The molecular structure of 4-*tert*-butylpyrazoles in the solid state and in solution: an X-ray, NMR and calorimetric study of the buttressing effect of a 4-*tert*-butyl substituent

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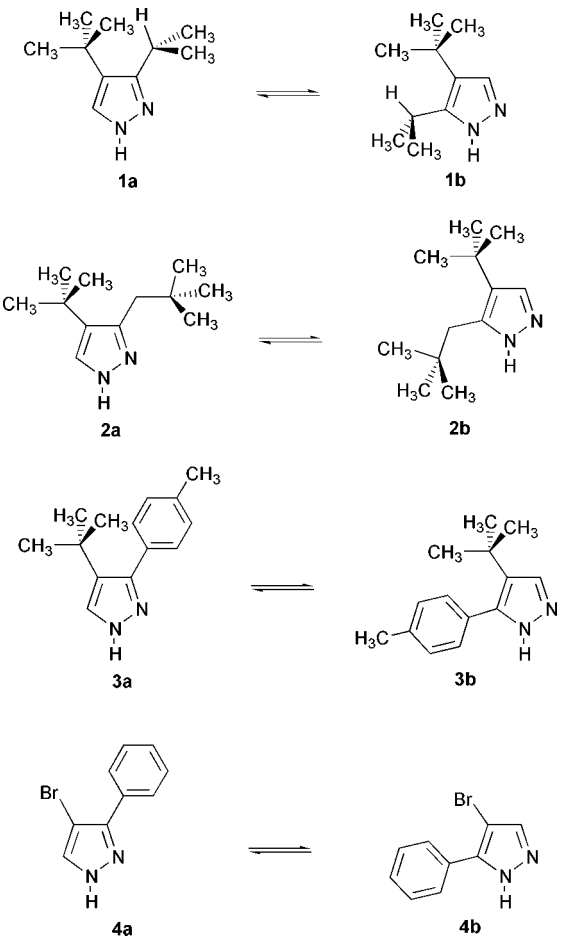
The molecular structures of three 4-*tert*-butylpyrazoles have been determined at 173 K: 4-*tert*-butyl-3(5)-isopropylpyrazole **1**, 4-*tert*-butyl-3(5)-neopentylpyrazole **2** and 4-*tert*-butyl-3(5)-*p*-tolylpyrazole **3**. ^{1}H, ^{13}C and ^{15}N NMR spectroscopies, in solution and in the solid state (CPMAS), have been used to complement the structural information. The major tautomers in solution correspond to the tautomers present in the crystal: 5-isopropyl **1b**, 5-neopentyl **2b** and 3-*p*-tolyl **3a**. All these compounds crystallise as tetramers, formed by four identical tautomers, through N–H···N hydrogen bonds, the tetramers corresponding to **1b** and **2b** being folded but that of **3a** is the first example of a planar tetramer.

We have been, and still are, interested in the behaviour in the solid crystalline state of 1*H*-pyrazoles unsubstituted on the nitrogen, sometimes called *N*H-pyrazoles. Two properties of these compounds mainly interest us, the annular tautomerism, *i.e.* which nitrogen atom bears the proton, and the pattern formed by the N–H···H hydrogen bonds present in these compounds. Therefore, we decided to extend these studies to three pyrazoles **1**–**3** (Scheme 1) having in common the presence of a *tert*-butyl substituent at position 4 of the pyrazole ring.

We have found that, concerning tautomerism, alkyl groups clearly prefer position 5 (tautomer **b**) while aryl groups seem to prefer position 3 (tautomer **a**).[1,2] Concerning the network formed by the hydrogen bonds (secondary structure),[2] the substituent at position 4 plays a minor role by pushing away the adjacent substituents (buttressing effect). The presence at position 3(5) of a *tert*-butyl group with position 5 unoccupied leads to the formation of dimers or tetramers (our model does not distinguish these two situations) as opposed to trimers or catemers (chains). Since isopropyl and neopentyl groups can be considered similar to *tert*-butyl groups, especially if one takes into account the buttressing effect, we predict for **1** and **2** the formation of tetramers of type $[\mathbf{1b}]_4$ and $[\mathbf{2b}]_4$.

