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3,6-Bis(4-*tert*-butylphenyl)-1,2,4,5-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-dione

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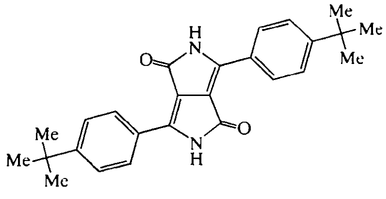
Abstract

The molecule of the title compound, $C_{26}H_{28}N_2O_2$, has no molecular symmetry (C_1). The phenyl rings are asymmetrically twisted by 7.9 (3) and 9.0 (3)° in opposite directions with respect to their attached five-membered ring of the heterocyclic ring system. The heterocyclic ring system is not entirely planar, but is folded in the middle, with a dihedral angle of 176.7 (3)° between the two halves. The molecules are stacked nearly in a 'bricks in a brick wall' fashion.

Comment

The title compound, 3,6-bis(4-*tert*-butylphenyl)-1,2,4,5-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-dione (TB–DPP), is a commercial yellow–red pigment based on a novel chromophore of diketopyrrolopyrrole (Iqbal *et al.*, 1988). The appealing feature of DPP pigments is that they exhibit a variety of vivid red colors, depending on the molecular arrangement in the solid state. A series of investigations has been carried out on DPP pigments with special attention being paid to the correlation between the crystal and electronic structures (Mizuguchi & Wooden, 1991; Mizuguchi & Rihs, 1992; Mizuguchi *et al.*, 1993). The present structure determination was undertaken as a continuation of this investigation.



TB–DPP

An *ORTEP*II (Johnson, 1976) diagram of TB–DPP is shown in Fig. 1. The TB–DPP molecule possesses no molecular symmetry (C_1) in contrast to the C_i symmetry of *meta* or *para*-chlorinated DPP (Mizuguchi *et al.*, 1993) or non-substituted DPP (Mizuguchi *et al.*, 1992) (Fig. 1). This causes a dipole moment of about 0.3 D (1 D = 3.33564 × 10^{-30} C m) to appear. The phenyl rings, having a bulky *tert*-butyl group at the *para* site, deviate asymmetrically from the heterocyclic ring system by about 7.9 (3) and 9.0 (3)° in opposite directions ('propeller type'). As a consequence, there are two molecular configurations in the crystal. The heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of 176.7 (3)° between the two halves. The molecular stack of TB–DPP is shown in Fig. 2. In each molecular layer, hydrogen bonds between the N—H group and the O atom link molecules along the *c* axis [N4—H4···O1: N—H···O 171.31°, O···H 1.87, N—H 0.95 and N···O 2.82 Å; N3—H3···O2: N—H···O 168.80°, O···H 1.88, N—H 0.95 and N···O 2.82 Å]. The hydrogen-bond pair is characterized by a homochiral pair. It is also apparent that the chirality of the molecule is different in each layer and each column. The molecules are stacked in a quasi-'bricks in a brick wall' fashion. Between two columns, there are two kinds of heterochiral pairs in a diagonal direction; one has greater π–π overlap than the other. The formation of the dimeric stacking is presumably attributed to the induced dipole moment on going from solution to the solid state. So the polar molecules are apt to dimerize so as to reduce the electrostatic energy, leading to stabilization of the ground state of the total system. The present molecular arrangement is quite different from that of other DPP pigments and is found to be responsible for a different shade of TB–DPP caused by exciton coupling effects. Details on this are under investigation and will be given elsewhere.

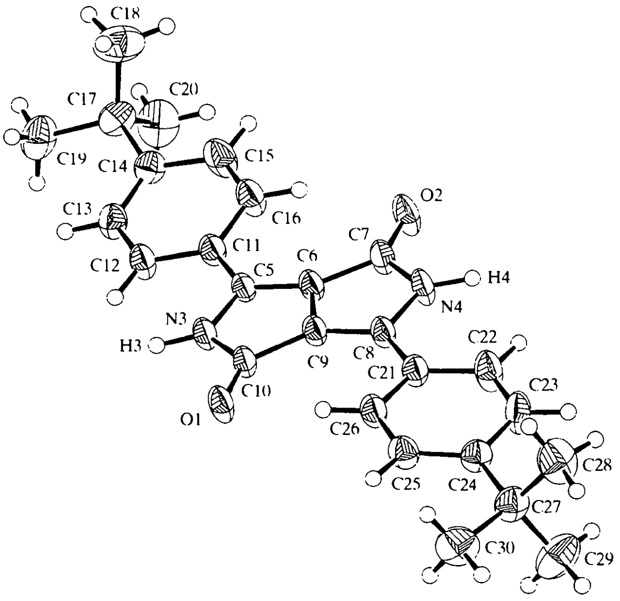


Fig. 1. *ORTEP*II (Johnson, 1976) plot of TB-DPP showing the numbering of the non-H atoms. Displacement ellipsoids are scaled to the 40% probability level.

