



STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 78 (2022)

Supporting information for article:

Dynamic simulation of orientational disorder in organic crystals: methyl groups, trifluoromethyl groups and whole molecules

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**Dynamic simulation of orientational disorder in organic crystals:
methyl groups, trifluoromethyl groups and whole molecules****Supplementary information**

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S-1. A template of a .oeh file type for use in the MiCMoS environment

```
#ENEHUB P212121 esp charges
0
  4.622  16.171  16.572  90.00  90.00  90.00
  0.0
28
1  0.4079  0.7488  0.2721  1 18 -0.6111
2  0.5362  0.7343  0.3418  1 12  0.3762
3  0.5477  0.6564  0.3798  1 12 -0.4343
4  0.4141  0.5908  0.3442  1 12  0.4336
5  0.2627  0.6035  0.2707  1 14 -0.4422
6  0.2729  0.6843  0.2363  1 12  0.6215
7  0.6669  0.8086  0.3811  1 12  0.4909
8  0.4880  0.8381  0.4332  1 41 -0.1493
9  0.9130  0.7825  0.4208  1 41 -0.2216
10 0.7600  0.8640  0.3304  1 41 -0.1453
11 0.4230  0.5075  0.3824  1 13 -0.1378
12 0.2679  0.4900  0.4571  1 13  0.0071
13 0.5734  0.5018  0.4573  1 23 -0.2321
14 0.1041  0.5413  0.2300  1 12 -0.0056
15 -0.0333  0.5577  0.1588  1 12 -0.1480
16 -0.0187  0.6357  0.1240  1 12 -0.0770
17 0.1303  0.6986  0.1611  1 12 -0.1642
18 0.1509  0.7825  0.1232  1 13  0.4598
19 0.4231  0.8049  0.1078  1 41 -0.1553
20 0.0332  0.8419  0.1680  1 41 -0.1569
21 0.0126  0.7849  0.0516  1 41 -0.1674
22 0.6608  0.6488  0.4363  1  2  0.1800
23 0.4300  0.4764  0.3248  1  3  0.1448
24 0.1759  0.4296  0.4680  1  3  0.0974
25 0.1257  0.5355  0.4835  1  3  0.0888
26 0.0916  0.4800  0.2556  1  2  0.0765
27 -0.1548  0.5094  0.1292  1  2  0.1404
28 -0.1257  0.6470  0.0671  1  2  0.1309
0
4  0
1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0
0.000000 0.000000 0.000000
1.0  0.0  0.0  0.0 -1.0  0.0  0.0  0.0 -1.0
```

```

0.500000  0.500000  0.000000
-1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  -1.0
0.000000  0.500000  0.500000
-1.0  0.0  0.0  0.0  -1.0  0.0  0.0  0.0  1.0
0.500000  0.000000  0.500000
  1
  0

```

S-2 Algebra for the rotations in program Cryrot.for

Let $\mathbf{r}_{0,i}$ be the atomic fractional coordinates of a reference molecule and $\mathbf{r}_{m,i}$ the coordinates of symmetry-related molecules:

$$\mathbf{r}_{m,i} = \mathbf{M}_m \mathbf{r}_{0,i} + \mathbf{t}_m$$

where \mathbf{M}_m and \mathbf{t}_m are matrix and vector of a given symmetry operation. Let the corresponding orthogonalized vectors be $\mathbf{x}_{0,i}$ and $\mathbf{x}_{m,i}$. Let \mathbf{B}_0 and \mathbf{b}_0 be the matrix and vector that transform from the cell reference system to the local reference system, say the system with the x-direction along the C-C(Me) bond, or the inertial reference system:

$$\mathbf{w}_{0,i} = \mathbf{B}_0(\mathbf{x}_{0,i} + \mathbf{b}_0)$$

A rotation in this local system is represented by an Euler-type rotation matrix \mathbf{C}_0 :

$$\mathbf{w}'_{0,i} = \mathbf{C}_0 \mathbf{w}_{0,i}$$

where the prime denotes rotated vectors. Transforming back into the orthogonalized cell reference system in which intermolecular distances are ultimately computed, one gets, after rearranging, the final coordinates of the atoms undergoing the rotation:

$$\mathbf{x}'_{0,i} = \mathbf{S}_0 \mathbf{x}_{0,i} + \mathbf{S}_0 \mathbf{b}_0 - \mathbf{b}_0$$

$$\mathbf{S}_0 = \mathbf{B}_0^{-1} \mathbf{C}_0 \mathbf{B}_0$$

S-3 Program Cryrot for ZL rotation in crystals

```

      program cryrot
c
c      rigid group rotation in crystal
c
      character*2 symbol
      character*4 titolo(10)
      dimension xf(100,3),q(100),qtot(100),tco(100,3),tcp(100,3)
      dimension w(100),sma(3,3)
      dimension rm(100,3,3),tv(100,3),tvo(100,3),erot(200,6)
      dimension ispen(100),isptot(100),irot(100)
c      arrays for rotation matrix algebra
      dimension cze(3,3),bzer(3,3),bzm(3,3),t(3,3),sze(3,3),tem(100,3)
      dimension bze(3),or(3),ved(3)
      common xo(5000,100,3),xsa(100,3)
      common /sym/ symbol(70)
      common /ats/ wei(70),ravrg(70),ravdw(70),zeta(70),polat(70),
1qnum(70),zval(70),diffu(70),acdo(70),elneg(70),potio(70),difa(70)
c      CLP factors for charge,polarization,dispersion and repulsion
      common/potato/ pt(100,100,3),fq,fp,fd,fr
c      LJC 6-12 factors are in block data alldat
      common /lj/ c6(70),c12(70),clj(70,70,2)
      open (unit=1, file='cryrot.oeh')
      open (unit=2, file='cryrot.pri')
      fq=0.41
      fp=235.0
      fd=650.0

