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Thioketone Spin Traps as Mediating Agents for Free Radical Polymerization Processes

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SUPPLEMENTARY DATA SECTION

Synthesis of di-tert-butyl thione (DTBT)

Trimethylacetonitrile (16.6 g, Aldrich, 99%) and *tert*-butyl chloride (22.2 g, Alrich, 99%) were added under nitrogen over 1 hour to a well stirred suspension of sodium (9.2 g) in a mixture of light petroleum (40 mL), THF (20 mL) and methanol (1 mL) keeping the reaction temperature between 15° and 20°C. The mixture was stirred for 3 h at ambient temperature. Chlorobenzene (2 g) in THF (5 mL) was added drop-wise over 10 min and subsequent stirring continued for 1 h. Methanol (20 mL) was cautiously added over 30 min. This was followed by water until clear phases separated. The organic phase was removed and the water phase washed 3 times by diethyl ether (3 × 50 mL). The organic phases were combined, dried and the solvents removed via distillation. The resulting product was distilled to afford the pure imine (boiling point 62-63 °C).

Di-*tert*-butyl ketone imine (5.64 g) in dry light petroleum (Aldrich) under nitrogen was treated with ethereal methyl lithium. When the methane evolution has ceased, dry carbon disulphide (3.2 mL) is added and the mixture stirred for 3 h. The solvent is removed under reduced pressure. The brown residue is heated at 80 to 100 °C under vacuum and the practically pure thione is distilled into a round bottom flask into a liquid nitrogen trap. The DTBT is subsequently dried in vacuum. 300

MHz ^{1}H NMR ($CDCl_3$): δ [ppm] 1.45 (s). 75 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 278.51 (C=S), 53.51 (*q*-C), 32.77 ($\underline{C}H_3$). The above synthetic procedure was adapted from Ohno, A.; Nakamura, K.; Nakazima, Y.; Oka, S. *Bul. Chem. Soc. Jap.* **1975**, *48*, 2404-2404.

Molecular Weight Analysis

Molecular weight distributions were measured via size exclusion chromatography (SEC) on a Shimadzu modular system, comprising an auto injector, a Polymer Laboratories 5.0 μm bead-size guard column (50×7.5 mm), followed by three PL columns (10^5, 10^4 and 10^3 Å) and a differential refractive index detector. The eluent was tetrahydrofuran (THF) at 40 ºC with a flow rate of 1 mL min^{-1}. The system was calibrated using narrow polystyrene standards ranging from 540 to $2{\cdot}10^6$ g mol^{-1}.

Polymerizations

Styrene (Aldrich, 99%) was purified by drying for one day over molecular sieve (4 Å) and subsequent distillation in vacuum. The thermally decaying initiator 2,2'-azobisisobutyronitrile (AIBN, Aldrich, 99%) was purified twice by crystallization from ethanol. Solutions of styrene, DTBT and AIBN were prepared to give the concentrations indicated in the main text. The solutions were subsequently subjected to four freeze-pump-thaw cycles to remove any residual oxygen. The subsequent polymerizations were carried out in a thermostatted water bath (60 °C) and the reactions were stopped by cooling the solutions in an ice bath. The polymer was isolated by evaporating off the residual styrene; initially in a fume cupboard to remove the bulk of the liquid, and subsequently in a vacuum oven at 30 °C. Final conversions were measured by gravimetry.

Computational Procedures

Standard ab initio and density functional theory calculations were carried out using the GAUSSIAN 03[1] and Molpro 2000.6[2] software. Calculations were performed at a high level of theory, chosen on the basis of previous assessment studies for radical addition to C=S double bonds.[3] Geometries of all species were optimized at the B3-LYP/6-31G(d) level of theory, and care was taken to select the (global) minimum energy conformation via extensive conformational searching at this level. Improved energies were calculated via a three-layer ONIOM-based approach in which the "inner core" ($\bullet CH_3$ + $S{=}CH_2$) was calculated at W1,[4] the core was calculated using G3(MP2)-RAD[5] and the full system at RMP2/6-311+G(3df,2p). For the smaller $\bullet C(CH_3)_3$ + $S{=}C(C(CH_3)_3)_2$ reaction it was possible to treat the full system at G3(MP2)-RAD; for the larger $\bullet CH(Ph)CH_2CH(CH_3)Ph$ + $S{=}C(C(CH_3)_3)_2$ system, we used $\bullet CH(CH_3)Ph$ + $S{=}C(CH(CH_3)_2)_2$ as the core.