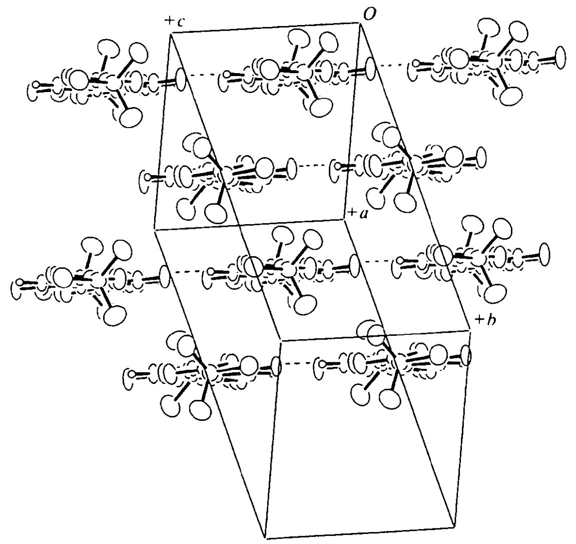


Fig. 2. Molecular stack showing quasi-'bricks in a brick wall' structure. The hydrogen bonds are depicted by dotted lines.

Experimental

TB–DPP ('Irgazin DPP Orange RA', Ciba Speciality Chemicals) was refined twice by vacuum sublimation using an apparatus described previously (Mizuguchi, 1981). Single crystals were then grown from the vapor phase using the same sublimation equipment. TB–DPP was sublimed at about 605 K, and the argon flow rate was controlled to 15 $\text{mm}^3\ \text{s}^{-1}$ using a mass flow meter (F-100/200, Bronkhorst BV). After 48 h of vapor growth, a number of platelets had been obtained. The density of TB–DPP was measured by flotation in benzene/carbontetrachloride

Crystal data

$C_{26}H_{28}N_2O_2$
$M_r = 400.52$
Triclinic
$P\bar{1}$
$a = 9.872\ (1)$ Å
$b = 15.779\ (1)$ Å
$c = 7.229\ (1)$ Å
$\alpha = 96.31\ (1)°$
$\beta = 91.13\ (1)°$
$\gamma = 82.20\ (1)°$
$V = 1108.9\ (2)$ Å^3
$Z = 2$
$D_x = 1.199$ Mg m^{-3}
$D_m = 1.150$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10.0–17.5°$
$\mu = 0.598$ mm^{-1}
$T = 298.2$ K
Platelet
$0.43 \times 0.18 \times 0.05$ mm
Orange

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3788 measured reflections
3788 independent reflections
2335 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 65°$
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -8 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 0.8%

Refinement

Refinement on F
$R = 0.061$
$wR = 0.087$
$S = 1.286$
2335 reflections
272 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00286|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.0010$

$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: type 2 Gaussian isotropic (Zachariasen, 1967)
Extinction coefficient: 0.05 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C10	1.234 (4)	C11—C16	1.390 (4)
O2—C7	1.234 (4)	C12—C13	1.377 (4)
N3—C5	1.390 (4)	C13—C14	1.381 (4)
N3—C10	1.380 (4)	C14—C15	1.402 (5)
N4—C7	1.388 (4)	C14—C17	1.528 (4)
N4—C8	1.400 (4)	C15—C16	1.370 (5)
C5—C6	1.383 (4)	C21—C22	1.399 (4)
C5—C11	1.448 (4)	C21—C26	1.393 (4)
C6—C7	1.450 (4)	C22—C23	1.380 (5)
C6—C9	1.424 (4)	C23—C24	1.403 (5)
C8—C9	1.373 (4)	C24—C25	1.380 (4)
C8—C21	1.443 (4)	C24—C27	1.528 (4)
C9—C10	1.447 (4)	C25—C26	1.378 (4)
C11—C12	1.392 (4)		
C5—N3—C10	112.8 (2)	O1—C10—C9	131.4 (3)
C7—N4—C8	112.4 (2)	N3—C10—C9	104.7 (2)
N3—C5—C6	106.2 (2)	C5—C11—C12	122.5 (3)
N3—C5—C11	122.5 (2)	C5—C11—C16	120.2 (3)
C6—C5—C11	131.3 (3)	C12—C11—C16	117.2 (3)
C5—C6—C7	143.2 (3)	C11—C12—C13	121.1 (3)
C5—C6—C9	109.2 (2)	C12—C13—C14	122.2 (3)
C7—C6—C9	107.4 (2)	C13—C14—C15	116.2 (3)
O2—C7—N4	123.8 (3)	C14—C15—C16	122.0 (3)
O2—C7—C6	131.9 (3)	C11—C16—C15	121.1 (3)
N4—C7—C6	104.4 (2)	C8—C21—C22	122.2 (3)
N4—C8—C9	106.4 (2)	C8—C21—C26	120.8 (2)
N4—C8—C21	121.7 (2)	C22—C21—C26	117.0 (3)
C9—C8—C21	131.8 (3)	C21—C22—C23	120.9 (3)
C6—C9—C8	109.4 (2)	C22—C23—C24	121.9 (3)
C6—C9—C10	107.2 (2)	C23—C24—C25	116.5 (3)
C8—C9—C10	143.3 (3)	C24—C25—C26	122.1 (3)
O1—C10—N3	123.9 (2)	C21—C26—C25	121.5 (3)

