

**Supporting information for:**

**Establishing the Ground State of the Disjoint**

**Diradical Tetramethyleneethane with Quantum Monte**

**Carlo**

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We include the scaled cc-pV5Z(sp)+2d-CDF basis set in Gaussian format. The basis is the standard cc-pV5Z-CDF basis<sup>S1</sup> for the  $s$  and  $p$  functions of carbon and  $s$  functions of hydrogen. The two  $d$  functions of the cc-pVDZ-CDF are added for carbon and the smaller exponent of the two  $d$  function is scaled by 1.5. For the  $p$  functions of hydrogen, the two cc-pVDZ-CDF  $p$  functions are employed with the smaller exponent scaled by 1.5.

We also include the optimized CASSCF(6,6)/cc-pVTZ geometry of TME in its lowest singlet and triplet states as a function of torsional angle. The absolute energies as a function of basis set and method is presented for each spin state and geometry, as well. Atomic units are employed with Bohr radius ( $a_0$ ) for length in the coordinates and Hartree (Ha) for energy. Each single-point energy is calculated at the presented geometry. All VMC and DMC calculations are performed using a truncated CAS(6,6) trial function.

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Table S1: Scaled cc-pV5Z(sp)+2d-CDF basis set in Gaussian format

Carbon			Hydrogen		
S	10.000000	1.000000	S	8.000000	1.000000
	31.367780	-0.002416		402.000000	0.000022
	19.537840	0.018709		60.240000	-0.000597
	12.191260	-0.078337		13.730000	0.013185
	7.615200	0.201296		3.905000	0.043733
	4.758170	-0.229367		1.283000	0.143398
	1.922630	-0.088946		0.465500	0.329949
	1.195500	0.094083		0.181100	0.437030
	0.510500	0.403249		0.072790	0.176123
	0.218000	0.501580	S	1.000000	1.000000
	0.093100	0.172148		1.283000	1.000000
S	1.000000	1.000000	S	1.000000	1.000000
	1.195500	1.000000		0.465500	1.000000
S	1.000000	1.000000	S	1.000000	1.000000
	0.510500	1.000000		0.181100	1.000000
S	1.000000	1.000000	S	1.000000	1.000000
	0.218000	1.000000		0.072790	1.000000
S	1.000000	1.000000	P	1.000000	1.000000
	0.093100	1.000000		0.736400	1.000000
P	10.000000	1.000000	P	1.000000	1.000000
	23.871530	-0.000983		0.212850	1.000000
	14.921780	0.007129			
	9.324360	-0.031091			
	5.829530	0.062401			
	3.159450	0.055414			
	1.974900	0.028564			
	1.232300	0.203529			
	0.508000	0.369212			
	0.209400	0.366562			
	0.086300	0.168151			
P	1.000000	1.000000			
	1.232300	1.000000			
P	1.000000	1.000000			
	0.508000	1.000000			
P	1.000000	1.000000			
	0.209400	1.000000			
P	1.000000	1.000000			
	0.086300	1.000000			
D	1.000000	1.000000			
	0.558600	1.000000			
D	1.000000	1.000000			
	0.227100	1.000000			

Table S2: Absolute energies for the  $^1A$  state of TME at a  $0^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.66626127
	CASSCF(2,2)	-231.74696848
	CAS(2,2)PT2	-232.56906306
	CASSCF(6,6)	-231.83094313
	CAS(6,6)PT2	-232.56400872
cc-pVTZ	RHF	-231.73401235
	CASSCF(2,2)	-231.80933242
	CAS(2,2)PT2	-232.80583171
	CASSCF(6,6)	-231.89192329
	CAS(6,6)PT2	-232.79962123
cc-pVTZ'	RHF	-231.72489830
	CASSCF(6,6)	-231.88365441
	CAS(6,6)PT2	-232.71462052
cc-pVQZ	RHF	-231.75104501
	CASSCF(2,2)	-231.82418592
	CAS(2,2)PT2	-232.88053094
	CASSCF(6,6)	-231.90638228
	CAS(6,6)PT2	-232.87357165
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64836361
	VMC (3-term Jastrow/CAS(6,6))	-38.611721 $\pm$ 0.000889
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.690705 $\pm$ 0.000041
	DMC ( $\tau = 0.005$ au)	-38.691973 $\pm$ 0.000014
	DMC ( $\tau = 0.0075$ au)	-38.692473 $\pm$ 0.000033
	DMC ( $\tau = 0.01$ au)	-38.693276 $\pm$ 0.000032

Table S3: Geometry of the  $^1A$  state of TME at a  $0^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.410161827
C	0.000000000	0.000000000	1.410161827
C	0.000000000	2.260970430	-2.761770903
C	0.000000000	2.260970430	2.761770903
C	0.000000000	-2.260970430	-2.761770903
C	0.000000000	-2.260970430	2.761770903
H	0.000000000	2.218513341	-4.786963031
H	0.000000000	-2.218513341	-4.786963031
H	0.000000000	-2.218513341	4.786963031
H	0.000000000	2.218513341	4.786963031
H	0.000000000	4.080818902	-1.892343703
H	0.000000000	-4.080818902	-1.892343703
H	0.000000000	-4.080818902	1.892343703
H	0.000000000	4.080818902	1.892343703

