

Structure of 6-Pentyl-2,5-bis(phenethylamino)-1,4-benzoquinone, a Reaction Product of 2-Phenylethylamine with Primin

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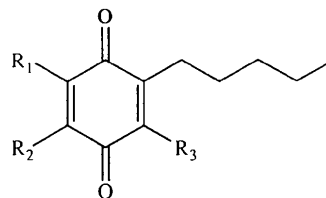
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Abstract. $C_{27}H_{32}N_2O_2$, $M_r = 416.565$, triclinic, $P\bar{1}$, $a = 4.951$ (3), $b = 14.946$ (2), $c = 15.988$ (6) Å, $\alpha = 95.80$ (2), $\beta = 91.06$ (4), $\gamma = 96.14$ (2)°, $V = 1169.8$ (1.4) Å³, $Z = 2$, $D_x = 1.183$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.69$ cm⁻¹, $F(000) = 448$, $T = 295$ K, $R = 0.074$ for 2403 observed unique reflections. The angle between the quinone ring plane and the mean plane defined by the aliphatic pentyl chain atoms is 91.5 (4)°; the angles between the ethylamine groups and the quinone ring at positions 2 and 5 are 92.9 (4) and 56.3 (4)°, respectively. The planes of the quinone ring and the phenyl ring of the amino group at C(2) are approximately parallel to each other but are at different heights; the dihedral angle is 2.0 (4)°, while the corresponding dihedral angle with the other phenyl group is twisted out of the plane by 51.8 (4)°. The average $C_{sp^3}-C_{sp^3}$ bond distances and angles of the pentyl chain are 1.520 (6) Å and 113.4 (4)°. The average dimensions of the quinone ring are C—C 1.470 (5), C=C 1.360 (5), C=O 1.236 (5) Å, C—C—C 119.1 (4), C=C—C 120.4 (4), O=C—C 120.4 (4)°. Owing to delocalization of π electrons and resonance with the amino groups significant differences of quinone ring bond lengths and angles between the title compound and primin are observed. The structure is stabilized by N—H...O hydrogen bonds and van der Waals forces. Hydrogen-bonding dimensions are: H(2)...O(1ⁱ) 2.07 (4), N(2)...O(1ⁱ) 2.912 (5) Å, N(2)—H(2)...O(1ⁱ) 149 (4)°; H(5ⁱⁱ)...O(4) 2.31 (4), N(5ⁱⁱ)...O(4) 3.068 (5) Å, N(5ⁱⁱ)—H(5ⁱⁱ)...O(4) 143 (4)° [(i) $-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$].

Introduction. The naturally occurring toxic and irritant principle of the *Primulae* species, primin [2-methoxy-6-pentyl-1,4-benzoquinone (1a)] is well known for its sensitizing potency as reported by Hjorth, Fregert & Schildknecht (1969), Hausen (1978, 1979) and Schulz, Garbe, Hausen &

Simatupang (1979). Structural details of primin and the sensitizing capacity of substituted *p*-benzoquinones have been discussed and the positions for covalent binding to a receptor protein of epidermal cells were assumed to be at C(3) and/or C(5) of the quinonoid ring system (Schulz *et al.*, 1979; Schmalle, Jarchow, Hausen & Schulz, 1984; Cremer, Hausen & Schmalle, 1987). These positions can be attacked by nucleophiles of the receptor protein, *e.g.* SH and NH₂ groups of amino acids. To verify these assumptions, preliminary binding experiments with primin were performed with 2-phenylethylamine, and experiments with amino acids are in progress. The initial experiments were successful: substitution of the methoxy group at position C(2) and a Michael-type addition reaction at position C(5), as competitive reactions, yielded the main product (1c). Its structure was assigned by spectroscopic methods and mechanistic reasoning. X-ray structure determination has been carried out in order to obtain more structural details of the product, and to confirm the spectroscopic results.



