Azolides. Part 12.† Carbon-13 Nuclear Magnetic Resonance Study of *N*-Methyl and *N*-Acetyl Derivatives of Azoles and Benzazoles

By **Mikael Begtrup,*** Institute of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark
Rosa Maria Claramunt and **José Elguero,** Laboratoire de Chimie Moléculaire, Université d'Aix-Marseille III, Rue H. Poincaré, 13397 Marseille Cédex 4, France

^{13}C N.m.r. chemical shifts and C–H coupling constants of methyl- and acetyl-benzazoles have been derived from data for the corresponding uncondensed azoles by addition of increments which depend on the position and nature of the azole nitrogen atoms present. Use of ^{13}C n.m.r. parameters by estimation of conformer distribution in acetylazoles or -benzazoles proved reliable only when the individual conformers were observable. In the absence of steric effects the composition of equilibrium mixtures of isomeric *N*-substituted azoles is independent of the nature of the *N*-substituent.

THE distribution between *Z*- and *E*-conformers of some *N*-acylazoles and -benzazoles have been determined by ^{1}H n.m.r. spectroscopy (see references in Table 6). However, ^{13}C n.m.r. chemical shift differences between conformers normally exceed the ^{1}H n.m.r. shift differences. In addition, the proton-decoupled ^{13}C spectra give distinct peaks, of particular advantage in the analysis of benzazoles. Therefore, ^{13}C n.m.r. spectra of *N*-acetyl-azoles and -benzazoles have now been compared with data for the corresponding *N*-methyl compounds in order to obtain information about conformation of the acetyl compounds. A comparison of azole with benzazole data simultanously allows analysis of changes in ^{13}C n.m.r. shifts and C–H coupling constants induced by the annellation of the azoles.

^{13}C *N.m.r. Signal Assignments.*—The ^{13}C n.m.r. data of the *N*-methylazoles (1a)—(13a), (14a; X = H and Br) and the known *N*-acetylazoles (1b)—(10b), (12b), and (14b; X = H and Br) are presented in Table 1a—c. The signals were assigned using (i) reported assignments of spectra of (1a)—(6a),[1,2] (7a),[3] and (1b) [4] which were all

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† Part 11, A. Maquestiau, Y. Van Haverbeke, R. Flammang, R. M. Claramunt, and J. Elguero, *Bull. Soc. chim. France*, 1975, 2693.

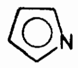
[1] J. Elguero, C. Marzin, and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 357.

[2] M. Begtrup, *J.C.S. Perkin II*, 1976, 736.

[3] R. G. Parker and J. D. Roberts, *J. Org. Chem.*, 1970, **35**, 996.

[4] S. Combrisson and B. P. Roques, *Tetrahedron*, 1976, **32**, 1507.

rerun for standard solvent and concentration in order to obtain values suitable for comparison; (ii) selective proton decoupling [3] based on analysed ^{1}H n.m.r. spectra [5–7] which permitted assignment of all tertiary carbon atoms of (8a), (14a),* and (7b). Assignment of indazole signals were confirmed by carbon spectra of their *C*-nitro-derivatives.[11] (iii) Annellation effects (Table 2), discussed below, are remarkably consistent and allow assignment of all quaternary carbon atoms in condensed azoles. (iv) One bond C–H couplings determined from coupled carbon spectra were compared with values obtained from proton satellite spectra [12] allowing assignment of C-3 and C-5 of 1-acetyl-1,2,4-triazole (5b).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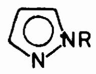
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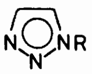
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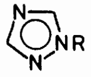
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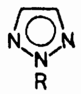
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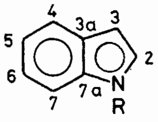
a; R = Me
b; R = Ac



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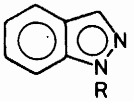
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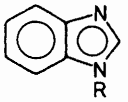
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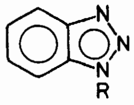
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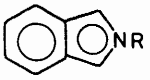
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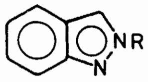
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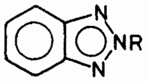
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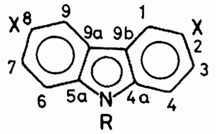

