

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

Direct comparison can be made with the homologous Ru compound (2), and with $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NMe})_2$ (5) (Doedens, 1969). All three compounds possess the same molecular framework, with two NR nitrene ligands triply-bridging an approximately isosceles M_3 triangle, to which all CO ligands are attached terminally. A very similar arrangement is observed for $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NNCPh}_2)_2$ (Baikie & Mills, 1967), but insufficient details are available for a comparison of all the relevant geometrical features.

As is the case for both (2) and (5), the two $M-M$ bond lengths in (4) are significantly different. Comparison of all three structures suggests that the major cause of this asymmetry is the arrangement of the nine CO groups, rather than the orientation of the Ph rings in (2) and (4). In each case, the longer $M-M$ bond is the one with a staggered rather than eclipsed arrangement of CO ligands. The structures of (5) and (4) are remarkably similar in detail, (4) benefitting from higher precision. The differences between these and (2) can be attributed to the change in metal from Fe to Ru. Despite the minor nature of these differences, (2) and (4) are not isomorphous.

Because of the short $\text{N}\cdots\text{N}$ distance of 2.405 (11) Å in (2), some direct $\text{N}-\text{N}$ interaction was postulated, and an alternative description of the structural core is as an Ru_3N_2 trigonal-bipyramidal cluster, with two Ru atoms occupying axial sites. In the iron complexes, the shorter Fe-N bonds necessitate a correspondingly shorter $\text{N}\cdots\text{N}$, 2.301 (6) Å in the case of (4).

The geometry of the phenyl rings is normal, and the CO groups are essentially linear, with C-O 1.124 (3)–1.145 (3) Å and Fe-C-O 174.2 (2)–178.6 (2)°.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles for the ligands have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39698 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

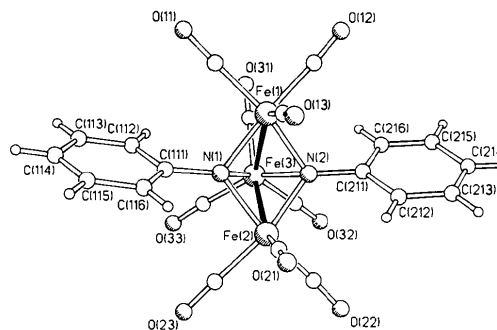


Fig. 1. Molecular structure of (4), showing the atom-labelling scheme. Carbonyl C atoms take the same numbers as the corresponding O atoms; H atoms take the same numbers as the corresponding phenyl C atoms.

We thank the Fonds der Chemischen Industrie for financial support.

References

- AIME, S., GERVASIO, G., MILONE, L., ROSSETTI, R. & STANGHELLINI, P. L. (1978). *J. Chem. Soc. Dalton Trans.* pp. 534–540.
- ALPER, H. & AMARATUNGA, S. (1980). *Tetrahedron Lett.* **21**, 2603–2604.
- BAIKIE, P. E. & MILLS, O. S. (1967). *Chem. Commun.* pp. 1228–1229.
- BHADURI, S., GOPALKRISHNAN, K. S., CLEGG, W., JONES, P. G., SHELDRIK, G. M. & STALKE, D. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1765–1767.
- BHADURI, S., GOPALKRISHNAN, K. S., SHELDRIK, G. M., CLEGG, W. & STALKE, D. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2339–2341.
- CLEGG, W. (1981). *Acta Cryst.* **A37**, 22–28.
- CLEGG, W., SHELDRIK, G. M., STALKE, D., BHADURI, S. & GOPALKRISHNAN, K. S. (1984). *Acta Cryst.* **C40**, 927–929.
- DOEDENS, R. J. (1969). *Inorg. Chem.* **8**, 570–574.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- SAPPA, E. & MILONE, L. (1973). *J. Organomet. Chem.* **61**, 383–388.
- SHELDRIK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1984). **C40**, 2047–2049

