organic compounds

Apparent shortening of the Csp^3–Csp^3 bond analysed via a variable-temperature X-ray diffraction study in racemic 1,1′-binaphthalene-2,2′-diyl diethyl bis(carbonate)

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Crystal structure determination at room temperature [292 (2) K] of racemic 1,1′-binaphthalene-2,2′-diyl diethyl bis(carbonate), $C_{26}H_{22}O_6$, showed that one of the terminal carbon–carbon bond lengths is very short [Csp^3–Csp^3 = 1.327 (6) Å]. The reason for such a short bond length has been analysed by collecting data sets on the same crystal at 393, 150 and 90 K. The values of the corrected bond lengths clearly suggest that the shortening is mainly due to positional disorder at two sites, with minor perturbations arising as a result of thermal vibrations. The positional disorder has been resolved in the analysis of the 90 K data following the changes in the unit-cell parameters for the data sets at 150 and 90 K, which appear to be an artifact of a near centre of symmetry relationship between the two independent molecules in the space group $P\bar{1}$ at these temperatures. Indeed, the unit cell at low temperature (150 and 90 K) is a supercell of the room-temperature unit cell.

Comment

The appearance of a short carbon–carbon bond is often encountered in crystal structure determinations and is explained either as a consequence of thermal effects or as a structural disorder of some kind; theoretical calculations support both these observations. In crystal structures, long and short bonds have been treated as a consequence of rotational oscillations of molecules in crystals, as proposed by Cruickshank (1956). Dunitz (1999) has observed that 'the discrepancy between the 'curiously short' carbon–carbon double bond distance in 3-ethynylcyclopropene, as measured experimentally by X-ray analysis [1.255 (2) Å], compared with the value derived from high level *ab initio* calculations (*ca* 1.28 Å), is largely due to neglect of corrections for molecular motion in

the crystal'. It was suggested that THMA (thermal motion analysis; Dunitz, Maverick & Trueblood, 1988; Dunitz, Shomaker & Trueblood, 1988; Dunitz, 1995) clearly brings out the importance of thermal corrections between the X-ray distances and theoretically computed values. On the other hand, the shortening of the bond has been explained as either due to ring strain (Xie & Schaffer, 1989; Ermer & Lex, 1987) or owing to special electronic effects (Ermer et al., 1989; Allen, 1980, 1981; Hagen et al., 1972; Traetteberg et al., 1984; Irngartinger et al., 1984). It has been argued that hybridization alone is not the cause for short C—C bonds; indeed, symmetry and geometrical constraints play a significant role (Huntley et al., 2005). We have observed a very short Csp^3—Csp^3 bond length of 1.327 (6) Å in one of the terminal ethyl groups of racemic 1,1′-binaphthalene-2,2′-diyl diethyl bis(carbonate), (I), at room temperature.
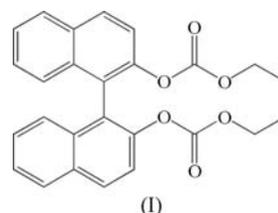
In this structure, there are no strains involved and no significant electronic effects in the molecule. One would expect that analysis of the structure determined at different temperatures (in this case at 393, 150 and 90 K) for the same crystal should reveal whether the shortening is due either entirely to thermal effects or to positional disorder. Bond-length corrections for thermal effects were applied on the basis of a THMA (Dunitz, Maverick & Trueblood, 1988; Dunitz, Shomaker & Trueblood, 1988; Dunitz, 1995) analysis before comparisons of variations in bond lengths. It is of interest to note that the unit cell at 150 K is a supercell of that observed at 292 K, and this feature, as shown in Fig. 1, explains the near doubling of the unit-cell volume observed at lower temperatures (150 and 90 K). The transformation matrix is ($\bar{1}$10, $\bar{1}$01, 011).

At 292 K, the compound crystallizes in the space group $P\bar{1}$ with Z = 2. Fig. 2 shows the molecular structure with the atom
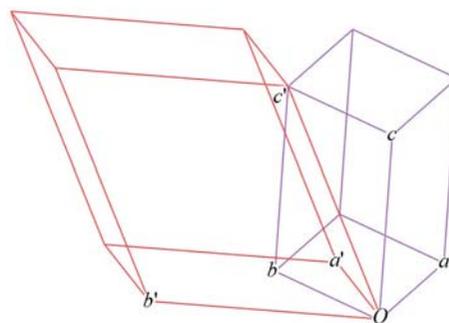

