The Structure of Some Phenol-Formaldehyde Condensates for Wood Adhesives

R. Smit[ab]; A. Pizzi[ac]; C. J. H. Schutte[d]; S. O. Paul[d]

[a] Processing and Chemical Manufacturing Technology Division CSIR, Pretoria, Republic of South Africa [b] Department of Chemistry, UNISA, Pretoria, South Africa [c] Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa [d] Department of Chemistry, University of South Africa (UNISA), Pretoria, Republic of South Africa

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THE STRUCTURE OF SOME PHENOL-FORMALDEHYDE CONDENSATES FOR WOOD ADHESIVES

R. SMIT † and A. PIZZI ‡

Processing and Chemical Manufacturing Technology Division
CSIR
P.O. Box 395, Pretoria 0001, Republic of South Africa

C. J. H. SCHUTTE and S. O. PAUL

Department of Chemistry
University of South Africa (UNISA)
P.O. Box 392, Pretoria 0001, Republic of South Africa

ABSTRACT

The probable minimum-energy structures of three dimeric, three tri-
meric, and two hexameric phenol-formaldehyde (PF) condensates were
determined by using a simplified model where the total energy was cal-
culated as the sum of the van der Waals, hydrogen bonding, torsional,
and electrostatic energies. The minimum-energy conformation was de-
fined as that with internal angles of rotation that correspond to the
overall minimum in the total energy. Representations of the structures
of these PF condensates in the minimum-energy conformations were
obtained. The results obtained indicated that the van der Waals energy,
and in some cases the hydrogen bonding energy, make the most impor-
tant contributions to the total energy. The phenol-formaldehyde dimers
and trimers are predicted by this model to have nonplanar structures,
and the longer phenol-formaldehyde condensates, such as the hexamers,
probably exist in helical conformations.

†Present address: Department of Chemistry, UNISA, Pretoria,
South Africa.
‡Present address: Department of Chemistry, University of the
Witwatersrand, P.O. Wits 2050, Johannesburg, South Africa.

INTRODUCTION

Phenol-formaldehyde (PF) resins are currently produced in large quantities for many uses, for instance, the manufacture of exterior-grade wood adhesives. Many aspects of the chemistry of phenolic resins have been examined and described in the last half-century [1]. However, the structure of such systems is still unknown, with the exception of 3,3″-dichloro-4,4″-dihydroxydiphenylmethane [2], which is related to the PF-dimers to be described below.

The molecular structure of simple PF condensates like dimers and trimers is of importance to an understanding of the structure of the PF resins and warrant further study. These molecules are too big for a formal quantum mechanical treatment or even for semiempirical molecular-orbital studies, and further approximate methods are needed for the computation of molecular geometry. The methods of molecular mechanics focus upon the internal forces in the molecules exemplified by force constants and should present a reasonable model.

It was, however, decided to use another approach, namely to investigate the appropriateness of an even simpler model in which the basic bond-distance and interbond-angle geometry of the molecule were assumed, and the atom groups were allowed to rotate freely around the methylene and OH bonds under the influence of electrostatic forces upon the atoms, van der Waals forces, and hydrogen-bond forces. This model allows calculations to be executed for simple potential functions with a computer program [3], and the total relative molecular energies can be expressed as the sum of the van der Waals energy, the hydrogen bonding energy, electrostatic energy, and the energy of torsion around the bonds. The systematic variation of the torsional angles around the methylene and OH bonds allowed the determination of the relative minimum total energy and, hence, the most stable geometrical conformation. The model thus permits the determination of the most probable molecular conformation as well as two-dimensional plots of the van der Waals and the relative total energies as functions of the $-CH_2-$ torsional angles (van der Waals and total energy maps). It must be pointed out that 1) all energies reported are relative energies, and 2) the study leads to comparison of the conformations of relative total minimum energy of the various molecules investigated.

The present calculations show that this very simple model predicts the correct geometrical conformations of molecules like acetone, and of the x-ray-derived conformation of 3,3′-dichloro-4,4′-dihydroxydiphenylmethane [2], which form a rather stringent test for any geometrical investigation.

The input for the electrostatic part of the calculation consists of the par-

TABLE 1. Molecular Dimensions Used for the Phenol-Formaldehyde Condensates

Bond	Length, Å
$C_{phenyl\ ring}-C_{phenyl\ ring}$	1.38
$C_{phenyl\ ring}-C_{methylene}$	1.50
$C_{phenyl\ ring}-O$	1.37
$C-H$	0.98
$O-H$	0.90

Bond	Angle, degrees
$C_{phenyl\ ring}-C_{methylene}-C_{phenyl\ ring}$	112.5
$C_{phenyl\ ring}-C_{phenyl\ ring}-C_{phenyl\ ring}$	120
$C_{phenyl\ ring}-O-H$	110
$C_{phenyl\ ring}-C_{phenyl\ ring}-H$	120

tial electrostatic charges on the various atoms. These charges on the various atoms were obtained from semiempirical molecular orbital calculations with the MNDO/3 (QCPE Programme 485) [4]. The charges give a fair indication of the electron distribution in the molecules and are consistent with the bond orders found experimentally for similar compounds.

