

2237

**Flow Diagrams for Computation  
of Spatial Locations  
of Atoms of a Chain Molecule  
Undergoing Intramolecular Rotations**

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Fortran II Program for Computing Backbone Chain  
Plus Two Side Atoms on Each Chain Atom

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*1005
  DIMENSION A(3,22),B(3),E(22),F(3),G(3),UJ(20),UO(20),DU(20),
  1R(21),V(21),X(3,22),H2(3),H3(3),H4(3),EH(21),HCH(21),XLINE(3),
  LXH(3)
  RADIN=1.745329252E-02
101 READ 200,N,NSMPL
200 FORMAT (I2,I4)
  DO 1 L=1,2
    READ 201,X(1,L),X(2,L),X(3,L)
  1 READ 201,A(1,L),A(2,L),A(3,L)
201 FORMAT (3F14.10)
  KK=N+3
  DO 2 L=1,KK
    READ 202,E(L),V(L),UO(L),DU(L),R(L)
    READ 202,HCH(L),EH(L)
202 FORMAT (5F14.10)
  V(L)=V(L)*RADIN
  UO(L)=UO(L)*RADIN
  DU(L)=DU(L)*RADIN
  2 HCH(L)=HCH(L)*RADIN
  L=1
  LF=1
  LD=1
  UJ(1)=0.0
  VSIN=1.0
  ISOMR=1
  GO TO 503
500 LF=L
  51 IF(V(LF))53,52,53
  52 LF=LF-1
  IF(LF-1)54,54,51
  54 VSIN=1.0
  GO TO 503
  53 VSIN=SINF(V(LF))
503 LX=L+1
  DO 3 I=1,3
  3 B(I)=A(I,L+1)
  IF(VSIN)50,504,50
  50 DO 4 I=1,3
  GO TO (5,6,7),I
  5 J=2
  K=3
  GO TO 4
  6 J=3
  K=1
  GO TO 4
  7 J=1
  K=2
  4 F(I)=(A(J,LF)*A(K,LF+1)-A(J,LF+1)*A(K,LF))/VSIN

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Fortran II Program (Cont.)

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119 PSI=(V(LX)-3.141592654)/2.0
    CALL DRCTN (B, H2, PSI, H3)
    THETA=HCH(LX)/2.0
    DO 42 KH=1,2
    CALL DRCTN (H3, G, THETA, H4)
    DO 40 I=1,3
40 XH(I)=X(I,LX)+EH(LX)*H4(I)
    PRINT 207,L,XH(1),XH(2),XH(3)
207 FORMAT (6H      HI5,3F15.10)
    IF (THETA)42,43,42
42 THETA=-THETA
43 IF (L-N-1)20,21,20
21 PRINT 205,ISOMR
205 FORMAT (I4/)
    KK=N+3
    DO 39 J=1,KK
    LX=J-1
    39 PUNCH 208,ISOMR,LX,X(1,J),X(2,J),X(3,J),NSMPL
208 FORMAT (I5,I3,3F15.10,22X,I5)
    PRINT 209
209 FORMAT (//)
    ISOMR=ISOMR+1
20 L=L+LD
    IF (LD)22,23,23
23 IF (L-N-1)24,24,25
25 LD=-1
    GO TO 20
24 UJ(L)=UO(L)
    GO TO 500
22 IF (L-2)100,26,26
26 UJ(L)=UJ(L)+DU(L)
    IF (UJ(L)-6.283185)27,25,25
27 LD=1
    GO TO 500
100 PAUSE
    GO TO 101
    END
*1005
    SUBROUTINE DRCTN (FROM,TO,ANGLE,XLINE)
    DIMENSION FROM(3),TO(3),XLINE(3)
    DO 600 I=1,3
600 XLINE(I)=FROM(I)*COSF (ANGLE)+TO(I)*SINF (ANGLE)
    RETURN
    END

```

Card Inputs Required by Fortran Program

Using the Symbolism of the Flow Diagrams

In order of reading:

n	Sample No.				
