References

Bosch, J. & Bonjoch, J. (1988). *Studies in Natural Product Chemistry*, edited by A. Rahman. Amsterdam: Elsevier.

Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.

Davies, K. (1983). *SNOOPI. Program for Drawing Crystal and Molecular Diagrams*. Univ. of Oxford, England.

Götz, P. H., Bats, J. W. & Fritz, H. (1986). *Justus Liebigs Ann. Chem.* pp. 2065–2080.

Magnus, P., Sear, N. L., Kim, C. S. & Vicker, N. (1992). *J. Org. Chem.* **57**, 70–78.

Patır, S. (1991). *Chim. Acta Turcica*, **19**, 129–133.

Patır, S. & Fritz, H. (1990). *Chim. Acta Turcica*, **18**, 455–460.

Patır, S. & Götz, P. (1993). In preparation.

Volker, O. I. (1979). *Synthesis*, p. 136.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Watkin, D. J., Carruthers, J. R. & Betteridge, D. W. (1985). *CRYSTALS. Program for Crystal Structure Solution*. Univ. of Oxford, England.

Acta Cryst. (1994). C**50**, 453–456

2-(2,6-Di-*tert*-butylphenoxy)-2′,4,4,4′,4′,6,6,6′,6′-nonachloro-2,2′-bi(cyclotri-λ^5-phosphazene)

TUNCER HÖKELEK*

Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey

ZEYNEL KILIÇ

Ankara University, Department of Chemistry, Tandoğan, Ankara, Turkey

ADEM KILIÇ

İnönü University, Department of Chemistry, Malatya, Turkey

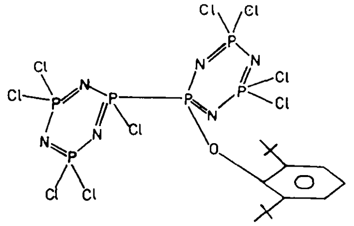
(*Received* 11 *March* 1993; *accepted* 9 *August* 1993)

Abstract

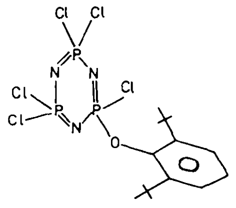
The title compound consists of the bulky 2,6-di-*tert*-butylphenoxy group and two phosphazene rings joined by a P—P bond [2.193 (2) Å]. The bulky group plays a predominant role in the distortion of the molecule as a whole. This distortion results in deviations of the benzene and phosphazene rings from planarity and twists the rings with respect to each other. In monocyclophosphazenes, the endocyclic angles about the P atom decrease while the exocyclic angles increase. This is in contrast to the behaviour of the title compound (a bicyclophosphazene) in which the exo- and endocyclic angles about the P atoms both decrease on substitution.

Comment

During the last two decades, the structure and properties of halophosphazenes have prompted an interest in the synthesis of new small-molecule organocyclophosphazenes and new inorganic backbone macromolecules (Allcock, Mang, McDonnel & Parvez, 1987). The organophosphazene derivatives are used in polymer synthesis and the resulting polymers are expected to have unique physical properties (Allcock, 1972; Allcock *et al.*, 1987). Polyphosphazenes with aryloxy, alkoxy and metallocenyl side groups are of special interest (Allcock, Riding & Whittle, 1984; Allcock *et al.*, 1987; Allcock, Manners, Mang & Parvez, 1990). We have investigated the reaction of sodium 2,6-di-*tert*-butylphenoxide and hexachlorocyclotriphosphazene, $N_3P_3Cl_6$. It is a highly complex reaction and yields at least two different products, a bicyclophosphazene derivative (I) and a monocyclophosphazene derivative (II).



(I)



(II)

During the reaction, the Cl atoms of compounds (I) and (II) can be substituted with 2,6-di-*tert*-butylphenoxy groups and the structural isomers (geminal, *cis–trans*) are probably formed. In this study, 2,6-di-*tert*-butylphenoxide was prepared from the reaction of 2,6-di-*tert*-butylphenol with metallic sodium (Çetinkaya, Gümrükçü & Lappert, 1980). The title compound (I), a bicyclophosphazene, was then synthesized by the reaction of hexachlorocyclotriphosphazene with the prepared sodium 2,6-di-*tert*-butylphenoxide and separated from the reaction mixture by column chromatography.

