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Unusually Short Ethylene Bond and Large Amplitude Torsional Motion of (*E*)-Stilbenes in Crystals. X-ray Crystallographic Study of ‘Stiff’ Stilbenes

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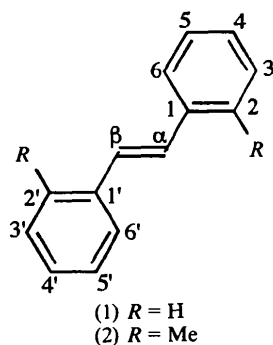
Abstract

Crystal structures of (*E*)-4,4'-dimethyl-1,1'-biindanylidene, (*E*)-5,5'-dimethyl-1,1'-biindanylidene, (*E*)-6,6'-dimethyl-1,1'-biindanylidene, (*E*)-7,7'-dimethyl-1,1'-biindanylidene and (*E*)-2,2,2',2'-tetramethyl-1,1'-biindanylidene were determined by X-ray diffraction at 296 and 120 K. The observed ethylene bond length is 1.35–1.36 Å, independent of the temperature and the compound, which agrees well with the length estimated from the molecular mechanics calculations. The results make a sharp contrast with those for ordinary (*E*)-stilbenes and strongly support the interpretation that the unusual short ethylene bond in the X-ray structures of (*E*)-stilbenes is an artifact which originates from the large-amplitude torsional motion of the C—Ph bonds in crystals. The true length of the ethylene bond in (*E*)-stilbenes is safely estimated to be 1.35–1.36 Å.

Introduction

The molecular structure of (*E*)-stilbene (1) has been studied for a long time by various methods

(Waldeck, 1991; Mazzucato & Momicchioli, 1991). However, it has been a long-standing problem that the ethylene bond in the X-ray structure is unusually short (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992). Since the ethylene bond is conjugated with the benzene rings, it is expected to be longer than an isolated C=C bond, whose standard bond length is 1.337 (6) Å (*International Tables for X-ray Crystallography*, 1968, Vol. III). Theoretical calculations gave the value 1.35–1.36 Å for the ethylene bond length (Warshel, 1975). The observed length remains, however, in the range 1.28–1.34 Å, which is significantly shorter than the theoretical value (Robertson & Woodward, 1937; Finder, Newton & Allinger, 1974; Bernstein, 1975; Hoekstra, Meertens & Vos, 1975; Bouwstra, Schouten & Kroon, 1984). A similar tendency is found for various compounds that have the (*E*)-stilbene skeleton (Jungk, Fronczek & Gandour, 1984; Tirado-Rives, Oliver, Fronczek & Gandour, 1984; Zobel & Ruban, 1978, 1983; Butters, Haller-Pauls & Winter, 1982; Arrieta, Domínguez, Lete, Villa & Germain, 1984; Krohn *et al.*, 1986; Bruce, Snow & Tiekink, 1987; Tirado-Rives, Fronczek & Gandour, 1985).



This problem was partially solved by the X-ray studies of (1) repeatedly carried out throughout 1984. It was revealed that there are two independent molecules lying at inversion centers in the unit cell and that one shows orientational disorder. Due to the disorder, the ethylene bond showed an apparent shrinkage as large as 0.05 Å (Bernstein, 1975; Hoekstra, Meertens & Vos, 1975; Bouwstra, Schouten & Kroon, 1984).

Recently we found in the literature that the ethylene bond at the nondisordered site is also short [1.313 (4)–1.326 (2) Å] at room temperature (Bernstein, 1975; Hoekstra, Meertens & Vos, 1975; Bouwstra, Schouten & Kroon, 1984) and revealed that the shrinkage is ascribed to an artifact caused by a dynamical disorder which originates from the large-amplitude torsional motion of the C—Ph bonds (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992). We demonstrate here further evidence that supports this interpretation and report the most reliable value ever experimentally determined for the ethylene bond length of the (*E*)-stilbenes, based on the X-ray study of model compounds of (*E*)-stilbenes in which the large amplitude torsional motion of the C—Ph bonds is suppressed.

The previous paper showed that the shrinkage of the ethylene bond without the orientational disorder

widely occurs in the X-ray structures of the compound having the (*E*)-stilbene skeleton, among which the results for (*E*)-2,2'-dimethylstilbene (2) are the most remarkable and characteristic (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992; Ogawa *et al.*, 1988). The X-ray structure of (2) shows a strong temperature dependence of the molecular structure, as well as an unusually short ethylene bond length [1.283 (3) Å at room temperature]. As the temperature is lowered, the ethylene bond length increases [1.321 (2) Å at 118 K], the bond angles $C\beta-C\alpha-C1$ and $C\alpha-C\beta-C1'$ decrease [128.3 (1)° at 298 K, 126.4 (1)° at 118 K], and the absolute values of the torsion angles of the C—Ph bonds $C\beta-C\alpha-C1-C6$ and $C\alpha-C\beta-C1'-C6'$ increase [11.7 (3)° at 298 K, 18.0 (2)° at 118 K].* Other geometrical parameters hardly change with the variation of the temperature.

These results were successfully explained by assuming unresolved disorder and/or vibration in the direction almost perpendicular to the molecular plane, as shown in Fig. 1 (the dynamical disorder model). According to this model, the observed molecular structure is an average of two conformers that are interconverted by the torsional vibration of the C—Ph bonds, during which the movement of the benzene rings is restrained to be as small as possible. The temperature dependence of the observed molecular structure is due to a slight energy difference between the two conformers in the crystal.

On the basis of this interpretation, we can make the following prediction: No shrinkage of the ethylene bond or no temperature dependence of the molecular structure will be observed by X-ray diffraction for the compound having the (*E*)-stilbene skeleton in which the internal rotation of the C—Ph bonds is severely restricted by the alkylene chains. Such compounds are known as 'stiff' stilbenes, *i.e.* indenoidene (3), tetrahydrochrysene (4) and (*E*)-1,1'-biindanylidene [(5) Ogawa, Suzuki & Futakami, 1988]. The ethylene bond length obtained from X-ray diffraction of these compounds must be the most reliable value ever observed for the ethylene bond of (*E*)-stilbenes. This paper reports the

* As the molecule is centrosymmetric, the torsion angles $C\beta-C\alpha-C1-C6$ and $C\alpha-C\beta-C1'-C6'$ have identical absolute values with opposite signs.

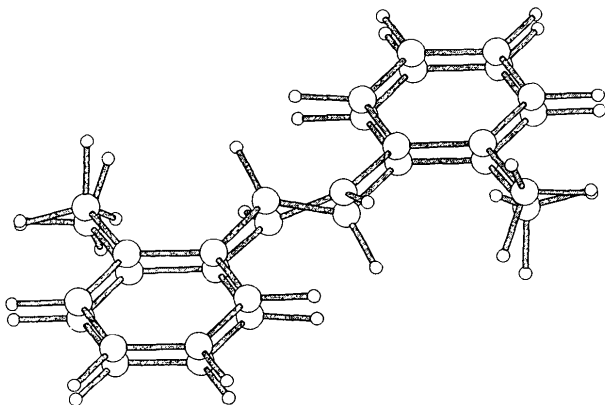


Fig. 1. Conformational interconversion due to the internal rotation around the C—Ph bonds.