$x_0$	$y_0$	$z_0$			Format for all these numbers is F14.10, except n, which is I2, and Sample No., which is I4.
$s_0$	$t_0$	$u_0$			
$x_1$	$y_1$	$z_1$			
$s_1$	$t_1$	$u_1$			Note that the sequencing places only two side atoms on each chain atom. Therefore, in order to accommodate a methyl group at each end of the chain, the chain atoms numbered 0 and n+2 must be hydrogens.
0.0	0.0	0.0	0.0	$R_0$	
0.0	0.0				
0.0	$V_1$	$J_{1,0}$	$\Delta J_1$	$R_1$	In order to accommodate a single side atom, such as a carbonyl oxygen, set the corresponding HCH angle = 0.0.
$\angle HC_1H$	$LH_1$				
$L_2$	$V_2$	$J_{2,0}$	$\Delta J_2$	$R_2$	In order to accommodate a chain atom having no side atoms, such as an ether oxygen, set both $\angle HCH$ and $LH = 0.0$ .
$\angle HC_2H$	$LH_2$				
$L_3$	$V_3$	$J_{3,0}$	$\Delta J_3$	$R_3$	
$\angle HC_3H$	$LH_3$				
.	.	.	.	.	
.	.	.	.	.	
.	.	.	.	.	
.	.	.	.	.	
$L_n$	$V_n$	$J_{n,0}$	$\Delta J_n$	$R_n$	
$\angle HC_nH$	$LH_n$				
$L_{n+1}$	$V_{n+1}$	0.0	0.0	$R_{n+1}$	
$\angle HC_{n+1}H$	$LH_{n+1}$				
$L_{n+2}$	0.0	0.0	0.0	$R_{n+2}$	
0.0	0.0				

## Specifications for Fortran Program

- (1) The program computes one chain of atoms having individual characteristics with two (or less) identical side atoms symmetrically attached to each chain atom except the first and last.
- (2) Maximum length of chain = 21 atoms    Maximum value of n = 18.
- (3) Number of side atoms per chain atom is governed by  $\angle HC_pH$  and  $LH_p$ . If both are non-zero, two identical side atoms will be placed symmetrically on chain atom p. If  $\angle HC_pH$  is zero, only one side atom will be attached, as for a carbonyl oxygen or an olefinic hydrogen. If  $LH_p$  is zero, no side atom will be placed on the chain atom, as for the chain oxygen atom of an ether, alcohol, or ester.
- (4) Since a maximum of two side atoms can be placed on a chain atom, a three-atom set such as the hydrogens of a methyl, at one end of the chain, requires that chain atom numbered zero or n+2 must be a hydrogen.
- (5) Input: All angles in degrees, all lengths in the same unit, such as Angstroms, in order of entry shown on page 13.
- (6) Output: Printed output gives coordinates and interatomic distances for each new location of each chain atom and coordinates of each side atom. Each location is printed only once, although the atom at this location may be involved in several isomers. Punched card output consists of a complete summary of the coordinates of the chain atoms for each rotational isomer, for use in further computations of molecular properties such as electric moment, interaction energy, moment of inertia, etc. Output format is given below.

## Output Format for Fortran Program

### Printout format:

(Chain Atom No.)	(3 coordinates of numbered atom of chain)	(Angle J of chain)
(0)	(Distance between numbered atom and Atom 0)	
(1)	(Distance between numbered atom and Atom 1)	
(2)	(Distance between numbered atom and Atom 2)	
.	.	
.	.	
.	.	
H (Chain Atom No.)	(3 coordinates of side atom attached to numbered chain atom)	
H (Chain Atom No.)	(3 coordinates of other side atom)	
(Isomer No.)		

### Punched card format:

(Isomer No.) (Chain atom No.) (3 coordinates of numbered chain atom) (Sample No.)