Figure 1
Diagram showing the supercell at 90 K, with unit-cell parameters defined as a', b' and c', along with the subcell at 292 K, defined with cell parameters a, b and c, with respect to a common origin (0, 0, 0).
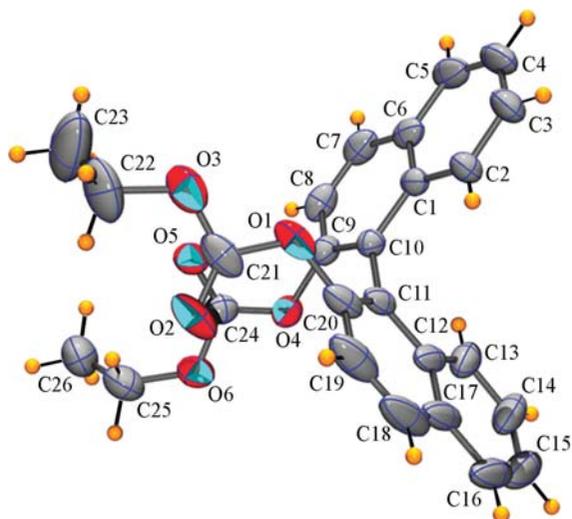
Figure 2
The molecular structure at 292 K, shown with 30% probability displacement ellipsoids.

Figure 3
The packing of molecules at 292 K in the unit cell, shown in the same orientation as the resulting supercell at low temperature.

numbering. All displacement ellipsoids are large and, in particular, those associated with the short-bond atoms C22 and C23 are very large. Thermal motion analysis using the program *THMA* (Dunitz, Maverick & Trueblood, 1988; Dunitz, Shomaker & Trueblood, 1988; Dunitz, 1995) was used to obtain corrected bond lengths for all bonds; however, the C22—C23 bond continues to be exceptionally short [1.327 (6) Å]. From a search of the Cambridge Structural Database (Version 5.29 of 2008; Allen, 2002), this is one of a number of short single C—C bonds found in the literature for a molecule of this type, *i.e.* one in which there is either no highly strained ring or no electronic effect due to conjugation.
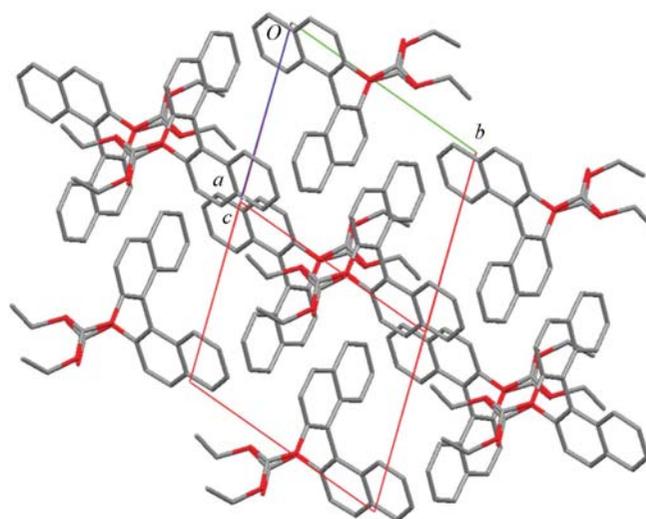
Fig. 3 is a packing diagram, with the orientation of the unit cell and hence its contents similar to that of the resulting supercell at low temperatures to ensure easy comparison. The packing in the lattice is mainly through weak interactions involving an intermolecular π–π [3.880 (2) Å] stacking interaction between the centroids of the C12–C17 rings at (x, y, z) and $(-x + 2, -y, -z)$.

