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X–RAY DETERMINATION OF UNIT CELL DIMENSIONS OF SODIUM BENZOYLACETONATE

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Abstract. Sodium benzoylacetonate has not been studied by X-ray diffraction methods. There is no X-ray information on their interplaner spacings and lattice dimensions.

Sodium benzoylacetonate showed anomalous electrical properties when heated at 90°. There is a phase transformation at this particular temperature.

X-ray powder diffraction methods were used to study the original sample and the new phase formed at 90°. The lattice spacings and the geometry of the two crystals before and after heating were evaluated. The results showed that crystals of sodium benzoylacetonate are monoclinic while the crystals of the preheated sample at 90° are triclinic.

The indexing of monoclinic patterns with four parameters and triclinic patterns involving six parameters, is very difficult. A number of investigators have tackled the problem. Vand[1,2] has described several methods of indexing powder patterns of compound with large interplaner spacings. Zsoldos[3] started from Vand's third graphical method and developed a general method for indexing powder pattern of low symmetry crystals. This method is probably most advantageous in the monoclinic case. Ito[4,5] attacked the problem without making any assumptions as to the symmetry and dimensions of the unit cell. The method is based on the fact that each reflection of a powder pattern corresponds to a vector in the reciprocal lattice. Three noncoplaner vectors define the edges of a possible unit cell, and three additional vectors fix their interaxial angles. Once an appropriate unit cell is selected, it should be possible to index all lines in the pattern.

Ito's method was used in the present work for indexing powder patterns of sodium benzoylacetonate before and after heating at 90°

Experimental and Results

Material. Sodium benzoylacetonate ($C_{10}H_9O_2Na$) was prepared according to the method given by Vogel[6]. The sample was in the powder form grain size suitable for study by the X–ray diffraction method. The specimen was mounted on a glass fibre and rotated in the collimated X–ray beam. The diffraction pattern was recorded using a Philips powder camera (114.6 mm dia) and Co k_α radiation. The material was heated to 90° for 30 min, then cooled to room temperature. The diffraction pattern was recorded again under the same conditions.

Measurements Technique. The interplaner spacings and corresponding Q values of sodium benzoylacetonate are listed in Table 1. The three lines of smallest Q's were assigned indices 100, 010 and 001. The high order reflections were also selected to correct the Q values of the first order reflections. The computed and the observed of these values were tabulated in Table 2. From this Table it was conducted that:

$$Q_{100} = 0.0039 - 0.0002 = 0.0037 = a^{*2}$$

$$Q_{010} = 0.0059 - 0.0009 = 0.0050 = b^{*2}$$

$$Q_{001} = 0.0095 - 0.0004 = 0.0091 = c^{*2}$$

From these particular values of Q_{001} and Q_{010} the values of Q'_{110} and Q'_{011} become

$$Q'_{110} = \sqrt{Q_{110} + Q_{\bar{1}10}} = a^{*2} + b^{*2} = 0.0087$$

and

$$Q'_{011} = \sqrt{Q_{011} + Q_{0\bar{1}1}} = b^{*2} + c^{*2} = 0.0141$$

A check of Table 1 for a pair of Q's symmetrically disposed about Q'_{110} and Q'_{011} that satisfies these relations reveals that lines 3 and 5 have Q's values of 0.0095 and 0.0146 respectively. This would indicate that $Q'_{110} = Q_{110}$ i.e. $\cos\gamma^* = 0$ or $\gamma^* = 90^\circ$ and $Q'_{011} = Q_{011}$, i.e. $\cos\alpha^* = 0$ or $\alpha^* = 90^\circ$. To verify this conclusion several other values of Q_{hko} and Q_{okl} for several reflections were computed and were compared with the observed Q's values (Tables 3,4). It could be observed that the given values could not be appreciably improved by changing the values of either a^{*2} or b^{*2} The slight difference between the two values may be attributed to errors in measuring the interplaner spacings or in the computation of Q'_{110} or Q'_{011}

