References

Atovmyan, L. O., D'yachenko, O. A. & Soboleva. S. V. (1970). *Zh. Strukt. Khim.* **2**, 557–558.

Bergen, A. van den, Murray, K. S., O'Connor, M. J., Rehak, N. & West, B. O. (1968). *Austral. J. Chem.* **21**, 1505–1515.

Blow, D. M. (1960). *Acta Cryst.* **13**, 168.

Coggon, P., McPhail, A. T., Mabbs, F. E. & McLachlan, V. N. (1971). *J. Chem. Soc.* (*A*), pp. 1014–1019.

Davies, J. E. & Gatehouse, B. M. (1972*a*). *Acta Cryst.* B**28**, 3641–3645.

Davies, J. E. & Gatehouse, B. M. (1972*b*). *Cryst. Struct. Commun.* **1**, 115–120.

Davies, J. E. & Gatehouse, B. M. (1973). *Acta Cryst.* **B29**, 1934–1942.

Fleischer, E. & Hawkinson, S. (1967). *J. Amer. Chem. Soc.* **89**, 720–721.

Gardner, A. P. (1970). M. Sc. Thesis, Monash University.

Gerloch, M., McKenzie, E. D. & Towl, A. D. C. (1969). *J. Chem. Soc.* (*A*), pp. 2850–2858.

Germain, P., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* B**26**, 274–285.

Hoffman, A. B., Collins, D. M., Day, V. W., Fleischer, E. B., Scrivastava, T. S. & Hoard, J. L. (1972). *J. Amer. Chem. Soc.* **94**, 3620–3626.

Ibers, J. A. (1962). *International Tables for X-ray Crystallography*, Vol. 3. Birmingham: Kynoch Press.

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

Lewis, J., Mabbs, F. E. & Richards, A. (1967). *J. Chem. Soc.* (*A*), pp. 1014–1018.

Lingafelter, E. C. & Braun, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951–2956.

Lippard, S. J., Schugar, H. & Walling, C. (1967). *Inorg. Chem.* **6**, 1825–1831.

Shiono, R. (1968). *S. F.* Block-diagonal least-squares refinement program. Univ. of Pittsburgh, U.S.A.

Trotter, J., Whitlow, S. H. & Zobel, T. (1966). *J. Chem. Soc.* (*A*), pp. 353–356.

White, J. C. B. (1965). Melbourne University Fourier Program *MUFR*3. See Rollett, J. S. (1961) in *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by Pepinsky, Robertson & Speakman, p. 87. Oxford: Pergamon Press.

Wooster, W. A. (1962). *Diffuse X-ray Reflections from Crystals*, pp. 153–173. Oxford: Clarendon Press.

Acta Cryst. (1973). B**29**, 2658

Crystal Structure of 3,5-Dimethyl-4-nitrobenzoic Acid

By M. C. Apreda,* P. Smith-Verdier and S. García-Blanco

Instituto de Química-Física 'Rocasolano' C.S.I.C., Serrano 119, *Madrid* 6, *Spain*

(*Received* 31 *May* 1973; *accepted* 19 *June* 1973)

The crystals have the space group $P2_1/a$ with four molecules per unit cell and $a = 11·965$, $b = 10·207$, $c = 8·364$ Å, $\beta = 110°36'$. The structure was solved by direct methods and hydrogen atoms were located in a differential synthesis. Refinement by full-matrix least-squares methods resulted in a final R value of 0·088 for 1409 observed reflexions. The structure consists of dimers linked together by hydrogen bonds. The benzene ring is planar and C–C distances average 1·391 Å. The carboxyl group is twisted 18°04′ from this plane and the nitro group, 86°16′ from the same plane.

Introduction

The study of the crystalline structure of 3,5-dimethyl-4-nitrobenzoic acid has been carried out in an attempt to reveal the interaction between methyl groups and the carboxyl group, together with the influence of the nitro group in the molecular packing.

Molecular structures of derivatives of benzoic acids have been studied by Anca, Martínez-Carrera & García-Blanco (1967), Martínez-Perez & Martínez-Carrera (1967), Florencio & Smith (1970), Smith, Florencio & García-Blanco (1971), Cano, Martínez-Carrera & García-Blanco (1970), and this work was undertaken as a continuation of these previous studies.

Experimental

Crystals of 3,5-dimethyl-4-nitrobenzoic acid were recrystallized from an ethanolic solution. The density was measured by flotation in an aqueous potassium iodide solution.

Crystal data

$a = 11·965$, $b = 10·207$, $c = 8·364$ Å, $\beta = 110°36'$, $D_m = 1·36$ g cm^{-3}, $D_x = 1·356$ g cm^{-3}, $Z = 4$, $F(000) = 408$, $\mu(\text{Cu } K\alpha) = 9·329$ cm^{-1}. Systematic absences are: $0k0$ with $k = 2n+1$ and $h0l$ with $h = 2n+1$, and the space group is $P2_1/a$.