In the case of 3(5)-arylpyrazoles, our model predicts the formation of trimers or catemers, without considering that the buttressing effect can increase the apparent steric demand of the 3(5)-substituent. For instance, 4-bromo-3(5)-phenylpyrazole **4** crystallise in trimers formed by the 3-phenyl tautomer $[\mathbf{4a}]_3$.[3]

One of the open problems is how to transform this qualitative model into a quantitative one. The property of the substituent that better relates to the model is the Molar Refractivity (*MR*).[4] When the *MR* value is 2.4 or higher the compound should crystallise in dimers or tetramers and when lower than 2.4 it would form trimers or catemers.[2] The phenyl group has $MR = 2.54$, therefore compound **4** should have



Scheme 1

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Table 1 Crystallographic data of: 4-*tert*-butyl-3(5)-isopropylpyrazole **1**, 4-*tert*-butyl-3(5)-neopentylpyrazole **2** and 4-*tert*-butyl-3(5)-*p*-tolylpyrazole **3**

	1	**2**	**3**
Empirical formula	$C_{10}H_{18}N_2$	$C_{12}H_{22}N_2$	$C_{14}H_{18}N_2$
Formula weight	166.26	194.32	214.30
Space group	$C2/c$	$I4_1/a$	$P\bar{1}$
a/Å	12.7395(4)	18.9969(10)	11.7417(2)
b/Å	28.0431(7)	18.9969(10)	15.7638(2)
c/Å	12.2071(3)	13.3498(10)	16.3452(2)
α/°			61.8921(3)
β/°	98.0824(19)	90	88.7569(8)
γ/°			78.1825(9)
V/Å^3	4317.7(3)	4817.7(11)	2602.20(7)
Z	16	16	8
T/K	173(2)	173(2)	173(2)
μ(Mo-Kα)/cm^{-1}	0.61	0.63	0.65
$R(F)$ (%)	6.85	6.09	6.46
$R(wF^2)$ (%)	13.08	11.23	16.78

crystallised in dimers or tetramers, but its MR value is very close to the borderline. The *p*-tolyl group has $MR = 3.00$ and, consequently, the compound should form dimers or tetramers. The MR values for isopropyl and neopentyl substituents are, respectively, 1.50 and 2.42. Therefore, and ignoring the buttressing effect, **1b** should crystallise in trimers or catemers while **2b** should be on the borderline. To solve these problems and to advance in the quantification of the model, we have undertaken a study of compounds **1**–**3**.

We would like to stress that these pyrazoles are intended to be used to prepare novel homoscorpionate (trispyrazolylborate) ligands. It is expected that the free rotation of the 3-R substituents would be curtailed by the 4-*tert*-butyl group, leading to the presence of one favoured rotamer, disposed in such manner as to minimise its non-bonding interaction with the 4-*tert*-butyl group.

The chosen synthetic approach involved heating the appropriate pyrazole with *tert*-butyl chloride in an autoclave at 200–220 °C, for 4–8 h. The unoptimised yields were poor, in the 10–15% range, as the reaction yielded, in addition to the desired product, also the corresponding 3R-1-*tert*-butylpyrazoles, 3R-1,4-bis(*tert*-butyl)pyrazoles and, possibly, also some quaternary salts. Still, this was a single step reaction, and the desired novel pyrazoles could be separated from the by-products, and obtained in good purity, by distillation and recrystallisation.

Experimental

All chemicals were commercial reagent grade used as received. The compounds 3(5)-isopropylpyrazole,[5] 3(5)-neopentylpyrazole[6] and 3(5)-(*para*-tolyl)pyrazole[7] were prepared according to the literature. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE.

Synthesis of 3(5)-substituted-4-*tert*-butylpyrazoles

4-*tert*-Butyl-3(5)-isopropylpyrazole 1. A mixture of 3(5)-isopropylpyrazole (159 g, 1.45 mol)[5] and *tert*-butyl chloride (210 g, 2.27 mol) was heated in an autoclave for 6 h at 220 °C. After cooling, the product mixture was stirred with an excess of ice-cold dilute sodium hydroxide solution, and the products were extracted with methylene chloride. After stripping the solvent, the residue was distilled *in vacuo*. The top cut partly solidified, and was recrystallised from heptane, yielding 22 g (13%) of product **1**, mp 126–127 °C. Calc. for $C_{10}H_{18}N_2$: C, 72.24, H, 10.91; N, 16.85. Found: C, 72.40; H, 10.99; N, 16.71%.

