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Tetrathiafulvalene revisited

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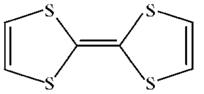
Monoclinic (α) tetrathiafulvalene [systematic name: 2-(1,3-dithiol-2-ylidene)-1,3-dithiole], $C_6H_4S_4$, undergoes a reversible second-order phase transition at *ca* 190 K through a displacive modulation with doubling of the *a* parameter. The low-temperature phase (γ) contains two crystallographically non-equivalent (but centrosymmetric) molecules of very similar geometry.

Comment

The electron donor 2,2′-bis(1,3-dithiole), or tetrathiafulvalene (TTF), synthesized by Wudl *et al.* (1970), is of paramount importance as a component of charge-transfer (CT) salts and complexes, organic metals, and superconductors. Knowing its precise structural parameters is obviously useful, especially since Reith *et al.* (1988) and Clemente & Marzotto (1996) have demonstrated simple linear relations between the degree of CT and bond lengths in the TTF molecule.



TTF

TTF appears in two polymorphic modifications, *viz.* the orange monoclinic α form (or TTF1) and the yellow triclinic β form (or TTF2). The crystal structure of α-TTF was determined at room temperature (Cooper *et al.*, 1971, 1974) and never revisited, evidently because of the high quality of the original study. The β phase, which is more stable at elevated temperatures (Bozio *et al.*, 1979; Venuti *et al.*, 2001), was discovered by LaPlaca *et al.* (1975), who reported its lattice parameters (Weidenborner *et al.*, 1977). The full structure determination was carried out by Ellern *et al.* (1994), also at room temperature. The low-temperature crystallography of TTF remained unexplored, although β-TTF was known to convert occasionally into α-TTF after slow cooling to 80 K (Venuti *et al.*, 2001). Temkin *et al.* (1977) studied the Raman spectra of α-TTF at 2, 80 and 300 K, and observed ten low-frequency (intermolecular) modes at low temperatures, instead of the six expected for two molecules per unit cell. A more detailed Raman spectroscopic study of both α- and β-TTF from 300 to 80 K was carried out by Venuti *et al.* (2001), who reported no unusual effects.

We undertook a variable-temperature study of α-TTF to obtain the standard bond lengths free of the spurious shortening caused by thermal libration (for which no corrections had been made in the earlier studies). On cooling the sample below 190 K, additional reflections emerged, which corresponded to the doubling of the lattice parameter *a*. The sample remained a single crystal and the transition was fully reversible; five cycles of cooling/warming across it did not cause any appreciable deterioration of the crystal quality. No further changes of the diffraction pattern were detected down to 95 K. Full sets of data were collected at 290, 150 and 98 K and used for structure determination. At 290 K, our results agree with those of Cooper *et al.* (1971, 1974). The molecule (Fig. 1*a*) lies at a crystallographic inversion centre and participates in an infinite stack, running parallel to the *y* axis, with rigorously uniform interplanar separations of 3.60 Å (calculated between the central C_2S_4 groups).

For the low-temperature phase, all 'new' reflections (with odd *h*) were systematically weaker than the 'old' (with even *h*). At 150 K, the intensities differ by an average factor of 13, but at 98 K only by a factor of 8. Nevertheless, the 'new' reflections are not negligible. Thus, 62% of reflections with *h* odd have *I* greater than $3\sigma(I)$ at 150 K, and 72% at 98 K (*cf.* 85 and 88% for *h* even). At 150 K, the mean $I/\sigma(I)$ ratio is 24.1 for *h* even and 9.2 for *h* odd; at 98 K, this ratio is, respectively, 26.4 and 13.5.

Thus, at around 190 K, α-TTF undergoes a second-order phase transition into a new low-temperature modification, γ-TTF. From systematic absences, the latter has $P2_1/n$ symmetry rather than $P2_1/c$. For example, the 98 K data set contained 374 reflections of *h*0*l* type with both *h* and *l* odd, giving the average $I/\sigma(I)$ ratio of 22.1. Of these, 342 reflections (91%) had *I* greater than $3\sigma(I)$. On the other hand, 386 reflections of *h*0*l* type with *h* odd and *l* even had the average $I/\sigma(I)$ equal to 0.7; only 59 reflections (15%) had *I* exceeding $3\sigma(I)$, and those only very slightly. The mean absolute intensities of the former and the latter class related as 91:1.