Table S4: Absolute energies for the  $^3B_1$  state of TME at a  $0^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.74449544
	CASSCF(2,2)	-231.74449544
	CAS(2,2)PT2	-232.56199483
	CASSCF(6,6)	-231.82494676
	CAS(6,6)PT2	-232.55803745
cc-pVTZ	RHF	-231.80636003
	CASSCF(2,2)	-231.80636003
	CAS(2,2)PT2	-232.79839363
	CASSCF(6,6)	-231.88569986
	CAS(6,6)PT2	-232.79296129
cc-pVQZ	RHF	-231.82104031
	CASSCF(2,2)	-231.82104031
	CAS(2,2)PT2	-232.87295498
	CASSCF(6,6)	-231.90008376
	CAS(6,6)PT2	-232.86668317
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64208457
	VMC (3-term Jastrow/CAS(6,6))	-38.603166 $\pm$ 0.000877
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.684296 $\pm$ 0.000077
	DMC ( $\tau = 0.005$ au)	-38.685692 $\pm$ 0.000035
	DMC ( $\tau = 0.0075$ au)	-38.868650 $\pm$ 0.000034
	DMC ( $\tau = 0.01$ au)	-38.687124 $\pm$ 0.000035

Table S5: Geometry of the  $^3B_1$  state of TME at a  $0^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.424855393
C	0.000000000	0.000000000	1.424855393
C	0.000000000	2.256922880	-2.780737032
C	0.000000000	2.256922880	2.780737032
C	0.000000000	-2.256922880	-2.780737032
C	0.000000000	-2.256922880	2.780737032
H	0.000000000	2.209170773	-4.805523909
H	0.000000000	-2.209170773	-4.805523909
H	0.000000000	-2.209170773	4.805523909
H	0.000000000	2.209170773	4.805523909
H	0.000000000	4.079476490	-1.915130035
H	0.000000000	-4.079476490	-1.915130035
H	0.000000000	-4.079476490	1.915130035
H	0.000000000	4.079476490	1.915130035

Table S6: Absolute energies for the  $^1A$  state of TME at a  $10^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.66557903
	CASSCF(2,2)	-231.74733985
	CAS(2,2)PT2	-232.56952696
	CASSCF(6,6)	-231.83121736
	CAS(6,6)PT2	-232.56432639
cc-pVTZ	RHF	-231.73305866
	CASSCF(2,2)	-231.80959899
	CAS(2,2)PT2	-232.80617873
	CASSCF(6,6)	-231.89214279
	CAS(6,6)PT2	-232.79977422
cc-pVQZ	RHF	-231.74996440
	CASSCF(2,2)	-231.82441541
	CAS(2,2)PT2	-232.88083260
	CASSCF(6,6)	-231.90658503
	CAS(6,6)PT2	-232.87366828

Table S7: Geometry of the  $^1A$  state of TME at a  $10^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.410148599
C	0.000000000	0.000000000	1.410148599
C	0.197296111	2.255104866	-2.756812895
C	-0.197296111	2.255104866	2.756812895
C	-0.197296111	-2.255104866	-2.756812895
C	0.197296111	-2.255104866	2.756812895
H	0.195942726	2.220267912	-4.782193452
H	-0.195942726	-2.220267912	-4.782193452
H	0.195942726	-2.220267912	4.782193452
H	-0.195942726	2.220267912	4.782193452
H	0.423309545	4.056550064	-1.876370778
H	-0.423309545	-4.056550064	-1.876370778
H	0.423309545	-4.056550064	1.876370778
H	-0.423309545	4.056550064	1.876370778

Table S8: Absolute energies for the  $^3B_1$  state of TME at a  $10^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.74531587
	CASSCF(2,2)	-231.74531587
	CAS(2,2)PT2	-232.56296039
	CASSCF(6,6)	-231.82566293
	CAS(6,6)PT2	-232.55890476
cc-pVTZ	RHF	-231.80715766
	CASSCF(2,2)	-231.80715766
	CAS(2,2)PT2	-232.79931156
	CASSCF(6,6)	-231.88641180
	CAS(6,6)PT2	-232.79377105
cc-pVQZ	RHF	-231.82183132
	CASSCF(2,2)	-231.82183133
	CAS(2,2)PT2	-232.87385546
	CASSCF(6,6)	-231.90079550
	CAS(6,6)PT2	-232.86747960

Table S9: Geometry of the  $^3B_1$  state of TME at a  $10^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.423769745
C	0.000000000	0.000000000	1.423769745
C	0.197017482	2.251920119	-2.772809060
C	-0.197017482	2.251920119	2.772809060
C	-0.197017482	-2.251920119	-2.772809060
C	0.197017482	-2.251920119	2.772809060
H	0.172136712	2.216126761	-4.797803193
H	-0.172136712	-2.216126761	-4.797803193
H	0.172136712	-2.216126761	4.797803193
H	-0.172136712	2.216126761	4.797803193
H	0.449610288	4.052208767	-1.895441946
H	-0.449610288	-4.052208767	-1.895441946
H	0.449610288	-4.052208767	1.895441946
H	-0.449610288	4.052208767	1.895441946

