Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N3	0.95	2.60	2.835 (2)	94
C12—H121···O1	0.90 (2)	2.24 (3)	2.649 (2)	108 (2)
O1—H1···N2^{i}	1.07 (3)	1.66 (3)	2.719 (2)	173 (2)

Symmetry code: (i) $x, 1+y, z$.

All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically, 0.95 Å from their parent atoms; the H atoms of O1 and C12 were refined for a few cycles. For all H atoms except H1, H121 and H122, a riding model was used with $U_{eq}(H) = 1.3U_{eq}(C)$.

Data collection and cell refinement were carried out with *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). *MolEN* (Fair, 1990) was used for data reduction, structure solution, structure refinement, molecular graphics and to prepare material for publication. Hydrogen bonds were calculated with *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1359). Services for accessing these data are described at the back of the journal.

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Tenfold Interpenetration of Giant Hexagonal $R^{12}_{12}(126)$ Nets in the Hydrogen-Bonded Structure of 1,1,1-Tris(4-hydroxyphenyl)ethane–4,4′-Bipyridyl (2/3)

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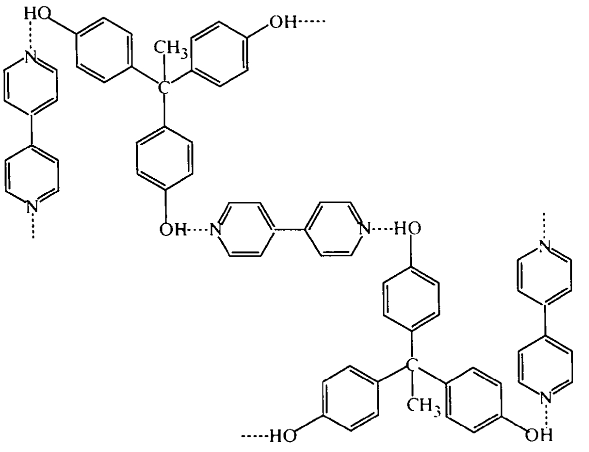
Abstract

In the 2:3 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane [or ethane-1,1,1-triyltris(4-phenol)] and 4,4′-bipyridyl, $2C_{20}H_{18}O_3.3C_{10}H_8N_2$, the components are linked by O—H···N hydrogen bonds [N···O 2.780 (2), 2.745 (2) and 2.731 (2) Å] into puckered two-dimensional nets built from giant hexagons, each involving six units of each component. There are ten such independent nets, all multiply interwoven, within the structure.

Comment

The hydrogen-bonded adducts of 1,3,5-trihydroxybenzene with 4,4′-bipyridyl (Coupar *et al.*, 1996) and with hexamethylenetetramine (Coupar, Glidewell & Ferguson, 1997) have stoichiometry $(triol)_2.(amine)_3$, and in both adducts the structural motif is that of a 'chain-of-rings' (Bernstein *et al.*, 1995). Each ring is formed from two molecules of the triol and two molecules of the amine; these four-component rings are linked into chains by the third amine molecule. In each structure, the triol acts as a triple donor and the amine as a double acceptor of hydrogen bonds, all of which are of the O—H···N type.

In the larger tris-phenol 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$, the hydrogen-bond-donor hydroxy groups are separated by *ca* 9.4 Å in a rather rigid triangle. Thus, in an adduct of this tris-phenol with a diamine such as 4,4′-bipyridyl, in which the hydrogen-bond acceptors are separated by *ca* 7.2 Å at opposite ends of a rigid and effectively linear framework, small-ring formation, as observed in the adducts of 1,3,5-trihydroxybenzene, is precluded by the fixed disposition of the hydrogen-bond donor and acceptor sites in the molecular components. The distance between, and the relative orientation of, the COH groups in the tris-phenol strongly suggests that the preferred structural motif in such an adduct will in fact be a network built from giant hexagons, with tris-phenol molecules at the nodes of the network and 4,4′-bipyridyl molecules along edges of the hexagonal reticulations. By making plausible assumptions about the dimensions of the molecular components and their van der Waals surfaces, it can be calculated that in such a structure the hexagons would, if regular and as nearly planar as possible, have radii of *ca* 20 Å, and that a structure built from just one such network would have a density of no more than *ca* 0.16 g cm^{-3}. Since phenol–amine adducts of this general type typically have densities in the range 1.2–1.4 g cm^{-3} (Coupar, Glidewell & Ferguson, 1997; Ferguson, Coupar & Glidewell, 1997; Ferguson, Bell *et al.*, 1997), the occurrence of multiple networks in the structure, possibly around eight in number, is to be expected. We report here the formation and structure of the adduct 1,1,1-tris(4-hydroxyphenyl)ethane–4,4′-bipyridyl (2/3), (I), which contains ten independent interwoven networks, each built from giant hexagons.



