

rigid body thermal parameters and the thermal ellipsoid of the anthracene molecule have real significance.

The final difference map of the TCNB molecule is presented in Fig. 6. There are maxima at the middle of the bonds, whereas minima appear at the middle of the C≡N bond and at both ends of the bonds. The height of the positive regions is approximately $0.18 \text{ e.}\text{\AA}^{-3}$ for $C_{ar}-C_{ar}$, $0.11 \text{ e.}\text{\AA}^{-3}$ for $C_{ar}-C$ and $0.10 \text{ e.}\text{\AA}^{-3}$ for $C_{ar}-H$; the minima range from -0.08 to $-0.20 \text{ e.}\text{\AA}^{-3}$. The systematic arrangement of the maxima and minima seems to suggest that electron density has moved to the centre of the bonds. In the middle of the C≡N bond no maximum appears as in the case of *cis*-1,2,3-tricyanocyclopropane (Hartman & Hirshfeld, 1966). This might be related to the fact that the C≡N bond length is shorter when measured with X-rays than when measured with neutrons or when determined spectroscopically (Little, Paulter & Coppens, 1971). But the section perpendicular to and through the midpoint of the C≡N bond shows the residual electron density surrounding the bond in the form of a torus.

The maximum is $0.07 \text{ e.}\text{\AA}^{-3}$ and lies at a distance of 0.7 \AA from the C≡N bond. It may be noted that the π -electron density calculation on the basis of a wave function of the form $\varphi(2p_x) = Nx \cdot \exp(-cr/2)$ (Coulson, 1961) shows a maximum of $0.12 \text{ e.}\text{\AA}^{-3}$ 0.70 \AA from the midpoint of the carbon and nitrogen atoms.

The calculations were carried out on the FACOM 270-30 computer at this Institute with a local version of the Universal Crystallographic Computation Pro-

gram System, UNICS (Crystallographic Society of Japan, 1967). This research was aided in part by a Scientific Research Grant of the Ministry of Education.

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The Crystal and Molecular Structure of Bis[bis(dicyclohexylphosphino)methane]nickel

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Bis[bis(dicyclohexylphosphino)methane]nickel, $\{[(C_6H_{11})_2P]_2CH_2\}_2Ni$, crystallizes in the space group $P2_1/c$ with the unit-cell constants $a = 19.404$ (5), $b = 12.193$ (5), $c = 22.310$ (6) \AA , $\beta = 100.41$ (3) $^\circ$, $Z = 4$, $D_c = 1.12 \text{ g.cm}^{-3}$. Integrated intensities of 5844 unique reflexions were collected at room temperature with a computer-controlled Siemens-Hoppe diffractometer, using Cu $K\alpha$ radiation. The structure was solved by a combination of direct and Fourier methods and refined by full-matrix least-squares calculations to a reliability index $R = 0.069$, using 3982 observed reflexions. The coordination around the nickel is distorted-tetrahedral. The presence of bent Ni-P bonds is indicated by comparison of the bond angles about the nickel atom with those of the ideal sp^3 hybridization. All cyclohexyl rings are in the chair conformation and bonded equatorially to the phosphorus.

Introduction

Low valent nickel is known to form phosphine-adducts of variable stoichiometry $Ni(PR_3)_n$, $n = 2, 3, 4$, (Wilke, Englert & Jolly, 1971; Jolly, Jonas, Krüger & Tsay,

1971; Heimbach, 1964), depending on experimental conditions and ligand properties. Structural determinations have been reported for $(PF_3)_4Ni$ (Marriott, Salthouse, Ware & Freeman, 1970; Almenningen, Andersen & Astrup, 1970) and in part for (piperidine-

$\text{PF}_2)_4\text{Ni}$ (Greenberg, Amendola & Schmutzler, 1963).

