d), 8.9 (2 H, Py α-H, d); IR (Nujol)[12] ν_{max} 3200, 2800–2300 (NH$^+$ stretching), 1640, 1500, 1065, 750 cm^{-1}; MS,[13] m/e 213, 183, 108, 107, 106, 105 (base peak), 77, 36 (HCl), 27 (HCN); ^{13}C NMR (Me$_2$SO$_4$; 25.2 MHz) δ 76.0 (C-OH, d), 76.9 (C-CN, s), 119.0 (CN, s), 126.1 (Py β-C, d), 127.4 (d), 128.1 (d), 128.8 (d), 138.5 (Ph, s), 141.0 (Py α-C, d), 158.6 (Py γ-C, s).

Anal. Calcd for $C_{13}H_{13}N_2O_2Cl$: C, 58.97; H, 4.91; N, 10.58. Found: C, 59.0; H, 4.8; N, 10.6.

Registry No. 1, 10425-22-6; 2, 78387-03-8; 3, 81390-08-1; 4, 5650-40-8; 5, 81390-09-2; 6, 81390-10-5; *erythro*-7, 63031-61-8; *threo*-7, 81390-11-6; *erythro*-8, 81390-12-7; *threo*-8, 81390-13-8; *meso*-9, 81390-14-9; *dl*-9, 81390-15-0; 10, 81390-16-1; 11, 81390-17-2; *erythro*-12, 63031-62-9; *threo*-12, 81390-18-3; *erythro*-13, 81390-19-4; *threo*-13, 81390-20-7; 14, 81390-21-8; *meso*-15, 20445-38-9; *dl*-15, 20445-39-0; 16, 81390-22-9; 17, 81390-23-0; 18, 81390-24-1; 19, 81390-25-2; TiCl$_3$, 7705-07-9; benzoyl cyanide, 613-90-1; benzoylformic acid, 611-73-4; methyl benzoylformate, 15206-55-0; ethyl pyruvate, 617-35-6; 2-acetylpyridine, 1122-62-9; acetone, 67-64-1; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; 4-acetylpyridine, 1122-54-9; 4-pyridinecarboxaldehyde, 872-85-5.

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[12] The apparent absence of the CN group absorption may be explained by its triple-bond character which can be greatly modified by interaction with neighboring hydroxyl groups: Raaen, V. R. *J. Org. Chem.* **1966**, *31*, 3310, note 9.

[13] The mass spectrum of 19 does not show the molecular ion because of the complete loss of HCN due to its thermal decomposition. The presence of the CN group is confirmed by the very intense m/e 27 ion corresponding to HCN loss.

Crystal Structure of "Homoaromatic" 6-Ethyl-3-phenyl-1,6-dihydro-1,2,4,5-tetrazine[1a]

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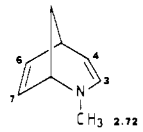
Received November 17, 1981

The crystal structure of 6-ethyl-3-phenyl-1,6-dihydro-1,2,4,5-tetrazine (3) was elucidated by X-ray structure analysis. This analysis revealed that the molecule is in a boat conformation with C(6) and C(3) pointing upward with dihydral angles of 49.3° and 26.7°, respectively. N(1) was found to be sp^2 hybridized, and the N(1)–N(2), N(2)–N(3), C(3)–N(4), and N(4)–N(5) bond distances were found to be between single and double bond length, in agreement with the expected electron delocalization.

^{1}H NMR spectroscopy[2] revealed that 1,6-dihydro-1,2,4,5-tetrazines are homoaromatic[3,4] species. The aromatic sextet is formed by the four electrons in the two double bonds and the lone pair of N(1); therefore, a 1,6-dihydro-1,2,4,5-tetrazine can be considered as a monohomotetrazole. In order to enable electron delocalization in the aromatic part, homoaromatic compounds have to be nonplanar with one methylene group pointing out of the plane; consequently, the p$_z$ orbitals of the atoms adjacent to the methylene bridge are canted. Therefore, the overlap here becomes restricted to single lobes at the side of the molecule opposite the bridging atom. For this reason 1,6-dihydro-1,2,4,5-tetrazines were considered[2] to contain an approximately planar tetrazine ring (see Figure 1) with a shortened N(1)–N(5) distance with respect to the corresponding distance in 1,2,4,5-tetrazine, so that overlap and delocalization are possible.