(I)

The asymmetric unit (Fig. 1) consists of one molecule each of the tris-phenol and the bipyridyl lying in general positions, with a further bipyridyl molecule lying across a centre of inversion, thus giving a tris-phenol to bipyridyl ratio of 2:3. These molecular building blocks are connected by hydrogen bonds, with the tris-phenol acting as a triple donor and each type of bipyridyl as a double acceptor; the conventional hydrogen-bonding capacity is thus fully utilized by the exclusive formation of O—H···N hydrogen bonds. Although the hydrogen-bonding scheme appears to be simple, with just three types of O—H···N hydrogen bond (Table 2), the large sizes of the molecular components combined with the many symmetry elements of the space group generate a structure of some complexity.

Within the asymmetric unit, the O1 atom acts as a hydrogen-bond donor to atom N44. Atom O2 in the unit at (x, y, z) acts as donor to atom N54 in the unit at ($\frac{1}{2}+x$, $-\frac{3}{2}-y$, $\frac{1}{2}+z$), while O2 in this latter unit acts as donor to N54 in the unit at ($1+x$, y, $1+z$), so generating a chain in the [101] direction, produced by the action of the *n* glide plane at $y = -\frac{3}{4}$. The unitary- and binary-level graph sets for this chain are *DD* and $C_2^2(21)$ (Etter, 1990; Bernstein *et al.*, 1995). Atom O3 in the unit at (x, y, z) acts as hydrogen-bond donor to atom N64, and the symmetry-related N atom in the same bipyridyl unit, at ($1-x$, $1-y$, $1-z$), accepts a hydrogen bond from atom O3 in the tris-phenol molecule at ($1-x$, $1-y$, $1-z$). Atom O2 at ($1-x$, $1-y$, $1-z$) acts as donor to N54 in the bipyridyl at ($\frac{1}{2}-x$, $\frac{5}{2}+y$, $\frac{1}{2}-z$), and N44 in this bipyridyl unit is a hydrogen-bond acceptor from atom O1 in the triol of the same unit. The O3 atom at ($\frac{1}{2}-x$, $\frac{5}{2}+y$, $\frac{1}{2}-z$) acts as donor to N64 in the same unit, while the symmetry-related N atom in the same bipyridyl molecule, at ($-\frac{1}{2}+x$, $\frac{7}{2}-y$, $-\frac{3}{2}+z$), acts as acceptor from atom O3 in the tris-phenol molecule also at ($-\frac{1}{2}+x$, $\frac{7}{2}-y$, $-\frac{3}{2}+z$). Finally, O2 in this last tris-phenol acts as hydrogen-bond donor to atom N54 at (x, $5+y$, z), thus completing a chain in the **b** direction, with unitary- and binary-level graph sets *DD* and $C_4^4(42)$, the repeat unit of which spans five unit cells. There are thus

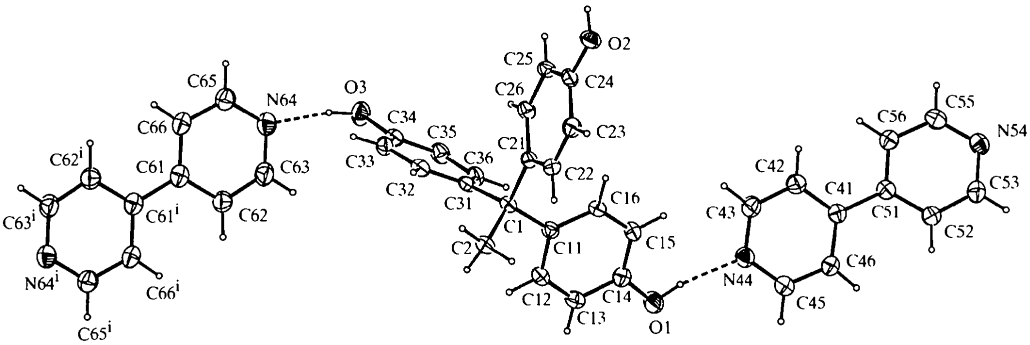


Fig. 1. A view of the three-component molecular aggregate in (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $1-x$, $1-y$, $1-z$.]

five independent chain units based upon the asymmetric units at (x, $n+y$, z) for n = 0–4; the overall repeat motif over five cells is described by the graph set $C_8^8(84)$.

