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Note

Binuclear complexes from 1,8-substituted anthracene derivatives. The crystal structure of [{μ-[1,8-anthracenedicarboxaldehydebis(dimethylhydrazone)]}tetrachlorobis(η^2-ethylene)di-platinum]

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Abstract

Oxidative addition of anthracene 1,8-dicarbonylchloride to the three-coordinate [Pt(2,9-Me_2-1,10-phenanthroline)(dimethylmaleate)], leads to a binuclear species with trigonal bipyramidal coordination around each platinum atom. Some reactions of this complex are described. The crystal structure of the related ethylene four-coordinate species [{μ-[1,8-anthracenedicarboxaldehydebis(dimethylhydrazone)]}tetrachlorobis(η^2-ethylene)di-platinum], is reported. The complex crystallizes in the triclinic space group $P\bar{1}$ with: $a=7.185(3)$, $b=13.379(7)$, $c=14.943(7)$ Å, $\alpha=103.49(4)$, $\beta=93.48(4)$, $\gamma=97.78(4)°$, $Z=2$, $R=0.065$.

Key words: Crystal structures; Platinum complexes; Anthracene complexes; Binuclear complexes

Introduction

The chemistry of polynuclear complexes is of wide interest. In this area binuclear species in which the two metal centers are present in separate, but potentially interacting, coordination environments are representative systems. Preliminary results achieved in our laboratory [1] demonstrated the ability of anthracene derivatives bearing donor groups in 1,8-positions to behave as bridging ligands in Pt(II) ethylene binuclear complexes.

As a follow-up to our preliminary study, we prepared four new binuclear species, with carbon–metal bonds between the anthracene ligand and coordinatively saturated platinum(II) (Fig. 1).

As an example among the bimetallic anthracene derivatives available to date, we report the X-ray analysis of a complex obtained in our preliminary investigation [1], $[C_{14}H_8(CH{=}NNMe_2)_2Pt_2Cl_4(C_2H_4)_2]$ (**E**). This was chosen due to its more representative planar coordination around the metal.

Experimental

Commercial 2,9-dimethyl-1,10-phenanthroline (DMPHEN) was purified by sublimation *in vacuo*. Dimethylmaleate (DMM) was commercially available. The three-coordinate substrate [Pt(DMPHEN)(DMM)] [2] and anthracene 1,8-dicarbonylchloride [3] were prepared according to literature methods.

^{1}H NMR spectra were recorded at 200 or 270 MHz. $C_2D_2Cl_4$ and CD_3NO_2 were used as solvents (references: $C_2H_2Cl_4$, 5.98 ppm; CHD_2NO_2, 4.33 ppm). Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad peak.

Preparation of A

To a solution of [Pt(DMPHEN)(DMM)] (0.060 g, 0.11 mmol) in 2 ml of chloroform, anthracene 1,8-dicarbonylchloride was added (0.016 g, 0.052 mmol) and the mixture was stirred for 3 h at room temperature. Filtration afforded a white solid. This was washed with chloroform and dried *in vacuo* (yield 0.060 g, 78%).

^{1}H NMR data ($C_2D_2Cl_4$, ^2J(Pt–H) in parentheses): δ 7.62 (d, 4H), 7.28 (s, 4H), 7.20 (s, 1H), 7.08 (d, 4H), 6.91 (d, 2H), 6.50–6.35 (m, 4H), 6.02 (s, 1H), 4.24 (80 Hz, s, 4H), 3.82 (s, 12H), 3.24 (s, 12H) ppm. *Anal.* Calc. for $C_{56}H_{48}Cl_2N_4O_{10}Pt_2$: C, 48.11; H, 3.46; N, 4.01. Found: C, 47.81; H, 3.45; N, 3.91%.

*Preparation of **B***

To a suspension of **A** (0.050 g, 0.036 mmol) in 4 ml of methylene chloride/nitromethane (1:1) was added $AgBF_4$ (0.014 g, 0.072 mmol) in 1 ml acetonitrile. The mixture was stirred at room temperature for 30 min. After filtration of AgCl on Celite, the solvent was removed *in vacuo* from the resulting solution. The residue was dissolved in the minimum amount of nitromethane/chloroform (1:1) and crystallization of a yellow product was obtained by careful addition of diethyl ether (yield 0.045 g, 80%).

