Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m*/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Williams, D. E. (1984). *PCK83*. A crystal and molecular packing analysis program. Univ. of Louisville, USA. QCPE Program No. 481, Department of Chemistry, Indiana Univ., Indiana, USA.
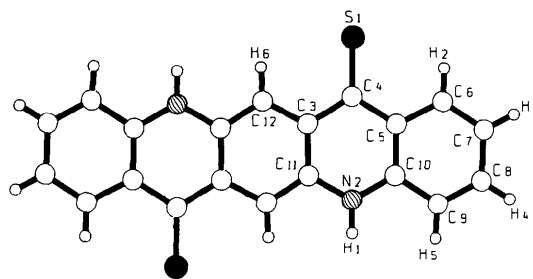
Fig. 1. Chemical structure of DTQ showing the numbering of the non-H atoms used in Tables 1 and 2.

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Structure of 5,7,12,14-Tetrahydroquinolino-[2,3-*b*]acridine-7,14-dithione

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Abstract

The molecule of the title compound, commonly called dithioquinacridone, belongs to point group $\bar{1}$ (C_i) and is planar. The maximal deviation from the best plane through the molecule is less than 0.04 (1) Å. In the crystal alternating molecules lie in the same plane and are stacked along the *b* axis at an inclination angle of 42.4 (2)°, in such a way that the molecular planes in the different columns are nearly perpendicular. The two sorts of stacking columns bond together, along a direction perpendicular to the stacking axis, through intermolecular hydrogen bonding between the NH group and the S atom. One molecule is hydrogen-bonded to four neighbouring molecules lying in the other columns.

Comment

5,7,12,14-Tetrahydroquinolino[2,3-*b*]acridine-7,14-dithione, commonly called dithioquinacridone (DTQ shown in Fig. 1), is a thionated derivative of linear *trans*-unsubstituted quinacridone (QA) which is known as a pigment of outstanding light, heat and chemical fastness. Several colours of QA pigments are available, depending on the polymorphic forms, although their detailed structures have not yet been

clarified (Koyama, Scheel & Laves, 1966; Ohmasa & Süsse, 1976; Lincke, 1980).

DTQ has recently attracted attention because of its near-IR absorption which is applicable to GaAs-diode laser printers (Rochat, Jaffe & Mizuguchi, 1988) and to information storage systems (Mizuguchi & Rochat, 1990). The near-IR absorption is, however, only available when the evaporated film of DTQ is exposed to the vapours of certain organic solvents. This vapour treatment brings about a rearrangement of molecules (phase transition) to give an intense near-IR absorption. The present structure determination has been undertaken in order to gain more insight into the correlation between crystal structures and optical properties.

DTQ was prepared from commercially available unsubstituted quinacridone by using a Lawesson's reagent as the thionation agent (Rochat, Jaffe & Mizuguchi, 1988). The single crystal was grown from the vapour phase using an apparatus which has been described previously (Mizuguchi, 1981). DTQ was sublimated at about 633 K, and the argon flow rate was controlled to 13 mm^3 s^{-1} using a mass flow meter (F-100/200, Bronkhorst BV).

The atomic positional and equivalent isotropic displacement parameters are listed in Table 1. Table 2 details the interatomic distances and bond angles together with their e.s.d.'s. The molecule is entirely planar with the exception of the S atoms which lie slightly out of plane by 0.04 (1) Å. It should be noted that the bonds C3—C4 and C4—C5 are significantly longer than aromatic C—C bonds, whereas the bonds C11—N2 and N2—C10 are shorter. Furthermore, the bonds C6—C7, C7—C8 and C8—C9 at the corner of the phenyl ring are slightly shorter than the bonds C5—C6, C5—C10 and C9—C10.

Fig. 2 shows the stereodiagram of the crystal structure of DTQ. Alternating molecules lie in the same plane and are stacked along the *b* axis at an inclination angle of 42.4 (2)°, in such a way that the molecular planes in the different columns are nearly perpendicular. The two sorts of stacking columns bond together, along a direction perpendicular to the stacking axis, through intermolecular bonding

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S1	0.2882 (1)	0.1233 (2)	0.63948 (6)	0.069 (1)
N2	0.3631 (2)	0.1551 (5)	0.3592 (2)	0.040 (1)
C3	0.4095 (3)	0.3226 (5)	0.5191 (2)	0.034 (1)
C4	0.3155 (3)	0.1382 (6)	0.5366 (2)	0.040 (1)
C5	0.2457 (3)	−0.0305 (6)	0.4574 (2)	0.039 (1)
C6	0.1504 (3)	−0.2165 (8)	0.4636 (3)	0.055 (1)
C7	0.0892 (3)	−0.3776 (7)	0.3886 (3)	0.058 (1)
C8	0.1195 (3)	−0.3637 (7)	0.3044 (3)	0.053 (1)
C9	0.2089 (3)	−0.1870 (6)	0.2943 (3)	0.047 (1)
C10	0.2730 (3)	−0.0189 (6)	0.3710 (2)	0.039 (1)
C11	0.4307 (3)	0.3260 (6)	0.4296 (2)	0.036 (1)
C12	0.4810 (3)	0.4980 (7)	0.5888 (2)	0.039 (1)