The bond lengths and bond angles were obtained from an extensive literature search of compounds that are similar to these PF dimers and trimers and contain the basic dihydroxydiphenylmethane unit. Such compounds are o-cresol [5], p-cresol [6], m-cresol [7], catechol [8], resorcinol [9], and diphenylmethane [10]. The aromatic bond lengths were assumed to be all equal to 1.38 Å. The bond lengths and interbond angles used are given in Table 1. These data differ somewhat from those of the compound 3,3″-dichloro-4,4″-dihydroxydiphenylmethane, the structure of which was determined by Whittaker [2] and which shows an anomalous and inexplicable variation of the aromatic C–C bond distances, as well as a deviation of 12° in the C–C–C interbond angle at the methylene bridge. This interbond angle was taken to be 112.5° in the present study, which is the corresponding angle in diphenylmethane.

FIGURE I (a)

STRUCTURAL FORMULAE FOR THE PHENOL FORMALDEHYDE
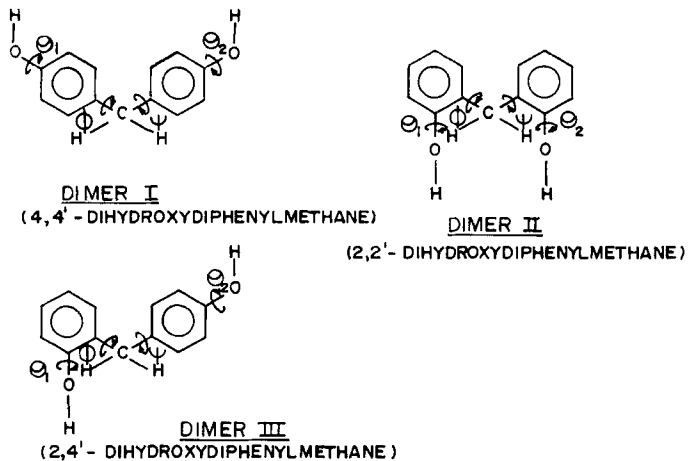(PF) - DIMERS, TRIMERS AND HEXAMERS

DIMER I
(4,4' - DIHYDROXYDIPHENYLMETHANE)

DIMER II
(2,2'- DIHYDROXYDIPHENYLMETHANE)

DIMER III
(2,4'- DIHYDROXYDIPHENYLMETHANE)

FIGURE I (b)

PF - TRIMERS

TRIMER I
(2,4-BIS [(4-HYDROXYPHENYL) METHYL]
PHENOL)

TRIMER II
(2,6 -BIS [(4-HYDROXYPHENYL) METHYL]
PHENOL)

TRIMER III
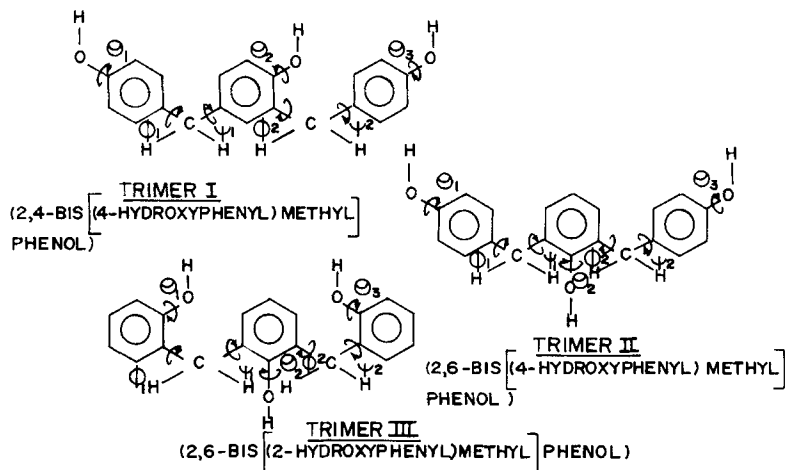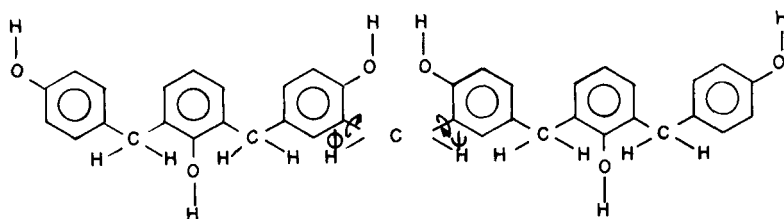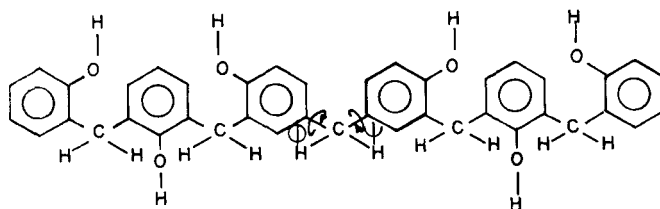(2,6-BIS [(2-HYDROXYPHENYL)METHYL] PHENOL)

