Aminopyrazoles and Their Conjugated Acids. An X-Ray Study of 3,5-Dimethyl-4-aminopyrazole and the Picrate of 3(5)-Aminopyrazole

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The crystal structure determination of 3,5-dimethyl-4-aminopyrazole (**3**) and of 3(5)-aminopyrazolium picrate salt (**5a**) have been undertaken. The packing in **3** is characterized by the formation of sheets in which the N-H of the pyrazole and one H atom of the amino group are involved. The remaining HB donor interconnects sheets. In **5a**, the anions and the cations are linked by a two-dimensional network of hydrogen bonds in the *ab* plane. Each N-H and C-H in the cation are involved in hydrogen interactions with the O atoms of the anion. *Ab initio* molecular orbital methods at the HF and B3LYP levels using a 6-31G** basis set have been carried out to compare the relative stability of the tautomeric forms of the 3(5)-aminopyrazolium and 4-aminopyrazolium cations.

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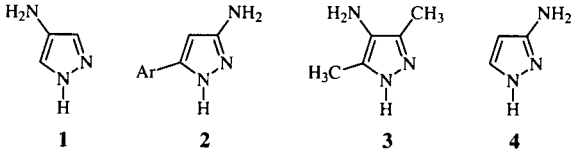
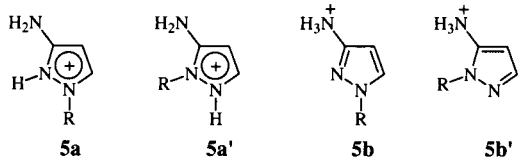
Amongst pyrazole derivatives, *C*-aminopyrazoles are the most used in heterocyclic chemistry as starting materials due to their versatility in reactions with conjugated ketones, esters and nitriles. In this way, a very large variety of fused and condensed heterocyclic derivatives have been prepared starting from *C*-aminopyrazoles [1-7]. We have already devoted two publications to these compounds, namely to the structure and polymorphism of 4-aminopyrazole (**1**) [8] and to the structure and tautomerism of a series of 3(5)-amino-5(3)-arylpyrazoles (**2**) [9]. The present work reports the study of another 4-aminopyrazole derivative, **3**, as well as that of the picrate salt of 3(5)-aminopyrazole (**4**).



1 **2** **3** **4**

Although evident [10], it is often ignored that the equilibrium between conjugated acids is also a case of tautomerism. Therefore, it has to be approached with similar methods and with the same precautions as tautomerism between neutral species. For example, protonation of a 3- or 5-aminopyrazole can afford two kinds of cations, those protonated on the annular nitrogen atom, **a** and **a'** (3-aminopyrazolium cations), and those protonated on the amino group, **b** and **b'** (3- or 5-ammoniopyrazoles). When R = H, cations **5b** and **5b'** are in equilibrium, the so-called annular tautomerism [10].



5a **5a'** **5b** **5b'**

The most stable tautomer is, in general, dependent on the phase in which the study is carried out. We will summarize below the knowledge of the tautomerism of salts **5** in solution and in the gas phase. In solution, using pK_a measurements [11], ^{13}C nmr spectroscopy [12], ^{15}N nmr spectroscopy [13], and uv spectroscopy [13], it was established that **5a** and **5a'** are the most stable tautomers. Since the present study deals with the 1-unsubstituted derivatives (R = H), **a** and **a'** become identical and from now on, only **5a** structure will be discussed.

In the gas phase, a study by Ion Cyclotron Resonance spectroscopy combined with 6-31G *ab initio* calculations demonstrates that the compound obtained by protonation of 3(5)-aminopyrazole (**4**) has the structure **5a** [14]. This result is in agreement with a study using Ion Mobility Spectrometry according to which aminopyrazoles protonate on the ring nitrogen (**5a**, **5a'**) in the gas phase [15]. Theoretical calculations for R = H on these different

cations have been carried out several times using different approximations. According to INDO calculations [11], cation **5a** is much more stable than cations **5b** and **5b'**. AM1 calculations on the protonation enthalpies (determined by Ion Cyclotron Resonance) of a very large set of pyrazoles shows that **4** behaves like all other pyrazoles, *i.e.* it protonates on the ring nitrogen [16]. A later paper was devoted to the equilibrium **5b** ⇄ **5b'** (R = H, annular tautomerism) where, according to 6-31G calculations, cation **5b** is more stable than **5b'** by 18 kcal mol^{-1} [17].

To determine whether the tautomer present in the solid-state has the same structure as the predominant tautomer in solution, we decided to establish experimentally, by X-ray crystallography, if the salt obtained by protonation of **4** has the structure **5a**.

