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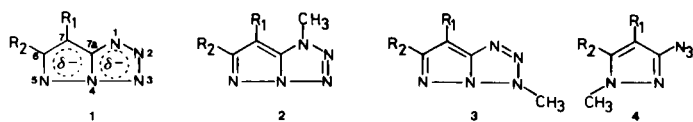
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The molecular structure of 1,6-dimethyl-7-ethoxycarbonylpyrazolo[1,5-*d*]tetrazole, a 3a-azapentalene derivative having only nitrogens as ring heteroatoms, has been determined by X-ray diffraction. The compound crystallizes in the space group $P2_1/a$ with four molecules in a unit cell of dimensions $a = 10.184$, $b = 28.827$, $c = 4.090$ Å, $\beta = 123.37^\circ$. The structure, which was solved by direct methods and refined to a final value of $R = 0.039$, shows a clear difference in bond localization in the two fused rings, in agreement with CNDO/2 calculations. The position of the *N*-methyl group corroborates an empirical rule based on pmr.

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Following our research work in the field of azapentalenic systems (1) we have investigated the structure and spectroscopic properties of the pyrazolo[1,5-*d*]tetrazole system. In previous papers (2,3) we showed that the methylation of bicyclic anions 1 yielded 1-methyl pyrazolo[1,5-*d*]tetrazoles (2), 3-methylpyrazolo[1,5-*d*]tetrazoles (3) and 1-methyl-3-azidopyrazoles (4), and we assigned the structures of the bicyclic isomers on the basis of proton nmr spectroscopy using the empirical rule (4) that the chemical shifts of *N*-methyl protons in compounds 2 should appear at lower frequencies than those in products 3.



a

b

c

R ₁	Ph	H	CO ₂ Et
R ₂	H	H	Me

Although this relationship has been applied to pairs of compounds 2 and 3 (3), it could be confusing and lead to an erroneous assignment (5) when only one isomer is available. In order to verify this rule and afford additional evidence for the structures of pyrazolo[1,5-*d*]tetrazoles, the corresponding 1,6-dimethyl-7-ethoxycarbonyl derivative 2c (3) has been examined by X-ray crystallography.

Bond lengths and angles are shown in Figure 1, which was drawn with the aid of the ORTEP program (6). Estimated standard deviations for the bond lengths are 0.0025-0.0038 Å, and for the bond angles the e.s.d.'s are 0.18-0.22°.

The experimental bond lengths are also reported in the 4th column of Table I. In the 3rd column are those calculated from π -bond orders. There is a good agreement, tak-

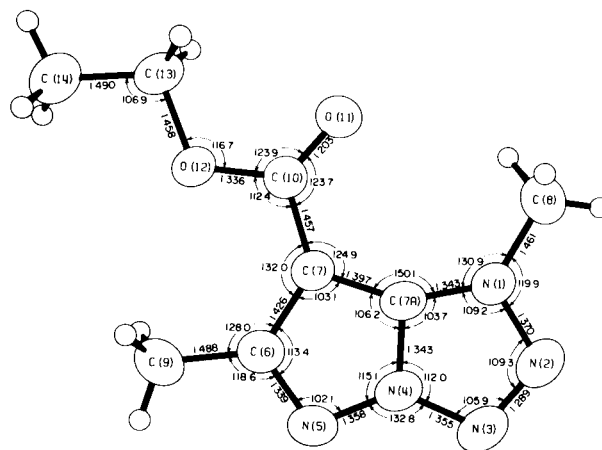


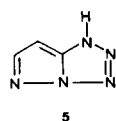
Figure 1. Final bond lengths and angles. The thermal ellipsoid outlines enclose 50% probability.

ing into account that derivative 2c is substituted in positions 1, 6 and 7, whereas the compound utilized for the CNDO/2 calculations (7) is not. Moreover, the geometry utilized in those calculations is an ideal, non optimized geometry consisting in two regular pentagons, 1.39 Å side.

