SUPPORTING INFORMATION

Reversible Formation of Organyl(oxo)boranes RBO (R = C_6H_5, CH_3) from Boroxins $(RBO)_3$: A Matrix Isolation Study

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Pyrolysis of trimethylboroxin with trapping in Xe

and subsequent 10 Hz laser irradiation

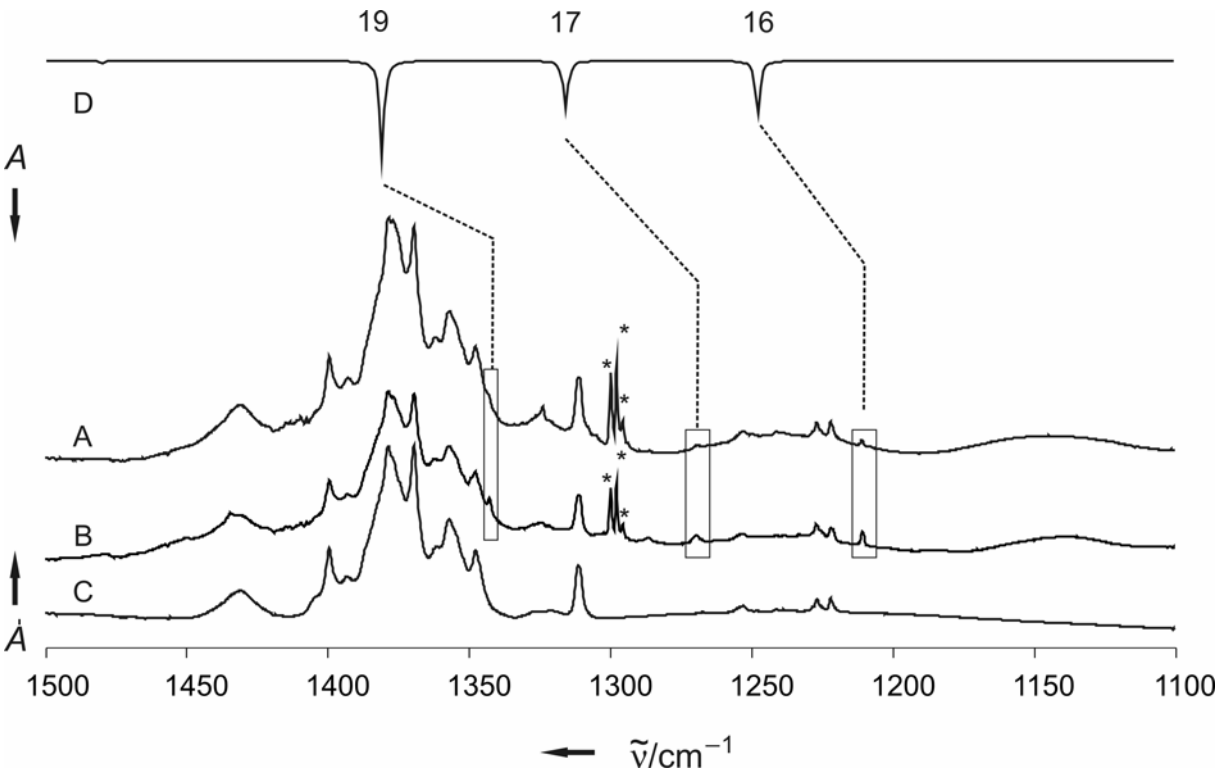

Figure S1. IR spectra of the pyrolysate of trimethylboroxin (**3b**) trapped in xenon. (A) 0.2% **3b** in Xe, FVP at 725 °C, trapping temperature 30K; (B) After 248 nm irradition (10 min, 10 Hz); (C) **3b** in Xe (0.2%, 30 K) for comparison; (D) Theoretical spectrum computed at the MP2/cc-pVTZ level for **7b**. The group of signals labeled with an asterisk in A and B is due to **1b** and **6b**.

Cartesian Coordinates (in Angstrom), absolute energies (in a.u.), and zero-point vibrational energies (in kcal mol^{-1}) of stationary points:

1. Phenyl(oxo)borane, **1a**

```
  13
MP2/cc-pVTZ
C     0.000000    1.207283   -1.537260
C     0.000000    1.210678   -0.145834
C     0.000000    0.000000    0.562551
C     0.000000   -1.210678   -0.145834
C     0.000000   -1.207283   -1.537260
C     0.000000    0.000000   -2.233305
H     0.000000    2.143908   -2.077210
H     0.000000    2.150087    0.390403
H     0.000000   -2.150087    0.390403
H     0.000000   -2.143908   -2.077210
H     0.000000    0.000000   -3.314653
B     0.000000    0.000000    2.089011
O     0.000000    0.000000    3.308109

EUMP2 =     -331.10029; ZPE = 61.5
```

2. Methyl(oxo)borane, **1b**

```
   6
MP2/aug-cc-pVTZ
C     0.000000    0.000000    1.300586
B     0.000000    0.000000   -0.237333
O     0.000000    0.000000   -1.456844
H     0.000000    1.020036    1.679265
H    -0.883377   -0.510018    1.679265
H     0.883377   -0.510018    1.679265

EUMP2 =    -139.78891; ZPE(cc-pVTZ) = 27.4
```

