Acta Cryst. (1977). B**33**, 266–268

1,1′-Carbonyldipyrazole

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(*Received* 10 *August* 1976; *accepted* 27 *August* 1976)

Abstract. $C_7H_6N_4O$, M_r = 162·08, orthorhombic, $Pna2_1$, a = 17·378 (3), b = 3·938 (1), c = 10·713 (2) Å, V = 733·1 Å^3, D_o = 1·46 (2), Z = 4, D_x = 1·47 g cm^{-3}. Mo $K\alpha_1$ radiation, λ = 0·70926 Å, F(000) = 336, T = 22 ± 1 °C. Final R = 0·043 for 526 diffractometer-measured reflexions (>2·3σ). The molecule is approximately planar. The two pyrazolyl rings are asymmetrically disposed about the C—O bond. Marked differences between C—C and between C—N bonds indicate that delocalization is not extensive.

Introduction. The title compound was prepared by the reaction between sodium pyrazolide and phosgene in a water-free solvent (benzene or ether are suitable) under reduced pressure (Thé & Peterson, 1973). Single crystals were grown by sublimation in an inert, dry atmosphere.

Photographs indicated *mmm* Laue symmetry; systematic absences $h0l$, $h = 2n + 1$ and $0kl$, $k + l = 2n + 1$ indicated space groups $Pna2_1$ or $Pnam$. Intensities and cell dimensions were obtained from an approximately spherical crystal with a diameter varying from 0·30 to 0·38 mm. The compound was sensitive to moisture and common adhesive solvents, and so the crystal was sealed in a Lindemann glass capillary.

Cell dimensions were determined by least squares from the 2θ values (2θ > 35°) for 14 strong reflexions centred on the Mo $K\alpha_1$ (λ = 0·70926 Å) peak on a Picker FACS-1 automated diffractometer. Intensity measurements for 690 unique reflexions with 0° < 2θ < 50° were made by the θ–2θ scan technique (Nb-filtered Mo $K\alpha$ radiation, scan speed = 2° min^{-1}, scan width = 2°), the crystal b axis being coincident with the φ axis. Of the 690 reflexions measured, 526 were classed as observed with $I/\sigma(I) > 2{\cdot}3$, where $\sigma(I) = [T + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$, and T = total scan count, B_1 and B_2 background counts, t_s = scan time, t_b = total background count time, k is constant at 0·03 and I = net count. Corrections for Lorentz and polarization effects were applied; absorption was not corrected [μ(Mo $K\alpha$) = 1·15 cm^{-1}].

Since a unique space group was not indicated and the $|E|$ statistics showed no clear indication, structure solution was first attempted for $Pnam$ by symbolic addition methods. As no structure was elucidated, tangent-refinement methods were applied to $Pna2_1$. The subsequent successful structure determination and refinement confirms this choice of space group.

Table 1. *Coordinates and thermal parameters*

(*a*) Fractional coordinates with e.s.d.'s

	x	y	z
O	0·3789 (2)	0·074 (1)	0·4220
C(1)	0·3918 (3)	0·001 (1)	0·3157 (5)
N(1)	0·4606 (2)	−0·163 (1)	0·2850 (5)
N(2)	0·4851 (2)	−0·243 (1)	0·1676 (5)
C(2)	0·5538 (3)	−0·374 (2)	0·1840 (6)
C(3)	0·5747 (4)	−0·386 (2)	0·3100 (6)
C(4)	0·5150 (3)	−0·250 (2)	0·3714 (6)
N(3)	0·3411 (2)	0·077 (1)	0·2198 (5)
N(4)	0·2776 (3)	0·267 (1)	0·2506 (6)
C(5)	0·2382 (3)	0·285 (2)	0·1468 (7)
C(6)	0·2728 (3)	0·113 (2)	0·0484 (7)
C(7)	0·3372 (3)	−0·018 (2)	0·0964 (5)
H(2)	0·580 (4)	−0·46 (2)	0·107 (6)
H(3)	0·617 (3)	−0·52 (2)	0·322 (6)
H(4)	0·499 (3)	−0·22 (2)	0·453 (6)
H(5)	0·192 (2)	0·41 (1)	0·145 (5)
H(6)	0·251 (3)	0·09 (1)	−0·040 (5)
H(7)	0·381 (3)	−0·15 (1)	0·057 (6)

