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Synthesis and crystal structures of two potential *gem*-di(pyrazolyl)cycloalkane ligands, 1,1-di(pyrazol-1-yl)cyclohexane [$C_6H_{10}(C_3N_2H_3)_2$] and 1,1-di(pyrazol-1-yl)cyclopentane [$C_5H_8(C_3N_2H_3)_2$]

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The species 1,1-di(pyrazol-1-yl)cyclohexane, $C_{12}H_{16}N_4$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.340(2)$, $b = 14.281(5)$, $c = 10.153(3)$ Å, $\beta = 106.86(2)°$, and $Z = 4$. The cyclohexane moiety has the chair conformation. The congener, 1,1-di(pyrazol-1-yl) cyclopentane, $C_{11}H_{14}N_4$, while not isomorphous, also crystallizes in space group $P2_1/c$ with $a = 14.350(2)$, $b = 6.776(1)$, c = 11.043(2) Å, $\beta = 100.68(1)°$, and $Z = 4$. The cyclopentane ring has a conformation in which four carbon atoms are essentially coplanar, while the fifth (that with the two pyrazolyl substituents) lies 0.63 Å from this plane, resulting in a bend of 41.3° across the C(2)···C(5) vector. The hydrogen atoms in each structure were located directly and their coordinates refined.

KEY WORDS: Pyrazolyl derivative; substituted cyclopentane; substituted cyclohexane; crystal structure; bidentate ligand.

Introduction

We have recently been involved in the determination of the detailed geometric properties of a series of polydentate ligands containing nitrogen donor atoms. We have previously reported the X-ray structural characterization of the *tridentate* ligands 2,2′:6′,2″-terpyridine and 2,6-bis(pyrazol-l-yl)pyridine,[1] and the *bidentate* ligands di(pyrazol-l-yl)methane,[2] 2,2-di(pyrazol-l-yl)propane,[3] and 3,3-di(pyrazol-l-yl)pentane.[4] We now report the syntheses and crystal structures of two *gem*-di(pyrazol-l-yl) species based on cycloalkanes, which are of importance as potential *bidentate* ligands.

Experimental

Synthesis

Synthesis of 1,1-diethoxycyclohexane. A 1-L roundbottomed flask was charged with (in order) 70.0 g of montmorillonite K, 400 mL of hexanes, and 115 g of triethyl orthoformate (0.777 mol) and the mixture was stirred for 15 min. Cyclohexanone (51.0 g; 0.52 mol) was added and the mixture was stirred for 1 h, at which time GC/MS analysis indicated that the reaction was complete. The montomorillonite was removed by filtration, washed with hexanes and the combined filtrates were washed with 200 mL of 0.5% Na_2CO_3. The organic layer was dried over $MgSO_4$,

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filtered, and the hexanes removed by use of a rotary evaporator. The resulting liquid was distilled and a 43.3 g (42%) fraction obtained at 75–77°C (21 mm Hg) was judged by GC/MS to be the desired product.

Synthesis of 1,1-di(pyrazol-1-yl)cyclohexane. A 300-mL round-bottomed flask was charged with 150 mL toluene, 9.80 g (0.139 mol) pyrazole, 8.00 g (0.047 mol) 1,1-diethoxycyclohexane, and 25 mg *p*-toluenesulfonic acid. The flask was fitted with a Soxhlet apparatus in which the thimble is charged with 20 g of 4-E molecular sieves (activated at 400°C for 5 h). The Soxhlet apparatus was topped by a nitrogen T-tube and the reaction mixture was heated to reflux for 5 days. The progress of the reaction was monitored by TLC (alumina/toluene). The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated to an oil which was placed in a freezer overnight. The crystals which resulted were triturated with hexanes, filtered, and rinsed with hexanes and methanol. In this manner, 5.35 g (53%) of white crystals (m.p. 68–70°C) were obtained. ^1H NMR ($CDCl_3$) ppm 1.5–2.9 (m, 10 H); 6.0–6.3 (m, 2H); 7.39 (d of d, 2H, J = 3.2, 0.6 Hz); 7.50–7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) ppm 22.4; 24.7; 35.7; 95.9; 106.1; 127.2; 139.6.