The three-dimensional data were obtained with Cu $K\alpha$ radiation and the multiple-film integrated Weissenberg procedure for nine layers with the crystal oscillated about the unique b axis and for six layers with oscillation about the c axis. The intensities of 1944

---

* On leave from Departamento de Física, Facultad de Ciencias Exactas, U.N.L.P., Calle 115 esq. 49, La Plata, Buenos Aires, Argentine.

Table 1. *Observed and calculated structure factors*

Structure factor list of $C_9H_9O_4N$ No observed reflexions with *

H	K	L	FOBS	FCAL
12	0	0	3.7	4.1
10	0	0	3.4	1.9
8	0	0	[illegible]	17.1
6	0	0	[illegible]	12.7
4	0	0	[illegible]	[illegible]
12	0	1	[illegible]	9.6
10	0	1	1.4	.2*
8	0	1	5.9	5.3
6	0	1	1.1	.7*
4	0	1	[illegible]	17.6
2	0	1	16.1	13.5
0	0	1	17.6	21.1
-4	0	1	24.2	25.5
-6	0	1	27.9	20.5
-8	0	1	[illegible]	11.7
-10	0	1	14.7	15.7
-12	0	1	1.4	1.2*
-14	0	1	3.9	4.9
12	0	2	2.5	2.5
10	0	2	1.4	.1*
8	0	2	1.4	[illegible]
6	0	2	17.9	17.5
4	0	2	22.5	22.7
2	0	2	19.6	[illegible]
0	0	2	57.2	[illegible]
-2	0	2	15.7	11.7
-4	0	2	34.5	31.7
-6	0	2	21.5	19.7
-8	0	2	[illegible]	22.1
-10	0	2	21.1	[illegible]
-12	0	2	6.4	[illegible]
-14	0	2	1.0	.7*
12	0	3	.7	1.4*
10	0	3	1.2	[illegible]
8	0	3	3.6	3.6
6	0	3	2.3	.0*
4	0	3	29.5	[illegible]
2	0	3	8.0	7.6
0	0	3	.6	[illegible]
-2	0	3	44.9	44.4
-4	0	3	8.6	9.3
-6	0	3	19.6	19.9
-8	0	3	12.5	11.9
-10	0	3	42.4	46.2
-12	0	3	13.2	13.2
-14	0	3	1.0	1.2*
10	0	4	2.3	3.2
8	0	4	3.7	4.1
6	0	4	6.6	7.2
4	0	4	16.0	16.1
2	0	4	30.6	29.6
0	0	4	15.1	14.4
-2	0	4	25.5	22.9
-4	0	4	13.9	13.2
-6	0	4	1.1	2.0*
-8	0	4	6.2	5.1
-10	0	4	4.2	3.2
-12	0	4	12.1	12.2
-14	0	4	[illegible]	1.1*
10	0	[illegible]	.7	[illegible]
8	0	5	1.2	2.7
6	0	5	3.3	3.4
4	0	5	12.1	12.0
2	0	5	4.4	4.9
0	0	5	20.8	21.6
-2	0	5	11.4	9.3
-4	0	5	6.0	3.4
-6	0	5	8.1	7.3
-8	0	5	1.3	.0*
-10	0	5	9.9	10.3
-12	0	5	1.3	.6*
8	0	6	.9	1.8*
6	0	6	2.6	4.2
4	0	6	1.4	2.4
2	0	6	1.4	.1*
0	0	6	4.4	5.5
-2	0	6	5.0	3.7
-4	0	6	2.9	1.7
-6	0	6	22.9	20.9
-8	0	6	11.5	9.3
-10	0	6	3.1	2.9
-12	0	6	1.3	3.2
6	0	7	1.0	1.6*
4	0	7	1.3	1.3*
2	0	7	1.4	2.4
0	0	7	4.9	6.1
-2	0	7	1.4	1.3*
-4	0	7	6.9	5.9
-6	0	7	1.4	2.3
-8	0	7	5.7	6.3
-10	0	7	2.0	1.3*
-12	0	7	1.2	.5*
4	0	8	1.0	1.9*
2	0	8	2.6	4.5
0	0	8	1.4	.9*
-2	0	8	1.4	7.5
-4	0	8	2.7	2.6
-6	0	8	3.3	3.7
-8	0	8	1.4	1.2*
-10	0	8	1.2	2.5
-12	0	8	1.0	1.7
-2	0	9	7.5	6.1
-4	0	9	7.8	5.8
-6	0	9	5.5	5.9
-8	0	9	1.2	.1*
-10	0	9	3.8	3.8
-12	0	9	.7	1.5*
14	1	0	.8	.2*
13	1	0	1.2	.1*
12	1	0	2.3	2.6
11	1	0	4.0	4.5
10	1	0	7.2	7.6
9	1	0	10.7	10.3
8	1	0	16.6	17.0
7	1	0	8.1	7.7
6	1	0	11.1	9.8
5	1	0	8.8	8.2
4	1	0	34.3	38.7
3	1	0	6.9	8.1
2	1	0	25.5	27.3
1	1	0	40.5	43.3
13	1	1	4.1	4.1
12	1	1	2.0	2.3
11	1	1	2.3	[illegible]
10	1	1	2.5	2.5
9	1	1	13.1	13.2
8	1	1	8.3	9.9
7	1	1	1.3	.0*
6	1	1	3.5	3.9
5	1	1	32.3	31.9
4	1	1	35.0	37.0
3	1	1	12.9	11.8
2	1	1	49.5	62.3
1	1	1	[illegible]	[illegible]
0	1	1	7.5	3.9
-1	1	1	6.1	5.4
-2	1	1	29.4	[illegible]
-3	1	1	17.3	17.9
-4	1	1	16.1	16.3
-5	1	1	21.3	20.5
-6	1	1	21.4	21.4
-7	1	1	[illegible]	9.4
-8	1	1	11.4	[illegible]
-9	1	1	25.6	[illegible]
-10	1	1	15.1	[illegible]
-11	1	1	[illegible]	[illegible]
-12	1	1	[illegible]	[illegible]
-13	1	1	[illegible]	[illegible]
-14	1	1	3.4	3.4
13	1	2	.6	2.3*

