

Crystal Structure and Absolute Configuration of a New Highly Strained Helical Heterocyclic Molecule: (+)₃₆₅-(P)-N-(4-Tolylsulfonyl)-8-thiomethyl-1-thia-10-aza[2.2]metacyclophane

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(+)₃₆₅-(P)-N-(4-Tolylsulfonyl)-8-thiomethyl-1-thia-10-aza[2.2]metacyclophane, C₂₂H₂₁NO₂S₃, has been synthesized by a caesium-assisted high-dilution method and the pure (+)₃₆₅-enantiomer was separated using HPLC with poly(triphenylmethyl methacrylate) [(+)-PTrMA, (Okamoto-resin)] as a chiral phase. The crystal structure and the absolute configuration of this highly strained helical molecule was determined by X-ray diffraction. The compound crystallizes in an acentric orthorhombic space group *P*2₁2₁ (No. 19) with cell dimensions: *a* = 10.540(1), *b* = 11.491(1), *c* = 16.768(1) Å and *V* = 2030.8(4) Å³ with *Z* = 4. Full-matrix least-squares refinement of 253 parameters gave *R* = 0.028 for 1610 averaged reflections [*I* > 3.0σ(*I*)]. The insertion of the thiomethyl group into the ten-membered ring at position C(8) induces extra strain to the already highly strained cyclophane molecule causing the helicity-defining torsion angles, α, β, γ and δ, to have values of 10.23, 3.56, 3.59 and 18.20°, respectively. Also the transannular C(8)-C(16) distance is affected by the large thiomethyl group and has now a value of 2.720(4) Å, which is somewhat larger than in similar compounds in which the thiomethyl group at C(8) is absent.

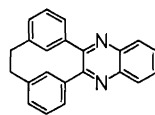
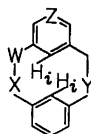
Whereas [2.2]metacyclophane (**1**)^{1,2} and also the dithia analogue (**2**)^{3,4} are well known compounds, analogous ring systems containing two different heteroatoms in the bridges e.g. **3** and **4**⁵ have been synthesized only recently. Heterocyclic compounds such as **10a** containing substituents other than hydrogen in position eight [C(8)] causing extra strain to the already highly strained molecule due to the large size of the substituent, were hitherto unknown. Due to the increased strain of the molecules an increase of the helicity-defining angles α-δ is observed for compounds **10a, b** compared with those of the well known molecules **3-9** (Table 4).

Apart from the synthetic and ring-strain problems these monoheteraphanes are of fundamental structural and stereochemical interest: they constitute a new family of low molecular weight helical compounds,⁵ their ring strain is dependent on the carbon-heteroatom bond lengths, and their crystal structures can be related to their chiroptical properties.⁶⁻⁹

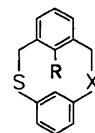
In this work we report the crystal structure and the first determination of the absolute configuration of an optically pure highly strained helical cyclophane, namely (+)₃₆₅-(P)-N-(4-tolylsulfonyl)-8-thiomethyl-1-thia-10-aza[2.2]metacyclophane.

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No.	W	X	Y	Z
1	CH ₂	CH ₂	CH ₂	CH
2	CH ₂	S	S	CH
3	CH ₂	S	O	CH
4	CH ₂	S	NTs	CH
5	CH ₂	O	CH ₂	N
6	CH ₂	NTs	CH ₂	CH
7	O	CH ₂	S	CH
8	CH ₂	S	CH ₂	CH

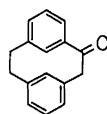


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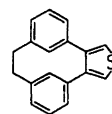


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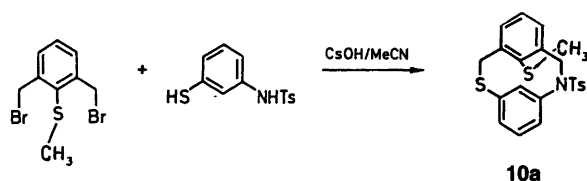
- a: R = SMe
- b: R = OMe
- c: R = COOMe
- d: R = CH₃
- e: R = SO₂CH₃
- f: R = C₆H₅



11



12



Experimental

Preparation of 10a. Compound **10a** was obtained by the cyclization of 1,3-bis(bromomethyl)-2-thiomethylbenzene and *N*-(4-toluenesulfonyl)-3-mercaptoaniline using cesium hydroxide^{10,11} as base in acetonitrile under high-dilution conditions.^{12,13,14}

The separation of the enantiomers was done using HPLC with poly(triphenylmethyl methacrylate) [(+)-PTMMA], ('Okamoto-resin')¹⁵ as a chiral phase. The crystals of the pure (+)₃₆₅-enantiomer were recrystallized from ethanol.

