anion [1·688 (5) Å]. Up to now the longest value found for a P—N bond was that due to the zwitterionic monoamidophosphate anion in the corresponding potassium salt [1·800 (4) Å; Cameron, Chan & Chute, 1980].

In this case the nitrogen lone pair is unable to form donor $p\pi(N) \rightarrow d\pi(P)$ bonding because of the additional bonding of a proton.

The longer P—N distance in $C_6H_5N.PS_2Cl$ of 1·849 (2) Å means that the P—N bond is only relatively weak without any π back donation. The P—N bond length is of the same order as that found in the adduct of ammonia with phosphorus pentafluoride [1·842 (2) Å; Storzer, Schomburg, Röschenthaler & Schmutzler, 1983] and only slightly shorter than in the corresponding pyridine adduct of PF_5 [1·885 (4) Å; Sheldrick, 1974]. This should be expected because bond distances in penta- and hexacoordinated phosphorus adducts are generally longer than in tetracoordinated ones.

The P—S distances ($\overline{P–S} = 1·920 \pm 0·002$ Å) are typical for P—S double bonds which normally lie within the range 1·90 to 1·95 Å, whereas the P—Cl distance of 2·058 Å is considerably longer than the average value for the P—Cl single-bond length of 2·02 ± 0·01 Å (Corbridge, 1974).

Based on the determined bond lengths one can conclude that the compound $C_6H_5N.PS_2Cl$ is preferably formulated as a donor stabilized dithiophosphoryl monochloride corresponding to form (1). This is supported by the large S—P—S bond angle of 123·68° which is of the same order as that found for the threefold coordinated planar dithioxo(tri-*tert*-butylphenyl)phosphorane, $C_{18}H_{29}PS_2$ (126°; Appel, Knoch & Kunze, 1983). In normal dithiophosphates containing strongly tetrahedrally coordinated P atoms the S—P—S angles vary only between 108 and 118° (Aurivillius & Stålhandske, 1975).

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X-ray Study of 3-*tert*-Butyl-1-methyl-2-phenylindole, the Product of an Unexpected *tert*-Butylation Reaction

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Abstract. $C_{19}H_{21}N$, $M_r = 263·4$, orthorhombic, $Pbca$, $a = 20·152$ (4), $b = 18·267$ (4), $c = 8·488$ (2) Å, $V = 3124·6$ (12) Å^3, $Z = 8$, $D_x = 1·12$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 4·6$ cm^{-1}, $F(000) = 1136$, $T = 293$ K, final $R = 0·052$ for 1755 symmetry-independent observed reflections. The indole nucleus adopts an almost planar conformation with a dihedral angle between the mean planes of the two

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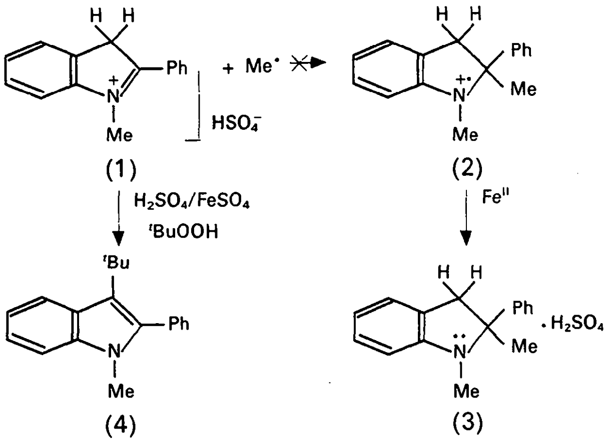
individual rings of 1·1 (1)°. The mutual interactions between the phenyl and *tert*-butyl substituents give rise to deformations in their internal geometry.

Introduction. In our attempts to synthesize an indoline such as (3), we planned a direct radical methylation of the protonated form (1) of 1-methyl-2-phenylindole.



In fact, it is well known that one of the most used methods to methylate protonated heteroaromatic bases is the decomposition of *tert*-butyl hydroperoxide by iron(II) (Itokawa *et al.*, 1978; Minisci, Vismara, Fontana, Morini, Serravalle & Giordano, 1987, and references therein):

$$ {}^tBuOOH + Fe^{II} \rightarrow {}^tBuO\cdot + OH^- + Fe^{III} $$

$$ {}^tBuO \rightarrow MeCOMe + Me $$

The reaction, carried out by adding the *tert*-butyl hydroperoxide to a solution of the indole and $FeSO_4.7H_2O$ in 60% aqueous sulfuric acid at room temperature, did not afford the indoline (3) but an unexpected product which, from spectroscopic investigation and X-ray analysis, was shown to be 3-*tert*-butyl-1-methyl-2-phenylindole (4): yield 37%, m.p. 444–445 K from ligroin 60–80°C; ^1H NMR in $CDCl_3$ *vs* TMS: 1·2 (9H, *s*, ᵗBu), 3·3 (3H, *s*, Me), 7·1–7·5 (8H, *m*, arom.), 7·9 (1H, *m*, arom.); mass spectroscopy: *m*/*e* (relative intensity): 263 (22), 248 (100), 232 (9), 212 (12), 193 (5).