The calculated geometries, frequencies and energies were then used to calculate the equilibrium constant (and associated thermodynamic functions), using standard formulae, as outlined previously.[6] In calculating the partition functions, the low frequency (< 300 cm^{-1}) torsional modes were treated as one-dimensional hindered internal rotations. For each mode, full rotational potentials were obtained at the B3-LYP/6-31G(d) level of theory by performing a relaxed scan through the 360° in steps of 10°. These were then fitted with a Fourier series of up to 18 terms, and the corresponding energy levels were found numerically by solving the one dimensional Schrödinger for a rigid rotor, using a Fortran program described previously.[7,8] Where the rotational potentials could be fitted with a simple cosine potential, the enthalpy and entropy associated with each mode were obtained from the Pitzer[9] tables. These two alternative approaches yield identical results for the special case of simple cosine potentials.

Full geometries in the form of Gaussian archive entries are provided in Table S1, rotational potentials (or barriers) and associated partition functions for the low frequency torsional modes are provided in Table S2, and total energies and entropies are provided in Table S3.

References

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Table S1 B3-LYP/6-31G(d) Optimized Geometries

•$C(CH_3)_3$


```
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 0543532,1.7616707466,0.\C,-1.3291518262,0.6720547343,0.\C,-0.063598760
 4,-0.1288255571,0.\C,0.6742610965,-0.3163631938,1.2896997828\C,0.67426
 10964,-0.3163631938,-1.2896997829\H,-1.9400616179,0.4675010949,0.88858
 77545\H,-1.940061618,0.4675010949,-0.8885877544\H,1.2835911529,0.56875
 54926,1.555440113\H,-0.0116451147,-0.4829080616,2.1301907067\H,1.36782
 79377,-1.165692268,1.2415727567\H,1.2835911528,0.5687554926,-1.5554401
 131\H,-0.0116451148,-0.4829080615,-2.1301907067\H,1.3678279377,-1.1656
 92268,-1.2415727567\\Version=DEC-AXP-OSF/1-G98RevA.11.3\State=2-A'\HF=
 -157.7983276\S2=0.75402\S2-1=0.\S2A=0.750012\RMSD=4.543e-09\RMSF=2.179
 e-06\Dipole=0.0334859,0.0680061,0.\PG=CS [SG(C2H1),X(C2H8)]\\@
```


•$CH(CH_3)Ph$


```
1\1\GINC-SC30\FOpt\UB3LYP\6-31G(d)\C8H9(2)\MLC501\25-May-2004\0\\# B3L
 YP/6-31G* OPT FREQ MAXDISK=268435456\\EtPh-cs-6dub3\\0,2\H,2.076652979
 1,-1.7071221701,0.\C,1.8330785143,-0.6472341403,0.\C,2.9648478287,0.33
 29041964,0.\C,0.4615044195,-0.296422334,0.\C,-2.3017509074,0.350177759
 9,0.\C,-0.5414638247,-1.3098262805,0.\C,0.01601966,1.0572057614,0.\C,-
 1.3371627939,1.3659918739,0.\C,-1.8898621213,-0.9905058968,0.\H,-0.229
 1124677,-2.3517513472,0.\H,0.7487305703,1.8588289809,0.\H,-1.649403422
 1,2.4074639039,0.\H,-2.6317608755,-1.785156805,0.\H,-3.3593148857,0.59
 85933381,0.\H,3.930913811,-0.179956881,0.\H,2.94101482,0.9926776704,0.
 8806011513\H,2.94101482,0.9926776704,-0.8806011513\\Version=DEC-AXP-OS
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 0613\RMSD=8.432e-09\RMSF=3.493e-05\Dipole=0.1484688,0.0260889,0.\PG=CS
  [SG(C8H7),X(H2)]\\@
```