Crystal structure analysis and determination of the absolute configuration of 10a. The crystal data and conditions for the data collection are given in Table 1. * The lattice parameters were determined by measuring 25 reflections using Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation at room temperature (296 K). Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using Mo K_{α} radiation and $\omega/2\theta$ scan mode. The intensity data was corrected for Lorentz and polarization effects but not for extinction. An empirical absorption correction using psi scan data on 10 degree intervals was carried out for the data set, the maximum transmission being 99.98% and the minimum 93.34% on intensity. The structure was solved by direct methods using the MULTAN11/82 program.¹⁶ The final refinements were carried out by full-matrix least-squares using the SDP program package,¹⁷ anisotropically for all non H-atoms. The H-atom coordinates were calculated to their ideal positions (C-H distance 1.00 \AA) and used as riding atoms in final refinements with a fixed isotropic temperature factor ($B = 5.0 \text{ \AA}^2$). The absolute configuration was determined by refining the Rogers polarity parameter,¹⁸ η , and the Flack's enantiomer parameter,¹⁹ x , with the data set containing all Friedel pairs. These refinements were carried out using the CRYSTALS program package²⁰ with all non H-atoms with unit weights and gave the values, $\eta = 0.936$ and $x = -0.041$, indicating the correct absolute configuration (the other enantiomorph gave the values, $\eta = -0.936$ and $x = 1.045$). The atomic scattering factors were taken from Ref. 21. The final coordinates are quoted in Table 2.

The calculations were performed on a μ -VAX II computer at the Department of Chemistry, University of Jyväskylä. In addition to the programs quoted the PLUTO²² and SCHAKAL²³ programs were used.

* Lists of structure factors, anisotropic temperature factors, least-squares planes, H-atom coordinates and torsion angles may be obtained from one of the authors (K.R.) on request.

Table 1. Crystal and experimental data for the helical cyclophane **10a**.

Compound	<i>N</i> -(4-Tolylsulfonyl)-8-thiomethyl-1-thia-10-aza[2.2]metacyclophane
Formula	C ₂₂ H ₂₁ NO ₂ S ₃
M_r	427.61
$a/\text{\AA}$	10.540(1)
$b/\text{\AA}$	11.491(1)
$c/\text{\AA}$	16.768(1)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2030.8(4)
Z	4
$d_{\text{calc}}/\text{Mg m}^{-3}$	1.398
μ/mm^{-1}	0.37
$\lambda(\text{Mo } K_{\alpha})$	0.71073
$F(000)$	896
Space group	$P2_12_12_1$, (No. 19)
T/K	296 \pm 1
Crystal size/mm	0.15 \times 0.18 \times 0.20
Refl. for latt. meas.	25
θ range for latt. meas./ $^\circ$	8–12
Scan method	$\omega/2\theta$
Scan speed/ $^\circ \text{ min}^{-1}$	1–17
Scan width (ω)/ $^\circ$	0.50 + 0.34 tan θ
θ range/ $^\circ$	2–25
h range	–12 \rightarrow 12
k range	–13 \rightarrow 13
l range	–19 \rightarrow 19
Variation of std. refl.	None
Refl. measured	4120 (Friedel pairs)
Number of unique refl.	2060 (merged)
Condition of obs. refl.	$I > 3.0\sigma(I)$
Refl. used in refinement	1610
Max. shift/error	0.01
No. of parameters	253
Max./min. in final $\Delta\rho/\text{e}\text{\AA}^{-3}$	0.19(3)/–0.18(3)
Rogers polarity parameter η	0.936
Flack's enantio parameter x	–0.041
S	1.50
R_{int}	0.015
R	0.028
R_w	0.041
$w = 1/[(\sigma F_o)^2 + (a F_o)^2]$	$a = 0.06$

Results and discussion

The bond distances and angles of **10a** are shown in Table 3. Comparison of the helicity defining torsion angles, α , β , γ and δ , between the thiomethylcyclophane (**10a**) and various other cyclophanes is presented in Table 4. Fig. 1 shows a view of **10a** with the numbering scheme. A stereoscopic view of the molecule is presented in Fig. 2.

