An All-nitrogen Aromatic Ring System: Structural Study of 4-Dimethylaminophenylpentazole

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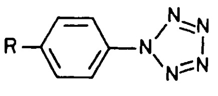
The crystal structure of the title compound at 128 K confirms the presence of the pentazole ring which, as a substituent, appears to have an inductive effect similar to that of the nitro group.

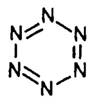
The thermally unstable product obtained by Huisgen and Ugi by the reaction of benzenediazonium chloride with lithium azide in methanol at −40 °C was formulated by them (in 1957) as phenylpentazole (1) on the basis of ^{15}N labelling studies.[1] Subsequent work[2] showed that electron-donating substituents in the 4-position of the benzene ring stabilized the pentazole system, and a series of 4-substituted derivatives was then isolated as crystalline solids at low temperature.[3] Support for their constitution was provided by u.v. solution spectra, which resembled those of the corresponding tetrazoles rather than those of diazonium salts. The most stable derivative, (2), reported to decompose at 50 °C, has a 4-dimethylamino substituent. Since we are interested in this compound as a possible candidate for accurate electron density studies, as a first step we have determined its crystal structure to confirm the molecular constitution.

Crystal data: (2) $C_8H_{10}N_6$, $M = 190.2$, monoclinic, $a = 4.077(3)$, $b = 10.925(9)$, $c = 10.042(6)$ Å, $\beta = 98.37(6)°$, space group $P2_1/m$, $Z = 2$, $D_c = 1.43$ g cm^{-3}, λ (Mo-K_α) = 0.71069 Å, $T = 128$ K.



(1) R = H

(2) R = NMe$_2$



(3)

Needle-shaped crystals of (2) were grown from a dichloromethane solution at −15 °C. The crystal quality quickly deteriorates at room temperature so the crystal chosen for diffraction measurements was cooled to 128 K. The structure was solved with MULTAN 80[4] and refined by full-matrix least-squares analysis with the SHELX[5] and XRAY 72[6] packages using 664 independent reflections ($\theta_{max} = 29°$) with $I \geqslant 3\sigma(I)$. A modified weighting scheme[7] with $r = 6.0$ Å^2 was used, but no extinction correction was applied ($R = 0.036$). The results† of the analysis confirm formula (2). Molecular dimensions are shown in Figure 1.

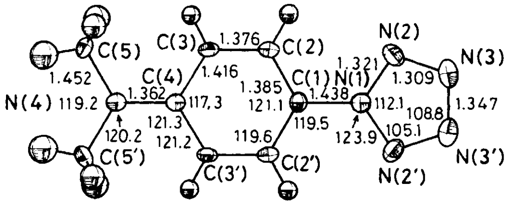


Figure 1. An ORTEP (ref. 8) plot of 4-dimethylaminophenylpentazole showing vibrational ellipsoids at the 50% probability level. E.s.d.s. are in the range 0.002—0.004 Å for indicated bond lengths, and 0.1—0.2° for bond angles.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

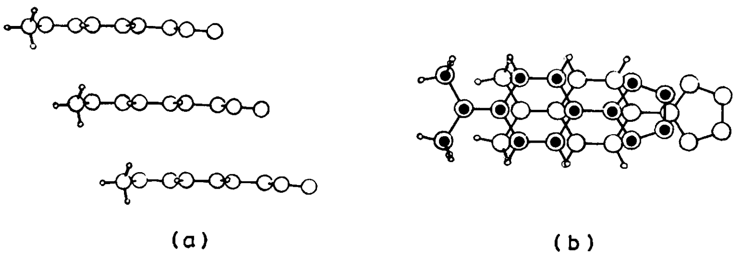

Figure 2. (a) Stacking of molecules related by the *a* axis translation; (b) stacking diagram, both drawn with PLUTO (ref. 17).

This is the first *X*-ray analysis of a compound containing a five-membered ring composed exclusively of nitrogen atoms. (The structure of a triaziridine derivative has been reported.[9]) The N–N bond distances in (**2**) lie in the range 1.30—1.35 Å, intermediate between single bonds (hydrazine,[10] 1.449 Å) and double bonds (*trans*-diimine,[11] 1.252 Å), so the pentazole ring, with its 6π electrons, can be regarded as aromatic. The theoretical N–N distance[12] of 1.29 Å calculated for D_{6h} hexazine (**3**) fits in nicely with the average N–N distance of 1.32 Å in the pentazole; the difference is about the same as the one between the observed C–C bond lengths in the carbocyclic 6π electron analogues: 1.396 Å in D_{6h} benzene[13] and 1.428—1.433 Å in C_5H_5 rings (from recent low temperature crystal structure measurements on metallocenes).[14]

Bond lengths in the framework formed by the benzene ring of (**2**) and its two exocyclic bonds to nitrogen are similar to those in 4-nitroaniline:[15] N(1)–C(1), N(4)–C(4), and C(2)–C(3) are short while C(3)–C(4) is long. The patterns of bond angles are also similar. Adopting the angular substituent parameters derived by Domenicano and Murray-Rust[16] for the NMe_2 group and assuming additivity of substituent effects, we obtained parameters for the pentazole substituent ($\Delta\alpha = +2.8°, \Delta\beta = -1.8°, \Delta\gamma = 0.6°, \Delta\delta = -0.3°$) that suggest it is very similar to the $-NO_2$ group as far as its inductive effect is concerned. Its place in the mesomeric (resonance) scale is less clear, mainly because of the small range of $\Delta\gamma$, the angular parameter used in the correlation.[16]

The two nitrogen atoms attached to the benzene ring are nearly, but not quite, coplanar with their respective three bonded atoms, N(1) being displaced by 0.019(1)Å, from the plane containing C(1), N(2), and N(2′), and N(4) by 0.047(1) Å in the same direction from the plane containing C(5), C(5′), and C(4). The benzene ring is also slightly nonplanar, the whole molecule being bowed so that C(5) and C(5′) are displaced by 0.096 Å from the mean plane of the benzene ring, N(3) and N(3′) by 0.192 Å on the same side. The molecules pack in parallel stacks (Figure 2) along the *a* axis, the overlap between adjacent molecules being shown in Figure 2(b). The shortest intermolecular contacts of different types are: N(1) . . . N(3) 3.39; N(2) . . . C(2) 3.41, N(1) . . . C(1) and N(3) . . . C(1) 3.48; C(1) . . . C(4) 3.51 and C(2) . . . C(3) 3.54 Å. Figure 2 suggests that there may even be a specific interaction between N(1) of one molecule and the N(3)–N(3′) bond of the next. Adjacent stacks in the *b* direction are antiparallel since they are related by the crystallographic 2_1 axis.

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