

Predicting the Right Mechanism for Hypervalent Iodine Reagents

by Applying Two Types of Hypervalent Twist Models:

Apical Twist and Equatorial Twist

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Computational details

All density functional theory (DFT) calculations were conducted with the Gaussian 16 program.^[1] The relative free energies (at 298.15K) are in kcal/mol. Keyword `int=grid=99770` was used for all M06-2X tasks to eliminate the unexpected small imaginary frequency. Solvent effects were evaluated with the SMD solvation model (Acetonitrile).^[2] Intrinsic reaction coordinates (IRC) calculations were performed for the saddle points to confirm that each saddle-point structure indeed connects to two relevant minima on the potential surface (keyword `LQA` was used).^[3] NBO6 was used to do the analysis.^[4]

IRC calculations

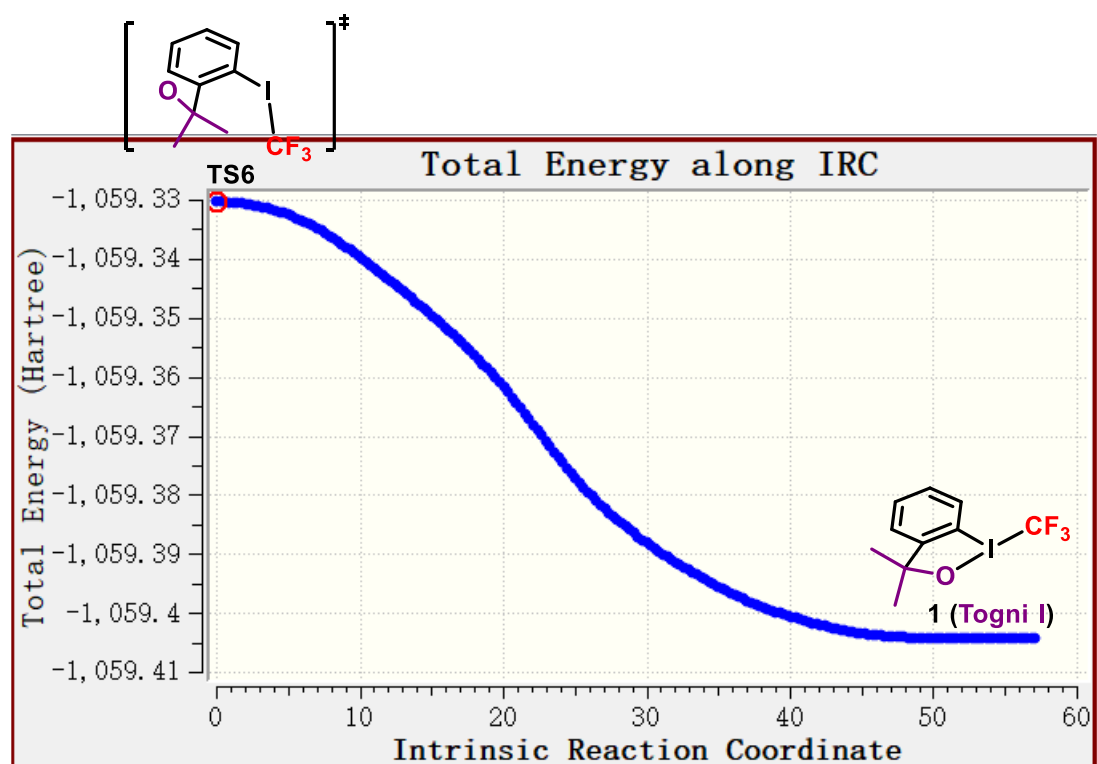


Figure S1. IRC calculations from TS6 to intermediate 1(Togni I).

