Single crystal formation by solid state reaction between 8-hydroxyquinoline and 2,4,5-trichlorophenol

Nakshatra B. Singh,[a] **Archana Srivastava**[a] **and Roland Fröhlich**[b]

[a] *Department of Chemistry, D D U Gorakhpur University, Gorakhpur-273009, India*
[b] *Department of Organic Chemistry, University of Münster, Münster, Germany*

Received (in Cambridge, UK) 21st February 2000, Accepted 12th March 2001
First published as an Advance Article on the web 3rd April 2001

8-Hydroxyquinoline reacts with 2,4,5-trichlorophenol in solution as well as in the solid state forming a 1 : 1 addition compound. In the solid state, reaction proceeds by the diffusion of 8-hydroxyquinoline into the crystal lattice of 2,4,5-trichlorophenol and the reaction product separates in the form of single crystals. The crystal structure of the reaction product has been determined by X-ray diffraction techniques and belongs to a monoclinic system.

Introduction

It is generally accepted that reactions in the solid state tend to occur with a minimum of atomic and molecular motion.[1] Apart from this concept, several other ideas have been put forward to explain organic solid state reactivity.[2] In recent years another breakthrough in this field has been crystal engineering[3] which now includes design strategies for a wide variety of supramolecular and organized structures. A major focus of interest in solid state chemistry is now the utilization of the crystalline state to lock molecules into orientations favoring a desired reaction.[4] It is possible to design, or preordain or at least modify the reactivity of organic materials, by adjustment of certain crystallographic and topochemical factors.

A number of organic solid state reactions between 8-hydroxyquinoline (8-HQ) and other organic solids **X** (**X** = 1,2,3-trihydroxybenzene, *p*-nitrobenzoic acid, *p*-chloranil,† picric acid) have been studied[5–8] and it is found that the stoichiometry and rate of reactions are different in different systems. In all the cases the 8-HQ molecules diffuse into the crystal lattice of **X**. It appears that different functional groups present in **X** engineer molecules in such a way as to have specific geometry and crystal packing. In the case of the 8-HQ–1,2,3-trihydroxybenzene system, the reaction product separates in the form of single crystals. These types of reaction are novel and important in the sense that single crystals can be prepared by solid state reactions.

In an attempt to prepare single crystals by solid state reactions, the study of the present system was undertaken. The mechanism of reaction and structure of the reaction product have been discussed in this paper.

Experimental

Materials

2,4,5-Trichlorophenol (2,4,5-TCP) (CDH) (white colour) was purified by repeated crystallization from benzene. The melting point of the pure compound was found to be 68 °C.

8-Hydroxyquinoline (8-HQ) (Merck) (white colour) was used without further purification. Its melting point was 75 °C.

Methods

Reaction between 2,4,5-TCP and 8-HQ in solution. A benzene solution of the two components in 1 : 1 molar ratio was mixed and allowed to remain at room temperature for 7 days, where a yellow coloured reaction product separated in the form of a single crystal. The melting point of the compound was found to be 74 °C. Lattice determinations of single crystals show within the standard deviations the same unit cell as that of crystals obtained from solid state reactions.

Reaction between 2,4,5-TCP and 8-HQ in the solid state leading to the formation of the reaction product in the form of single crystals. Two glass tubes (internal diameter 1.8 cm) fitted with standard joints and closed at one end were taken. One tube was filled with powdered 8-HQ and the other with powdered 2,4,5-TCP. The two tubes were then connected with each other in such a way that an air-gap of approximately 5.5 cm was created between the surfaces of the two reactants. The assembly was kept in an incubator at 50 °C. After 15 days it was observed that tiny crystals were formed at the surface of the 2,4,5-TCP. The crystals were yellow in colour. The size of the crystals increased with time. After approximately two months, the maximum size and thickness of the crystals were about 5 and 1 mm respectively. The melting point of the reaction product was found to be 74 °C.

A single crystal of dimensions 0.30 × 0.30 × 0.10 mm was chosen for X-ray crystallographic analysis.‡

DSC studies

The differential scanning calorimetric studies of the reaction products obtained from solution and solid state reaction were performed from room temperature to 150 °C under ambient conditions.

FTIR spectral studies

FTIR spectra of 2,4,5-TCP, 8-HQ and the reaction product obtained from the solid state reaction were recorded.

