

(2) Dans les motifs Mo_6X_8 , les distances Mo–X intra-motifs diffèrent très peu dans les deux phases, la valeur moyenne de cette longueur de liaison étant de 2,45 dans la phase sulfurée et de 2,58 Å dans la phase sélénée. Par contre, les distances Mo–X intermotifs sont respectivement de 2,55 et 2,72 Å.

(3) Alors que les différentes distances X–X intra- et interchaînes présentent des variations importantes dans les phases comportant un petit cation, elles deviennent plus régulières, de même que les angles, dans le cas du plomb. La longueur moyenne de la liaison S–S est de 3,48 et celle de la liaison Se–Se de 3,63 Å. Le faible écart entre ces deux valeurs confirme encore le caractère métallique du réseau de sélénium déjà mis en évidence dans les phases Mo_3Se_4 (Bars, Guillevic & Grandjean, 1973b) et $\text{Ni}_{0,33}\text{Mo}_3\text{Se}_4$ (Bars *et al.*, 1973a).

En conclusion, l'étude cristallographique de ces deux phases de composition définie nous a permis: (a) de leur attribuer une formule 'structurale' $\text{M}_x\text{Mo}_3\text{X}_4$ identique à celle des solutions solides, (b) de montrer que, si l'introduction de gros cations dans la structure

de base Mo_3X_4 ne modifie pas la disposition des atomes de molybdène et des atomes X, elle régularise par contre sensiblement le réseau des atomes X comme l'indiquent les distances interatomiques, les angles de valence et les plans moyens correspondants.

Références

- BARS, O., GUILLEVIC, J. & GRANDJEAN, D. (1973a). *J. Solid State Chem.* **6**, 335–339.
 BARS, O., GUILLEVIC, J. & GRANDJEAN, D. (1973b). *J. Solid State Chem.* **6**, 48–57.
 CHEVREL, R., SERGENT, M. & PRIGENT, J. (1971). *J. Solid State Chem.* **3**, 515–519.
 GUILLEVIC, J., BARS, O. & GRANDJEAN, D. (1973). *J. Solid State Chem.* **7**, 158–162.
 GUILLEVIC, J., BARS, O. & GRANDJEAN, D. (1976). *Acta Cryst.* **B32**, 1338–1342.
 MAREZIO, M., DERNIER, P. D., REMEIK, J. P., CORENZWIT, E. & MATTHIAS, B. T. (1973). *Mater. Res. Bull.* **8**, 657–668.
 SERGENT, M. & CHEVREL, R. (1973). *J. Solid State Chem.* **6**, 433–437.

Acta Cryst. (1976). **B32**, 1345

The Crystal Structure of Phenyl Benzoate

BY J. M. ADAMS AND IN PART BY S. E. MORSI*

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed, SY23 1NE, Wales

(Received 9 October 1975; accepted 11 October 1975)

The structure of $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$ has been determined from 844 microdensitometer-measured intensities. All bond lengths and angles are normal. The –COO group is twisted 9.8° out of the plane of the benzene ring to which it is attached, and 65.1° out of the plane of the second ring. The dihedral angle between the two benzene rings is 55.7° .

Introduction

There has recently been some interest in the solid-state decomposition kinetics of dibenzoyl peroxide (Morsi & Khalil, 1973, 1974; Morsi, Thomas & Williams, 1975) and, since phenyl benzoate is one of the products of the decomposition, this investigation was undertaken to give information necessary for a detailed explanation of the mechanism of the reaction. Part of the interest in this material arises from the exceptionally low activation energy (substantially less than the –O–O– bond dissociation energy) of solid-state decomposition of the parent dibenzoyl peroxide.

Experimental

The crystals used (maximum dimension ~ 0.5 mm) were grown from methanol at room temperature and

their density measured by flotation. Oscillation and Weissenberg photographs gave the space group $P2_1/c$; high-angle reflexions were used to deduce the cell parameters (Table 1). $0kl-3kl$ and $h0l-h1l$ data were collected on a Stoe–Weissenberg camera (with different crystals for the two data sets) and were measured on an Optronics International P1000 microdensitometer by the SRC Microdensitometer Service.

