Tetrahedron. Vol. 30, pp. 3045 to 3051. Pergamon Press 1974. Printed in Great Britain

A NUCLEAR MAGNETIC RESONANCE STUDY OF HINDERED ROTATION IN 8-PHENYLPURINES

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(*Received in the UK* 3 *October* 1973; *Accepted for publication* 5 *November* 1973)

Abstract—In the PMR spectrum of 8-phenylpurines, the multiplet of the o-protons appears downfield of the multiplet, characteristic for m,p-protons. The separation of the centres of these two signals (Δ-value) diminishes with increasing steric interference between the phenyl ring and substituents in the imidazole moiety. The contribution of the purine ring current to the chemical shifts of the aromatic protons was calculated according to the theory of Johnson and Bovey, and the torsion angles θ between the phenyl ring and the plane of the purine system were derived. For 8-phenylpurines with an NH-group in the imidazole ring, θ is 10–15°; for compounds with an N-methyl group in this ring, $\theta \sim 35$–45°; in 3,9-dimethyl derivatives, Δ becomes zero, while θ is about 50°.

In a recent study on the alkylation of 8-phenylpurines,[1] it was noted that methyl substituents in the imidazole ring cause a marked *hypsochromic* shift of λ_{max}. This behavior is in contrast with that of purines with a free 8-position, where introduction of a 7- or 9-methyl substituent causes, in general, slight bathochromic displacements of λ_{max} (the absorption maxima of hypoxanthine, its 9-methyl and its 1,7-dimethyl derivatives are 249, 250 and 255 nm, respectively[2] while the corresponding values in the 8-phenyl series are 286, 271 and 275 nm[1]). This was interpreted in terms of steric hindrance, preventing coplanarity of the phenyl ring with the purine system. In the present investigation we shall show that PMR measurements support this assumption and can give certain quantitative information about the degree of interference.

We have studied four series **a**–**d** of 8-phenylpurines (Table 1). With the exception of **9c** and **d**, the signals of the five phenyl protons are separated into two groups, the one integrating for two protons appearing downfield relative to the second group, integrating for three protons (Fig 1). The multiplet at higher field may represent the combination of the p-proton signal with either the two o- or m-protons. Calculations of the chemical shifts of the phenyl protons due to ring current (see below) show that the latter assignment is correct.

Similar conclusions were reached by Lynch and Hung[3] and by Tensmeyer and Ainsworth[4] for the PMR spectra of N- and C-phenyl substituted pyrazoles.

In the following discussion, Δ designates the difference between the centre of the multiplets representing the o- and m,p-protons.

The data in Table 1 and the summary in Table 2 for PMR measurements on neutral molecules lead to the following generalisations: (1) In 8-phenylpurines, bearing an NH-group in the imidazole ring, Δ is 0·76 ± 0·05 ppm (class B in Table 2). (2) Alkylation at N-1 or N-3, which changes the "aromatic" structure of 8-phenylpurine **1a** into a "quinoid" form and thus eliminates the NH-group in the imidazole moiety, e.g. **2a** (Fig 2),

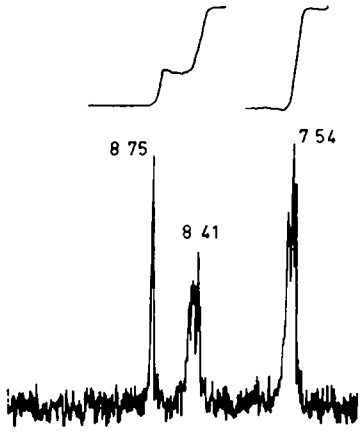
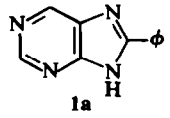
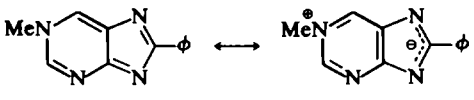


Fig 1. PMR spectrum of 3-methyl-6-methylthio-8-phenylpurine (**3b**) in d_6-DMSO-D_2O = 9:1, at 70°. Note the 2H-signal at 8·75 ppm, the center of the multiplet for the two o-hydrogens at 8·41 and of the multiplet for the three m,p-hydrogens at 7·54, i.e. Δ = 0·87.