Preparation of a single crystal of 1,1-di(pyrazol-1-yl)cyclohexane. A 50-mg sample was dissolved in a minimum of warm cyclohexane. The solution was cooled slowly in the dark and uncovered until complete evaporation of the solvent occurred (approximately 2 days). A number of clear, colorless crystals (approximately 2 mm × 2 mm × 3 mm) were collected from the container. The ^1H NMR spectrum of the crystals was consistent with the ^1H NMR spectrum reported above and the melting point of the crystals was 75.5–76°C. A crystal of size 0.45 × 0.25 × 0.15 mm was cut carefully from a larger crystal and used for the X-ray diffraction study.

Synthesis of 1,1-diethoxycyclopentane. A 1-L roundbottomed flask was charged with (in order) 70.0 g montmorillonite K, 400 mL hexanes, and 115 g triethyl orthoformate, (0.777 mol) and the mixture was stirred for 15 min. Cyclopentanone (43.7 g; 0.52 mol) was added and the mixture was stirred for 1 h, at which time GC/MS analysis indicated the reaction was complete. The montmorillonite was removed by filtration, washed with hexanes, and the combined filtrates were washed with 200 mL of 0.5% Na_2CO_3. The organic layer was dried over $MgSO_4$, filtered, and the hexanes removed by rotary evaporator. The resulting liquid was distilled and a 34.9 g (46%) fraction obtained at 77–78°C (30 mm Hg) was judged by GC/MS to be the desired product.

Synthesis of 1,1-di(pyrazol-1-yl)cyclopentane. A 300-mL roundbottomed flask was charged with 7.49 g (0.47 mol) of 1,1-diethoxycyclopentane, 7.01 g (0.103 mol) pyrazole, 150 mL cyclohexane and 25 mg *p*-toluenesulfonic acid. The flask was fitted with a Soxhlet apparatus in which the thimble is charged with 20 g of 4-E molecular sieves (activated at 400°C for 5 h). The Soxhlet apparatus was topped by a nitrogen T-tube and the reaction mixture is heated to reflux for 15 h. The progress of the reaction was monitored by TLC (alumina/toluene). The organic layer was separated, dried over $MgSO_4$, and filtered. Evaporation of the organic layer to a volume of 25 mL resulted in a deposit of white crystals (6.2 g, 65% yield) which have a melting point of 126–131°C. ^1H NMR ($CDCl_3$) ppm 1.7–2.0 (m, 4 H); 2.8–3.1 (m, 4H); 6.22 (d of d, 2H, J = 3.2, 0.6 Hz); 7.4–7.7 (m, 4H). ^{13}C NMR ($CDCl_3$) ppm 22.4; 37.8; 86.6; 106.3; 127.7; 139.5.

Preparation of a single crystal of 1,1-di(pyrazol-1-yl)cyclopentane. A 50-mg sample was dissolved in a minimum of warm cyclohexane. The solution was cooled slowly in the dark and uncovered until complete evaporation of the solvent occurred (approximately 2 days). A number of clear, colorless crystals (approximately 1 mm × 1 mm × 3 mm) were collected from the container. The ^1H NMR spectrum of the crystals was consistent with the ^1H NMR spectrum reported above and the melting point of the crystals was 130–131°C. A crystal of size 0.4 × 0.4 × 0.5 mm, cut from a larger crystal, was used in the X-ray diffraction study.

Crystallographic studies

Diffraction data were collected as described previously;[5] details are provided in Table 1. All calculations were performed on a VAXstation 3100 computer with the use of the SHELXTL PLUS[6,7] (Release 4.11 (VMS)) program package. Analytical scattering factors were employed[8a] with the assumption of neutral atoms; these were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[8b] The following items should be noted.

