the $MCl_4/M'(Hg)$ system (M/M' = U/Na, U/Li or Ti/Li) (Ephritikhine & Villiers, 2004). During this work, we have prepared di-*tert*-butyl ketone hydrazone, (I), and the new



compound di-*tert*-butyl ketone triphenylphosphoranylidene hydrazone, (II), by analogy with the synthesis reported for the two corresponding benzophenone derivatives (Barton *et al.*, 1974; Bestmann & Fritzsche, 1961). The crystal structure of benzophenone triphenylphosphoranylidenehydrazone, (III), has been reported previously (Bethell *et al.*, 1992). Compound (II) could not be transformed into tetra-*tert*-butylethylene.

The asymmetric unit in (I) contains one hydrazone molecule. The C1=N2 and N1—N2 bond lengths (Table 1) are in agreement with the mean values reported for similar hydrazones in the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002), which are 1.282 (11) and 1.38 (3) Å, respectively. The C1—C2 and C1—C6 bond lengths and the C2—C1—C6 angle are also in agreement with the mean values for similar di-*tert*-butyl-substituted sp^2-hybridized C atoms reported in the CSD, which are 1.56 (5) Å and 123 (3)°. The value of the N2—C1—C6 angle is lower by about 11° than those of the other two angles around C1, which is likely due to the minimal crowding in the corresponding sector, atom N1 being on the same side as C2. The five atoms N1, N2, C1, C2 and C6 define a plane with an r.m.s. deviation of 0.005 Å. Centrosymmetric dimers are formed through double hydrogen bonding between the N—NH_2 groups of two neighbouring molecules, with the formation of a six-membered ring (Fig. 1 and Table 2).

The asymmetric unit in (II) contains two independent but nearly identical molecules, denoted *A* and *B* (molecule *A* is represented in Fig. 2). These two molecules fit to one another with an overall r.m.s. deviation of 0.143 Å (the largest deviations, up to 0.29 Å, are those of atoms in the *tert*-butyl groups and aromatic rings) (OFIT in *SHELXTL*; Bruker, 1999). The C1=N2 bond lengths [Table 3; mean value 1.2905 (15) Å], as well as the angles around C1, match those in (I), but the N1—N2 distances [mean value 1.4205 (5) Å] are slightly larger than those in compounds (I) and (III) [1.388 (4) Å] and are also larger than the mean value for N—N bond lengths in triphenylphosphoranylidene hydrazone C=N—N=P-$(C_6H_5)_3$ groups reported in the CSD [1.384 (19) Å]. This may be due to the crowding induced by the simultaneous presence of *tert*-butyl groups and aromatic rings in (II). However, the mean P1=N1 bond length of 1.6017 (9) Å is slightly shorter than the mean value of 1.616 (13) Å from the CSD and the value of 1.606 (3) Å in (III). These bond lengths indicate the presence of double bonds between C1 and N2 and between P1 and N1. However, their slight deviation from the values tabulated for single and double bonds has been considered as

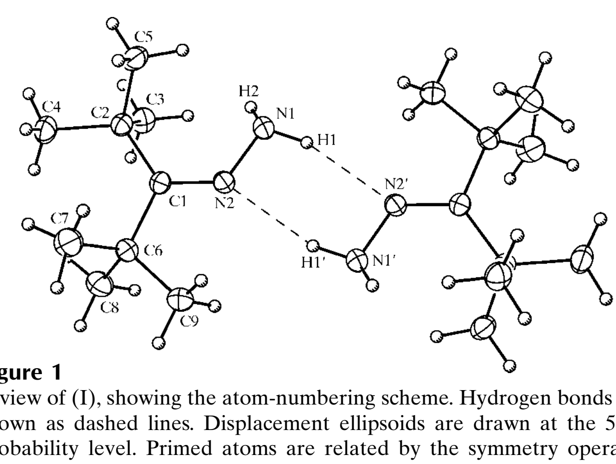


Figure 1
A view of (I), showing the atom-numbering scheme. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related by the symmetry operator ($-x$, $-y$, $-z$).

possible evidence of π-conjugation over the whole of the triphenylphosphoranylidene hydrazone moiety (Bethell *et al.*, 1992). This moiety adopts a *trans* geometry with respect to the central N1—N2 bond in (II), as is usual in such compounds (Bethell *et al.*, 1992; Minutolo *et al.*, 1999).

