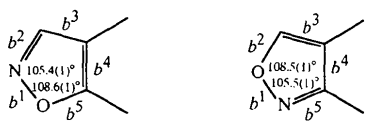
Datensammlung

Kuma Diffraction KM-4 Diffraktometer
$\omega/2\theta$ Abtastung
Absorptionskorrektur: ψ scan
T_{min} = 0,839, T_{max} = 0,902
10013 gemessene Reflexe
9651 unabhängige Reflexe
8523 Reflexe mit $I > 2\sigma(I)$
R_{int} = 0,021
θ_{max} = 70,31°
$h = -7 \rightarrow 7$
$k = -37 \rightarrow 37$
$l = 0 \rightarrow 16$
2 Kontrollreflexe
alle 100 Reflexen
Intensitätsschwankung: 3,2%

Verfeinerung

Verfeinerung auf F^2
$R[F^2 > 2\sigma(F^2)]$ = 0,036
$wR(F^2)$ = 0,105
S = 1,003
9651 Reflexe
614 Parameter
H-atome: mit geometrischen Bedingungen
$w = 1/[\sigma^2(F_o^2) + (0{,}0660P)^2 + 0{,}3267P]$ wobei $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0{,}022$
$\Delta\rho_{max}$ = 0,189 e Å^{-3}
$\Delta\rho_{min}$ = −0,164 e Å^{-3}
Extinktionskorrektur: *SHELXL*93 (Sheldrick, 1993)
Extinktionskoeffizient: 0,00088 (12)
Atomformfaktoren aus *International Tables for Crystallography* (Bd C)
Absolute Konfiguration: Flack (1983)
Flack-Parameter = 0,14 (17)

Tabelle 1. *Vergleich der für (2a) und (4a) gefundenen Bindungslängen b^1–b^5 (Å) im Isoxazolring mit Literatur-Daten für die Ringsysteme I und II*



I

II

	(2a)	(4a) Molekül A	(4a) Molekül B	I†	II
b^1	1,421 (2)	1,416 (2)	1,419 (3)	1,415 (2)	1,416 (2)
b^2	1,298 (3)	1,295 (3)	1,307 (3)	1,312 (2)	1,349 (2)
b^3	1,415 (2)	1,420 (2)	1,418 (3)	1,427 (2)	1,358 (2)
b^4	1,334 (2)	1,344 (3)	1,346 (3)	1,354 (2)	1,425 (2)
b^5	1,351 (2)	1,347 (2)	1,359 (2)	1,352 (2)	1,310 (2)

† Mittelwerte von 54 Strukturen mit Ringsystem I bzw. 56 Strukturen mit Ringsystem II [CSD, $R < 0{,}07$ (Allen *et al.*, 1993)].

Alle H-Atome wurden in (2*a*) und (4*a*) aus Differenz-Fourier-Synthesen ermittelt und mit Hilfe eines Reitermodells verfeinert. Die H-Atome der Methylgruppen wurden als starre Gruppen betrachtet; U(H) = 1,1$U_{äq}$(C). Bei der Bestimmung der absoluten Konfiguration von (2*a*) bzw. (4*a*) wurden 2250 bzw. 4888 Friedel-Reflexenpaare ausgewertet.

Datensammlung für (2*a*) und (4*a*): *Kuma KM-4 Software* (Kuma Diffraction, 1991); Zellverfeinerung: *Kuma KM-4 Software*; Datenreduktion: *Kuma KM-4 Software*; Lösung der Strukteren: *SHELXS*86 (Sheldrick, 1985); Verfeinerung der Strukteren: *SHELXL*93 (Sheldrick, 1993); Molekülgrafik: *ORTEP*II (Johnson, 1976); Programm für die Herstellung von Veröffentlichungsmaterialien: *SHELXL*93.

Ergänzende Daten für diese Veröffentlichung können vom elektronischen Archiv des IUCr (Referenz: JZ1306) bezogen werden. Zugangsmöglichkeiten für diese Daten werden auf der dritten Umschlagseite beschrieben.