We have undertaken the structural determination of bis[bis(dicyclohexylphosphine)methane]nickel $\{[(\text{C}_6\text{H}_{11})_2\text{P}]_2\text{CH}_2\}_2\text{Ni}$ in order to obtain additional information on the coordination around the nickel atom in these complexes as well as to establish the steric arrangement of the ligand. These data are pertinent to our interest in catalytically active organometallic compounds.

Experimental

The title compound was prepared by Jonas (1971) in this institute by addition of a solution of the phosphine ligand to an ethereal solution of *t,t,t*-cyclododecatriene-nickel. Preliminary Weissenberg and precession photographs indicated that the crystals were monoclinic with the systematic absences $h0l$, $l=2n+1$, and $0k0$, $k=2n+1$, consistent with the space group $P2_1/c$ (C_{2h}^5 , No. 14).

A crystal of approximate dimensions $0.64 \times 0.72 \times 0.38$ mm was sealed in a capillary under dry argon and

was used for all subsequent X-ray studies. The crystal was mounted with the $[010]$ direction parallel to the φ axis of the diffractometer. Accurate unit-cell dimensions were obtained by a least-squares refinement using 2θ angles of 39 reflexions. These values were determined by $\theta/2\theta$ scans with a narrow receiving slit. The derived values are given with other information of the unit cell in Table 1.

Table 1. *Crystal data*

$\text{NiP}_4\text{C}_{50}\text{H}_{92}$	$a=19.404$ (5) Å
M. W. 876	$b=12.193$ (5) Å
$Z=4$	$c=22.310$ (6) Å
$D_c=1.12$ g.cm $^{-3}$	$\beta=100.41$ (3)°
Space group $P2_1/c$ (C_{2h}^5)	
$\mu=15.2$ cm $^{-1}$	

Integrated intensities for hkl and $\bar{h}kl$ reflexions ($2\theta < 120^\circ$, $\lambda=1.54178$ Å) were measured on a computer-controlled diffractometer (PDP-8+Siemens-Hoppe) by a modified five-step $\theta-2\theta$ scan method (Hoppe, 1965; Krüger, 1970). Each reflexion was scanned twice and stationary background measurements were taken at both ends of the scans. The scan width of each reflexion was treated as a function of θ ; the size of the counter aperture used, 0.4×1.0 mm, was determined photographically by the spot-size of some representative reflexions. The primary beam collimator, used in connection with a fine-focus tube with copper target, had a diameter of 1 mm. The crystal-to-counter distance was set to 16 cm.

A pre-measurement of the reflexion to be scanned allowed the computer to choose variable scanning times and, if the intensity was stronger than preset limits of the optimal counter capability, one of five nickel-foil attenuators of various width was automatically introduced into the primary beam.

A standard reflexion (0,0,10) was measured after every 20 reflexions and was used to detect any crystal decay or mispositioning. The five measurements for each reflexion were collected and punched automatically on cards with the corresponding Eulerian angles, filter number, measuring time and hkl values during the data collection procedure. A subsequent program scaled these data to a relative scale with the appropriate time and filter factors and applied approximate

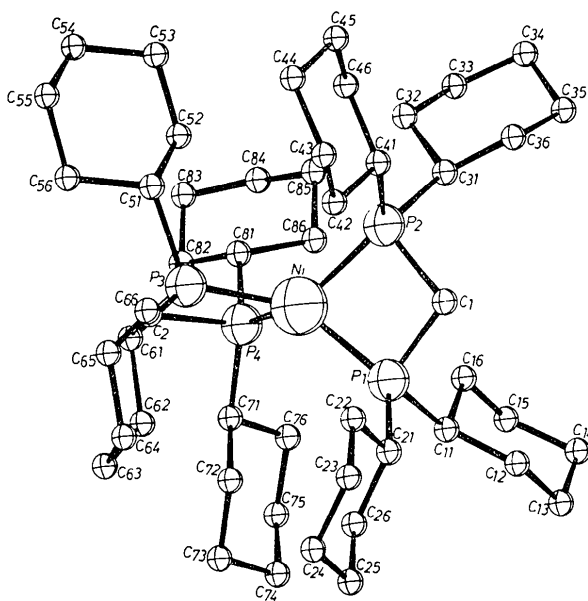


Fig. 1. The molecular structure, showing the numbering scheme used.