Table 1 (*cont.*)

reflexions were measured by means of a double-beam microdensitometer; 1409 represented observed reflexions.

Data from the two axes were corrected for Lorentz and polarization effects. No correction for absorption was made. The data were reduced to structure amplitudes in the usual way, and placed on the same relative scale by comparing common reflexions on different films.

Determination of the structure and refinement

The X-RAY System programs of Stewart, Kundell & Baldwin (1970) were used (*a*) to compute both a scale and an overall temperature factor by a Wilson plot, (*b*) to convert the structure factor amplitudes to normalized E values and (*c*) to sort out the 329 reflexions with $|E| \geq 1{\cdot}50$. The scattering factors for the carbon, nitrogen and oxygen atoms were those given by Hanson, Herman, Lea & Skillman (1964). Those for the hydrogen atoms were interpolated from the values given by Stewart, Davidson & Simpson (1965).

The structure was finally determined by direct methods with the multiple solution technique by means of the automatic phasing program *MULTAN* of Germain, Main & Woolfson (1971). The solution of the structure did not present difficulties: of the 4 sets, the one that had the highest figure of merit was chosen. The coordinates of the 14 non-hydrogen atoms were readily obtained from an E map computed with the 329 normalized observed factors, giving a value for the reliability index of 0·296.

The scale factor, atomic parameters and individual isotropic temperature factors, were refined by three cycles of least-squares calculations, with unit weight for all the atoms; the R value dropped to 0·181. Further refinement of the structure was carried out by three cycles of least squares with anisotropic temperature factors, neglecting the hydrogen atoms, and a value for R of 0·103 was obtained. A three-dimensional difference Fourier synthesis, based on the last cycle of least squares and including structure factors with $\sin\theta < 0{\cdot}45$, was calculated to obtain the positions of the hydrogen atoms. No definite peaks were observed, but positive regions around the carbon atoms to which hydrogen atoms are attached were visible. The new agreement index was 0·097. The temperature factors of the hydrogen atoms were set equal to those of the corresponding binding atoms, but were not allowed to vary. At this stage the weighting scheme of Cruickshank was used: $w_{hkl} = [a + b|F_o| + c|F_o|^2]^{-1/2}$. The constants a, b and c were obtained by a least-squares fit with experimental data. Finally, three new cycles of least squares reduced the R value to 0·088. The value for σ_1, the e.s.d. of an observation of unit weight, was equal to 0·937. σ_1 is given by the expression $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = 1409 reflexions and NV = 127 variables.

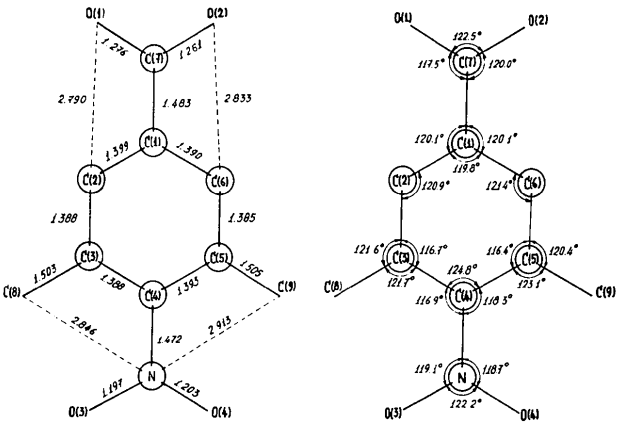

Fig. 1. Bond lengths and valence angles in the 3,5-dimethyl-4-nitrobenzoic acid molecule.