Table 1. *Crystal data*

$\text{C}_{13}\text{H}_{10}\text{O}_2$
 Space group $P2_1/c$; $a=5.74$ (1), $b=14.75$ (2), $c=12.45$ (2) Å
 (Cu $K\alpha$, $\lambda=1.5418$ Å), $\beta=101.0$ (2) $^\circ$
 $Z=4$, $d_m=1.28$, $d_c=1.27$ g cm $^{-3}$

Determination of the structure

The data were corrected for Lorentz and polarization effects and were initially scaled with the $h0l$ and $h1l$ data. Reflexions that had been too weak to be recorded by the microdensitometer were given half the intensity

* Permanent address: Dept. of Chemistry, Centre-Delta University, Tanta, Egypt.

of the weakest observed reflexion on the appropriate film. A Wilson plot gave an overall temperature factor of 2.1 \AA^2 and E values were generated.

The direct-method programs of Germain, Main & Woolfson (1970) were used to solve the structure. The set of signs with the highest figure of merit (1.15) produced an E map with all the heavy atoms immediately recognizable. Refinement of the positional and isotropic thermal parameters reduced R to 0.108. A cycle of full-matrix least squares with anisotropic thermal parameters reduced R to 0.088 at which point a difference synthesis enabled all the H atoms to be located. The final R was 0.047. The average shift in the atomic parameters was 0.05 of the e.s.d. and the largest shift/e.s.d. was 0.43 in the y parameter of H(7). Throughout the refinement the weights were taken as unity and scale factors for the different levels were refined separately. The scattering factors used were those listed in *International Tables for X-ray Crystallography* (1974). Final atomic and thermal parameters are given in Tables 2 and 3.* All calculations apart from the structure solution were performed on a CDC 7600 computer with the X-RAY System of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion

The molecular dimensions (Table 4) are similar to the normal values, with C-C (aromatic) ranging from

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31451 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates and their standard deviations ($\times 10^4$)

	x	y	z
C(1)	3481 (9)	1393 (3)	4357 (4)
C(2)	2920 (11)	1996 (3)	3480 (4)
C(3)	918 (10)	2542 (3)	3385 (4)
C(4)	-540 (11)	2487 (4)	4156 (4)
C(5)	22 (10)	1897 (3)	5035 (4)
C(6)	2030 (8)	1360 (3)	5120 (3)
C(7)	4468 (9)	841 (3)	6780 (4)
C(8)	4628 (8)	125 (3)	7631 (3)
C(9)	2774 (9)	-477 (3)	7695 (4)
C(10)	3044 (11)	-1139 (4)	8491 (4)
C(11)	5189 (11)	-1205 (4)	9240 (4)
C(12)	7046 (10)	-611 (4)	9189 (4)
C(13)	6753 (10)	49 (3)	8396 (4)
O(1)	2459 (6)	734 (2)	5995 (2)
O(2)	5869 (6)	1436 (2)	6758 (3)
H(1)	5040 (90)	950 (40)	4470 (40)
H(2)	3970 (90)	2010 (40)	2890 (50)
H(3)	510 (70)	2960 (30)	2740 (30)
H(4)	-2030 (120)	2840 (40)	4030 (50)
H(5)	-1100 (80)	1870 (30)	5630 (40)
H(6)	1150 (80)	-480 (30)	7110 (40)
H(7)	1690 (100)	-1630 (40)	8440 (40)
H(8)	5390 (80)	-1630 (30)	9790 (40)
H(9)	8540 (90)	-610 (30)	9830 (40)
H(10)	8060 (100)	410 (40)	8330 (40)

Table 3. Thermal vibration parameters (\AA^2) with standard deviations

All U_{ij} are multiplied by 10^3 , all U are multiplied by 10^2 .

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	52 (4)	51 (3)	50 (3)	-2 (3)	9 (2)	-8 (2)
C(2)	62 (4)	60 (3)	41 (3)	-3 (3)	14 (3)	-4 (2)
C(3)	53 (4)	53 (3)	44 (3)	-3 (3)	0 (2)	4 (3)
C(4)	59 (5)	56 (3)	53 (3)	4 (3)	0 (3)	4 (3)
C(5)	48 (4)	56 (3)	47 (3)	1 (3)	8 (2)	-4 (3)
C(6)	43 (4)	46 (3)	38 (2)	-4 (3)	0 (2)	0 (2)
C(7)	48 (4)	44 (3)	43 (3)	-1 (3)	7 (2)	-4 (2)
C(8)	37 (3)	40 (2)	42 (2)	-1 (2)	10 (2)	-5 (2)
C(9)	45 (4)	53 (3)	46 (3)	-1 (3)	9 (2)	-3 (2)
C(10)	69 (5)	54 (3)	55 (3)	-6 (3)	7 (3)	4 (3)
C(11)	74 (5)	52 (3)	48 (3)	6 (3)	8 (3)	10 (3)
C(12)	59 (5)	58 (3)	50 (3)	0 (3)	-5 (3)	5 (3)
C(13)	49 (4)	47 (3)	56 (3)	-3 (3)	0 (3)	-5 (2)
O(1)	55 (3)	53 (2)	53 (2)	-11 (2)	-3 (2)	14 (2)
O(2)	70 (4)	61 (2)	60 (2)	-25 (2)	-4 (2)	11 (2)