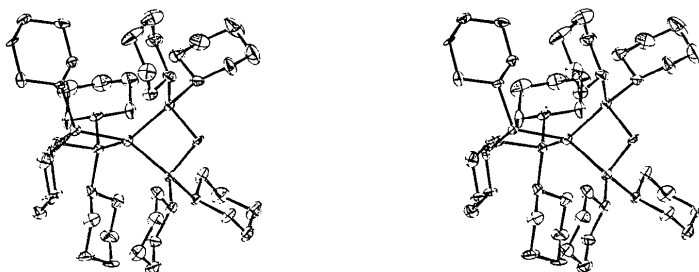


Fig. 2. Stereoscopic view of the molecule, oriented as in Fig. 1, showing the 50% probability thermal ellipsoids.

Table 2. Starting reflexions for the iterative symbolic addition procedure

<i>h</i>	<i>k</i>	<i>l</i>	Sign	<i>E</i>	Symb. Sign	Interactions
-5	6	8	+	3.06	A	35
-6	3	8	+	3.11	B	37
-6	4	9	+	3.38	C	31
-8	1	11	-	2.97	D	29
-3	2	1	+	2.87	E	25
1	3	14	-	2.56	F	31

decay correction factors based on the variation of the intensity of the monitoring reflexion. With the aid of the five intensity measurements, the program also determined and indicated reflexions that probably suffered from counter errors, severe mis-setting errors, or white-streak distortions. A standard data reduction was then carried out and reflexions with a net intensity of less than 25 counts were considered unobserved. Of the 5844 unique reflexions measured, 1862 were considered unobserved and omitted from the least-squares refinements. No absorption correction was applied to the data.

The structure was solved by applying iterative direct methods as programmed by Dewar (1968) and adapted to our computer system. A Wilson statistics plot indicated the scale factor and the overall temperature

factor which were used to compute a set of *E* values; the reflexions given in Table 2 were chosen as starting reflexions for the iterative symbolic addition procedure. After 7 cycles, in which the starting probability factor of 0.995 was lowered subsequently to 0.985, 428 signed

Table 3. Final atomic coordinates with their standard deviations ($\times 10^4$), and thermal parameters ($\times 10^3$)

	X	SD(X)	Y	SD(Y)	Z	SD(Z)	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
H 1	7565.	2.	659.	2.	177.	2.	29.	2.9	2.5	2.	2.	2.
P 1	665.	2.	957.	2.	127.	2.	27.	2.7	2.1	2.	1.	1.
P 2	6854.	2.	933.	2.	117.	2.	31.	3.1	2.6	2.	1.	1.
P 3	5692.	2.	1415.	2.	116.	2.	27.	2.7	2.2	2.	1.	1.
P 4	5844.	2.	1741.	2.	445.	2.	33.	3.3	2.9	2.	1.	1.
C 1	6823.	3.	574.	3.	972.	3.	28.	2.8	2.2	2.	1.	1.
C 2	5868.	3.	522.	3.	231.	3.	33.	3.3	2.7	2.	1.	1.
C 3	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 4	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 5	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 6	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 7	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 8	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 9	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 10	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 11	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 12	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 13	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 14	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 15	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 16	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 17	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 18	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 19	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 20	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 21	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 22	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 23	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 24	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 25	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 26	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 27	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 28	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 29	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 30	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 31	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 32	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 33	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 34	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 35	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 36	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 37	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 38	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 39	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 40	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 41	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 42	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 43	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 44	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 45	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 46	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 47	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 48	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 49	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 50	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 51	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 52	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 53	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 54	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 55	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 56	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 57	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 58	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 59	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 60	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 61	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 62	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 63	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 64	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 65	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 66	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 67	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 68	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 69	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 70	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 71	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 72	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 73	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 74	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 75	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 76	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 77	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 78	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 79	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 80	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 81	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 82	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 83	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 84	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 85	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 86	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 87	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 88	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 89	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 90	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 91	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 92	6823.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 93	6511.	3.	2248.	3.	1247.	3.	21.	2.1	1.7	2.	1.	1.
C 94	6823.											