The observed and calculated structure factors are given in Table 1.

Final parameters

Final atomic parameters and their standard deviations, and the bond lengths together with the valence angles, are shown in Tables 2 and 3 respectively. The bond lengths and angles are also shown on Fig. 1. The following equations for the different mean-square planes have been calculated (Schomaker, Waser, March & Bergman, 1959) with respect to orthogonal crystallographic axes a, b and c'.

(*a*) All atoms:

$$-0{\cdot}1635X' - 0{\cdot}3684Y + 0{\cdot}9152Z' - 0{\cdot}9509 = 0.$$

(*b*) Benzene ring:

$$-0{\cdot}2038X' - 0{\cdot}3712Y + 0{\cdot}9059Z' - 0{\cdot}7725 = 0.$$

(*c*) Carboxyl group and C(1):

$$0{\cdot}0773X' - 0{\cdot}3541Y + 0{\cdot}9320Z' - 2{\cdot}1185 = 0.$$

(*d*) Nitro group and C(4):

$$0{\cdot}9541X' - 0{\cdot}1255Y + 0{\cdot}2717Z' - 4{\cdot}6968 = 0.$$

Deviations of the atoms from the mean-square planes are given in Table 5. In Table 6 have been listed the hydrogen atom parameters. Intermolecular distances less than 4·0 Å are shown in Table 4 and on Fig. 2.

Table 2. *Final atomic parameters*

Estimated standard deviations in parentheses.

The temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \cdots + 2\beta_{23}kl) \times 10^{-4}]$.

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
71 (3)	54 (3)	134 (6)	−5 (2)	33 (3)	−7 (3)
59 (3)	69 (4)	149 (7)	−3 (2)	28 (3)	−15 (4)
70 (3)	63 (4)	129 (6)	1 (2)	32 (3)	−5 (4)
82 (3)	49 (3)	114 (6)	−13 (2)	33 (3)	−4 (3)
68 (3)	61 (3)	141 (6)	−13 (2)	23 (3)	−1 (4)
67 (3)	67 (4)	160 (7)	2 (3)	32 (3)	−7 (4)
73 (3)	63 (4)	139 (6)	−2 (3)	28 (3)	−12 (4)
77 (3)	83 (4)	277 (9)	10 (3)	61 (5)	−34 (5)
72 (3)	97 (5)	313 (9)	−29 (3)	34 (5)	−28 (6)
105 (3)	60 (3)	151 (6)	−13 (2)	39 (3)	−19 (4)
90 (2)	73 (3)	240 (6)	−22 (2)	72 (3)	−39 (3)
80 (2)	70 (3)	293 (7)	−2 (2)	61 (3)	−52 (4)
419 (9)	140 (5)	224 (9)	−118 (6)	182 (7)	−102 (5)
337 (9)	58 (3)	261 (9)	−28 (4)	106 (7)	7 (4)

	x/a	y/b	z/c
C(1)	0·4526 (3)	0·1897 (3)	0·3375 (4)
C(2)	0·5494 (3)	0·1159 (3)	0·3312 (5)
C(3)	0·5331 (3)	−0·0101 (3)	0·2643 (4)
C(4)	0·4169 (3)	−0·0576 (3)	0·2050 (4)
C(5)	0·3173 (3)	0·0124 (3)	0·2061 (4)
C(6)	0·3382 (3)	0·1370 (4)	0·2756 (5)
C(7)	0·4713 (3)	0·3256 (4)	0·4043 (5)
C(8)	0·6361 (4)	−0·0909 (4)	0·2566 (6)
C(9)	0·1921 (4)	−0·0410 (4)	0·1349 (7)
N	0·3988 (3)	−0·1904 (3)	0·1317 (4)
O(1)	0·5704 (2)	0·3806 (3)	0·4197 (4)
O(2)	0·3912 (2)	0·3823 (3)	0·4440 (4)
O(3)	0·3872 (6)	−0·2047 (4)	−0·0153 (5)
O(4)	0·3927 (5)	−0·2808 (3)	0·2208 (5)

