

Bei der Brom-Verbindung ist die Bindungslänge P–C(1) (zum halogen-substituierten Ring) mit 1,795 Å etwas verkürzt gegenüber den Bindungslängen P–C(7) (1,812 Å) und P–C(13) (1,814 Å).

Bei der Chlorverbindung stimmen dagegen alle drei Längen: 1,806, 1,804 und 1,806 Å im Rahmen der Messgenauigkeit überein. Ein ähnlicher Einfluss des Bromatoms wurde auch bei den (allerdings ungenaueren) Messungen des *p*-Bromphenyl-diphenylphosphins (Kuhn, 1968) gefunden, während beim Triphenylphosphin (Daly, 1964) natürlich alle drei Abstände im Rahmen der Messgenauigkeit gleich sind. Dass die Mittelwerte der P–C-Bindungslängen mit 1,824 bzw. 1,828 Å bei den beiden letztgenannten Verbindungen wesentlich grösser sind als bei den hier untersuchten (1,807 bzw. 1,805 Å) dürfte auf den unterschiedlichen Bindungscharakter zurückzuführen sein: Bei den dreibindigen Phosphinen gehen die drei *p*-Orbitale des Phosphors Bindungen mit den Kohlenstoffatomen ein; diese Bindungen besitzen eine relative Stärke von 1,73 (Pauling, 1968) und stehen senkrecht aufeinander, während beim vierbindigen Phosphor eine *sp*³-Bindung der Stärke 2,0 und einer tetraedrischen Anordnung realisiert ist. Demzufolge betragen die Bindungswinkel C–P–C bei den Phosphinen im Mittel 103,0° und 103,5° (die Aufweitung gegenüber dem theoretischen Wert 90° ist sicherlich auf den Raumbedarf der Benzolringe zurückzuführen), während bei den beiden Phosphin-Oxiden 106,9 und 107,0° realisiert sind (theoretischer Tetraederwinkel 109,5°).

Der Phosphor-Sauerstoff-Atomabstand beträgt bei der Bromverbindung 1,496 und 1,485 Å bei der Chlorverbindung. Mit $2,4 \cdot \sigma$ liegt die Differenz zwischen beiden Werten dicht unterhalb der Signifikanzgrenze.

Bei den intermolekularen Abständen ist besonders der Wert für O(1)–H(6) bemerkenswert: Mit 2,39 bzw. 2,46 Å ist er in beiden Verbindungen erheblich kürzer als die Summe der van der Waals-Radien (2,6 Å); zumindest bei der Chlorverbindung ist diese Abweichung mit $5 \cdot \sigma$ eindeutig signifikant. Hier könnte sich also das Vorhandensein einer schwach ausgeprägten O–H-Brückenbindung andeuten, die das gesamte Phosphin-Sauerstoff-System durch die Anlagerung eines aromatischen Systems zusätzlich stabilisiert.

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The Structure of *p*-Toluic Acid*

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Crystals of *p*-toluic acid, CH₃C₆H₄COOH, are triclinic, space group *P* $\bar{1}$, with $a = 8.88$, $b = 7.87$, $c = 7.59$ Å; $\alpha = 121.4^\circ$, $\beta = 118.7^\circ$, $\gamma = 93.9^\circ$; ρ_o , 1.251 g.cm⁻³; ρ_c for $Z = 2$, 1.256 g.cm⁻³. The structure was refined by the method of least squares to an *R* value of 0.106 for 852 observed reflexions. The molecular dimensions are compared with those of related molecules. The molecules as usual form dimers; the C–O bonds of the carboxylic group are both 1.292 ± 0.008 Å long. The carboxylic group has pronounced torsional oscillation with a root-mean-square amplitude of about 12°; the methyl group has a considerable vibration normal to the C–C bond.

