A Comparison of Geometry Optimization with Internal, Cartesian, and Mixed Coordinates

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Abstract

Improvements in MO programs and computer speeds have dramatically increased the size of molecules that can be optimized by MO methods. This has put a considerable strain on existing geometry optimization techniques. For a given molecular system, the performance of a geometry optimization method can vary significantly depending on the coordinates used. Nonredundant internal coordinates (e.g., Z-matrix coordinates) are easily constructed and behave well for acyclic molecules but can be quite troublesome for cyclic systems. Cartesian coordinates behave well for rigid, cyclic molecules but can be quite poor for flexible, acyclic systems. Mixed cartesian and internal coordinates have been suggested as a means of combining the best of both approaches and are particularly convenient for cyclic systems with flexible substituents. The efficiency of these different approaches is compared for a number of molecules. © 1992 John Wiley & Sons, Inc.

Introduction

Geometry optimization is one of the important steps in almost any quantum chemical study. With the advent of efficient methods for computing energy gradients for *ab initio* molecular orbital calculations [1] and the use of gradient-based optimization algorithms [2], finding equilibrium geometries has become almost routine for many simple molecules [3]. The key to the efficiency of any optimization is the choice of a suitable coordinate system. Strong coupling between coordinates, narrow gullies, and curved valleys cause serious problems for even the best optimizers [2]. Many geometry optimizations in quantum chemical calculations are carried out using nonredundant internal coordinates, for example, Z-matrix coordinates or similar definitions of internal coordinates. This is both convenient and efficient for many small molecules, since the Z-matrix is constructed from the natural coordinates of a molecule, that is, bondlengths, valence angles, and torsions about bonds. Such internal coordinates are normally not very strongly coupled, and the optimization proceeds efficiently [3,4]. However for cyclic molecules, it is very difficult to set up a nonredundant coordinate system without strong coupling [4]. There are a number of ways around this problem: cartesian coordinates, redundant internal coordinates, or a nonredundant linear combination of cartesian or redundant internal coordinates (e.g., symmetry adapted coordinates). Pulay [5] recently demonstrated that suitable combinations of redundant coordinates can be used very efficiently in geometry optimization. Generating an appropriate redundant

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internal coordinate system that minimizes coupling requires some skill or a suitable program [6]. The effort in constructing such a coordinate system is rewarded by significant improvements in the efficiency of the geometry optimization [5]. The other alternative, cartesian coordinates, is routinely used in molecular mechanics [7]. Cartesian coordinates are unambiguous and easy to set up, but are moderately strongly coupled. Traditionally, cartesian coordinates have been avoided in molecular orbital calculations because it was thought they would slow down optimization significantly. Recently Hehre et al. [8] showed that with a suitable initial guess for the hessian and the geometry, cartesian coordinate-based optimization could be quite comparable to internal coordinate-based methods. Cartesian coordinates were better for cyclic and rigid molecules, but were poorer for flexible, acyclic systems. Cartesian coordinates also make constraints more difficult to impose (however, see Refs. [9]–[11]). As an alternative to pure cartesian or pure internal coordinates, Head [11] and Obara et al. [12] have suggested the use of mixed cartesian and internal coordinates. In this article we compare the efficiency of geometry optimization based on internal, cartesian, and mixed coordinates.

Methodology

All molecular orbital calculations were carried out with the GAUSSIAN 92 series of programs [13]. The Hartree–Fock level of theory was used with the STO–3G basis set [14]. Geometries were optimized with two different sets of internal coordinates, cartesian coordinates, and mixed cartesian/internal coordinates. Starting geometries were obtained by molecular mechanics minimization using MacroModel [15] and the MM2 force field [7] (the C—H bonds were shortened by 0.03 Å to take into account the systematic difference between MM2 and *ab initio* MO computed C—H bondlengths). Internal, cartesian, and mixed internal/cartesian coordinate optimizations were started from the same geometry. The initial estimates of the hessians were generated from a simple valence force field transformed to the coordinate system used in the optimization [16]. The standard optimization routine in GAUSSIAN was used for all minimizations [17].

