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^{13}C-NMR Spectra of Phenyl-substituted Azoles: a Conformational Study

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^{13}C-NMR Spectra of a number of 1-phenyl-pyrazoles and 1-phenyl-1,2,3-triazoles have been obtained. The effects of substitution with methyl, chlorine, or bromine on δ-values and coupling constants have been measured. The chemical shifts of the benzene carbon atoms depend on the dihedral angle between the rings, a consistency obtaining also in 2-phenyl-1,2,3-triazoles, 1-, 2-, or 4-phenyl-imidazoles, 1-phenyl-pyrrole, and in 1- or 5-phenyl tetrazoles. The parameters most susceptible to changes in the dihedral angle are $\delta_{ortho-C}$ and the difference $\delta_{meta-C} - \delta_{ortho-C}$. Values for these parameters have been determined and their usefulness for conformational studies of phenyl substituted azoles demonstrated.

In unhindered phenyl-substituted azoles, azines, or benzenes the π-electrons are extensively delocalized over both rings. Steric factors, such as bulky substituents may, however, impede delocalization as a result of augmented torsional energy barriers.[1–10]

The pattern of the phenyl ring protons in the ^{1}H-NMR-spectra: multiplet in highly delocalized systems, singlets, or nearly so, in less flexible systems, has been widely used in conformational studies of biphenyls,[1] 2-phenyl-pyridines,[2] 3-phenyl-pyridazines,[3] 2-phenyl-triazines,[2] 3-phenyl-tetrazines,[2] 1-phenyl-pyrazoles,[4–8] 1-phenyl- and 2-phenyl-1,2,3-triazoles,[7,9] 1-phenyl- and 4-phenyl-1,2,4-triazoles,[7] 1-phenyl-tetrazoles,[7] and 5-phenyl-tetrazoles.[10] However, exceptions to the pattern are known. Thus, in contrast to 2-phenyl-imidazole,[11,12] 1-phenyl-imidazole, an extensively delocalized system,[11,13,14] exhibits a phenyl group singlet at δ 7.4 (*cf.* Experimental). Conversely, the phenyl group of 1-methyl-2-phenyl-imidazole with an expected higher torsional energy barrier,[12] appears as a multiplet, (see Experimental).

The marked deshielding of the *o*-protons of the phenyl groups in delocalized systems may be caused by several factors the relative weights of which are poorly understood.[1,4,5,7,8,10,15] Presumably, the anisotropy effects induced by the phenyl-substituted ring play a major role. Hence, ^{1}H-NMR-spectroscopy

is not an infallible method for conformation analysis of biaromatic systems. The high susceptibility of ^{13}C-NMR-signals to variation in electron densities of the individual carbon atoms, paired with their relatively small sensitivity to anisotropy factors,[16a,17a] renders ^{13}C-NMR-spectroscopy a potentially useful tool in studying the extent of delocalization in such systems. We have confirmed experimentally the virtues of ^{13}C-spectroscopy for this purpose and report the results from studies of a number of phenyl-substituted pyrazoles, imidazoles, 1,2,3-triazoles, and tetrazoles.

RESULTS

The proton-noise-decoupled ^{13} C-NMR-data of a series of methyl-, chloro-, and bromo-substituted phenyl-azoles are presented in Table 1.