Table 2. *Geometric parameters* (Å, °)

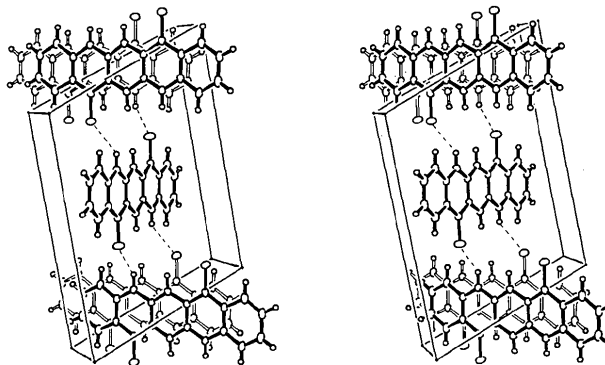| S1—C4	1.643 (4)	C5—C6	1.417 (5)
N2—C10	1.362 (4)	C5—C10	1.404 (5)
N2—C11	1.371 (4)	C6—C7	1.367 (5)
C3—C4	1.460 (4)	C7—C8	1.389 (6)
C3—C11	1.416 (5)	C8—C9	1.357 (5)
C3—C12	1.392 (4)	C9—C10	1.410 (4)
C4—C5	1.451 (4)	C11—C12*	1.392 (5)
C10—N2—C11	122.6 (3)	C6—C7—C8	120.7 (3)
C4—C3—C11	120.2 (2)	C7—C8—C9	120.7 (3)
C4—C3—C12	121.8 (3)	C8—C9—C10	119.4 (4)
C11—C3—C12	118.0 (3)	N2—C10—C5	120.6 (3)
S1—C4—C3	122.3 (2)	N2—C10—C9	118.2 (3)
S1—C4—C5	121.5 (3)	C5—C10—C9	121.2 (3)
C3—C4—C5	116.2 (3)	N2—C11—C3	119.9 (3)
C4—C5—C6	122.4 (3)	N2—C11—C12*	119.1 (3)
C4—C5—C10	120.5 (3)	C3—C11—C12*	121.0 (3)
C6—C5—C10	117.0 (3)	C3—C12—C11*	120.9 (3)
C5—C6—C7	121.0 (4)		

Symmetry code: (*) $1 - x, 1 - y, 1 - z$.

Fig. 2. Stereoview of the crystal structure of DTQ. Intermolecular hydrogen bonds between the NH group and the S atom are represented by dotted lines. One DTQ molecule is hydrogen bonded to four neighbouring molecules.

Experimental

Crystal data

$C_{20}H_{12}N_2S_2$	$\theta = 12\text{-}18°$
$M_r = 344.45$	$V = 763.9\ (4)$ Å³
Monoclinic	$Z = 2$
$P2_1/c$	$D_x = 1.470$ Mg m⁻³
$a = 10.657\ (1)$ Å	$D_m = 1.497$ Mg m⁻³
$b = 5.120\ (1)$ Å	Cu $K\alpha$
$c = 14.813\ (2)$ Å	$\lambda = 1.5418$ Å
$\beta = 109.06\ (1)°$	$\mu = 3.11$ mm⁻¹
Cell parameters from 25 reflections	$T = 293$ K
	$0.20 \times 0.14 \times 0.06$ mm
	Black

Data collection

Nonius CAD-4 diffractometer	$R_{int} = 0$
	$\theta_{max} = 75°$
Absorption correction: none	$h = -13 \rightarrow 13$
	$k = 0 \rightarrow 6$
1827 measured reflections	$l = 0 \rightarrow 18$
1539 independent reflections	3 standard reflections
1285 observed reflections	frequency: 120 min
$[I > 3\sigma(I)]$	intensity variation: 0.4%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.08$
Final $R = 0.056$	$\Delta\rho_{max} = 0.362$ e Å⁻³
$wR = 0.066$	$\Delta\rho_{min} = -0.371$ e Å⁻³
$S = 1.48$	
1285 reflections	Atomic scattering factors
133 parameters	from *International Tables*
All H-atom parameters refined	*for X-ray Crystallography* (1974, Vol. IV, Table
$w = 1/\sigma^2(F_o)$	2.2B)

between the NH group and the S atom. One DTQ molecule is hydrogen bonded to four neighbouring molecules lying in the other columns.

The intermolecular hydrogen bonds based on NH···S are as follows: N2—H···S1 = 140 (3)°, S1···H1 = 2.53 (5), N2—H1 = 0.93 (5) and N2···S1 = 3.290 94) Å. The hydrogen-bond-forming power is known to decrease greatly as the atoms deviate from linearity (about 0.42 kJ mol⁻¹ per 6°) (Pauling, 1960). Thus, an angle of 140 (3)° is not favourable for strong hydrogen bonding. On the other hand, the N2···S1 distance of 3.290 (4) Å is shorter and, therefore, more favourable for hydrogen bonding than thionated pyrrolopyrrole pigments of similar type [3.435 (3), 3.440 (5) and 3.359 (5) Å in modifications (I), (II) and (III), respectively, determined by Mizuguchi, Rochat & Rihs, (1990) and Mizuguchi, Arita & Rihs, (1991)].