For optimizations using mixed cartesian and internal coordinates, variable cartesian coordinates are treated analogous to variable internal coordinates. The transformations for the coordinates and gradients from cartesian to internal coordinates is

$$\delta q = B\delta x \quad \text{and} \quad g_q = (\mathrm{BMB}^t)^{-1}\mathrm{BM}g_x$$

where B is the Wilson B matrix [18]. If the Z-matrix orientation is used for the cartesian coordinates of the molecule, M is an identity matrix with the diagonal elements for x_1, y_1, z_1, x_2, y_2, y_3 set to zero (i.e., for those cartesian coordinates that are always zero in the Z-matrix orientation). To add a few cartesian coordinates to the internal coordinates, one simply defines the appropriate B-matrix elements for cartesian displacements (i.e., an identity matrix). This approach has been implemented in GAUSSIAN 92 [13]. The current specification of the Z-matrix geometry input already includes the possibility of defining some (or all) of the atoms

by cartesian coordinates and the remainder by internal coordinates. Unlike earlier implementations of mixed coordinate optimization [12], the present approach allows full coupling between the cartesian and internal coordinates.

For full cartesian coordinate optimization, the structure input can be via cartesian coordinates or *Z*-matrix internal coordinates (the cartesian variable names are generated automatically and passed to the same optimizer used for internal coordinates [17]). Even though translational and rotational invariance of the gradient should assure that the molecule does not undergo overall translation or rotation during the optimization, the hessian for cartesian coordinate optimization is adjusted so that the coordinates for overall translation or rotation have large positive force constants, effectively freezing these degrees of freedom (this is similar to the frozen coordinates that can be used in regular geometry optimizations [13]).

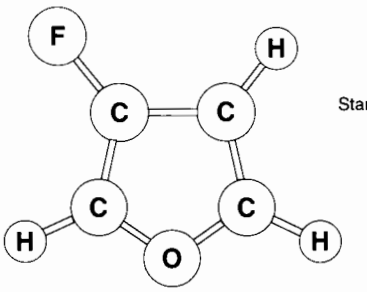
Results and Discussion

Table I presents a selection of some monocyclic, bicyclic, and tricyclic molecules. A number of these have been used in previous articles [5,8] to test the performance of geometry optimization methods. To assess the variability in performance of optimizations in internal coordinates, a number of molecules were optimized with two different sets of internal coordinates. Those in set (a) were constructed according to the suggestions of Ref. [4] so as to minimize the coupling between coordinates and to maintain the symmetry of the molecule during the optimization. These internal coordinates, along with the starting geometries are shown in Figure 1. The internal coordinates of set (b) were chosen in a more cavalier manner without regard to problems of strong coupling (e.g., a six-membered ring is constructed as a simple chain of six atoms). For cartesian coordinates, all 3 N coordinates are allowed to vary. For mixed coordinates, the n atoms in the rings are described by $3n - 6$ cartesian coordinates, while the substituents are attached using internal coordinates.

TABLE I. Comparison of geometry optimization performance using internal, cartesian, and mixed interal/cartesian coordinates.

Molecule	Number of atoms	Symmetry	Number of variables	Number of optimization steps			
				Internal (a)	Internal (b)	Cartesian	Mixed
2 fluoro furan	9	C_s	15	7	8	7	7
norbornane	19	C_{2v}	15	7	6	5	5
bicyclo[2.2.2]octane	22	D_3	11	11	25	19	14
bicyclo[3.2.1]octane	22	C_s	33	6	5	6	7
endo hydroxy bicyclopentane	14	C_1	36	8		18	9
exo hydroxy bicylopentane	14	C_1	36	10		20	11
ACTHCP	16	C_1	42	65		>81	72
1,4,5 trihydroxy anthroquinone	27	C_s	51	10		11	17
histamine H^+	18	C_1	48	42		>100	47

2 fluoro furan



Starting geometry & internal coorinate set (a)

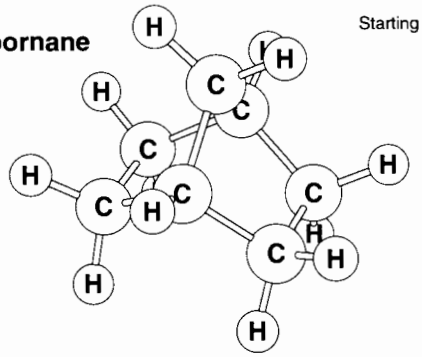
```
C
C 1 r1
C 1 r2 2 a2
C 2 r3 1 a3 3  0.
O 1 r4 2 a4 3  0.
F 1 r5 2 a5 3 180.
H 2 r6 1 a6 3 180.
H 3 r7 1 a7 2 180.
H 4 r8 2 a8 1 180.
```

