Crystal and molecular structure of the symmetrical bidentate ligand 3,3-di(1-pyrazolyl)pentane, CH₃CH₂C(C₃H₃N₂)₂CH₂CH₃

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Received March 26, 1998

The title compound crystallizes in the centrosymmetric space group C2/c with a = 14.4005(23), b = 7.0494(12), c = 11.2462(20) Å, $\beta = 101.572(13)^{\circ}$ and Z = 4; the molecule lies on a crystallographic C_2 axis. Hydrogen atoms were both located and refined.

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

Introduction

We have recently been involved in the determination of the detailed geometric properties of a series of nitrogen-containing polydentate ligands. We have previously reported the X-ray structural characterization of the *tridentate* ligands 2,2':6',2"-terpyridine and 2,6-bis(1-pyrazolyl)pyridine,¹ and the *bidentate* ligands di(1-pyrazolyl)methane² and 2,2-di(1-pyrazolyl)propane;³ we have now extended these studies to 3,3-di(1-pyrazolyl)pentane.

Experimental

Synthesis

The synthetic method is a modification of a previous published procedure.⁴

Synthesis of 3,3-dimethoxypentane. A 1 L roundbottomed flask was charged with (in order) 70.0 g of montmorillonite K, 400 mL of hexanes, and 82.5 g of trimethyl orthoformate (0.777 mol) and the mixture was stirred for 15 min. 3-pentanone (44.8 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 and washed with hexanes and the combined filtrates were washed with 200 mL of 0.5% Na₂CO₃. The organic layer was dried over MgSO₄, filtered and the hexanes were removed by rotary evaporator. Distillation at atmospheric pressure (125–128°C) yielded 62 g (67%) of a liquid which was judged by GC/MS to be the desired product.

Synthesis of 3,3-di(1-pyrazolyl)pentane. A 300 mL round-bottomed flask was charged with 7.82 g (0.053 mol) 3,3-dimethoxypentane, 7.02 g (0.103 mol) pyrazole, 150 mL of toluene, and 25 mg of p-toluenesulfonic acid. The mixture was heated to reflux (the methanol being removed) for 48 h. The reaction was worked up as described above and the organic residue remaining after evaporation of the organic layer was dissolved in 25 mL hexane. Filtration yielded 3.1 g of product which was recrystallized from hot cyclohexane to give 2.23 g (20% yield) of white crystals (m.p. 50–56°C). ¹H NMR (CDCl₃): ppm 0.79 (t, 6H, J = 7.3 Hz); 2.73 (q, 4H, 7.3 Hz); 6.26 (d of d, 2H, J = 3.2, 0.6 Hz); 7.4–7.6 (m, 4H). ¹³C NMR (C₆H₆): ppm 7.7, 29.5, 83.1, 105.9, 127.6, 139.2.

Preparation of a single crystal of 3,3-di(1-pyrazo-lyl)pentane. A 30-mg sample of 3,3-di(1-pyrazolyl)-

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pentane was dissolved in a minimum amount of toluene. Cyclohexane was slowly added until cloudiness was observed. A very small amount of toluene was then carefully added until the mixture became clear. The solution was left undisturbed in the dark and uncovered until complete evaporation of the solvent occurred (approximately 4 days). A number of clear, colorless crystals (approximately $1 \times 1 \times 3$ mm) were isolated from the container. The ¹H NMR spectrum of the crystals was consistent with the ¹H NMR spectrum of 3,3-di(1-pyrazolyl)pentane and the melting point of the crystals was 58–59°C.

The crystallographic structural analysis

A colorless block, of approximate orthogonal dimensions $0.5 \times 0.35 \times 0.25$ mm, was cut from a larger crystal and sealed into a thin-walled glass capillary. It was aligned on a Siemens R3m/V automated with its extended direction close-to-parallel with the instrumental ϕ -axis. Diffraction data were collected as described in general previously;⁵ details specific to the present analysis are provided in Table 1.