Di-2-pyridyl Ketone 2-Pyridylhydrazone, $\text{C}_{16}\text{H}_{13}\text{N}_5$

BY CHE FAUZIAH ISHAK, RONALD T. PFLAUM AND NORMAN C. BAENZIGER

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, USA

(Received 11 July 1984; accepted 8 August 1984)

Abstract. $M_r = 275.34$, orthorhombic, $P2_12_12_1$, $a = 7.9213$ (13), $b = 10.603$ (3), $c = 16.499$ (2) Å, $V = 1386$ Å³, $Z = 4$, $D_m = 1.304$ (10), $D_x = 1.320$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.91$ cm⁻¹, $F(000) =$

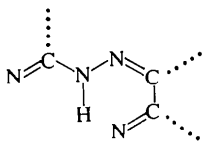
2304.2, $T = 295$ K, $R_w = 0.039$ for 1751 independent reflections. One pyridyl ring of the dipyridyl ketone group is coplanar with the 2-pyridylhydrazone moiety. The planarity results from the hydrogen bond formed

0108-2701/84/122047-03\$01.50

© 1984 International Union of Crystallography

between the N atom of one pyridyl ring from the dipyridyl ketone group and the hydrazone N atom which carries an H atom.

Introduction. Much interest has been shown in the chelating capability of the title compound (DPPH) for the spectrophotometric trace analyses of Zn^{II} , Cd^{II} , Cu^{II} and V^V . The chromogenic group of DPPH is the $N=CNH=CC=N$ chain as shown below.



DPPH acts as a bi- or tridentate chelating agent (Alexaki-Tzivanidou, 1977) and forms mono, bis, or tris complexes according to the preferred metal coordination number. Substituted hydrazones react slowly with metal ions to form very stable chelate complexes. It has long been assumed that chelation is reasonably slow owing to the necessary rupture of the hydrogen bond assumed to be present in the free ligand before it can act as a bidentate or tridentate ligand. The elucidated structure shows planarity resulting from hydrogen bonding. The structure confirms the long-used explanation of complex formation, and provides a base for comparing the structural parameters of the ligand when bound to a metal ion.

Experimental. DPPH was synthesized by refluxing for 8 h an ethanolic solution of equimolar quantities (0.4 M) of di-2-pyridyl ketone and 2-hydrazinopyridine (both from Aldrich Chemical Co., Inc.). The hydrazone was separated after cooling and recrystallized from ethanol (light-yellow needles: m.p. 410.7–411.7 K). D_m determined by the pycnometer (water) technique. A full sphere of X-ray intensity data ($2\theta = 3-45^\circ$, $h = -8$ to 8 , $k = -11$ to 11 , $l = -17$ to 17 ; 10 817 total reflections, 1823 independent in the Laue symmetry sense, 1751 with intensities greater than three standard deviations above background; reflections 400, 060, 008 measured after every 60 reflections were used to correct the data, max. and min. correction factors 1.08 and 0.96; average agreement among equivalent reflections 0.039) collected using a four-circle automated diffractometer, graphite-monochromated $Mo K\alpha$ X-rays and a stepped scan (7 to 15 steps centered on peak, basic step $0.10^\circ 2\theta$; step size varied to compensate for dispersion; background measured at ± 10 steps from peak maximum) (Baenziger, Foster, Howells, Howells, Vander Valk & Burton, 1977). Crystal $0.38 \times 0.50 \times 0.58$ mm. No absorption correction as the correction factor was expected to vary only from 1.03 to 1.05. Cell parameters determined from 12 reflections (between 34 and $45^\circ 2\theta$) carefully centered on the diffractometer. Structure solved by *MULTAN*

(Germain, Main & Woolfson, 1971), and refined by least-squares methods that minimized $\sum w(\Delta F)^2$ (program *LESQUI*, 1971). H atoms found from electron density difference maps. Non-hydrogen atoms were refined with anisotropic temperature parameters and H atoms with isotropic thermal parameters for a total of 242 parameters. In addition, an extinction parameter was varied to allow for apparent extinction effects in the low-angle data. Weights $w = 1/(S_F^2 + c^2F^2)$ where S_F is the estimated standard deviation in F from counting statistics and $c = 0.025$. In the last refinement cycle (1751 observed reflections) $(\Delta/\sigma)_{\max} = 0.04$. Max. and min. values in $\Delta\rho$ map within $\pm 0.4 e \text{ \AA}^{-3}$. $R = 0.027$, $R_w = 0.039$, $S = 1.10$. Scattering factors for C and N from *International Tables for X-ray Crystallography* (1974). H-atom scattering factors from Stewart, Davidson & Simpson (1965). All plots made by *ORTEP* (Johnson, 1965).

