Colour Polymorphism of a Bis(quinoxaline) Compound

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Synthesis of 2(1*H*)-quinoxalinone *O*-(2′-quinoxalinyl)oxime (**3**) results in two easily distinguishable crystal forms with different colours, providing a rare example of colour polymorphism. The crystal structures of the two forms have been determined and compared. Intermolecular interactions and light-absorption characteristics of the polymorphs have been analysed by a mixed quantum chemical/molecular mechanical method. In one of the polymorphic forms the crystal field stabilises relatively high energy conformations by enhanced electrostatic interactions. The difference in the light absorption is found to be caused partly by a conformational difference of the molecules. The crystal field increases the difference in the absorption wavelengths and shift them towards higher values.

Introduction

Polymorphism of drug substances is a matter of increasing concern in the pharmaceutical industry.[1][2] Predictions of crystal structures and of the polymorphic behaviour of materials are still in their infancy.[3] Therefore, it is important to find and describe simple model systems that exhibit this kind of behaviour. It is also of interest to try to account for the observed differences in properties, as far as possible, on the basis of structural findings. A rare example of polymorphism among organic substances is when the different polymorphs have different colours.[4−8] Such a system provides an opportunity to determine the crystal structures of the different forms, to calculate or to predict some of their properties, and to interpret other experimental findings (e.g. stability) on structural grounds.

One of the earliest reports of colour polymorphism was that of Byrn et al.[4] They described colourless and yellow forms of a terephthalic acid derivative. It was suggested that the different colours of the polymorphic forms, which persisted in solution, could be explained in terms of differential electron delocalization due to different intramolecular hydrogen-bonding arrangements.

Fletton et al.[5] have described an intermolecular hydrogen-bonding system in one (colourless) polymorphic form of a nitroacetanilide derivative, and an intramolecular arrangement in a second (yellow) form. They attributed the yellow colour of the latter to the intramolecular hydrogen bonding, which allowed a planar geometry and consequently more extensive π-electron delocalization in the molecule. On the contrary, the intermolecular hydrogen-bonding system in the colourless form resulted in a nonplanar conformation, which could not be excited by visible light.

Stephenson et al.[6] have reported an example of conformational polymorphism where the structures of three crystal forms displayed different colours. An attempt was made to correlate these findings with the significantly different interplanar angles of the nitroaniline and substituted thiophene rings.

Finally, Bernstein et al.[7][8] have published a series of benzylidene−aniline structures that share some characteristics with the structures we wish to discuss in the present paper. Both sets of compounds have two aromatic systems connected by a two-atom bridge. However, in the structures of Bernstein et al., rotation about the central bond (−CH=N−) of the bridge is not possible, although the terminal torsion angles are relatively free to move around. Two members of the set provide an example of polymorphism. In one of the crystal forms, a totally flat molecule can be found,[7] while in another[8] the aniline and benzylidene rings form an angle of 24.8° with the plane formed by the two bridge atoms and the two other nonhydrogen atoms directly connected to them. The crystals of the first form are described as pale-yellow, while those of the latter are said to be yellow.

In this paper, we describe a pair of polymorphs with different colours and attempt to interpret the structural and colour differences on a theoretical basis.

Results and Discussion

In the course of screening compounds as *N*-methyl-D-aspartate (NMDA) receptor inhibitors, we have found quinoxaline derivatives that constitute a pair of polymorphs displaying different colours. Quinoxaline chemistry has been the subject of intense interest, since some of these com-

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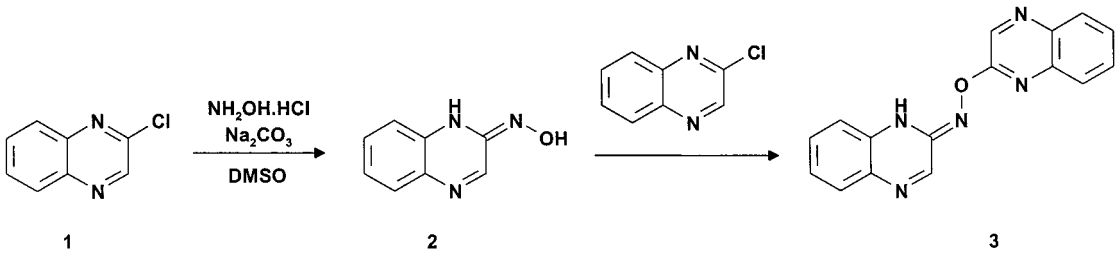

Scheme 1. Synthesis of **3**

pounds exhibit remarkable biological activity.[9] Although a large number of quinoxalines have been reported in the literature, relatively few crystal structures have been determined.