```

```
fr=77000.0
nin=0
1100 continue
c read oeh file -----
read(1,12,end=1002) (tito1o(kg),kg=1,10)
12 format(1x,10a4)
write(2,13) (tito1o(kg),kg=1,10)
13 format(/5x,' group rotation module-- ', 2x,10a4)
nin=nin+1
read(1,*) inopt
read(1,*) cela,celb,celc,ali,bei,gai
c write(2,15) cela,celb,celc,ali,bei,gai
c 15 format(1x,' cell parameters',3x,3f9.4,3f8.2)
pz=0.01745329
cali=cos(ali*pz)
cbei=cos(bei*pz)
cgai=cos(gai*pz)
sgai=sin(gai*pz)
vabc=1.0-cali**2-cbei**2-cgai**2+2.0*cali*cbei*cgai
vabc=sqrt(vabc)
vcell=vabc*cela*celb*celc
cccs=(cali-cbei*cgai)/sgai
read(1,*) dhsubl
read(1,*) natom
c read atom data -----
do 22 i=1,natom
read(1,*) nu,xx,yy,zz,mldum,isp,qar
if(mldum.ne.1) call emerg(2)
ispn(nu)=isp
q(nu)=qar
w(nu)=wei(isp)
c orthogonal coordinates of central molecule
xo(1,nu,1)=xx*cela+yy*celb*cgai+zz*celc*cbei
xo(1,nu,2)=yy*celb*sgai+zz*celc*cccs
xo(1,nu,3)=zz*celc*vabc/sgai
c save original non-rotated coordinates
xsa(nu,1)=xo(1,nu,1)
xsa(nu,2)=xo(1,nu,2)
xsa(nu,3)=xo(1,nu,3)
c save fractional coordinates
xf(nu,1)=xx
xf(nu,2)=yy
22 xf(nu,3)=zz
read(1,*) nhyd
read(1,*) npe
do 24 i=1,npe
read(1,*)((rm(i,j,k),k=1,3),j=1,3)
read(1,*)(tv(i,j),j=1,3)
24 continue
c print level 0,1,2,ipots=0 CLP,=1 LJC; frac of Ri+Rj for short dist
read(1,*) ipri,ipots,facra
if(ipri.eq.0) go to 225
open (unit=3, file='cryrot.xyz')
write(2,21) natom
21 format(5x,i5,' atom information, fragm.,species,charge ')
do 25 i=1,natom
isp=ispn(i)
write(2,23) i,symbol(isp),(xsa(i,j),j=1,3),ispn(i),q(i),w(i)
23 format(i5,1x,a2,3f10.4,i4,f8.4,f8.3)
25 continue
225 continue
if(ipots.eq.0) write(2,16) fq,fp,fd,fr
16 format(' Coulomb-London-Pauli potential coefficients',
1./2x,3f10.3,f11.1)
if(ipots.eq.1) write(2,17)
17 format(2x,'Lennard-Jones-Coulomb potentials ')
c reference system record -----
c il1>0: two atoms defining rot. axis,atom in the xy plane (0 now)
c il1<0: inertial reference system
read(1,*) il1,il2,il3
c read number of atoms to rotate, then limits and steps
c nrot < 0 rotate all atoms
read(1,*) nrot
```

```
      if(nrot.lt.0) go to 18
      read(1,*) (irot(i),i=1,nrot)
      go to 19
18  nrot=natom
      do 20 i=1,natom
20  irot(i)=i
c   iax=1, 2, 3 around x, y, z
19  iax=1
      tmin=0.0
      tmax=360.
      step=5.
      read(1,*) iax,tmin,tmax,step
c   orthogonal coordinates of 125 cells -----
      nm=1
      do 31 j=1,5
      ttx=float(j-3)
      do 31 k=1,5
      tty=float(k-3)
      do 31 m=1,5
      ttz=float(m-3)
      do 32 jj=1,npe
      if(jj.eq.1.and.j.eq.3.and.k.eq.3.and.m.eq.3) go to 32
      nm=nm+1
      do 33 kk=1,natom
      xxp=rm(jj,1,1)*xf(kk,1)+rm(jj,1,2)*xf(kk,2)+rm(jj,1,3)*xf(kk,3)
      yyp=rm(jj,2,1)*xf(kk,1)+rm(jj,2,2)*xf(kk,2)+rm(jj,2,3)*xf(kk,3)
      zzp=rm(jj,3,1)*xf(kk,1)+rm(jj,3,2)*xf(kk,2)+rm(jj,3,3)*xf(kk,3)
      xxp=xxp+tv(jj,1)+ttx
      yyp=yyp+tv(jj,2)+tty
      zzp=zzp+tv(jj,3)+ttz
      xo(nm,kk,1)=xxp*cela+yyp*celb*cgai+zzp*celc*cbei
      xo(nm,kk,2)=yyp*celb*sgai+zzp*celc*cccs
33  xo(nm,kk,3)=zzp*celc*vabc/sgai
32  continue
31  continue
      if(ipri.eq.0) go to 44
      write(2,40) (titolo(kg),kg=1,10)
40  format('TITL',10a4)
      write(2,42) 1.,1.,1.,90.,90.,90.
42  format('CELL',6f8.1)
      do 41 i=1,nm
      do 41 j=1,natom
      ispe=ispen(j)
      jw=100+j
      write(2,45) symbol(ispe),jw,(xo(i,j,mm),mm=1,3)
45  format('ATOM',2x,a2,i3,3f10.4)
41  continue
      write(2,43)
43  format('END ')
44  continue
c   load potential parameters -----
      call potljc
      if(ipots.eq.1) go to 38
      do 36 i=1,natom
      q(i)=q(i)*fq
      do 36 j=1,natom
      do 36 k=1,3
36  pt(i,j,k)=0.0
      do 37 i=1,natom
      isptot(i)=ispen(i)
37  qtot(i)=q(i)
      call potclp (natom,isptot,qtot)
38  continue
      if(i11.gt.0) go to 1001
c   i11<0, local reference system is inertial frame
c   form matrices bzer and bzm and vector bze (origin)
      comx=0.0
      comy=0.0
      comz=0.0
      we=0.0
      do 70 i=1,natom
      we=we+w(i)
      comx=comx+xo(1,i,1)*w(i)
```

```
comy=comy+xo(1,i,2)*w(i)
70 comz=comz+xo(1,i,3)*w(i)
c origin is center of mass
  bze(1)=-comx/we
  bze(2)=-comy/we
  bze(3)=-comz/we
  c1=0.0
  c2=0.0
  c3=0.0
  sx=0.0
  sy=0.0
  sz=0.0
c fill inertial matrix
do 71 i=1,natom
  ps=w(i)
  x1=xo(1,i,1)+bze(1)
  y1=xo(1,i,2)+bze(2)
  z1=xo(1,i,3)+bze(3)
  c1=c1+ps*x1*x1
  c2=c2+ps*y1*y1
  c3=c3+ps*z1*z1
  sx=sx-ps*x1*y1
  sy=sy-ps*x1*z1
71 sz=sz-ps*y1*z1
  sma(1,1)=c2+c3
  sma(2,2)=c1+c3
  sma(3,3)=c1+c2
  sma(1,2)=sx
  sma(1,3)=sy
  sma(2,3)=sz
  sma(2,1)=sma(1,2)
  sma(3,1)=sma(1,3)
  sma(3,2)=sma(2,3)
  call jacob (sma,bzm)
  call inv(bzm,bzer)
  go to 1000
1001 continue
c rotation around il1-il2 axis
c transform coordinates of molecule 1 for group rotation
c around il2-il1 axis
write(2,207) iax,il1,il2,il3
206 format(' atoms ',10i4)
write(2,206) (irot(k),k=1,nrot)
207 format(' rotation around axis 'i3,2x,3i5)
c bze is the origin in il1, or is il2-il1 vector
do 39 j=1,3
  bze(j)=-xsa(il1,j)
39 or(j)=xsa(il2,j)-xsa(il1,j)
  com=or(1)**2+or(2)**2
  che=sqrt(com)
  rr=sqrt(com+or(3)**2)
  cchi=or(1)/che
  schi=-or(2)/che
  czet=che/rr
  szet=-or(3)/rr
c matrix product of axis rotation around z and then around y
  bzer(1,1)=ccchi*czet
  bzer(1,2)=-czet*schi
  bzer(1,3)=-szet
  bzer(2,1)=schi
  bzer(2,2)=ccchi
  bzer(2,3)=0.0
  bzer(3,1)=ccchi*szet
  bzer(3,2)=-schi*szet
  bzer(3,3)=czet
  call inv(bzer,bzm)
1000 continue
write(2,246)
246 format(' coordinates in local reference system ')
do 240 j=1,natom
do 240 k=1,3
240 tco(j,k)=xo(1,j,k)+bze(k)
do 242 j=1,natom
```

```

    do 241 k=1,3
      tcp(j,k)=0.0
      do 241 m=1,3
241    tcp(j,k)=tcp(j,k)+bzer(k,m)*tco(j,m)
      write(2,243) j,ispn(j),(tcp(j,k),k=1,3)
243    format(i5,i4,3f10.4)
242    continue
c    open loops for rotation around new axis-----
      write(2,199) tmin,tmax,step
199    format(/2x,' start rotations teta min,max,step ',3f8.1)
      nst=1.0+(tmax-tmin)/step
      do 200 i=1,nst
        teta=tmin+float(i-1)*step
        cte=cos(teta*0.0174533)
        ste=sin(teta*0.0174533)
c      Acta Cryst 1975
c      cze is main rotation matrix c0
      go to (201,202,203),iax
201    cze(1,1)=1.0
      cze(1,2)=0.0
      cze(1,3)=0.0
      cze(2,1)=0.0
      cze(2,2)=cte
      cze(2,3)=-ste
      cze(3,1)=0.0
      cze(3,2)=ste
      cze(3,3)=cte
      go to 204
202    cze(1,1)=cte
      cze(1,2)=0.0
      cze(1,3)=-ste
      cze(2,1)=0.0
      cze(2,2)=1.0