Discussion. Atom coordinates are given in Table 1 and the main bond distances and angles in Table 2.* The molecular structure of DPPH and the atom numbering system used are shown in Fig. 1(a). Fig. 1(b) shows an edge view of the molecule rotated approximately 90° from Fig. 1(a). Within the three pyridyl rings, no bond lengths or angles depart significantly from accepted aromatic values. The bond distances and angles in the three pyridyl rings are essentially equivalent. The absolute configuration of the molecule is unknown. (The anomalous corrections to the scattering factors when $Mo K\alpha$ radiation is used are small and the imaginary terms were neglected in the calculations. This neglect does not lead to significant errors in positional parameters.)

In a review of the internal bond angles at N in six-membered rings it was pointed out (Singh, 1965) that the angle is significantly larger than 120° when the N atom is carrying an extra-annular H atom, and less than 120° when the N atom has no H atom attached to it. DPPH conforms to this principle, as all the angles at the ring N atoms are $< 120^\circ$, and no protons were found attached to these N atoms. The N(2)–C(3) bond distance suggests that there is a fairly well localized double bond between these two atoms. The C–N bond length of $1.306(2) \text{ \AA}$ corresponds to a bond order of 1.6 (Wheatley, 1955).

The molecule of DPPH is not planar, as can be seen clearly in Fig. 1(b). One pyridyl ring of the dipyridyl ketone group is forced to twist out of the plane. The rest of the molecule, however, is nearly planar. The

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, additional intramolecular distances and angles and thermal-motion-corrected bond distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39683 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

planarity must certainly result from the interaction of the N(5*b*) from the (*b*) pyridyl ring of the dipyridyl ketone group and the proton H(1) attached to N(1) of the hydrazone group giving a non-linear N—H...N hydrogen-bond distance of 2.607 (2) Å (N—H...N angle 129°). The edge view shows a slight bend in the plane of the (*c*) pyridyl ring from the (*b*) pyridyl ring (dihedral angle 10.9°).

