Table IX. Averaged Parameters of the Porphine Skeleton in Metalloporphyrins as a Function of the Radius of the Central Core, C_t-N

	Ni(DEUT)[a]	MoO(TTP)	Mo(Cl)$_2$- (TTP)	Sn(Cl)$_2$- (TPP)[b]
Distances (Å)				
C_t-N	1.960	2.011	2.074	2.098
M-N	1.960 (4)	2.110 (6)	2.074 (6)	2.098 (2)
$\Delta P_M{}^c$	0.0	0.73	0.0	0.0
N-C_α	1.383 (3)	1.392 (7)	1.385 (6)	1.370 (2)
C_β-C_β	1.350 (5)	1.343 (12)	1.376 (11)	1.380 (3)
C_α-C_m	1.375 (4)	1.395 (7)	1.402 (7)	1.407 (2)
Angles (deg)				
C_α-N-C_α	104.5 (6)	105.7 (6)	107.8 (6)	109.2 (2)
C_α-C_m-C_α	123.9 (4)	124.4 (7)	126.3 (7)	126.4 (2)
N-C_α-C_β	110.0 (5)	109.3 (4)	108.7 (4)	108.2 (2)

[a] T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, 87, 2305 (1965). [b] Reference 18. [c] ΔP_M denotes the deviation of the metal M from the mean plane of the porphine skeleton.

radius. Hoard has noted this tendency and points out[19] that an increase in the C_α-N-C_α angle is conducive to stronger complexing, but the amount of expansion of this angle is limited by the need to keep the N-C_α-C_β angle as large as possible. As a conclusion, the Mo(IV) ion is possibly more strongly complexed in Mo(Cl)$_2$(TTP) than in MoO(TTP).

Registry No. I, 69501-68-4; II, 64024-41-5; MoO(Cl)(TTP)·HCl, 69484-02-2; MoOCl$_3$, 13814-74-9.

Supplementary Material Available: Listings of observed and calculated structure factors, positional atomic and anisotropic thermal parameters, and Tables V and VIII (interatomic distances) (33 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Structure of Bis(*tert*-butyl isocyanide)(*meso*-tetraphenylporphyrinato)iron(II)–Bis(toluene)
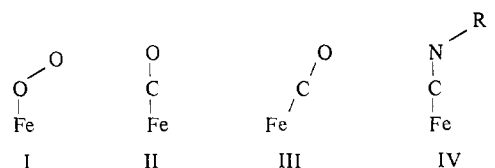
GEOFFREY B. JAMESON and JAMES A. IBERS*

The structure of bis(*tert*-butyl isocyanide)(*meso*-tetraphenylporphyrinato)iron(II)–bis(toluene) has been determined by three-dimensional, single-crystal X-ray diffraction methods. The material crystallizes with four formula units in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions a = 22.113 (7) Å, b = 12.581 (4) Å, c = 19.455 (8) Å, β = 94.55 (1)°, and V = 5396 Å³ at −150 °C. The structure described by 408 variable parameters has been refined by full-matrix, least-squares techniques to values of the agreement index R (on F^2, 8186 data including $F_o^2 < 0$) of 0.071 corresponding to a value of R (on F, 6747 data having $F_o^2 > 3\sigma(F_o^2)$) of 0.049. The geometry about the iron atom is approximately tetragonal with Fe–N(porph) separations of 2.000 (1), 2.010 (2), 2.005 (2), and 2.004 (2) Å and with Fe–C(*t*-BuNC) separations of 1.901 (3) and 1.900 (3) Å. Although there are large deviations of the Fe–C–N–C moiety of the Fe-*t*-BuNC groups from linearity (Fe–C–N angles, 168.1 (2) and 169.9 (2)°; CNC angles, 159.1 (3) and 165.2 (3)°), we conclude, from crystal packing considerations, that the isocyanide geometry is essentially linear. Such a linear geometry may be expected in the corresponding isocyanide adducts of hemoproteins.

Introduction

Of the small molecules, L = O_2, CO, NO, and RNC which bind to ferrous hemoproteins,[1] X-ray crystal structures of simple Fe^{II}(porphyrinato)(L)(base) complexes are available for all except isocyanide, L = RNC.[2-5] In a classic paper on the bonding of these ligands to the heme center,[6] Pauling predicted an angular iron–dioxygen geometry, I, and a linear iron–carbonyl geometry, II. These have been strongly supported by the structures of model complexes.[2-4] Geometry I for dioxygen is consistent with the present structure of

oxymyoglobin.[7,8] The apparently bent geometry claimed[9-11] for several carbonyl hemoglobin compounds[9-12] is probably better interpreted as a tilted but linear geometry, III.[4,13] An angular geometry has been observed in the structure of the
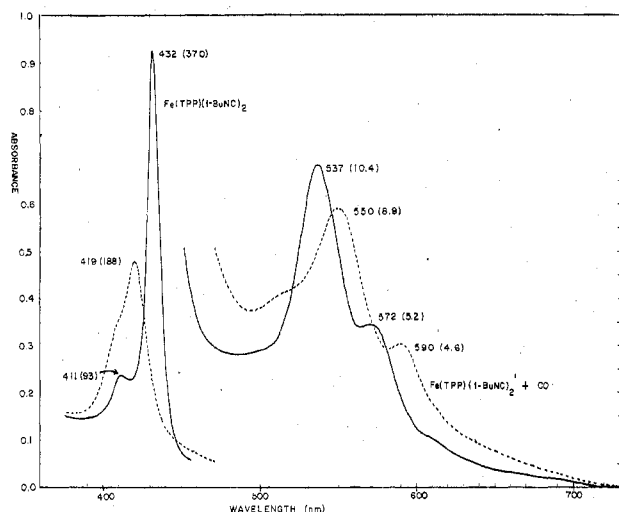
Figure 1. UV–visible spectra for Fe(TPP)(t-BuNC)$_2$ and its carbonyl adduct, in toluene. Extinction coefficients (×10^{-3}) are given in parentheses following λ_{max} (nm).

nitrosyl compound Fe(TPP)(NO)(1-MeIm),[5,14] although the bond angle is more obtuse than for iron–dioxygen complexes. For heme–isocyanide complexes, Pauling implicitly predicted that the CNR moiety would be substantially bent (apparently ~120°); the FeCN group was predicted to be linear (geometry IV).

A large number of isocyanide complexes have now been characterized structurally.[15-72] Except for some[22,29,36] of the zerovalent complexes[22,29-41] and most[23-26,28,29] of the complexes where the isocyanide ligand bridges two metal atoms,[23-29] the M–CNR group is usually described as being "essentially linear", and the small deviations from linearity (usually less than 10°) have generally been attributed to crystal packing effects. Structural studies of porphyrin isocyanide complexes appear to be nonexistent. In fact not even approximate, dianionic macrocyclic analogues appear to have been characterized structurally. Nonetheless the linear linkage generally observed when the metal center is in a normal oxidation state[15-21,42-72] might also be expected for a (porphyrin)(isocyanide)iron(II) species.