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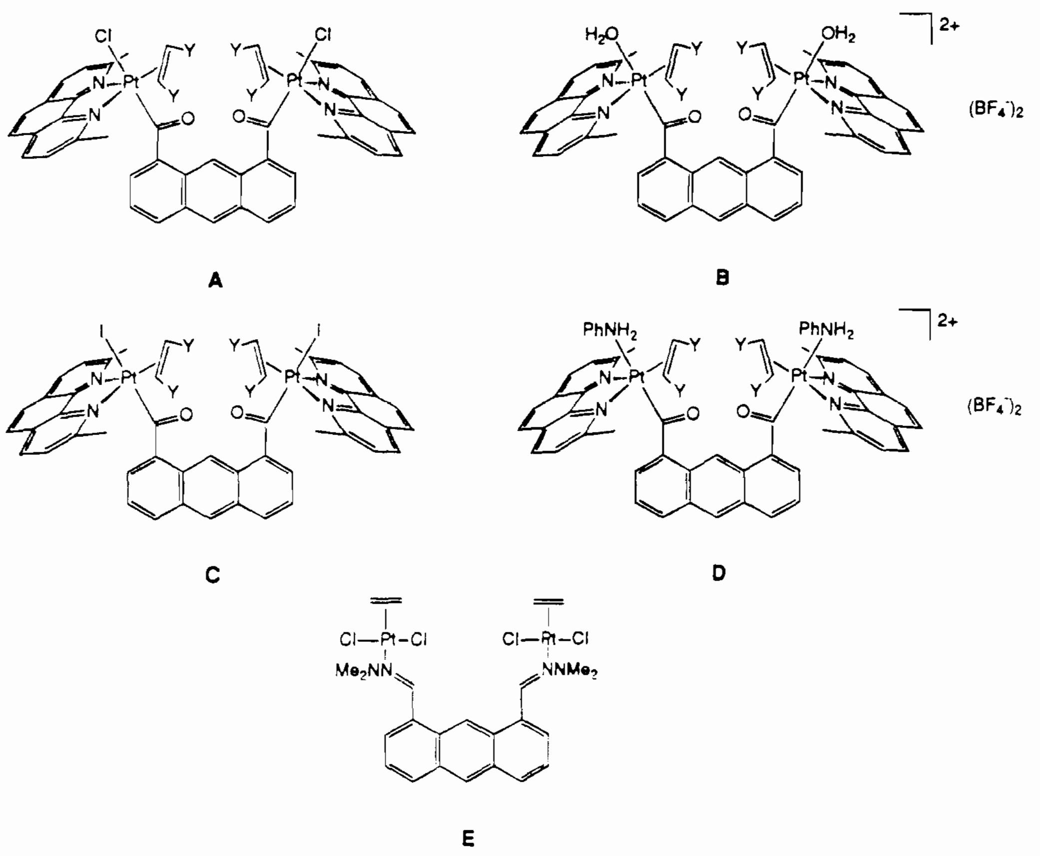


Fig. 1. The orientation of Y groups (Y = COOMe) does not imply configurational assignment.

^{1}H NMR (CD_3NO_2, ^2J(Pt–H) in parentheses): δ 7.82 (d, 4H), 7.40 (d, 4H), 7.35 (s, 1H), 7.18 (s, 4H), 7.07 (d, 2H), 6.57 (t, 2H), 6.24 (d, 2H), 6.06 (s, 1H), 4.13 (60 Hz, s, 4H), 3.83 (s, 12H), 3.04 (s, 12H) ppm. *Anal.* Calc. for $C_{56}H_{52}B_2F_8N_4O_{12}Pt_2$: C, 43.78; H, 3.39; N, 3.65. Found: C, 43.71; H, 3.55; N, 3.40%.

Preparation of **C**

To a solution of **B** (0.040 g, 0.025 mmol) in 2 ml of nitromethane, NaI (0.300 g) in 2 ml of acetone was added. After 2 h yellow crystals of **C** were filtered, washed with acetone, and dried *in vacuo* (yield 0.030 g, 75%).