There are very few reports in the literature about homoaromatic compounds containing heteroatoms in their ring: e.g., the UV spectrum of *N*-methyl-2-azabicyclo[3.2.1]octa-3,6-diene (1)[5] can be explained by the assumption of a homoaromatic contribution; the 1,4-dihydropyridyl anion (2)[6], on the contrary, was not found to be a homoaromatic species. By use of ^{1}H NMR spectroscopy, 6-ethyl-3-phenyl-1,6-dihydro-1,2,4,5-tetrazine (3) was found to exist in one conformation in solution.[2] The hydrogen at the sp^3 carbon atom is above the tetrazole ring, and the alkyl group is in the exo position. In contrast, at room temperature, 3-phenyl-1,6-dihydro-1,2,4,5-tetrazine (4) undergoes an inversion between two conformations, one with the methylene group pointing upward and the other with the methylene downward.[2] Since 3 is easily obtained in crystalline form, it is possible to obtain direct information about the correctness of the assumed conformation by a crystal structure determination.



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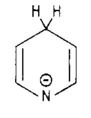

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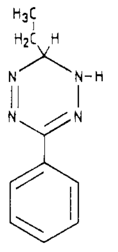

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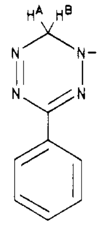

4

Results and Discussion

The crystals of 3 (from pentane/ether) are orthorhombic, with space group P_{bca}. The unit cell which has dimensions a = 8.349 (1), b = 10.252 (1), and c = 23.041 (2) Å and contains eight molecules of 3, leading to a calculated density of 1.267 g cm^{-3}. A total of 1454 reflections were collected at 223 K (because the compound decomposes at room temperature) on a Nonius CAD-4 automatic fractometer by using graphite-monochromatized Cu Kα radiation. No absorption correction was applied (crystal

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[1] (a) Part 6 on 1,2,4,5-tetrazines and their derivatives. For part 5 see: Counotte-Potman, A.; Van der Plas, H. C.; Van Veldhuizen, A.; Landheer, C. A. *J. Org. Chem.* **1981**, *46*, 5102. (b) Laboratory of Crystallography, J. H. van't Hoff Institute, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WS Amsterdam, The Netherlands.

[2] Counotte-Potman, A.; van der Plas, H. C.; Van Veldhuizen, A. *J. Org. Chem.* **1981**, *46*, 2138.

[3] Winstein, S. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 22.

[4] Paquette, L. A. *Angew. Chem.* **1978**, *90*, 114.

[5] Anastasiou, A. G.; Kasmai, H. *J. Chem. Soc., Chem. Commun.* **1975**, 201.

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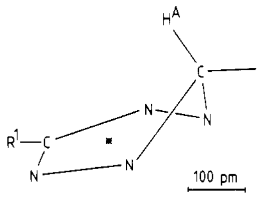

Figure 1. Perspective drawing of 1,6-dihydro-1,2,4,5-tetrazine.

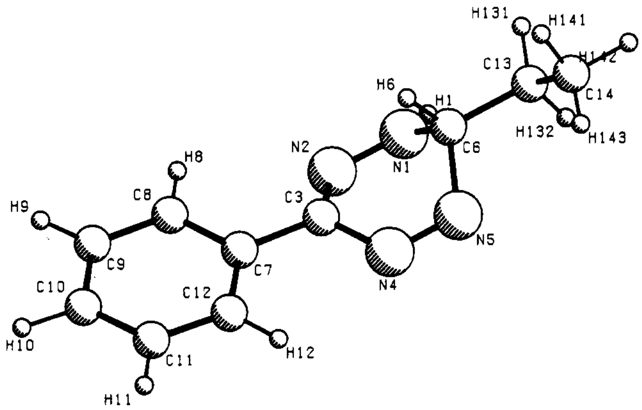

Figure 2. Three-dimensional structure of 3.