1a



2a

Fig 2.

Table 1. Signals of o- and m,p-protons in the NMR spectrum of 8-phenylpurines

Compound	N-Methyl groups at positions	Series a 8-phenylpurines			Series b 6-methylthio-8-phenylpurines			Series c 8-phenylhypoxanthines			Series d 8-phenyl-6-thiopurines		
		o	m + p	Δ[a]	o	m + p	Δ	o	m + p	Δ	o	m + p	Δ
1	—	8·30–8·44	7·50–7·68	0·75	8·20–8·33	7·50–7·60	0·72	8·24–8·35	7·54–7·61	0·72	8·27–8·35	7·50–7·56	0·78
2	1	8·41–8·57	7·53–7·65	0·90	8·36–8·47	7·51–7·58	0·87	8·29–8·39	7·49–7·57	0·81	8·34–8·40	7·57–7·64	0·76
3	3	8·42–8·58	7·60–7·70	0·85	8·35–8·46	7·51–7·60	0·85	8·27–8·37	7·54–7·61	0·74	8·25–8·37	7·45–7·54	0·80
4	7	—	—		7·81–7·93	7·64–7·74	0·18	—	—		7·85–7·94	7·65–7·71	0·22
5	9	7·97–8·15	7·68–7·80	0·31	7·87–8·02	7·66–7·73	0·24	7·97–8·04	7·70–7·78	0·26	7·94–8·03	7·66–7·73	0·29
6	1,7							7·97–8·07	7·77–7·85	0·21	7·91–8·01	7·72–7·79	0·20
7	1,9							7·98–8·09	7·74–7·81	0·26	7·99–8·08	7·72–7·79	0·28
8	3,7							—	—		7·93–8·03	7·72–7·79	0·22
9	3,9							7·96		0	7·94		0
10	1,3							8·28–8·40	7·49–7·58	0·80	—	—	

[a] Δ = difference between centre of o- and m,p-multiplets.

Table 2. Centre values of the Multiplets of o- and m,p-proton signals in the Neutral Molecules of 8-phenylpurines

Class	δ(ppm) of centre of o-hydrogens	δ(ppm) of centre of m,p-hydrogens	Δ
A[a]	8·45	7·58	0·87 ± 0·03
B[b]	8·32	7·56	0·76 ± 0·05[f]
C[c]	8·01	7·73	0·28 ± 0·04
D[d]	7·95	7·74	0·21 ± 0·02
E[e]	7·95	7·95	0

[a] Class A comprises all 1- and 3-methyl-derivatives of 8-phenylpurine and 6-methylthio-8-phenylpurine: **2a,b**; **3a,b**.

[b] Class B comprises all 8-phenylpurines with an aromatic pyrimidine ring and an NH-group in the imidazole moiety: **1a-d**; **2c,d**; **3c,d**.

[c] Class C consists of all 9-methyl derivatives: **5a-d**; **7c,d**.

[d] Class D comprises all 7-methyl derivatives: **4b,d**; **6c,d**; **8d**.

[e] Class E consists of the 3,9-dimethyl derivatives **9c** and **9d**.

[f] The zwitterion **10c** exhibits a centre of the o-protons at 8·34 ppm and of the m,p-protons at 7·54 ppm; Δ = 0·80.

increases the Δ-value to about 0·87, due to a downfield shift of the o-hydrogen signals, the m,p-multiplet remaining practically unchanged (class A in Table 2). (3) The Δ-value is drastically reduced by introduction of methyl substituents into the imidazole ring, the 7-methyl group (class D, Δ ~ 0·21 ppm) being more effective than a 9-methyl substituent (class C, Δ ~ 0·28 ppm). (4) In the 3,9-dimethyl derivatives **9c** and **d** (class E), the signals of all five aromatic protons are contracted into a rather narrow singlet (half-width about 2 Hz).

