

Supplementary Material for

The photoelectron spectra of the isomeric 1- and 2-methyltetrazoles; their equilibrium structures and vibrational analysis by *ab initio* configuration interaction studies.

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SM1. Synthesis and characterization of 1- and 2-methyltetrazoles.

These experiments require care and skill. *Tetrazole* prepared by diazotization of 5-aminotetrazole hydrate in the presence of hypophosphorous acid¹ was converted to its anion by aqueous sodium hydroxide. Addition of iodomethane (1 mole equivalent) and reflux for 3 hours gave a mixture of 1- and 2-Methyltetrazoles, after extraction with CH₂Cl₂.² The isomers were separated by distillation behind a safety shield. The considerable difference in

boiling points was important. Kugelrohr distillation at atmospheric pressure gave *2-methyltetrazole* as a colourless liquid bp150°C (lit.³143–144°C) Vacuum distillation at the same temperature then gave 1-methyltetrazole as a colourless solid bp150°C at 20Torr (lit.³148–150°C at 18 Torr). The spectral identification using ¹H NMR (300MHz) and ¹³C NMR (75MHz) both in CDCl₃ show good agreement with literature values.^{3,4}

2-Methyltetrazole: ¹H: δ 4.40 (3H) and 8.51(1H); ¹³C: δ 39.2(CH₃) and 152.8 (CH).

1-Methyltetrazole: ¹H: δ 4.21 (3H) and 8.76 (1H); ¹³C: δ 34.3 (CH₃) and 143.3 (CH).

SM1.1. References to synthesis and characterization.

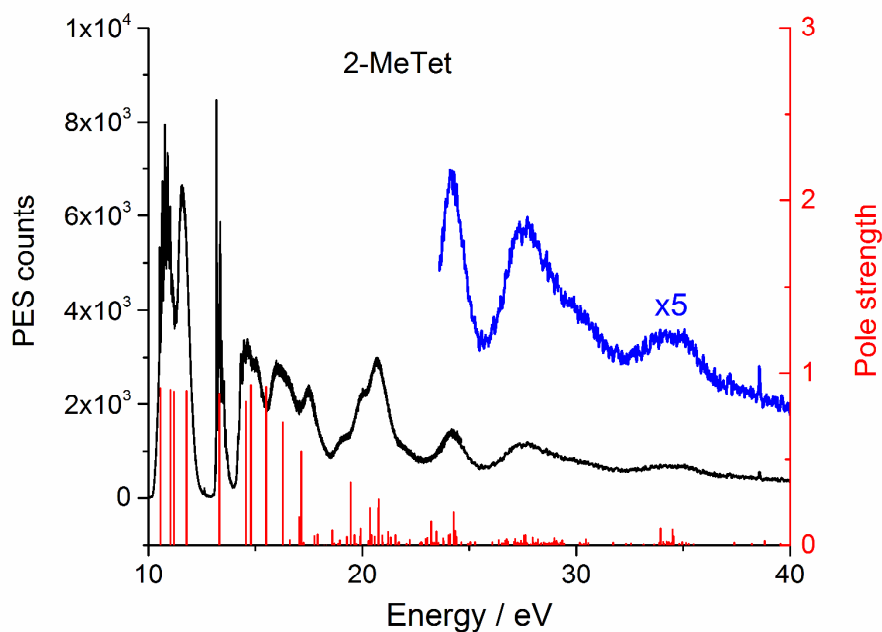
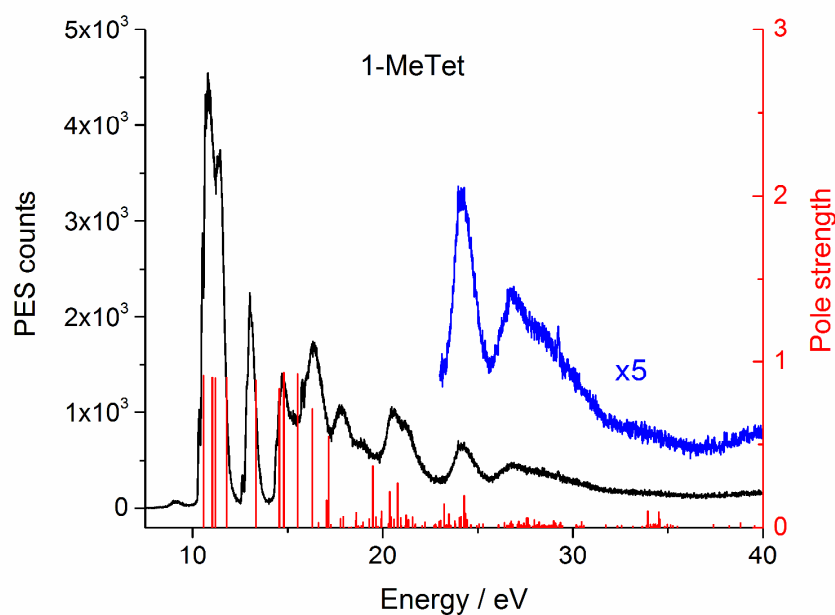
1. R. A. Henry and W.G. Finnegan, J. Amer. Chem. Soc., **76**, 290–291 (1954).
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SM2. The wide scan PES for both compounds with Tamm-Dancoff approximation¹⁻³ (TDA) calculated pole strengths included.