Table 1 (Continued)

Correlation of Systems of Symbols

<u>Item</u>	<u>J. Chem. Phys.</u>	<u>Flow Diagrams</u>	<u>Fortran</u>
Supplement of bond angle at p	$V_B$	$V_p$	V(L)
Supplement of bond angle at p+1	$V_C$	$V_{p+1}$	V(L+1)
Length of bond between atom p+1 and atom p+2	L	$L_{p+2}$	E(L+2)
Dihedral angle	J	$J_p$	UJ(L)
Initial value of dihedral angle		$J_{p0}$	UO(L)
Increment for dihedral angle		$\Delta J_p$	DU(L)
Angle between bonds to side atoms on chain atom p		$\angle HC_pH$	HCH(L)
Length of bond between side atom and chain atom p		$LH_p$	EH(L)

Table 2

Coordinates of hydroxyl group for selected rotational isomers

<u>Hydrogen atom</u>			<u>Oxygen atom</u>		
<u>x</u>	<u>y</u>	<u>z</u>	<u>x</u>	<u>y</u>	<u>z</u>
-0.760	1.754	$\pm 1.146$	-0.205	2.537	$\pm 1.168$
-0.689	1.708	$\pm 1.291$	-0.166	2.512	$\pm 1.248$
-0.037	1.285	$\pm 2.069$	0.522	2.065	$\pm 2.068$
0.085	1.206	$\pm 2.153$	0.589	2.022	$\pm 2.115$
0.976	0.627	$\pm 2.438$	1.530	1.411	$\pm 2.415$
1.116	0.536	$\pm 2.438$	1.607	1.361	$\pm 2.415$

Carbon atoms of the double bond

-0.6685	0	0	0.6885	0	0
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## ACKNOWLEDGMENT

I wish to express my appreciation to Kenneth A. Tabler, Linda E. Preiss, and Elizabeth A. Eddy for assistance in various phases of this project.

Table 1

## Correlation of Systems of Symbols

Item	J. Chem. Phys.	Flow Diagrams	Fortran
Serial number of atom	---	$p = 0, 1, 2 \dots$	$L = p$ (basic comput. unit) $L = p+1$ (cycling and input-output)
Maximum value of $p$	---	$n$	$N = n$
Maximum value of $L$	---		$N + 1$
Serial number of atom during distance loop	---	$q = 0, 1, 2 \dots$	$LJ = q + 1$ $JI = q$
Increment or decrement	---	$\Delta p$	$LD$
Coordinate number subscript	$i = 0, 1, 2$		$I = 1, 2, 3$
Direction cosines of bond AB pointing from atom $p-1$ to atom $p$ .	$\alpha_0$ $\alpha_1$ $\alpha_2$	$s_p$ $t_p$ $u_p$	$A(1, L)$ $A(2, L)$ $A(3, L)$
Direction cosines of bond BC pointing from atom $p$ to atom $p+1$	$\beta_0$ $\beta_1$ $\beta_2$	$s_{p+1}$ $t_{p+1}$ $u_{p+1}$	$A(1, L+1) = B(1)$ $A(2, L+1) = B(2)$ $A(3, L+1) = B(3)$
Direction cosines of bond CD pointing from atom $p+1$ to atom $p+2$	$\gamma_0$ $\gamma_1$ $\gamma_2$	$s_{p+2}$ $t_{p+2}$ $u_{p+2}$	$A(1, L+2)$ $A(2, L+2)$ $A(3, L+2)$
Direction cosines of line BF	$\lambda_0$ $\lambda_1$ $\lambda_2$	$\lambda_0$ $\lambda_1$ $\lambda_2$	$F(1)$ $F(2)$ $F(3)$
Direction cosines of lines BG and CG'	$\mu_0$ $\mu_1$ $\mu_2$	$\mu_0$ $\mu_1$ $\mu_2$	$G(1)$ $G(2)$ $G(3)$
Coordinates of atom $p+1$	$C_0$ $C_1$ $C_2$	$x_{p+1}$ $y_{p+1}$ $z_{p+1}$	$X(1, L+1)$ $X(2, L+1)$ $X(3, L+1)$
Coordinates of atom $p+2$	$D_0$ $D_1$ $D_2$	$x_{p+2}$ $y_{p+2}$ $z_{p+2}$	$X(1, L+2)$ $X(2, L+2)$ $X(3, L+2)$

For starting the iterative procedure, it is necessary to specify numerical values for the coordinates of Atoms 0 and 1, along with their direction cosines. Direction cosines pointing toward Atom 0 ( $s_0, t_0, u_0$ ) have no molecular significance. They merely control the plane in which Atom 2 is to be placed, and, in so doing they define the orientation of the coordinate frame of reference. The program automatically sets  $V_0=90^\circ$  and  $J_0=0^\circ$ ; therefore  $s_0, t_0, u_0$  must be chosen as a line perpendicular to the bond between Atoms 0 and 1, pointing toward Atom 0 from a position trans to Atom 2, and lying in the plane desired for Atoms 0, 1, and 2. Interrelations within the plane chosen for Atoms 0, 1, and 2 are illustrated in figure 2.