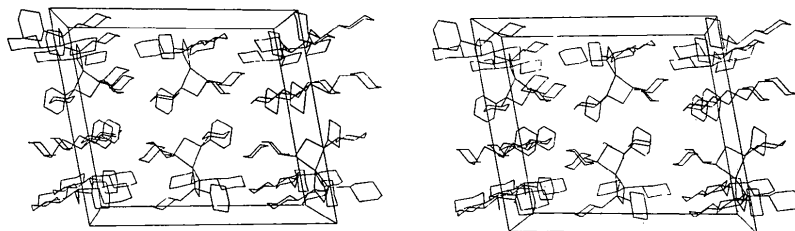


Fig. 5. Stereoscopic view of the unit cell along the $-b$ axis. The c axis is horizontal.

reflexions with E values greater than 1.38 were generated. The signs given in Table 2 were obtained from the 292 symbol equivalences at a probability level of 0.85.

An E map computed with these signs showed the nickel atom and two of the phosphorus atoms of the molecule. The positions of the remaining two phosphorus atoms were not discernible, because of ghost peaks due to Fourier ripples around the heavy atom. A Fourier map based on phases produced by only these three initial atoms was used to locate the remaining two phosphorus atoms. A subsequent Fourier map yielded the atomic positions for the remaining 50 carbon atoms.

Five cycles of full-matrix least-squares refinement on positional and isotropic temperature parameters gave a conventional R value of 12.0%. Five additional cycles of anisotropic temperature factor refinement reduced the R value to 10.5%. Hydrogen atom positions of all six-membered rings were then calculated based on the positions of the carbon atoms of the cyclohexyl groups and checked against positions found in a difference Fourier map. The hydrogen atom positions at the two methylene groups were determined solely from a difference Fourier map.

A final R value of 6.9% was achieved when the hydrogen atoms were included in 5 additional cycles of anisotropic refinement (hydrogen atoms refined isotropically). The resulting positional and thermal parameters are given in Table 3. A comparison of the final signed structure factors showed that only 18 of the 434 signs obtained by the direct method were incorrectly determined. The $|F_o|$ and $|F_c|$ based on the final parameters are obtainable as Supplementary Publication No. SUP 30005 (22 pp., 1 microfiche).*

Atomic scattering factors used were those of Cromer & Waber (1965) for the heavier atoms, and those of Stewart, Davidson & Simpson (1965) for hydrogen. The real parts of the anomalous dispersion for nickel and phosphorus were corrected for with values given by Cromer & Liberman (1970). In all our least-squares refinements, the weighting scheme used was $w = 1.0/\sigma^2(|F_o|)$.

The molecular structure with its numbering scheme is illustrated in Fig. 1. Fig. 2 shows the 50% probability thermal ellipsoids. Intramolecular distances and angles are listed in Table 4. The estimated standard deviations were calculated from the inverse matrix of the last least-squares cycle. A final difference Fourier map indicated no extra density larger than $1.5 \text{ e.}\text{\AA}^{-3}$.

Table 4. Intramolecular distances and angles

(a) Bond lengths (\AA) and standard deviations ($\times 10^3$)

