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(1*RS*,2*SR*,3*RS*,5*SR*)-2-Benzoyl-4,4-dicyano-1,3,5-triphenylcyclohexanol at 120 K: complex sheets built from C—H···O and C—H···N hydrogen bonds

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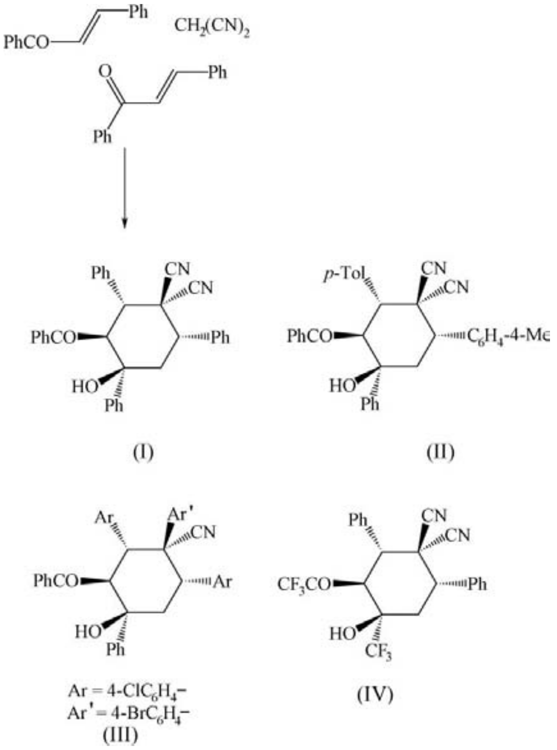
At 120 K, the title compound [systematic name: (2*RS*,3*SR*,4*RS*,6*SR*)-3-benzoyl-4-hydroxy-2,4,6-triphenylcyclohexane-1,1-dicarbonitrile], $C_{33}H_{26}N_2O_2$, has unit-cell dimensions apparently different from those reported at 294 K [Rong, Li, Yang, Wang & Shi (2006). *Acta Cryst.* E**62**, o1766–o1767]. The molecules are linked by two C—H···O hydrogen bonds and three C—H···N hydrogen bonds into complex sheets, and the hydrogen-bonded structures at the two temperatures are the same, although incorrectly described in the earlier report. The significance of the present study lies in its correct description of the hydrogen bonding and in its analysis of the unit-cell dimensions; the differences between the cell angles at 120 and 294 K arise from the fact that one such angle in the triclinic cell is extremely close to 90° so that a very small change in this angle can induce significant changes in the reduced cell.

Comment

As part of a programme for the synthesis of highly substituted hydropyridone derivatives as potential bioactive compounds, we have considered the use, as a synthetic intermediate, of the Michael adduct obtained from malononitrile and 1,3-diphenylprop-2-en-1-one (chalcone). However, we have now found that under basic conditions this reaction provides not the expected simple adduct (López *et al.*, 2001) but instead a mixture of compounds (Victory *et al.*, 1991), from which the title compound, (I), was obtained in crystalline form. We report here the molecular and crystal structures of (I) (Fig. 1) at 120 K.

The structure of (I) has been reported using diffraction data collected at 294 K (Rong *et al.*, 2006), but the unit cell reported by these authors [a = 10.996 (2) Å, b = 12.017 (2) Å, c = 12.109 (2) Å, α = 89.950 (4)°, β = 67.150 (3)° and γ = 67.821 (3)°] appears to differ significantly from that found here. While the repeat vectors are very similar, the reduced unit-cell angles at 294 K are all close to the supplementary values of the reduced angles at 120 K, *i.e.* each reduced angle θ



