

Synthesis and Structure of the Picrate Salt of 2,2'-Bis[2*N*-(1,1,3,3-tetramethylguanidino)]biphenyl

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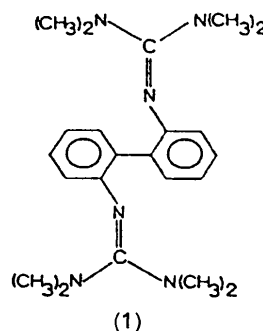
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Abstract. 2,2'-(2,2'-Biphenyldiyl)bis(1,1,3,3-tetramethylguanidinium) dipicrate, $C_{22}H_{34}N_6^{2+} \cdot 2C_6H_2N_3O_7^-$, $M_r = 838.74$, tetragonal, $P4_12_12$, $a = 12.372$ (5), $c = 25.370$ (10) Å, $V = 3882.95$ Å³, $Z = 4$, $D_x = 1.435$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu = 1.064$ cm⁻¹, $F(000) = 1752$, $T = 291$ K, $R_m = 0.0572$ for 2694 unique reflections. The dihedral angle between the planes of the two benzene rings is 80.4 (12)° and the inter-ring C—C bond length is 1.466 (15) Å, one of the shortest observed in biphenyl compounds. Evidence of the delocalization of the positive charge onto all three N atoms of the tetramethylguanidino group is given by the similarity and shortness of all three C—N bond lengths: N(2)—C(7) = 1.339 (14), N(1)—C(7) = 1.311 (13) and N(3)—C(7) = 1.335 (13) Å.

Introduction. There has been considerable research activity recently on a class of diamines which have enhanced basicity owing to the fact that protonation leads to the release of steric strain in the substrate molecule. Such compounds are known as 'proton sponges', as a result of the trade name introduced by the Aldrich Chemical Company for the first example of this type of compound, 1,8-bis(dimethylamino)naphthalene (Alder, Bowman, Steele & Winterman, 1968). Recently, proton sponges have been investigated with a variety of rigid carbon skeletons to which dimethylamino groups were attached in positions inducing steric strain in the molecule (Staab & Saupe, 1988). This work was extended to the biphenyl system in which two *ortho*-dimethylamino groups induced no steric strain in the substrate molecule because they were able to move away from each other by rotation about the central inter-ring C—C bond. Thus, although 2,2'-bis(dimethylamino)biphenyl is not a proton sponge because it is not a sterically strained molecule, it was shown that it gives a monohydrobromide when reacted with hydrogen bromide in *n*-hexane, and the X-ray structure of the cation showed that the proton formed an almost linear bridge between the two N atoms which are 2.65 Å apart (Staab & Saupe, 1988).

This paper extends the above work with an investigation of the characteristics of the tetramethylguanidino group substituted in place of the dimethylamino groups, by the preparation of 2,2'-bis[2*N*-(1,1,3,3-tetramethylguanidino)]biphenyl (1).



Experimental. 2,2'-Bis[2*N*-(1,1,3,3-tetramethylguanidino)]biphenyl was prepared by the reaction of the salt formed between phosgene, tetramethylurea and 2,2'-diaminobiphenyl. A solution of tetramethylurea (11 g in toluene) at 273 K was added dropwise to 100 ml of 0.193*M* phosgene in toluene and stirred for 2 h. The solvent was evaporated under vacuum leaving a white salt to which 200 ml of dry acetonitrile was added. A solution of 2,2'-diaminobiphenyl (5 g in 20 ml of dry acetonitrile) was added and the reaction mixture refluxed overnight. After evaporation of the acetonitrile, the solid residue was triturated with ether and 25% aqueous NaOH. The ether extract was dried and evaporated to yield 5.0 g of the product (48% yield based on the 2,2'-diaminobiphenyl). ¹³C NMR δ : C1 133.7, C2 150.6, C3 122.7, C4 127.1, C5 119.4, C6 131.7, C7 157.9, C8 39.7. ¹H NMR δ : 6.78–7.30 (8H, *m*), 2.50 (24H, *s*); mass spectrum (relative intensity, %) 380 (69), 336 (25), 180 (27), 146 (37), 100 (100), 85 (66).

The picrate of the biphenyl base was prepared by dissolving the biphenyl in absolute ethanol and titrating this solution with a saturated solution of picric acid in ethanol using a glass electrode. The precipitate was dissolved by heating the suspension and, after cooling, the crystals were filtered. A

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second crystallization from ethanol was followed by drying in a vacuum desiccator.