The size of the ligand-binding pocket in hemoglobins, normal and abnormal, and subunit heterogeneity may be probed more sensitively with isocyanide ligands than with the other small molecules, O$_2$, CO, and NO, because the steric demands of the isocyanide ligand may be varied by changing R. Hence the precise geometry of a simple (porphyrinato)(base)(isocyanide)iron(II) complex is of interest. Toward this end we have prepared and characterized such a complex, Fe(TPP)(t-BuNC)$_2$. The facile formation of bis(isocyanide)–heme complexes has been previously observed.[73] Other studies on the chemistry of porphyrin–isocyanide complexes appear to be rare, although cobalt–glyoxime isocyanide complexes have been prepared.[74-76]

Experimental Section

Preparation of Fe(TPP)(t-BuNC)$_2$·2(toluene). Typically for preparation of large crystals, 1.5 mL of a 2 mM toluene solution of t-BuNC was added to a toluene solution of Fe(TPP)(py)$_2$ (24 mg in 3.0 mL). Aliquots were then transferred by syringe to crystallizing vessels. Crystallization was readily achieved by vapor or solvent diffusion of hexane into the solution at 5 °C. Solutions of Fe(TPP)(t-BuNC)$_2$ appear to be moderately stable in air. The UV-visible spectrum of Fe(TPP)(t-BuNC)$_2$ is shown in Figure 1. The C≡N stretching vibration occurs at 2129 cm^{-1} (Nujol mull) and at 2125 cm^{-1} (toluene solution). All solvents used were dry and deoxygenated, and all manipulations were performed under purified dinitrogen using standard Schlenk apparatus and techniques.

Table I. Crystal Data and Data Collection Procedures for Fe(TPP)(t-BuNC)$_2$·2(toluene)

formula	C$_{68}$H$_{62}$FeN$_6$
formula wt, amu	1019.14
space group	C_{2h}^5-$P2_1/c$
a, Å	22.113 (7)
b, Å	12.581 (4)
c, Å	19.455 (8)
β, deg	94.55 (1)
V, Å^3	5396
Z	4
temp, °C	~−150^a
crystal shape	7-sided lump, ~0.75 × 0.60 × 0.52 mm
crystal vol, mm^3	0.260
radiation	graphite-monochromated Mo Kα, λ(Kα$_1$) 0.7093 Å
linear abs coef, cm^{-1}	3.24
transmission factors	0.82-0.88
detector aperture	4.0 mm wide, 4.2 mm high, 32 cm from crystal
takeoff angle, deg	2.6
scan speed	2.0° in 2θ/min
λ^{-1}(sin θ) limits, Å^{-1}	0.0431-0.5701 (3.5 < 2θ(Mo Kα$_1$) < 47.7°)
background counts	10 s at each end of scan, with rescan option^b
scan range	0.8° below Kα$_1$, 0.8° above Kα$_2$
data collected	±h, +k, +l
p	0.05
unique data	8186
unique data with $F_o^2 > 3\sigma(F_o^2)$	6747

^{a} The low-temperature system is based on a design by J. C. Huffman, Ph.D. Thesis, Indiana University, 1974. ^{b} P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975).

Crystallographic Study of Fe(TPP)(t-BuNC)$_2$·2(toluene). Upon exposure to air, the crystals rapidly lost their ability to diffract, presumably through loss of toluene solvate molecules. Symmetry and systematic absences uniquely consistent with the monoclinic space group C_{2h}^5-$P2_1/c$ were observed by precession and Weissenberg photography of a crystal sealed in a capillary. The crystal selected for data collection upon a Picker FACS-I automatic diffractometer was chipped from a much larger crystal which also provided material for spectroscopic studies. Crystal mosaicities (peak width at half peak height) as determined by ω scans were typically less than 0.15° for intense low-angle reflections. Lattice parameters at −150 °C were obtained as previously described[77] by the hand centering of 17 reflections in the range 0.2804 < λ^{-1} sin θ < 0.3177 Å^{-1} with Mo Kα$_1$ radiation (λ 0.709 30 Å). The rapid loss of solvate precluded a satisfactory density measurement; however, for four FeC$_{68}$N$_6$H$_{62}$ units per unit cell the calculated density of 1.25 g cm^{-3} is typical for metalloporphyrins. Important features of data collection are summarized in Table I.

Standard procedures and programs were used to solve and refine this structure.[4,77] In the initial stages calculations were done by using the Vogelback Computer Center's CDC6600 at Northwestern University. The Lawrence Berkeley Laboratory CDC7600 computer at Berkeley was used for the final refinements. Coordinates for the iron atom and the whole of the *meso*-tetraphenylporphyrinato skeleton were deduced from an unsharpened Patterson map. A Fourier synthesis, with phases derived from this initial model, revealed the positions of the remaining nonhydrogen atoms, including two toluene solvate molecules. Atoms in the six phenyl rings were constrained as rigid groups with D_{6h} geometry (C–C = 1.395 Å) and with each atom being assigned an isotropic thermal parameter. The 62 hydrogen atoms were then unambiguously located in difference maps and were included as a fixed contribution to F_c at their calculated idealized positions (C–H = 0.95 Å, thermal parameter B_H = B_C + 1.0 Å^2, and, for methyl hydrogen atoms, C–C–H = 109.5°).

All data, corrected for absorption effects and including $F_o^2 < 0$, were utilized in the final two cycles of full-matrix least-squares refinement in which all nongroup atoms were allowed anisotropic thermal parameters. The model was described by 408 variable parameters, and at convergence the values for R and R_w on F^2 were
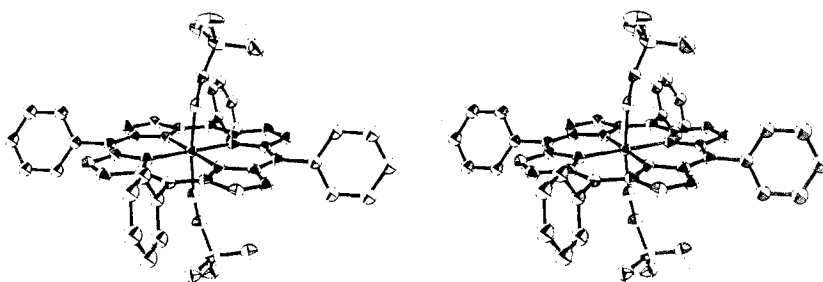
Figure 2. A stereo diagram of the Fe(TPP)(t-BuNC)$_2$ molecule. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 70% probability level.
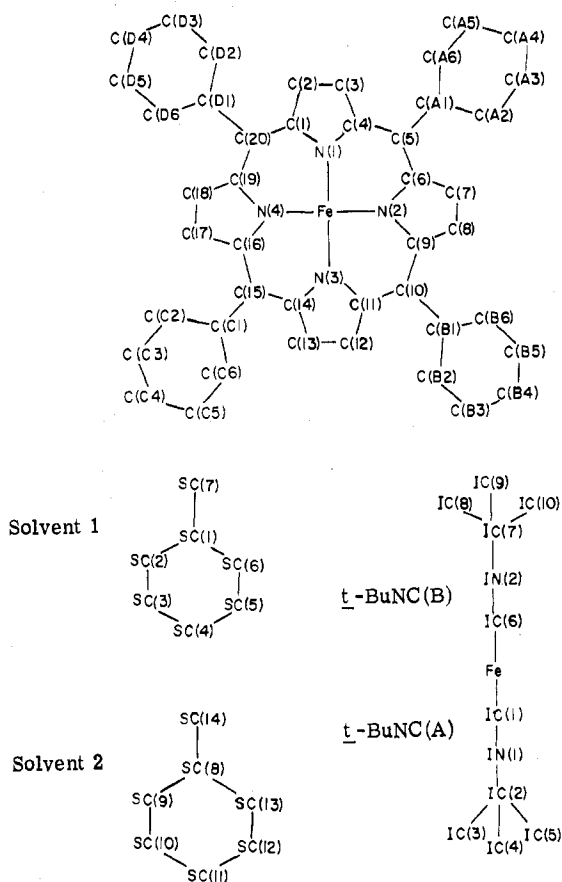

Figure 3. Atom labeling scheme for Fe(TPP)(t-BuNC)·2(toluene).