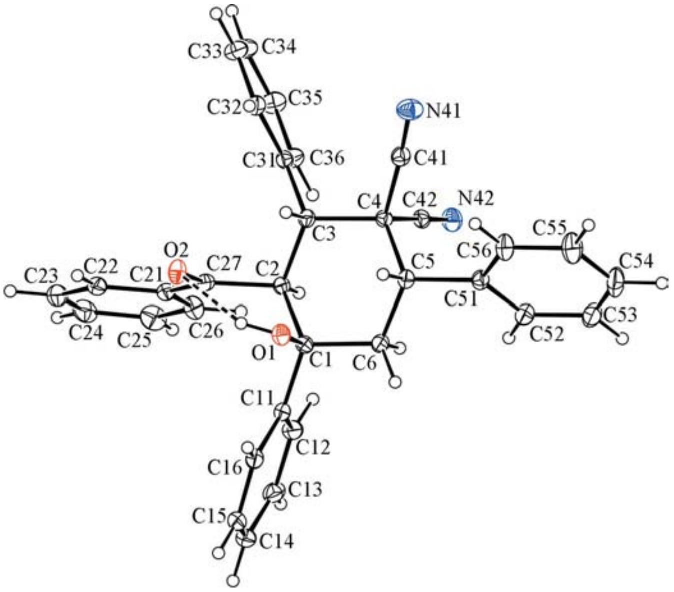


Figure 1
The 1*R*,2*S*,3*R*,5*S* isomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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($\theta = \alpha$, β or γ) at 294 K corresponds closely to ($180^\circ - \theta$) at 120 K, with a maximum difference of *ca* 0.57° occurring in the angles γ; the corresponding atomic coordinates at the two temperatures are very precisely related by the transformation ($1 - x, y, z$). Furthermore, the crystal structure was described as a three-dimensional array of C—H···O and C—H···N hydrogen bonds (Rong *et al.*, 2006), whereas at 120 K we find that the hydrogen-bonded structure is two-dimensional. We first describe the structure at 120 K and shall return below to both these points concerning the structure reported at 294 K.

The cyclohexane ring in (I) adopts the usual chair conformation, and the benzoyl and the three phenyl substituents all occupy equatorial sites, so that the hydroxy substituent necessarily occupies an axial site. There are four stereogenic centres and the configuration in the selected asymmetric unit is 1*R*,2*S*,3*R*,5*S*; since the compound crystallizes in a centrosymmetric space group, the overall configuration for the racemic mixture can be described as 1*RS*,2*SR*,3*RS*,5*SR*. The bond lengths and angles present no unusual features.

There is an intramolecular O—H···O hydrogen bond (Table 1), and the molecules are linked into complex sheets by a combination of three C—H···N hydrogen bonds and two C—H···O hydrogen bonds. The sheet formation is readily analysed in terms of two one-dimensional substructures, one of which utilizes just one hydrogen bond, while the other utilizes four hydrogen bonds. In the simpler of the two substructures, atom C24 in the benzoyl group of the molecule at (x, y, z) acts as a hydrogen-bond donor to atom N41 in the equatorial cyano substituent of the molecule at ($-1 + x, y, -1 + z$); in this way a *C*(11) (Bernstein *et al.*, 1995) chain is generated by translation along the [101] direction (Fig. 2).

The second and more complex of the one-dimensional substructures is built from two C—H···O and two C—H···N hydrogen bonds. Aryl atoms C32 and C56 in the molecule at (x, y, z) act as donors, respectively, to atoms O1 and O2, both in the molecule at ($1 - x, 1 - y, 1 - z$). Within the resulting dimeric unit the two hydrogen bonds acting independently generate centrosymmetric $R_2^2(14)$ and $R_2^2(18)$ rings, respectively, while their combination generates a noncentrosymmetric $R_2^2(14)$ motif. In addition, aryl atoms C12 and C26 in the molecule at (x, y, z) both act as hydrogen-bond donors to the axial cyano atom N42 in the molecule at ($1 - x, 2 - y, 1 - z$); in combination, these interactions generate an $R_2^1(10)$ motif, while individually, each independently generates a centrosymmetric $R_2^2(18)$ ring. The combination of these four hydrogen bonds then generates a complex chain of rings running parallel to the [010] direction, with the centrosymmetric rings built from C—H···O hydrogen bonds and centred at ($\frac{1}{2}, \frac{1}{2} + n, \frac{1}{2}$) (where *n* represents zero or an integer) alternating with the corresponding rings built from C—H···N hydrogen bonds and centred at ($\frac{1}{2}, n, \frac{1}{2}$) (where *n* represents zero or an integer) (Fig. 3). The combination of the chains along [010] and [101] generates a complex sheet lying parallel

