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1,3,4,6-Tetramethyl-1,4-dihydro-1,2,4,5-tetrazine, C₆H₁₂N₄

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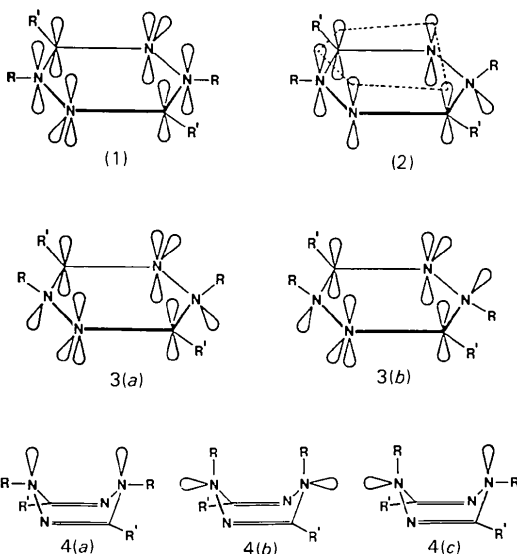
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Abstract. $M_r = 140.19$, monoclinic, $P2_1/n$, $a = 10.612$ (3), $b = 6.820$ (1), $c = 10.975$ (2) Å, $\beta = 95.31$ (2)°, $V = 790.9$ (5) Å³, $Z = 4$, $D_m = 1.13$ (5) (floatation), $D_x = 1.177$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.848$ cm⁻¹, $F(000) = 304$, $T = 295$ K, $R = 0.077$ for 704 observed reflections. This potentially antiaromatic or homoaromatic ring system has a flattened boat conformation with both N-methyls in equatorial positions. Bond angles and distances (excluding H's) predicted to be symmetry equivalent exhibit variations of 0.002–0.014 Å and 0.0–2.0°. Substantial delocalization of the electron lone pairs of N(1) and N(4) is found.

Introduction. In the past, planar antiaromatic (1), homoaromatic (2) and nonaromatic (3a), (3b) formulations as well as boat shapes (4) have been considered for the 8 π -electron-available 1,4-dialkyl-1,4-dihydro-1,2,4,5-tetrazines (Kohn & Olofson, 1972; Hoskin, Wooden & Olofson, 1982). In a boat conformation, both N-alkyl groups may be axial, both equatorial or one axial and one equatorial (4a)–(4c). Previous NMR studies indicate that in solution the system is either symmetrical or rapidly inverting (Kohn & Olofson, 1972). An earlier attempt to resolve the structural ambiguity by solving the structure of 1,4-

dimethyl-1,4-dihydro-1,2,4,5-tetrazine failed because the molecule was disordered in the crystal (Hoskin, 1981). A single-crystal X-ray diffraction study of the 1,3,4,6-tetramethyl-substituted 1,4-dihydro-1,2,4,5-tetrazine [(1)–(4), $R = R' = \text{Me}$] is presented here.



Experimental. Preparation by reaction of ethyl acetimidate.HCl with methylhydrazine (adapted from Kohn & Olofson, 1972), m.p. 363–365 K, lit. 364–365 K (Skorianetz & Kovats, 1972); very volatile solid slowly crystallized from dried hexanes; irregularly shaped piece (0.30 × 0.30 × 0.64 mm) cut from larger crystal and mounted in capillary. Unit-cell parameters (least squares) from 20 reflections in θ range 6–13°; Enraf–Nonius CAD-4 diffractometer (graphite monochromator); data corrected for Lorentz and polarization factors but not for absorption; min. $(\sin\theta)/\lambda = 0.040$, max. $(\sin\theta)/\lambda = 0.5323 \text{ \AA}^{-1}$; h, k, l min. 0, 0, -11, max. 11, 7, 11; 3 standard reflections every hour (drift correction: empirical 0.996–1.000, intensity variation 0.9%, anisotropic 0.990–1.038); 1168 reflections measured, 1004 unique; $R_{\text{int}} = 0.014$; 300 unobserved [$I < 2\sigma(I)$]; structure solved by direct methods (*MULTAN78*) with all non-H atoms refined anisotropically; * H's located from difference Fourier maps and refined with B_{iso} fixed at 5.0 \AA^2 ; 127 parameters refined; $R = 0.077$, $wR = 0.097$, $S = 2.69$; Corfield, Doedens & Ibers (1967) weighting scheme, $p = 0.06$, $w = F^2/\sigma^2(F^2)$; max. $\Delta/\sigma = 0.02$; max. height in final difference Fourier map = 0.166 e \AA^{-3} ; f, f'' from Cromer & Waber (1974) compilation; programs: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *SDP-Plus* version 1.0 (Frenz, 1983), *ORTEPII* (Johnson, 1965).