3. 1:1 Dimer complex, **6b**

```
  12
MP2/aug-cc-pVTZ
B     0.143235    1.586264    0.000000
O     1.270204    1.112133    0.000000
C    -1.270204    2.181797    0.000000
H    -1.986547    1.361951    0.000000
H    -1.428137    2.796190    0.884097
H    -1.428137    2.796190   -0.884097
O    -1.270204   -1.112133    0.000000
B    -0.143235   -1.586264    0.000000
C     1.270204   -2.181797    0.000000
H     1.986547   -1.361951    0.000000
H     1.428137   -2.796190    0.884097
H     1.428137   -2.796190   -0.884097
```

EUMP2 = -279.58825; ZPE(cc-pVTZ) = 55.3

4. 1,3-Dimethyl-1,3-dioxa-2,4-boretane, **7b**

```
  12
MP2/aug-cc-pVTZ
B     0.000000    0.914793    0.000000
O     0.000000    0.000000    1.080143
O     0.000000    0.000000   -1.080143
B     0.000000   -0.914793    0.000000
C    -0.026606    2.464517    0.000000
H    -1.066950    2.797713    0.000000
H     0.446378    2.872936    0.890452
H     0.446378    2.872936   -0.890452
C     0.026606   -2.464517    0.000000
H    -0.446378   -2.872936   -0.890452
H     1.066950   -2.797713    0.000000
H    -0.446378   -2.872936    0.890452
```

EUMP2 = -279.63906; ZPE(cc-pVTZ) = 56.9

5. Complex **8b**

```
  18
MP2/aug-cc-pVTZ
B    -0.903089    1.001155   -0.276458
O    -1.870686    0.364682    0.534008
O    -0.372699   -0.144531   -0.936948
B    -1.310626   -0.773146   -0.079618
C    -0.528356    2.497179   -0.399828
H    -1.410911    3.132203   -0.343747
H     0.113474    2.747582    0.447480
H     0.018044    2.710532   -1.315774
C    -1.588055   -2.280585    0.156546
H    -1.320344   -2.884598   -0.707681
H    -0.981574   -2.616310    1.001278
H    -2.629168   -2.456960    0.419671
B     2.070811   -0.098235    0.486061
C     2.739570   -0.890491   -0.646033
H     2.516580   -0.417222   -1.599879
H     3.817843   -0.935858   -0.507648
H     2.343730   -1.904054   -0.672343
O     1.556871    0.532248    1.398515
```

EUMP2 = -419.43677; ZPE(cc-pVTZ) = 84.8

6. Trimethylboroxin, **3b**

```
  18
MP2/aug-cc-pVTZ
O     0.000000   -1.378286   -0.022722
O    -1.193631    0.689143   -0.022722
O     1.193631    0.689143   -0.022722
B     1.205458   -0.695971   -0.019979
B     0.000000    1.391943   -0.019979
B    -1.205458   -0.695971   -0.019979
C     0.000000    2.954739    0.018448
```

```
C     2.558879   -1.477370    0.018448
C    -2.558879   -1.477370    0.018448
H     0.000000    3.279462    1.061453
H     2.840097   -1.639731    1.061453
H    -2.840097   -1.639731    1.061453
H     0.889532    3.373575   -0.445235
H     3.366367   -0.916430   -0.445235
H     2.476836   -2.457144   -0.445235
H    -0.889532    3.373575   -0.445235
H    -3.366367   -0.916430   -0.445235
H    -2.476836   -2.457144   -0.445235

EUMP2 = -419.50676; ZPE(cc-pVTZ) = 87.4
```

7. **TS1**

```
  12
MP2/aug-cc-pVTZ
B     0.017449    1.126627    0.000000
O    -1.132193    0.631632    0.000000
C     1.132193    2.185603    0.000000
H     0.710708    3.189135    0.000000
H     1.761056    2.055848    0.878925
H     1.761056    2.055848   -0.878925
O     1.132193   -0.631632    0.000000
B    -0.017449   -1.126627    0.000000
C    -1.132193   -2.185603    0.000000
H    -0.710708   -3.189135    0.000000
H    -1.761056   -2.055848    0.878925
H    -1.761056   -2.055848   -0.878925

EUMP2 = -279.57542; ZPE(cc-pVTZ) = 55.3
```

8. **TS2**

```
  18
MP2/aug-cc-pVTZ
B     0.176260    1.007927    0.047546
O     1.274523    0.704291   -0.820879
O     0.263105   -0.245527    0.842574
B     1.380362   -0.418429    0.000252
C    -0.202370    2.416290    0.605287
H     0.613915    2.791813    1.224636
H    -0.359177    3.123641   -0.207803
H    -1.103087    2.385591    1.216352
C     2.462047   -1.539887    0.021030
H     2.073973   -2.471164    0.429822
H     2.868052   -1.719534   -0.972761
H     3.291365   -1.226277    0.658477
B    -1.727179   -0.487110   -0.354710
C    -2.314622   -1.758159    0.256297
H    -2.379219   -1.638365    1.336112
H    -3.304903   -1.959933   -0.148080
H    -1.661023   -2.602535    0.045369
O    -1.394808    0.553156   -0.939601

EUMP2 = -419.43064; ZPE(cc-pVTZ) = 85.2
```