Results and Discussion.

X-Ray Crystallographic Study.

The structure of the 3,5-dimethyl-4-aminopyrazole (**3**) and that of 3(5)-aminopyrazolium picrate (**5a**) have been solved by X-ray analysis (Table 1 and Figure 1). The geometry of the pyrazole ring in **3** is similar to that observed in the two polymorphic forms of 4-aminopyrazole [8]. Most of the bond lengths and angles present nor-

Table 1

Intra and Intermolecular Parameters. Cpz and Cph mean the Centroids of the Pyrazole (N1,...,C5) and Phenyl (C7,...,C12) Rings Respectively

Compound **3**

N1-N2	1.353(2)	N2-C3	1.348(2)	C3-C4	1.398(3)
C4-C5	1.376(3)	N1-C5	1.355(3)	C3-C6	1.489(3)
C4-N7	1.423(3)	C5-C8	1.490(3)	N2-N1-C5	112.5(2)
N1-N2-C3	104.9(2)	N2-C3-C4	110.4(2)	C3-C4-C5	106.2(2)
N1-C5-C4	106.1(2)	N2-C3-C6	120.6(2)	C4-C3-C6	129.0(2)
C3-C4-N7	128.4(2)	C5-C4-N7	125.1(2)	N1-C5-C8	122.7(2)
C4-C5-C8	131.3(2)	Σα(N7)	343(3)	N2-C3-C4-N7	174.1(2)
C3-C4-N7-H71	13(2)	C3-C4-N7-H72	149(2)		
D-H···A	D-H	D···A	H···A	D-H···A	
N1-H1···N7(-x, 1/2+y, 1/2-z)	0.89(3)	2.946(2)	2.07(3)	169(3)	
N7-H72···N2(x, 1/2-y, 1/2+z)	0.93(3)	3.091(2)	2.17(3)	176(2)	
N7-1471···N2(1-x, y-1/2, 1/2-z)	0.94(3)	3.350(2)	2.45(3)	160(2)	
C6-H63···Cpz(1-x, y-1/2, 1/2-z)	0.99(5)	3.738(2)	2.96(5)	137(3)	

Compound **5a**

N1-N2	1.354(4)	N2-C3	1.338(5)	C3-C4	1.398(5)
C4-C5	1.360(6)	NI-C5	1.331(6)	C3-N3	1.348(5)
N2-N1-C5	108.3(3)	N1-N2-C3	108.6(3)	N2-C3-C4	107.9(3)
C3-C4-C5	105.6(4)	N1-C5-C4	109.6(4)	N2-C3-N3	121.5(4)
C4-C3-N3	130.6(4)	Σα(N3)	353(8)	N1-N2-C3-N3	180.0(4)
N2-C3-N3-H31	13(5)	N2-C3-N3-H32	164(4)		
C7-C8	1.436(5)	C8-C9	1.378(5)	C9-C10	1.387(5)
C10-C11	1.371(5)	C11-C12	1.376(5)	C7-C12	1.458(5)
C7-O1	1.242(4)	C8-N4	1.459(5)	N4-O41	1.209(5)
N4-O42	1.221(5)	C10-N5	1.448(4)	N5-O51	1.230(4)
N5-O52	1.222(4)	C12-N6	1.444(5)	N6-O61	1.217(5)
N6-O62	1.213(5)	C8-C7-C12	112.3(3)	C7-C8-C9	124.9(3)
C8-C9-C10	117.9(3)	C9-C10-C11	122.1(3)	C10-C11-C12	119.5(3)
C11-C12-C7	123.2(3)	C8-C7-O1	123.4(3)	C12-C7-O1	124.2(3)
C7-C8-N4	119.5(3)	C9-C8-N4	115.6(3)	C9-C10-N5	118.2(3)
C11-C10-N5	119.7(3)	C7-C12-N6	120.2(3)	C11-C12-N6	116.6(3)
C12-C7-C8-N4	174.1(3)	C8-C9-C10-N5	179.5(3)	C8-C7-C12-N6	-177.1(3)
C7-C8-N4-O41	21.2(5)	C9-C10-N5-O51	5.4(5)	C7-C12-N6-O61	179.4(4)
D-H···A	D-H	D···A	H···A	D-H···A	
N2-H2···O1	0.98(4)	2.602(4)	1.74(4)	144(4)	
N2-H2···O62	0.98(4)	2.979(4)	2.22(4)	133(3)	
N3-H31···O41	0.86(6)	3.161(5)	2.36(6)	155(5)	
N3-H31···O1	0.86(6)	2.886(5)	2.22(6)	134(6)	
N1-H1···O42(1+x,y,z)	0.93(5)	2.860(5)	1.94(5)	170(4)	
N3-H32···O51(1/2-x, 1/2+y, 1/2-z)	0.93(6)	3.078(5)	2.18(6)	164(5)	
N3-H32···O52(1/2-x, 1/2+y, 1/2-z)	0.93(6)	3.284(5)	2.50(6)	142(4)	