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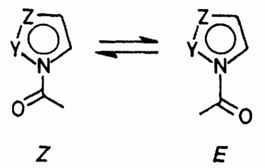

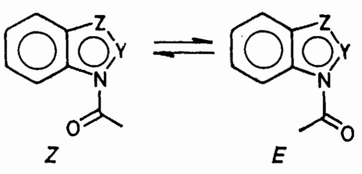

(v) Effects on carbon shifts induced by replacement of CH with imine nitrogen can be deduced from spectra assigned on the above mentioned criteria. The approximately additive contributions allow assignment of the tertiary carbon atoms in (10a), (11a), (13a), (2b)—(4b), and (10b), but do not permit distinction between C-4 and C-5 in (10a). (vi) Shift difference between methyl and acetyl compounds estimated ultimately by comparison of (7a)[3] with (7b) [method (ii)] and listed in Table 3 were used to assign C-4 ($\Delta\delta$ 1.5), C-5 ($\Delta\delta$ 2.5), and C-6 ($\Delta\delta$ 3.5 p.p.m.) of (8b), (9b), and (12b). On the other hand, C-4 and C-5 of (10a) could be identified from the corresponding shifts of (10b).

Spectra assigned using the above mentioned criteria reveal that (a) $^1J_{CH}$ of carbon atoms α to nitrogen is larger than $^1J_{CH}$ of benzenoid carbon atoms. This allows identification of C-3 in (8b) and (12b) and of C-2 in (9b). (b) C-7 is the homocyclic carbon atom with the largest one-bond C-H coupling (and the highest carbon shift). This permits assignment of C-7 in (8b)—(10b) and (12b), and of C-4 ≡ C-6 in the *N*-acetylcarbazoles (14b).

Generalization of Carbon Shifts and C–H *Couplings in Azoles and Benzazoles.*—Carbon shifts and C–H couplings of azoles are predictable from values for benzene and cyclopentadiene anion by addition of effects from imino nitrogen atoms, amino nitrogen atoms and their substituents, and from annellation, provided that these incre-

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* The ^{1}H spectrum of (14a; X = H) was analysed like that of carbazole [8] using proton double resonance which revealed that $\delta_{H-1} > \delta_{H-4} > \delta_{H-3} > \delta_{H-2}$. For the bromo-derivatives (14; X = Br) comparison with calculated bromine substitution effects on benzenoid carbon atoms [9] and absence of a three-bond C–H coupling for C-4 ≡ C-6 [10] allowed complete assignment.

[5] M. H. Palmer, R. Findlay, S. M. F. Kennedy, and P. S. McIntyre, *J.C.S. Perkin II*, 1975, 1695.

[6] J. Elguero, A. Fruchier, and R. Jacquier, *Bull. Soc. chim. France*, 1966, 2075.

[7] L. Pappalardo, J. Elgüero, and A. Fruchier, *Anales de Quim.*, 1975, **71**, 598.

[8] P. J. Black and M. L. Heffernan, *Austral. J. Chem.*, 1965, **18**, 353.

[9] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley, New York, 1972, p. 81.

[10] J. Karliner and R. Rodebaugh, *Tetrahedron Letters*, 1975, 3783.

[11] P. Bouchet, A. Fruchier, G. Joncheray, and J. Elguero, *Org. Magnetic Resonance*, in the press.

[12] J. Elguero, C. Marzin, and L. Pappalardo, *Bull. Soc. chim. France*, 1974, 1137.

ments are independent and additive. However, effects from more than one nitrogen atom are non-additive in monocyclic azoles[1] and the present data demonstrate that this is true for benzazoles, too. Thus replacement of C-2 with nitrogen induces shift changes of C-3a from —4.6 in (7a) and (8a) to 2.3 p.p.m. in (9a) and (10a).

Annellation-induced changes of carbon shifts or of one-bond C-4 couplings (Tables 2 and 4) are remarkably consistent. The amino nitrogen atom which determines the π-bond structure is the main source of annellation effects. However, additional imino nitrogen atoms cause significant contributions to the shifts of C-5, C-6, C-3a, and C-7a (but remarkably hardly to C-7) and to the C–H couplings of C-5 and C-6. The effect of more nitrogen atoms seems additive except for one bond couplings of C-4 and C-7 where a reinforcement of the contributions is observed. The difference in shift and coupling constants between corresponding signals of methyl and acetyl compounds depend on the position of the amino nitrogen atom (Table 3). If it is at position 2, C-4 and C-6 exhibit larger shift differences than the carbon atoms situated closer to nitrogen.