The signals of 1-phenyl-pyrazole *1a*, 1-phenyl-3-bromo-pyrazole *1c*, 1-phenyl-4-bromo-pyrazole *2c*, and 1-phenyl-5-bromo-pyrazole *3c* were assigned through the proton-undecoupled spectra (Table 2). The signals with the largest splittings were ascribed to the heterocyclic carbon atoms.[17b] The signals which solely exhibited small couplings were assigned to quaternary carbon atoms. Thus, C-3* of *1c* and C-5 of *3c* appeared as broad doublets, and C-4 of *2c* as a triplet. In *1c*, *2c*, and *3c* it was found that $\delta_{C-3} > \delta_{C-5} > \delta_{C-4}$. Consequently, this order is assumed to be valid also in 1-phenyl-pyrazole *1a*. The signal which only exhibited multiplet fine structure due to small couplings was assigned to C-1′. The other benzene carbon atoms showed, besides large $^1J_{CH}$ couplings, smaller coupling constants; the latter were used for the assignments. This fine structure is dominated by coupling to protons in the *m*-positions due to the fact that $J_{CCCH} > J_{CCH}$ and J_{CCCCH} in benzene derivatives.[17c] Thus the signal, exhibiting triplet fine structure in the doublet branches, was attributed to C-4′, the triplet pattern arising from coupling with the two identical *m*-protons. In addition, the C-4′ signal had a lower intensity than signals corresponding to C-2′ and C-3′. The signal with doublet fine structure in its doublet branches, was attributed to C-3′, the small doublets arising from coupling to one *m*-proton. The doublet branches due to C-2′ appeared as frequently blurred triplets or quartets. The fine splitting is caused by coupling to two different *m*-protons. A representative spectrum, illustrating the identification, is shown in Fig. 1.

In the proton-noise-decoupled spectra of *1a*, *1c*, *2c*, and *3c* the intensity of the signals decreased in the order C-3′ > C-2′ > C-4′ > C-3 and C-4 > C-5 > C-1′. Carbon-atoms carrying a substituent appeared with strongly reduced intensity due to loss of Overhauser-enhancement and increase in relaxation time.[16b] The order of intensities was used to identify the signals of the methyl- and chloro-pyrazoles *1d*, *3d*, *1b*, *2b*, and *3b*. The signals of the dihalogeno- and trihalogeno-pyrazoles and of the benzyl-pyrazoles (Table 1) were identified in the same way. If the identity of a signal was considered uncertain, or if

* The heterocyclic carbon atoms are numbered according to the IUPAC nomenclature.[18] The phenyl carbon atoms are denoted with a dash. Counting starts with the substituted atom (C-1′).

Table 1. ^{13}C-NMR chemical shifts (δ ppm) of phenyl-substituted azoles.