Introduction

The structure analyses of *p*-toluic acid and *p*-nitrotoluene (Barve & Pant, 1971) were undertaken in

order to study the influence on the molecular structure of methyl group substitution in *para* position in mono-substituted benzenes containing electron withdrawing groups. The methyl group is a weaker electron donor than the amino group; the structures of *p*-aminobenzoic acid and *p*-nitroaniline have been determined with great accuracy. It is of interest to compare these

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structures with those of corresponding methyl-substituted compounds. The structure of *p*-nitrotoluene is given in the following paper (Barve & Pant, 1971).

$c=7.59$ $\gamma=93.9$
 $\rho_0, 1.251 \text{ g.cm}^{-3}$;
 $\rho_c \text{ for } Z=2, 1.256 \text{ g.cm}^{-3}$
 $\mu \text{ for Cu } K\alpha, 9.2 \text{ cm}^{-1}$.

Experimental

The crystals grown from solution in toluene are triclinic, space group $P\bar{1}$ with

$a=8.88 \text{ \AA}$ $\alpha=121.4^\circ$
 $b=7.87$ $\beta=118.7$

The axial lengths were determined from several high-angle reflexions having θ values between 64° and 75° on zero layer Weissenberg photographs. Graphs were plotted between $d_{100}, d_{010}, d_{001}$ respectively and $\sin^2 \theta$; the extrapolated values of spacings at $\theta=90^\circ$ were used to calculate axial lengths. The maximum scatter of

Table 1. Final atomic and thermal parameters

The anisotropic thermal parameters ($\times 10^4$) are of the form $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl)]$. The e.s.d.'s are given in parentheses and refer to last significant figures.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₂₃	<i>b</i> ₁₃
C(1)	0.3607 (6)	0.1762 (7)	0.0007 (8)	175 (9)	296 (14)	348 (19)	93 (9)	226 (15)	158 (12)
C(2)	0.5453 (6)	0.3086 (8)	0.2299 (9)	200 (11)	325 (16)	390 (21)	90 (11)	215 (16)	172 (13)
C(3)	0.6910 (7)	0.3828 (8)	0.2307 (10)	181 (10)	332 (17)	505 (25)	67 (11)	248 (18)	177 (14)
C(4)	0.6588 (7)	0.3264 (8)	0.0039 (11)	240 (12)	324 (16)	719 (31)	148 (12)	363 (20)	314 (17)
C(5)	0.4754 (7)	0.1973 (9)	-0.2229 (11)	263 (13)	490 (22)	545 (27)	190 (14)	373 (22)	272 (17)
C(6)	0.3268 (7)	0.1204 (9)	-0.2298 (10)	233 (12)	437 (20)	438 (23)	132 (12)	349 (19)	206 (14)
C(7)	0.2030 (6)	0.0964 (7)	-0.0031 (9)	195 (10)	293 (15)	448 (22)	108 (10)	256 (16)	205 (13)
C(8)	0.8208 (8)	0.4053 (10)	0.0097 (10)	302 (15)	528 (25)	915 (41)	190 (16)	542 (29)	391 (22)
O(1)	0.2385 (4)	0.1586 (6)	0.2099 (6)	208 (8)	448 (13)	389 (14)	66 (8)	246 (12)	185 (9)
O(2)	0.0376 (4)	-0.0311 (6)	-0.2187 (6)	154 (7)	499 (14)	372 (14)	49 (8)	273 (12)	123 (8)
H(1)	0.580 (7)	0.322 (9)	0.382 (10)						
H(2)	0.809 (7)	0.459 (9)	0.377 (10)						
H(3)	0.455 (8)	0.171 (10)	-0.335 (11)						
H(4)	0.202 (8)	0.025 (10)	-0.393 (11)						
H(5)	0.778 (9)	0.420 (10)	-0.103 (11)						
H(6)	0.891 (9)	0.345 (10)	0.038 (11)						
H(7)	0.897 (9)	0.560 (10)	0.129 (11)						