Table 1. Crystal data and structure refinement for **3**

Identification code	Form **A**	Form **B**
Empirical formula	$C_{16}H_{11}N_5O$	$C_{16}H_{11}N_5O$
Formula weight	289.30	289.30
Temperature [K]	293(2)	293(2)
Wavelength [A]	1.54178	1.54178
Crystal system	monoclinic	monoclinic
Space group	*P*21/*n*	*P*21/*n*
a [Å]	11.988(2)	8.665(5)
b [Å]	11.178(6)	14.780(15)
c [Å]	20.708(2)	11.392(3)
β [°]	92.380(8)	110.75(3)
Volume [Å]	2773(2)	1364(2)
Z	8	4
Density (calculated)	1.386 g/cm^3	1.408 g/cm^3
Absorption coefficient	0.754 mm^{-1}	0.767 mm^{-1}
F(000)	1200	600
Crystal size [mm]	0.4 × 0.1 × 0.1	0.4 × 0.2 × 0.2
θ range for data collection	4.19−75.13°	5.12−75.08°
Index ranges	$0 \le h \le 13$	$-9 \le h \le 10$
	$0 \le k \le 13$	$-17 \le k \le 18$
	$-25 \le l \le 25$	$-13 \le l \le 14$
Reflections collected	4928	2810
Independent reflections	4672	2642
R_{int}	0.0648	0.0583
Absorption correction	ψ scans	none
Max. and min. transmission	1.000 and 0.937	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4672/0/399	2642/0/200
Goodness-of-fit on F^2	1.008	0.981
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0500$	$R1 = 0.0545$
	$wR2 = 0.1178$	$wR2 = 0.1302$
R indices (all data)	$R1 = 0.2324$	$R1 = 0.1505$
	$wR2 = 0.1842$	$wR2 = 0.1830$
Extinction coefficient	0.00058(11)	none
Largest difference peak	0.250	0.240
Largest difference hole	−0.214 eA^{-3}	−0.250 eA^{-3}

Here, we present the crystal structures of two polymorphic forms of **3** (Scheme 1). Form **A** (Table 1) is light-yellow, while form **B** is orange. This is evidenced by the superimposed UV/Vis spectra of the two polymorphic forms (Figure 1). Both, a shift towards the longer wavelength as well as increased absorption intensity in the form **B** is evident from the spectra.[10] Figure 1 also shows the spectrum of the solution which is identical for the solution prepared from the two polymorphic forms, as expected. The peak belonging to the visible region of the spectrum of the solution shifted towards the UV region by about 15 nm and 25 nm as compared to the yellow and orange forms, respectively. We also detected that crystals of form **A** are needle-shaped, whereas those of form **B** are plates. While crystals of form **B** contain a totally flat molecule of **3** in the crystal structure (Figure 2), those of form **A** have two different conformers (crystallographically independent molecules) in their asymmetric unit, which are asymmetrically bent about the connecting N−O bond (Figure 3 and Table 2). It seems that the extent of bending of the given torsion angle correlates directly with the length of the N9′−O9 bond. The greater the deviation of this torsion angle from 180°, the longer the N9′−O9 bond (cf. Table 2). The increased delocalization between the two condensed ring systems through the N9′−O9 bond may be responsible for the deeper colour of form **B**. The formation of the energetically less favourable bent conformations in form **A** is probably counterbalanced by the appearance of the two relatively stronger bifurcated hydrogen bonds (cf. Table 3 and Figure 4b).

Apart from the hydrogen bonds, other crystal packing interactions are also noteworthy. In crystals of form **B**, the planes of pairs of molecules are totally parallel (Figure 5). The interplanar distances are around 3.6 Å and they may reflect to a weak π-π type interaction. On the contrary, in crystals of form **A** the almost perpendicular orientation of the two independent molecules is the most striking structural feature (Figure 4a).

The a priori prediction of crystal structures and hence also the prediction of the polymorphic behaviour of a given material is one of the great challenges in contemporary science, which is also attracting great industrial interest. Due to the complicated interactions in molecular crystals, no general method is available for the prediction or interpretation of the properties of such systems. However, the recently developed SCMP-NDDO method[11] calculates the wavefunction of polar molecular crystals and has been shown to adequately reproduce experimental lattice energies. In the present study, this method has been employed to compare interactions and to characterize the light absorption properties of the two polymorphic forms of **3**. The SCMP-NDDO method has been described previously[11] and some specific aspects related to the present study are briefly discussed in the Experimental Section.

