ELSEVIER

Dyes and Pigments 45 (2000) 169–176

DYES and PIGMENTS

Visible spectra of crystalline anthraquinone colorants: the impact of crystal packing

A.V. Yatsenko [a,]*, V.V. Chernyshev [a], S.I. Popov [b], E.J. Sonneveld [c], H. Schenk [c]

[a]*Department of Chemistry, Moscow State University, 119899 Moscow, Russia*
[b]*Institute of Organic Intermediates and Dyes, 103787 Moscow, Russia*
[c]*Laboratory for Crystallography, Amsterdam University, 1018 WV Amsterdam, The Netherlands*

Received 16 December 1999; received in revised form 14 January 2000; accepted 9 February 2000

Abstract

The crystal structures of purpurin monohydrate and 1,4-dihydroxy-5,8-di-*p*-toluidinoanthraquinone were determined from single-crystal and powder X-ray diffraction data, respectively, and the visible reflection spectra of 18 crystalline colorants, (anthraquinones and related compounds) were obtained. Twelve of the compounds showed moderate (440–1090 cm^{-1}) bathochromic shifts of their absorption maxima, compared to the solutions; other compounds exhibited greater bathochromic (up to 2900 cm^{-1}) or hypsochromic (up to -1130 cm^{-1}) shifts. For some of the compounds, the differences in colour between crystals and solutions are ascribable to the changes in molecular conformations or to the impact of hydrogen bonds.

Keywords: Anthraquinone; Crystal structure; Reflectance spectroscopy

---

1. Introduction

In previous papers, we studied the relationship between molecular conformation and visible spectra of some amino derivatives of anthraquinone [1,2]. It was found that for some compounds (e.g., 1-methylphenylaminoanthraquinone), the molecular conformation in the solution phase differed from that in the crystal phase and these differences were accompanied by considerable shifts in absorption maxima. Recent examination of the orientational dependence of the colour of crystals of 1,4-di-*p*-toluidinoanthraquinone revealed the appearance of a new absorption band at 19 200 cm^{-1} which was attributed to intermolecular charge transfer, a phenomenon that was not observed in solution [3]. This finding provoked us to compare the visible spectra of solutions and crystals of several anthraquinone colorants and analogous compounds (Fig. 1) in relation to their crystal structures. In this study we also determined the crystal structures of purpurin monohydrate (**14**) from single-crystal experiments and 1,4-dihydroxy-5,8-di-*p*-toluidinoanthraquinone (**11**) from powder diffraction data.

According to current molecular crystal theory, each electronic transition of an isolated molecule in a crystal splits into *n* excitonic components (so-called Davydov splitting). The centre of the excitonic multiplet differs from the excitation energy

---

* Corresponding author. Fax: +7-95-939-0898.

E-mail address: yatsenko@biocryst.phys.msu.su (A.V. Yatsenko).

