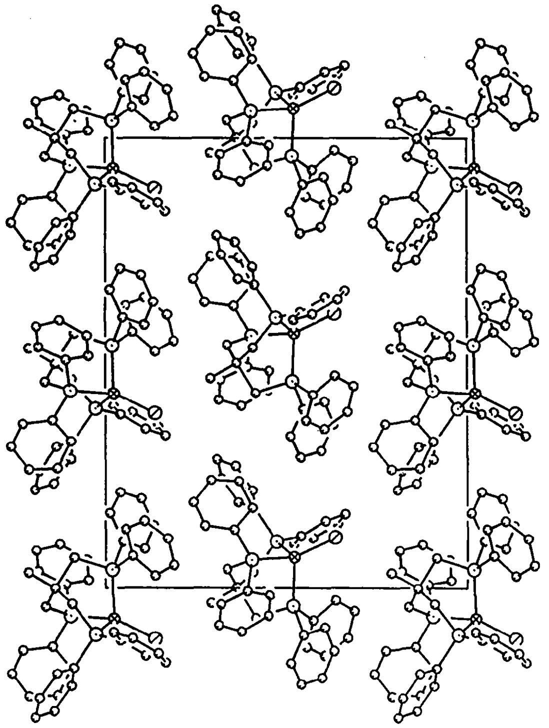

Fig. 2. Unit-cell packing diagram for [({(C_6H_5)$_2$PCH$_2$}$_3$CCH$_3$)CuCl] projected along the *b* axis.

with Cl—Cu—P(av.) = 122.4 and P—Cu—P(av.) = 93.4°. This strain almost certainly affects the orbital overlap of the P—Cu bond. The electronic transition in the arylphosphines has been described in terms of a $\sigma,d\rightarrow a_\pi$ transition (Fife, Moore & Morse, 1984*a*). The σ,d indicates that a synergistic bonding is involved in the transition. Preliminary experiments show considerable difference in the triplet sensitization of norbornadiene by the two compounds. Photochemical constants are being experimentally determined to better compare the electronic properties of these analogous compounds.

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Structure of [3,5-(C_6H_5)$_2$$C_3H_2N_2$]$_4$. A 3,5-Diphenylpyrazole Tetramer Linked by Hydrogen Bonds

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Abstract. 3,5-Diphenylpyrazole, $C_{15}H_{12}N_2$, M_r = 220.1, monoclinic, *C*2/*c* (No. 15), a = 16.948 (4) Å, b = 17.163 (4) Å, c = 17.677 (6) Å, β = 109.59 (2)°, V = 4844 (2) Å^3, Z = 32, D_x = 1.21 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.07 mm^{-1}, $F(000)$ = 1861.6, T = 298 K, final R = 0.056 and wR = 0.058 for 259 variable parameters and 2073 reflections with $F_o^2 > 3\sigma(F_o^2)$. The asymmetric unit consists of a hydrogen-bonded dimer of 3,5-diphenylpyrazole which is further hydrogen bonded to form four discrete tetrameric aggregates per unit cell. Each tetrameric unit forms a twelve-membered (N—N—H)$_4$ heterocycle.

Introduction. Pyrazolato anions of the type 3,5-R_2pz (R = alkyl group, pz = C_3HN_2) are extensively used in the synthesis of transition-metal complexes (Trofimenko, 1972, 1986) where they can act as mono- or bidentate ligands. We have been particularly interested in the homoleptic complexes [M(μ-3,5-Ph$_2$pz)]$_3$, M is a Group 11 metal, which contain a triangular arrangement of the metal core (Raptis

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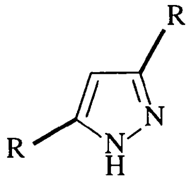
& Fackler, 1988; Murray, Raptis & Fackler, 1988).