FIGURE I (c)

PF - HEXAMERS

HEXAMER I

HEXAMER II

FIG. 1. Structural formulas of the phenol-formaldehyde dimers, trimers, and hexamers examined.

THE PF CONDENSATES EXAMINED

Figure 1 displays the structural formulas of the dimers, trimers, and hexamers of the PF condensates examined in this study, as well as the relevant torsional angles around the OH group (θ angles) and the CH_2 groups (ϕ and ψ angles). Some of the C—O—H bonds are shown linear for the sake of clarity.

The dimers represent all the possible PF dimer structures since the OH group on the phenyl groups can only be in a position which is either *ortho*

or *para* to the methylene carbon. The three trimers studied were those which had been previously isolated from phenol-formaldehyde condensates [11]. The hexamers represent a possible precursor to a PF polymer and were, therefore, examined to obtain a probable relative minimum-energy conformation which would allow extrapolation to the polymeric structure.

ROTATION OF BONDS

Four, seven, and two rotational angles were defined for the PF dimers, trimers, and hexamers, respectively, as indicated in Fig. 1. The arbitrary initial conformation (before any optimization of the structure started by the rotation around bonds) was chosen to be the same for all PF condensates examined, namely, with all the atoms of the phenolic rings of each PF condensate in the same plane (only the methylene bridge of angles are not in this plane). For the initial conformation a value of $0°$ was assigned to the bond rotational angles of each PF condensate. The convention of rotation is such that the arrows on the structural formulas in Fig. 1 indicate *positive rotation* from the initial conformation. All bond rotational angles must be rotated simultaneously in order to optimize the structure. This was possible for the PF dimers and hexamers, but long computer execution times made it impractical for the PF trimers. The bond rotational angles of the PF trimers, therefore, had to be rotated in groups, using procedures described in
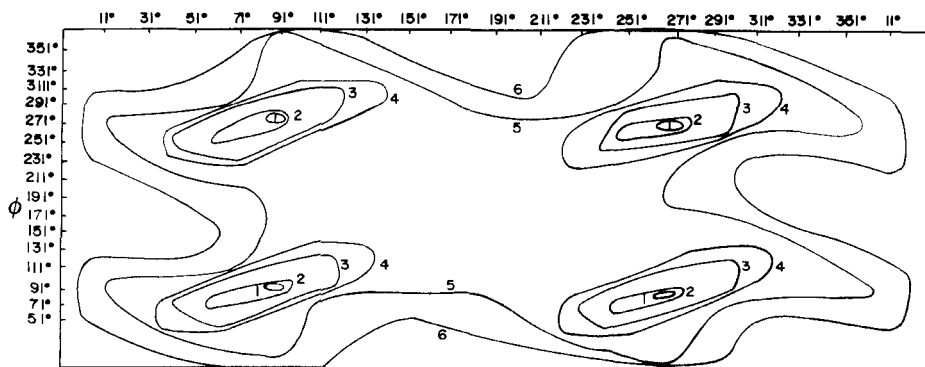
FIG. 2. Total energy map for Dimer 1. Energies in kJ/mol: 1, 260.16; 2, 260.45; 3, 261.08; 4, 261.82; 5, 265.68; 6, 343.09.
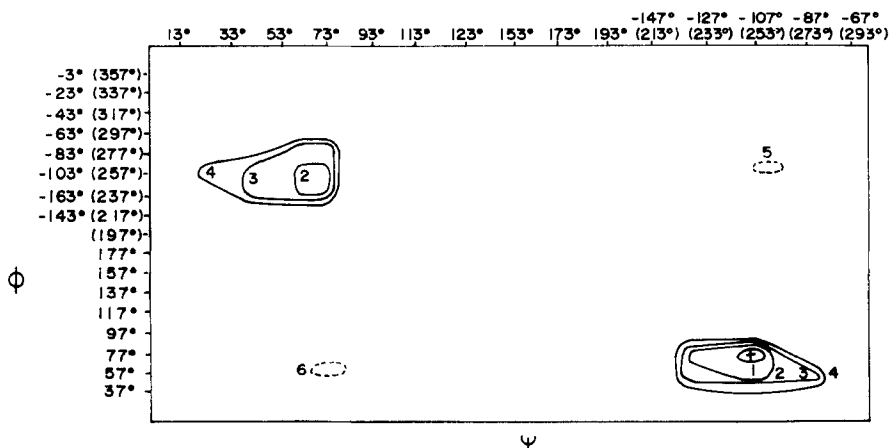
FIG. 3. Total energy map for Dimer II; $(\theta_1, \theta_2) = (-99°, -57°)$. Energies in kJ/mol: 1, 246.19; 2, 259.41; 3, 264.43; 4, 267.78; 5, 268.62; 6, 273.05. The symbol + indicates the minimum energy structure.