0143-7208/00/$ - see front matter
PII: S0143-7208(00)00021-8

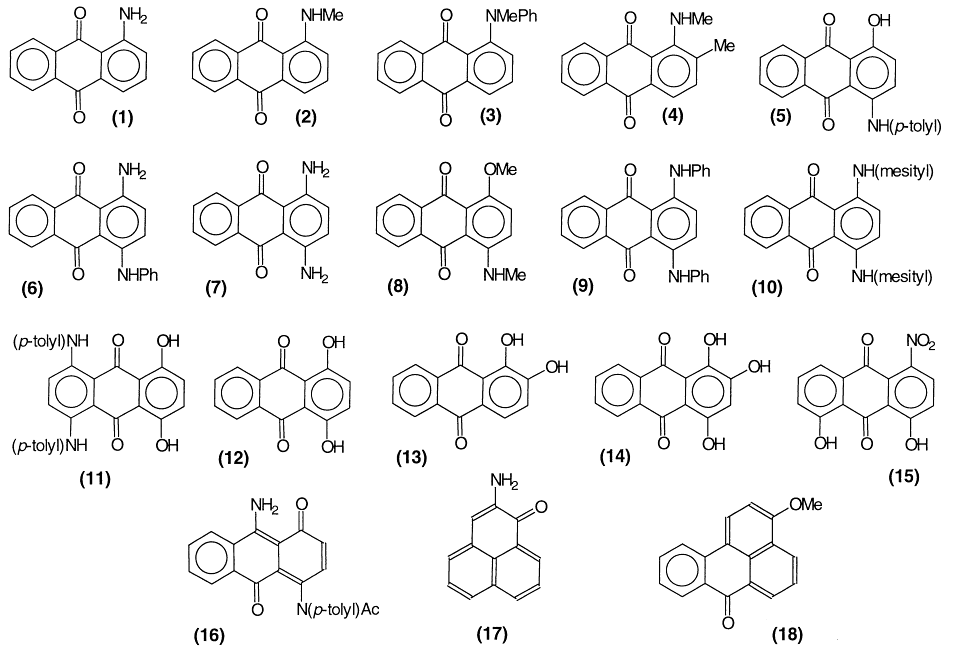

Fig. 1. Chemical diagrams and reference numbers of investigated compounds.

of the isolated molecule by the matrix shift, which, in principal, is in nature analogous to solvatochromism in solution (because in the solid state, intermolecular contacts are closer than in solutions, crystal packing acts like an extremely polar solvent). An additional shift in the absorption maximum occurs because the intensities of the bands of the excitonic multiplet differ [4]. The effects of intermolecular charge–transfer interactions as well as geometrical distortions of molecules in crystals are outside the scope of this approach, although these aspects have been used to explain the colour changes that occur in, for example, several phases of titanylphthalocyanine [5].

Exciton theory was used to show that an empirical correlation occurred between the position of the absorption maximum and the overlap of neighbouring molecules within the crystal stack for a series of perylene-bis(dicarboximide) pigments [6]. These results were interpreted in terms of the different levels of exciton theory [7,8]. The existence of two variously coloured polymorphs of 4-(β,β-dicyanovinyl)-3-methyl-*N*-methyl-*N*-benzylaniline also was qualitatively interpreted in terms of exciton theory using a point-dipole model [9]. However, for two polymorphs of pendimethalin, interpretation using the exciton theory was difficult and the inherent colour change was modelled on the ZINDO level, taking into account small changes in the conformation of the amino group [10]. In addition, for a pyrrolopyrrole pigment, calculations based on exciton theory failed to explain the observed wavelength shift whereas consideration of intermolecular hydrogen bonding allowed quantitative explanation to be achieved [11]. Of especial interest in terms of crystal packing, are the yellow and red forms of 2,3-bis(2-phenylethenyl)-5,6-dicyanopyrazine, which, although displaying essentially identical packing arrangements, differ in terms of the interplanar distance insofar as the orange form is 0.1 Å shorter than the yellow form [12]. Unfortunately, because of the complexity of exciton theory, only approximate models can be considered.

2. Experimental

Yellow, single crystals of purpurin monohydrate (**14**) were grown from solution in 95% ethanol by slow evaporation. X-ray measurements were carried out using an Enraf-Nonius CAD-4 diffractometer (Mo K_α radiation, ω-scan technique). Crystal data: $a = 9.077(2)$, $b = 20.872(5)$, $c = 6.796(2)$ Å, $\beta = 116.20(3)°$, $V = 1155.3$ Å^3, $Z = 4$, space group C2/c. The structure was solved using SHELXS 96 [13] and refined using SHELXL93 [14], R(F) = 0.076 for 750 reflections with $I > 2\sigma(I)$, and $R(F^2) = 0.191$ for all 1135 reflections with $\theta \leqslant 26°$. The crystal packing motif is presented in Fig. 2 from which it is evident that the molecule of (**14**) is situated on the two-fold axis and the O2 atom is disordered over two sets of sites. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (No. 136012).

