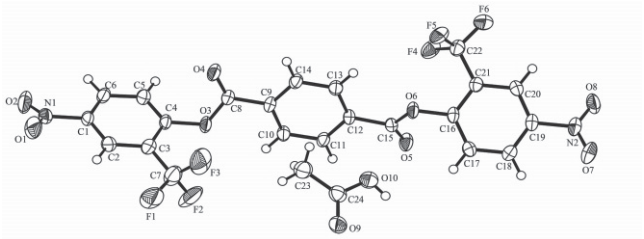
# Crystal structure of bis(2-trifluoromethyl-4-nitrophenyl) terephthalate — acetic acid (1:1), $C_{24}H_{14}F_6N_2O_{10}$

Wei Chen, Mian Ji and Shiyong Yang*

Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100190, P. R. China

Received December 23, 2014, accepted June 01, 2015, available online June 09, 2015, CCDC no. 1267/4322




**Abstract**

$C_{24}H_{14}F_6N_2O_{10}$, triclinic, $P\bar{1}$ (no. 2), $a$ = 9.985(2) Å, $b$ = 11.496(3) Å, $c$ = 12.721(2) Å, $\alpha$ = 107.297(9)°, $\beta$ = 112.982(9)°, $\gamma$ = 94.214(14)°, $V$ = 1253.4 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.0656, $wR_{ref}(F^2)$ = 0.1427, $T$ = 173 K.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colourless blocks, size 0.13×0.21×0.36 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 1.53 cm$^{-1}$ |
| Diffractometer, scan mode: | MM007-HF CCD(Saturn 724+), $\omega$ at fixed $\chi$ = 45° |
| $2\theta_{max}$: | 54.96° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 16660, 5718 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 4 |
| $N(param)_{refined}$: | 381 |
| Programs: | OLEX2, SHELX [3, 4] |

## Source of material

In a three-necked flask with magnetic agitation and nitrogen inlet/outlet, 4-nitro-2-(trifluoromethyl) benzenol (44 mmol, 4.56 g) and triethyl amine (10 ml) were first dissolved in anhydrous DMF (25 ml), then a solution of terephthaloyl chloride (10 mmol, 2.03 g) in dry DMF was added dropwise. The mixture reacted at room temperature for 2 h and heated at 60 °C for another 2 h. After cooling down, the reaction mixture was poured into 400 ml of solution consisting of methanol-water (1:1, by volume) and washed repeatedly. The light brown precipitate was recrystallized from glacial acetic acid to provide white needles, the obtained product was finally dried under vacuum at 80 °C for 12 h. Yield: 87%, the melting point is 361K. Elemental analysis (%): calced. for $C_{22}H_{10}F_6N_2O_8$: C, 48.54; H, 1.85; N, 5.15%; Found C,48.69; H, 2.11; N, 4.95%.

## Experimental details

The hydrogen atoms were added using riding models with $U_{iso}$(H) = 1.2$U_{eq}$.

## Discussion

The title compound bis (2-trifluoromethyl-4-nitrophenyl) terephthalate can be used as an important intermediate in the synthesis of corresponding diamine, which acts as a monomer for the preparation of polyimide films with low coefficients of thermal expansion (CTE). Low CTE polyimides have been widely used in a variety of micro and optoelectronic applications, because of their combined excellent properties, including high glass transition temperature, high resistance to chemicals and radiation, and good mechanical properties [1]. The ester linkages in the title compound contribute to the stiff and almost linear structure, consequently improving the in-plane orientation during imidization and reducing CTE of the derived PIs [2]. The introduction of trifluoromethyl group also promote transparency of the polyimide films. The title molecule exhibits a symmetrical structure and its crystal structure is build up by the $C_{22}H_{10}F_6N_2O_8$ molecule and one $CH_3COOH$ molecule. The bond lengths are $d$(F1–C7) = 1.335(3) Å, d(O1–N1) = 1.213(3) Å, $d$(O3–C4) = 1.397(2) Å, $d$(O3–C8) = 1.372(3) Å, $d$(O4–C8) = 1.200(3) Å, $d$(N1–C1) = 1.472(3) Å, $d$(C3–C7) = 1.496(4) Å and $d$(C8–C9) = 1.477(3) Å. The angles are C8–O3–O4 = 116.15(16)°, O1–N1–O2 = 124.4(2)°, F1–C7–C3 = 112.2(2)°, F1–C7–F2 = 106.4(3)°, O3–C8–C9 = 111.69(17)° and O3–C8–O4 = 122.11(19)°. The nitro group (O1–N1–O2) attached at C1 forms dihedral angles of 22.4° with the benzene ring. In the trifluoromethyl group, the three C–F bond lengths are nearly equal, at about 107°. The dihedral angles between the benzene ring 2 which attach to ester groups (C9-C14) and the benzene ring 1 which attach to nitro group (C1-C6) and benzene ring 3 which attach to nitro group (C16-C21) is 80.17° (almost perpendicular) and 49.96°, respectively. In the crystal structure acetic acid molecules are pairwise connected by hydrogen bonds of O–H···O type to form the typical dimers. Parameters of these bonds are follwing: O10··O9$^{\#1}$ = 2.654(3) Å, O10–H10A···O9$^{\#1}$ = 166.4°.