A crystal of approximate dimensions $0.05 \times 0.15 \times 0.5$ mm was mounted on a glass fibre. An Enraf-Nonius CAD-4 diffractometer was used to measure the unit-cell dimensions and to collect the data [2θ 4–46°; hkl : 0–13, 0–13, 0–27; $\omega/2\theta$ scan; ω -scan width $(1 + 0.35 \tan \theta)^\circ$ at 1.6 – $3.3^\circ \text{ min}^{-1}$, extended 25% on each side for background measurement; three standards measured every hour (no intensity loss); 3123 reflections measured, 2694 unique, 1083 with $I > 3\sigma(I)$]. The unit-cell constants were obtained by least-squares analysis of the diffractometer setting angles of 25 well centred reflections in the range $2\theta = 28$ – 32° . While the small needle crystals diffracted well up to $2\theta = 32^\circ$, the intensities of the reflections fell off sharply after this angle and there were few significant reflections recorded above $2\theta = 40^\circ$. Attempts were made to collect the data at low temperatures but the crystal crumbled to dust at a temperature just below 273 K. The intensities were reduced to a standard scale using routine procedures (Cameron & Cordes, 1979). Lorentz and polarization corrections were applied and absorption corrections (Walker & Stuart, 1983) were performed. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and were corrected for the real and imaginary parts of anomalous dispersion. The structure was solved by using *SHELXS86* (Sheldrick, 1985), calculations and refinements were performed by using *SHELX76* (Sheldrick, 1976).

The systematically absent reflections confirmed the space group as $P4_12_12$. The positions of most atoms were determined from an E map (*SHELXS86*) and the remaining non-H atoms were located in subsequent difference Fourier syntheses. The structure was refined initially by a full-matrix least-squares procedure with independent isotropic temperature factors on the atoms. Absorption corrections were then applied (maximum/minimum transmission coefficients 1.15/0.56). H atoms were placed in their geometrically calculated positions (C—H = 1.08 Å) and then refined riding on C atoms [except the positional parameters of H(1) attached to N(1) which are not uniquely defined by the geometry]. The final refinements were with anisotropic temperature factors on the non-H atoms and individual isotropic temperature factors on the H atoms. A two-block-matrix least-squares method was employed with the cation in one block and the anion in the second block (159 and 147 variables). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where w is the weight. From the different weighting schemes tested the best results were obtained when unit weights were used during refinement. Final $R = 0.0684$. $S = 2.242$. No correction for extinction was applied. The final

difference map had no recognizable residual features (maximum $\Delta\rho = 0.3 \text{ \AA}^{-3}$, $\Delta/\sigma = 0.78$). Figs. 1 and 2 were produced with *CHEMGRAF* (Davies, 1983).

Discussion. The atomic positional parameters are listed in Table 1, the bond lengths and bond angles in Table 2, and a view of the molecule is shown in Fig. 1.* The crystal structure of the molecule shows that the biphenyl cation contains a crystallographic twofold axis which bisects the C—C bond connecting the two biphenyl groups. There are thus two picrate anions associated with each biphenyl cation, *i.e.* each N atom attached to a phenyl ring is protonated. Therefore, unlike 2,2'-bis(dimethylamino)biphenyl, the title compound does not exhibit properties analogous to proton sponges.

While the biphenyl fragment seems to be well behaved crystallographically, the picrate ion clearly suffers from considerable static or dynamic disorder. An examination of the unit-cell packing diagram* shows that the picrate ion sits in a channel which runs along c . This leaves ample scope for the ion to move within the structure. A rigid-body TLS analysis was performed (Schomaker & Trueblood, 1968) as implemented in *CRYSTALS* (Carruthers & Watkin, 1989), on this ion and showed two significant librations. The first is about an axis perpendicular to the plane of the ring and passes close to atom C(22) [Fig. 2(a)]. The second, perpendicular to the first, passes below the ring plane and is approximately in the C(21)—C(23) direction [Fig. 2(b)]. These librations have amplitudes of ± 4.6 and $\pm 5.3^\circ$ respectively. An examination of the diagrams in Fig. 2 indicates a qualitative agreement with these analyses, but the motion (or disorder) must be much more complex than this since the correlation between the observed and the calculated anisotropic thermal parameters is not good, $R = 14.9\%$ with an r.m.s. discrepancy almost 50% greater than the e.s.d.'s of the U_{ii} values determined from the X-ray data. In view of the poor TLS correlation, and thus the poor refinement model, the bond lengths and angles in the picrate ion were not corrected for thermal motion and must be regarded with considerable caution. The cation, on the other hand, seems to be thermally well behaved with no unusual anisotropic thermal parameters and no significant rigid-body librations.