At 393 K, the cell parameters and the packing of the molecules in the unit cell are similar to those at room temperature. However, the displacement parameters of all atoms show the expected increase, and in particular those of both C22 and C23 are remarkably enhanced (Fig. 1S, supplementary material). It
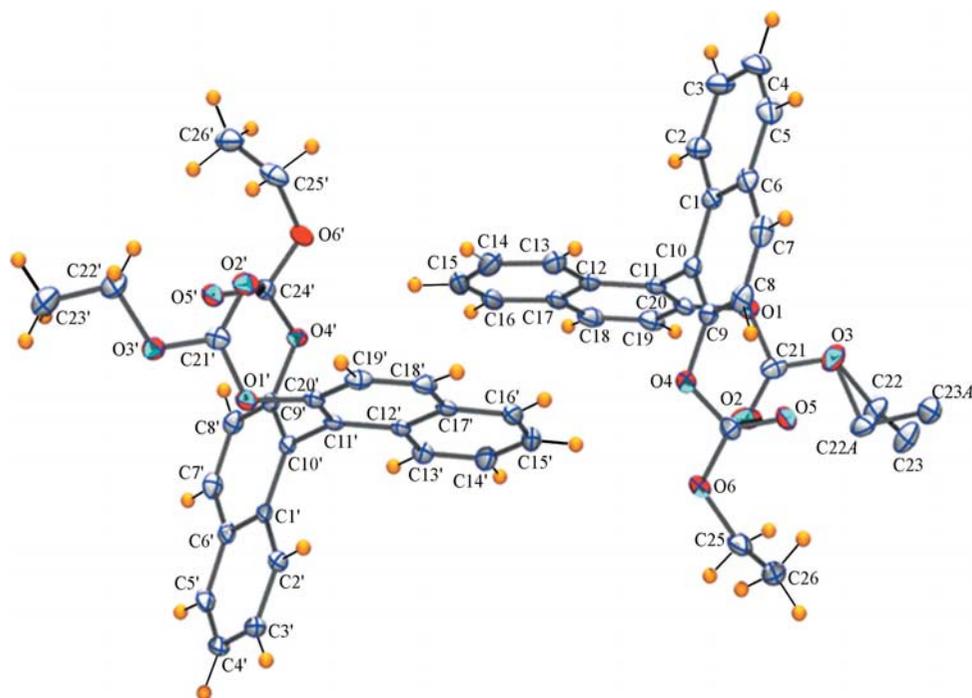

Figure 4
The molecular structure at 90 K, showing the atom labelling for all non-H atoms and 50% probability displacement ellipsoids. The H atoms of the disordered ethyl group have been omitted for clarity.

is noteworthy that the THMA analysis results in a C22—C23 bond length of 1.326 (1) Å, suggesting that the bond shortening is certainly not due to thermal effects alone.

The same crystal when cooled to 150 K indexes uniquely with $Z = 4$ and a cell volume almost double that of the 292 K structure. It is noteworthy that the short C—C bond is now associated with only one molecule (THMA-corrected C22—C23 = 1.343 Å), and the second molecule shows a closer to normal bond length (THMA-corrected C22′—C23′ = 1.453 Å). Thus, it appears that resolution of the overlap of molecules is beginning to take place at this temperature. The molecule is shown in Fig. 2S (supplementary material), and details of the C—H⋯O hydrogen bonding present are given in Table 1.

At 90 K, the cell volume contracts slightly compared with that at 150 K; however, the disorder at the C22—C23 site is now resolved. Fig. 4 shows the molecular structure of the compound, and the features of the positionally disordered C22 and C23 atoms now correspond to normal bond lengths (the THMA corrected bond lengths for C22—C23 and C22′—C23′ are 1.520 and 1.482 Å, respectively). The refinements suggest an occupancy ratio of 58:42 for disordered atoms C22 and C22A, respectively. The refinements were carried out keeping the constraint on occupancy for C22 and C23 as one block and that for C22A and C23A as another block. The packing in the lattice (Fig. 5) is mainly through weak interactions involving intermolecular C—H⋯O contacts (Table 2) and π–π stacking interactions [with centroid–centroid distances of 3.849 (2) and 3.960 (1) Å between the centroids of rings C12–C17 and C12′–C17′ and between the centroid of C1–C6, and that of C1′/C6′–C10′ at $(x, y, z + 1)$]. There are two types of C—H⋯π interactions {C3—H3⋯π[ring C12–C17 at $(-x, -y + 2, -z + 1)$] and C3′—H3′⋯π[ring C11′/C12′/C17′–C20′ at $(-x + 1, -y + 1, -z)$], with H⋯π distances of 2.86 and 2.88 Å, respectively}.

In conclusion, the formation of a terminal short bond without the influence of strain or hybridization is of fundamental importance. The results clearly indicate that positional disorder could be the cause, and the structural analysis at different temperatures clearly brings out the salient features of such an effect. 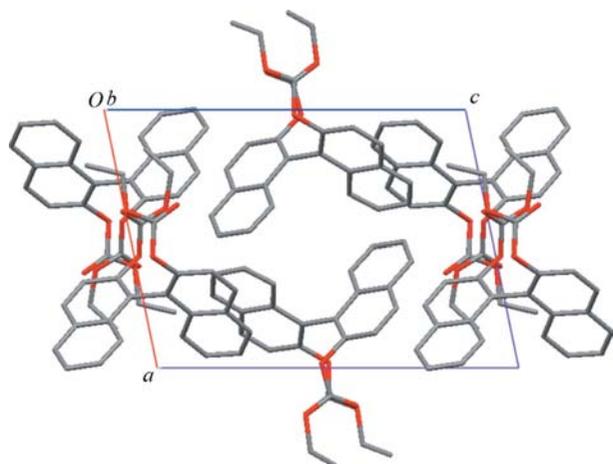It is to be noted that thermal effects alone cannot resolve such unusual observed bond lengths. The unit cell at 150 K and below shows a supercell formation.