Table 2. Observed and calculated structure factors

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
1	0	0	15.9	18.5	2	0	0	2.7	-3.2	3	1	1	2.0	2.1					
1	0	1	14.5	14.7	2	1	0	2.2	-2.9	3	0	1	2.8	-3.2					
1	0	2	6.4	6.7	2	0	1	1.7	-1.5	3	1	0	1.3	-0.9					
1	0	3	7.4	7.9	2	1	1	4.7	-4.5	3	0	1	2.6	-2.4					
1	0	4	2.2	1.9	2	0	2	1.0	-1.0	3	1	1	4.6	-3.9					
1	0	5	4.9	5.3	2	1	2	3.8	-3.9	3	0	2	13.8	14.8					
1	0	6	3.2	3.1	2	0	3	1.8	-1.4	3	1	2	3.1	-3.1					
1	0	7	2.1	1.9	2	1	3	2.2	2.1	3	0	3	1.3	-1.3					
1	0	8	1.6	1.5	2	0	4	1.4	-1.1	3	1	3	1.3	-1.3					
1	0	9	3.2	3.1	2	1	4	1.4	-1.1	3	0	4	2.9	-2.9					
1	0	10	4.4	4.4	2	0	5	0.6	-0.9	3	1	4	1.2	-1.3					
1	0	11	11.4	12.2	2	1	5	9.4	9.5	3	0	5	2.9	-2.9					
1	0	12	2.9	2.9	2	0	6	1.2	-1.2	3	1	5	1.8	-1.8					
1	0	13	15.5	17.3	2	1	6	11.2	11.9	3	0	6	1.8	-1.8					
1	0	14	18.0	17.6	2	0	7	2.0	1.0	3	1	6	2.1	-2.1					
1	0	15	9.1	9.8	2	1	7	11.2	11.0	3	0	7	1.8	-1.8					
1	0	16	1.1	1.1	2	0	8	11.0	10.1	3	1	7	1.5	-1.5					
1	0	17	6.3	6.3	2	1	8	6.9	-6.1	3	0	8	1.7	-1.7					
1	0	18	2.5	2.5	2	0	9	4.3	4.4	3	1	8	3.2	-3.2					
1	0	19	6.3	6.6	2	1	9	13.3	12.3	3	0	9	4.3	-3.5					
1	0	20	2.6	2.6	2	0	10	11.0	-11.1	3	1	9	10.3	-9.5					
1	0	21	1.0	0.9	2	1	10	1.9	-2.0	3	0	10	19.6	-17.4					
1	0	22	9.9	9.9	2	0	11	1.1	1.3	3	1	10	8.3	-8.2					
1	0	23	1.4	1.1	2	1	11	3.0	2.8	3	0	11	18.1	-16.7					
1	0	24	2.1	2.3	2	0	12	13.0	-11.9	3	1	11	28.0	-21.5					
1	0	25	3.2	3.2	2	1	12	13.3	11.9	3	0	12	4.7	-4.7					
1	0	26	3.2	3.2	2	0	13	13.3	11.9	3	1	12	16.4	-16.2					
1	0	27	3.2	3.2	2	1	13	13.3	11.9	3	0	13	2.6	-2.5					
1	0	28	3.2	3.2	2	0	14	3.4	3.2	3	1	13	4.7	-4.7					
1	0	29	3.2	3.2	2	1	14	1.1	1.3	3	0	14	8.3	-8.2					
1	0	30	3.2	3.2	2	0	15	1.9	-2.0	3	1	14	16.0	-16.2					
1	0	31	3.2	3.2	2	1	15	1.1	1.3	3	0	15	2.6	-2.5					
1	0	32	3.2	3.2	2	0	16	1.1	1.3	3	1	15	4.7	-4.7					
1	0	33	3.2	3.2	2	1	16	1.1	1.3	3	0	16	8.3	-8.2					
1	0	34	3.2	3.2	2	0	17	1.1	1.3	3	1	16	16.0	-16.2					
1	0	35	3.2	3.2	2	1	17	1.1	1.3	3	0	17	2.6	-2.5					
1	0	36	3.2	3.2	2	0	18	1.1	1.3	3	1	17	4.7	-4.7					
1	0	37	3.2	3.2	2	1	18	1.1	1.3	3	0	18	8.3	-8.2					
1	0	38	3.2	3.2	2	0	19	1.1	1.3	3	1	18	16.0	-16.2					
1	0	39	3.2	3.2	2	1	19	1.1	1.3	3	0	19	2.6	-2.5					
1	0	40	3.2	3.2	2	0	20	1.1	1.3	3	1	20	4.7	-4.7					
1	0	41	3.2	3.2	2	1	20	1.1	1.3	3	0	20	8.3	-8.2					