The group defined by atoms P1, N1, N2, C1, C2 and C6 is close to planarity in both molecules of (II), with r.m.s. deviations of 0.010 and 0.024 Å and P1—N1—N2—C1 torsion angles of 179.55 (14) and 175.93 (14)° in molecules *A* and *B*, respectively. One of the aromatic rings in both molecules (atoms C10–C15) is nearly coplanar with the triphenylphosphoranylidene hydrazone mean plane, with dihedral angles of 8.70 (12) and 2.78 (12)° in molecules *A* and *B*, respectively (but with, however, out-of-plane displacements as large as 0.4 Å). Such a geometry has previously been observed in a related triphenylphosphoranylidene hydrazone compound, (2,4-cyclopentadien-1-ylidenehydrazono)triphenylphosphorane, (IV), and considered as indicative of the possibility of π-conjugation between the two fragments, which was supported by the corresponding P—C bond length being slightly smaller than those of the other two, by about 0.011 Å (Minutolo *et al.*, 1999). The P1—C10 bonds in (II) are also slightly shorter than P1—C16 and P1—C22, by about 0.01–0.02 Å, which confirms the previous observation. However, the C—N, N—N, P—N and P—C bonds in (II) are all longer, by 0.01–0.05 Å, than their counterparts in (IV) (the largest difference corresponds to N—N), which may partly be due to the data collection temperature difference of 98 K, but also to the presence in (IV) of a Cp ring instead of the two *tert*-butyl groups in (II), with possible additional conjugation effects. The aromatic C—C bond lengths in (II) are in the usual range in all three rings.

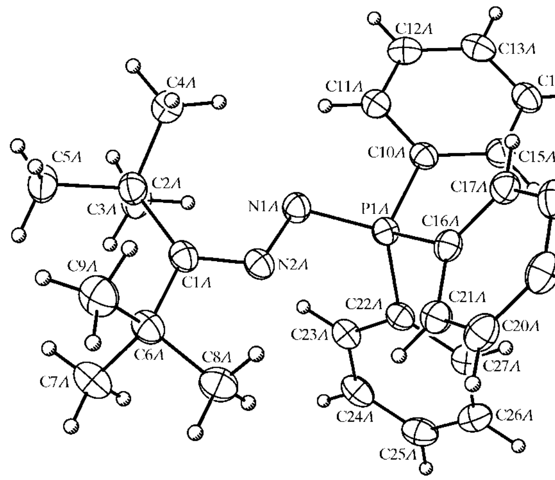


Figure 2
A view of molecule *A* in (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

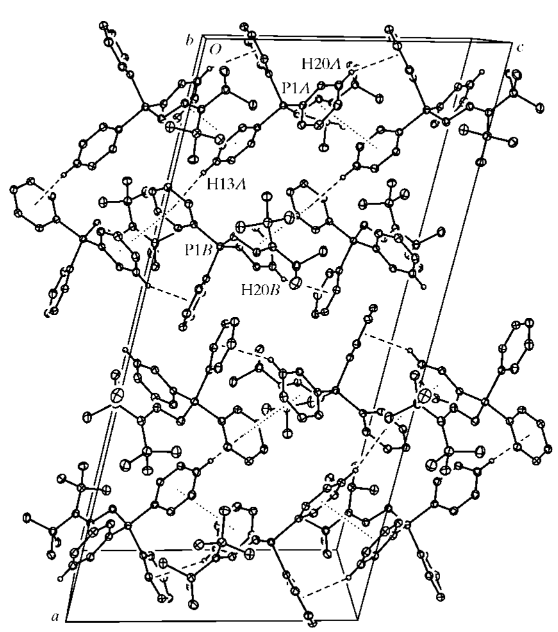


Figure 3
A view of (II), showing the double chains along the *c* axis. C—H$\cdots\pi$ and π–π stacking interactions are represented by dashed and dotted lines, respectively. Displacement ellipsoids are drawn at the 30% probability level.

The aromatic rings in (II) are involved in several weak intermolecular interactions. π–π stacking interactions are possibly present between rings C10–C15 (centroid *Cg*1) and C16–C21 (centroid *Cg*2) of molecules related by a glide plane for both *A* and *B* molecules [$Cg1A\cdots Cg2A^{i}$ = 3.76 Å, dihedral angle = 7.0°, centroid offset = 1.65 Å and shortest interatomic contact = 3.26 Å for *A* molecules; $Cg1B\cdots Cg2B^{i}$ = 3.64 Å, dihedral angle = 6.5°, centroid offset = 1.22 Å and shortest interatomic contact = 3.36 Å for *B* molecules; symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$]. Although the shortest interatomic contacts are shorter than twice the out-of-plane van der Waals radius of C (1.7 Å; Bondi, 1964), these interactions are weak at best, due to the large offset values.

Three significant C—H$\cdots\pi$ interactions are also present. One of them links molecules *A* and *B* in the asymmetric unit ($H13A\cdots Cg1B$ = 2.74 Å and $C13A—H13A\cdots Cg1B$ = 153°) and the other two involve two sets of adjacent *A* or *B* molecules [$H20A\cdots Cg3A^{ii}$ = 2.68 Å and $C20A—H20A\cdots Cg3A^{ii}$ = 154°; $H20B\cdots Cg3B^{ii}$ = 2.60 Å and $C20B—H20B\cdots Cg3B^{ii}$ = 147°; *Cg*3 is the centroid of the C22–C27 ring; symmetry code: (ii) $x, \frac{3}{2} - y, z + \frac{1}{2}$]. Molecule *A* thus acts as a hydrogen-bond donor to two neighbouring molecules and as an acceptor from one, whereas molecule *B* acts as a single donor and double acceptor. These interactions result in double chains of *A* and *B* molecules running along the *c* axis (Fig. 3).