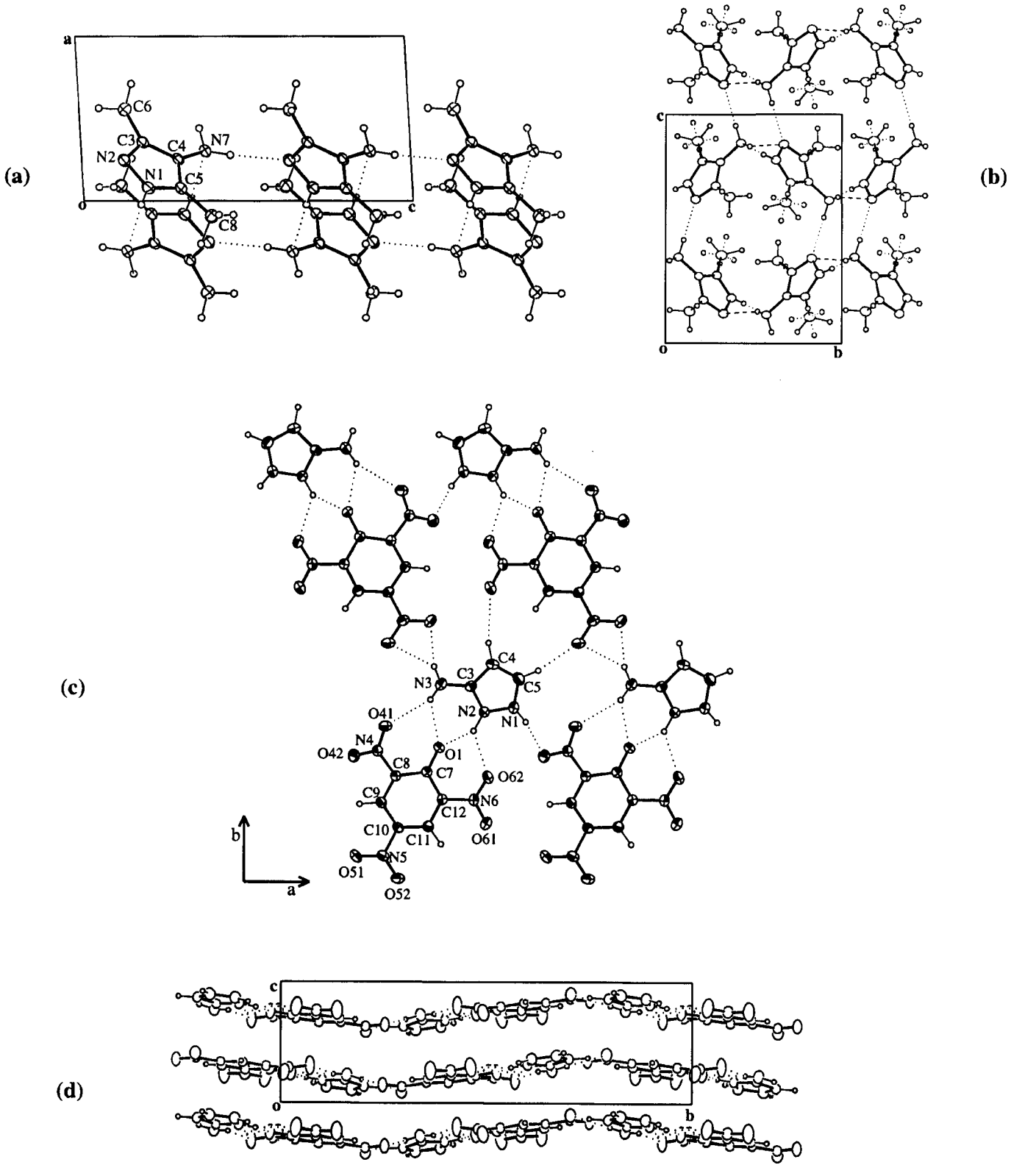


Figure 1. (a) Secondary structure of **3**. (b) Crystal packing of **3** down the *a* axis displaying the disorder model of the C8 methyl group. (c) Molecular arrangement of **5a** within a sheet. (d) Packing of the layers in **5a** along the *a* axis. Each drawing shows 30% probability displacement ellipsoids. Dashed and dotted lines represent the disorder model and the hydrogen bond systems.

mal values, and small internal angular distortions at C3 and C4 and, to a lesser extent, at C5 are probably due to the influence of the methyl groups [18,19]. There is a dissymetry in the C-C bond lengths, the C4-C5 bond being significantly shorter than the C3-C4 one. The amino group presents an analogous distorted sp^3 hybridization and a perpendicular conformation similar to that of polymorph I of **1**.

