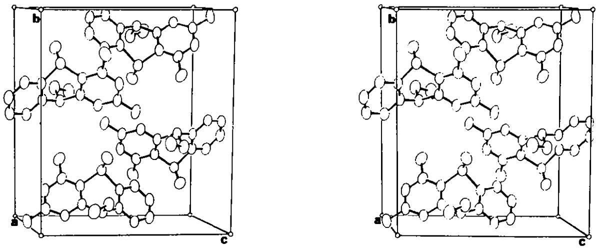

Fig. 3. The molecular packing of *cis*-9-ethyl-2,4-dimethylthioxanthene 10-oxide in a unit cell.

in the crystal is shown in Fig. 3. There are no intermolecular contacts shorter than van der Waals distances.

The equations of the least-squares planes of the two benzene rings are $0{\cdot}7339x - 0{\cdot}5991y + 0{\cdot}1872z = 1{\cdot}280$ and $-0{\cdot}7749x + 0{\cdot}5358y + 0{\cdot}4653z = 1{\cdot}410$ (where x, y, and z are in Å) for rings A and B (Fig. 1), respectively. The deviations of atoms from the planes range from 0·001 to 0·007 Å. The deviations of the two methyl substituents on the benzene ring, C(15) and C(16), from plane A are 0·03 and 0·05 Å, respectively. The folding angle between the planes of the two benzene rings is 141·5°, compared with 147·3° in *cis*-2,4,9-trimethylthioxanthene 10-oxide (Chu, Rosenstein & Ternay, 1979). The difference in the folding angle is apparently due to the effect of the different 9 substituent since the C—S—C and C—C—C bond angles involving the *meso* atoms within the central ring are both smaller in the title compound.

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References

Chu, S. S. C. (1975). *Acta Cryst.* **B31**, 1082–1087.

Chu, S. S. C., Kou, W. W. & van der Helm, D. (1978). *Acta Cryst.* **B34**, 308–312.

Chu, S. S. C. & Rosenstein, R. (1980). *Acta Cryst.* **B36**, 989–991.

Chu, S. S. C., Rosenstein, R. & Ternay, A. L. Jr (1979). *Acta Cryst.* **B35**, 2430–2433.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Shiono, R. (1971). Tech. Rep. 49, Crystallography Department, Univ. of Pittsburgh.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1981). **B37**, 777–779

Structure of *p*-Cyanobenzoic Acid

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Abstract. $C_8H_5NO_2$, triclinic, $P\bar{1}$, $a = 13{\cdot}000\,(2)$, $b = 7{\cdot}406\,(3)$, $c = 3{\cdot}831\,(1)$ Å, $\alpha = 101{\cdot}68\,(4)$, $\beta = 89{\cdot}93\,(2)$, $\gamma = 101{\cdot}69\,(3)°$, $Z = 2$, $D_x = 1{\cdot}382$ Mg m^{-3}; final $R = 0{\cdot}086$ for 1050 reflections collected photographically. The molecule has approximate twofold symmetry with normal molecular dimensions, and the carboxyl group is disordered. The crystal structure consists of layers of molecules parallel to (201). The molecules are linked by hydrogen bonds forming dimers, which are gathered together *via* antiparallel contacts of the cyano groups. In addition, the short intermolecular contacts suggest some contribution of Coulombic interaction in the crystal.

Introduction. As part of a study on the molecular packing of benzonitriles, the crystal structure of *p*-cyanobenzoic acid has been determined. Colourless wedge-shaped crystals were grown in ethanol solution by slow evaporation.

Intensity data were measured on a Syntex AD1 autodensitometer from equi-inclination Weissenberg photographs about the b ($h0l$–$h4l$) and c axes ($hk0$–$hk2$), with Ni-filtered Cu $K\alpha$ radiation. 1050 reflection data were obtained by application of the usual corrections. An absorption correction [μ(Cu $K\alpha$) = 0·808 mm^{-1}] was also applied, taking into consideration the irregular shape of the crystal used for the data

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collection. The wedge-shaped crystal measured *ca* 0·02 × 0·61 × 0·46 mm. The space group $P\bar{1}$ was determined from the statistical behaviour of the intensity data.