Ni—P(1)	2.214 (2)
Ni—P(2)	2.215 (2)
Ni—P(3)	2.193 (2)
Ni—P(4)	2.218 (2)
P(1)—C(1)	1.861 (6)
P(1)—C(11)	1.877 (7)
P(1)—C(21)	1.902 (7)
P(2)—C(1)	1.866 (6)
P(2)—C(31)	1.865 (7)
P(2)—C(41)	1.872 (7)
P(3)—C(2)	1.862 (7)
P(3)—C(51)	1.892 (6)
P(3)—C(61)	1.883 (7)
P(4)—C(2)	1.881 (7)
P(4)—C(71)	1.885 (7)
P(4)—C(81)	1.887 (7)
C(11)—C(12)	1.539 (10)
C(12)—C(13)	1.526 (11)
C(13)—C(14)	1.531 (11)
C(14)—C(15)	1.532 (12)
C(15)—C(16)	1.534 (10)
C(16)—C(11)	1.518 (10)
C(21)—C(22)	1.507 (10)
C(22)—C(23)	1.548 (10)
C(23)—C(24)	1.511 (11)
C(24)—C(25)	1.496 (11)
C(25)—C(26)	1.559 (10)
C(26)—C(21)	1.519 (9)
C(31)—C(32)	1.543 (10)
C(32)—C(33)	1.517 (11)
C(33)—C(34)	1.543 (12)
C(34)—C(35)	1.533 (13)
C(35)—C(36)	1.529 (12)
C(36)—C(31)	1.527 (10)
C(41)—C(42)	1.545 (11)
C(42)—C(43)	1.544 (11)
C(43)—C(44)	1.537 (12)
C(44)—C(45)	1.506 (12)
C(45)—C(46)	1.517 (11)
C(46)—C(41)	1.546 (10)
C(51)—C(52)	1.530 (9)
C(52)—C(53)	1.543 (9)
C(53)—C(54)	1.525 (11)
C(54)—C(55)	1.494 (10)
C(55)—C(56)	1.548 (9)
C(56)—C(51)	1.569 (9)

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Table 4 (cont.)