Compound[a]	C-2	C-3	C-4	C-5	C-1′	C-2′	C-3′	C-4′	CH_2 or CH_3
1-Phenyl-pyrrole[b]	119.0	110.1			140.4	120.2	129.1	125.3	
1-Benzyl-pyrazole [30]		139.2	105.7	129.0	136.3	127.4	128.5	127.7	55.7
1-Benzyl-3-chloro-pyrazole [31]		138.9	105.1	130.9	135.3	127.7	128.6	128.0	56.3
1-Benzyl-4-chloro-pyrazole [31]		137.5	110.1	126.8	135.4	127.5	128.6	128.0	56.7
1-Benzyl-5-chloro-pyrazole [31]		139.5	104.9	128.2	135.8	127.2	128.6	127.7	52.5
1-Phenyl-pyrazole *1a* [32], [b]		140.7	107.3	126.2	140.7	118.8	129.1	126.0	
1-Phenyl-3-chloro-pyrazole *1b* [31]		141.4	106.8	128.2	139.3	118.5	129.2	126.6	
1-Phenyl-4-chloro-pyrazole *2b* [33]		139.0	112.1	124.5	139.4	118.7	129.1	126.6	
1-Phenyl-5-chloro-pyrazole *3b* [34]		140.3	106.3	126.9	138.3	124.7	128.6	128.0	
1-Phenyl-3,5-dichloro-pyrazole *5b* [35]		140.7	105.6	128.1	137.2	124.7	128.8	128.4	
1-Phenyl-3-bromo-pyrazole *1c* [31]		127.9	110.4	128.4	139.4	118.8	129.2	126.7	
1-Phenyl-4-bromo-pyrazole *2c* [36]		141.3	95.5	126.8	139.4	118.8	129.4	129.9	
1-Phenyl-5-bromo-pyrazole *3c* [31], [a]		141.1	110.2	112.5	138.5	125.4	128.7	128.2	
1-Phenyl-3,4-dibromo-pyrazole *4c* [31]		128.5	98.9	129.4	138.9	118.6	129.4	127.3	
1-Phenyl-3,5-dibromo-pyrazole *5c* [37]		128.8	112.5	114.0	138.1	125.4	128.8	128.2	
1-Phenyl-4,5-dibromo-pyrazole *6c*[31]		141.3	98.9	114.9	139.1	125.2	128.8	128.8	
1-Phenyl-3,4,5-tribromo-pyrazole *7c* [31]		128.9	101.8	116.2	138.4	125.2	129.2	129.9	
1-Phenyl-3-methyl-pyrazole *1d* [38]		153.3	107.1	127.0	139.9	118.6	129.1	126.0	13.7
1-Phenyl-5-methyl-pyrazole *3d* [39]		139.4	106.5	138.3		124.5	128.5	127.3	14.6
1-Phenyl-imidazole *8*[40]	135.0		129.9	117.8	136.7	121.0	129.4	128.0	
2-Phenyl-imidazole *9a*[c,d]	146.7		122.7	122.7	130.0	125.2	128.4	128.3	
1-Methyl-2-phenyl-imidazole *9d* [41]	147.2		127.8	121.9	130.1	128.0	128.0	128.0	34.4
4-Phenyl-imidazole *10a* [42], [d]						124.7	128.5	126.7	
1-Methyl-4-phenyl-imidazole *10a* [43]	141.7	137.4	115.5	122.2	133.6	124.3	128.1	126.2	
1-Phenyl-1,2,3-triazole *11a* [44]			134.1	121.5	136.9	120.4	129.4	128.5	
1-Phenyl-4-chloro-1,2,3-triazole *11b* [33]				118.9		120.1	129.5	128.9	
1-Phenyl-5-chloro-1,2,3-triazole *12b* [45]			131.6		134.6	124.5	129.1	129.1	
1-Phenyl-4-methyl-1,2,3-triazole *11d* [44]			143.5	119.0	136.7	120.0	129.2	128.0	
1-Phenyl-5-methyl-1,2,3-triazole *12d* [46]			132.8		135.9	124.4	129.0	129.9	
2-Phenyl-1,2,3-triazole *13a* [47]			139.4	139.4	135.2	118.7	129.3	128.9	
2-Phenyl-4-methyl-1,2,3-triazole *13d* [47]			144.9	134.6	139.6	118.3	128.8	126.6	
1-Phenyl-tetrazole *14*[e]				140.3	133.4	120.8	129.8	129.6	
1-Methyl-5-phenyl-tetrazole *15* [48]						128.1	128.8	130.8	35.0
2-Methyl-5-phenyl-tetrazole *16* [48]						126.4	128.5	129.9	39.4

[a] The compounds were prepared as described in the references given. [b] The material is commercially available. [c] ^{13}C-NMR data in benzene solution have been published previously.[49] [d] The ^{13}C-NMR spectrum was obtained in a saturated solution accumulating 10 000 scans. [e] The material was kindly supplied by Dr. C. Christoffersen, Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen, Denmark.

Table 2. ^{13}C-^{1}H NMR-coupling constants of phenyl-substituted azoles.[a]

Compound	The carbon to which the coupling takes place							
	C-2	C-3	C-4 $^{1}J_{CH}$ $^{2}J_{CCH}$ Hz $^{3}J_{CXCH}$	C-5	C-1′	C-2′	C-3′	C-4′
1-Phenyl-pyrrole	185	170				160	161	165
1-Phenyl-pyrazole *1a*		186	177	185		164	161	162
		8[b]	10; 10	7[b]				
		5		3		5	7	7
1-Phenyl-3-bromo-pyrazole *1c*			183	188		162	161	162
		11	8	9				
		1			9	6	6	7
1-Phenyl-4-bromo-pyrazole *2c*		193		194		165	161	163
		6		5				
						10	5	6
1-Phenyl-5-bromo-pyrazole *3c*		189	182			162	162	162
		6	11	6				
					3	6		
1-Phenyl-imidazole *8*	208		190	188[c]		160	162	160
			10	16				
	10; 6		10	3		6	6	6
1-Methyl-2-phenyl-imidazole *9d*			190	188		160	160	160
			10	19				
					7			
1-Phenyl-1,2,3-triazole *11a*			195	194		160		162
			11	15				
1-Phenyl-4-chloro-1,2,3-triazole *11b*				202		165	161	162
						5	7	7
1-Phenyl-5-chloro-1,2,3-triazole *12b*			201			164	162	164
					5	6; 5	4	3
2-Phenyl-1,2,3-triazole *13a*			194	194		165	161	161
			14	14				
						6	7	8
1-Phenyl-tetrazole *14*				216		162	164	
						5		