Microstructural studies

A clean glass slide was kept at 74 °C in an oven and a small amount of 2,4,5-TCP was placed on the slide and immediately melted. The temperature of the oven was lowered and the molten 2,4,5-TCP was allowed to crystallize in one direction with the help of a cover slip (a very thin layer crystallized). This was examined under microscope and photographed.[9] The photo-

---

† The IUPAC name for *p*-chloranil is 2,3,5,6-tetrachloro-1,4-benzoquinone.

‡ CCDC reference number 160321. See http://www.rsc.org/suppdata/p2/b0/b001412p/ for crystallographic files in .cif or other electronic format.

DOI: 10.1039/b001412p

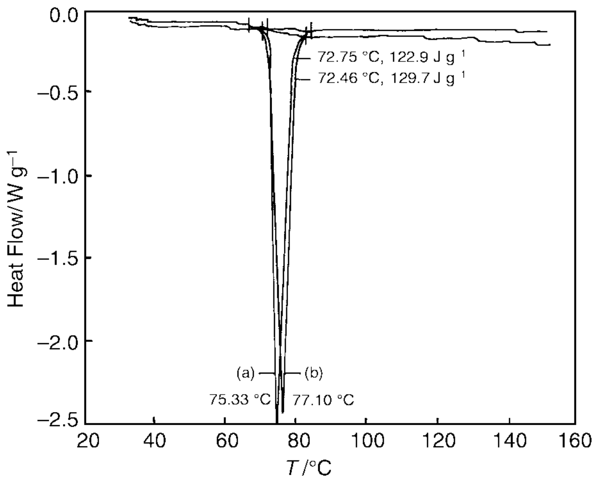


Fig. 1 Differential scanning calorimetric curves of (a) reaction product obtained by solid state reaction; (b) reaction product obtained from solution.

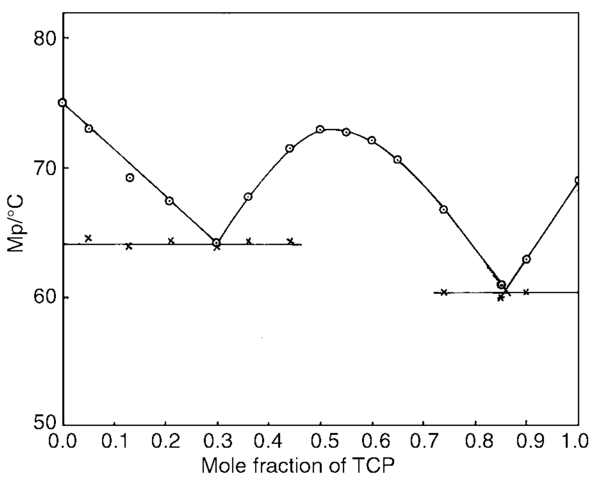


Fig. 2 Phase-diagram of the 8-hydroxyquinoline–2,4,5-trichlorophenol system.

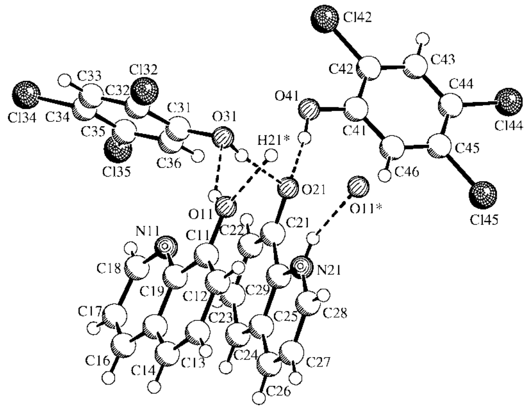


Fig. 3 Crystal structure of (8-hydroxyquinoline)$_1$(2,4,5-trichlorophenol)$_1$.

graph showed a very thin layer of crystallized 2,4,5-TCP which represented the microstructure of 2,4,5-TCP.

In a small beaker 8-HQ was taken and heated so that the beaker was filled with vapours of 8-HQ. A slide of 2,4,5-TCP was kept on top of the beaker filled with vapours of 8-HQ and covered with a bigger beaker and kept at 70 °C for 5 and 30 minutes. 2,4,5-TCP reacted with the vapours of 8-HQ and the change in microstructure was photographed.