Table S10: Absolute energies for the  $^1A$  state of TME at a  $20^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.66288763
	CASSCF(2,2)	-231.74820584
	CAS(2,2)PT2	-232.57030206
	CASSCF(6,6)	-231.83173373
	CAS(6,6)PT2	-232.56482576
cc-pVTZ	RHF	-231.72973215
	CASSCF(2,2)	-231.81024498
	CAS(2,2)PT2	-232.80668500
	CASSCF(6,6)	-231.89254649
	CAS(6,6)PT2	-232.79990774
cc-pVQZ	RHF	-231.74636092
	CASSCF(2,2)	-231.82499196
	CAS(2,2)PT2	-232.88124903
	CASSCF(6,6)	-231.90695947
	CAS(6,6)PT2	-232.87369047

Table S11: Geometry of the  $^1A$  state of TME at a  $20^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.410470798
C	0.000000000	0.000000000	1.410470798
C	0.394081205	2.234945572	-2.746196406
C	-0.394081205	2.234945572	2.746196406
C	-0.394081205	-2.234945572	-2.746196406
C	0.394081205	-2.234945572	2.746196406
H	0.393128895	2.217198904	-4.771944545
H	-0.393128895	-2.217198904	-4.771944545
H	0.393128895	-2.217198904	4.771944545
H	-0.393128895	2.217198904	4.771944545
H	0.794061984	3.995754713	-1.841696822
H	-0.794061984	-3.995754713	-1.841696822
H	0.794061984	-3.995754713	1.841696822
H	-0.794061984	3.995754713	1.841696822

Table S12: Absolute energies for the  $^3B_1$  state of TME at a  $20^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.74721171
	CASSCF(2,2)	-231.74721171
	CAS(2,2)PT2	-232.56494102
	CASSCF(6,6)	-231.82725417
	CAS(6,6)PT2	-232.56070568
cc-pVTZ	RHF	-231.80901595
	CASSCF(2,2)	-231.80901595
	CAS(2,2)PT2	-232.80119045
	CASSCF(6,6)	-231.88799922
	CAS(6,6)PT2	-232.79545888
cc-pVQZ	RHF	-231.82368448
	CASSCF(2,2)	-231.82368448
	CAS(2,2)PT2	-232.87570717
	CASSCF(6,6)	-231.90238727
	CAS(6,6)PT2	-232.86914973



Table S13: Geometry of the  $^3B_1$  state of TME at a  $20^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.421979230
C	0.000000000	0.000000000	1.421979230
C	0.393854313	2.233658807	-2.755923303
C	-0.393854313	2.233658807	2.755923303
C	-0.393854313	-2.233658807	-2.755923303
C	0.393854313	-2.233658807	2.755923303
H	0.363983591	2.221910950	-4.781423281
H	-0.363983591	-2.221910950	-4.781423281
H	0.363983591	-2.221910950	4.781423281
H	-0.363983591	2.221910950	4.781423281
H	0.833537930	3.985770459	-1.851552931
H	-0.833537930	-3.985770459	-1.851552931
H	0.833537930	-3.985770459	1.851552931
H	-0.833537930	3.985770459	1.851552931

Table S14: Absolute energies for the  $^1A$  state of TME at a  $30^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.65751544
	CASSCF(2,2)	-231.74919038
	CAS(2,2)PT2	-232.57079239
	CASSCF(6,6)	-231.83214935
	CAS(6,6)PT2	-232.56515495
cc-pVTZ	RHF	-231.72358325
	CASSCF(2,2)	-231.81100325
	CAS(2,2)PT2	-232.80684072
	CASSCF(6,6)	-231.89283528
	CAS(6,6)PT2	-232.79981191
cc-pVQZ	RHF	-231.73993683
	CASSCF(2,2)	-231.82569526
	CAS(2,2)PT2	-232.88133420
	CASSCF(6,6)	-231.90722614
	CAS(6,6)PT2	-232.87350419

Table S15: Geometry of the  $^1A$  state of TME at a  $30^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.411526210
C	0.000000000	0.000000000	1.411526210
C	0.589194052	2.198902139	-2.733327602
C	-0.589194052	2.198902139	2.733327602
C	-0.589194052	-2.198902139	-2.733327602
C	0.589194052	-2.198902139	2.733327602
H	0.586421317	2.203308088	-4.759352991
H	-0.586421317	-2.203308088	-4.759352991
H	0.586421317	-2.203308088	4.759352991
H	-0.586421317	2.203308088	4.759352991
H	1.135668610	3.907311020	-1.801363122
H	-1.135668610	-3.907311020	-1.801363122
H	1.135668610	-3.907311020	1.801363122
H	-1.135668610	3.907311020	1.801363122

Table S16: Absolute energies for the  $^3B_1$  state of TME at a  $30^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.74919250
	CASSCF(2,2)	-231.74919250
	CAS(2,2)PT2	-232.56676134
	CASSCF(6,6)	-231.82885550
	CAS(6,6)PT2	-232.56239079
cc-pVTZ	RHF	-231.81095857
	CASSCF(2,2)	-231.81095857
	CAS(2,2)PT2	-232.80288013
	CASSCF(6,6)	-231.88958564
	CAS(6,6)PT2	-232.79700971
cc-pVQZ	RHF	-231.82563145
	CASSCF(2,2)	-231.82563145
	CAS(2,2)PT2	-232.87739196
	CASSCF(6,6)	-231.90398210
	CAS(6,6)PT2	-232.87070286