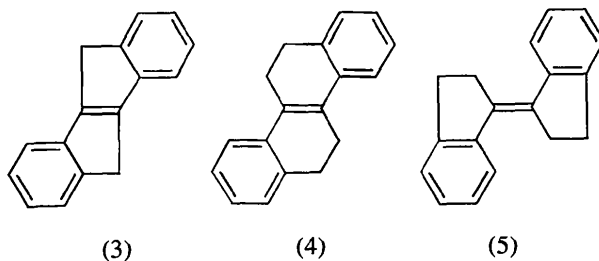


Table 1. Crystallographic data for (6)–(10)

Formula	(6)		(7)		(8)		(9)		(10)	
	C ₂₀ H ₂₀		C ₂₀ H ₂₀		C ₂₀ H ₂₀		C ₂₀ H ₂₀		C ₂₂ H ₂₄	
Crystal system	Monoclinic		Monoclinic		Monoclinic		Triclinic		Triclinic	
Space group	P2 ₁ /n		C2/c		P2 ₁ /n		P $\bar{1}$		P $\bar{1}$	
Z	2		4		2		4		4	
Temperature (K)	296	120	296	120	296	120	296	120	296	120
a (Å)	5.225 (3)	5.182 (1)	21.776 (2)	21.710 (2)	5.627 (2)	5.605 (3)	13.302 (3)	13.188 (2)	10.703 (2)	10.555 (1)
b (Å)	5.420 (2)	5.376 (2)	8.620 (2)	8.553 (2)	5.050 (2)	4.979 (3)	14.763 (2)	14.693 (2)	15.902 (2)	15.815 (2)
c (Å)	24.260 (2)	24.079 (1)	7.709 (2)	7.528 (2)	23.987 (3)	23.835 (4)	7.757 (1)	7.6702 (7)	10.302 (2)	10.206 (1)
α (°)	90	90	90	90	90	90	97.75 (1)	98.444 (8)	90.65 (1)	90.47 (1)
β (°)	92.67 (2)	93.42 (2)	95.22 (2)	95.73 (1)	92.31 (3)	92.58 (4)	98.94 (2)	98.961 (9)	90.01 (2)	90.14 (1)
γ (°)	90	90	90	90	90	90	90.53 (2)	90.522 (9)	103.86 (1)	103.64 (1)
V (Å ³)	686.3 (5)	669.6 (2)	1441.0 (6)	1390.9 (4)	681.1 (3)	664.5 (6)	1490.5 (5)	1451.5 (3)	1702.2 (5)	1655.5 (4)
D _x (Mg m ⁻³)	1.260	1.290	1.200	1.243	1.271	1.301	1.160	1.192	1.125	1.157
F(000)	280	280	560	560	280	280	560	560	624	624
Crystal size (mm)	0.30 × 0.20 × 0.20		0.25 × 0.20 × 0.20		0.25 × 0.20 × 0.20		0.25 × 0.20 × 0.20		0.20 × 0.20 × 0.20	
μ (mm ⁻¹)	0.49	0.51	0.47	0.49	0.50	0.51	0.46	0.47	0.44	0.45
θ_{\max}	60	60	60	60	60	60	60	60	60	60
h range	0 → 5	0 → 5	0 → 24	0 → 24	0 → 6	0 → 6	0 → 14	0 → 14	0 → 12	0 → 11
k range	0 → 6	0 → 6	0 → 9	0 → 9	0 → 5	0 → 5	-16 → 16	-16 → 16	-17 → 17	-17 → 17
l range	-27 → 26	-26 → 26	-8 → 8	-8 → 8	-26 → 26	-26 → 26	-8 → 8	-8 → 8	-11 → 11	-11 → 11
No. of reflections measured	1173	1198	1130	1112	1161	1238	4751	4516	5400	5328
No. of unique reflections	1014	990	1068	1038	1011	990	4426	4159	4982	4865
No. of observed reflections*	928	918	930	962	936	943	3398	3529	2677	3343
R	0.043	0.045	0.049	0.043	0.049	0.045	0.043	0.039	0.056	0.053
wR	0.052	0.061	0.057	0.057	0.065	0.058	0.048	0.044	0.058	0.059
No. of parameters	131	131	131	131	131	131	521	521	589	589
(Δ/σ) _{min}	0.133	0.038	0.175	0.008	0.002	0.001	0.771	0.002	0.003	0.015
ρ_{\min} (e Å ⁻³)	-0.430	-0.270	-0.294	-0.324	-0.308	-0.336	-0.287	-0.271	-0.441	-0.413
ρ_{\max} (e Å ⁻³)	0.754	0.180	0.227	0.243	0.173	0.191	0.189	0.160	0.366	0.322
Weight, g†	0.0001	0.0002	0.0002	0.0002	0.0002	0.0001	0.0002	0.0002	0.0002	0.0002

* $I \geq 2\sigma(I)$.† $w = [\sigma^2(F_o) + gF_o^2]^{-1}$.

confirmation of this prediction on the basis of the X-ray crystallographic analysis of methylated derivatives of (5), *i.e.* (*E*)-4,4'-dimethyl-1,1'-biindanylidene (6), (*E*)-5,5'-dimethyl-1,1'-biindanylidene (7), (*E*)-6,6'-dimethyl-1,1'-biindanylidene (8), (*E*)-7,7'-dimethyl-1,1'-biindanylidene (9) and (*E*)-2,2,2',2'-tetramethyl-1,1'-biindanylidene (10), at different temperatures.

Experimental

Melting points were determined on a hot stage apparatus and are uncorrected. All the reactions were carried out under an atmosphere of argon. Tetrahydrofuran (THF) was freshly distilled under argon over Na/benzophenone prior to use. 4-Methyl-1-indanone, 5-methyl-1-indanone, 6-methyl-1-indanone, and 7-methyl-1-indanone were prepared according to the published procedures (Koo, 1953; Elsner & Parker, 1957; Money, Raphael, Scott & Young, 1961; Elvidge & Foster, 1963; Budhram, Palaniswamy & Eisenbraun, 1986). (10) was prepared according to the procedure by Lemmen & Lenoir (1984).

Synthesis of (*E*)-4,4'-dimethyl-1,1'-biindanylidene (6)

The procedure reported by Lenoir was applied (Lenoir, 1977). Titanium tetrachloride (3.1 ml,

28 mmol) was added dropwise to a stirred suspension of zinc powder (3.64 g, 56 mmol) in THF (80 ml) at 273 K. The resulting dark mixture was heated under reflux for 1 h. Pyridine (1.6 ml) was then added. The mixture was cooled to room temperature and a solution of 4-methyl-1-indanone (3.40 g, 23 mmol) in THF (40 ml) was added. The mixture was refluxed and stirred for 18 h and allowed to cool to room temperature. The reaction mixture was poured into 10% aqueous potassium carbonate (150 ml). The mixture was extracted with chloroform (400 ml × 3). The organic layers were combined and washed successively with water (300 ml), water containing a trace of hydrochloric acid (200 ml) and brine (300 ml). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was evaporated to give a yellow solid (2.17 g). The solid was recrystallized from a mixture of ethanol and chloroform, affording (6) as pale yellow crystals (1.20 g, 40%), m.p. 512.8–513.3 K. Analysis: calc. for C₂₀H₂₀: C 92.26, H 7.74; found: C 92.05, H 7.72%. Single crystals of (6) for the X-ray diffraction were obtained by slow evaporation of the chloroform solution at room temperature.