Moreover, the unequivocal establishment of the conformation of this compound may allow a better approach to the interpretation of its anomalous formation.

Experimental. Colorless prismatic tabular crystals obtained by slow crystallization from benzene–petroleum ether. Siemens AED diffractometer on-line to a General Automation Jumbo 220 microcomputer, Ni-filtered Cu $K\alpha$ radiation, θ–2θ scan, scan width from $(\theta - 0{\cdot}60)$ to $[\theta + 0{\cdot}60 + (\Delta\lambda/\lambda)\mathrm{tg}\theta]°$; scan speed 3·0° min^{-1}. Crystal dimensions 0·19 × 0·38 × 0·57 mm. Cell dimensions based on 29 $(\theta,\chi,\varphi)_{hkl}$ measured intensities; 3393 symmetry-independent reflections ($0 \le h \le 24$, $0 \le k \le 22$, $0 \le l \le 10$, $3 \le \theta \le 70°$) collected at $T = 293$ K with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One standard reflection every 50, no significant variation. Correction for Lorentz and polarization effects.

Structure solved by direct methods (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). 1755 observed reflections [$I > 3\sigma(I)$], 226 parameters in full-matrix least-squares refinement; all H atoms located in the difference Fourier map refined isotropically: methyl and *tert*-butyl substituents refined as rigid groups. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2 F_o + 0{\cdot}025 F_o^2]^{-1}$; *SHELX*76 system (Sheldrick, 1976); maximum shift of parameters $0{\cdot}2\sigma$ for N and C, $0{\cdot}8\sigma$ for H; $\Delta\rho_{max} = 0{\cdot}15$, $\Delta\rho_{min} = -0{\cdot}23$ e Å^{-3}. Final refinement converged to $R = 0{\cdot}052$, $wR = 0{\cdot}059$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The arbitrary numbering scheme used in the crystal analysis is shown in Fig. 1, which represents a perspective view of the molecule. Bond distances, bond angles and selected torsion angles are reported in Table 2.

The intramolecular bond lengths and angles of the indole nucleus are in line with the hybridization expected for the atoms involved and in agreement with those found in related compounds (Thewalt & Bugg, 1972; Schmelter, Bradaczek & Luger, 1973; Greci & Sgarabotto, 1984; Chakraborty &

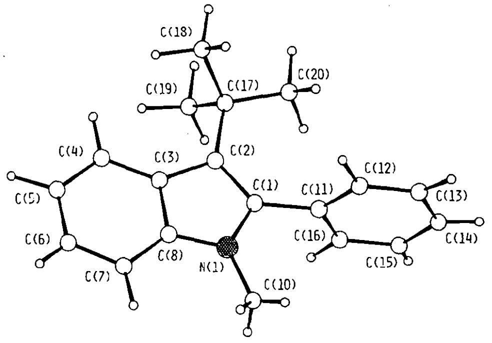


Fig. 1. Perspective view of the molecule showing the atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52101 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^4$) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
N(1)	955 (1)	543 (1)	2952 (2)	492 (6)
C(1)	1037 (1)	−146 (1)	3619 (3)	435 (7)
C(2)	1460 (1)	−103 (1)	4882 (3)	454 (7)
C(3)	1654 (1)	657 (1)	5005 (3)	454 (7)
C(4)	2074 (1)	1059 (2)	6012 (4)	607 (9)
C(5)	2158 (2)	1796 (2)	5754 (4)	727 (11)
C(6)	1828 (2)	2158 (2)	4545 (5)	781 (12)
C(7)	1408 (2)	1786 (1)	3525 (4)	633 (10)
C(8)	1327 (1)	1038 (1)	3785 (3)	485 (8)
C(10)	579 (2)	725 (2)	1558 (4)	806 (13)
C(11)	686 (1)	−766 (1)	2871 (3)	458 (7)
C(12)	47 (1)	−964 (2)	3328 (4)	600 (10)
C(13)	−273 (1)	−1550 (2)	2627 (4)	693 (11)
C(14)	29 (2)	−1931 (2)	1439 (4)	676 (10)
C(15)	662 (1)	−1742 (2)	946 (3)	652 (10)
C(16)	981 (1)	−1160 (1)	1655 (3)	566 (8)
C(17)	1697 (1)	−708 (1)	5984 (2)	595 (9)
C(18)	1526 (1)	−501 (1)	7715 (2)	960 (17)
C(19)	2470 (1)	−769 (1)	5831 (2)	879 (13)
C(20)	1416 (1)	−1468 (1)	5599 (2)	1051 (17)