In the literature, only a few cyclophosphazene dimers are reported (Allcock, Connoly & Harris, 1982; Allcock, Karen, Riding, Suszko & Whittle, 1984). The structure determination of the title compound was undertaken in order to elucidate the effects of the steric interactions of the bulky 2,6-di-*tert*-butylphenoxy group with the phosphazene rings, and to compare the obtained values with the reported structural results of a bicyclophosphazene, $[Fe(N_3P_3Cl_4)_2(\eta\text{-}C_5H_4)_2]$, already reported in the literature (Allcock, Karen *et al.*, 1984). A view of the molecule and the atomic numbering scheme is shown in Fig. 1.

As can be seen from Table 2, the P4—Cl5 bond length [2.016 (2) Å] is the longest of the P—Cl bonds. In the bicyclophosphazene $[Fe(N_3P_3Cl_4)_2(\eta\text{-}C_5H_4)_2]$, the P—P bond length is reported as 2.219 (1) Å (Allcock, Karen *et al.*, 1984). It is slightly longer than P1—P4 [2.193 (2) Å] in the title compound. The average P—N bond length is 1.576 (5) Å in the *A* (P1, N1, P3, N3, P2, N2) and *B* (P4, N4, P5, N5, P6, N6) rings, and along with P1—O1 [1.575 (4) Å] and C1—O1 [1.440 (6) Å] these distances are comparable with the reported values of P—N [1.575 (5) Å], P—O [1.579 (5) Å] and C—O [1.393 (8) Å] in $N_3P_3(OC_6H_4Cl\text{-}p)_6$ (Bandoli *et al.*, 1989).

The C1—O1 bond length might be longer because of the 2,6-di-*tert*-butyl groups on the benzene ring. The effect of the 2,6-di-*tert*-butylphenoxy group is greater on ring *A* than on ring *B*. The *A* and *B* rings are appreciably distorted and an examination of the deviations from the individual-ring least-squares planes shows that these rings are not planar and have maximum deviations for N3 [−0.182 (7) Å] and N5 [0.100 (8) Å]. If the substituents bonded to the P atoms are the same, then phosphazene rings are generally expected to be planar. On the other hand, if the substituents are different, phosphazene rings deviate from planarity (Allcock, 1972; Contractor, Hursthouse, Shaw, Shaw & Yılmaz, 1985). The *C* ring (C1, C2, C3, C4, C5, C6) is also non-planar with a maximum deviation for C1 [−0.087 (6) Å] from the least-squares plane. The rings are twisted with respect to each other. The dihedral angles between the least-squares planes are $A/B = 19.0$ (6), $A/C = 62.7$ (2) and $B/C = 43.9$ (2)°. In monocyclophosphazenes, it is observed that endocyclic angles about P decrease while exocyclic angles increase (Contractor *et al.*, 1985; Fincham, Hursthouse, Parkes, Shaw & Shaw, 1986). The title compound, a bicyclophosphazene, is somewhat different. The exocyclic angles Cl5—P4—P1 [98.1 (1)°] and O1—P1—P4 [98.7 (1)°] are smaller [3.3 (1) and 2.7 (1)°, respectively] than the average Cl—P—Cl value [101.4 (1)°]. On the other hand, the endocyclic angles N4—P4—N6 [118.0 (3)°] and N1—P1—N2 [116.7 (2)°] decrease [0.5 (3) and 1.8 (3)°, respectively] compared to the average value [118.5 (3)°] of the other N—P—N angles. Thus, the exo- and endocyclic angles about the P1 and P4 atoms decrease at the same time.

The interatomic distances C8···O1 [2.785 (8) Å], H83···O1 [2.346 (8) Å], C13···O1 [2.765 (9) Å] and H133···O1 [2.328 (9) Å] may indicate possible hydrogen bonds, leading to a decrease in the value of the exocyclic O1—P1—P4 angle.