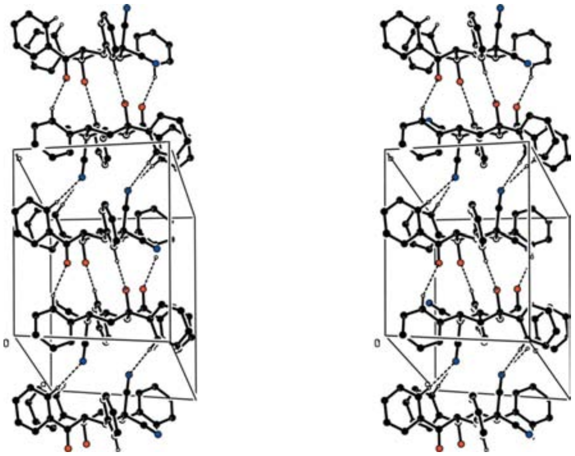

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain of rings along [010]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

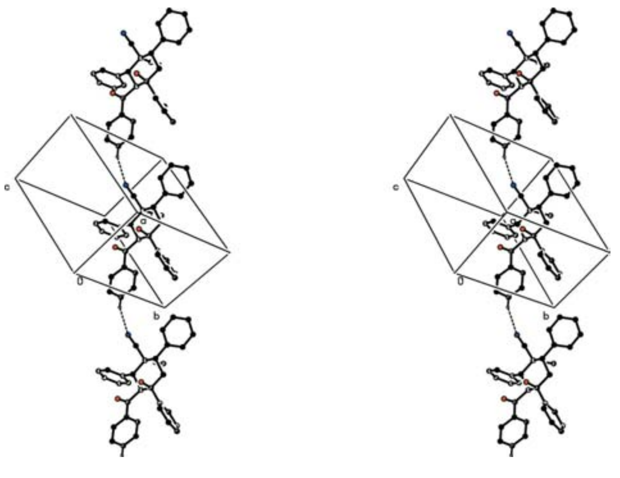

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded *C*(11) chain along [101]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

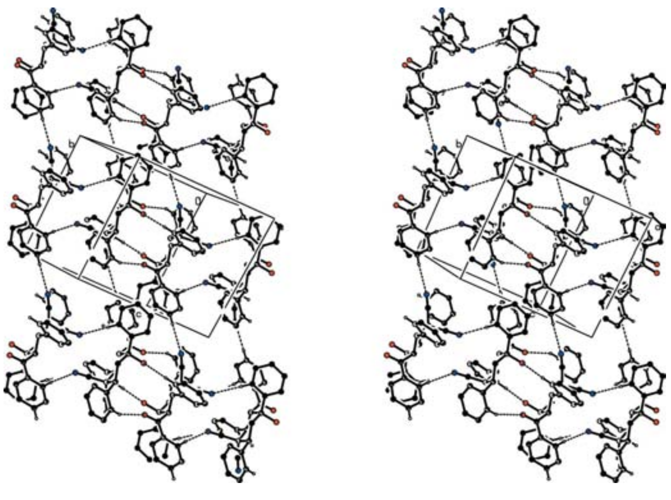

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet parallel to (10$\bar{1}$). For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

to ($10\overline{1}$) (Fig. 4). The only direction-specific interaction linking the adjacent sheets is a single C—H$\cdots\pi$(arene) interaction (Table 1).

As expected, the repeat vectors reported at 294 K (Rong *et al.*, 2006) are greater than those found here at 120 K, with the maximum difference of 0.240 (3) Å (*ca* 2%) occurring in the vector **b**. Similarly, for the unit-cell angles the magnitudes of the differences between θ at 294 K and (180° − θ) at 120 K range from 0.234 (9)° in β to 0.57 (2)° in γ. However, at both temperatures the cell angle α is very close to 90° and the angle reported at 294 K is 89.950 (4)°. If this value is artificially set to be 90.050 (4)°, then the resulting reduced cell has values of β and γ corresponding almost exactly to those found at 120 K. Hence, the apparently substantial differences between the unit-cell dimensions at 120 and 294 K are most plausibly explained as a consequence of a small change in the angle α from one side of 90° to the other, resulting in a change in the reduced cell angles and a concomitant change in the atom coordinates. It has been suggested, although without formal proof (Andrews *et al.*, 1980), that the combination of reduced cell lengths in real and reciprocal spaces together with the reduced cell volume provides a unique description of a crystal lattice. Accordingly, the use of this set of parameters enables comparison of lattices or of unit cells without reference to the cell angles. This proposal was developed specifically in response to the large and discontinuous jumps in the unit-cell angles that can occur when there are only very small changes in the overall lattice, exactly as in the example described here.