0.071 and 0.137. The standard error in an observation of unit weight is 1.71 e^2. For the portion of data having $F_o^2 > 3\sigma(F_o^2)$ the values for R and R_w on F are 0.049 and 0.067. Except for one peak of height 1.15 e/Å^3 associated with one of the porphyrinato phenyl rings, the final difference Fourier map is flat and generally featureless (but see Discussion). The minimized function is independent of the magnitude of $|F_o|$; there is a slight dependence on the magnitude of $\lambda^{-1} \sin\theta$ with

low-angle data having highest values. Since the thermal parameters of atoms in rigid groups at −150 °C are very small and because there are a large number of extra parameters involved, little improvement in the accuracy of the remainder of the structure would have accompanied the release of group constraints.

Final nonhydrogen parameters are listed in Tables II and III. Hydrogen atom parameters are given in Table IV.[78] Table V lists the values of 10$|F_o|$ vs. 10$|F_c|$.[78] A negative entry indicates that $F_o^2 \le 0$.

Description and Discussion of the Structure

General Information. The crystal structure consists of monomeric molecules of bis(*tert*-butyl isocyanide)(*meso*-tetraphenylporphyrinato)iron(II), as illustrated in Figure 2, and of toluene solvate molecules. No symmetry is imposed on molecular species. The geometry about the iron atom is approximately tetragonal; the average Fe–N(porph) separation is 2.005 (4) Å and the average Fe–C separation is 1.901 (3) Å. The atom labeling scheme is defined in Figure 3. Figure 4 illustrates the crystal packing arrangement. While there are no unusually close contacts (Tables VI and VII[78]), there are effects of crystal packing on the geometry of the Fe–CNR species and these will be discussed later. The pronounced layering of solvate molecules that is apparent in Figure 4 may be the cause of the facile egress of solvate molecules from crystals exposed to air at room temperature.

Inspection of the tables of bond distances and angles, Tables VIII and IX, shows that with few exceptions, which are delineated later, chemically equivalent bond distances and angles show statistically insignificant differences. This internal consistency allows some confidence to be placed on the significance of differences which in absolute terms are rather small. Furthermore the high precision and internal consistency of this analysis tempted us to investigate the disposition of residual electron density in the porphyrinato plane.

The Coordination Sphere and Conformation of the Isocyanides. Table X lists a selection of iron porphyrinato complexes. The Fe–N(porph) separations observed here are typical of a low-spin, six-coordinate iron(II) porphyrinate.[79] The UV–visible spectrum, typical of hemochrome species such as Fe(TpivPP)(1-MeIm)$_2$,[80] and the reversible binding of CO to give, presumably, Fe(TPP)(CO)(t-BuNC), see Figure 1,

Figure 4. Unit cell of Fe(TPP)(t-BuNC)·2(toluene). Hydrogen atoms have been omitted for clarity.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of Fe(TPP)(t-BuNC)₂·2(toluene)

ATOM	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
FE	-0.243598(15)	0.231614(28)	0.153421(18)	5.97(9)	19.53(27)	7.37(11)	-0.18(11)	6.24(7)	-0.28(12)
N(1)	-0.306083(89)	0.17734(16)	0.08200(10)	6.45(45)	23.2(15)	8.19(58)	0.76(65)	0.68(40)	-0.97(73)
C(1)	-0.33391(11)	0.07933(20)	0.07948(13)	6.14(53)	26.0(18)	8.82(71)	-0.46(79)	0.70(48)	-1.61(89)
C(2)	-0.37560(11)	0.07220(21)	0.01898(13)	7.41(55)	26.8(18)	10.87(75)	-1.48(81)	0.27(51)	-1.80(93)
C(3)	-0.37447(11)	0.16613(21)	-0.01364(13)	6.79(54)	35.3(19)	8.48(71)	0.66(82)	-0.65(49)	-0.94(94)
C(4)	-0.33099(11)	0.23221(20)	0.02552(13)	5.82(52)	27.3(18)	8.13(71)	1.08(77)	-0.27(48)	-1.65(88)
C(5)	-0.31807(11)	0.33581(20)	0.00771(13)	6.67(53)	26.2(18)	9.53(72)	2.70(79)	0.78(49)	-0.56(89)
N(2)	-0.242043(90)	0.37198(17)	0.10428(10)	6.89(45)	22.2(14)	8.25(59)	0.39(65)	0.46(41)	-1.38(73)
C(6)	-0.27645(11)	0.40096(20)	0.04516(13)	7.01(54)	23.7(17)	8.28(70)	2.54(78)	-0.81(49)	1.08(87)
C(7)	-0.26301(12)	0.50854(21)	0.02673(13)	8.65(57)	26.6(18)	10.29(74)	2.03(82)	0.01(52)	3.13(92)
C(8)	-0.22080(11)	0.54526(20)	0.07449(13)	8.72(57)	20.6(17)	10.83(75)	-0.56(79)	1.56(52)	0.88(89)
C(9)	-0.20784(11)	0.46037(20)	0.12312(13)	6.88(54)	22.5(17)	9.14(71)	0.60(78)	2.43(49)	0.09(87)
C(10)	-0.16477(11)	0.46625(20)	0.17940(13)	7.29(54)	21.5(17)	10.10(73)	-0.41(77)	2.71(50)	-2.21(89)
N(3)	-0.181023(91)	0.28641(16)	0.22491(10)	6.94(45)	22.1(14)	8.19(59)	0.39(65)	0.89(41)	-0.23(72)
C(11)	-0.15251(11)	0.38369(20)	0.22598(13)	5.95(52)	23.6(17)	9.18(71)	-0.04(77)	0.77(48)	-1.99(88)
C(12)	-0.10853(11)	0.38975(20)	0.28484(13)	7.71(55)	26.3(18)	9.45(73)	-1.53(80)	0.32(50)	-3.08(91)
C(13)	-0.11059(11)	0.29681(21)	0.31876(13)	7.45(56)	29.4(18)	9.15(73)	1.77(82)	-0.75(50)	-0.86(92)
C(14)	-0.15593(11)	0.23224(20)	0.28156(13)	5.91(52)	24.4(17)	8.55(71)	1.84(77)	0.19(48)	-1.85(87)
C(15)	-0.17129(11)	0.12889(20)	0.30041(13)	7.24(55)	26.1(18)	7.82(69)	2.89(79)	0.59(48)	1.38(89)
N(4)	-0.246231(91)	0.09208(16)	0.20282(10)	7.15(46)	21.7(14)	8.94(60)	0.47(65)	0.23(42)	-0.07(73)
C(16)	-0.21378(11)	0.06480(20)	0.26368(13)	7.01(54)	23.1(17)	9.46(72)	0.79(79)	1.19(50)	0.59(89)
C(17)	-0.23055(12)	-0.03988(21)	0.28470(13)	8.05(56)	28.0(18)	10.76(75)	0.07(82)	0.24(52)	3.67(93)
C(18)	-0.27250(12)	-0.07647(20)	0.23681(14)	8.86(58)	22.2(17)	12.47(78)	-1.66(81)	-0.24(54)	1.38(93)
C(19)	-0.28221(11)	0.00545(20)	0.18506(13)	6.67(54)	20.2(17)	10.41(73)	-0.12(76)	1.46(50)	-0.18(87)
C(20)	-0.32363(11)	-0.00214(20)	0.12792(13)	7.30(55)	22.1(17)	10.91(75)	-0.76(78)	2.24(51)	-3.16(90)
1C(1)	-0.30430(12)	0.29757(21)	0.20271(13)	8.74(58)	24.0(17)	7.86(71)	-3.34(86)	-0.93(52)	3.67(91)
1N(1)	-0.33704(10)	0.35368(18)	0.22829(11)	10.10(51)	27.9(16)	12.14(66)	0.88(76)	1.38(47)	1.72(83)
1C(2)	-0.36957(12)	0.45168(21)	0.24302(14)	10.39(61)	26.2(18)	14.88(83)	4.79(85)	1.70(56)	-0.42(98)
1C(3)	-0.32282(13)	0.54064(23)	0.24525(15)	12.68(68)	38.2(21)	17.53(90)	1.03(96)	2.57(62)	-3.1(11)
1C(4)	-0.41804(13)	0.46684(24)	0.18458(16)	11.85(66)	37.1(21)	18.80(92)	0.73(95)	-0.89(62)	2.0(11)
1C(5)	-0.39709(14)	0.43909(24)	0.31122(16)	16.04(74)	41.8(22)	18.89(95)	1.6(10)	6.41(67)	1.3(12)
1C(6)	-0.17559(12)	0.18152(20)	0.10902(13)	9.86(62)	18.0(17)	7.59(78)	-2.10(82)	-1.13(52)	0.92(86)
1N(2)	-0.12922(10)	0.15391(17)	0.09115(11)	8.87(52)	30.6(16)	9.61(63)	0.23(73)	0.79(46)	-1.26(78)
1C(7)	-0.06539(12)	0.12779(23)	0.08661(14)	7.18(57)	41.2(20)	14.75(84)	4.04(88)	1.47(54)	4.1(11)
1C(8)	-0.05361(14)	0.02126(27)	0.12117(17)	14.49(74)	53.7(25)	23.4(11)	9.1(11)	1.45(70)	7.1(13)
1C(9)	-0.05294(15)	0.12506(29)	0.01110(17)	16.68(77)	79.6(29)	19.2(10)	16.3(12)	9.86(70)	6.4(13)
1C(10)	-0.02925(14)	0.21575(27)	0.12483(19)	9.58(66)	60.7(27)	31.9(12)	-1.7(11)	-2.18(71)	1.2(14)