Table I. Bond Distances[a] and Interbond Angles[b] in 6-Ethyl-3-phenyl-1,6-dihydro-1,2,4,5-tetrazine (3)[c]

N(1)-N(2)	1.319 (4)	N(1)-N(2)-C(3)	113.4 (3)
N(1)-H(1)	.94 (4)	N(2)-N(1)-H(1)	123 (2)
N(2)-C(3)	1.333 (4)	C(6)-N(1)-H(1)	119 (2)
C(3)-N(4)	1.388 (4)	N(2)-C(3)-N(4)	117.9 (3)
N(4)-N(5)	1.271 (4)	N(2)-C(3)-C(7)	120.0 (3)
N(5)-C(6)	1.493 (4)	C(6)-N(5)-N(4)	111.7 (3)
C(6)-N(1)	1.435 (4)	C(3)-N(4)-N(5)	119.9 (3)
C(6)-H(6)	1.07 (4)	N(1)-C(6)-N(5)	102.9 (3)
C(6)-C(13)	1.509 (4)	N(2)-N(1)-C(6)	117.7 (3)
C(3)-C(7)	1.466 (4)	N(1)-C(6)-H(6)	105 (2)
C(7)-C(8)	1.398 (4)	N(5)-C(6)-C(13)	111.9 (3)
C(8)-C(9)	1.381 (5)	N(5)-C(6)-H(6)	107 (2)
C(9)-C(10)	1.408 (5)	C(13)-C(6)-H(6)	115 (2)
C(10)-C(11)	1.368 (6)	N(1)-C(6)-C(13)	114.4 (3)
C(11)-C(12)	1.381 (5)	N(4)-C(3)-C(7)	119.7 (3)
C(12)-C(7)	1.405 (4)	C(3)-C(7)-C(8)	120.4 (3)
		C(3)-C(7)-C(12)	121.2 (3)

[a] In angstroms (1 Å = 100 pm). [b] The average value of the C(*n*)-C(*m*)-H(*m*) bond angle is 120° in the case where C(*m*) is sp^2 hybridized and 109° in the case where C(*m*) is sp^3 hybridized. [c] The estimated standard deviations are in parentheses.

dimensions 0.25 × 0.25 × 0.05 mm; $\mu = 6.1\ \text{cm}^{-1}$).

The crystal structure was determined by a straightforward application of the symbolic addition program system SIMPEL.[7] Refinement proceeded by block-diagonal least-squares calculations, anisotropic for C and N and isotropic for H. The H atoms were located in a ΔF synthesis. The final *R* value was 0.053.

The conformation of the molecule and the atomic numbering are shown in Figure 2. As predicted from the ^1H NMR spectroscopic data[2], H(6) is indeed found above the tetrazole ring, and the ethyl group is in the exo position. The bond distances and angles are listed in Table I.

In Table II the distances of the tetrazine ring atoms from the best plane through N(1)–N(2)–N(4)–N(5) are given. From this table it is seen that the tetrazine ring is in a boat conformation, and, consequently, the tetrazole part of the homotetrazole is not planar as originally suggested (Figure 1). The planes through N(2)–C(3)–N(4) and through N(1)–C(6)–N(5) make dihedral angles of 26.7° and 49.3°, respectively, with the plane through N(1)–N(2)–N(4)–N(5). C(3) deviates significantly from plane. The angles around C(3) add up to only 357.5°, and the distance from the plane through N(2), N(4), and C(7) is 0.13 Å. This, however, will not noticeably afffect the sp^2 character of C(3). The benzene ring is planar within 0.013 Å (Table II). C(3) deviates significantly (0.049 (3) Å) from this plane.