4-*tert*-Butyl-3(5)-neopentylpyrazole 2. A mixture of 3(5)-neopentylpyrazole (182 g, 1.31 mol)[6] and *tert*-butyl chloride (200 g, 2.15 mol) was heated in an autoclave for 8 h at 220 °C. After cooling, the product mixture was treated as above. The final cut was collected from the point when solid started appearing in the distillate, partly solidified, and it was recrystallised from hexane, yielding 25 g (10%) of product **2**, mp 128–129 °C. Calc. for $C_{12}H_{22}N_2$: C, 74.17, H, 11.41; N, 14.42. Found: C, 74.45; H, 11.39; N, 14.60%.

4-*tert*-Butyl-3(5)-*p*-tolylpyrazole 3. This compound was prepared as above, starting from 3(5)-*p*-tolylpyrazole,[7] and was obtained, after recrystallisation of the final cut, which also contained 1,4-bis(*tert*-butyl)pyrazole and starting pyrazole, from octane in 12% yield. mp 165–166 °C. Calc. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.7. Found: C, 78.48; H, 8.56; N, 13.30%.

Crystallographic structural determination

Crystal data collection and refinement parameters are given in Table 1. No evidence of symmetry higher than triclinic was observed in the diffraction data of **3**. The systematic absences in the diffraction data are uniquely consistent for the reported space group for **2** and consistent for the space groups, *Cc* and *C*2/*c* for **1**. *E*-statistics, as well as the value of Z, suggested the centrosymmetric options, *C*2/*c* and $P\bar{1}$ for **1** and **3**, respectively, which yielded chemically reasonable and computationally stable refinements. The structures were solved using direct methods, completed by subsequent Fourier difference syntheses and refined by full-matrix least-squares procedures. SADABS absorption corrections were applied to all data sets.[8] The asymmetric units of **1** and **3** contain two molecules of 4-*tert*-butyl-5-isopropylpyrazole **1b** and two molecules of 4-*tert*-butyl-3-*p*-tolylpyrazole **3a**, respectively. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms of **2** and the N–H atoms of **1** and **3** were located from difference maps and free to refine. All other hydrogen atoms were treated as idealised contributions.

The crystals used were always colourless blocks. The diffractometer used was a Siemens P4/CCD and the radiation Mo-Kα ($\lambda = 0.710\,73$ Å). All software and sources of scattering factors are contained in the SHELXTL (5.10) program library.[9]

CCDC reference numbers 163025–163027. See http://www.rsc.org/suppdata/nj/b1/b101733k/ for crystallographic data in CIF or other electronic format.

NMR measurements

^{1}H (400 MHz), ^{13}C (100 MHz) and ^{15}N NMR (40.56 MHz) spectra were obtained using a Bruker DRX 400 instrument. Variable temperature ^{1}H, ^{13}C and ^{15}N NMR experiments were recorded on the same spectrometer using CD_3OD as solvent. 2-D Inverse proton detected heteronuclear shift correlation spectra, HMBC, were obtained using the standard pulse sequence.[10] CPMAS NMR spectra have been obtained on a

Bruker AC-200 spectrometer at 298 K using a 7 mm Bruker DAB 7 probehead that achieves rotational frequencies of about 3.5–4.5 kHz. Samples (approximately 200 mg of material) were carefully packed in ZrO_2 rotors and the standard CPMAS pulse sequence was applied.[11]

Results and discussion

Molecular structures

All known *N*-unsubstituted (NH) pyrazoles crystallise in four classes as far as hydrogen bonding (HB) is concerned: catemers, dimers, trimers and tetramers, all of them similarly populated.[2,12] We have summarised in Table 2 the situations found in the four compounds, the three new ones (see Fig. 1–4) and **4**.

The tautomer present in the case of compound **1** is the 5-isopropyl **1b** and even more interesting is that it forms tetramers although the *i*Pr group has a $MR = 1.50$. To accommodate this result to our quantitative model, one has to assume that the 4-*tert*-butyl group somewhat increases the volume (MR is not a pure steric effect and also includes polarisability) of the isopropyl group.

In the case of compound **2** everything is normal, the tautomerism and the HB pattern, $[\mathbf{2b}]_4$. The buttressing effect should make the neopentyl group lose its free rotation (gear effect)[14] and the most populated rotamer would have the conformation **2b** represented in Scheme 1, which is very space demanding.