Our reflection spectra measurements of DTQ single crystals revealed that a prominent peak appears at 13815 cm⁻¹ (*ca* 724 nm), accompanied by two weak bands at 16704 and 15333 cm⁻¹ (*ca* 597 and 652 nm, respectively), and a broad band at 21741 cm⁻¹ (*ca* 460 nm). No near-IR absorption is found with the present crystal modification.

The density of the single crystal was measured by flotation in a mixture of chloroform and dichloromethane. Program used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Refinement was made by full-matrix least-squares methods.

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References

Koyama, H., Scheel, H.-J. & Laves, F. (1966). *Naturwissenschaften*, **53**, 700.

Lincke, G. (1980). *Farbe Lack*, **85**, 966–972.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Mizuguchi, J. (1981). *Krist. Tech.* **16**, 695–700.

Mizuguchi, J., Arita, M. & Rihs, G. (1991). *Acta Cryst.* C47, 1952–1956.

Mizuguchi, J. & Rochat, A. C. (1990). European Patent Application No. 0401791.

Mizuguchi, J., Rochat, A. C. & Rihs, G. (1990). *Acta Cryst.* C46, 1899–1903.

Ohmasa, M. & Süsse, P. (1976). *Naturwissenschaften*, **63**, 387–388.

Pauling, L. (1960). *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, ch. 12. Cornell Univ. Press.

Rochat, A. C., Jaffe, E. E. & Mizuguchi, J. (1988). US Patent No. 4760004.

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Structure of Sodium Hydrogen Succinate at 123 K

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Abstract

The hydrogen succinate anion has $\bar{1}$ site symmetry and the residues are linked into infinite chains by very short crystallographically symmetric hydrogen bonds with an O···O separation of 2.4277(5) Å. The acidic H atom was best modelled by two equally populated sites on either side of the inversion centre.

Comment

Acid salts (MHY) of dibasic carboxylic acids (H_2Y) have been the subject of numerous structural and physical investigations (Speakman, 1972; Hadzi, 1965). The salts classified as type A_2 are particularly interesting in view of their very short crystallographically symmetric hydrogen bonds which link carboxyl groups of different anions.

A recent structural study of some alkylammonium salts of the hydrogen succinate anion has suggested that the H atom in the short hydrogen bond is best described by two equally populated sites on either side of the centre of the bond, *i.e.* a double-minimum potential function rather than a single-minimum potential function with the H atom located on the site of $\bar{1}$ symmetry (Kalsbeek & Larson, 1991; Kalsbeek, 1991). This conclusion was reached following consideration of the more reasonable H-atom thermal parameters given by the double-potential-minimum model.

Structure analysis of the title compound (which was shown by IR spectroscopy to be a type A_2 salt) was undertaken to check its suitability for a high-resolution charge-density investigation of the symmetric hydrogen-bond environment.

A view of the hydrogen succinate anion with atom labelling is shown in Fig. 1. This anion has $\bar{1}$ symmetry and the sodium cation occupies a site of symmetry 2, as in many other acid salts where the molecular symmetry is dictated by crystallographic symmetry. The bond lengths and angles of the hydrogen succinate residue are in very good agreement with those recently reported for the alkylammonium salts (Kalsbeek & Larson, 1991; Kalsbeek, 1991), and also for the lithium, potassium and caesium salts (Küppers, 1982; McAdam, Currie & Speakman, 1971; McAdam & Speakman, 1971) with which the sodium salt is not isomorphous. Unlike the majority of the succinate salts, the anion deviates markedly from planarity (see Table 2) with C(2^i) displaced 1.28 Å from the mean plane defined by O(1), O(2), C(1) and C(2). The C(2^i)—C(2)—C(1)—O(1) and C(2^i)—C(2)—C(1)—O(2) torsion angles are $-116.3(1)$ and $62.4(1)°$ respectively.

The position of the acidic hydrogen, H(3), was initially fixed at the site of $\bar{1}$ symmetry (1/4, 1/4, 0). Refinement of U_{iso} for this position gave a value of 0.062 (1) Å². This was considered unreasonable when compared with the
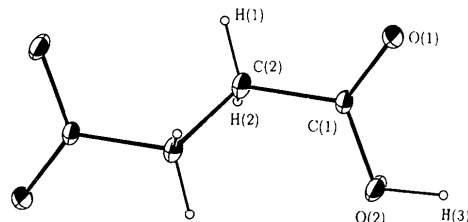

Fig. 1. The molecular structure of the anion showing the atom-labeling scheme. Thermal ellipsoids are shown at the 50% probability level except for the H atoms which are depicted as spheres of arbitrary size.