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Structures of 3,6-Diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione and 2,5-Dimethyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione

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Abstract

Crystal data for 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP) are: $C_{18}H_{12}N_2O_2$, $M_r = 288.310$, triclinic, $P\bar{1}$, $a = 3.817(1)$, $b = 6.516(1)$, $c = 13.531(2)$ Å, $\alpha = 93.11(1)$, $\beta = 86.97(1)$, $\gamma = 95.02(1)°$, $V = 334.3(2)$ Å^3, $Z = 1$, $D_x = 1.432$, $D_m = 1.410$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 0.73$ mm^{-1}, $F(000) = 150$, $T = 293$ K, $R = 0.059$ for 1076 reflections. Crystal data for 2,5-dimethyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DM-DPP) are: $C_{20}H_{16}N_2O_2$, $M_r = 316.359$, orthorhombic, *Pbcn*, $a = 11.666(1)$, $b = 12.003(1)$, $c = 10.779(1)$ Å, $V = 1509.4(2)$ Å^3, $Z = 4$, $D_x = 1.392$, $D_m = 1.388$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 0.54$ mm^{-1}, $F(000) = 522$, $T = 293$ K, $R = 0.054$ for 1470 reflections. The DPP and DM-DPP molecules, both of which belong to the point group C_i, are not entirely planar. The phenyl rings are twisted in the same direction; out of the plane of the planar heterocyclic system by 7(1)° in DPP and by 31 (1)° in DM-DPP. The DPP molecules align in nearly the same molecular plane and parallel to each other due to intermolecular hydrogen bonding. By contrast, the DM-DPP molecules are arranged in a herringbone fashion along the stacking axis.

Introduction

3,6-Diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP, see Fig. 1) is a new heterocyclic pigment of red color whose chlorinated derivative is now on the market. This pigment features a completely new chromophore system of pyrrolo[3,4-*c*]pyrrole-1,4-dione (Iqbal, Jost, Kirchmayr, Pfenninger, Rochat & Wallquist, 1988).

The heterocyclic chromophore of DPP is so small that DPP appears only pale yellow in solution. In the solid state, however, it is an intense red pigment. There is a significant resemblance in spectral shape between the absorption spectra in solution and in the solid state. The solid-state spectrum can therefore be pictured as the solution spectrum with a bathochromic shift of about 40 nm (*ca* 1400 cm^{-1}). The mechanism of this large bathochromic displacement has been tackled in a previous investigation from the standpoint of intermolecular hydrogen bonding between the N—H of one molecule and the oxygen of another (Mizuguchi & Wooden, 1991). These experiments were conducted using DPP as the compound with hydrogen bonding and 2,5-dimethyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (DM-DPP, see Fig. 2) as the reference compound with no hydrogen bonds: DPP has two NH groups and DM-DPP two N—CH_3 groups. The studies

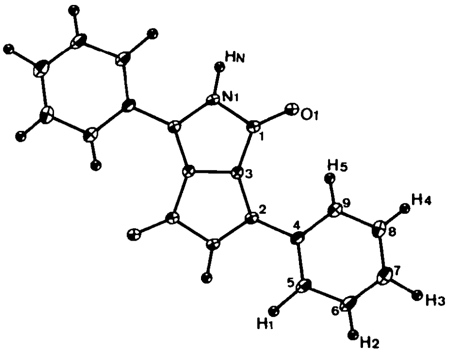

Fig. 1. Conformation of DPP.

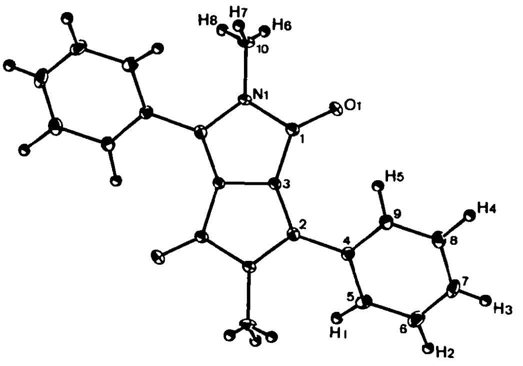

Fig. 2. Conformation of DM-DPP.