Table 1. Crystal data and	structure refinement
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$C_{11}H_{16}N_4$
CCDC-1003/5553
Colorless
204.3
296 K
Monoclinic
C2/c (No. 15)
$a = 14.4005(23), \text{\AA}$
b = 7.0494(12) Å
c = 11.2462(20) Å
$\beta = 101.572(13)^{\circ}$
1118.25(33) Å ³
4
1.213 mg/m ³
0.072 mm^{-1}
440
5.0 to 45.0°
$-15 \le h \le 15, -7 \le k \le 7,$
$-12 \le l \le 12$
2933
736 ($R_{\rm int} = 0.68\%$)
632 ($F > 6.0\sigma(F)$)
$\Sigma w (F_{\rm o} - F_{\rm c})^2$
$\chi = 0.005(2)$, where
$F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1}$
$w^{-1} = \sigma^2(F) + 0.0003F^2$
102
2.23
R = 0.0340, wR = 0.0335
R1 = 0.0394, wR = 0.0507

The crystal gave rise to a diffraction pattern of C_{2h} (2/m) symmetry, indicative of the monoclinic crystal system. The systematic absences (*hkl* for h + k = 2n + 1; *h0l* for both l = 2n + 1 and h = 2n + 1) are consistent with space groups Cc (No. 9)^{6a} or C2/c (No. 15).^{6b} Intensity statistics⁷ favored the latter, centrosymmetric, possibility. With Z = 4, this requires that the molecule lies on a site of crystallographic C_2 (2) or C_i (\overline{l}) symmetry;^{6b} only the former is possible for an *ordered* structure.

A complete sphere of X-ray diffraction data (Mo $K\overline{\alpha}$ radiation, $\overline{\lambda} = 0.710730$ Å, $^{8}2\theta = 5.0-45.0^{\circ}$), representing four equivalent general forms, was collected. The 2933 observed reflections were reduced to a unique set of 736 data (with the remarkably satisfactory averaging index of R(int) = 0.68%); 632 data (85.9%) were observed with $|F_{o}| > 6\sigma(|F_{o}|)$.

The structure was solved by direct methods under the SHELXTL PLUS Release 4.11 (VMS) system of crystallographic routines.^{9,10} Calculations were based upon the analytical expressions for neutral atoms;^{11a} corrections were made for the small real $(\Delta f')$ and imaginary $(i\Delta f'')$ components of anomalous dispersion.^{11b} Nonhydrogen atoms were quickly located from an electron density map, which showed the molecule to lie about a site of two-fold symmetry at 1/2, y, 1/4 (Wyckoff notation e^{6b}). Positional and anisotropic displacement coefficients for all nonhydrogen atoms (with $U_{12} = U_{23} = 0$ for atom C(13), which lies on a site of C_2 symmetry^{11c}) were refined, following which all hydrogen atoms were located unambiguously from a difference-Fourier map. Refinement of positional and anisotropic displacement coefficients for non-hydrogen atoms, positional and isotropic displacement coefficients for all hydrogen atoms, the scale factor and a secondary extinction parameter¹² led to convergence $[(\Delta/\sigma)_{max} = 0.002]$ with R = 3.94% for all 736 reflections and R = 3.40%for those 632 reflections above $6\sigma(|F_0|)$. Final atomic coordinates are given in Table 2.

Discussion

The 3,3-di(1-pyrazolyl)pentane molecule lies on a site of crystallographic C_2 symmetry, which passes through atom C(13). The crystallographic asymmetric unit consists of one-half of the molecule. The atomic labeling scheme is shown in Fig. 1. Atoms in the primary unit are labeled normally; those in the "other-half" of the molecule, related to the primary unit by the transformation (1 - x, y, 1/2 - z), are