TABLE 1. OBSERVED Q VALUES FOR ($C_{10}H_9O_2Na$) BEFORE HEATING

Line	d A'	I/I_o	$Q=1/d^2$	Line	dA^o	I/I_o	$Q=1/d^2$	Line	dA^o	I/I_o	$Q=1/d^2$
1	15.95	S	0.0039	11	4.53	M	0.0484	21	3.20	M	0.0876
2	12.98	M	0.0059	12	4.20	M	0.0567	22	3.05	M	0.1075
3	10.27	W	0.0095	13	4.10	W	0.0595	23	2.97	M	0.1134
4	8.88	V.S	0.0126	14	3.88	S	0.0664	24	2.90	M	0.1189
5	8.29	M	0.0146	15	3.70	W	0.0730	25	2.88	M	0.1206
6	7.25	S	0.0190	16	3.56	S	0.0789	26	2.80	W	0.1275
7	5.63	M	0.0315	17	3.46	M	0.0835	27	2.73	W	0.1342
8	5.34	W	0.0351	18	3.35	W	0.0891	28	2.69	W	0.1382
9	4.89	V.S.	0.0418	19	3.29	W	0.0924	29	2.65	W	0.1424
10	4.73	M	0.0447	20	3.23	M	0.0958	30	2.60	W	0.1479

TABLE 2. SELECTION OF Q_{100} AND Q_{001} FROM TABLE 1.

Q_{hkl}	Comp.	Obs.	Error in Q_{hkl}	Q_{hkl}	Comp.	Obs.	Error in Q_{hkl}
Q_{100}	--------	0.0039	--------	Q_{030}	0.0531	0.0567	+0.0004
Q_{200}	0.0156	0.0146	-0.0002	Q_{040}	0.0944	0.0958	+0.0001
Q_{300}	0.0351	0.0351	0.0000	Q_{001}	--------	0.0095	--------
Q_{400}	0.0624	0.0595	-0.0002	Q_{002}	0.0380	0.0351	-0.0007
Q_{010}	--------	0.0059	--------	Q_{003}	0.0855	0.0835	-0.0002
Q_{020}	0.0236	0.0190	-0.0011	Q_{004}	0.1520	--------	--------

TABLE 3. AGREEMENT OF COMPUTED AND OBSERVED Q_{hko}'s

Q_{hko}	Comp.	Obs.	Diff.	Q_{hko}	Comp.	Obs.	Diff.
110	0.0085	0.0095	+0.0010	310	0.0365	0.0351	-0.0014
120	0.2350	--------	--------	230	0.0590	0.0595	+0.0005
210	0.0190	0.0190	0.0000	320	0.0515	0.0487	-0.0029
220	0.0340	0.0351	+0.0011	330	0.0765	0.0789	+0.0024
130	0.0485	0.0487	+0.0002	-----	--------	--------	--------

TABLE 4. AGREEMENT OF COMPUTED AND OBSERVED Q_{okl}'s

Q_{okl}	Comp.	Obs.	Diff.	Q_{okl}	Comp.	Obs.	Diff.
011	0.0139	0.0146	+0.0007	031	0.0539	0.0567	+0.0028
012	0.0417	0.0418	+0.0001	023	0.1001	0.976	–0.0025
021	0.0289	----------	----------	032	0.0806	0.0789	–0.0017
022	0.0556	0.0567	+0.0011	033	0.1251	0.1275	+0.0024
013	0.0851	0.0835	–0.0016	------	----------	----------	----------

β^* can be calculated by help of the following relation

$$\cos \beta^* = \frac{Q_{101} - Q_{10\bar{1}}}{4 \quad a^* \quad c^*}$$

$$Q'_{101} = Q_{100} + Q_{001} = 0.0037 + 0.0091 = 0.0128$$

The pair of Q's symmetrically placed about Q'_{101} shows that lines 2 and 6, Table 1, come closest to satisfying the relation, $\sqrt{Q_{101} + Q_{\bar{1}01}} = c^{*2} + a^{*2} = Q'_{101}$

This requires that

$$Q_{101} - Q'_{101} = Q'_{101} - Q_{\bar{1}01}$$

Substituting the Q value of line 6 for Q_{101},

$$Q_{101} - Q'_{101} = Q_6 - Q'_{101} = 0.0190 - 0.0128 = 0.0062$$

Similarly, substituting the Q value of line 2 for Q_{101}

$$Q'_{101} - Q_{101} = Q'_{101} - Q_2 = 0.0128 - 0.0059 = 0.0069$$

The slight discrepancy between the values can be attributed to errors in the measured values of Q_{101} and $Q'_{\bar{1}01}$ or in the computation of $Q'_{\bar{1}01}$. Thus with the new values of $a^{*2} = 0.0035$ and $c^{*2} = 0.0089$, the two sides of the above relation become

$$Q'_{\bar{1}01} - Q'_{101} = Q'_{101} - Q_{10\bar{1}}$$
$$0.0190 - 0.0124 = 0.0124 - 0.0059$$
$$0.0066 = 0.0065$$

Thus both sides are the same within an acceptable errors. Subtituting the values of Q_2 and Q_6'

$$\beta^* = \cos^{-1} \frac{0.0190 - 0.0059}{4(0.0592 \times 0.0940)} = 54^\circ,\bar{2}$$

To verify the value of β^*, several values of $Q_{\bar{h}ol}$ and Q_{hol} for several reflections were computed and were compared with the observed Q's, Table 5.