Table 3. *Bond lengths and valence angles*

C(1)–C(2)	1·399 (5) Å	C(1)–C(2)–C(3)	120·9 (3)°
C(2)–C(3)	1·388 (5)	C(2)–C(3)–C(4)	116·7 (3)
C(3)–C(4)	1·388 (5)	C(3)–C(4)–C(5)	124·8 (3)
C(4)–C(5)	1·393 (5)	C(4)–C(5)–C(6)	116·4 (3)
C(5)–C(6)	1·385 (5)	C(5)–C(6)–C(1)	121·4 (3)
C(6)–C(1)	1·390 (5)	C(6)–C(1)–C(2)	119·8 (3)
C(1)–C(7)	1·483 (5)	C(2)–C(3)–C(8)	121·6 (3)
C(7)–O(1)	1·276 (5)	C(6)–C(5)–C(9)	120·4 (3)
C(7)–O(2)	1·261 (5)	C(8)–C(3)–C(4)	121·7 (3)
C(3) C(8)	1·503 (6)	C(9)–C(5)–C(4)	123·1 (3)
C(5)–C(9)	1·505 (5)	C(3)–C(4)–N	116·9 (3)
C(4)–N	1·472 (5)	C(5)–C(4)–N	118·3 (3)
O(3)–N	1·197 (6)	C(4)–N—O(3)	119·1 (4)
O(4)–N	1·203 (5)	C(4)–N—O(4)	118·7 (4)
		O(3)–N—O(4)	122·2 (4)
		C(2)–C(1)–C(7)	120·1 (3)
		C(6)–C(1)–C(7)	120·1 (3)
		C(1)–C(7)–O(2)	120·0 (3)
		C(1)–C(7)–O(1)	117·5 (3)
		O(1)–C(7)–O(2)	122·5 (3)

Table 4. *Intermolecular distances less than* 4 Å

The roman supscripts give the symmetry relationship of the atoms concerned.

None	x	y	z	vi	$1-x$	$1-y$	$1-z$
i	$1-x$	$-y$	$1-z$	vii	$\frac{3}{2}-x$	$-\frac{1}{2}+y$	$1-z$
ii	$1-x$	$-y$	$-z$	viii	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	z
iii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z	ix	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$-z$
iv	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-z$	x	x	$1+y$	z
v	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	z				

C(1)···C(3$^{\rm i}$)	3·753 Å	C(7)···N($^{\rm i}$)	3·891 Å
C(1)···C(4$^{\rm i}$)	3·833	C(7)···O(1$^{\rm vi}$)	3·453
C(1)···O(3$^{\rm ii}$)	3·821	C(7)···O(2$^{\rm vi}$)	3·426
C(1)···O(4$^{\rm i}$)	3·623	C(7)···O(4$^{\rm i}$)	3·017
C(2)···C(3$^{\rm i}$)	3·992	C(8)···O(1$^{\rm vii}$)	3·614
C(2)···C(4$^{\rm i}$)	3·803	C(8)···O(2$^{\rm i}$)	3·974
C(2)···C(5$^{\rm i}$)	3·859	C(8)···O(2$^{\rm iii}$)	3·598
C(2)···O(2$^{\rm iii}$)	3·859	C(8)···O(3$^{\rm ii}$)	3·586
C(2)···O(3$^{\rm ii}$)	3·129	C(8)···O(4$^{\rm viii}$)	3·447
C(2)···O(4$^{\rm i}$)	3·940	C(9)···O(1$^{\rm v}$)	3·595
C(3)···C(6$^{\rm i}$)	3·833	C(9)···O(3$^{\rm iv}$)	3·608
C(3)···O(3$^{\rm ii}$)	3·384	C(9)···O(4$^{\rm iv}$)	3·849
C(4)···C(8$^{\rm ii}$)	3·986	N ···C(6$^{\rm ix}$)	3·994
C(5)···O(3$^{\rm iv}$)	3·758	N ···C(7$^{\rm i}$)	3·891
C(6)···C(8$^{\rm i}$)	3·844	O(1)···O(1$^{\rm vi}$)	3·489
C(6)···N$^{\rm iv}$	3·994	O(1)···O(4$^{\rm i}$)	3·056
C(6)···O(1$^{\rm v}$)	3·805	O(2)···O(2$^{\rm vi}$)	3·423
C(6)···O(3$^{\rm iv}$)	3·239	O(2)···O(4$^{\rm x}$)	3·916
C(7)···C(7$^{\rm vi}$)	3·864	O(2)···O(4$^{\rm i}$)	3·243
		O(1)···O(2$^{\rm vi}$)	2·646*