The two types of chain, along **b** and along the [101] direction, intersect at each tris-phenol unit to form continuous nets built from giant hexagonal $R_{12}^{12}(126)$ rings (Fig. 2), each involving six tris-phenol units at the nodes and six bipyridyl units along the edges. The approximate maximum internal dimensions of these hexagons are 30 × 40 Å. Each net utilizes 0.8 tris-phenol and 1.2 bipyridyl molecules per unit cell, so that this set of nets utilizes only half the contents of the unit cell, namely the units at (x, y, z), ($-x$, $-y$, $-z$), ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) and ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$). These in isolation would define the space group $P2_1/n$, a subgroup of the observed space group $C2/c$. A second, entirely independent, set of five nets is generated by the other half of the unit-cell contents [the units at ($\frac{1}{2}+x$, $\frac{1}{2}+y$, z), (x, $-y$, $\frac{1}{2}+z$), ($-x$, y, $\frac{1}{2}-z$) and ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$)] and is related to the first set by the action of the twofold axes.

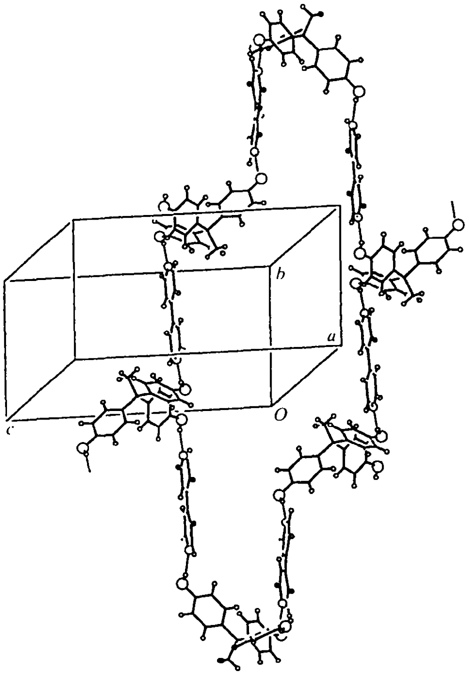


Fig. 2. A view of one of the giant hexagonal nets, viewed approximately normal to ($10\bar{1}$).

Inspection of a projection, along the [101] direction, of the fivefold set of nets generated by the translations along the **b** direction showed that these are all interwoven; furthermore, this set of nets is also interwoven with a second fivefold set of nets generated from the first set by the twofold axis at (0, y, $\frac{1}{4}$), so generating tenfold interwoven sheets parallel to ($10\bar{1}$). Between neighbouring multiple sheets, however, there are only van der Waals contacts. The tenfold interweaving of $R_{12}^{12}(126)$ nets in compound (I) may be contrasted with the twofold interweaving of square $R_4^4(32)$ nets in 4,4′-sulfonyldiphenol (Glidewell & Ferguson, 1996) and of hexagonal $R_6^6(48)$ nets in the 1:1 adduct of 1,1,1-tris(4-hydroxyphenyl)-ethane with hexamethylenetetramine (Coupar, Ferguson & Glidewell, 1997), and with the threefold interweaving in a 2:3 adduct of trimesic acid and 4,4′-bipyridyl (Sharma & Zaworotko, 1996), in all of which the interweaving produces two-dimensional structures, as well as with the interwoven three-dimensional networks in the 4:3 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane with piperazine (Ferguson, Bell *et al.*, 1997). Other multiply interwoven three-dimensional networks, which depend upon the cooperative effects of multiple hydrogen bonds, occur in methanetetraacetic acid (Ermer & Eling, 1988), adamantane tetracarboxylic acid (Ermer, 1988) and trimesic acid (Duchamp & Marsh, 1969), as well as in some tetrakis(2-pyridone) derivatives and their clathrates with carboxylic acids (Simard *et al.*, 1991; Wang *et al.*, 1994).