Experimental

Reaction of di-*tert*-butyl ketone (5.70 g, 0.04 mol) with hydrazine hydrate (6 ml, 0.12 mol) in diethylene glycol (14 ml) gave compound (I) (5.90 g) in 94% yield. The ^{1}H NMR spectrum of (I) in $CDCl_3$ is identical to that described previously (Hartzler, 1971). Reaction of (I) (1.56 g, 0.01 mol) with dibromotriphenylphosphorane (4.22 g, 0.01 mol) gave compound (II) (2.50 g) in 60% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.08 (*s*, 9H, ^{t}Bu), 1.56 (*s*, 9H, ^{t}Bu), 7.33–7.51 (*m*, 9H, *ortho*- and *para*-Ph_3P), 7.61–7.74 (*m*, 6H, *meta*-Ph_3P). Single crystals of both compounds were obtained by slow evaporation of pentane solutions.

Compound (I)

Crystal data

$C_9H_{20}N_2$	D_x = 1.040 Mg m^{-3}
M_r = 156.27	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 23020 reflections
a = 11.5299 (8) Å	θ = 3.1–25.7°
b = 8.0975 (4) Å	μ = 0.06 mm^{-1}
c = 10.8937 (8) Å	T = 100 (2) K
β = 101.111 (3)°	Irregular, colourless
V = 998.01 (11) Å^3	0.23 × 0.19 × 0.16 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	R_{int} = 0.038
φ and ω scans	θ_{max} = 25.7°
23020 measured reflections	h = −14 → 13
1884 independent reflections	k = −9 → 0
1717 reflections with $I > 2\sigma(I)$	l = 0 → 13

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.3197P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.039	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.105	$(\Delta/\sigma)_{max}$ < 0.001
S = 1.03	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
1884 reflections	$\Delta\rho_{min}$ = −0.15 e Å^{-3}
112 parameters	
H atoms: see below	

Table 1
Selected geometric parameters (Å, °) for (I).

N1—N2	1.3992 (13)	C1—C2	1.5585 (14)
C1—N2	1.2864 (14)	C1—C6	1.5504 (15)
N1—N2—C1	123.28 (9)	N2—C1—C6	112.76 (9)
N2—C1—C2	123.39 (9)	C2—C1—C6	123.83 (9)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2^{i}	0.930 (15)	2.230 (15)	3.0937 (13)	154.1 (12)

Symmetry code: (i) $-x, -y, -z$.

Compound (II)

Crystal data

$C_{27}H_{33}N_2P$	D_x = 1.160 Mg m^{-3}
M_r = 416.52	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 122758 reflections
a = 29.1768 (16) Å	θ = 2.9–25.7°
b = 11.6848 (7) Å	μ = 0.13 mm^{-1}
c = 14.3768 (6) Å	T = 100 (2) K
β = 103.243 (3)°	Platelet, colourless
V = 4771.1 (4) Å^3	0.17 × 0.15 × 0.10 mm
Z = 8	

Data collection

Nonius KappaCCD area-detector diffractometer	R_{int} = 0.036
φ and ω scans	θ_{max} = 25.7°
122758 measured reflections	h = −35 → 34
9059 independent reflections	k = −14 → 0
6960 reflections with $I > 2\sigma(I)$	l = 0 → 17

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 1.2906P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.044	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.118	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.99	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
9059 reflections	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
553 parameters	
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for (II).

P1*A*—N1*A*	1.6025 (16)	P1*B*—N1*B*	1.6008 (16)
P1*A*—C10*A*	1.8030 (18)	P1*B*—C10*B*	1.8006 (18)
P1*A*—C16*A*	1.811 (2)	P1*B*—C16*B*	1.8114 (19)
P1*A*—C22*A*	1.8214 (19)	P1*B*—C22*B*	1.8212 (19)
N1*A*—N2*A*	1.421 (2)	N1*B*—N2*B*	1.420 (2)
C1*A*—N2*A*	1.292 (2)	C1*B*—N2*B*	1.289 (2)
C1*A*—C2*A*	1.552 (3)	C1*B*—C2*B*	1.555 (3)
C1*A*—C6*A*	1.548 (3)	C1*B*—C6*B*	1.552 (3)
P1*A*—N1*A*—N2*A*	109.19 (12)	P1*B*—N1*B*—N2*B*	109.58 (12)
N1*A*—N2*A*—C1*A*	119.47 (16)	N1*B*—N2*B*—C1*B*	119.41 (16)
N2*A*—C1*A*—C2*A*	123.44 (17)	N2*B*—C1*B*—C2*B*	123.49 (17)
N2*A*—C1*A*—C6*A*	112.72 (17)	N2*B*—C1*B*—C6*B*	112.55 (17)
C2*A*—C1*A*—C6*A*	123.80 (16)	C2*B*—C1*B*—C6*B*	123.95 (16)

The two H atoms bound to N1 in (I) were found in a difference Fourier map and they were refined with $U_{iso}(H) = 1.2U_{eq}(N1)$. All other H atoms in both compounds were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (aromatic CH) or 0.96 Å (CH_3), and with $U_{iso}(H) = 1.2U_{eq}(CH)$ or $1.5U_{eq}(CH_3)$.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3003). Services for accessing these data are described at the back of the journal.

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