(1) A complete sphere of X-ray diffraction data

Table 1. Data for the X-Ray Diffraction Studies

	Cyclohexane Deriv.	Cyclopentane Deriv.
Formula	$C_{12}H_{16}N_4$	$C_{11}H_{14}N_4$
CCDC deposit no.	CCDC-1003/5604	CCDC-1003/5605
Molecular weight	216.3	202.3
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	8.340(2)	14.350(2)
b, Å	14.281(5)	6.776(1)
c, Å	10.153(3)	11.043(2)
β, deg	106.86(2)	100.68(1)
V, Å^3	1157.3(6)	1055.2(3)
Z	4	4
D_c(g/cm^3)	1.241	1.273
μ(Mo $K\alpha$), mm^{-1}	0.073	0.076
F(000)	464	432
Temperature (K)	296	296
Diffractometer (scan)	Siemens R3m/V ($2\theta-\theta$)	[a]
2θ range, deg	5–45	5–45
Index ranges	$-8 \leq h \leq 8$ $-15 \leq k \leq 15$ $-10 \leq \ell \leq 10$	$-15 \leq h \leq 15$ $-7 \leq k \leq 7$ $-11 \leq \ell \leq 11$
Reflections collected	6009	5474
Independent reflections	1510	1376
R(int), %	1.17	2.23
Reflections $> 3\sigma(I)$	986	1078
Absorption method	N/A	Semi-empirical χ-scans
Transmission factors, min/max	N/A	0.9515/0.9749
Computing	SHELXTL PLUS 4.11 (VMS)	[a]
Solution	Direct methods	[a]
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0002F^2$	$\sigma^2(F) + 0.0013F^2$
Extinction parameter (χ)	0.0032(4)	0.023(2)
Final R (data $> 3\sigma(I)$)	$R = 3.12\%$, $wR = 3.27\%$	$R = 2.78\%$, $wR = 3.88\%$
R (all data)	$R = 6.00\%$, $wR = 4.14\%$	$R = 3.94\%$, $wR = 4.77\%$
Largest difference peak and hole (e$^-$/Å^3)	+0.10, −0.13	+0.12, −0.12

[a] Information is same as for entry in previous column.

(Mo $K\overline{\alpha}$ radiation, $\overline{\lambda} = 0.710730$ Å, $2\theta = 5.0$–$45.0°$) was collected for each crystal. Since each compound crystallizes in space group $P2_1/c$, corresponding to Laue symmetry 2/m, four equivalent forms of data were measured.

(2) Least-squares refinement involved anisotropic thermal parameters for each nonhydrogen atom, isotropic thermal parameters for each hydrogen atom and positional parameters for each atom (carbon, nitrogen *and hydrogen*).

(3) Crystals were of excellent quality, although the intensity of data did drop off rather rapidly as a function of 2θ. Secondary extinction proved to have a significant effect on strong, low-angle, reflections. Final values for χ, the secondary extinction parameter,[9] were 0.0032(4) for the cyclohexane, and 0.023(2) for the cyclopentane, derivative.

Final atomic coordinates for the two structures are provided in Tables 2 and 3.

Discussion

(1) 1,1-di(pyrazol-1-yl)cyclohexane, $C_6H_{10}(C_3N_2H_3)_2$

The crystal is composed of discrete molecular units of $C_6H_{10}(C_3N_2H_3)_2$ separated by normal van der Waals' distances. The packing of molecules in the

Table 2. Final Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (U(eq), Å^2 × 10^3) for 1,1-Di(pyrazol-1-yl)cyclohexane

	x	*y*	*z*	*U*(eq)
C(1)	3147(3)	3202(2)	1877(2)	39(1)
C(2)	2687(3)	3632(2)	3091(3)	50(1)
C(3)	3039(4)	4684(2)	3232(3)	60(1)
C(4)	2203(4)	5194(2)	1903(3)	68(1)
C(5)	2711(4)	4778(2)	718(3)	59(1)
C(6)	2319(3)	3736(2)	551(3)	47(1)
N(11)	2600(2)	2210(1)	1724(2)	43(1)
N(12)	975(2)	2012(2)	1148(3)	73(1)
C(13)	898(4)	1086(2)	1267(3)	71(1)
C(14)	2404(4)	696(2)	1900(3)	64(1)
C(15)	3477(4)	1435(2)	2188(3)	61(1)
N(21)	4969(2)	3186(1)	2130(2)	38(1)
N(22)	5615(2)	3059(2)	1064(2)	52(1)
C(23)	7247(3)	2961(2)	1665(3)	56(1)
C(24)	7656(3)	3006(2)	3073(3)	55(1)
C(25)	6181(3)	3145(2)	3347(3)	47(1)
H(2A)	3215(25)	3284(15)	3943(24)	53(7)
H(2B)	1513(29)	3510(14)	2926(21)	54(7)
H(3A)	4264(29)	4781(15)	3469(21)	53(7)
H(3B)	2675(28)	4928(18)	4024(27)	73(8)
H(4A)	2489(29)	5878(20)	2025(25)	77(8)
H(4B)	993(33)	5131(19)	1726(25)	75(8)
H(5A)	3933(27)	4882(14)	874(21)	51(7)
H(5B)	2139(27)	5072(16)	−192(24)	63(7)
H(6A)	1147(31)	3641(15)	409(23)	63(8)
H(6B)	2643(25)	3456(15)	−214(24)	52(7)
H(13)	−130(32)	806(19)	883(26)	78(9)
H(14)	2695(29)	67(19)	2076(24)	81(9)
H(15)	4635(35)	1444(18)	2621(28)	89(9)
H(23)	7930(29)	2863(15)	1114(23)	60(8)
H(24)	8685(30)	2961(17)	3749(25)	71(8)
H(25)	5890(23)	3210(14)	4091(21)	45(6)