The structural criteria of aromaticity, based in the absence of bond alternation, shows, considering the experimental or the calculated bond lengths, that the pyrazolic half-ring is more "aromatic" than the tetrazolic counterpart. The last has a N₂-N₃ bond shorter than all the others N-N bonds, whereas in the pyrazolic part all bonds (N-C or C-C) have approximately the same length. The C₆-C₇ bond is experimentally 0.03 Å longer than the C₇-C_{7a} bond, but the calculated values are almost identical (1.390 and 1.395 Å). We think that the small experimental difference can probably be ascribed to interatomic repulsion between the adjacent substituents on C(6) and C(7) (causing a slight lengthening of the C(6)-C(7) bond). Such re-

Table I

Comparison of Observed Bond Distances and those Predicted from CNDO/2 Calculations.

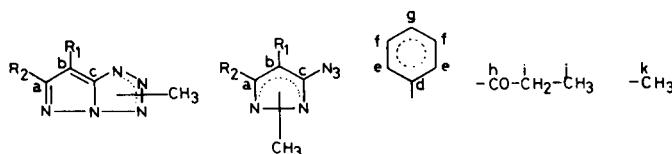


Bonds	π -Bond order (7)	Predicted Distance (a)	Observed Distance
N (1)-N (2)	0.439	1.385	1.370
N (2)-N (3)	0.822	1.310	1.289
N (3)-N (4)	0.394	1.395	1.355
N (4)-N (5)	0.396	1.395	1.358
N (5)-C (6)	0.690	1.325	1.339
C (6)-C (7)	0.652	1.390	1.426
C (7)-C (7a)	0.631	1.395	1.397
C (7a)-N (1)	0.421	1.375	1.343
N (4)-C (7a)	0.542	1.350	1.343

(a) Calculated from the following empirical equations: $R_{CC}(\text{\AA}) = 1.51 - 0.18 p_{CC}$ (8), $R_{CN}(\text{\AA}) = 1.45 - 0.18 p_{CN}$ (8), and $R_{NN}(\text{\AA}) = 1.47 - 0.19 p_{NN}$ (9) for the unsubstituted 1H-pyrazolo[1,5-d]tetrazole (5).

Table II

Carbon-13 Chemical Shifts in ppm from TMS.



Compound	C _a	C _b	C _c	N-CH ₃	R ₁	R ₂
3 (5)-azido-4-phenylpyrazole	131.4	110.7	143.4	----	C ₆ H ₅ : 129.0 (d) 126.1 (e) 128.6 (f) 126.1 (g)	----
2a	144.9	96.7	134.9	37.2	C ₆ H ₅ : 130.6 (d) 126.4 (e) 129.1 (f) 126.1 (g)	----
3a	143.4	97.8	131.4	42.8	C ₆ H ₅ : 128.6 (d) 123.9 (e) 129.0 (f) 125.2 (g)	----
4a	131.1	111.1	142.5	37.5	C ₆ H ₅ : 130.8 (d) 125.8 (e) 128.6 (f) 126.1 (g)	----
3 (5)-azidopyrazole	131.2	95.4	147.0	----	----	----
2b	146.9	78.2	138.4	35.7	----	----
3b	146.8	80.8	149.8	42.4	----	----
4b	133.5	95.9	146.2	38.8	----	----
1-methyl-5-azidopyrazole	138.4	94.6	137.2	34.5	----	----
2c	159.1	87.1	138.5	36.7	CO ₂ Et: 161.3 (h) 59.9 (i) 14.1 (j)	CH ₃ : 14.6
3c	160.8	87.8	149.8	42.7	CO ₂ Et: 161.8 (h) 59.5 (i) 14.4 (j)	CH ₃ : 14.7

pulsion is also evident in the enlarged C(7)-C(6)-C(9) and C(6)-C(7)-C(10) angles (See Fig. 1). Localization of bonds in one of the two fused rings in 3a-azapentalenes has been previously proposed on spectroscopic grounds (10-12), but this is the first clear structural demonstration.