Calculated lattice energy components and the relative lattice energies for the two polymorphs are shown in Table 4. The difference in lattice energies amounts to 8.4 kJ/mol. The magnitude of this difference is consistent with the exist-

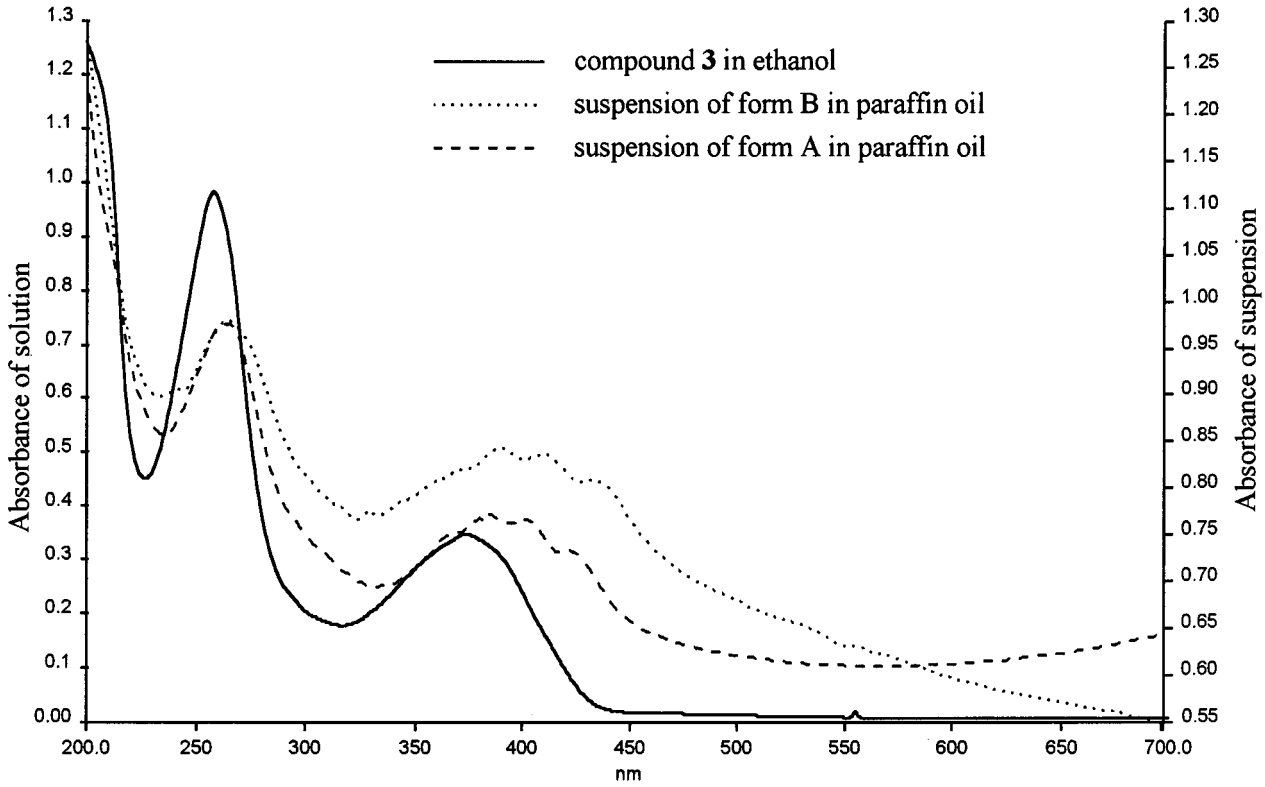

Figure 1. UV/Vis spectra of **3** in solution and in suspensions of form **A** and **B**

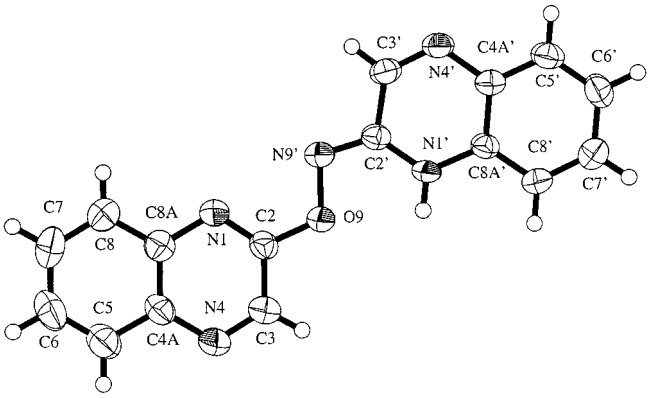

Figure 2. Structure and atomic numbering of a molecule of **3** as found in the crystal of form **B**