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Dimorphism of 2,3,5,6-tetraphenylpyrazine

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Abstract

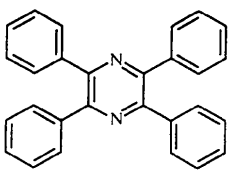
Two forms of 2,3,5,6-tetraphenylpyrazine (TPP), $C_{28}H_{20}N_2$, have been crystallized. The first variety (α) is primitive monoclinic ($P2_1/c$), in which the TPP molecule is centrosymmetric. The second variety (β) is *C*-face-centred monoclinic ($C2/c$) with two symmetry-independent molecules having binary axis symmetry, where in one of the molecules, the binary axis passes through the two N atoms of the pyrazine ring, while in the second molecule, the binary axis passes through the midpoints of the two C—C bonds of the pyrazine ring. In these two compounds, the phenyl rings are differently disposed, showing a wing-like conformation in the α form and a propeller-like conformation for the two molecules in the β form. The rotations of the phenyl rings, given by the dihedral angles between the pyrazine

rings and the phenyl rings, are in the range 37.56 (8)–49.72 (8)°.

Comment

In polyarylarenes, such as hexaphenylbenzene and tetrapyridylpyrazine, the tendency of the individual aromatic nuclei to adopt a coplanar conformation is counteracted by the steric repulsion between the *ortho*-H atoms of vicinal rings. The crystal structure of one of the polymorphic forms of hexaphenylbenzene shows a propeller conformation. The peripheral rings are twisted with dihedral angles in the range 62.0 (1)–70.7 (1)° with respect to the central ring (Bart, 1968). For tetra(2-pyridyl)pyrazine, two forms are described: a monoclinic one (Bock *et al.*, 1992) and a tetragonal one (Greaves & Stoeckli-Evans, 1992). In both forms, the molecule is centrosymmetric. The difference is in the orientation of the pyridine rings, which in the tetragonal form are almost antiparallel to those in the monoclinic form. Nevertheless, the N atoms of the vicinal pyridyl rings are on opposite sides of the pyrazine ring plane for the monoclinic form and on the same side for the tetragonal form.

Two forms of tetraphenylpyrazine, TPP, have been mentioned as early as 1889 (Grossmann, 1889), but the nature of this dimorphism has not been determined until now. Both forms have the same melting point and crystallize under similar conditions. In a preliminary crystal study, Seal (1896) attributes a triclinic cell to the α form.



TPP

In the α form, the asymmetric unit is defined by half a TPP molecule. Thus the molecule is centrosymmetric. The phenyl groups are twisted in the same direction about the N···N axis, leading to a wing-like conformation (Fig. 1). The dihedral angles between the mean planes of the phenyl and pyrazine rings are 41.10 (13) and 48.83 (13)° for the two phenyl groups incorporating C21 and C31, respectively. The inversion centre dictates that the diagonally opposite phenyl groups are exactly parallel one to another.

In the β form, the asymmetric unit is defined by two half TPP molecules situated about binary axes. Thus the crystal shows the TPP molecules in two conformations. In the first one (Fig. 2*a*), the twofold axis passes through the two N atoms of the pyrazine ring. The dihedral angles between the mean planes of the phenyl and pyrazine rings are 49.72 (8) and

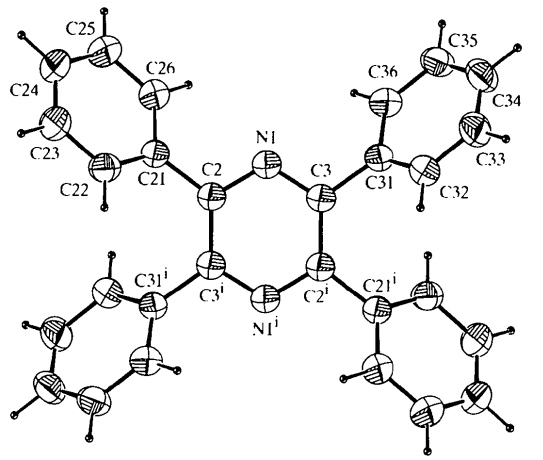


Fig. 1. Molecular structure of the α form of TPP showing 30% probability displacement ellipsoids. H atoms are arbitrarily scaled. [Symmetry code: (i) $-x, 1-y, -z$.]