Each five-membered ring is planar within experimental error (± 0.003 Å) with a dihedral angle between the fused ring planes of 1.6° . The whole molecule (excluding hydrogens) is planar within ± 0.14 Å. The ethoxycarbonyl group is in all-*trans* conformation, the torsional angles C(7a)-C(7)-C(10)-O(12), C(7)-C(10)-O(12)-C(13), and C(10)-O(12)-C(13)-C(14) being -174.4 , 177.4 and 177.3° respectively. The approximate coplanarity of C(14) with the rest of the molecule is apparently due to packing constraints.

In the crystal structure, molecules are stacked along the *c* direction, with mean interplanar spacing of 3.40 Å. There is essentially no overlap of the five-membered rings in adjacent layers; N(3) and N(4) of one molecule lie nearly over C(7a) and C(7) respectively of the adjacent molecule. Intermolecular contacts within a layer correspond to the van der Waals interactions.

The crystal structure reported here is of interest, being the first X-ray determination of a 3a-azapentalene derivative with only nitrogens as ring heteroatoms. Previous related X-ray studies (13-17) have been of sulfur derivatives.

This analysis shows unambiguously that the *N*-methyl group is in position 1, as deduced from the empirical relationship proposed by Butler (4), and thus demonstrates

Table III

Final Fractional Coordinates and Thermal Parameters (a,b)
(Standard deviations, in parentheses, refer to the least significant digit.)

Atom	x/a	y/b	z/c	U ₁₁ or B	U ₂₂	U ₃₃	2U ₂₃	2U ₁₃	2U ₁₂
N (1)	0.4363 (2)	0.29956 (6)	0.8776 (5)	44 (1)	48 (1)	67 (1)	- 1 (2)	67 (2)	4 (2)
N (2)	0.5692 (2)	0.30021 (7)	0.8702 (6)	51 (1)	64 (1)	81 (1)	3 (2)	84 (2)	16 (2)
N (3)	0.6188 (2)	0.34230 (7)	0.9117 (6)	46 (1)	69 (1)	79 (1)	5 (2)	80 (2)	9 (2)
N (4)	0.5170 (2)	0.36860 (6)	0.9474 (5)	38 (1)	54 (1)	55 (1)	3 (2)	55 (2)	- 2 (2)
N (5)	0.5062 (2)	0.41498 (6)	0.9867 (5)	47 (1)	51 (1)	65 (1)	1 (2)	65 (2)	-15 (2)
C (6)	0.3758 (2)	0.41797 (7)	0.9905 (6)	44 (1)	48 (1)	47 (1)	1 (2)	50 (2)	- 6 (2)
C (7)	0.3035 (2)	0.37417 (7)	0.9526 (6)	38 (1)	44 (1)	49 (1)	0 (2)	47 (2)	0 (2)
C (7a)	0.4020 (2)	0.34302 (7)	0.9245 (6)	35 (1)	49 (1)	48 (1)	2 (2)	44 (2)	- 6 (2)
C (8)	0.3571 (3)	0.25563 (8)	0.8363 (9)	79 (2)	46 (1)	121 (2)	-27 (3)	134 (4)	-12 (3)
C (9)	0.3221 (3)	0.46461 (8)	1.0258 (7)	68 (2)	45 (1)	76 (2)	- 3 (2)	89 (3)	-12 (2)
C (10)	0.1614 (2)	0.36136 (7)	0.9355 (6)	45 (1)	43 (1)	54 (1)	4 (2)	58 (2)	2 (2)
O (11)	0.1195 (2)	0.32193 (5)	0.9195 (6)	64 (1)	44 (1)	125 (2)	- 4 (2)	129 (2)	-10 (2)
O (12)	0.0821 (2)	0.39831 (5)	0.9347 (5)	42 (1)	46 (1)	68 (1)	- 1 (1)	70 (2)	1 (1)
C (13)	-0.0658 (2)	0.38923 (8)	0.9008 (7)	42 (1)	59 (1)	68 (2)	- 1 (2)	70 (2)	- 2 (2)
C (14)	-0.1279 (3)	0.43494 (9)	0.9262 (8)	58 (2)	68 (2)	86 (2)	3 (3)	95 (3)	13 (2)
H (81)	0.409 (3)	0.232 (1)	0.834 (9)	6.1 (8)					
H (82)	0.302 (4)	0.256 (1)	0.955 (9)	7.1 (9)					
H (83)	0.279 (5)	0.254 (1)	0.618 (12)	11.1 (12)					
H (91)	0.381 (3)	0.488 (1)	1.030 (8)	4.8 (7)					
H (92)	0.313 (3)	0.466 (1)	1.244 (8)	5.0 (7)					
H (93)	0.219 (3)	0.471 (1)	0.803 (8)	5.5 (7)					
H (131)	-0.043 (3)	0.367 (1)	1.113 (6)	2.5 (5)					
H (132)	-0.134 (3)	0.372 (1)	0.654 (7)	3.2 (5)					
H (141)	-0.058 (3)	0.451 (1)	1.157 (8)	4.3 (6)					
H (142)	-0.222 (3)	0.432 (1)	0.909 (7)	4.3 (6)					
H (143)	-0.143 (3)	0.456 (1)	0.727 (7)	4.2 (6)					