(*b*) Anisotropic thermal motion parameters (×10^3 Å^2) in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	76 (2)	153 (4)	51 (2)	0 (3)	6 (2)	−29 (3)
C(1)	55 (3)	79 (4)	42 (3)	−18 (3)	10 (2)	−13 (3)
N(1)	52 (3)	68 (3)	38 (2)	−9 (2)	−2 (2)	−5 (2)
N(2)	61 (2)	94 (4)	38 (2)	8 (2)	3 (2)	−6 (3)
C(2)	66 (3)	86 (4)	56 (3)	4 (3)	7 (3)	−2 (3)
C(3)	70 (4)	82 (4)	58 (3)	0 (3)	−5 (3)	9 (3)
C(4)	75 (4)	110 (5)	41 (3)	−9 (4)	−1 (3)	13 (3)
N(3)	51 (2)	61 (2)	50 (3)	−10 (2)	4 (2)	−7 (2)
N(4)	62 (3)	78 (3)	69 (3)	6 (3)	16 (2)	−13 (3)
C(5)	57 (3)	82 (4)	83 (5)	−3 (3)	4 (4)	−1 (4)
C(6)	64 (4)	93 (5)	69 (4)	−4 (4)	−7 (3)	−8 (4)
C(7)	59 (3)	79 (4)	54 (3)	−4 (3)	0 (3)	−19 (3)

(*c*) Isotropic thermal motion parameters (×10^2 Å^2)

	U		U
H(2)	11 (2)	H(5)	5 (1)
H(3)	12 (3)	H(6)	8 (2)
H(4)	9 (2)	H(7)	8 (2)

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A Fourier map following the phasing procedure gave coordinates for nine non-hydrogen atoms. Approximate positions for the three remaining non-hydrogen atoms were calculated. Refinement of positional and isotropic thermal parameters by full-matrix least squares yielded an R of 0·123. Examination of a difference map showed that anisotropic thermal parameters for N(1), N(3), C(1) and O would be justified. Their inclusion reduced R to 0·089.

All six H atoms were then located in a difference map. Further refinement with anisotropic thermal parameters for all N atoms and the constituents of the carbonyl group and with isotropic thermal parameters for the remaining C and H atoms reduced R to 0·064. Two final cycles of refinement in which all non-hydrogen atoms were treated anisotropically gave a final R of 0·043. A final difference map showed no peaks greater than $3\sigma(\rho)$.

Table 2. *Deviations of atoms from least-squares planes* (Å)

(*a*) Plane through N(1), N(2), C(2), C(3), C(4)

O	−0·142	C(3)	0·003
C(1)	−0·070	C(4)	−0·001
N(1)	−0·001	H(2)	0·049
N(2)	0·003	H(3)	0·093
C(2)	−0·004	H(4)	

The equation of the plane with reference to an orthogonal system of axes *a,b,c* is

$$-0{\cdot}4115x + 0{\cdot}0836y - 0{\cdot}9076z + 2{\cdot}4537 = 0.$$

χ^2 for the plane is 1·29.

(*b*) Plane through N(3), N(4), C(5), C(6), C(7)

O	0·230	C(6)	−0·002
C(1)	0·069	C(7)	0·003
N(3)	−0·004	H(5)	−0·014
N(4)	0·003	H(6)	0·027
C(5)	−0·001	H(7)	−0·043

The equation of the plane with reference to an orthogonal system of axes *a,b,c* is

$$-0{\cdot}4940x + 0{\cdot}2536y - 0{\cdot}8317z + 2{\cdot}5790 = 0.$$

χ^2 for the plane is 1·49.

Angle between plane (*a*) and plane (*b*) is 11·7°.

Unobserved reflexions were excluded from the refinement. For the initial refinement, unit weights were used but in the final two cycles weights ($=1/\sigma^2F$) were given in terms of $\sigma F = \sigma I/(\mathrm{Lp})2F_o$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and the programs used were those described by Einstein & Jones (1972).

Final coordinates and thermal parameters are given in Table 1.* Interatomic distances and angles are displayed in Fig. 1. Table 2 shows least-squares planes.

Discussion. Crystallographically the molecule has no symmetry, but potentially could have symmetry as high as *mm*2. While the two C(1)–N distances are equivalent within experimental error, the two pyrazolyl rings are not placed symmetrically with respect to the C=O bond; the imino N(2) and N(4) are *trans* to the N–C–N bridge.