1	0	42	3.2	3.2	2	0	21	1.1	1.3	3	1	21	16.0	-16.2					
1	0	43	3.2	3.2	2	1	21	1.1	1.3	3	0	21	2.6	-2.5					
1	0	44	3.2	3.2	2	0	22	1.1	1.3	3	1	22	4.7	-4.7					
1	0	45	3.2	3.2	2	1	22	1.1	1.3	3	0	22	8.3	-8.2					
1	0	46	3.2	3.2	2	0	23	1.1	1.3	3	1	23	16.0	-16.2					
1	0	47	3.2	3.2	2	1	23	1.1	1.3	3	0	23	2.6	-2.5					
1	0	48	3.2	3.2	2	0	24	1.1	1.3	3	1	24	4.7	-4.7					
1	0	49	3.2	3.2	2	1	24	1.1	1.3	3	0	24	8.3	-8.2					
1	0	50	3.2	3.2	2	0	25	1.1	1.3	3	1	25	16.0	-16.2					
1	0	51	3.2	3.2	2	1	25	1.1	1.3	3	0	25	2.6	-2.5					
1	0	52	3.2	3.2	2	0	26	1.1	1.3	3	1	26	4.7	-4.7					
1	0	53	3.2	3.2	2	1	26	1.1	1.3	3	0	26	8.3	-8.2					
1	0	54	3.2	3.2	2	0	27	1.1	1.3	3	1	27	16.0	-16.2					
1	0	55	3.2	3.2	2	1	27	1.1	1.3	3	0	27	2.6	-2.5					
1	0	56	3.2	3.2	2	0	28	1.1	1.3	3	1	28	4.7	-4.7					
1	0	57	3.2	3.2	2	1	28	1.1	1.3	3	0	28	8.3	-8.2					
1	0	58	3.2	3.2	2	0	29	1.1	1.3	3	1	29	16.0	-16.2					
1	0	59	3.2	3.2	2	1	29	1.1	1.3	3	0	29	2.6	-2.5					
1	0	60	3.2	3.2	2	0	30	1.1	1.3	3	1	30	4.7	-4.7					
1	0	61	3.2	3.2	2	1	30	1.1	1.3	3	0	30	8.3	-8.2					
1	0	62	3.2	3.2	2	0	31	1.1	1.3	3	1	31	16.0	-16.2					
1	0	63	3.2	3.2	2	1	31	1.1	1.3	3	0	31	2.6	-2.5					
1	0	64	3.2	3.2	2	0	32	1.1	1.3	3	1	32	4.7	-4.7					
1	0	65	3.2	3.2	2	1	32	1.1	1.3	3	0	32	8.3	-8.2					
1	0	66	3.2	3.2	2	0	33	1.1	1.3	3	1	33	16.0	-16.2					
1	0	67	3.2	3.2	2	1	33	1.1	1.3	3	0	33	2.6	-2.5					
1	0	68	3.2	3.2	2	0	34	1.1	1.3	3	1	34	4.7	-4.7					
1	0	69	3.2	3.2	2	1	34	1.1	1.3	3	0	34	8.3	-8.2					
1	0	70	3.2	3.2	2	0	35	1.1	1.3	3	1	35	16.0	-16.2					
1	0	71	3.2	3.2	2	1	35	1.1	1.3	3	0	35	2.6	-2.5					
1	0	72	3.2	3.2	2	0	36	1.1	1.3	3	1	36	4.7	-4.7					
1	0	73	3.2	3.2	2	1	36	1.1	1.3	3	0	36	8.3	-8.2					
1	0	74	3.2	3.2	2	0	37	1.1	1.3	3	1	37	16.0	-16.2					
1	0	75	3.2	3.2	2	1	37	1.1	1.3	3	0	37	2.6	-2.5					
1	0	76	3.2	3.2	2	0	38	1.1	1.3	3	1	38	4.7	-4.7					
1	0	77	3.2	3.2	2	1	38	1.1	1.3	3	0	38	8.3	-8.2					
1	0	78	3.2	3.2	2	0	39	1.1	1.3	3	1	39	16.0	-16.2					
1	0	79	3.2	3.2	2	1	39	1.1	1.3	3	0	39	2.6	-2.5					
1	0	80	3.2	3.2	2	0	40	1.1	1.3	3	1	40	4.7	-4.7					
1	0	81	3.2	3.2	2	1	40	1.1	1.3	3	0	40	8.3	-8.2					
1	0	82	3.2	3.2	2	0	41	1.1	1.3	3	1	41	16.0	-16.2					
1	0	83	3.2	3.2	2	1	41	1.1	1.3	3	0	41	2.6	-2.5					
1	0	84	3.2	3.2	2	0	42	1.1	1.3	3	1	42	4.7	-4.7					
1	0	85	3.2																