The structure of the low-temperature phase was solved successfully in the space group $P2_1/n$, with two crystallographically non-equivalent molecules (*A* and *B*; Fig. 1*b*) lying at inversion centres at $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Thus, the asymmetric unit comprises two half-molecules, which would be related by an *a*/2 translation (equivalent to an *a* translation in α-TTF) but for a slight misalignment (Fig. 1*c*). At 150 K, atoms C3 of *A* and *B* deviate by 0.053 (1) Å from an ideal *a*/2 translation, atoms S1 and S2 by 0.180 (1) and 0.173 (1) Å, and the peripheral atoms C1 and C2 by 0.248 (2) and 0.245 (2) Å. At 98 K, the deviations slightly increase, *viz.* 0.064 (2) Å for C3, 0.218 (1) Å for S1, 0.210 (1) Å for S2, 0.300 (2) Å for C1 and 0.299 (2) Å for C2. The mean deviation for all non-H atoms increases from 0.18 Å at 150 K to 0.22 Å at 98 K. The angle between the central C_2S_4 planes of molecules *A* and *B* increases from 2.3 (1)° at 150 K to 2.8 (1)° at 98 K, and the angle between the long axes of these molecules from 4.5 (1) to 5.4 (1)°. Owing to the smallness of these deviations, γ-TTF can

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be regarded as displacively modulated α-TTF. In fact, using only the (low-temperature) data with h even, the structure of γ-TTF can be solved and refined as a 1:1 disordered structure having a lattice similar to that of the α phase and $P2_1/c$ symmetry. The refinement converges at nearly the same R factor (on half the number of reflections, of course).

An alternative model of γ-TTF was tested, assuming one independent molecule occupying a general position [with the molecular centroid at *ca* $(\frac{1}{4}, 0, 0)$]. The refinement was unstable and produced absurd atomic displacement parameters and an R value greater than 0.12. Refinements in $P2_1/c$ symmetry were equally unsuccessful.

In both α and γ phases, the TTF molecule shows a small but significant chair-like distortion, folding along the S1$\cdots$S2 vector by 2.0 (1)° in the α phase and by 2.3 (1) and 1.8 (1)° in molecules A and B of the γ phase. The same conformation was found in β-TTF, which (unlike the α and γ phases) does not have a stacking motif, whereas in the gas phase, TTF adopts a boat conformation, with a 13.5° folding of both rings (Hargittai *et al.*, 1994). Both *ab initio* calculations (Batsanov *et al.*, 1995) and a survey of the Cambridge Structural Database (Wang *et al.*, 1997) indicate that the TTF molecule is indeed rather flexible conformationally.

Although γ-TTF contains two symmetrically non-equivalent types of stacks, the differences between their geometries are negligible. The mean interplanar separation is 3.53 Å at 150 K and 3.51 Å at 98 K. In α-TTF, atom S1 forms with its symmetry equivalent an inter-stack contact, S1$\cdots$S1$^{\rm ii}$, of 3.400 (1) Å, considerably shorter than twice the van der Waals radius of S (1.81 Å; Rowland & Taylor, 1996), while S2 is 'wedged' between two molecules of the adjacent stack, at equal distances [3.575 (1) Å] from S2$^{\rm iii}$ and S2$^{\rm iv}$ (symmetry codes as in Figs. 1 and 2). In γ-TTF, this pattern remains essentially the same. The S1$\cdots$S1$^{\rm ii}$ contact becomes S1$A\cdots$S1$B^{\rm ii}$ of 3.353 (1) (150 K) or 3.341 (1) Å (98 K). The S2$\cdots$S2$^{\rm iii}$ and S2$\cdots$S2$^{\rm iv}$ contacts become S2$A\cdots$S2$B^{\rm iii}$ and S2$A\cdots$S2$B^{\rm iv}$, respectively, which are no longer symmetrically equivalent but nevertheless are equidistant within experimental error, averaging 3.514 (1) Å at 150 K and 3.498 (1) Å at 98 K.

The observed and libration-corrected [by the **TLS** model of Schomaker & Trueblood (1968) in *PLATON* (Spek, 2003)] bond distances are listed in Table 1, and in Table 2 the average values are compared with the earlier results. It is worth noting that the 'outer' S—C1,2 bonds are significantly shorter than the 'inner' S—C3 bonds, and the difference is even more pronounced after the libration correction and/or at low temperature.