detail elsewhere [12]. All bond rotations were initially done from 0 to 360° with a 20° increment to identify the relative energy minima. This process was repeated successively with a 10, 5, 2, and a final 1° increment to determine the final minimum. The energy maps obtained were numerical and were transformed into the contour-line types shown in Figs. 2-4 by drawing energy contour lines obtained by joining graphically angle conformations with definitely the same energy.

RESULTS AND DISCUSSION

There are two and four sets of optimum values for the hydroxyl bond rotational angles for the dimers and trimers, respectively, with the exception of Trimer III, for which there is only a single set. For each of these sets there are four sets of optimum values for the methylene bond rotational angles (i.e., four rotamers), one of which corresponds to the *global* relative energy minimum (minimum-energy conformation), while the remaining three are *local* relative energy minima. Therefore, each dimer has eight rotamers, while each trimer has 16 rotamers (with the exception of Trimer III, which has only four rotamers). The results for the dimers and trimers are given in Table 2.
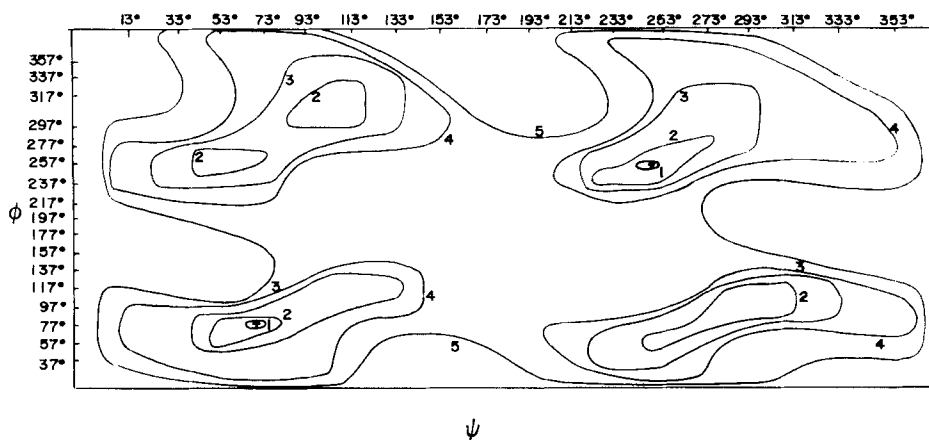
FIG. 4. Van der Waals energy map for Dimer II. Energies in kJ/mol:
1, 219.24; 2, 221.75; 3, 223.43; 4, 233.05; 5, 376.56. The symbol + indicates the minimum van der Waals energy.

For Dimer I (similarly for Dimer III and Trimers I and II), the van der Waals energy is the main contributor to the total energy (hydrogen bonding is absent). Figure 2 indicates the small difference in total energy between the four rotamers for $(\theta_1,\theta_2) = (\pm89°,\pm89°)$. In fact, there is only a small total energy difference between all eight rotamers of Dimer I. In Fig. 2, as well as in Figs. 3 and 4, the global relative energy minimum is indicated with a "+" sign and the energy associated with each of the isoenergy contour lines is given underneath. The two p-hydroxyl groups of Dimer I do not place any restriction on rotation of the methylene bond rotational angles θ_1 and θ_2 and therefore the optimum values for θ_1 and θ_2 agree with the values determined for diphenylmethane [10], and the minimum-energy structure of Dimer I in Fig. 5 is that of diphenylmethane with two p-hydroxyl groups.