The suggestion that pyrazole and 3,5-dimethylpyrazole form stable hydrogen-bonded trimers (Anderson, Duncan & Rossotti, 1961) gave birth to the idea that replacing the bridging hydrogens with two-coordinate metal atoms would generate trimeric metallocyclic complexes. This idea was successfully explored (Bonati, Minghetti & Banditelli, 1974) and several complexes of the general formula $[\mathrm{Au}(\mu\text{-}3,5\text{-}R_2\mathrm{pz})]_3$ were prepared (Banditelli, Bandini, Minghetti & Bonati, 1981; Banditelli, Bandini, Bonati, Goel & Minghetti, 1982). In the case of $R = \mathrm{CF}_3$, a crystallographic study confirmed the expected trimeric structure (Bovio, Bonati & Banditelli, 1984). Our work, which aimed at the expansion of the studies of the Italian group into other late transition-metal pyrazolato complexes, has resulted in the structural characterization of the homologous series $[M(\mu\text{-}3,5\text{-}\mathrm{Ph_2pz})]_3$, $M = \mathrm{Cu^I}$, $\mathrm{Ag^I}$, $\mathrm{Au^I}$ (Raptis & Fackler, 1988; Murray, Raptis & Fackler, 1988), as well as the characterization of a mixed-valence complex $[\mathrm{Au}(\mu\text{-}3,5\text{-}\mathrm{Ph_2pz})]_3\mathrm{Cl}_2$ (Raptis, Murray & Fackler, 1988). In the course of our investigations, we also characterized the hexameric complex $[\mathrm{Au}(\mu\text{-}3,5\text{-}\mathrm{Ph_2pz})]_6$ (Raptis, Murray & Fackler, 1987). This was the first proof that homoleptic pyrazolato complexes can be other than trimeric. It has been reported that the silver-pyrazolato complex is tetrameric in its acetone solution (Trofimenko, 1972). These results prompted us to investigate the solid-state structure of 3,5-diphenylpyrazole (3,5-$\mathrm{Ph_2pzH}$), (I).



(I)

Experimental. 3,5-Diphenylpyrazole (Lancaster Synthesis Ltd) was used without purification. The crystal used for the X-ray diffraction experiment was grown by slow evaporation of a $\mathrm{CH_2Cl_2}$ solution.

A single multi-faceted colorless crystal of approximate dimensions 0.30 × 0.40 × 0.50 mm was mounted in a random orientation on a glass fiber (Nicolet *R3m/E* diffractometer, graphite-monochromated Mo $K\alpha$ radiation). Refined cell parameters were obtained from the setting angles of 25 reflections with $20 < 2\theta < 30°$. Data collection was carried out at room temperature using the Wyckoff scanning technique in bisecting geometry. 4593 intensities were measured for 4271 unique reflections ($h < 21$, $k < 21$, $|l| < 22$) with $3 < 2\theta < 50°$; no symmetry equivalent reflections were collected. Scan rate variable, 3–30° $\mathrm{min^{-1}}$; scan range 0.9, scan width 0.9. Three low-angle standards (310, 023, $\bar{2}44$) were measured every 97 data. The data were corrected for decay (3%) by scaling on the three standards. Absorption correction was applied (minimum and maximum transmission 0.98 and 1.00, normalized). Structure solution and refinement was carried out with the *SHELXTL* collection of crystallographic software (Sheldrick, 1981). Initial positional parameters for two N and 21 C atoms were determined from a direct-methods program solution; all remaining atoms were located on difference electron density maps. The four bridging H atoms were located on difference electron-density maps, two in general positions and two along the twofold rotation axis, and their positional parameters were fixed. Due to the low number of reflections, phenyl rings were refined as idealized polygons (C—C = 1.395 Å, C—C—C = 120°) using H atoms placed in calculated positions (C—H = 0.960 Å) with their thermal parameters riding on those of the C atoms [$U(\mathrm{H}) = 0.08$ Å^2]. All non-H atoms were refined anisotropically. Refinement of H atoms restrained to lie on the twofold axis or on a plane bisecting N(1) and N(3) led to large U_{iso} values (>0.17 Å^2) and therefore the asymmetric model was preferred. Refinement was based on F with weights of the form $w^{-1} = [\sigma^2(F) + 0.00069(F^2)]$. Scattering factors, including terms for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). One intense low-angle reflection (110) with extinction problems was rejected from the final refinements. Convergence to conventional R values of $R = 0.058$ and $wR = 0.062$ was obtained using 259 variable parameters and 2073 reflections with $F_o^2 > 3\sigma(F_o^2)$. For final cycle, maximum shift/σ was 0.02 with a goodness-of-fit indicator of 1.608. Maximum and minimum residual electron density on final difference Fourier map were 0.28 and -0.35 e Å^{-3} in the vicinity of C(44).