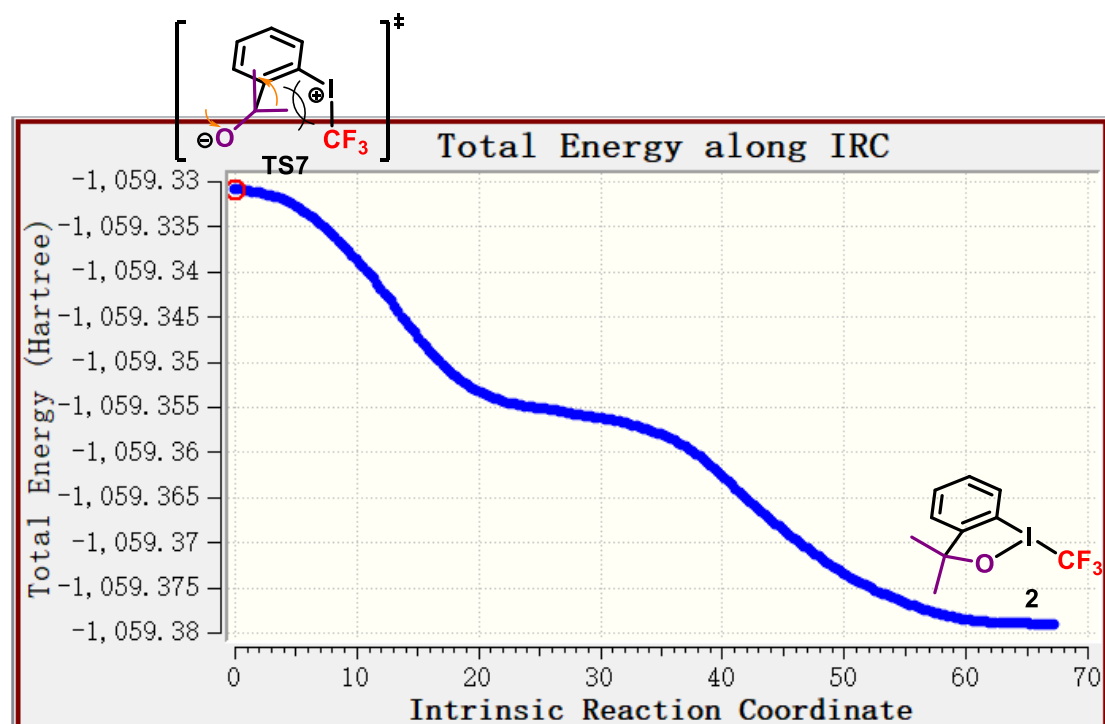


Figure S2. IRC calculations from TS7 to intermediate 2.

Reference:

- [1] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [2] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* 2009, 113, 6378.
- [3] (a) Fukui, K. *J. Phys. Chem.* 1970, 74, 4161. (b) Fukui, K. *Acc. Chem. Res.* 1981, 14, 363.
- [4] (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* 1980. 102, 7211-7218. (b) NBO 6.0. E. D. Glendening. J. K.; Badenhoop, A. E.; Reed, J. E.; Carpenter, J. A.; Bohmann, C. M.; Morales, C. R.; Landis; Weinhold, F. *Theoretical Chemistry Institute, University of Wisconsin, Madison*, 2013.

Cartesian Coordinates

1

C	-0.01927500	2.09846300	-0.20852600
C	-0.49813700	0.80389600	-0.12096900
C	-1.83608500	0.49272500	0.02215700
C	-2.73529600	1.55275600	0.11104600
C	-2.28953800	2.86457700	0.03397900
C	-0.93796800	3.13794000	-0.13313400
H	1.02803900	2.32178800	-0.34584500
H	-3.79116700	1.34949600	0.24031100
H	-3.00097000	3.67808200	0.09788900
H	-0.58987300	4.15983300	-0.20934800
C	-2.23951200	-0.98155400	0.10439800
C	-3.51690500	-1.24896800	-0.68501700
H	-3.72060200	-2.32066000	-0.66552000
H	-4.37443900	-0.73031900	-0.25487900
H	-3.39432900	-0.93454000	-1.72249200
C	-2.43162900	-1.35563100	1.57754400
H	-2.69919000	-2.41157500	1.64843700
H	-1.50604100	-1.19169200	2.13448200
H	-3.22215400	-0.75854500	2.03595100
O	-1.21010100	-1.74176500	-0.46701200
I	0.70549800	-0.93050200	-0.18285100
C	2.56284000	0.30352800	0.13748500
F	2.94628600	1.07455100	-0.89535800
F	3.56226400	-0.57695500	0.33742300
F	2.53860900	1.10060900	1.21837800