The total relative energy map for Dimer II (Fig. 3) shows that one of the Dimer II rotamers (minimum-energy conformation) has a considerably lower total energy than the remaining three for $(\theta_1,\theta_2) = (-99°,-57°)$. That is the effect of a difference in hydrogen bonding energy between these four rotamers. Figure 6 shows that, in the structure of the minimum-energy conformation, the hydroxyl groups are oriented in an optimum position for hydrogen bonding (the hydrogen bonding energy $E_{HB} = -18.912$ kJ/mol). The conformation $(\theta_1,\theta_2,\phi,\psi) = (-99°,-57°,-103°,73°)$ has a less favorable orientation of the hydroxyl groups for hydrogen bonding ($E_{HB} = -6.19$

TABLE 2. Minimum Energy Conformations for the PF Dimers and Trimers

	Optimum values for	Minimum energy conformations	Total energy, kJ/mol	Hydrogen bonding energy, kJ/mol
Dimer I	(89°,89°)	(89°,89°,91°,91°)[a]	260.103	0
	(89°,-89°)	(89°,-89°,91°,-89°)	260.103	0
Dimer II	(-99°,-57°)	(-99°,-57°,77°,-107°)[a]	246.191	-18.912
	(57°,99°)	(57°,99°,107°,77°)	246.208	
Dimer III	(-81°,-89°)	(-81°,-89°,-111°,65°)[a]	260.065	0
	(80°,-88°)	(80°,-88°,111°,115°)	260.073	0
Trimer I	(-91°,-81°,91°)	(-91°,-81°,91°,-84°,-89°,77°,69°)[a]	469.441	0
	(87°,-81°,91°)	(87°,-81°,91°,96°,-89°,77°,69°)	469.449	0
	(-91°,-81°,-87°)	(-91°,-81°,-87°,-84°,89°,77°,-111°)	469.491	0
	(87°,-81°,-87°)	(87°,-81°,-87°,96°,-89°,77°,-111°)	469.503	0
Trimer II	(89°,90°,89°)	(89°,90°,89°,-61°,117°-117°,-61°)[a]	466.445	0
	(-89°,90°,89°)	(-89°,90°,89°,119°,117°,-117°,61°)	466.445	0
	(-89°,90°,-89°)	(-89°,90°,-89°,-61°,117°,-117°,61°)	466.453	0
	(89°,90°,-89°)	(89°,90°,-89°,-61°,117°,-117°,119°)	466.453	0
Trimer III	(57°,99°,-89°)	(57°,99°,-89°,-73°,-79°,-111°,-102°)[a]	427.856	-39.497

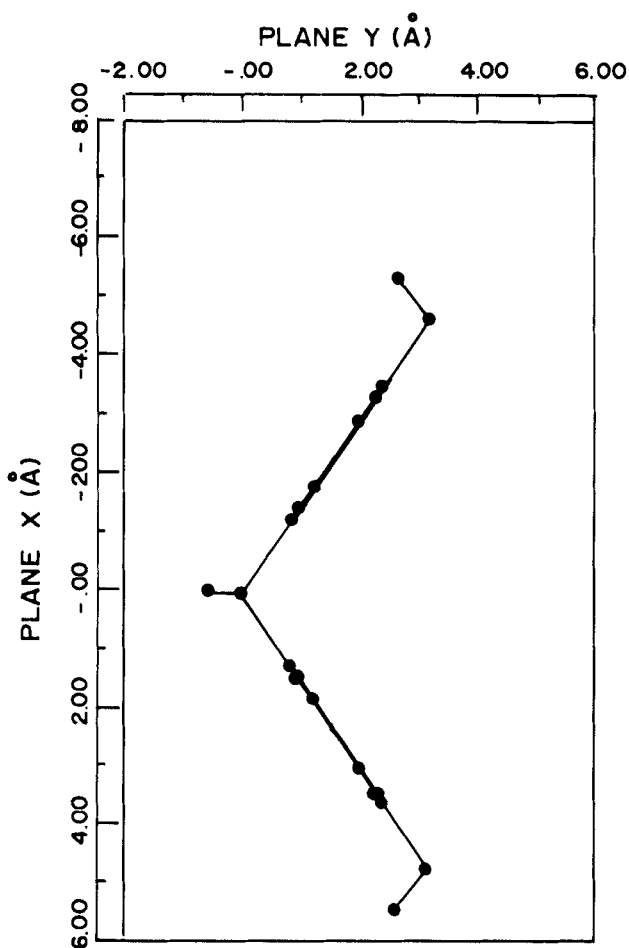[a] Conformations of which structure representations are given.

