

The Crystal Structure of Toluene- α ,2-dicarboxylic Acid, $C_9H_8O_4$

BY M. P. GUPTA AND M. SAHU

Department of Physics, University of Ranchi, Ranchi-8, Bihar, India

(Received 15 December 1970)

The crystal structure of dicarboxylic homophthalic acid, $C_9H_8O_4$, has been determined using three-dimensional X-ray diffraction data and refined by the method of least-squares to an R value of 0.107. The crystals are triclinic, $a=8.44$, $b=10.77_3$, $c=5.21_5$ Å, $\alpha=80^\circ 3'$, $\beta=116^\circ 10'$, $\gamma=96^\circ 44'$, with two molecules in a unit cell, space group symmetry $P\bar{1}$. In the crystal structure, homophthalic acid molecules form an extended system of hydrogen bonds, each molecule being linked through its two carboxyl groups to two nearest neighbours, the hydrogen bonds being 2.66 and 2.62 Å in length across centres of symmetry. The two hydrogen bonds are in nearly mutually perpendicular planes and the two carboxyl groups themselves in the molecule are rotated out of the central aromatic ring by $8^\circ 30'$ & $89^\circ 54'$.

Homophthalic acid (toluene- α ,2-dicarboxylic acid), $C_9H_8O_4$, is a dicarboxylic acid and is expected to show, like most other aliphatic or aromatic dicarboxylic acids, interesting features of hydrogen bonding. Moreover, the stereochemistry of the molecule is also of interest since there is the possibility of large rotations, without much steric hindrance, of the two end carboxyl groups in the molecule around the C(1)–C(2) or C(8)–C(9) single bonds (Fig. 1). A determination of the crystal structure of homophthalic acid was, therefore, undertaken to unravel the scheme of the hydrogen bond system and to establish the exact spatial geometry of the two carboxyl groups *vis à vis* the central aromatic ring (Fig. 1).

Crystal data

Crystals of homophthalic acid were first studied using X-ray diffraction techniques by Gupta & Bose (1969). The details of crystal morphology and unit-cell measurements for this acid are given by the above authors and the unit-cell parameters (determined by the use of high $\sin \theta$ reflexions on Weissenberg films on which silver lines had been superimposed at one end, as internal standards for calibration) reported below are similar. These values are:

$$\begin{array}{ll} a=8.44 \text{ \AA} & \alpha=80^\circ 3' \\ b=10.77_3 & \beta=116^\circ 10' \\ c=5.21_5 & \gamma=96^\circ 44' \end{array}$$

$$\rho_{\text{calc}}=1.423 \text{ g.cm}^{-3} \quad \rho_{\text{obs}}=1.41 \text{ g.cm}^{-3}$$

Number of molecules in the unit cell, $Z=2$

Linear absorption coefficient for Cu $K\alpha$ $\mu=9.77 \text{ cm}^{-1}$. Space group: $P\bar{1}$ (confirmed by pyroelectricity tests and $N(z)\%$ test (Howells, Philips & Rogers, 1950).

A total number of 621 reflexions with non-zero values of intensity were collected by the use of normal beam (for hko , $0kl$, $h0l$, hkh , hkh reflexions) and equi-

inclination Weissenberg photographs with unfiltered Cu K radiation and multiple film technique (for the upper levels around the $[001]$ axis, *viz* hkl , $hk2$, $hk3$, $hk\bar{1}$, $hk\bar{2}$, $hk\bar{3}$). This gives about 5 reflexions for each parameter (positional, thermal and scale) in structure, excluding the hydrogen atoms. Intensities of reflexions were estimated visually and corrected for the geometrical factors and also for spot-size and shape (for the upper level Weissenberg photographs). The $|F|$ values were brought to a nearly absolute scale by statistical methods.

