Title
TRIS(METHYLCYCLOPENTADIENYL)URANIUM(III)AMMONI A

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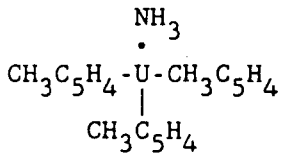
Abstract. $(MeC_5H_4)_3U{\cdot}NH_3$, M_r = 492.43, monoclinic, Im, a = 12.129(3), b = 24.197(5), c = 8.725(3) Å, β = 92.85°, V = 2557.5 Å^3, Z = 6, D_x = 1.92 g/cm^3, λ(MoKα) = 0.71073 Å, μ = 90.2 cm^{-1}, F(000) = 1386, T = 296 K, R = 0.037 [4247 data, $F^2 > 3\sigma(F^2)$]. There are two independent molecules, one of which is across the mirror plane. The uranium atom is bonded to three cyclopentadienyl rings and to an ammonia molecule, with <U-C>, <U-ring> and <U-N> distances of 2.81(5), 2.55(3) and 2.61(3) Å, respectively.

Introduction. The crystal structure of $(MeC_5H_4)_3U{\cdot}NH_3$ was determined in order to examine the role of steric effects on the U-L bond length in a series of $(MeC_5H_4)_3U{\cdot}L$ compounds, where L = ammonia, 4-dimethylaminopyridine, and quinuclidine. A structural representation of the complex is shown below.



Experimental. The title compound was prepared by the addition of an ammonia-saturated toluene solution to a solution of $(MeC_5H_4)_3U{\cdot}OC_4H_8$, and the red-brown needles were crystallized from ether at -20°. An air-sensitive crystal, 0.1 x 0.2 x 0.7 mm, was sealed inside a quartz capillary in an argon filled dry box. X-ray diffraction intensities (θ-2θ scans) were obtained using a modified Picker FACS-I automatic diffractometer equipped with a graphite monochromator. Cell dimensions from 30 reflections, 20° < 2θ < 33°; 2θ scan width 1.5+0.693tanθ, 2θ scan speed 2-8° min^{-1}; analytical absorption correction, range 1.5-2.9; max $\sin\theta/\lambda$ = 0.65, h -15 to 15, k 0 to 31, ℓ -11 to 11; three standard reflections, 1.6%,1.2%,1.6% variation in standards intensities from average, intensities adjusted isotropically; 6046 data (with 4247, $F^2 > 3\sigma$) Friedel pairs not averaged; structure solved by Patterson and Fourier methods; refined on F, 246 parameters; 37 hydrogen atoms in calculated positions and fixed isotropic thermal paramters; anisotropic thermal parameters for 26 of the 32 non-hydrogen atoms; distance restraints applied to 10 ring C-C and to 4 C-C(methyl) distances, 1.39 Å and 1.54 Å respectively; R = 0.075 for all the data, R = 0.037 for $F^2 > 3\sigma$ data,

wR = 0.043, S = 1.07; $w=4F^2[\sigma^2(F^2)+(0.055F^2)^2]^{-1}$; max (shift/$\sigma$) < 0.09; no extinction correction indicated; max. and min of ΔF synthesis 2.4 and -2.0 e $Å^{-3}$; Rogers (1981) parameter η (an indicator of absolute configuration and twinning in non-centric structures) = 0.95(3); atomic f for neutral U, Cl and C, and spherical bonded H from International Tables (1974); local unpublished programs and ORTEP (Johnson, 1965). Atomic parameters are listed in Table I*. A list of selected distances and angles is given in Table II. Figures 1 and 2 show the two independent molecules and the numbering scheme.

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*Lists of anisotropic thermal parameters, calculated hydrogen positions, additional distances and angles, distance restraints, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. XXXXX (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results. There are two independent molecules in the unit cell. In the first molecule, Fig. 1, the atoms are all in general positions. The second molecule is astride the mirror plane and is shown in Fig. 2. Although the orientation of components of the two molecule are different, the bond distances and angles are comparable within the estimated statistics, and chemically the two are identical.