[a] All coupling constants have been obtained by first order analysis. [b] The $^{2}J_{CCH}$ coupling constants were distinguished from $^{3}J_{CCCH}$ coupling constants since the former are of the same order of magnitude as $^{2}J_{CCH}$ of the bromo-substituted pyrazoles *1c*, *2c*, and *3c*. [c] The $^{2}J_{CCH}$ coupling constants were distinguished from the $^{3}J_{CXCH}$ coupling constants since the former is of the same order of magnitude as $^{2}J_{CCH}$ of 1-methyl-2-phenyl-imidazole *9d*.

signals coincided, the identity was established by analysis of the proton-undecoupled spectra, as described above.

The ^{13}C-NMR-signals of 1-phenyl-1,2,3-triazole *11a* and of the 4-chloro- and the 5-chloro-derivatives *11b* and *12b*, respectively (Table 1), were identified analogously through the proton-undecoupled spectra (Table 2).

In the proton-noise-decoupled spectra of *11a*, *11b*, and *12b* the intensity decreased in the order C-3′ > C-2′ > C-4′ > C-4 > C-5 > C-1′. Again, carbon-atoms

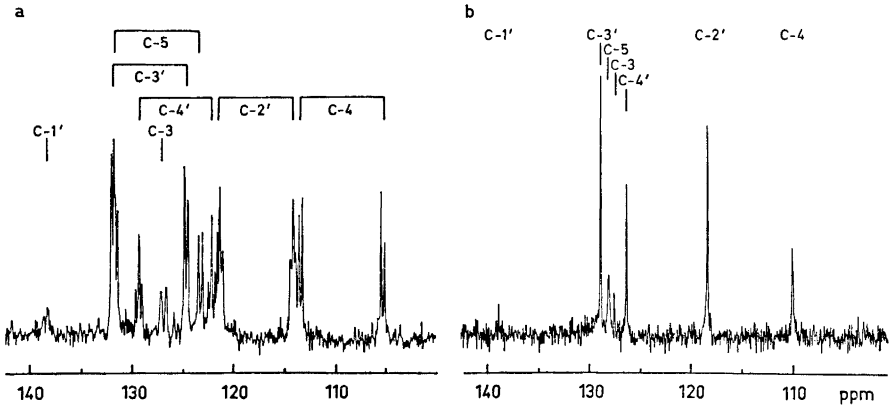
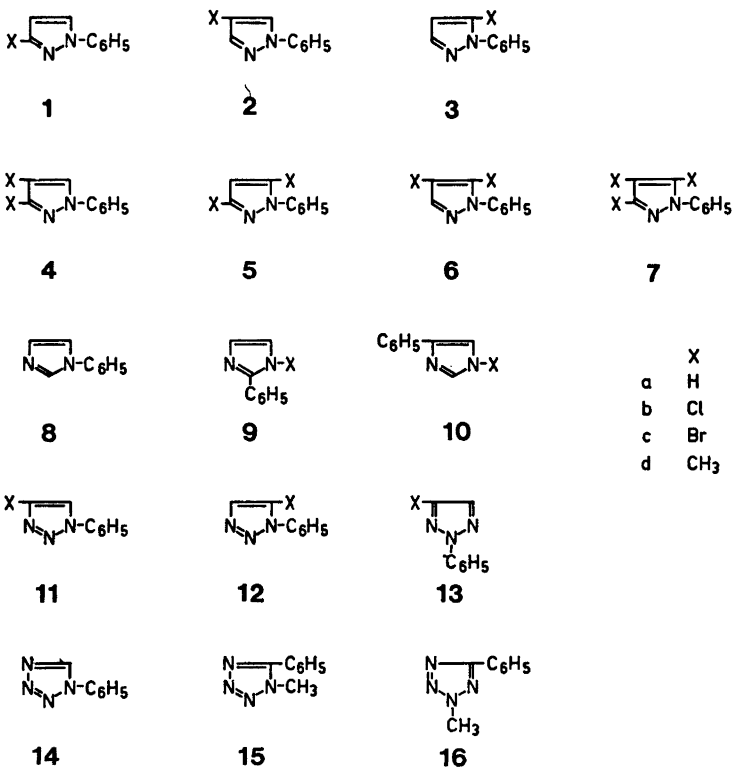


