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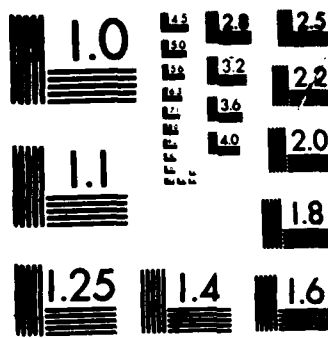
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Technical Report No. 1

A ROTATIONAL ISOMERIC STATE MODEL FOR THE POLYCARBONATE
OF 2,2' - BIS (4-HYDROXYPHENYL) PROPANE

by

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A ROTATIONAL ISOMERIC STATE MODEL FOR THE POLYCARBONATE OF 2,2'-BIS(4-HYDROXYPHENYL)PROPANE

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Recently, the conformations of fragments of the polycarbonate of 2,2'-bis(4-hydroxyphenyl)propane (hereafter abbreviated PC) have been the subject of several detailed studies in which quantum chemical^{1,2} and molecular mechanical^{3,5,7} methods have been used. The rotational isomeric state (RIS) model for this chain molecule has not been revised accordingly, and Williams and Flory's⁶ RIS scheme is usually used unchanged.^{8,12} It seems appropriate and timely to incorporate the newer structural and conformational data into a revised RIS model.

Based mainly on the data provided by Bicerano and Clark¹ and Perez and Scaringe² we formulate the following RIS model; all torsion angles are zero in the planar ("zig-zag") conformation depicted in Figure 1. Geometric data is collected in Table 1. Statistical weight matrices and the associated sets of torsion angles are shown in Table 2.

The limiting unperturbed mean-square end-to-end distance of PC, calculated with this RIS model, is

$$\lim_{M \rightarrow \infty} \langle r^2 \rangle_0 / M = 0.85 \text{ \AA}^2 \text{ mol g}^{-1}$$

This compares favorably to the reported experimental values of 0.75 $\text{\AA}^2 \text{ mol g}^{-1}$ (light scattering¹²), 0.87 $\text{\AA}^2 \text{ mol g}^{-1}$ ($[\eta]$ ¹²), and 0.98 $\text{\AA}^2 \text{ mol g}^{-1}$ (light scattering¹³).

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We gratefully acknowledge financial support of MH by IBM through a Program of Polymer Science and Technology (PPST) Fellowship at MIT, and of UWS by the Bayer Professorship at MIT. We would especially like to thank Drs. Joseph Bicerano, Hayden Clark, and Alan Letton from Dow Chemical Company for providing us with preprints of their work prior to publication, and for many invigorating discussions.

TABLE 1: Geometric Data

Bond Number	"Real" Length, \AA	RIS Bond Length, \AA
1	1.54	4.30
2	1.54	4.30
*	2.76	(Phenyl rings included in t_1, t_2)
3	1.41	1.41
4	1.33	1.33
5	1.33	1.33
6	1.41	1.41
Bond Angles, degrees		
$\pi - \phi_1$		109.8
$\pi - \phi_2$		117.7
$\pi - \phi_3$		105.8
$\pi - \phi_4$		117.7

TABLE 2: RIS Parameters

At ca. Room Temperature

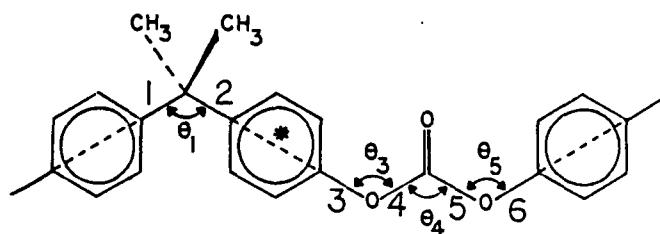
Bond Number i	(ϕ_i) , degrees	U_i
1	45, 135, 225, 315	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$
2	45, 135, 225, 315	$\begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}$
3	45, 135, 225, 315	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$
4	0, 180	$\begin{bmatrix} 1 & \gamma \\ 1 & \gamma \\ 1 & \gamma \\ 1 & \gamma \end{bmatrix}$
5	0, 180	$\begin{bmatrix} 1 & \gamma \\ 1 & 0 \end{bmatrix}$
6	45, 135, 225, 315	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$

where $\gamma = \exp(-500/T)$ with T in K.

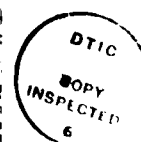
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FIGURE 1



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