3,3-Di(l-pyrazolyl)pentane

Uх y z N(1) 4157(1)149(2) 2324(1) $46(1)^{a}$ N(2) 3914(1) -668(2)3306(1) $63(1)^{a}$ C(3) 3191(1) -1785(3)2841(2) $67(1)^{a}$ C(4) 2972(1) -1717(3)1606(2) $66(1)^{a}$ -491(3)C(5) 3605(1)1292(2) $58(1)^{a}$ C(11) 4203(2)4060(4)1106(4)98(1)^a 4984(1)2578(3) 1360(2) C(12) $65(1)^{a}$ C(13) 5000 1390(3) 2500 $48(1)^{a}$ 3382(19) H(3) 2925(13) 2536(28) 84(6) H(4) 2481(13) -2336(29)1027(18) 82(6) H(5) 3703(13) -127(24)549(19) 64(5)H(11A) 4149(17) 4588(37) 299(25) 112(9) H(11B) 3585(20) 3530(27) 1035(24)116(9) 129(10) H(11C) 4306(21) 5017(45) 1786(27) H(12A) 5599(13) 3202(28) 1500(16) 72(5) H(12B) 4955(12) 1760(29) 696(18) 68(5)

Table 2. Atomic coordinates ($\times 10^4$) and isotropic displacements $(U, \text{\AA}^2 \times 10^3)$ for atoms in 3,3-di(1-pyrazolyl)pentane

^{*a*} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ii} tensor.

labeled with the suffix "A." Intramolecular distances and angles are listed in Table 3.

Bond lengths within the pyrazolyl system are (given cyclically), N(1)-N(2) = 1.351(2), N(2)-C(3) = 1.327(2), C(3)-C(4) = 1.361(3), C(4)-C(5) = 1.354(3), and C(5)-N(1) = 1.346(2) Å; these are in excellent agreement with those found previously in 1,1-di(pyrazolyl)methane² and 2,2-di (pyrazolyl)propane³ (see Table 4).



Fig. 2. Packing of molecules in the unit cell, as viewed down *c*. The *a*-axis is vertical and the *b*-axis horizontal. [ORTEP2 diagram; 30% ellipsoids, with hydrogen atoms artificially reduced.]

The pyrazolyl ligands are close-to-planar, the constituent nonhydrogen atoms having a mean deviation of only 0.0051 Å from their least-squares plane. The interplanar angle between the two symmetry-related pyrazolyl systems is 82.6° . The N(1)…N(1A) distance is 2.381 Å. Atoms N(2) and N(2A), which have lone pairs of electrons available



Fig. 1. Labeling of atoms in the CH₃CH₂C($C_3H_3N_2$)₂CH₂CH₃ molecule. The crystallographic C_2 -axis is vertical and passes through atom C(13). This is an ORTEP2 diagram showing 30% probability envelopes for all atoms, including hydrogens.



Fig. 3. Packing of molecules viewed down b, the unique axis. The *c*-axis is horizontal and the *a*-axis lies at about 11.6° from the vertical.

(A) Distances within the C ₃ N ₂ r	ing		
N(1) - N(2)	1.351(2)	C(3) - C(4)	1.361(3)
N(1) - C(5)	1.346(2)	C(4) - C(5)	1.354(3)
N(2) - C(3)	1.327(2)		
(B) N(pyrazolyl)-C(pentane) l	inkages		
N(1) - C(13)	1.477(2)	N(1A) - C(13)	1.477(2)
(C) Bond lengths within the per	ntane backb	one	
C(11) - C(12)	1.519(4)	C(13) - C(12A)	1.528(3)
C(12) - C(13)	1.528(3)	C(12A) - C(11A)	1.519(4)
(D) Carbon-hydrogen distance	es		
C(3)-H(3)	0.94(2)	C(11) - H(11B)	0.95(3)
C(4) - H(4)	0.96(2)	C(11)-H(11C)	1.01(3)
C(5) - H(5)	0.91(2)	C(12)-H(12A)	0.97(2)
C(11)-H(11A)	0.97(3)	C(12) - H(12B)	0.94(2)
(E) Internal angles of the pyraz	olyl ring		
N(2) - N(1) - C(5)	110.9(1)	C(3) - C(4) - C(5)	105.0(2)
N(1) - N(2) - C(3)	104.0(1)	N(1) - C(5) - C(4)	107.5(2)
N(2) - C(3) - C(4)	112.6(2)		
(F) Angles on the exterior of th	ne pyrazolyl	ring	
N(2) - N(1) - C(13)	118.9(1)	C(3) - C(4) - H(4)	131.4(13)
C(5) - N(1) - C(13)	129.8(1)	C(5) - C(4) - H(4)	123.6(13)
N(2) - C(3) - H(3)	117.8(11)	N(1) - C(5) - H(5)	121.5(11)
C(4) - C(3) - H(3)	129.5(11)	C(4) - C(5) - H(5)	130.9(11)
(G) C-C-C, N-C-C and N	-C-N ang	les associated with the pe	entane
backbone			
C(11) - C(12) - C(13)	114.9(2)	N(1) - C(13) - C(12)	109.8(1)
C(12) - C(13) - C(12A)	113.5(2)	N(1) - C(13) - C(12A)	108.1(1)
C(12) - C(13) - N(1A)	108.1(1)	N(1) - C(13) - N(1A)	107.4(2)
N(1A) - C(13) - C(12A)	109.8(1)		