Table 3. Final Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (U(eq), Å^2 × 10^3) for 1,1-Di(pyrazol-1-yl)cyclohexane

	x	*y*	*z*	*U*(eq)
C(1)	2340(1)	6069(2)	2757(1)	37(1)
C(2)	2216(1)	4545(3)	1729(2)	47(1)
C(3)	2857(2)	2850(3)	2279(2)	59(1)
C(4)	2949(2)	3011(3)	3674(2)	60(1)
C(5)	2354(1)	4794(3)	3899(2)	47(1)
N(11)	1590(1)	7556(2)	2591(1)	39(1)
N(12)	1352(1)	8445(2)	3588(1)	53(1)
C(13)	731(1)	9816(3)	3105(2)	61(1)
C(14)	578(1)	9829(3)	1835(2)	60(1)
C(15)	1142(1)	8366(3)	1527(2)	49(1)
N(21)	3260(1)	7089(2)	2838(1)	35(1)
N(22)	3577(1)	7573(2)	1799(1)	46(1)
C(23)	4361(1)	8596(3)	2193(2)	48(1)
C(24)	4550(1)	8797(3)	3456(2)	51(1)
C(25)	3829(1)	7844(3)	3841(2)	45(1)
H(2A)	2357(12)	5079(25)	961(16)	44(5)
H(2B)	1535(13)	4148(26)	1593(15)	51(5)
H(3A)	2560(15)	1628(35)	1991(20)	76(6)
H(3B)	3467(15)	2947(29)	2029(18)	61(6)
H(4A)	2724(15)	1841(35)	4037(20)	79(7)
H(4B)	3613(17)	3168(31)	4051(19)	75(7)
H(5A)	2596(12)	5474(26)	4682(16)	49(5)
H(5B)	1703(14)	4405(26)	3896(16)	55(5)
H(13)	469(14)	10582(33)	3660(18)	72(6)
H(14)	170(15)	10623(34)	1315(20)	77(7)
H(15)	1257(15)	7876(28)	712(20)	66(6)
H(23)	4709(13)	9108(30)	1596(18)	62(6)
H(24)	5066(13)	9519(28)	3953(16)	58(5)
H(25)	3694(13)	7681(25)	4584(19)	47(5)

unit cell is shown in Fig. 1; there are no abnormally close intermolecular contacts. Figure 2 shows the numbering of all atoms in the molecule; interatomic distances and angles are collected in Table 4. The carbocyclic frame of the cyclohexane system takes up the usual chair conformation. Dimensions within this ring fall in the following ranges: d(C—C) = 1.509(5)—1.529(4) Å (av. = 1.521 Å) and (C—C—C) = 110.9(2)–112.7(3)° (av. = 111.5°). The ten refined C—H distances range 0.960(24)—1.004(28) Å, averaging 0.985 Å (*cf.* the average overall X-ray determined C—H distance of ~0.95 Å[10]). The angle between the two bulky pyrazolyl ligands, ∠N(11)—C(1)—N(21) = 106.0(2)° is, surprisingly, the *smallest* of all external angles of the three organic rings; the largest values are for the chemically equivalent angles, ∠C(1)—N(11)—C(15) = 129.4(2)° and ∠C(1)—N(21)—C(25) = 128.5(2)°. Distances within the pyrazolyl rings are similar to those in related species (see Table 4 of ref. 4).

(2) 1,1-di(pyrazol-1-yl)cyclopentane, $C_5H_8(C_3N_2H_3)_2$

The labeling of atoms is illustrated in Fig. 3. Interatomic distances and angles are collected in Table 5. As can be seen from Fig. 4, the packing of molecules in the unit cell is stabilized by intermolecular N···H—C hydrogen bonding along the *c*-axis. Even though they crystallize in a different space group ($C2/c$, rather than $P2_1/c$), the packing of 2,2-