TABLE 1

^{13}C N.m.r. chemical shifts (p.p.m. relative to the $CDCl_3$ centre peak at δ 76.90) and ^{13}C–H coupling constants in Hz of *N*-methyl- and *N*-acetyl-azole derivatives dissolved in deuteriochloroform (concentration 15% w/v)

a, Azoles

	C-2		C-3		C-4		C-5		C=O		CH_3	
Compound	δ	*J* [a]	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*
(1a)	121.0	184.0	107.7	170.0	107.7	170.0	121.0	184.0			35.2	
(1b)	119.0	191.3	112.9	172.1	112.9	172.1	119.0	191.3	167.5		21.9	129.0
(2a)			138.7	185.5	105.1	176.7	129.3	185.5			38.4	
(2b)			143.6	187.1 6.1; 9.2	109.3	178.7 8.8; 11.8	127.8	190.3 4.4; 8.8	169.2		21.3	
(3a)	137.6				129.3	188.1	119.7	189.5			32.9	
(3b)	136.2	214.6 5.6; 9.6			130.5	192.3 9·8; 11.2	115.9	195.0 0; 15.6	166.3	7.0	22.3	129.8
(4a)					133.6	194.3 11.7	124.1	196.6 15.4			36.2	
(4b)					134.2	195.4 10.3	121.1	198.0 16.8	188.3		22.1	
(5a)			150.7	206.6			142.7	209.2			35	
(5b)			152.8	210.4 12.9			143.0	217.5 7.0	167.8	7.0	21.8	130.5
(6a)					133.8	192.5 12.8	133.8	192.5 12.8			41.0	
(6b)					138.1	191.3 10.7	138.1	191.3 10.7	165.7	7.0	21.8	130.6

b, Benzazoles

	C-2		C-3		C-4		C-5		C-6		C-7		C-7a		C-3a		C=O		CH_3	
	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	*J*
(7a)	128.6	181.5	100.8	173 3; 7	119.1	161.5	120.7	160	121.3	160.5 1.5; 7	109.0	160	136.6		128.4				32.4	136.5
(7b)	125.0	187.5 9.5	108.7	175 3; 5.5	120.6	161 8	123.4	158.5 7.5	124.8	160 9	116.0	170. 7	135.2		130.2		168.2		23.5	128
(8a)			132.4	188 2.5	120.8	161	120.2	161.5	125.9	159 5.5; 8	108.6	161	139.7		123.8				35.2	138
(8b)			139.4	190 2.5	120.6	163.5	124.1	161.5	129.2	157.5	115.3	174	139.4		126.1		170.7	6.5	22.7	130.5
(9a)	143.1	202 4			119.7	160.5	121.5	159.5	122.4	158.5 8	108.9	160.5	134.1		143.2				30.4	139.4
(9b)	141.2	210.5			120.2	163	124.7	161 8.5	125.5	163.5 8	115.1	170	131.2		143.6	6	166.9	6	23.3	129.5
(10a)					119.3	165 4	123.4	162 3; 6	126.8	160.5 2; 8	108.8	165.5 8	133.1		145.5				33.7	140.5
(10b)					119.9	167.5 7.5	125.8	162.5 8	130.0	163 2; 8	114.1	173.5 7.5	130.7		146.0		169.3		22.8	130.8
(11a)			111.3 [b]	186.5	119.1	163.0	120.2	159.5	120.2	159.5	119.1	163.0	124.3		124.3				37.1	140
(12a)			123.1	186.5 0	119.6	162.5 7	121.2	159 8	125.4	157.5 9.5	116.8	162.5 5.5	148.7		121.8				39.7	140
(12b)			122.1	191.5 0.5	124.0	160.5 9	121.4	165 7.5	129.0	161 9	118.8	167 6.5	150.7		122.1		170.8		21.8	130.5
(13a)					117.5	167.0	125.9	160.0	125.9	160.0	117.5	167.0	144.3	1.3; 4.5	144.3			1.3; 4.5	42.8	