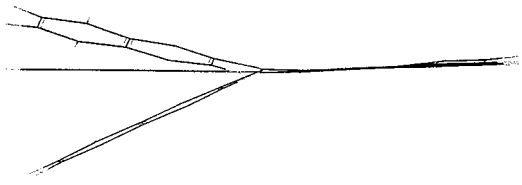

Figure 3. Superposition of the three conformations found in the two polymorphic forms (superposition of the nonhydrogen atoms of the quinoxaline rings protonated at the N1′ atoms)

ence of the polymorphs. Considering the individual contributions, it can be seen that molecules in form **A** adopt relatively high energy conformations [E^{iso}(**A**) − E^{iso}(**B**) = 13.7 kJ/mol] and that the energy increase associated with the structural deformation is largely compensated by the increased interaction between the molecules. Clearly, it is the electrostatic component (E^{ele}) that is responsible for this compensation (Table 4). Other intermolecular components favour **B** over **A**. It is also interesting to note that the ratio of the electrostatic and polarisation energies (E^{ele}/E^{pol}) for **B** is near to 4. A similar ratio has been found for several previously studied molecular crystals[1] and it has been suggested that a constant ratio may justify the use of an approximation where instead of an explicit evaluation, E^{pol} is taken into account in an exaggerated value for E^{ele}. On the other hand, E^{ele}/E^{pol} is found to be nearly 7 in **A**. This observation highlights the danger of adopting any approximation that neglects an explicit evaluation of E^{pol}, even in cases where energies of lattices built-up from the same molecule are compared.

Both, form **A** and form **B** absorb visible light. Form **A** absorbs at a lower wavelength than form **B**. The present implementation of SCMP-NDDO method allows the study of the absorption bands in the single transition approximation (STA).[12] This approach does not make it possible to quantitatively reproduce experimental electronic spectra; however, it may help to interpret the observed differences in the electronic excitation of the two polymorphs. In order to establish the usefulness of the STA in the present problem, the excitation energies of the monomers as obtained from STA and from configuration interaction (CI) calculations were compared. In the CI expansions the four highest occupied and the four lowest unoccupied orbitals were considered and all single excitations together with doubles

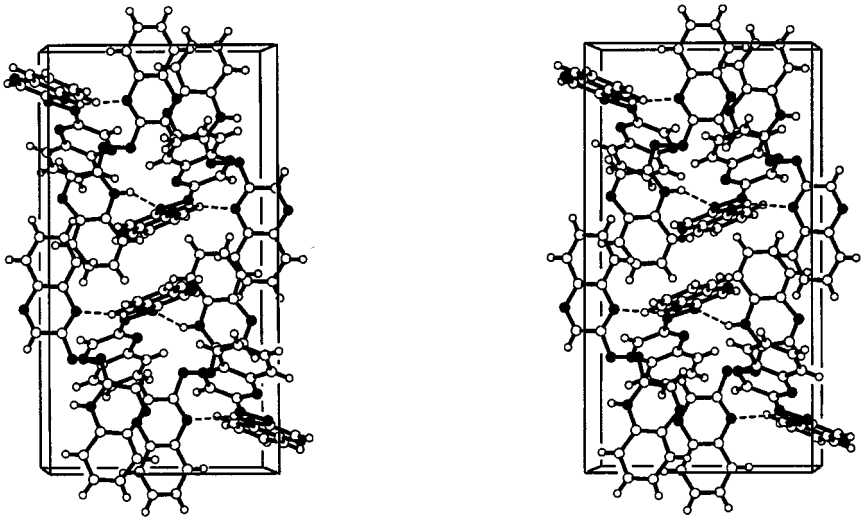

Figure 4a. Stereo view showing the packing of the molecules in crystals of form **A**

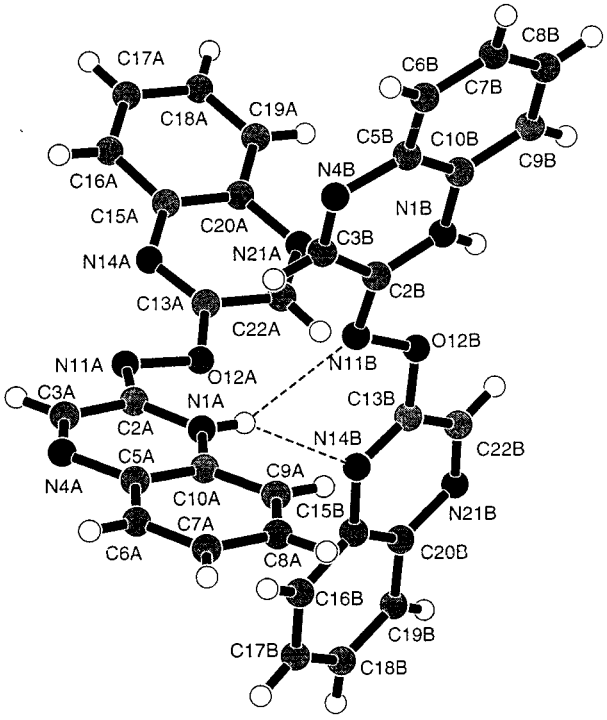

Figure 4b. Hydrogen-bonded pairs of two crystallographically independent molecules of **3** in crystals of form **A**