The tris-phenol component could, in principle, adopt a skeletal conformation of C_3 symmetry; in the event, this component does not exhibit even approximate symmetry, as judged by the C2—C1—Cn1—Cn2 (n = 1, 2, 3) torsion angles (Table 1). In the centrosymmetric bipyridyl molecule (that containing N64), the two rings are necessarily parallel, although not exactly coplanar: these rings are stepped by 0.0094 (15) Å. However, in the other bipyridyl molecule, the twist angle between the rings is quite substantial [24.3 (1)°]; a similar variation was observed among the conformations of the three crystallographically independent 4,4′-bipyridyl units in the adduct with 1,3,5-trihydroxybenzene (Coupar *et al.*, 1996). As in the 1,3,5-trihydroxybenzene adduct, none of the inter-ring C· · ·C or C· · ·N distances in compound (I) is significantly less than the sum of the van der Waals radii. The bond distances are all typical of their types.

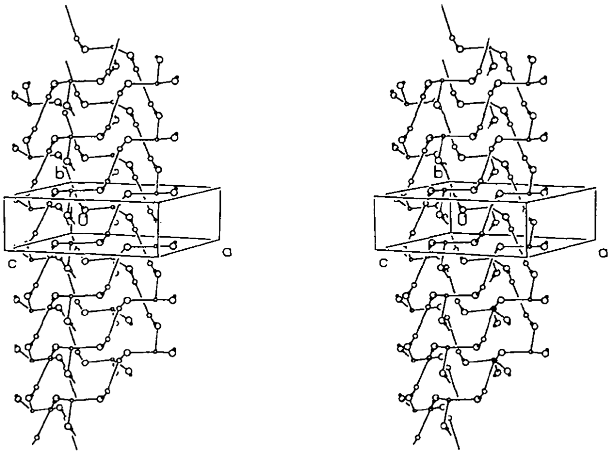


Fig. 3. Stereoview of the fivefold set of nets generated by translation along [010]; for the sake of clarity, the second set generated by the action of the twofold axis has been omitted.

Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the structure.

Experimental

1,1,1-Tris(4-hydroxyphenyl)ethane (1.53 g, 5.0 mmol) and 4,4′-bipyridyl (0.78 g, 5.0 mmol) were dissolved separately in ethanol (50 ml). The solutions were mixed and then set aside to crystallize, yielding analytically pure compound (I). Analysis: found C 77.8, H 5.4, N 7.8%; $C_{70}H_{60}N_6O_6$ requires C 77.8, H 5.6, N 7.8%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$2C_{20}H_{18}O_3.3C_{10}H_8N_2$
$M_r = 1081.28$
Monoclinic
$C2/c$
$a = 29.1351$ (9) Å
$b = 10.4189$ (2) Å
$c = 20.0512$ (6) Å
$\beta = 116.766$ (1)°
$V = 5434.5$ (3) Å^3
$Z = 4$
$D_x = 1.322$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 23 347 reflections
$\theta = 2.82$–$26.30°$
$\mu = 0.085$ mm^{-1}
$T = 130$ (1) K
Lath
0.30 × 0.15 × 0.06 mm
Colourless

Data collection

Nonius Kappa-CCD diffractometer
ω scans
Absorption correction: none
23 347 measured reflections
5498 independent reflections

3879 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.068$ (all reflections)
$\theta_{\rm max} = 26.30°$
$h = 0 \rightarrow 36$
$k = 0 \rightarrow 12$
$l = -25 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.108$
$S = 0.938$
5498 reflections
378 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$

$\Delta\rho_{\rm max} = 0.239$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.290$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient: 0.0019 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C14	1.3583 (18)	C43—N44	1.3415 (19)
O2—C24	1.3676 (17)	N44—C45	1.335 (2)
O3—C34	1.3674 (19)	C53—N54	1.3398 (19)
C1—C11	1.535 (2)	N54—C55	1.335 (2)
C1—C31	1.540 (2)	C61—C61$^{\rm i}$	1.493 (3)
C1—C21	1.5441 (19)	C63—N64	1.333 (2)
C1—C2	1.5547 (18)	N64—C65	1.336 (2)
C41—C51	1.4865 (19)		
O1—C14—C13	116.92 (13)	O3—C34—C35	118.82 (14)
O1—C14—C15	124.91 (13)	C43—N44—C45	116.26 (13)
O2—C24—C23	117.94 (14)	C53—N54—C55	116.41 (13)
O2—C24—C25	122.88 (13)	C63—N64—C65	116.42 (13)
O3—C34—C33	122.51 (14)		
C2—C1—C11—C12	49.18 (18)	C2—C1—C31—C32	48.40 (17)
C2—C1—C21—C22	36.39 (18)		

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N44	0.86 (2)	1.94 (2)	2.780 (2)	166.1 (13)
O2—H2···N54$^{\rm i}$	0.92 (2)	1.85 (2)	2.745 (2)	164.9 (12)
O3—H3···N64	0.93 (2)	1.81 (2)	2.731 (2)	168.0 (17)

Symmetry code: (i) $\frac{1}{2} + x, -\frac{3}{2} - y, \frac{1}{2} + z$.