Table 5. *Intramolecular bond lengths and angles*The unprimed atoms are at x, y, z and the O(2') atom at $\bar{x}, \bar{y}, \bar{z}$.

	Bond length (Å)			E.s.d.	Angle
	Uncorrected	Corrected			
C(1)–C(2)	1.394 Å		0.009 Å	C(6)–C(1)–C(2)	118.7 ± 0.7°
C(2)–C(3)	1.379		0.009	C(1)–C(2)–C(3)	120.2 ± 0.7
C(3)–C(4)	1.398		0.010	C(2)–C(3)–C(4)	121.4 ± 0.7
C(4)–C(5)	1.383		0.010	C(3)–C(4)–C(5)	118.5 ± 0.7
C(5)–C(6)	1.379		0.010	C(4)–C(5)–C(6)	121.5 ± 0.7
C(6)–C(1)	1.421		0.009	C(5)–C(6)–C(1)	119.8 ± 0.7
C(1)–C(7)	1.476		0.009	C(3)–C(4)–C(8)	120.2 ± 0.8
C(4)–C(8)	1.499	1.514 Å	0.011	C(5)–C(4)–C(8)	121.4 ± 0.8
C(7)–O(1)	1.272	1.292	0.008	C(2)–C(1)–C(7)	120.9 ± 0.7
C(7)–O(2)	1.275	1.292	0.008	C(6)–C(1)–C(7)	120.5 ± 0.7
O(1)–O(2')	2.629		0.006	C(1)–C(7)–O(1)	118.3 ± 0.6
				C(1)–C(7)–O(2)	118.8 ± 0.6
C(2)–H(1)	0.98		0.07	O(1)–C(7)–O(2)	122.9 ± 0.6
C(3)–H(2)	0.89		0.07	C(7)–O(1)–O(2')	117.2 ± 0.6
C(5)–H(3)	0.68		0.08		
C(6)–H(4)	0.97		0.07		
C(8)–H(5)	0.83		0.09		
C(8)–H(6)	0.82		0.09		
C(8)–H(7)	0.96		0.09		

the refinement, the unobserved reflexions having a threshold value less than F_c were also used. The first three cycles of refinement, including the ring hydrogen atoms only in the structure factor calculations and keeping their parameters constant, did not improve the R value. Four more cycles of refinement were given including the ring as well as the methyl group hydrogen atoms in the structure factor calculations and using Hughes's weighting scheme ($F_{\min} = 3$). During these cycles, atomic parameters of hydrogen atoms were also refined although their thermal parameters were kept constant. The final R for the observed reflexions was 0.107 (0.106 on applying an overall scale factor to F_o). The final atomic and thermal parameters along with their estimated standard deviations (e.s.d.'s) (obtained from the diagonal terms of the least-squares inverse matrices) are given in Table 1 and F_o and F_c in Table 2.