Table S17: Geometry of the  $^3B_1$  state of TME at a  $30^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.420294539
C	0.000000000	0.000000000	1.420294539
C	0.589097637	2.198542311	-2.737474509
C	-0.589097637	2.198542311	2.737474509
C	-0.589097637	-2.198542311	-2.737474509
C	0.589097637	-2.198542311	2.737474509
H	0.566211384	2.211910390	-4.763412589
H	-0.566211384	-2.211910390	-4.763412589
H	0.566211384	-2.211910390	4.763412589
H	-0.566211384	2.211910390	4.763412589
H	1.166316045	3.895863247	-1.803070566
H	-1.166316045	-3.895863247	-1.803070566
H	1.166316045	-3.895863247	1.803070566
H	-1.166316045	3.895863247	1.803070566

Table S18: Absolute energies for the  $^1A$  state of TME at a  $40^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.64957346
	CASSCF(2,2)	-231.75019369
	CAS(2,2)PT2	-232.57080852
	CASSCF(6,6)	-231.83237850
	CAS(6,6)PT2	-232.56533409
cc-pVTZ	RHF	-231.71484805
	CASSCF(2,2)	-231.81186558
	CAS(2,2)PT2	-232.80656566
	CASSCF(6,6)	-231.89297064
	CAS(6,6)PT2	-232.79965658
cc-pVQZ	RHF	-231.73096346
	CASSCF(2,2)	-231.82653960
	CAS(2,2)PT2	-232.88102872
	CASSCF(6,6)	-231.90735641
	CAS(6,6)PT2	-232.87331159
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64911672
	VMC (3-term Jastrow/CAS(6,6))	-38.612569 $\pm$ 0.00078
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.690693 $\pm$ 0.000073
	DMC ( $\tau = 0.005$ au)	-38.691789 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.692128 $\pm$ 0.000033
	DMC ( $\tau = 0.01$ au)	-38.692814 $\pm$ 0.000032

Table S19: Geometry of the  $^1A$  state of TME at a  $40^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.412858466
C	0.000000000	0.000000000	1.412858466
C	0.780917939	2.145554403	-2.719906754
C	-0.780917939	2.145554403	2.719906754
C	-0.780917939	-2.145554403	-2.719906754
C	0.780917939	-2.145554403	2.719906754
H	0.775318076	2.174009885	-4.746120577
H	-0.775318076	-2.174009885	-4.746120577
H	0.775318076	-2.174009885	4.746120577
H	-0.775318076	2.174009885	4.746120577
H	1.463406584	3.791467886	-1.762629019
H	-1.463406584	-3.791467886	-1.762629019
H	1.463406584	-3.791467886	1.762629019
H	-1.463406584	3.791467886	1.762629019

Table S20: Absolute energies for the  $^3B_1$  state of TME at a  $40^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.75056186
	CASSCF(2,2)	-231.75056186
	CAS(2,2)PT2	-232.56781799
	CASSCF(6,6)	-231.82994232
	CAS(6,6)PT2	-232.56339858
cc-pVTZ	RHF	-231.81227327
	CASSCF(2,2)	-231.81227327
	CAS(2,2)PT2	-232.80375443
	CASSCF(6,6)	-231.89062429
	CAS(6,6)PT2	-232.79783656
cc-pVQZ	RHF	-231.82695361
	CASSCF(2,2)	-231.82695361
	CAS(2,2)PT2	-232.87827063
	CASSCF(6,6)	-231.90502798
	CAS(6,6)PT2	-232.87153630
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64681418
	VMC (3-term Jastrow/CAS(6,6))	-38.609351 $\pm$ 0.000852
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.688833 $\pm$ 0.000076
	DMC ( $\tau = 0.005$ au)	-38.690221 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.690747 $\pm$ 0.000035
	DMC ( $\tau = 0.01$ au)	-38.691561 $\pm$ 0.000034

Table S21: Geometry of the  $^3B_1$  state of TME at a  $40^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.419526365
C	0.000000000	0.000000000	1.419526365
C	0.780908749	2.145529153	-2.721326496
C	-0.780908749	2.145529153	2.721326496
C	-0.780908749	-2.145529153	-2.721326496
C	0.780908749	-2.145529153	2.721326496
H	0.772361104	2.178806605	-4.747484921
H	-0.772361104	-2.178806605	-4.747484921
H	0.772361104	-2.178806605	4.747484921
H	-0.772361104	2.178806605	4.747484921
H	1.470425986	3.786986708	-1.760956398
H	-1.470425986	-3.786986708	-1.760956398
H	1.470425986	-3.786986708	1.760956398
H	-1.470425986	3.786986708	1.760956398

Table S22: Absolute energies for the  $^1A$  state of TME at a  $45^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.65367189
	CASSCF(2,2)	-231.75069453
	CAS(2,2)PT2	-232.57067334
	CASSCF(6,6)	-231.83243885
	CAS(6,6)PT2	-232.56541993
cc-pVTZ	RHF	-231.71896520
	CASSCF(2,2)	-231.81234514
	CAS(2,2)PT2	-232.80633083
	CASSCF(6,6)	-231.89300736
	CAS(6,6)PT2	-232.79964312
cc-pVTZ'	RHF	-231.70991244
	CASSCF(6,6)	-231.88477401
	CAS(6,6)PT2	-232.71487718
cc-pVQZ	RHF	-231.73526962
	CASSCF(2,2)	-231.82702668
	CAS(2,2)PT2	-232.88079119
	CASSCF(6,6)	-231.90739817
	CAS(6,6)PT2	-232.87329918
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64915411
	VMC (3-term Jastrow/CAS(6,6))	-38.608681 $\pm$ 0.000852
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.690250 $\pm$ 0.000074
	DMC ( $\tau = 0.005$ au)	-38.691434 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.692012 $\pm$ 0.000028
	DMC ( $\tau = 0.01$ au)	-38.692614 $\pm$ 0.000021