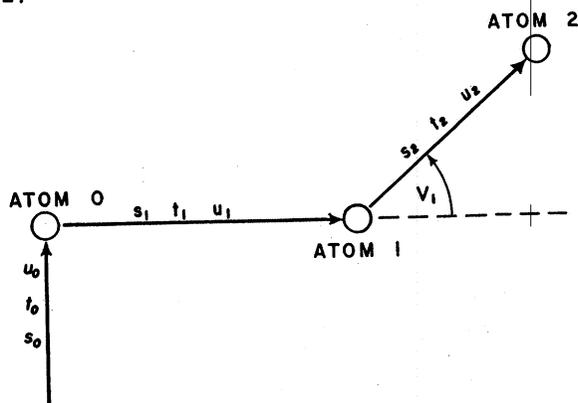


Fig. 2  
Directed lines in the plane of Atoms 0, 1, and 2, showing the relation between  $s_0, t_0, u_0$  and Atom 2 for starting the iterations.

As  $p$  is incremented along the chain, the coordinates of each atom are computed by the basic computational unit and printed out, until the other end of the chain has been reached. This gives the conformation of the molecule for one starting set of values of the  $J$ 's; for example, those corresponding to a fully extended chain.

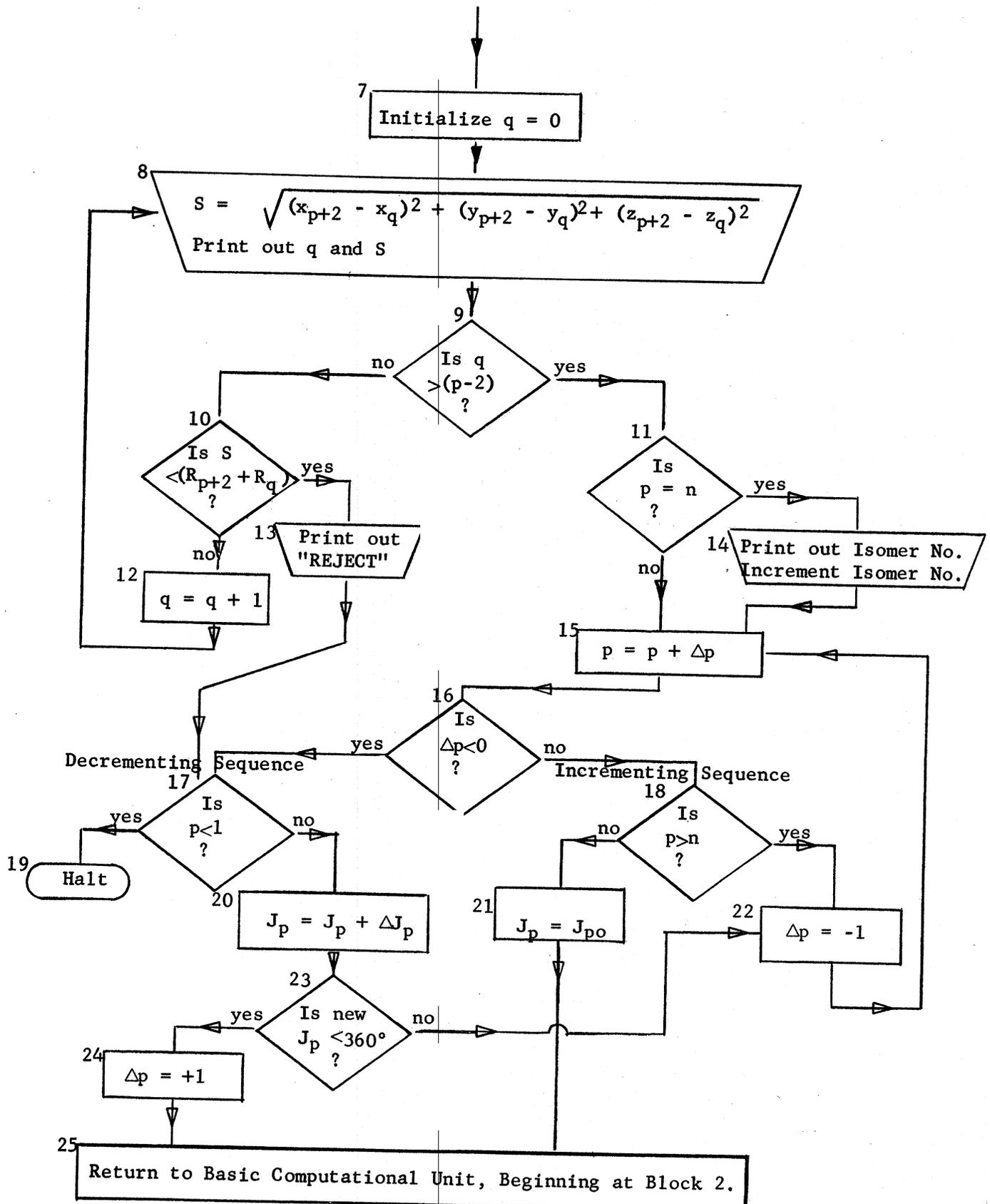
The index  $p$  then follows either of two different sequences, depending on whether it is incrementing or decrementing. During the incrementing sequence, for each new value of  $p$ ,  $J_p$  is reset to its lowest value. During the decrementing sequence, for each new value of  $p$ , the existing value of  $J_p$  is increased to its next higher value and tested. If  $J_p$  has already passed through all of its allowed values,  $p$  continues to decrement; if  $J_p$  has not yet passed through all of its allowed values,  $p$  is switched to its incrementing sequence. Whenever a  $J_p$  is changed to a new allowable value, the location of the corresponding D atom (numbered  $p+2$ ) is computed. Whenever  $p$  exceeds its upper limit, it is switched to the decrementing sequence. When  $p$  falls below its lower limit, computation ceases because all  $J$ 's have passed through all their allowed values and the atom locations for all possible rotational isomers have been printed out.