The average U-N distance of 2.61(3) Å in the ammonia complex may be compared with other trivalent uranium coordination complexes with nitrogen-containing donor ligands: 2.64(2) Å in $(MeC_5H_4)_3U\cdot p\text{-}NC_5H_4Me$ (Zalkin &

Brennen, 1987), and 2.764(4) Å in $(MeC_5H_4)_3U{\cdot}N(CH_2CH_2)CH$ (Brennan, Stults, Andersen & Zalkin, 1988). The large variation in these distances reflects the relative steric demands of the ligands. The title compound has a U-N distance similar to that found in the dimethylaminopyridine adduct, consistent with their similar steric nature. This is in marked contrast to the quinuclidine complex. Solution based-competition studies further reflect this difference: the ammonia and dimethylaminopyridine complexes are similar in their coordinative affinity for uranium, and both are better Lewis bases than quinuclidine (Brennan, 1985; Rosen, 1988).

The average Cp-U-Cp and Cp-U-N angles also reflect the steric differences between these ligands, although the differences are small. In $(MeC_5H_4)_3U{\cdot}NH_3$, these angles are 118° and 97°, respectively, while in $(MeC_5H_4)_3{\cdot}p\text{-}NC_5H_4Me$ and $(MeC_5H_4)_3U{\cdot}N(CH_2CH_2)CH$ the Cp-U-Cp angles are 117° and 116° and the Cp-U-N angles are 100° and 101°. Thus, the title compound shows a slightly greater tendency towards an idealized geometry of trigonal pyramidal, suggesting that ammonia is slightly less bulky than either of these other ligands. Although these values are consistent with the solution equilibrium studies, they are not significant crystallographically.

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Table I. Atomic Parameters

$$B_{eq} = 1/3\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Atom	x	y	z	B*/Beq
U1	0	0.18783(2)	0	3.75(1)
U2	0.51053(6)	0	0.25804(8)	3.47(2)
N1	-0.1344(10)	0.2713(6)	-0.0174(15)	4.7(3)
N2	0.7237(16)	0	0.2139(25)	5.8(6)
C1	0.0938(15)	0.2091(8)	0.2965(18)	6.3(5)
C2	0.1735(14)	0.1816(8)	0.2149(23)	6.8(5)
C3	0.2080(12)	0.2180(11)	0.1077(20)	7.7(6)
C4	0.1510(16)	0.2689(8)	0.1165(20)	7.5(6)
C5	0.0771(13)	0.2623(6)	0.2397(16)	5.6(4)
C6	-0.1489(17)	0.1448(8)	0.2051(21)	7.3(6)
C7	-0.0729(16)	0.1008(9)	0.1803(24)	8.0(6)
C8	-0.0861(21)	0.0796(10)	0.035(3)	9.4(8)
C9	-0.1712(25)	0.1076(15)	-0.0291(27)	11.1(10)
C10	-0.2106(13)	0.1460(11)	0.0670(28)	9.1(8)
C11	0.0374(29)	0.1355(15)	-0.300(4)	15.1(11)*
C12	-0.0430(18)	0.1780(11)	-0.3231(19)	8.8(8)
C13	0.0046(21)	0.2310(9)	-0.2965(18)	7.9(7)
C14	0.1123(20)	0.2197(10)	-0.2560(19)	8.1(7)
C15	0.1338(15)	0.1651(9)	-0.2459(20)	7.0(5)
C16	0.4931(18)	0.0605(9)	0.5354(26)	7.8(5)*
C17	0.4143(17)	0.0802(6)	0.4316(23)	10.3(8)
C18	0.4521(14)	0.1088(7)	0.3039(18)	6.5(5)
C19	0.5640(15)	0.1085(6)	0.3296(20)	8.9(7)
C20	0.5833(18)	0.0821(10)	0.4709(26)	9.8(6)*
C21	0.362(4)	0	0.006(3)	9.8(14)
C22	0.4255(25)	0.0466(12)	-0.0202(27)	12.8(12)
C23	0.5295(21)	0.0290(8)	-0.0394(21)	12.7(14)
C24	0.0039(19)	0.3063(8)	0.3041(25)	9.3(7)
C25	0.0020(21)	0.0781(17)	0.313(3)	16.9(16)
C26	0.054(4)	0.0725(16)	-0.307(5)	19.7(16)*
C27	0.6900(28)	0.0666(21)	0.565(5)	20.4(16)*
C28	0.244(4)	0	0.065(10)	26.7(34)*