	U		U		U
H(1)	5 (2)	H(5)	3 (1)	H(8)	2 (1)
H(2)	6 (2)	H(6)	3 (1)	H(9)	4 (2)
H(3)	2 (1)	H(7)	6 (2)	H(10)	4 (2)
H(4)	8 (2)				

1.371 (6) to 1.401 (7) \AA and ring angles within 3σ of 120° . The geometry involving H atoms is reasonable with no obviously spurious bond lengths or angles. The molecule is made up of three planar regions, the two benzene rings and the C(8), C(7), O(2), O(1), C(6) group of atoms. All the atoms lie on these planes (Table 5), within three e.s.d.'s in the atomic parameters. The -COO group is twisted by 9.8° with respect to the C(1)-C(6) ring - a figure in keeping with those previously found for unsubstituted benzoates [0-14°; see, e.g. Iball & MacKay (1962); Skinner, Stewart & Speakman (1954); Verhoef & Boeyens (1969)] - the C(8)-C(13) ring being twisted in the opposite sense 55.7° from the first ring. The angle between the -COO group and the C(8)-C(13) ring is 65.1° , the axes of rotation of these planes being almost parallel.

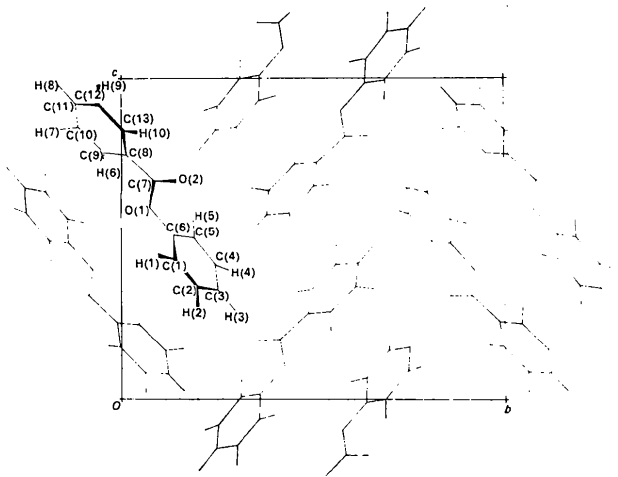


Fig. 1. Projection of the structure down the a axis.

Table 4. Bond distances (Å) and angles (°) with their standard deviations

C(1)—C(2)	1.398 (7)	C(1)—C(2)—C(3)	119.9 (5)
C(1)—C(6)	1.379 (8)	C(2)—C(3)—C(4)	120.3 (5)
C(2)—C(3)	1.389 (8)	C(3)—C(4)—C(5)	120.0 (5)
C(3)—C(4)	1.390 (9)	C(4)—C(5)—C(6)	118.9 (5)
C(4)—C(5)	1.387 (7)	C(5)—C(6)—C(1)	122.0 (4)
C(5)—C(6)	1.386 (8)	C(6)—C(1)—C(2)	118.7 (5)
C(6)—O(1)	1.413 (5)	C(1)—C(6)—O(1)	120.9 (4)
O(1)—C(7)	1.371 (6)	C(5)—C(6)—O(1)	116.9 (4)
C(7)—O(2)	1.194 (6)	C(6)—O(1)—C(7)	118.3 (4)
C(7)—C(8)	1.487 (6)	O(1)—C(7)—C(8)	110.9 (4)
C(8)—C(9)	1.400 (7)	O(1)—C(7)—O(2)	123.1 (4)
C(9)—C(10)	1.379 (7)	O(2)—C(7)—C(8)	126.0 (4)
C(10)—C(11)	1.399 (8)	C(7)—C(8)—C(9)	123.1 (4)
C(11)—C(12)	1.390 (8)	C(8)—C(9)—C(10)	120.5 (5)
C(12)—C(13)	1.374 (7)	C(9)—C(10)—C(11)	119.5 (5)
C(13)—C(8)	1.401 (7)	C(10)—C(11)—C(12)	120.7 (5)
C(1)—H(1)	1.09 (5)	C(11)—C(12)—C(13)	119.3 (5)
C(2)—H(2)	1.04 (6)	C(13)—C(8)—C(9)	118.9 (4)
C(3)—H(3)	1.01 (4)	C(13)—C(8)—C(7)	117.9 (4)
C(4)—H(4)	0.98 (7)	C(6)—C(1)—H(1)	119 (3)
C(5)—H(5)	1.07 (5)	C(2)—C(1)—H(1)	122 (3)
C(9)—H(6)	1.07 (4)	C(1)—C(2)—H(2)	119 (3)
C(10)—H(7)	1.05 (6)	C(3)—C(2)—H(2)	121 (3)
C(11)—H(8)	0.91 (4)	C(2)—C(3)—H(3)	119 (3)
C(12)—H(9)	1.06 (5)	C(4)—C(3)—H(3)	120 (3)
C(13)—H(10)	0.93 (6)	C(3)—C(4)—H(4)	118 (4)
		C(5)—C(4)—H(4)	121 (4)
		C(4)—C(5)—H(5)	119 (2)
		C(6)—C(5)—H(5)	122 (2)
		C(8)—C(9)—H(6)	122 (2)
		C(10)—C(9)—H(6)	117 (2)
		C(9)—C(10)—H(7)	117 (3)
		C(11)—C(10)—H(7)	123 (3)
		C(10)—C(11)—H(8)	121 (3)
		C(12)—C(11)—H(8)	118 (3)
		C(11)—C(12)—H(9)	119 (3)
		C(13)—C(12)—H(9)	121 (3)
		C(12)—C(13)—H(10)	118 (3)
		C(8)—C(13)—H(10)	120 (3)