The extra strain, which is due to the steric effects caused by the large thiomethyl group occupying position eight [C(8)], induces opening of the heteroatom–carbon bond angle together with a small increase in the heteroatom–carbon bond distances in **10a**. The angle C(2)–S(1)–C(15) together with the C(2)–S(1) and C(15)–S(1) bond distances have now slightly larger values [101.2°, 1.873(4) and 1.776(3) \AA , respectively] than those found in 1-thia-10-(*p*-tol-

Table 2. Fractional coordinates and equivalent isotropic temperature factors^a for **10a** with e.s.d.s in parentheses.

Atom	x	y	z	B _{eq} Å ²
S(1)	1.29530(8)	0.9125(1)	0.78498(5)	4.75(2)
S(2)	1.11629(9)	0.97877(8)	0.99578(5)	3.99(2)
S(3)	0.69297(7)	0.93500(7)	0.81729(5)	3.42(1)
O(1)	0.7132(2)	0.9611(2)	0.7350(1)	4.30(5)
O(2)	0.6328(2)	0.8281(2)	0.8393(2)	4.52(5)
N(10)	0.8320(2)	0.9354(2)	0.8595(2)	3.76(5)
C(2)	1.3059(4)	0.8467(3)	0.8869(2)	4.30(7)
C(3)	1.1863(3)	0.7857(3)	0.9080(2)	4.41(6)
C(4)	1.1633(4)	0.6739(3)	0.8776(2)	4.06(7)
C(5)	1.0450(4)	0.6254(3)	0.8808(2)	4.28(8)
C(6)	0.9432(4)	0.6905(3)	0.9079(2)	3.98(7)
C(7)	0.9622(3)	0.8023(3)	0.9380(2)	3.10(6)
C(8)	1.0861(3)	0.8438(3)	0.9464(2)	3.00(6)
C(9)	0.8494(3)	0.8836(3)	0.9414(2)	3.72(6)
C(11)	0.9349(3)	1.0041(3)	0.8289(2)	3.22(6)
C(12)	0.9394(4)	1.1243(3)	0.8359(2)	3.80(7)
C(13)	1.0528(4)	1.1812(3)	0.8195(2)	4.25(7)
C(14)	1.1612(3)	1.1199(3)	0.8018(2)	4.15(7)
C(15)	1.1558(3)	0.9982(3)	0.7943(2)	3.37(6)
C(16)	1.0400(3)	0.9433(3)	0.8020(2)	3.06(5)
C(17)	1.0632(5)	0.9449(3)	1.0960(2)	5.28(9)
C(18)	0.6021(3)	1.0475(3)	0.8596(2)	3.33(6)
C(19)	0.5711(3)	1.1458(3)	0.8161(2)	4.01(7)
C(20)	0.4893(4)	1.2275(3)	0.8481(2)	4.25(7)
C(21)	0.4381(3)	1.2131(3)	0.9223(2)	4.20(7)
C(22)	0.3427(4)	1.2986(3)	0.9542(3)	5.44(9)
C(23)	0.4736(4)	1.1166(3)	0.9671(2)	4.73(8)
C(24)	0.5544(4)	1.0330(3)	0.9364(2)	4.25(7)

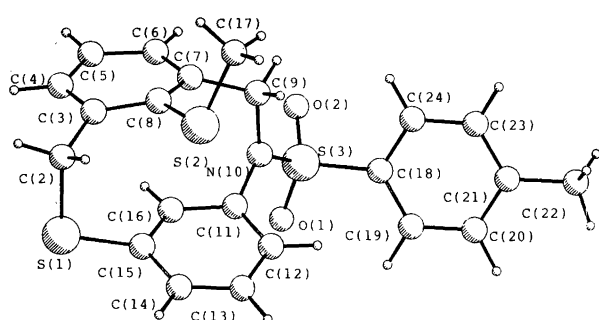
$$^a B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$$

Table 3. Bond distances (Å) and angles (°) for the helical cyclophane **10a**.