FIG. 5. Planar projection of the minimum total energy structure of Dimer I.

kJ/mol), while no hydrogen bonding is present for the remaining two rotamers for $(\theta_1, \theta_2) = (-99°, -57°)$. There is no substantial difference between the relative van der Waals energies of these four rotamers, but the two rotamers with hydrogen bonding absent have the lowest relative van der Waals energies, as is evident from Fig. 4.
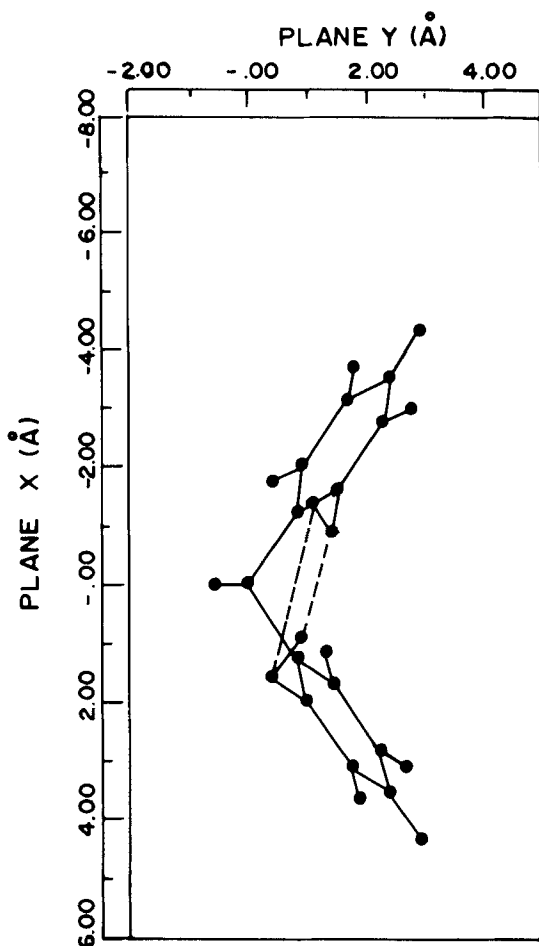
FIG. 6. Planar projection of the minimum total energy structure of
Dimer II. Broken lines indicate the location of hydrogen bonds.

If undissolved (e.g., in a cured PF resin), Dimer II will probably exist in
the conformations of lowest relative total energy (cf. Table 2), the structure
of which is shown in Fig. 6, where the broken lines indicate hydrogen bond-
ing. When dissolved in a solvent which forms intermolecular hydrogen bond-
ing with the dimer molecules (e.g., in a PF resin being applied to timber),
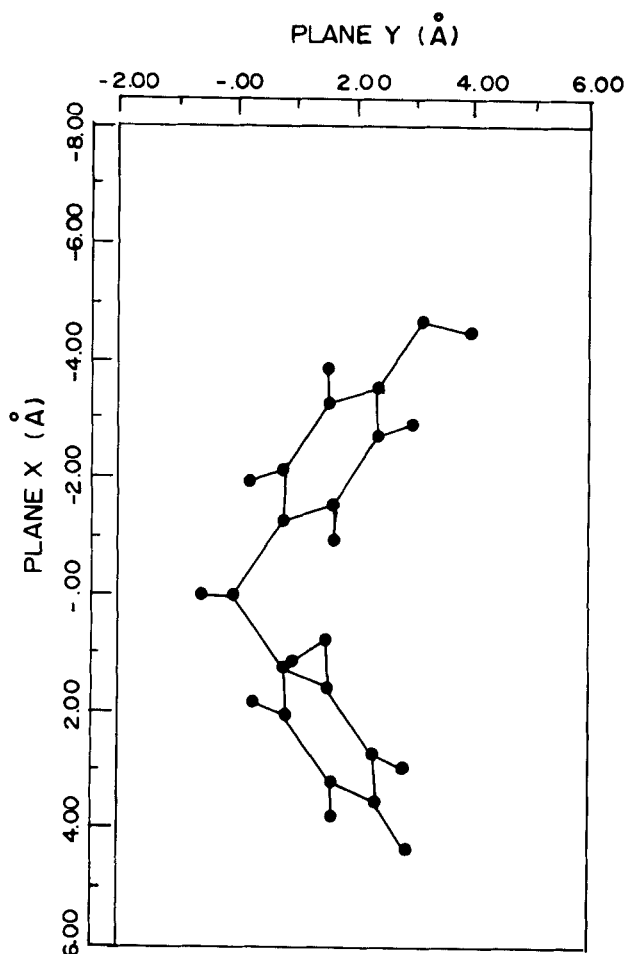
PLANE Y (Å)

FIG. 7. Planar projection of the minimum total energy structure of Dimer III.