Determination and refinement of the structure

Patterson projections failed to give any clue regarding the orientation of the molecule. A three-dimensional Patterson function (with limited data) proved equally difficult to interpret. Optical transform methods (Lipson & Taylor, 1958) gave a structure which failed to refine further. Extensive trial and error methods, based on packing and other physico-chemical considerations also proved to be of little help. At this stage, all the observed values of structure amplitudes were converted into normalized structure factors (E_h) using the expression given by Karle & Karle (1966), evaluated on a desk calculator. Three reflexions (272, $0\bar{2}1$, 720) with large absolute values of E_h were given positive signs and using algebraic symbols for the undetermined signs of other reflexions, signs of 108 reflexions out of 612 were determined either in the form of + or – or expressed in terms of the algebraic symbols, the number of the latter being reduced to one. Lack of local computer facilities prevented the calculation of three-dimensional Fourier syntheses giving the algebraic symbols values of either + or – but it was noticed that the majority of the reflexions of the type $0kl$, with large $|F|$ values, had their signs expressed in terms of only one unknown symbol. This unknown symbol was given the value + and a two-dimensional

Table 1. Observed and calculated structure factors

h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc
1	0	0	10.0	10.0	1	0	0	10.0	10.0	1	0	0	10.0	10.0	1	0	0	10.0	10.0
1	1	0	10.0	10.0	1	1	0	10.0	10.0	1	1	0	10.0	10.0	1	1	0	10.0	10.0
1	2	0	10.0	10.0	1	2	0	10.0	10.0	1	2	0	10.0	10.0	1	2	0	10.0	10.0
1	3	0	10.0	10.0	1	3	0	10.0	10.0	1	3	0	10.0	10.0	1	3	0	10.0	10.0
1	4	0	10.0	10.0	1	4	0	10.0	10.0	1	4	0	10.0	10.0	1	4	0	10.0	10.0
1	5	0	10.0	10.0	1	5	0	10.0	10.0	1	5	0	10.0	10.0	1	5	0	10.0	10.0
1	6	0	10.0	10.0	1	6	0	10.0	10.0	1	6	0	10.0	10.0	1	6	0	10.0	10.0
1	7	0	10.0	10.0	1	7	0	10.0	10.0	1	7	0	10.0	10.0	1	7	0	10.0	10.0
1	8	0	10.0	10.0	1	8	0	10.0	10.0	1	8	0	10.0	10.0	1	8	0	10.0	10.0
1	9	0	10.0	10.0	1	9	0	10.0	10.0	1	9	0	10.0	10.0	1	9	0	10.0	10.0
1	10	0	10.0	10.0	1	10	0	10.0	10.0	1	10	0	10.0	10.0	1	10	0	10.0	10.0
1	11	0	10.0	10.0	1	11	0	10.0	10.0	1	11	0	10.0	10.0	1	11	0	10.0	10.0
1	12	0	10.0	10.0	1	12	0	10.0	10.0	1	12	0	10.0	10.0	1	12	0	10.0	10.0
1	13	0	10.0	10.0	1	13	0	10.0	10.0	1	13	0	10.0	10.0	1	13	0	10.0	10.0
1	14	0	10.0	10.0	1	14	0	10.0	10.0	1	14	0	10.0	10.0	1	14	0	10.0	10.0
1	15	0	10.0	10.0	1	15	0	10.0	10.0	1	15	0	10.0	10.0	1	15	0	10.0	10.0
1	16	0	10.0	10.0	1	16	0	10.0	10.0	1	16	0	10.0	10.0	1	16	0	10.0	10.0
1	17	0	10.0	10.0	1	17	0	10.0	10.0	1	17	0	10.0	10.0	1	17	0	10.0	10.0
1	18	0	10.0	10.0	1	18	0	10.0	10.0	1	18	0	10.0	10.0	1	18	0	10.0	10.0
1	19	0	10.0	10.0	1	19	0	10.0	10.0	1	19	0	10.0	10.0	1	19	0	10.0	10.0
1	20	0	10.0	10.0	1	20	0	10.0	10.0	1	20	0	10.0	10.0	1	20	0	10.0	10.0
1	21	0	10.0	10.0	1	21	0	10.0	10.0	1	21	0	10.0	10.0	1	21	0	10.0	10.0
1	22	0	10.0	10.0	1	22	0	10.0	10.0	1	22	0	10.0	10.0	1	22	0	10.0	10.0
1	23	0	10.0	10.0	1	23	0	10.0	10.0	1	23	0	10.0	10.0	1	23	0	10.0	10.0
1	24	0	10.0	10.0	1	24	0	10.0	10.0	1	24	0	10.0	10.0	1	24	0	10.0	10.0
1	25	0	10.0	10.0	1	25	0	10.0	10.0	1	25	0	10.0	10.0	1	25	0	10.0	10.0
1	26	0	10.0	10.0	1	26	0	10.0	10.0	1	26	0	10.0	10.0	1	26	0	10.0	10.0
1	27	0	10.0	10.0	1	27	0	10.0	10.0	1	27	0	10.0	10.0	1	27	0	10.0	10.0
1	28	0	10.0	10.0	1	28	0	10.0	10.0	1	28	0	10.0	10.0	1	28	0	10.0	10.0
1	29	0	10.0	10.0	1	29	0	10.0	10.0	1	29	0	10.0	10.0	1	29	0	10.0	10.0
1	30	0	10.0	10.0	1	30	0	10.0	10.0	1	30	0	10.0	10.0	1	30	0	10.0	10.0