The integer  $n$  specifies the upper limit of  $p$ . Since the chain of atoms runs from Atom 0 to Atom  $n+2$ ,  $n$  must be assigned a value lower by 3 than the number of atoms in the chain. For iterating  $J$ 's, the initial angles,  $J_{p0}$ , must be specified, along with the incremental angle for each bond,  $\Delta J_p$ , based on rotational restrictions of the assumed model. The upper limit of  $J_p$  is taken as  $360^\circ$ . If computation for only one rotational isomer is desired, setting each  $\Delta J_p$  equal to  $361^\circ$  will cause the computer to stop after passing along the chain only once.

Cases that are mathematically possible but physically impossible are eliminated by assigning a minimum radius to each atom,  $R_p$ . As each D atom is located, its distances from all previous atoms are computed. If any one of these distances is less than the sum of the two corresponding minimum radii, that rotational isomer is eliminated from further computation. If the chain atom carries no attached atoms, its van der Waals radius can be used

Figure 4

Flow diagram, Part 2, showing recycling sequence for case of skeletal atoms of chain molecule





## ABSTRACT

Flow diagrams are presented for a computer program which calculates the coordinates in space of atoms of a chain molecule, for all possible rotational isomers consistent with given bond lengths, bond angles, and restrictions on rotation about single bonds. A Fortran program illustrates one form of this computation, and modifications are outlined for application to other than chain molecules.