Table II. Distances (Å) from the Best Planes through N(1), N(2), N(4), and N(5) (A) and C(7)-C(12) (B)

A		B	
atom	distance	atom	distance
N(1)	0.002 (2)	C(7)	0.009 (3)
N(2)	−0.002 (2)	C(8)	−0.013 (3)
N(4)	0.002 (3)	C(9)	0.008 (4)
N(5)	−0.002 (2)	C(10)	0.002 (4)
C(3)	0.315 (3)	C(11)	−0.007 (4)
C(6)	0.690 (3)	C(12)	0.002 (3)
		C(3)	−0.049 (3)

Table III. Bond Lengths (Å) and Bond Orders for Bonds between C and N Atoms in Which Both Atoms Are Assumed to Have sp^2 Hybridization

	bond order		
bond type	1.0	1.5	2.0
C-C	1.48	1.39	1.34
C-N	1.45	1.34	1.27
N-N	1.41	1.31	1.23

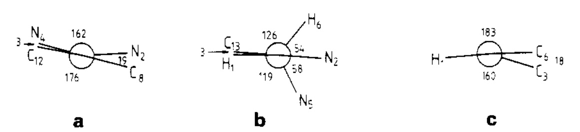

Figure 3. Newman projections: a, along the C(7)–C(3) bond; b, along the N(1)–C(6) bond; c, along the N(1)–N(2) bond.

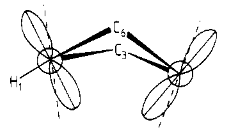

Figure 4. Newman projections along the N(1)–N(2) and the N(5)–N(4) bonds: closed lines, p_z orbitals of N(1) and N(5); dotted lines, p_z orbitals of N(2) and N(4).

The Newman projection along C(7)–C(3) (see Figure 3a) shows the position of the benzene ring relative to the tetrazine ring. N(1) is involved in a hydrogen bond of 2.97 Å with N(4) of the molecule at $^1/_2 - x, {}^1/_2 + y, z$. [Another important piece of information from this X-ray structural determination is the fact that N(1), which carries the hydrogen, is sp^2 hybridized.] The coplanarity of H(1) with N(1), N(2), and C(6) [H(1) is at 0.04 (4) Å from the plane of these three atoms] leaves no doubt about the sp^2 character of N(1). This can also be seen from the Newman projections along the N(1)–N(2) and the N(1)–C(6) bonds in Figure 3b,c.

The sp^2 hybridization of N(1) is essential to the proper orientation of the lone-pair electrons, necessary for overlap and electron delocalization. Connection of the Newman projections along the N(1)–N(2) and the N(5)–N(4) bonds results in Figure 4.

The p_z orbitals of the nitrogen atoms are perpendicular to the plane of the sp^2-hybridized orbitals as indicated in Figure 4. From this figure it is clear that the p_z orbitals of N(1) and N(5) are pointing toward each other and that

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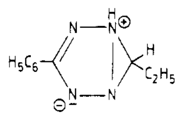
[7] Overbeek, R. A.; Schenk, H. In "Computing in Crystallography"; Schenk, H.; Olthof, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978.

consequently the homoallylic participation[2,8] is probable. A review of the relation between bond lengths and bond order for bonds between sp^2-hybridized carbon and nitrogen atoms was found in the literature[9] (see Table III). A localized single bond has a bond order of 1.0 and a localized double bond a bond order of 2.0.

The dimensions of 1,2,4,5-tetrazine[10] are as follows: C–N, 1.33 Å; N–N, 1.32 Å; C–N–N, 115°; N–C–N, 127°. Comparison with the bond angles and distances in **3** (see Table I) reveals that both the N(1)–N(2) (1.32 Å) and the N(4)–N(5) (1.27 Å) distances are larger than that in the localized double bond (1.23 Å) and smaller than that in the single bond (1.41 Å). Especially, the N(1)–N(2) distance is of the same magnitude as in 1,2,4,5-tetrazine (1.32 Å). Also the N(2)–C(3) (1.33 Å) and the N(4)–C(3) (1.39 Å) bond lengths are between those of the single and double bond lengths. These intermediate bond lengths are in agreement with the delocalization of the π electrons over these ring atoms. It is striking that especially the N(1)–N(2) bond is so aromatic.