References

1. L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 205 (1977).
2. J. Schirmer and L. S. Cederbaum, J. Phys. B: At. Mol. Phys. **11**, 1889 (1978).
3. L. S. Cederbaum, W. Domcke, J. Schirmer, and H. Koppel, J. Chem. Phys. **72**, 1348 (1980).

These are not central to the present study, but are presented here.



SM3. Internal rotation in 1- and 2-MeTet.

The energies for internal rotation of the methyl group are very small relative to both electronic excitation and ionization. For *2-MeTet*, minima occur when the $H_{ip}-CN_1N_2$ dihedral angle is 0° , 120° and 240° ; the energy is 178 cm^{-1} higher at the maxima. The minima

for **1-MeTet** occur at 60° , 180° and 300° with the maxima 92 cm^{-1} higher; the barriers are smaller where the in-plane **H**-atom eclipses lone pairs on the ring.

A scan of the potential energy surface for the internal rotation of the **CH₃** group for the X^1A' state of **1-MeTet**, showed two C_s conformers, where the in-plane **H**-atom (**H_{ip}**) is eclipsed (*cis*, to N_2), ie dihedral angle $H_{ip}CN_1C_5 = 180^\circ$, or staggered (*trans* to N_2), ie $H_{ip}CN_1C_5 = 0^\circ$. Only the *cis* conformer, has all 24 vibration frequencies positive; in contrast, the *trans* conformer, is a saddle point with one imaginary frequency. This shows that the **H_{ip}** to **H₅** eclipsing in the preferred *cis* conformation is less important than the out-of-plane (**H_{oop}**) interactions with the LP_N at N_2 ; this is shown in Fig. 2. In contrast, **2-MeTet** which has LP_N on both sides, has an energy difference between the *cis* and *trans* **H_{ip}** to C_5 and N_2 of 178 cm^{-1} ; all vibration frequencies are positive for the *cis* $H_{ip}CN_2N_3$ conformer.

Figure SM3.1 Internal rotation of the methyl group in 1-MeTet

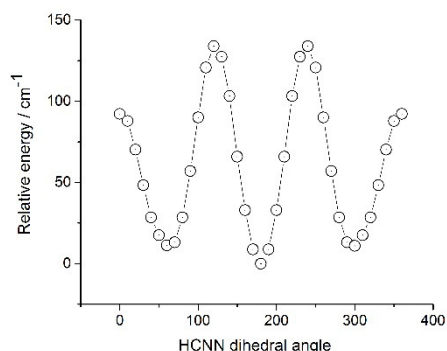
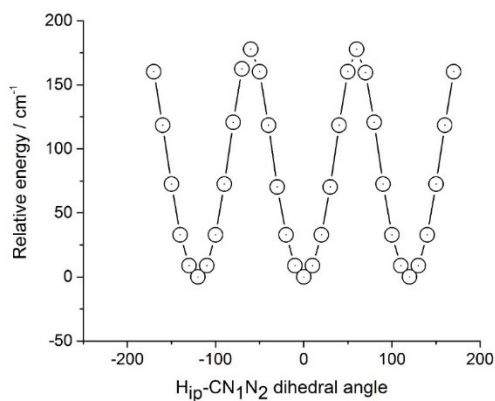