The May 2006 version of the Cambridge Structural Database (Allen & Taylor, 2004) lists over 150 structures containing unsubstituted TTF groups. Most of these materials are salts or CT complexes, in which the TTF group bears a net charge varying between 0 and +1 (Salmeron-Valverde *et al.*, 2003; Salmeron-Valverde & Bernes, 2005, and references therein). Accumulation of positive charge substantially alters the molecular geometry, the S—C bonds contracting and the C=C bonds lengthening in comparison with neutral TTF (Reith *et al.*, 1988; Clemente & Marzotto, 1996). However, low-temperature studies of some cocrystals, where CT is ruled out by spectroscopic and conductivity evidence, have revealed a TTF molecular geometry very similar to the present results (see Table 1).

Venuti *et al.* (2001) have made interesting predictions of the structure and energy of solid TTF by quasi-harmonic lattice dynamics, using three different molecular-mechanical models, *viz*. a 6-exp type atom–atom potential (W) parametrized by Williams & Cox (1984), the same with added Coulombic term (W+C) and another 6-exp potential specially devised by Della Valle *et al.* (1999) for bis(ethylenedithio)tetrathiafulvalene systems, also with a Coulombic term (ET+C). Both the W+C and the ET+C models predict that, on cooling from 300 to 0 K, the a and b cell parameters will contract but the c parameter

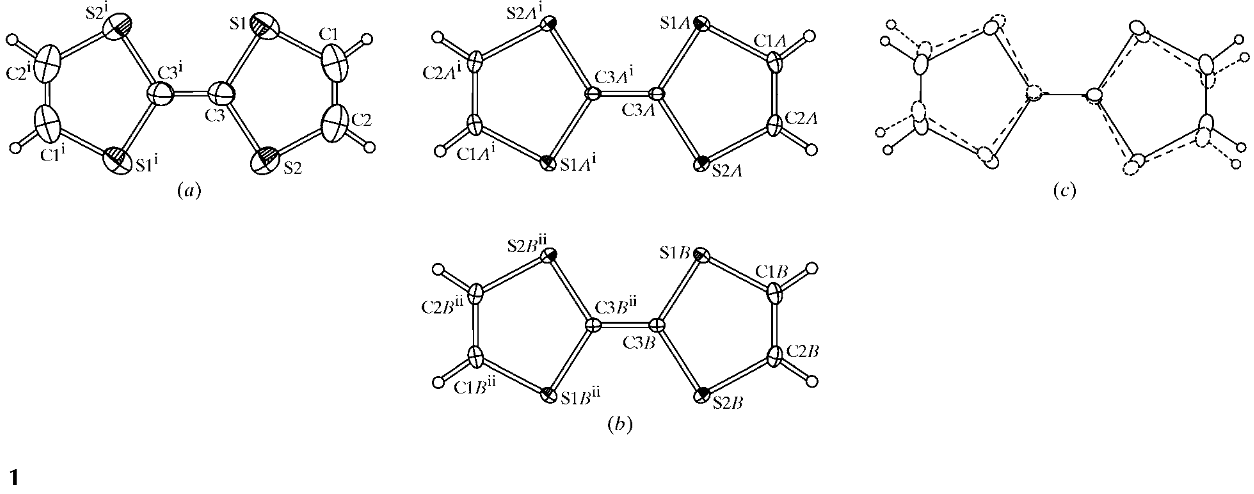

Figure 1

The molecular structure of TTF, showing (*a*) the α phase at 290 K, (*b*) the γ phase at 98 K, and (*c*) the overlap of molecules A and B (shifted by $a/2$) in the γ phase. Atomic displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.]

will expand, whereas the W method predicts a uniform contraction of all three parameters (see Table 3). Since the space-group symmetry was taken as datum, the phase transition obviously could not be forseen. Apart from this, our results show better agreement with W than with Coulombic corrected models. It is also noteworthy that W accurately predicted the β angle, which in the other two models was off the mark by 2–5°.

The same authors determined phonon wavenumbers of TTF from Raman data at 300 and 295 K, and at eight other temperatures ranging from 200 to 80 K. It is noteworthy that between 80 and 190 K each wavenumber shows a gentle linear dependence on temperature, but the values for 200 K are uniformly shifted down from the corresponding regression lines, which may be a manifestation of the phase transition. Unfortunately, no measurements were taken between 200 and 295 K, which makes comparison with the present results difficult.

For the preliminary publication on the phase traisition in TTF, see Batsanov *et al.* (1998).

