X-ray powder diffraction data for three red azo pigments: sodium, barium, and ammonium lithol salts

Alicja Rafalska-Łasocha,[1,a)] Marta Grzesiak-Nowak,[1] Piotr Goszczycki,[1] Katarzyna Ostrowska,[1] and Wiesław Łasocha[1,2]
[1]*Faculty of Chemistry, Jagiellonian University, 30-060 Krakow, Poland*
[2]*Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, 30-239 Krakow, ul. Niezapominajek 8, Poland*

(Received 8 February 2017; accepted 25 April 2017)

Lithol reds belong to the group of azo pigments, which were popular artists' colouring materials in the first half of the twentieth century. These pigments were also used in many branches of industry. Here, we report X-ray powder diffraction data, unit-cell parameters, and space groups for three compounds from this group: sodium (E)-2-((2-hydroxynaphthalen-1-yl)diazenyl)naphthalene-1-sulphonate monohydrate (Na lithol red), monoclinic, space group $C2/c$, with cell parameters $a = 33.343(7)$, $b = 6.667(2)$, $c = 16.397(4)$ Å, $\beta = 90.83°$, $V = 3644.51$ Å^3, $Z = 8$; barium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate trihydrate (Ba lithol red), monoclinic, space group $P21/m$, with cell parameters $a = 17.758(9)$, $b = 6.209(4)$, $c = 16.857(8)$ Å, $\beta = 92.07°$, $V = 1857.39$ Å^3, $Z = 2$; and ammonium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate monohydrate (NH4 lithol red), monoclinic, space group $P2/c$, with cell parameters $a = 17.721(5)$, $b = 6.428(3)$, $c = 16.911(5)$ Å, $\beta = 100.31(3)°$, $V = 1895.31$ Å^3, and $Z = 4$. In the first and third cases we synthesised the pigments in their monohydrate form, performed X-ray powder diffraction measurements, and indexed all of the obtained diffraction maxima. In the case of the barium compound, despite many efforts in the course of the synthesis procedure, the powder diffraction patterns of the obtained samples were not of the best quality. Nevertheless, we indexed the best one and found a reliable space group and cell parameters. © *2017 International Centre for Diffraction Data.*
[doi:10.1017/S0885715617000616]

Key words: azo pigments, lithol salts, powder diffractometry

I. INTRODUCTION

Lithol red, due to its reasonably low price, great tinctorial strength, good working properties, and clean bright hue, was a popular pigment in the early and middle twentieth century. It was used in alkyd resin enamels and lacquers, paper coatings, emulsion paints, polystyrene and amide-based plastics, artists' materials, colouring plastics (Ash and Ash, 1996), elastomers (Herbst and Hunger, 1997), architectural paints, and toy finishes (Alphen, 1998). Under the name lithol red pigment, one can find a family of sodium (PR 49), barium (PR 49:1), calcium (PR 49:2), and strontium (PR 49:3) salts of diazotised Tobias (2-naphthylamine-1-sulphonic) acid coupled with 2-naphthol. The colour of the pigment ranges from yellowish red (sodium salt) to bluish red (strontium salt), depending on the metal cation. The main drawback of lithol red is its very poor lightfastness, which has profound implications for its artistic use. As an example, we can mention Mark Rothko's Seagram and Harvard Murals, painted in the middle of the twentieth century (Standeven, 2008). Nowadays, in cases where brightness, bleed resistance, and low cost are of primary importance, pigments from the group of lithol reds are still used (mainly in the USA) in great quantities in the printing industry.

Sodium salt is the starting compound for production of the other lithol salts by means of a simple ion-exchange process whereby Ba, NH_4, Ca, or Sr ions replace the Na ions. This process is inefficient; some Na salt almost always remains. Therefore, it is very difficult to obtain a pure lithol salt. The sodium form is usually present in all of the PR 49 types. This explains the absence of crystallographic characterisations of lithol salts in the PDF files. To date only potassium lithol salt ($C_{20}H_{13}KN_2O_4S$, powder diffraction data PDF 46-1638 and PDF 46-1639) is represented in PDF-4+ (ICDD, 2015). However, within the PDF characterisation, only 2θ, interplanar d-spacing and intensities are present. These patterns are not indexed and lattice parameters have not been determined.