      cze(2,3)=0.0
      cze(3,1)=ste
      cze(3,2)=0.0
      cze(3,3)=cte
      go to 204
203    cze(1,1)=cte
      cze(1,2)=-ste
      cze(1,3)=0.0
      cze(2,1)=ste
      cze(2,2)=cte
      cze(2,3)=0.0
      cze(3,1)=0.0
      cze(3,2)=0.0
      cze(3,3)=1.0
204    continue
c    matrix S is bzm*cze*bzer
      do 210 j=1,3
      do 210 k=1,3
      t(j,k)=0.0
      do 210 m=1,3
210    t(j,k)=t(j,k)+cze(j,m)*bzer(m,k)
      do 211 j=1,3
      do 211 k=1,3
      sze(j,k)=0.0
      do 211 m=1,3
211    sze(j,k)=sze(j,k)+bzm(j,m)*t(m,k)
c    form vector S0*b0-b0
      do 212 j=1,3
      ved(j)=0.0
      do 212 k=1,3
212    ved(j)=ved(j)+sze(j,k)*bze(k)
      do 213 j=1,3
213    ved(j)=ved(j)-bze(j)
c    final conversion of coords of rotated atoms back to cluster
      do 221 j=1,nrot
      jr=irof(j)
      do 220 k=1,3
      tem(jr,k)=0.0
      do 223 m=1,3
223    tem(jr,k)=tem(jr,k)+sze(k,m)*xsa(jr,m)
```

```
220 tem(jr,k)=tem(jr,k)+ved(k)
    xo(1,jr,1)=tem(jr,1)
    xo(1,jr,2)=tem(jr,2)
    xo(1,jr,3)=tem(jr,3)
221 continue
c   prepare xyz file with rotating model
    if(ipri.eq.0) go to 333
    write(3,231) natom
    write(3,233) teta
233 format(' rotation ',f8.1)
231 format(i5)
232 format(1x,a2,3f10.4)
    do 230 k=1, natom
        isp=ispn(k)
        write(3,234) symbol(isp), (xo(1,k,m),m=1,3)
234 format(1x,a2,2x,3f10.4)
230 continue
333 continue
c   now compute energy
    etot=0.0
    erep=0.0
    edisp=0.0
    ecoul=0.0
    epol=0.0
    do 51 m=2, nm
        do 52 j=1, natom
            x1=xo(1,j,1)
            y1=xo(1,j,2)
            z1=xo(1,j,3)
            q1=q(j)
            is1=ispn(j)
            do 52 k=1, natom
                q2=q(k)
                is2=ispn(k)
                rr=(x1-xo(m,k,1))**2+(y1-xo(m,k,2))**2+(z1-xo(m,k,3))**2
                rr=sqrt(rr)
                if(rr.lt.facra) write(2,54) teta,m,j,symbol(is1),k,symbol(is2),rr
54 format(f8.1,' short R,mol,atoms ',i4,1x,i4,1x,a2,i4,1x,a2,2f8.3)
                ecoul=ecoul+q1*q2/rr
                if(ipots.eq.1) go to 53
                erep=erep+pt(j,k,3)*rr**(-12)
                edisp=edisp-pt(j,k,2)*rr**(-6)
                epol=epol-pt(j,k,1)*rr**(-4)
                go to 52
53 erep=erep+clj(is1,is2,2)*rr**(-12)
                edisp=edisp-clj(is1,is2,1)*rr**(-6)
52 continue
51 continue
    ecoul=ecoul*1389.355
    etot=ecoul+epol+edisp+erep
c   close loop on main rotation on angle teta
    erot(i,1)=teta
    erot(i,2)=ecoul
    erot(i,3)=epol
    erot(i,4)=edisp
    erot(i,5)=erep
    erot(i,6)=etot
200 continue
c   prepare output of rotational profile
c   find minimum and maximum energy
    etomin=999.
    etomax=-999.
    do 50 i=1, nst
        if(erot(i,6).gt.etomin) go to 58
        etomin=erot(i,6)
        ecomin=erot(i,2)
        edimin=erot(i,4)
        eremin=erot(i,5)
        temin=erot(i,1)
58 if(erot(i,6).lt.etomax) go to 50
        etomax=erot(i,6)
        temax=erot(i,1)
50 continue
```

```
barr=etomax-etomin
ezero=erot(1,6)-etomin
write(2,57) (titolo(kg),kg=1,4),temin,temax,ezero,barr
write(6,57) (titolo(kg),kg=1,4),temin,temax,ezero,barr
57 format(1x,4a4,' tetamin,tetamax, Ezero, barrier ',4f9.1)
do 56 i=1,nst
  etorel=erot(i,6)-etomin
  ecorel=erot(i,2)-ecomin
  edirel=erot(i,4)-edimin
  ererel=erot(i,5)-eremin
c   write(2,55) erot(i,1),erel,erot(i,6),(erot(i,k),k=2,5)
  write(2,55) erot(i,1),etorel,ecorel,edirel,ererel,erot(i,6)
55 format(8f10.2)
56 continue
c end of business for one structure-----
go to 1100
c
c end of data stream
c
1002 continue
write(2,1003) nin
1003 format(' normal end of operation, crystals read',i5)
stop
end
subroutine emerg (n)
if(n.eq.2) write(2,2)
2 format(' more than one mol in asymm unit ')
stop
end
subroutine potclp (natot,isptot,qtot)
common /ats/ wei(70),ravrg(70),ravdw(70),zeta(70),polat(70),
1qnum(70),zval(70),diffu(70),acdo(70),elneg(70),potio(70),difa(70)
common/potato/ pt(100,100,3),fq,fp,fd,fr
dimension isptot(100),qtot(100)
do 1 i=1,natot
  is1=isptot(i)
  q1=qtot(i)
  qn1=qnum(is1)
  zv1=zval(is1)
  dif1=diffu(is1)
  pol1=polat(is1)*((zv1-q1)/zv1)
  pot1=potio(is1)
  do 2 j=1,natot
    is2=isptot(j)
    q2=qtot(j)
    zv2=zval(is2)
    qn2=qnum(is2)
    dif2=diffu(is2)
    dd=sqrt(dif1*dif2)
    pol2=polat(is2)*((zv2-q2)/zv2)
    pot2=potio(is2)
    alfeff=sqrt(pol1*pol2)
    absq=abs(q1*q2)
    qnef=qn1*qn2
    potef=sqrt(pot1*pot2)
c polarization coefficient, r**(-4)
    pt(i,j,1)=alfeff*absq*fp
c dispersion coefficient, r**(-6)
    pt(i,j,2)=alfeff*qnef*potef*fd
    dij=(zv1-q1)
    dkm=(zv2-q2)
    pt3=dij*dkm*dd
    hbo=acdo(is1)*acdo(is2)
    if(hbo.lt.0.0) pt3=(1.0+hbo)*pt3
c repulsion coefficient, r**(-12)
    pt(i,j,3)=pt3*fr
  2 continue
1 continue
return
end
c lennard-jones 6-12 potential coefficients
subroutine potljc
common /lj/ c6(70),c12(70),clj(70,70,2)
```

```

maxspe=70
c 6-12 coefficients are in block data alldat
do 1 i=1,maxspe
1  clj(i,i,1)=c6(i)
   clj(i,i,2)=c12(i)
do 20 i=1,maxspe
do 20 j=1,maxspe
   clj(i,j,1)=sqrt(clj(i,i,1)*clj(j,j,1))
   clj(i,j,2)=sqrt(clj(i,i,2)*clj(j,j,2))
20 continue
return
end
subroutine inv(bzer,bzm)
dimension bzer(3,3),bzm(3,3)
c matrix inversion routine
R11=bzer(1,1)
R12=bzer(1,2)
R13=bzer(1,3)
R21=bzer(2,1)
R22=bzer(2,2)
R23=bzer(2,3)
R31=bzer(3,1)
R32=bzer(3,2)
R33=bzer(3,3)
DET=R11*R22*R33+R12*R23*R31+R21*R32*R13-R13*R22*R31
DET=DET-R11*R23*R32-R12*R21*R33
bzm(1,1)=(R22*R33-R23*R32)/DET
bzm(2,1)=-(R21*R33-R23*R31)/DET
bzm(3,1)=(R21*R32-R22*R31)/DET
bzm(1,2)=-(R12*R33-R13*R32)/DET
bzm(2,2)=(R11*R33-R13*R31)/DET
bzm(3,2)=-(R11*R32-R12*R31)/DET
bzm(1,3)=(R12*R23-R13*R22)/DET
bzm(2,3)=-(R11*R23-R13*R21)/DET
bzm(3,3)=(R11*R22-R12*R21)/DET
return
end
SUBROUTINE JACOB (f,v)
c diagonalize matrix f, put eigenvectors in v
DIMENSION F(3,3),V(3,3)
character*4 flab
common/ope1/ alfa(20000,3),rm(20000,3,3)
common/ope2/ peso(250),ispn(250),mlc(250),flab(250),rain(250),
1 nass(10),nide(10,250),qrg(250),numas
common/ope3/cutoff,ilevel(5),totale,tipo(30,30,3),natom,ntot,nclu,
2 na,naa,nb,nc,nd,ne,nf,ng,nh,ni,nl,nm,nee,nem,nef,nel,nep,
3 ndd,nde,ndf,ndg,ndh
DOUBLE PRECISION SINT,COST,FUNNO,FUNT
N=3
RHO=0.000001
TE=0.0
FUNNO=1.0
DO 20 I=1,3
DO 21 J=1,3
V(I,J)=0.0
21 CONTINUE
V(I,I)=1.0
20 CONTINUE
DO 1 I=2,N
K=I-1
DO 1 J=1,K
TE=TE+2.*F(I,J)*F(I,J)
1 CONTINUE
TE=SQRT(TE)
MA=0
A=N
2 TE=TE/A
IF(TE.LT.RHO)TE=RHO
3 DO 14 II=2,N
IJ=II-1
DO 14 JJ=1,IJ
IF (ABS(F(II,JJ))-TE)14,4,4
4 MA=1

