Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A series of three bis[2-(methyl/trifluoromethyl)-4*H*-3,1-benzoxazin-4-one] compounds

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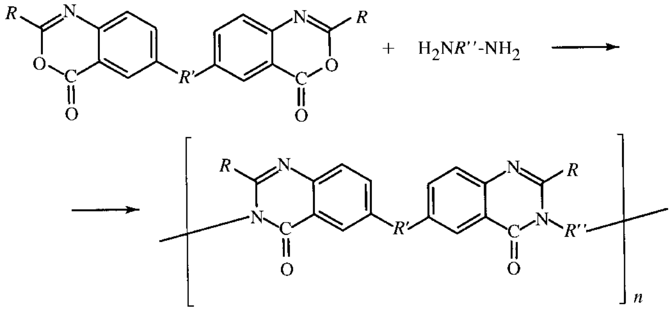
Received 20 July 1999
Accepted 3 November 1999

Each of the three title compounds, namely 6,6′-methylenebis(2-methyl-4*H*-3,1-benzoxazin-4-one), $C_{19}H_{14}N_2O_4$, 6,6′-methylenebis(2-trifluoromethyl-4*H*-3,1-benzoxazin-4-one), $C_{19}H_8F_3N_2O_4$, and 6,6′-bi(2-trifluoromethyl-4*H*-3,1-benzoxazin-4-one), $C_{18}H_6F_6N_2O_4$, contains two planar benzoxazinone fragments. In the first two compounds, these planes are virtually perpendicular to each other, while the third compound is planar overall. The electronic effects of the substituent groups on the oxazine moiety result in distortion of the bond angles at the C atoms of the C=O and C=N bonds, and in redistribution of electronic density in the oxazine rings. The latter leads to different bond lengths within this ring in the three molecules. All the molecules form stacks in their crystals with distances of 3.2–3.6 Å between adjacent molecules in a stack.

Comment

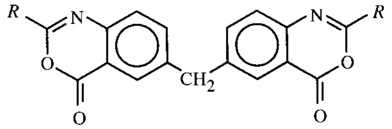
Polyquinazolones (PQs, see scheme below) are an important class of polyheteroarylenes which possess high thermal and hydrolytic stability, and have good solubility in organic solvents. PQs are usually synthesized from diamines and bis[2-(alkyl/phenyl)-4*H*-3,1-benzoxazin-4-one] compounds



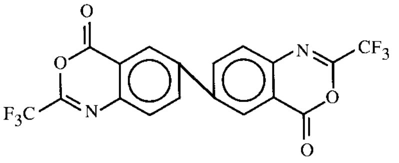
R, *R*″ = alkyl, aryl; *R*′ = alkyl, Ph

Films obtained from PQs based on aromatic diamines have thermal, dielectric and physico-mechanical properties comparable with those of common polyimides. It was also shown that, as a rule, PQs have dielectric indices exceeding those of the famous DuPont 'KAPTON' film (Odnoralova & Vasilyeva-Sokolova, 1978; Ponomarev *et al.*, 1992; de Gaudemaris *et al.*, 1965).

It is well known that when studying polymers, accurate knowledge of the molecular structure of the corresponding monomers is very important. For this reason, we undertook the current X-ray stuctural analysis of three 2-substituted bis-benzoxazinones, (I)–(III), which are of interest as PQ precursors.



(I) R = Me
(II) R = CF_3



(III)

The three molecules display symmetry. Each molecule of (III) has a crystallographic inversion center which coincides with the midpoint of the C6*A*—C6*A*^{i} bond, whereas (I) and (II) each has a twofold axis passing through C11. The twofold symmetry is approximate (and non-crystallographic) in (I) but crystallographic in (II). Furthermore, bond angles at C11 are close to tetrahedral values in (I) (Fig. 1), but somewhat distorted in (II) (Fig. 2), where the C6*A*—C11—C6*A*^{i} bond angle is 115.6 (4)°.