Number of optimization steps

internal coordinates (a)	7
internal coordinates (b)	8
cartesian coordinates	7
mixed coordinates	7

```
r1=1.4558/r2=1.3375/r3=1.3395
r4=2.1286/r5=1.3336/r6=1.0721
r7=1.0724/r8=1.0726/a2=102.5826
a3=101.6686/a4= 70.3774/a5=128.8779
a6=129.0378/a7=126.9982/a8=126.7146
```

norbornane



Starting geometry & internal coordinate set (a)

```
C
C 1 r1
C 1 r1 2 a1
C 2 r2 1 a2 3  d2
C 2 r2 1 a2 3 -d2
C 3 r2 1 a2 2  d2
C 3 r2 1 a2 2 -d2
H 1 r3 2 a3 3 a3  1
H 1 r3 2 a3 3 a3 -1
H 2 r4 1 a4 3 180.
H 3 r4 1 a4 2 180.
H 4 r5 2 a5 1  d5
H 4 r6 2 a6 1  d6
H 5 r5 2 a5 1 -d5
H 5 r6 2 a6 1 -d6
H 6 r5 3 a5 1  d5
H 6 r6 3 a6 1  d6
H 7 r5 3 a5 1 -d5
H 7 r6 3 a6 1 -d6
```

Number of optimization steps

internal coordinates (a)	7
internal coordinates (b)	6
cartesian coordinates	5
mixed coordinates	5

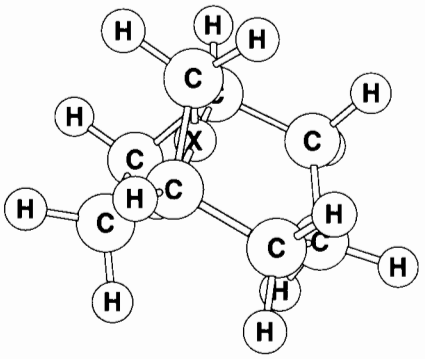
```
r1=1.5378/r2=1.5418/r3=1.0863
r4=1.0876/r5=1.0869/r6=1.0858
a1= 92.5394/a2=102.1580/a3=113.4070
a4=115.0850/a5=110.2372/a6=112.0658
d2=-56.4782/d5=-81.9032/d6=157.5936
```

Figure 1. Structures, starting geometries, and internal coordinate set (a) for the molecules in Table I.

The table shows that for a variety of systems internal coordinates perform as well as or better than cartesian coordinates, in agreement with Baker and Hehre [8]. Secondly, the number of steps taken by optimizations using mixed cartesian and internal coordinates is generally intermediate between pure cartesian coordinates and well-chosen internal coordinates. Since mixed coordinate systems do not require the careful crafting of good internal coordinates for rings [4], and since their performance is equal to or better than cartesian coordinates, there is some merit to using mixed coordinates.

Fluorofuran, hydroxybicyclopentane, norbornane, and 2 bicyclooctanes are fairly rigid and are well represented by the MM2 force field. Thus, relatively few steps are

bicyclo [3.2.1] octane



Starting geometry & internal coordinate set (a)

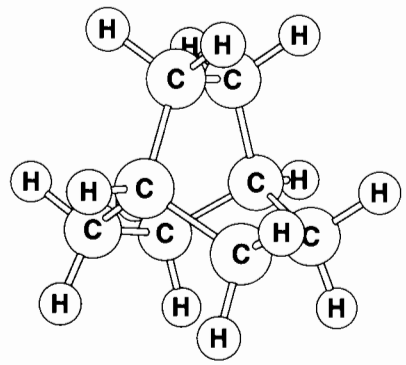
```
-
c 1 r1
c 1 r2  2 90.
c 1 r2  2 90. 3 180.
c 3 r3  1 a3  2  d3
c 4 r3  1 a3  2 -d3
c 3 r4  1 a4  2  d4
c 4 r4  1 a4  2 -d4
c 1 r5  2 a5  3  90.
h 2 r6  3 a6  4  a6 -1
h 2 r7  3 a7  4  a7  1
h 3 r8  2 a8  4  d8
h 4 r8  2 a8  3 -d8
h 5 r9  3 a9  6  d9
h 5 r10 3 a10 6  d10
h 6 r9  4 a9  5 -d9
h 6 r10 4 a10 5 -d10
h 7 r11 3 a11 9  d11
h 7 r12 3 a12 9  d12
h 8 r11 4 a11 9 -d11
h 8 r12 4 a12 9 -d12
h 9 r13 7 a13 8 a13  1
h 9 r14 7 a14 8 a14 -1
```

