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CONFORMATIONAL ANALYSIS OF POLY-2,5-BENZOIMIDAZOLE (ABPBI),
POLY-2,5-BENZOXAZOLE (ABPBO), AND POLY-2,6-BENZOTHIAZOLE
(ABPBT) DIMERS BY THE MODIFIED NEGLECT OF DIATOMIC OVERLAP
(MNDO) AND AUSTIN METHOD 1 (AM1) SEMIEMPIRICAL MOLECULAR
ORBITAL METHODS

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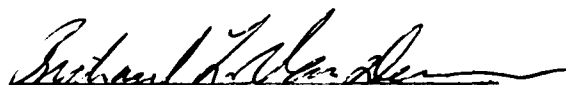Final Report for Period August 1986 - September 1986

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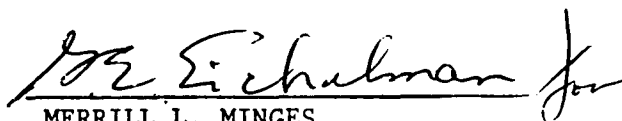This technical report has been reviewed and is approved for publication.

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07	04		Poly-2,5-benzoimidazole Austin Method 1
11	04		Poly-2,6-benzothiazole Molecular Orbital

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The two repeat unit analogs of three, aromatic, heterocyclic polymers were studied as part of the Materials Laboratory's research program to develop high-performance polymers with good environmental resistance. The Modified Neglect of Diatomic Overlap (MNDO) and Austin Method 1 (AM1) semiempirical orbital methods were used to calculate the change in energy of the molecules with rotation about the bond connecting the two repeat units. Curves of torsion angle versus heat of formation were obtained where minima on the curves represent the most thermodynamically stable conformations of the molecules.

The AM1 method was found to be superior to the MNDO method in all cases. The MNDO method produced near perpendicular minima while AM1 gave planar or near planar minima, consistent with x-ray studies of the polymers.

In all three cases the transoid conformations were lower in energy than the cisoid. However, the barrier to rotation was so low, 2.5 kcal/mol in the highest case, that (cont)

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Poly-2,5-benzoxazole (ABPBO), and Poly-2,6-benzothiazole (ABPBT) Dimers by the Modified Neglect of Diatomic Overlap (MNDO) and Austin Method 1 (AM1) Semiempirical Molecular Orbital Methods

19. ABSTRACT (Cont)

free rotation would occur about the connecting bond at room temperatures. Extended chains can be formed by attaching repeat units in a transoid fashion, while coiled structures occur if the cisoid conformation is used.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structure Resins." During the period of August 1986 to September 1986 the work was administered under the direction of Materials Laboratory (ML), Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command (AFSC), Wright-Patterson Air Force Base, Ohio, 45433-6533 with Dr. I. J. Goldfarb as the ML Project Scientist. The report was released by the author 2Lt Scott G. Wierschke, Air Force Wright Aeronautical Laboratories, Materials Laboratory, Polymer Branch (AFWAL/MLBP) in February 1987.

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SECTION I

INTRODUCTION

The need to correlate the properties of isolated molecules with those of the bulk materials they form has prompted the use of molecular modeling and computational chemical methods, both empirical and molecular orbital, to study polymers. Computational techniques can give insight into the structure and conformations of a molecule which may be difficult or impossible to obtain by any experimental method. Useful information is obtained in a short time and can be used to guide future experiments.

Polymer systems are too large for the use of rigorous ab initio quantum mechanical calculations with today's computers. These computations are too long to be practical, even on a Cray. Therefore, the semiempirical methods, Modified Neglect of Diatomic Overlap (MNDO) (Reference 1) and Austin Method 1 (AM1) (Reference 2), which speed up the calculations by approximating the electron repulsion and exchange integrals generated by the quantum mechanical treatment, are used. These methods are just beginning to be used to characterize polymer systems. Much work is needed to make them useful tools for polymer study.

In this study, the effect of torsion angle on heat of formation has been examined for molecules containing two repeat units of the poly-2,5-benzoimidazole (ABPBI), poly-2,5-benzoxazole (ABPBO), and poly-2,6-benzothiazole (ABPBT) polymers. The torsion is performed around the bond connecting the two repeat units. The minimum energy conformations for the molecules are determined and discussed. Both the MNDO and AM1 methods were used to give a good comparison of the two techniques.

ABPBI, ABPBO and ABPBT are all polymers of interest in the Air Force Ordered Polymers Research Program to develop high-performance polymers with good environmental resistance for aerospace applications. ABPBI has been studied as a component of a molecular composite (Reference 3), while extensive studies of ABPBO fibers have been done in the Polymer Branch (Reference 4). This computational study will aid in the understanding of these materials on a molecular level.

SECTION II

COMPUTATIONAL DETAILS

The MNDO and AM1 semiempirical molecular orbital programs in the MOPAC, version 3.10 (Reference 5), program package were used. The "precise" keyword was employed which increases the optimization criteria 100 times.

Single repeat units, capped by hydrogen atoms at the connection points, of ABPBI, ABPBO, and ABPBT were built and fully optimized with both the MNDO and AM1 methods. These optimized structures were used to construct dimers, again with hydrogen atoms capping the ends, of each polymer.