* atoms refined isotropically

Table II. Selected Distances(Å) and Angles(°)[a]

<U2	- C>	2.78(6)	Cp1 - U1 - Cp3		118.1
U1	- Cp1	2.54	Cp2 - U1 - Cp3		118.1
U1	- Cp2	2.57	Cp4 - U2 - Cp4'		114.4
U1	- Cp3	2.58	Cp4 - U2 - Cp5		120.5
U2	- Cp4	2.53	N1 - U1 - Cp1		98.1
U2	- Cp5	2.51	N1 - U1 - Cp2		97.4
U1	- N1	2.595(12)	N1 - U1 - Cp3		97.6
U2	- N2	2.633(19)	N2 - U2 - Cp4		98.5
			N2 - U2 - Cp5		94.5

[a] Cp1, Cp2, Cp3, Cp4, and Cp5 are the centroids of cyclopentadienyl ring atoms C1-C5, C6-C10, C11-C15, C16-C20, and (C21,C22,C22',C23,C23') respectively. Primed positions represent the equivalent groups or atoms at x,-y,z.

Fig 1. ORTEP drawing of the molecule in the general position; thermal ellipsoids at 50% probability level.

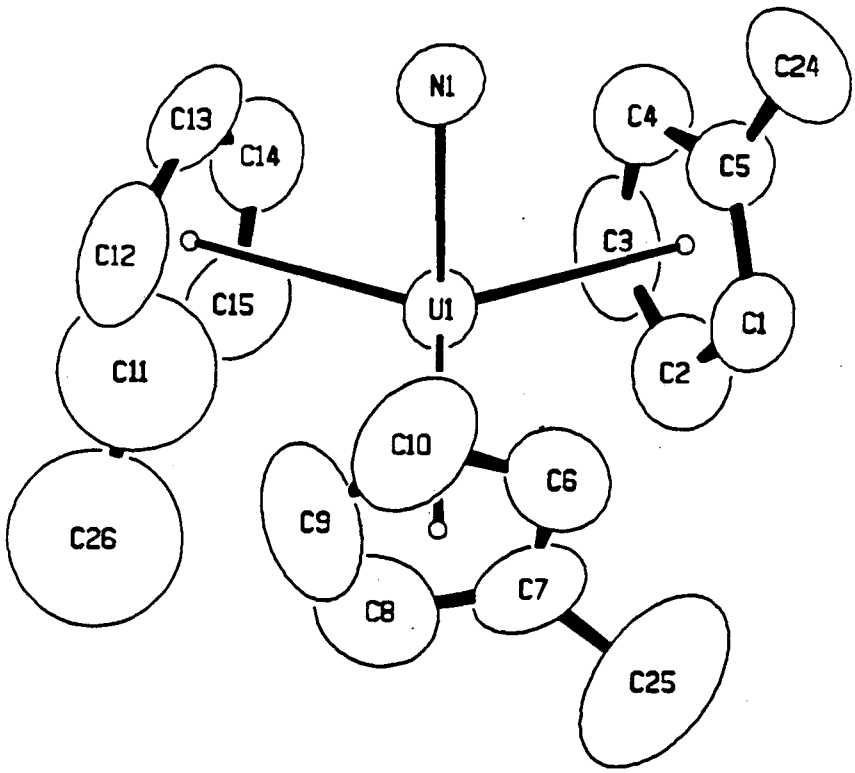
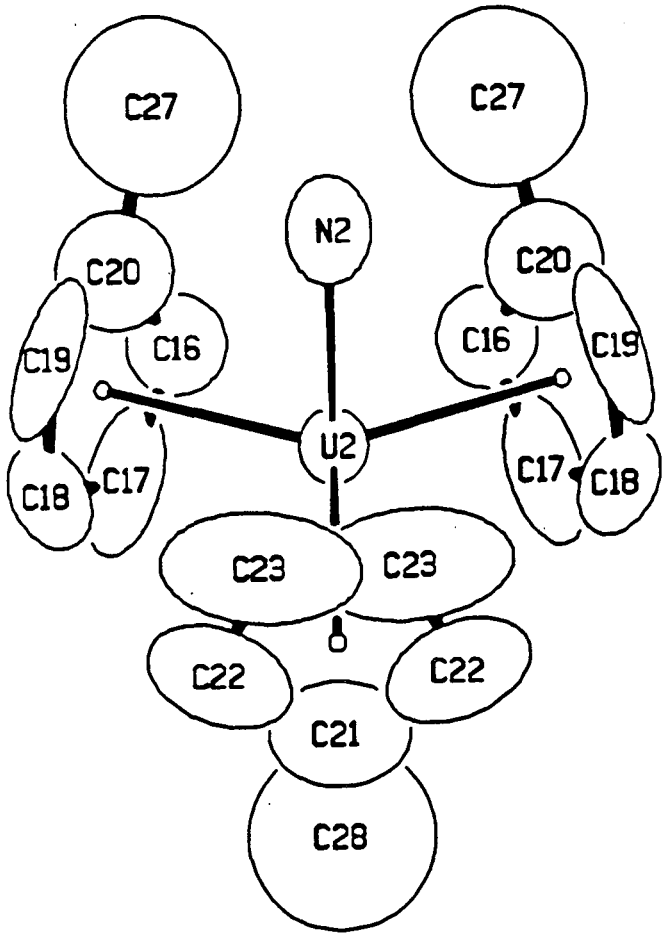


Fig 2. ORTEP drawing of the molecule on the mirror plane; thermal ellipsoids at 50% probability level.



Supplemental Materials

Tris(methylcyclopentadienyl)uranium(III)ammonia

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Abstract. $(MeC_5H_4)_3U{\cdot}NH_3$, M_r = 492.43, monoclinic, Im, a = 12.129(3), b = 24.197(5), c = 8.725(3) Å, β = 92.85°, V = 2557.5 Å^3, Z = 6, D_x = 1.92 g/cm^3, λ(MoKα) = 0.71073 Å, μ = 90.2 cm^{-1}, F(000) = 1386, T = 296 K, R = 0.037 [4247 data, $F^2 > 3\sigma(F^2)$]. There are two independent molecules, one of which is across the mirror plane. The uranium atom is bonded to three cyclopentadienyl rings and to an ammonia molecule, with <U-C>, <U-ring> and <U-N> distances of 2.81(5), 2.55(3) and 2.61(3) Å, respectively.

Supplemental Table 1. Anisotropic Thermal Parameters ($Å^2$) with Estimated Standard Deviations for $(MeC_5H_4)_3UNH_3$