* Hydrogen bond

Discussion of the structure

The benzene ring is practically planar. The C–C distances are normal, in agreement with accepted values. The average distance is 1·391 Å. The C(5)–C(9) and C(8)–C(3) lengths are normal: 1·505 and 1·503 Å respectively. The C(7)–C(1) bond of 1·483 Å indicates an sp^2 hybridization state. Similar values have been found in *para*-substituted derivatives of benzoic acid, such as 2,4,6-trimethylbenzoic (Florencio & Smith, 1970) and 3,4,5-trimethylbenzoic acids (Cano, Martínez-Carrera & García-Blanco, 1970), in contrast to the *ortho* and *meta*-substituted compounds, *e.g.* 2,6-dimethylbenzoic (Anca, Martínez-Carrera & García-Blanco, 1967) and 2,3-dimethylbenzoic acids (Smith, Florencio & García-Blanco, 1971). In the last two compounds, the bond length C(7)–C(1) is 1·516 Å. The value found for the C(3)–C(4)–C(5) bond angle is greater than 120·0°, which is the normal value, and the C(2)–C(3)–C(4) and C(4)–C(5)–C(6) angles are smaller. This indicates a degree of shrinkage of the benzene ring, due, possibly, to the presence of the $-NO_2$ group in the *para* position. This can be corroborated by comparing this structure with that of 3,4,5-trimethylbenzoic acid.

The bond length C(7)–O(1) of 1·276 Å exceeds that of C(7)–O(2) (1·261 Å) and the angle O(1)–C(7)–C(1) of 117·5° is smaller than O(2)–C(7)–C(1) (120·0°). This clearly indicates that the hydrogen atom is attached to the O(1) atom. It is worth while remarking that the difference between the lengths of these bonds is less than those found in the *ortho* and *meta* substituted compounds studied so far. This may be due to the influence of the nitro group in the *para* position, as it occurs in terephthalic acid (Bailey & Brown, 1967). The carbon atom of the carboxyl group, C(9) of the methyl group, and the nitrogen atom, show remarkable deviations, all in the same sense, with respect to the least-squares plane through the ring. The C(8) atom is practically undeviated. C(7) and the carbon atom of

Table 5. *Displacements of the atoms from the various planes*

(I) Plane through all the atoms.
(II) Plane through benzene-ring atoms.
(III) Plane through carboxyl group and C(1).
(IV) Plane through nitro group and C(4).

	(I)	(II)	(III)	(IV)
C(1)	0·031 Å	0·001 Å	0·000 Å	−0·003 Å
C(2)	0·072	−0·003	0·313	1·202
C(3)	0·065	−0·001	0·279	1·222
C(4)	0·018	0·006	−0·075	−0·003
C(5)	−0·042	−0·008	−0·413	−1·231
C(6)	−0·020	0·004	−0·353	−1·199
C(7)	−0·006	−0·046	−0·002	−0·008
C(8)	0·109	−0·005	0·612	2·507
C(9)	−0·141	−0·048	−0·839	−2·543
N	−0·008	−0·010	−0·130	0·010
O(1)	−0·289	−0·377	0·001	1·041
O(2)	0·241	0·241	0·001	−1·022
O(3)	−1·055	−1·059	−1·129	−0·004
O(4)	1·025	1·032	0·820	−0·004

Table 6. *Hydrogen atom parameters*

	x/a	y/b	z/c	B
H[C(2)]	0·621	0·134	0·368	2·48
H[C(6)]	0·275	0·192	0·298	2·83
H[C(8)]	0·697	−0·121	0·355	3·90
H[C(8)]	0·680	−0·043	0·226	3·90
H[C(8)]	0·620	−0·156	0·166	3·90
H[C(9)]	0·174	−0·100	0·019	4·46
H[C(9)]	0·120	0·020	0·107	4·46
H[C(9)]	0·180	−0·120	0·200	4·46
H[O(2)]	0·428	0·539	0·480	3·87

the methyl group in the *para* position in 3,4,5-trimethylbenzoic acid, show more remarkable deviations. This is more noticeable in the carboxylic carbon atom of 2,4,6-trimethylbenzoic acid. It could be remarked that in the *para*-substituted derivatives the bigger the twist angle of the -COOH group, the bigger is the deviation of the C(7) atom from the plane of the benzene ring. The values of the torsion angles for the 2,4,6- and 3,4,5-trimethylbenzoic acids are 48°29′ and 5°16′ respectively.

The O(3) and O(4) atoms in the nitro group show a marked deviation from the benzene-ring plane as a consequence of the rotation with respect to that plane. The twist of the nitro group around the C(4)-N bond is 86°16′ away from the plane of the ring and the twist of the carboxyl group around the C(7)-C(1) bond, 18°04′; both rotations are in the same sense. The twisting of the $-NO_2$ group is very remarkable and this effect could be ascribed to steric interaction between this group and the methyl group in the *ortho* position. If there are no *ortho* substituents, the rotation of the nitro group is less marked, as has been found in *p*-nitrobenzoic acid where the angle of twist is equal to 13°42′ (Sakore & Pant, 1966). The fact that both the -COOH and $-NO_2$ groups are twisted proves the lack of a polar effect in this compound since the *para* substituents in this case are both electron-withdrawing groups.