Fig. 1. ^{13}C-NMR-spectra of 1-phenyl-3-bromo-pyrazole, *1c*. *a*. Undecoupled. *b*. Proton noise-decoupled.



carrying a substituent appeared with strongly reduced intensity. The order of intensities was used to identify the signals of the methyl-1,2,3-triazoles *11c* and *12d*.

The signals of 2-phenyl-1,2,3-triazole *13a*. 1-phenyl-imidazole *8*, 1-methyl-2-phenyl-imidazole *9d*, 1-methyl-4-phenyl-imidazole *10d*, 1-phenyl-tetrazole *14*, 1-methyl-5-phenyl-tetrazole *15*, 2-methyl-5-phenyl-tetrazole *16*, and of 1-phenyl-pyrrole (Table 1) were identified analogously through their proton-undecoupled spectra (Table 2), taking account of the fact that heterocyclic carbon atoms β to nitrogen absorb at higher field than those α to nitrogen, while carbon atoms flanked by two nitrogen atoms absorb at the lowest fields.[17e] C-4 and C-5 of *8* and *9d* were assigned assuming the same order as C-3 and C-5 of 1-phenylpyrazole *1a* and 1-methyl-pyrazole,[17e] respectively. The signals of 2-phenyl- and 4-phenyl imidazole, *9a* and *10a*, were identified on the basis of their relative intensity.

A bromine atom shields the bromine-carrying pyrazole ring carbon, C-4 of the pyrazole ring is less shielded than C-3 and C-5. A methyl group deshields the substituent-carrying pyrazole ring carbon. A chlorine atom deshields the substituted carbon, chlorine at C-4 producing larger shifts than chlorine at C-3 or C-5. Carbon atoms adjacent to the substituent are influenced to a minor extent; yet, chlorine at C-3 has a rather large influence on δ_{C-5}. Contributions from more substituent on δ_{C-3} and δ_{C-4} are additive inside a maximum range of 0.8 ppm (see Table 1). Contributions from more substituents on δ_{C-5} are only approximately additive. In this case the maximum difference between δ_{C-5} observed and δ_{C-5} calculated by addition of the single contributions from the substituents is 2.2 ppm.

The effects of substituents are different from those found in benzene derivatives,[17d] here obviously depending on the position of substituents, the ring type (compare substituted 1-phenyl-pyrazoles and 1,2,3-triazoles), and finally, the nature of the nitrogen-substituent (compare the chloro-substituted 1-phenyl- and 1-benzyl-pyrazoles).

$^1J_{CH}$ of the heteroaromatic carbons are, as expected,[17b] larger the more electron attracting the surroundings are. Thus $^1J_{HC-5}$ of *14* $>$ $^1J_{HC-2}$ of *8* $>$ $^1J_{HC-4}$ and $^1J_{HC-5}$ of *11a* and $^1J_{HC-4}$ of *13a* $>$ $^1J_{HC-4}$ and $^1J_{HC-5}$ of *8* $>$ $^1J_{HC-3}$ and $^1J_{HC-5}$ of *1a* $>$ $^1J_{HC-4}$ of *1a*. $^1J_{CH}$ for carbon atoms adjacent to an imine-nitrogen atom is larger than $^1J_{CH}$ for carbon atoms adjacent to an amine-nitrogen atom. (Thus, $^1J_{HC-4} > {}^1J_{HC-5}$ in *8*, $^1J_{HC-3} > {}^1J_{HC-5}$ in *1a*, and $^1J_{HC-4} > {}^1J_{HC-5}$ in *11a*).