Phase-diagram studies

Phase-diagram studies were made by using the thaw–melt method.[10] Homogeneous mixtures of two components in different proportions were prepared and their melting points were determined using a precision thermometer.

Kinetic studies of reaction between 2,4,5-TCP and 8-HQ in the solid state

Kinetic studies were carried out by the capillary technique as described earlier.[11] A glass capillary of length 5 cm and internal diameter 0.186 cm was taken. Half of the glass capillary tube, sealed at one end with a sealing wax, was filled with powdered 2,4,5-TCP (particle size <350 mesh) and the tube was tapped for 5 minutes in order to have an uniform packing density. The remaining half of the capillary tube was filled with powdered 8-HQ (particle size <350 mesh), sealed and placed horizontally in a constant temperature incubator. The reaction propagated towards the side of 2,4,5-TCP. The kinetics were studied by measuring the thickness of the yellow coloured reaction product at 30, 35, 40 and 45 °C with the help of a travelling microscope.

Results and discussion

The reaction products obtained from solution and solid state reaction were yellow in colour and melted at 74 °C. The differential scanning calorimetric curves of the products are almost superimposable on each other (Fig. 1). These two results clearly indicate that reaction products obtained from solution and solid state reaction are the same. Phase-diagram studies (Fig. 2) show that a 1 : 1 addition compound is formed between 2,4,5-TCP and 8-HQ. Since the maximum is broad, it suggests that a stable addition compound is formed in the solid state which may dissociate in the molten state or in solution.[12]

IR spectral studies of the components and the reaction product give some information regarding the nature of the interaction. 8-HQ in the solid state exists as a dimer and the association is due to hydrogen bonding.[13] A broad maximum at around 3500 cm^{-1} confirms this point. 2,4,5-Trichlorophenol also shows a broad maximum between 3400–3500 cm^{-1} due to a hydrogen bonded OH group. IR spectra of the reaction product obtained by solid state reaction show two peaks at 3412.9 and 3529.8 cm^{-1}. The first peak may be due to formation of –NH in 8-HQ molecules and the second peak may be due to hydrogen bonded OH. These results have been confirmed by X-ray diffraction studies.

The crystal structure is shown in Fig. 3. On one quinoline molecule a hydrogen shift from oxygen to nitrogen has occurred, driven by the hydrogen bonding system formed by four trichlorophenol molecules and four quinolines. Two of them have hydrogen located at nitrogen atom N21, and for the other two, the hydrogen is on O11, forming a hydroxy group. Half of this system is shown in the figure. All bond lengths and angles in the skeleton of the formed product are comparable with those found in the structure of 8-HQ[14] and the addition product of 2,4,5-TCP with aniline.[15] The only differences can be found in the bond lengths C21–O21 (1.319(3) Å) and C11–O11 (1.369(3) Å), showing a typical C–O single bond due to hydrogen shift to O11. All hydrogen atoms involved in the bridging are located from difference Fourier maps. The bond lengths and bond angles involved in bridging are given in Table 1. The packing stereo diagram of the crystal is given in Fig. 4.[16]

When powders of 8-HQ and 2,4,5-TCP were kept in a glass capillary, in contact, the reaction started with a colour change at the surface of 2,4,5-TCP. As the reaction progressed, the thickness of the reaction boundary increased and moved towards 2,4,5-TCP. This indicates that 8-HQ is the diffusing species. The kinetics were followed by measuring the thickness

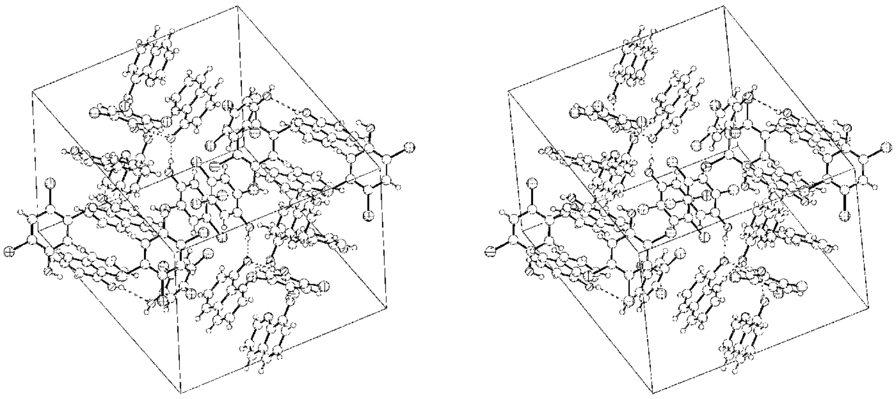


Fig. 4 Stereo packing diagram of crystalline (8-hydroxyquinoline)$_1$(2,4,5-trichlorophenol)$_1$.