The connecting carbon-carbon bond between the repeat units is the torsion bond. The torsion angle is labeled θ (Figure 1). A $\theta = 0^{\circ}$ denotes a cisoid planar structure, i.e., like groups on same side. A $\theta = 180^{\circ}$ denotes a transoid planar structure, i.e., like groups on opposite sides (Figures 2-4).
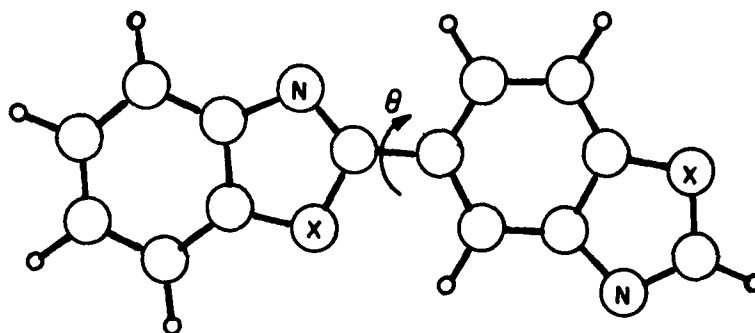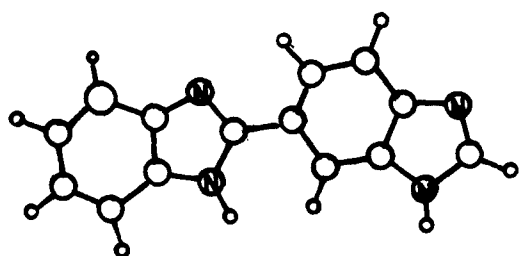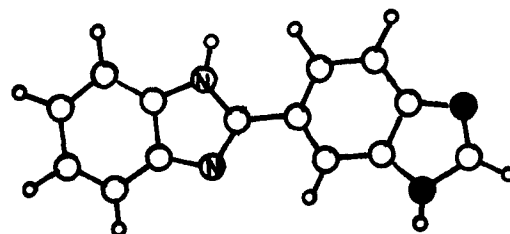

Figure 1. The Torsion Angle θ

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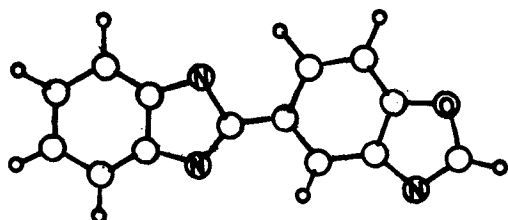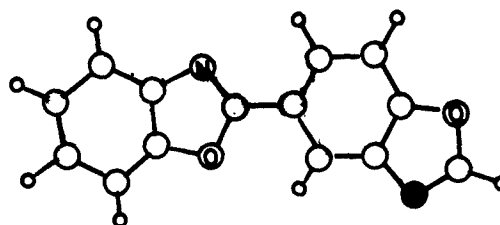(i) Cisoid   (ii) Transoid

Figure 2. Cisoid and Transoid Conformations of ABPBI

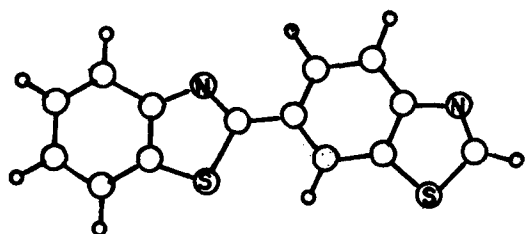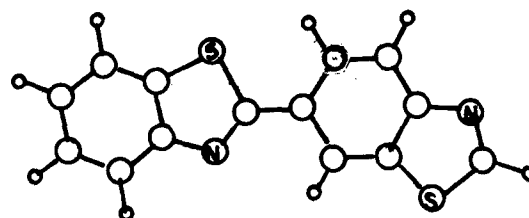(i) Cisoid   (ii) Transoid

Figure 3. Cisoid and Transoid Conformations of ABPBO

(i) Cisoid   (ii) Transoid

Figure 4. Cisoid and Transoid Conformations of ABPBT

The geometries of each dimer were optimized, using both AM1 and MNDO, at every 10° increment of θ between 0° and 180°. These were full optimizations; i.e., all bond lengths, bond angles, and dihedral angles were optimized, for ABPBI and ABPBT. Since the ABPBT repeat units showed no deviation from planarity during the rotation, the repeat unit dihedral angles for ABPBO were set to give a planar repeat unit and not optimized. The ABPBI repeat unit wouldn't be expected to stay perfectly planar during the rotation since it contains an sp^3 nitrogen. The rotation from 0° to 180° gives the mirror image of the energy curve that would be obtained from a 0° to -180° scan because of the C_s symmetry of the molecules. Thus, a full 360° rotation can be studied in half the time using the 0° to 180° scan.

