Conformational stability of poly(trimethylene sulphide)

Masaru Ohsaku and Akira Imamura

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730, Japan (Received 13 May 1983)

CNDO/2 calculations with the spd basis set using the tight-binding approximation for polymers were performed on species of poly(trimethylene sulphide) (PTM3), assuming several typical molecular conformations. From the results of the calculations, the conformational stability of PTM3 is discussed in comparison with that of poly(trimethylene oxide) (POM3).

Keywords Conformation; CNDO/2; MO; sulphide; poly(trimethylene sulphide)

INTRODUCTION

Molecular and electronic structures of molecules of the type $\{(CH_2)_m O\}_n$ have been very extensively studied up to the present time 1-8. On the other hand, for the sulphur analogues such as $[(CH_2)_m S]_n$, crystal structures have been analysed on the species m = 1-3, for example⁹⁻¹¹. With the MO treatments, the CNDO/2 sp and spd calculations were performed previously¹² on the species m=1. Typical conformations for the series $f(CH_2)_m X_{n}^{-1}$ (m=1-3, X=S or O) are shown in Figure 1. It is well known that, in the oxygen analogues, the all-trans conformation becomes favourable with increasing m in the series¹³. However, in the case of the sulphur analogues, such a tendency is not so clearly seen in general in the series for m = 1-3. That is, the stable form in the crystalline state of the species m = 1-3 in the series $[(CH_2)_m]_n$ reported is GG, $\bar{G}TGGT\bar{G}$ and GGGG, respectively. Moreover, in the oxygen analogues, more than two conformations exist independently in the crystalline state¹⁻⁶. However, in the sulphur compounds, only one conformation was reported for each species⁹⁻¹¹.

In the present study, in order to clarify the reasons, the CNDO/2 MO calculations were performed on the species m=3, poly(trimethylene sulphide) (PTM3).

METHOD OF CALCULATION

Calculations were carried out as in previous papers^{7,14,15} using the tight-binding approximation¹⁶. Geometries used were as follows: r(C-H) = 1.09 Å, r(C-S) = 1.81 Å, r(C-C) = 1.54 Å, $\phi(CSC) = 100^{\circ}$, and angles around the carbon atom were assumed to be tetrahedral. Torsional angles used for the *trans* and *gauche* conformations were 180° and 68°, respectively, and the calculations were performed on the four typical conformations, TTTT, TTGT, TGGT and GGGG. The basis set used was the spd.

RESULTS AND DISCUSSION

Table 1 shows the calculated total energies for the TTTT, TTGT, TGGT and GGGG conformations of PTM3. The conformation of the form GGGG was calculated as the

0032-3861/84/040511-02\$03.00 © 1984 Butterworth & Co. (Publishers) Ltd. most stable one. The present result, therefore, reproduces very well the experimental result¹¹ which was concluded from the X-ray analysis of PTM3. The energy difference calculated among the forms is much larger in PTM3 than in the oxygen analogue⁸. The present calculation reflects the experimental result that only one form of PTM3 exists in the crystalline state¹¹. Here the calculated total energy is in the order GGGG < TGGT < TTTT < TTGT.

We now discuss in some detail the energy difference among the different molecular conformations. The partitioned energy according to equations (1)-(4) of ref. 7 are as follows:

Total energy, GGGG < TGGT < TTTT < TTGT. Total intrasegment, TGGT < TTTT < GGGG < TTGT.

Total intersegment, GGGG < TTGT < TTTT < TGGT.

The GGGG form is destabilized by the intrasegment term, but is stabilized by the intersegment term. A similar situation was already seen¹² in the species m=1. The stabilization energy in the intersegment term sufficiently compensates the destabilization in the intrasegment term.



Figure 1 Typical conformations for the species $\{(CH_2)_mX\}_n$ (m=1-3, X=0 or S). Conformations with brackets are the stable forms for oxygen analogues and conformation with asterisk is the most stable one

POLYMER, 1984, Vol 25, April 511

Table 1 Total energy (eV) of $\frac{1}{4}(CH_2)_3S_{\frac{1}{2}n}$

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



	ттт	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
(°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 (°C8, 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), (0 H10, ¹S1) and (0 C8, ¹C2) of PTM3 for example correspond to those of (0 H13, ¹O1), (0 H20, 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.

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, for which the authors express their gratitude. We are also grateful to the Information Processing Center of Hiroshima University and the Computer Center of the Institute for Molecular Science for their general permission to use HITAC M-200H systems.

REFERENCES

- Uchida, T. and Tadokoro, H. J. Polym. Sci. A-2 1967, 5, 63 1
- 2 Carazzolo, G. and Mammi, M. J. Polym. Sci. A 1963, 1, 965
- Tadokoro, H., Chatani, Y., Yoshihara, T., Tahara, S. and 3
- Murahashi, S. Makromol. Chem. 1964, 73, 109 Takahashi, Y., Sumita, I. and Tadokoro, H. J. Polym. Sci., Polym. 4 Phys. Edn. 1973, 11, 2113
- 5 Tadokoro, H., Takahashi, Y., Chatani, Y. and Kakida, H. Makromol. Chem. 1967, 109, 96
- 6 Kakida, H., Makino, D., Chatani, Y., Kobayashi, M. and Tadokoro, H. Macromolecules 1970, 3, 569
- Ohsaku, M. and Imamura, A. Macromolecules 1978, 11, 970 7 8 Ohsaku, M., Izouka, T., Murata, H. and Imamura, A. Polymer
- 1981. 22, 624 9
- Carazzolo, G. and Valle, G. Makromol. Chem. 1966, 90, 66
- 10 Takahashi, Y., Tadokoro, H. and Chatani, Y. J. Macromol. Sci., Phys. 1968, 2, 361
- Sakakibara, E., Takahashi, Y. and Tadokoro, H. Abstracts. 11 SPSJ, 18th Annual Meeting, Tokyo, 11 November 1969, p. 407
- 12 Ohsaku, M., Murata, H., Imamura, A. and Tachibana, A. Polymer 1981, 22, 1346
- 13 Tadokoro, H. 'Kobunshi no Kozo' (Molecular Structure of Polymers), Kagakudojin, Kyoto, 1976
- Imamura, A. and Fujita, H. J. Chem. Phys. 1974, 61, 115 Pople, J. A. and Beveridge, D. L. 'Approximate Molecular 14 15
- Orbital Theory', McGraw-Hill, New York, 1970
- For example, Slater, J. C. 'Quantum Theory of Molecules and 16 Solids', McGraw-Hill, New York, 1965