confirm the formal oxidation state of the iron atom as Fe(II). The small but significant scatter of the Fe–N_p bonds about their mean bond length in relation to the estimated standard deviation of an individual bond has been observed previously[5,81] and is probably a crystal packing phenomenon. A similar situation occurs for the N_p–Fe–N_p bond angles. The Fe–C separations do not appear to be unusual, although there is an almost entire lack of basis for comparison. The compound Fe(TPP)(1-MeIm)₂,[82] has a Fe–N(imid) separation of 2.016 (5) Å. In view of the considerably less sterically demanding nature of the t-BuNC ligand compared with the 1-MeIm ligand, the average Fe–C separation of 1.901 (3) Å may not be unusually short. With respect to those iron–isocyanide complexes listed in Table XI where the isocyanide is a terminal (i.e., nonbridging) ligand, the Fe–C separations for Fe-(TPP)(t-BuNC)₂ are significantly longer.

Of somewhat more interest is the angular geometry of the Fe–CNR group. Consideration of the two valence-bond structures

$$Fe{\leftarrow}:C{\equiv}NR \text{ and } Fe{=}C{=}N_{\diagdown}^{\diagup R}$$

shows that increasing 3d(Fe) → π*(C–N) π bonding should lead to bending of the C–N–R bond angle. The Fe–C–N bond angle remains invariant and linear. Recently in a number of complexes where the isocyanide ligand is in a bridging mode or where the metal is in an unusually low valence state (e.g., 0) with the other ligands being poorer π acceptors, the C–N–R bond angle has been found to be markedly bent (see Table XI). In other cases, including non-iron isocyanide complexes,[42-72] it is rare for the C–N–R angle to be much less than 170° or for M–C–N angles to be much less than 175°. But for Fe-(TPP)(t-BuNC)₂, the Fe–CNR geometry is markedly non-

Table III. Derived Parameters for the Rigid Group Atoms of Fe(TPP)(t-BuNC)₂·(toluene)₂

ATOM	X	Y	Z	B, Å²	ATOM	X	Y	Z	B, Å²
C(A1)	-0.352044(73)	0.38230(13)	-0.055439(67)	1.59(5)	C(D2)	-0.332982(51)	-0.19436(13)	0.103269(97)	1.83(5)
C(A2)	-0.398940(77)	0.45448(14)	-0.047861(65)	2.08(5)	C(D3)	-0.368027(69)	-0.28985(10)	0.092185(98)	2.14(5)
C(A3)	-0.430656(70)	0.49802(13)	-0.106014(85)	2.41(6)	C(D4)	-0.430780(67)	-0.28508(10)	0.095192(98)	2.11(5)
C(A4)	-0.415478(77)	0.46938(14)	-0.171745(70)	2.23(5)	C(D5)	-0.458487(50)	-0.18881(13)	0.109444(98)	1.91(5)
C(A5)	-0.368583(80)	0.39719(14)	-0.179324(62)	2.15(5)	C(D6)	-0.423442(66)	-0.09732(10)	0.120688(93)	1.77(5)
C(A6)	-0.336866(68)	0.35366(13)	-0.121171(81)	1.88(5)	SC(1)	0.394060(52)	0.23588(11)	0.133048(69)	2.17(5)
C(B1)	-0.128723(65)	0.56777(10)	0.189385(91)	1.51(5)	SC(2)	0.423017(65)	0.24767(14)	0.198958(64)	2.25(5)
C(B2)	-0.156547(52)	0.66260(12)	0.206541(96)	1.80(5)	SC(3)	0.484108(67)	0.22073(16)	0.211381(70)	2.46(6)
C(B3)	-0.122393(71)	0.75560(10)	0.21484(10)	2.16(5)	SC(4)	0.516242(54)	0.18200(15)	0.157734(90)	2.75(6)
C(B4)	-0.060415(69)	0.75377(10)	0.20598(10)	2.27(5)	SC(5)	0.487286(67)	0.17021(16)	0.091824(79)	2.84(6)
C(B5)	-0.032592(52)	0.65893(13)	0.18882(10)	2.30(5)	SC(6)	0.426195(67)	0.19715(15)	0.079481(61)	2.45(5)
C(B6)	-0.066746(67)	0.56594(10)	0.180527(94)	1.89(5)	SC(7)	0.327452(57)	0.26526(18)	0.11959(11)	3.11(6)
C(C1)	-0.139648(73)	0.08470(13)	0.365346(64)	1.49(5)	SC(8)	0.201455(61)	0.028743(99)	0.066184(69)	2.10(5)
C(C2)	-0.098229(77)	0.00155(13)	0.362133(64)	1.75(5)	SC(9)	0.177263(82)	0.09104(13)	0.118685(63)	2.37(5)
C(C3)	-0.068397(73)	-0.03830(12)	0.422570(83)	2.13(5)	SC(10)	0.152933(90)	0.19078(12)	0.093521(84)	2.99(6)
C(C4)	-0.079983(78)	0.00499(14)	0.486219(66)	2.24(5)	SC(11)	0.152797(84)	0.22822(11)	0.026017(94)	3.33(7)
C(C5)	-0.121401(81)	0.08813(14)	0.489432(63)	2.05(5)	SC(12)	0.176989(94)	0.16592(13)	-0.024483(72)	3.12(6)
C(C6)	-0.151234(71)	0.12798(12)	0.428995(80)	1.78(5)	SC(13)	0.201319(82)	0.06618(12)	-0.007319(66)	2.55(6)
C(D1)	-0.360689(64)	-0.10209(10)	0.117521(92)	1.50(5)	SC(14)	0.22798(10)	-0.08000(12)	0.07801(11)	2.98(6)