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(2) | 2*i* | –0.0166 | 0.2791 | 0.8322 | 0.043 |
| H(5) | 2*i* | 0.4062 | 0.5502 | 0.9069 | 0.036 |
| H(6) | 2*i* | 0.3396 | 0.5572 | 1.0649 | 0.037 |
| H(10) | 2*i* | 0.2531 | 0.4437 | 0.4987 | 0.033 |
| H(11) | 2*i* | 0.2854 | 0.4211 | 0.3233 | 0.032 |
| H(13) | 2*i* | 0.5855 | 0.2106 | 0.4175 | 0.034 |
| H(14) | 2*i* | 0.5600 | 0.2408 | 0.5968 | 0.034 |
| H(17) | 2*i* | 0.3164 | 0.1250 | –0.0227 | 0.036 |
| H(18) | 2*i* | 0.3606 | 0.0850 | –0.1959 | 0.035 |
| H(20) | 2*i* | 0.8020 | 0.1962 | 0.0179 | 0.033 |
| H(10A) | 2*i* | 0.1257 | 0.0658 | 0.0667 | 0.074 |
| H(23A) | 2*i* | 0.1556 | 0.1494 | 0.3489 | 0.066 |
| H(23B) | 2*i* | 0.2164 | 0.0266 | 0.3335 | 0.066 |
| H(23C) | 2*i* | 0.0545 | 0.0239 | 0.3233 | 0.066 |

* Correspondence author (e-mail: shiyang@iccas.ac.cn)