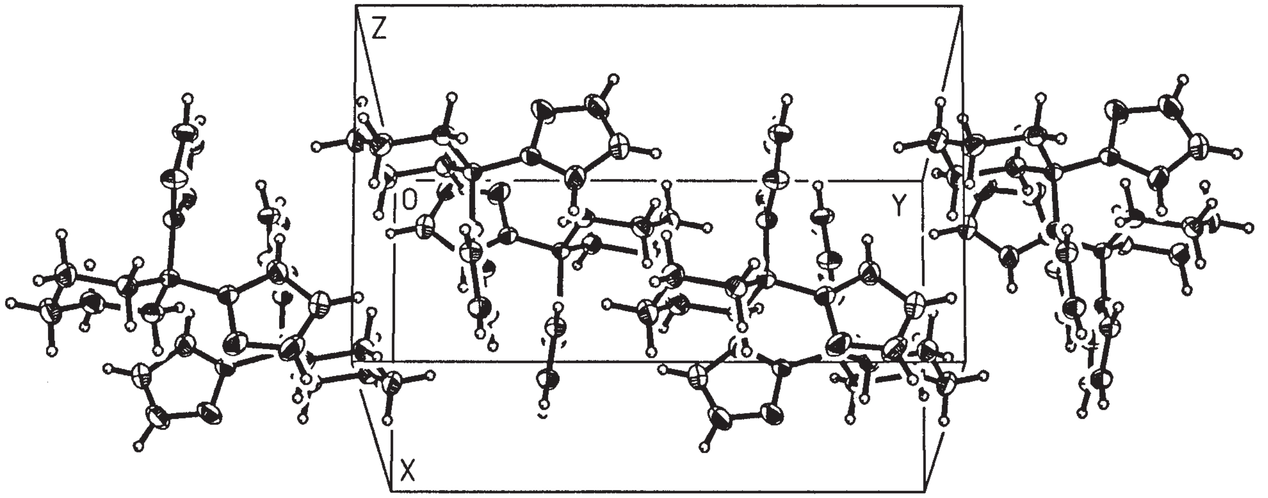

Fig. 1. Packing of $C_6H_{10}(C_3N_2H_3)_2$ molecules in the unit cell. (ORTEP2 diagram, 30% probability envelopes for non-hydrogen atoms, with H atoms artificially reduced.)

di(pyrazol-1-yl)propane[3] and 3,3-di(pyrazol-1-yl) pentane[4] molecules is remarkably similar to that for the present 1,1-di(pyrazol-1-yl)cyclopentane molecules, with analogous N···H–C interactions propagated along "*c*" by *c*-glide operations.

The cyclopentane ring takes up an unusual conformation such that the four atoms C(2) → C(5) are

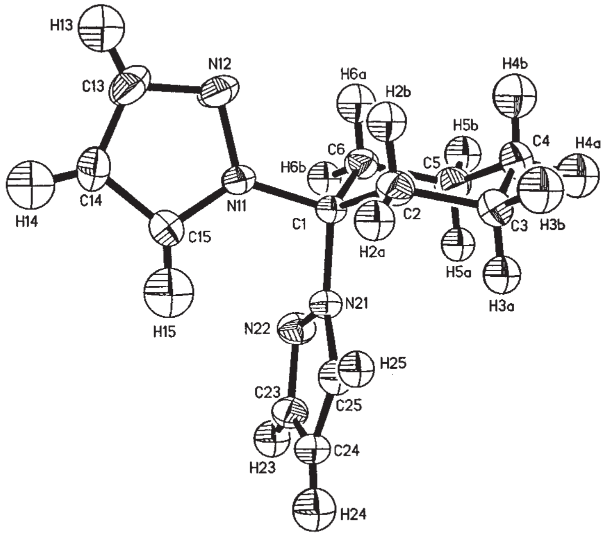

Fig. 2. Labeling of atoms in the $C_6H_{10}(C_3N_2H_3)_2$ molecule (ORTEP2 diagram, 30% probability envelopes for all atoms, including hydrogen atoms).

Table 4. Intramolecular Distances (Å) and Angles (°) for 1,1-Di(pyrazol-1-yl)cyclohexane