Atom	B11	B22	B33	B12	B13	B23
U1	3.873(18)	4.147(23)	3.244(19)	0	0.459(13)	0
U2	4.00(3)	3.47(3)	2.982(28)	0	0.481(22)	0
N1	5.0(6)	4.5(6)	4.6(6)	0.5(5)	0.2(4)	0.7(5)
N2	5.6(9)	5.2(10)	6.9(11)	0	3.0(8)	0
C1	8.0(10)	6.2(8)	4.6(7)	-0.2(8)	-1.0(7)	0.1(7)
C2	5.1(7)	8.0(11)	7.2(10)	1.7(7)	-1.3(7)	-0.7(8)
C3	4.8(7)	12.7(16)	5.7(8)	-2.3(9)	0.3(6)	-2.2(10)
C4	8.6(10)	6.9(10)	6.8(9)	-3.9(8)	-1.1(8)	1.1(8)
C5	7.3(8)	5.3(8)	4.2(6)	-1.7(6)	1.2(5)	0.5(6)
C6	8.3(10)	6.7(10)	7.0(10)	-3.1(9)	2.5(8)	-0.1(8)
C7	9.4(12)	6.9(11)	7.6(11)	-4.4(10)	-1.8(9)	3.3(9)
C8	9.1(13)	8.5(13)	10.6(16)	-6.4(12)	0.7(12)	0.9(12)
C9	10.4(16)	15.4(24)	7.8(12)	-9.1(17)	2.0(12)	-3.4(14)
C10	4.9(8)	13.1(18)	9.1(13)	-2.9(9)	-0.4(8)	3.4(13)
C12	8.4(11)	14.0(19)	4.1(7)	-3.1(12)	0.8(7)	1.1(9)
C13	12.3(15)	8.2(12)	3.4(7)	-0.7(12)	2.6(8)	2.9(7)
C14	11.5(14)	9.0(14)	4.1(7)	-3.3(12)	3.0(8)	0.2(8)
C15	7.4(9)	8.0(11)	5.7(8)	2.8(8)	2.5(7)	0.5(8)
C17	12.0(14)	4.8(9)	14.8(19)	-1.5(9)	8.0(14)	-6.7(11)
C18	8.1(10)	5.0(8)	6.5(9)	1.7(7)	0.0(7)	0.5(7)
C19	12.1(13)	4.4(7)	11.0(13)	-4.9(8)	8.4(11)	-3.7(8)
C21	13.4(28)	13.3(31)	2.6(10)	0	-0.8(13)	0
C22	16.4(25)	15.2(24)	6.1(11)	3.6(20)	-5.3(15)	4.8(13)
C23	10.6(13)	22.2(38)	5.3(8)	-2.0(15)	0.1(8)	7.5(14)
C24	11.8(14)	6.5(10)	9.4(13)	2.5(10)	-3.0(11)	-3.1(9)
C25	14.2(22)	24.7(37)	12.0(20)	-7.1(25)	1.3(17)	7.5(21)

* The anisotropic temperature factor has the form $T = -0.25\exp(\Sigma h_i h_j B_{ij} a_i^* a_j^*)$

Supplemental Table 2. Positional and Thermal Parameters of Fixed Atoms for $(MeC_5H_4)_3UNH_3$

