3934 measured reflections
3638 independent reflections

3 standard reflections
frequency: 50 min
intensity variation: −8.5%

Refinement

Refinement on F
Final R = 0.060
wR = 0.082
S = 2.87
2776 reflections
333 parameters
Refinement of all H atoms except those in ethanol
$w = 1/\sigma$
$(\Delta/\sigma)_{\max}$ = 0.01

$\Delta\rho_{\max}$ = 0.47 (7) e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 (7) e Å^{-3}
Extinction correction: $|F_c|/(1+gI_c)$
Extinction coefficient: 2.73 × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}
C1	1.2153 (4)	0.3426 (2)	0.9046 (2)	4.26 (6)
C1*a*	1.0809 (3)	0.3632 (2)	0.8318 (2)	3.79 (6)
C2	1.2825 (4)	0.3928 (2)	0.9780 (2)	4.19 (6)
C3	1.2226 (3)	0.4682 (2)	0.9796 (2)	3.86 (6)
N3	1.2903 (3)	0.5195 (1)	1.0535 (2)	4.75 (6)
C3*a*	1.2596 (4)	0.6019 (2)	1.0398 (2)	5.43 (8)
C3*b*	1.4331 (4)	0.4970 (2)	1.1267 (2)	5.17 (7)
C4	1.0904 (3)	0.4902 (2)	0.9033 (2)	3.81 (6)
C4*a*	1.0200 (3)	0.4374 (2)	0.8318 (2)	3.66 (6)
C5	0.9981 (4)	0.3043 (2)	0.5842 (2)	4.73 (7)
C5*a*	0.9617 (4)	0.3422 (2)	0.6610 (2)	4.05 (6)
C6	0.9476 (4)	0.3362 (2)	0.4924 (2)	5.03 (7)
C7	0.8636 (4)	0.4059 (2)	0.4748 (2)	5.12 (7)
N7	0.8098 (4)	0.4367 (2)	0.3835 (2)	6.53 (8)
C7*a*	0.7325 (5)	0.5112 (2)	0.3681 (2)	7.1 (1)
C7*b*	0.8211 (5)	0.3927 (3)	0.3031 (2)	7.7 (1)
C8	0.8366 (4)	0.4468 (2)	0.5537 (2)	4.73 (7)
C8*a*	0.8862 (4)	0.4142 (2)	0.6443 (2)	4.10 (6)
S9	0.84843 (9)	0.46599 (4)	0.74065 (5)	4.57 (2)
N10	1.0060 (3)	0.3102 (1)	0.7553 (1)	4.14 (5)
C11	0.9361 (4)	0.2401 (2)	0.7703 (2)	4.33 (6)
O11	0.8658 (3)	0.1990 (1)	0.7022 (1)	5.41 (5)
N12	0.9509 (3)	0.2196 (1)	0.8612 (2)	5.25 (6)
C13	0.8893 (5)	0.1450 (2)	0.8838 (3)	6.7 (1)
O1(solv.)	0.5658 (4)	0.2388 (2)	0.5697 (2)	8.60 (8)
C1(solv.)	0.4956 (8)	0.2949 (4)	0.7008 (4)	14.2 (2)
C2(solv.)	0.4829 (9)	0.2626 (6)	0.6266 (4)	18.8 (3)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C1—C1*a*	1.383 (4)	C5*a*—N10	1.427 (3)
C1—C2	1.370 (4)	C6—C7	1.385 (4)
C1*a*—C4*a*	1.379 (4)	C7—N7	1.383 (4)
C1*a*—N10	1.443 (3)	C7—C8	1.418 (4)
C2—C3	1.396 (4)	N7—C7*a*	1.431 (5)
C3—N3	1.387 (3)	N7—C7*b*	1.417 (5)
C3—C4	1.405 (3)	C8—C8*a*	1.385 (4)
N3—C3*a*	1.441 (4)	C8*a*—S9	1.763 (3)
N3—C3*b*	1.441 (4)	N10—C11	1.390 (4)
C4—C4*a*	1.385 (3)	C11—O11	1.231 (3)
C4*a*—S9	1.762 (2)	C11—N12	1.339 (4)
C5—C5*a*	1.402 (4)	N12—C13	1.457 (5)
C5—C6	1.395 (4)	C5*a*—C8*a*	1.387 (4)
C1—C1*a*—N10	122.1 (2)	C4*a*—C1*a*—N10	119.5 (2)
C2—C3—N3	121.5 (2)	N3—C3—C4	121.2 (2)
C3—N3—C3*a*	119.6 (2)	C3—N3—C3*b*	119.5 (2)
C3*a*—N3—C3*b*	116.9 (2)	C1*a*—C4*a*—S9	119.9 (2)
C4—C4*a*—S9	119.1 (2)	C5—C5*a*—N10	121.9 (2)
C8*a*—C5*a*—N10	119.9 (2)	C6—C7—N7	121.8 (3)
N7—C7—C8	120.1 (3)	C7—N7—C7*a*	120.6 (3)
C7—N7—C7*b*	120.5 (3)	C7*a*—N7—C7*b*	118.8 (3)
C5*a*—C8*a*—S9	119.4 (2)	C8--C8*a*—S9	118.5 (2)
C4*a*—S9—C8*a*	99.0 (1)	C1*a*—N10—C5*a*	116.3 (2)
C1*a*—N10—C11	123.0 (2)	C5*a*—N10—C11	118.1 (2)
N10—C11—O11	120.5 (3)	N10—C11—N12	117.2 (2)
O11—C11—N12	122.4 (3)	C11—N12—C13	120.8 (2)