**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| F(1) | 2*i* | –0.1208(2) | 0.1864(2) | 0.6128(2) | 0.058(1) | 0.091(2) | 0.050(1) | –0.029(1) | 0.0096(9) | 0.016(1) |
| F(2) | 2*i* | –0.0422(2) | 0.3167(2) | 0.5493(2) | 0.073(1) | 0.101(2) | 0.0321(9) | –0.009(1) | –0.0001(9) | 0.031(1) |
| F(3) | 2*i* | 0.0689(2) | 0.1684(2) | 0.5743(2) | 0.092(2) | 0.071(1) | 0.053(1) | –0.004(1) | 0.034(1) | –0.014(1) |
| F(4) | 2*i* | 0.7936(2) | 0.3492(1) | 0.3135(1) | 0.0550(9) | 0.0371(8) | 0.0283(7) | 0.0116(7) | 0.0104(7) | 0.0030(6) |
| F(5) | 2*i* | 0.8134(2) | 0.1597(1) | 0.2915(1) | 0.0488(9) | 0.0458(9) | 0.0308(7) | 0.0142(7) | 0.0109(6) | 0.0200(7) |
| F(6) | 2*i* | 0.9374(2) | 0.2704(2) | 0.2367(1) | 0.0300(8) | 0.067(1) | 0.0398(8) | 0.0007(7) | 0.0095(7) | 0.0162(8) |
| O(1) | 2*i* | 0.0420(3) | 0.3245(3) | 1.0498(2) | 0.061(1) | 0.130(2) | 0.054(1) | –0.012(2) | 0.030(1) | 0.046(2) |
| O(2) | 2*i* | 0.1708(3) | 0.5124(2) | 1.1530(2) | 0.085(2) | 0.079(2) | 0.040(1) | 0.049(1) | 0.043(1) | 0.031(1) |
| O(3) | 2*i* | 0.2682(2) | 0.4083(2) | 0.6799(1) | 0.0407(9) | 0.0421(9) | 0.0250(8) | 0.0174(7) | 0.0217(7) | 0.0182(7) |
| O(4) | 2*i* | 0.4527(2) | 0.3111(2) | 0.7518(1) | 0.048(1) | 0.0401(9) | 0.0248(8) | 0.0199(8) | 0.0206(7) | 0.0169(7) |
| O(5) | 2*i* | 0.4197(2) | 0.3676(2) | 0.1819(2) | 0.052(1) | 0.042(1) | 0.0346(9) | 0.0232(8) | 0.0283(8) | 0.0239(8) |
| O(6) | 2*i* | 0.5095(2) | 0.1977(2) | 0.2033(1) | 0.0405(9) | 0.0360(9) | 0.0273(8) | 0.0159(7) | 0.0232(7) | 0.0172(7) |
| O(7) | 2*i* | 0.5146(2) | 0.0485(2) | –0.3096(2) | 0.070(1) | 0.041(1) | 0.0274(9) | 0.0087(9) | 0.0247(9) | 0.0066(8) |
| O(8) | 2*i* | 0.7324(2) | 0.1701(2) | –0.1971(2) | 0.050(1) | 0.061(1) | 0.046(1) | 0.0151(9) | 0.0358(9) | 0.0255(9) |
| N(1) | 2*i* | 0.1205(2) | 0.4179(3) | 1.0621(2) | 0.038(1) | 0.082(2) | 0.039(1) | 0.028(1) | 0.025(1) | 0.039(1) |
| N(2) | 2*i* | 0.6128(2) | 0.1167(2) | –0.2115(2) | 0.050(1) | 0.032(1) | 0.029(1) | 0.0151(9) | 0.0243(9) | 0.0136(8) |
| C(1) | 2*i* | 0.1590(3) | 0.4163(2) | 0.9613(2) | 0.035(1) | 0.051(2) | 0.027(1) | 0.021(1) | 0.020(1) | 0.024(1) |
| C(2) | 2*i* | 0.0673(3) | 0.3333(3) | 0.8461(2) | 0.030(1) | 0.051(2) | 0.034(1) | 0.008(1) | 0.016(1) | 0.022(1) |
| C(3) | 2*i* | 0.1031(3) | 0.3325(2) | 0.7507(2) | 0.034(1) | 0.040(1) | 0.027(1) | 0.008(1) | 0.013(1) | 0.015(1) |
| C(4) | 2*i* | 0.2329(2) | 0.4117(2) | 0.7767(2) | 0.035(1) | 0.035(1) | 0.024(1) | 0.0161(9) | 0.0185(9) | 0.0171(9) |
| C(5) | 2*i* | 0.3216(3) | 0.4963(2) | 0.8923(2) | 0.033(1) | 0.034(1) | 0.028(1) | 0.0076(9) | 0.0154(9) | 0.0140(9) |
| C(6) | 2*i* | 0.2829(3) | 0.4997(2) | 0.9865(2) | 0.037(1) | 0.038(1) | 0.021(1) | 0.014(1) | 0.0142(9) | 0.0119(9) |
| C(7) | 2*i* | 0.0026(3) | 0.2507(3) | 0.6218(3) | 0.053(2) | 0.057(2) | 0.033(1) | –0.007(1) | 0.016(1) | 0.009(1) |
| C(8) | 2*i* | 0.3826(2) | 0.3513(2) | 0.6749(2) | 0.032(1) | 0.028(1) | 0.022(1) | 0.0069(9) | 0.0135(9) | 0.0101(8) |