Atom	x	y	z	B(Å^2)
H1	0.0552	0.193	0.3818	10.000
H2	0.1995	0.1437	0.2313	10.000
H3	0.2646	0.2099	0.0345	10.000
H4	0.1603	0.3016	0.0524	10.000
H5	-0.1556	0.1681	0.2961	10.000
H6	-0.0422	0.0503	-0.0106	10.000
H7	-0.2013	0.1009	-0.1336	10.000
H8	-0.273	0.1707	0.0426	10.000
H9	-0.1207	0.1717	-0.3539	10.000
H10	-0.0322	0.2673	-0.3053	10.000
H11	0.168	0.2485	-0.2364	10.000
H12	0.2037	0.1485	-0.2081	10.000
H13	0.4829	0.0369	0.6263	15.000
H14	0.3345	0.0754	0.4426	15.000
H15	0.4098	0.1253	0.2166	15.000
H16	0.6210	0.1229	0.2649	15.000
H17	0.3999	0.0847	-0.0251	15.000
H18	0.5939	0.0528	-0.0494	15.000
H19	0.0435	0.3277	0.3849	15.000
H20	-0.0604	0.2884	0.3464	15.000
H21	-0.0206	0.331	0.2203	15.000
H22	-0.0333	0.0483	0.3686	15.000
H23	0.0224	0.1082	0.3839	15.000
H24	0.0685	0.0639	0.2669	15.000
H25	0.0736	0.0622	-0.4106	20.000
H26	-0.0172	0.0575	-0.2843	20.000
H27	0.1112	0.0579	-0.2325	20.000
H28	0.7073	0.0969	0.6353	20.000
H29	0.749	0.0637	0.4906	20.000
H30	0.6837	0.032	0.6191	20.000
H31	0.1936	0	-0.0272	20.000
H32	0.2307	0.033	0.1257	20.000
H33	-0.0961	0.303	-0.0506	15.000
H34	-0.1610	0.2788	0.0802	15.000
H35	-0.1933	0.2638	-0.087	15.000
H36	0.7634	0	0.3095	15.000
H37	0.742	0.0317	0.1585	15.000

* The isotropic temperature factor has the form: $T = \exp[-B(\sin\theta/\lambda)^2]$.

Supplemental Table 3. Distances in $(MeC_5H_4)_3UNH_3$

Atoms	d(Å)	Atoms	d(Å)	Atoms	d(Å)
U1 - Cp1	2.542	C14 - U1	2.782(16)	C25 - C7	1.536(13)
U1 - Cp2	2.572	C15 - U1	2.808(15)	C9 - C8	1.33(4)
U1 - Cp3	2.579	N2 - U2	2.633(18)	C10 - C9	1.35(3)
U2 - Cp5	2.508	C16 - U2	2.845(17)	C12 - C11	1.425(30)
U2 - Cp4	2.534	C17 - U2	2.757(13)	C15 - C11	1.43(3)
U2 - Cp4'	2.534	C18 - U2	2.760(16)	C26 - C11	1.538(13)
N1 - U1	2.595(13)	C19 - U2	2.77(3)	C13 - C12	1.421(29)
C1 - U1	2.822(16)	C20 - U2	2.830(17)	C14 - C13	1.364(18)
C2 - U1	2.752(16)	C21 - U2	2.77(3)	C15 - C14	1.348(30)
C3 - U1	2.746(14)	C22 - U2	2.825(17)	C20 - C16	1.359(18)
C4 - U1	2.837(15)	C23 - U2	2.709(18)	C18 - C17	1.407(17)
C5 - U1	2.882(15)	C5 - C1	1.391(23)	C19 - C18	1.365(17)
C6 - U1	2.806(15)	C2 - C1	1.397(24)	C20 - C19	1.398(18)
C7 - U1	2.797(15)	C3 - C2	1.365(27)	C27 - C20	1.544(13)
C8 - U1	2.842(19)	C2 - C3	1.365(27)	C22 - C21	1.391(13)
C9 - U1	2.845(18)	C4 - C3	1.415(27)	C28 - C21	1.541(13)
C10 - U1	2.836(16)	C5 - C4	1.442(23)	C23 - C22	1.35(3)
C11 - U1	2.96(4)	C24 - C5	1.512(24)	C23 - C23	1.40(4)
C12 - U1	2.851(17)	C10 - C6	1.387(26)		
C13 - U1	2.794(14)	C7 - C6	1.431(28)		

Supplemental Table 4. Distance Restraints in Least-Squares

C15	C11	1.39(4)	C19	C20	1.39(2)
C11	C12	1.39(4)	C21	C22	1.39(1)
C13	C14	1.39(2)	C23	C23'	1.39(2)
C16	C17	1.39(2)	C25	C7	1.54(1)
C17	C18	1.39(2)	C26	C11	1.54(1)
C18	C19	1.39(2)	C27	C20	1.54(1)
C16	C20	1.39(2)	C28	C21	1.54(1)