On the basis of our model of homoaromaticity (see Figure 1), we would have expected that the N(1)–N(5) distance would have been shorter than the 2.29 Å actually found. It indicates that the contribution of the mesomeric structures **8** and **9** is small. It remains unanswered as to whether this is necessarily in conflict with the homoaromatic character, although the concept of homoaromaticity seems in our opinion to be the only explanation of the results of the ^{1}H and ^{13}C NMR[2,15] data measured in solution.



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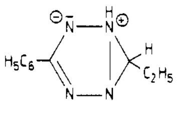
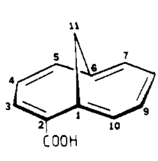


9

In some homoaromatic systems a similar distance has been observed by X-ray crystal analysis. For example in 1,6-methano[10]annulene-2-carboxylic acid (**5**) the 1,6-distance is 2.26 Å, and in bicyclo[5.4.1]dodecapentaenylium ion (**6**) the 1,6-distance is 2.30 Å;[12] yet in these compounds a considerable 1,6-overlap was established.[13] It is regrettable, however, that there are not more crystal structural data available for comparison.



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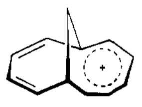

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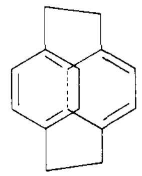

7

As the tetrazine part of **3** is boat shaped, the tetrazole ring of the homotetrazole is not planar but is puckered. There are some examples of "bent aromaticity" in the literature. An example is the [2.2]paracyclophane system (**7**).[14] In this strained molecule the benzene rings are boat shaped. Although the gradients amount to 13°, the benzene rings have preserved their normal aromatic properties. Also in the above-mentioned annulenes (**5** and **6**) the carbon atoms forming the 10-π-electron system are puckered.[11,12] From these examples it is clear that electron delocalization can occur in a not perfectly planar system.

In conclusion we want to stress the point that the crystal structure determination of **3** is not in conflict with our previous proposal of homoaromaticity, based on ^{1}H NMR data, but on the other hand is also not a dramatic affirmation of this phenomenon.

Editor's Note. This paper and the following paper by Hoskin, Wooden, and Olofson were reviewed together; both authors were invited to comment on the other paper.

Registry No. 3, 76630-76-7.

Supplementary Material Available: Final atomic parameters, thermal parameters, and bond distance (3 pages). Ordering information is given on any current masthead page.

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[13] Dewey, N. J., Deger, H.; Fröhlich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412.

[14] Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204.

Homoaromaticity and the 1,1,4-Trimethyl-1,4-dihydro-1,2,4,5-tetrazinium Cation: Evidence from a Crystal Structure Determination

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Received January 6, 1981 (Revised Manuscript Received January 6, 1982)

Because the ^{1}H and ^{13}C NMR spectra of the title cation (**2**) are most easily rationalized by including a strong "ring current" effect, **2** has previously been assigned a homoaromatic structure. The fluorosulfate salt of **2** has now been prepared, and crystals suitable for a single crystal X-ray structure determination have been obtained: $C_5H_{11}FN_4O_3S$, orthorhombic, space group $P2_12_12_1$, cell dimensions a = 9.376 (2) Å, b = 16.716 (5) Å, c = 6.181 (7) Å, V = 969 (2) Å^3, Z = 4, final R = 0.060. The quaternary nitrogen (N1) is tetrahedral which causes the ring to assume a boat shape. There is evidence for substantial delocalization of the N4 electron pair (hybridization between trigonal and tetrahedral; N1 is 0.51 Å above the N2–C3–N5–C6 plane while N4 is only 0.26 Å above the same plane).

In 1972, the methylation of the dihydrotetrazine (**1**) to give the novel trimethyldihydrotetrazinium fluoroborate (**2a**, Chart I) was reported by this laboratory.[1] Because the ^{1}H NMR absorption of the methyls attached to the

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