The energy minima and maxima were found by fully optimizing the geometries from low and high points in the energy curves. Force constants were calculated to ensure that these points were indeed minima and maxima. The results were plotted as heat of formation vs torsion angle (Figures 5-10).
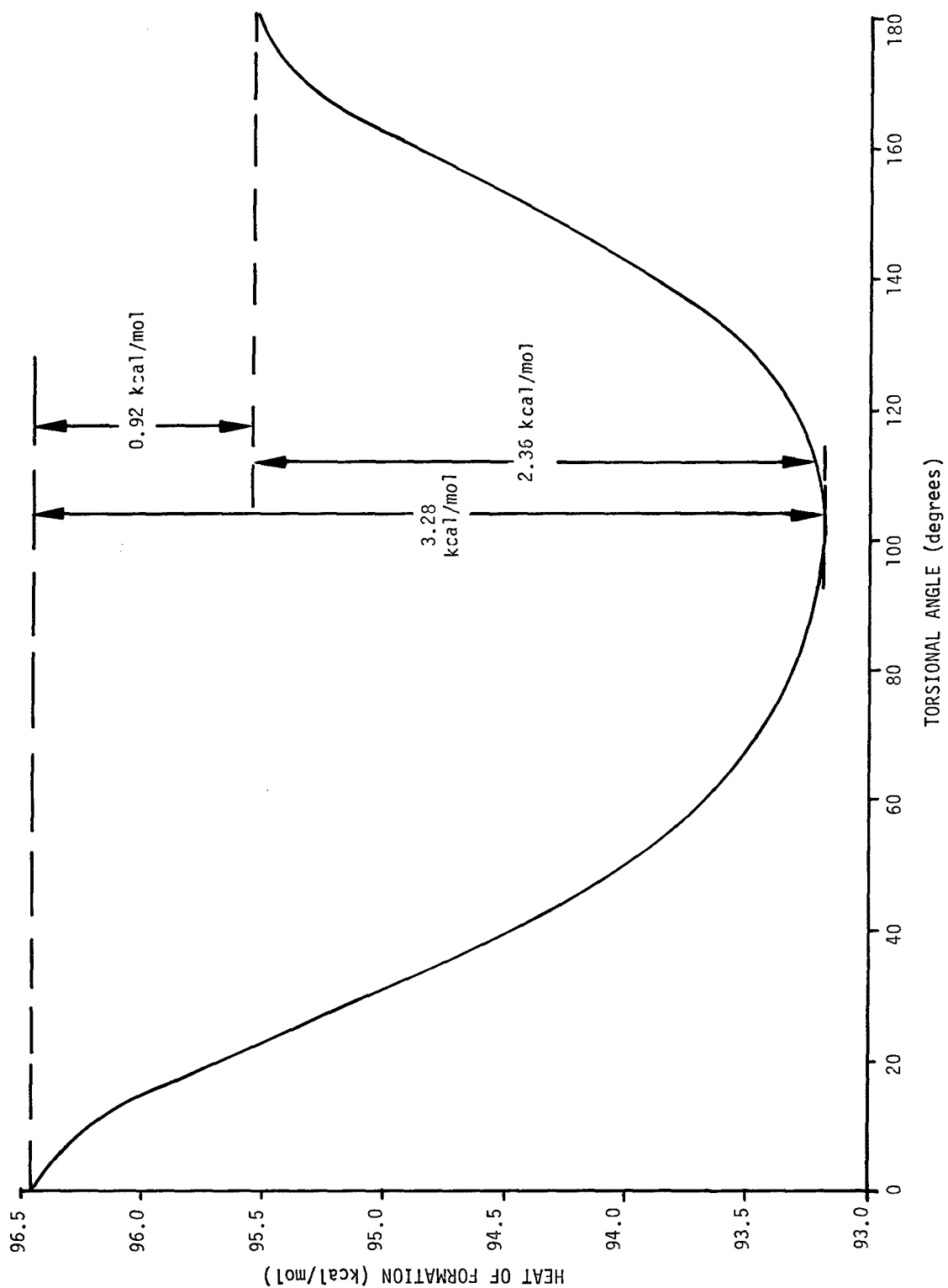
Figure 5. MNDO ABPBI Dimer Torsional Scan 0-180°