Table 2a. Selected bond lengths [Å] and angles [°] for form **A**

C2(1)−O9(1)[a]	1.365(5)
O9(1)−N9′(1)	1.450(5)
C2′(1)−N9′(1)	1.304(6)
C2′(1)−C3′(1)	1.438(7)
C2(2)−O9(2)	1.363(6)
O9(2)−N9′(2)	1.435(5)
C2′(2)−N9′(2)	1.304(6)
C2′(2)−C3′(2)	1.443(7)
C2(1)−O9(1)−N9′(1)	113.3(4)
C2′(1)−N9′(1)−O9(1)	106.7(4)
C2(2)−O9(2)−N9′(2)	112.4(4)
C2′(2)−N9′(2)−O9(2)	107.9(4)
C2(1)−O9(1)−N9′(1)−C2′(1)	160.3(4)
C2(2)−O9(2)−N9′(2)−C2′(2)	168.8(4)

[a] The numbers in parentheses denote the number of different molecules present in the crystallographic asymmetric unit.

Table 2b. Selected bond lengths [Å] and angles [°] for form **B**

C2−O9	1.375(4)
O9−N9′	1.418(3)
C2′−N9′	1.311(5)
C2′−C3′	1.460(5)
C2−O9−N9′	113.1(3)
C2′−N9′−O9	106.1(3)
C2−O9−N9′−C2′	177.2(3)

gained by exciting an intact pair of electrons were used. This CI expansion was shown to describe excitation energies reasonably.[13] STA calculations were performed with the SCMP-NDDO program with switching off the intermolecular potentials, while CI calculations were done with MOPAC 6.0.[14] The results of these calculations (Table 5) suggest that, at least for the present system, the excitation energy difference of STA well approximates that of the AM1 CI calculations. This finding combined with the results of ref.[13] places confidence in the STA based interpretation of the excitation energy differences.

As it is described earlier,[11] the SCMP-NDDO wave function of a crystal is a Hartree product of normalised, antisymmetrised strongly orthogonal subsystem wavefunctions. In the present study the subsystems of both polymorphs were chosen as the crystallographic asymmetric units. However, the proper description of excited states may require to make allowance for orbital delocalization between molecules. Therefore, subsystems including the molecule in the asymmetric unit and one of its neighbours were constructed. This results in subsystems with two molecules for form **B**. In the case of form **A** an analogous procedure results in 4 molecules in the subsystem. Wavefunctions and excitation energies in STA were calculated for crystals with several subsystems constructed this way. In the case of form **B** a significant lowering of the excitation energy was obtained when the subsystems included two molecules whose

Table 3. Hydrogen bond geometry

Form **A**	Form **B**
N···N distances [Å]	
3.0685 (0.0061) N1′(1)−N9′(2)	3.050 (0.004) N1′−N4′$2[b]
3.1291 (0.0061) N1′(1)−N1(2)	
3.1139 (0.0058) N1′(2)−N9′(1)$1[a]	
3.1524 (0.0060) N1′(2)−N1(1)$1	
H···N distances [Å]	
2.4050 H1′(1)−N9′(2)	2.214 (0.004) H1′−N4′$2
2.3349 H1′(1)−N1(2)	
2.3632 H1′(2)−N9′(1)$1	
2.4209 H1′(2)−N1(1)$1	
NH···N angles [°]	
134.36 N1′(1)−H1′(1)−N9′(2)	164.03 (0.12) N1′−H1′−N4′$2
153.69 N1′(1)−H1′(1)−N1(2)	
146.06 N1′(2)−H1′(2)−N9′(1)$1	
143.27 N1′(2)−H1′(2)−N1(1)$1	

[a] $1 is a symmetry operation defining an equivalent molecule: $-x + 3/2, y - 1/2, -z + 1/2$. − [b] $2 is a symmetry operation defining an equivalent molecule: $-x - 1/2, -y + 3/2, z - 1/2$.