The benzoxazinone systems in all three molecules are planar, in agreement with earlier experimental data (Etter *et al.*, 1982; Pink *et al.*, 1993). Only in (III) does atom C10*A* of the trifluoromethyl group deviate from the oxazine plane, by 0.147 (2) Å. There appears to be no obvious way to rationalize this observation in terms of intramolecular interactions, since there are neither sterically bulky groups nor strong electronic ones in the molecule. Although not conclusive, the fact that the molecules form stacks suggests that intermolecular factors may be significant.

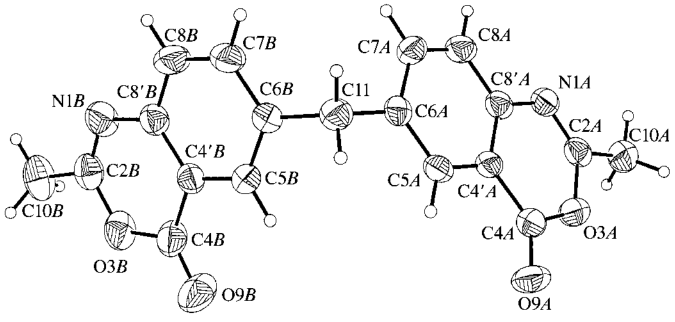


Figure 1
A view of (I) with displacement ellipsoids drawn at the 50% probability level. H atoms are shown with an arbitrary radius.

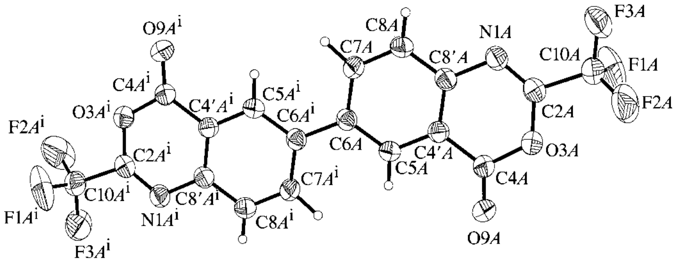


Figure 2
A view of (II) with displacement ellipsoids drawn at the 50% probability level. H atoms are shown with an arbitrary radius. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

While bond lengths involving O3*A* and O3*B* are almost equal in (I), the values for O3*A*—C2*A* are much shorter than those for O3*A*—C4*A* in compounds (II) and (III). Moreover, in all three structures, the bond angles at C2*A* and C4*A* (or C4*B*) are distorted from their ideal values of 120°. These observations are probably best explained by the concerted electronic effects of adjacent substituents, namely the trifluoromethyl and carbonyl groups.

The planes of the benzoxazinone moieties in (I) are virtually perpendicular to each other, as shown by the dihedral angle of 82.42 (5)°; the corresponding angle in (II) is 74.79 (7)°.

Molecules of (III) (Fig. 3) are planar overall despite the presence of unfavorable short intramolecular H7*A*···H5*A*$(-1 + x, -1 - y, -z)$ interactions of 2.12 (4) Å [the sum of the corresponding van der Waals radii is 2.32 Å (Zefirov & Zorkii, 1989)]. One F atom of each trifluoromethyl group in (II) and (III) lies in an approximately eclipsed conformation with respect to the adjacent C═N bond, as shown by the torsion angles N1*A*—C2*A*—C10*A*—F2*A* of −11.3 (5)° for (II) and N1*A*—C2*A*—C10*A*—F3*A* of 15.8 (3)° for (III).

Molecules of all three compounds form stacks [along the crystallographic *a* axis for (I) and along the *b* axis for (II) and (III)], with the distance between successive molecules in the range 3.2–3.6 Å. However, in (I), only the benzoxazinone moieties where the atoms carry the suffix *B* (Fig. 1) form stacks; the moieties identified by the suffix *A* occupy the space between them. In (III), adjacent stacks are connected by weak intermolecular H7*A*···F3*A*′$(2 - x, -1 - y, -z)$ interactions of 2.55 (3) Å [the sum of the corresponding van der Waals radii is 2.57 Å (Zefirov & Zorkii, 1989)].