- (1a) $R_1 = \text{OCH}_3$, $R_2 = R_3 = \text{H}$
 (1b) $R_1 = \text{OCH}_3$, $R_2 = \text{H}$, $R_3 = \text{NH}(\text{CH}_2)_2\text{Ph}$
 (1c) $R_1 = R_3 = \text{NH}(\text{CH}_2)_2\text{Ph}$, $R_2 = \text{H}$
 (1d) $R_1 = \text{OCH}_3$, $R_2 = R_3 = \text{NH}(\text{CH}_2)_2\text{Ph}$
 (1e) $R_1 = R_2 = R_3 = \text{NH}(\text{CH}_2)_2\text{Ph}$

Experimental. The structure of 6-pentyl-2,5-bis(phenethylamino)-1,4-benzoquinone was determined by mass and ¹³C NMR spectroscopy (a full account of spectral data will be published elsewhere) and was

confirmed by X-ray analysis using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The binding reactions of primin (1a) with phenylethylamine were carried out by stirring (1a) (11 mg) with a 50-fold excess of 2-phenylethylamine in absolute dichloromethane at room temperature for 2 days. Chromatography and crystallization from methanol afforded the purple-coloured main product (1c) (8 mg). Recrystallization of (1c) (m.p. 383.5–384.5 K) by slow diffusion of hexane into a CHCl₃ solution of (1c) yielded crystals suitable for X-ray analysis. The wedge-shaped crystal selected for the X-ray measurements had dimensions of approximately $0.82 \times 0.29 \times 0.15 \text{ mm}$. The unit-cell parameters were determined by least-squares refinement of the setting angles of 24 automatically centred reflections in the range $6.8 < \theta < 11.2^\circ$. Intensities of 7090 reflections (including 84 standards) in the interval $-6 < h < 6$, $-21 < k < 21$, $-22 < l < 0$ with θ between 1.0 and 30.0° were collected using the ω - 2θ -scan technique and zigzag mode. The scan rate varied from 1.49 to $8.24^\circ \text{ min}^{-1}$, the maximum measuring time was 50 s. Three standard reflections were monitored every 3 h of measuring time, no loss of intensities was noted. Orientation was controlled every 350 reflections using two standard reflections. A numerical absorption correction ($\mu = 0.69 \text{ cm}^{-1}$) based on six indexed crystal faces and carefully measured distances between faces was applied with *SHELX76* (Sheldrick, 1976). The transmission factors ranged from 0.994 to 0.987. Data reduction led to 6784 unique reflections (444 reflections averaged, $R_{\text{int}} = 0.0148$). The data were corrected for Lorentz and polarization effects. 2408 reflections were considered observed with $I \geq 2\sigma(I)$, 4376 reflections were unobserved.

The phase problem was solved using the Patterson interpretation routine of the program *SHELXS86* (Sheldrick, 1985) in the space group $P\bar{1}$. Hypercentricity of the structure afforded a shift of the atomic coordinates of $x + 0.13$, $y - 0.37$ and $z + 0.05$ to match the correct centre of symmetry. [A similar effect was observed with the solution of the structure of primin (Schmalle *et al.*, 1984).] The structure was refined by full-matrix least-squares calculations with *SHELX76* (Sheldrick, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for the non-H atoms. The phenyl rings were converted into regular hexagons. All 32 H atoms were localized by difference Fourier syntheses. The positional parameters of the H atoms were varied, their displacement parameters were fixed at values equal to the isotropic displacement parameters of the attached C and N atoms. The phenyl H atoms were refined with constraint bond lengths of 1.08 \AA within an e.s.d. of 0.015 \AA . The final refinement converged at $R/wR =$

$7.41/5.89\%$, with 352 variable parameters and 2403 observed reflections; five reflections were omitted because secondary extinction was suspected. The maximum shift-to-e.s.d. ratio was 0.72 for an H-atom parameter and 0.34 for a vibrational parameter of C(24). Maximum and minimum electron densities in the final difference Fourier synthesis were 0.227 e \AA^{-3} [0.61 \AA from C(18)] and $-0.289 \text{ e \AA}^{-3}$. Calculations were performed on Hitachi AS XL 60 and PDP 11/34 computers. Neutral atomic scattering factors were those of *SHELX76*. The final atomic coordinates and equivalent isotropic displacement parameters U_{eq} are listed in Table 1.* The $\sigma(U_{\text{eq}})$ values were calculated by the method of Schomaker & Marsh (1983).