II. EXPERIMENTAL

A. Synthesis of lithol salts

1. Synthesis of sodium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl] naphthalene-1-sulphonate monohydrate

The sodium lithol salt was prepared by modified literature procedure (Stenger *et al.*, 2010). Initially 2-aminonaphtalene-1-sulphonic acid (8.92 g, 40 mmol) was suspended in a mixture of 160 ml of water and 4.2 ml of concentrated HCl. The mixture was heated to about 90 °C for 30 min and then cooled to 0 °C. To the cooled and vigorously stirred suspension,

---

[a)] Author to whom correspondence should be addressed. Electronic mail: rafalska@chemia.uj.edu.pl

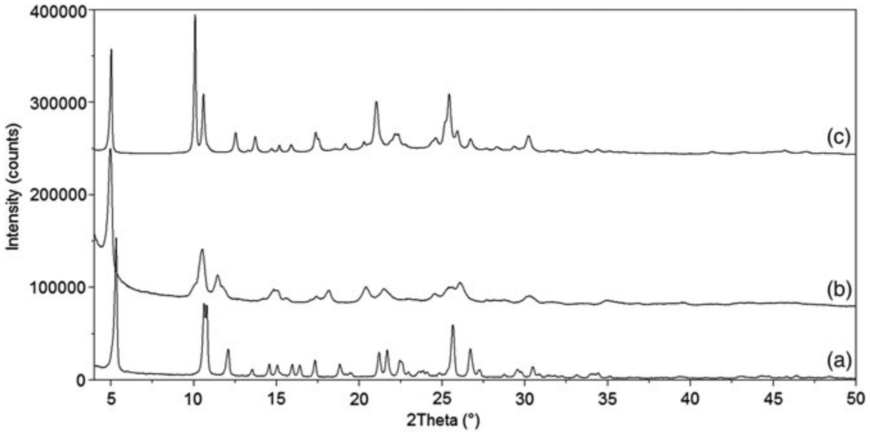


Figure 1. Experimental powder diffraction patterns of the investigated lithol salts. Na lithol red (*A*), Ba lithol red (*B*), and NH_4 lithol red (*C*).

TABLE I. X-ray powder diffraction data for sodium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate monohydrate.

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs}	*H*	*k*	*l*	θ_{cal} (°)	d_{calc} (Å)	$\Delta 2\theta$
5.300	16.6745	100	2	0	0	5.302	16.6699	−0.002
10.619	8.3313	51	4	0	0	10.614	8.3349	0.004
10.792	8.1981	48	0	0	2	10.792	8.1978	−0.001
12.089	7.3213	21	2	0	2	12.101	7.3141	−0.012
13.539	6.5403	5	1	1	0	13.546	6.5371	−0.007
14.580	6.0756	10	−1	1	1	14.574	6.0783	0.006
			1	1	1	14.603	6.0663	−0.023
15.056	5.8846	9	−4	0	2	15.048	5.8879	0.008
15.277	5.8000	2	4	0	2	15.271	5.8023	0.006
15.503	5.7159	1	−3	1	0	15.501	5.7168	0.002
15.953	5.5557	10	6	0	0	15.950	5.5566	0.002
16.415	5.4003	9	−3	1	1	16.383	5.4108	0.032
17.300	5.1260	14	−1	1	2	17.327	5.1182	−0.027
18.844	4.7094	10	5	1	0	18.824	4.7145	0.020
			−3	1	2	18.858	4.7059	−0.014
19.170	4.6300	2	−6	0	2	19.165	4.6312	0.005
19.440	4.5663	3	6	0	2	19.430	4.5686	0.009
21.183	4.1943	20	−1	1	3	21.160	4.1989	0.023
			1	1	3	21.221	4.1870	−0.038
21.671	4.1010	21	−5	1	2	21.648	4.1053	0.022
			0	0	4	21.682	4.0989	−0.012
22.421	3.9655	10	2	0	4	22.413	3.9669	0.008
			−3	1	3	22.422	3.9654	−0.001
22.578	3.9383	9	3	1	3	22.593	3.9357	−0.016
22.948	3.8756	3	7	1	0	22.949	3.8754	−0.002
23.562	3.7760	3	−7	1	1	23.527	3.7816	0.035
23.800	3.7387	4	−8	0	2	23.810	3.7372	−0.011
24.090	3.6944	3	−4	0	4	24.055	3.6997	0.035
			8	0	2	24.098	3.6932	−0.008
24.822	3.5871	3	−5	1	3	24.814	3.5882	0.007
25.320	3.5176	3	−7	1	2	25.304	3.5199	0.016
25.630	3.4758	43	−1	1	4	25.620	3.4772	0.010
26.702	3.3386	23	−3	1	4	26.666	3.3431	0.036
			10	0	0	26.740	3.3340	−0.039
27.235	3.2745	6	6	0	4	27.225	3.2757	0.010
28.749	3.1054	2	−5	1	4	28.713	3.1092	0.036
			−10	0	2	28.760	3.1042	−0.012
29.529	3.0251	6	−9	1	2	29.531	3.0249	−0.003
29.775	3.0006	3	9	1	2	29.797	2.9986	−0.021
30.467	2.9340	9	−1	1	5	30.464	2.9344	0.004
30.801	2.9030	2	8	0	4	30.822	2.9011	−0.021
			−4	2	2	30.827	2.9007	−0.026
30.914	2.8926	1	4	2	2	30.940	2.8903	−0.026
31.349	2.8534	1	−3	1	5	31.347	2.8537	0.002
31.548	2.8359	1	3	1	5	31.557	2.8352	−0.008
			−7	1	4	31.583	2.8329	−0.035