The crystals were grown from an ethanol solution at 281 K. A crystal sealed in a glass capillary with N_2 gas was used for the diffraction experiments. An anisotropic decay correction was applied and refinement was by full-matrix least-squares methods.

Program used throughout the analysis: *MolEN* (Fair, 1990). Program used to solve structure: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Program used to draw figure: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71114 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1005]

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Acta Cryst. (1993). C**49**, 1541–1543

Structure of 5,5′,6,6′-Tetraphenyl-3,3′-bi-1,2,4-triazine

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(*Received* 25 *September* 1992; *accepted* 10 *February* 1993)

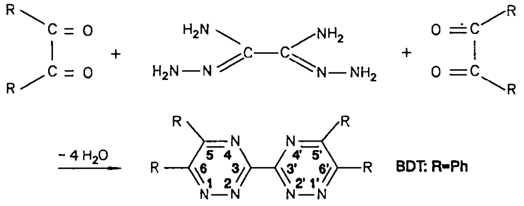
Abstract

The title compound (BDT) crystallizes in an *s-trans* conformation, the inversion center lying on the bond between the two triazine rings. The triazine rings are coplanar with the phenyl rings twisted 26.5 and 54.2° relative to them. Steric crowding caused by the adjacent phenyl groups is reflected in a distortion (±5°) of the exocyclic bond angles. The heteroaromatic rings deviate significantly from planarity; 0.046 (3) Å being the maximum deviation from the least-squares plane. The observed molecular dimensions are in good agreement with published structures of 1,2,4-triazines.

Comment

Due to their potential application as photosensitizers, polypyridyl complexes of Ru^{II} have received extensive scrutiny. An important goal of these studies has been the tuning of ground and excited-state properties. Key approaches involve peripheral substitution of the parent 2,2′-bipyridine with electron-donating or electron-withdrawing groups or polyimine ligands such as bipyrimidine, bipyridazine *etc.* (Ernst & Kaim, 1986; Juris, Balzani, Barigelletti, Campagna Belser & von Zelewsky, 1988; Kalyanasundaram, Nazeeruddin, Grätzel, Viscardi, Savarino & Barni, 1992; Kawanishi, Kitamura & Tazuke, 1989).