S(1)–C(2)	1.873(4)	C(3)–C(4)	1.403(5)	C(14)–C(15)	1.406(5)
S(1)–C(15)	1.776(3)	C(3)–C(8)	1.406(4)	C(15)–C(16)	1.380(4)
S(2)–C(8)	1.787(3)	C(4)–C(5)	1.366(6)	C(18)–C(19)	1.383(4)
S(2)–C(17)	1.814(3)	C(5)–C(6)	1.385(5)	C(18)–C(20)	1.392(5)
S(3)–O(1)	1.428(2)	C(6)–C(7)	1.395(4)	C(19)–C(24)	1.383(5)
S(3)–O(2)	1.431(2)	C(7)–C(8)	1.397(4)	C(20)–C(21)	1.366(5)
S(3)–N(10)	1.627(3)	C(7)–C(9)	1.513(5)	C(21)–C(22)	1.504(5)
S(3)–C(18)	1.758(3)	C(11)–C(12)	1.387(4)	C(21)–C(23)	1.391(5)
N(10)–C(9)	1.509(4)	C(11)–C(16)	1.385(4)	C(23)–C(24)	1.383(5)
N(10)–C(11)	1.437(4)	C(12)–C(13)	1.390(5)	C(2)–C(3)	1.485(5)
C(13)–C(14)	1.375(5)				
C(2)–S(1)–C(15)	101.1(2)	C(3)–C(4)–C(5)	121.2(3)	C(13)–C(14)–C(15)	119.7(3)
C(8)–S(2)–S(17)	100.9(2)	C(4)–C(5)–C(6)	119.9(3)	S(1)–C(15)–C(14)	121.7(2)
O(1)–S(3)–O(2)	119.7(2)	C(5)–C(6)–C(7)	120.4(3)	S(1)–C(15)–C(16)	119.1(2)
O(1)–S(3)–N(10)	106.6(1)	C(6)–C(7)–C(8)	119.0(3)	C(14)–C(15)–C(16)	118.9(3)
O(1)–S(3)–C(18)	108.4(1)	C(6)–C(7)–C(9)	118.0(3)	C(11)–C(16)–C(15)	120.5(3)
O(2)–S(3)–N(10)	106.8(1)	C(8)–C(7)–C(9)	121.3(3)	S(3)–C(18)–C(19)	121.1(2)
O(2)–S(3)–C(18)	106.6(1)	S(2)–C(8)–C(3)	119.4(2)	S(3)–C(18)–C(24)	118.8(2)
N(10)–S(3)–C(18)	108.3(1)	S(2)–C(8)–C(7)	120.6(2)	C(19)–C(18)–C(24)	120.0(3)
S(3)–N(10)–C(9)	120.3(2)	C(3)–C(8)–C(7)	119.6(3)	C(18)–C(19)–C(20)	119.8(3)
S(3)–N(10)–C(11)	121.7(2)	N(10)–C(9)–C(7)	107.8(2)	C(19)–C(20)–C(21)	121.2(3)
C(9)–N(10)–C(11)	116.8(2)	N(10)–C(11)–C(12)	122.9(3)	C(20)–C(21)–C(22)	120.6(3)
S(1)–C(2)–C(3)	110.9(2)	N(10)–C(11)–C(16)	116.3(3)	C(20)–C(21)–C(23)	118.8(3)
C(2)–C(3)–C(4)	119.5(3)	C(12)–C(11)–C(16)	120.2(3)	C(22)–C(21)–C(23)	120.6(3)
C(2)–C(3)–C(8)	121.5(3)	C(11)–C(12)–C(13)	118.8(3)	C(21)–C(23)–C(24)	121.2(3)
C(4)–C(3)–C(8)	118.1(3)	C(12)–C(13)–C(14)	121.1(3)	C(18)–C(24)–C(23)	118.9(3)

Table 4. Torsion angles, α , β , γ and δ ($^\circ$) and transannular distance [C(8)–C(16)], d (\AA), for various helical cyclophanes.