•$CH(Ph)CH_2CH(CH_3)Ph$


```
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3249473,-0.2306189065\C,4.9866434022,-0.6149116332,-0.0702524875\C,5.1
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89,-2.219418854,-0.2110854093\H,-5.5367614668,-1.420128658,-0.75243871
3\H,-6.0547281376,1.0141572333,-0.6849129762\H,-4.2661427363,2.6312659
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01075\H,0.0426418865,0.7751383174,-0.5908563495\H,-1.2909463363,-0.710
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\@
```


S=$C(CH(CH_3)_2)_2$


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 ,-0.7397396479,-0.4718184714\H,1.9138139718,-0.5042998326,0.2882215209
 \C,-0.1007738848,0.0414311416,-0.0990834793\C,-0.2229362362,0.35709008
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 573,0.5030381769,-1.2032000869\C,0.8417709149,-2.2515085176,-0.3479450
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3088\H,1.7535862345,-2.8353197596,-0.5165171644\H,0.4521131667,-2.5119
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43301131,0.5685711898,3.0070364933\H,-2.2451271003,1.1693190215,1.4456
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4807332,1.9071023549,2.73668169\\Version=IA64L-G03RevC.02\State=1-A\HF
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7,0.7543252\PG=C01 [X(C7H14S1)]\\@

$S=C(C(CH_3)_3)_2$

1\1\GINC-AC14\FOpt\RB3LYP\6-31G(d)\C9H18S1\MLC501\14-Jun-2005\0\\# B3L
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$(CH_3)_3C–SC•(C(CH_3)_3)_2$

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$PhCH(CH_3)–SC•(CH(CH_3)_2)_2$

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PhCH(CH$_3$)CH$_2$CH(PH)–SC•(C(CH$_3$)$_3$)$_2$

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,-0.0705417193,0.499100173\C,-0.065628253,-0.025719982,0.872185629\H,0
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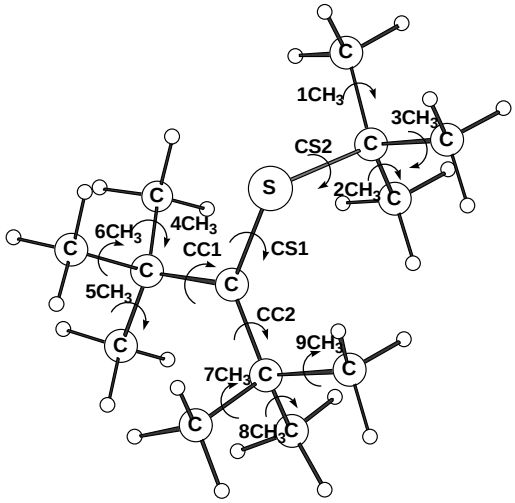
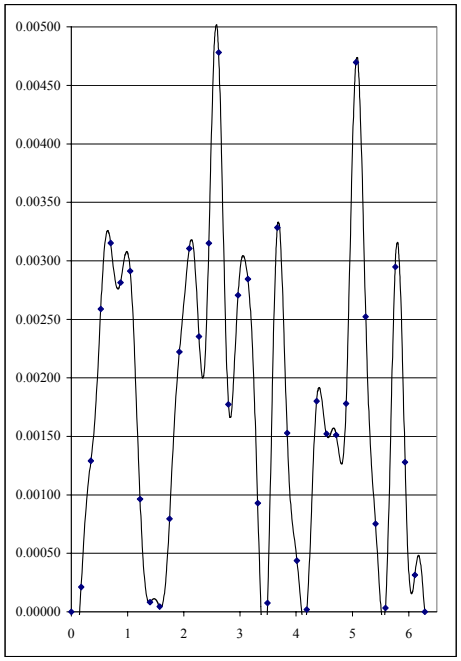
,-0.1913651\PG=C01 [X(C25H35S1)]\\@

Table S2. Optimized structures at B3LYP/6-31G(d) of the attacking radicals, the thioketone agent and the forming radicals; the rotational potentials (B3LYP/6-31G(d)) of individual functional groups and assigned low-mode vibrational frequencies for corresponding rotations used for calculated of the equilibrium constants.

