Supplementary Material for Faraday Discussions

The Application of No Barrier Theory to the Aldol Addition Reaction

J. Peter Guthrie*, Alexander R. Bannister, and Sriyawathie Peiris

Department of Chemistry, University of Western Ontario,
London, Ontario, Canada N6A 5B7

Supporting Information.

1. Structures of the reactants and products in Z-matrix format.

2. Distortion energies for all reactions.

1. Structures of the reactants and products in Z-matrix format.

a. enolates

acetaldehyde enolate

```
%chk=/scratch/pguthrie/enolal
%rwf=/scratch/pguthrie/enolal
%nosave
#T pm6 POpt Test

enolal

 -1   1
C
H       1 R2
H     1 R3     2 A3
C     1 R4     2 A4     3 D4
O     4 R5     1 A5     2 D5
H     4 R6     1 A6     2 D6
Variables:
R2    =    1.06215
R3    =    1.05827
A3    =  115.00397
R4    =    1.36955
A4    =  121.73643
D4    = -180.00002
R5    =    1.26513
A5    =  127.98124
D5    =    0.00000
R6    =    1.11057
A6    =  117.44091
D6    = -180.00002
```

acetone enolate

```
%chk=/scratch/pguthrie/enolao
%rwf=/scratch/pguthrie/enolao
%nosave
#T pm6 POpt Test

acetoneenolate

 -1 1
C
```

```
C      1 R2
C      2 R3     1 A3
O      2 R4     1 A4     3 D4
H      1 R5     2 A5     3 D5
H      1 R6     2 A6     3 D6
H      3 R7     2 A7     1 D7
H      3 R8     2 A8     1 D8
H      3 R9     2 A9     1 D9
Variables:
R2    =    1.36874
R3    =    1.55221
A3    =  117.92410
R4    =    1.25737
A4    =  127.93846
D4    =  180.00002
R5    =    1.05709
A5    =  123.93339
D5    =    0.00000
R6    =    1.06166
A6    =  120.94179
D6    = -180.00002
R7    =    1.08544
A7    =  112.08395
D7    =   -0.02798
R8    =    1.08869
A8    =  108.58824
D8    =  121.15556
R9    =    1.08868
A9    =  108.58446
D9    = -121.20984

acetophenone enolate

%chk=/scratch/pguthrie/enolap
 %rwf=/scratch/pguthrie/enolap
 %nosave
 #P PM6 POpt Test

 enolap.mop

  -1   1
 C
 C      1 R2
 C      2 R3     1 A3
 C      3 R4     2 A4     1 D4
 C      3 R5     2 A5     1 D5
```

C 5 R6 3 A6 2 D6
C 6 R7 5 A7 3 D7
C 4 R8 3 A8 2 D8
H 4 R9 3 A9 2 D9
H 5 R10 3 A10 2 D10
H 6 R11 5 A11 3 D11
H 7 R12 6 A12 5 D12
H 8 R13 4 A13 3 D13
O 2 R14 1 A14 3 D14
H 1 R15 2 A15 3 D15
H 1 R16 2 A16 3 D16

Variables:

R2 = 1.365
R3 = 1.540
A3 = 116.271
R4 = 1.402
A4 = 119.674
D4 = 127.852
R5 = 1.401
A5 = 121.090
D5 = -52.904
R6 = 1.398
A6 = 120.395
D6 = -179.736
R7 = 1.399
A7 = 120.141
D7 = -0.031
R8 = 1.397
A8 = 120.452
D8 = 179.968
R9 = 1.089
A9 = 118.537
D9 = 0.970
R10 = 1.088
A10 = 119.014
D10 = 0.398
R11 = 1.085
A11 = 119.906
D11 = 179.977
R12 = 1.083
A12 = 120.192
D12 = -179.873
R13 = 1.085
A13 = 119.967
D13 = 179.895
R14 = 1.254

A14 = 129.369
D14 = 179.180
R15 = 1.060
A15 = 123.984
D15 = -0.321
R16 = 1.064
A16 = 120.849
D16 = -179.432

b. carbonyl compounds

formaldehyde

%chk=/scratch/pguthrie/form
%rwf=/scratch/pguthrie/form
%nosave
#P PM6 POpt Test

form.mop

0 1
O
C 1 R2
H 2 R3 1 A3
H 2 R4 1 A4 3 D4
Variables:
R2 = 1.211
R3 = 1.097
A3 = 122.017
R4 = 1.097
A4 = 122.008
D4 = -180.000