Number of optimization steps

internal coordinates (a)	6
internal coordinates (b)	5
cartesian coordinates	6
mixed coordinates	7

```
r1=0.9863/r2=1.1768/r3=1.5408
r4=1.5404/r5=2.2660/r6=1.0856
r7=1.0871/r8=1.0889/r9=1.0871
r10=1.0855/r11=1.0865/r12=1.0868
r13=1.0872/r14=1.0859/a3= 74.7408
a4= 93.5429/a5=130.0092/a6=113.4879
a7=110.7039/a8=111.4780/a9=109.6191
a10=112.0531/a11=108.8747/a12=109.9315
a13=110.3734/a14=109.2114/d3=-132.2131
d4=115.7902/d8=166.7660/d9=117.9400
d10=-123.1354/d11=-121.1057/d12=122.3794
```

bicyclo [2.2.2] octane



Starting geometry & internal coordinate set (a)

```
C
C 1 r1
C 1 r2 2 a2
C 1 r2 2 a2 3 120.
C 1 r2 2 a2 3 240.
C 2 r2 1 a2 3 d2
C 2 r2 1 a2 6 120.
C 2 r2 1 a2 6 240.
- 1 1. 2 90. 3 0.
- 2 1. 1 90. 6 0.
H 1 r3  9 90. 2 180.
H 2 r3 10 90. 1 180.
H 3 r4 1 a4 2 d4
H 3 r5 1 a5 2 d5
H 4 r4 1 a4 2 d4
H 4 r5 1 a5 2 d5
H 5 r4 1 a4 2 d4
H 5 r5 1 a5 2 d5
H 6 r4 2 a4 1 d4
H 6 r5 2 a5 1 d5
H 7 r4 2 a4 1 d4
H 7 r5 2 a5 1 d5
H 8 r4 2 a4 1 d4
H 8 r5 2 a5 1 d5
```

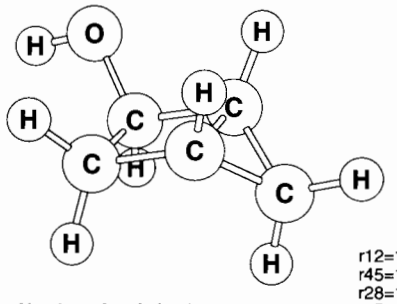
Number of optimization steps

internal coordinates (a)	11
internal coordinates (b)	25
cartesian coordinates	19
mixed coordinates	14

```
r1=2.5790/r2=1.5396/r3=1.0895
r4=1.0867/r5=1.0868/a2= 70.0910
a4=109.2484/a5=110.4824/d2=6.3053
d4=114.9771/d5=-127.9986
```

Figure 1. (*Continued*)

2 hydroxy bicyclopentane



Number of optimization steps

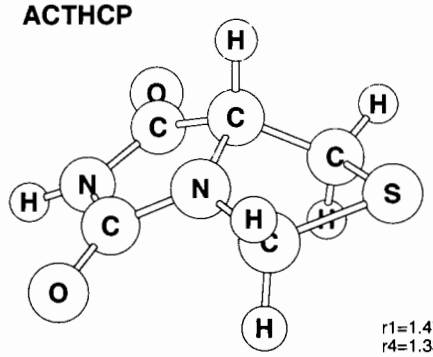
internal coordinates (a)	10
cartesian coordinates	20
mixed coordinates	11

Starting geometry and internal coordinate set (a)

```
C
C 1 r12
C 1 r13 2 a213
C 1 r14 2 a214 3 d3214
C 4 r45 1 a145 2 d2145
O 4 r46 1 a146 2 d2146
H 1 r17 2 a217 3 d3217
H 2 r28 1 a128 3 d3128
H 3 r39 1 a139 2 d2139
H 3 r3A 1 a13A 2 d213A
H 4 r4B 1 a14B 2 d214B
H 5 r5C 4 a45C 1 d145C
H 5 r5D 4 a45D 1 d145D
H 6 r6E 4 a46E 1 d146E
```

```
r12=1.5447/r13=1.4892/r14=1.5367
r45=1.5374/r46=1.4064/r17=1.0875
r28=1.0877/r39=1.0845/r3A=1.0839
r4B=1.0877/r5C=1.0854/r5D=1.0851
r6E=0.9423/a213=58.7631/a214=89.4219
a145=90.6265/a146=111.3076/a217=109.2699
a128=109.1552/a139=116.0099/a13A=115.6587
a14B=113.6734/a45C=114.7176/a45D=113.3309
a46E=108.0277/d3214=125.1018/d2145=-0.3599
d2146=114.4321/d3217=-113.9872/d3128=114.3015
d2139=-107.2585/d213A=107.0506/d214B=-118.5685
d145C=115.4893/d145D=-113.2697/d146E=177.3806
```