RIGID GROUP PARAMETERS

GROUP	X_C	Y_C	Z_C	DELTA	EPSILON	ETA
PHEN-A	-0.383761(51)	0.425839(89)	-0.113592(59)	-2.3184(14)	2.45312(83)	1.6236(15)
PHEN-B	-0.094569(50)	0.660769(80)	0.197683(57)	-2.12173(85)	2.8633(11)	-0.0757(11)
PHEN-C	-0.109815(50)	0.044841(87)	0.425782(57)	0.6335(13)	-2.52671(82)	-1.7387(14)
PHEN-D	-0.395734(50)	-0.193585(89)	0.106356(56)	1.00329(82)	-2.9348(11)	0.1143(11)
SOLV-1	0.455151(51)	0.208939(92)	0.145391(61)	-1.81737(85)	-3.04614(74)	1.8215(12)
SOLV-2	0.177126(55)	0.128479(96)	0.043101(64)	0.40390(87)	2.93242(75)	1.7223(13)

[a] X_C, Y_C, and Z_C are the fractional coordinates of the origin of the rigid group. [b] The rigid group orientation angles delta, epsilon, and eta (radians) have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

Table VI. Nonbonded Contacts (<3.75 Å and Excluding Hydrogen Atoms) for Fe(TPP)(t-BuNC)₂·2(toluene)

C(2)-SC(5)	3.661 (3)	C(19)-C(A5)	3.593 (3)
C(3)-IC(5)	3.653 (4)	IC(1)-C(A5)	3.716 (3)
C(3)-SC(14)	3.732 (4)	IN(1)-C(A5)	3.725 (3)
C(4)-SC(14)	3.703 (3)	IC(3)-SC(2)	3.641 (4)
N(2)-C(C5)	3.648 (3)	IC(3)-C(D3)	3.735 (4)
C(6)-C(C5)	3.680 (3)	IC(4)-C(D4)	3.573 (3)
C(6)-C(C6)	3.728 (3)	IC(4)-C(A3)	3.594 (3)
C(7)-C(C5)	3.489 (3)	IC(6)-SC(13)	3.711 (3)
C(7)-C(C6)	3.663 (3)	IN(2)-SC(13)	3.529 (3)
C(7)-C(D3)	3.730 (3)	IC(10)-C(B4)	3.736 (4)
C(8)-C(C5)	3.311 (3)	C(A3)-SC(1)	3.494 (2)
C(8)-C(C4)	3.727 (3)	C(A3)-SC(2)	3.686 (3)
C(9)-C(C5)	3.403 (3)	C(A4)-SC(2)	3.601 (3)
C(12)-SC(9)	3.654 (3)	C(B2)-SC(9)	3.733 (3)
C(13)-C(B5)	3.624 (3)	C(B5)-C(C2)	3.705 (2)
C(13)-SC(14)	3.733 (4)	C(C3)-C(C4)	3.629 (2)
N(4)-C(A5)	3.685 (3)	C(C3)-SC(11)	3.662 (2)
C(16)-C(A5)	3.712 (3)	C(C4)-C(C4)	3.538 (4)
C(17)-C(A5)	3.656 (3)	C(D3)-SC(6)	3.671 (3)
C(18)-C(A5)	3.580 (3)	C(D4)-SC(6)	3.583 (3)
C(18)-SC(7)	3.713 (4)		

linear. Not only do the Fe–C–N bond angles depart by more than 10° and the C–N–C bond angles by more than 15° from 180° but the isocyanide groups are tilted such that the Fe–C vectors are nonparallel to the perpendicular to the porphyrinato plane. The angles of tilt are 5.8° and 5.9° for t-BuNC (A)

and t-BuNC (B), respectively. For the following reasons we believe that these deviations arise from crystal packing effects; that is, the geometry observed does not pertain to an isolated molecule. First, bending of the Fe–C–N and C–N–C angles may be avoided by tilting. Second, if the Fe–CNC moieties are made linear and perpendicular to the normal to the porphyrinato plane, intermolecular contacts become unrealistically close (see Table XII). Third, the group which shows the greatest bending, t-BuNC (A), also shows the larger number of intermolecular contacts less than 3.75 Å, contacts which become shorter upon idealization of the Fe–CNR geometry. Fourth, inspection of Figure 4 shows that above the methyl carbon atoms of each t-BuNC group resides, coplanarly, a toluene solvate molecule. Thus while purely electronic considerations for the observed geometry cannot be excluded, for the reasons noted we believe that the nonlinearity is a crystal packing phenomenon.

Nonbonded intramolecular contacts appear to be responsible for the somewhat larger scatter of the isocyanide N–C–CH₃ bond angles about their mean than that predicted from the estimated standard deviation of an individual bond angle. Specifically and more notably for t-BuNC (A), the IN(1)–IC(2)–IC(5) bond angle is nearly 2° more obtuse than the other two analogous angles. Opening up of the bond angle relieves the intramolecular porphyrin–IC(5) contact (observed separation 3.65 Å, see also Figure 2).