```

```
V1=F(JJ,JJ)
V2=F(II,JJ)
V3=F(II,II)
U=.5*(F(JJ,JJ)-F(II,II))
IF(ABS(U)-RHO)5,6,6
5 OMEGA=-1.0
GO TO 7
6 FUX=SQRT(F(II,JJ)*F(II,JJ)+U*U)
OMEGA=-F(II,JJ)/FUX
Z=1.
IF (U.LT.0.)Z=-Z
OMEGA=OMEGA*Z
7 FUX=1.0-OMEGA*OMEGA
FEX=2.0*(1.0+SQRT(FUX))
SINT=OMEGA/SQRT(FEX)
FUNT=FUNNO-SINT*SINT
COST=SQRT(FUNT)
DO 13 I=1,N
IF(I-II)9,8,8
8 TEM=F(I,JJ)*COST-F(I,II)*SINT
F(I,II)=F(I,JJ)*SINT+F(I,II)*COST
F(I,JJ)=TEM
GO TO 12
9 IF(I-JJ)10,11,11
10 TEM=F(JJ,I)*COST-F(II,I)*SINT
F(II,I)=F(JJ,I)*SINT+F(II,I)*COST
F(JJ,I)=TEM
GO TO 12
11 TEM=F(I,JJ)*COST-F(II,I)*SINT
F(II,I)=F(I,JJ)*SINT+F(II,I)*COST
F(I,JJ)=TEM
12 TEM=V(I,JJ)*COST-V(I,II)*SINT
V(I,II)=V(I,JJ)*SINT+V(I,II)*COST
V(I,JJ)=TEM
13 CONTINUE
F(JJ,JJ)=V1*COST*COST+V3*SINT*SINT-2.*V2*SINT*COST
F(II,II)=V1*SINT*SINT+V3*COST*COST+2.*V2*SINT*COST
F(II,JJ)=2.*U*SINT*COST+V2*(COST*COST-SINT*SINT)
14 CONTINUE
IF(MA-1)16,15,15
15 MA=0
GO TO 3
16 IF(TE-RHO)17,17,2
17 CONTINUE
310 IF(F(1,1)-F(2,2)) 100,101,101
101 IF(F(2,2)-F(3,3)) 102,102,103
103 IND=6
GO TO 200
102 IF(F(1,1)-F(3,3)) 104,104,105
104 IND=2
GO TO 200
105 IND=5
GO TO 200
100 IF(F(2,2)-F(3,3)) 107,107,108
107 IND=1
GO TO 200
108 IF(F(1,1)-F(3,3)) 109,109,110
109 IND=4
GO TO 200
110 IND=3
200 GO TO (116,115,116,115,115,201),IND
115 F33=F(2,2)
F(2,2)=F(3,3)
F(3,3)=F33
DO 120 I=1,3
VC=V(I,3)
V(I,3)=V(I,2)
120 V(I,2)=VC
116 IF(IND.EQ.5) GO TO 201
GO TO (118,119,119,118) ,IND
118 F33=F(1,1)
F(1,1)=F(3,3)
F(3,3)=F33
```



```
c   number of valence electrons
   data zval/
1  1.,1.,1.,0.,1.,1.,1.,1.,1.,4.,
2  4.,4.,4.,4.,0.,5.,5.,5.,5.,5.,
3  5.,0.,6.,6.,0.,0.,6.,6.,6.,6.,
4  6.,6.,0.,6.,6.,6.,6.,5.,0.0,0.0,
5  7.,7.,17.,17.,6*0.0,
6  4.,5.,6.,7.,8.,9.,10.,11.,12.,0.0,
7  2.,8.,8.,18.,18.,8.,8.,8.,18.,18./
c   quantum number of valence electrons
   data qnum/
1  1.0,1.0,1.0,0.0,1.0,1.0,1.0,1.0,1.0,2.0,
2  2.0,2.0,2.0,2.0,0.0,2.0,2.0,2.0,2.0,2.0,
3  2.0,0.0,2.0,2.0,0.0,0.0,2.0,2.0,2.0,2.0,
4  2.0,2.0,0.0,3.0,3.0,3.0,3.0,3.0,0.0,0.0,
5  2.0,3.0,4.0,5.0,6*0.0,
6  3.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,0.0,
7  1.0,2.0,3.0,4.0,5.0,3.0,2.0,3.0,4.0,5.0/
c   AA-clp and PIXEL atomic polarizabilities
c   adapted from Miller JACS 112,8573,1990
   data polat/
1  0.39,0.39,0.39,0.00,0.39,0.39,0.39,0.39,0.39,1.05,
2  1.35,1.35,1.05,1.90,0.00,1.00,1.00,1.05,1.00,1.00,
3  1.00,0.00,0.75,0.75,0.00,0.00,0.75,0.75,0.75,0.75,
4  0.75,0.75,0.00,3.00,3.00,3.00,3.00,1.54,0.0,0.0,
5  0.40,2.50,3.27,5.00,6*0.00,
6  4.18,3.31,2.86,2.93,2.81,2.62,2.61,2.81,3.63,0.00,
7  0.10,0.20,0.30,0.40,0.30,0.70,0.40,2.50,3.27,5.00/
c   AA-clp diffuseness factors
   data diffu/
1  0.60,0.62,0.64,0.00,0.75,0.80,0.80,0.80,0.80,1.00,
2  1.00,1.00,1.00,1.00,0.00,0.63,0.63,0.58,0.70,0.63,
3  0.63,0.00,0.45,0.70,0.00,0.00,0.50,0.50,0.45,0.50,
4  0.75,0.75,0.00,2.00,2.00,2.50,2.00,3.00,0.00,0.00,
5  0.20,2.40,1.50,5.00,6*0.00,
6  0.80,0.80,0.80,0.80,0.80,0.80,0.80,0.80,0.80,0.00,
7  0.20,0.30,1.50,3.00,5.00,1.50,0.50,3.00,4.00,5.00/
c   AA-clp acceptor-donor index
   data acdo/
1  0.20,0.10,0.05,0.00,0.99,0.99,0.90,0.99,0.99,0.00,
2  0.00,0.00,0.00,0.00,0.00,0.00,-0.97,-0.99,-0.70,0.00,
3  -0.85,0.00,-0.90,-0.99,0.00,0.00,-0.99,-0.90,-0.97,-0.95,
4  -0.90,-0.90,0.00,-0.50,-0.50,0.00,-0.50,0.00,0.00,0.00,
5  0.00,-0.20,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,
6  -0.50,-0.50,-0.50,-0.50,-0.50,-0.50,-0.50,-0.50,-0.50,0.0,
7  0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00,0.00/
c   Pauling electronegativities
   data elneg/
1  2.10,2.10,2.10,0.00,2.10,2.10,2.10,2.10,2.10,2.50,
2  2.50,2.50,2.50,2.50,0.00,3.00,3.00,3.00,3.00,3.00,
3  3.00,0.00,3.50,3.50,0.00,0.00,3.50,3.50,3.50,3.50,
4  3.50,3.50,0.00,2.50,2.50,2.50,2.50,2.10,0.00,0.00,
5  4.00,3.00,2.80,2.50,6*0.00,
6  1.32,1.45,1.56,1.60,1.64,1.70,1.75,1.75,1.66,0.00,
7  0.50,0.50,0.50,0.50,0.50,0.50,4.00,3.00,2.80,2.50/
c   ionization potentials
   data potio/
1  0.500,0.500,0.500,0.000,0.500,0.500,0.500,0.500,0.500,0.414,
2  0.414,0.414,0.414,0.414,0.000,0.534,0.534,0.534,0.534,0.534,
3  0.534,0.000,0.500,0.500,0.000,0.000,0.500,0.500,0.500,0.500,
4  0.500,0.500,0.000,0.381,0.381,0.381,0.381,0.386,0.000,0.000,
5  0.640,0.477,0.434,0.384,6*0.0,
6  0.251,0.248,0.249,0.273,0.289,0.289,0.281,0.284,0.345,0.000,
7  1.000,0.850,0.700,0.500,0.450,0.700,0.750,0.650,0.500,0.400/
c   Lennard-Jones 6-12 coefficients for hydrogen to iodine
   data c6/
1  73.8,73.8,73.8,6*0.0,2280.0,
2  2280.,2280.,2280.,2280.,0.0,2200.,2200.,2200.,2200.,2200.,
3  2200.,0.0,1650.,2600.,0.0,0.0,1650.,1650.,1650.,1650.,
4  1650.,1650.,0.0,10000.,10000.,10000.,10000.,0.0,0.0,0.0,
5  1080.,6400.,11900.,14280.,26*0.0/
   data c12/
1  14500.,14500.,14500.,6*0.0,4.5d+06,
```

```
2 4*4.5d+06,0.0,5*2.32d+06,  
3 2.32d+06,0.0,1.22d+06,2.6d+06,2*0.0,4*1.22d+06,  
4 1.22d+06,1.22d+06,0.0,4*1.3d+07,3*0.0,  
5 7.6d+05,7.65d+06,1.58d+07,1.90d+07,26*0.0/  
end
```