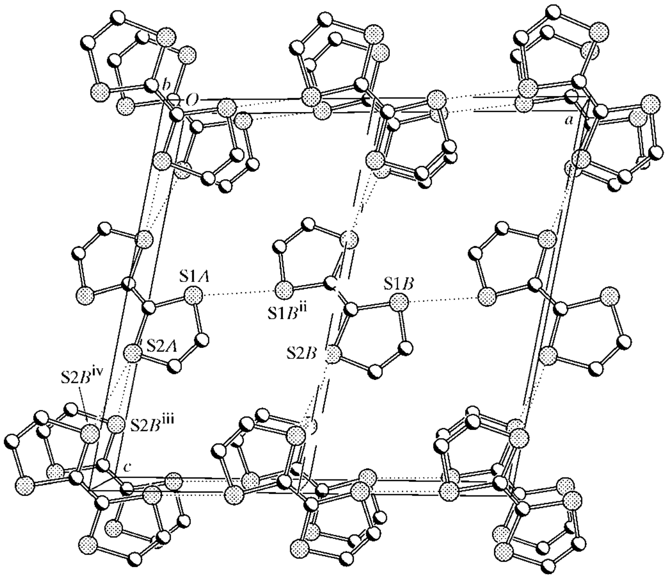

Figure 2
The crystal packing in γ-TTF. Dashed lines indicate the unit cell of α-TTF. [Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+\frac{1}{2}, -\frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$].

Experimental

Commercial TTF was recrystallized from heptane at room temperature.

TTF at 290 K

Crystal data

$C_6H_4S_4$
$M_r = 204.33$
Monoclinic, $P2_1/c$
$a = 7.352$ (2) Å
$b = 4.0181$ (11) Å
$c = 13.901$ (4) Å
$\beta = 101.426$ (10)°
$V = 402.5$ (2) Å^3
$Z = 2$
$D_x = 1.686$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.09$ mm^{-1}
$T = 290$ (2) K
Block, orange
0.20 × 0.16 × 0.14 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: integration (*XPREP* in *SHELXTL*; Bruker, 2001); $R_{int} = 0.040$ before correction
$T_{min} = 0.786$, $T_{max} = 0.875$
3571 measured reflections
926 independent reflections
813 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.065$
$S = 1.12$
926 reflections
55 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 0.1703P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.132 (7)

Table 1
Observed and libration-corrected[a] bond distances (Å).

T (K)	S1—C1	S2—C2	S1—C3	S2—C3	C1=C2	C3=C3^{i}
290	1.736 (2)	1.735 (2)	1.7556 (17)	1.7569 (17)	1.319 (3)	1.341 (3)
Corrected	1.741	1.741	1.763	1.764	1.325	1.345
150, *A*[b]	1.7462 (17)	1.7444 (17)	1.7607 (14)	1.7613 (14)	1.329 (2)	1.345 (3)
Corrected	1.749	1.747	1.765	1.765	1.332	1.347
150, *B*	1.7450 (17)	1.7453 (17)	1.7577 (14)	1.7608 (14)	1.328 (2)	1.349 (3)
Corrected	1.748	1.749	1.761	1.765	1.331	1.351
98, *A*	1.7482 (14)	1.7467 (14)	1.7613 (12)	1.7612 (13)	1.3337 (19)	1.348 (2)
Corrected	1.750	1.748	1.764	1.764	1.336	1.349
98, *B*	1.7447 (14)	1.7477 (14)	1.7609 (13)	1.7625 (13)	1.3349 (19)	1.346 (2)
Corrected	1.747	1.749	1.763	1.765	1.337	1.347

Notes: (*a*) using the **TLS** model (Schomaker & Trueblood, 1968); (*b*) *A* and *B* signify the two independent molecules.

TTF at 150 K

Crystal data

$C_6H_4S_4$
$M_r = 204.33$
Monoclinic, $P2_1/n$
$a = 14.641$ (3) Å
$b = 3.933$ (1) Å
$c = 13.832$ (3) Å
$\beta = 100.98$ (1)°
$V = 781.9$ (3) Å^3
$Z = 4$
$D_x = 1.736$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.13$ mm^{-1}
$T = 150$ (2) K
Block, orange
0.20 × 0.16 × 0.14 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: integration (*XPREP* in *SHELXTL*; Bruker, 2001); $R_{int} = 0.040$ before correction
$T_{min} = 0.779$, $T_{max} = 0.875$
8728 measured reflections
2072 independent reflections
1757 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 29.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.16$
2072 reflections
108 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.3828P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0300 (15)

Table 2
Mean bond distances (Å) in TTF.