(*E*)-5,5'-Dimethyl-1,1'-biindanylidene (7)

The procedure was the same as for the preparation of (6), except that 5-methyl-1-indanone (2.67 g,

18 mmol) was used instead of 4-methyl-1-indanone. The yellow solid (2.1 g) obtained from the organic extracts of the reaction mixture was recrystallized from hexane, affording yellow crystals (1.33 g, 56%), m.p. 460.8–461.2 K. Analysis: calc. for $C_{20}H_{20}$: C 92.26, H 7.74; found: C 92.30, H 7.76. Single crystals of (7) for X-ray diffraction were obtained by the slow evaporation of a hexane solution at room temperature.

(*E*)-6,6'-Dimethyl-1,1'-biindanylidene (8)

The procedure was the same as for the preparation of (6) except that 6-methyl-1-indanone (4.53 g, 31 mmol) was used instead of 4-methyl-1-indanone. The yellow solid (2.65 g) obtained from the organic extracts of the reaction mixture was recrystallized from a mixture of ethanol and chloroform, affording pale yellow crystals (0.97 g, 24%), m.p. 539.6–540.8 K. Analysis: calc. for $C_{20}H_{20}$: C 92.26, H 7.74; found: C 92.13, H 7.85. Single crystals of (8) for X-ray diffraction were obtained by the slow evaporation of the chloroform solution at room temperature.

(*E*)-7,7'-Dimethyl-1,1'-biindanylidene (9)

The procedure was the same as for the preparation of (6) except that 7-methyl-1-indanone (3.00 g, 21 mmol) was used instead of 4-methyl-1-indanone. The yellow solid (2.67 g) obtained from the organic extracts of the reaction mixture was recrystallized from hexane, affording colorless crystals (1.57 g, 59%), m.p. 424.8–425.2 K. Analysis: calc. for $C_{20}H_{20}$: C 92.26, H 7.74; found: C 92.00, H 7.74. Single crystals of (9) for X-ray diffraction were obtained by the slow evaporation of the hexane solution at room temperature.

(*E*)-2,2,2',2'-Tetramethyl-1,1'-biindanylidene (10)

Single crystals for X-ray diffraction were obtained by the slow evaporation of the methanol solution at room temperature. M.p. 399.5–403.4 K.

X-ray crystallography

All diffraction measurements were made on a Rigaku AFC-6A diffractometer with graphite-monochromated $Cu K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). An Oxford Cryostream cooler was used for the low-temperature measurements. The temperature was held constant to within $\pm 0.2 \text{ K}$ during the measurement. The integrated intensities were corrected in the $2\theta-\omega$ scan mode with an ω rate of 4.0 or $8.0^\circ \text{ min}^{-1}$. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Three standard reflections were measured after every 50 or 100 reflections during the data collection to monitor

the decay of the crystal. No significant decrease in the intensity of the standard reflections was observed. The structures were solved by direct methods with *SHELXS86* (Sheldrick, 1985) or *XTAL* (Hall & Stewart, 1990; Hall, Flack & Stewart, 1992). Structures were refined by full-matrix least squares using the *XTAL* system. All H atoms were located from difference maps. All C atoms were refined anisotropically. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Calculations of geometrical parameters and drawings of *ORTEPII* (Johnson, 1971) diagrams were performed using *XTAL*. The crystal and experimental data are summarized in Table 1.

Results and discussion

For the purpose of this work, the parent stiff stilbenes (3), (4) and (5) are expected to be the compounds of choice. However, we could not obtain good-quality single crystals of these compounds for X-ray diffraction. We synthesized the methylated derivatives of (5), *i.e.* (6), (7), (8), (9) and (10), by reductive coupling of the corresponding ketones using low-valent titanium reagents. All the compounds, which are new except (10) (Gano, Park, Pinkerton & Lenoir, 1990), fortunately gave good-quality single crystals for X-ray diffraction.

X-ray diffraction measurements of (6)–(10) were carried out at 120 and 296 K. The atomic coordinates are listed in Table 2* and the selected geometrical parameters in Table 3. The definition of the geometrical parameters is given in Fig. 2. Perspective views of the molecules are shown in Fig. 3.

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS0668). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

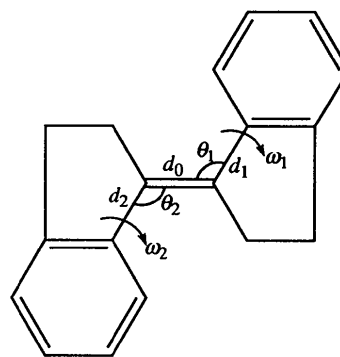


Fig. 2. Definition of the geometrical parameters for the (*E*)-stilbene skeleton.

Table 2. Atomic positional and isotropic displacement parameters (\AA^2) for (6)–(10)

