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Structure of the β-Form of *p*-Formylcinnamic Acid, $C_{10}H_8O_3$, a Photodimerizable Crystal

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Abstract. $M_r = 176\cdot2$, monoclinic, $P2_1/n$, $a = 6\cdot261\ (2)$, $b = 4\cdot825\ (1)$, $c = 27\cdot614\ (9)$ Å, $\beta = 91\cdot54\ (2)°$, $V = 833\cdot9\ (4)$ Å^3, $Z = 4$, $D_m = 1\cdot40$, $D_x = 1\cdot403$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1\cdot5418$ Å, $\mu = 0\cdot88$ mm^{-1}, $F(000) = 368$, $T = 298$ K. Final $R = 0\cdot058$ for 1286 unique observed reflexions. Nearly planar molecules are piled up along the short *b* axis to form a parallel plane-to-plane stack. The *b*-axial length is just the shortest intermolecular distance between reactive double bonds, indicating that the double bonds related by the **b** translation would react to form a cyclobutane ring with a mirror symmetry. This conforms with the experimental results, though 4·825 Å is the longest separation so far found for solid-state photodimerization. Since the plane-to-plane perpendicular distance between reactive molecules is fairly short (3·888 Å), it may be concluded that the topochemical behaviour is better understood by π-interactions between reactive molecules than by the distances between functional groups.

Introduction. *p*-Formylcinnamic acid (*p*-FCA) crystallizes in two polymorphic modifications; that is, the photodimerizable β-form from ethanol solution and the photostable γ-form from acetone solution (Nakanishi, Nakanishi, Tasai, Suzuki & Hasegawa, 1974). Solid-state photodimerization of the β-form of *p*-FCA is of interest in that the reaction proceeds more effectively with incorporation of surrounding water molecules (Nakanishi, Nakanishi, Tsuchiya & Hasegawa, 1976; Hasegawa, Katsuki & Iida, 1981). In addition, it has been recently found that the β-form of *p*-FCA, when exposed to HCl gas and suspended in alcohol, undergoes acetal formation *via* a solid–liquid heterogeneous reaction, whereas the γ-form does not (Nakanishi, Ishii & Nakanishi, 1984). The present crystal-structure analysis has been carried out to clarify the topochemical characteristics in these reactions.

Experimental. *p*-FCA prepared by condensation of terephthalaldehyde with malonic acid (Wiley & Hobson, 1949); colourless plate-like crystals (from vacuum sublimation), 0·40 × 0·35 × 0·05 mm. D_m by flotation in a mixture of cyclohexane and carbon tetrachloride. Nicolet automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit-cell dimensions determined by least squares with 2θ values of 25 high-angle reflexions. Intensity data in range $2\theta < 140°$ (range of *hkl*: 0→8, 0→6, −34→34), $2\theta/\omega$ scanning, scanning speed 5–16° (2θ)min^{-1}, scan width 1·0° (ω) plus $\alpha_1-\alpha_2$ divergence. Three reflexions monitored periodically showed no significant intensity deterioration; no absorption correction. Structure solved by direct methods and refined using *SHELX76* (Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1\cdot0$; H (from difference map) isotropic; final $R = 0\cdot058$ for 1286 reflexions $[|F_o| > 5\sigma(|F_o|)]$. $|\Delta/\sigma|_{\max} = 0\cdot18$. $\Delta\rho$ excursions $-0\cdot26$–$0\cdot16$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters and bond distances and angles are listed in Tables 1* and 2 respectively. The numbering system used is shown in Fig. 1.

The H atom of the carboxyl group is bound at two positions. One is located at a distance of 0·74 Å from O(13) with an occupancy factor of 0·55 and the other is at 1·18 Å from O(12) with 0·45 occupancy. The benzene ring and ethylene and carboxyl groups are planar.* Dihedral angles are 1·2 (3)° between benzene and ethylene planes, 3·3 (3)° between benzene and carboxyl planes, and 5·5 (3)° between benzene and formyl carbonyl planes. Thus, the molecule as a whole is nearly planar, within a deviation of 0·07 Å from the mean plane.*

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* Lists of structure factors, anisotropic thermal parameters of C and O atoms, least-squares planes of the expected planar moieties, atomic coordinates of H atoms and bond distances between H and non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39704 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The crystal structure viewed along the *a* axis is shown in Fig. 2. The molecules form cyclic hydrogen-bonded pairs around the centre of symmetry, and are piled up along the *b* axis to form a parallel plane-to-plane stack. The length of the *b* axis (4·825 Å) is just the shortest intermolecular distance between reactive double bonds. The second shortest distance of 5·287 Å is found between the molecules related by the centre of symmetry. Therefore, it is most probable that the double bonds related by the **b** translation react to form a cyclobutane ring with a mirror symmetry. In fact, the photodimerization of the β-form crystal gives rise to the dimer with a mirror symmetry (4,4′-diformyl-β-truxinic acid)* in a quantitative yield (Nakanishi *et al.*, 1974). 4·825 Å is the longest separation so far found for topochemical photodimerization, and is in the range of photostable modifications (Schmidt, 1967). Fig. 1 shows the overlapping of reactive molecules where the plane-to-plane perpendicular distance is 3·388 Å, implying that π-electron interactions between these two molecules must be large. Thus, it may be concluded that topochemical behaviour is better understood by π-interactions between reactive molecules than by the distance between functional groups, as has been pointed out by Frank & Paul (1973).