Phase	*T* (K)	S—C1,2	S—C3	C1═C2	C3═C3^{i}
α-TTF^{a}	295	1.731 (2)	1.757 (2)	1.314 (3)	1.349 (3)
α-TTF^{b}	290	1.736 (2)	1.756 (2)	1.319 (3)	1.341 (3)
Corrected	290	1.741	1.764	1.325	1.345
γ-TTF^{b}	150	1.745 (2)	1.760 (2)	1.329 (2)	1.347 (3)
Corrected	150	1.748	1.764	1.332	1.349
γ-TTF^{b}	98	1.747 (1)	1.761 (1)	1.334 (2)	1.347 (2)
Corrected	98	1.749	1.764	1.337	1.348
β-TTF^{c}	298	1.731 (6)	1.755 (3)	1.309 (4)	1.337 (4)
Gas^{d}	433	1.739 (4)	1.758 (4)	1.338 (4)	1.354 (5)
TTF·Q^{e}	150	1.740 (7)	1.763 (4)	1.328 (2)	1.336 (4)
TTF·OFN^{f}	120	1.749 (1)	1.765 (2)	1.328 (2)	1.352 (2)

Notes: (*a*) Cooper *et al.* (1971, 1974); (*b*) this work, libration corrections using the **TLS** model; (*c*) Ellern *et al.* (1994); (*d*) electron diffraction study by Hargittai *et al.* (1994); (*e*) Batsanov *et al.* (1994), Q is 1-oxo-2,6-dimethyl-4-dicyanomethylenecyclohexa-2,5-diene; (*f*) Batsanov *et al.* (2001), OFN is octafluoronaphthalene.

TTF at 90 K

Crystal data

$C_6H_4S_4$
$M_r = 204.33$
Monoclinic, $P2_1/n$
$a = 14.625$ (3) Å
$b = 3.909$ (1) Å
$c = 13.812$ (3) Å
$\beta = 100.90$ (1)°
$V = 775.4$ (5) Å^3
$Z = 4$
$D_x = 1.750$ Mg m^{-3}
Mo *K*α radiation
$\mu = 1.14$ mm^{-1}
$T = 98$ (2) K
Block, orange
0.20 × 0.16 × 0.14 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: integration (*XPREP* in *SHELXTL*; Bruker, 2001);
$R_{\rm int} = 0.036$ before correction
$T_{\rm min} = 0.778$, $T_{\rm max} = 0.874$
8696 measured reflections
2064 independent reflections
1842 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 29.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.060$
$S = 1.12$
2064 reflections
108 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 0.4237P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.52$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0307 (14)

All H atoms were refined isotropically [Csp^2—H = 0.88 (3) and 0.94 (2) Å at 290 K, and 0.91 (2)–0.95 (2) Å at low temperatures]. The highest peaks of residual electron density (which increase from 0.20–0.32 e Å^{-3} at 290 K to 0.32–0.43 e Å^{-3} at 150 K to 0.32–0.52 e Å^{-3} at 98 K) lie near the mid-points of the C—S and C═C bonds, while the deepest 'holes' are found in the area of *p*π orbitals of the C atoms. The relatively large (*ca* 2.2) ratio of the maximum/minimum electron density may be due to the anisotropy of extinction, for which only an isotropic correction was applied.

For all determinations, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001).

The author thanks Professor M. R. Bryce for a sample of crystalline TTF and Professor J. A. K. Howard for valuable advice.

Table 3
Experimental and calculated unit-cell parameters (Å, °) of α- and γ-TTF.

Source	*T* (K)	*a*	*b*	*c*	*β*
X-ray^{a}	295	7.364	4.023	13.922	101.42
X-ray^{b}	290	7.352 (2)	4.018 (1)	13.901 (4)	101.43 (1)
X-ray^{b}	150	14.641 (3)	3.933 (1)	13.832 (3)	100.98 (1)
X-ray^{b}	98	14.625 (3)	3.909 (1)	13.812 (3)	100.90 (1)
W^{c}	300	7.582	3.859	14.205	101.64
W^{c}	0	7.426	3.764	14.184	101.29
W+C^{c,d}	300	7.340	4.429	13.764	105.40
W+C^{c,d}	0	7.252	3.987	13.931	103.65
ET+C^{c,d}	300	7.375	4.204	13.894	106.66
ET+C^{c,d}	0	7.244	4.067	14.040	106.35

Notes: (*a*) Cooper *et al.* (1971, 1974), no s.u. values were published; (*b*) this work; (*c*) calculations by Venuti *et al.* (2001); (*d*) molecule treated as flexible.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3012). Services for accessing these data are described at the back of the journal.

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