(A) Distances within cyclohexane ring			
C(1)−C(2)	1.523(4)	C(4)−C(5)	1.509(5)
C(2)−C(3)	1.529(4)	C(5)−C(6)	1.522(4)
C(3)−C(4)	1.514(4)	C(6)−C(1)	1.526(3)
(B) Distances within pyrazolyl rings			
N(11)−N(12)	1.341(3)	N(21)−N(22)	1.354(3)
N(12)−C(13)	1.332(4)	N(22)−C(23)	1.327(3)
C(13)−C(14)	1.354(4)	C(23)−C(24)	1.372(4)
C(14)−C(15)	1.360(4)	C(24)−C(25)	1.353(4)
C(15)−N(11)	1.334(3)	C(25)−N(21)	1.352(3)
(C) Inter-ring linkages			
C(1)−N(11)	1.483(3)	C(1)−N(21)	1.466(3)
(D) Internal angles of cyclohexane ring			
C(6)−C(1)−C(2)	110.9(2)	C(3)−C(4)−C(5)	110.9(3)
C(1)−C(2)−C(3)	112.7(2)	C(4)−C(5)−C(6)	111.9(3)
C(2)−C(3)−C(4)	111.3(2)	C(5)−C(6)−C(1)	111.2(2)
(E) Internal angles of pyrazolyl rings			
C(15)−N(11)−N(12)	111.1(2)	C(25)−N(21)−N(22)	111.1(2)
N(11)−N(12)−C(13)	103.8(2)	N(21)−N(22)−C(23)	103.8(2)
N(12)−C(13)−C(14)	112.9(3)	N(22)−C(23)−C(24)	112.7(3)
C(13)−C(14)−C(15)	104.2(3)	C(23)−C(24)−C(25)	104.8(2)
C(14)−C(15)−N(11)	108.0(2)	C(24)−C(25)−N(21)	107.5(3)
(F) External angles			
C(2)−C(1)−N(11)	109.1(2)	C(1)−N(11)−N(12)	119.2(2)
C(2)−C(1)−N(21)	110.9(2)	C(1)−N(11)−C(15)	129.4(2)
C(6)−C(1)−N(11)	109.7(2)	C(1)−N(21)−N(22)	119.7(2)
C(6)−C(1)−N(21)	110.1(2)	C(1)−N(21)−C(25)	128.5(2)
N(11)−C(1)−N(21)	106.0(2)		

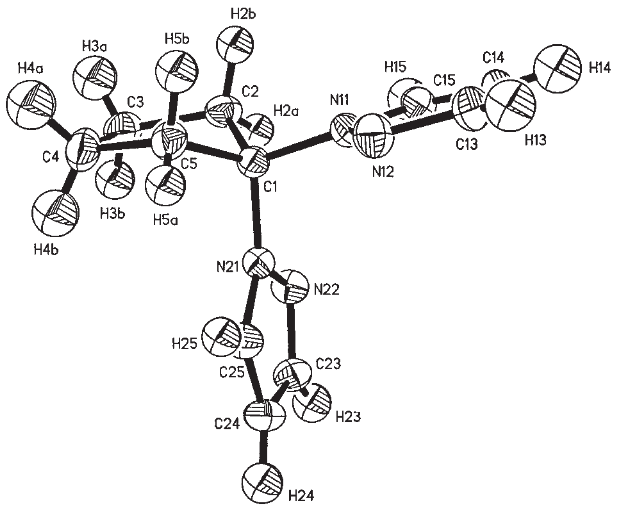

Fig. 3. Labeling of atoms in the $C_5H_8(C_3N_2H_3)_2$ molecule (ORTEP2 diagram, 30% probability envelopes for all atoms, including hydrogen atoms).

essentially coplanar (individual atomic deviations from the least-squares plane are 0.0011 Å for C(2), −0.0018 Å for C(3), 0.0018 Å for C(4), and −0.0011 Å for C(5)), while atom C(1) lies 0.6303 Å from this plane. The interplanar angle C(2)−C(3)−C(4)−C(5)/C(2)−C(1)−C(5) is 41.3°. This geometric arrangement is more similar to the bending observed in metal-cyclopentadiene complexes (e.g., $(C_5H_5)Co(C_5H_5Ph)$[11,12] or $(C_5H_5)Co(C_5H_5COPh)$[13–15]) than to the usual "puckered" conformation found in simple cyclopentane derivatives. Dimensions within the pentatomic carbocyclic ring include the following: d(C−C) = 1.520(2)−1.526(3) Å (av. = 1.524 Å) and ∠(C−C−C) = 102.4(1)–106.4(2)° (av. = 104.4°). The C−C−C angles are, of course, substantially smaller (by 7.1°) than those for the cyclohexane analogue (*vide supra*) as a geometric requirement for the smaller ring size. The eight refined C−H distances range 0.958(23)–0.997(19) Å, averaging 0.975 Å. The angle between the two pyrazolyl rings is N(11)−C(1)−N(21) = 108.3(1)°. Once again, the largest