TS1

C	1.54195000	-2.11808400	-0.01269000
C	1.29656000	-0.76180200	-0.04135000
C	2.27450000	0.21718600	0.01825400
C	3.59419100	-0.20913400	0.11004700
C	3.88495200	-1.56771400	0.13726500
C	2.87104700	-2.51634100	0.07672000
H	0.73837800	-2.83985300	-0.06433400
H	4.39323800	0.52051200	0.16252600
H	4.91622800	-1.88896300	0.20466300
H	3.10993400	-3.57162900	0.09412600
C	1.82922400	1.66789900	0.04018000
C	2.69039900	2.56935500	-0.82395700
H	2.26104000	3.57119500	-0.84342600
H	3.69296700	2.63405100	-0.40054000
H	2.75484500	2.18246400	-1.84050700

C	1.73304200	2.17338500	1.47169700
H	1.36391100	3.19938800	1.47478100
H	1.06324400	1.54789600	2.06553800
H	2.72141000	2.14872500	1.93206900
O	0.51214900	1.72085900	-0.58726800
I	-0.57389200	0.17245200	-0.16795500
C	-3.60323900	-0.12436600	0.02319400
F	-2.89652100	-1.34838000	0.24313100
F	-4.48537800	-0.52490700	-0.97556000
F	-4.43701700	-0.11703200	1.13653900

2

C	-0.06043100	2.28767800	-0.10332800
C	-0.43621500	0.95532100	-0.08515300
C	-1.74674900	0.55372900	0.00729300
C	-2.74427200	1.52124600	0.08802400
C	-2.39450800	2.86613800	0.06188500
C	-1.06031500	3.25162600	-0.03521100
H	0.98259500	2.57598600	-0.17128400
H	-3.78566600	1.23374500	0.17270900
H	-3.16832900	3.62148500	0.11820400
H	-0.79941000	4.30234700	-0.05764600
C	-1.97522400	-0.95306700	0.06989800
C	-3.11484600	-1.38088100	-0.84670100
H	-3.21181700	-2.46713300	-0.82450500
H	-4.05759000	-0.94382600	-0.51545200
H	-2.91684300	-1.06339800	-1.87103500
C	-2.23689500	-1.37086000	1.51567600
H	-2.38228500	-2.45144200	1.56486600
H	-1.38583000	-1.10135700	2.14614100
H	-3.12704100	-0.87480100	1.90642800
O	-0.81164300	-1.60408900	-0.40502900
I	0.97412200	-0.66538000	-0.08693900
C	1.38977000	-2.89600100	-0.15460100
F	1.08313800	-3.51982900	-1.30065000
F	0.81570500	-3.59709400	0.83353300
F	2.72368400	-3.02813600	0.00649600

TS2

C	1.52939500	-2.07553300	0.43155700
C	0.92269300	-0.90103300	0.00417500
C	1.56310500	0.32559900	-0.03789800
C	2.89801400	0.32631200	0.38239000
C	3.53890600	-0.82895500	0.80094300

C	2.85661400	-2.03859800	0.82582300
H	0.96956400	-3.00122800	0.46075100
H	3.45141700	1.25647100	0.36778600
H	4.57551100	-0.78373300	1.11039400
H	3.34530900	-2.94534200	1.15768900
C	0.90457500	1.62194700	-0.55941300
C	1.43410200	1.84204400	-1.99037400
H	1.00216400	2.76188400	-2.38953900
H	2.52308800	1.92570200	-2.00483600
H	1.13319900	1.00879200	-2.62820400
C	1.31893800	2.82499000	0.30588800
H	0.72451500	3.68082500	-0.01812700
H	1.12331600	2.64735000	1.36336600
H	2.37212300	3.08234300	0.18783600
O	-0.46153600	1.49707700	-0.64058000
I	-1.10031600	-1.11163800	-0.55134500
C	-1.66307800	0.76633400	0.85182600
F	-2.51228700	1.64710600	0.38775500
F	-0.79487200	1.23037700	1.72633500
F	-2.45778600	-0.04172300	1.63436900