The arrangement of the molecules within the unit cell is shown in Fig. 1. The shortest intramolecular contacts involving O(2) are one of 2.89 (5) from H(1) and another of 2.60 (5) Å from H(10), this latter being almost exactly the sum of the van der Waals radii. There are no intermolecular contacts less than the van der Waals distances — the shortest are 2.52 (5) from O(2)—H(5) [at $1+x, y, z$], 2.45 (7) from H(9)—H(9) [at $2-x, -y, 2-z$] and 2.56 (7) Å from H(5)—H(7) [at $-x, \frac{1}{2}+y, \frac{3}{2}-z$].

The authors thank Professor J. M. Thomas for suggesting the problem and also for his interest in this work.

Table 5. Least-squares planes and the deviations of atoms from them (Å)

(a) Plane defined by C(1)—C(6)			
$2.5883x + 10.5121y + 5.4960z = 4.7651$			
C(1)	-0.0060	H(1)	-0.005
C(2)	0.0015	H(2)	-0.037
C(3)	0.0048	H(3)	-0.017
C(4)	-0.0067	H(4)	-0.094
C(5)	0.0022	H(5)	0.010
C(6)	0.0042	O(1)	-0.0624
(b) Plane defined by C(8)—C(13)			
$-2.7393x + 9.2746y + 8.6364z = 5.4418$			
C(8)	-0.0034	H(6)	-0.063
C(9)	0.0009	H(7)	-0.126
C(10)	0.0008	H(8)	0.026
C(11)	0.0001	H(9)	0.140
C(12)	-0.0027	H(10)	-0.074
C(13)	0.0044	C(7)	-0.0310
(c) Plane defined by O(1), C(7), O(2), C(8), C(6)			
$-3.5436x + 8.6165y + 7.9060z = 4.5006$			
O(1)	-0.0003	C(8)	0.0000
C(7)	0.0004	C(6)	0.0001
O(2)	-0.0002		
(d) Plane defined by C(6), O(1), C(7)			
$-3.5466x + 8.6089y + 7.9068z = 4.4995$			

References

- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
- IBALL, J. & MACKAY, K. J. H. (1962). *Acta Cryst.* **15**, 148–156.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MORSI, S. E. & KHALIL, S. M. (1973). *Egypt. J. Chem.* **16**, 543–549.
- MORSI, S. E. & KHALIL, S. M. (1974). *Egypt. J. Chem.* **17**, 69–73.
- MORSI, S. E., THOMAS, J. M. & WILLIAMS, J. O. (1975). *J. Chem. Soc. Faraday*, **1**, 71, 1857–1867.
- SKINNER, J. M., STEWART, G. M. D. & SPEAKMAN, J. C. (1954). *J. Chem. Soc.* pp. 180–184.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. H. & HALL, S. R. (1972). The X-RAY System—version of June 1972. Update of April 1974. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.
- VERHOEF, L. H. W. & BOEYENS, J. C. A. (1969). *Acta Cryst.* **B25**, 607–611.