Concerning the tautomerism of compound **3** the result, **3a**, is that expected. On the one hand, the compound crystallises as a tetramer, $[\mathbf{3a}]_4$, this being consistent with the prediction of the quantitative model but, on the other hand, it is the first example of a planar tetramer. To this moment, the literature has reported eleven tetramers[2] and we have recently described a twelfth one.[11] In all these cases, the conformation of the tetramers can be represented as a "tub". Using the centroids of the four pyrazole rings, the "tub" conformation can be described by the average distance between the centroids (d_i) and the folding angle (ψ_i).[2,7] For the twelve reported compounds these parameters oscillate between $d_i = 4.91$–5.16 Å

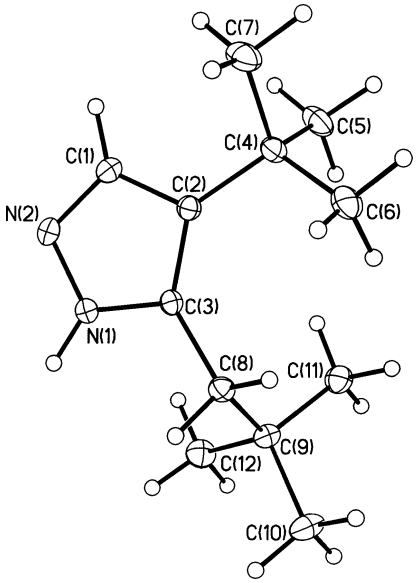

Fig. 2 An ORTEP diagram of 4-*tert*-butyl-5-neopentylpyrazole **2b** showing the labelling scheme.

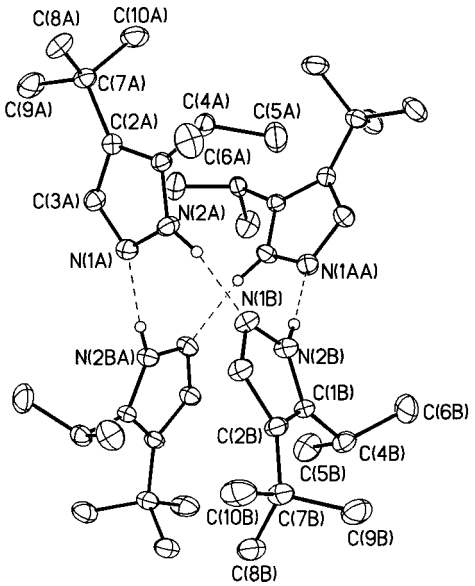

Fig. 1 An ORTEP[13] diagram of 4-*tert*-butyl-5-isopropylpyrazole **1b** showing the labelling scheme and hydrogen bonds among four molecules, two of which are crystallographically independent.

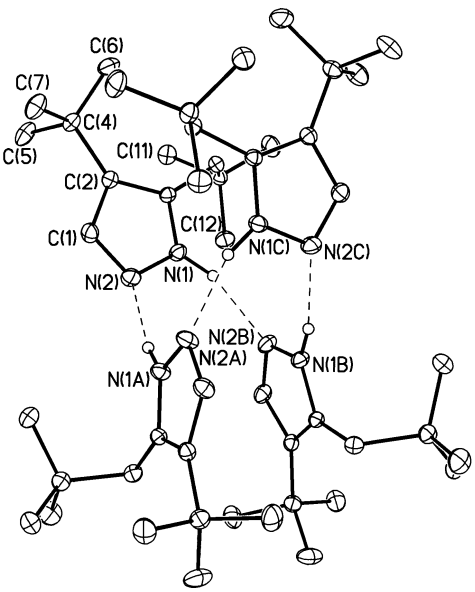

Fig. 3 An ORTEP diagram of **2b** showing the hydrogen bonds among four molecules.

Table 2 Description of the HB network using the centroids of the pyrazole rings (d_i and ψ_i values for compounds **1**, **2**, **3** and **4** are average values)

Compound	Tautomer	Motif	Proton disorder	Centroids	d_i/Å	ψ_i/°
1	**1b**	Tetramer	No	Folded	4.96	60.0
2	**2b**	Tetramer	No	Folded	4.57	57.4
3	**3a**	Tetramer	No	**Planar**	5.25	89.8
Literature results on tetramers			—	Folded	4.91–5.16	41.5–64.0
4	**4a**	Trimer	No	—	5.12	60.0

Table 3 ^{1}H chemical shifts (δ) of compounds **1**–**3** at RT unless otherwise indicated