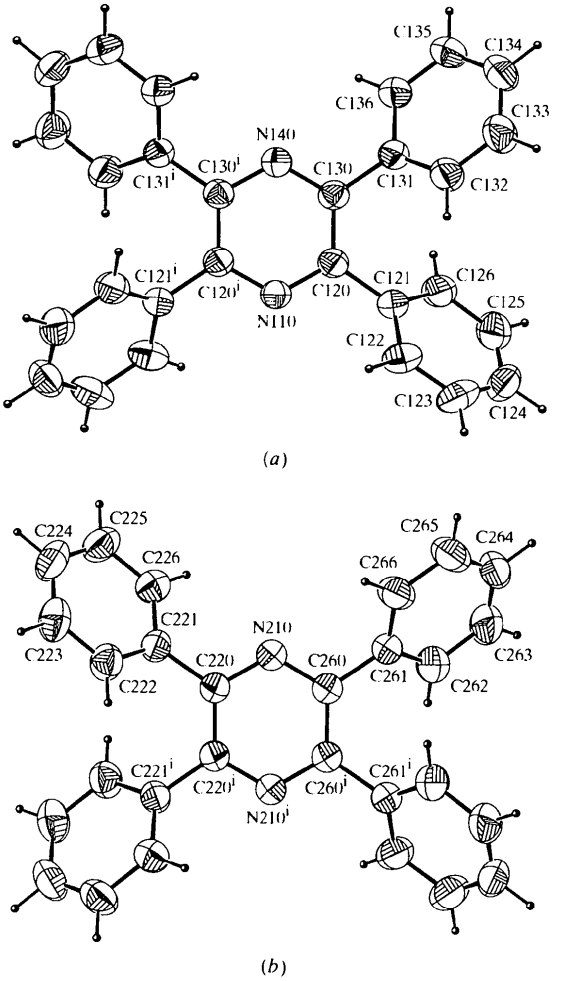


Fig. 2. (*a*) First molecule and (*b*) second molecule of the β form of TPP showing 30% probability displacement ellipsoids. H atoms are arbitrarily scaled. [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

37.56 (8)° for the two phenyl groups incorporating C121 and C131, respectively. In the second TPP molecule (Fig. 2*b*), the twofold axis passes through the midpoints of the two pyrazine C—C bonds. The dihedral angles between the mean planes of the phenyl and pyrazine rings are 39.30 (14) and 47.15 (15)° for the two phenyl groups incorporating C221 and C261, respectively. In this crystal, the phenyl rings adopt a propeller-like conformation for each of the two independent molecules. The diagonally opposite phenyl groups are almost perpendicular one to another, their mean planes making angles of 87.28 (8) for the first molecule and 86.45 (15)° for the second molecule.

Experimental

TPP was obtained by dimerization of 2,6-diphenylazirine on a SiO_2 column and recrystallized from CH_2Cl_2 (β form) or a mixed solvent (CH_2Cl_2/CH_3CN). In the latter case, two types of crystals appear simultaneously, plates (α form) and needles (β form).

α form

Crystal data

$C_{28}H_{20}N_2$
M_r = 384.48
Monoclinic
$P2_1/c$
a = 15.210 (2) Å
b = 5.5390 (6) Å
c = 17.192 (2) Å
β = 134.45 (1)°
V = 1034.0 (3) Å^3
Z = 2
D_x = 1.235 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54056 Å
Cell parameters from 25 reflections
θ = 19.31–57.50°
μ = 0.56 mm^{-1}
T = 291 K
Plate
0.60 × 0.40 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–5/3θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.816, T_{max} = 0.874
1956 measured reflections
1956 independent reflections

1915 reflections with $I_{net} > 0$
R_{int} = 0.025
θ_{max} = 73.0°
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 6$
$l = -21 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 3.0%

Refinement

Refinement on F
R = 0.060
wR = 0.137
S = 1.9
1915 reflections
137 parameters
H-atom parameters not refined

$w = 4F_o^2[\sigma^2(I) + (0.12F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{max}$ 0.01
$\Delta\rho_{max}$ = 0.296 e Å^{-3}
$\Delta\rho_{min}$ = −0.260 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

β form

Crystal data

$C_{28}H_{20}N_2$
M_r = 384.48
Monoclinic
$C2/c$
a = 18.654 (3) Å
b = 23.509 (2) Å
c = 9.576 (1) Å
β = 92.18 (1)°
V = 4196.6 (8) Å^3
Z = 8
D_x = 1.217 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54056 Å
Cell parameters from 25 reflections
θ = 8.55–50.10°
μ = 0.55 mm^{-1}
T = 291 K
Needle
0.52 × 0.30 × 0.06 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–4/3θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.913, T_{max} = 0.992
4043 measured reflections
4043 independent reflections

3583 reflections with $I_{net} > 0$
R_{int} = 0.022
θ_{max} = 73°
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 29$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 0.2%

Refinement

Refinement on F
R = 0.057
wR = 0.077
S = 1.24
3583 reflections
272 parameters
H-atom parameters not refined

$w = 4F_o^2[\sigma^2(I) + (0.04F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max}$ = 0.206 e Å^{-3}
$\Delta\rho_{min}$ = −0.197 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The H atoms were placed in geometrically calculated positions and their positions were held fixed.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *SDP* (Frenz, 1982); program(s) used to solve structures: *SDP*; program(s) used to refine structures: *SDP*; molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1076). Services for accessing these data are described at the back of the journal.