c, Carbazoles

	C-1 = C-9		C-2 = C-8		C-3 = C-7		C-4 = C-6		C-4a = C-5a	C-9a = C-9b	C=O	CH_3	
	δ	*J*	δ	*J*	δ	*J*	δ	*J*	δ	δ	δ	δ	*J*
(14a; X = H)	120.1	160.5 7.5	118.7	160.5 7.5	125.5	158 8	108.2	159 8	140.9	122.7		29.6	137.5
(14b; X = H)	119.4	161 8.5	123.2	163 6.5	126.9	162.5 8	115.8	168.5	138.3	126.0	169.6	27.2	
(14a; X = Br) [c]	123.3	167.5	111.3		128.8	165.0 6	111.4	165.0	139.6	122.8		29.3	
(14b; X = Br) [c]	124.3	162 5.5	117.1		131.4	160.5 5	119.1	168.5 2	138.3	127.5	171.4	28.3	

[a] Three and two bond couplings are given below the one bond couplings. [b] C-3 = C-1. [c] Dissolved in [$^2H_6$]DMSO.

Taking the special combined effect of two imino nitrogen atoms into account, combination of the values in Tables 2—4 allows estimation of shifts and one-bond C–H couplings in any alkyl- or acyl-benzazole.

Conformer Distribution in Acyl-azoles and -benzazoles.— In order to determine this distribution low temperature spectra of pyrrole (1) and carbazole (14) derivatives were recorded (Table 5) as for reported proton spectra.[12,13] By analogy with recently assigned low temperature spectra of 1-acetylpyrrole[4] it was assumed that $\delta_{C\text{-}4a} >$

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[13] J. Elguero, C. Marzin, and M. E. Peek, *Org. Magnetic Resonance*, 1975, **6**, 445.

TABLE 2

^{13}C N.m.r. shift replacements caused by the annellation of methylazoles to methylbenzazoles

	Carbon atom	Annellation shift[a] (p.p.m.)	Increment (p.p.m.) in the presence of imino-N at position 1	position 2	position 3
Amino-N at position 1	2	7.5		0.5	
	3	−7.0			−2
	4	−9.5		1.5	0.5
	5	−8.0		−0.5	1
	6	−7.0		4.5	1
	7	−19.5		−0.5	0
	7a	15.5		−4	−1
	3a	21.5		−3	−8
	CH_3	−3.0		3	−2
Amino-N at position 2	3	−9.5	3.5		
	4	−9.5	0.5		−2
	5	−8.5	1		4.5
	6	−8.5	5		0.5
	7	−9.5	−2.5		0.5
	7a	16.5	−6.5		0
	3a	16.5	0		6.5
	CH_3	2	2.5		2.5

[a] The shift replacements of C-4—C-7 are relative to the benzene signal (128.5 p.p.m.) whereas those of C-2, C-3, C-3a, C-7a, and CH_3 are relative to the shifts of the uncondensed azoles (Table 1). Positive values correspond to downfield shifts.

TABLE 4

$^1J_{CH}$ Changes caused by the annellation of methyl- or acetyl-azoles to their benzo-derivatives

	Carbon atom	Annellation induced change of J_{CH} (Hz)[a]	Increment (Hz) in the presence of imino-N at position 1	position 2	position 3
Amino-N at position 1	2	−2.5 (−4)			1 (−0.5)
	3	3 (4)		0 (−1)	
	4	2.5 (2)		−0.5 (2.5)	−1 (2)
	5	1 (−0.5)		1.5 (3)	0 (2.5)
	6	1.5 (1)		−1.5 (−2.5)	−2 (3.5)
	7	1 (11)		1 (4)	0.5 (0)
Amino-N at position 2	3	2.5	−1.5		
	4	4	−0.5		−0.5
	5	0.5	−0.5		−2
	6	0.5	−2		−0.5
	7	4	−0.5		−0.5

[a] Values in parentheses obtain for acetylbenzazoles.