Discussion. The structure consists of two 3,5-diphenylpyrazole molecules in the asymmetric cell which generates the tetramer by the crystallographic twofold axis. The unit cell contains four such tetramers. Views of the structure are given in Fig. 1. Atomic positional and isotropic thermal parameters for all non-H atoms are presented in Table 1.* Bond angles and distances are summarized in Table 2.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and a difference electron-density contour map have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71173 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1006]

The pyrazole molecules of the $(3,5\text{-}Ph_2pzH)_4$ tetramer form hydrogen bonds with their neighboring molecules, thus generating a twelve-membered $(\text{—N—N—H—})_4$ heterocycle. A twofold axis runs through two of the bridging H atoms. Assuming that all four H atoms are equivalent and ignoring the orientation of the phenyl groups, this tetramer has D_{2d} symmetry, which is reduced to only C_2 for the crystallographically characterized form (two pairs of crystallographically non-equivalent bridging H atoms). Two of the bridging H atoms form symmetrical hydrogen bonds, N—H 1.443 (5) and 1.456 (4) Å, while the other two bridge asymmetrically, N—H 1.12 (4) and 1.74 (4) Å, although this observation should be treated with caution (see below).

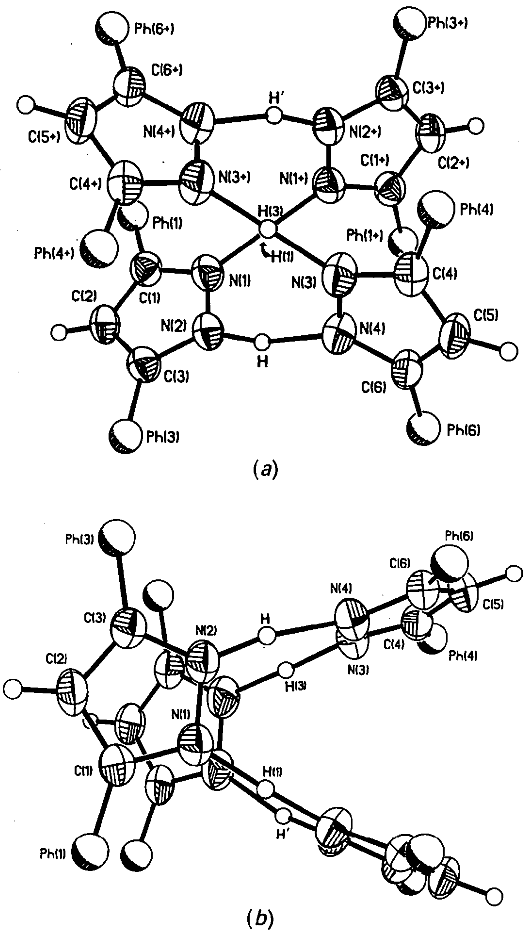

Fig. 1. Views of the $[3,5\text{-}(C_6H_5)_2C_3H_2N_2]_4$ structure showing (*a*) a view down the C_2 axis, and (*b*) a view at an angle to the C_2 axis. Thermal ellipsoids have been drawn at the 50% probability level. Phenyl groups are represented by their ipso C atoms of arbitrary radii for clarity [Ph(1): C(11)–C(16); Ph(3): C(31)–C(36), *etc.*]. H atoms are shown as open circles of arbitrary radii.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses for* $[3,5\text{-}(C_6H_5)_2C_3H_2N_2]_4$