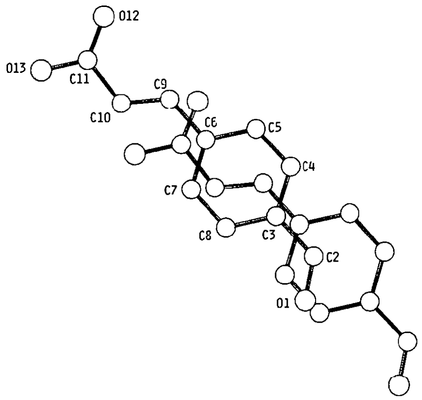

Fig. 1. The crystal structure viewed along the *a* axis.

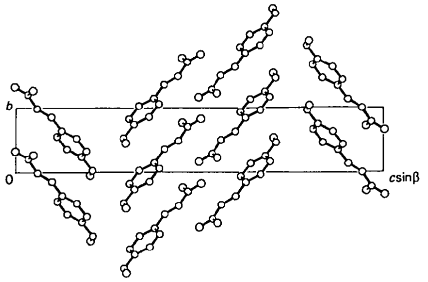

Fig. 2. The overlapping of reactive molecules viewed along the normal to the mean plane of the molecule.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for p-FCA*

$$U_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i U_{ii}.$$

	x	y	z	U_{eq}(Å^2)
O(1)	−0·3349 (3)	1·5401 (5)	0·2949 (1)	0·0669
C(2)	−0·1542 (5)	1·4656 (6)	0·2898 (1)	0·0475
C(3)	−0·0432 (5)	1·2531 (5)	0·3194 (1)	0·0396
C(4)	0·1604 (4)	1·1687 (6)	0·3076 (1)	0·0461
C(5)	0·2660 (4)	0·9670 (6)	0·3344 (1)	0·0453
C(6)	0·1713 (4)	0·8491 (5)	0·3744 (1)	0·0406
C(7)	−0·0324 (4)	0·9374 (6)	0·3865 (1)	0·0483
C(8)	−0·1393 (4)	1·1361 (6)	0·3592 (1)	0·0451
C(9)	0·2880 (4)	0·6360 (5)	0·4025 (1)	0·0441
C(10)	0·2196 (5)	0·5055 (6)	0·4409 (1)	0·0494
C(11)	0·3451 (4)	0·2884 (5)	0·4662 (1)	0·0462
O(12)	0·5285 (3)	0·2268 (4)	0·4534 (1)	0·0594
O(13)	0·2522 (3)	0·1675 (4)	0·5013 (1)	0·0409

Table 2. *Bond distances* (Å) *and angles* (°)

O(1)–C(2)	1·200 (3)	C(8)–C(3)	1·387 (3)
C(2)–C(3)	1·474 (3)	C(6)–C(9)	1·471 (3)
C(3)–C(4)	1·385 (3)	C(9)–C(10)	1·315 (4)
C(4)–C(5)	1·381 (4)	C(10)–C(11)	1·474 (4)
C(5)–C(6)	1·388 (4)	C(11)–O(12)	1·247 (3)
C(6)–C(7)	1·394 (4)	C(11)–O(13)	1·283 (3)
C(7)–C(8)	1·382 (4)		
O(1)–C(2)–C(3)	125·0 (3)	C(7)–C(6)–C(9)	122·1 (2)
C(2)–C(3)–C(4)	119·7 (2)	C(6)–C(7)–C(8)	120·9 (2)
C(2)–C(3)–C(8)	121·0 (2)	C(7)–C(8)–C(3)	120·1 (2)
C(4)–C(3)–C(8)	119·3 (2)	C(6)–C(9)–C(10)	126·4 (3)
C(3)–C(4)–C(5)	120·7 (2)	C(9)–C(10)–C(11)	122·8 (3)
C(4)–C(5)–C(6)	120·5 (2)	C(10)–C(11)–O(12)	121·2 (2)
C(5)–C(6)–C(7)	118·6 (2)	C(10)–C(11)–O(13)	115·7 (3)
C(5)–C(6)–C(9)	119·3 (2)	O(12)–C(11)–O(13)	123·0 (3)

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* Truxinic acid is 3,4-diphenyl-1,2-cyclobutanedicarboxylic acid.