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showed that intermolecular hydrogen bonding in DPP involves partial electron transfer from oxygen to the N—H bond in the solid state thereby increasing the electron density on the N atom. As a consequence, there is more overall electron density in the chromophore which contributes to the bathochromic shift.

Since intermolecular hydrogen bonding exerts such a profound influence on the electronic spectra, structure analyses of DPP and DM-DPP were carried out. The structure of DPP has been reported previously (Iqbal, Jost, Kirchmayr, Pfenninger, Rochat & Wallquist, 1988). The present analysis was carried out on a better quality crystal, which resulted in a final R value of 0.059.

Experimental

DPP was synthesized from benzonitrile and dimethyl succinate by the method described previously (Rochat, Cassar & Iqbal, 1986). The product was washed three times with acetone for initial purification purposes. The DPP powder was further purified four times by sublimation under argon atmosphere using equipment described previously (Mizuguchi, 1981). A single crystal was grown from the vapor phase using argon as the carrier gas in the same sublimation apparatus. DPP sublimed at about 608 K, and the argon flow rate was controlled to 15 $mm^3 s^{-1}$ using a mass flow meter (F-100/200, Bronkhorst BV). After 24 h of vapor growth, a number of single crystals were obtained in the form of rectangular and parallelgram platelets. The dimensions of the single crystal used for the structure analysis were 0.39 × 0.13 × 0.03 mm.

DM-DPP was prepared according to the method previously reported (Jost, Iqbal & Rochat, 1986). The single crystal was grown from DM-DPP solution in dioxane. The dimensions of the single crystal used for the analysis were 0.6 × 0.52 × 0.25 mm.

The crystal structures were analyzed at 293 K using an Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). θ–2θ scans. Unit-cell dimensions: DPP from 25 reflections ($10 < \theta < 15°$); DM-DPP from 25 reflections ($10 < \theta < 15°$). 1425 independent reflections obtained in the range $4 < 2\theta < 56°$ for DPP, $-4 \leq h \leq 4$, $-8 \leq k \leq 8$, $0 \leq l \leq 16$. 1799 independent reflections in the range $4 < 2\theta < 150°$ for DM-DPP, $0 \leq h \leq 14$, $0 \leq k \leq 15$, $0 \leq l \leq 13$. Of these, 1076 and 1470 reflections with $I > 3\sigma(I)$ were used for structure refinement for DPP and DM-DPP, respectively. Corrections for absorption and secondary extinction were not applied. Three standard reflections monitored every 2 h during data collection showed no significant change in intensity. The densities of the single crystals were measured by flotation in a mixture of chloroform and methylene chloride. The crystallographic data are given in the *Abstract*.

Structure determination and refinement

The structures of DPP and DM-DPP were determined by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The structures were refined on $|F|$ by full-matrix least-squares calculations using the *SDP* package (Frenz, 1985). In both cases, refinement was carried out with anisotropic atomic displacement parameters, neglecting H atoms, up to $R = 0.082$ for DPP and $R = 0.086$ for DM-DPP. Six H atoms for DPP and eight H atoms for DM-DPP were then located in difference electron density maps. Final $R = 0.059$, $wR = 0.067$, $S = 0.51$ (124 parameters varied) for DPP, and $R = 0.054$, $wR = 0.068$, $S = 0.81$ (141 parameters varied) for DM-DPP. Weights of each reflection in refinement were $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ being the e.s.d. based on counting statistics, $(\Delta/\sigma)_{\max} = 0.06$ for DPP and 0.08 for DM-DPP. The maximum heights in the final difference electron density maps were 0.42 and 0.41 e $Å^{-3}$ for DPP and DM-DPP, respectively. Atomic scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic positional and equivalent isotropic displacement parameters appear in Tables 1 and 2.*

Discussion

Molecular geometry

The conformations of DPP and DM-DPP are given in Figs. 1 and 2, respectively, where the atoms are represented by displacement ellipsoids according to *ORTEP* (Johnson, 1971). The interatomic distances and bond angles together with their e.s.d.'s are listed in Table 3. The DPP and DM-DPP molecules, both of which belong to the point group C_i, are not entirely planar. The phenyl rings are twisted in the same direction: out of the plane of the planar heterocyclic system by 7(1)° in DPP and by 31 (1)° in DM-DPP.