3

C	2.89498500	-0.07293800	-0.33128500
C	1.53089400	0.02085700	-0.07231800
C	0.89968400	1.26791700	0.04472800
C	1.71057800	2.39641800	-0.10198800
C	3.07158700	2.30957300	-0.35097800
C	3.66985200	1.06755900	-0.46976300
H	3.35459800	-1.04762300	-0.42310600
H	1.27296800	3.37996600	-0.02268100
H	3.65430200	3.21557100	-0.45570200
H	4.72980900	0.97577100	-0.66930800
C	-0.58610400	1.46735400	0.36891900
C	-1.06622700	2.89212300	0.12578700
H	-2.13694800	2.94673800	0.30622200
H	-0.58362700	3.57881800	0.81909700
H	-0.86036700	3.20823500	-0.89671900
C	-0.87197100	1.07653800	1.81552000
H	-1.92199500	1.23655500	2.06309700
H	-0.60212800	0.04601100	2.03293000
H	-0.27327800	1.73314500	2.44751000
O	-1.27333800	0.61431300	-0.61366100
I	0.58350800	-1.85372800	0.11613000
C	-2.50129200	0.15094100	-0.43474700

F	-2.62885800	-0.70883200	0.58608000
F	-3.42477900	1.10477200	-0.22758000
F	-2.85552400	-0.50432100	-1.54035400
CF₃+			
C	2.89498900	0.48636500	0.19415800
F	2.81698000	1.02400200	-0.90569700
F	3.46455700	-0.59398200	0.31103100
F	2.40339300	1.03001300	1.17748400
4			
C	-2.99877500	0.43278400	0.23343700
C	-3.07869900	1.81663000	0.15556600
C	-1.94329600	2.58014700	-0.09314700
C	-0.70188200	1.97478900	-0.25738200
C	-0.65091000	0.59836600	-0.15404300
C	-1.76801700	-0.18433300	0.07040900
H	-3.87798100	-0.17351300	0.40900700
H	-4.03582900	2.30651700	0.27868400
H	-2.02051500	3.65716800	-0.16545300
H	0.18017000	2.56437900	-0.46486600
C	-1.59318700	-1.67534600	0.08239200
O	-2.51185200	-2.43577700	0.27768600
O	-0.36275900	-2.04972300	-0.16097600
I	1.10548900	-0.52353900	-0.32967400
O	1.59406400	-0.86171900	1.34099300
O	2.15142800	1.11164000	-0.47782700
C	2.46532100	1.86223500	0.69513000
H	3.32321100	1.42797900	1.20825500
H	2.71081800	2.87239800	0.36610300
H	1.62661100	1.91093200	1.39305500
TS3			
C	-3.29271900	-1.38439500	-0.14256800
C	-2.26142800	-2.30126000	-0.32238700
C	-0.94203400	-1.87105700	-0.36003300
C	-0.71348000	-0.51491600	-0.21032900
C	-1.71137000	0.42251200	-0.03279300
C	-3.02351600	-0.02995900	0.00096600
I	1.26826700	0.12838800	-0.25572700
O	1.83042000	-1.00269500	-1.49714000
C	-1.34480000	1.88914800	0.10894700
O	-2.22684200	2.71501900	0.27893200
O	1.70266400	-1.00395900	1.23879500

C	1. 19908500	-0. 60200700	2. 52541400
O	-0. 08649000	2. 10649800	0. 03095000
H	1. 57076900	-1. 34232100	3. 23094200
H	0. 10698400	-0. 60828800	2. 53414600
H	1. 57176800	0. 38500700	2. 80406900
H	-0. 12744000	-2. 56935500	-0. 50586200
H	-2. 48213900	-3. 35459400	-0. 43524300
H	-4. 31731800	-1. 73248000	-0. 11642300
H	-3. 82018900	0. 68954100	0. 13780700

5

C	-0. 01387500	2. 10208300	-0. 02394100
C	-0. 47459100	0. 79964900	0. 02098600
C	-1. 81886600	0. 47731100	0. 03857200
C	-2. 74630900	1. 51266900	0. 01016800
C	-2. 31949100	2. 82948700	-0. 03725400
C	-0. 96065400	3. 11950900	-0. 05400000
H	1. 03463700	2. 35583100	-0. 03828900
H	-3. 79845100	1. 25936100	0. 02405300
H	-3. 04336100	3. 63346300	-0. 06230900
H	-0. 62250300	4. 14686500	-0. 09214300
O	-1. 28003500	-1. 80308700	0. 08196200
I	0. 78356800	-0. 89117800	0. 05800600
C	2. 63838400	0. 30469600	0. 04214400
F	2. 79433400	1. 05275800	-1. 04966700
F	3. 64186900	-0. 57589000	0. 07119500
F	2. 77412700	1. 10308100	1. 10059700
C	-2. 25640000	-0. 96487800	0. 08183900
O	-3. 44034700	-1. 25346600	0. 11139000