acetaldehyde

%chk=/scratch/pguthrie/al
%rwf=/scratch/pguthrie/al
%nosave
#P PM6 POpt Test

al.mop

0 1
C
C 1 R2
O 2 R3 1 A3

```
H     1 R4    2 A4    3 D4
H     1 R5    2 A5    3 D5
H     1 R6    2 A6    3 D6
H     2 R7    1 A7    4 D7
Variables:
R2    =     1.500
R3    =     1.210
A3    =   122.739
R4    =     1.101
A4    =   111.744
D4    =     0.073
R5    =     1.098
A5    =   111.648
D5    =  -119.913
R6    =     1.098
A6    =   111.641
D6    =   120.053
R7    =     1.102
A7    =   115.482
D7    =  -179.924
```

benzaldehyde

```
%chk=/scratch/pguthrie/bl
%rwf=/scratch/pguthrie/bl
%nosave
#T pm6 POpt Test

bl

 0  1
C
C     1 R2
C     2 R3    1 A3
C     3 R4    2 A4    1 D4
C     4 R5    3 A5    2 D5
C     1 R6    2 A6    3 D6
C     3 R7    2 A7    1 D7
H     7 R8    3 A8    2 D8
H     1 R9    2 A9    3 D9
H     2 R10   1 A10   6 D10
H     4 R11   3 A11   2 D11
H     5 R12   4 A12   3 D12
H     6 R13   1 A13   2 D13
O     7 R14   3 A14   2 D14
Variables:
```

R2 = 1.39743
R3 = 1.40260
A3 = 120.04217
R4 = 1.40339
A4 = 119.93675
D4 = 0.00000
R5 = 1.39609
A5 = 119.89762
D5 = 0.00000
R6 = 1.39807
A6 = 119.88757
D6 = 0.00000
R7 = 1.48916
A7 = 119.77193
D7 = 180.00002
R8 = 1.10267
A8 = 115.90584
D8 = 180.00002
R9 = 1.08903
A9 = 119.97026
D9 = -180.00002
R10 = 1.09403
A10 = 120.84109
D10 = -180.00002
R11 = 1.08990
A11 = 120.26821
D11 = -180.00002
R12 = 1.08879
A12 = 120.06918
D12 = -180.00002
R13 = 1.09003
A13 = 119.96366
D13 = -180.00002
R14 = 1.21302
A14 = 122.74567
D14 = 0.00000

acetone

%chk=/scratch/pguthrie/ao
%rwf=/scratch/pguthrie/ao
%nosave
#T pm6 POpt Test

ao

```
 0  1
C
C     1 R2
C     2 R3    1 A3
O     2 R4    1 A4    3 D4
H     1 R5    2 A5    3 D5
H     1 R6    2 A6    3 D6
H     1 R7    2 A7    3 D7
H     3 R8    2 A8    1 D8
H     3 R9    2 A9    1 D9
H     3 R10   2 A10   1 D10
Variables:
R2    =    1.50371
R3    =    1.50341
A3    =  115.80209
R4    =    1.20959
A4    =  122.04448
D4    = -180.00002
R5    =    1.10031
A5    =  111.23029
D5    = -180.00002
R6    =    1.09705
A6    =  111.79154
D6    =   60.12611
R7    =    1.09707
A7    =  111.79822
D7    =  -60.10917
R8    =    1.10037
A8    =  111.25677
D8    =  180.00002
R9    =    1.09714
A9    =  111.78433
D9    =  -60.12138
R10   =    1.09715
A10   =  111.79194
D10   =   60.09335

acetophenone

%chk=/scratch/pguthrie/ap
 %rwf=/scratch/pguthrie/ap
 %nosave
 #P PM6 POpt Test

 ap.mop
```

```
 0  1
C
O      1 R2
C      1 R3     2 A3
H      3 R4     1 A4     2 D4
H      3 R5     1 A5     2 D5
H      3 R6     1 A6     2 D6
C      1 R7     2 A7     3 D7
C      7 R8     1 A8     2 D8
C      8 R9     7 A9     1 D9
C      9 R10    8 A10    7 D10
C     10 R11    9 A11    8 D11
C      7 R12    1 A12    2 D12
H      8 R13    7 A13    1 D13
H      9 R14    8 A14    7 D14
H     10 R15    9 A15    8 D15
H     11 R16   10 A16    9 D16
H     12 R17    7 A17    1 D17
Variables:
R2    =     1.214
R3    =     1.502
A3    =   120.941
R4    =     1.097
A4    =   111.998
D4    =  -119.389
R5    =     1.097
A5    =   111.973
D5    =   119.128
R6    =     1.102
A6    =   110.450
D6    =    -0.116
R7    =     1.497
A7    =   120.963
D7    =  -179.995
R8    =     1.405
A8    =   117.682
D8    =     0.122
R9    =     1.396
A9    =   120.339
D9    =  -179.984
R10   =     1.398
A10   =   119.869
D10   =     0.009
R11   =     1.399
A11   =   120.056
D11   =    -0.009
```