In DPP, the interatomic distances H(1)—H(N) and H(5)—O(1) shown in Fig. 1 are 2.19 (6) and 2.31 (5) Å, respectively. These distances are considerably shorter than the sum of the van der Waals radii of the corresponding atoms: 2.4 and 2.6 Å, respec-

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55083 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BX0577]

Table 1. *Positional and isotropic displacement parameters for* DPP, *with e.s.d.'s in parentheses*

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
O1	0.9477 (8)	0.3188 (4)	−0.1055 (2)	0.045 (1)
N1	0.6913 (9)	0.2982 (5)	0.0534 (2)	0.039 (1)
C1	0.764 (1)	0.2203 (5)	−0.0440 (3)	0.036 (1)
C2	0.488 (1)	0.1578 (5)	0.1085 (3)	0.034 (1)
C3	0.582 (1)	0.0168 (6)	−0.0476 (3)	0.035 (1)
C4	0.386 (1)	0.2047 (6)	0.2119 (3)	0.038 (1)
C5	0.461 (1)	0.4033 (6)	0.2554 (3)	0.047 (1)
C6	0.360 (1)	0.4399 (7)	0.3551 (3)	0.057 (1)
C7	0.188 (1)	0.2885 (8)	0.4089 (4)	0.061 (1)
C8	0.113 (1)	0.0924 (8)	0.3663 (4)	0.060 (1)
C9	0.211 (1)	0.0498 (7)	0.2670 (3)	0.049 (1)
H1	0.64 (1)	0.530 (8)	0.218 (4)	0.038 (8)*
H2	0.42 (1)	0.564 (8)	0.387 (4)	0.039 (8)*
H3	0.12 (1)	0.345 (9)	0.486 (5)	0.063 (8)*
H4	−0.03 (1)	−0.015 (8)	0.402 (4)	0.042 (8)*
H5	0.17 (1)	−0.081 (8)	0.236 (4)	0.046 (8)*
HN	0.825 (9)	0.435 (6)	0.068 (3)	0.013 (7)*

* Atoms refined isotropically.

Table 2. *Positional and isotropic displacement parameters for* DM-DPP, *with e.s.d.'s in parentheses*

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
O1	0.4290 (3)	0.7692 (3)	−0.0569 (3)	0.061 (1)
N1	0.5624 (3)	0.8483 (3)	0.0771 (3)	0.027 (1)
C1	0.4751 (4)	0.8528 (3)	−0.0148 (4)	0.024 (1)
C2	0.6005 (4)	0.9549 (3)	0.1096 (4)	0.027 (1)
C3	0.4612 (3)	0.9711 (3)	−0.0392 (4)	0.024 (1)
C4	0.6878 (3)	0.9765 (4)	0.2036 (4)	0.025 (1)
C5	0.7795 (4)	0.9034 (4)	0.2284 (5)	0.035 (1)
C6	0.8579 (4)	0.9280 (5)	0.3221 (5)	0.043 (1)
C7	0.8478 (4)	1.0254 (5)	0.3900 (5)	0.041 (1)
C8	0.7604 (4)	1.1011 (4)	0.3634 (4)	0.035 (1)
C9	0.6805 (4)	1.0772 (4)	0.2703 (4)	0.028 (1)
C10	0.6006 (5)	0.7415 (4)	0.1269 (5)	0.042 (1)
H1	0.794 (5)	0.843 (5)	0.161 (6)	0.038 (9)*
H2	0.928 (5)	0.885 (5)	0.326 (5)	0.042 (9)*
H3	0.895 (4)	1.037 (4)	0.451 (5)	0.025 (8)*
H4	0.752 (4)	1.179 (4)	0.424 (4)	0.029 (9)*
H5	0.613 (5)	1.138 (5)	0.261 (5)	0.035 (9)*
H6	0.562 (4)	0.704 (4)	0.134 (4)	0.032 (9)*
H7	0.694 (4)	0.715 (4)	0.073 (5)	0.039 (9)*
H8	0.593 (3)	0.747 (3)	0.223 (3)	0.013 (8)*