The equations of the various planes referred to the a, b', c' orthogonal axes such that ab and ab' planes are the same, are given in Table 3 along with the angles between them and the deviations of the atoms from the different planes. The equations of the planes were obtained by the method of Schomaker, Waser, Marsh & Bergman (1959). The thermal parameters b_{ij} were used to calculate the direction cosines of the principal axes of the individual atomic vibration ellipsoids referred to the a, b', c' orthogonal axes; these are given in Table 4 along with the angles between the principal axes of the vibration ellipsoids and the aromatic plane as well as those between the principal axes and the molecular axis [*i.e.* C(1)–C(4) direction, Fig. 1].

The intramolecular bond lengths and angles along with the e.s.d.'s obtained in the usual way assuming isotropic errors are shown in Fig. 1 and listed in Table 5. Examination of Table 4 indicates that there is considerable torsional oscillation of the carboxylic group about the C(1)–C(7) bond; the methyl group also

shows considerable intramolecular vibration. In order to apply corrections to the C(7)–O(1), C(7)–O(2) and C(4)–C(8) distances arising from large thermal vibrations, mean square displacements of atoms C(7), O(1), O(2), C(4) and C(8) along required directions were obtained (Table 6). The corrections were evaluated assuming spread parameter q^2 to be 0.13 Å² (Cruickshank, 1956) and amounted to 0.020, 0.017 and 0.015 Å for C(7)–O(1), C(7)–O(2) and C(4)–C(8) bonds respectively; corrections for bond angles and for other bond lengths are expected to be within experimental errors and are neglected.

Table 6. *Some mean square displacements (Å² × 10³)*

	Direction of displacement*		
	Normal to the plane†	In the plane normal to the bond	Parallel to the bond
O(1)	102	65	45
C(7)	51	(a) 50	O(1) 47
		(b) 41	O(2) 75
O(2)	111	39	42
C(4)	49	98	38
C(8)	86	117	44

* Values parallel and normal to the bond for C(4) are given only for the C(4)–C(8) bond. The atoms listed besides certain values in the Table indicate the direction of the bond in question.

† The vibration directions of O(1), O(2) and C(7) are with respect to the plane through C(1), C(7), O(1) and O(2) whereas the vibration directions of C(4) and C(8) are with respect to the benzene plane.

Discussion

The average length of the aromatic bonds in *p*-toluic acid (1.392 Å) is normal; the central bonds C(2)–C(3) and C(5)–C(6) are both 1.379 Å long while the average length of the other four aromatic bonds is 1.399 Å. The general picture thus resembles that found in the

cases of *p*-aminobenzoic acid (Lai & Marsh, 1967), *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), β -*p*-nitrophenol (Coppens & Schmidt, 1965), β -sulphanilamide (O'Connell & Maslen, 1967) and terephthalic acid (Bailey & Brown, 1967); in these molecules, the central bonds of the aromatic ring are shortened, the average lengths being 1.375, 1.375, 1.380, 1.381 and 1.370 Å respectively; the e.s.d.'s in bond lengths in these structure analyses are of the order of 0.005 Å and in the case of terephthalic acid the two central bonds of the benzene ring are related by a centre of symmetry. The corresponding length in *p*-nitrobenzoic acid, 1.393 Å (Sakore & Pant, 1966) is normal. Except for terephthalic acid and *p*-nitrobenzoic acid, all the compounds mentioned above have an electron donor and an acceptor group in *para* positions. The shortening of the central bonds of the benzene ring in terephthalic acid as well probably implies that cooperative electronic interaction between the *para* substituents in the other molecules (having donor and acceptor groups in *para* positions) must be only partly responsible for the

shortening of the central bonds of the benzene ring.