ACTHCP



Number of optimization steps

internal coordinates (a)	65
cartesian coordinates	>81
mixed coordinates	72

Starting geometry & internal coordinate set (a)

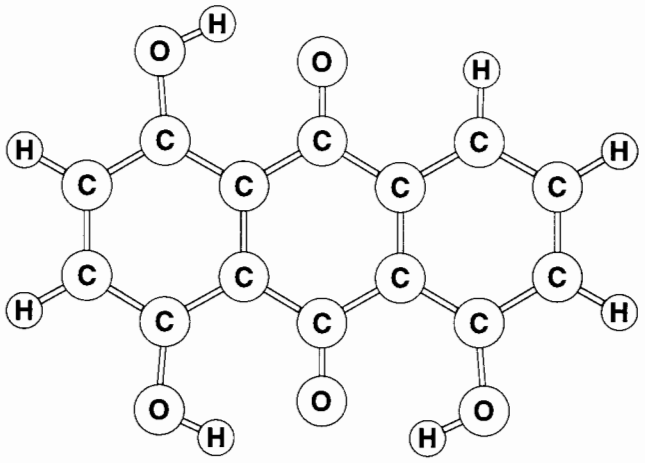
```
C
N 1 r1
C 1 r2 2 a2
N 1 r3 2 a3 3 d3
C 2 r4 1 a4 3 d4
C 1 r5 2 a5 3 d5
C 2 r6 1 a6 6 d6
S 1 r7 2 a7 6 d7
H 1 r8 2 a8 3 d8
O 3 r9 1 a9 2 d9
H 4 rA 3 aA 1 dA
O 5 rB 2 aB 1 dB
H 6 rC 1 aC 2 dC
H 6 rD 1 aD 2 dD
H 7 rE 2 aE 1 dE
H 7 rF 2 aF 1 dF
```

```
r1=1.4763/r2=1.5142/r3=2.3316
r4=1.3397/r5=1.5277/r6=1.4667
r7=2.6282/r8=1.0872/r9=1.2263
rA=1.0141/rB=1.2516/rC=1.0851
rD=1.0841/rE=1.0843/rF=1.0835
a2= 99.1882/a3= 64.9195/a4=112.8177
a5=101.7456/a6=122.6016/a7= 69.6216
a8=110.1242/a9=127.3698/aA=124.2840
aB=126.5097/aC=110.4262/aD=111.8364
aE=110.9696/aF=111.1680/d3=-6.3596
d4=5.3108/d5=122.7439/d6=-34.1633
d7=29.1542/d8=-115.5422/d9=173.4622
dA=-179.3990/dB=-179.3990/dC=-75.3678
dD=163.4138/dE=123.1421/dF=-113.1194
```

Figure 1. (*Continued*)

required for the optimizations for any of the coordinate systems. Bicyclo [2.2.2] octane can twist about the C_3 axis and this may account for the greater number of steps taken by the cartesian based optimization. For the hydroxybicyclopentanes, optimization of the rotation of the hydroxyl groups may be more difficult in cartesian coordinates. Rigid planar molecules such as fluorofuran and trihydroxyanthroqui-

1,4,5 trihydroxy anthroquinone



Starting geometry & internal coordinate set (a)

```
C
C  1 r1
C  1 r2   2 a2
C  3 r3   1 a3   2 180.
C  4 r4   3 a4   1 180.
C  2 r5   1 a5   3   0.
C  6 r6   2 a6   1 180.
C  7 r7   6 a7   2 180.
C  1 r8   2 a8   3 180.
C  9 r9   1 a9   3 180.
C 10 r10  9 a10  1 180.
C  2 r11  1 a11  3 180.
C 12 r12  2 a12  1 180.
C 13 r13 12 a13  2 180.
O  1 r14  3 r14  2 180.
O  4 r15  3 a15  1   0.
H 16 r16  4 a16  3   0.
H  5 r17  4 a17  3 180.
H  8 r18  7 a18  6 180.
O  7 r19  6 a19  2   0.
H 20 r20  7 a20  6   0.
O  2 r21  6 a21  7   0.
O 13 r22 12 a22  2   0.
H 23 r23 13 a23 12   0.
H 14 r24 13 a24 12 180.
H 11 r25 10 a25  9 180.
H 10 r26  9 a26  1   0.
```