Bromide and chlorine increase the one bond coupling constant of the adjacent carbon atom with 5.5 – 6.5 Hz and the β-carbon atom with 3.0 – 3.7 Hz.

$^2J_{CCH}$ of the heteroaromatic carbon atoms is particularly dependent on the surroundings of the hydrogen atom. The value becomes larger the more electron withdrawing the surroundings of the hydrogen atom are. (Thus, $^2J_{HCC-4} > {}^2J_{HCC-3}$ and $^2J_{HCC-5}$ in *1a*. In addition, $^2J_{HCC-4}$ and $^2J_{HCC-5}$ of *8* and *11a* and $^2J_{HCC-4}$ in *13a* are all larger than $^2J_{HCC-3}$ and $^2J_{HCC-5}$ in *1a*. Finally, $^2J_{HCC-5} > {}^2J_{HCC-4}$ in *8* and in *11a*).

DISCUSSION

In 1-benzyl-pyrazole, C-1′ resonates at lower field than C-2′, C-3′, and C-4′ due to the electron-attracting amine nitrogen atom. The latter three carbon atoms have similar chemical shifts since they are influenced only by remote inductive effects. A chlorine atom in the heterocyclic ring of 1-benzyl-pyrazole has only a minor influence on the benzene ring carbon atoms, even when chlorine is situated at the 5-position.

In 1-phenyl-pyrazole *1a*, 1-phenyl-3-bromo-pyrazole *1c*, and 1-phenyl-4-bromo-pyrazole *2c* full interannular conjugation prevails.[4–8,11,19,20] C-2′ and C-4′ resonate at higher field than C-3′ because the lone pair of N-1 is delocalized over the *o*- and *p*-positions. C-1′ absorbs at lower field than C-3′ due to the inductive effect of the adjacent nitrogen atom. The chemical shifts of the different benzene carbon atoms vary less than 1.3 ppm in *1a*, *1c*, and *2c*. Thus bromine in the pyrazole ring shields C-1′. The shielding increases when the bromine is moved from C-4 to C-3. C-2′ is not influenced but C-3′ and C-4′ are deshielded by bromine in the pyrazole ring. The deshielding increases when the bromine is moved from C-4 to C-3.

Whereas bromine in the unhindered 3- and 4-bromo compounds *1c* and *2c* exerts little effect on the phenyl group signals, bromine in 1-phenyl-5-bromo-pyrazole *3c* causes strong low field displacements of C-2′ and C-4′. C-1′ and C-3′ are much less affected. This may be attributable to steric factors interfering with extensive interannular conjugation.[19–21]

Similar results were found for the other compounds studied. Thus, introduction of chlorine at C-3 or C-4 of 1-phenyl-pyrazole *1a* causes small variations in the position of the benzene carbon signals: C-1′ is shielded. The shielding increases when the chlorine is moved from C-4 to C-3. C-3′ is not influenced, but C-2′ is shielded and C-4′ is deshielded, the more so when chlorine is moved from C-4 to C-3.

In contrast, chlorine at C-5 causes major displacements similar to those observed when bromine is introduced at C-5.

A methyl group at C-3 of 1-phenyl-pyrazole *1a* does not influence C-3′ and C-4′ but shields C-2′ slightly. In contrast, a methyl group at C-5 again causes displacements similar to those observed with bromine in the 5-position.