(a) Anisotropic temperature factors given by $\exp[-2\pi^2(U_{11a}^2h^2 + U_{22b}^2k^2 + U_{33c}^2l^2 + 2U_{23b}^*c^*k\ell + 2U_{13a}^*c^*h\ell + 2U_{12a}^*b^*hk)]$. (b) The U_{ij} values are $\times 10^3$; B values (in \AA^2) are given for hydrogen atoms instead of U_{11} .

the validity of the assumptions made in our preceding paper (3) based on this rule.

In the case of 1-methyl-7-phenyl and 3-methyl-7-phenyl pyrazolo[1,5-d]tetrazoles (**2a** and **3a**), respectively, the appearance in proton nmr of the signal corresponding to the phenyl group in deuteriochloroform permits us to distinguish between both derivatives: a singlet (7.37 ppm) is observed for the sterically hindered phenyl in compound **2a** and a multiplet (7.08-7.85 ppm) for the coplanar phenyl in **3a** (see Experimental).

Carbon-13 Nmr Results.

We also tried to use ^{13}C nmr spectroscopy as a tool to differentiate methylated pyrazolo[1,5-d]tetrazole isomers **2** and **3**. We found that the carbon chemical shift of the *N*-methyl groups appeared (Table II) at about 36 ppm and 42 ppm from TMS for compounds **2** (a-c) and **3** (a-c) respectively (18).

Two conclusions can be drawn from the Table II values. The first one concerns the difference between chemical shifts of carbons *ortho* (e) and *meta* (f) to the phenyl group in pyrazolo[1,5-d]tetrazole derivatives; as in proton nmr $\Delta\delta_{ef}$ depends on the dihedral angle between the phenyl

group and the heterocycle (19): $\Delta\delta_{ef}$ (**2a**) = 2.7 and $\Delta\delta_{ef}$ (**3a**) = 5.1 ppm. The other one concerns the influence of the azido group on pyrazolic carbon chemical shifts. The magnitude of the azido-substitution effect can be obtained by comparison with 1-methylpyrazole (20). The azide causes a downfield shift of 7.3 ppm at the site of substitution, C_c , an upfield shift of 10 ppm on carbon b and a small shift (-0.6 to 3.7 ppm depending on the position of the *N*-methyl group) on carbon a.

EXPERIMENTAL

Melting points were determined on a Buchi apparatus and are uncorrected. Pmr spectra were obtained on a Varian EM-360 spectrometer (TMS as internal standard). The ir and uv spectra were taken with a Perkin Elmer Model 577 instrument and a Cary 14 spectrophotometer, respectively. Tlc was carried out on Merk F₂₅₄ silica gel plates. For column chromatography, silica gel 60 Merk, 70-230 mesh ASTM, was used. ^{13}C nmr were recorded on a Varian CFT-20

Methylation of the Bicyclic Anion **1a**.