These changes in the Δ-values will first be interpreted on the basis of steric interference. The smallest influence in free rotation of the phenyl group is to be expected when the imidazole bears no substituent at all, as in the members of class A. Here, deshielding of the o-hydrogens is maximal and Δ reaches its highest value (0·85 to 0·90, see Tables 1 and 2). Introduction of an NH-group into the imidazole ring (class B: **1a–d**, **2c,d** and **3c,d**) causes an upfield shift of the signals of the o-protons, while the centres of the m,p-multiplets remain practically unchanged; thus the Δ-value is lowered to 0·76.

In class C and D, the centre of the o-signals is shifted upfield by ~ 0·34 ppm, while that of the m,p-protons is displaced downfield by ~ 0·18 ppm, relative to the corresponding values in class A and B. These changes are ascribed to the fact that coplanarity of the 8-phenyl substituent is prevented by a 7- or 9-methyl group.

Finally when passing from classes C and D to E, the o-hydrogen signal is not changed measurably, while the centre of the m,p-band has shifted downfield by about 0·2 ppm, so that a singlet results.

All aromatic protons in 8-phenylpurines are deshielded relative to benzene (δ = 7·2 ppm), but to a different degree. This expresses the influence of the purine ring current, which decreases with greater distance of a proton from C-8. Similar conclusions have been drawn by Tensmeyer and Ainsworth[4] for phenylpyrazoles. Thus in 3-phenylpyrazoles, which are comparable to the present class B, the multiplet of the o-hydrogens centres at 7·73 and that of the m,p-protons at 7·37 ppm. When a methyl substituent is introduced α to the phenyl group, the resonance of all five aromatic protons becomes a singlet, δ ~ 7·42 ppm. Thus in the phenylpyrazole series, conditions for coplanarity are more stringent than in 8-phenylpurines.

In general, ring current influences o- and m,p-protons in the same direction. However, transition from classes A,B to C,D causes opposite shifts—the o-proton signals undergo an upfield shift, while the m,p-multiplets move to lower field. This shows that additional factors are involved (see below).

We have attempted to calculate the contribution of ring current to the chemical shifts of the aromatic protons, as function of the torsion angle θ between the plane of the purine system and that of the benzene ring, according to the semiclassical theory of Johnson and Bovey,[5] as presented by Mallion.[6] This approach is preferable to that of McWeeny[7] in predicting the relative position of the aromatic proton signals.

In a polycyclic system, let J_i be the strength of the ring current in ring i. Calculation of J_i will be discussed below. If we assume that each ring contributes additively to the shielding of a proton, placed at distance r_i from its centre,[8] then these contributions are given by Eq (1) where Δσ = shielding:

$$\Delta\sigma = \frac{ne^2}{6\pi mc^2 a} \sum_i J_i K(r_i). \qquad (1)$$

Here n = number of electrons circulating in a loop of radius at a distance p (see Eq 2), above and below ring i. The value of Johnson and Bovey[5] for benzene (p = 0·46) was used in all our calculations; m = mass of the electron and e = its charge; c = velocity of light. $K(r_i)$ is a geometric factor, reflecting the effect of the current in ring i on the secondary field at the proton, characterised by its cylindrical coordinates ρ and z with respect to the center of ring i, as shown in Eq (2).

$$K(r_i) = \frac{1}{[(1+\rho_i)^2 + (z_i - p)^2]^{1/2}} K(k_-) + \frac{1-\rho_i^2-(z_i-p)^2}{(1-\rho_i)^2+(z_i-p)^2} E(k_-) + \frac{1}{[(1+\rho_i)^2+(z_i+p)^2]^{1/2}} K(k_+) + \frac{1-\rho_i^2-(z_i+p)^2}{(1-\rho_i)^2+(z_i+p)^2} E(k_+) \qquad (2)$$

where K and E are the complete elliptic integrals with modulus k_- and k_+:

$$k_- = \left(\frac{4\rho}{(1+\rho)^2+(z-p)^2}\right)^{1/2} \quad (3a)$$

$$k_+ = \left(\frac{4\rho}{(1+\rho)^2+(z+p)^2}\right)^{1/2}. \quad (3b)$$

The intensities J_i of the ring currents were calculated according to McWeeny,[7] using the program elaborated by Figeys and Dedieu.[9] The latter authors employed self-consistent iterative functions for the different resonance integrals, introducing the special characters of the bonds by bond order-bond length relations. They presented functions for a variety of C—C, C—O and C—N linkages, but not for C—S bonds, needed for some of the purines in Table 1. We have therefore utilised Häfelinger's[10] values for the resonance integrals and the bond order-bond length relations for C—S bonds (in series b) and C=S linkages (in series d of Table 1). We have thus obtained the following iterative functions for these links:[11]

$$\beta_{C-S} = 0{\cdot}405 + 0{\cdot}077P_{C-S} \quad (4a)$$

$$\beta_{C=S} = 0{\cdot}517 + 0{\cdot}063P_{C=S} \quad (4b)$$

where P = bond order.

Initial parameters for all other bonds, involved in the present calculations, were taken from Pullman and Pullman.[12]

For calculation of the geometrical factors $K(r_i)$, we accepted the Watson geometry for the purine system,[13] assuming a length of d = 1·52 A for the C(8)-phenyl bond.[14] When this link is shortened by partial double bond character, deshielding of all hydrogens due to the magnetic anisotropy of the purine ring current may become more powerful. Therefore the influence of the length of this bond on the proton signals in the benzene ring was calculated. However, even when this bond is shortened from 1·52 to 1·40 A (the length of the C—C bond in benzene), the maximal increase in Δ is 0·05 ppm. Thus a partial double bond at C(8)-phenyl which would produce a bond length between the above two limits, can make only a minor contribution to the Δ-values.

With the help of Eqs (1) and (2), the shielding effect of the ring current on o-, m- and p-hydrogens was calculated. The results clearly showed stronger shielding of the m- and p- than of the o-protons; e.g. for **1b** we find $\delta_{o\text{-}H} = 8{\cdot}43$; $\delta_{m\text{-}H} = 7{\cdot}8$; $\delta_{p\text{-}H} = 7{\cdot}76$ ppm, as compared to the centre values in Table 1, $\delta_{o\text{-}H} = 8{\cdot}42$; $\delta_{m,p} = 7{\cdot}55$ ppm. Thus these calculations support the assignments in Table 1.

The data obtained by our calculations are collected in Table 3. The J_i-values for the phenyl group are included, although the contribution of its ring current to the Δ-values cancels out. It should be noted that the J_i-values for the pyrimidine ring are higher than those for the imidazole moiety in all 8-phenylpurines lacking a substituent at position 6 (series a in Table 1). This is also true for the 7-methyl derivative **4a** (which was not available): J_i (imidazole) 9·52; J_i (pyrimidine) 11·46. The reverse relation is characteristic for all derivatives bearing 6-substituents (series b-d), the only exception being 9-methyl-6-methylthio-8-phenylpurine **5b** (see Table 3).

It is evident that ring current accounts only in part for the Δ-values in Table 2. Therefore the influence of a possible additional factor was studied.

The chemical shift of an aromatic proton reflects the π-electron charge on the carbon atom, to which it is bound.[15] In order to calculate the Δ-values to be expected from this source, we have used Schug's[16] equation as follows:

$$\Delta = 6{\cdot}63(q_{meta} - q_{ortho}) + 1{\cdot}686 \sum_{meta\ \nu} (q_\nu - 1) - \sum_{ortho\ \nu} (q_\nu - 1). \quad (5)$$

Here q is the charge of the carbon atom under consideration; summation in the second term is carried out over all nearest neighbours ν. These calculations led to Δ-values of ~0·015; they cannot account for the absolute Δ-values found or for the changes of Δ as function of substitution in the imidazole ring.