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
x	y	z	U_{eq}
(6) at 296 K			
C(1)	0.0396 (3)	0.4226 (3)	0.52055 (6)
C(2)	0.2475 (3)	0.2265 (3)	0.51668 (7)
C(3)	0.2673 (3)	0.0938 (3)	0.57272 (7)
C(4)	0.0288 (3)	0.1733 (3)	0.66199 (7)
C(5)	-0.1601 (4)	0.3102 (4)	0.68629 (8)
C(6)	-0.2943 (4)	0.4923 (4)	0.65684 (8)
C(7)	-0.2425 (3)	0.5445 (4)	0.60271 (8)
C(8)	-0.0542 (3)	0.4086 (3)	0.57701 (7)
C(9)	0.0776 (3)	0.2233 (3)	0.60712 (7)
C(10)	0.1763 (5)	-0.0230 (5)	0.69353 (9)
(6) at 120 K			
C(1)	0.0394 (3)	0.4214 (3)	0.52081 (7)
C(2)	0.2488 (3)	0.2231 (3)	0.51744 (7)
C(3)	0.2675 (3)	0.0879 (3)	0.57400 (7)
C(4)	0.0256 (3)	0.1682 (3)	0.66320 (7)
C(5)	-0.1651 (3)	0.3068 (4)	0.68715 (7)
C(6)	-0.3003 (3)	0.4918 (3)	0.65707 (7)
C(7)	-0.2473 (3)	0.5440 (3)	0.60262 (7)
C(8)	-0.0559 (3)	0.4069 (3)	0.57729 (7)
C(9)	0.0760 (3)	0.2192 (3)	0.60815 (7)
C(10)	0.1746 (4)	-0.0308 (4)	0.69514 (8)
(7) at 296 K			
C(1)	0.47073 (8)	0.4953 (2)	0.5238 (2)
C(2)	0.42997 (8)	0.6336 (2)	0.5542 (3)
C(3)	0.36763 (8)	0.5686 (2)	0.5978 (3)
C(4)	0.33301 (8)	0.2830 (2)	0.6304 (2)
C(5)	0.34794 (8)	0.1264 (2)	0.6255 (2)
C(6)	0.40679 (9)	0.0875 (2)	0.5857 (3)
C(7)	0.45000 (9)	0.1975 (2)	0.5499 (3)
C(8)	0.43507 (7)	0.3556 (2)	0.5547 (2)
C(9)	0.37574 (7)	0.3950 (2)	0.5958 (2)
C(10)	0.3024 (1)	0.0025 (3)	0.6627 (4)
(7) at 120 K			
C(1)	0.47076 (7)	0.4957 (2)	0.5235 (2)
C(2)	0.42974 (7)	0.6356 (2)	0.5534 (2)
C(3)	0.36668 (7)	0.5701 (2)	0.5952 (2)
C(4)	0.33138 (7)	0.2819 (2)	0.6262 (2)
C(5)	0.34682 (7)	0.1238 (2)	0.6219 (2)
C(6)	0.40627 (7)	0.0836 (2)	0.5846 (2)
C(7)	0.44994 (7)	0.1952 (2)	0.5499 (2)
C(8)	0.43451 (6)	0.3545 (2)	0.5541 (2)
C(9)	0.37498 (6)	0.3950 (2)	0.5939 (2)
C(10)	0.30058 (8)	-0.0017 (2)	0.6549 (2)
(8) at 296 K			
C(1)	-0.0744 (3)	0.5356 (3)	0.52040 (7)
C(2)	-0.2692 (3)	0.7455 (4)	0.51473 (7)
C(3)	-0.3967 (3)	0.7496 (4)	0.57019 (8)
C(4)	-0.3183 (4)	0.4647 (4)	0.65886 (8)
C(5)	-0.1764 (4)	0.2751 (4)	0.68581 (8)
C(6)	0.0143 (3)	0.1616 (4)	0.65968 (7)
C(7)	0.0600 (3)	0.2376 (4)	0.60515 (8)
C(8)	-0.0822 (3)	0.4270 (3)	0.57724 (7)
C(9)	-0.2707 (3)	0.5423 (3)	0.60540 (7)
C(10)	0.1677 (4)	-0.0431 (5)	0.68883 (9)
(8) at 120 K			
C(1)	-0.0748 (3)	0.5351 (3)	0.52039 (7)
C(2)	-0.2714 (3)	0.7475 (3)	0.51471 (7)
C(3)	-0.3994 (3)	0.7495 (3)	0.57072 (7)
C(4)	-0.3212 (3)	0.4565 (4)	0.65977 (7)
C(5)	-0.1775 (3)	0.2640 (3)	0.68674 (7)
C(6)	0.0157 (3)	0.1504 (3)	0.66021 (7)
C(7)	0.0614 (3)	0.2297 (3)	0.60565 (7)

Table 2. (cont.)

	x	y	z	U_{eq}
C(8)	-0.0823 (3)	0.4226 (3)	0.57772 (7)	0.0105 (5)
C(9)	-0.2723 (3)	0.5381 (3)	0.60583 (7)	0.0118 (5)
C(10)	0.1706 (3)	-0.0589 (4)	0.68963 (7)	0.0170 (6)
(9) at 296 K				
C(101)	0.3143 (2)	0.7004 (1)	-0.0852 (3)	0.0368 (7)
C(102)	0.3941 (2)	0.6459 (2)	-0.1717 (3)	0.0445 (8)
C(103)	0.3676 (2)	0.6614 (2)	-0.3658 (3)	0.0544 (9)
C(104)	0.3116 (2)	0.8141 (2)	-0.4762 (3)	0.0544 (9)
C(105)	0.2742 (2)	0.8997 (2)	-0.4317 (4)	0.059 (1)
C(106)	0.2505 (2)	0.9255 (2)	-0.2649 (4)	0.0552 (9)
C(107)	0.2595 (2)	0.8661 (1)	-0.1378 (3)	0.0451 (8)
C(108)	0.2931 (1)	0.7782 (1)	-0.1869 (3)	0.0388 (7)
C(109)	0.3224 (2)	0.7543 (2)	-0.3528 (3)	0.0432 (8)
C(110)	0.2417 (3)	0.9007 (2)	0.0458 (4)	0.065 (1)
C(111)	0.2608 (2)	0.6710 (1)	0.0310 (3)	0.0378 (7)
C(112)	0.1543 (2)	0.6999 (2)	0.0577 (4)	0.0490 (9)
C(113)	0.0996 (2)	0.6079 (2)	0.0612 (4)	0.057 (1)
C(114)	0.1771 (2)	0.4689 (2)	0.2019 (3)	0.060 (1)
C(115)	0.2663 (2)	0.4274 (2)	0.2634 (3)	0.061 (1)
C(116)	0.3599 (2)	0.4678 (2)	0.2601 (3)	0.0507 (9)
C(117)	0.3689 (2)	0.5497 (1)	0.1900 (3)	0.0405 (7)
C(118)	0.2787 (2)	0.5881 (1)	0.1188 (3)	0.0373 (7)
C(119)	0.1841 (2)	0.5497 (2)	0.1330 (3)	0.0459 (8)
C(120)	0.4721 (2)	0.5952 (2)	0.2071 (4)	0.0493 (9)
C(201)	-0.2004 (2)	0.8181 (1)	0.0570 (3)	0.0398 (7)
C(202)	-0.1036 (2)	0.8472 (2)	-0.0048 (3)	0.0512 (9)
C(203)	-0.1326 (2)	0.8328 (2)	-0.2066 (4)	0.061 (1)
C(204)	-0.3063 (2)	0.8670 (2)	-0.3838 (3)	0.064 (1)
C(205)	-0.4080 (2)	0.8832 (2)	-0.3764 (4)	0.071 (1)
C(206)	-0.4468 (2)	0.8809 (2)	-0.2218 (4)	0.063 (1)
C(207)	-0.3867 (2)	0.8605 (1)	-0.0682 (3)	0.0464 (8)
C(208)	-0.2849 (2)	0.8401 (1)	-0.0780 (3)	0.0412 (7)
C(209)	-0.2453 (2)	0.8472 (2)	-0.2341 (3)	0.0492 (8)
C(210)	-0.4319 (2)	0.8684 (2)	0.0986 (4)	0.056 (1)
C(211)	-0.2043 (2)	0.7652 (1)	0.1842 (3)	0.0381 (7)
C(212)	-0.2933 (2)	0.7033 (2)	0.1989 (3)	0.0449 (8)
C(213)	-0.2418 (2)	0.6154 (2)	0.2503 (3)	0.0493 (9)
C(214)	-0.0671 (2)	0.6040 (2)	0.4477 (3)	0.0515 (9)
C(215)	0.0235 (2)	0.6495 (2)	0.5260 (3)	0.0547 (9)
C(216)	0.0415 (2)	0.7347 (2)	0.5017 (3)	0.0484 (8)
C(217)	-0.0278 (2)	0.7852 (1)	0.3940 (3)	0.0413 (7)
C(218)	-0.1167 (2)	0.7374 (1)	0.3074 (3)	0.0371 (7)
C(219)	-0.1376 (2)	0.6485 (3)	0.3407 (3)	0.0410 (7)
C(220)	-0.0087 (2)	0.8855 (2)	0.3927 (4)	0.056 (1)
(9) at 120 K				
C(101)	0.3160 (1)	0.7006 (1)	-0.0847 (2)	0.0173 (5)
C(102)	0.3967 (2)	0.6454 (1)	-0.1719 (2)	0.0204 (6)
C(103)	0.3697 (2)	0.6596 (1)	-0.3698 (2)	0.0242 (6)
C(104)	0.3138 (1)	0.8134 (1)	-0.4809 (2)	0.0235 (6)
C(105)	0.2760 (1)	0.9001 (1)	-0.4348 (3)	0.0254 (6)
C(106)	0.2517 (1)	0.9264 (1)	-0.2648 (3)	0.0242 (6)
C(107)	0.2606 (1)	0.8671 (1)	-0.1368 (2)	0.0198 (6)
C(108)	0.2947 (1)	0.7783 (1)	-0.1871 (2)	0.0181 (6)
C(109)	0.3245 (1)	0.7538 (1)	-0.3555 (2)	0.0195 (6)
C(110)	0.2414 (2)	0.9022 (1)	0.0494 (3)	0.0288 (7)
C(111)	0.2615 (1)	0.6714 (1)	0.0326 (2)	0.0181 (6)
C(112)	0.1542 (1)	0.7011 (1)	0.0599 (3)	0.0228 (6)
C(113)	0.0981 (1)	0.6088 (1)	0.0623 (3)	0.0250 (6)
C(114)	0.1756 (2)	0.4684 (1)	0.2021 (2)	0.0254 (6)
C(115)	0.2656 (2)	0.4260 (1)	0.2627 (2)	0.0269 (7)
C(116)	0.3604 (2)	0.4665 (1)	0.2590 (2)	0.0230 (6)
C(117)	0.3701 (1)	0.5489 (1)	0.1903 (2)	0.0180 (6)
C(118)	0.2789 (1)	0.5881 (1)	0.1200 (2)	0.0169 (5)
C(119)	0.1832 (1)	0.5499 (1)	0.1338 (2)	0.0209 (6)
C(120)	0.4745 (1)	0.5943 (1)	0.2071 (3)	0.0224 (6)
C(201)	-0.2004 (1)	0.8180 (1)	0.0572 (2)	0.0191 (6)
C(202)	-0.1027 (1)	0.8474 (1)	-0.0047 (2)	0.0230 (6)
C(203)	-0.1323 (2)	0.8332 (1)	-0.2093 (3)	0.0261 (7)
C(204)	-0.3078 (2)	0.8693 (1)	-0.3863 (3)	0.0265 (7)
C(205)	-0.4109 (2)	0.8860 (1)	-0.3783 (3)	0.0296 (7)
C(206)	-0.4492 (2)	0.8835 (1)	-0.2207 (3)	0.0263 (6)
C(207)	-0.3886 (1)	0.8614 (1)	-0.0670 (2)	0.0210 (6)