Compound (I) crystallized in the monoclinic system; space group *C*2/*c* or *Cc* was indicated by the systematic absences. *C*2/*c* was assumed and confirmed by the analysis. Preliminary studies were made using a Rigaku AFC-7*S* diffractometer and room-temperature measurements. These allowed the structure (gross connectivity) to be determined but only gave some 25% of the data as 'observed' at the 2σ level. Full three-dimensional data were then recollected at 130 K using a Kappa-CCD diffractometer (Nonius, 1997*a*) and measurements (60 s) of 205 frames in 1° steps from a crystal in a random orientation gave an abundance of data. Measurements of equivalent reflections showed that there was no decay during the data collection. The final cell data were refined using the θ values of all 23 347 measurements. All H atoms were clearly visible in difference maps at intermediate stages of the analysis; those bonded to C were treated as riding atoms (C—H 0.93–0.96 Å). There was no evidence at all for transfer of a hydroxy H atom to a bipyridyl N atom and the three hydroxy H atoms were treated using an algorithm to keep the C—O—H angle at a tetrahedral value, but allow the O—H distance to refine.

Data collection: *Kappa-CCD Control Software* (Nonius, 1997*a*). Cell refinement: *DENZO* (Nonius, 1997*b*). Data reduction: *DENZO*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *NRCVAX*96 (Gabe *et al.*, 1989) and *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1190). Services for accessing these data are described at the back of the journal.

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1,8-Bis(2-thienyl)-1,3,5,7-octatetrayne

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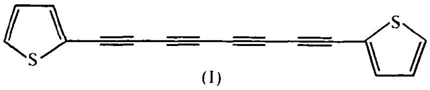
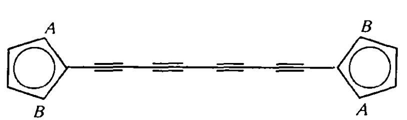
Abstract

Although the title compound, $C_{16}H_6S_2$, has parallel stacking of the molecules along the *c* axis, and the intermolecular distances between the C atoms of the triple bonds are within the required distance of 4.0 Å, these atoms are not positioned to form a 1,4-addition polymer. The thiophene rings are disordered over two different orientations, with 87:13 relative occupancies. The molecule has $\bar{1}$ symmetry.

Comment

Diacetylenes are known to undergo solid-state 1,4-addition polymerization upon thermal, UV or γ irradiation, to give polydiacetylenes (PDA; Wegner, 1972; Bloor & Chance, 1985). The reaction is a topochemical one, and in a few cases, a single-crystal monomer to single-crystal polymer transformation can be achieved (Wegner, 1972). The quasi-one-dimensional π-conjugation of PDA has attracted attention in the field of third-order non-linear optics. With the aim of preparing a third-order non-linear optical material with enhanced π-conjugation, we prepared 1,8-bis(2-thienyl)-1,3,5,7-octatetrayne, (I) (Sarkar *et al.*, 1998). Like diacetylenes, the tetraynes are also expected to polymerize topochemically. However, crystal packing plays a vital role in determining the reactivity of the monomer. The stacking angle, ϕ, and contact distance, *d*, need to be in a particular range (*ca* 45° and *ca* 5 Å, respectively) for the monomer to undergo 1,4-addition polymerization (Baughman, 1974; Wegner, 1977; Bloor, 1982). The side groups, *R* and *R'*, have a profound influence on the crystal packing, *via* steric and electronic effects. Therefore, it is of the utmost importance to investigate the effect of the side groups on the crystal packing. Here we report the crystal structure of the title compound, (I), which is unreactive towards topochemical polymerization under normal conditions, although at elevated temperatures it reacts in the solid state.


(I)



(II)

The distance between S1 and C5 [1.706 (2) Å] is perhaps different from that of S1—C2 [1.697 (2) Å], but they both still compare well with C—S bond lengths in thiophene (1.712 Å). However, these values for the S—C bond lengths are uncertain because the thiophene ring was found to be disordered over different orientations, as shown in structure (II) above. Approximately 87% of the S atom occupies position *A*, while the remaining 13% occupies position *B*. In turn, the occupancy of the C atom at position *B* is about 87%, while the remaining 13% is at position *A*. As a result, the bond