^{1}H NMR ($C_2D_2Cl_4$, ^2J(Pt–H) in parentheses): δ 7.59 (d, 4H), 7.29 (d, 4H), 7.23 (s, 1H), 7.06 (s, 4H), 6.97 (d, 2H), 6.47 (t, 2H), 6.23 (s, 1H), 6.09 (d, 2H), 4.17 (70 Hz, s, 4H), 3.85 (s, 12H), 3.27 (s, 12H) ppm. *Anal.* Calc. for $C_{56}H_{48}I_2N_4O_{10}Pt_2$: C, 42.54; H, 3.06; N, 3.54. Found: C, 42.60; H, 3.03; N, 3.45%.

Preparation of **D**

To a solution of **B** (0.080 g, 0.050 mmol) in 2 ml of nitromethane, $PhNH_2$ (0.010 g, 0.11 mmol) was added. After 3 h stirring the volume of the solution was reduced under vacuum and the product crystallized by slow addition of diethyl ether. The light yellow solid was washed with diethyl ether and dried *in vacuo* (yield 0.067 g, 80%).

^{1}H NMR (CD_3NO_2): δ 7.65 (d, 4H), 7.54 (s, 4H), 7.51 (d, 4H), 7.33 (s, 1H), 7.03 (d, 2H), 6.61 (dd, 2H), 6.31 (d, 2H), 6.23 (s, 1H), 6.01 (m, 6H), 5.47 (d, 4H), (4H, overlapped by other signals), 4.01 (s, 12H), 3.28 (s, 12H) ppm. *Anal.* Calc. for $C_{68}H_{62}B_2F_8N_6O_{10}Pt_2$: C, 48.41; H, 3.70; N, 4.98. Found: C, 48.76; H, 3.91; N, 5.03%.

X-ray diffraction of **E**

A fresh sample of the complex was obtained as previously reported [1].

The very low solubility of **E** in most of the common solvents made extremely difficult its recrystallization. Only from chloroform could we obtain crystals, which were of poor quality. The very small dimensions of the crystals (*c.* 0.02×0.02×0.12 mm) caused difficulties in the intensity measurements.

A single crystal was mounted on an Enraf-Nonius CAD-4 automatic diffractometer, using Zr filtered Mo Kα radiation. Standard centering and autoindexing procedures indicated a triclinic lattice. The space group $P\bar{1}$ was initially assigned and later confirmed by a well-behaved refinement process. 1920 reflections were collected, in the ω-scan method, 792 of which with $I \geqslant 3\sigma(I)$

were considered for the refinement. Two standard reflections monitored periodically during data collection showed only random fluctuations. Lorentz and polarization corrections were applied but no correction was used for absorption on account of the very small size of the crystal and the relatively small value of μ (50.6 cm^{-1}). The structure was solved by direct methods using the program Multan 82 [4]. The E-map evaluated with the set of phases corresponding to the highest combined figure of merit showed all Pt and Cl atoms. Successive Fourier maps evidenced all the non-hydrogen atoms. Crystal data and details of intensity data collection are given in Table 1.

Determination and refinement of the structure

Blocked-cascade least-square refinement was used. Owing to the small ratio (experimental data/parameters to be refined) we introduced constraints on bond lengths, bond and torsion angles on the anthracene moiety, (C–C = 1.395 Å, C–C–C = 120°, C–C–C–C = 0°) and on the C–C=N–N frames (C–C = 1.46 Å, C=N = 1.28 Å, N–N = 1.37 Å, C=N = 1.45 Å, C–C=N = 120° and C–C=N–N = 180°). Only the Pt and the Cl atoms were anisotropized; the hydrogen atoms were treated as idealized contributions, they were included in the calculation of structure factors but not refined. The conventional R index converged to the final value of 0.065. A unitary weighting scheme was used. Scattering factors for the atoms were taken from Cromer and Waber [5]: the scattering factors for Pt and Cl were corrected for the real and imaginary parts of anomalous dispersion using Cromer's values [6]. All computations were performed using the SHELX-76 program [7]. The final positional and thermal parameters of the non-hydrogen atoms are listed in Table 2.