intramolecular hydrogen bonding between dimer molecules will be masked (prevented) and Dimer II molecules will probably exist as the rotamers of lowest relative van der Waals energy. The same applies for Trimer III. In the cases of Dimer I, Dimer III, Trimer I, and Trimer II with hydrogen bonding absent, the dimer and trimer molecules will probably exist in the confor-
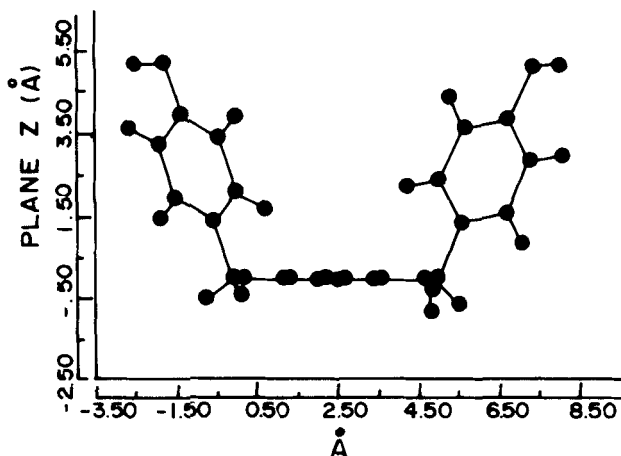
FIG. 8. Planar projection of the minimum total energy structure of Trimer I.

mations of lowest total energy, which also have the lowest van der Waals energies. in the undissolved and dissolved states.

Figures 7–10 represent the minimum-energy structures of Dimer III, Trimer I, Trimer II, and Trimer III. In Trimer I and Trimer II with hydrogen bonding absent, the two outer phenolic rings are on the same side of the middle ring (*cis* conformation) to minimize the relative van der Waals energy, while hydrogen bonding is the driving force for the *trans* conformation of Trimer III.

The results obtained for the hexamers indicate that longer phenol-formaldehyde polymers probably exist in helical conformations and that the shape of the helix depends on the nature of the methylene bridging in the structure. Figures 11 and 12 are representations of the relative minimum-energy conformations of (helical structures) Hexamers I and II.

CONCLUSIÓNS

The results of this study can be useful in an examination of the interaction between phenol-formaldehyde condensates and cellulose in both the undissolved and dissolved states for which a model of the behavior of phenol-formaldehyde resins has been developed[13,14].Such a model may be used to explain
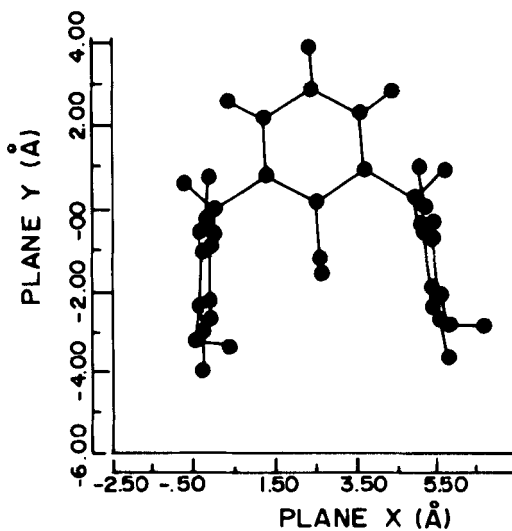
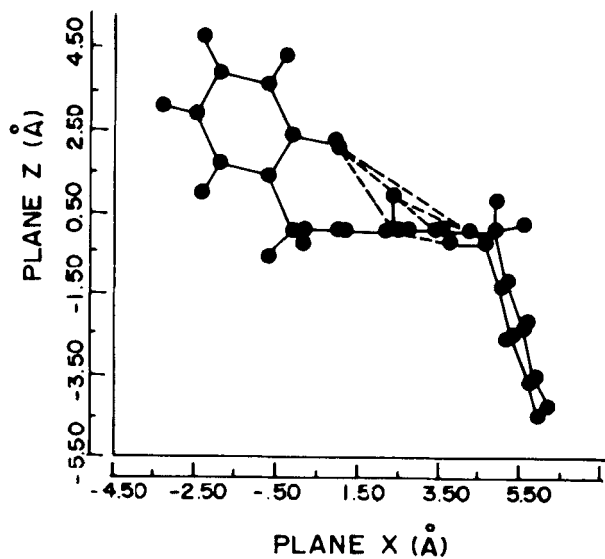FIG. 9. Planar projection of the minimum total energy structure of Trimer II.