Continued

TABLE I. Continued

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs}	H	k	l	θ_{cal} (°)	d_{calc} (Å)	$\Delta 2\theta$
31.807	2.8135	1	6	2	1	31.820	2.8124	−0.014
32.224	2.7779	1	12	0	0	32.221	2.7783	0.004
33.129	2.7041	2	−6	2	2	33.114	2.7054	0.016
			−5	1	5	33.117	2.7052	0.013
			−2	0	6	33.145	2.7030	−0.015
33.944	2.6410	3	−12	0	2	33.918	2.6431	0.027
34.169	2.6241	2	−11	1	2	34.151	2.6256	0.019
34.421	2.6055	4	−4	0	6	34.389	2.6080	0.033
			−10	0	4	34.427	2.6052	−0.005
			11	1	2	34.436	2.6045	−0.014
35.105	2.5563	1	−2	2	4	35.066	2.5591	0.039
			−9	1	4	35.098	2.5569	0.007
36.329	2.4729	1	8	2	2	36.307	2.4745	0.023
			−3	1	6	36.334	2.4727	−0.004
36.719	2.4475	1	11	1	3	36.683	2.4499	0.036

TABLE II. X-ray powder diffraction data for barium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1- sulphonate trihydrate.

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs}	h	k	l	θ_{cal} (°)	d_{calc} (Å)	$\Delta 2\theta$
4.950	17.8518	100	1	0	0	4.979	17.7467	−0.029
9.980	8.8628	7	2	0	0	9.968	8.8734	0.012
10.502	8.4234	41	0	0	2	10.502	8.4230	−0.001
11.437	7.7368	18	2	0	1	11.438	7.7362	−0.001
			−1	0	2	11.464	7.7185	−0.027
11.786	7.5085	6	1	0	2	11.792	7.5048	−0.006
14.720	6.0178	6	2	0	2	14.760	6.0014	−0.041
15.017	5.8995	8	3	0	0	14.976	5.9156	0.041
15.670	5.6551	3	−3	0	1	15.696	5.6458	−0.026
17.433	5.0869	5	2	1	0	17.432	5.0871	0.000
18.133	4.8921	10	−2	1	1	18.110	4.8981	0.022
20.250	4.3852	12	−2	1	2	20.204	4.3951	0.046
20.510	4.3302	12	−4	0	1	20.515	4.3292	−0.005
21.474	4.1379	9	−1	0	4	21.508	4.1314	−0.034
21.795	4.0777	3	−1	1	3	21.788	4.0790	0.006
24.620	3.6158	5	4	1	0	24.662	3.6098	−0.042
25.434	3.5019	10	4	1	1	25.385	3.5085	0.048
			−5	0	1	25.457	3.4988	−0.024
26.070	3.4179	14	4	0	3	26.043	3.4214	0.027
28.745	3.1056	2	0	2	0	28.757	3.1044	−0.012
30.070	2.9718	3	−3	0	5	30.043	2.9743	0.026
30.295	2.9502	4	5	0	3	30.272	2.9523	0.022
30.575	2.9237	2	−5	1	2	30.577	2.9236	−0.001
34.876	2.5724	2	−3	0	6	34.871	2.5728	0.005
			−6	1	2	34.914	2.5697	−0.038
35.059	2.5594	2	0	1	6	35.076	2.5582	−0.017