Table VIII. Bond Distances for Fe(TPP)(*t*-BuNC)₂·2(toluene)₂ (Å)

atoms	distance	avᵃ	atoms	distance	av
Fe-N(1)	2.000 (2)	2.005 (4)	C(1)-C(20)	1.399 (4)	1.393 (5)
Fe-N(2)	2.010 (2)		C(4)-C(5)	1.384 (4)	
Fe-N(3)	2.005 (2)		C(6)-C(5)	1.394 (4)	
Fe-N(4)	2.004 (2)		C(9)-C(10)	1.395 (4)	
Fe-IC(1)	1.901 (3)	1.901 (3)	C(11)-C(10)	1.391 (4)	
Fe-IC(6)	1.900 (3)		C(14)-C(15)	1.400 (4)	
N(1)-C(1)	1.377 (3)	1.377 (3)	C(16)-C(15)	1.392 (4)	
N(1)-C(4)	1.375 (3)		C(19)-C(20)	1.387 (4)	
N(2)-C(6)	1.377 (3)		C(5)-C(A1)	1.507 (3)	1.506 (3)
N(2)-C(9)	1.378 (3)		C(10)-C(B1)	1.510 (3)	
N(3)-C(11)	1.376 (3)		C(15)-C(C1)	1.502 (3)	
N(3)-C(14)	1.375 (3)		C(20)-C(D1)	1.506 (3)	
N(4)-C(16)	1.378 (3)		IC(1)-IN(1)	1.152 (3)	1.157 (7)
N(4)-C(19)	1.377 (3)		IC(6)-IN(2)	1.162 (3)	
C(1)-C(2)	1.439 (4)	1.440 (4)	IN(1)-IC(2)	1.467 (3)	1.463 (6)
C(3)-C(4)	1.442 (4)		IN(2)-IC(7)	1.459 (3)	
C(6)-C(7)	1.437 (4)		IC(2)-IC(3)	1.522 (4)	1.516 (6)
C(8)-C(9)	1.440 (4)		IC(2)-IC(4)	1.511 (4)	
C(11)-C(12)	1.444 (4)		IC(2)-IC(5)	1.511 (4)	
C(13)-C(14)	1.440 (4)		IC(7)-IC(8)	1.513 (4)	
C(16)-C(17)	1.436 (4)		IC(7)-IC(9)	1.516 (4)	
C(18)-C(19)	1.445 (4)		IC(7)-IC(10)	1.524 (4)	
C(2)-C(3)	1.342 (4)	1.344 (4)			
C(7)-C(8)	1.346 (4)				
C(12)-C(13)	1.345 (4)				
C(17)-C(18)	1.343 (4)				

ᵃ The standard deviation in parentheses is the larger of that calculated for an individual parameter from the inverse matrix or of that calculated for an individual observation on the assumption that the values averaged are from the same population.

Table IX. Bond Angles for [Fe(TPP)(*t*-BuNC)₂]·2(toluene) (Deg)

atoms	angle	avᵃ	atoms	angle	av	atoms	angle	av
N(1)-Fe-N(2)	90.37 (9)	90.0 (7)	C(1)-N(1)-C(4)	105.8 (2)	105.7 (3)	N(2)-C(9)-C(10)	125.3 (2)	125.7 (4)
N(2)-Fe-N(3)	89.48 (8)		C(6)-N(2)-C(9)	105.3 (2)		N(3)-C(11)-C(10)	126.1 (2)	
N(3)-Fe-N(4)	90.76 (9)		C(11)-N(3)-C(14)	105.9 (2)		N(3)-C(14)-C(15)	125.4 (2)	
N(4)-Fe-N(1)	89.39 (9)		C(16)-N(4)-C(19)	105.6 (2)		N(4)-C(16)-C(15)	125.5 (2)	
N(1)-Fe-N(3)	179.84 (8)	179.5 (5)	N(1)-C(1)-C(2)	109.9 (2)	110.0 (2)	N(4)-C(19)-C(20)	126.0 (2)	
N(2)-Fe-N(4)	179.25 (8)		N(1)-C(4)-C(3)	109.9 (2)		C(4)-C(5)-C(6)	124.3 (2)	124.2 (6)
IC(1)-Fe-N(1)	91.3 (1)		N(2)-C(6)-C(7)	110.3 (2)		C(9)-C(10)-C(11)	123.9 (2)	
IC(1)-Fe-N(2)	84.0 (1)		N(2)-C(9)-C(8)	110.3 (2)		C(14)-C(15)-C(16)	124.9 (2)	
IC(1)-Fe-N(3)	88.6 (1)		N(3)-C(11)-C(12)	109.7 (2)		C(19)-C(20)-C(1)	123.5 (2)	
IC(1)-Fe-N(4)	95.3 (1)		N(3)-C(14)-C(13)	110.1 (2)		IC(1)-IN(1)-IC(2)	159.1 (3)	
IC(6)-Fe-N(1)	95.7 (1)		N(4)-C(16)-C(17)	110.1 (2)		IC(6)-IN(2)-IC(7)	165.2 (2)	
IC(6)-Fe-N(2)	91.8 (1)		N(4)-C(19)-C(18)	109.8 (2)		IN(1)-IC(2)-IC(3)	106.3 (2)	107.4 (11)
IC(6)-Fe-N(3)	84.4 (1)		C(1)-C(2)-C(3)	107.3 (2)		IN(1)-IC(2)-IC(4)	106.8 (2)	
IC(6)-Fe-N(4)	88.9 (1)		C(2)-C(3)-C(4)	107.1 (2)		IN(1)-IC(2)-IC(5)	108.7 (2)	
IC(1)-Fe-IC(6)	171.9 (1)		C(6)-C(7)-C(8)	107.3 (2)		IN(2)-IC(7)-IC(8)	107.8 (2)	
Fe-N(1)-C(1)	127.8 (2)	127.2 (5)	C(7)-C(8)-C(9)	106.9 (2)		IN(2)-IC(7)-IC(9)	108.3 (2)	
Fe-N(1)-C(4)	126.5 (2)		C(11)-C(12)-C(13)	107.2 (2)	107.2 (2)	IN(2)-IC(7)-IC(10)	106.2 (2)	
Fe-N(2)-C(6)	126.9 (2)		C(12)-C(13)-C(14)	107.0 (2)		IC(3)-IC(2)-IC(4)	111.6 (2)	111.5 (3)
Fe-N(2)-C(9)	127.8 (2)		C(16)-C(17)-C(18)	107.2 (2)		IC(3)-IC(2)-IC(5)	111.8 (2)	
Fe-N(3)-C(11)	127.3 (2)		C(17)-C(18)-C(19)	107.2 (2)		IC(4)-IC(2)-IC(5)	111.3 (2)	
Fe-N(3)-C(14)	126.7 (2)		N(1)-C(1)-C(20)	125.7 (2)		IC(8)-IC(7)-IC(9)	111.9 (3)	
Fe-N(4)-C(16)	126.7 (2)		N(1)-C(4)-C(5)	126.5 (2)		IC(8)-IC(7)-IC(10)	111.2 (2)	
Fe-N(4)-C(19)	127.7 (2)		N(2)-C(6)-C(5)	125.4 (2)		IC(9)-IC(7)-IC(10)	111.1 (3)	
Fe-IC(1)-IN(1)	168.1 (2)							
Fe-IC(6)-IN(2)	169.9 (2)							

ᵃ See footnote to Table VIII.

Fe(TPP)(*t*-BuNC)₂ as a Model for Hemoprotein Isocyanide Complexes. A linear Fe-CNR geometry is observed for a wide range of ligand systems providing the isocyanide ligand is not in a bridging mode or the iron atom is not formally zerovalent (see Table XI). Hence, regarding the Fe-CNR geometry observed for Fe(TPP)(*t*-BuNC)₂ as being essentially linear, a similar geometry may be expected for a complex where one of the *t*-BuNC ligands is replaced by a nitrogenous base, such as 1-methylimidazole, even though a strong σ-donor but weak π-acceptor ligand, such as 1-methylimidazole or pyridine, will enhance π back-bonding from the metal dπ to isocyanide π* (C-N) orbitals.