The mean C-H distance in the C(9) methyl group is 1·044 Å and in the C(8) methyl group, 0·913 Å. The methyl groups have the expected tetrahedral configuration; mean values of the H-C-H angles are 100·9 and 101·6° respectively. The C-C-H angles have the average values 116·1 and 115·9° in the C(8) and C(9) methyl groups respectively.

The bond angles C(8)-C(3)-C(4) of 121·7° and C(9)-C(5)-C(4) of 123·1° are rather greater than those calculated for 3,4,5-trimethylbenzoic acid, which has a methyl carbon in the *para* position.

The intramolecular distances O(1)···C(2), O(2)···C(6), C(8)···N, C(9)···N and O(1)···O(2) are somewhat shorter than the sums of the corresponding van der Waals radii (3·16, 3·37 and 2·72 Å respectively; Kitaigorodskii, 1961), which shows once more the effect of the molecular overcrowding.

Noteworthy is the dimerization by double hydrogen bonds, which is a common feature in most carboxyl derivatives. The structure, viewed along the *b* axis, is shown in Fig. 2. The hydrogen bonds, which occur in pairs about centres of symmetry, have a length of 2·646 Å, similar to other values given for benzoic acids. The structure is isomorphous with that of 3,4,5-trimethylbenzoic acid.

All the calculations were performed on the 1108 UNIVAC computer of the 'Centro de Proceso de Datos del Ministerio de Educación y Ciencia' (Madrid-Spain). We express our appreciation to Dr S. Martínez-Carrera, Dr F. Florencio and Dr F. H. Cano for invaluable assistance.

References

Anca, R., Martínez-Carrera, S. & García-Blanco, S. (1967). *Acta Cryst.* 23, 1010-1016.

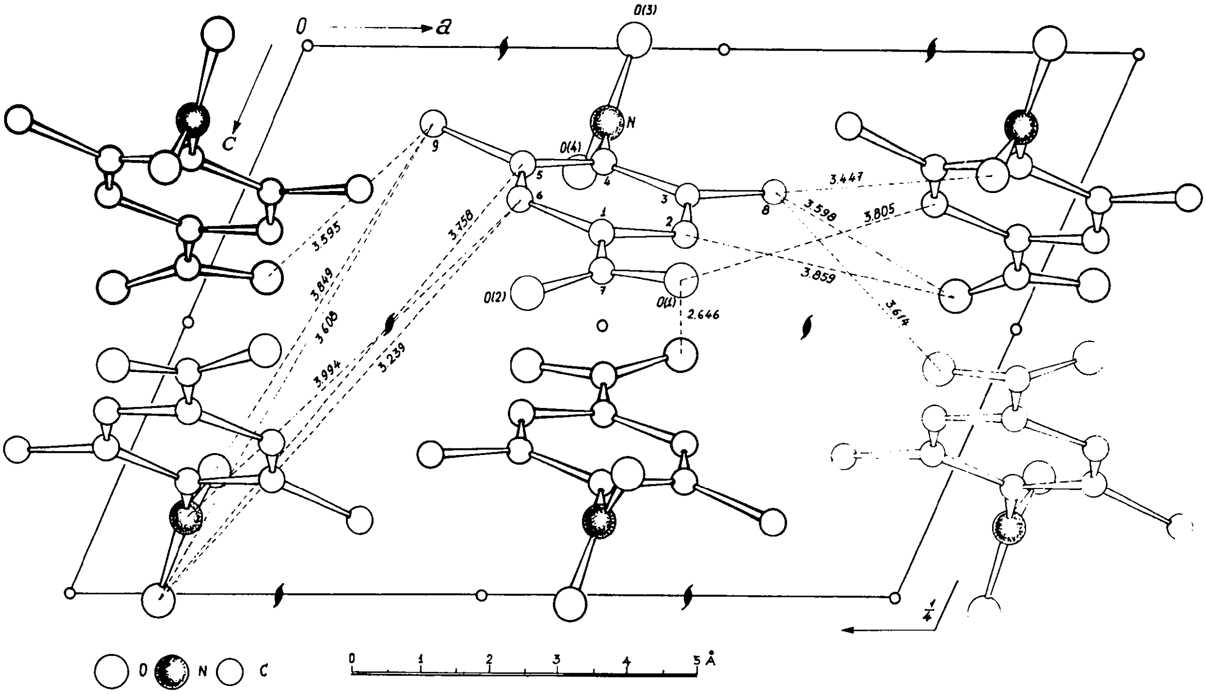

Fig. 2. Projection of the structure along the *b* axis. Some molecular distances less than 4·0 Å are shown.

BAILEY, M. & BROWN, C. J. (1967). *Acta Cryst.* **22**, 387–391.

