

Table 1 Total energy (eV) of $\text{-(CH}_2\text{)}_3\text{S-}_n$

Energy ^a	TTTT	TTGT	TGGT	GGGG
Total	-1023.45	-1023.18	-1023.46	-1023.62
Total intrasegment	-988.14	-987.66	-988.31	-987.79
Total one centre	-779.81	-780.25	-780.15	-779.94
Total two centre	-208.33	-207.40	-208.16	-207.85
Resonance	-211.79	-210.94	-211.69	-211.42
Exchange	-46.90	-46.82	-46.86	-46.73
Electrostatic	50.36	50.36	50.38	50.30
Total intersegment	-35.31	-35.52	-35.15	-35.83
0-1 ^b total	-17.65	-17.76	-17.57	-17.91
Resonance	-17.64	-17.78	-17.64	-17.95
Exchange	-2.61	-2.62	-2.57	-2.66
Electrostatic	2.60	2.64	2.64	2.70

^a Meanings of the energy terms are shown in ref. 7

^b For simplicity, 0-1 (segments) means the interaction energy between the central and the first nearest neighbour segments. In this article, up to 0-2 segments were taken into consideration. The 0-2 terms are not listed because the absolute values are less than 0.01 eV

Table 2 Large contributing elements on the energy difference^a of the intersegment two-centre terms among three forms $\text{-(CH}_2\text{)}_3\text{S-}_n$

	TTTT	TGGT	GGGG
(⁰ H3, ¹ S1) ^b	0.00	-0.13	-0.13
(⁰ C5, ¹ S1)	-0.83	-0.74	-0.72
(⁰ C8, ¹ S1)	-16.35	-16.21	-16.22
(⁰ H10, ¹ S1)	-0.25	-0.26	-0.37
(⁰ C8, ¹ C2)	0.05	0.03	-0.08
Total	-17.64	-17.64	-17.95

^a Energy in eV

^b Notations of the elements are the same as in ref. 7

As a result, the intersegment term is dominant in stabilizing the GGGG form. In the total intersegment term, the dominant term in governing the energy difference among the four conformations is the 0-1 interaction term, i.e. between the nearest neighbours. Moreover, it can be seen in the 0-1 intersegment term, that the resonance term is dominant in governing the energy difference among the forms.

To see in more detail the resonance elements, a fairly large energy difference appeared in the elements as is summarized in Table 2. Absolute values of the energy difference among the forms of PTM3 are much larger than those in the oxygen analogue⁸, POM3. As can be easily recognized from this Table, the elements (⁰H10, ¹S1) and (⁰C8, ¹C2) are the dominant ones in stabilizing the GGGG form among the four forms. The type of interaction can be understood with the help of Figure 2. The elements (⁰H3, ¹S1), (⁰H10, ¹S1) and (⁰C8, ¹C2) of PTM3 for example correspond to those of (⁰H13, ¹O1), (⁰H20, ¹O1) and (⁰C18, ¹C2) of POM3 (see also Figure 1 of ref. 8). However, a remarkably large value did not appear in these elements of POM3. We can, therefore, recognize from these results that the electronic situation in PTM3 is quite different from that of POM3. One reason for the different situation may be the widely spread electron of the sulphur atom in PTM3.

CONCLUSION

The conformational stability on PTM3 has been explained by the CNDO/2 calculations using the spd basis set. It was found that the elements governing the energy difference among the forms of PTM3 are different from

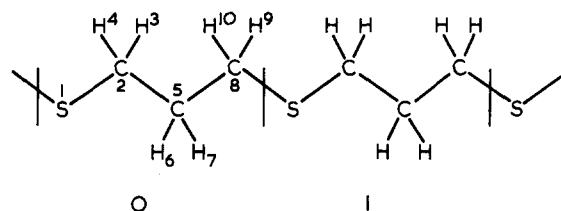


Figure 2 Schematic structure, and atom and segment numberings of PTM3

those in oxygen analogue, POM3. This may be partly due to the wide electronic distribution of the sulphur atoms in PTM3.

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