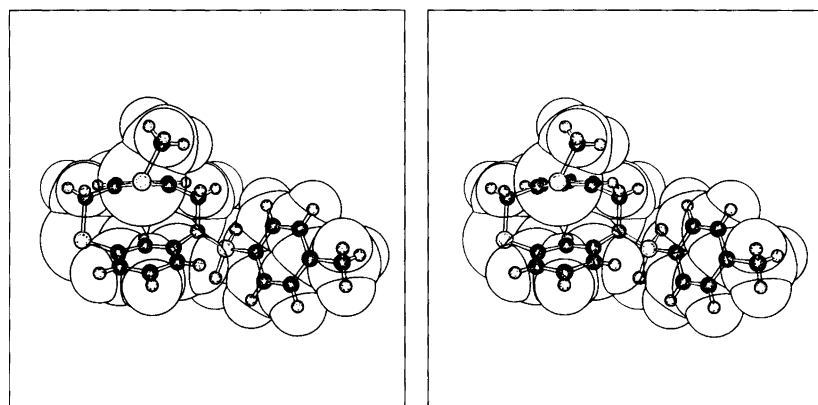
Cyclophane	α	β	γ	δ	d	Reference
10a	10.23	3.56	3.59	18.20	2.720(4)	This work
3	4.4	6.3	5.6	6.9	2.62	5
4	2.4	4.9	6.9	5.4	2.57	5
5	2.00	4.50	3.20	3.60	2.579	7
6	4.28	0.74	5.43	4.33	2.613	8
7	3.9	4.1	8.1	7.1	2.639	9
	9.1	7.3	31.0	8.3	2.59	27
8	2.6	2.9	5.6	3.1	2.681	24
9	7.2	10.1	33.8	7.2	2.58	28
10b	5.45	4.01	6.77	5.78	2.68	12
10c	15.65	4.92	3.63	15.10	2.72	12

Fig. 1. PLUTO plot and the numbering scheme for the helical cyclophane **10a**.

ylsulfonyl)-10-aza[2.2]metacyclophane,⁵ [99.6(3) $^\circ$, 1.851(7) and 1.756(7) \AA , respectively], which does not contain a large substituent in position eight. The C'–S–C'' angle and C'–S and C''–S bond distances are quite close to those observed in a related sulfone,⁹ but markedly different from those found in 1-thia[2.2]metacyclophane.²⁴ The C'–N–C'', C'–N–S and C''–N–S angles and C'–N, C''–N and N–S bond distances are affected as much by the thiomethyl group, and are comparable to the values found in tosyl-group-containing cyclophanes.^{5,8} The chiral N-atom has

nearly planar trigonal coordination, the angles being close to 120 $^\circ$ and the out-of-plane deformation from the least-squares plane [C(9)–C(11)–S(3)] is only 0.096(3) \AA . Due to the very small out-of-plane deformation, the absolute chirality of the N-atom is not very clear, but it could be assigned as *R*. The planarity of the benzene rings [C(3)–C(8) and C(11)–C(16)] is lost due to the steric effects caused by the heteroatom bridges and the large thiomethyl group. The C(5), C(8), C(13) and C(16) benzene ring carbons are deformed out of the benzene planes [–0.053(3), –0.086(3), 0.041(3) and 0.061(3) \AA , respectively] pointing away from the center of the molecule (boat conformation). The transannular distance, d , between the carbons at positions eight and sixteen is also greatly affected by the increasing steric hindrance and the value 2.720(4) \AA is the largest yet found and comparable to distances observed¹² in related cyclophanes **10b** and **10c** (Table 4).

The determination of the absolute chirality of the compound is based on the correct set of coordinates (see the Experimental) and on the helicity defining torsion angles α , β , γ and δ . The definition⁵ of the angles α , β , γ and δ is presented in Fig. 3. According to the data obtained now the absolute chirality of this thiomethyl-substituted cyclophane is assigned⁵ to *P* (for plus of a right-handed helix). The

Fig. 2. Stereoscopic SCHAKAL plot for the helical cyclophane **10a**.