TABLE 1. Summary of crystal and intensity collection data

Formula	$C_{26}H_{30}Cl_4N_4Pt_2$
Molecular weight	930.55
a (Å)	7.185(3)
b (Å)	13.379(7)
c (Å)	14.943(7)
α (°)	103.49(4)
β (°)	93.48(4)
γ (°)	97.78(4)
V ($Å^3$)	1377
Z	2
D_{calc} (g/cm^3)	2.24
D_{exp} (g/cm^3)	2.23
Space group	$P\bar{1}$
Radiation (Å)	Mo Kα (0.7107)
μ (cm^{-1})	50.67
2θ Limit (°)	40
Data collected	1920
Data unique	1498
Data used ($I \geq 3\sigma(I)$)	792
hkl Range	$-6 \leq h \leq 6$, $-12 \leq k \leq 12$, $0 \leq l \leq 14$
Weighting	1
$F(000)$	425.97
Refined parameters	167
R_{obs} [a]	0.0649
$R_{all\ data}$ [a]	0.0789

[a] $R = \Sigma \Delta F / \Sigma F_o$.

TABLE 2. Positional and thermal parameters of the non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z	U_{iso}	U_{eq} [a]
Pt(1)	0.1989(5)	0.2021(3)	0.6420(2)		0.0582
Pt(2)	0.7755(5)	0.8397(3)	0.8061(3)		0.0664
Cl(1)	0.108(3)	0.362(2)	0.671(2)		0.0820
Cl(2)	0.209(3)	0.041(2)	0.614(2)		0.0873
Cl(3)	0.509(3)	0.712(2)	0.758(1)		0.0909
Cl(4)	1.047(3)	0.961(2)	0.854(2)		0.0932
C(1)	0.749(5)	0.486(2)	0.846(1)	0.0163	
C(2)	0.665(5)	0.397(2)	0.870(1)	0.0321	
C(3)	0.576(6)	0.312(2)	0.801(2)	0.0486	
C(4)	0.493(7)	0.222(2)	0.825(2)	0.0563	
C(5)	0.482(7)	0.223(2)	0.918(2)	0.0628	
C(6)	0.566(8)	0.309(3)	0.987(2)	0.0872	
C(7)	0.655(6)	0.397(2)	0.963(2)	0.0454	
C(8)	0.743(7)	0.483(2)	1.031(1)	0.1031	
C(9)	0.827(5)	0.572(2)	1.007(1)	0.0426	
C(10)	0.897(7)	0.662(2)	1.076(1)	0.0526	
C(11)	0.986(7)	0.750(2)	1.052(2)	0.1204	
C(12)	1.009(5)	0.747(2)	0.959(2)	0.0204	
C(13)	0.929(7)	0.659(2)	0.890(2)	0.0772	
C(14)	0.838(5)	0.572(2)	0.914(5)	0.0264	
N(1)	0.479(7)	0.270(4)	0.640(2)	0.0448	
N(2)	0.540(9)	0.275(5)	0.555(3)	0.0972	
N(3)	0.939(9)	0.727(4)	0.757(3)	0.0954	
N(4)	0.953(8)	0.711(4)	0.665(3)	0.0668	
C(15)	0.609(5)	0.308(4)	0.706(2)	0.0332	
C(16)	0.45(1)	0.193(5)	0.476(5)	0.0723	
C(17)	0.48(1)	0.362(2)	0.525(7)	0.1232	
C(18)	0.963(7)	0.651(3)	0.794(2)	0.0144	
C(19)	1.02(1)	0.624(6)	0.607(6)	0.1126	
C(20)	1.04(1)	0.797(6)	0.633(6)	0.1124	
C(21)	0.63(1)	0.933(7)	0.905(6)	0.0306	
C(22)	0.59(1)	0.966(6)	0.827(6)	0.0731	
C(23)	−0.101(9)	0.138(5)	0.599(4)	0.0366	
C(24)	−0.053(8)	0.137(5)	0.701(4)	0.0309	

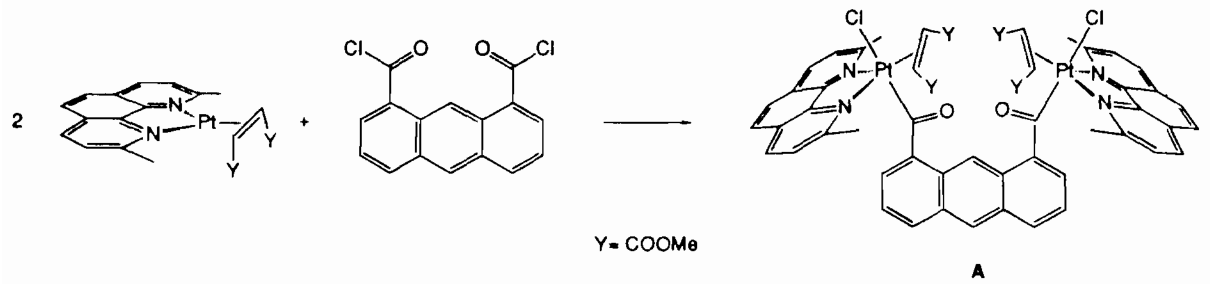
[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Results and discussion