From the previous results it could be concluded that the reciprocal edges and interaxial angles of sodium benzoylacetonate becomes:

$a^* = 0.0592$	$\alpha^* = 90^\circ$
$b^* = 0.0707$	$\beta^* = 54^\circ,2'$
$c^* = 0.0940$	$\gamma^* = 90^\circ$

From these values every line in the observed powder pattern could be indexed. The complete set of observed and computed Q values was listed in Table 6.

Calculating the reciprocal volume and by using the equations of transformation[7] the direct unit cell edges could be computed.

$a = 20.87$ Å	$\alpha = 90^\circ$
$b = 14.14$ Å	$\beta = 125^\circ,58'$
$c = 13.14$ Å	$\gamma = 90^\circ$

A least -squared refinement of them against their quoted d-values were carried out using a computer programme and a more exact fit of the data was obtained. The refined cell dimensions were:

$a = 20.79$, $b = 14.38$, $c = 13.39$ Å, $\beta = 126^\circ.97$.

Sodium benzoylacetonate showed anomalous electrical behaviour when heated at 90° then other metal complexes of this group[8] The new phase formed at this particular temperature was studied. The interplaner spacings and the corresponding Q's values of the preheated $C_{10}H_9O_2Na$ to 90° were arranged in Table 7 .

Following the procedures adopted before, the reciprocal cell dimensions of the preheated sample were determined. The results were shown in Tables 8-12. The reciprocal and the direct unit cell dimensions are:

$a^* = 0.0608$	$\alpha^* = 82^\circ.\bar{1}$
$b^* = 0.0721$	$\beta^* = 73^\circ.\overline{36}$
$c^* = 0.1049$	$\gamma^* = 53^\circ.\overline{32}$

TABLE 5. AGREEMENT OF COMPUTED AND OBSERVED Q_{hol}'s AND $Q_{\bar{h}ol}$'s

Q_{hol}	Comp.	Obs.	Diff.	$Q_{\bar{h}ol}$	Comp.	Obs.	Diff.
101	0.0190	0.0190	0.0000	103	0,0638	0.0664	+0.0026
101	0.0058	0.0059	+0.0001	301	0.0602	0.0595	−0.0007
102	0.0523	0.0567	+0.0044	301	0.0206	0.0190	−0.0016
102	0.0259	----------	----------	203	0.1337	0.1342	+0.0005
201	0.0361	0.0351	−0.0010	203	0.0554	0.0567	+0.0013
201	0.0097	0.0095	−0.0002	302	0.1067	0.1075	+0.0008
202	0.0760	0.0730	−0.0030	302	0.0275	----------	----------
202	0.0232	----------	----------	303	0.1710	----------	----------
103	0.0934	0.0924	−0.0010	303	0.0522	0.0567	+0.0045

TABLE 6. AGREEMENT OF OBSERVED AND COMPUTED $Q_{hkl's}$

Line	Obs.	Comp.	hkl.	Line	Obs.	Comp.	hkl.
1	0.0039	0.0039	100	16	0.0789	0.0806	032,003
2	0.0059	0.0059	010,101	17	0.0835	0.0851	013
3	0.0095	0.0095	001,201	18	0.0891	----------	----------
4	0.0126	0.0136	011	19	0.0924	0.0934	103,333
5	0.0146	0.0145	211	20	0.0958	0.0962	232,222
6	0.0190	0.0190	101	21	0.0976	0.1001	023
7	0.0315	0.0318	312	22	0.1075	0.1067	302,113
8	0.0351	0.0351	201,002	23	0.1134	0.1133	331,312
9	0.0418	0.0417	012,222	24	0.1189	0.1195	223,232
10	0.0447	0.0442	321,122	25	0.1206	0.1218	123
11	0.0487	0.0485	130,131	26	0.1275	0.1291	232,322
12	0.0567	0.0556	203,122	27	0.1342	0.1340	133,203
13	0.0595	0.0602	301,230	28	0.1382	0.1363	142,213
14	0.0664	0.0638	103,311	29	0.1424	----------	----------
15	0.0730	0.0737	331,223	30	0.1479	0.1468	242,133