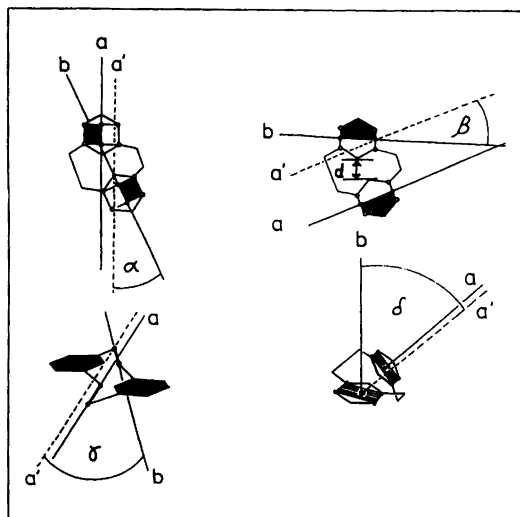


Fig. 3. Comparison of the torsion angles α , β , γ and δ in helical cyclophanes and the intra-annular distance, d . Definition of the angles: a , b , strictly defined lines; a' ; projected line parallel to a (a/a'); a' and b , cross in a well-defined point. α , β , γ and δ are angles formed by the lines a' and b .

values of α and δ are markedly different (Table 4) from those of the other helical cyclophanes. The increase in the torsion angles is caused by the addition of the thiomethyl group into the position eight.

As a consequence of the similarity of the CD spectra of the compounds **4**⁵ and **10a-f**¹² it seems possible to assign a *P*-helicity to the (+)-enantiomers **4**⁵ and **10a-f**¹² due to their common positive Cotton effects at 220–240 nm (Table 5 and Fig. 4).

Interestingly, this correlation is in contrast with the *M*-helicity of the compound (+)-**4**, which was derived earlier⁵ from known absolute configurations of 1-oxo[2.2]metacyclophane (**11**)²⁵ and the thiophenophane (**12**)²⁶ by comparison of the CD spectra.

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Table 5. Absolute configurations of (+)-enantiomers of compounds **10a-f**.

No.	R	Chirality
4	H	(+)- <i>P</i>
10a	SCH ₃	(+)- <i>P</i>
10b	OCH ₃	(+)- <i>P</i>
10c	COOCH ₃	(+)- <i>P</i>
10d	CH ₃	(+)- <i>P</i>
10e	SO ₂ CH ₃	(+)- <i>P</i>
10f	C ₆ H ₅	(+)- <i>P</i>

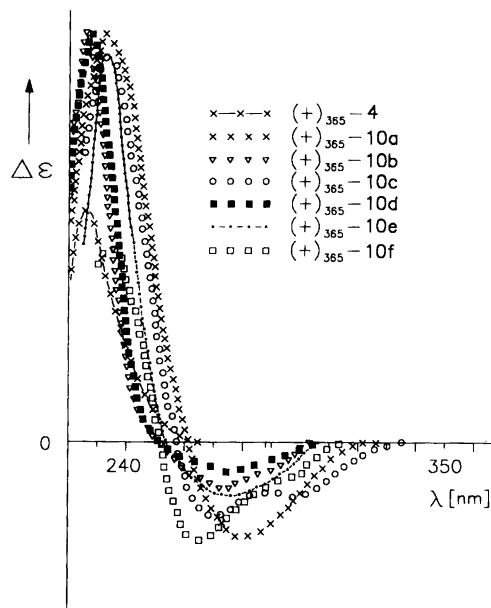


Fig. 4. CD spectra of compounds **4** and **10a-f**, (1,4-dioxane): **10a**: $\Delta\epsilon_{232} = +31.2$, $\Delta\epsilon_{278} = -7.7$; **10b**: $\Delta\epsilon_{227} = +80.4$, $\Delta\epsilon_{276} = -6.5$, $\Delta\epsilon_{291} = -4.0$; **10c**: $\Delta\epsilon_{232} = +23.5$, $\Delta\epsilon_{270} = -4.4$, $\Delta\epsilon_{295} = -3.2$; **10d**: $\Delta\epsilon_{227} = +60.8$, $\Delta\epsilon_{276} = -4.7$; **10e**: $\Delta\epsilon_{232} = +23.4$, $\Delta\epsilon_{276} = -3.2$; **10f**: $\Delta\epsilon_{235} = +11.5$, $\Delta\epsilon_{265} = -5.9$, $\Delta\epsilon_{295} = -1.8$.

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