Using the general procedure indicated in reference (3), the final residue obtained from the reaction was chromatographed (eluted with petroleum ether 50-70°-benzene) to afford a first fraction

that crystallized on standing: 1-methyl-3-azido-4-phenylpyrazole (**4a**) (28% yield), m.p. 70-73° (2); ir (potassium bromide): 2130 cm^{-1} (ν as N_3); λ max (ethanol 95%): 267 nm ($\log \epsilon$ 4.20), 250 sh (4.09); pmr (deuteriochloroform) δ : 3.75 (s, N-CH₃), 7.10-7.60 (m, phenyl protons), 7.38 (s, H₆); (DMSO- d_6) δ : 3.80 (s, N-CH₃), 7.10-7.60 (m, phenyl protons), 8.05 (s, H₆).

The second fraction from the column was 1-methyl-7-phenylpyrazolo[1,5-*d*]tetrazole (**2a**) (36% yield), m.p. 101-103°; λ max (ethanol 95%): 298 nm sh ($\log \epsilon$ 3.46), 257 (4.15); pmr (deuteriochloroform) δ : 4.20 (s, N-CH₃), 7.37 (s, phenyl protons), 7.93 (s, H₆); (DMSO- d_6) δ : 4.27 (s, N-CH₃), 7.17-7.83 (m, phenyl protons), 8.23 (s, H₆); ms: m/e (relative intensity) M^+ 199 (40), 103 (11), 102 (100), 76 (12), 52 (10), 51 (13), 50 (10), 28 (11).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{N}_5$: C, 60.3; H, 4.5; N, 35.2. Found: C, 59.9; H, 4.5; N, 35.5.

Finally, using benzene-chloroform, a third fraction was obtained, 3-methyl-7-phenylpyrazolo[1,5-*d*]tetrazole (**3a**) (16% yield), m.p. 138-139° (3); λ max (ethanol 95%): 346 nm ($\log \epsilon$ 3.15), 268 (3.85), 264 (2.86), 258 (3.85); pmr (deuteriochloroform) δ : 4.46 (s, N-CH₃), 7.08-7.85 (m, phenyl protons), 8.22 (s, H₆); (DMSO- d_6) δ : 4.56 (s, N-CH₃), 7.06-7.96 (m, phenyl protons), 8.53 (s, H₆); ms: m/e (relative intensity) M^+ 199 (43), 142 (19), 130 (13), 129 (100), 128 (19), 115 (16), 102 (22), 101 (67), 88 (10), 77 (19), 76 (13), 75 (42), 74 (15), 63 (13), 62 (10), 51 (35), 50 (17), 43 (25), 39 (13), 28 (17).

Methylation of the bicyclic Anion **1b**.

Proceeding in a similar way as described for **1a** the elution with benzene yielded us a first fraction of 1-methyl-3-azidopyrazole (**4b**) (15% yield), oil; ir (neat): 2120 cm^{-1} (ν as N_3); pmr (deuteriochloroform) δ : 3.80 (s, N-CH₃), 5.80 (d, H₇), 7.20 (d, H₆), $J_{67} = 2.4$ Hz; (DMSO- d_6) δ : 3.78 (s, N-CH₃), 5.92 (d, H₇), 7.62 (d, H₆).

Anal. Calcd. for $\text{C}_4\text{H}_5\text{N}_5$: C, 39.0; H, 4.1; N, 56.9. Found: C, 39.1; H, 4.0; N, 56.9.

The use of benzene-chloroform afforded a second fraction, 1-methylpyrazolo[1,5-*d*]tetrazole (**2b**) (48% yield), m.p. 115-116°; λ max (ethanol 95%): 320 nm ($\log \epsilon$ 3.28), 276 (3.73); pmr (deuteriochloroform) δ : 4.11 (s, N-CH₃), 5.80 (d, H₇), 7.76 (d, H₆), $J_{67} = 2.4$ Hz; (DMSO- d_6) δ : 4.16 (s, N-CH₃), 6.10 (d, H₇), 7.90 (d, H₆).

Anal. Calcd. for $\text{C}_4\text{H}_5\text{N}_5$: C, 39.0; H, 4.1; N, 56.9. Found: C, 38.8; H, 4.1; N, 57.1.