Table 2. (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(208)	-0.2859 (1)	0.8404 (1)	-0.0785 (2)	0.0188 (6)
C(209)	-0.2463 (1)	0.8477 (1)	-0.2362 (2)	0.0212 (6)
C(210)	-0.4339 (2)	0.8679 (1)	0.1025 (3)	0.0244 (6)
C(211)	-0.2044 (1)	0.7649 (1)	0.1853 (2)	0.0182 (6)
C(212)	-0.2945 (1)	0.7032 (1)	0.1999 (2)	0.0208 (6)
C(213)	-0.2433 (1)	0.6144 (1)	0.2506 (3)	0.0223 (6)
C(214)	-0.0663 (1)	0.6032 (1)	0.4496 (2)	0.0228 (6)
C(215)	0.0261 (1)	0.6489 (1)	0.5279 (2)	0.0239 (6)
C(216)	0.0447 (1)	0.7389 (1)	0.5043 (2)	0.0213 (6)
C(217)	-0.0256 (1)	0.7853 (1)	0.3957 (2)	0.0194 (6)
C(218)	-0.1159 (1)	0.7370 (1)	0.3088 (2)	0.0174 (6)
C(219)	-0.1374 (1)	0.6478 (1)	0.3423 (2)	0.0190 (6)
C(220)	-0.0058 (2)	0.8862 (1)	0.3940 (3)	0.0251 (6)

(10) at 296 K

C(101)	0.3438 (4)	0.5874 (3)	0.3327 (4)	0.039 (2)
C(102)	0.3077 (4)	0.5838 (3)	0.1858 (4)	0.045 (2)
C(103)	0.3249 (6)	0.6822 (3)	0.1569 (5)	0.054 (2)
C(104)	0.5153 (5)	0.8068 (3)	0.2367 (5)	0.057 (2)
C(105)	0.6115 (5)	0.8317 (4)	0.3295 (6)	0.064 (2)
C(106)	0.6246 (5)	0.7781 (3)	0.4283 (6)	0.061 (2)
C(107)	0.5393 (5)	0.6970 (3)	0.4391 (5)	0.049 (2)
C(108)	0.4395 (4)	0.6715 (3)	0.3499 (4)	0.043 (2)
C(109)	0.4313 (4)	0.7254 (3)	0.2471 (4)	0.047 (2)
C(110a)	0.1685 (6)	0.5358 (4)	0.1527 (6)	0.059 (2)
C(110b)	0.4045 (7)	0.5507 (4)	0.1033 (6)	0.062 (3)
C(111)	0.2901 (4)	0.5310 (3)	0.4254 (4)	0.037 (2)
C(112)	0.2781 (8)	0.5496 (3)	0.5733 (4)	0.043 (2)
C(113)	0.1438 (5)	0.4896 (3)	0.6046 (5)	0.049 (2)
C(114)	0.0546 (5)	0.3318 (3)	0.5191 (5)	0.054 (2)
C(115)	0.0649 (5)	0.2722 (4)	0.4230 (6)	0.064 (2)
C(116)	0.1533 (5)	0.2934 (3)	0.3241 (5)	0.059 (3)
C(117)	0.2297 (5)	0.3778 (3)	0.3155 (5)	0.051 (2)
C(118)	0.2158 (4)	0.4400 (3)	0.4074 (4)	0.043 (2)
C(119)	0.1322 (4)	0.4161 (3)	0.5105 (4)	0.045 (2)
C(120a)	0.2763 (6)	0.6438 (3)	0.6090 (6)	0.054 (2)
C(120b)	0.3805 (6)	0.5193 (4)	0.6527 (6)	0.056 (2)
C(201)	0.1575 (4)	0.9148 (3)	0.0809 (4)	0.040 (2)
C(202)	0.1931 (4)	0.9143 (3)	-0.0658 (4)	0.040 (2)
C(203)	0.1736 (5)	0.8158 (3)	-0.0923 (5)	0.050 (2)
C(204)	-0.0177 (5)	0.6942 (3)	-0.0103 (6)	0.060 (2)
C(205)	-0.1146 (6)	0.6738 (4)	0.0803 (6)	0.069 (2)
C(206)	-0.1285 (5)	0.7297 (4)	0.1773 (6)	0.062 (2)
C(207)	-0.0411 (5)	0.8111 (3)	0.1874 (5)	0.050 (2)
C(208)	0.0596 (4)	0.8318 (3)	0.0987 (4)	0.043 (2)
C(209)	0.0683 (4)	0.7749 (3)	-0.0015 (4)	0.047 (2)
C(210a)	0.0955 (6)	0.9469 (4)	-0.1496 (6)	0.060 (2)
C(210b)	0.3313 (5)	0.9610 (4)	-0.1005 (6)	0.055 (2)
C(211)	0.2132 (4)	0.9727 (3)	0.1731 (4)	0.041 (2)
C(212)	0.2264 (4)	0.9588 (3)	0.3208 (4)	0.044 (2)
C(213)	0.3658 (5)	1.0129 (3)	0.3461 (5)	0.053 (2)
C(214)	0.4615 (5)	1.1684 (3)	0.2612 (6)	0.059 (2)
C(215)	0.4497 (6)	1.2277 (4)	0.1676 (6)	0.069 (2)
C(216)	0.3592 (6)	1.2074 (3)	0.0693 (6)	0.063 (2)
C(217)	0.2781 (5)	1.1236 (3)	0.0616 (5)	0.053 (2)
C(218)	0.2916 (4)	1.0620 (3)	0.1522 (4)	0.045 (2)
C(219)	0.3797 (4)	1.0866 (3)	0.2540 (5)	0.049 (2)
C(220a)	0.1327 (6)	0.9982 (4)	0.3983 (6)	0.058 (2)
C(220b)	0.2159 (6)	0.8647 (4)	0.3636 (6)	0.057 (2)