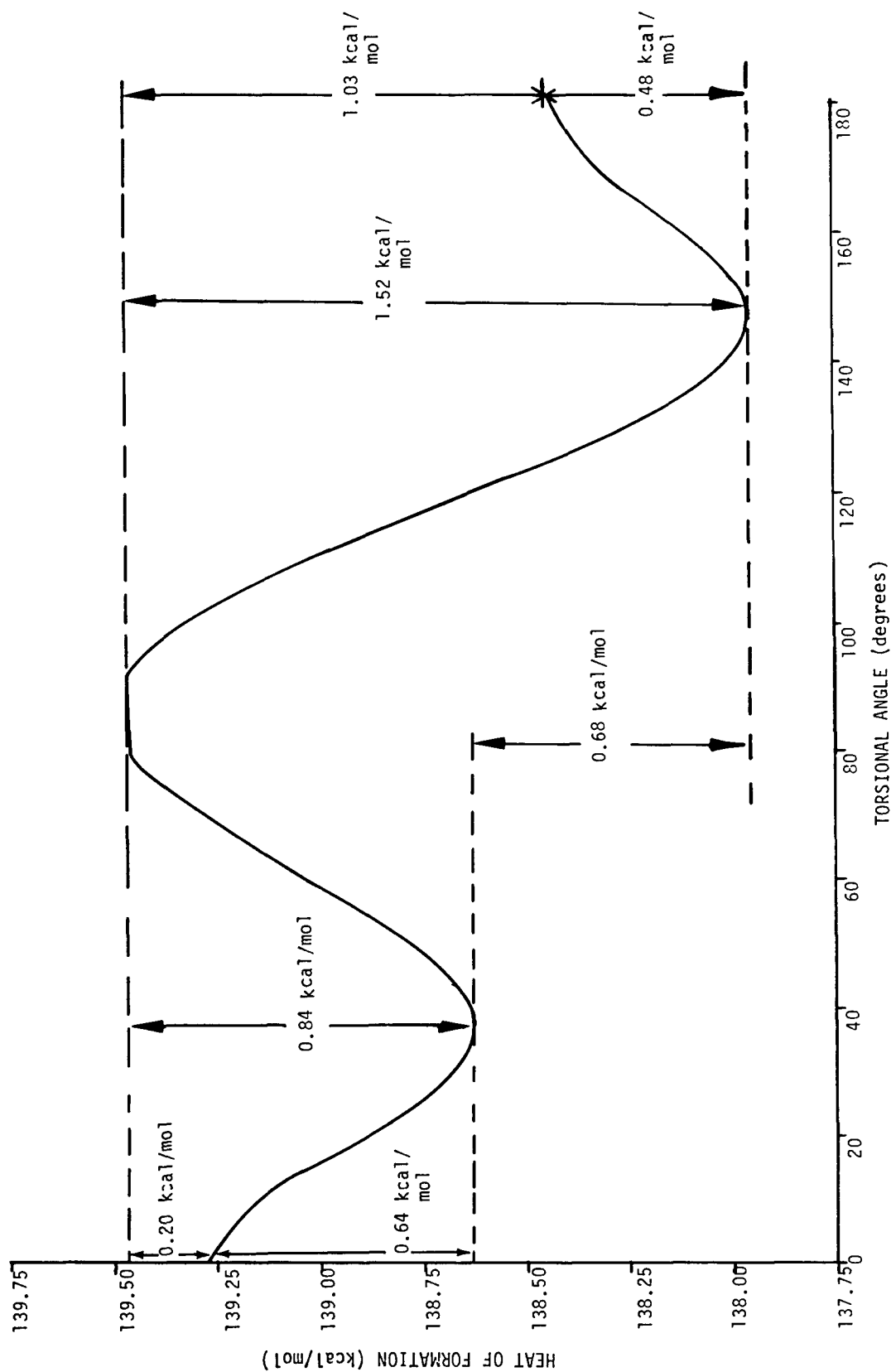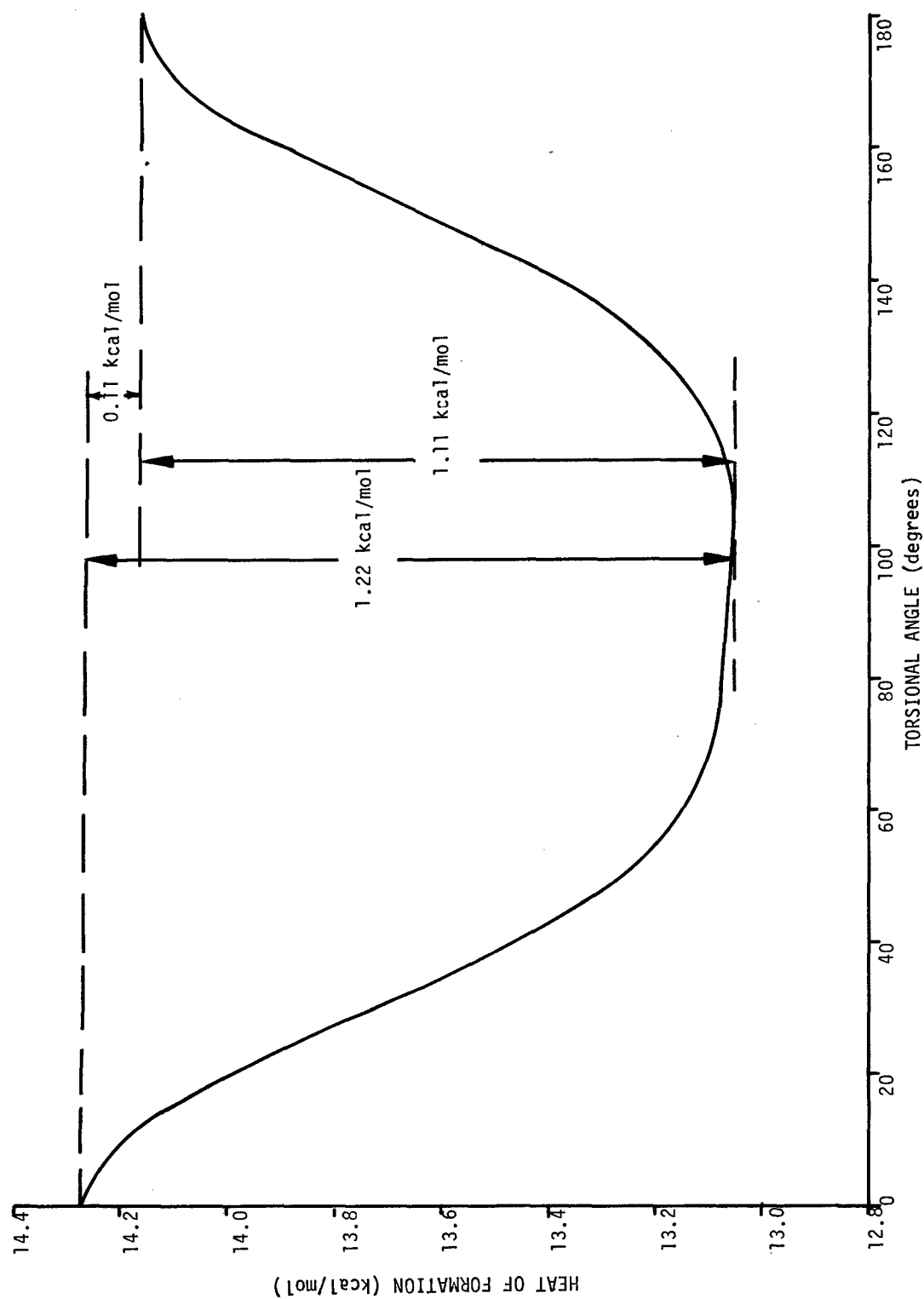Figure 6. AM1 ABPBI Dimer Torsional Scan 0-180°