R12 = 1.402
A12 = 122.806
D12 = -179.848
R13 = 1.095
A13 = 119.046
D13 = 0.025
R14 = 1.089
A14 = 120.003
D14 = -179.993
R15 = 1.090
A15 = 119.980
D15 = 179.988
R16 = 1.089
A16 = 119.955
D16 = 179.998
R17 = 1.090
A17 = 120.592
D17 = -0.033

trifluoroacetophenone

%chk=/scratch/pguthrie/tfap
%rwf=/scratch/pguthrie/tfap
%nosave
#P PM6 POpt Test

tfap.mop

0 1
C
O 1 R2
C 1 R3 2 A3
F 3 R4 1 A4 2 D4
F 3 R5 1 A5 2 D5
F 3 R6 1 A6 2 D6
C 1 R7 2 A7 3 D7
C 7 R8 1 A8 2 D8
C 8 R9 7 A9 1 D9
C 9 R10 8 A10 7 D10
C 10 R11 9 A11 8 D11
C 7 R12 1 A12 2 D12
H 8 R13 7 A13 1 D13
H 9 R14 8 A14 7 D14
H 10 R15 9 A15 8 D15
H 11 R16 10 A16 9 D16
H 12 R17 7 A17 1 D17

Variables:

R2	=	1.204
R3	=	1.568
A3	=	115.832
R4	=	1.340
A4	=	114.941
D4	=	-119.111
R5	=	1.340
A5	=	114.914
D5	=	118.870
R6	=	1.337
A6	=	111.872
D6	=	-0.103
R7	=	1.476
A7	=	125.146
D7	=	179.979
R8	=	1.411
A8	=	116.127
D8	=	0.062
R9	=	1.394
A9	=	120.383
D9	=	-179.951
R10	=	1.400
A10	=	119.860
D10	=	-0.005
R11	=	1.398
A11	=	120.039
D11	=	-0.014
R12	=	1.403
A12	=	124.414
D12	=	-179.897
R13	=	1.095
A13	=	119.253
D13	=	0.044
R14	=	1.090
A14	=	120.037
D14	=	179.999
R15	=	1.091
A15	=	119.971
D15	=	179.994
R16	=	1.090
A16	=	119.947
D16	=	179.999
R17	=	1.090
A17	=	121.784
D17	=	-0.048

2. Distortion energies for all reactions.

For the aldol additions studied there is no energy difference between reactive conformation and equilibrium conformation for the enolate, but there generally is for the product. This energy difference was calculated as described in the text.

Distortions for addition of acetone enolate to six carbonyl compounds.

Corner	formaldehyde	acetaldehyde	benzaldehyde	acetone	acetophenone	trifluoroacetophenone
000	0.000	0.000	0.000	0.000	0.000	0.000
100	49.461	61.105	53.203	82.057	84.467	101.709
010	28.197	29.882	26.928	34.430	34.625	33.505
001	6.07	6.08	6.26	6.37	6.68	7.14
110	22.209	22.014	10.815	23.899	22.219	30.026
101	29.816	36.757	27.473	41.340	35.645	44.942
011	34.27	35.96	33.19	40.80	41.31	40.65
111	1.542	1.565	8.485	2.750	5.479	7.042

Distortions for addition of acetone enolate to six carbonyl compounds.

Corner	formaldehyde	acetaldehyde	benzaldehyde	acetone	acetophenone	trifluoroacetophenone
000	0.000	0.000	0.000	0.000	0.000	0.000
100	67.151	62.365	57.939	87.945	84.288	106.869
010	28.567	28.625	27.541	32.696	32.268	31.462
001	6.53	6.40	6.58	6.20	7.74	7.19
110	20.953	24.088	24.924	25.047	23.659	31.572
101	28.956	30.440	27.734	48.121	39.404	56.523
011	35.1	35.03	34.12	38.90	40.01	38.65
111	1.903	7.869	8.797	2.203	5.204	5.751

Distortions for addition of acetophenone enolate to six carbonyl compounds.

Corner	formaldehyde	acetaldehyde	benzaldehyde	acetone	acetophenone	trifluoroacetophenone
000	0.000	0.000	0.000	0.000	0.000	0.000
100	55.388	65.618	55.926	85.600	03.256	104.409
010	27.754	29.281	28.175	33.029	29.448	31.372
001	7.76	7.66	6.07	7.58	5.42	6.40
110	26.236	25.989	23.796	27.962	24.294	32.706
101	37.231	39.441	21.405	52.897	33.053	54.893
011	35.51	36.94	34.25	40.61	34.87	37.77
111	0.000	0.737	10.401	1.168	1.310	1.911