sodium nitrite $NaNO_2$ (3.1 g, 45 mmol) in 30 ml of water was added dropwise to maintain the reaction temperature as close to 0 °C as possible. Following the addition of sodium nitrite, the reaction mixture was stirred for 20 min and a solution of β-naphthol (6.06 g, 42 mmol) in 100 ml of sodium hydroxide solution (2.4 g, 60 mmol) was added dropwise to maintain the temperature between 0 and 5 °C. After this addition, the reaction mixture was stirred in an ice bath for about 3 h; then the thick suspension was filtered and washed with water and left to dry, yielding 13 g of crude product (86%). For further purification, 2 g of the obtained sodium salt was suspended in 100 ml of distilled water, heated to about 100 °C for 30 min, and then left overnight to cool and settle. The product was then filtered and washed with two 10-ml portions of water and finally with 10 ml of methanol. Following methanol washing, some floating yellow impurities were decanted off. The purified product was dried at approximately 100 °C to yield 1.8 g of pure product (90%). Anal. calcd for $C_{20}H_{13}N_2NaO_4S \times H_2O$: C, 57.41; H, 3.61; N, 6.70; S, 7.66%; found: C, 57.64; H, 3.77; N, 6.66; S, 6.11%.

2. Synthesis of barium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl] naphthalene-1-sulphonate trihydrate

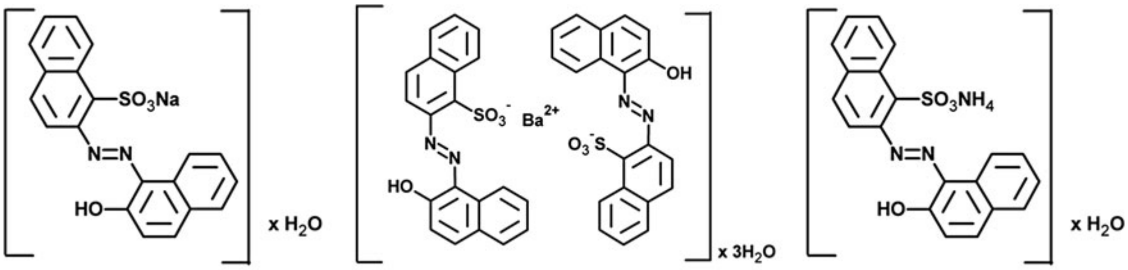
The sodium salt obtained in the previous step (500 mg, 1.25 mmol) was added to 75 ml of near-saturated solution of $BaCl_2 \times 2H_2O$ (18.39 g, 75.3 mmol) and heated to about

TABLE III. X-ray powder diffraction data for ammonium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate monohydrate.