* Atoms refined isotropically.

tively (Pauling, 1960). The C(2)—C(4) distance consequently becomes shorter than the value expected for the carbon–carbon single bond of 1.54 Å (Pauling, 1960). The observed value of 1.455 (5) Å (Table 3) is much shorter, for example, than the value of 1.496 (3) Å found in biphenyl (Charbonneau & Delugeard, 1976). The present bond shortening is presumably caused by well-delocalized π-electrons in the diketopyrrolopyrrole chromophore which give some double-bond character to the C(2)—C(4) bond.

A similar bond shortening also operates in DM-DPP as shown in Table 3. The C(2)—C(4) bond is 1.460 (6) Å. This is slightly longer than in DPP but still much shorter than in biphenyl.

Table 3. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

	DPP	DM-DPP
O1—C1	1.230 (5)	1.226 (5)
N1—C1	1.409 (5)	1.422 (6)
N1—HN	1.00 (3)	
N1—C10		1.460 (6)
N1—C2	1.372 (5)	1.399 (5)
C1—C3	1.442 (5)	1.453 (6)
C2—C3	1.383 (5)	1.371 (6)
C2—C4	1.455 (5)	1.460 (6)
C3—C3	1.422 (5)	1.419 (6)
C4—C5	1.404 (5)	1.409 (6)
C4—C9	1.391 (6)	1.409 (6)
C5—C6	1.397 (6)	1.394 (7)
C5—H1	1.15 (5)	1.05 (6)
C6—C7	1.360 (7)	1.385 (8)
C6—H2	0.92 (5)	0.97 (6)
C7—C8	1.386 (7)	1.396 (7)
C7—H3	1.11 (6)	0.87 (5)
C8—C9	1.394 (6)	1.399 (6)
C8—H4	0.98 (5)	1.15 (5)
C9—H5	0.94 (5)	1.08 (6)
C10—H6		0.64 (4)
C10—H7		1.27 (5)
C10—H8		1.04 (4)
C1—N1—C2	112.1 (3)	111.5 (3)
C1—N1—HN	112 (2)	
C1—N1—C10		120.5 (4)
C2—N1—HN	136 (2)	
C2—N1—C10		127.9 (4)
O1—C1—N1	123.0 (4)	122.7 (3)
O1—C1—C3	132.8 (4)	133.2 (4)
N1—C1—C3	104.2 (4)	104.1 (4)
N1—C2—C3	107.3 (3)	106.7 (3)
N1—C2—C4	121.4 (3)	123.9 (4)
C3—C2—C4	131.4 (4)	129.4 (3)
C1—C3—C2	143.5 (4)	142.3 (4)
C1—C3—C3	107.7 (3)	107.4 (4)
C2—C3—C3	108.8 (3)	110.4 (4)
C2—C4—C5	120.8 (4)	123.4 (4)
C2—C4—C9	118.9 (3)	117.7 (4)
C5—C4—C9	120.3 (4)	118.9 (3)
C4—C5—C6	118.5 (4)	120.2 (5)
C4—C5—H1	123 (3)	115 (3)
C6—C5—H1	117 (3)	123 (3)
C5—C6—C7	121.1 (3)	120.4 (5)
C5—C6—H2	120 (3)	118 (3)
C7—C6—H2	118 (3)	120 (3)
C6—C7—C8	120.5 (5)	120.2 (5)
C6—C7—H3	112 (3)	119 (3)
C8—C7—H3	128 (3)	121 (3)
C7—C8—C9	120.0 (4)	120.0 (4)
C7—C8—H4	122 (3)	119 (3)
C9—C8—H4	118 (3)	121 (3)
C4—C9—C8	119.5 (4)	120.1 (4)
C4—C9—H5	118 (3)	125 (3)
C8—C9—H5	122 (3)	115 (3)
N1—C10—H6		116 (4)
N1—C10—H7		108 (2)
N1—C10—H8		106 (2)
H6—C10—H7		119 (5)
H6—C10—H8		82 (4)
H7—C10—H8		123 (3)