Synthesis and characterization of the complexes

The neutral compound **A** was obtained adapting the known procedure [8] suitable for the attainment of mononuclear acyl-olefin five-coordinate derivatives. This involves oxidative addition to three-coordinate Pt(0) species (according to eqn. (1)).

Treatment of **A** with $AgBF_4$ in the presence of acetonitrile afforded the cationic compound **B**. This



(1)

complex is fairly soluble in nitromethane, while **A** is poorly soluble in the common organic solvents.

The presence of H_2O in **B** was suggested by the elemental analysis and confirmed by recording the ^{1}H NMR spectrum in dry deuteronitromethane. The amount of water was equimolar to that of DMPHEN and DMM, as evaluated through the integration of the pertaining peaks. Although the preference for the coordination of water with respect to acetonitrile is generally not observed in related platinum(II) cationic mononuclear species [9, 10], this is not the first report of such a finding [11].

Two attempts to replace the coordinated H_2O of **B** were performed. Thus, treatment of the complex with an anionic ligand (I^-) affords the neutral complex **C**. Alternatively, another cationic complex (**D**) can be obtained, by the substitution of water with a neutral ligand, i.e. $PhNH_2$. The easy exchange of the apical ligands reveals a strict analogy with the reactivity of related mononuclear species [9] including a *trans*-activating apical C–Pt bond.

All the complexes were characterized by elemental analysis and ^{1}H NMR spectroscopy. The latter shows the equivalence of the two halves of DMPHEN and DMM. This observation, together with the large high field shift of the olefin protons with respect to the value observed for the free olefin, points to a TBP arrangement around Pt, stabilized by sterical influences of DMPHEN [12]. The protons on the two external rings of the anthracene moiety are also equivalent. As a whole the NMR data suggest that the molecule presents an average mirror plane coincident with the anthracene plane, which leads to the overall symmetry C_{2v}. The same feature was displayed by the ^{1}H NMR spectrum of **E** at 298 K [1]. In the latter case the symmetry exhibited seemed to reflect a rapid '*syn–anti*' interconversion, i.e. involving conformations bearing the two coordination spheres on the same or on opposite sides of the anthracene plane. In fact, lowering of the temperature to 248 K allows the observation of two different spectral patterns for **E**, in agreement with the existence of two different slowly interconverting conformers. It is to be noted that the '*syn–anti*' interconversion seems to be quite difficult in the case of **E**, owing to conformational constraints, as deduced from an investigation using molecular models. In fact, short intramolecular contact distances would arise between Pt(1) and C(4) (Pt(2) and C(12)) (<2.5–2.7 Å) and the hydrogen atoms bonded to these carbon atoms (<1.7–1.8 Å), but these constraints do not prohibit the interconversion, according to the NMR spectrum at 298 K.

Description of the structure of E

The molecular structure of **E** is shown in Fig. 2 with the adopted labelling scheme. Selected geometrical parameters are listed in Table 3.

The relatively high standard errors of some molecular parameters do not allow a thorough analysis of structural details, nonetheless the main molecular features can be described with a fairly good degree of confidence.