The non-H atoms were refined anisotropically by full-matrix least-squares methods. H atoms were included but not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1057). Services for accessing these data are described at the back of the journal.

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1,3-Diphenylguanidinium Trifluoroacetate

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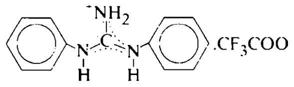
Abstract

The two phenyl rings of the title compound, $C_{13}H_{14}N_3^+.CF_3CO_2^-$, assume a *syn* conformation with respect to the unsubstituted N atom of the cation. Bond lengths and angles within the guanidinium moiety are close to those expected for a central C_{sp^2} atom, accounting for some charge delocalization between the three C—N bonds. The structure is stabilized by a two-dimensional network of intermolecular hydrogen bonds, where the carboxylate O atoms of the anions are acceptors from the N—H groups of the diphenylguanidinium cations.

Comment

Guanidine compounds and their salts continue to attract interest because of their biological and pharmaceutical (*e.g.* neuroleptic and antipsychotic) activities. *N*,*N*′-Di-*o*-tolylguanidine and its congeners are selective ligands for the haloperidol-sensitive σ receptor (Weber *et al.*, 1986; Largent *et al.*, 1987; Largent *et al.*, 1988). Certain *N*,*N*′-diarylguanidines are potent ligands for the *N*-methyl-D-aspartate/PCP receptor, and such compounds have neuroprotective properties against glutamate-induced neuronal cell death (Olney *et al.*, 1989). In addition, guanidine compounds are regarded as potentially interesting for non-linear optical applications (Zyss *et al.*, 1993). The structure determination of the title compound, (I), was undertaken as part of a current research project to study the structural, optical and dielectric properties of a series of diphenylguanidine (dpg) compounds.



(I)

The CN_3 fragment of the guanidinium group has the planar geometry expected for a central C_{sp^2} atom. The C1—N1 [1.329 (3) Å] and C1—N3 [1.334 (3) Å] bond lengths are comparable with literature averages for substituted and unsubstituted guanidinium cations (1.321 and 1.328 Å, respectively; Allen *et al.*, 1987), while the C1—N2 bond length [1.318 (3) Å] is slightly shorter. These values are larger than the mean value of a C_{sp^2}=N bond [1.295 Å], indicating that some charge delocalization occurs within the guanidinium fragment. With regard to the bond angles in the guanidinium group, there are small deviations from the ideal value of 120°, the angle opposite to the unsubstituted N atom being significantly smaller than the other two.

Both phenyl rings lie *syn* to the unsubstituted N2 atom, the dihedral angle between the planes of the phenyl rings being 70.53 (10)°. This conformation is similar to that of dpg$^+$ hydrogenselenite monohydrate (Paixão *et al.*, 1997), but different from the *syn-anti* conformation found in the molecular crystal of the free base (Zakharov *et al.*, 1980), as well as in dpg$^+$ *m*-chlorobenzeneseleninate (Antolini *et al.*, 1991) and dpg$^+$ perchlorate (Paixão *et al.*, 1998). These differences in conformation arise from the low value of the barrier of rotation of the phenyl rings, as can be shown by comparing the dihedral angles between the ring planes and the plane defined by the central guanidine fragment. In the present compound, these angles are 62.86 (11) (C2–C7) and 53.54 (8)° (C8–C13), and may be compared with the corresponding values in dpg$^+$ hydrogenselenite monohydrate [45.74 (13) and 48.35 (15)°; Paixão *et al.*, 1997], dpg$^+$ perchlorate [69.00 (13) and 79.26 (15)°; Paixão *et al.*, 1998] and dpg$^+$ *m*-chlorobenzeneseleninate [119.1 and 138.0°; Antolini *et al.*, 1991].

The geometry of the anion is unexceptional. The bond lengths in the carboxylate group are equal within estimated uncertainty and have a value compatible with a full proton transfer to the dpg molecule. As the F atoms are not involved in strong hydrogen bonds (see below), one might expect some degree of rotational disorder of the CF_3 group, however, the refinement shows that the position of this group is well defined in a single minimum, with reasonable displacement parameters for the F atoms.

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