Sample input : whole molecule rotation

#BENZEN06 'P b c a'

```
0 0.0  
7.3600 9.3750 6.7030 90.00 90.00 90.00  
0.1100  
12  
1 -0.0615 0.1408 -0.0059 1 12 -0.1100  
2 -0.1400 0.0441 0.1273 1 12 -0.1100  
3 0.0778 0.0966 -0.1333 1 12 -0.1100  
4 -0.0778 -0.0966 0.1333 1 12 -0.1100  
5 0.1400 -0.0441 -0.1273 1 12 -0.1100  
6 0.0615 -0.1408 0.0059 1 12 -0.1100  
7 -0.1086 0.2499 -0.0104 1 2 0.1100  
8 -0.2483 0.0780 0.2252 1 2 0.1100  
9 0.1376 0.1714 -0.2367 1 2 0.1100  
10 -0.1376 -0.1714 0.2367 1 2 0.1100  
11 0.2483 -0.0780 -0.2252 1 2 0.1100  
12 0.1086 -0.2499 0.0104 1 2 0.1100  
0  
4  
1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0  
0.110000 0.110000 0.110000  
-1.0 0.0 0.0 0.0 -1.0 0.0 0.0 0.0 1.0  
0.500000 0.110000 0.500000  
1.0 0.0 0.0 0.0 -1.0 0.0 0.0 0.0 -1.0  
0.500000 0.500000 0.110000  
-1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 -1.0  
0.110000 0.500000 0.500000  
0 1 2.0  
-1 0 0  
-1  
1 0. 120. 2.
```

Sample input: rotation of atoms 14, 15, 16 around the 11-13 axis

#EFITAO 'P -1'

```
0 0.0  
7.572 8.281 9.562 68.31 88.67 78.57  
0.0  
24  
1 0.3399 0.2309 -0.1203 1 34 -0.2314  
2 0.4264 0.3498 -0.2937 1 10 0.8244  
3 0.2924 0.4766 -0.3862 1 21 -0.8375  
4 0.1221 0.4972 -0.3318 1 10 0.8875  
5 0.1224 0.3603 -0.1773 1 12 -0.1779  
6 -0.0301 0.3521 -0.1043 1 12 -0.2067  
7 -0.0671 0.2329 0.0451 1 14 0.3858  
8 0.0573 0.0871 0.1405 1 12 -0.2428  
9 0.0101 -0.0167 0.2804 1 12 -0.0688  
10 -0.1602 0.0198 0.3290 1 12 -0.1380  
11 -0.2860 0.1632 0.2352 1 12 -0.1231  
12 -0.2401 0.2683 0.0947 1 12 -0.3160  
13 -0.4727 0.1999 0.2847 1 13 1.0177  
14 -0.5657 0.0797 0.2857 1 41 -0.3146  
15 -0.5680 0.3573 0.1963 1 41 -0.3078  
16 -0.4759 0.2005 0.4239 1 41 -0.3160  
17 0.5834 0.3198 -0.3215 1 27 -0.4949  
18 -0.0049 0.6111 -0.3998 1 27 -0.5379  
19 -0.1460 0.4503 -0.1661 1 2 0.1264  
20 0.1916 0.0553 0.1045 1 2 0.1868  
21 0.1085 -0.1283 0.3528 1 2 0.1324  
22 -0.1956 -0.0621 0.4388 1 2 0.1356  
23 -0.3395 0.3791 0.0225 1 2 0.1737  
24 0.3164 0.5529 -0.4906 1 7 0.4430  
0  
2 0  
1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0
```

```

0.000000 0.000000 0.000000
-1.0 0.0 0.0 0.0 -1.0 0.0 0.0 0.0 -1.0
0.000000 0.000000 0.000000
0 1 2.0
11 13 0
3
14 15 16
1 0. 360. 5.