C(61)–C(62)	1.540 (9)	C(15)–C(16)–C(11)	111.4 (6)
C(62)–C(63)	1.524 (10)	C(16)–C(11)–C(12)	110.4 (6)
C(63)–C(64)	1.489 (10)	C(21)–C(22)–C(23)	111.8 (6)
C(64)–C(65)	1.527 (10)	C(22)–C(23)–C(24)	111.2 (6)
C(65)–C(66)	1.524 (10)	C(23)–C(24)–C(25)	112.4 (6)
C(66)–C(61)	1.506 (10)	C(24)–C(25)–C(26)	111.3 (6)
C(71)–C(72)	1.537 (10)	C(25)–C(26)–C(21)	110.9 (6)
C(72)–C(73)	1.530 (10)	C(26)–C(21)–C(22)	112.4 (6)
C(73)–C(74)	1.518 (12)	C(31)–C(32)–C(33)	110.9 (6)
C(74)–C(75)	1.506 (11)	C(32)–C(33)–C(34)	113.2 (7)
C(75)–C(76)	1.525 (10)	C(33)–C(34)–C(35)	110.4 (7)
C(76)–C(71)	1.538 (10)	C(34)–C(35)–C(36)	111.9 (7)
C(81)–C(82)	1.548 (10)	C(35)–C(36)–C(31)	110.4 (6)
C(82)–C(83)	1.554 (11)	C(36)–C(31)–C(32)	111.4 (6)
C(83)–C(84)	1.511 (12)	C(41)–C(42)–C(43)	114.7 (6)
C(84)–C(85)	1.522 (12)	C(42)–C(43)–C(44)	111.1 (7)
C(85)–C(86)	1.534 (10)	C(43)–C(44)–C(45)	112.4 (7)
C(86)–C(81)	1.527 (10)	C(44)–C(45)–C(46)	111.4 (7)
		C(45)–C(46)–C(41)	115.1 (6)
		C(46)–C(41)–C(42)	108.6 (6)
		C(51)–C(52)–C(53)	110.4 (5)
		C(52)–C(53)–C(54)	112.0 (4)
		C(53)–C(54)–C(55)	110.5 (6)
		C(54)–C(55)–C(56)	111.3 (6)
		C(55)–C(56)–C(51)	110.7 (5)
		C(56)–C(51)–C(52)	109.1 (5)
		C(61)–C(62)–C(63)	111.6 (6)
		C(62)–C(63)–C(64)	113.4 (6)
		C(63)–C(64)–C(65)	112.1 (6)
		C(64)–C(65)–C(66)	110.7 (6)
		C(65)–C(66)–C(61)	112.8 (5)
		C(66)–C(61)–C(62)	112.7 (6)
		C(71)–C(72)–C(73)	113.5 (6)
		C(72)–C(73)–C(74)	109.8 (6)
		C(73)–C(74)–C(75)	110.6 (6)
		C(74)–C(75)–C(76)	111.3 (7)
		C(75)–C(76)–C(71)	111.3 (6)
		C(76)–C(71)–C(72)	108.4 (6)
		C(81)–C(82)–C(83)	109.8 (6)
		C(82)–C(83)–C(84)	113.1 (7)
		C(83)–C(84)–C(85)	111.4 (7)
		C(84)–C(85)–C(86)	111.8 (6)
		C(85)–C(86)–C(81)	111.6 (6)
		C(86)–C(81)–C(82)	110.9 (6)
Bond angles (°) and standard deviations ($\times 10$)			
P(1)–Ni–P(3)	136.4		
P(2)–Ni–P(4)	134.1		
P(1)–Ni–P(4)	121.0		
P(1)–Ni–P(2)	77.7		
P(3)–Ni–P(4)	77.3		
P(3)–Ni–P(2)	119.8		
Ni–P(1)–C(1)	92.9 (2)		
Ni–P(2)–C(1)	92.7 (2)		
Ni–P(1)–C(21)	129.4 (2)		
Ni–P(2)–C(41)	125.6 (2)		
Ni–P(2)–C(31)	125.0 (2)		
Ni–P(1)–C(11)	120.5 (2)		
Ni–P(3)–C(2)	94.4 (2)		
Ni–P(4)–C(2)	93.0 (2)		
Ni–P(3)–C(51)	119.9 (2)		
Ni–P(3)–C(61)	127.4 (2)		
Ni–P(4)–C(71)	125.7 (2)		
Ni–P(4)–C(81)	122.7 (2)		
P(1)–C(1)–P(2)	96.4 (3)		
P(3)–C(2)–P(4)	94.8 (3)		
C(1)–P(1)–C(11)	103.6 (3)		
C(1)–P(1)–C(21)	105.1 (3)		
C(1)–P(2)–C(31)	101.6 (3)		
C(1)–P(2)–C(41)	102.0 (3)		
C(2)–P(3)–C(61)	106.0 (3)		
C(2)–P(3)–C(51)	104.4 (3)		
C(2)–P(4)–C(81)	103.1 (3)		
C(2)–P(4)–C(71)	100.7 (3)		
C(11)–P(1)–C(21)	100.9 (3)		
C(31)–P(2)–C(41)	103.0 (3)		
C(51)–P(3)–C(61)	101.4 (3)		
C(71)–P(4)–C(81)	104.9 (3)		
P(1)–C(11)–C(16)	111.3 (3)		
P(1)–C(11)–C(12)	115.4 (3)		
P(1)–C(21)–C(22)	110.6 (3)		
P(1)–C(21)–C(26)	109.9 (3)		
P(2)–C(31)–C(36)	118.3 (3)		
P(2)–C(31)–C(32)	113.5 (3)		
P(2)–C(41)–C(46)	115.8 (3)		
P(2)–C(41)–C(42)	109.9 (3)		
P(3)–C(51)–C(52)	110.5 (3)		
P(3)–C(51)–C(56)	115.6 (3)		
P(3)–C(61)–C(62)	110.9 (3)		
P(3)–C(61)–C(66)	109.7 (3)		
P(4)–C(71)–C(72)	109.0 (3)		
P(4)–C(71)–C(76)	115.6 (3)		
P(4)–C(81)–C(82)	117.5 (3)		
P(4)–C(81)–C(86)	112.4 (3)		
C(11)–C(12)–C(13)	111.7 (6)		
C(12)–C(13)–C(14)	113.2 (6)		
C(13)–C(14)–C(15)	108.4 (6)		
C(14)–C(15)–C(16)	111.9 (6)		