Fourier synthesis was calculated. This synthesis, however, was not one of the best resolved ones and the resulting map only showed the gross orientation of the molecule as well as the rotations in the two carboxyl groups in the molecule. Structure factor calculations soon confirmed the model to be a correct one and $R(0kl)$ reduced to 0.28. Work was then concentrated on the projection down the [001] axis, the best resolved projection. Packing considerations soon gave reasonable x coordinates and reiterative Fourier refinements reduced $R(hk0)$ to 0.25. At this stage, least-squares refinement of the complete three-dimensional data was undertaken by using first only an overall isotropic

temperature factor, then individual isotropic temperature factors for each atom and finally anisotropic temperature factors for each atom and unit weight for all the observed reflexions in the last stages of refinement. The program of Busing, Martin & Levy (1962) using full-matrix refinement (modified by Hamilton, Ibers, Johnson & Srikanta for use on the CDC-3600

Table 2. Atomic coordinates and anisotropic temperature factors

(a) Atomic coordinates in fractions of cell edges and their standard deviations ($\times 10^4 \text{ \AA}$) in parentheses

	x/a	y/b	z/c
C(1)	2200 (21)	1001 (12)	1682 (37)
C(2)	3991 (21)	1631 (12)	3036 (31)
C(3)	5390 (19)	1357 (12)	2637 (38)
C(4)	7030 (20)	1931 (12)	3909 (33)
C(5)	7317 (20)	2819 (13)	5606 (34)
C(6)	5927 (21)	3104 (12)	6249 (36)
C(7)	4200 (21)	2562 (11)	4904 (32)
C(8)	2768 (21)	2952 (12)	5408 (31)
C(9)	1478 (27)	3832 (13)	2904 (45)
O(1)	2118 (14)	0230 (09)	-0078 (22)
O(2)	0912 (14)	1117 (09)	2059 (27)
O(3)	0165 (16)	4072 (10)	3275 (26)
O(4)	1757 (15)	4230 (10)	0785 (27)