```

S-4 Detail of Monte Carlo and Molecular Dynamics simulations

The following are samples of the topology files for Monte Carlo (rigid body + CF3 free rotation) and Molecular Dynamics (full motion of all degrees of freedom):

```

#EFITAO    renumbered topology Monte Carlo
21
1 0.06049 1.14972 2.93511 34 -0.2314
2 0.04870 0.38652 4.53619 10 0.8244
3 -0.04118 -0.96404 4.41291 21 -0.8375
4 -0.04869 -1.50276 3.14032 10 0.8875
5 -0.02969 -0.40346 2.13034 12 -0.1779
6 -0.07114 -0.69395 0.82735 12 -0.2067
7 -0.06961 0.17354 -0.35155 14 0.3858
8 -0.12894 1.56904 -0.31625 12 -0.2428
9 -0.10840 2.30280 -1.48539 12 -0.0688
10 -0.03776 1.68232 -2.71083 12 -0.1380
11 0.01030 0.29642 -2.76546 12 -0.1231
12 -0.00864 -0.44959 -1.59918 12 -0.3160
13 0.03848 -0.38558 -4.08984 13 1.0177
14 0.12268 1.00891 5.57054 27 -0.4949
15 -0.04988 -2.68498 2.90421 27 -0.5379
16 -0.11261 -1.75023 0.60549 2 0.1264
17 -0.19136 2.07848 0.63410 2 0.1868
18 -0.14826 3.38106 -1.43655 2 0.1324
19 -0.01981 2.26628 -3.61937 2 0.1356
20 0.02364 -1.52799 -1.65558 2 0.1737
21 -0.09914 -1.55114 5.22013 7 0.4430
1 nslav-u
22 23 24 13 11 12 41 -0.3128
0 ncore-v
0 nslav-v
202.3 0.0 volu-u,volu-v
0 nstr-u
0 nstr-v
0 nbend-u
0 nbend-v
1 ntors-u
22 13 11 12 0.3 -1.0 2.0
0 ntors-v
0 nlist-u
0 nlist-v
0.0 0.0 0.0 0.0
0 nextr

```

```

#EFITAO    renumbered topology Molecular dynamics
24
1 0.06049 1.14972 2.93511 34 -0.2314
2 0.04870 0.38652 4.53619 10 0.8244
3 -0.04118 -0.96404 4.41291 21 -0.8375
4 -0.04869 -1.50276 3.14032 10 0.8875
5 -0.02969 -0.40346 2.13034 12 -0.1779
6 -0.07114 -0.69395 0.82735 12 -0.2067
7 -0.06961 0.17354 -0.35155 14 0.3858
8 -0.12894 1.56904 -0.31625 12 -0.2428
9 -0.10840 2.30280 -1.48539 12 -0.0688
10 -0.03776 1.68232 -2.71083 12 -0.1380
11 0.01030 0.29642 -2.76546 12 -0.1231
12 -0.00864 -0.44959 -1.59918 12 -0.3160
13 0.03848 -0.38558 -4.08984 13 1.0177
14 0.12268 1.00891 5.57054 27 -0.4949
15 -0.04988 -2.68498 2.90421 27 -0.5379
16 -0.11261 -1.75023 0.60549 2 0.1264
17 -0.19136 2.07848 0.63410 2 0.1868

```

18	-0.14826	3.38106	-1.43655	2	0.1324
19	-0.01981	2.26628	-3.61937	2	0.1356
20	0.02364	-1.52799	-1.65558	2	0.1737
21	-0.09914	-1.55114	5.22013	7	0.4430
22	-1.11825	-0.29292	-4.73064	41	-0.3146
23	0.31754	-1.68454	-3.98918	41	-0.3078
24	0.95297	0.12446	-4.91395	41	-0.3160
0	nslav-u				
0	ncore-v				
0	nslav-v				
202.3	0.0	volu-u,volu-v			
25	nstr-u				
1	2	1.774	3000.0	S- C	
1	5	1.752	3000.0	S- C	
2	3	1.359	5398.5	C- N	
2	14	1.209	8355.7	C- O	
3	4	1.382	4859.3	N- C	
3	21	1.000	5300.0	N- H	
4	5	1.493	2713.1	C- C	
4	15	1.206	8442.2	C- O	
5	6	1.336	6025.9	C- C	
6	7	1.464	3329.4	C- C	
6	16	1.080	3600.0	C- H	
7	8	1.397	4729.0	C- C	
7	12	1.396	4756.2	C- C	
8	9	1.380	5081.3	C- C	
8	17	1.080	3600.0	C- H	
9	10	1.375	5188.5	C- C	
9	18	1.080	3600.0	C- H	
10	11	1.388	4926.8	C- C	
10	19	1.080	3600.0	C- H	
11	12	1.385	4994.7	C- C	
11	13	1.490	2776.5	C- C	
12	20	1.080	3600.0	C- H	
13	22	1.326	4000.0	C- F	
13	23	1.332	4000.0	C- F	
13	24	1.333	4000.0	C- F	
0	nstr-v				
40	nbend-u				
1	2	3	110.00	500.0	S- C- N
1	2	14	123.00	500.0	S- C- O
1	5	4	110.00	500.0	S- C- C
1	5	6	130.00	500.0	S- C- C
2	1	5	92.00	500.0	C- S- C
2	3	4	118.00	590.2	C- N- C
2	3	21	121.00	460.0	C- N- H
3	2	14	126.00	702.0	N- C- O
3	4	5	110.00	515.9	N- C- C
3	4	15	124.00	702.0	N- C- O
4	3	21	121.00	460.0	C- N- H
4	5	6	120.00	583.8	C- C- C
5	4	15	126.00	781.8	C- C- O
5	6	7	131.00	661.0	C- C- C
5	6	16	114.00	580.0	C- C- H
6	7	8	125.00	618.9	C- C- C
6	7	12	117.00	562.7	C- C- C
7	6	16	114.00	580.0	C- C- H
7	8	9	121.00	590.8	C- C- C
7	8	17	120.00	505.0	C- C- H
7	12	11	121.00	590.8	C- C- C
7	12	20	120.00	505.0	C- C- H
8	7	12	118.00	569.7	C- C- C
8	9	10	121.00	590.8	C- C- C
8	9	18	119.00	517.5	C- C- H
9	8	17	120.00	505.0	C- C- H
9	10	11	119.00	576.7	C- C- C
9	10	19	120.00	505.0	C- C- H
10	9	18	120.00	505.0	C- C- H
10	11	12	120.00	583.8	C- C- C
10	11	13	120.00	583.8	C- C- C
11	10	19	120.00	505.0	C- C- H
11	12	20	120.00	505.0	C- C- H
11	13	22	112.00	601.0	C- C- F