Arrangement of molecules

Fig. 3 and 4 show stereodiagrams of the crystal structures of DPP and DM-DPP, respectively. In DPP, the molecules align in nearly the same plane and are parallel to each other. Along the ⟨110⟩ direction in the molecular plane, there are chains of intermolecular hydrogen bonds between the N—H group of one molecule and the carbonyl oxygen of the neighboring one. There are van der Waals contacts along the *c* axis. In DM-DPP, by contrast, all molecules are arranged in a herringbone fashion along the *c* axis. In each column, molecules face each other alternately, forming a dimeric stacking structure.

The overlap of the two molecules along the stacking axis is shown in Figs. 5(*a*) and 5(*b*) for DPP and DM-DPP, respectively. There is significant overlap between the heterocyclic ring systems in DPP causing π–π interactions [interplanar spacing 3.36 (1) Å]. On the other hand, no such overlap is observed in DM-DPP. Instead, there are π–π contacts between the heterocyclic ring and the phenyl ring.

Hydrogen bonding

In DPP, there are intermolecular hydrogen bonds along the ⟨110⟩ direction. The NH···O angle is 173 (3)° and the distances between O/H, N/H and N/O are 1.82 (3), 1.00 (3) and 2.817 (4) Å, respectively. The hydrogen-bonding atoms lie in the plane of the heterocyclic system.

Intermolecular hydrogen bonding is extremely important for pigments in order to limit solubility. A strong intermolecular NH···O bond is generally linear (to within 10°) on the same axis, and the N/O distance is about 2.8 Å (Pauling, 1960). Hydrogen bonding in DPP satisfies these general conditions well. In fact, DPP is highly insoluble in organic solvents.

Since intermolecular hydrogen bonding is strong in DPP, the molecules are held together firmly so as to arrange themselves along the molecular plane. On the other hand, DM-DPP molecules are mainly associated together by van der Waals forces. Because of this, the molecular arrangement is very different in DPP compared with DM-DPP.

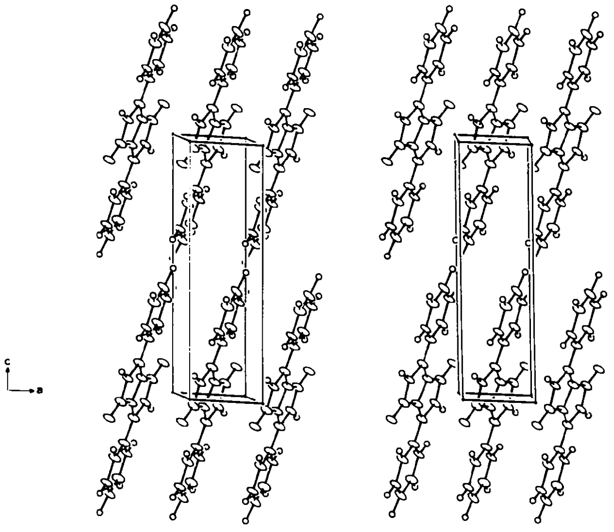


Fig. 3. Stereoview of the crystal structure of DPP (triclinic).