The effects of the 5-substituents increase in the order Me, Cl, Br, possibly reflecting an increase in steric hindrance in that order. Inspection of the data reveal $\delta_{C-2'}$ and $\delta_{C-3'} - \delta_{C-2'}$ as the parameters most sensitive to the degree of interannular conjugation. The results indicate that if $\delta_{C-2'} \sim 118.5$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 10.5$ ppm in methyl- or chloro-substituted 1-phenyl-pyrazoles the delocalization is extensive. If, however, $\delta_{C-2'} \sim 124.6$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 4.0$ ppm delocalization is impeded as a result of higher torsional energy barrier. In bromo-substituted 1-phenylpyrazoles delocalization is extensive if $\delta_{C-2'} \sim 118.8$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 10.5$ ppm and strongly diminished if $\delta_{C-2'} \sim 125.4$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 3.3$ ppm. The values for 1-phenyl-pyrazole *1a* itself are similar to those of a unhindered bromo-substituted derivative.

N-Phenyl substituted 1,2,3-triazoles, -imidazoles, and -tetrazoles behave in the same way as the 1-phenyl-pyrazoles. Thus, introduction of chlorine at

C-4 of 1-phenyl-1,2,3-triazole *11a* causes small displacements of the ^{13}C-NMR-signals of the benzene ring. In contrast, introduction of chlorine at C-5 causes a large low field shift of C-2′ and a minor shift of C-3′ and C-4′. Similarly, introduction of a methyl group at C-4 of 1-phenyl-1,2,3-triazole *11a* or of 2-phenyl-1,2,3-triazole *13a* produces minor shifts of the benzene carbon signals. However, introduction of a methyl group at C-5 of 1-phenyl-1,2,3-triazole *11a* results in a large low field shift of C-2′ and minor shifts of C-3′ and C-4′. The effect of chlorine is larger than that of methyl as in the pyrazole series.

This indicates that interannular conjugation is extensive in methyl- or chlorine substituted 1-phenyl-1,2,3-triazoles[22] if $\delta_{C-2'} \sim 120$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 9.4$ ppm but reduced if $\delta_{C-2'} \sim 124.5$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 4.6$ ppm. In the unhindered 2-phenyl-1,2,3-triazoles *13a*[12,22] and *13d* $\delta_{C-2'} \sim 118.3$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 10.6$ ppm. In the unhindered 1-phenyl-imidazole *8*[11,13,14] $\delta_{C-2'} = 121.0$ ppm and $\delta_{C-3'} - \delta_{C-2'} = 9.4$ ppm. In the unhindered 1-phenyl-tetrazole *14* $\delta_{C-2'}$ is 120.8 ppm and $\delta_{C-3'} \sim \delta_{C-2'}$ is 9.0 ppm. In the unhindered 1-phenyl pyrrole [11,23–27] $\delta_{C-2'} = 120.2$ ppm and $\delta_{C-3'} - \delta_{C-2'} = 8.9$ ppm.

The ^{13}C-NMR chemical shifts of C-1′ and C-2′ of the unhindered *C*-phenyl substituted compounds 2-phenyl-imidazole *9a*,[11,12] 4-phenyl-imidazole *10a*.[11,12] 1-methyl-4-phenyl-imidazole *10d*, and 2-methyl-5-phenyl-tetrazole *16*[10] are different from those of the unhindered *N*-phenyl substituted azoles. Thus, C-1′ of *9a*, *10a*, *10d*, and *16* was found to be more shielded than C-1′ of the *N*-phenyl azoles in which C-1′ is deshielded by the adjacent nitrogen atom. C-2′ of *9a*, *10a*, *10d*, and *16* were deshielded compared to C-2′ of the unhindered *N*-phenyl azoles. This may be caused by the ability of *C*-phenyl groups to both accept and donate π-electrons, whereas the latter effect is far less conspicuous in π-excessive azoles.[28] However, it reduces the electron density at C-2′ (and C-4′) relative to C-3′ and, hence, $\delta_{C-3'} - \delta_{C-2'}$ as compared to the *N*-phenyl substituted azoles, where the phenyl groups act solely as π-electron acceptors.