The coordination geometry about the two Pt atoms is slightly distorted square-planar, with metal–ligand distances and angles within the normal values. The two metals together with their coordination sphere are disposed in a *syn* conformation with respect to the anthracene plane. This feature is favored if compared with the alternative *anti* conformation, since it affords the possibility to establish in the crystal propitious interactions between adjacent arenic moieties through attractive London's dispersion effects. Actually, the

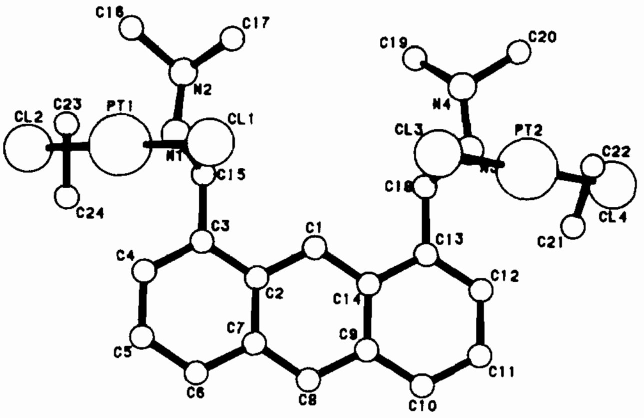


Fig. 2. Molecular structure of $[C_{14}H_8(CH{=}NNMe_2)_2Pt_2Cl_4(C_2H_4)_2]$.

TABLE 3. Selected geometrical parameters for **E**; the two columns refer to the two pseudo-symmetrical molecular halves

Bond distances (Å)			
Pt(1)–Cl(1)	2.27(2)	Pt(2)–Cl(3)	2.34(2)
Pt(1)–Cl(2)	2.29(2)	Pt(2)–Cl(4)	2.32(2)
Pt(1)–M(1)	2.08(3)	Pt(2)–M(2)	2.08(3)
Pt(1)–N(1)	2.10(4)	Pt(2)–N(3)	2.06(4)
N(2)–C(16)	1.44(2)	N(4)–C(20)	1.44(2)
N(2)–C(17)	1.45(2)	N(4)–C(19)	1.45(2)
Bond angles (°)			
Cl(1)–Pt(1)–N(1)	90(1)	Cl(3)–Pt(2)–N(3)	88(2)
Cl(1)–Pt(1)–M(1)	89(2)	Cl(3)–Pt(2)–M(2)	91(2)
Cl(1)–Pt(1)–Cl(2)	170(2)	Cl(3)–Pt(2)–Cl(4)	178(1)
M(1)–Pt(1)–Cl(2)	80(1)	M(2)–Pt(2)–Cl(4)	85(2)
M(1)–Pt(1)–N(1)	178(2)	M(2)–Pt(2)–N(3)	175(2)
Cl(2)–Pt(1)–N(1)	100(2)	Cl(4)–Pt(2)–N(3)	95(1)
Torsion angles (°)			
C(4)–C(3)–C(15)–N(1)	50	C(12)–C(13)–C(18)–N(3)	−50
C(15)–N(1)–N(2)–C(16)	149	C(18)–N(3)–N(4)–C(20)	−143
C(15)–N(1)–N(2)–C(17)	−100	C(18)–N(3)–N(4)–C(19)	−10

M(1) and M(2) indicate the middle point of the ethylene groups bonded to Pt(1) and Pt(2), respectively.

crystal structure shows a kind of dimeric association of molecular **E** units about inversion centers at $\frac{1}{2}$, $\frac{1}{2}$, 0, with almost superimposed anthracene rings *c*. 3.4–3.5 Å apart. The coordination planes of the two metal nuclei form an angle of *c*. 25° and are both almost orthogonal to the anthracene plane (the corresponding dihedral angles are *c*. 75–80°). The torsion angles C(4)–C(3)–C(15)–N(1) (*c*. 50°) and C(12)–C(13)–C(18)–N(3) (*c*. −50°) lead to an almost optimal orientation of the arene system with respect to the vicinal double bonds C(15)=N(1) and C(18)=N(3) (respectively) and cooperate to relieve the repulsive interaction between Cl(1) and Cl(3), which are in this structure at a distance of *c*. 5 Å.

The overall molecular structure displays a clear C_s pseudo-symmetry as evidenced in Fig. 2 (see also Table 3) with a mirror plane orthogonal to the anthracene ring through C(1) and C(8). The only relevant deviation from this symmetry regards the two methyl atoms C(17) and C(19). The methyl groups bonded to N(2) and N(4) are in the two most stable alternative 'eclipsing' conformations [13], of which that on N(2) is less favored by *c*. 1 Kcal/mol [14]. This conformation, which is not imposed by the necessity to avoid short intramolecular contact distances between C(19) and C(17), is likely to depend upon packing influences in the crystal regions near the inversion centers at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and 0, $\frac{1}{2}$, $\frac{1}{2}$.

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