The equivalent isotropic U is defined as one third of the trace of the U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	9097 (2)	2597 (2)	2228 (2)	48 (1)
N(2)	8742 (2)	3085 (2)	2624 (2)	48 (1)
C(1)	8486 (2)	2275 (2)	1613 (2)	42 (1)
C(2)	7723 (2)	2564 (2)	1618 (2)	48 (1)
C(3)	7904 (2)	3073 (2)	2256 (2)	44 (1)
C(11)	8037 (1)	1433 (2)	406 (1)	63 (2)
C(12)	8209 (1)	885 (2)	−101 (1)	81 (2)
C(13)	9022 (1)	605 (2)	68 (1)	89 (3)
C(14)	9664 (1)	872 (2)	743 (1)	83 (2)
C(15)	9492 (1)	1420 (2)	1249 (1)	65 (2)
C(16)	8679 (1)	1700 (2)	1081 (1)	49 (1)
C(31)	7619 (1)	3854 (2)	3332 (1)	77 (2)
C(32)	7086 (1)	4326 (2)	3587 (1)	93 (2)
C(33)	6282 (1)	4491 (2)	3067 (1)	89 (2)
C(34)	6009 (1)	4185 (2)	2291 (1)	91 (2)
C(35)	6541 (1)	3714 (2)	2035 (1)	70 (2)
C(36)	7346 (1)	3548 (2)	2556 (1)	51 (1)
N(3)	10357 (2)	4472 (2)	3373 (2)	53 (1)
N(4)	10000 (2)	3967 (2)	3761 (2)	52 (1)
C(4)	10974 (2)	4866 (2)	3927 (2)	46 (1)
C(5)	11005 (2)	4609 (2)	4681 (2)	51 (1)
C(6)	10399 (2)	4038 (2)	4558 (2)	46 (1)
C(41)	11771 (2)	5285 (2)	3044 (1)	65 (2)
C(42)	12335 (2)	5790 (2)	2876 (1)	86 (2)
C(43)	12646 (2)	6433 (2)	3369 (1)	96 (3)
C(44)	12391 (2)	6571 (2)	4030 (1)	97 (3)
C(45)	11826 (2)	6066 (2)	4198 (1)	74 (2)
C(46)	11516 (2)	5423 (2)	3705 (1)	53 (1)
C(61)	10490 (2)	3743 (1)	5957 (1)	61 (2)
C(62)	10315 (2)	3271 (1)	6523 (1)	75 (2)
C(63)	9848 (2)	2591 (1)	6281 (1)	82 (2)
C(64)	9557 (2)	2382 (1)	5471 (1)	86 (2)
C(65)	9732 (2)	2853 (1)	4905 (1)	71 (2)
C(66)	10199 (2)	3533 (1)	5147 (1)	50 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *for* $[3,5\text{-}(C_6H_5)_2C_3H_2N_2]_4$

N(1)—N(2)	1.354 (4)	N(1)—H(1)	1.443 (5)
N(3)—N(4)	1.367 (5)	N(2)—H	1.118 (41)
N(1)—C(1)	1.343 (4)	N(3)—H(3)	1.456 (53)
N(2)—C(3)	1.350 (4)	N(4)—H	1.741 (42)
N(3)—C(4)	1.350 (4)	C(2)—H(2)	0.959 (40)
N(4)—C(6)	1.348 (4)	C(5)—H(5)	0.986 (40)
C(1)—C(2)	1.388 (5)	C(1)—C(16)	1.471 (4)
C(2)—C(3)	1.376 (5)	C(3)—C(36)	1.473 (5)
C(4)—C(5)	1.389 (5)	C(4)—C(46)	1.466 (5)
C(5)—C(6)	1.383 (5)	C(6)—C(66)	1.478 (5)