11	13	23	113.00	601.0	C-	C-	F				
11	13	24	113.00	601.0	C-	C-	F				
12	11	13	120.00	583.8	C-	C-	C				
22	13	23	107.00	600.0	F-	C-	F				
22	13	24	106.00	600.0	F-	C-	F				
23	13	24	106.00	600.0	F-	C-	F				
0	nbend-v										
25	ntors-u										
22	13	11	12	0.30	-1.0	2.0	C-	C-	C-	F	cf3
5	1	2	3	50.00	-1.0	1.0	C-	S-	C-	N	5-ring
2	1	5	4	50.00	-1.0	1.0	C-	S-	C-	C	
1	2	3	4	50.00	-1.0	1.0	S-	C-	N-	C	
2	1	3	14	100.00	-1.0	1.0	C-	S-	N-	O	
2	3	4	5	50.00	-1.0	1.0	C-	N-	C-	C	
3	2	4	21	100.00	-1.0	1.0	N-	C-	C-	H	
3	4	5	1	50.00	-1.0	1.0	N-	C-	C-	S	
4	3	5	15	100.00	-1.0	1.0	C-	N-	C-	O	
5	1	4	6	100.00	-1.0	1.0	C-	S-	C-	C	
1	5	6	7	50.00	-1.0	1.0	S-	C-	C-	C	bridge
5	6	7	8	50.00	-1.0	1.0	C-	C-	C-	C	
6	5	7	16	100.00	-1.0	1.0	C-	C-	C-	H	
6	7	8	9	50.00	1.0	1.0	C-	C-	C-	C	6-ring
6	7	12	11	50.00	1.0	1.0	C-	C-	C-	C	
7	6	8	12	100.00	-1.0	1.0	C-	C-	C-	C	
7	8	9	10	50.00	-1.0	1.0	C-	C-	C-	C	
8	7	9	17	100.00	-1.0	1.0	C-	C-	C-	H	
8	9	10	11	50.00	-1.0	1.0	C-	C-	C-	C	
9	8	10	18	100.00	-1.0	1.0	C-	C-	C-	H	
9	10	11	12	50.00	-1.0	1.0	C-	C-	C-	C	
10	9	11	19	100.00	-1.0	1.0	C-	C-	C-	H	
10	11	12	7	50.00	-1.0	1.0	C-	C-	C-	C	
11	10	12	13	100.00	-1.0	1.0	C-	C-	C-	C	
12	7	11	20	100.00	-1.0	1.0	C-	C-	C-	H	
0	ntors-v										
0	nlist-u										
0	nlist-v										
0.0	0.0	0.0	0.0	0.0							
0	nextr										

S-5 Refcodes of Ph-CH3 crystals for ZL calculations

#ANUWOX	'P 21 21 21'	ordered	1.237	100.0	2015.	2.58
#BAZFUG	'P 21 21 21'		1.285	297.0	2017.	3.77
#CETLET	'C 2/c'		1.283	298.0	2006.	4.80
#CUVQIT	'P b c a'		1.304	295.0	2000.	4.10
#DERTEA	'P 21 21 21'		1.323	137.0	2006.	3.61
#EBAMAY	'P 21/n'		1.428	90.0	2014.	3.07
#EVOSIS	'P -1'		1.504	296.0	2011.	3.07
#GOFNEW	'P 21/n'		1.386	296.0	2014.	4.88
#HAHRIT	'P n a 21'		1.618	295.0	2011.	3.45
#JIZKUY	'P 21/a'		1.333	295.0	1991.	4.10
#KERZIR	'P 21 21 21'		1.286	293.0	2006.	4.17
#KIDVEA	'P -1'		1.594	173.0	2013.	3.92
#KIMRUV	'P -1'		1.532	100.0	2012.	3.53
#LOJDIY	'C 2/c'		1.302	100.0	2008.	4.58
#LUPKUD	'P 21/n'		1.176	173.0	2009.	3.73
#NIFGIT01	'P n a 21'		1.134	297.0	2008.	4.07
#OMONEJ	'P b c a'		1.193	130.0	2004.	4.25
#PAXMIM	'P -1'		1.514	293.0	2012.	4.84
#QAKDAJ	'P 21/c'		1.151	293.0	2011.	4.77
#TEFKIA	'C 2/c'		1.551	200.0	2012.	2.90
#TUNPOI	'P 21/n'		1.272	299.0	2010.	5.00
#UMOWOK	'P 21 21 21'		1.303	181.0	2016.	4.25
#WOGMIQ	'P n a 21'		1.261	100.0	2014.	3.32
#WULPEZ	'P 21/c'		1.528	100.0	2009.	2.95
#XALMEF	'P 21/c'		1.544	100.0	2017.	4.00
#XAZFEL	'P 21/c'		1.439	100.0	2012.	3.15
#YELRIT	'P 21 21 21'		1.338	296.0	2016.	2.59
#YODDOL	'P b c a'		1.631	299.0	2008.	3.35
#ZUWFII	'P 21 21 21'		1.575	173.0	2015.	2.72
#XADRUP	'C 2/c'	disordered				
#AYOYAP	'P 21/c'					
#XIHMOQ	'P b c a'					

#XIHSUD 'P 21 21 2
#ZIXDIV 'P -1'

S-6 Refcodes of Ph-CF₃ crystals for ZL calculations

AGAVUA	'P 21/c'	1.587	133.0	2008.	3.83
AZAXEE	'P 21/c'	1.352	295.0	2003.	5.00
AZAXII	'P 21/c'	1.498	295.0	2003.	4.80
BAVVID	'P b c a'	1.707	295.0	1999.	5.08
BURTAL	'P -1'	1.542	123.0	2015.	4.21
CARBUS	'P -1'	1.606	295.0	1983.	5.12
CEGZAS	'P -1'	1.651	100.0	2017.	5.19
CEWDEQ	'P -1'	1.420	240.0	2017.	5.54
DAXBAG	'P 21/n'	1.528	273.0	2005.	13.61
EDOROG01	'P 21 21 21'	1.665	90.0	2012.	3.37
ENEHUB	'P 21 21 21'	1.647	293.0	2011.	5.31
EVAJOB	'P 21/n'	1.456	296.0	2011.	4.44
FMPHTZ	'P 21 21 21'	1.570	295.0	1976.	7.30
FUGWEK	'P -1'	1.501	296.0	2009.	9.96
GEJDIJ	'P 21/n'	1.519	120.0	2006.	5.64
GERBUA	'P -1'	1.484	295.0	1988.	8.20
GIDJIM10	'P c c n'	1.510	295.0	1990.	3.80
GISZIR01	'P -1'	1.481	295.0	1998.	6.67
GITKUQ	'P 21/n'	1.678	294.0	2008.	4.87
GOKKAU	'P 21/c'	1.517	180.0	2011.	5.31
GUGLOL	'P 21/c'	1.482	150.0	2015.	7.51
HIRNIG	'P 21/c'	1.518	298.0	2007.	2.99
HODHIS	'P 21/c'	1.411	298.0	2008.	5.30
ICULUN	'P 21/c'	1.560	293.0	2001.	5.70
IFABEX	'P n a 21'	1.604	298.0	2006.	6.93
LASJOG	'P c c n'	1.567	120.0	2012.	5.38
NAJWUS	'P b c a'	1.746	295.0	2009.	5.48
REZSIZ	'P 21/n'	1.546	100.0	2007.	4.60
TIDNUP	'P n a 21'	1.721	130.0	1996.	4.24
TIHQIL	'P 21 21 21'	1.424	296.0	2007.	7.60
VIFQIL01	'P 21/c'	1.493	293.0	2006.	4.72
VILBOH	'P c c n'	1.520	295.0	1991.	4.66
VILBUN	'P 21 21 21'	1.516	295.0	1991.	7.50
VOQLUJ	'P -1'	1.481	298.0	2009.	6.80
WIGZAO	'P 21/c'	1.544	298.0	2007.	4.88
#DAHDOF	'P 21/c'				
#EFATOU	'P 21/n'				
#MEKMof	'P 21/c'				
#RIJDUM	'P 21/c'				
#UFAZOQ	'P 21/n'				
#UNUZIN	'P 21/c'				
#CEWDIU	'P 21/c'				
#DEJXEY	'P -1'				
#EFITAO	'P -1'				
#FPAMCA	'C 2/c'				
#GULTAK	'P 21/c'				
#HUYHUG	'P 21/c'				
#OBIXUV	'P 21/n'				
#OKEHUJ	'C 2/c'				
#PETJIJ	'P 21/n'				
#PETLAD	'P 21/c'				
#SASYAN	'P -1'				
#YAZGOY	'P n a 21'				