In **5a**, the X-ray analysis reveals that the hydrogen atom of the hydroxyl group in the picric acid molecule has been transferred to the N2 of the pyrazole and therefore, tautomer **5a** (Figure 1c) is present in the structure. The protonation of symmetrical pyrazoles in the annular nitrogen results in a delocalized structure of C_{2v} symmetry; in the case of **5a**, the loss of this class of symmetry is due to the amino substituent. The amino group at C3, that presents a sp^2 hybridization, breaks the symmetry mainly closing the corresponding internal angle, N2-C3-C4 < N1-C5-C4 (Table 1). The C-N(amino) distance is similar to the average value of 1.374(14) (standard deviation of the sample in parentheses) reported for this bond in eighteen 3(5)-aminopyrazole derivatives [9,20]. The geometry of the picrate anion in **5a** is also similar to that observed in other previously reported studies [20-23].

The crystal structure of **3** and those of the two polimorphic forms I and II of **1** [8] show different hydrogen-bonding topologies although the N-H hydrogen of the pyrazole and the hydrogen atoms of the amino group in the present compound and in the polymorph I are bonded between them in a similar way. The strongest N1-H1···N7 and N7-H72···N2 interactions (Table 1) form waved sheets perpendicular to the *a* axis (Figure 1a) cross-linked

Table 2

Crystal Analysis Parameters.

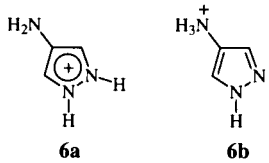
Compound	**3**	**5a**
Crystal data		
Formula	$C_5H_9N_3$	$C_3H_6N_3{\cdot}C_6H_2N_3O_7$
Crystal habit	Colourless, plate	Colourless, plate
Crystal size (mm)	0.33 x 0.30 x 0.17	0.53 x 0.13 x 0.10
Symmetry	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Unit cell determination:	Least-squares fit from 40 reflexions (θ<45°)	Least-squares fit from 63 reflexions (θ<45°)
Unit cell dimensions (Å, °)	a = 5.8418(3)	a = 8.9746(4)
	b = 8.7463(5)	b = 21.3846(12)
	c = 11.5750(10)	c = 6.6737(3)
	90, 93.160(9), 90	90.0, 106.916(3), 90.0
Packing: V(Å^3), Z	590.52(6), 4	1225.39(8), 4
Dc(g/cm^3), M, F(000)	1.250, 111.15, 240	1.692, 312.20, 640
μ(cm^{-1})	6.60	12.99
Experimental Data		
Technique	Four circle diffractometer: Philips PW 1100, Bisecting geometry. Graphite oriented monochromator.CuKα radiation. $\omega/2\theta$ scans. θ_{max} = 65 Detector apertures 1 x 1°. 1 min./reflex. Scan width 1.50°	
Temperature	200K	295K
Number of reflexions:		
Independent	1002	2082
Observed (2σ(I) criterion)	879	1720
Standard reflexions:	2 reflexions every 90 min. No variation	
Solution	Direct methods: Sir92	
Refinement:		
Least-Squares on Fo	Full matrix	
Secondary extinction (10^4)	–	0.169(7)
Parameters:		
Number of variables	121	231
Degrees of freedom	758	1489
Ratio of freedom	7.3	7.4
Final shift/error	0.002	0.001
H atoms	From difference synthesis	
Weighting-scheme	Empirical as to give no trends in $\langle\omega\Delta^2F\rangle$ vs. $\langle\lvert Fobs\rvert\rangle$ and $\langle\sin\theta/\lambda\rangle$	
Max. thermal value (Å^2)	U22(C8) = 0.057(1)	U33(O62) = 0.180(4)
Final ΔF peaks (eÅ^{-3})	±0.23	±0.34
Final R and Rw	0.049, 0.052	0.064, 0.081

by N7-H71···N2 and C6-H63···Cpz interactions (Figure **1b**). In **5a**, all potential acceptor atoms in the anion and all H atoms in the cation are involved in hydrogen bonds (HBs, Figure 1c). Each cation is linked to four neighbour anions by a total of nine HBs (two of them correspond to C-H···O contacts) forming layers perpendicular to the *c* axis (Figure **1d**). Some degree of overlapping between the ions is observed (Table 1). There are no voids in the structures and the total packing coefficients are 0.688 and 0.733 for **3** and **5a** respectively.

