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4-ISOPROPYLIDENE-3,3,5,5-TETRAMETHYL-Δ^1-PYRAZOLINE - AN ALMOST FLAT PYRAZOLINE

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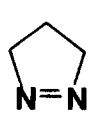
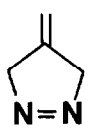
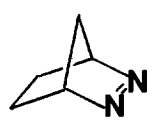
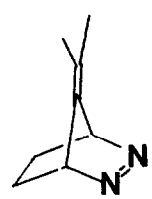
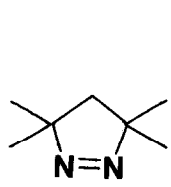
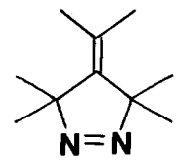
Abstract: The X-ray crystallographic structure of the title compound 6 shows that it is almost planar. This helps to explain a number of peculiar features in the chemistry of α-methylated pyrazolines.

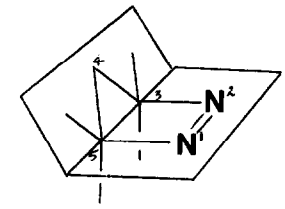
The rate of thermal deazetation of azoalkanes R-N=N-R normally depends on the stability of the alkyl radicals produced.[1] In the case of Δ^1-pyrazoline 1 the introduction of a radical stabilising alkylidene substituent in the 4-position (as in compound 2) lowers the energy barrier to nitrogen loss by ca. 10 kcal/mol and a similar effect is observed in the case of the bicyclic pyrazolines 3 and 4.[2]

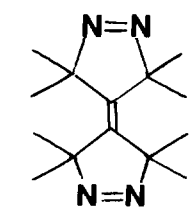





	1	2	3	4	
E_a deazetation	42.4	32.6	37.3	28	kcal/mol.





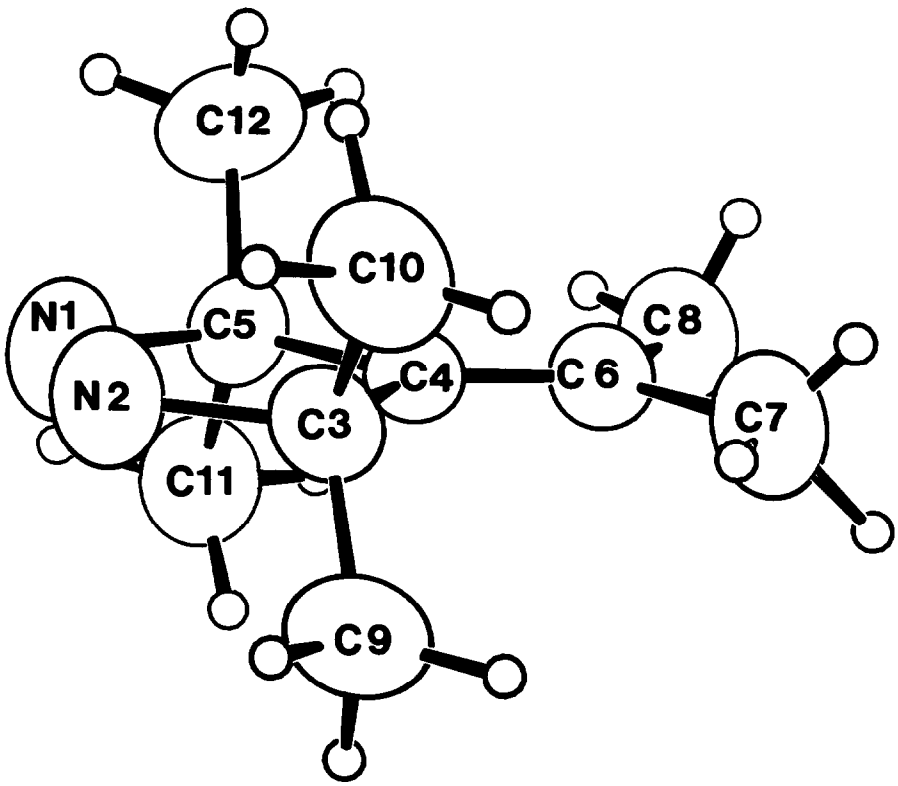




	5	6	7	8
E_a deazetation	37.7	45.5	kcal/mol	

For the α-methylated pyrazolines 5 and 6, however, introduction of a 4-alkylidene substituent does not lower the barrier to nitrogen loss.[3] The reason for this anomaly is probably conformational.[3,4] Pyrazolines normally adopt a folded "envelope" conformation 7 and a survey of eight monocyclic pyrazolines for which detailed X-Ray Crystallographic data is available, shows an average angle between the plane through atoms C3,C4,C5 and that defined by atoms N1,N2,C3,C5 of 24 ± 9°.[5] A similar folding is, of course, forced on the bicyclic pyrazolines 3 and 4 and, in the case of compound 4, it is 51°.[6] This folding leads to overlap between the Π bond of a 4-alkylidene substituent and the breaking C-N bonds and subsequent stabilisation of the radicals produced. In the case of the α-methylated pyrazolines 5 and 6, however, the more the ring is folded the greater becomes the steric clash between the methyl groups on C3 and C5. It has been suggested that the presence of these α-substituents flattens the ring so that in 6 the alkylidene substituent Π bond and the breaking C-N bonds become orthogonal and the accelerating effect is lost.[4] This would also explain why further extension of the conjugated system in compound 6 does not produce the expected increase in reaction rate[4] and why 6 and its relatives show a strong tendency to give "least motions" products, apparently arising from a bis orthogonal TMM biradical.[7] The only X-Ray Crystallographic study of an α-methylated pyrazoline available, compound 8, shows some flattening of the rings (fold of 16°) but this is a rather special case.[8] In this compound the final conformation is a compromise between flattening of the rings which reduces the C3/C5 methyl group repulsion and folding which allows the methyls on opposite rings to intercollate. We therefore decided to determine the X-ray crystallographic structure of the α-methylated pyrazoline 6, as a more "typical" representative of the series and, as anticipated, the pyrazoline ring was almost flat.

4-Isopropylidene-3,3,5,5-tetramethyl-Δ^1-pyrazoline was prepared as previously described[9] and purified by sublimation. Since it is a highly volatile material the crystal had to be mounted in a sealed capillary. The crystal was monoclinic, space group $P2_1/n$, with $\underline{a}$ = 8.280(6), $\underline{b}$ = 16.417(10), $\underline{c}$ = 7.880(4) Å, and β = 93.20(5)°, with 4 molecules per cell. The structure was determined using the 857 reflections with $I > 2\sigma(I)$. Least-squares refinement with allowance for anisotropic vibrations for C and N and isotropic vibrations for H gave a final R of 5.79%. As may be seen in the Figure the ring is very nearly planar. C4 lies only 0.031 Å from the mean plane of N1-N2-C3-C5 while N1 and N2 are 0.042 and 0.049 Å from the C3-C4-C5 plane, and the dihedral angle is 1.9°.



ORTEP drawing of the molecular structure of pyrazoline 6

The positional standard deviations of the ring atoms are ∿ 0.005 Å.

Bond lengths are:- N_1-N_2 1.240(5), N_2-C_3 1.492(5), C_3-C_4 1.526(5), C_4-C_5 1.520(5), C_4-C_6 1.317(5), C_6-C_7 1.507(6), C_6-C_8 1.500(7), C_3-C_9 1.542(6), C_3-C_{10} 1.518(7), C_5-C_{11} 1.530(7), C_5-C_{12} 1.551(7).

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