Discussion. The atom-numbering scheme and the vibrational ellipsoids are presented with the *ORTEPII* (Johnson, 1971) drawing of Fig. 1. The thermal motion in the molecule increases significantly with increasing distance from the central quinone ring (see U_{eq} values in Table 1 and the corresponding ellipsoids in Fig. 1). Bond distances and angles for non-H atoms are shown in Table 2. The bond lengths and angles of the quinonoid ring differ significantly from values observed in primin (Schmalle *et al.*, 1984) and in other 6-alkyl-1,4-benzoquinones (Schmalle, Jarchow, Adiwidjaja, König, Heitsch, Rathmann, Hausen & Schulz, 1988; Ulrich, Klaska, Jarchow, Schmalle, König, Heitsch, Rathmann, Hausen & Schulz, 1990), owing to delocalization of C=C π electrons of the quinone ring and resonance with the amino groups at C(2) and C(5). The C(2)=C(3) and C(5)=C(6) double bonds are lengthened to $1.354(5)$ and $1.367(5) \text{ \AA}$, which is in accordance with substituted *p*-benzoquinone structures (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The delocalization of the π electrons is scattered over the atomic sequences O(1)=C(1)—C(6)=C(5)—N(5) and O(4)=C(4)—C(3)=C(2)—N(2), which are separated by relatively long distances of $1.518(5)$ and $1.540(5) \text{ \AA}$ for C(1)—C(2) and C(4)—C(5).

The quinonoid ring, the phenyl chain atoms, both of the ethylamino groups and their attached phenyl rings were used for plane calculations. The planes are indicated in the *ORTEP* stereoplot of Fig. 2. The maximum out-of-plane deviation of the quinone ring C(1) to C(6) (plane *A*) is $-0.023(6) \text{ \AA}$ for C(3). Atoms O(1), O(4), N(2), N(5) and C(7) deviate

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53728 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters with *e.s.d.*'s in parentheses
$$U_{eq} = \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O(1)	-0.0519 (6)	0.0894 (2)	0.4407 (2)	0.0616 (9)
O(4)	0.5465 (6)	0.4019 (2)	0.5329 (2)	0.074 (1)
C(1)	0.0763 (8)	0.1650 (3)	0.4599 (2)	0.043 (1)
C(2)	0.3014 (8)	0.1702 (3)	0.5266 (2)	0.043 (1)
C(3)	0.4485 (9)	0.2503 (3)	0.5520 (3)	0.050 (1)
C(4)	0.4093 (9)	0.3287 (3)	0.5149 (3)	0.050 (1)
C(5)	0.1801 (8)	0.3236 (3)	0.4475 (2)	0.047 (1)
C(6)	0.0210 (8)	0.2444 (3)	0.4232 (2)	0.042 (1)
C(7)	-0.2084 (9)	0.2313 (3)	0.3585 (3)	0.047 (1)
C(8)	-0.1176 (8)	0.2221 (3)	0.2677 (3)	0.052 (1)
C(9)	-0.3396 (9)	0.2371 (4)	0.2042 (3)	0.057 (1)
C(10)	-0.2616 (11)	0.2218 (4)	0.1147 (3)	0.077 (2)
C(11)	0.4728 (13)	0.2470 (5)	0.0525 (4)	0.097 (2)
N(2)	0.3343 (8)	0.0910 (2)	0.5540 (2)	0.054 (1)
C(12)	0.5252 (10)	0.0777 (3)	0.6215 (3)	0.054 (1)
C(13)	0.4076 (10)	0.0990 (4)	0.7065 (3)	0.064 (1)
C(14)	0.6112 (6)	0.0911 (2)	0.7759 (2)	0.057 (1)
C(15)	0.6270 (6)	0.0069 (2)	0.8051 (2)	0.092 (2)
C(16)	0.8150 (6)	-0.0022 (2)	0.8690 (2)	0.108 (2)
C(17)	0.9871 (6)	0.0730 (2)	0.9036 (2)	0.087 (2)
C(18)	0.9713 (6)	0.1572 (2)	0.8745 (2)	0.080 (2)
C(19)	0.7834 (6)	0.1662 (2)	0.8106 (2)	0.066 (1)
N(5)	0.1742 (7)	0.4056 (2)	0.4213 (2)	0.058 (1)
C(20)	0.0021 (10)	0.4408 (3)	0.3608 (3)	0.062 (2)
C(21)	0.1710 (11)	0.4855 (4)	0.2970 (3)	0.074 (2)
C(22)	-0.0028 (7)	0.5249 (3)	0.2358 (2)	0.060 (1)
C(23)	-0.1330 (7)	0.6009 (3)	0.2616 (2)	0.091 (2)
C(24)	-0.3016 (7)	0.6357 (3)	0.2050 (2)	0.132 (3)
C(25)	-0.3401 (7)	0.5946 (3)	0.1228 (2)	0.139 (3)
C(26)	-0.2100 (7)	0.5186 (3)	0.0970 (2)	0.132 (3)
C(27)	-0.0413 (7)	0.4838 (3)	0.1536 (2)	0.094 (2)