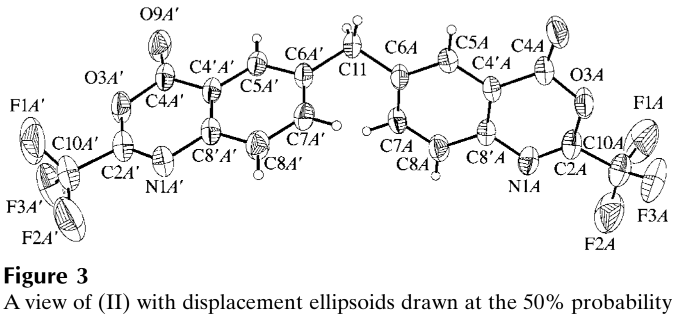


Figure 3
A view of (II) with displacement ellipsoids drawn at the 50% probability level. H atoms are shown with an arbitrary radius. [Symmetry code: (i) $1 - x, -1 - y, -z$.]

Experimental

The compounds studied were synthesized by analogous reactions of 5,5′-methylenebisanthranilic or 5,5′-bianthranilic acids (0.01 mol) with the corresponding anhydride (20 ml) [acetic anhydride for the preparation of (I) and hexafluoroacetic anhydride for the preparation of (II) and (III)] under reflux for 10 h. Crystals of the products suitable for X-ray structure determination were obtained after the reaction mixtures had been cooled and allowed to stand for several days.

Compound (I)

Crystal data

$C_{19}H_{14}N_2O_4$
$M_r = 334.32$
Triclinic, $P\overline{1}$
$a = 7.162$ (2) Å
$b = 8.2217$ (15) Å
$c = 13.807$ (4) Å
$\alpha = 98.10$ (2)°
$\beta = 99.40$ (2)°
$\gamma = 102.51$ (2)°
$V = 769.8$ (3) Å^3
$Z = 2$
$D_x = 1.442$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–12°
$\mu = 0.103$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.50 × 0.20 × 0.20 mm

Data collection

Siemens *P*3/PC four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2964 measured reflections
2722 independent reflections
1399 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$
2 standard reflections every 98 reflections intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.189$
2710 reflections
228 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Compound (II)

Crystal data

$C_{19}H_8F_6N_2O_4$
$M_r = 442.28$
Monoclinic, $C2/c$
$a = 25.643$ (17) Å
$b = 5.206$ (2) Å
$c = 16.211$ (10) Å
$\beta = 126.35$ (4)°
$V = 1743.0$ (17) Å^3
$Z = 4$
$D_x = 1.685$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–12°
$\mu = 0.161$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colorless
0.40 × 0.30 × 0.30 mm

Data collection

Siemens *P*3/PC four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2596 measured reflections
2544 independent reflections
1468 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.116$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 36$
$k = 0 \rightarrow 7$
$l = -22 \rightarrow 18$
2 standard reflections every 98 reflections intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.209$
$S = 1.157$
2492 reflections
145 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1162P)^2 + 2.6524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Compound (III)

Crystal data

$C_{18}H_6F_6N_2O_4$
$M_r = 428.24$
Monoclinic, $P2_1/n$
$a = 10.509$ (2) Å
$b = 5.0144$ (7) Å
$c = 15.397$ (3) Å
$\beta = 95.35$ (2)°
$V = 807.8$ (3) Å^3
$Z = 2$

$D_x = 1.761$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–12°
$\mu = 0.171$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, yellow
0.50 × 0.30 × 0.30 mm

Data collection

Siemens *P*3/PC four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2066 measured reflections
1962 independent reflections
1357 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$

$\theta_{\max} = 28.06°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 6$
$l = -20 \rightarrow 20$
2 standard reflections every 98 reflections intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.146$
$S = 1.248$
1939 reflections
148 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

All H atoms were found by difference Fourier syntheses. Methyl H atoms in (I) were refined as part of an idealized group which was allowed to rotate about the local C—C vector but not to deform or tip; the other H atoms were treated as riding [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$], as were those of (II). The H atoms of (III) were refined isotropically [C—H 0.89 (2)–1.01 (2) Å].

For all compounds, data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by the Russian Foundation for Basic Research (grant Nos. 97-03-33783a and 96-15-97367).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1366). Services for accessing these data are described at the back of the journal.

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