Figure 7. MNDO ABPBO Dimer Torsional Scan 0-180^0
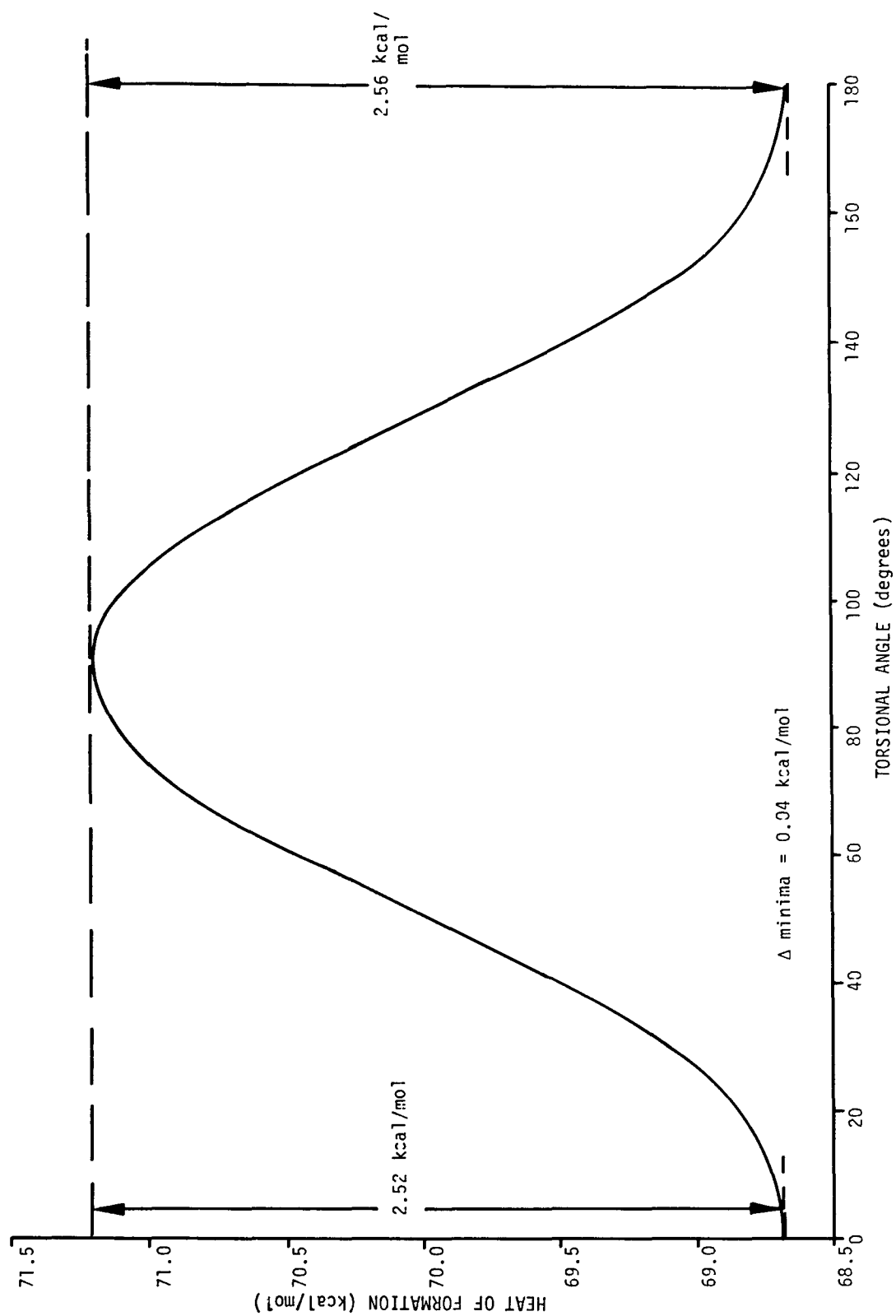
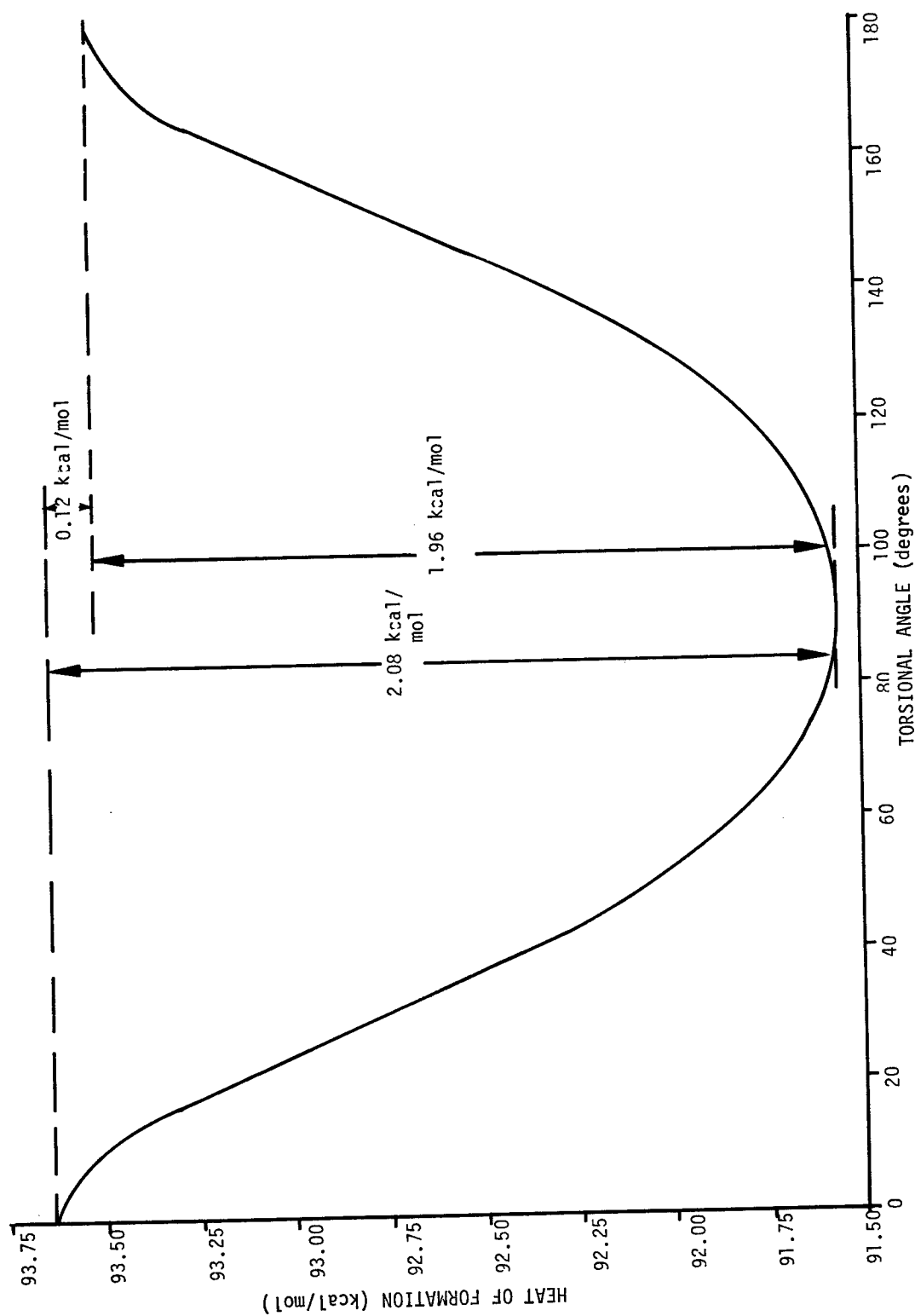Figure 8. AM1 ABPBO Dimer Torsional Scan 0-180°