TABLE 7. OBSERVED Q VALUES FOR ($C_{10}H_9O_2$ Na) AFTER HEATING

Line	dA	I/I_o	$Q=1/d^2$	Line	d A^o	I/I_o	$Q=1/d^2$	Line	d A^o	I/I_o	$Q=1/d^2$
1	16.45	S	0.0037	12	4.59	V.S.	0.0474	23.	3.39	W	0.0870
2	13,81	S	0.0052	13	4.48	W	0.0498	24	3.30	W	0.0918
3	9.50	V.S.	0.0111	14	4.41	W	0.0514	25	3.25	W	0.0947
4	8.42	W	0.0141	15	4.23	V.S.	0.0559	26	3.22	M	0.0964
5	7.39	S	0.0183	16	4.06	W	0.0607	27	3.16	M	1.001
6	6.93	M	0.0208	17	3.89	M	0.0659	28	3.14	W	0.1014
7	5.91	V.S.	0.0286	18	3.72	M	0.0722	29	3.06	W	0.1068
8	5.59	W	0.0320	19	3.59	W	0.0776	30	2.98	M	0.1126
9	5.41	M	0.0342	20	3.45	W	0.0835	31	2.81	M	0.1266
10	4.93	W	0.0411	21	3.44	S	0.0845	32	2.79	W	0.1284
11.	4.77	M	0.0440	22	3.42	W	0.0855				

V. S = very strong M = medium, S = strong

TABLE 8. SELECTION OF Q_{100} AND Q_{001} FROM TABLE 7.

Q_{hkl}	Comp.	Obs.	Error in Q_{hkl}	Q_{hkl}	Comp.	Obs.	Error
Q_{100}	-------	0.0037	--------	Q_{030}	0.0468	0.0474	0.0000
Q_{200}	0.0148	0.0141	–.0002	Q_{040}	0.0832	0.0835	0.0000
Q_{390}	0.0333	0.0346	+.0001	Q_{001}	--------	0.0111	--------
Q_{400}	0.0592	0.0607	+.0001	Q_{002}	0.0443	0.0443	0.0000
Q_{010}	--------	0.0052	0.0000	Q_{003}	0.0997	0.1001	0.0000
Q_{020}	0.0208	0.0208	0.0000	Q_{004}	0.1773	--------	--------

TABLE 9. AGREEMENT OF COMPUTED AND OBSERVED Q_{okl}'s

Q_{okl}	Comp	Obs.	Diff.	Q_{okl}	Comp.	Obs.	Diff.
011	0.0183	0.0183	0.0000	013	0.0979	0.0964	0.0015
011	0.0141	0.0141	0.0000	031	0.0641	0.0659	+0.0018
012	0.0534	0.0514	−0.0020	031	0.0515	0.0514	−0.0001
012	0.0450	0.0440	−0.0010	023	0.1324	0.1325	+0.0001
021	0.0360	0.0342	−0.0018	023	0.1072	0.1068	−0.0004
021	0.0276	0.0286	+0.0010	032	0.1034	0.1014	−0.0020
022	0.0732	0.0722	−0.0010	032	0.0782	0.0776	−0.0006
022	0.0564	0.0559	−0.0005	033	0.1647	--------	--------
013	0.1105	0.1126	+0.0021	033	0.1269	0.1263	−0.0006

TABLE 10. AGREEMENT OF COMPUTED AND OBSERVED Q_{hol}'s

Q_{hol}	Comp.	Obs.	Diff.	Q_{hol}	Comp.	Obs.	Diff.
101	0.0173	0.0183	+0.0010	103	0.0919	0.0918	−0.0001
101	0.0111	0.0111	0.0000	301	0.0561	0.0559	−0.0002
102	0.0549	0.0559	+0.0010	301	0.0345	0.0342	−0.0003
102	0.0405	0.0411	+0.0006	203	0.1354	----------	----------
201	0.0330	0.0320	−0.0010	203	0.0922	0.0918	−0.0004
201	0.0186	0.0183	−0.0003	302	0.0999	0.1001	+0.0002
202	0.0732	0.0722	−0.0010	302	0.0567	0.0559	−0.0008
202	0.0444	0.0440	−0.0004	303	0.1657	--------	----------
103	0.1135	0.1126	−0.0009	303	0.1009	0.1014	+0.0005