3,3′-Bi-1,2,4-triazines are readily accessible in high yields by cyclocondensation of α,β-diketones with oxamidodihydrazone (Case, 1965; Culbertson & Parr, 1967; Dedichen, 1936; Jensen & Pflaum, 1965; Kiss, 1984) and various substituents *R* can be easily introduced to the bi-triazine frame:



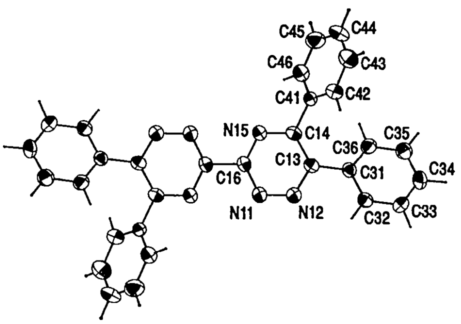


Fig. 1. *ORTEP* (Johnson, 1965) plot of 5,5′,6,6′-tetraphenyl-3,3′-bi-1,2,4-triazine showing the atom-labeling scheme. Thermal ellipsoids are scaled to enclose 50% probability. H atoms are scaled to an arbitrary size.

In a typical reaction the title compound (BDT, *R* = phenyl) was synthesized by refluxing oxamidodihydrazone (3.52 g; 30.03 mmol) and benzil (12.76 g; 60.7 mmol) with a few drops of HCl added in ethanol (200 ml) for about 3 h. Yield: 12.81 g; 91%.

Suitable single crystals were obtained by slow evaporation of a solution of BDT in DMF at slightly elevated temperature (313 K). Important interatomic distances and angles were calculated by the *CRYSTAL STRUCTURE UTILITY* program (Vickovic, 1988) and are listed in Table 2. Fig. 1 shows a view of the molecule and the numbering system.

Like 2,2′-bipyridine, BDT crystallizes in an *s-trans* conformation with the inversion center lying on the bond between C16 and C16^{i}. The triazine rings are coplanar and steric crowding caused by adjacent phenyl groups is reflected in the exocyclic bond angles at C13 and C14. The heteroaromatic rings deviate significantly from planarity with a maximum deviation of 0.046 (3) Å from the least-squares plane. While the deviations of the heteroaromatic rings from planarity [maximum: 0.012 (2) Å and 0.013 (1) Å, respectively] are less pronounced for published 1,2,4-triazine structures (Oeser, 1973; Atwood, Krass & Pandler, 1974), the observed molecular dimensions are in good agreement.

Experimental

Crystal data

$C_{30}H_{20}N_6$
$M_r = 464.5$
Tetragonal
$I4_1/a$ (origin at $\bar{1}$ on glide *b*)
$a = 27.699$ (3) Å
$c = 6.169$ (1) Å
$V = 4732.7$ (7) Å^3
$Z = 8$
$D_x = 1.30$ Mg m^{-3}
Cu $K\alpha$ radiation

$\lambda = 1.54185$ Å
Cell parameters from 25 reflections
$\theta = 8.0$–$16.5°$
$\mu = 0.6$ mm^{-1}
$T = 297$ K
Bar
0.29 × 0.10 × 0.06 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{\min} = 0.9457$, $T_{\max} = 0.9744$
3339 measured reflections
1209 independent reflections

2578 observed reflections $[I>\sigma(I)]$
$R_{\rm int} = 0.031$
$\theta_{\max} = 50.0°$
$h = -27 \rightarrow 27$
$k = 0 \rightarrow 27$
$l = -4 \rightarrow 6$
3 standard reflections
frequency: 100 min
intensity variation: none

Refinement

Refinement on *F*
Final $R = 0.066$

$w = 1.1434\sigma_F^{-2}$
$(\Delta/\sigma)_{\max} = 0.021$

$wR = 0.034$
$S = 2.1$
1209 reflections
204 parameters
All H-atom parameters refined

$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

H atoms were refined with a common but variable C—H bond length.