The molecular dimensions suggest that delocalization is not extensive. In pyrazole (Larsen, Lehman, Søtofte & Rasmussen, 1970) the differences between the C–C and C–N distances are only on the verge of significance. In the present determination there are significant differences in C–C and C–N distances and our interpretation is that the molecule is best thought of

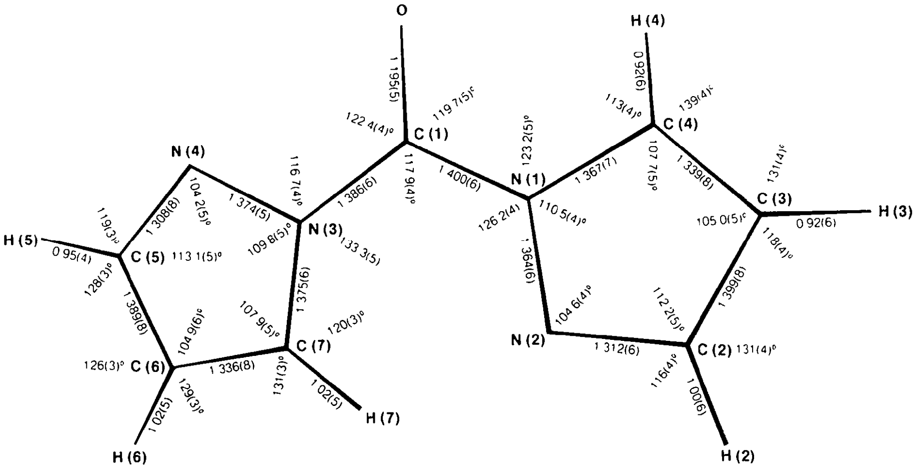

Fig. 1. Interatomic distances and angles and their standard deviations.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32064 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

as having localized C–N(imino) double bonds and two C–C double bonds. Molecular orbital calculations made with the CNDO program (kindly provided by Professor P. G. Perkins) support this view, giving average bond indices (Armstrong, Perkins & Stewart, 1973) of 1·65 for the C–N and C–C double bonds, 1·23 for the C–C single bond and 1·14 for the C–N(amino) single bond.

Intramolecular hydrogen bonding does not appear to be an important factor in determining the orientation of the two rings; O–H(4) and H(7)–N(2), the two pertinent contacts, are 2·40 and 2·19 Å respectively. The asymmetric disposition of the rings adopted about the C=O bond would appear to alleviate an otherwise unfavourable lone-pair repulsion between N(2) and N(4).

We acknowledge financial support from the National Research Council of Canada in the form of grants to F. Einstein and L. Peterson.

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Acta Cryst. (1977). B**33**, 268–271

Ferrocenyldiphenylsilane

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(*Received* 4 *August* 1976; *accepted* 30 *August* 1976)

Abstract. $C_{22}H_{20}FeSi$, $M_r = 368{\cdot}34$; monoclinic; $P2_1/c$, $a = 10{\cdot}797\ (3)$, $b = 24{\cdot}639\ (7)$, $c = 7{\cdot}707\ (3)$ Å, $\beta = 116{\cdot}95\ (2)°$; $Z = 4$, $D_m = 1{\cdot}33\ (1)$, $D_c = 1{\cdot}34$ g cm^{-3}, $U = 1828\ (1)$ Å^3, $\mu(\text{Mo } K\alpha) = 9{\cdot}1$ cm^{-1}. The two planar cyclopentadienyl rings in the ferrocenyl moiety are tilted 2·7° from parallel and twisted approximately 13·3° from the fully eclipsed configuration. The distance between the cyclopentadienyl ring centroids is 3·28 Å. The mean silicon–phenyl carbon bond length is 1·871 (4) Å; the silicon–cyclopentadienyl carbon bond length is 1·856 (4) Å.

Introduction. Crystals of the title compound were prepared by the method reported for ferrocenyltriphenylsilane (Benkeser, Goggin & Schroll, 1954). A crystal, 0·22 × 0·15 × 0·12 mm, was mounted on a Syntex $P2_1$ diffractometer and data were collected to a 2θ of 55° with Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation (graphite monochromator) and the θ–2θ scan technique at 2° min^{-1}. Backgrounds were measured at each end of the scan (2θ scan range: 2θMo $K\alpha_1 - 1{\cdot}0°$ to 2θMo $K\alpha_2 + 1{\cdot}0°$) for a total time equal to one-half the scan time. Systematic absences were $h0l$, l odd; $0k0$, k odd, uniquely determining the space group $P2_1/c$. Fifteen reflections with 2θ between 7 and 24° were centered with a programmed centering routine; cell parameters were obtained by least-squares refinement of these angles. During data collection, the intensities of three standard reflections were measured every 97 reflections with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those described previously (Schmonsees, 1974). Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0{\cdot}03I)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background count, and K = ratio of scan time to background time. No corrections for absorption were made. The 2160 data with $F_o^2 > 3\sigma(F_o^2)$ from 4632 data

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