Polish J. Chem., **77**, 1427–1435 (2003)

Structure of Pyridine-2-azo-*p*-phenyltetramethylguanidine*

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(Received February 28th, 2003; revised manuscript June 25th, 2003)

Replacement of dimethylamino group in pyridine-2-azo-p-dimethylaniline (PADA) by a stronger electron – releasing tetramethylguanidil (TMG) group forms a new complexing agent, pyridine-2-azo-*p*-phenyltetramethylguanidine (PAPT). The substitution does not enhance the expected complexing ability of PAPT in comparison with that of PADA. For steric reasons the tetramethylguanidil substituent CN_3 and phenyl ring are not coplanar, which makes the resonance between them limited. This manifests in small contribution of quinoid form in the canonical structure distribution. The additivity of angular parameters in the phenyl ring is preserved.

Key words: pyridine-2-azo-*p*-phenyltetramethylguanidine (PAPT), chelate ligand of metal-d, through resonance of *p*-substituents, canonical structure distribution, quinoid form contribution, additivity of angular parameters

Pyridine-2-azo-*p*-dimethylaniline (PADA), originally synthesized by Faessinger and Brown [1], has been thoroughly examined with respect to its ability to chelate several metal ions with d-orbitals [2–4]. Taking into account the usefulness of PADA as a chelating agent of several metal ions, in particular nickel(II) [5], Leffek and Jarczewski assumed that PADA analogue with a stronger electron-releasing group, tetramethylguanidil (TMG) instead of dimethylamino group could have a stronger ability to bond metal ions with d-orbitals than PADA itself [6]. The strongly electron-releasing effect of TMG group was already proved [7]. The new compound, pyridine-2-azo-*p*-phenyltetramethylguanidine (PAPT) was synthesized by a modified Faessinger method [1] and carefully examined in water and acetonitrile solvents [6].

The dissociation constants of the conjugate acid in water are $pK'_a = 10.41$ and $pK''_a = 2.62$ and in acetonitrile $pK'_a = 18.0$ and $pK''_a = 10.4$. The properties of metal-ligand chelates in acetonitrile have been examined and the stability constants of Ni^{2+}, Co^{2+} and Zn^{2+} complexes determined [6]. PAPT was also studied by osmometric method and FT-IR spectroscopy and the results suggest that PAPT exists in acetonitrile as a monomer, whereas the monoprotonated and Li^+ complexes are in the form of dimers with the intramolecular hydrogen or lithium bonds, $N^+–H\cdots N$ and $N^+–Li\cdots N$ bonds, respectively [8]. In general, the expected enhancement of the metal ion complexing ability of PAPT was not found. This was due to its strong proton acceptor pro-

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

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perties, so the trace of water in solution converts the PAPT to its mono- and diprotonated cations [6].

The aim of this paper is to determine the crystal structure of PAPT, so that the acid-base and chelating properties of this compound could be better understood.

RESULTS AND DISCUSSION

The asymmetric unit contains one molecule of PAPT. The perspective view of the molecule together with the numbering scheme is given in Fig.1 and the selected bond lengths and bond angles are presented in Table 1.

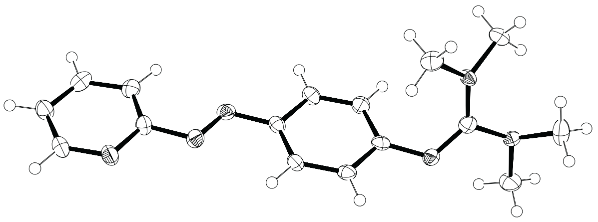

Figure 1. Displacement ellipsoid representation and the labeling scheme of the pyridine-2-azo-*p*-phenyltetramethylguanidine (PAPT). The ellipsoids are drawn at 50% probability level, hydrogen atoms are spheres of arbitrary radii.

Table 1. Selected bond lengths (Å) and bond angles (deg).

N(7)–N(8)	1.261(4)	C(16)–N(18)	1.378(4)
N(7)–C(2)	1.441(4)	N(17)–C(19)	1.474(4)
N(8)–C(9)	1.417(4)	C(12)–N(15)	1.391(4)
C(9)–C(10)	1.417(5)	N(15)–C(16)	1.307(5)
C(10)–C(11)	1.368(5)	C(16)–N(17)	1.348(5)
C(11)–C(12)	1.410(5)	C(16)–N(18)	1.378(4)
C(12)–C(13)	1.413(5)	N(17)–C(19)	1.474(4)
C(13)–C(14)	1.377(5)	N(17)–C(20)	1.462(5)
C(14)–C(9)	1.395(5)	N(18)–C(21)	1.472(4)
C(16)–N(17)	1.348(5)	N(18)–C(22)	1.469(5)
C(9)–C(10)–C(11)	120.7(4)	C(12)–N(15)–C(16)	122.5(4)
C(10)–C(11)–C(12)	121.1(4)	N(15)–C(16)–N(17)	126.9(4)
C(11)–C(12)–C(13)	117.7(4)	N(15)–C(16)–N(18)	118.1(4)
C(12)–C(13)–C(14)	121.3(4)	N(17)–C(16)–N(18)	115.0(4)
C(13)–C(14)–C(9)	120.5(4)	C(16)–N(17)–C(19)	122.8(3)
C(14)–C(9)–C(10)	118.6(3)	C(16)–N(17)–C(20)	123.9(3)
C(2)–N(7)–N(8)	112.4(3)	C(16)–N(18)–C(21)	120.4(3)
N(7)–N(8)–C(9)	114.2(3)	C(16)–N(18)–C(22)	117.8(3)