TABLE 5

^{13}C N.m.r. chemical shifts (p.p.m. relative to the [$^2H_6$]acetone centre peak at δ 29.22) of *N*-methyl- and *N*-acetyl-azoles dissolved in hexadeuterioacetone

Compound	Temperature (°C)	C-2	C-3	C-4	C-5	C=O	CH_3
(1a)	34	121.6	108.0				35.3
	−63	121.3	107.7				35.1
	−93	121.2	107.6				34.9
(1b)	34	119.5	112.8	112.8	119.5	167.9	21.7
$Z \equiv E$	−63	118.0	112.7	112.7	120.7	168.1	21.7
	−93	117.9	112.8	112.8	120.9	168.4	21.8

Compound	Temperature (°C)	C-4	C-3	C-2	C-1	C-9	C-8	C-7	C-6	C-5a	C-9a	C-9b	C-4a	C=O
(14a; X = H)	34	109.4	126.3	119.5	120.8	120.8	119.5	126.3	109.4	141.8	111.6	111.6	141.8	
(14b; X = H)	−93	117.2	127.0	119.6	123.1	123.8	120.2	127.6	115.2	137.2	125.9	125.3	138.7	170.5
$Z \equiv E$														

$\delta_{C\text{-}5a} > \delta_{C\text{-}9a} > \delta_{C\text{-}9b}$ in the single conformer of 1-acetylcarbazole. C-4 was distinguished from C-6 since its shift on replacement of acetyl with methyl was similar to that of C-7 in (7b), known from ^{1}H n.m.r.,[13] dipole moment measurements,[14] and *X*-ray analysis [15] to adopt the *Z*-form. C-1—C-3, and C-7—C-9 of (14b; X = H) were tentatively assigned in the same way by comparison with C-4—C-6 of (7b).

TABLE 3

^{13}C N.m.r. shift differences (p.p.m.) between methyl- and acyl-benzazoles

	C-2	C-3	C-4	C-5	C-6	C-7	C-7a	C-3a
Amino-N at position 1	−3	7.5	0.5	3.0	3.5	6.5	−1.5	1
Amino-N at position 2		−1	4.5	0	3.5	2	2	0.5

A comparison of the low temperature spectra of methyl- and acetyl-pyrrole in $CDCl_3$ indicates that C-2 and C-5 in (1b) exhibit upfield shifts of 2.6 and 1.5 p.p.m. with respect to C-2 in (1a). If these shift values are significant information about distribution between *Z*- and *E*-forms in rapidly equilibrating acetylazoles may be obtained. Thus, C-5 of 1-acetylpyrazole exhibits at 1.5 p.p.m. upfield shift with respect to C-5 of 1-methylpyrazole (Table 1) suggesting a predominance of the *Z*-form in the equilibrium. The results obtained for the other acetylazoles are shown in Table 6.

Information about conformer distribution in *N*-acetylbenzazoles (8b)—(12b) may likewise be obtained by comparison with the fixed conformer of (14b; X = H) in

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[14] J. P. Fayet, M. C. Vertut, P. Mauret, R. M. Claramunt, and J. Elguero, *Rev. Roumaine Chim.*, 1977, **22**, 471.

[15] J. P. Mornon, J. Delettré, and E. Surcouf, to be published.

which the benzenoid carbon atoms α and β to nitrogen are those most sensitive to conformational change. Thus, the shift difference between C-7a in (8a and b), 0.3 p.p.m. (Table 1), exceeds the shift difference between C-4a in (14a and b; X = H). This suggests predominance of the *Z*-form of (8b). The results of similar reasoning for (9b)—(12b) are depicted in Table 6.

TABLE 6

Conformer distribution in *N*-acetyl-azoles and -benzazoles obtained from ^{13}C n.m.r. shift differences between analogous carbon atoms of *N*-acetyl and *N*-methyl compounds

Compound	Approximate conformer distribution (%*Z*) at 34 °C	Position for which the shift difference has been calculated [a]	Conformer distribution (%*Z*) obtained by other methods	References
1-Acetylpyrazole (2b)	100	C-5	0	12, 14, 16, 17
1-Acetylimidazole (3b)	0	C-2	35—75	12, 18
	0	C-5 [b]		
1-Acetyl-1,2,3-triazole (4b)	0	C-5 [b]	5	12, 17
1-Acetyl-1,2,4-triazole (5b)	100	C-5 [b]	0	12, 17
1-Acetylindole (7b)	0	C-2 [b]		
	100	C-7a [b]	100	13, 15, 17
	60	C-7		
1-Acetylindazole (8b)	100	C-7a [b]	55—100	6, 19, 20
	45	C-7		
1-Acetylbenzimidazole (9b)	35	C-2	70—90	7, 14, 21
	100	C-7a		
	20	C-7		
1-Acetylbenzotriazole (10b)	100	C-7a [b]	90	22
	0	C-7 [b]		
2-Acetylindazole (12b)	75	C-3	0	6, 19, 20
1-Acetyltetrazole	0 [c]	C-5	3 [d]	12