In the guanadinium ion, the C(1)—C(1') bond distance of 1.466 (15) Å is one of the shortest distances found among a substantial number of

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55100 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic positional parameters and equivalent isotropic temperature factors (\AA^2) for $C_{22}H_{34}N_6^{2+} \cdot 2C_6H_2N_3O_7^-$

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$$

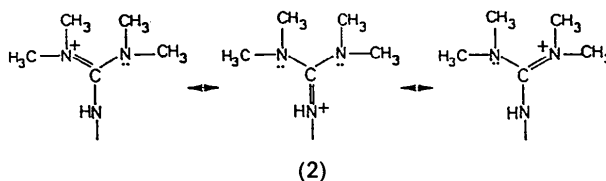
	x	y	z	U_{eq}
C(1)	0.5689 (8)	0.4860 (7)	-0.0041 (4)	0.0644
C(2)	0.6667 (8)	0.4884 (8)	0.0206 (4)	0.0603
C(3)	0.7432 (9)	0.4072 (8)	0.0125 (4)	0.0702
C(4)	0.7173 (10)	0.3208 (8)	-0.0190 (4)	0.0734
C(5)	0.6194 (10)	0.3130 (10)	-0.0450 (4)	0.0836
C(6)	0.5447 (9)	0.3982 (8)	-0.0349 (4)	0.0772
N(1)	0.8105 (6)	0.6476 (6)	0.1164 (3)	0.0607
N(2)	0.6933 (7)	0.5735 (6)	0.0586 (3)	0.0586
N(3)	0.8673 (6)	0.6252 (7)	0.0310 (3)	0.0620
C(7)	0.7914 (8)	0.6150 (7)	0.0681 (4)	0.0526
C(8)	0.7679 (9)	0.5958 (9)	0.1626 (4)	0.0830
C(9)	0.8704 (10)	0.7492 (10)	0.1258 (4)	0.0993
C(10)	0.9820 (8)	0.6238 (9)	0.0412 (3)	0.0746
C(11)	0.8412 (8)	0.6352 (8)	-0.0238 (3)	0.0755
O(21)	-0.0454 (6)	0.1729 (6)	0.1221 (3)	0.0978
C(21)	0.0447 (9)	0.1680 (10)	0.0997 (4)	0.0736
C(22)	0.1092 (9)	0.2624 (9)	0.0940 (3)	0.0623
N(22)	0.0662 (10)	0.3666 (9)	0.1092 (4)	0.0936
O(221)	0.1331 (10)	0.4370 (9)	0.1226 (3)	0.1665
O(222)	-0.0295 (9)	0.3815 (7)	0.1039 (3)	0.1227
C(23)	0.2066 (11)	0.2566 (11)	0.0750 (4)	0.0914
C(24)	0.2553 (9)	0.1653 (15)	0.0594 (4)	0.0980
N(24)	0.3621 (12)	0.1587 (14)	0.0393 (5)	0.1437
O(241)	0.3962 (8)	0.0760 (11)	0.0225 (4)	0.1672
O(242)	0.4169 (9)	-0.2400 (13)	0.0432 (5)	0.2041
C(25)	0.1965 (11)	0.0695 (11)	0.0581 (4)	0.0943
C(26)	0.0948 (10)	0.0733 (9)	0.0759 (4)	0.0820
N(26)	0.0326 (14)	-0.0286 (12)	0.0729 (7)	0.2055
O(262)	-0.0428 (12)	-0.0336 (9)	0.1041 (6)	0.2413
O(261)	0.0646 (12)	-0.0983 (9)	0.0490 (6)	0.2477

Table 2. Interatomic distances (\AA) and interbond angles ($^\circ$) for $C_{22}H_{34}N_6^{2+} \cdot 2C_6H_2N_3O_7^-$