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs}	h	k	l	θ_{cal} (°)	d_{calc} (Å)	$\Delta 2\theta$
5.080	17.3824	73	1	0	0	5.064	17.4349	0.015
10.123	8.7312	100	2	0	0	10.139	8.7175	−0.016
10.634	8.3127	41	0	0	2	10.626	8.3191	0.008
12.576	7.0331	14	1	0	2	12.573	7.0349	0.003
13.314	6.6449	1	−2	0	2	13.321	6.6411	−0.008
13.764	6.4286	11	0	1	0	13.765	6.4282	−0.001
14.746	6.0026	2	0	1	1	14.762	5.9962	−0.016
15.216	5.8183	5	3	0	0	15.233	5.8116	−0.018
15.935	5.5573	5	1	1	1	15.924	5.5610	0.011
			2	0	2	15.975	5.5433	−0.041
17.405	5.0911	12	−2	1	1	17.387	5.0962	0.017
			0	1	2	17.420	5.0866	−0.016
17.607	5.0332	6	−1	1	2	17.606	5.0333	0.000
18.510	4.7896	0	2	1	1	18.477	4.7980	0.032
18.670	4.7489	0	1	1	2	18.684	4.7454	−0.014
19.197	4.6197	4	−2	1	2	19.200	4.6189	−0.004
20.361	4.3582	4	4	0	0	20.358	4.3587	0.002
21.084	4.2103	34	−1	1	3	21.063	4.2145	0.021
21.912	4.0531	3	−3	1	2	21.908	4.0537	0.003
			−2	0	4	21.950	4.0460	−0.039
22.190	4.0029	8	−2	1	3	22.200	4.0010	−0.011
22.415	3.9632	7	1	1	3	22.422	3.9621	−0.007
22.818	3.8942	2	1	0	4	22.831	3.8919	−0.014
24.437	3.6397	3	−4	1	1	24.441	3.6390	−0.005
			3	1	2	24.465	3.6355	−0.029
24.670	3.6058	6	4	1	0	24.658	3.6076	0.012
			4	0	2	24.677	3.6048	−0.007
25.222	3.5282	14	−1	1	4	25.225	3.5278	−0.003
25.481	3.4929	37	0	1	4	25.486	3.4922	−0.005
25.962	3.4293	12	−2	1	4	26.001	3.4242	−0.039
26.776	3.3268	7	1	1	4	26.756	3.3292	0.019
27.720	3.2156	0	−3	1	4	27.733	3.2141	−0.014
			0	2	0	27.733	3.2141	−0.014
28.370	3.1433	2	4	1	2	28.363	3.1442	0.008
29.420	3.0336	3	−5	1	2	29.405	3.0351	0.015
30.270	2.9503	11	−4	1	4	30.271	2.9502	−0.001
31.479	2.8396	1	1	1	5	31.473	2.8402	0.006
			4	1	3	31.497	2.8381	−0.018
32.219	2.7761	2	0	0	6	32.256	2.7730	−0.037
33.747	2.6538	2	−6	1	2	33.782	2.6512	−0.035
34.450	2.6012	2	6	0	2	34.438	2.6022	0.013
			−3	2	3	34.454	2.6010	−0.003
			−4	2	1	34.490	2.5984	−0.039
35.124	2.5528	2	6	1	1	35.148	2.5512	−0.024
41.379	2.1802	2	8	0	0	41.397	2.1794	−0.018
46.099	1.9674	2	7	2	0	46.066	1.9687	0.033
			−9	0	2	46.133	1.9660	−0.034
46.994	1.9320	2	−6	1	7	46.986	1.9323	0.008

TABLE IV. X-ray crystal structure data for sodium, barium, and ammonium lithol reds.

Pigment	Na lithol red $C_{20}H_{13}N_2NaO_4S.H_2O$	Ba lithol red $C_{40}H_{26}N_4BaO_8S_2.3H_2O$	NH_4 lithol red $C_{20}H_{17}N_3O_4S.H_2O$
System	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2$_1$/*m*	*P*2/*c*
Z	8	2	4
$D_{calc.}$(g cm^{-3})	1.46	1.69	1.45
a (Å)	33.343(7)	17.758(9)	17.721(5)
b (Å)	6.667(2)	6.209(4)	6.428(3)
c (Å)	16.397(4)	16.857(8)	16.911(5)
β (°)	90.83	92.07	100.31(3)
V (Å^3)	3644.51	1857.39	1895.31
$M_{(20)}$	12.81	4.98	13.47
$F_{(30)}$	36.98	7.72	35.32



sodium (*E*)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate monohydrate

barium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate trihydrate

ammonium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl]naphthalene-1-sulphonate monohydrate

Figure 2. Structural diagram of the investigated lithol red salts.

100 °C for 2 h. At the outset, 5 ml of ethanol was added to increase the solubility and reduce the surface tension of the solution. The suspension was stirred for 3 days and then filtered and washed with two 10-ml portions of water and 10 ml of methanol. Some floating yellow impurities were decanted off during methanol washing. The product was left to dry in the funnel to yield 500 mg of product (90%). Anal. calcd for $C_{40}H_{26}BaN_4O_8S_2{\times}3H_2O$: C, 50.78; H, 3.41; N, 5.92; S, 6.78%; found: C, 50.01; H, 3.45; N, 5.75; S, 6.37%.

3. Synthesis of ammonium (E)-2-[(2-hydroxynaphthalen-1-yl)diazenyl] naphthalene-1-sulphonate monohydrate

Sodium salt (500 mg, 1.25 mmol) was added to 50 ml of ammonium chloride (4.03 g, 75.3 mmol) and heated to about 100 °C for 2 h. The suspension was stirred for 3 days and then filtered and washed with two 10-ml portions of water and 10 ml of methanol. Some yellow impurities floating in the methanol wash were decanted off. The product was dried at about 100 °C, yielding 450 mg of ammonium salt (91%). Anal. calcd for $C_{20}H_{17}N_3O_4S \times H_2O$: C, 58.10; H, 4.63; N, 10.16; S, 7.76%; found: C, 58.14; H, 4.55; N, 10.01; S, 8.06%.