Table 2. Bond distances (\AA), bond angles ($^\circ$) and hydrogen-bonding contacts ($\text{\AA}, ^\circ$)

C(1)—O(1)	1.242 (4)	C(1)—C(6)	1.427 (5)
C(1)—C(2)	1.518 (5)	C(2)—C(3)	1.354 (5)
C(2)—N(2)	1.328 (5)	C(3)—C(4)	1.396 (5)
C(4)—C(5)	1.540 (5)	C(4)—O(4)	1.230 (4)
C(5)—C(6)	1.367 (5)	C(5)—N(5)	1.336 (5)
C(6)—C(7)	1.505 (5)	C(7)—C(8)	1.525 (6)
C(8)—C(9)	1.532 (6)	C(9)—C(10)	1.491 (6)
C(10)—C(11)	1.531 (8)	N(2)—C(12)	1.463 (5)
C(12)—C(13)	1.507 (6)	C(13)—C(14)	1.507 (5)
C(14)—C(15)	1.395	C(14)—C(19)	1.395
C(15)—C(16)	1.395	C(16)—C(17)	1.395
C(17)—C(18)	1.395	C(18)—C(19)	1.395
N(5)—C(20)	1.452 (6)	C(20)—C(21)	1.495 (7)
C(21)—C(22)	1.496 (5)	C(22)—C(23)	1.395
C(22)—C(27)	1.395	C(23)—C(24)	1.395
C(24)—C(25)	1.395	C(25)—C(26)	1.395
C(26)—C(27)	1.395		
O(1)—C(1)—C(2)	116.5 (4)	C(2)—C(1)—C(6)	120.0 (4)
O(1)—C(1)—C(6)	123.5 (4)	C(1)—C(2)—C(3)	120.2 (4)
C(1)—C(2)—N(2)	113.6 (4)	C(3)—C(2)—N(2)	126.1 (4)
C(2)—C(3)—C(4)	121.5 (4)	C(3)—C(4)—C(5)	118.3 (4)
C(3)—C(4)—O(4)	123.9 (4)	C(5)—C(4)—O(4)	117.8 (4)
C(4)—C(5)—C(6)	121.4 (4)	C(4)—C(5)—N(5)	108.7 (3)
C(6)—C(5)—N(5)	129.9 (4)	C(5)—C(6)—C(1)	118.5 (4)
C(1)—C(6)—C(7)	115.4 (4)	C(5)—C(6)—C(7)	126.2 (4)
C(6)—C(7)—C(8)	114.3 (4)	C(7)—C(8)—C(9)	113.1 (4)
C(8)—C(9)—C(10)	113.9 (4)	C(9)—C(10)—C(11)	113.3 (5)
C(2)—N(2)—C(12)	124.9 (4)	N(2)—C(12)—C(13)	110.9 (4)
C(12)—C(13)—C(14)	110.9 (4)	C(13)—C(14)—C(15)	119.0 (2)
C(13)—C(14)—C(19)	121.0 (2)	C(15)—C(14)—C(19)	120.0
C(14)—C(15)—C(16)	120.0	C(15)—C(16)—C(17)	120.0
C(16)—C(17)—C(18)	120.0	C(17)—C(18)—C(19)	120.0
C(18)—C(19)—C(14)	120.0	C(5)—N(5)—C(20)	133.0 (4)
N(5)—C(20)—C(21)	110.5 (4)	C(20)—C(21)—C(22)	111.1 (4)
C(21)—C(22)—C(23)	120.2 (3)	C(21)—C(22)—C(27)	119.8 (3)
C(23)—C(22)—C(27)	120.0	C(22)—C(23)—C(24)	120.0
C(23)—C(24)—C(25)	120.0	C(24)—C(25)—C(26)	120.0
C(25)—C(26)—C(27)	120.0	C(26)—C(27)—C(22)	120.0