All attempts to prepare suitable single crystals of (**11**) were unsuccessful. Cell parameters and intensities of reflections were determined from the Guinier Cu $K_{\alpha 1}$ data, $a = 26.128(7)$, $b = 18.181(6)$, $c = 4.613(1)$ Å, $V = 2191$ Å^3, $Z = 4$, space group $P2_12_12_1$. Details of the experimental technique and data reduction have been described previously [15,16]. A molecular model was built using the molecular structure of 1,4-dianilinoanthraquinone [17] and its position and orientation in the unit cell was determined using the grid search procedure [18]. Rietveld refinement was carried out using the MRIA program [19], bond lengths and angles were restrained, but torsion angles, which determine the orientation of tolyl groups with respect to anthraquinone tricycle, were free to refine. Final refinement gave $R_p = 0.048$ and $R_B = 0.132$ in the 2θ range 4.8–64.0°. The crystal packing motif is presented in Fig. 3 and details of the structure determination are available from the authors upon request.

Reflection spectra in the region 11 500–40 000 cm^{-1} were recorded on a Specord M-40 (Carl Zeiss, Jena) spectrophotometer. Crystalline colorants were ground and then mixed with barium sulphate. The data obtained for the absorption maxima of solid samples and *i*-propanol solutions are presented in Table 1.

3. Results and discussion

The molecules of (**14**) stack in columns, parallel to [001]. The normal to the molecular planes are inclined 4.4° to the stack axis. The adjacent molecules within the column are related through inversion centres, with interplanar distances of 3.38 and 3.40 Å. Each water molecule made a strong hydrogen bond to O2 (O4...O2 = 2.641(3) Å) as H-acceptor, and two weak hydrogen bonds to O1 (O4...O1 = 2.916(3) Å) as H-donor.

In structure **11**, the molecules are arranged in columns with an interplanar spacing of 3.32 Å by [001] translation and the normal to the plane of

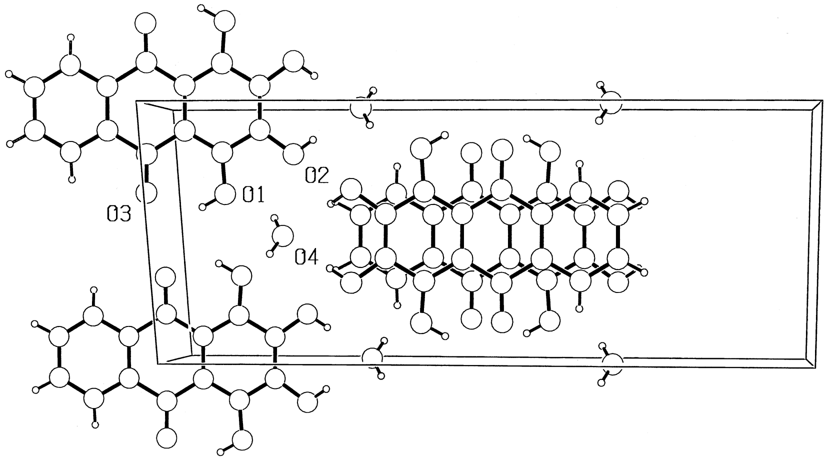

Fig. 2. Crystal packing diagram of purpurin monohydrate viewed down [001]. One hydroxy group [O(2)] is disordered over two sets of sites.