Table 1. Atomic parameters for DPPH

B values for nonhydrogen atoms are $\frac{1}{3}$ trace B_{ij} .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
N(1)	0.6575 (2)	0.6208 (1)	0.64183 (9)	3.8
N(2)	0.7288 (2)	0.5449 (1)	0.58588 (8)	3.3
N(5 <i>a</i>)	0.9767 (2)	0.2915 (1)	0.54482 (8)	3.9
N(5 <i>b</i>)	0.9072 (2)	0.5610 (1)	0.73734 (8)	3.8
N(5 <i>c</i>)	0.4329 (2)	0.7296 (1)	0.69111 (8)	4.1
C(3)	0.8704 (2)	0.4864 (1)	0.60096 (9)	3.0
C(4 <i>a</i>)	0.9236 (2)	0.4088 (1)	0.53006 (9)	3.1
C(6 <i>a</i>)	1.0151 (2)	0.2199 (2)	0.4799 (1)	4.5
C(7 <i>a</i>)	1.0004 (3)	0.2599 (2)	0.4021 (1)	4.6
C(8 <i>a</i>)	0.9481 (3)	0.3791 (2)	0.3878 (1)	4.5
C(9 <i>a</i>)	0.9084 (2)	0.4563 (2)	0.4517 (1)	3.8
C(4 <i>b</i>)	0.9701 (2)	0.4912 (1)	0.67630 (9)	3.0
C(6 <i>b</i>)	0.9957 (3)	0.5696 (2)	0.8063 (1)	4.4
C(7 <i>b</i>)	1.1476 (3)	0.5106 (2)	0.8182 (1)	4.7
C(8 <i>b</i>)	1.2129 (3)	0.4393 (2)	0.7562 (1)	4.6
C(9 <i>b</i>)	1.1249 (2)	0.4301 (2)	0.6841 (1)	3.9
C(4 <i>c</i>)	0.4953 (2)	0.6646 (1)	0.62905 (9)	3.3
C(6 <i>c</i>)	0.2740 (3)	0.7702 (2)	0.6837 (1)	4.5
C(7 <i>c</i>)	0.1759 (3)	0.7519 (2)	0.6172 (1)	4.8
C(8 <i>c</i>)	0.2437 (2)	0.6879 (2)	0.5515 (1)	4.4
C(9 <i>c</i>)	0.4059 (2)	0.6425 (1)	0.5570 (1)	3.7
H(1)	0.714 (2)	0.636 (2)	0.695 (1)	4.7 (4)
H(6 <i>a</i>)	1.053 (3)	0.134 (2)	0.489 (1)	6.2 (5)
H(7 <i>a</i>)	1.034 (3)	0.206 (2)	0.368 (1)	5.3 (5)
H(8 <i>a</i>)	0.935 (3)	0.414 (2)	0.339 (1)	5.4 (5)
H(9 <i>a</i>)	0.875 (2)	0.539 (2)	0.443 (1)	4.0 (4)
H(6 <i>b</i>)	0.947 (3)	0.621 (2)	0.851 (1)	5.0 (4)
H(7 <i>b</i>)	1.210 (3)	0.521 (2)	0.873 (1)	5.9 (5)
H(8 <i>b</i>)	1.314 (3)	0.394 (2)	0.765 (1)	5.7 (5)
H(9 <i>b</i>)	1.169 (3)	0.374 (2)	0.636 (1)	6.3 (5)
H(6 <i>c</i>)	0.232 (2)	0.813 (2)	0.728 (1)	3.8 (4)
H(7 <i>c</i>)	0.069 (3)	0.780 (2)	0.617 (1)	4.7 (4)
H(8 <i>c</i>)	0.173 (3)	0.674 (2)	0.496 (1)	6.4 (5)
H(9 <i>c</i>)	0.461 (3)	0.596 (2)	0.509 (1)	4.4 (4)

Table 2. Bond distances (Å) and angles (°) in DPPH

N(1)—N(2)	1.349 (2)	N(1)—H(1)	1.00 (2)
N(2)—C(3)	1.306 (2)	C(3)—C(4 <i>a</i>)	1.491 (2)
N(1)—C(4 <i>c</i>)	1.382 (2)	C(3)—C(4 <i>b</i>)	1.474 (2)
N(1)—N(5 <i>b</i>)	2.607 (2)	H(1)—N(5 <i>b</i>)	1.86 (2)
	Ring (<i>a</i>)	Ring (<i>b</i>)	Ring (<i>c</i>)
C(4)—N(5)	1.335 (2)	1.345 (2)	1.330 (2)
N(5)—C(6)	1.348 (2)	1.339 (2)	1.336 (3)
C(6)—C(8)	1.357 (3)	1.370 (3)	1.358 (3)
C(7)—C(8)	1.351 (3)	1.373 (3)	1.387 (3)
C(8)—C(9)	1.371 (3)	1.382 (3)	1.375 (3)
C(9)—C(4)	1.393 (2)	1.393 (3)	1.403 (2)
C(6)—H(6)	0.97 (2)	1.00 (2)	0.92 (2)
C(7)—H(7)	0.85 (2)	1.04 (2)	0.90 (2)
C(8)—H(8)	0.89 (2)	0.95 (2)	1.08 (2)
C(9)—H(9)	0.93 (2)	1.05 (2)	1.03 (2)
N(2)—N(1)—C(4 <i>c</i>)	119.0 (1)	C(3)—C(4 <i>a</i>)—N(5 <i>a</i>)	117.4 (1)
N(1)—N(2)—C(3)	120.8 (1)	C(3)—C(4 <i>b</i>)—N(5 <i>b</i>)	116.9 (1)
N(2)—C(3)—C(4 <i>a</i>)	110.8 (1)	N(1)—C(4 <i>c</i>)—N(5 <i>c</i>)	113.7 (2)
N(2)—C(3)—C(4 <i>b</i>)	127.2 (1)	C(3)—C(4 <i>a</i>)—C(9 <i>a</i>)	120.3 (1)
C(4 <i>a</i>)—C(3)—C(4 <i>b</i>)	122.0 (1)	C(3)—C(4 <i>b</i>)—C(9 <i>b</i>)	122.3 (1)
	Ring (<i>a</i>)	Ring (<i>b</i>)	Ring (<i>c</i>)
N(5)—C(4)—C(9)	122.2 (1)	120.9 (1)	123.4 (2)
C(4)—N(5)—C(6)	116.8 (2)	118.6 (2)	116.6 (2)
N(5)—C(6)—C(7)	123.8 (2)	123.4 (2)	124.5 (2)
C(6)—C(7)—C(8)	119.0 (2)	118.4 (2)	118.7 (2)
C(7)—C(8)—C(9)	119.6 (2)	119.3 (2)	118.8 (2)
C(8)—C(9)—C(4)	118.6 (2)	119.4 (2)	118.0 (2)