C(1)—C(1')	1.466 (15)	C(21)—C(22)	1.42 (2)
C(1)—C(6)	1.37 (2)	C(21)—C(26)	1.46 (2)
C(1)—C(2)	1.364 (15)	C(22)—N(22)	1.45 (2)
C(2)—C(3)	1.39 (2)	C(22)—C(23)	1.30 (2)
C(3)—C(4)	1.37 (2)	N(22)—O(221)	1.25 (2)
C(4)—C(5)	1.38 (2)	N(22)—O(222)	1.21 (2)
C(5)—C(6)	1.42 (2)	C(23)—C(24)	1.34 (2)
C(2)—N(2)	1.466 (14)	C(24)—N(24)	1.42 (2)
N(2)—C(7)	1.339 (14)	C(24)—C(25)	1.39 (2)
C(7)—N(1)	1.311 (13)	N(24)—O(241)	1.19 (2)
C(7)—N(3)	1.335 (13)	N(24)—O(242)	1.22 (2)
N(1)—C(8)	1.436 (14)	C(25)—C(26)	1.34 (2)
N(1)—C(9)	1.479 (15)	C(26)—N(26)	1.48 (2)
N(3)—C(10)	1.443 (14)	N(26)—O(262)	1.23 (2)
N(3)—C(11)	1.434 (14)	N(26)—O(261)	1.13 (2)
O(21)—C(21)	1.252 (14)		
C(1)—C(1)—C(6)	118.9 (10)	C(22)—C(21)—C(26)	112.2 (10)
C(1)—C(1)—C(2)	122.7 (10)	C(21)—C(22)—N(22)	119.9 (10)
C(6)—C(1)—C(2)	118.3 (10)	C(21)—C(22)—C(23)	120.9 (11)
C(1)—C(2)—C(3)	121.3 (10)	N(22)—C(22)—C(23)	119.2 (11)
C(2)—C(3)—C(4)	119.2 (10)	C(22)—N(22)—O(221)	116.8 (11)
C(3)—C(4)—C(5)	122.5 (11)	C(22)—N(22)—O(222)	117.8 (11)
C(4)—C(5)—C(6)	115.6 (11)	O(221)—N(22)—O(222)	125.0 (12)
C(5)—C(6)—C(1)	123.1 (10)	C(22)—C(23)—C(24)	124.9 (13)
C(1)—C(2)—N(2)	121.2 (9)	C(23)—C(24)—N(24)	125.0 (14)
C(3)—C(2)—N(2)	117.5 (9)	C(23)—C(24)—C(25)	119.4 (13)
C(2)—N(2)—C(7)	126.6 (9)	N(24)—C(24)—C(25)	115.4 (13)
N(2)—C(7)—N(1)	116.6 (9)	C(24)—N(24)—O(241)	126.7 (14)
N(2)—C(7)—N(3)	123.2 (9)	C(24)—N(24)—O(242)	116.2 (14)
N(1)—C(7)—N(3)	120.1 (9)	O(241)—N(24)—O(242)	123 (2)
C(7)—N(1)—C(8)	124.0 (9)	C(24)—C(25)—C(26)	117.0 (13)
C(7)—N(1)—C(9)	120.1 (9)	C(21)—C(26)—C(25)	124.6 (12)
C(8)—N(1)—C(9)	115.6 (9)	C(21)—C(26)—N(26)	119.0 (12)
C(7)—N(3)—C(10)	124.4 (9)	C(25)—C(26)—N(26)	116.3 (12)
C(7)—N(3)—C(11)	122.2 (9)	C(26)—N(26)—O(262)	114.0 (15)
C(10)—N(3)—C(11)	113.3 (8)	C(26)—N(26)—O(261)	120 (2)
O(21)—C(21)—C(22)	120.4 (11)	O(262)—N(26)—O(261)	125 (2)
O(21)—C(21)—C(26)	127.3 (11)		

Symmetry code: (') $x, y, -z$.

biphenyl structure determinations in the literature. However, it is within 1.5σ of the theoretically calculated value of 1.488 \AA between two sp^2 -hybridized C atoms (Dewar & Schmeising, 1968) and in view of the disordered anion, this shortening may have little significance. The mean value of the six C—C bond distances (1.328 \AA) of the benzene ring in the biphenyl cation and the C(2)—N(2) bond distance of 1.466 (14) \AA are normal, but the other three C—N bond lengths in the tetramethylguanidino group do not correspond to the structure shown as (1). Upon protonation of N(2) the structure becomes a resonance hybrid of the three structures (2).