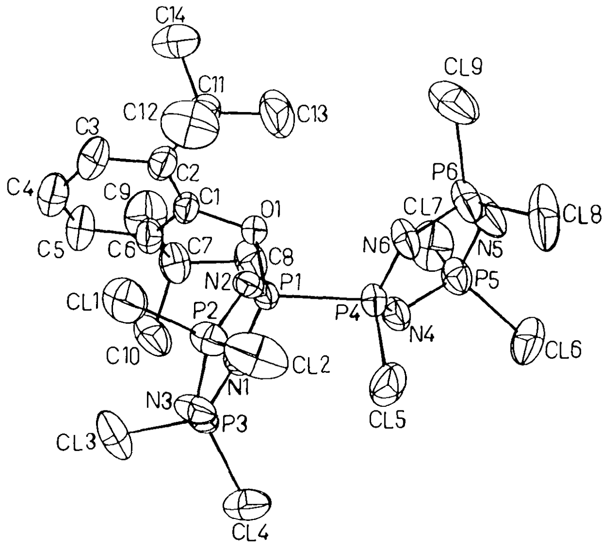


Fig. 1. A *SNOOPI* (Davies, 1983) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

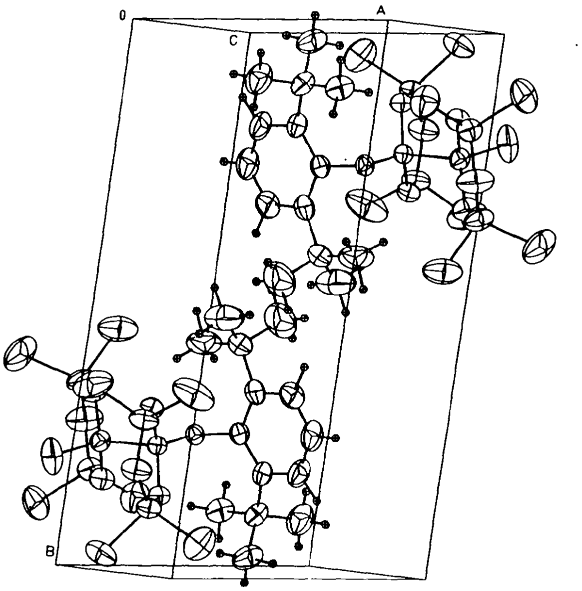


Fig. 2. Perspective view of the crystal packing.

As can be seen from the crystal packing in Fig. 2, 2,6-di-*tert*-butylphenoxy groups are close to each other due to the van der Waals interactions and they are packed parallel to the *b* axis of the unit cell. The bulky 2,6-di-*tert*-butylphenoxy group is effective in determining the shape of the molecule.

Experimental

Crystal data

$C_{14}H_{21}Cl_9N_6OP_6$
$M_r = 794.28$
Triclinic
$P\bar{1}$
$a = 11.933$ (2) Å
$b = 16.400$ (3) Å
$c = 9.471$ (3) Å
$\alpha = 92.20$ (2)°
$\beta = 118.15$ (2)°
$\gamma = 93.85$ (3)°
$V = 1625.4$ (7) Å^3
$Z = 2$

$D_x = 1.623$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 9$-30°
$\mu = 10.36$ mm^{-1}
$T = 293$ K
Rod
0.70 × 0.50 × 0.25 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.075$, $T_{\max} = 0.286$
7296 measured reflections

6322 independent reflections
4292 observed reflections $[F \geq 3\sigma(F)]$
$\theta_{\max} = 75°$
$h = -14 \rightarrow 12$
$k = -20 \rightarrow 20$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 180 min
intensity variation: 1%

Refinement

Refinement on F
$R = 0.061$
$wR = 0.069$
3773 reflections
325 parameters
H-atom parameters not refined