TS4

C	-0. 15456200	2. 44120800	0. 77905300
C	-0. 41395500	1. 08358000	0. 65294200
C	-1. 57469700	0. 54781400	0. 12236700
C	-2. 53228900	1. 46472400	-0. 31224700
C	-2. 30593400	2. 82933900	-0. 21824200
C	-1. 12156200	3. 32196000	0. 32280700
H	0. 76925500	2. 79596000	1. 21559300
H	-3. 46086600	1. 09280400	-0. 72855500
H	-3. 06301000	3. 52075300	-0. 56643600
H	-0. 95132900	4. 38779400	0. 39710100
O	-2. 43751400	-1. 46389500	0. 96558500
I	1. 04504300	-0. 24895300	1. 35441200
C	2. 35642700	-0. 04878600	-0. 39201300

F	1.62813700	0.08194300	-1.47345200
F	3.10104800	-1.12811600	-0.47153700
F	3.12387200	1.00912800	-0.25010800
C	-1.81978500	-0.96020100	0.01295600
O	-1.36037700	-1.49552300	-1.00934600

6

C	-0.62276300	2.50599600	0.40697600
C	-0.68798400	1.13102800	0.23170300
C	-1.78411900	0.46501800	-0.29810500
C	-2.86196200	1.26528500	-0.66988100
C	-2.83082300	2.64453300	-0.52339600
C	-1.71422600	3.26833500	0.01649000
H	0.25444000	2.97153600	0.83458400
H	-3.73129600	0.76895900	-1.08041200
H	-3.68371600	3.23628700	-0.83096900
H	-1.68441000	4.34325700	0.13679800
O	-3.01211500	-1.51757200	-0.64768400
I	0.97897600	0.08336900	0.95953100
C	1.86613000	-0.50264100	-0.95715800
F	1.15125400	-0.01390500	-1.94019200
F	1.94738600	-1.80623400	-1.04847000
F	3.08498500	0.00554300	-1.00929000
C	-1.86958800	-1.05578200	-0.52606100
O	-0.77490100	-1.65411100	-0.58087400

TS5

C	-0.15649000	2.39237700	0.91081400
C	-0.45036000	1.03859600	0.79294000
C	-1.61977900	0.59152400	0.18815000
C	-2.49967500	1.55788900	-0.30261500
C	-2.21297000	2.91115000	-0.21824200
C	-1.03757800	3.33035000	0.39230300
H	0.75199200	2.71187700	1.40395400
H	-3.42319000	1.21956800	-0.75583500
H	-2.90720200	3.63817800	-0.62051100
H	-0.80441800	4.38447400	0.47401300
O	-3.17374700	-1.17647100	0.26765900
I	0.92779000	-0.30153200	1.64715900
C	1.42472500	-1.59549300	-1.34411900
F	1.01709400	-2.74562200	-1.21168900
F	2.58335300	-1.33092000	-0.99678100
F	0.79774500	-0.76028000	-1.99200400
C	-1.99804900	-0.88038300	0.00927600