The pyridine-azophenyl moiety of PAPT displays most of azobenzene structural features, which have been found for the non-disordered molecule in the room temperature and for the structure determined at 82 K [9–11]. Thus, the observed length of N(7)=N(8) of 1.261(4) Å compares well with that in azobenzene at 82 K. On the other hand, the bond lengths N(7)–C(2) and N(8)–C(9) are unequivalent in contrast to azobenzene, they differ by 5σ but the molecule does not indicate any features of disorder. The azo-part of the PAPT molecule is flat, torsion angles around C(2)–N(7) and C(9)–N(8) are 0.6(5)° and –1.5(5)°, respectively. The adequate torsions in two independent azobenzene molecules in the structure of azobenzene are ±21.0(2)° and ±10.1(2)°, respectively [11]. The configuration of the azo-moiety indicated by the torsion angle C(2)–N(7)–N(8)–C(9) of –178.4(3)° is (*E*) in relation to N(7)=N(8) double bond.

The CN_3 fragment of the TMG substituent is flat and exists in the imino tautomeric form with the shortest bond length C(16)–N(15) of 1.307(5)Å. In general, the three C–N bonds are highly differentiated in neutral derivatives of guanidine [12], too. It is also the case of the TMG substituent. The C(16)–N(15) bond is slightly elongated in comparison with the C–N double bond – 1.28 Å (room temperature data). It is worth emphasizing that due to the frozen thermal motion at 100 K, the temperature of the PAPT data collection, all bond lengths are elongated in comparison with those derived from room temperature measurement. The scarcity of low temperature determinations makes all the comparisons difficult*.

The other two C–N bonds in the CN_3 group are longer than C(16)–N(15), namely, the C(16)–N(17) and C(16)–N(18) bonds are 1.348(5) Å and 1.378(4) Å, respectively, the difference between them is 5σ, both of them have partial double-bond character. These values correlate with the sum of the bond angles around N(17) and N(18) being 359.8(5)° and 351.2(5)°, respectively. The observed unequivalent bond lengths and a slight pyramidalization of the N(18) atom are probably caused by the steric strain which also exists in the other derivatives of neutral guanidine [12,13]. This conclusion is supported by the structure of protonated guanidines in which owing to the fact that protonation leads to the release of steric strain, all three C–N bond lengths are equalized and the cation is stabilized by the Y delocalization effect [12,14].

The steric hindrance from the methyl groups of the TMG is also the reason for a large torsion around the C(12)–N(15) bond, dihedral angle between the CN_3 group and the phenyl ring is as large as 62.8(1)°, what's more, the C(12) atom is out of the CN_3 plane by 0.525(6) Å. This conformation should strongly affect the extent of conjugation of the TMG group with the phenyl ring.

It has been found that in monosubstituted benzenes the skeletal deformations induced by the substitution do not extend beyond the half of the ring nearest the substi-

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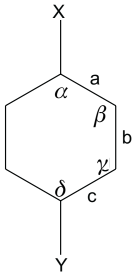
* Standard deviations for the bond lengths in PAPT are rather high as for the low temperature structure determination: they are within limits of 0.004–0.005 Å. This rather unsatisfying precision is caused probably by poor quality of the crystal. Similar difficulties were described by Tanatani *et al.*, [12].

tuent [15] and they concern both, the bond lengths and bond angles. The introduction of a second substituent *para* to the first one is expected, therefore, to have no appreciable effect on the geometry of the opposite part of the ring [16], unless through resonance between *para* substituents takes place. In PAPT the azopyridil fragment of the molecule, which possesses π-acceptor properties, is coplanar with the phenyl ring, whereas the *para* TMG substituent, a strong π-electron donor is twisted outwards of the phenyl ring as mentioned above and for this reason, the through resonance with the azo-group is expected to be hindered. The effect of through resonance manifests in lengthening of the *a* and *c* bonds accompanied by a "quinoidal" shortening of the *b* bonds [16] (Scheme 1).