Compound	Solvent	H3/H5	Substituent
1	DMSO-d_6	7.16	1.23 (9H) *tert*-butyl 3.19 (1H), 1.21 (3H) and 1.19 (3H) (isopropyl)
1a	CD_3OD 185 K	7.36	1.29 (9H) *tert*-butyl 3.26 (1H), 1.25 (3H) and 1.23 (3H) (isopropyl)
1b	CD_3OD 185 K	7.25	1.29 (9H) *tert*-butyl 3.37 (1H), 1.26 (3H) and 1.25 (3H) (isopropyl)
2	DMSO-d_6	7.27	1.23 (9H) *tert*-butyl 2.58 (2H) and 0.97 (9H) (neopentyl)
3	DMSO-d_6	7.53	1.12 (9H) *tert*-butyl 7.24 (4H) and 2.34 (3H) (*p*-tolyl)

Table 4 ^{13}C chemical shifts (δ) of compounds **1**–**3** at RT unless otherwise indicated

Compound	Solvent	C3	C4	C5	Substituent
1a	DMSO-d_6	153.9	—	—	—
1b	DMSO-d_6	135.9	124.3	143.9	31.3 and 29.4 (*tert*-butyl) 25.4 and 23.1 (isopropyl)
1a	CD_3OD 185 K	155.8	126.1	127.6	31.6 and 30.8 (*tert*-butyl) 28.2 and 24.0 (isopropyl)
1b	CD_3OD 185 K	137.0	126.1	146.6	31.7 and 30.9 (*tert*-butyl) 26.9 and 23.4 (isopropyl)
1b	Without CPMAS	135.9	123.6 122.5	145.3	32.6, 31.1 and 30.2 (*tert*-butyl) 26.3, 24.4, 23.5, 22.3 and 21.5 (isopropyl)
2a	DMSO-d_6	146.3	—	—	—
2b	DMSO-d_6	124.4	127.3	137.3	31.8 and 29.6 (*tert*-butyl) 39.8, 31.6 and 30.2 (neopentyl)
2b	Without CPMAS	134.6	126.2 125.5	137.5	33.9 and 33.1 (*tert*-butyl) 39.5, 31.6 and 30.6 (neopentyl)
3a	DMSO-d_6	143.0	127.8	131.9	31.8 and 29.8 (*tert*-butyl) 137.3, 130.9, 130.0, 128.4 and 20.8 (*p*-tolyl)
3a	Without CPMAS	149.6	126.1	136.3	32.5 and 30.4 (*tert*-butyl) 137.9, 131.8, 128.8 and 22.6 (*p*-tolyl)

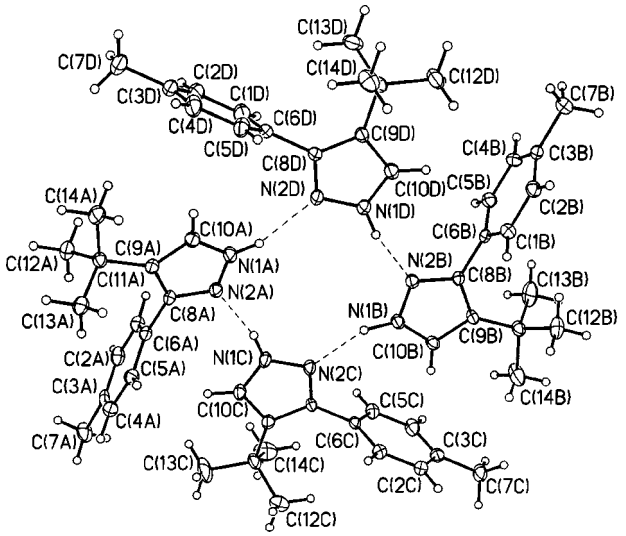

Fig. 4 An ORTEP diagram of 4-*tert*-butyl-3-*p*-tolylpyrazole **3a** showing the labelling scheme and hydrogen bonds for the four crystallographically independent molecules.

Table 5 ^{15}N chemical shifts[a] (δ) of compounds **1**–**3** in the solid state (CPMAS) referred to nitromethane

Compound	N(1)–H	–N(2)=
1b	−169.7	−101.6/−99.5
2b	−165.1	−94.9/−92.7
3a	−177.1	−89.9/−87.6

[a] The splitting of the –N(2)= signals is explained by the effect of two *tert*-butyl groups in different crystallographic situations. For compound **1b** at 40.58 MHz the two nitrogen atom signals were split: δ 170.3/168.6 and 101.5/98.8.

and $\psi_i = 41.5$–$64.0°$ (Table 2). A perfect tetrahedron has $\psi_i = 60.0°$ while a planar compound has $\psi_i = 90.0°$.