By analogy, in the absence of steric effects, a linear Fe-CNR geometry may be expected for myoglobin- or hemo-globin-isocyanide complexes. However, the steric constraints provided by the distal histidine group will probably lead to some bending of the Fe-CNR group and they will almost certainly lead to the CNR group being tilted from the normal to the heme plane in an entirely analogous way to that suggested for carbonylhemoglobins[4,12,13] where the ligand, CO, is considerably less bulky.

For an Fe(TPP)(*t*-BuNC)(1-MeIm) complex, an Fe-C separation considerably less than the 1.901-Å separation observed for Fe(TPP)(*t*-BuNC)₂ complex is expected by analogy with the related dioxygen, carbonyl, and nitrosyl complexes (see Table X).

Conformation of the Porphyrin. The porphyrinato skeleton is in the saddle conformation (i.e., D_{2d} symmetry) although

Table X. Selected Parameters for the Coordination Sphere of Some Metalloporphyrins

compound	Fe–N(porph)	Fe–N(ax)	Fe–L[a]	Σ[b]
Fe(TpivPP)(O$_2$)(1-MeIm)[c]	1.98 (1)	2.07 (2)	1.75 (2)	3.82
Fe(TpivPP)(O$_2$)(2-MeIm)[d]	1.996 (4)	2.107 (4)	1.898 (7)	4.01
Fe(TpivPP)(CO)(1-MeIm)[e]	2.00	2.06 (2)	1.61 (2)	3.67
Fe(TPP)(CO)(py)[f]	2.02 (3)	2.10 (1)	1.77 (2)	3.87
Fe(TPP)(NO)(1-MeIm)[g]	2.008 (9)	2.180 (4)	1.743 (4)	3.92
Fe(TPP)(1-MeIm)$_2$[h]	1.999 (4)	2.016 (5)		4.03
Fe(TPP)(pip)$_2$[i]	2.004 (4)	2.127 (3)		4.25
Fe^{III}(TPP)(Im)$_2$$^+$[j]	1.989 (5)	1.957 (4)		3.95
		1.991 (5)		
Fe(TPP)(t-BuNC)$_2$[k]	2.005 (4)	1.901 (3)		3.80

[a] L = O$_2$, CO, NO. [b] The sum of the axial bond lengths. [c] Reference 3. [d] G. B. Jameson, F. S. Molinaro, J. A. Ibers, J. P. Collman, J. I. Brauman, E. Rose, and K. S. Suslick, *J. Am. Chem. Soc.*, **100**, 6769 (1978). [e] Reference 79. [f] Reference 4. [g] Reference 5. [h] Reference 82. [i] L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2073 (1972). [j] D. M. Collins, R. Countryman, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2066 (1972). [k] This work.

Table XI. Parameters Involving the Isocyanide Ligand for Iron–Isocyanide Complexes[a]

compound	Fe–C, Å	C–N, Å	FeCN, deg	CNC, deg
Fe^{II}(MeNC)$_6$][Fe^{III}Cl$_4$]$_2$[b]	1.874(4)	1.166(12)	178.5(10)	178.8(3)
[Fe^{II}Cl(PPh(OEt)$_2$)$_3$((4-tolyl)NC)$_2$]-[ClO$_4$][c]	1.73(1)	1.23(1)	177(3)	172(2)
[Fe^{II}Cl(PPh$_3$)$_2$((4-tolyl)NC)$_3$][Fe^{III}Cl$_4$][d]	1.867(8)	1.145(5)	176.7(20)	176.6(20)
	1.813(4)	1.158(5)	176.8(7)	167.1(8)[e]
Fe(4-Cl-PhNC)$_2$(μ-S$_2$CNEt$_2$)$_2$ZnI$_2$[f]	1.832(17)	1.151(22)	177.6(15)	172.5(17)
Fe$_2$(Cp)$_2$(CO)$_3$(t-BuNC)[g]	1.81(1)	1.16(1)	178.5(8)	171.5(9)
Fe(t-BuNC)$_5$[h,i]	1.811(9)	1.21(1)	177.6(8)	135.0(16)
	1.823(17)	1.19(1)	177.1(8)	154.9(46)
	1.838(8)	1.18(2)	177.0(25)	169.4(54)
Fe$_2$(Cp)$_2$(CO)$_2$(μ-MeNC)$_2$[j]	1.937(14)	1.221(7)	139.1(26)	125.5(19)
Fe$_2$(Cp)$_2$(CO)$_2$(μ-CO)(μ-PhNC)[k]	1.90		(bent)	131
Fe(TPP)(t-BuNC)$_2$[l]	1.901(3)	1.157(7)	169.0(13)	162.2(43)

[a] See footnote to Table VIII. [b] Reference 16. [c] Reference 18. [d] Reference 20. [e] For the (4-tolyl)NC trans to Cl. [f] Reference 19. [g] Reference 21. [h] Geometry is distorted trigonal bipyramidal. The first entry is for two out of three radial t-BuNC; the second for an axial t-BuNC; the third for the remaining axial and radial t-BuNC. [i] Personal communication, J. A. K. Howard. There are two independent molecules in the unit cell. [j] Reference 23. [k] Reference 24. [l] This work.

Table XII. Comparison of Close Contacts for the Observed t-BuNC and for Linear and Perpendicular t-BuNC Geometry (Å)

atoms	distance[a]		atoms	distance[a]	
IC(1)–C(A5)	3.72	3.54	IC(6)–SC(13)		3.60
			IN(2)–SC(13)	3.53	3.18
IN(1)–C(A5)	3.73	3.19	IN(2)–SC(14)		3.41
IN(1)–C(A6)		3.46	IN(2)–SC(8)		3.52
IC(2)–C(A5)		3.31	IC(7)–SC(13)		3.22
IC(2)–SC(3)		3.39	IC(7)–SC(8)		3.29
IC(2)–C(A6)		3.44	IC(7)–SC(14)		3.49
IC(2)–SC(4)		3.69			
CH$_3$–solvate		2.27[b]	CH$_3$–solvate		2.42[b]

[a] First entry is the observed separation; second entry is the calculated separation for a linear and perpendicular t-BuNC geometry. [b] Numerous contacts less than 3.2 Å; only the closest intermolecular contact is quoted. Unreasonably close contacts with neighboring TPP units are also created.
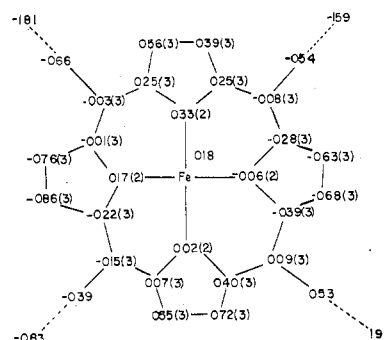

Figure 5. Displacements of atoms from the least-squares plane for the 24-atom porphyrinato skeleton. Estimated standard deviations in parentheses are given only for those atoms included in the calculation of the plane. The appropriate atom labels may be obtained from Figure 3; the porphyrinato skeletons are identically oriented.

displacements of atoms from the least-squares plane for the 24-atom porphyrinato core are fairly small (Figure 5). Three of the four phenyl substituents are angled "down"; the fourth is angled "up" (Figure 5). This may be correlated with the scatter in the Fe–N$_p$ distances and N$_p$–Fe–N$_p$ angles.