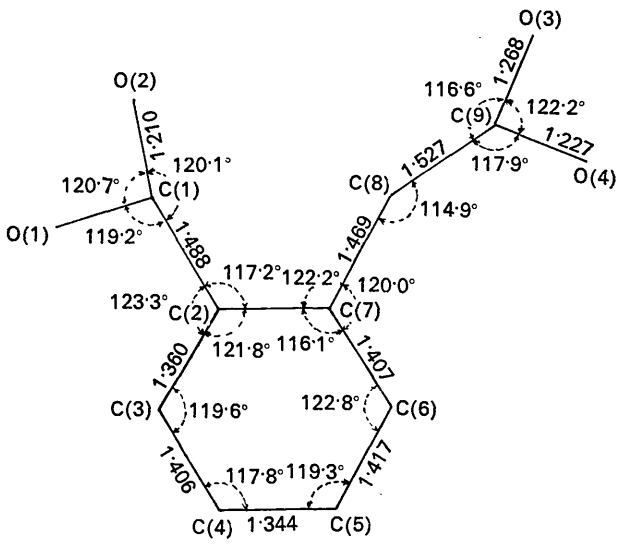


Fig. 1 The labelling scheme of atoms in the molecule with bond lengths and angles.

Table 2 (cont.)

(b) Anisotropic temperature factors and their estimated standard deviations ($\times 10^4 \text{\AA}^2$)

Thermal parameters are of the form

$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(2)	127 (31)	90 (14)	519 (111)	7 (16)	54 (48)	-46 (27)
C(2)	174 (34)	95 (14)	249 (97)	-2 (16)	5 (4)	-2 (23)
C(3)	135 (33)	84 (14)	752 (133)	44 (16)	-22 (52)	-38 (29)
C(4)	181 (35)	103 (14)	525 (116)	-3 (16)	146 (47)	-64 (28)
C(5)	197 (36)	103 (14)	474 (111)	-21 (17)	259 (48)	-41 (27)
C(6)	196 (34)	88 (13)	587 (116)	-10 (16)	233 (47)	-42 (25)
C(7)	215 (36)	78 (13)	344 (102)	-23 (16)	85 (48)	-46 (25)
C(8)	243 (38)	93 (14)	293 (99)	5 (18)	224 (45)	-7 (24)
C(9)	279 (48)	63 (13)	372 (127)	-1 (18)	66 (63)	-59 (25)
O(1)	261 (28)	117 (10)	624 (83)	-49 (13)	181 (37)	-148 (21)
O(2)	175 (25)	113 (11)	838 (94)	1 (13)	69 (40)	-173 (23)
O(3)	206 (28)	127 (12)	767 (91)	35 (15)	290 (36)	15 (22)
O(4)	189 (24)	126 (12)	449 (82)	43 (12)	194 (36)	-8 (23)

computer) was used. The final R value is 0.107 for all the observed reflexions only. This does not contain contributions from the hydrogen atoms which we have not tried to locate. Table 1 gives the list of observed and calculated structure factor amplitudes. Reflexions not observed have been excluded from the list.

Coordinates, bond lengths and angles and intermolecular contacts

Table 2(a) gives the final atomic coordinates together with their estimated standard deviations (in parentheses) while the thermal parameters with their e.s.d.'s in parentheses are given in Table 2(b). Tables 3 and 4 give the bond lengths and bond angles in the molecule together with their e.s.d.'s. Table 5 gives the significant intermolecular distances in the crystal structure up to 4 Å. The labelling scheme of atoms is given in Fig. 1. For example the notation ${}_a\text{C}(1)$ means carbon atom

Table 3. Bond lengths

	Length, l	$\sigma'(l)$
C(1)-C(2)	1.488 Å	0.020 Å
C(2)-C(3)	1.360	0.017
C(3)-C(4)	1.406	0.020
C(4)-C(5)	1.344	0.025
C(5)-C(6)	1.417	0.018
C(6)-C(7)	1.407	0.020
C(7)-C(2)	1.455	0.023
C(7)-C(8)	1.469	0.018
C(8)-C(9)	1.527	0.030
C(1)-O(1)	1.316	0.023
C(1)-O(2)	1.210	0.014
C(9)-O(3)	1.268	0.018
C(9)-O(4)	1.227	0.027