(10) at 120 K

C(101)	0.3445 (3)	0.5883 (2)	0.3319 (3)	0.016 (1)
C(102)	0.3085 (3)	0.5844 (2)	0.1837 (3)	0.017 (1)
C(103)	0.3245 (4)	0.6831 (2)	0.1549 (4)	0.021 (1)
C(104)	0.5161 (3)	0.8088 (2)	0.2348 (4)	0.022 (1)
C(105)	0.6140 (4)	0.8349 (2)	0.3285 (4)	0.025 (1)
C(106)	0.6274 (3)	0.7795 (2)	0.4297 (4)	0.023 (1)
C(107)	0.5420 (3)	0.6983 (2)	0.4409 (3)	0.020 (1)
C(108)	0.4409 (3)	0.6725 (2)	0.3494 (3)	0.016 (1)
C(109)	0.4316 (3)	0.7273 (2)	0.2455 (3)	0.017 (1)
C(110a)	0.1686 (4)	0.5358 (3)	0.1490 (4)	0.024 (1)
C(110b)	0.4074 (4)	0.5515 (3)	0.0998 (4)	0.025 (1)
C(111)	0.2901 (3)	0.5307 (2)	0.4258 (3)	0.016 (1)
C(112)	0.2781 (3)	0.5492 (2)	0.5746 (3)	0.016 (1)

Table 2. (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(113)	0.1425 (3)	0.4887 (2)	0.6070 (3)	0.019 (1)
C(114)	0.0528 (3)	0.3301 (2)	0.5195 (3)	0.022 (1)
C(115)	0.0645 (4)	0.2699 (2)	0.4225 (4)	0.025 (1)
C(116)	0.1541 (4)	0.2923 (2)	0.3222 (3)	0.024 (1)
C(117)	0.2304 (3)	0.3771 (2)	0.3136 (3)	0.020 (1)
C(118)	0.2158 (3)	0.4392 (2)	0.4068 (3)	0.017 (1)
C(119)	0.1307 (3)	0.4143 (2)	0.5112 (3)	0.018 (1)
C(120a)	0.2760 (4)	0.6428 (2)	0.6113 (4)	0.022 (1)
C(120b)	0.3812 (4)	0.5182 (3)	0.6554 (4)	0.023 (1)
C(201)	0.1568 (3)	0.9147 (2)	0.0800 (3)	0.017 (1)
C(202)	0.1920 (3)	0.9148 (2)	-0.0680 (3)	0.017 (1)
C(203)	0.1736 (3)	0.8154 (2)	-0.0952 (3)	0.020 (1)
C(204)	-0.0200 (4)	0.6932 (2)	-0.0129 (3)	0.024 (1)
C(205)	-0.1187 (4)	0.6710 (2)	0.0792 (4)	0.028 (1)
C(206)	-0.1321 (4)	0.7286 (2)	0.1777 (3)	0.024 (1)
C(207)	-0.0437 (3)	0.8097 (2)	0.1878 (3)	0.021 (1)
C(208)	0.0585 (3)	0.8315 (2)	0.0988 (3)	0.017 (1)
C(209)	0.0666 (3)	0.7740 (2)	-0.0034 (3)	0.018 (1)
C(210a)	0.0926 (4)	0.9473 (3)	-0.1517 (4)	0.024 (1)
C(210b)	0.3311 (3)	0.9615 (2)	-0.1042 (4)	0.022 (1)
C(211)	0.2141 (3)	0.9728 (2)	0.1731 (3)	0.016 (1)
C(212)	0.2272 (3)	0.9582 (2)	0.3221 (3)	0.018 (1)
C(213)	0.3683 (3)	1.0121 (2)	0.3491 (4)	0.021 (1)
C(214)	0.4650 (3)	1.1689 (2)	0.2628 (4)	0.023 (1)
C(215)	0.4539 (4)	1.2296 (2)	0.1688 (4)	0.026 (1)
C(216)	0.3609 (3)	1.2088 (2)	0.0701 (4)	0.024 (1)
C(217)	0.2791 (3)	1.1251 (2)	0.0612 (3)	0.020 (1)
C(218)	0.2932 (3)	1.0627 (2)	0.1526 (3)	0.019 (1)
C(219)	0.3825 (3)	1.0865 (2)	0.2558 (3)	0.019 (1)
C(220a)	0.1323 (4)	0.9981 (3)	0.4015 (4)	0.024 (1)
C(220b)	0.2164 (4)	0.8637 (2)	0.3658 (4)	0.023 (1)