[a] The shifts and shift differences are given in Table 1. [b] The shift difference exceeds the range obtaining for the fixed conformer of acetyl-pyrrole or -carbazole. [c] The difference between the C-5 shifts of 1-methyl- and 1-acetyl-tetrazole is 4.2 p.p.m.[23] [d] H-5 of 1-methyl- and 1-acetyl-tetrazole resonates at δ 8.51 and 9.34 ($CDCl_3$, values extrapolated to infinite solution). The difference corresponds to the presence of 97% of the *E*-form.[12]

TABLE 7

Distribution between *N*-isomers of some azoles and benzazoles under conditions of equilibrium [a]

Azole	Isomer	N–H (tautomer)	N–CHROH	$N–C(Me)_2OH$ (acetone; −80 °C)	$N–COCH_3$	$N–SiMe_3$
v-Triazole (4)	1,2,3-	50,[2] 15 [24]		45 [2,25]	20 [12]	
s-Triazole (5)	1,2,4-	100 [2,26]		100 [2,25]	100 [12]	100 [27]
Tetrazole	1,2,3,4-	80—90 [1,2,26]	100 [b]	85 [2,25]	95 [d]	100 [27]
Indazole (8)	N-1	100 [11,26]	100 [c] [20]	100 [28]	100 [6]	100 [29]
Benzotriazole (10)	N-1	100 [30]	100 [c] [31]	100 [28]	100 [22]	100 [29]

[a] Temperature 27 °C, unless otherwise stated. [b] R = Pr^i. [c] R = H. [d] Previously only the 1,2,3,4-isomer has been observed.[32] In $CDCl_3$ however, a ^1H n.m.r. signal at δ 8.92 indicates the presence of 5% of the 1,2,3,5-isomer in addition to the 1,2,3,4-isomer which resonates at δ 9.34.[33]

The shift differences for the acetyl-azoles and -benzazoles frequently exceed the range obtaining for the fixed conformers of acetyl-pyrrole or -carbazole. The results based on different carbon shift differences in a certain acetyl compound disagree in some cases [(8b)—(*10*b)]. In several cases, concordance with results obtained by other methods (Table 6) is not observed.

So far, therefore, ^{13}C n.m.r. chemical shifts give no reliable information about conformer distribution in *N*-acetyl-azoles or -benzazoles.

General Conclusion on N-*Isomerism in Azoles*.—The ^{13}C n.m.r. data allow unambiguous distinction between isomeric *N*-alkyl- or acyl-azoles (Tables 1—4). A combination of the present results with literature data dealing with the distribution between *N*-substituted isomers of azoles under conditions of equilibrium (Table 7) reveals

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that the composition of the equilibrium mixture is independent of the nature of the *N*-substituent in the absence of steric effects. This rule most likely obtains for other heterocycles (*e.g.* purines) and for other *N*-substituents (*e.g.* cyano).

EXPERIMENTAL

Compounds (1a), (3a), and (7a) are commercially available. The remaining compounds studied were prepared according to the following references: (1b);[12,13] (2a);[1,2] (2b);[12] (3b);[12] (4a);[1,2] (4b);[12] (5a);[1,2] (5b);[12] (6a);[1,2] (6b);[12] (7b);[13] (8a);[6] (8b);[12,15] (9a);[34] (9b);[7,21] (10a);[30] (10b);[22] (11a);[35] (12a);[6] (12b);[6,19] (13a);[30] (14a; X = H);[36] (14b; X = H);[13] (14a; X = Br);[13] and (14b; X = Br).[13]

^{13}C N.m.r. spectra were recorded in the Fourier transform mode on a Bruker WH-90 instrument. The digital resolution was 1.34 for ^{1}H decoupled and 2.68 points Hz^{-1} for coupled spectra. The latter were obtained using the gated decoupling technique.[37] Selective ^{1}H decouplings were performed on a Bruker HX-270S instrument (quadrature detection) irradiating in the 270 MHz region and observing in the 67.89 MHz region.

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