Experimental

Compound (I) at 292 K

Crystal data

$C_{26}H_{22}O_6$	$\gamma = 65.989 (2)°$
$M_r = 430.44$	$V = 1104.3 (3)$ Å^3
Triclinic, $P\overline{1}$	$Z = 2$
$a = 9.7614 (14)$ Å	Mo $K\alpha$ radiation
$b = 10.0379 (14)$ Å	$\mu = 0.09$ mm^{-1}
$c = 12.3947 (17)$ Å	$T = 292$ K
$\alpha = 89.490 (2)°$	$0.50 \times 0.31 \times 0.25$ mm
$\beta = 84.810 (2)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	11287 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	4176 independent reflections
$T_{min} = 0.907$, $T_{max} = 0.977$	2806 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	291 parameters
$wR(F^2) = 0.191$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
4176 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Compound (I) at 393 K

Crystal data

$C_{26}H_{22}O_6$	$\gamma = 65.578 (3)°$
$M_r = 430.44$	$V = 1130.4 (3)$ Å^3
Triclinic, $P\overline{1}$	$Z = 2$
$a = 9.8546 (18)$ Å	Mo $K\alpha$ radiation
$b = 10.0864 (19)$ Å	$\mu = 0.09$ mm^{-1}
$c = 12.539 (2)$ Å	$T = 393$ K
$\alpha = 89.469 (4)°$	$0.50 \times 0.31 \times 0.25$ mm
$\beta = 85.207 (4)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	12123 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	4606 independent reflections
$T_{min} = 0.909$, $T_{max} = 0.978$	2113 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$

Figure 5
The packing at 90 K, showing the molecules in the supercell.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.220$
$S = 1.03$
4606 reflections

291 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

Compound (I) at 150 K

Crystal data

$C_{26}H_{22}O_6$
$M_r = 430.44$
Triclinic, $P\bar{1}$
$a = 10.8028$ (18) Å
$b = 14.798$ (3) Å
$c = 15.926$ (3) Å
$\alpha = 63.692$ (2)°
$\beta = 72.394$ (3)°

$\gamma = 73.200$ (3)°
$V = 2139.2$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 150$ K
$0.50 \times 0.31 \times 0.25$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.906$, $T_{max} = 0.977$

22856 measured reflections
8704 independent reflections
6807 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.139$
$S = 1.04$
8704 reflections

581 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) at 150 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5′—H5′···O1^i	0.95	2.59	3.519 (2)	165
C7—H7···O2^{ii}	0.95	2.57	3.405 (3)	146
C16—H16···O5^{iii}	0.95	2.56	3.369 (3)	143

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

Compound (I) at 90 K

Crystal data

$C_{26}H_{22}O_6$
$M_r = 430.44$
Triclinic, $P\bar{1}$
$a = 10.7955$ (17) Å
$b = 14.726$ (2) Å
$c = 15.887$ (3) Å
$\alpha = 63.491$ (2)°
$\beta = 72.400$ (2)°

$\gamma = 73.011$ (2)°
$V = 2117.4$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 90$ K
$0.50 \times 0.31 \times 0.25$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.946$, $T_{max} = 0.981$

22555 measured reflections
8616 independent reflections
7378 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.114$
$S = 1.09$
8616 reflections

601 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) at 90 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5′—H5′···O1^i	0.95	2.57	3.497 (2)	166
C7—H7···O2^{ii}	0.95	2.54	3.369 (3)	146
C16—H16···O5^{iii}	0.95	2.54	3.327 (3)	140

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

The occupancy refinements for the 90 K data were carried out using the PART command in *SHELXL97* (Sheldrick, 2008). All H atoms were positioned geometrically, with C—H distances fixed in the range 0.93–0.99 Å, and refined using a riding model, with $U_{iso}(H)$ values of $1.5U_{eq}(C)$ for methyl groups or $1.5U_{eq}(C)$ otherwise.

In all cases, data collection: *SMART* (Bruker, 2004); cell refinement and data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997), *POV-RAY* (Persistence of Vision Team, 2004) and *CAMERON* (Watkin et al., 1993); software used to prepare material for publication: *PLATON* (Spek, 2009).

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