Table 3. Selected geometrical parameters for (6)–(10)*

	Origin	Temperature <i>T</i> (K)	Distance		Bond angle	Torsion angle
			d_0 (Å)	d_1, d_2 (Å)	θ_1, θ_2 (°)	ω_1, ω_2 (°)
(6)†	X-ray	296	1.353 (2)	1.478 (2)	127.7 (1)	±0.0 (3)
		120	1.355 (2)	1.476 (2)	127.7 (2)	±0.5 (3)
(7)†	X-ray	296	1.360 (3)	1.465 (2)	128.0 (1)	±2.0 (3)
		120	1.354 (3)	1.472 (2)	128.0 (1)	±2.5 (2)
(8)†	X-ray	296	1.362 (2)	1.472 (2)	127.6 (2)	±3.1 (3)
		120	1.358 (3)	1.479 (2)	127.4 (1)	±2.9 (3)
(9)‡	X-ray	296	1.343 (3)	1.483 (3)	128.4 (2)	40.9 (3)
			1.346 (3)	1.482 (3)	128.0 (2)	40.4 (4)
(10)‡	X-ray	120	1.354 (3)	1.483 (3)	127.0 (2)	40.5 (3)
			1.349 (3)	1.486 (3)	126.7 (2)	38.4 (4)
			1.348 (3)	1.483 (3)	128.2 (2)	41.0 (3)
			1.349 (3)	1.483 (3)	127.0 (2)	39.9 (3)
			1.349 (3)	1.485 (2)	127.9 (2)	40.3 (3)
		MM3	1.354	1.477	125.9	41.6
			1.349 (6)	1.486 (5)	127.7 (4)	33.8 (8)
			1.349 (6)	1.485 (5)	127.5 (4)	33.9 (8)
			1.349 (6)	1.489 (5)	127.9 (4)	35.1 (8)
			1.360 (4)	1.484 (6)	126.9 (4)	37.2 (8)
120	1.355 (4)	1.482 (4)	127.9 (3)	32.8 (6)		
	1.355 (4)	1.485 (4)	127.5 (3)	33.9 (6)		
	1.355 (4)	1.485 (4)	127.7 (3)	35.7 (6)		
	1.355 (4)	1.485 (4)	127.2 (3)	36.9 (6)		
	1.359	1.479	125.1	40.6		

* The definition of the geometrical parameters is given in Fig. 2.

† As the molecule is centrosymmetric, $d_1 = d_2$, $\theta_1 = \theta_2$ and $\omega_1 = \omega_2$.

‡ There are two independent molecules in a unit cell.

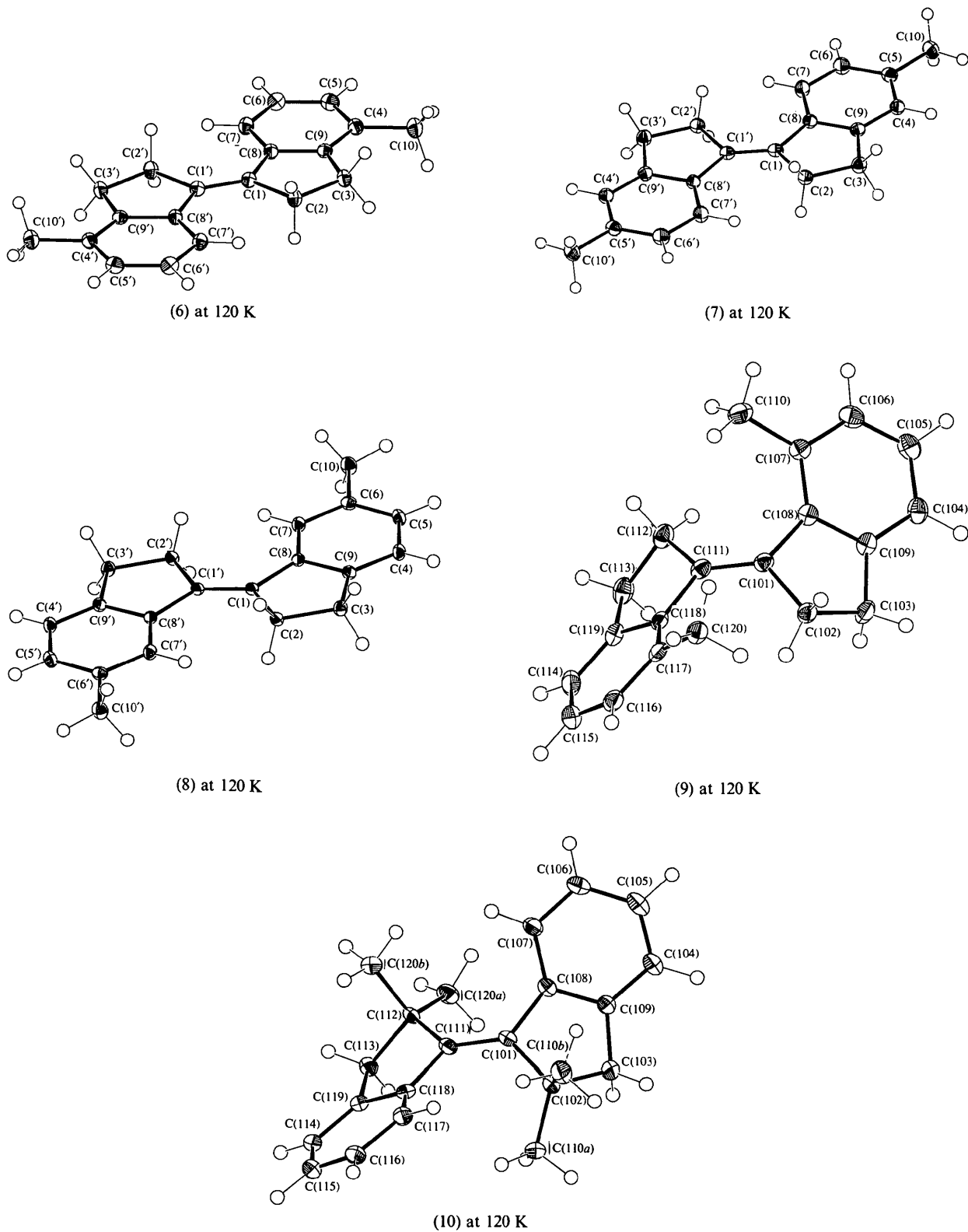
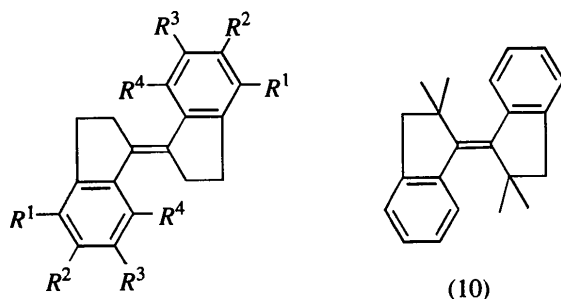


Fig. 3. ORTEP drawings (Johnson, 1971) of the (*E*)-1,1'-biindanylidene (6)–(10). The thermal ellipsoids of the C atoms are scaled to the 50% probability level; H atoms are shown as spheres of a fixed arbitrary size. For (9) and (10), one of the two independent molecules is drawn.