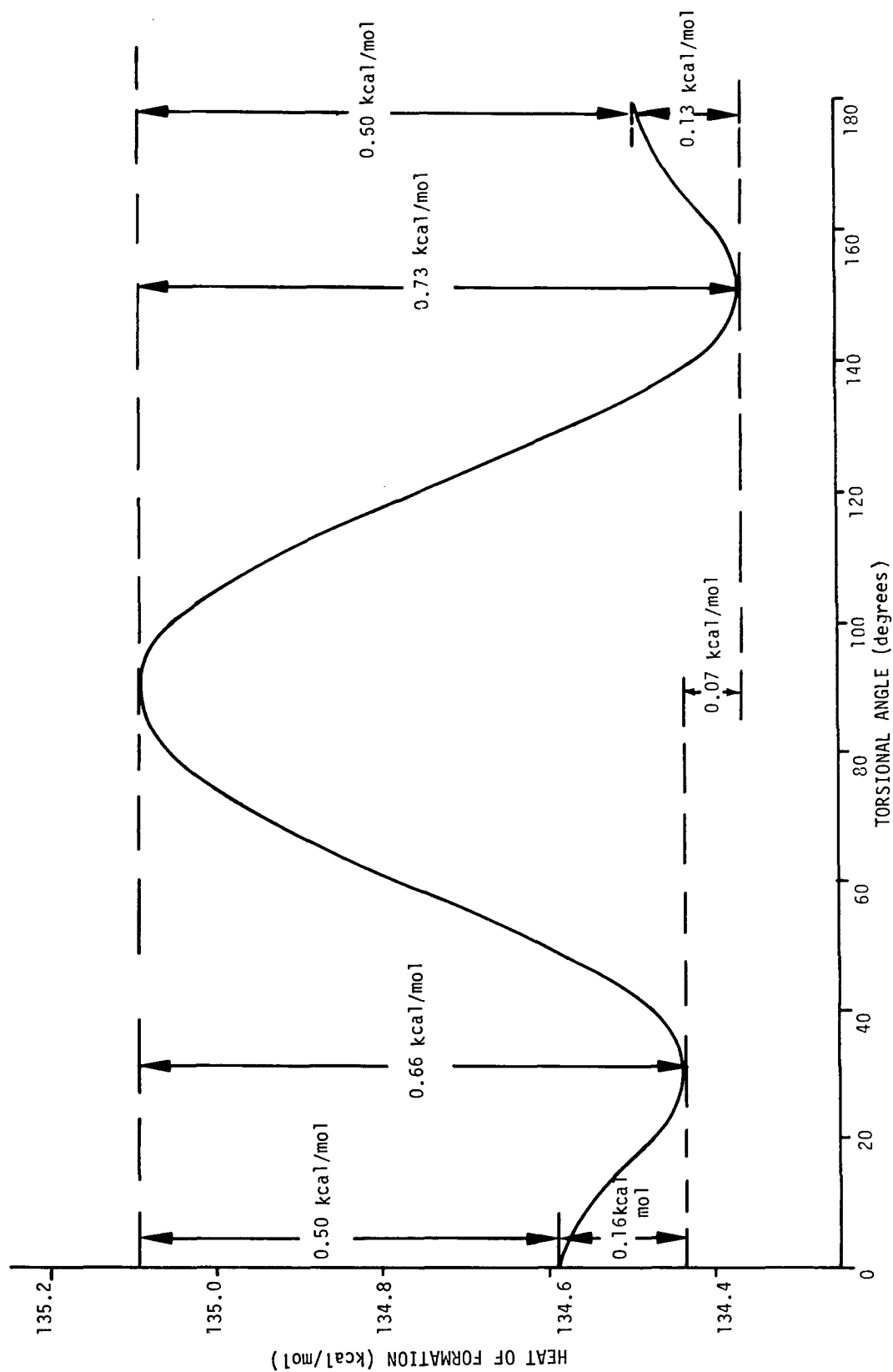Figure 9. _MNDO ABPBT Dimer Torsional Scan 0-180°_