0	-1.09090600	-1.63603100	-0.41005500
7			
C	3.00341300	-0.07219700	-0.37347000
C	1.64010700	-0.09734500	-0.11322700
C	0.94434800	1.10207500	0.03929300
C	1.62505000	2.31516400	-0.04822100
C	2.98168300	2.33767100	-0.32342600
C	3.66632800	1.14218700	-0.49044900
H	3.54886400	-1.00038500	-0.47640600
H	1.07407900	3.23744400	0.08698200
H	3.50063300	3.28332500	-0.40475800
H	4.72788400	1.14685000	-0.70255000
O	-1.23947800	0.48422200	-0.61811700
I	0.74004100	-1.96707400	0.17025300
C	-2.57771200	0.31603300	-0.41699600
F	-2.83662100	-0.25988900	0.74839600
F	-3.24210400	1.46089200	-0.47722500
F	-3.01697400	-0.47322200	-1.38200800
C	-0.51122800	1.18668600	0.32024700
O	-1.02465800	1.81238300	1.19184800
TS6			
C	-0.09725500	2.36137200	0.80991200
C	-0.40180300	1.01312200	0.59617800
C	-1.62794200	0.51534400	0.16011400
C	-2.57380200	1.53892200	-0.04958400
C	-2.31530700	2.88333500	0.13251500
C	-1.06451000	3.31193100	0.56322000
H	0.88254800	2.65312500	1.16227800
H	-3.56818400	1.25587300	-0.35903300
H	-3.10084900	3.60479900	-0.05585200
H	-0.84729900	4.36054800	0.71653500
O	-2.80037900	-1.21192400	1.23563400
I	1.26523500	-0.19690600	1.09542800
C	2.33909700	0.09554600	-0.78762800
F	1.51308300	-0.03528600	-1.80065600
F	3.28623500	-0.81546500	-0.85959800
F	2.87892400	1.29451600	-0.82344800
C	-2.17721900	-0.96621300	0.07028300
C	-3.13845000	-1.04550600	-1.14888100
H	-3.44391600	-2.08803700	-1.25411100
H	-4.04609100	-0.46579900	-0.98873700
H	-2.67477500	-0.72793300	-2.08900700

C	-1.08112900	-2.01667800	-0.23588500
H	-0.38412700	-1.73116400	-1.03025800
H	-0.52545500	-2.26864200	0.66342900
H	-1.59120600	-2.92859000	-0.55290000

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C	-0.02539000	2.19861000	0.82112300
C	-0.40247900	0.91743700	0.42477800
C	-1.70832000	0.49653400	0.19676300
C	-2.66074800	1.50476700	0.37974100
C	-2.33561200	2.79865900	0.75302600
C	-1.01249300	3.15548200	0.97995000
H	1.01362700	2.44365100	0.99465900
H	-3.68245100	1.18719800	0.20850800
H	-3.12080800	3.53511500	0.87503200
H	-0.74407000	4.15984500	1.28017100
O	-3.63461100	-0.87751400	-0.26199900
I	1.27065400	-0.36679500	0.19060300
C	1.86139000	0.42859600	-1.76410600
F	0.81486400	0.96016300	-2.35214900
F	2.33338300	-0.55756500	-2.49430200
F	2.79217200	1.34575300	-1.61434400
C	-2.29897100	-0.91917000	-0.20185400
C	-1.71297500	-1.31075000	-1.58116400
H	-2.15565600	-2.27102400	-1.85586500
H	-2.02665100	-0.57040100	-2.32088900
H	-0.62707900	-1.41439800	-1.63124000
C	-1.84448300	-1.93151300	0.87913300
H	-0.76590700	-2.06279700	0.99266500
H	-2.25971600	-1.62774300	1.84270600
H	-2.27224400	-2.90184900	0.61650000

TS7

C	0.05150400	2.33563400	0.88854100
C	-0.20975800	1.04004400	0.42925000
C	-1.47123600	0.46143200	0.30749000
C	-2.50457600	1.34904200	0.66859800
C	-2.29559400	2.63479500	1.12719800
C	-1.00644700	3.14200100	1.24980100
H	1.06661000	2.70174800	0.95435700
H	-3.52409400	1.00819800	0.57106400
H	-3.14769300	3.24911300	1.39118700
H	-0.82576300	4.14643200	1.60867300
O	-2.26080000	-0.64254700	-1.60816100

I	1.60409800	0.07691600	-0.07800300
C	1.54397000	0.56597200	-2.21540600
F	0.67158500	1.52498100	-2.41536400
F	1.21330800	-0.49153000	-2.92075800
F	2.74325700	0.97070700	-2.57892100
C	-1.92819100	-0.90901000	-0.33306600
C	-0.86130700	-2.02669700	-0.22909400
H	-1.36764000	-2.97131500	-0.43822800
H	-0.09861700	-1.90885000	-0.99521100
H	-0.38364200	-2.11172900	0.75254500
C	-3.13005300	-1.44492700	0.49416400
H	-2.90791300	-1.55945300	1.56052100
H	-4.01126100	-0.81537000	0.38249700
H	-3.38822900	-2.42593500	0.09121600