Discussion of the structure

The most interesting feature of the molecular structure of the title compound is the geometrical arrangement of the central part of the molecule. A detailed picture of the new heterocyclic four-membered spirane ring system is given in Fig. 3. The coordination around the nickel may be described as a distorted tetrahedron, wherein the formations of the four membered rings reduce the P–Ni–P angles substantially to 77.7 and 77.3°. Both ring systems are planar with deviations from the best planes of ± 0.03 Å. The equations of the best planes are:

$$P(1)NiP(2)C(1) \quad 1.461x + 12.16y - 0.297z - 2.098 = 0$$

$$P(3)NiP(4)C(2) \quad -0.631x + 3.192y - 21.04z + 0.973 = 0.$$

The dihedral angle between these planes is 80.8°, thus deviating by 9° from the ideal tetrahedral arrangement. Similar distortions from ideal symmetry have been noticed at other tetrahedral nickel compounds; however, no satisfactory explanations are known at the present time (Cotton, Deboer & Pipal, 1970). The angles around the phosphorus and ring-carbon atoms

are less affected by the ring strain. All C-P-C bond angles are very similar to those found in substituted non-coordinated phosphines (103°) (Daly, 1970). Thus the hybridization of the phosphorus atoms seems not to differ significantly from the tetrahedral sp^3 type. It is obvious on the other hand from the bonding angles of the heavy atom framework, e.g. the acute P-Ni-P angle (Fig. 3), that the orbital overlap has to take place through bent bonds, the region of maximum overlap being displaced by about 0.3 Å from the Ni-P axis, assuming exact tetrahedral hybridisation of the nickel (see Fig. 4). The contacts Ni-C(1) (2.963 Å) and Ni-C(2) (2.983 Å) seem to be too large to have any influence on the overall molecular arrangement.

All cyclohexyl rings are in the chair conformation and bonded equatorially to the phosphorus. The P-C distances are in the range of our previous measurements on similar compounds (Barnett & Krüger, 1972; Krüger & Tsay, 1972). The average C-C distance in the cyclohexyl rings is 1.529 Å. Fig. 5 shows a stereoscopic view of the unit-cell along the $-b$ axis.

Non-bonded distances

There are no abnormally short intermolecular distances. Thus it seems that the observed molecular

skeleton is not affected by packing forces. A list of contacts less than 4 Å is given in Table 5.

All computations were carried out on a PDP-10 time-sharing computer with local versions of commonly available crystallographic programs. Some programs were of local origin.

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Table 5. Interatomic contacts less than 4 Å

C(15)-C(64)	3.802 Å
C(24)-C(55)	3.810
C(33)-C(25)	3.998
C(46)-C(13)	3.959
C(54)-C(63)	3.934
C(63)-C(74)	3.941
C(64)-C(76)	3.945
C(65)-C(86)	3.719

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The Crystal and Molecular Structure of Monofluoroacetic Acid

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Crystals of monofluoroacetic acid are monoclinic with $a=4.30$, $b=7.55$, $c=9.98$ Å and $\beta=85.2^\circ$. The structure was solved by application of the $B_{3,0}$ formula to three-dimensional photographic data. It consists of centrosymmetrical dimers formed by carboxyl group coupling. The carbon-carbon distance is found to be extremely short.

Introduction

As a part of our research program on the structure and conformation of substituted mono and dicarboxylic acids the structures of tartronic acid (van Eijck, Kanters & Kroon, 1965) and monofluoromalonic acid

(Roelofsen, Kanters, Kroon & Vliegthart, 1971) were determined. These structures are remarkably similar in that the molecules form carboxyl-group coupled polymeric chains which are packed in almost identical ways. Strong chain interactions are absent in the two structures. This is reflected in the fact that the