| C(9) | 2*i* | 0.4023(2) | 0.3434(2) | 0.5640(2) | 0.035(1) | 0.025(1) | 0.019(1) | 0.0062(9) | 0.0143(9) | 0.0081(8) |
| C(10) | 2*i* | 0.3202(2) | 0.3978(2) | 0.4825(2) | 0.033(1) | 0.030(1) | 0.025(1) | 0.0109(9) | 0.0174(9) | 0.0116(9) |
| C(11) | 2*i* | 0.3386(2) | 0.3837(2) | 0.3774(2) | 0.032(1) | 0.030(1) | 0.023(1) | 0.0103(9) | 0.0140(9) | 0.0135(9) |
| C(12) | 2*i* | 0.4378(2) | 0.3127(2) | 0.3531(2) | 0.030(1) | 0.026(1) | 0.023(1) | 0.0059(8) | 0.0161(9) | 0.0102(8) |
| C(13) | 2*i* | 0.5200(2) | 0.2581(2) | 0.4344(2) | 0.032(1) | 0.031(1) | 0.027(1) | 0.0114(9) | 0.0158(9) | 0.0127(9) |
| C(14) | 2*i* | 0.5035(2) | 0.2751(2) | 0.5409(2) | 0.034(1) | 0.033(1) | 0.023(1) | 0.0111(9) | 0.0136(9) | 0.0138(9) |
| C(15) | 2*i* | 0.4518(2) | 0.2988(2) | 0.2382(2) | 0.025(1) | 0.031(1) | 0.024(1) | 0.0070(8) | 0.0141(9) | 0.0117(9) |
| C(16) | 2*i* | 0.5328(2) | 0.1803(2) | 0.0990(2) | 0.036(1) | 0.025(1) | 0.025(1) | 0.0103(9) | 0.0197(9) | 0.0125(8) |
| C(17) | 2*i* | 0.4133(3) | 0.1380(2) | –0.0150(2) | 0.028(1) | 0.036(1) | 0.031(1) | 0.0048(9) | 0.0170(9) | 0.014(1) |
| C(18) | 2*i* | 0.4392(3) | 0.1151(2) | –0.1182(2) | 0.034(1) | 0.029(1) | 0.023(1) | 0.0043(9) | 0.0112(9) | 0.0092(9) |
| C(19) | 2*i* | 0.5846(3) | 0.1380(2) | –0.1024(2) | 0.040(1) | 0.026(1) | 0.027(1) | 0.0105(9) | 0.021(1) | 0.0111(9) |
| C(20) | 2*i* | 0.7055(2) | 0.1811(2) | 0.0106(2) | 0.029(1) | 0.028(1) | 0.031(1) | 0.0081(9) | 0.0184(9) | 0.0125(9) |
| C(21) | 2*i* | 0.6789(2) | 0.2014(2) | 0.1130(2) | 0.031(1) | 0.024(1) | 0.025(1) | 0.0077(8) | 0.0137(9) | 0.0099(8) |
| C(22) | 2*i* | 0.8057(3) | 0.2453(2) | 0.2384(2) | 0.038(1) | 0.033(1) | 0.027(1) | 0.009(1) | 0.016(1) | 0.0091(9) |
| O(9) | 2*i* | –0.0565(2) | –0.0207(2) | 0.1007(2) | 0.033(1) | 0.068(1) | 0.039(1) | –0.0068(9) | 0.0154(8) | 0.0051(9) |
| O(10) | 2*i* | 0.1682(2) | 0.0735(2) | 0.1388(2) | 0.0340(9) | 0.064(1) | 0.040(1) | –0.0039(9) | 0.0130(8) | 0.013(1) |
| C(23) | 2*i* | 0.1297(3) | 0.0608(3) | 0.3065(2) | 0.043(1) | 0.045(2) | 0.039(1) | 0.010(1) | 0.016(1) | 0.009(1) |
| C(24) | 2*i* | 0.0717(3) | 0.0338(2) | 0.1732(2) | 0.035(1) | 0.036(1) | 0.039(1) | 0.007(1) | 0.017(1) | 0.006(1) |

*Acknowledgments.* This work is financially supported by National Basic Research Program of China (No.2014CB643604).

## References

1. Hasegawa, M.; Koseki, K.: Poly(ester imide)s possessing low CTE and low water absorption. High. Perform. Polym. **18** (2006) 697–717.
2. Hasegawa, M.; Tsujimura, Y.; Koseki, K.; Miyazaki, T.: Poly(ester imide)s possessing low CTE and low water absorption (II): effect of substituents. Polym. J. **40** (2008) 56–67.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: A complete structure solution, refinement and analysis program. J. Appl. Cryst. **42** (2009) 339–341.
4. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.