Table 4. Lattice energy components and relative lattice energies for polymorphic crystals of forms **A** and **B**[a] (see also Experimental Section)

	Form **A**	Form **B**
E^{ele}	−40.4	−30.4
E^{pol}	−6.2	−8.6
E^{DR}	−127.2	−129.6
E^{iso}(**A**) − E^{iso}(**B**)[b]	+13.7	
E^{lat}(**A** − **B**)[b]	+8.4	

[a] All energies are in kJ/mol. − [b] Energy of form **A** relative to form **B**; refer to text in Experimental Section.

planes are parallel with an interplanar distance of 3.6Å. In the case of form **A** an excitation energy lowering was obtained when two of the molecules in the subunit have parts of their ring systems lying parallel. Note, that in both forms, the structural motifs responsible for the orbital interactions are restricted to pairs of molecules. A visual examination of the crystal structures confirms that these pairs of molecules are the only candidates for significant orbital interactions. Thus, the observation that subunits containing other pairs of molecules (double pairs in form **A**) do not result in changes in calculated excitation energies, suggests that delocalization is taken into account satisfactorily.

Excitation energies calculated for the monomers and for the crystals are shown in Table 5. This is lower for monomer **B** than for both forms of monomer **A**. Crystal excitation energies are shifted towards lower values and the difference between the two forms is increased. The lower calculated excitation energy of crystal **B** is in accordance with the experimental spectrum. The 0.22 eV difference obtained from the calculation overestimates the 0.08 eV difference found experimentally for the lowest wave length absorption bands. As the excitation energy difference between crystals **A** and **B** is larger than that of the monomers, it can be concluded that conformational difference between the molecules is partly responsible for the excitation energy differences of the crystals. The role of the crystal field is to stabilize a relatively high energy conformation, to increase the difference between the excitation energies and to shift them towards lower values.

Table 5. Calculated (ΔE^{CI}, ΔE^{STA}) and experimental (ΔE^{exp}) excitation energies and their differences; all energies are in eV units

		ΔE^{CI}	ΔE^{STA}	ΔE^{exp}
Monomer	monomer (**A**1)[a]	3.90	4.39	
	monomer(**A**2)[a]	3.93	4.44	
	monomer (**B**)	3.84	4.32	
	A1 − **B**	0.06	0.07	
	A2 − **B**	0.09	0.12	
Crystal	crystal (**A**)		4.37	3.23
	crystal (**B**)		4.15	3.15
	A − **B**		0.22	0.08

[a] **A**1 and **A**2 refer to the two independent molecules in the asymmetric unit of form **A**.

Conclusion

We have described herein an interesting polymorphic system consisting of two crystal forms displaying different col-

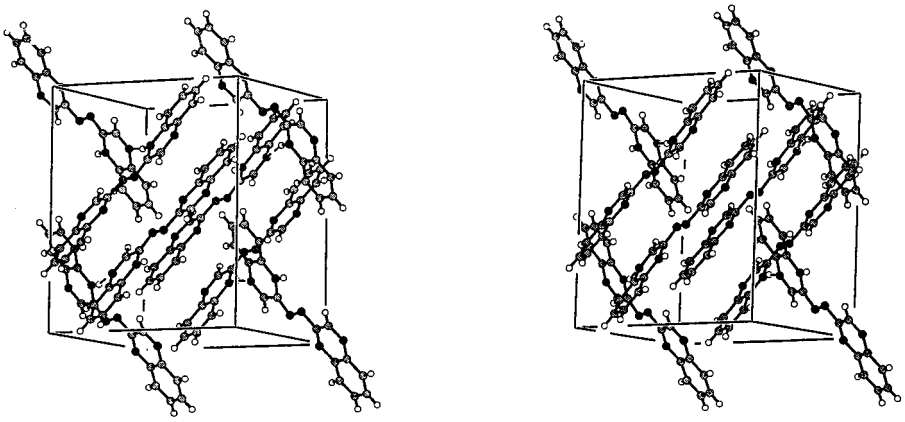

Figure 5. Stereo view of the packing of the molecules in crystals of form **B**

ours. A qualitative analysis of the crystal packing and of the conformations in the two crystal forms has been supported by mixed quantum chemical/molecular mechanical calculations. The dissection of the calculated lattice energies into components, as well as a comparison of the excitation energies of the isolated molecules and the crystals stress the importance of the crystal field, and in particular its electrostatic component, in governing the properties of these polymorphic crystal forms

Experimental Section

General Remarks: Melting points were determined in open capillary tubes with a Büchi 535 apparatus and are uncorrected. − Elemental analyses for C, H, N were carried out with a Carlo Erba Mod 1106 instrument. − NMR spectra were measured with a Bruker DRX-400 instrument at 400.13 (^{1}H), 100.6 MHz (^{13}C). − Mass spectra were measured with a VG-TS 250 instrument. − IR spectra: Bruker IFS-28 (KBr). − UV/Vis spectra: Perkin−Elmer Lambda 14200−700 nm in ethanol and in paraffin oil suspension.