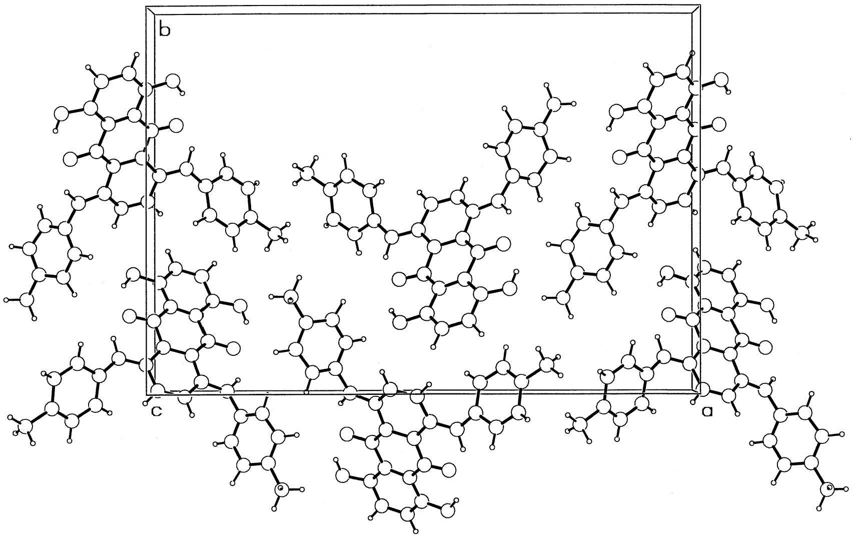

Fig. 3. Crystal packing diagram of 1,4-dihydroxy-5,8-di-*p*-toluidinoanthraquinone viewed down [001].

the anthraquinone tricycle is 44° offset with respect to the column axis. The tolyl groups make angles of 47 and 66° with the plane of the tricycle.

The visible spectra of several anthraquinone dyes in their solid state were studied by Rodionova et al. [20] employing a transmission technique (crystalline dyes were intensively milled with KBr, and then pressed into tablets). Our measurements on the same compounds revealed that for (**1**) and (**7**) the positions of absorption maxima compare well with those obtained by Rodionova et al [20] but, for compounds (**2**) and (**6**), they are shifted bathochromically by 800 and 1400 cm^{-1}, respectively. However, when the samples prepared by the evaporation of the solutions of colorants on the surface of pressed $BaSO_4$ tablets were used (i.e. the dyes were absorbed on the surface of $BaSO_4$ particles), the results closely matched the transmission data. It is proposed that the intensive disintegration necessary to obtain uniform transparent specimens caused disruption of the crystal structures.

Most of the compounds studied exhibited moderate bathochromic shifts of their absorption maxima (650 cm^{-1} on average), on going from the solution phase in polar solvent (*i*-propanol) to the solid state but there were some peculiar examples.

Firstly, there were several examples of greater bathochromic shifts. The origin of the 1700 cm^{-1} shift in the spectrum of (**3**) is the flattening of the whole molecule in the crystal as compared to solution [2]. Compound (**5**) shows the 2900 cm^{-1} shift of its second absorption band, whereas the shift of the long-wavelength band is only 1000 cm^{-1}. The former band has the same nature as the short-wavelength band in the spectra of 1,4-dianilinoanthraquinone and its derivatives, responsible for their green colour [1]. The behaviour of this band in other analogous compounds is quite different; compounds (**6**) and (**9**) exhibit the 1800 cm^{-1} red shift, whereas for (**10**) and (**11**) the shift is only 1000 and 300 cm^{-1}, respectively and, according to [3], for 1,4-di-*p*-toluidinoanthraquinone a blue shift is observed, although compounds (**3**), (**11**) and 1,4-di-*p*-toluidinoanthraquinone adopt the same packing motif (columns of molecules related by translation [21]).

Secondly, among hydroxyanthraquinones, only (**13**) and (**15**) show bathochromic shifts of 500 and 400 cm^{-1}, whilst compounds (**12**) and (**14**) exhibit hypsochromic shifts of 1100 and 100 cm^{-1}, respectively. Moreover, the absorption maximum of (**14**) monohydrate is displaced by 500 cm^{-1} to shorter wavelengths, as compared to that of the anhydrous (**14**). This fact can be rationalised if it is considered that molecule (**14**) forms hydrogen bonds through the hydroxy O1 atom, whereas the quinonoid oxygen atom is not involved in the

Table 1
Positions of absorption maxima (cm^{-1}) for the investigated compounds in the solid state and in the *i*-propanol solution