	R ¹	R ²	R ³	R ⁴
(6)	Me	H	H	H
(7)	H	Me	H	H
(8)	H	H	Me	H
(9)	H	H	H	Me

In the crystals of (6), (7) and (8), the observed molecular structures are centrosymmetric and have a planar geometry for the (*E*)-stilbene skeleton, both at low and room temperatures. The structures do not show temperature dependence and agree fairly well with the molecular structures obtained from the MM3 calculations (Allinger, 1992). Thus, the ethylene bond lengths are in the range 1.353 (3)–1.362 (3) Å, being distinctly longer than those ever observed for ordinary (*E*)-stilbenes. The C—Ph bond lengths [$d_1 = d_2 = 1.465$ (2)–1.479 (2) Å] are nearly equal to those of (*E*)-stilbenes. The torsion angle of the C—Ph bonds [$\omega_1 = -\omega_2 = \pm 0.0$ (3) – ± 3.1 (3)°] indicates the good planarity of the (*E*)-stilbene skeleton, slightly different from those of the parent (*E*)-stilbene (1). The bond angles $\theta_1 (= \theta_2)$ [X-ray, 127.4 (1)–128.0 (1)°; MM3, 127.2–127.3°] are significantly larger than those calculated for (*E*)-stilbenes from MM3 (124.9–125.1°), reflecting the fact that the ethylene bond of (6)–(8) is connected to the cyclopentene rings.

The observed molecular structures of (9) and (10), which have considerable steric congestion around the ethylene bond, are substantially different from those of (6)–(8). The C—Ph bonds are considerably twisted and the two benzene rings do not parallel within

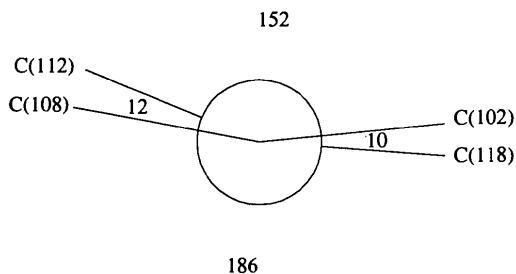


Fig. 4. Newman projection of the ethylene bond C(101)=C(111) for (9) at 120 K. Torsion angle values are given in °.

each of the molecules. That is, the molecular structure adopts a pseudo-*C*₂ symmetry. The ethylene bond is twisted by *ca* 10–20° and the C atoms are slightly pyramidal, as shown in Fig. 4. There is, nevertheless, no temperature dependence in the molecular structure or no shrinkage in the ethylene bond. The observed molecular structures essentially agree with those from the MM3 calculations.

It is to be noted that the ethylene bond is hardly elongated, irrespective of the considerable steric congestion around the bond. This indicates that the relief of the steric congestion is achieved primarily by the twisting of the C—Ph bonds and subsequently by the twisting of the ethylene bond.

All the results clearly show that the ethylene bond length observed for the stiff stilbenes is in the range 1.35–1.36 Å and hardly depends on the compound as well as the temperature. This makes a sharp contrast to the ordinary (*E*)-stilbenes such as (1), (2), (*E*)-2,2',4,4'-tetramethylstilbene or (*E*)-2,2',5,5'-tetramethylstilbene, where the observed ethylene bond length is in the range 1.28–1.34 Å, strongly dependent on the compound as well as the temperature. It therefore becomes further evident that the considerable variation in the ethylene bond length widely observed for the X-ray structures of the ordinary (*E*)-stilbenes is ascribed to an artifact caused by the large amplitude torsional motion of the C—Ph bonds and that the ethylene bond length is hardly changed by the steric congestion or the molecular packing. Thus, the true length of the ethylene bond in the (*E*)-stilbenes, of which a reliable value has not yet been obtained from X-ray diffraction due to the torsional motion, is safely estimated to be 1.35–1.36 Å.

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Structure and Thermochemical Properties of Some Alkyluracils

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Abstract

Crystalline 1,3,6-trisubstituted uracils have been analysed by X-ray diffraction. 1,3,6-Trimethyluracil, $C_7H_{10}N_2O_2$ (I), $M_r = 154.17$, triclinic, $P\bar{1}$, $a = 7.242(2)$, $b = 7.991(3)$, $c = 8.380(3)$ Å, $\alpha = 61.98(3)$, $\beta = 63.40(3)$, $\gamma = 82.09(3)^\circ$, $V = 381.2(2)$ Å³, $Z = 2$, $D_x = 1.343$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.79$ mm⁻¹, $F(000) = 164$, room temperature, final $R = 0.060$ for 1216 observed reflections. 1,3-Dimethyl-6-ethyluracil, $C_8H_{12}N_2O_2$ (II), $M_r = 168.20$, monoclinic, $P2_1/n$, $a = 4.107(1)$, $b = 9.806(1)$, $c = 20.994(2)$ Å, $\beta = 92.97(1)^\circ$, $V = 844.4(4)$ Å³, $Z = 4$, $D_x = 1.323$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.76$ mm⁻¹, $F(000) = 360$, room temperature, final $R = 0.049$ for 1284 observed reflections. 1,3-Dimethyl-6-propyluracil, $C_9H_{14}N_2O_2$ (III), $M_r = 182.22$, monoclinic, $P2_1/c$, $a = 10.738(1)$, $b = 11.735(1)$, $c = 23.056(2)$ Å, $\beta = 90.91(2)^\circ$, $V = 2904.9(4)$ Å³, $Z = 12$, $D_x = 1.250$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.70$ mm⁻¹, $F(000) = 1176$, room temperature, final $R = 0.049$ for 3048 observed reflections. 1,3-Dimethyl-6-butyluracil, $C_{10}H_{16}N_2O_2$ (IV), $M_r = 196.25$, monoclinic, $P2_1/c$, $a = 9.441(6)$, $b = 12.086(4)$, $c = 18.751(7)$ Å, $\beta = 100.53(4)^\circ$, $V = 2103(2)$ Å³, $Z = 8$, $D_x = 1.239$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.08$ mm⁻¹, $F(000) = 848$, room temperature, final $R = 0.063$ for 1812 observed reflections. In all structures, molecules are planar when only 'heavy' atoms are considered. A layered-type

structure was observed in all cases. In structures (III) and (IV), three and two independent molecules were found in the asymmetric unit, respectively. No conformational differences between the symmetrically non-equivalent molecules were detected. Correlations between thermochemical data and the properties of the compounds in the solid state are discussed.

Introduction

This investigation was undertaken as part of the thermochemical and structural studies of biologically significant nucleic acid bases and amino acids, which as part of the polynucleotide and polypeptide side chains are believed to be involved in the stereochemical control and recognition of substrates by those macromolecules. Methyl and other alkyl groups on pyrimidine and purine bases are known to play an important role in the formation of biologically active conformations of nucleic acids and contribute significantly to stacking interactions between both purine and pyrimidine bases in aqueous solutions. The number and position of attached alkyl groups determine the structure of their hydration shells and the character of the base–water interactions. The thermochemistry of aqueous solutions of alkylated pyrimidine bases was a subject of numerous investigations (Szemińska, Zielenkiewicz & Wierzchowski, 1979; Zielenkiewicz, Plesiewicz &