Scheme 1

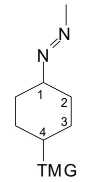
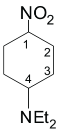
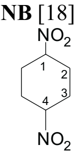
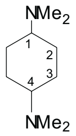


The analysis of the phenyl ring bond lengths in PAPT is interesting. Comparison of appropriate bond lengths in PAPT, diethyl-*p*-nitroaniline (DPNA) (π-electron cooperative effect) [17] and two reference compounds without the cooperative effect: *p*-dinitrobenzene (PDNB) [18] and tetramethyl-*p*-phenylenediamine (TMPD) [19] is given in Table 2.

The data indicate that the C2–C3 bond in PAPT is comparable with that in DPNA and is shorter than the appropriate bond lengths in the reference compounds PDNB and TMPD. The C1–C2 and C3–C4 bonds are in PAPT equal in their lengths and elongated in comparison with the bond lengths in unsubstituted benzene, also decreasing of C1–N and C4–N is found. This may be interpreted as a proof of a cooperative effect between the TMG and -N=N-R substituents, which induces certain contribution of the quinoid structure.

The bond length N(15)–C(12) is worth discussing. Its length of 1.391(4) Å is similar to that in *N*,*N*-dimethyl-4-nitro-2,6-xylidine (2,6-DNXY), 1.396(2) Å [20] and is significantly elongated in comparison with the N(amine)–C(phenyl) bond in *N*,*N*-diethyl-*p*-nitroaniline (DPNA), 1.354(4) Å [17]. In general, it follows from [21,22] that the C(phenyl)–N(amine) bond lengths are highly sensitive to steric hindrance. In 2,6-DNXY the steric hindrance of two *ortho*-methyl groups results also in a considerable dihedral angle between the planes of the amino and the phenyl ring equal to 60.4(2)°, the value similar to that found for PAPT.

Table 2. Comparison of bond lengths in PAPT, N,N-diethyl-*p*-nitroaniline (DPNA), *p*-dinitrobenzene (PDNB) and tetramethyl-*p*-phenylenediamine (TMPD) (Å).

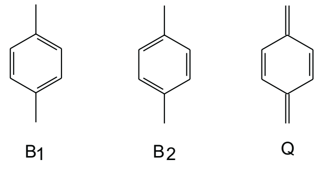
Compound	C1–N	C1–C2	C2–C3	C3–C4	C4–N
PAPT 	1.417(4)	1.406(4)[a]	1.375(4)[a]	1.412(4)[a]	1.391(4)
DPNA [17] 	1.433[b]	1.386[b]	1.366[b]	1.420[b]	1.354[b]
PDNB [18] 	1.478[a]	1.176[a]	1.387[a]		
TMPD [19] 			1.390[a]	1.401[a]	1.407[a]

[a] Mean values of two symmetrical bond length (C_{2v} symmetry of the phenyl ring assumed).
[b] Mean values of two molecules in the asymmetric unit and of all symmetrically equivalent bonds.

The observed geometry has been used to estimate the canonical structure distribution by applying the HOSE model [23,24][*].

Three canonical structures of the phenyl ring have been taken into account: B_1, B_2 and Q (Scheme 2):

Scheme 2



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[*] According to the analysis made by Krygowski *et al.* [23], the precision of PAPT determination is sufficient for successful application of the HOSE model.

The results obtained are as follows: $\%B_1 = 40.8$, $\%B_2 = 32.1$, and $\%Q = 27.1$.

Relatively small participation of the quinoid form indicates the hindered influence of through resonance between the substituents on the ring geometry. Our conclusion is in line with that obtained by Maurin and Krygowski [20] who found that the value of %Q for weakly interacting substituents is in the range of 26–32.

The application of the Domenicano and Murray-Rust angular parameters [15] allowed the estimation if additivity of angular distortions caused by substituent effect is fulfilled in the case of PAPT. Table 3 shows the observed and calculated bond angles in the phenyl ring. Non-additivity of angular distortions proposed by Maurin and Krygowski [17] is given by formula:

$$NA = \sum_{i=1}^{6} \left| \Phi_{obs} - \Phi_{calc} \right|$$

The value of NA for the phenyl ring in PAPT is 1.5°, *i.e.* 0.25° per angle. Since σ for PAPT = 0.3–0.4°, it follows that the angular geometry does not differ from the additivity scheme. For comparison, the NA value for A and B molecules of DPNA, the compound with a strong through resonance [17], is 0.90° and 0.72° per angle.

In conclusion, the additivity of angular parameters in the phenyl ring of PAPT confirms only weak through resonance between the both *para*-substituents.