$X-H\cdots Y$	$X-H$	$H\cdots Y$	$X\cdots Y$	$X-H\cdots Y$	Symmetry operation
N(2)—H(2) \cdots O(1)	0.93 (4)	2.07 (4)	2.912 (5)	149 (4)	-x, -y, 1-z
N(5)—H(5) \cdots O(4)	0.89 (4)	2.31 (4)	3.068 (5)	143 (4)	1-x, 1-y, 1-z

0.024 (5), 0.051 (5), 0.021 (6), 0.064 (6) and 0.031 (7) \AA , respectively. The angle between plane *A* and the pentyl chain (plane *B*) is $91.5 (4)^\circ$ for the title compound and $13.4 (4)^\circ$ for primin.

The dihedral angles between plane *A* and plane *C*, defined by the atoms N(5) to C(22), and plane *A* and plane *E*, defined by the atoms N(2) to C(14), are $56.3 (4)$ and $92.9 (4)^\circ$, respectively. Ring *A* and the phenyl ring *F* are approximately parallel to each other, but at different heights (see Fig. 2) with the normals to these planes making an angle of $2.0 (4)^\circ$; phenyl ring *D* is twisted out of the plane by a dihedral angle of $51.8 (4)^\circ$.

The structure is stabilized by N—H \cdots O hydrogen bonds and van der Waals forces. Hydrogen-bonding dimensions are shown in Table 2.

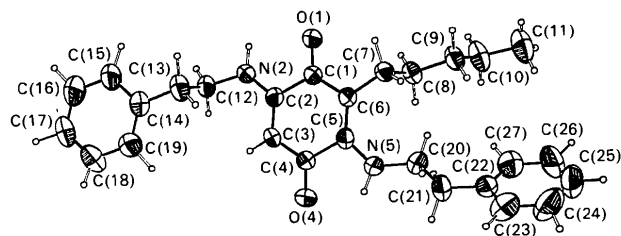


Fig. 1. ORTEP plot of 6-pentyl-2,5-bis(phenethylamino)-1,4-benzoquinone with numbering scheme and vibrational ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary size.