Table S23: Geometry of the  $^1A$  state of TME at a  $45^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.413312001
C	0.000000000	0.000000000	1.413312001
C	0.875012370	2.112466730	-2.712868237
C	-0.875012370	2.112466730	2.712868237
C	-0.875012370	-2.112466730	-2.712868237
C	0.875012370	-2.112466730	2.712868237
H	0.868569677	2.152608171	-4.739082085
H	-0.868569677	-2.152608171	-4.739082085
H	0.868569677	-2.152608171	4.739082085
H	-0.868569677	2.152608171	4.739082085
H	1.622454529	3.723989797	-1.744591448
H	-1.622454529	-3.723989797	-1.744591448
H	1.622454529	-3.723989797	1.744591448
H	-1.622454529	3.723989797	1.744591448

Table S24: Absolute energies for the  $^3B_1$  state of TME at a  $45^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.75092611
	CASSCF(2,2)	-231.75092611
	CAS(2,2)PT2	-232.56800090
	CASSCF(6,6)	-231.83023086
	CAS(6,6)PT2	-232.56358886
cc-pVTZ	RHF	-231.81260543
	CASSCF(2,2)	-231.81260543
	CAS(2,2)PT2	-232.80383292
	CASSCF(6,6)	-231.89087879
	CAS(6,6)PT2	-232.79792346
cc-pVQZ	RHF	-231.82728844
	CASSCF(2,2)	-231.82728844
	CAS(2,2)PT2	-232.87834688
	CASSCF(6,6)	-231.90528433
	CAS(6,6)PT2	-232.87162068
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64705729
	VMC (3-term Jastrow/CAS(6,6))	-38.610704 $\pm$ 0.000835
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.689223 $\pm$ 0.000075
	DMC ( $\tau = 0.005$ au)	-38.690586 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.691213 $\pm$ 0.000034
	DMC ( $\tau = 0.01$ au)	-38.691931 $\pm$ 0.000030

Table S25: Geometry of the  $^3B_1$  state of TME at a  $45^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.419530145
C	0.000000000	0.000000000	1.419530145
C	0.874825472	2.112015519	-2.715168977
C	-0.874825472	2.112015519	2.715168977
C	-0.874825472	-2.112015519	-2.715168977
C	0.874825472	-2.112015519	2.715168977
H	0.875059361	2.151729681	-4.741412815
H	-0.875059361	-2.151729681	-4.741412815
H	0.875059361	-2.151729681	4.741412815
H	-0.875059361	2.151729681	4.741412815
H	1.618623554	3.724058890	-1.744607378
H	-1.618623554	-3.724058890	-1.744607378
H	1.618623554	-3.724058890	1.744607378
H	-1.618623554	3.724058890	1.744607378

Table S26: Absolute energies for the  $^1A$  state of TME at a  $50^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.65866008
	CASSCF(2,2)	-231.75119010
	CAS(2,2)PT2	-232.57046867
	CASSCF(6,6)	-231.83247061
	CAS(6,6)PT2	-232.56551057
cc-pVTZ	RHF	-231.72426159
	CASSCF(2,2)	-231.81285518
	CAS(2,2)PT2	-232.80606696
	CASSCF(6,6)	-231.89303526
	CAS(6,6)PT2	-232.79968655
cc-pVQZ	RHF	-231.74069183
	CASSCF(2,2)	-231.82755372
	CAS(2,2)PT2	-232.88052991
	CASSCF(6,6)	-231.90743544
	CAS(6,6)PT2	-232.87335341
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64921969
	VMC (3-term Jastrow/CAS(6,6))	-38.608300 $\pm$ 0.000799
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.690006 $\pm$ 0.000887
	DMC ( $\tau = 0.005$ au)	-38.691417 $\pm$ 0.000046
	DMC ( $\tau = 0.0075$ au)	-38.692139 $\pm$ 0.000048
	DMC ( $\tau = 0.01$ au)	-38.692833 $\pm$ 0.000045

Table S27: Geometry of the  $^1A$  state of TME at a  $50^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.413779708
C	0.000000000	0.000000000	1.413779708
C	0.967572810	2.074966588	-2.706148474
C	-0.967572810	2.074966588	2.706148474
C	-0.967572810	-2.074966588	-2.706148474
C	0.967572810	-2.074966588	2.706148474
H	0.962494910	2.125483849	-4.732347673
H	-0.962494910	-2.125483849	-4.732347673
H	0.962494910	-2.125483849	4.732347673
H	-0.962494910	2.125483849	4.732347673
H	1.777585657	3.650393931	-1.728051529
H	-1.777585657	-3.650393931	-1.728051529
H	1.777585657	-3.650393931	1.728051529
H	-1.777585657	3.650393931	1.728051529