Figure SM3.2 Internal rotation of the methyl group in 2-MeTet



SM4. Comparison of the x-ray crystal structure for *1-MeTet* with the present equilibrium structure.

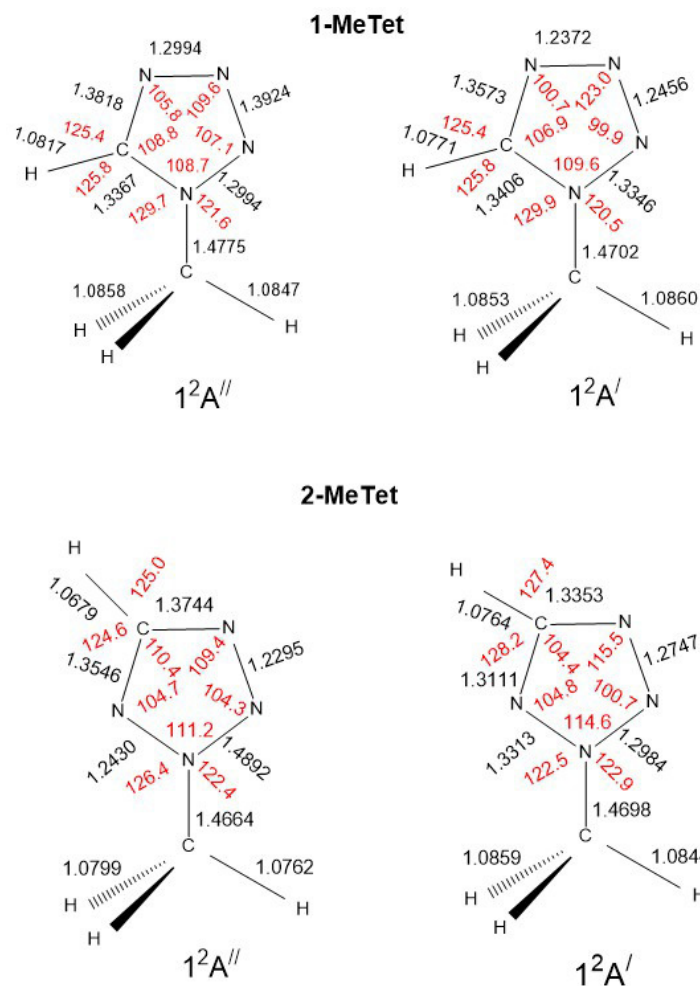
Differences between the experimental bond angles and our theoretical values, described in Table SM3.1, differ by less than 1°. The bond lengths differ up to 0.03 Å which may arise from intermolecular interactions in the solid state.

Table SM4.1. Comparison of the x-ray crystal structure for 1-MeTet with the present equilibrium structure.

Bond lengths / Å	C(Me)-N₁	N₁-N₂	N₂-N₃	N₃-N₄	N₄-C₅	C₅-N₁	
Crystal	1.455(2)	1.344(2)	1.299(2)	1.360(2)	1.315(2)	1.331(2)	
Theoretical	1.4464	1.3236	1.2504	1.3363	1.2887	1.3268	
Bond angles / °	CN₁N₅	CN₁N₂	N₂N₁C₅	N₃N₂N₁	N₄N₃N₂	C₅N₄N₃	N₁C₅N₄
Crystal	130.78(15)	120.81(13)	108.42(14)	106.23(12)	110.78(14)	105.39(14)	109.2(2)
Theoretical	131.24	121.58	107.17	107.37	111.11	105.52	108.82

SM4.1 Equilibrium molecular structures of the ionic states.