FIG. 10. Planar projection of the minimum total energy structure of Trimer III. Broken lines indicate the location of hydrogen bonds.
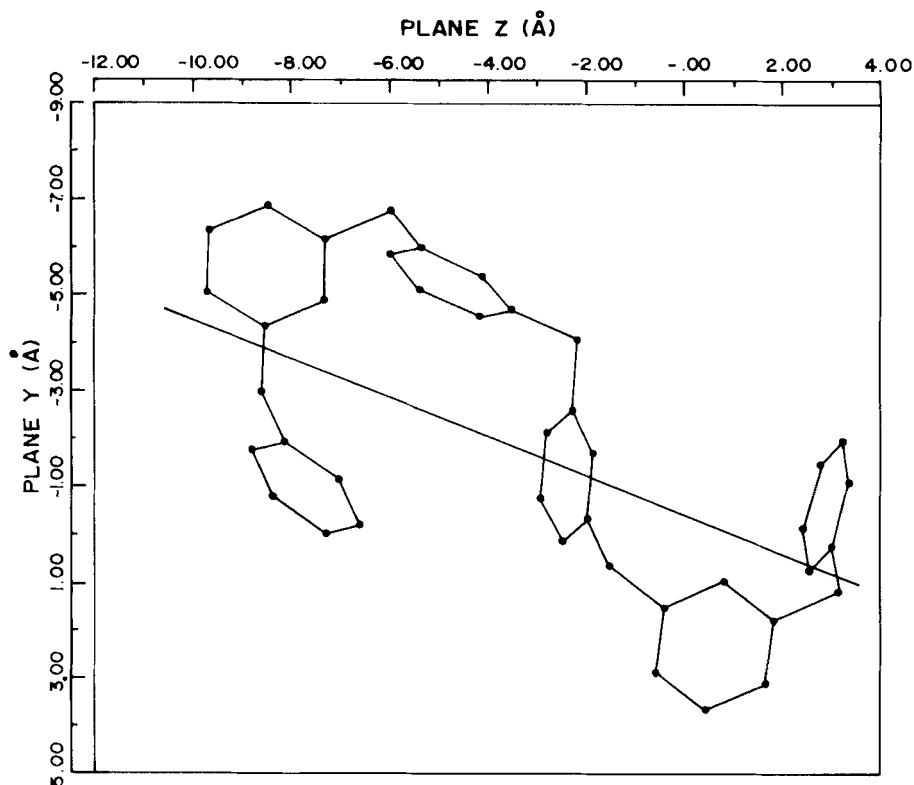
PLANE Z (Å)

FIG. 11. Planar projection of the minimum total energy structure of Hexamer I. The axis represents the control axis of the helix formed by the polymer.

many of the gluing characteristics of phenol-formaldehyde resins. It will also give an indication of the influence of hydroxyl group orientation in the phenol-formaldehyde condensates on gluing efficiency. Appropriate reaction conditions can be used to produce resins which are rich in phenol-formaldehyde [13, 14] condensates content with the most favorable hydroxy group orientation (e.g., all*ortho*) for a specific application. Such a model can, therefore, be helpful for the production of more effective adhesives.
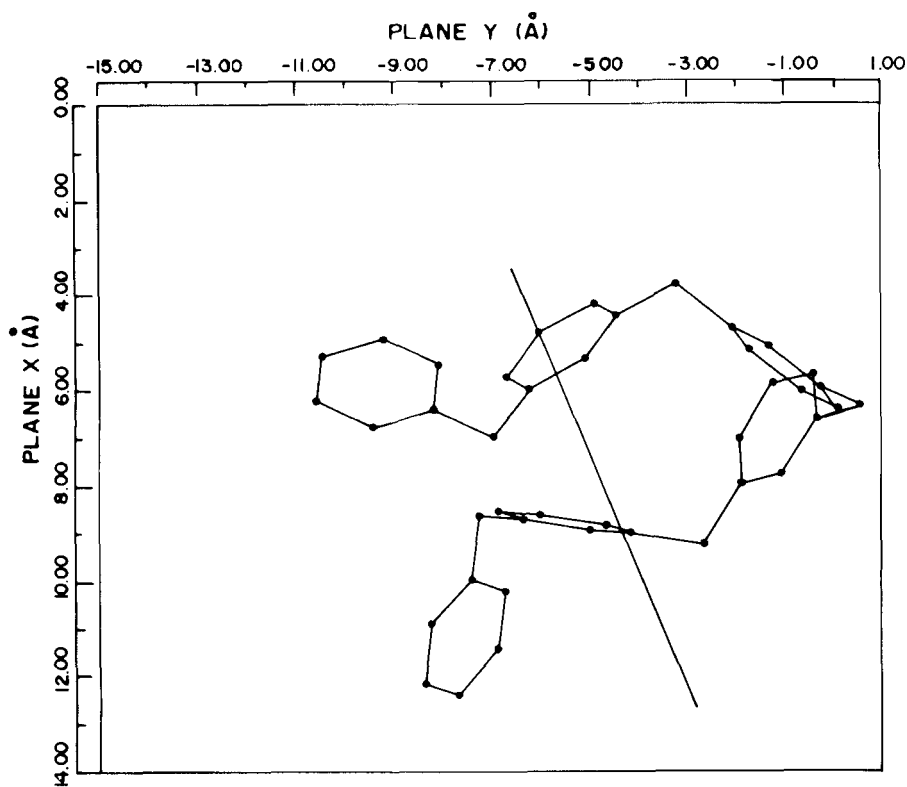
FIG. 12. Planar projection of the minimum total energy structure of Hexamer II. The axis represents the central axis of the helix formed by the polymer.

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