$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P1	0.9416 (1)	0.2339 (1)	0.4111 (2)	0.0340 (5)
P2	0.8922 (2)	0.2759 (1)	0.6596 (2)	0.0512 (5)
P3	0.8696 (2)	0.1149 (1)	0.5602 (2)	0.0435 (7)
P4	1.1424 (1)	0.2407 (1)	0.4655 (2)	0.0409 (6)
P5	1.2523 (2)	0.1932 (1)	0.2818 (2)	0.0491 (7)
P6	1.2846 (2)	0.3537 (1)	0.3941 (3)	0.0791 (8)
Cl1	0.7316 (3)	0.3237 (2)	0.6169 (4)	0.1092 (18)
Cl2	1.0148 (3)	0.3347 (1)	0.8680 (3)	0.1039 (16)
Cl3	0.6966 (2)	0.0536 (1)	0.4600 (3)	0.0873 (11)
Cl4	0.9776 (2)	0.0287 (1)	0.6773 (2)	0.0732 (11)
Cl5	1.2171 (2)	0.2068 (2)	0.6921 (2)	0.0794 (10)
Cl6	1.4016 (2)	0.1279 (1)	0.3759 (3)	0.0857 (13)
Cl7	1.1643 (2)	0.1474 (1)	0.0567 (2)	0.0813 (8)
Cl8	1.4548 (2)	0.3970 (2)	0.5715 (4)	0.1132 (16)
Cl9	1.2294 (3)	0.4509 (1)	0.2689 (4)	0.0991 (15)
O1	0.8815 (3)	0.2593 (2)	0.2331 (4)	0.0367 (17)
N1	0.8998 (4)	0.1413 (3)	0.4226 (5)	0.038 (2)
N2	0.9304 (5)	0.3007 (3)	0.5269 (6)	0.042 (2)
N3	0.8798 (6)	0.1827 (3)	0.6883 (7)	0.058 (3)
N4	1.1636 (5)	0.1732 (3)	0.3595 (7)	0.050 (3)
N5	1.3005 (7)	0.2860 (4)	0.2865 (9)	0.077 (4)
N6	1.1925 (5)	0.3324 (3)	0.4670 (7)	0.052 (3)
C1	0.7454 (5)	0.2634 (3)	0.1527 (7)	0.040 (2)
C2	0.7009 (6)	0.3393 (4)	0.1645 (7)	0.049 (3)
C3	0.5723 (7)	0.3349 (5)	0.1267 (9)	0.064 (3)
C4	0.4957 (6)	0.2615 (5)	0.0724 (9)	0.070 (3)
C5	0.5407 (6)	0.1934 (5)	0.0382 (9)	0.064 (3)
C6	0.6684 (5)	0.1915 (4)	0.0731 (7)	0.046 (3)
C7	0.7022 (6)	0.1176 (4)	−0.0003 (8)	0.052 (3)
C8	0.8378 (7)	0.1243 (4)	0.0207 (9)	0.057 (3)
C9	0.6118 (8)	0.1131 (6)	−0.1832 (9)	0.083 (4)
C10	0.6823 (7)	0.0380 (4)	0.0660 (10)	0.068 (4)
C11	0.7730 (7)	0.4251 (4)	0.1948 (4)	0.059 (3)
C12	0.7810 (10)	0.4704 (6)	0.3440 (10)	0.110 (7)
C13	0.9050 (9)	0.4274 (5)	0.2180 (10)	0.101 (6)
C14	0.6940 (10)	0.4729 (7)	0.0530 (10)	0.121 (7)

Table 2. *Selected geometric parameters* (Å, °)