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N(1)—C(1)	1·390 (3)	C(6)—C(7)	1·388 (5)
N(1)—C(8)	1·371 (3)	C(7)—C(8)	1·394 (3)
N(1)—C(10)	1·444 (4)	C(11)—C(12)	1·393 (3)
C(1)—C(2)	1·372 (3)	C(11)—C(16)	1·392 (3)
C(1)—C(11)	1·479 (3)	C(12)—C(13)	1·384 (5)
C(2)—C(3)	1·446 (3)	C(13)—C(14)	1·368 (5)
C(2)—C(17)	1·525 (3)	C(14)—C(15)	1·386 (5)
C(3)—C(4)	1·409 (4)	C(15)—C(16)	1·380 (4)
C(3)—C(8)	1·411 (3)	C(17)—C(18)	1·556 (3)
C(4)—C(5)	1·374 (5)	C(17)—C(19)	1·567 (3)
C(5)—C(6)	1·390 (5)	C(17)—C(20)	1·535 (3)
C(1)—N(1)—C(8)	108·8 (1)	N(1)—C(8)—C(7)	129·0 (2)
C(1)—N(1)—C(10)	127·2 (2)	C(3)—C(8)—C(7)	123·0 (2)
C(8)—N(1)—C(10)	123·9 (2)	C(1)—C(11)—C(12)	121·4 (2)
N(1)—C(1)—C(2)	109·9 (2)	C(1)—C(11)—C(16)	120·7 (1)
N(1)—C(1)—C(11)	117·5 (1)	C(12)—C(11)—C(16)	117·9 (2)
C(2)—C(1)—C(11)	132·6 (1)	C(11)—C(12)—C(13)	120·8 (2)
C(1)—C(2)—C(3)	106·2 (1)	C(12)—C(13)—C(14)	120·2 (2)
C(1)—C(2)—C(17)	129·2 (1)	C(13)—C(14)—C(15)	120·3 (3)
C(3)—C(2)—C(17)	124·5 (1)	C(14)—C(15)—C(16)	119·3 (2)
C(2)—C(3)—C(4)	134·9 (2)	C(11)—C(16)—C(15)	121·5 (2)
C(2)—C(3)—C(8)	107·1 (1)	C(2)—C(17)—C(18)	109·5 (1)
C(4)—C(3)—C(8)	117·9 (2)	C(2)—C(17)—C(19)	108·2 (1)
C(3)—C(4)—C(5)	119·2 (2)	C(2)—C(17)—C(20)	114·2 (1)
C(4)—C(5)—C(6)	121·6 (3)	C(18)—C(17)—C(19)	108·4 (1)
C(5)—C(6)—C(7)	121·3 (3)	C(18)—C(17)—C(20)	109·8 (1)
C(6)—C(7)—C(8)	116·9 (3)	C(19)—C(17)—C(20)	106·6 (1)
N(1)—C(8)—C(3)	108·0 (1)		
C(8)—N(1)—C(1)—C(11)	−178·8 (2)	C(11)—C(1)—C(2)—C(17)	−1·8 (4)
C(10)—N(1)—C(1)—C(2)	176·5 (3)	C(1)—C(2)—C(17)—C(18)	−123·5 (2)
C(10)—N(1)—C(1)—C(11)	−2·3 (4)	C(1)—C(2)—C(17)—C(19)	118·5 (2)
C(10)—N(1)—C(8)—C(7)	2·0 (4)	C(1)—C(2)—C(17)—C(20)	0·1 (3)
N(1)—C(1)—C(2)—C(17)	179·7 (2)		

Talapatra, 1986). The fused two-ring system is almost planar, the dihedral angle between the mean planes of the two individual rings being 1·1 (1)°.

From the study of the conformational geometry deduced from bond and torsion angles and from the analysis of the planarity reported in Table 3, it is possible to assert that the molecule is affected by a considerable degree of stretching as a consequence of the steric interaction between the phenyl and the *tert*-butyl substituents: in fact, significant deviations from the expected values are observed for the external angles at C(1) with an increase in C(2)—C(1)—C(11) and decrease in N(1)—C(1)—C(11) and similarly in the *tert*-butyl group for the angles C(2)—C(17)—C(20) and C(19)—C(17)—C(20); on the other hand, a significant deviation from coplanarity is also observed in the phenyl ring with regard to the C(12) atom. The dihedral angle between the phenyl and indole mean planes is 90·3 (1)°.

Table 3. *Distances* ($Å \times 10^3$) *of relevant atoms from the mean plane with e.s.d.'s in parentheses, and angles* (°) *between planes*

Starred atoms were not used to define the plane.

Plane *A*:	N(1), C(1), C(2), C(3), C(8) N(1) 0(2), C(1) 1(2), C(2) −1(2), C(3) 2(2), C(8) −1(2) C(10)* 73(4), C(11)* 30(2), C(17)* −9(2)
Plane *B*:	C(3)–C(8) C(3) 3(2), C(4) −5(3), C(5) 7(4), C(6) −3(4), C(7) 2(4) C(8) −2(2), N(1)* 22(2), C(2)* 27 (2)
Plane *C*:	C(11)–C(16) C(11) −7(2), C(12) 12(3), C(13) −4(3), C(14) 0(4), C(15) −3(3), C(16) 5(2), C(1)* −3(2)

A–B	1·1 (1)	*B–C*	90·5 (1)

The structure consists of individual molecules packed in the crystal with van der Waals forces; there are no unusual short intermolecular contacts and hence the packing interactions do not influence the geometry of the molecule.

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