Introduction of a methyl group in the 1-position of 2-phenyl-imidazole *9a* caused an appreciable low-field shift of C-2′ and minor shifts of C-3′ and C-4′. In fact, the signals of C-2′, C-3′, and C-4′ coincided. This clearly demonstrates that interannular conjugation has vanished in the hindered 1-methyl-2-phenyl-imidazole *9d*. Thus, conjugation is present in 2-phenyl-imidazoles if $\delta_{C-2'} \sim 125.2$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 3.2$ ppm but absent if $\delta_{C-2'} \sim 128.0$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 0$ ppm. Similarly, conjugation prevails in 4-phenyl-imidazoles if $\delta_{C-2'} \sim 124.7$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 3.8$ ppm.

Shift of a methyl group from N-2 to N-1 of 5-phenyl-tetrazole causes a low field shift of C-2′ and minor shifts of C-3′ and C-4′. The ^{13}C-NMR-data of the unhindered[10] 2-methyl-5-phenyl-tetrazole *16* and of the hindered[10] 1-methyl-5-phenyl-tetrazole *15* indicate that interannular conjugation in 5-phenyl-tetrazoles is extensive if $\delta_{C-2'} \sim 126.4$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 2.1$ ppm but impeded if $\delta_{C-2'} \sim 128.1$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 0.7$ ppm.

CONCLUSION

The results demonstrate that ^{13}C-NMR-spectroscopy is a useful tool for the study of the extent of interannular conjugation in *N*- or *C*-phenyl-azoles. The ^{13}C-NMR-spectra yield unambiguous results in contrast to the ^{1}H-NMR-spectra. The combined data indicate that interannular conjugation is extensive in simple *N*-phenyl-azoles if $\delta_{C-2'} \sim 118-121$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 9.0-10.6$ ppm but impeded if $\delta_{C-2'} \sim 124.5-125.5$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 3.3-4.6$ ppm. In simple *C*-phenyl substituted azoles interannular conjugation is extensive if $\delta_{C-2'} \sim 124.5-126.4$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 3.2-3.8$ ppm but impeded if $\delta_{C-2'} \sim 128-128.5$ ppm and $\delta_{C-3'} - \delta_{C-2'} \sim 0-0.7$ ppm.

So far, only a limited number of compounds have been studied, including very few *C*-phenyl-azoles. Supplementary data will undoubtedly extend the intervals given above. However, when the origin of these differences is taken into account, the differences between the values for unhindered and hindered cases are so large that overlap of the intervals seems unlikely. Thus, application of the ^{13}C-NMR method for assessing the extent of interannular conjugation in phenyl-azoles may most likely be useful in analogous cases.

Considering the origin of the different intervals observed, it seems likely that the ^{13}C-NMR method may be put to good use for conformational studies of phenyl-substituted azines and benzenes, as well as of phenyl-substituted, nonaromatic heterocyclic rings.

EXPERIMENTAL

^{1}H-NMR-spectra were obtained on a Varian A-60 instrument using deuteriochloroform as the solvent. Position of signals are given in ppm (δ-values) relative to tetramethylsilane.

All ^{13}C-NMR-spectra were obtained in deuteriochloroform solution. The compound (0.695 mmol) was dissolved in 1.20 ml of solvent. Position of signals were measured relative to the center peak of the deuteriochloroform triplet (δ 76.9 ppm [16c]) and are given in ppm (δ-values) relative to tetramethylsilane. The spectra were obtained on a BRUKER WH-90 instrument using Fast Fourier Transform pulse technique. Unless otherwise stated, 1000 scans were accumulated with 6000 Hz sweep using 8K computer memory. This corresponds to an accuracy of $\pm$ 0.07 ppm in the chemical shifts and of $\pm$ 3 Hz in the coupling constants. The repetition time was 3.0 sec. The decoupled spectra were obtained using proton-noise-decoupling. The undecoupled spectra were measured by the gated decoupling technique [29] in order to maintain part of the Overhauser enhancement of the signals. Thus, the proton-noise-decoupling was interrupted after 1.0 sec. After delay of 0.4 sec, the pulse (4 μsec) was turned on again. This cycle was repeated every 3.0 sec, 6000 scans being accumulated.

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