The structure was solved by the sharpened Patterson synthesis. The model was refined first by rigid-body least squares in which rotational motion of the carboxyl group was allowed, and subsequently by full-matrix least squares with anisotropic thermal parameters. The final R value was 0·086.

At a later stage of the refinement all the H atoms, except for that of the carboxyl, were located on the difference synthesis and included in the refinement with fixed positional and isotropic thermal parameters. On the difference synthesis calculated after several cycles of the refinement in which the carboxyl H atom was omitted, a slight peak was found at the expected position near the O(11) atom, but the following refinement including it made the C(9)—O(11) bond length shorter than C(9)—O(10). An alternative assumption of two H atoms with half occupancy also resulted in some distortion of the molecular dimensions. Thus the carboxyl H atom was neglected.

All the computations were carried out on a FACOM M-190 computer at the Data Processing Center, Kyoto University, using the programs of the KPAX system. Analytical expressions of the atomic scattering factors were used for all atoms; the coefficients were taken from *International Tables for X-ray Crystallography* (1974). The final atomic positional and thermal parameters are listed in Table 1.*

Discussion. The molecule of *p*-cyanobenzoic acid has approximate twofold symmetry and bond lengths and angles, shown in Fig. 1, are normal within experimental error. The molecule is slightly distorted from planarity (Table 2). The benzene ring is planar within 0·008 Å, while the cyano and the carboxyl groups deviate from it significantly. The thermal parameters of the atoms in both groups have larger components perpendicular to the benzene plane than those of the ring C atoms, indicating considerable out-of-plane motion. The carboxyl group is rotated about the exocyclic C—C bond out of the benzene plane by 7·7 (1)°.

The equality of the two C—O bond lengths, 1·271 (6) and 1·263 (6) Å, also of the two C—C—O angles, 118·6 (5) and 118·6 (4)°, indicates remarkable disorder in the carboxyl group. It is probably responsible for the difficulty in finding the carboxyl H atom during refinement. This kind of carboxyl disorder is often found in benzoic acids and was discussed by Leiserowitz (1976). Recently, Ichikawa (1979) indicated a continuous variation in the degree of disorder for cyclic hydrogen-bonded dimers.

The C—CN and C≡N bond lengths, 1·439 (8) and 1·149 (8) Å respectively, are in good agreement with those reported in related compounds.

In the benzene ring the mean C—C bond length, 1·392 Å, and the mean valence angle, 120·0°, are normal, but the mean length of the bond parallel to the long molecular axis, 1·378 Å, is appreciably shorter than the average of all six bonds. The shortening of the central C—C bond of the benzene ring seems to be a common feature in *para*-substituted benzonitriles: benzonitrile [1·371 Å (Fauvet, Massaux & Chevalier, 1978)], terephthalonitrile [1·376 Å (Drück & Littke, 1978); 1·382 Å (van Rij & Britton, 1977)], *p*-

Table 1. *Final positional parameters* (×10⁴) *and isotropic thermal parameters*

For the non-hydrogen atoms, the thermal parameters are the isotropic equivalents of the anisotropic thermal parameters (Hamilton, 1959), and estimated standard deviations of the positional parameters are given in parentheses.

	x	y	z	B_{iso} (Å^2)
C(1)	1775 (3)	7358 (6)	6745 (11)	2·61
C(2)	1498 (3)	5406 (7)	6502 (13)	2·84
C(3)	2173 (4)	4272 (7)	5075 (13)	3·09
C(4)	3140 (4)	5093 (7)	3876 (13)	3·01
C(5)	3433 (4)	7036 (8)	4159 (13)	3·21
C(6)	2746 (4)	8168 (7)	5565 (13)	3·10
C(7)	3806 (4)	3847 (8)	2274 (14)	3·54
N(8)	4291 (4)	2782 (8)	935 (15)	5·41
C(9)	1022 (3)	8557 (7)	8222 (13)	2·79
O(10)	200 (3)	7810 (5)	9583 (10)	3·66
O(11)	1231 (3)	10288 (5)	8043 (11)	4·16
H(2)	798	4848	7344	4·77
H(3)	1985	2881	4884	4·42
H(5)	4126	7589	3298	3·94
H(6)	2941	9558	5759	4·47

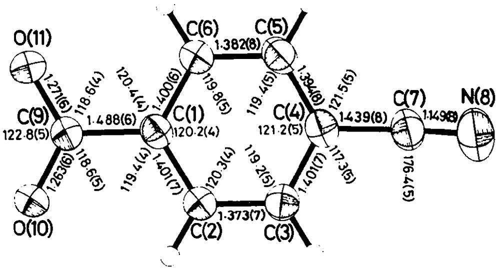

Fig. 1. Bond lengths (Å) and angles (°) of *p*-cyanobenzoic acid.