N(2)—N(1)—H(1)	117 (1)	N(1)—H(1)—N(1)′	176 (4)
N(1)—N(2)—H	116 (2)	N(3)—H(3)—N(3)′	179 (4)
N(4)—N(3)—H(3)	116 (2)	N(1)—C(1)—C(2)	108.3 (3)
N(3)—N(4)—H	115 (2)	C(1)—C(2)—C(3)	106.2 (3)
N(2)—N(1)—C(1)	108.5 (3)	N(2)—C(3)—C(2)	108.3 (3)
N(1)—N(2)—C(3)	108.6 (3)	N(3)—C(4)—C(5)	107.9 (3)
N(4)—N(3)—C(4)	108.6 (3)	C(4)—C(5)—C(6)	106.7 (3)
N(3)—N(4)—C(6)	108.4 (3)	N(4)—C(6)—C(5)	108.3 (3)
N(2)—H—N(4)	163 (3)		

The distances between N atoms bridged symmetrically by an H atom average 2.90 (2) Å, while between the asymmetrically bridged ones the distances average 2.83 (2) Å. These distances are, respectively, 6 and 9% shorter than the sum of the van der Waals radii for two N atoms (Porterfield, 1984), with the two symmetrically bridging H atoms almost linearly bound to two pyrazoles, N—H—N 176 (4)°.

These results are in good agreement with previous X-ray (Maslen, Cannon, White & Willis, 1974) and neutron (Moore, White & Willis, 1975) diffraction studies of tetrameric 3-methyl-5-phenylpyrazole, 3-Me-5-PhpzH. In $(3\text{-Me-5-PhpzH})_4$, adjacent pyrazole groups, bridged symmetrically by H atoms, showed N···N distances of 2.913 (5) and 2.824 (5) Å, while for those bridged by asymmetric hydrogen bonds, the measured N···N distance was 2.852 (5) Å. The corresponding symmetric N—H distances were found to be 1.458 (4) and 1.413 (4) Å with N—H—N angles of 176 (4) and 175 (2)°, while the asymmetric (but almost symmetric) ones were 1.44 (4) and 1.41 (4) Å with an N—H—N angle of 178 (3)°. Therefore, even though the positional parameters of the bridging H atoms of $(3,5\text{-Ph}_2\text{pzH})_4$ could not be refined, the results presented here agree with those of the studies of $(3\text{-Me-5-PhpzH})_4$.

The best-fit planes of consecutive pyrazole rings which are related by the twofold axis form dihedral angles of 82.5 (2) and 89.2 (2)°, while the dihedral angle of the asymmetrically bridged ones is 72.3 (2)°. The planes of alternate pyrazoles (the ones on the same side of the H_4 plane) form a dihedral angle of 41.3 (2)°. The N—N, C—N and C—C bonds within the pyrazole rings are unexceptional.

Recently, the proton transfer in the solid state of these pyrazoles has been communicated (Aguilar-Parrilla, Scherer, Limbach, Foces-Foces, Cano, Smith, Toiron & Elguero, 1992). The authors reported the structure of 3,5-diphenylpyrazole where they modelled the H atoms in a totally symmetrical system. This model was based on the comparison of the intracyclic angles within the pyrazole ring (Bonati, 1989).

Nothing obvious prevents the replacement of the H atoms of this structure with two-coordinate metals. Similar tetrameric complexes of copper, $[\text{Cu}(\mu\text{-1,3,-Me}_2\text{N}_3)]_4$ (O'Connor, Janusonis & Corey, 1968), and gold, $[\text{Au}(\mu\text{-1,3-Ph}_2\text{N}_3)]_4$ (Beck & Strähle, 1986) and $[\text{Au}(\mu\text{-MeCS}_2)]_4$ (Chiari, Piovesana, Tarantelli & Zanazzi, 1985), have been structurally characterized. The metal–metal distances measured for these complexes approximate the H···H distances in the H_4 quadrilateral of $[3,5\text{-Ph}_2\text{pzH}]_4$. The structure of a dimeric $[\text{Pt(pz)}_2(\text{pzH})_2]_2$ complex containing almost symmetrically hydrogen-bonded pyrazole and pyrazolato ligands has been determined (Burger & Strähle, 1986).

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