The azopyridil part of the molecule does not participate in the π-resonance: the N(7)–N(8) bond of 1.261(4) Å is a pure double bond, also the N(7)–C(2) bond of 1.441(4) Å, very long, does not prove any features of π-resonance. The internal bond angles of pyridine ring are highly changed but this effect is predominantly controlled by the σ-effects of the substituent [15].

All findings just presented are also confirmed by the enhanced basicity of PAPT: the dissociation constants of the conjugate acids in H_2O are $pK_a' = 10.41 \pm 0.06$ and $pK_a'' = 2.62 \pm 0.02$ [6]. The unprotonated form of PAPT exists only under strongly alkaline conditions, and already at pH = 10 two forms exist, the unprotonated form and the monoprotonated N(15) form. Strongly acid conditions, from pH = 2.5 to 1.0 shift the equilibrium to the diprotonated form (with the N(15) and N(1) protonated). Taking into account the acid-base behaviour of PAPT and its complexing abilities for Ni^{2+} [6], the PAPT molecule can be recognized rather as the one which consists of two separate compounds, each possessing a basic center: the first one is the TMG-phenyl part and the second – the azopyridil part with no interaction between them.

Table 3. Observed and calculated bond angles in the phenyl ring (deg)*.

Bond angle	Observed	Calculated
C(10)–C(9)–C(14)	118.6(3)	118.2(4)
C(9)–C(14)–C(13)	121.5(4)	121.1(2)
C(14)–C(13)–C(12)	121.3(4)	121.1(2)
C(13)–C(12)–C(11)	117.7(4)	117.8(4)
C(12)–C(11)–C(10)	121.1(4)	121.1(4)
C(11)–C(10)–C(9)	120.7(4)	121.1(2)

*Domenicano and Murray-Rust [15] angular parameters for -N=N-R and $-NMe_2$ substituents have been taken for calculation of the bond angles (the angular parameter for the TMG substituent has not been available).

EXPERIMENTAL

Single crystals of PAPT were obtained by slow evaporation of saturated heptane solution and a dark-red transparent crystal, m.p. 89°C; m/z (rel. int. %) 296(25.7), 268(12.6), 224(15.4), 197(12.9), 190(21.0), 146(20.3) was selected for the X-ray investigation. No phase transition was observed in the temperature range 293–100 K and the data collection was carried out at 100(2) K on a KUMA KM4CCD κ-geometry diffractometer with CCD detector [25], using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The measurement was performed in four separate runs (132 frames each). The ω width of each frame was 0.75°. The θ, κ and ϕ angles for the runs were chosen in such a way as to cover the appropriate part of the reflection sphere. Two reference frames were measured after every 50 frames of experiment; neither the geometry nor the intensity of the reflections in these frames changed during the data collection. Intensity data were corrected for Lorentz and polarization effects [26] but not for absorption. The unit cell parameters were calculated from the least-squares fit of the 1818 most intense reflections from the whole experiment [26]. Structure was solved with the SHELXS-97 program [27]. Full-matrix least squares refinement was carried out with the SHELXL-97 program [28]. Scattering factors incorporated in SHELXL-97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized with $w^{-1} = [\sigma^2(F_o)^2 + (0.0424P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Empirical extinction corrections were also applied according to the formula $F_c' = kF_c[1 + 0.001 \cdot x \cdot F_c^2\lambda^3/\sin2\Theta]^{-1/4}$ [28]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in idealized positions and refined using a "riding model". Crystal data and structure refinement details are given in Table 4.

Table 4. Crystal data and structure refinement.

Empirical formula	$C_{16}H_{20}N_6$
Formula weight	296.38
Temperature	100(2) K
Crystal system, space group	orthorhombic, $Pna2_1$
Unit cell dimensions	$a = 23.661(3)$ Å
	$b = 9.913(3)$ Å
	$c = 6.956(3)$ Å
Volume	1631.5(3) Å^3
Z, Calculated density	4, 1.207 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
$F(000)$	632

Table 4 (continuation)

Crystal size	0.05×0.25×0.35 mm
Theta range for data collection	3.30° to 24.98°
Index ranges	$-28 \leq h \leq 28, -7 \leq k \leq 11, -8 \leq l \leq 8$
Reflections collected / unique	8126/2857 [R(int) = 0.0684]
Completeness to theta = 24.98°	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2857/1/200
Goodness-of-fit on F^2	0.965
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1042
R indices (all data)	R1 = 0.1016, wR2 = 0.1155
Extinction coefficient	0.0122(15)
Largest diff. peak and hole	0.188 and –0.185 e·Å^{-3}

Additional crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 215035. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB 1EZ, UK. Fax: +44-1223-336033. e-mail: deposit@ccdc.cam.ac.uk

Acknowledgments

The authors are grateful for financial support from the Polish State Committee for Scientific Research (KBN grant 7 T09A 074 21), and for the funds from Faculty of Chemistry, A. Mickiewicz University.

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