Figure 10. AM1 ABPBT Dimer Torsional Scan 0-180°

SECTION III

RESULTS AND DISCUSSION

Table 1 contains the torsion angle vs heat of formation data, both MNDO and AM1, for ABPBI, ABPBO, and ABPBT. The minima are marked by *, the maxima by **. Figures 5-10 are heat of formation vs torsion angle plots for each system.

MNDO vs AM1. In comparing the MNDO and AM1 plots, we see that the two methods are giving opposite results. Each MNDO plot shows an energy minimum at θ about 90°, while the AM1 plots show maxima at $\theta = 90^o$. This is not surprising since MNDO is known to overestimate internuclear repulsions. Thus, in cases such as these where the extension of the conjugation should force the molecule into a more planar conformation, MNDO allows the repulsion terms to dominate giving the near perpendicular conformation as a minimum. The AM1 Hamiltonian has softer repulsion terms and seems to give better results in these cases. ABPBO and ABPBT have been shown, by x-ray diffraction, to adopt near planar, zigzag conformations (Reference 6). The MNDO results are given to show a comparison of the two methods.

ABPBI. In Figure 5 MNDO shows a minimum at 103.9^o. The minimum is 3.28 kcal/mol below the maximum at 0° and 2.36 kcal/mol below the maximum at 180°.

Figure 6 shows that AM1 gives minima at 36.2^o and 147.3^o. The second minima is 0.68 kcal/mol lower than the first. The barrier between the two minima is only 1.52 kcal/mol, suggesting there is free rotation in the dimer at room temperature. The nonplanar minima in this two repeat unit molecule is not surprising since the sp^3 nitrogen in ABPBI has a hydrogen atom and prefers bond angles nearer to tetrahedral than planar. An extended and near planar, zigzag, polymer chain could be constructed by putting the near transoid units together and alternating the torsional angle between 147.3 and -147.3^o.

ABPBO. In Figure 7 MNDO gives a minimum at 103.9^o. The minimum 1.22 kcal/mol lower than the maximum at 0° and 1.11 kcal/mol lower than the maximum at 180°.