P1—P4	2.193 (2)	P6—N5	1.559 (6)
P1—N2	1.577 (5)	P6—N6	1.578 (5)
P1—N1	1.591 (4)	P6—Cl9	1.983 (3)
P1—O1	1.575 (4)	P6—Cl8	1.987 (3)
P2—N2	1.584 (5)	C1—O1	1.440 (6)
P2—N3	1.572 (5)	C1—C2	1.407 (8)
P2—Cl1	1.987 (3)	C2—C3	1.397 (9)
P2—Cl2	1.976 (3)	C3—C4	1.380 (10)
P3—N3	1.569 (5)	C4—C5	1.360 (10)
P3—N1	1.576 (4)	C6—C1	1.392 (8)
P3—Cl4	1.976 (2)	C6—C5	1.402 (8)
P3—Cl3	1.993 (3)	C6—C7	1.543 (9)
P4—N4	1.578 (5)	C7—C8	1.529 (9)
P4—N6	1.576 (5)	C7—C9	1.550 (10)
P4—Cl5	2.016 (2)	C7—C10	1.523 (9)
P5—N4	1.573 (5)	C11—C2	1.542 (9)
P5—N5	1.583 (6)	C11—C12	1.530 (10)
P5—Cl7	1.968 (3)	C11—C13	1.480 (10)
P5—Cl6	1.987 (2)	C11—C14	1.510 (10)
N2—P1—P4	107.5 (2)	Cl8—P6—N6	108.7 (2)
N1—P1—P4	107.2 (2)	Cl8—P6—Cl9	101.7 (1)
N1—P1—N2	116.7 (2)	P3—N1—P1	122.1 (3)
O1—P1—P4	98.7 (1)	P2—N2—P1	121.5 (3)
O1—P1—N2	111.8 (2)	P3—N3—P2	120.1 (3)
O1—P1—N1	112.9 (2)	P5—N4—P4	121.2 (3)
N3—P2—N2	118.9 (3)	P6—N5—P5	120.9 (4)
Cl1—P2—N2	109.0 (2)	P6—N6—P4	120.8 (3)
Cl1—P2—N3	109.2 (2)	C1—O1—P1	116.0 (3)
Cl2—P2—N2	109.3 (2)	C2—C1—O1	117.4 (5)
Cl2—P2—N3	107.6 (2)	C6—C1—O1	117.4 (5)
Cl2—P2—Cl1	101.5 (1)	C2—C1—C6	125.2 (5)
N1—P3—N3	118.6 (2)	C1—C2—C11	127.2 (5)
Cl4—P3—N3	107.6 (2)	C3—C2—C11	117.7 (6)
Cl4—P3—N1	110.3 (2)	C3—C2—C1	114.7 (6)
Cl3—P3—N3	109.3 (2)	C4—C3—C2	121.2 (6)
Cl3—P3—N1	108.6 (2)	C5—C4—C3	120.2 (6)
Cl3—P3—Cl4	101.0 (1)	C4—C5—C6	122.4 (6)
N4—P4—P1	111.0 (2)	C1—C6—C5	114.1 (6)
N6—P4—P1	109.8 (2)	C1—C6—C7	127.8 (5)
N6—P4—N4	118.0 (3)	C5—C6—C7	117.5 (6)
Cl5—P4—P1	98.1 (1)	C8—C7—C6	115.5 (5)
Cl5—P4—N4	108.3 (2)	C9—C7—C6	106.2 (6)
Cl5—P4—N6	109.8 (2)	C9—C7—C8	106.0 (6)
N5—P5—N4	118.1 (3)	C9—C7—C10	109.7 (6)
Cl7—P5—N4	108.7 (2)	C10—C7—C6	111.5 (5)
Cl7—P5—N5	108.3 (3)	C10—C7—C8	107.7 (6)
Cl6—P5—N4	109.6 (2)	C12—C11—C2	110.0 (6)
Cl6—P5—N5	109.2 (3)	C13—C11—C2	116.1 (6)
Cl6—P5—Cl7	101.5 (1)	C13—C11—C12	107.0 (8)
N6—P6—N5	118.6 (3)	C14—C11—C2	107.2 (6)

Cl9—P6—N5	107.9 (3)	C14—C11—C12	107.3 (8)
Cl9—P6—N6	108.8 (2)	C14—C11—C13	109.0 (8)
Cl8—P6—N5	109.7 (3)		
C2—C1—C6—C7	154.9 (7)	O1—P1—P4—N6	66.5 (6)
C6—C1—C2—C11	−156.6 (7)	O1—P1—P4—Cl5	−179.4 (4)
C2—C1—O1—P1	90.9 (6)	O1—P1—P4—N4	−66.0 (6)
C1—O1—P1—P4	−179.1 (4)	N2—P1—O1—C1	−66.2 (7)
N1—P1—O1—C1	67.9 (6)	N2—P1—P4—N4	177.7 (6)

The H atoms were geometrically positioned 1.0 Å from their corresponding atoms and a riding model was used in the refinement process. Initially, a unit-weighting scheme was used, but in the final stages of the refinement the weights were assigned using the method described by Carruthers & Watkin (1979), as incorporated in the *CRYSTALS* package (Watkin, Carruthers & Betteridge, 1985). Other programs used were *SHELXS*86 (Sheldrick, 1990) and *SNOOPI* (Davies, 1983).