Compound	Solution	Solid state	Comments on packing motif[a]
1	20 640	20 040	t-stacks, $d = 3.25$ [28]
2	19 800	18 200	
3	18 840	17 120	a-stacks, $d > 3.54$ [2]
4	19 900	19 240	c-stacks, $d = 3.48$, 3.54 [2]
5	17 260, 17 720	16 500	t-stacks, $d = 3.50$ [21]
	27 800	24 920	
6	16 240, 17 400	15 380	dimers, $d = 3.37$ [29]
	26 640	24 840	
7	16 800, 18 040	17 760 (anhydrous)	
		15 960 (dihydrate)	t-stacks, $d = 3.37$ [24]
8	19 800	19 350	t-stacks[b]
9	15 700	14 680	dimers, $d = 3.42$ [17]
	16 760	16 000	
	24 920	23 160	
10	15 880	15 320	isolated molecules [1]
	17 100	16 600	
	26 240	25 240	
11	14 720	13 860	t-stacks, $d = 3.32$
	15 800	15 220	
	24 000	23 680	
12	20 750	21 880	c-stacks, $d = 3.38$,3.42 [30]
		20 830 (film) [13]	
13	23 000	22 520	t-stacks, $d = 3.42$–3.49 [31]
14	20 600	20 700 (anhydrous)	
		21 200 (monohydrate)	c-stacks, $d = 3.38$–3.40
15	23 200	22 760	dimers, $d > 3.32$ [32]
16	19 010	17 920	dimers, $d = 3.45$ [33]
17	20 680	19 640	t-stacks, $d = 3.48$ [34]
18	23 040	22 460	t-stacks, $d = 3.46$ [16]

[a] t-, c-, and a-stacks mean the stacks of molecules related by translation, inversion centre, and screw axis, respectively; d (Å) is the interplanar or shortest intermolecular distance within the stack or dimer.

[b] Crystal structure determination is not yet completed, but the presence of one short cell parameter (3.899 Å) gives an evidence that the molecules adopt stacking arrangement.

hydrogen-bond pattern. As electronic excitation of (**14**) is accompanied by charge transfer from the hydroxy groups to the carbonyls, participation of the hydroxy group in hydrogen bonds as H-acceptor destabilises the excited state of the molecule. The spectrum of the monohydrate sample dried at 150°C coincides closely with the spectrum of anhydrous (**14**). The absorption band of (**12**) consists of a number of vibrational sub-bands (in heptane solution, five individual maxima are well resolved [22]) and the observed shift of the main maximum is due to the redistribution of the intensities of sub-bands. The position of absorption maximum in the spectrum of a thin film of (**12**) essentially coincides with that in solution whereas the IR spectra indicate that the structure of this film and the crystal structure of (**12**) differ [23]. The blue shift observed for anhydrous (**7**) may be of the same nature because only one maximum is observed for solid samples instead of a well-resolved doublet in solutions.

Thirdly, compound **18** exhibits significant changes in the shape of its absorption band; a broadening in the solid state is observed and an additional maximum appears (Fig. 4b). These changes may arise from the fact that in crystals the methoxy group is closely coplanar to the benzanthrone system [16] whereas in solution, local deviations from planarity can take place, although the minimum-energy conformation is planar. The distinctions between