Supplemental Table 5. Angles in $(MeC_5H_4)_3UNH_3$

Atoms	Angle(°)	Atoms	Angle(°)
N1 - U1 -Cp1	98.06	C8 - C9 - C10	112.1(23)
N1 - U1 -Cp2	97.44	C6 - C10- C9	109.4(22)
N1 - U1 -Cp3	97.61	C12 - C11- C15	103.2(24)
Cp1 - U1 -Cp2	118.44	C12 - C11- C26	143(3)
Cp1 - U1 -Cp3	118.13	C15 - C11- C26	113(3)
Cp2 - U1 -Cp3	118.13	C11 - C12- C13	111.0(22)
N2 - U2 -Cp4	98.53	C12 - C13- C14	103.7(19)
N2 - U2 -Cp5	94.47	C13 - C14- C15	113.2(19)
Cp4 - U2 -Cp4	114.37	C11 - C15- C14	108.5(21)
Cp4 - U2 -Cp5	120.53	C17 - C16- C20	98.1(18)
C2 - C1 - C5	110.6(16)	C16 - C17- C18	116.8(17)
C1 - C2 - C3	106.6(17)	C17 - C18- C19	103.2(15)
C2 - C3 - C4	110.9(15)	C18 - C19- C20	105.5(14)
C3 - C4 - C5	105.6(15)	C16 - C20- C19	116.0(18)
C1 - C5 - C4	106.4(16)	C16 - C20- C27	110.9(26)
C1 - C5 - C24	126.7(15)	C19 - C20- C27	132.7(26)
C4 - C5 - C24	126.8(17)	C22 - C21- C22	108(4)
C7 - C6 - C10	102.0(18)	C22 - C21- C28	125.7(20)
C6 - C7 - C8	111.9(19)	C22 - C21- C28	125.7(20)
C6 - C7 - C25	120.9(26)	C21 - C22- C23	106(3)
C8 - C7 - C25	126.7(28)	C22 - C23- C23	108.4(14)
C7 - C8 - C9	104.6(24)		

Supplemental Table 6. Least Squares Planes and Deviations Therefrom

Plane #1

8.24368 a + 8.22671 b + 5.36898 c = 4.08227

Distance(Å) to the plane			
atoms in the plane		atoms not in plane	
C1	0.004(23)	U1	-2.537(10)
C2	-0.004(25)	C24	0.10(4)
C3	0.004(32)		
C4	0.000(25)		
C5	-0.002(20)		

Plane #2

7.99437 a + 16.18591 b - 3.28082 c = 0.46949

Distance(Å) to the plane			
atoms in the plane		atoms not in plane	
C6	0.010(27)	U1	2.571(12)
C7	-0.012(28)	C25	-0.22(6)
C8	0.014(36)		
C9	-0.002(43)		
C10	-0.011(34)		

Plane #3

-3.65388 a - 0.86732 b + 8.43420 c = -2.7331

Distance(Å) to the plane			
atoms in the plane		atoms not in plane	
C11	-0.049(45)	U1	2.568(12)
C12	0.009(36)	C26	-0.12(10)
C13	0.013(33)		
C14	-0.028(31)		
C15	0.025(29)		

Plane #4

-1.10342 a + 20.82145 b + 4.40761 c = 3.10341

Distance(Å) to the plane			
atoms in the plane		atoms not in plane	
C16	-0.029(29)	U1	-2.529(9)
C17	0.012(25)	C27	0.01(3)
C18	0.002(22)		
C19	-0.014(23)		
C20	0.037(30)		

Plane #5

1.94621 a + 2.19584 b + 8.49525 c = 0.75927

Distance(Å) to the plane			
atoms in the plane		atoms not in plane	
C21	0.0	U2	-2.426(49)
C22	0.0	C28	0.27(7)
C23	0.0	C22'	-0.20(10)
		C23'	-0.13(9)

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