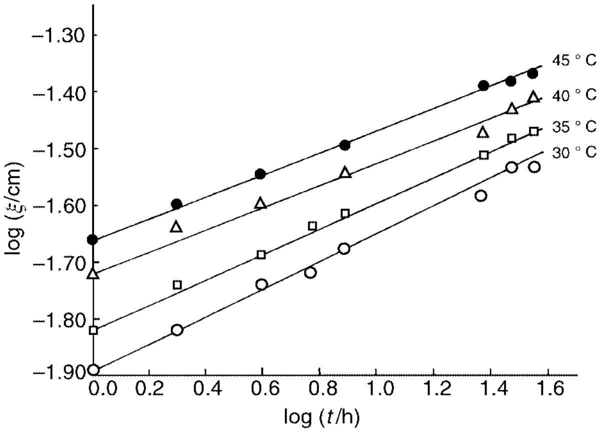


Fig. 5 Verification of kinetic eqn. (1).

Table 1 Bond lengths (Å) and angles (°) of the atoms involved in the bridging of the reaction product

N ··· H	N11–H11	2.25(4)
	N21–H21	0.83(3)
O ··· H	O11–H11	0.76(3)
	O31–H31	0.81(3)
	O41–H41	0.87(3)
	O31–H11	2.30(4)
	O21–H21	2.37(3)
	O21–H31	1.80(3)
	O21–H41	1.70(4)
	O11*–H21	2.19(3)
∠O ··· H ··· O	O11–H11–O31	148(4)
	O31–H31–O21	172(4)
	O41–H41–O21	171(4)
∠N ··· H ··· O	N21–H21–O21	104(2)
	N21–H21–O11*	150(3)
∠O ··· H ··· N	O11–H11–N11	118(3)

Table 2 Kinetic parameters of eqn. (1)

T/°C	$k \times 10^3$/cm h^{-1}	n	E/kJ mol^{-1}
30	12.88	0.23	27.5
35	14.79	0.22	
40	19.05	0.19	
45	21.88	0.18	

of the yellow coloured reaction product as a function of time and kinetic data obeyed eqn. (1)

$$\xi = k\, t^n \tag{1}$$

where ξ is the thickness of the reaction product at any time t, k is an apparent rate constant and n is a constant. The validity of eqn. (1) is tested by plotting log ξ *vs.* log t, where straight lines are obtained (Fig. 5). The values of k and n calculated from the straight lines are given in Table 2. From the Arrhenius plot, the