Table 2. *Deviations* (Å) *from the least-squares plane of the benzene ring*

The mean estimated standard deviation is 0·005 Å.

C(1)	0·004	C(5)	−0·008	C(9)	0·032
C(2)	−0·004	C(6)	0·002	O(10)	−0·100
C(3)	−0·001	C(7)	0·063	O(11)	0·196
C(4)	0·008	N(8)	0·143		

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35809 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

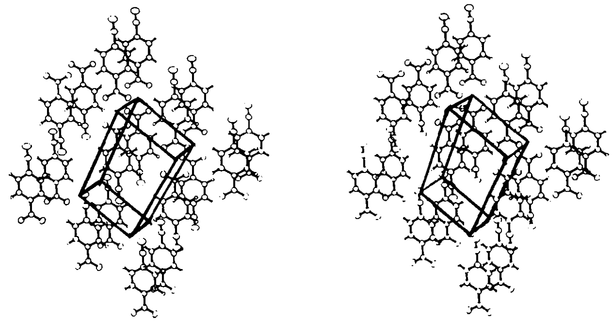

Fig. 2. Stereoscopic view of the crystal structure showing the layers of the molecules, viewed onto the (201) plane.

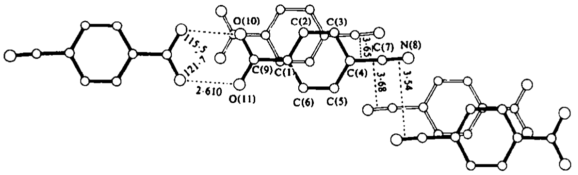

Fig. 3. Hydrogen bonds and cyano–cyano contacts, viewed along the normal of the least-squares plane of the molecule with the atom numbering. Estimated standard deviations are 0·006 Å for the O···O distance, 0·3–0·4° for the C—O···O angles, and 0·01–0·02 Å for the perpendicular distances between cyano groups.

hydroxybenzonitrile [1·375 Å (Higashi & Osaki, 1977*a*)], *p*-nitrobenzonitrile [1·380 Å (Higashi & Osaki, 1977*b*)], and *p*-bromobenzonitrile [1·370 Å (Britton, Konnert & Lam, 1977)]. Similar shortening of the central C—C bond of the benzene ring found in some *para*-substituted nitrobenzenes has been successfully explained by the cooperative electron interaction between the electron-withdrawing and electron-donating characters of two *para* substituents. However, except for *p*-hydroxybenzonitrile, the evidence for the *para*-substituted benzonitriles seems less conclusive. A further study of this point would be of interest.

The crystal structure, shown in Fig. 2, consists of layers of molecules parallel to the (201) plane with an interlayer spacing of 3·17 (1) Å. Each molecule is tilted by 9·8 (2)° out of the plane of the layer, the perpendicular distance to the adjacent molecule being 3·43 (13) Å. The stacking of the carboxyl groups belongs to one of the typical stacking modes found in benzoic acids (Leiserowitz, 1976).

Within the layer, a pair of molecules are linked by hydrogen bonds through the centre of symmetry forming a dimer, as found in most benzoic acids (Fig. 3). The O···O distance is 2·610 (6) Å and the C—O···O angles are 121·7 (4) and 115·5 (3)°.