Discussion. Atomic positional parameters are listed in Table 1 and significant bond distances and bond angles are given in Fig. 1 along with the crystallographic numbering system. From the stereoscopic view in Fig. 2, it is evident that the molecule has adopted a flattened boat shape with pyramidal N-methyl nitrogens [N(1) and N(4)] at the prow and stern. Bond distances and angles expected to be symmetry equivalent exhibit variations of 0.002–0.014 Å and 0.0–2.0° (excluding H's). Both N-methyls [C(7) and C(9)] are pseudo-equatorial and the relationship between the H's on C(7) and C(9) and the substituents along with the sp^3 part of the lone pairs on the attached N(1) and N(4) is a nicely staggered one. The H's on the methyls [C(8) and C(10)], while nearly staggered with respect to the substituents on C(3) and C(6), are somewhat skewed, possibly from an attractive interaction between H and the sp^2 lone pairs on N(2) and N(5). N(1) and N(4) are only 0.240 (3) and 0.249 (3) Å from the planes made by the attached N(2)–C(6)–C(7) and N(5)–C(3)–C(9), respectively. Thus, substantial delocalization of

the N(1) electron pair to N(5) [and of N(4) to N(2)] is predicted and is confirmed by the small difference between the lengths of the classically double-bonded C(6)=N(5) (1.32 Å) vs the single-bonded C(6)–N(1) (1.38 Å) [also C(3)–N(4) 1.39 and C(3)=N(2) 1.31 Å]. These differences are similar to those found for C(3)–N(4) (1.35 Å) and C(3)=N(2) (1.29 Å) in the 1,1,4-trimethyl-1,4-dihydro-1,2,4,5-tetrazinium cation (Hoskin, Wooden & Olofson, 1982). There both

Table 1. Positional coordinates and B_{eq} (Å²) values

$$B_{eq} = \frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$$

	x	y	z	B_{eq}
N(1)	0.0513 (3)	0.1650 (5)	0.7071 (3)	6.68 (8)
N(2)	-0.0606 (2)	0.1874 (4)	0.7562 (2)	4.11 (6)
N(4)	-0.0206 (3)	-0.1213 (5)	0.8375 (3)	7.34 (8)
N(5)	0.0567 (2)	-0.1683 (4)	0.7499 (2)	4.47 (6)
C(3)	-0.1043 (3)	0.0325 (5)	0.8098 (3)	5.34 (8)
C(6)	0.0818 (3)	-0.0237 (5)	0.6757 (3)	6.00 (8)
C(7)	0.0890 (3)	0.3272 (6)	0.6350 (3)	6.13 (9)
C(8)	-0.2144 (3)	0.0551 (6)	0.8763 (3)	5.71 (9)
C(9)	-0.0583 (4)	-0.2848 (6)	0.9087 (4)	6.7 (1)
C(10)	0.1772 (3)	-0.0566 (6)	0.5907 (3)	6.16 (9)

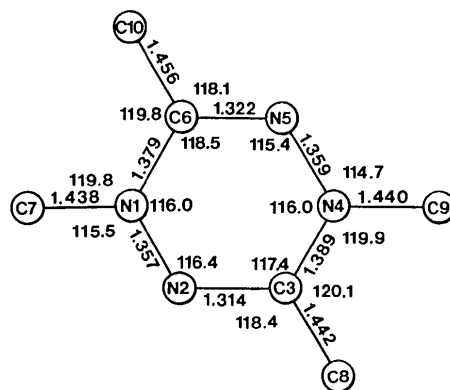


Fig. 1. Crystallographic numbering system with bond distances (Å) and angles (°) for non-H atoms (e.s.d. ranges are 0.003–0.004 Å and 0.2°).