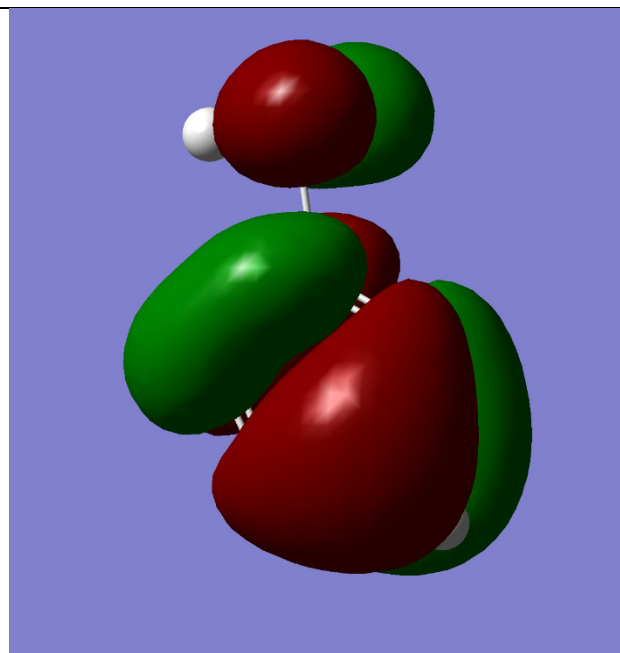
Our initial FC analysis, used CASSCF wave-functions since this allowed us to study a wider range of ionic states. In this method, the electrons are permuted among the active set of MOs, and all occupancy combination showing the desired symmetry are included. However, we found it necessary to only include MOs of the same type as the desired state symmetry. Thus, using C₅ symmetry, the π-ionic state calculations (²A'') only consisted of occupied π-MOs with π*-MOs. For the ²A' states, only σ and σ* MOs were in the active set. This restriction was essential to avoid 'state switching' at the structural optimization stage. Ideally, a mixture of π and σ-MOs would be present in each set, but state switching was severe, and no other means of control was found in the CASSCF.



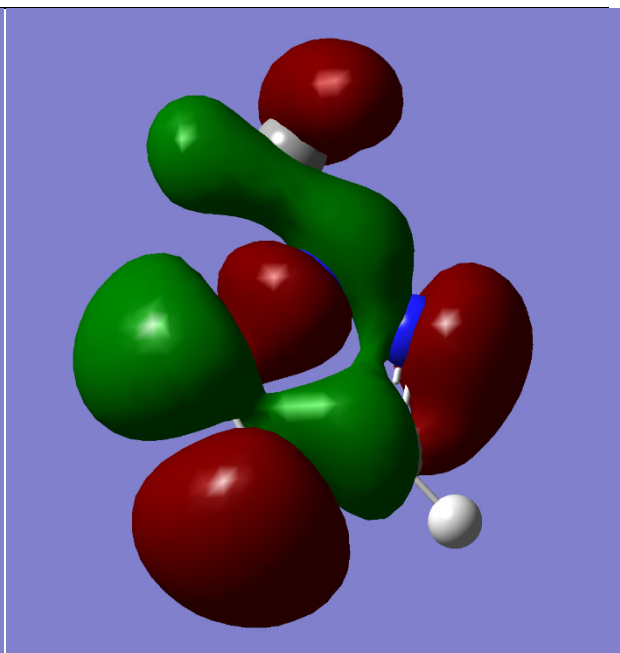
SM5. The highest occupied MOs (HOMOs) for 2-MeTet.

Fig.SM5.1 The highest occupied MOs (HOMOs) for 2-MeTet. All four views have a similar orientation, with the CH₃ at the top.

HOMO (22) 4a ^{''}	HOMO-1 (21) 18a [']
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HOMO-2 (20) 17a'



HOMO-3 (19) 3a''