This delocalization of the positive charge over all three N atoms in the tetramethylguanidino group gives each C—N bond length a very similar value: C(7)—N(2) 1.339 (14), C(7)—N(1) 1.311 (13) and C(7)—N(3) 1.335 (13) \AA . These are similar to the C—N bond lengths (1.32–1.34 \AA) found in other unsubstituted guanidinium ions (e.g. Haas, Harris & Mills, 1965). The C=N bond distance in an unprotonated tetramethylguanidino group attached to a phenyl ring is 1.282 (8) \AA (Pruszyński, Leffek, Cameron & Borecka, 1989). This result confirms the conclusion reached from pK_a and rate constants of protonation measurements that the positive charge is delocalized over all three N atoms of the tetramethylguanidino group (Leffek, Pruszyński & Thanapaalasingham, 1988; Pruszyński & Leffek, 1991).

The dihedral angle between the planes of the two benzene rings of 80.4 (12) $^\circ$ is typical of biphenyls with large groups substituted in the 2,2' positions, e.g. 2,2'-di(carbonyl chloride)biphenyl shows a dihedral angle of 83.1 $^\circ$ (Leser & Rabinovich, 1978), 2,2'-dibromooctafluorobiphenyl shows 75.9 $^\circ$ (Hamor

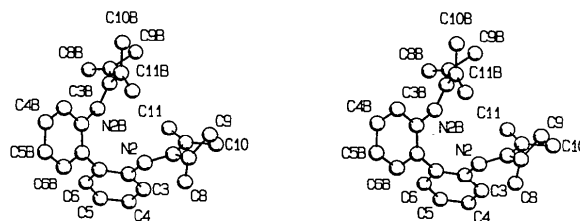


Fig. 1. The dication of 2,2'-bis[2N-(1,1,3,3-tetramethylguanidino)]-biphenyl; the twofold axis passes between the phenyl groups and between C(11) and C(11B).

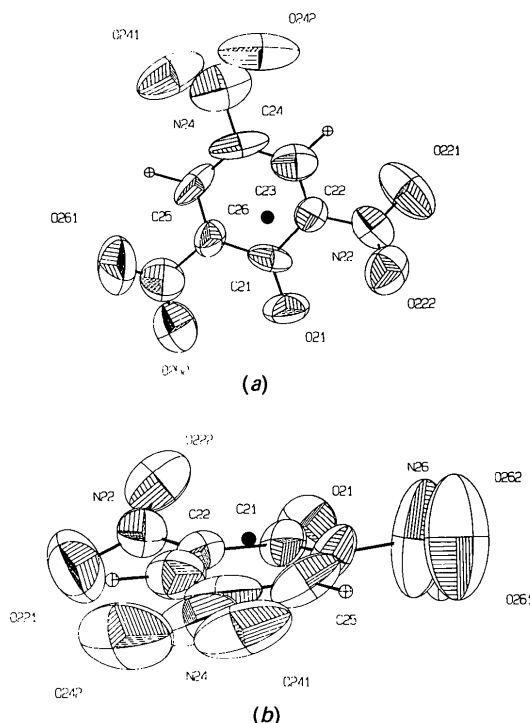


Fig. 2. The picrate ion showing (a) the plane of the major libration with the axis marked \bullet close to C(22), and (b) the plane of the second major libration with the axis marked \bullet .

& Hamor, 1980), 2,2',4,4',6,6'-hexachlorobiphenyl shows 87.3° (Singh & McKinney, 1979), and biphenyl-2,2'-bicarboxylic acid shows 71.3° (Fronczek, Davis, Gehring & Gandour, 1987). These values are in qualitative agreement with earlier predictions (Branch, Bryson, Gray, Ibbotson & Worrall, 1964).

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Structures of 1,1'-Dicyanobicyclopentyl, 1,1'-Dicyanobicyclohexyl and 1,1'-Dicyanobicycloheptyl

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Abstract. 1,1'-Bicyclopentane-1,1'-dicyanonitrile, $C_{12}H_{16}N_2$, (1), $M_r = 188.3$, orthorhombic, $Cmca$, $a = 9.711$ (2), $b = 6.885$ (1), $c = 16.258$ (2) Å, $V =$

1087.0 (3) Å³, $Z = 4$, $D_x = 1.150$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.064$ mm⁻¹, $F(000) = 408$, $T = 297$ K, $R = 0.042$ for 355 observed reflections. 1,1'-Bicyclohexane-1,1'-dicyanonitrile, $C_{14}H_{20}N_2$, (2), $M_r = 216.3$, monoclinic, $P2_1/n$, $a = 5.944$ (3), $b =$

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