Table 5. Intramolecular Distances (Å) and Angles (°) for 1,1-Di(pyrazol-1-yl) cyclopentane

(A) Distances within cyclopentane ring			
C(1)−C(2)	1.520(2)	C(4)−C(5)	1.526(3)
C(2)−C(3)	1.525(3)	C(5)−C(1)	1.525(2)
C(3)−C(4)	1.526(3)		
(B) Distances within pyrazolyl rings			
N(11)−N(12)	1.353(2)	N(21)−N(22)	1.350(2)
N(12)−C(13)	1.329(2)	N(22)−C(23)	1.323(2)
C(13)−C(14)	1.379(4)	C(23)−C(24)	1.377(3)
C(14)−C(15)	1.362(3)	C(24)−C(25)	1.353(3)
C(15)−N(11)	1.348(2)	C(25)−N(21)	1.349(2)
(C) Inter-ring linkages			
C(1)−N(11)	1.461(2)	C(1)−N(21)	1.478(2)
(D) Internal angles of cyclopentane ring			
C(5)−C(1)−C(2)	102.4(1)	C(3)−C(4)−C(5)	105.9(2)
C(1)−C(2)−C(3)	103.6(1)	C(4)−C(5)−C(1)	103.6(2)
C(2)−C(3)−C(4)	106.4(2)		
(E) Internal angles of pyrazolyl rings			
C(15)−N(11)−N(12)	112.1(1)	C(25)−N(21)−N(22)	111.0(1)
N(11)−N(12)−C(13)	103.7(2)	N(21)−N(22)−C(23)	104.3(1)
N(12)−C(13)−C(14)	112.4(2)	N(22)−C(23)−C(24)	112.4(2)
C(13)−C(14)−C(15)	105.0(2)	C(23)−C(24)−C(25)	104.6(2)
C(14)−C(15)−N(11)	106.7(2)	C(24)−C(25)−N(21)	107.7(2)
(F) External angles			
C(2)−C(1)−N(11)	113.1(1)	C(1)−N(11)−N(12)	119.8(1)
C(2)−C(1)−N(21)	110.0(1)	C(1)−N(11)−C(15)	127.7(1)
C(5)−C(1)−N(11)	113.0(1)	C(1)−N(21)−N(22)	120.0(1)
C(5)−C(1)−N(21)	109.9(1)	C(1)−N(21)−C(25)	128.6(1)
N(11)−C(1)−N(21)	108.3(1)		