Theoretical Calculations.

Theoretical calculation using the GAUSSIAN94 program [24] were carried out in order to obtain the relative stabilities of all the possible conjugated acids of **1** and **4** (**5a**, **5b**, **5b'** and **6a**, **6b**). The 6-31G** basis set and the HF and B3LYP methods were used for the optimization of the geometries. Tautomer **5a** has the lowest energy in agreement with that found in the solid state and with previous results [14-16]. Both methods of calculation predict the energies of the **5a** tautorner to differ by up to 14 and 11 kcal mol^{-1} (HF and B3LYP respectively) from those of the **5b**, **5b'**. Tautomer **6a** is more stable than **6b** by approximately 7 and 10 kcal mol^{-1} (HF and B3LYP). The X-ray determined geometrical parameters qualitatively agree with the theoretical prediction. The small differences between experimental and theoretical data and between those of both *ab initio* methods are of the same order of magnitude.

We have also optimized the geometry of the 4-amino-3,5-dimethylpyrazole compound (**3**) at the same level (HF and B3LYP/6-31G**). When comparing the geometry with that of **1** [8], the inclusion of two methyl groups results in the closing of the angles at C3 and C5 by 0.9° and the opening of the angle at C4 by 1.1° approximately, in accordance with the previously reported values [19].



6a **6b**

EXPERIMENTAL

Melting points were determined on an hot-stage microscope and are uncorrected. The nmr spectra were recorded on a Bruker DRX 400 spectrometer working at 400.13 and 100.62 MHz for ^1H and ^{13}C respectively. In all cases, tetramethylsilane was used as internal standard.

3,5-Dimethyl-4-aminopyrazole (**3**).

This compound was prepared according to reference [25]; its ^{13}C nmr study under neutral and acid conditions was reported in previous publications [12,26]. A picrate was prepared by mixing equimolar amounts of **3** and picric acid in ethanol, mp 175°; The ^1H nmr (dimethyl-d_6 sulfoxide): 2.16 (6H, CH_3), 8.58 (2H, picric acid); ^{13}C nmr in (dimethyl-d_6 sulfoxide): 9.7 (CH_3), 108.8 (pyrazole, C4), 137 (very broad, pyrazole C3 and C5), 124.5, 125.2, 141.8, 160.9 (picric acid). No suitable crystals were obtained of this picrate.

Anal. Calcd. for $C_{11}H_{12}N_6O_7$: C, 38.83; H, 3.55; N, 24.70. Found: C, 39.01; H 3.42; N, 24.68.

3-Aminopyrazole Picrate.

3-Aminopyrazole (**4**) is a commercial product (for its ^{13}C nmr study, see [12,26]). A picrate was prepared by mixing equimolar amounts of **4** and picric acid in ethanol, mp 218°; ^1H nmr in (dimethyl-d_6 sulfoxide): 5.92 (1H, H4, d, J = 2.6 Hz), 7.80 (1H, H5, d, J = 2.6 Hz), 8.57 (2H, picric acid); ^{13}C nmr in (dimethyl-d_6 sulfoxide): 94.6 (pyrazole, C4), 133.5 (pyrazole, C5), 145.9 (pyrazole C3), 124.2, 125.2, 141.8, 160.8 (picric acid). No suitable crystals were obtained of this picrate.

Anal. Calcd. for $C_9H_8N_6O_7$: C, 34.63; H, 2.58; N, 26.92. Found: C, 34.68; H, 2.51; N, 26.69.

X-Ray Analysis.

Single crystals of **3** and **5a** suitable for the X-ray study were grown from ethanol. The crystal of **3** used for data collection was cooled at 200K with an Oxford Cryostream device [27] since in the first data collection at room temperature the disorder model of one methyl group could not be properly established. Indications for two orientations of the C8 methyl H-atoms in **3** were noted during checking of difference density maps generated near the end of the refinement process. The crystal data and refinement parameters are reported in Table 2. Both structures were solved by direct methods (SIR92) [28] and refined by least-squares procedures on Fobs. Most of H atoms were found in difference maps and the remaining ones were placed geometrically. Two sets of methyl H atoms positions at C8 (Figure 1b) were included at half occupancy for each in the final refinement and all hydrogen atoms were refined freely. The scattering factors were taken from the International Tables for X-Ray Crystallography [29], and most of the calculations were carried out with the XTAL [30], PESOS [31] and PARST [32] set of programs running on an AXP 600 computer.

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