The authors are grateful to the Royal Society and TÜBİTAK (Scientific and Technical Research Council of Turkey) for financial support, and to Drs C. K. Prout and D. J. Watkin of the Chemical Crystallography Laboratory, University of Oxford, England, for provision of laboratory and computer facilities.

Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71574 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1081]

References

Allcock, H. R. (1972). *Chem. Rev.* **72**, 315–356.

Allcock, H. R., Connolly, M. S. & Harris, P. J. (1982). *J. Am. Chem. Soc.* **104**, 2482–2490.

Allcock, H. R., Karen, D. L., Riding, G. H., Suszko, P. R. & Whittle, R. R. (1984). *J. Am. Chem. Soc.* **106**, 2337–2347.

Allcock, H. R., Mang, M. N., McDonnel, G. S. & Parvez, M. (1987). *Macromolecules*, **20**, 2060–2067.

Allcock, H. R., Manners, I., Mang, M. N. & Parvez, M. (1990). *Inorg. Chem.* **29**, 522–529.

Allcock, H. R., Riding, G. H. & Whittle, R. R. (1984). *J. Am. Chem. Soc.* **106**, 5561–5567.

Bandoli, G., Casellato, U., Gleria, M., Grassi, A., Montoneri, E. & Pappalardo, G. C. (1989). *J. Chem. Soc. Dalton Trans.* pp. 757–760.

Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.

Çetinkaya, B., Gümrükçü, I. & Lappert, M. F. (1980). *J. Am. Chem. Soc.* **102**, 2086–2087.

Contractor, S. R., Hursthouse, M. B., Shaw, L. S., Shaw, R. A. & Yılmaz, H. (1985). *Acta Cryst.* B**41**, 122–131.

Davies, K. (1983). *SNOOPI. Program for Drawing Crystal and Molecular Diagrams*. Univ. of Oxford, England.

Fincham, J. K., Hursthouse, M. B., Parkes, H. G., Shaw, L. S. & Shaw, R. A. (1986). *Acta Cryst.* B**42**, 462–472.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Watkin, D. J., Carruthers, J. R. & Betteridge, D. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

Acta Cryst. (1994). C**50**, 456–458

N^1,N^2-Di(p-tolyl)benzamidine, $C_{21}H_{20}N_2$

N. W. ALCOCK, N. C. BLACKER, W. ERRINGTON AND M. G. H. WALLBRIDGE

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

J. BARKER

The Associated Octel Co. Ltd, Ellesmere Port, South Wirral L65 4HF, England

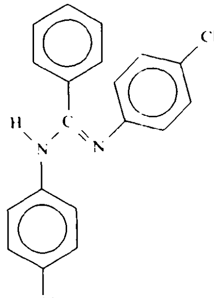
(*Received* 3 *March* 1993; *accepted* 24 *August* 1993)

Abstract

The C—N bonds in the amidine skeleton show distinct amine and imine characteristics; the N—C—N bond angle is 120.8 (7)°. An *E,Z* configuration is observed and the solid is held together in infinite chains containing N—H···N hydrogen bonding.

Comment

The structures of amidines continue to attract attention (Alcock, Barker & Kilner, 1988; Kosturkiewicz, Ciszak & Tykarska, 1992) because of their biological and ligating properties. The asymmetric unit in N^1,N^2-di(p-tolyl)benzamidine(1) contains two molecules, one of which is shown in Fig. 1.



(1)

The geometry of the amidine N—C—N skeleton is of interest since this is the portion which is particularly prone to structural changes upon coordination to a metal. The C—N bond lengths alternate as expected, with a mean C—N distance of 1.368 (10) Å and a mean C═N distance of 1.281 (11) Å; these values are not significantly different from those reported (Alcock, Barker & Kilner, 1988) for N^1,N^2-diphenylbenzamidine. The mean N—C—N bond angle of 120.8 (7)° is very close to the ideal value for