Table 4. Bond angles

	Angle, θ	$\sigma(\theta)$
C(2)-C(3)-C(4)	119.6°	1.7°
C(3)-C(4)-C(5)	117.8	1.7
C(4)-C(5)-C(6)	119.3	0.9
C(5)-C(6)-C(7)	122.8	1.05
C(6)-C(7)-C(2)	116.1	1.2
C(7)-C(2)-C(3)	121.8	1.55
C(1)-C(2)-C(3)	123.3	1.4
C(1)-C(2)-C(7)	117.2	1.5
O(1)-C(1)-C(2)	119.2	1.3
O(1)-C(1)-O(2)	120.7	1.5
O(2)-C(1)-C(2)	120.1	1.3
C(2)-C(7)-C(8)	122.9	1.2
C(8)-C(7)-C(6)	121.0	1.3
C(7)-C(8)-C(9)	114.9	1.6
C(8)-C(9)-O(3)	116.6	1.8
O(3)-C(9)-O(4)	122.2	1.4
C(8)-C(9)-O(4)	117.9	1.5

Table 5. Intermolecular distances

		Distance (Å)	
O(1) —	O(2)*	2.66	
O(3) —	$b\text{O}(4)^*$	2.62	
O(1) —	$-a\text{C}(4)$	4.00	O(2) — $a, c\text{C}(4)^*$ 3.74
O(3) —	$-a\text{C}(4)$	3.39	O(1) — $a, c\text{C}(4)^*$ 3.48
O(3) —	$-a\text{C}(5)$	3.20	C(3) — $a, c\text{C}(3)^*$ 3.70
O(4) —	$a, b, c\text{C}(5)^*$	3.82	C(2) — $a, c\text{C}(3)^*$ 3.55
O(4) —	$a, b, c\text{C}(6)^*$	3.26	C(9) — $a, b, c\text{C}(5)^*$ 3.45
O(1) —	$a, c\text{C}(5)^*$	3.60	C(9) — $a, b, c\text{C}(6)^*$ 3.51

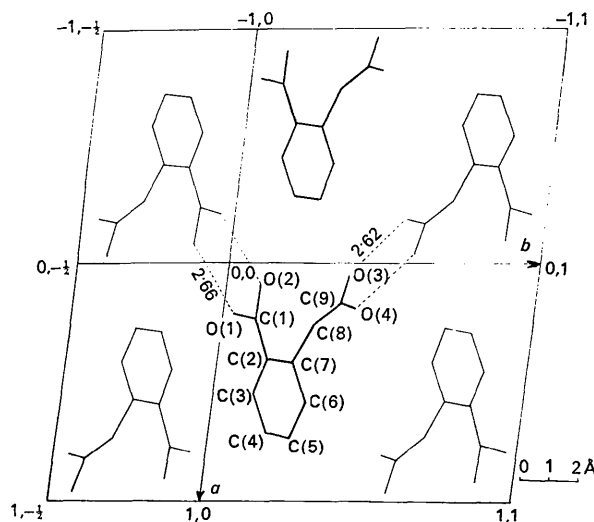


Fig. 2. Structure viewed down [001].

C(1) derived by unit a translation *etc.* An atom with an asterisk (*) mark is centrosymmetric to the corresponding atom in the reference molecule.

Equations of the best planes through the atom groups

The equation of the plane passing through the central aromatic ring (C(2)–C(3)–C(4)–C(5)–C(6)–C(7)) determined by the least-squares fit of data is given by

$$X + 19.62182 Y - 24.21691 Z - 7.36935 = 0 \quad (A)$$

The equations of the planes passing through the two end carboxyl groups (O(1)–C(1)–O(2)) and (O(3)–C(9)–O(4)) are, respectively.

$$X - 20.85043 Y + 24.17908 Z + 4.00329 = 0 \quad (B)$$

$$X + 3.08124 Y + 1.71849 Z - 16.69697 = 0 \quad (C)$$

X, Y, Z (in Å) are coordinates of atoms referred to orthogonal axes, a, b' and c' , b' being normal to a in the ab plane and c' being normal to both a and b' . Plane (B) makes an angle of $8^\circ 30'$ with the plane (A) while the angle that plane (C) makes with the plane (A) is $89^\circ 54'$. In other words, both the carboxyl groups are rotated out of the plane of the central aromatic ring and one of these (O(3)–C(9)–O(4)) is almost at right angles ($89^\circ 54'$) to it. The deviations of the atoms from the plane (A) and the e.s.d.'s of these deviations are given in Table 6. The direction cosines of the normals to the above three planes are given in Table 7.