 Table 3. Intramolecular distances (Å) and angles (deg.) for 3,3-di(1-pyrazolyl)-pentane

for coordination to such Lewis acids as transition metal cations, are separated with $N(2)\cdots N(2A) = 3.915$ Å. Rotation about the C(13)-N(1) and/or C(13)-N(1A) bonds is required before this molecule may function as a bidentate ligand—as it does in solution!

The pentane system is associated with the carbon-carbon distances C(11)-C(12) = 1.519(4), C(12)-C(13) = 1.528(3), C(13)-C(12A) = 1.528(3), and C(12A)-C(11A) = 1.519(4) Å. The pentatomic chain cannot take up the normal zig-zag conformation and its constituent carbon atoms are not coplanar. Indeed, atoms C(11) and C(11A) lie -1.099 and +1.099 Å, respectively, from the central C(12) - C(13) - C(12A) plane. The two symmetry-related pyrazolyl moieties lie at supplementary angles of 129.8 and 50.2° (respectively) to the C(12) - C(13) - C(12A) plane.

All eight crystallographically unique hydrogen atoms were refined; the resulting carbon—hydrogen

Table 4. Comparison of the bond lengths within three closely related pyrazolyl-containing species

	$CH_2(C_3H_3N_2)^2$	$CH_{3}C(C_{3}H_{3}N_{2})_{2}CH_{3}^{3}$	CH ₃ CH ₂ C(C ₃ H ₃ N ₂)CH ₂ CH ₃
N(1) - N(2)	1.347(2), 1.352(2)	1.349(2)	1.351(2)
N(2) - C(3)	1.325(3), 1.323(2)	1.325(2)	1.327(2)
C(3) - C(4)	1.376(3), 1.377(3)	1.368(3)	1.361(3)
C(4) - C(5)	1.356(3), 1.356(3)	1.350(3)	1.354(3)
C(5) - N(1)	1.342(2), 1.344(2)	1.346(2)	1.346(2)

3,3-Di(l-pyrazolyl)pentane

bond lengths range from C(5) - H(5) = 0.91(2) to C(11) - H(11C) = 1.01(3) Å, with an average value of 0.956 Å; this is in good agreement with the typical "X-ray determined" C-H distance of ~0.95 Å¹³ and is, of course, substantially reduced from the typical *internuclear* C-H distance of ~ 1.08 Å.

The packing of molecules within the unit cell is illustrated by Figs. 2 and 3. The structure is stabilized by weak hydrogen bonds involving N(2); thus N(2)…H(5) [x, -y, 1/2 + z] = 2.66 Å, and $\angle N(2)$ …H(5) $- C(5) = 175.2^{\circ}$. The closest intermolecular hydrogen \cdots hydrogen contact appears to be H(4)…H(4) [1/2 - x, -1/2 - y, -z] = 2.34 Å. (*Note that the above contacts are all based upon the "X-ray determined" positions of the hydrogen atoms.*)

Acknowledgments

The purchase of the diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

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