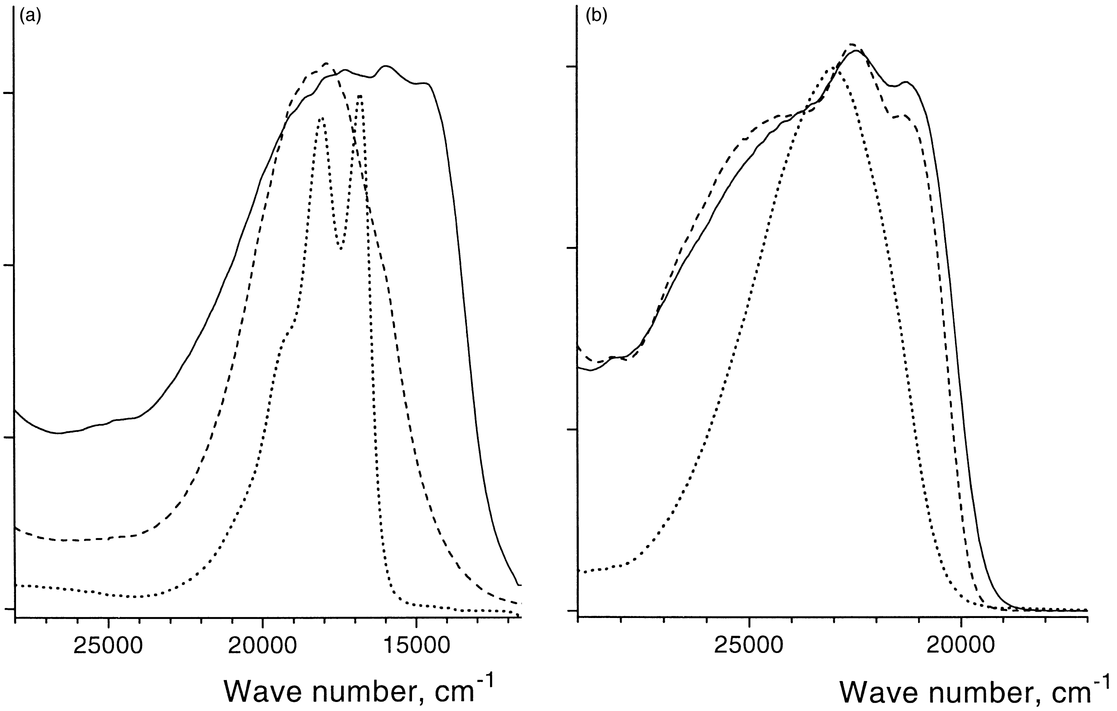

Fig. 4. Spectra of 1,4-diaminoanthraquinone (**7**) (a) and 3-methoxybenzanthrone (**18**) (b). Solid lines: ground crystalline specimens, dotted lines: *i*-propanol solutions, dashed lines: ground crystalline dihydrate of (**7**) (a) and the specimen evaporated on the $BaSO_4$ tablet (b). For the reflection spectra Kubelka–Munk function [27] is presented.

the spectra of anhydrous crystalline (**7**) and that of the crystalline dihydrate of (**7**) are demonstrated in Fig. 4a. In this structure, each water molecule as an H-donor forms hydrogen bonds with the oxygen atom of the carbonyl group and, as an H-acceptor, to the amino group [24]. In contrast to the monohydrate of (**14**), such a hydrogen-bond pattern stabilises the excited state of the molecule and so a red shift should be expected on going from solution to solid (**7**) dihydrate. However, after heating for 1 h at 150°C the sample loses crystallisation water, and its absorption spectrum becomes very similar to that of crystalline anhydrous (**7**).

In contrast to 1,4-di-*p*-toluidinoanthraquinone [3], the spectrum of solid (**11**) does not provide evidence of intermolecular charge transfer, although an inflection point at 19 500 cm^{-1} is observed. The stacking adopted by these compounds differs; in the former structure, the nitrogen atoms of one molecule overlap the oxygen atoms of the neighbouring molecule (i.e. only longitudal displacement of ca. 2.5 Å occurs), whilst in the latter structure both longitudal and transverse displacements of 2.6 and 1.4 Å, respectively, are present. Nonetheless, it was not possible to reproduce on the INDO/S level the appearance of an intermolecular charge-transfer band within the stack. It is noteworthy that only in the reflection spectra of 1,4-diarylamino-anthraquinones [(**9**), (**10**), (**11**)] were the absorption bands a well-resolved vibrational structure with two maxima and two inflection points.

The approach based on the combination of the matrix shift and the exciton theory does not provide a unified explanation of all the observed spectral phenomena. The relatively large red shifts observed for the crystals of dyes, which demonstrate only minor solvatochromism in solution, e.g. (**3**), (**6**), and (**9**), cannot be attributed to the matrix shift. Davydov splitting does not explain the shifts of relatively weak absorption bands [as the long-wavelength band of (**3**) and the second bands of (**5**), (**6**), and (**9**)], because the associated transition moments are small and so their interaction is to be relatively weak.