Table 6. Deviations (Å) from the least-squares planes of the central aromatic ring with their standard deviations

	Deviation	e.s.d.'s
C(1)	-0.048 Å	0.026 Å
C(2)	-0.016	0.024
C(3)	-0.032	0.026
C(4)	-0.016	0.025
C(5)	0.036	0.026
C(6)	-0.016	0.026
C(7)	0.009	0.024
C(8)	0.067	0.025
C(9)	1.440	0.031
O(1)	0.012	0.017
O(2)	0.128	0.019
O(3)	1.660	0.019
O(4)	2.640	0.019

Table 7. Direction cosines of normal to the planes

	l	m	n
Normal to plane (A)	0.0320	0.6287	-0.7759
Normal to plane (B)	0.0314	-0.6537	0.7580
Normal to plane (C)	0.2632	0.5477	0.4522

Description of the crystal structure

Figs. 2, 3 and 4 show views of the crystal structure down [001], [100] and [010]. In the crystal, each

molecule is linked through its two carboxyl groups to the two nearest neighbours, across centres of symmetry, in such a manner that there are short hydrogen bonds of 2.66 Å (across 0,0,0) and 2.62 Å, (across $0, \frac{1}{2}, 0$) between the oxygen atoms of the linked molecules. The different C–O bond lengths (1.31, 1.21; 1.27, 1.22 Å, Table 3) clearly indicate that oxygen atoms O(1) and O(3) are the donors while oxygen atoms O(2) and O(4) are the acceptors in the hydrogen bond formation. The angles C(1)–O(1)–O(2)* and C(9)–O(3)–O(4)* are 105° and $110^\circ 30'$ respectively, close to the tetrahedral value. The hydrogen bond system is an extended one and the molecules are linked to one another in a zigzag manner (Fig. 3). However, the two hydrogen bonds (2.66 and 2.62 Å) are in two nearly perpendicular planes as a consequence of the plane of one of the carboxyl groups [O(3)–C(9)–O(4)] being almost normal to the central aromatic ring. Other bonds which link the various molecules are of the van der Waals type (3.16 Å and upwards, Table 5).

Hydrogen positions

Although in a [001] difference Fourier synthesis (contributions of carbon and oxygen atoms only subtracted), the hydrogen atoms show up in the expected positions, we consider that these coordinates are not very reliable. The calculated positions for the hydrogen atoms assuming C–H = 1.08 Å and O–H = 1.05 Å are given below:

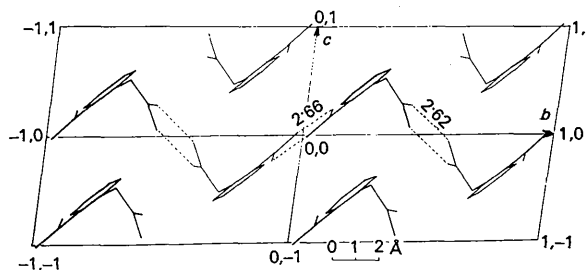


Fig. 3. Structure viewed down [100].

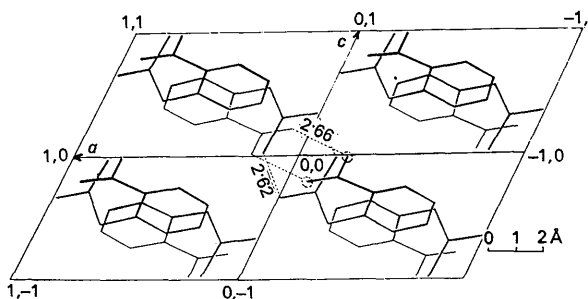


Fig. 4. Structure viewed down [010]. (Points encircled indicate atoms b -translated downwards.)