2(1*H*)-Quinoxalinone *O*-(2′-Quinoxalinyl)oxime (3): To a solution of 2-chloroquinoxaline (**1**) (3.29 g, 20 mmol) in dimethyl sulfoxide (6 mL) were added hydroxylamine hydrochloride (0.69 g, 10 mmol) and anhydrous sodium carbonate (1.17 g, 11 mmol). The reaction mixture was stirred at room temperature for 24 h. It was then diluted with water (20 mL), and the orange-yellow precipitate produced was filtered off and washed with water (20 mL). The crude product (a mixture of quinoxaline 2-oxime[15] **2** and **3**) (2.96 g, m.p. 145°C) was recrystallized from ethanol (100 mL). Compound **3** precipitated simultaneously as yellow needles (m.p. 152°C) and as orange plates (m.p. 150°C). The two polymorphic forms were separated mechanically. −^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 11.46 [d, br., *J* = 2.4 Hz, 1 H, N(1)−H], 9.06 (s, 1 H, 3′-H), 8.26 (d, 1 H, 3-H), 8.09 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1 H, 5′-H^a), 7.91 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1 H, 8′-H^a), 7.82 (ddd, *J* = 6.9 Hz, 1 H, 6′-H^b), 7.73 (ddd, 1 H, 7′-H^b), 7.60 (dd, *J* = 7.9, Hz, *J* = 1.5 Hz, 1 H, 5-H), 7.49 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1 H, 8-H), 7.43 (ddd, *J* = 7.3 Hz, 1 H, 7-H), 7.18 (ddd, 1 H, 6-H). (a, b: reversed assignment is also possible). − ^{13}C NMR (100 MHz, [D$_6$]DMSO) δ = 157.7, 147.4, 144.9, 139.9, 139.3, 137.3, 132.8, 131.3, 130.9, 130.5, 128.9, 128.7, 127.6, 127.3, 122.8, 115.5. − IR (KBr): form **B**: $\tilde{\nu}$ = 3144, 1630, 1610, 1576, 1549, 1499, 1297, 1199, 761 cm^{-1}; form **A**: $\tilde{\nu}$ = 3170, 1637, 1610, 1571, 1545, 1499, 1300, 1200, 756 cm^{-1}. − MS (EI); *m/z*: 289 [M$^+$]. − UV/Vis (EtOH): λ_{max} (lg ε) = 257 nm (4.52), 375 (4.07). − $C_{16}H_{11}N_5O$ (289.3): calcd. C 66.43, H 3.83, N 24.21; found C 66.61, H 3.92, N 24.05.

Quantum Chemical/Molecular Mechanical Calculations: The recently developed SCMP-NDDO method[11] used to study the two crystals uses a semiempirical Hamiltonian to calculate the molecular wavefunction for a subunit in the symmetrical environment made up of the same repeating subunit, the latter being represented by atomic point multipoles. These multipoles are calculated from the wavefunction and thus it is an iterative procedure yielding the self-consistent wavefunction and multipoles. The intermolecular potential is supplemented with an empirical dispersion−repulsion term. The SCMP-NDDO method with the AM1 Hamiltonian[16] has been shown to give sublimation enthalpies in good agreement with available experimental data for a series of molecular crystals.[11] A fundamental property of the method is that, besides electrostatics, it is able to account for the polarisation of the electron density caused by the crystal field.

Lattice energies and their components were calculated in the following way. First, an AM1 calculation was performed for the isolated molecule in the geometry observed in the crystal. Then, the density matrix relating to the isolated molecule was used to calculate the energy of the crystal. The energy obtained in this way includes the isolated monomer energy (E^{iso}) and the electrostatic interaction energy (E^{ele}), the latter being the interaction energy of the molecules obtained with the charge density of the isolated molecules. [Note that energies obtained from the SCMP-NDDO method refer to the asymmetric unit of the crystal. The asymmetric unit of form **A** contains 2 molecules while that of form **B** contains 1 molecule. In order to compare the energies of the two crystals, energies of form **A** are divided by two, such that E^{iso}(**A**) corresponds to the mean of the energies of the two molecules.]