We are thus left with ring current as the most important factor. We have attempted to establish better correlation between calculated and observed quantities by scaling (equation 6):

$$\Delta_{obs} = k\Delta_{calcd}. \quad (6)$$

For members of class A, for which we assume the torsion angle $\theta = 0$, the correlation parameter k is 1·53 ± 0·12 (see Table 3). The values of $\Delta_{obs/k}$ for the other classes are listed in column 4 of the Table. From these data, the corresponding torsion angles can be derived by comparison with the Δ-values calculated as function of θ (the cylindrical coordinates in Eq 2 are dependent on θ) (column 5). When d = 1·52 A, Δ becomes 0·01 ppm for $\theta = 50°$, i.e. this torsion angle is sufficient to eliminate any difference in the chemical shifts of o- and m,p-protons, as observed for **9c** and **9d**.* In class E, the 9-methyl substituent produces greater steric interference than in the corresponding 9-methyl derivatives **5c** and **5d**. This is in accordance with earlier conclusions, based on the marked downfield shift of both the 3- and 9-methyl signal in these purines.[17,18] The results of Table 3 show θ = about 10–15° for class B, 30–35° for class C and 35–40° for class D.

*If d = 1·40 A, the "limiting" value of θ is 60°.

Table 3. Ring current intensities J_i, Δ-values and torsion angles θ in 8-phenylpurines

1. Class A—Torsion angle $\theta = 0$

Compound	$J_i(\times 10^{-2})$ Imidazole	Pyrimidine	Phenyl	Δ_{obs}	r = 1·52 A Δ_{calcd}	k	r = 1·40 A Δ_{calcd}	k
2a	9·73	11·05	10·48	0·90	0·62	1·45	0·67	1·34
3a	9·60	11·08	10·46	0·85	0·615	1·38	0·66	1·29
2b	8·98	7·86	10·37	0·87	0·54	1·61	0·59	1·47
3b	8·17	7·97	10·29	0·85	0·50	1·70	0·54	1·57
						Av. 1·535		Av. 1·42

2. Calculation of torsion angles θ for classes B-E

Compound	$J_i(\times 10^{-2})$ Imidazole	Pyrimidine	Phenyl	Δ_{obs}	r = 1·52 A Δ_{calcd}	$\Delta_{obs/k}$	θ (degrees)	r = 1·40 A Δ_{calcd}	$\Delta_{obs/k}$	θ (degrees)
Class B										
1a	9·83	11·61	10·51	0·75	0·63	0·49	15–20	0·68	0·52	15–20
1b	9·20	8·82	10·39	0·72	0·57	0·47	10–15	0·61	0·47	15–20
1c	9·50	8·79	10·49	0·72	0·58	0·47	10–15	0·63	0·50	15–20
1d	9·08	8·30	10·41	0·78	0·55	0·51	10	0·60	0·54	10–15
2c	9·36	8·43	10·45	0·81	0·57	0·53	5–10	0·62	0·56	10–15
2d	9·01	8·05	10·38	0·76	0·55	0·50	10	0·59	0·53	10–15
3c	9·28	8·58	10·44	0·74	0·57	0·48	10–15	0·61	0·51	15–20
3d	8·91	8·07	10·36	0·80	0·54	0·52	0–5	0·59	0·55	5–10
							Av. 10·6			Av. 14·4
Class C										
5a	9·45	11·40	10·48	0·31	0·61	0·20	30–35	0·66	0·22	35–40
5b	7·68	8·56	10·29	0·24	0·48	0·16	30–35	0·53	0·17	35–40
5c	9·16	8·55	10·44	0·26	0·55	0·17	30–35	0·61	0·18	35–40
5d	8·79	8·02	10·36	0·29	0·54	0·19	30–35	0·58	0·20	35–40
7c	9·06	8·33	10·44	0·21	0·55	0·14	35–40	0·60	0·15	40–45
7d	9·04	7·82	10·39	0·28	0·54	0·18	30–35	0·59	0·19	35–40
							Av. 33·3			Av. 38·3
Class D										
4b	9·03	8·82	10·41	0·18	0·56	0·12	35–40	0·60	0·13	40–45
4d	8·77	8·17	10·38	0·22	0·53	0·14	35	0·58	0·15	40–45
6c	9·21	8·45	10·48	0·26	0·56	0·17	30–35	0·61	0·18	35–40
6d	8·86	8·03	10·40	0·20	0·54	0·13	35	0·59	0·14	40–45
8d	8·79	8·08	10·29	0·22	0·54	0·14	35	0·59	0·15	40–45
							Av. 35			Av. 41·5
Class										
9c	8·75	8·15	10·42	0	0·53	0	50	0·58	0	58–59
9d	8·64	7·98	10·35	0	0·53	0	50	0·57	0	58–59