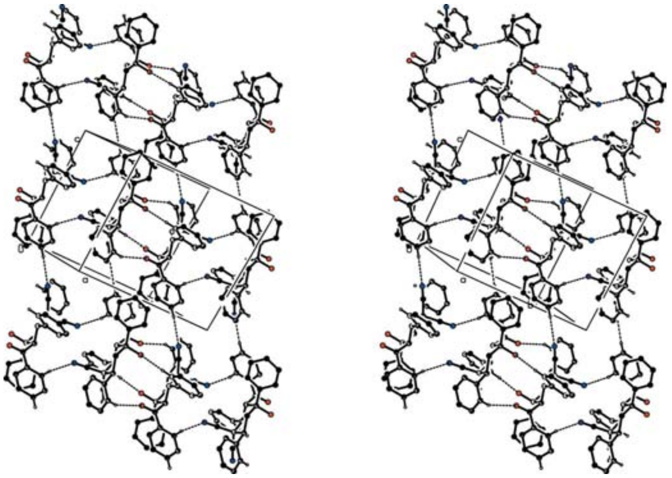

Figure 5
A stereoview of part of the crystal structure of (I) at 294 K, using the atomic coordinates of Rong *et al.* (2006), showing the formation of a hydrogen-bonded sheet parallel to (101). Note the different orientation of the unit cell in comparison with that in Fig. 4. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

The overall hydrogen-bonded structures are the same at the two temperatures. Although Rong *et al.* (2006) described their hydrogen-bonded structure as three-dimensional, an analysis based on the hydrogen bonds found at 294 K shows clearly that the structure is two-dimensional, exactly as at 120 K (Fig. 5). The packing diagram presented in the earlier report (Rong *et al.*, 2006) in fact shows a centrosymmetric aggregate of four molecules, those at (x, y, z), ($-1 + x$, y, $1 + z$), ($1 - x$, $1 - y$, $1 - z$) and ($2 - x$, $1 - y$, $-z$), which does not illustrate a repeating unit even in one dimension, far less the three-dimensional network postulated.

An interesting comparison can be made with the 3,5-bis(4-methylphenyl) analogue (II) [Cambridge Structural Database (CSD; Allen, 2002) refcode JEVYEO (Al-Arab, 1990)], which also crystallizes in the space group $P\overline{1}$. The unit-cell angles for (II) are rather similar to those reported for (I) at 294 K, except that now it is the cell angle γ = 89.46 (2)° which is very close to 90°, while the atomic coordinates can be related to those reported here for corresponding atoms by the transformation ($\frac{1}{2} - z$, y, x). The **a** and **b** unit-cell vectors reported for (II) at 130 K are almost identical to the values of **b** and **c**, respectively, found here for (I) at 120 K, but there has been a reordering of the repeat vectors, thus (**cab**). This, and the

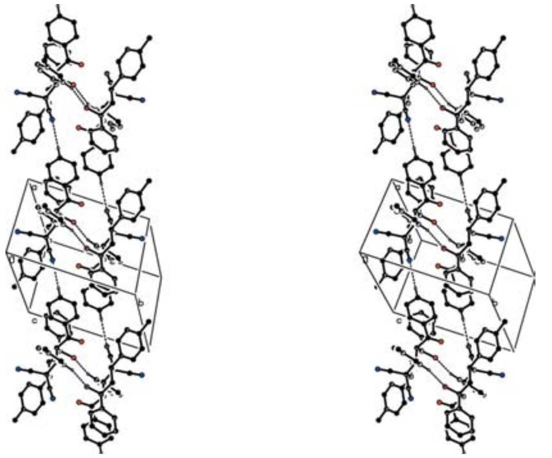

Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain of alternating $R_2^2(14)$ and $R_4^4(36)$ rings. The original atom coordinates (Al-Arab, 1990) have been used and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