The deformation of the charge density of the isolated molecule in the crystal field can be obtained in a self-consistent field (SCF) procedure. The energy lowering due to this charge deformation is the polarisation energy (E^{pol}). A further component of the lattice energy of the crystal is the dispersion−repulsion term (E^{DR}), which is calculated classically. Thus, the lattice energy (E^{lat}) can be obtained from Equation 1 where E^{lat} can be dissected into components according to Equation 2.

$$E^{lat} = E^{tot} - E^{iso} \quad (1)$$

$$E^{lat} = E^{ele} + E^{pol} + E^{DR} \quad (2)$$

As shown by Equation 1, the lattice energy is calculated as the difference between the total energy of the crystal and the energy of the isolated monomer. If it is supposed that the geometry of the molecule is not deformed in the field of the crystal, E^{iso} can be calculated for the geometry observed in the crystal. This procedure was successfully used in an earlier study.[11] However, this is clearly not a valid approximation in the present problem. The two molecules in the asymmetric unit of form **A** have different geometries, and the corresponding energies of the isolated molecules differ by 3.1 kJ/mol. Furthermore, the energy of the isolated molecule in the geometry of form **B** is 12 kJ/mol lower than that of the more stable molecule in form **A**. Thus, on calculating E^{tot}(**A**) = E^{iso}(**A**) + E^{ele}(**A**) + E^{pol}(**A**) + E^{DR}(**A**) and E^{tot}(**B**) = E^{iso}(**B**) + E^{ele}(**B**) + E^{pol}(**B**) + E^{DR}(**B**) for crystal forms **A** and **B**, respectively, E^{iso}(**A**) and E^{iso}(**B**) are found to be different. This contradicts the fact that both crystals produce the same molecule upon sublimation.

The above considerations show that no uniquely defined isolated monomer energy is available and, consequently, no absolute lattice energies can be calculated in the manner followed in ref.[11] The inaccuracy in E^{lat}(**A**) stems from the fact that E^{iso}(**A**) includes not only the internal energy of the isolated molecule but also the energy required for its deformation into the structure observed in form **A**. An analogous situation is found for E^{lat}(**B**). Thus, a relative lattice energy, E^{lat}(**A** − **B**), can be calculated for the two polymorphic crystals according to Equation 3.

$$E^{lat}(\mathbf{A} - \mathbf{B}) = E^{lat}(\mathbf{A}) - E^{lat}(\mathbf{B}) + E^{iso}(\mathbf{A}) - E^{iso}(\mathbf{B}) = E^{tot}(\mathbf{A}) - E^{tot}(\mathbf{B}) \quad (3)$$

We note that a possible means of calculating absolute lattice energies would be to use E^{tot} and E^{iso} in the geometries optimised by the SCMP-NDDO and the standard AM1 methods, respectively. Such a procedure would be expected to preserve two distinct polymorphic forms and a common isolated monomer. The implementation of forces into the SCMP-NDDO method with a view to performing such calculations is currently underway.

Excitation energies of molecules in the single transition approximation (STA)[12] are calculated as the energy difference between the spin-adapted determinental wavefunction of the excited state

and the ground state SCF determinant. The excited-state wavefunction is constructed from the ground-state orbitals. Thus, the energy difference between a singly excited singlet and a closed-shell ground state is calculated according to Equation 4 where ε is the orbital energy, J is the Coulomb integral and K is the exchange integral.

$$\Delta E = \varepsilon_{j^*} - \varepsilon_k - J_{kj^*} + 2\,K_{kj^*} \quad (4)$$

Equation 4 corresponds to an electron promotion $\phi_k - \phi_{j^*}$. In the SCMP approach the excitation energy in STA takes the form of Equation 5.

$$\Delta E(\mathrm{M}) = \varepsilon(\mathrm{M})_{j^*} - \varepsilon(\mathrm{M})_k - J_{kj^*} + 2\,K_{kj^*} - J(\mathrm{M})_{kj^*} + 1/2\,J(\mathrm{M})_{kk} + 1/2\,J(\mathrm{M})_{j^*j^*} \quad (5)$$

Where $J(\mathrm{M})_{kj^*}$ is a Coulomb integral including two terms; the interaction of an electron on orbitals *k* in the subsystem with all electrons on orbital *j** of other subunits and the interaction of an electron on orbital *j** in the subsystem with all electrons on orbital *k* of other subunits.

X-ray Crystallographic Study: Data were collected with a Rigaku AFC6S diffractometer. The structures were solved with teXsan[17] and refined with SHELXL-93.[18] Positional parameters, anisotropic displacement parameters for nonhydrogen atoms, and groupwise isotropic displacement parameters for hydrogen atoms were refined. The crystal of form **A** was found to contain two molecules in the asymmetric unit. Bond lengths and angles in these two molecules, as well as those found in crystals of form **B**, were found to be equal within experimental error, with the exception of those indicated in Tables 2a and 2b. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-112573 and CCDC-112574. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax (internat.): +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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