r1=2.8128/r2=1.4007/r3=1.4025/r4=1.3934
r5=1.4009/r6=1.4025/r7=1.3934/r8=1.3998
r9=1.3986/r10=1.3926/r11=1.3999/r12=1.4025
r13=1.3945/r14=1.2122/r15=1.3656/r16=0.9757
r17=1.0735/r18=1.0735/r19=1.3653/r20=0.9747
r21=1.2141/r22=1.3652/r23=0.9750/r24=1.0734
r25=1.0737/r26=1.0735/a2= 59.7891
a3=119.9130/a4=119.8322/a5= 59.7502
a6=119.9728/a7=119.8749/a8= 59.4339
a9=119.4018/a10=120.5069/a11= 59.9316
a12=120.5476/a13=119.9462/a14=120.1535
a15=123.2100/a16=112.4815/a17=119.9896
a18=119.9769/a19=123.2140/a20=112.5473
a21=120.3804/a22=123.0024/a23=112.3739
a24=119.9078/a25=120.2592/a26=121.6324

Number of optimization steps

internal coordinates (a)	10
cartesian coordinates	11
mixed coordinates	17

Figure 1. (*Continued*)

none optimize readily in all three coordinate systems since there are no flexible rings or internal rotors to cause problems. For trihydroxyanthroquinone, Baker and Hehre were unable to achieve convergence with internal coordinates, but the present choice of internal coordinates performed as well as cartesian coordinates. ACTHCP and protonated histamine were the most troublesome molecules in the present study. Both contain a very flexible five-membered ring that changes conformation during the course of the optimization. Baker and Hehre found a minimum for ACTHCP only with cartesian coordinates (90 cycles) [8]. In the present study, internal and mixed coordinates both converged in somewhat fewer cycles (65 and 72, respectively). Internal and mixed coordinates behaved similarly for histamine H^+; cartesian coordinate-based optimization had difficulties adjusting the flexible hydrogen-bonded side chain and did not converge with 100 cycles.

With the reduction in computational cost and the improvements in *ab initio* MO calculations over the last decade, it is possible to contemplate optimizing the ge-

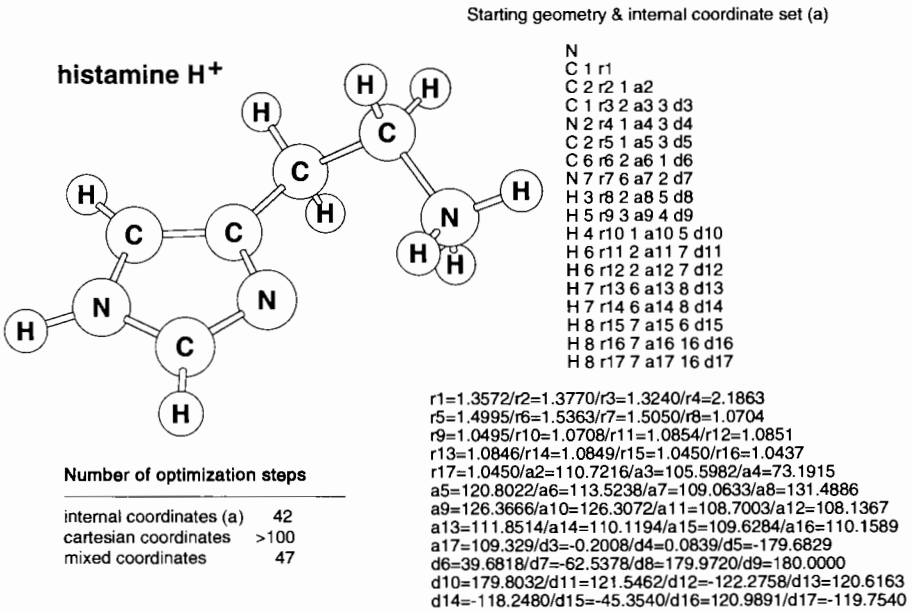


Figure 1. (*Continued*)