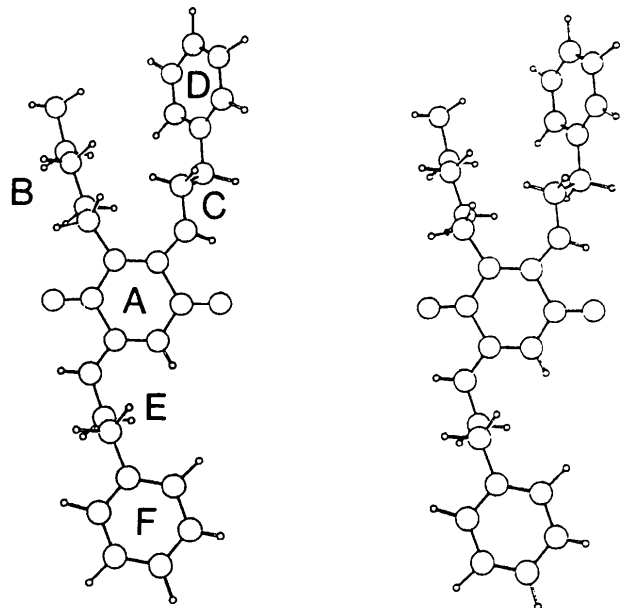


Fig. 2. ORTEP stereoplots of the molecule indicating the least-squares planes: *A* = quinone ring, *B* = pentyl chain, *C* and *E* = amino groups, *D* and *F* = phenyl rings.

The main product (1c) clearly demonstrates an addition/elimination reaction took place *via* a Michael-type addition at the electronically favourable position C(5) and the concomitant, well known (Finley, 1974) substitution of the C(2) methoxy group by the *N*-nucleophile (formally an amination/dealkoxylation of a vinylogous ester). As is expected from a mechanistic point of view, C(3) was not attacked, a fact which was not fully accounted for in a recent book (Hausen, 1988). However, the assumption that the nucleophilic attack may occur at position C(3) was made considering that the side chain was anchored in the lipid layer of the cell membrane of a stimulator cell, *i.e.* the position C(5) would not be available for a nucleophilic attack, and an elimination reaction at C(2) instead of a Michael-type addition reaction at C(3) was not taken into account. Thus, neither the product (1d) nor (1e) was formed, which correlates well with the experimental finding that 2,5-disubstituted *p*-benzoquinones exhibit no or only weak sensitizing properties *in vivo*.

The addition/elimination reaction proceeds surprisingly slow *in vitro* and only in the presence of a remarkable excess of the amine. Therefore, the mono-addition/elimination product (1b) could not be observed under the conditions studied.

Rotation of the methoxy methyl group was assumed to be a feature for enhanced reactivity between nucleophile and quinone (Cremer *et al.*, 1987). The result of this experiment, however, supports the assumption that methoxy groups at positions C(2) of strong quinonoid contact allergens like primin can be substituted by nucleophiles of the

receptor protein, most probably supported by enzymatic reactions *in vivo*.

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Structures of Three Unsymmetrical Diester Derivatives of Dibenzobarrelene

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Abstract. $T = 295$ K. 9-Isopropyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-9,11-dicarboxylate (Me/9-^{*i*}Pr), C₂₂H₂₀O₄, $M_r = 348.40$, monoclinic, $C2/c$, $a = 17.059$ (1), $b = 8.5405$ (3), $c = 25.894$ (1) Å, $\beta = 108.883$ (3)°, $V = 3569.5$ (3) Å³, $Z = 8$, $D_x = 1.296$ g cm⁻³, Cu $K\alpha_1$, $\lambda = 1.54056$ Å, $\mu = 6.8$ cm⁻¹, $F(000) = 1472$, $R = 0.049$ for 2542 reflections. 10-Isopropyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-10,11-dicarboxylate (Me/10-^{*i*}Pr), C₂₂H₂₀O₄, $M_r = 348.40$, monoclinic, $P2_1/a$, $a =$

15.388 (3), $b = 8.091$ (1), $c = 16.437$ (2) Å, $\beta = 117.86$ (1)°, $V = 1809.3$ (5) Å³, $Z = 4$, $D_x = 1.279$ g cm⁻³, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, $\mu = 0.82$ cm⁻¹, $F(000) = 736$, $R = 0.042$ for 2286 reflections. 10-(–)-Menthyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-10,11-dicarboxylate (Me/10-Men), C₂₉H₃₂O₄, $M_r = 444.57$, orthorhombic, $P2_12_12_1$, $a = 8.462$ (1), $b = 14.383$ (2), $c = 19.988$ (3) Å, $V = 2432.7$ (5) Å³, $Z = 4$, $D_x = 1.213$ g cm⁻³, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, $\mu = 0.81$ cm⁻¹, $F(000) = 952$, $R =$