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A new orthorhombic phase of *N,N′*-diphenylguanidine

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Abstract

A new orthorhombic phase of the title compound, $C_{13}H_{13}N_3$, is reported. There are two symmetry-independent molecules in the unit cell, as in the monoclinic phase, both having a *syn-anti* conformation of the phenyl rings with respect to the unsubstituted N atom. This orthorhombic phase differs from the monoclinic one in the hydrogen-bonding scheme and molecular packing. Bond lengths and angles within the guanidine moiety are close to those expected for a central Csp^2 atom with one C=N and two C—N bonds. The *anti* ring binds to the guanidine moiety as C_{aryl}—NH—C and the *syn* ring as C_{aryl}—N=C.

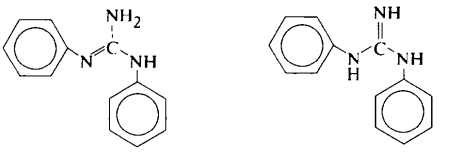
Comment

The title compound, also known as melaniline, is used as a cure accelerator in the rubber industry. It is marked under the trade name of 'Vulkazit'. Certain *N,N′*-diarylguanidines are potent ligands for the *N*-methyl-D-aspartate/PCP(Phencyclidine) receptor and have neuroprotective properties against glutamate-induced neuronal cell death (Olney *et al.*, 1989). *N,N′*-Di-*ortho*-tolylguanidine and its congeners are selective ligands for the haloperidol-sensitive σ receptor (Weber *et al.*, 1986; Largent *et al.*, 1987). As such, di-substituted guanidine compounds are of considerable interest in pharmaceutical applications, as neuroleptic and antipsychotic drugs. From the point of view of their physical properties, guanidine compounds are potentially interesting for non-linear optics applications (Zyss *et al.*, 1993).

This work is part of an on-going research project to study the structural, optical and dielectric properties of diphenylguanidine (dpg) salts. It is known that dpg is a very flexible molecule due to the low potential barrier for rotation of the phenyl rings and a number of different molecular conformations (*syn-syn*, *syn-anti* and *anti-anti*) have been found both in solution (Alagona *et al.*, 1994) and in several salts (Antolini *et al.*, 1991; Paixão *et al.*, 1997; Matos Beja *et al.*, 1998; Paixão *et al.*, 1998*a,b,c*). The effect of the counter ion of the protonated molecule on the relative stability of the different conformers has also been studied theoretically from both *ab initio* and Monte–Carlo calculations (Nagy & Durant, 1996). The dipole moment and polarizability of protonated dpg molecules, and therefore the optical and dielectric properties of dpg salts, depend on the orientation of the rings, which justifies the need to determine accurate structural data for these compounds.

The structure of monoclinic dpg was reported by Zakharov *et al.* (1980). We have found that under certain conditions, namely crystallization from weak acidic media, crystals of a new, orthorhombic phase of the free base grew from the solution. The structure of this new polymorph is reported here.

There are two symmetry-independent molecules in the asymmetric unit cell, I and II, as in the monoclinic phase. The CN_3 fragment of the guanidinium group has the planar geometry expected for a central Csp^2 atom. The bond lengths C1—N1 [I 1.366 (3), II 1.367 (3) Å] and C1—N2 [I 1.356 (3), II 1.336 (3) Å] are larger than literature averages for unsubstituted and substituted guanidinium cations, 1.321 and 1.328 Å, respectively (Allen *et al.*, 1987). They are closer to the standard value of a single C—N bond than in dpg^+ salts, where protonation is followed by a relevant charge delocalization within the guanidine moiety. The bond length C1—N3 [I 1.278 (3), II 1.292 (3) Å] is significantly shorter than the C1—N1 and C1—N2 bonds and has a value closer to that expected for a C=N bond. This fact, and the objective localization of the H atoms on a difference Fourier map confirm the observation of Zakharov *et al.* (1980) that the tautomeric form (*a*) is preferred over form (*b*).



(*a*) (*b*)

The sums of the valence angles around C1 and C1′ are 360.0 (4) and 359.9 (4)°, respectively, but the N—C—N angles differ considerably from the mean value of 120°. The largest deviation is that of N1—C1—N2 [I 112.9 (2), II 113.2 (2)°].