Table S28: Absolute energies for the  $^3B_1$  state of TME at a  $50^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.75108043
	CASSCF(2,2)	-231.75108043
	CAS(2,2)PT2	-232.56798017
	CASSCF(6,6)	-231.83035666
	CAS(6,6)PT2	-232.56359149
cc-pVTZ	RHF	-231.81272831
	CASSCF(2,2)	-231.81272831
	CAS(2,2)PT2	-232.80370974
	CASSCF(6,6)	-231.89096863
	CAS(6,6)PT2	-232.79782438
cc-pVQZ	RHF	-231.82741264
	CASSCF(2,2)	-231.82741264
	CAS(2,2)PT2	-232.87821582
	CASSCF(6,6)	-231.90537452
	CAS(6,6)PT2	-232.87151333
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64713861
	VMC (3-term Jastrow/CAS(6,6))	-38.610704 $\pm$ 0.000835
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.689172 $\pm$ 0.000075
	DMC ( $\tau = 0.005$ au)	-38.690470 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.691299 $\pm$ 0.000033
	DMC ( $\tau = 0.01$ au)	-38.691829 $\pm$ 0.000032



Table S29: Geometry of the  $^3B_1$  state of TME at a  $50^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.419602899
C	0.000000000	0.000000000	1.419602899
C	0.967150199	2.074060294	-2.709932884
C	-0.967150199	2.074060294	2.709932884
C	-0.967150199	-2.074060294	-2.709932884
C	0.967150199	-2.074060294	2.709932884
H	0.975469511	2.118399830	-4.736211152
H	-0.975469511	-2.118399830	-4.736211152
H	0.975469511	-2.118399830	4.736211152
H	-0.975469511	2.118399830	4.736211152
H	1.764875122	3.655515052	-1.731112218
H	-1.764875122	-3.655515052	-1.731112218
H	1.764875122	-3.655515052	1.731112218
H	-1.764875122	3.655515052	1.731112218

Table S30: Absolute energies for the  $^1A$  state of TME at a  $60^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.66681372
	CASSCF(2,2)	-231.75210267
	CAS(2,2)PT2	-232.56996676
	CASSCF(6,6)	-231.83246306
	CAS(6,6)PT2	-232.56569721
cc-pVTZ	RHF	-231.73302586
	CASSCF(2,2)	-231.81388394
	CAS(2,2)PT2	-232.80556624
	CASSCF(6,6)	-231.89307309
	CAS(6,6)PT2	-232.79991587
cc-pVQZ	RHF	-231.74966141
	CASSCF(2,2)	-231.82863407
	CAS(2,2)PT2	-232.88004371
	CASSCF(6,6)	-231.90750015
	CAS(6,6)PT2	-232.87362101

Table S31: Geometry of the  $^1A$  state of TME at a  $60^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.414267257
C	0.000000000	0.000000000	1.414267257
C	1.147275458	1.987139383	-2.693391901
C	-1.147275458	1.987139383	2.693391901
C	-1.147275458	-1.987139383	-2.693391901
C	1.147275458	-1.987139383	2.693391901
H	1.151398274	2.052869933	-4.719504704
H	-1.151398274	-2.052869933	-4.719504704
H	1.151398274	-2.052869933	4.719504704
H	-1.151398274	2.052869933	4.719504704
H	2.077945741	3.484561338	-1.699099280
H	-2.077945741	-3.484561338	-1.699099280
H	2.077945741	-3.484561338	1.699099280
H	-2.077945741	3.484561338	1.699099280

Table S32: Absolute energies for the  $^3B_1$  state of TME at a  $60^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.75089137
	CASSCF(2,2)	-231.75089137
	CAS(2,2)PT2	-232.56748698
	CASSCF(6,6)	-231.83023192
	CAS(6,6)PT2	-232.56317695
cc-pVTZ	RHF	-231.81248524
	CASSCF(2,2)	-231.81248524
	CAS(2,2)PT2	-232.80303387
	CASSCF(6,6)	-231.89077611
	CAS(6,6)PT2	-232.79722640
cc-pVQZ	RHF	-231.82716757
	CASSCF(2,2)	-231.82716757
	CAS(2,2)PT2	-232.87750456
	CASSCF(6,6)	-231.90517860
	CAS(6,6)PT2	-232.87088049

Table S33: Geometry of the  $^3B_1$  state of TME at a  $60^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.420389970
C	0.000000000	0.000000000	1.420389970
C	1.146029577	1.984981455	-2.703111563
C	-1.146029577	1.984981455	2.703111563
C	-1.146029577	-1.984981455	-2.703111563
C	1.146029577	-1.984981455	2.703111563
H	1.166776012	2.033870980	-4.729411523
H	-1.166776012	-2.033870980	-4.729411523
H	1.166776012	-2.033870980	4.729411523
H	-1.166776012	2.033870980	4.729411523
H	2.054251906	3.499446841	-1.713543383
H	-2.054251906	-3.499446841	-1.713543383
H	2.054251906	-3.499446841	1.713543383
H	-2.054251906	3.499446841	1.713543383