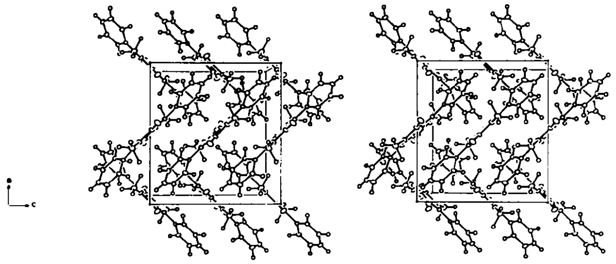
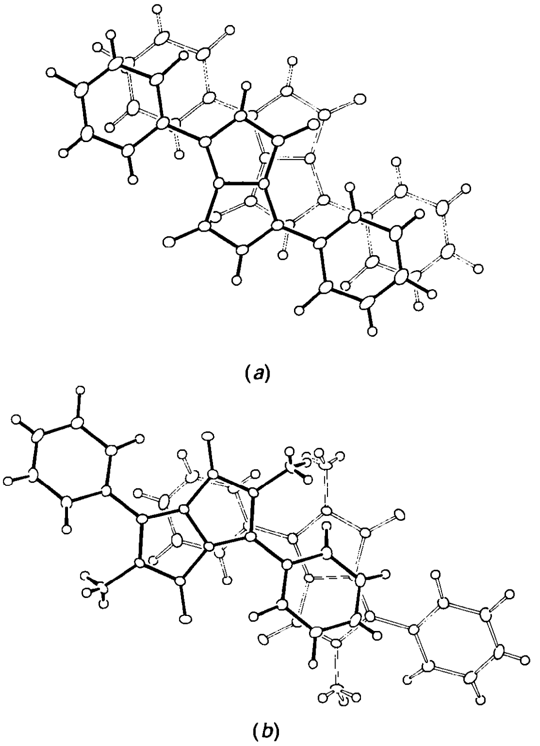


Fig. 4. Stereoview of the crystal structure of DM-DPP (orthorhombic).



(*a*)

(*b*)

Fig. 5. Overlap of the two molecules along the stacking axis: (*a*) DPP and (*b*) DM-DPP.

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Nature of the Hydrogen Bond: Crystallographic *versus* Theoretical Description of the O—H···N(sp^2) Hydrogen Bond

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Abstract

In order to analyze the characteristics of OH···N(sp^2) hydrogen bonds a survey of R—OH···N(sp^2) intermolecular interactions in organic crystals has been performed using the Cambridge Structural Database. Two subfiles of data, one containing 304 hydroxyl groups and the other 120 water molecules as donors, were selected and subjected to statistical analysis. In both sets the highest concentration of hydrogen-bond interactions occurs for almost linear arrangements. The strength of interactions involving R—OH groups depends on R, increasing as follows: C(sp^3) < N < C(sp^2). To complete this study we have carried out SCF calculations on 72 pyridine–water complexes at the 3-21G level. The nature of the hydrogen-bond interaction was also investigated by means of a topological analysis of both the charge density and the Laplacian of the charge density. This analysis revealed not only that charge-transfer interactions are sizeable but that they bear a direct relationship to the stability of the complex. Therefore, either the value of $\nabla^2\rho$ at the points of maximum charge concentration corresponding to the N(sp^2) lone pair, or the charge density at the hydrogen-bond critical point can be used as a suitable index for investigation of the relative stability of these hydrogen-bonded complexes. Our results show that there is fairly good agreement between the most outstanding features of the statistical survey and the SCF results.

Introduction

There is no need to stress the importance of the hydrogen bond in chemistry and in biology (Pimentel & McClellan, 1960; Schuster, Zundel & Sandorfy, 1976; Etter, 1990), and the increasing efforts towards a quantitative description of the hydrogen bond in LFER (linear free-energy relationships) (Taft, Abboud, Kamlet & Abraham, 1985). Nevertheless, different methods consider the hydrogen bond differently. Two of the more extreme pictures arise from classical crystallography (classical to differentiate it from electron density determinations) and from theoretical calculations. From a crystallographic point of view a hydrogen bond is a problem of the geometry of three particles D, H and A (D—H···A), namely the D—A distance and the angle at the hydrogen ($\angle D$HA). From these values, it is possible to conclude whether a hydrogen bond is present or not in a crystal and if it is strong or weak: a strong hydrogen bond is characterized by a short D—A distance and a $\angle D$HA value near 180°. Although not categorically stated as such, this is the definition assumed by Taylor and Kennard (Taylor, 1981; Allen, Kennard & Taylor, 1983; Taylor, Kennard & Versichel, 1983,

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