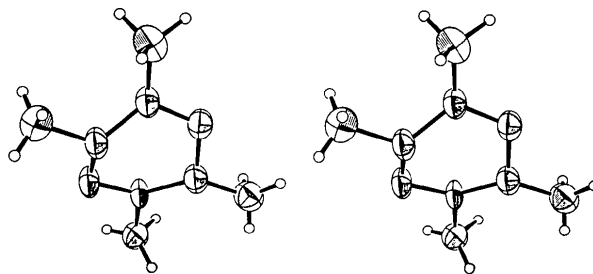


Fig. 2. Stereoscopic view with thermal ellipsoids for non-H atoms at 35% probability.

* Complete bond distances and angles, least-squares planes, anisotropic thermal parameters, structure factors and a stereo packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39677 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds in an unsymmetrically flattened boat are somewhat shorter because of the attractive effect of the positive charge. Since C(3) is only 0.162 (3) Å from the N(2)—N(4)—C(8) plane [and C(6) 0.151 (3) Å from N(1)—C(5)—C(10)], near sp^2 hybridization at C(3) [and C(6)] is indicated. The symmetry of the system is further evident from a comparison of the distances of related atoms from the C(7)—N(1)—N(4)—C(9) plane (0.002–0.003 Å): N(2) 0.283 (2) vs N(5) 0.272 (3) Å, C(3) 0.443 (3) vs C(6) 0.406 (3) Å, C(8) 0.584 (4) vs C(10) 0.519 (4) Å; similarly using the C(10)—C(6)—C(3)—C(8) plane (0.005–0.011 Å): N(1) 1.131 (3) vs N(4) 1.117 (3) Å, N(2) 1.169 (3) vs N(5) 1.177 (3) Å, C(7) 2.399 (4) vs C(9) 2.392 (4) Å.

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Struktur von 1,8-Di-2-pyridyl-3,6-dithiaoctan, $C_{16}H_{20}N_2S_2$

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Abstract. $M_r = 304.48$, monoclinic, $P2_1/c$, $a = 15.189$ (3), $b = 4.825$ (9), $c = 11.833$ (2) Å, $\beta = 107.64$ (1)°, $V = 826.3$ Å³, $Z = 2$, $D_x = 1.224$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 3.015$ cm⁻¹, $F(000) = 324$, $T = 293$ K, final $R = 0.057$ for 1032 significant [$I > 2\sigma(I)$] reflections. In the crystal structure the molecule exhibits the form of a chain, the pyridine rings being *trans* orientated. There are no unusual bond distances or angles.

Einleitung. 1,8-Di-2-pyridyl-3,6-dithiaoctan (bpdto) kann als vierzähliger N,S,S',N' - und als zweizähliger N,N' -Chelatligand fungieren (Castineiras, Molleda, Masaguer & Coto, 1983). Im Rahmen unserer Untersuchungen über Komplexe von Kobalt(II) mit bpdto (Castineiras, Hiller, Strähle, Paredes & Sordo, 1984) als Modellsubstanzen für die homogene Katalyse berichten wir im folgenden über die Kristallstruktur des Chelatliganden bpdto.

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Experimentelles. Farblose Kristallnadeln von bpdto wurden durch Umsetzung von 1,2-Ethandithiol mit 2-Vinylpyridin erhalten (Goodwin & Lions, 1960). Die Substanz kristallisiert in schlechter Qualität. Kristallgröße 0,9 × 0,15 × 0,1 mm, Buerger-Präzessionsaufnahmen: monoklin, $P2_1/c$. Vierkreisdiffraktometer CAD-4 von Enraf-Nonius, Mo $K\alpha$ -Strahlung, Graphitmonochromator. Ermittlung der Gitterkonstanten anhand von 25 genau zentrierten Reflexen hoher Beugungswinkel ($3^\circ < \theta < 27^\circ$). Registrierung der Intensitäten mit $2\theta/\theta$ -scan, $\theta_{\max} = 31^\circ$. Keine signifikante Änderung der Intensitäten der Kontrollreflexe im Verlauf der Messung. $h + 22$, $k \pm 7$, $l \pm 17$. 3599 gemessene Reflexe, 2629 unabhängige Reflexe, 1032 Reflexe mit einer Intensität $I > 2\sigma(I)$, die für die Verfeinerung verwendet wurden. LP-Korrektur, Extinktionskorrektur, auf eine Absorptionskorrektur wurde verzichtet. Strukturaufklärung mit *MULTAN80* (Main *et al.*, 1980); H-Atomlagen wurden einer

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