Table S34: Absolute energies for the  $^1A$  state of TME at a  $70^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.67229982
	CASSCF(2,2)	-231.75281838
	CAS(2,2)PT2	-232.56946621
	CASSCF(6,6)	-231.83238935
	CAS(6,6)PT2	-232.56582315
cc-pVTZ	RHF	-231.73905741
	CASSCF(2,2)	-231.81476740
	CAS(2,2)PT2	-232.80516364
	CASSCF(6,6)	-231.89308100
	CAS(6,6)PT2	-232.80018086
cc-pVQZ	RHF	-231.75583651
	CASSCF(2,2)	-231.82957320
	CAS(2,2)PT2	-232.87966326
	CASSCF(6,6)	-231.90753789
	CAS(6,6)PT2	-232.87393104

Table S35: Geometry of the  $^1A$  state of TME at a  $70^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.414889922
C	0.000000000	0.000000000	1.414889922
C	1.318004655	1.882305720	-2.683906180
C	-1.318004655	1.882305720	2.683906180
C	-1.318004655	-1.882305720	-2.683906180
C	1.318004655	-1.882305720	2.683906180
H	1.338550787	1.953578729	-4.710079536
H	-1.338550787	-1.953578729	-4.710079536
H	1.338550787	-1.953578729	4.710079536
H	-1.338550787	1.953578729	4.710079536
H	2.359579822	3.297247487	-1.678344523
H	-2.359579822	-3.297247487	-1.678344523
H	2.359579822	-3.297247487	1.678344523
H	-2.359579822	3.297247487	1.678344523

Table S36: Absolute energies for the  $^3B_1$  state of TME at a  $70^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.75036392
	CASSCF(2,2)	-231.75036392
	CAS(2,2)PT2	-232.56672046
	CASSCF(6,6)	-231.82984294
	CAS(6,6)PT2	-232.56250040
cc-pVTZ	RHF	-231.81193059
	CASSCF(2,2)	-231.81193059
	CAS(2,2)PT2	-232.80215287
	CASSCF(6,6)	-231.89034472
	CAS(6,6)PT2	-232.79643203
cc-pVQZ	RHF	-231.82660908
	CASSCF(2,2)	-231.82660908
	CAS(2,2)PT2	-232.87658169
	CASSCF(6,6)	-231.90474390
	CAS(6,6)PT2	-232.87004706

Table S37: Geometry of the  $^3B_1$  state of TME at a  $70^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.421357510
C	0.000000000	0.000000000	1.421357510
C	1.315654918	1.878949949	-2.699996774
C	-1.315654918	1.878949949	2.699996774
C	-1.315654918	-1.878949949	-2.699996774
C	1.315654918	-1.878949949	2.699996774
H	1.347755934	1.927126979	-4.726386915
H	-1.347755934	-1.927126979	-4.726386915
H	1.347755934	-1.927126979	4.726386915
H	-1.347755934	1.927126979	4.726386915
H	2.337738628	3.315664426	-1.705012549
H	-2.337738628	-3.315664426	-1.705012549
H	2.337738628	-3.315664426	1.705012549
H	-2.337738628	3.315664426	1.705012549

Table S38: Absolute energies for the  $^1A$  state of TME at a  $80^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.67536953
	CASSCF(2,2)	-231.75325290
	CAS(2,2)PT2	-232.56910603
	CASSCF(6,6)	-231.83230502
	CAS(6,6)PT2	-232.56587672
cc-pVTZ	RHF	-231.74251102
	CASSCF(2,2)	-231.81533956
	CAS(2,2)PT2	-232.80490383
	CASSCF(6,6)	-231.89306667
	CAS(6,6)PT2	-232.80036204
cc-pVQZ	RHF	-231.75937676
	CASSCF(2,2)	-231.83018664
	CAS(2,2)PT2	-232.87942460
	CASSCF(6,6)	-231.90754725
	CAS(6,6)PT2	-232.87414840

Table S39: Geometry of the  $^1A$  state of TME at a  $80^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.415317945
C	0.000000000	0.000000000	1.415317945
C	1.478202391	1.761653010	-2.678163943
C	-1.478202391	1.761653010	2.678163943
C	-1.478202391	-1.761653010	-2.678163943
C	1.478202391	-1.761653010	2.678163943
H	1.517457346	1.828835819	-4.704420324
H	-1.517457346	-1.828835819	-4.704420324
H	1.517457346	-1.828835819	4.704420324
H	-1.517457346	1.828835819	4.704420324
H	2.621819588	3.090767297	-1.666120742
H	-2.621819588	-3.090767297	-1.666120742
H	2.621819588	-3.090767297	1.666120742
H	-2.621819588	3.090767297	1.666120742

Table S40: Absolute energies for the  $^3B_1$  state of TME at a  $80^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.74986508
	CASSCF(2,2)	-231.74986508
	CAS(2,2)PT2	-232.56609008
	CASSCF(6,6)	-231.82948193
	CAS(6,6)PT2	-232.56193972
cc-pVTZ	RHF	-231.81141904
	CASSCF(2,2)	-231.81141904
	CAS(2,2)PT2	-232.80145612
	CASSCF(6,6)	-231.88995870
	CAS(6,6)PT2	-232.79580321
cc-pVQZ	RHF	-231.82609505
	CASSCF(2,2)	-231.82609505
	CAS(2,2)PT2	-232.87585547
	CASSCF(6,6)	-231.90435757
	CAS(6,6)PT2	-232.86939201