CANO, F. H., MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1970). *Acta Cryst.* B**26**, 972–979.

FLORENCIO, F. & SMITH, P. (1970). *Acta Cryst.* B**26**, 659–666.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HANSON, H. P., HERMAN, F., LEA, L. P. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography.* New York: Consultants Bureau.

MARTÍNEZ-PEREZ, C. & MARTÍNEZ-CARRERA, S. (1967). *An. Real. Soc. Fis. Quim.* **43**(A), 313–328.

SAKORE, T. D. & PANT, L. M. (1966). *Acta Cryst.* **21**, 715–719.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

SMITH, P., FLORENCIO, F. & GARCÍA-BLANCO, S. (1971). *Acta Cryst.* B**27**, 2255–2260.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY System of Crystallographic Programs. Univ. of Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1973). B**29**, 2664

Structure Determination of Non-Linear Metallocenes. IV. The Crystal and Molecular Structure of Benzene-1,2-dithiolene-di-(π-cyclopentadienyl)tungsten(VI)

BY T. DEBAERDEMAEKER AND A. KUTOGLU

Fachbereich Geowissenschaften, Philipps-Universität Marburg, D 355 Marburg, Germany (BRD)

(*Received* 30 *April* 1973; *accepted* 21 *June* 1973)

The chelate complex $(C_5H_5)_2WS_2C_6H_4$ crystallizes in the orthorhombic crystal system. The cell dimensions are $a=16{\cdot}088$, $b=11{\cdot}148$ and $c=7{\cdot}735$ Å; the space group is *Pnma* and $Z=4$. The coordination polyhedron around the tungsten atom, defined by the cyclopentadienyl ring centroids and the sulphur atoms, is a distorted tetrahedron of nearly C_{2v} symmetry. The $S_2C_6H_4$ plane is inclined to the WS_2 plane at an angle of 8°. One of the two cyclopentadienyl rings occupies statistically the two possible positions with respect to the space-group symmetry (mirror plane).

Introduction

Of the series of 'dithiolene chelates', those with en-1,2-dithiolene ligands and also two π-cyclopentadienyl ligands bound to the central metallic atom are an important group. Although there are many metallocene dithiolene chelates, only a few of the crystal structures are known (McCleverty, 1968). From these analyses it appears that the geometry around the central metallic atom is disturbed from C_{2v} symmetry, as proposed by McCleverty (1968), to C_s or C_1 symmetry. Köpf (1961) postulates a different endithiolene-dithio-α-dicetene mesomery depending on whether the complexes are formed with metals of the fourth or the sixth subgroup; as was pointed out by Ballhausen & Dahl (1961), they have different φ_0 orbitals.

The work described in this paper is part of a contribution to a better knowledge of these complexes.

Experimental

Yellow-orange crystals were kindly supplied by Köpf (Berlin), for a crystal structure analysis. The cell parameters were obtained from the least-squares refinement of 25 strong reflexions found by the 'peak-hunting program' provided with the Philips PW 1100 automatic four-circle diffractometer. The crystallographic data are given in Table 1.

Table 1. *Crystal data*

Orthorhombic crystal symmetry
Systematic absences $0kl$: $k+l=2n+1$, $hk0$: $h=2n+1$
Space group: *Pnma* or $Pn2_1a$

$a=16{\cdot}088\pm0{\cdot}008$ Å	$V=1387{\cdot}26$ Å^3
$b=11{\cdot}148\pm0{\cdot}007$	$Z=4$
$c=\ \ 7{\cdot}735\pm0{\cdot}005$	$d_{\text{meas}}=2{\cdot}16$g cm^{-3} (in KI/H_2O solution)
M.W. 454·27	$d_{\text{cal}}=2{\cdot}18$g cm^{-3}

$F(000)=864$
$\lambda=0{\cdot}7107$ Å (Mo $K\alpha$)
Graphite monochromator

2082 independent reflexions were measured with a 2θ–ω scan. Each reflexion was measured in a 60 s scan with a scan rate of 0·02° s^{-1}; the stationary background was measured at both ends of the scan for 10 s. Two reference reflexions were checked every hour for intensity stability and for crystal orientation, but no appreciable variation was observed. Lorentz and polarization corrections were computed for each reflexion, but no absorption correction was applied. A reflexion was considered as unobserved and set to zero when $I_{hkl}\le 2*\sigma(I_{hkl})$, $[\sigma(I_{hkl})=\sqrt{(B_1+B_2+I_{\text{peak}})}]$. All the computation was carried out on the IBM 370/145 (150 kbytes) of our department and the TR 4 computer of the Zentralen Rechenanlage der Universität Marburg. The programs used were from the X-RAY 70 system or our own programs. The atomic form factors used in