The pyrrole rings are planar to within 0.011 Å and their geometry is also typical.[79] Despite the presence of two identical axial ligands, a small doming of the porphyrinato skeleton is observed (0.011 Å). Again, crystal packing effects may be invoked. The dihedral angles between the phenyl rings and porphyrinato skeleton are, as is commonly observed, well removed from 90°. More pronounced rotations have been observed.[83] Tables XIII and XIV summarize parameters describing selected least-squares planes and the dihedral angles between them.

Bonding Electron Density in the Porphyrinato Skeleton. A final difference Fourier synthesis was calculated with sections parallel to the porphyrinato skeleton. Fourfold symmetry was apparent, with residual electron density being concentrated in interatomic regions. To reduce the effects of random noise, the map was averaged assuming fourfold symmetry about the iron atom. A plot of this averaged map is shown in Figure 6. The lack of very high angle data,[84–89] precludes a rigorous interpretation of this map. However, two qualitative features are apparent. First, the maxima of electron density, which are concentrated in interatomic regions, lie close to but not exactly on the interatomic vectors. This is consistent with the now-accepted notion of bent σ bonds in strained rings. Second, around the metal atom there is a hole along the Fe–N vector and a saddle between such vectors. Such a pattern is expected for a $(t_{2g})^6(e_g)^0$ electronic configuration of a low-spin iron(II) system. The large positive peak at the iron position and the negative shell around it may reflect the infelicities in the

Table XIII. Least-Squares Planes for Fe(TPP)(t-BuNC)$_2$[a]

name	coefficients $Ax + By + Cz - D = 0$[a]				atoms defining the plane displacement[b]						displacement of other atoms[b]
	A	B	C	D							
I	17.033	−4.337	−11.595	−6.939	N(1) 006 (2)	N(2) −006 (2)	N(3) 006 (2)	N(4) −006 (2)			Fe 007
II	16.904	−4.456	−11.627	−6.956	C(5) −007 (3)	C(10) 007 (3)	C(15) −007 (3)	C(20) 007 (3)			Fe 022
pyrrole-1	17.035	−4.360	−11.568	−6.942	N(1) 006 (2)	C(1) −011 (3)	C(2) 010 (3)	C(3) −003 (3)	C(4) −004 (3)		Fe 008
pyrrole-2	17.004	−4.122	−11.833	−6.886	N(2) 003 (2)	C(6) −003 (3)	C(7) 001 (3)	C(8) 002 (3)	C(9) −003 (3)		Fe −027
pyrrole-3	16.487	−4.710	−11.843	−6.998	N(3) 001 (2)	C(11) −000 (3)	C(12) −001 (3)	C(13) 001 (3)	C(14) −001 (3)		Fe 074
pyrrole-4	16.963	−4.887	−11.086	−6.871	N(4) −004 (2)	C(16) 005 (3)	C(17) −001 (3)	C(18) −003 (3)	C(19) 006 (3)		Fe −094
phenyl-A	14.495	9.500	0.793	−1.427	C(A1) 0	C(A2) 0	C(A3) 0	C(A4) 0	C(A5) 0	C(A6) 0	
phenyl-B	2.589	−2.615	18.653	1.715	C(B1) 0	C(B2) 0	C(B3) 0	C(B4) 0	C(B5) 0	C(B6) 0	
phenyl-C	16.497	8.321	−2.656	−2.570	C(C1) 0	C(C2) 0	C(C3) 0	C(C4) 0	C(C5) 0	C(C6) 0	
phenyl-D	0.734	−2.589	18.917	2.223	C(D1) 0	C(D2) 0	C(D3) 0	C(D4) 0	C(D5) 0	C(D6) 0	
porphyrin	16.916	−4.431	−11.638	−6.950	see Figure 5						

[a] The plane is in crystal coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965). [b] The displacement in A is generated by placing a decimal point in front of the first digit.

Table XIV. Angles between Planes for Fe(TPP)(t-BuNC)$_2$·(toluene)[a]

	porphyrin	I	pyrrole-1	pyrrole-2	pyrrole-3	pyrrole-4	phenyl-A	phenyl-B	phenyl-C	phenyl-D
porphyrin		0.6	0.5	1.5	1.8	2.7	76.7	111.2	67.7	115.4
I			0.1	1.2	2.4	2.9				
pyrrole-1				1.3	2.3	2.8				
pyrrole-2					3.0	4.1				
pyrrole-3						2.8				

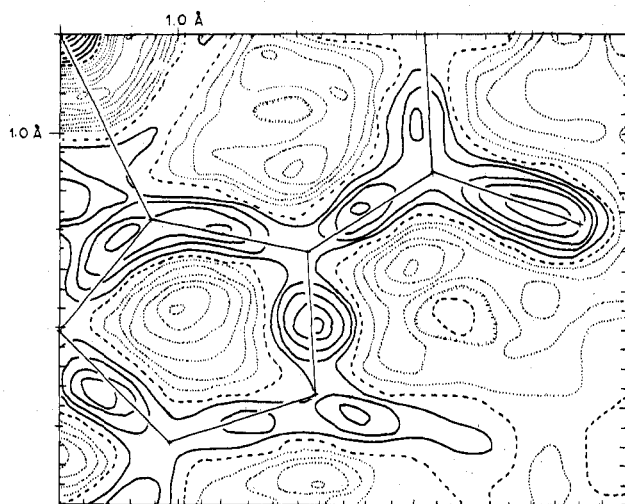[a] See Table XIII for definition of planes.

Figure 6. Residual electron density in the porphyrinato plane. Fourfold symmetry has been assumed and the unique quadrant is shown together with the porphyrinato skeleton. Contours are drawn at intervals of approximately 0.035 e/Å^3. The dashed line is the zero contour; positive contours are solid lines; negative contours are dotted lines. The calculated error is 0.006 e/Å^3.

scattering model for iron. That the bond of highest order does not have the highest peak is not an uncommon feature; reasons for this have been discussed by Coppens.[90]

A concentration of electron density in the C≡N interatomic region is observed for both t-BuNC ligands but there is, as previously observed with triple bonds,[88,89] no sign of a four-leaf clover pattern indicative of orthogonally oriented π bonds.

Summary

The structure of Fe(TPP)(t-BuNC)$_2$·2(toluene) has been precisely determined. Both Fe–CNR groups have essentially linear geometry although the large distortions from linearity of up to 12° at the coordinated carbon atom and up to 21° at the nitrogen atom suggest that the isocyanide ligand is susceptible to crystal packing influences. A similar geometry is expected to pertain to the isocyanide adducts of hemoproteins such as myoglobin.

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(14) Abbreviations: TPP, *meso*-tetraphenylporphyrinato; Im, imidazole; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; *t*-BuNC, *tert*-butyl isocyanide; 4-tolylNC, 4-tolyl isocyanide; 4-ClPhNC, *p*-chlorophenyl isocyanide; py, pyridine; pip, piperidine; Cp, cyclopentadienyl; Ph, phenyl; Et, ethyl.

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