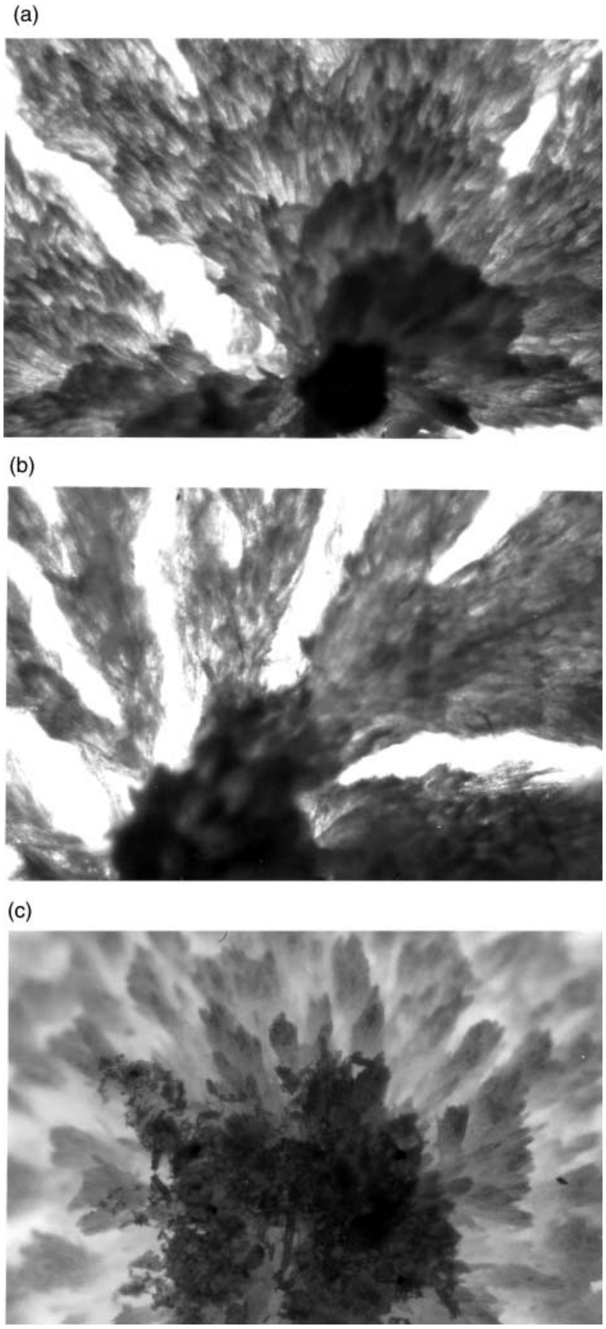
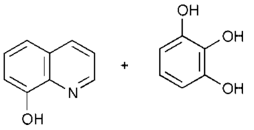
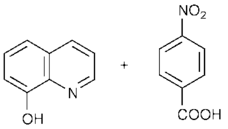
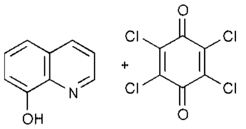
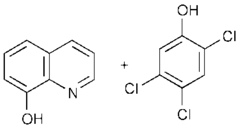
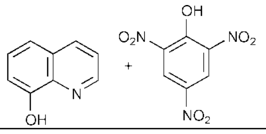


Fig. 6 (a) Microstructure of 2,4,5-trichlorophenol—5 × 4; (b) microstructure of 2,4,5-trichlorophenol exposed to vapours of 8-hydroxyquinoline for 5 minutes—5 × 4; (c) microstructure of 2,4,5-trichlorophenol exposed to vapours of 8-hydroxyquinoline for 30 minutes—5 × 4.

Table 3 Comparison of rate constants and energies of activation for the solid state reactions between 8-HQ and other reactants (8-HQ is the diffusing species)

System no.	Reaction system	Stoichiometry of the reaction product	$k \times 10^2$/cm h^{-1}	E/kJ mol^{-1}	Ref.
1		2 : 1	2.39 (50 °C)	28.7	5
2		1 : 1	3.60 (50 °C)	30.1	6
3		2 : 1	1.71 (50 °C)	32.2	7
4		1 : 1	2.18 (45 °C)	27.5	
5		1 : 1	6.6 (50 °C)	13	8

energy of activation was calculated and found to be 27.5 kJ mol^{-1}. This value is much lower than the heat of sublimation[17] of 8-HQ (108.7 kJ mol^{-1}). This shows that diffusion of 8-HQ is not a vapour phase dominated process. An easier way of diffusion is also involved during the course of reaction in addition to vapour phase diffusion. This may be surface migration. It has already been proved that surface migration of 8-HQ on the surface of glass is not uncommon.[18] When the reaction was allowed to occur in a glass tube for the preparation of a single crystal it was seen that the reaction did not occur uniformly but nuclei of reaction products were formed at different places on the surface of the 2,4,5-TCP powder which grew in size and ultimately the entire surface was covered with single crystals of $(2,4,5\text{-TCP})_1(8\text{-HQ})_1$. It appears that reaction started at the sites where some sort of defect was present.

When a molten material is allowed to crystallize on a glass slide (only a very thin layer) in one direction, the structure observed under an optical microscope is known as the microstructure of the material. Two slides of 2,4,5-TCP were made and exposed to vapours of 8-HQ for 5 and 30 minutes respectively. The structural changes are given in Fig. 6. Fig. 6(a) shows that 2,4,5-TCP crystallizes from one point and spreads over in all the directions. When the slide with 2,4,5-TCP was allowed to react with the vapours of 8-HQ for 5 minutes [Fig. 6(b)] reaction started at the central point from which crystallization started in the case of 2,4,5-TCP. When it was further exposed for 30 minutes [Fig. 6(c)] reaction starting from a central point spread in other directions. These results show that during solid state reaction between 8-HQ and 2,4,5-TCP, reaction started at a specific point where some sort of defect was present. This then nucleated and grew in size giving single crystals of reaction product.