B. Specimen preparation and powder diffraction data collection

X-ray powder diffraction measurements were performed at the Faculty of Chemistry Jagiellonian University, using an X'PERT PRO MPD apparatus, Cu$K\alpha$ radiation ($\lambda = 1.541\,78$ Å) at 40 kV and 30 mA, a diffracted-beam graphite monochromator, and a PIXcel PSD detector in a 2θ range from 5° to 90°, with an interpolated step size of 0.02° [2θ]. The divergence of the incident X-ray beam was 0.25. Prior to each measurement the samples were thoroughly ground and placed from the back side in a sample holder.

III. RESULTS AND DISCUSSION

Obtained powder diffraction data (see supplementary material) were elaborated, first with the use of diffractometer software and subsequently with the PROSZKI package (Łasocha and Lewinski, 1994). Experimental powder diffraction patterns are depicted in Figure 1.

The X-ray powder diffraction data obtained for the investigated compounds are shown in Tables I–III. The crystallographic characteristics and indexing figures of merit (de Wolff, 1968; Smith and Snyder, 1979) for all three compounds are collected in Table IV. Figure 2 presents the structural formulas of the investigated compounds.

The chemistry of lithol red salts turned out to be quite complex (Kennedy *et al.*, 2004). Apart from difficulties connected with their preparation using ion-exchange procedures, they are sensitive to the solvents in which the procedure is carried out and usually crystallise in forms containing molecules of solvents in their crystal structures (Stenger *et al.*, 2010). Obtaining pure monophase samples is a demanding task, which is why the results of crystallographic studies of lithol reds are so rarely reported in the literature.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715617000616.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Philippe Walter from the Laboratory of Molecular and Structural Archaeology, Université Pierre et Marie Curie in Paris, for a fruitful discussion concerning the stability of lithol red pigments, which was the starting point of our interest in the presented research. This study was partially supported by ICDD Grant-in-Aid No. 97-04, 2016/17.

Alphen, M. (**1998**). *Paint Film Components*, National Environmental Health Forum Monographs (National Environmental Health Forum, Australia), General Series No. 2, p. 137. http://www.cffet.net/ait/X1_paint.pdf

Ash, I. and Ash, M. (**1996**). *Handbook of Paint and Coating Raw Materials, Volume 1: Trade Name Products* (Gower, Aldershot), p. 402.

de Wolff, P. M. (**1968**). "A simplified criterion for the reliability of a powder pattern indexing", J. Appl. Crystallogr. **1**, 108–113.

Herbst, W. and Hunger, K. (**1997**). *Industrial Organic Pigments: Production, Properties, Applications* (Wiley-VCH, Weinheim), 2nd ed., p. 318.

ICDD (**2015**). PDF-4+ 2015 (Database) edited by Dr. Soorya Kabekkodu, International Centre for Diffraction Data, Newton Square, PA, USA.

Kennedy, A. R., Jennifer, B. A., Kirkhouse, J. B. A., McCarney, K. M., Puissegur, O., Smith, W. E., Staunton, E., Teat, S. J., Cherryman, J. C., and James, R. (**2004**). "Supramolecular motifs in s-block metal-bound sulfonated monoazo dyes, part 1: structural class controlled by cation type and modulated by sulfonate aryl ring position", Chem. Eur. J. **10**, 4606–4615.

Łasocha, W. and Lewinski, K. (**1994**). "PROSZKI – a system of programs for powder diffraction data analysis", J. Appl. Cryst. **27**, 437–438.

Smith, G. S. and Snyder, R. L. (**1979**). "F_n: a criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing", J. Appl. Crystallogr. **12**, 60–65.

Standeven, H. A. L. (**2008**). "The History and Manufacture of Lithol Red, a Pigment Used by Mark Rothko in his Seagram and Harvard Murals of the 1950s and 1960s", Tate Papers, 10, Autumn 2008, http://www.tate.org.uk/research/publications/tate-papers/10/history-and-manufacture-of-lithol-red-pigment-used-by-mark-rothko-in-seagram-and-harvard-murals-1950s-and-1960s (accessed 10 January 2017).

Stenger, J., Kwan, E. E., Eremin, K., Speakman, S., Kirby, D., Stewart, H., Huang, S. G., Kennedy, A. R., Newman, R., and Khandekar, N. (**2010**). "Lithol red salts: characterization and deterioration", e-PS **7**, 147–157.