Atom	Attached to	x/a	y/b	z/c
H(1)...	C(3)	0.518	0.067	0.121
H(2)...	C(4)	0.811	0.169	0.352
H(3)...	C(5)	0.861	0.328	0.660
H(4)...	C(6)	0.614	0.379	0.764
H(5)...	C(8)	0.299	0.344	0.722
H(6)...	C(8)	0.233	0.233	0.685
H(7)...	O(1)	0.092	-0.030	-0.088
H(8)...	O(3)	-0.059	0.534	0.167

We also thank Dr S. M. Prasad of this laboratory for his valuable help in the completion of this work.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Oak Ridge National Laboratory Report ORNL-TM-305.
- GUPTA, M. P. & BOSE, S. (1969). *Indian J. Phys.* **43**, 45.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
- KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* **21**, 860.
- LIPSON, H. & TAYLOR, C. A. (1958). *Fourier Transforms and X-ray Diffraction*. Appendix II, p. 65. London: Bell.

Grateful acknowledgement is made of the computing facilities at TIFR, Colaba, on the CDC-3600. The optical transform method was tried using the facilities available at the Physics Department of Gauhati University, Assam for which we express our thanks.

Acta Cryst. (1971). B27, 2473

The Crystal Structure of *N,N'*-Dibenzyl-4,4'-bipyridylium diiodide

BY J. H. RUSSELL* AND S. C. WALLWORK

Department of Chemistry, University of Nottingham, England

(Received 28 December 1970)

($C_6H_5 \cdot CH_2 \cdot NC_5H_4 \cdot C_5H_4N \cdot CH_2 \cdot C_6H_5$)²⁺ 2I⁻ forms red monoclinic crystals, space group $P2_1/c$, and each unit cell of dimensions $a = 7.009$, $b = 12.99$, $c = 12.74$ Å, $\beta = 90.2^\circ$ contains two bipyridylium ions and four iodide ions. Although the iodide ion does not lie directly over the pyridylium ring, close interatomic approaches indicate that charge transfer from the iodide ion to the bipyridylium ion occurs.

Introduction

The crystal structures of a series of quaternary salts of *N,N'*-substituted-4,4'-bipyridyls have been determined as part of a programme aimed at investigating possible interactions between the anion and cation in relation to observed properties of the compounds. The first of these papers (Russell & Wallwork, 1969) reported the structure of the dimethyl substituted tetrachlorocuprate and a future paper will report the structures of the dimethyl substituted dichloride, dibromide and diiodide. This paper describes the crystal structure of *N,N'*-dibenzyl-4,4'-bipyridylium diiodide.

Bipyridylium salts possess a number of interesting properties, one of which has enabled them to find commercial application as herbicides (Boon, 1964). Some have also been shown to be charge transfer complexes, (Macfarlane & Williams, 1969) as exhibited by their spectra. It is hoped that the present investigations will shed further light on the nature of the charge transfer interactions by studying the relative dispositions of the ions; this aspect will be discussed in a future paper.

Experimental

The material, in the form of red crystals suitable for X-ray photography, was supplied by the Mond Division of Imperial Chemical Industries Ltd. Oscillation and equi-inclination Weissenberg photographs were

* Present address: Agricultural Division, Imperial Chemical Industries Ltd., Billingham, Teesside, England.

Table 1. *Analysis of agreement between F_o and final F_c (both on 50 times absolute scale)*

$ F_o $ range	No. of reflexion	$\sum F_o - F_c $	R	Av. $\sum w(F_o - F_c)^2 10^{-3}$
0-999	1057	112402	0.185	32.7
1000-1999	412	47058	0.081	24.3
2000-2999	146	26262	0.074	10.1
3000-3999	86	24367	0.082	17.9
4000-4999	43	13084	0.068	7.4
5000-5999	24	13396	0.103	49.9
6000-7999	21	8813	0.060	6.3
8000-9999	2	1358	0.077	11.5
> 9999	3	2999	0.094	16.7