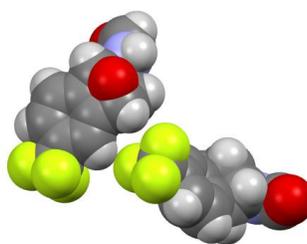
S-7 Monte Carlo simulations

EFITAO (P1-), VILBUN (P2₁2₁2₁): rigid molecule except for CF₃ rotation with intramolecular barrier of 0.6 kJ mol⁻¹, MI-LJC crystal potentials, crystal box 360 molecules (dimensions 42-50 Å) with periodic boundary conditions, 3 million steps NPT simulation at 298 K and 1 atm, IIE pressure control;
HODHIS (P2₁/c): all as above, box 256 molecules (dimensions 40-44) Å, simulation at 298 and 100 K;

CORONE ($P2_1/n$): fully rigid molecule, box 168 molecules (dimensions 33-47 Å), 2 million steps at 300, 400, 500 K, box 192 molecules, 2 million steps at 700 K.

S-8 EFITAO-VILBUN, difference in barrier and difference in structure

What is the structural reason for the different behavior of CF_3 in two similar compounds at the same temperature?. In the ordered structure one F atom nests in the bay area between two C-H groups in a neighbor molecule (Figure 10a), in what is sometimes invoked as a stabilizing C-H...F "bond" that could prevent rotation. However, in the wholly disordered structure (Figure 10b) there is also a similar C-H bay area, which the fluorine atoms do not approach closely. A conservative view is that in both cases there is a weak local stabilization due to nearby positive (hydrogen) and negative (fluorine) regions, probably stronger in the case of the ordered structure.

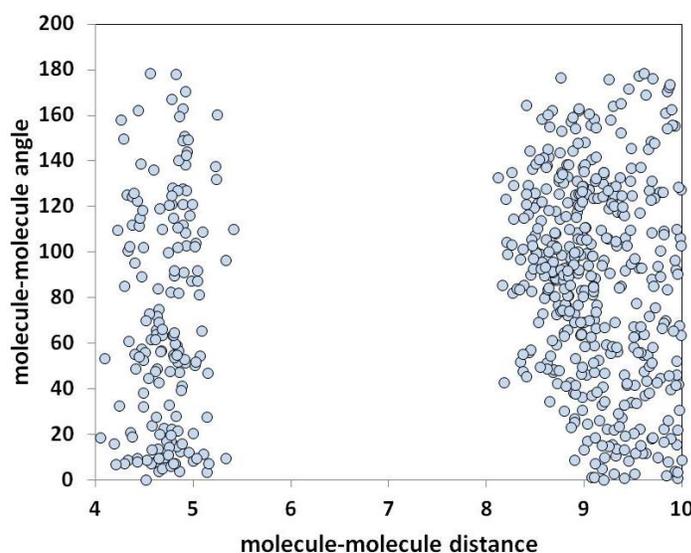


EFITAO ordered

VILBUN disordered

Nearest-neighbor molecular pairs in the structure with CF_3 ordered (*a*) and with CF_3 disordered (*b*), in which fluorine atoms seem more free from short contact.

S-9 Coronene: Monte Carlo simulation at 700 K



MC simulation of the coronene crystal ($P2_1/n$, $Z = 2$): distribution of mutual in-plane rotation angles against distances between molecular centers of mass (ordered crystal values: 0° at 4.69 and 9.39 Å; 132° at 8.42 Å, red circles). Spread in distance and angle at 700 K.

S-10 Molecular dynamics details

Trifluoromethylbenzene, TFMB (XOGJAG, Pbc_a): box 160 molecules, dimension 30 Å, 5000 steps of 0.002 ps, NPT simulation at 213 K with weak thermostat coupling with relaxation factor 0.6, 1 atm with comprs = 0.35, trajectory written every 0.1 ps

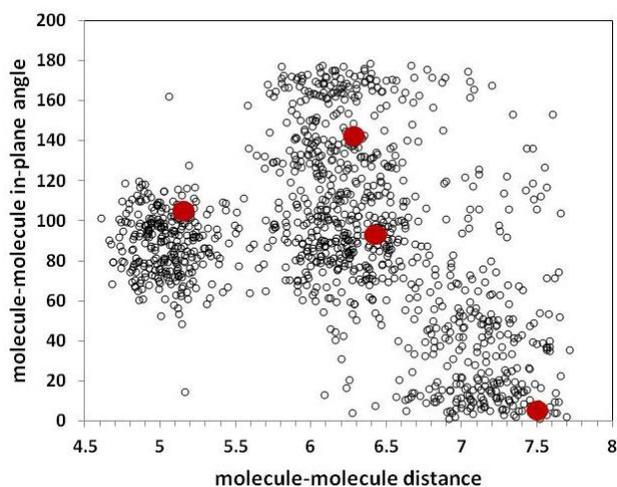
trifluoromethylbenzylidene) thiazolidine-2,4-dione, TFTD (EFITAO, P1-) box 160 molecule, dimensions 33-38 Å, room temperature, rest all as above;

trifluoromethylphenylpropanoic acid (TPPA (VOQLUJ, P1-) box 160 molecules, dimensions 33-39 Å, room temperature, 1 atm with comprs = 0.2, rest all as above.

S-11 Torsion angle trajectories

A problem in the analysis of torsional trajectories, plots of torsion angle as a function of time, is that the angle is defined in the -180° to $+180^\circ$ range, according to the standard convention (in the A-B-C-D atom sequence, torsion is positive if looking from A down the B-C vector the D atom turns to the right side). Therefore, discontinuities may occur for values close to $\text{abs}(180^\circ)$: e.g. a clockwise rotation of 10° from $+175^\circ$ would bring the angle to -175° . Moreover, in principle it is impossible to determine if a transition has occurred by clockwise $\Delta\tau$ or counterclockwise $360-\Delta\tau$; in practice, however, for small time intervals, taking the smaller of the two values and working $\text{mod}(360)$ is sufficient to obtain a seamless trajectory, if at the price of having angles $>\text{abs}(180^\circ)$.

S-12 Final frame of the MD simulation for 1,4-cyclohexadiene



In-plane reciprocal angle against distance for pairs of molecules. The red dots are the values for the ordered crystal.