On the simplest level of the exciton theory, we can consider a one-dimensional stack of molecules instead of the whole crystal, because the distances between the centres of neighbouring molecules within the stack are much shorter than the inter-stacking ones. If the molecules in the stack are related by translation, as in eight structures shown in Table 1, the shift depends on the angle subtended by the translation and the transition dipole moment. Angles smaller than 55° should yield a red shift of the absorption band; larger angles cause a blue shift [25]. Transition moments were calculated on the INDO/S level using the GRINDOL program [26]. Among the structures considered, the observed red shift could be explained in this manner only for the long-wavelength bands of (**7**) and (**11**) (angles of 44 and 50°, respectively); for other compounds this model predicts the blue shift.

4. Conclusions

Anthraquinone colorants exhibit a tendency for aggregation (stacking or dimerisation) in the solid state, but no simple relation was found between crystal packing and the colour of the crystals. The most striking differences in colour between the solid state and solution state can be interpreted in terms of intermolecular hydrogen bonds or conformational changes but not through exciton theory. The further progress in understanding the origin of crystallochromy requires simultaneous spectral and structural studies of organic colorants.

Acknowledgements

This work was supported by The Netherlands Organisation for Fundamental Research (NWO).

References

[1] Yatsenko AV, Tafeenko VA, Zakharov VN, Popov SI, Schenk H. An INDO/S study of the second ππ* transition in the spectra of 1,4-diaminoanthraquinones responsible for their green hue. Dyes and Pigments 1998;37(3):273–82.

[2] Yatsenko AV, Paseshnichenko KA, Popov SI. Structural studies of two hindered aminoanthraquinones. Z. Kristallogr, in press.

[3] Saito T, Liu C, Lynch VM, Bard AJ. Orientational dependence of the color and photoconductivity of 1,4-di-*p*-toluidinoanthraquinone single crystals. Chem Mater 1997;9(6):1318–27.

[4] Broude VL, Rashba EI, Sheka EF. Spectroscopy of molecular excitons. Berlin: Springer-Verlag, 1985.

[5] Mizuguchi J, Rihs G, Karfunkel HR. Solid-state spectra of titanylphthalocyanine as viewed from molecular distortion. J Phys Chem 1995;99(44):16217–27.

[6] Klebe G, Graser F, Hädicke E, Berndt J. Crystallochromiy as a solid-state effect: correlation of molecular conformation, crystal packing and colour in perylene-3,4:9,10-bis(dicarboximide) pigments. Acta Cryst 1989;B45(1):69–77.

[7] Kazmaier PM, Hoffmann R. A theortical study of crystallochromy. Quantum interference effects in the spectra of perylene pigments. J Am Chem Soc 1994;116(21):9684–91.

[8] Johnson E, Aroca R. Molecular orientation and stacking of perylenetetracarboxylic diimide derivatives in Langmuir–Blodgett monolayers. Appl Spectrosc 1995;49(4):472–7.

[9] Abe J, Shirai Y, Sakai K, Tsubomura T. Ab initio MO and X-ray studies of excited states in molecular crystals of 4-(β,β-dicyanovinyl)-3-methyl-*N*-methyl-*N*-benzylaniline. J Phys Chem 1995;99(20):8108–20.

[10] Stockton GW, Godfrey R, Hitchcock P, Mendelsohn R, Mowery PC, Rajan S, Walker AF. Crystal polymorphism in pendimethalin herbicide is driven by electronic delocalisation and changes in itramolecular hydrogen bonding. A crystallographic, spectroscopic and computational study. J Chem Soc, Perkin Trans 1998;2(9):2061–71.

[11] Adachi M, Nakamura S. Absorption spectrum shift in the solid state, a MO study of pyrrolopyrrole pigment. J Phys Chem 1994;98(7):1796–801.

[12] Kim JH, Matsuoka M, Fukunishi K. Selective topochemical photoreaction of crystallized 2,3-bis(2-phenylethenyl)-4,5-dicyanopyrzines. Chem Lett 1999;2:143–4.

[13] Sheldrick GM. SHELXS96. Program for the solution of crystal structures. Germany: University of Göttingen, 1996.

[14] Sheldrick GM. SHELXL93. Program for the solution of crystal structures. Germany: University of Göttingen, 1993.