The C(1)–C(7) bond length, 1.476 ± 0.009 Å agrees with that found in terephthalic acid, 1.483 ± 0.003 Å (Bailey & Brown, 1967), is a little smaller than the corresponding length in *p*-nitrobenzoic acid, 1.501 ± 0.008 Å (Sakore & Pant, 1966) and a little longer than its values in the two crystallographically independent molecules of *p*-aminobenzoic acid, 1.455 ± 0.006 Å and 1.464 ± 0.006 Å (Lai & Marsh, 1967). The two C–O bond lengths of the carboxylic group are both 1.292 ± 0.008 Å (1.272 and 1.275 Å without correction for librational effects); these values agree with the corresponding lengths in terephthalic acid, 1.262 ± 0.003 Å and 1.272 ± 0.003 Å without correction for librational effects (Bailey & Brown, 1967).

The carbon atom C(8) of the methyl group is 0.034 Å away from the aromatic plane. The C(4)–C(8) bond length, 1.514 ± 0.011 Å (1.499 Å without correction for librational effects) agrees with the corresponding lengths in 2-amino-3-methylbenzoic acid, 1.501 ± 0.002 Å without correction for librational effect (Brown & Marsh, 1963) and 1,1-di-*p*-tolylethylene, 1.503 ± 0.005 Å and 1.509 ± 0.005 Å without correction for librational effects (Casalone, Gavezzotti, Mariani, Mugnoli & Simonetta, 1970).

The methyl group and the oxygen atoms of the carboxylic group show considerable thermal anisotropy. The mean square displacements of the atoms O(1), O(2) and C(7) normal to the plane containing the carboxylic group and the atom C(1) (0.102 , 0.111 and 0.051 Å² respectively, Table 6) imply a root-mean-square (r.m.s.) amplitude of oscillation of the carboxylic group about the C(1)–C(7) bond of about 12° . Larger r.m.s. displacements of atoms C(2), C(3), C(5) and C(6) across the molecular plane compared with the corresponding displacements for C(7), C(1) and C(4) (Table 4) suggest some rigid body oscillation of the entire molecule as well about its long axis. The methyl group has a considerable vibration normal to the C(4)–C(8) bond.

The arrangement of molecules in the unit cell is shown in Fig. 2 in which the principal intermolecular distances (< 3.8 Å) are also given. The crystal structures of *p*-toluic acid and terephthalic acid (Bailey & Brown, 1967) are quite similar; in both structures, infinite chains of molecules are held together by normal van der Waals interactions. In *p*-toluic acid, the molecules in any chain are bonded with neighbouring molecules by double OH...O hydrogen bonds of length 2.63 Å on one side and by van der Waals bonds between methyl groups (C–C distance, 3.50 Å) on the other.

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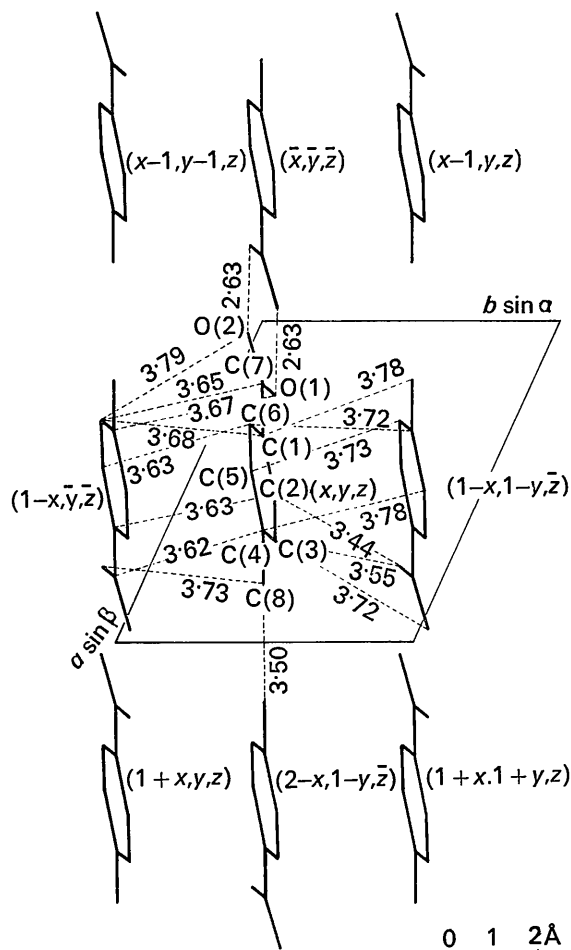