Compound **1** is a perfect tetrahedron regarding its angles and **3** is nearly perfectly planar. This exceptional behaviour of compound **3** (see Table 2) is also apparent in the distances between centroids (5.250 Å), which are longer than in any other tetramer. It must be understood that averages do not exactly reflect the complexities of these tetramers, except for compound **3**. It consists of four independent molecules, but in their planar arrangement they are very regular and there are only small variations among the independent centroid–centroid distances and angles. In compound **1** there are two independent molecules, which requires a single symmetry operation to generate the tetramer. In this case there are one short (4.4165 Å) and five long distances (5.063 Å), but the angles are much more regular and vary only by a few degrees ($60 \pm 2.0°$).

For compound **2**, there is only one independent molecule; the other three are symmetry generated. In the roughly tetrahedral arrangement of centroids, there are two short (4.167 Å) and four long (4.971 Å) distances, and the angles vary from 49.6 to 65.2°, the larger angle being associated with the short distances.

DSC

The DSC records were obtained with a Seiko DSC 220C instrument with a scanning rate of 2° min^{-1}. Compounds **1** and **2** behave normally (mp 126.7 and 128.3 °C, respectively). Compound **3** presents a phase transition at 113.0 °C before melting at 165.7 °C.

NMR results

The NMR data are reported in Tables 3 (^{1}H), 4 (^{13}C) and 5 (^{15}N).

The ^{1}H NMR spectra (Table 3) are consistent with the structures. In the case of compound **1** we have recorded the NMR spectra in methanol-d_4 at different temperatures. At 185 K both tautomers are clearly observed in a 35/65 **a**/**b** relationship (assigned by a 2-D spectrum ^{1}H–^{13}C, see below). A simulation of the spectrum at $T = 185$ K, using the WIN-DYNAMICS program,[15] yields a rate of $k = 0.1$ s^{-1} and at the coalescence temperature (253 K), $k = 200$ s^{-1}, which corresponds to $\Delta G^{\ddagger}_{253} = 51$ kJ mol^{-1}. This value is consistent with activation energies determined in this solvent for other pyrazoles.[16]

The ^{13}C NMR (Table 4) results are the richer in information and will be discussed in detail. The ^{15}N NMR data (Table 5) obtained in the solid state (CPMAS) are consistent with those of other pyrazoles recorded under the same conditions but cannot be used to determine the tautomeric structure.[17] Let us examine now the results of Table 4, where there was no problem to assign the signals of the pyrazoles nor those of the substituents.[18,19] The broadening of the signals hinders the observation of C4 and C5 of the minor tautomer in DMSO-d_6 at room temperature.

(i) Compounds **1** and **2** exist in solution, both in DMSO-d_6 and in methanol-d_4, as 35/65 mixtures of tautomers **a** and **b**, while **3** seems to be present predominantly as tautomer **3a** in DMSO-d_6 solution. Therefore, also in this case, the rule that asserts that the most abundant tautomer in solution is the same as the tautomer found in the solid state is verified.[16]

(ii) The presence of two independent molecules (see the crystallographic discussion) in the case of **1b** and **3a** but only one in the case of **2b** is reflected in the CPMAS spectra by a splitting of all signals in the case of **1b** (C4, *tert*-butyl and isopropyl). In the case of **2b** only C4 is split and in the case of **3a** no signal shows this phenomenon. Therefore, splitting in CPMAS NMR and crystallography are not simply related.

(iii) The chemical shifts of tautomers **1b** and **2b** in solution and in the solid state are very similar verifying simultaneously the assignment in solution and the **b** structure in the crystal. In the case of **3**, the values in the solid state are consistent with its **3a** structure.[18] The values in DMSO-d_6 indicate that some amount of **3b** is present but the percentages cannot be estimated.

Conclusion

In our attempt to rationalise the structure of NH-pyrazoles in the solid state[1,2,11] we have solved the structure of three new compounds. We have discovered that our method of prediction works well concerning the hydrogen-bonded motives (tetramers) and the tautomerism (5-alkyl *vs.* 3-aryl), but we were surprised to find a planar tetramer when this situation, similar to a planar conformation for *o*-tetraphenylene, was thought to be not stable.[2]

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