[15] Goubitz K, Sonneveld EJ, Chernyshev VV, Yatsenko AV, Zhukov SG, Reiss CA, Schenk H. Crystal structure determination of a series of benzene derivatives from powder data. Z Kristallogr 1999;214(3):469–74.

[16] Yatsenko AV, Chernyshev VV, Zhukov SG, Sonneveld EJ, Schenk H. Crystal structure of 3-methoxybenzanthrone from X-ray powder diffraction. Powder Diffraction 1999;14(2):133–5.

[17] Yatsenko AV, Tafeenko VA, Zhukov SG, Medvedev SV, Popov SI. Crystal structure of 1,4-bis(phenylamino)-anthracene-9,10-dione, $C_{26}H_{18}N_2O_2$. Z Kristallogr 1995; 210(2):969–70.

[18] Chernyshev VV, Schenk H. A grid search procedure of positioning a known molecule in an unknown crystal structure with the use of powder diffraction data. Z Kristallogr 1998;213(1):1–3.

[19] Zlokazov VB, Chernyshev VV. MRIA — a program for the full profile analysis of powder multiphase neutron-diffraction time-of-flight (direct and Fourier) spectra. J Appl Crystallogr 1992;25(4):447–51.

[20] Rodionova GN, Krutovskaya IV, Rodionov AN, Tuchin YuG, Karpov VV. Electronic spectra and structure of some amino derivatives of anthraquinone in different states of matter. Zh Prikl Spektrosk 1980;32(4):623–8.

[21] Yatsenko AV, Zhukov SG, Medvedev SV, Stalnaya TV. Phase transition and expected non-linear polarizability in 1-hydroxy-4-(4-methylphenylamino)-9,10-anthracenedione. Acta Cryst 1996;C52(7):1853–6.

[22] Gillispie GD, Van Benthem MH, Balakrishnan N. Electronic energy shifts in α,α'-substituted anthraquinones. J Phys Chem 1989;93(1):55–8.

[23] Bernede JC. Is a hydrogen bond responsible for the optical properties of some dihydroxyanthraquinones. Quinizarin and anthraflavic? J Phys Chem Solids 1995;56(9):1239–51.

[24] Kahino S, Senoo K, Haisa M. Structure of 1,4-diaminoanthraquinone dihydrate. Acta Cryst 1988;C44 (6):1044–6.

[25] Czikkely V, Forsterling HD, Kuhn H. Extended dipole model for aggregates of dye molecules. Chem Phys Lett 1970;6(3):207–10.

[26] Lipinski J. Modified all-valence INDO/spd method for ground and excited state properties of isolated molecules and molecular complexes. Int J Quantum Chem 1988;34(5):423–35.

[27] Wendlandt WW, Hecht HG. Reflectance spectroscopy. New York: Interscience Publishers, 1966.

[28] Yatsenko AV, Chernyshev VV, Aslanov LA, Schenk H. 1-Aminoanthraquinone: crystal data and a model of molecular packing. Powder Diffraction 1998;13(2):85–8.

[29] Kurucsev T, Snow MR, Tiekink ERT. 1-Amino-4-phenylamino-9,10-anthracenedione. Acta Crystallogr 1987; C43(11):2226–8.

[30] Nigam GD, Deppisch B. Redetermination of the structure of 1,4-dihydroxyanthraquinone. Z Kristallogr 1980;151(3-4):185–91.

[31] Guilhem J. Determination by X-ray diffraction of the crystal structure of dihydroxyanthraquinones. II. Crystal structure of alizarin. Bull Soc Chim Fr 1967;5:1666–75.

[32] Yatsenko AV, Paseshnichenko KA, Popov SI. 4,5-Dihydroxy-1-nitroanthracene-9,10-dione. Acta Cryst 1996;C52 (12):3258–60.

[33] Yatsenko AV, Tafeenko VA, Zhukov SG, Medvedev SV, Popov SI. Structures and tautomeric interconversions of anthraquinone imine derivatives. Struct Chem 1997;8 (3):197–204.

[34] Yatsenko AV, Chernyshev VV, Schenk H. 2-Aminophenalenone: crystal data and molecular packing. Powder Diffraction 1999;14(1):42–4.