The reactions of 8-HQ with a number of organic compounds in the solid state have been studied. The rate constants and energies of activation for different reactions are given in Table 3. In all the systems given in Table 3, 8-HQ is the diffusing species and the energies of activation are almost the same except in the 8-HQ–picric acid systems. This shows that the mechanism of diffusion is probably the same but the rate constants are different. 8-HQ migrates over the surface of other reactants and at the same time it penetrates into the crystal lattice through defects and cavities. Since the crystal geometry and symmetry of reactants other than 8-HQ are different, it offers a different amount of hindrance during the course of diffusion of 8-HQ molecules. As a result the rate of reaction becomes different.

Out of all the solid state reactions listed in Table 3, the reaction product separated in the form of single crystals only in the 8-HQ–1,2,3-trihydroxybenzene system and in the present reaction system. In first case the proton of the middle OH group of 1,2,3-trihydroxybenzene is transferred to the N-atom of 8-HQ whereas in the present system the H-atom of the OH group of 8-HQ is transferred to the N-atom and oxygen is hydrogen bonded with the H-atom of the OH group of 2,4,5-TCP. This hydrogen bonding extends in a systematic manner in the solid state. As a result the reaction product separates in the form of a single crystal. The hydrogen bond is the master-key interaction in crystal engineering because it combines directionality with strength and has become a major element in the quest for controlled supramolecular synthesis.[19]

References

1 M. D. Cohen and G. M. J. Schmidt, *J. Chem Soc.*, 1964, 1996.
2 N. B. Singh, R. J. Singh and N. P. Singh, *Tetrahedron*, 1994, **50**, 6441.
3 G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.
4 D. Y. Curtin, I. C. Paul, E. N. Duesler, T. W. Lewis, B. J. Mann and W. I. Shian, *Mol. Cryst. Liq. Cryst.*, 1979, **50**, 25.
5 N. B. Singh, N. P. Singh, V. Kumar and D. Nethaji, *J. Chem. Soc., Perkin Trans. 2*, 1994, 361.
6 N. B. Singh, K. Singh and R. Singh, *Indian J. Chem.*, 1998, **37B**, 429.
7 N. B. Singh, R. J. Singh and N. N. Singh, *Indian J. Chem.*, 1989, **28A**, 639.
8 N. B. Singh, K. Singh and R. Singh, *Mol. Cryst. Liq. Cryst.*, 1999, **333**, 269.
9 N. B. Singh and N. B. Singh, *J. Cryst. Growth*, 1975, **28**, 267.
10 R. P. Rastogi and K. T. R. Verma, *J. Phys. Chem.*, 1958, **62**, 641.
11 R. P. Rastogi, P. S. Bassi and S. L. Chaddha, *J. Phys. Chem.*, 1962, **66**, 2707.
12 R. P. Rastogi, *J. Chem. Educ.*, 1964, **41**, 443.

13 C. K. Prout and A. G. Wheeler, *J. Chem. Soc. A*, 1967, 469.

14 P. Roychowdhary, B. N. Das and B. S. Basak, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **34**, 1047.

15 P. I. van Bellingen, G. Germain, P. Piret and M. van Meerssche, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **27**, 553.

16 Crystallographic details: chemical formula—$(C_9H_7ON)_2(C_6H_3Cl_3O)_2$; formula weight—685.18 g mol^{-1}; crystal system—monoclinic; space group—$P2_1/n$ (No. 14); unit cell dimensions—$a = 11.023(1)$, $b = 16.872(1)$; $c = 16.682(1)$ Å; $\beta = 107.57(1)°$; unit cell volume—2957.8(4) Å^3; temperature of data collection—20 °C; $z = 4$; $\mu = 6.21$ cm^{-1}; measured, independent reflections and R(int)—9690, 5016, 0.030; R_1 ($I > 2$) = 0.041, $wR^2 = 0.091$.

17 *Lange's Handbook of Chemistry*, 13th edn., ed. J. A. Dean, McGraw Hill Book Company, New York, 1985, 9-153, 9-158.

18 R. P. Rastogi, N. B. Singh and R. P. Singh, *Indian J. Chem.*, 1977, 941.

19 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.