Table S41: Geometry of the  $^3B_1$  state of TME at a  $80^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.422155919
C	0.000000000	0.000000000	1.422155919
C	1.474922110	1.757743724	-2.698878412
C	-1.474922110	1.757743724	2.698878412
C	-1.474922110	-1.757743724	-2.698878412
C	1.474922110	-1.757743724	2.698878412
H	1.513906195	1.803682999	-4.725334020
H	-1.513906195	-1.803682999	-4.725334020
H	1.513906195	-1.803682999	4.725334020
H	-1.513906195	1.803682999	4.725334020
H	2.611368943	3.104271772	-1.701547802
H	-2.611368943	-3.104271772	-1.701547802
H	2.611368943	-3.104271772	1.701547802
H	-2.611368943	3.104271772	1.701547802

Table S42: Absolute energies for the  $^1A$  state of TME at a  $90^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.67635028
	CASSCF(2,2)	-231.75339588
	CAS(2,2)PT2	-232.56897526
	CASSCF(6,6)	-231.83226856
	CAS(6,6)PT2	-232.56588832
cc-pVTZ	RHF	-231.74363060
	CASSCF(2,2)	-231.81553480
	CAS(2,2)PT2	-232.80481270
	CASSCF(6,6)	-231.89305702
	CAS(6,6)PT2	-232.80042275
cc-pVTZ'	RHF	-231.73469760
	CASSCF(6,6)	-231.88489671
	CAS(6,6)PT2	-232.71580565
cc-pVQZ	RHF	-231.76052565
	CASSCF(2,2)	-231.83039700
	CAS(2,2)PT2	-232.87934194
	CASSCF(6,6)	-231.90754673
	CAS(6,6)PT2	-232.87422274
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64930415
	VMC (3-term Jastrow/CAS(6,6))	-38.611174 $\pm$ 0.000863
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.689950 $\pm$ 0.000076
	DMC ( $\tau = 0.005$ au)	-38.691505 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.692358 $\pm$ 0.000033
	DMC ( $\tau = 0.01$ au)	-38.693082 $\pm$ 0.000036



Table S43: Geometry of the  $^1A$  state of TME at a  $90^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.415490855
C	0.000000000	0.000000000	1.415490855
C	2.300251989	0.000000000	-2.676251273
C	-2.300251989	0.000000000	-2.676251273
C	0.000000000	2.300251989	2.676251273
C	0.000000000	-2.300251989	2.676251273
H	2.379156665	0.000000000	-4.702539099
H	-2.379156665	0.000000000	-4.702539099
H	4.052453338	0.000000000	-1.662046859
H	-4.052453338	0.000000000	-1.662046859
H	0.000000000	-4.052453338	1.662046859
H	0.000000000	4.052453338	1.662046859
H	0.000000000	-2.379156665	4.702539099
H	0.000000000	2.379156665	4.702539099

Table S44: Absolute energies for the  $^3B_1$  state of TME at a  $90^\circ$  torsional angle

Basis Set	Method	Absolute Energy (Ha)
cc-pVDZ	RHF	-231.74966706
	CASSCF(2,2)	-231.74966706
	CAS(2,2)PT2	-232.56584657
	CASSCF(6,6)	-231.82933802
	CAS(6,6)PT2	-232.56174609
cc-pVTZ	RHF	-231.81121922
	CASSCF(2,2)	-231.81121923
	CAS(2,2)PT2	-232.80119356
	CASSCF(6,6)	-231.88980832
	CAS(6,6)PT2	-232.79559912
cc-pVQZ	RHF	-231.82589463
	CASSCF(2,2)	-231.82589463
	CAS(2,2)PT2	-232.87558312
	CASSCF(6,6)	-231.90420795
	CAS(6,6)PT2	-232.86918133
cc-pV5Z(sp)+2d-CDF	CASSCF(6,6)	-37.64601074
	VMC (3-term Jastrow/CAS(6,6))	-38.608053 $\pm$ 0.000866
	DMC (extrap. $\tau \rightarrow 0$ . au)	-38.686816 $\pm$ 0.000074
	DMC ( $\tau = 0.005$ au)	-38.688039 $\pm$ 0.000034
	DMC ( $\tau = 0.0075$ au)	-38.688581 $\pm$ 0.000033
	DMC ( $\tau = 0.01$ au)	-38.689237 $\pm$ 0.000031

Table S45: Geometry of the  $^3B_1$  state of TME at a  $90^\circ$  torsional angle

Atom	X ( $a_0$ )	Y ( $a_0$ )	Z ( $a_0$ )
C	0.000000000	0.000000000	-1.422298593
C	0.000000000	0.000000000	1.422298593
C	2.294665488	0.000000000	-2.698653844
C	-2.294665488	0.000000000	-2.698653844
C	0.000000000	2.294665488	2.698653844
C	0.000000000	-2.294665488	2.698653844
H	2.355766085	0.000000000	-4.725142620
H	-2.355766085	0.000000000	-4.725142620
H	4.056454112	0.000000000	-1.700866755
H	-4.056454112	0.000000000	-1.700866755
H	0.000000000	-4.056454112	1.700866755
H	0.000000000	4.056454112	1.700866755
H	0.000000000	-2.355766085	4.725142620
H	0.000000000	2.355766085	4.725142620

## References

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