TABLE 1. Torsion Angle vs Heat of Formation Data
(Angles in degrees, Energies in kcal/mol)

ABPBI Dimer (AM1)		ABPBO Dimer (AM1)		ABPBT Dimer (AM1)	
**0.0	139.26	*0.0	68.68	**0.0	134.59
10.0	139.14	10.0	68.72	10.0	134.55
20.0	138.87	20.0	68.84	20.0	134.47
30.0	138.67	30.0	69.09	*30.0	134.43
*36.2	138.62	40.0	69.48	40.0	134.48
40.0	138.63	50.0	69.97	50.0	134.61
50.0	138.78	60.0	70.46	60.0	134.78
60.0	139.03	70.0	70.86	70.0	134.94
70.0	139.29	80.0	71.12	80.0	135.05
80.0	139.45	**90.0	71.21	**90.0	135.09
**90.0	139.46	100.0	71.11	100.0	135.05
100.0	139.30	110.0	70.84	110.0	134.93
110.0	139.00	120.0	70.42	120.0	134.75
120.0	138.61	130.0	69.93	130.0	134.56
130.0	138.24	140.0	69.45	140.0	134.42
140.0	138.00	150.0	69.06	*150.0	134.36
*147.3	137.95	160.0	68.81	160.0	134.39
150.0	137.96	170.0	68.68	170.0	134.46
160.0	138.10	*180.0	68.65	180.0	134.49
170.0	138.32				
**180.0	138.43				

ABPBI Dimer (MNDO)		ABPBO Dimer (MNDO)		ABPBT Dimer (MNDO)	
**0.0	96.46	**0.0	14.27	**0.0	93.64
10.0	96.22	10.0	14.19	10.0	93.51
20.0	95.67	20.0	13.99	20.0	93.19
30.0	95.04	30.0	13.72	30.0	92.77
40.0	94.46	40.0	13.46	40.0	92.37
50.0	94.00	50.0	13.27	50.0	92.04
60.0	93.67	60.0	13.15	60.0	91.81
70.0	93.45	70.0	13.09	70.0	91.67
80.0	93.31	80.0	13.07	80.0	91.59
90.0	93.22	90.0	13.06	90.0	91.56
100.0	93.17	100.0	13.06	*93.14	91.56
*103.9	93.17	*103.9	13.05	100.0	91.58
110.0	93.19	110.0	13.06	110.0	91.64
120.0	93.29	120.0	13.10	120.0	91.77
130.0	93.51	130.0	13.20	130.0	91.99
140.0	93.87	140.0	13.38	140.0	92.30
150.0	94.35	150.0	13.62	150.0	92.69
160.0	94.89	160.0	13.88	160.0	93.09
170.0	95.34	170.0	14.08	170.0	93.40
**180.0	95.54	**180.0	14.16	**180.0	93.51

*Energy minima
**Energy maxima

The AM1 plot (Figure 8) shows minima at 0° and 180°, the transoid minimum is 0.04 kcal/mol lower in energy than the cisoid minimum. The barrier between the minima is 2.56 kcal/mol, again suggesting free rotation. The sp^3 oxygen with no third group attached can keep a near tetrahedral bond angle and still be planar with respect to the rest of the molecule, giving the planar minima. An extended planar, zigzag chain can be achieved by tacking single repeat units together in a transoid fashion. Tacking the repeat units together in a cisoid fashion would give a spiralling chain with about 16 repeat units per full turn.

ABPBT. In Figure 9 MNDO gives a minimum at 93.1^O. The minimum is 2.08 kcal/mol below the maximum at 0° and 1.96 kcal/mol below the maximum at 180°.

Note that there are no AM1 parameters for sulfur as of yet, so the AM1 scan (Figure 10) used MNDO parameters for sulfur and AM1 parameters for all other atoms. The minima are at 30° and 150° with the second only 0.07 kcal/mol below the first. The barrier between minima is 0.7 kcal/mol, indicating free rotation in the dimer. The barrier to a planar minimum is only 0.13-0.16 kcal/mol. This suggests that with AM1 parameters for sulfur ABPBT would be analogous to ABPBO. When sulfur parameters are available this system will be rerun. An extended near planar, zigzag chain can be made by attaching repeat units in the near transoid conformation and alternating the torsion angle between 150° and -150°.

SECTION IV

CONCLUSIONS

The results of a torsion angle study, using the MNDO and AM1 semiempirical molecular orbital methods, on two repeat unit molecules of ABPBI, ABPBO, and ABPBT were presented. The AM1 method was found to be better suited for the types of systems studied than MNDO. The AM1 minimum structures gave reasonably good agreement with the structures obtained in x-ray studies of the actual polymers (Table 2). We saw that although the transoid, or near transoid, conformations were more thermodynamically favored than the cisoid, or near cisoid, the energy barriers between the minima were too small to prevent free rotation in the dimers at room temperature. Obviously, these dimers cannot be used to completely describe the polymers they represent, but they do give an idea as to what is occurring at the junction between repeat units. The information obtained in this study would have been difficult, if not impossible to get experimentally. The use of these methods in the study of polymer systems will be the subject of future work.

Table 2. Calculated Minimum- and X-ray Torsion Angles

	MNDO	AM1	X ray
ABPBI	103.9^o	147.3^o	-----
ABPBO	103.9^o	180.0^o	180.0^o
ABPBT	93.9^o	150.0^o	180.0^o

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