ometry for each point on a potential surface scan. Such a relaxed surface scan requires one or more coordinates to be constrained (i.e., the coordinate(s) defining the surface) while the remaining coordinates are minimized. Internal coordinates such as bond lengths and dihedral angles are often the most convenient and meaningful for surface scans. However, constraints on internal coordinates are more complicated to impose when the optimization is carried out in cartesian coordinates [9–11]. With mixed internal and cartesian coordinates, the surface coordinates can be expressed in terms of internals, whereas cartesian coordinates can be used for rings. Figure 2 shows an example of a relaxed scan for protonated histamine as a function of the two dihedral angles of the side chain. The five-membered ring is defined in terms of cartesian coordinates; internal coordinates are used for all of the substituents. The dihedral angles were stepped in 60° increments and the relaxed energies were fitted to a double fourier expansion. The surface shows a deep diagonal valley where the RNH_3^+ group forms a strong hydrogen bond to the imidazole nitrogen. The narrow, diagonal nature of the valley indicates strong coupling between the 2 dihedral angles. Provided both angles change in a concerted manner, the ring formed by the hydrogen-bonded side chain can flex above and below the plane of the imidazole without significant change in energy. This deep, narrow valley with a flat bottom probably is the reason for the slow convergence in the geometry optimization of this molecule (Table I).

Conclusions

Coordinate systems with a mixture of internal and cartesian coordinates are useful alternatives to pure cartesians or pure internals for geometry optimization

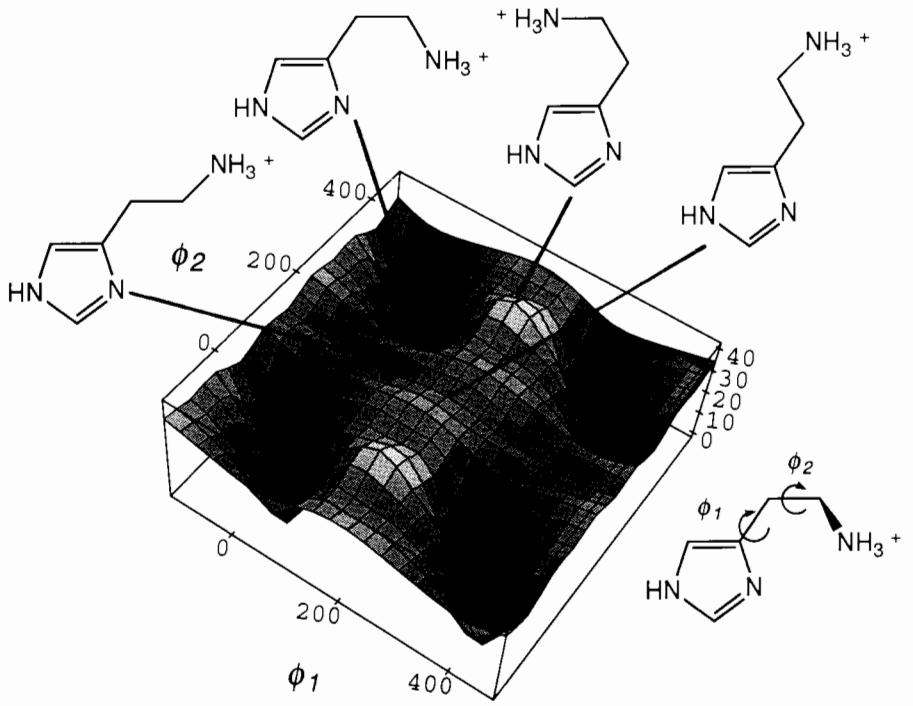


Figure 2. Potential energy surface scan for protonated histamine. The dihedral angles ϕ_1 and ϕ_2 were stepped in 60° intervals and all of the remaining degrees of freedom were optimized using mixed internal/cartesian coordinates.

and have been incorporated in GAUSSIAN 92. Rings can be represented more easily in cartesian coordinates; side chains can be readily described by internal coordinates. The performance of mixed coordinate optimizations is generally intermediate between cartesian and well-chosen internal coordinate systems. Well-chosen internal coordinates and mixed coordinates may require a bit more work to set up but generally performed as well as or better than cartesian coordinates for the examples considered in this study. Internal and mixed coordinates also have some advantages for relaxed potential surface scans.

Acknowledgments

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