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

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N11	0.4653 (1)	0.5211 (1)	0.2257 (5)	0.0426 (9)
N12	0.4705 (1)	0.5511 (1)	0.3952 (5)	0.0407 (9)
C13	0.5138 (1)	0.5702 (1)	0.4409 (6)	0.0328 (10)
C14	0.5547 (1)	0.5568 (1)	0.3175 (6)	0.0319 (10)
N15	0.5490 (1)	0.5298 (1)	0.1395 (5)	0.0360 (8)
C16	0.5039 (1)	0.5147 (1)	0.1002 (5)	0.0325 (10)
C31	0.5135 (1)	0.6054 (1)	0.6231 (6)	0.0325 (10)
C32	0.4778 (1)	0.6015 (1)	0.7827 (6)	0.0356 (11)
C33	0.4776 (1)	0.6330 (1)	0.9575 (7)	0.0434 (12)
C34	0.5117 (2)	0.6686 (1)	0.9726 (7)	0.0533 (13)
C35	0.5461 (1)	0.6742 (1)	0.8113 (7)	0.0556 (14)
C36	0.5468 (1)	0.6425 (1)	0.6372 (7)	0.0441 (12)
C41	0.6053 (1)	0.5688 (1)	0.3713 (7)	0.0349 (11)
C42	0.6243 (1)	0.5574 (1)	0.5739 (8)	0.0487 (14)
C43	0.6726 (2)	0.5670 (2)	0.6150 (9)	0.0690 (17)
C44	0.7012 (2)	0.5886 (2)	0.4607 (10)	0.0737 (18)
C45	0.6827 (2)	0.6004 (2)	0.2605 (9)	0.0632 (16)
C46	0.6346 (2)	0.5899 (1)	0.2161 (7)	0.0456 (12)

Table 2. *Geometric parameters* (Å, °)

N11—N12	1.343 (4)	C14—N15	1.338 (5)
N11—C16	1.332 (4)	C14—C41	1.478 (4)
N12—C13	1.341 (4)	N15—C16	1.340 (4)
C13—C14	1.414 (4)	C16—C16^i	1.496 (4)
C13—C31	1.488 (5)		
N12—N11—C16	116.7 (3)	C13—C14—C41	125.4 (3)
N11—N12—C13	120.2 (3)	N15—C14—C41	115.0 (3)
N12—C13—C14	120.0 (3)	C14—N15—C16	115.7 (3)
N12—C13—C31	114.4 (3)	N11—C16—N15	127.0 (3)
C14—C13—C31	125.7 (3)	N11—C16—C16^i	115.9 (3)
C13—C14—N15	119.6 (3)	N15—C16—C16^i	117.0 (3)

Symmetry code: (i) $1 - x, 1 - y, -z$.

The generous support given by the Hanns Seidel Stiftung e. V. is gratefully acknowledged. We thank Dr U. Klement for the collection of diffractometer data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes deviations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71093 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1020]

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Acta Cryst. (1993). C**49**, 1543–1547

Structure of 1,4-Benzenedicyanamide Dianion Derivatives

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(*Received* 9 *April* 1992; *accepted* 8 *February* 1993)

Abstract

The crystal structures of four tetraphenylarsonium salts of 1,4-dicyanamidebenzene derivatives, namely, bis(tetraphenylarsonium) 1,4-benzenedicyanamide(2−), bis(tetraphenylarsonium) 2,5-dimethyl-1,4-benzenedicyanamide(2−), bis(tetraphenylarsonium) 2,5-dichloro-1,4-benzenedicyanamide(2−) and bis(tetraphenylarsonium) 2,3,5,6-tetrachloro-1,4-benzenedicyanamide(2−), were determined. All of the derivatives are essentially planar with the cyanamide groups in an *anti* configuration, suggesting a significant degree of π coupling between the cyanamide groups and phenyl ring. No evidence was seen of π stacking for any of the 1,4-dicyanamidebenzene dianion derivatives.

Acta Crystallographica Section C
ISSN 0108-2701 ©1993