EXPERIMENTAL

PMR spectra were measured with a Jeol MH-100 instrument, in d_6-DMSO-D_2O = 9:1, v/v, at 70°C. TSP (= sodium 3-trimethylsilylpropionate-2,2,3,3-d_4 of Merck, Sharp and Dohme, Canada) served as internal standard.

Solvents for paper chromatography (descending method): A—acidic solvent-n-butanol–acetic acid–water = 12:3:5, v/v, B—basic solvent-2-propanol–DMF–25% ammonia = 13:5:2, v/v, C—neutral solvent—95% ethanol–DMF–water = 3:1:1, v/v. Spots were located by their fluorescence at $\lambda \sim 255$ nm

Materials. The following compounds were prepared according to known methods: **1a, 1b** and **3c**;[19] **1c**;[20] **1d, 3b** and **3d**;[21] **2b, 2d, 4b, 4d, 5b-d, 6c-d, 7c-d, 8d, 9c** and **9d**;[1] **2c** and **10c**.[22]

New purines

2a, 3a and **5a** were synthesised as follows:

Method A. A solution of the 6-thio derivatives (**2d, 3d** or **5d**) (3 g) in DMF (100 ml) was stirred with thoroughly washed, neutralised, Raney nickel and heated to 95° for 90 min. The catalyst was filtered off and the filtrate brought to dryness *in vacuo*. Crystallisation of the dethiation products is described in Table 4.

Method B. (For synthesis of **2a** only). A solution of 8-phenylpurine[5] (2 g) in acetonitrile (70 ml) and DMF (20 ml) was refluxed with methyl iodide (10 ml) for 90 min. The volatile components were removed *in vacuo* and the residue dissolved in a small volume of water. The free base of **2a** was precipitated by addition of sodium bicarbonate. For purification of **2a** see Table 4.

Table 4. Physical properties and analyses of new derivatives of 8-phenylpurine

No.	Methyl substituent at position	Method used[a]	Yield %	m.p. °C	Solvent for crystallisation	Crystal form and color	R_f in solvent[b] A	B	C	λ_{max} (nm)[c] at pH 1	8
2a	1	A	40	282–284	water	colorless needles	0·73	0·73	0·69	238(4·13)	243(4·26)
		B	93	(dec)						308(4·40)	308(4·34)
3a[d]	3	A	30	227 (dec)	ethanol	pale yellow needles	0·77	0·76	0·70	233(4·05) 318(4·46)	232(4·06) 316(4·42)
5a	9	A	50	168–169	ethyl acetate	colorless needles	0·80	0·65	0·75	238(4·16) 289(4·17)	228(4·05) 281(4·26)

Analyses. Calcd. for $C_{12}H_{10}N_4$: C, 68·6; H, 4·8; N, 26·7%

No.	Found % C	H	N
2a	68·2	4·8	26·2
3a	68·7	4·8	26·2
5a	68·5	5·0	26·6

[a] For methods see Experimental.
[b] For solvents, see Experimental.
[c] Figures in brackets indicate log ϵ_{max}.
[d] This purine has been previously isolated only as picrate (Ref 19).

Calculations were performed on a CDC 6400 computer, employing Tables of complete elliptic integrals.[23] The program of Figeys and Dedieu,[9] written in FORTRAN IV, was used.

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