This is a report of work done at the  
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FLOW DIAGRAMS FOR COMPUTATION OF SPATIAL LOCATIONS OF ATOMS  
OF A CHAIN MOLECULE UNDERGOING INTRAMOLECULAR ROTATIONS

C. Roland Eddy

This bulletin supplements the note that appeared in the Journal of Chemical Physics (4)\* by giving flow diagrams for a digital-computer program.

The equations on the flow diagrams are obtained from the equations in the Journal by two transformations: (1) The subscript  $i$  is given in turn the three values 0, 1, 2 to cover the three coordinates. Arithmetical operations on  $i$  are performed modulo 3. (2) In order to make the computation iterative, an integral number  $p$  is assigned to each atom in the chain, beginning at one end, where the first three atoms are placed in known positions to specify the coordinate system. For any value of  $p$  during the course of the iteration, Atom B is designated Atom  $p$ , Atom A is  $p-1$ , Atom C is  $p+1$ , etc. Direction cosines  $s_p$ ,  $t_p$ ,  $u_p$  are for the directed line from Atom  $p-1$  pointing toward Atom  $p$ . Bond length  $L_p$  is the distance from Atom  $p-1$  to Atom  $p$ . Bond angle  $V_p$  is for the angle at Atom  $p$ , expressed as the supplement of the angle formed by the three atoms  $p-1$ ,  $p$ ,  $p+1$ . Dihedral angle  $J_p$  is the angle of rotation of the BCD plane about the bond joining Atoms  $p$  and  $p+1$ . The zero of  $J_p$  is taken as the trans position of Atom  $p+2$  relative to Atom  $p-1$ , with all four atoms  $p-1$ ,  $p$ ,  $p+1$ ,  $p+2$  lying in the same plane. Positive  $J_p$  is defined as counterclockwise rotation of Atom  $p+2$  from the  $J_p=0$  position, as viewed from Atom  $p$  looking toward Atom  $p+1$ . These designations of the variables are illustrated in figure 1.

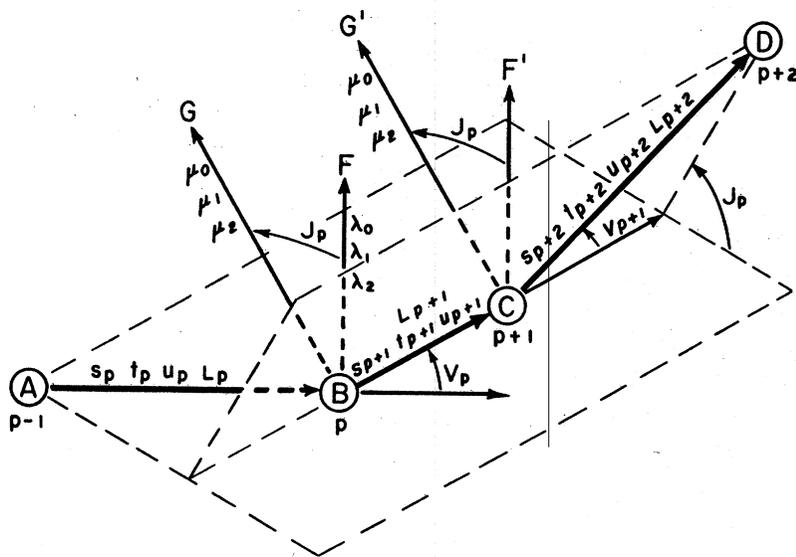


Fig. 1  
Directed lines and angles for any given portion of the molecular chain as a function of subscript  $p$ .

\* Figures in parentheses refer to Literature Cited at end of report.