The molecules are also gathered together *via* antiparallel contacts of the cyano groups across the centre of symmetry at $x = \frac{1}{2}$ (Fig. 3). Each cyano group has two nearest antiparallel neighbours with perpendicular distances between the cyano groups of 3·54 (2) and 3·68 (2) Å, indicating dipole–dipole interactions in the crystal. Both contacts, of which the shorter occurs in the layer of molecules, are probably responsible for the slight deformation of the cyano group from twofold symmetry. Thus, the C—C≡N angle is 176·4 (5)° and the two exocyclic C—C—CN valence angles are 117·3 (5) and 121·5 (5)°. The antiparallel arrangement of the cyano groups has been reported in 4-pyridinecarbonitrile (Laing, Sparrow & Sommerville, 1971), in terephthalonitrile (Drück & Littke, 1978; van Rij & Britton, 1977), and in *p*-fluorobenzonitrile (Britton & Gleason, 1977).

In addition, some short intermolecular contacts listed in Table 3, in which H···N, H···O, O···C, and N···C pairs are dominant, seem to indicate a third interaction in the crystal: Coulombic interactions between opposite charges if we assume some residual charge on each atom, negative on O and N, positive on C and H.

Table 3. *Intermolecular distances* (Å)

Roman numerals represent equivalent positions: (i) *x*,*y*,*z*; (ii) −*x*,−*y*,−*z*; other symbols represent cell translations. Mean estimated standard deviations are 0·01 Å for the distances in (*a*) and 0·007 Å in (*b*).

(*a*) Distances shorter than 3·2 Å involving H atoms

H(3)···O(11, i − *b*)	2·51	H(2)···O(10, ii + *b* + 2*c*)	2·62
H(5)···N(8, ii + *a* + *b*)	2·64	H(2)···H(2, ii + *b* + *c*)	2·82
H(2)···H(2, ii + *b* + 2*c*)	2·91	H(3)···O(11, i − *b* − *c*)	2·95
H(6)···N(8, i + *b* + *c*)	3·02	H(3)···H(6, i − *b*)	3·05
H(2)···O(10, ii + *b* + *c*)	3·08	H(5)···N(8, ii + *a* + *b* + *c*)	3·11

(*b*) Distances shorter than 3·6 Å between non-hydrogen atoms

O(10)···O(11, ii + 2*b* + 2*c*)*	2·61	O(10)···O(10, ii + 2*b* + 2*c*)	3·34
O(10)···C(9, ii + 2*b* + 2*c*)	3·36	O(11)···C(3, i + *b*)	3·38
O(10)···C(9, i + *c*)	3·38	O(10)···C(2, ii + *b* + *c*)	3·41
O(11)···C(9, ii + 2*b* + 2*c*)	3·45	O(10)···C(3, ii + *b* + *c*)	3·47
N(8)···C(5, ii + *a* + *b* + *c*)	3·47	O(10)···C(2, ii + *b* + 2*c*)	3·48
C(3)···C(4, i + *c*)	3·49	C(1)···C(6, i + *c*)	3·50
O(10)···O(11, i + *c*)	3·50	O(11)···O(11, ii + 2*b* + 2*c*)	3·52
O(10)···C(1, i + *c*)	3·54	N(8)···C(5, ii + *a* + *b*)	3·54
N(8)···C(7, ii + *a* + *b*)	3·55	O(11)···C(3, i + *b* + *c*)	3·58
C(3)···C(7, i + *c*)	3·58		

* Hydrogen bond.

References

Britton, D. & Gleason, W. B. (1977). *Acta Cryst.* B**33**, 3926–3928.

Britton, D., Konnert, J. & Lam, S. (1977). *Cryst. Struct. Commun.* **6**, 45–48.

Drück, U. & Littke, W. (1978). *Acta Cryst.* B**34**, 3095–3096.

Fauvet, G., Massaux, M. & Chevalier, R. (1978). *Acta Cryst.* B**34**, 1376–1378.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Higashi, T. & Osaki, K. (1977*a*). *Acta Cryst.* B**33**, 607–609.

Higashi, T. & Osaki, K. (1977*b*). *Acta Cryst.* B**33**, 2337–2339.

Ichikawa, M. (1979). *J. Cryst. Mol. Struct.* **9**, 87–105.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.

Laing, M., Sparrow, N. & Sommerville, P. (1971). *Acta Cryst.* B**27**, 1986–1990.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

Rij, C. van & Britton, D. (1977). *Acta Cryst.* B**33**, 1301–1303.