TABLE 11. AGREEMENT OF COMPUTED AND OBSERVED Q_{hko}'s

Q_{hko}	Comp.	Obs.	Diff.	Q_{hko}	Comp.	Obs.	Diff.
110	0.0141	0.0141	0.0000	130	0.0349	0.0342	−0.0007
110	0.0037	0.0037	0.0000	310	0.0541	0.0559	+ 0.0018
120	0.0349	0.0342	−0.0007	310	0.0229	0.0208	−0.0021
120	0.0104	0.0111	+ 0.0007	230	0.0928	0.0918	−0.0010
210	0.0304	0.0320	+ 0.0016	230	0.0304	0.0320	+ 0.0016
210	0.0096	0.0111	+ 0.0015	320	0.0853	0.0855	+ 0.0002
220	0.0564	0.0559	−0.0005	320	0.0229	----------	----------
220	0.0148	0.0141	−0.0007	330	0.1269	0.1266	−0.0003
130	0.0661	0.0659	−0.0002	330	0.0333	0.0342	+ 0.0009

a = 21.09 Å $\alpha^* = 87^\circ.28$
b = 17.24 Å $\beta^* = 104^\circ.29$
c = 9.39 Å $\gamma^* = 125^\circ.46$

Conclusion and Discussion of Results

X-ray results showed that the crystal of sodium benzoylacetonate belongs to a monoclinic system while the cystal of the preheated sample at 90° belongs to a triclinic system. At this particular temperature the original unit cell dimensions were affected and, therefore, the atomic positions within the unit cell were changed.

The unit cell determined from Ito's method is often not the most desirable cell for describing the crystal concerned. It is merely a possible cell and does not exhibit the full symmetry of the lattice. The

TABLE 12. AGREEMENT OF OBSERVED AND COMPUTED $Q_{hkl's}$ FOR PREHEAT ($C_{10}H_9O_2Na$)

Line	Q_{obs}	Q_{comp}	hkl	Line	Q_{obs}	Q_{comp}	hkl
1	0.0037	0.0037	100	17	0.0722	0.0732	022
2	0.0052	0.0052	010	18	0.0776	0.0782	032
3	0.0111	0.0111	001	19	0.0835	0.0832	040
4	0.0141	0.0141	011	20	0.0845	0.0848	331
5	0.0183	0.0183	011	21	0.0855	0.0853	320
6	0.0208	0.0208	020	22	0.0870	0.0867	312
7	0.0286	--------	----	---	--------	--------	----
8	0.0320	0.0319	121	23	0.0918	0.0919	103
9	0.0342	0.0345	301	24	0.0947	0.0943	141
10	0.0411	0.0405	102	25	0.0964	0.0970	113
11	0.0440	0.0443	002	26	0.1001	0.0999	302
12	0.0474	0.0495	212	28	0.1014	0.1016	103
13	0.0498	0.0495	212	28	0.1068	0.1072	023
14	0.0514	0.0515	031	29	0.1126	0.1115	332
15	0.0559	0.0561	301	30	0.1266	0.1269	330
16	0.0607	0.0602	202	32	0.1284	0.1279	303
17	0.0659	0.0652	222				

analytical method of analysis is usually not enough to give any picture of the structure. The structure determination needs X-ray studies using single crystal methods.

References

1. V. Vand, Acta Cryst.,**1**, 109 (1948).
2. V. Vand, Acta Cryst,**1** , 290 (1948).
3. L. Zsoldos, Acta Cryst., **11**, 835 (1958).
4. T. Ito, Nature, **164**, 755 (1949).
5. T. Ito, *X-Ray Studies on Polymorphism* (Maruzen Co., Ltd., Tokyo (1950)) pp. 187 - 228.
6. Vogel and I. Arther, *A Text Book of Practical Organic Chemistry* (Longmans , 1956),3rd edition, p. 865.
7. G. H. Stout and L. H. Jensen, *X-Ray Structure Determination, A Practical Guide* (Macmillan, London, 1968), p. 29.
8. A. El-Shafie, Electrical Properties of Some Organo-Metalic Solid Compounds, M.Sc., Thesis Submitted to Faculty of Science, Cairo University (1976).