Fig. 2. The structure of *p*-toluic acid projected along the *c* axis.

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The Structure of *p*-Nitrotoluene*

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Crystals of *p*-nitrotoluene, $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$, are orthorhombic, space group *Pcab*, with $a=6.43$, $b=14.07$, $c=15.66$ Å²; ρ_o , 1.294 g.cm⁻³; ρ_c for $Z=8$, 1.287 g.cm⁻³. The structure was refined by the method of least squares to an *R* value of 0.107 for 467 observed reflexions. The molecular dimensions are compared with those of related molecules. The nitro group has pronounced torsional oscillation; as in *p*-toluic acid, the methyl group is vibrating normal to the C-C bond.

Experimental

The pale yellow needle-like crystals grown from aqueous alcohol are orthorhombic. The cell dimensions determined from equatorial Weissenberg photographs are $a=6.43$, $b=14.07$, $c=15.66$ Å; the data reported by Prasad & Merchant (1938) are $a=6.41$, $b=14.10$, $c=15.39$ Å; space group, *Pcab*. a was measured from four reflexions having θ between 46° and 76°, b from five having θ between 41° and 61° and c from four reflexions having θ between 51° and 75°; the maximum scatter from mean values was 0.01 Å for a , 0.03 Å for b and 0.02 Å for c . The observed systematic absences confirmed the space group reported by Prasad & Merchant (1938). The other crystal data are ρ_o , 1.294 g.cm⁻³; ρ_c for $Z=8$, 1.287 g.cm⁻³; μ for Cu $K\alpha$, 9.8 cm⁻¹.

The crystals sublime on exposure to the atmosphere and had to be enclosed and sealed within thin walled glass capillaries in order to use them for collecting intensity data. Data were collected with unfiltered Cu radiation from zero to fifth layer equi-inclination Weissenberg photographs about the a axis and from zero to second layer photographs about the b axis; the crystals used for the two sets of photographs had the cross sections 1.0 × 0.8 and 1.0 × 0.9 mm² and lengths 2 and 1 mm respectively. Of the 469 independent reflex-

ions, 96 were present in both sets of photographs. The intensities were corrected for various factors and brought to a common scale in the usual way (Takwale & Pant, 1971).

Determination and refinement of the structure

The structure was solved in the (100) projection with the help of a (100) sharpened Patterson projection and ($\frac{1}{2}$, y , 0) and (0 , $\frac{1}{2}$, z) Harker lines on the basis of a plane molecule with usual bond lengths and angles; x parameters were determined with the help of the (x , 0, $\frac{1}{2}$) Harker line. The structure was first refined with the help of $0kl$ and $h0l$ reflexions to an *R* value of about 0.3 for general reflexions using an overall temperature factor (4.6 Å²) obtained by Wilson's method. Six cycles of least-squares refinement of atomic parameters and individual isotropic temperature factors and correction of some numerical and indexing errors reduced *R* to about 0.18. Further refinement was carried out with anisotropic temperature factors using the block diagonal approximation; to start with, unit weights were given to all F 's and later the following weighting scheme was used:

$$w = \frac{1}{a + |F_o| + c|F_o|^2},$$

where $a=2F_{\min}$ and $c=2/F_{\max}$ (Cruickshank, 1965); *R* at this stage was about 0.13. The atomic parameters of the hydrogen atoms of the benzene ring were ob-

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