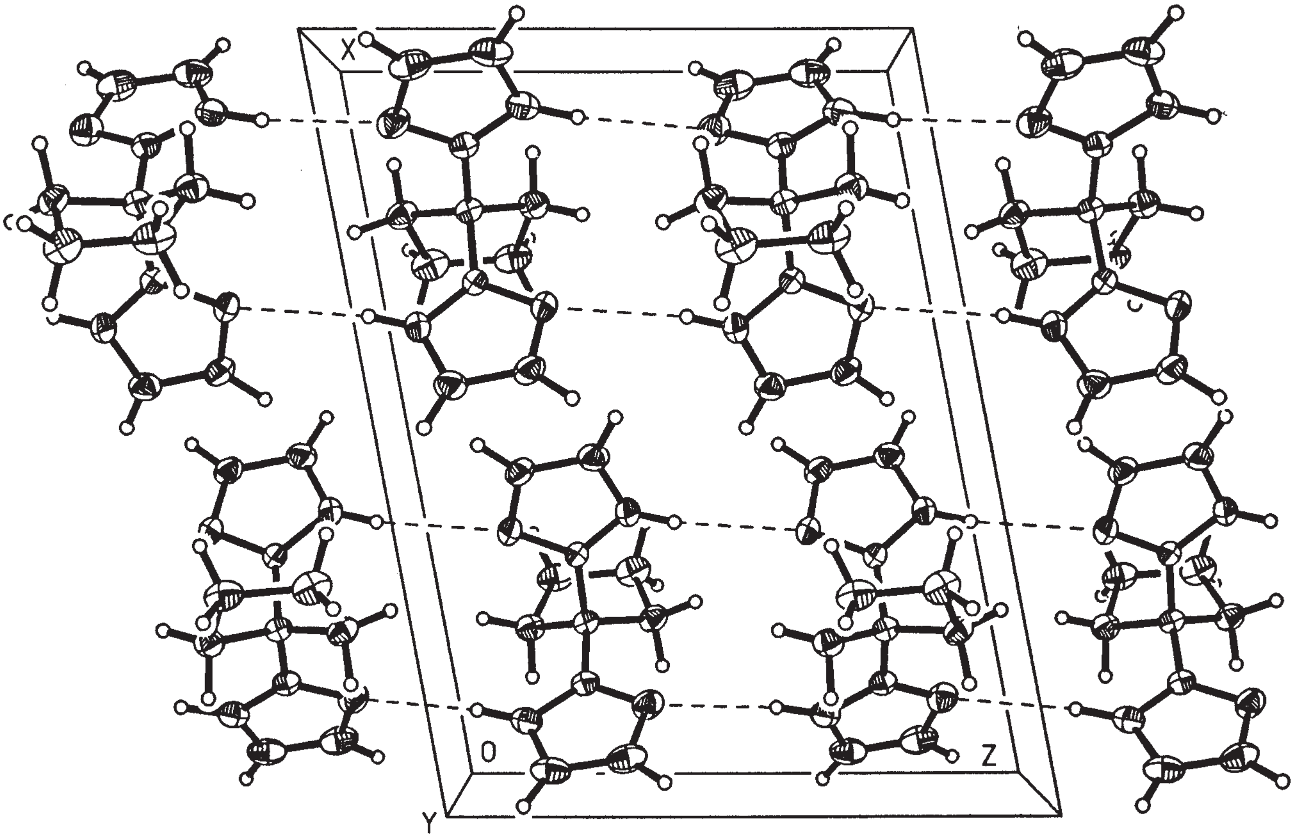

Fig. 4. Packing of $C_5H_8(C_3N_2H_3)_2$ molecules in the unit cell (ORTEP2 diagram, 30% probability envelopes for nonhydrogen atoms, with H atoms artificially reduced).

angles in the molecule are the chemically equivalent pair, C(1)—N(21)—C(25) = 128.6(1)° and C(1)—N(11)—C(15) = 127.7(1)°. Distances and angles within the pyrazolyl rings are similar to those for the cyclohexane analogue.

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References

1. Bessel, C.A.; See, R.F.; Jameson, D.L.; Churchill, M.R.; Takeuchi, K.J. *J. Chem. Soc. Dalton Trans.* **1992,** 3223.
2. Churchill, M.R.; Churchill, D.G.; Huynh, M.H.V.; Takeuchi, K.J.; Castellano, R.K.; Jameson, D.L. *J. Chem. Crystallogr.* **1996,** *26,* 93.
3. Churchill, M.R.; Churchill, D.G.; Huynh, M.H.V.; Takeuchi, K.J.; Castellano, R.K.; Jameson, D.L. *J. Chem. Crystallogr.* **1996,** *26,* 179.
4. Churchill, M.R.; Churchill, D.G.; Huynh, M.H.V.; Takeuchi, K.J.; Distefano, A.J.; Jameson, D.L. *J. Chem. Crystallogr.* **1999,** *29,* 461.
5. Churchill, M.R.; Lashewycz, R.A.; Rotella, F.J. *Inorg. Chem.* **1977,** *16,* 265.
6. Sheldrick, G.M.; *SHELXTL PLUS;* Siemens Analytical Instruments, Madison, WI, 1989.
7. Sheldrick, G.M.; *SHELXTL PLUS. An Integrated System for Solving. Refining and Displaying Crystal Structures from Diffraction Data. For Nicolet R3m/V;* University of Göttingen: Germany, 1987.
8. *International Tables for X-Ray Crystallography. Vol. 4;* Kynoch Press: Birmingham, England, 1974 (a) Table 2.2B on pp 99–101; (b) Table 2.3.1 on pp 149–150.
9. (a) Zachariasen, W.H. *Acta Crystallogr.* **1963,** *16,* 1139; (b) *idem, ibid.* **1967,** *23,* 558.
10. Churchill, M.R. *Inorg. Chem.* **1973,** *12,* 1213.
11. Churchill, M.R.; Mason, R. *Proc. Chem. Soc.* **1963,** 112.
12. Churchill, M.R.; Mason, R. *Proc. Roy. Soc.* **1964,** *A279,* 191.
13. Churchill, M.R. *J. Organomet. Chem.* **1965,** *4,* 258.
14. Churchill, M.R.; Mason, R. *Adv. Organomet. Chem.* **1967,** *5,* 93.
15. Churchill, M.R. *Transac. New York Acad. Sci.* **1969,** *31,* 280.