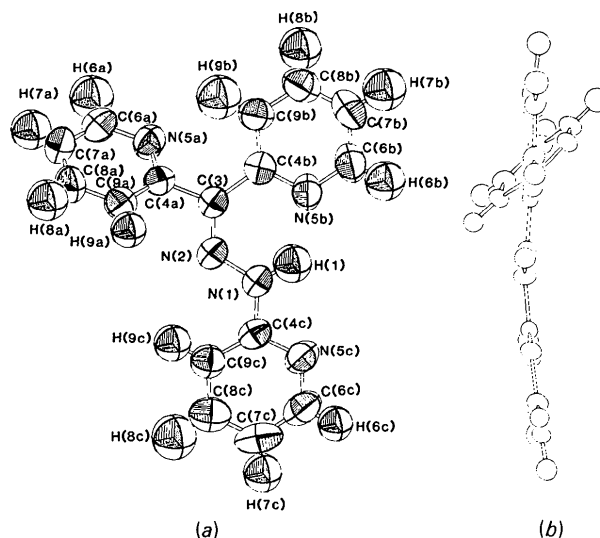


Fig. 1. (a) View of DPPH showing the atom labeling. (b) Edge view showing the planarity of the molecule.

The thermal-motion parameters of the non-hydrogen atom were fit by a model which assumed the whole molecule behaved as a rigid body, and the components of the tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were found which best reproduced the individual atomic vibrational ellipsoids. Assuming **S**=0 gave 0.0443 (13), 0.0400 (17), 0.0388 (15), -0.0035 (14), 0.0012 (12), 0.0038 (14) Å² for the components of **T** (11, 22, 33, 12, 13, 23) and 6.7 (7), 4.0 (8), 2.0 (6), -1.3 (5), -0.2 (4), 0.5 (4)° as the comparable components of **L**. Allowing for screw coupling of **T** and **L** did not significantly improve the fit. Using the values of **L** to correct the bond distances increased the values on average 0.002 Å (range 0.00 to 0.003 Å). It is clear from the values of **T** and **L** that the dominant contribution to the thermal motion is translational, and produces the rather small corrections to the bond lengths.

References

- ALEXAKI-TZIVANIDOU, H. (1977). *Microchem. J.* **22**, 388–395.
- BAENZIGER, N. C., FOSTER, B. A., HOWELLS, M., HOWELLS, R., VANDER VALK, P. & BURTON, D. J. (1977). *Acta Cryst.* **B33**, 2327–2329.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LESQUI (1971). Lawrence Berkeley Laboratory full-matrix least-squares computer program modified for local use by F. J. HOLLANDER.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WHEATLEY, P. J. (1955). *Acta Cryst.* **8**, 224–226.