The last fraction eluted was 3-methylpyrazolo[1,5-*d*]tetrazole (**3b**), oil; pmr (deuteriochloroform) δ : 4.43 (s, N-CH₃), 6.05 (d, H₇), 7.86 (d, H₆), $J_{67} = 2.8$ Hz; (DMSO- d_6) δ : 4.50 (s, N-CH₃), 6.20 (d, H₇), 7.96 (d, H₆).

Anal. Calcd. for $\text{C}_4\text{H}_5\text{N}_5$: C, 39.0; H, 4.1; N, 56.9. Found: C, 39.3; H, 3.9; N, 57.0.

Methylation of 3-Azidopyrazole.

A mixture of 3-azidopyrazole (0.45 g., 0.004 mole), 6 ml. of 1 *M* sodium methoxide, 1.5 ml. of methyl iodide in 10 ml. of dry methanol was stirred at room temperature for 24 hours. After evaporation of the solvent, water (200 ml.) was added and the aqueous solution extracted several times with ether, the ether extracts washed with sodium thiosulfate and dried. The proton nmr of a portion of the residue obtained after evaporation of the ether, showed that it was a mixture of 3-azidopyrazole (9%), 1-methyl-3-azidopyrazole (**4b**) (68%) and 1-methyl-5-azidopyrazole (23%).

1-Methyl-5-azidopyrazole.

This compound had pmr (deuteriochloroform) δ : 3.61 (s, N-CH₃), 5.96 (d, H₄), 7.40 (d, H₃), $J_{34} = 2.0$ Hz; (DMSO- d_6) δ : 3.57 (s, N-CH₃), 6.16 (d, H₄), 7.39 (d, H₃).

X-Ray Data Collection.

1,6-Dimethyl-7-ethoxycarbonylpyrazolo[1,5-*d*]tetrazole (**2c**) crystallizes from water-methanol as needles which have monoclinic symmetry with $a = 10.184$ (4), $b = 28.827$ (9), $c = 4.090$ (5) Å, $\beta = 123.37$ (5)°. Systematic absences of $h0l$ reflections with h odd, and of $0k0$ with k odd, define the space group as $\text{P}2_1/a$. There are four molecules per unit cell, corresponding to a calculated density of 1.836 g/cm^3 .

Three-dimensional intensity data were collected with a Picker diffractometer using Ni-filtered Cu radiation ($\lambda = 1.5418$ Å). All 1699 independent reflections in the range $2\theta \leq 130^\circ$ were measured, using the $\theta/2\theta$ scan technique. The (2θ) scan speed was 2°min^{-1} , and the scan ranges were 2° for $2\theta < 100^\circ$, and 3° otherwise. Instrumental and crystal stability were monitored by measuring a "check" reflection at intervals of about 30 reflections. No significant fluctuations were recorded. A reflection was considered observed only if its net count was ≥ 12 and at least one-tenth of the total background count. Lorenz and polarization corrections were applied, but absorption corrections were considered unnecessary ($\mu = 8.9 \text{ cm}^{-1}$).

Structure Solution and Refinement.

The structure was solved routinely by the symbolic addition procedure. Refinement was by block-diagonal least-squares calculations, applying anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms, which were all located on a difference map, were refined isotropically. The weighting function used in the least-squares calculations was

$$w = (25.0/|F_o|)^2 \quad \text{if } |F_o| \geq 25.0, \text{ otherwise } w = 1.0.$$

Five reflections were given zero weights in the final cycles; four of these appear to be affected by extinction and one by double reflection. All scattering factor values were taken from "International Tables for X-ray Crystallography" (21). The final R value ($= \sum |F_o| - |F_c| / \sum |F_o|$) was 0.039 for the 1303 observed reflections used in this analysis. All calculations were done with the NRC set of crystallographic programs (22) and ORTEP (6). The final fractional coordinates and thermal parameters are listed in Table III. A table of observed and calculated structure factors has been placed in the Depository of Unpublished Data (23).

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