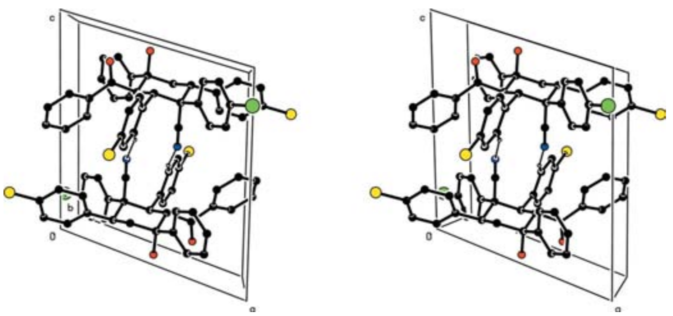

Figure 7
A stereoview of part of the crystal structure of (III), showing the formation of a hydrogen-bonded dimer containing an $R_2^2(14)$ ring. The original atom coordinates (Al-Arab *et al.*, 1992) have been used and, for the sake of clarity, H atoms not involved in the motif shown have been omitted, along with the solvent molecules.

interchange of the x and z coordinates, results from the slight 'stretching' of the crystal structure, predominantly in one direction, which is a consequence of the introduction of methyl groups into two of the aryl rings. As a result of this stretching of the structure of (II) as compared with that of (I), only two of the intermolecular contacts found in (I) are still within effective hydrogen-bonding distances in (II), one each of the C—H···O and C—H···N types. These form, respectively, a centrosymmetric $R_2^2(14)$ ring and a $C(11)$ chain generated by translation, exactly analogous to the corresponding motifs in (I). In combination, these two hydrogen bonds link the molecules of (II) into a chain of alternating centrosymmetric $R_2^2(14)$ and $R_4^4(36)$ rings (Fig. 6).

In the more heavily substituted analogue (III) [CSD refcode PEHYUW (Al-Arab *et al.*, 1992)], which crystallizes in $P\overline{1}$ as a stoichiometric acetic acid solvate with the cyano group occupying an axial site, the molecules of the cyclohexanol component are linked by paired C—H···N hydrogen bonds into a centrosymmetric $R_2^2(14)$ dimer (Fig. 7), while the acetic acid component independently forms the usual $R_2^2(8)$ dimer. The structure of the trifluoromethyl derivative (IV) has been reported [CSD code NAVZAL (Sanin *et al.*, 1997)], but no H-atom coordinates are deposited in the CSD, so that useful discussion of the intermolecular aggregation is not possible.

Experimental

Sodium methoxide (1.44 mmol) was added to a mixture of malononitrile (1.44 mmol) and 1,3-diphenylprop-2-en-1-one (chalcone, 1.44 mmol) dissolved in methanol (20 ml), and the reaction mixture was then stirred at ambient temperature for 6 h. The mixture was neutralized with 10% aqueous acetic acid solution and then evaporated to dryness under reduced pressure. The resulting solid product was recrystallized from aqueous methanol to give (I) in 38% yield as colourless crystals suitable for single-crystal X-ray diffraction.

Crystal data

$C_{33}H_{26}N_2O_2$
$M_r = 482.56$
Triclinic, $P\overline{1}$
$a = 10.9251\ (18)$ Å
$b = 11.777\ (3)$ Å
$c = 11.9438\ (12)$ Å
$\alpha = 90.417\ (13)°$
$\beta = 112.616\ (9)°$
$\gamma = 112.750\ (14)°$
$V = 1286.1\ (5)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 120\ (2)$ K
$0.59 \times 0.47 \times 0.35$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.946$, $T_{\max} = 0.973$
33243 measured reflections
5800 independent reflections
3387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.086$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.128$
$S = 1.04$
5800 reflections
334 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

Cg represents the centroid of the C11–C16 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.84	1.97	2.702 (2)	145
C12—H12···N42$^{\rm i}$	0.95	2.59	3.536 (3)	177
C24—H24···N41$^{\rm ii}$	0.95	2.56	3.449 (3)	157
C26—H26···N42$^{\rm i}$	0.95	2.51	3.451 (3)	171
C32—H32···O1$^{\rm iii}$	0.95	2.42	3.325 (3)	159
C56—H56···O2$^{\rm iii}$	0.95	2.48	3.379 (3)	157
C54—H54···$Cg^{\rm iv}$	0.95	2.85	3.690 (3)	148

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x-1, y, z-1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+2, -y+2, -z+1$.

Crystals of (I) are triclinic; the space group $P\overline{1}$ was selected and confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.99 (CH_2) or 1.00 Å (aliphatic C—H) and O—H distances of 0.84 Å, and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(O).

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3114). Services for accessing these data are described at the back of the journal.

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