$(CH_3)_3C–SC•(C(CH_3)_3)_2$

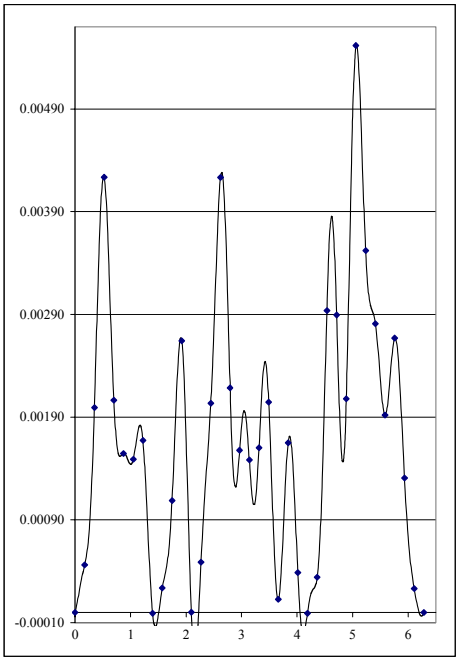


Rotation around the CC1 bond



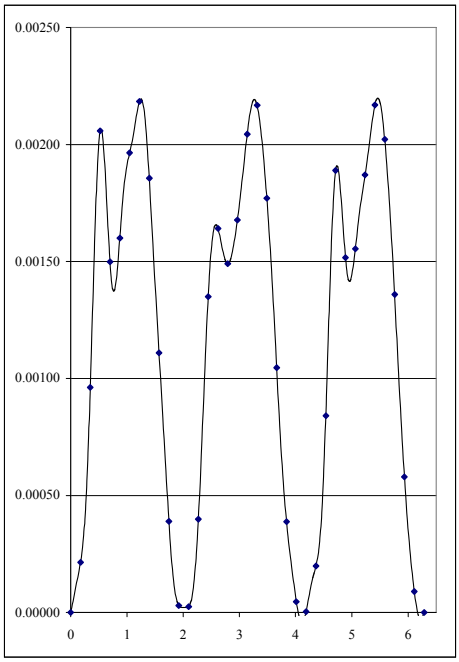
Assigned frequency 105.0 cm^{-1}

Rotation around the CC2 bond



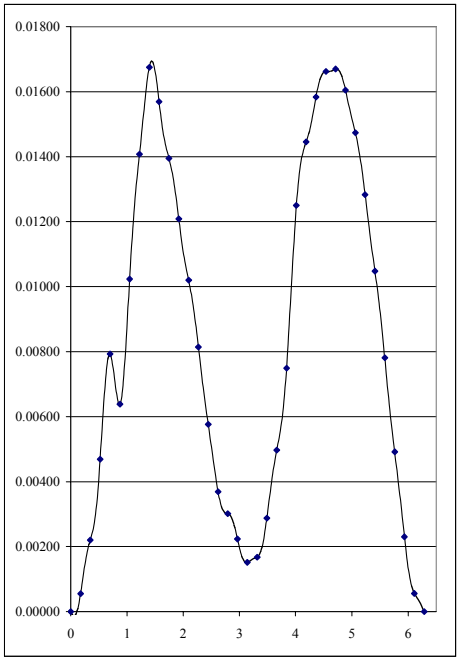
Assigned frequency 76.0 cm^{-1}

Rotation around the CS1 bond



Assigned frequency 29.8 cm^{-1}

Rotation around the CS2 bond

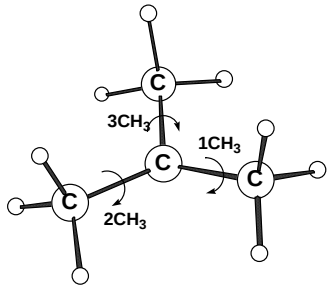


Assigned frequency 68.3 cm^{-1}

Rotational barriers for the CH_3-group rotations

	1CH_3	**2CH_3**	**3CH_3**	**4CH_3**	**5CH_3**	**6CH_3**	**7CH_3**	**8CH_3**	**9CH_3**
Barrier, Hartree	0.00657	0.00583	0.00398	0.00641	0.00561	0.00398	0.00497	0.00398	0.00807
Assigned Frequency, cm^{-1}	300.2	237.6	232.1	207.2	248.2	364.4	252.2	174.0	337.3

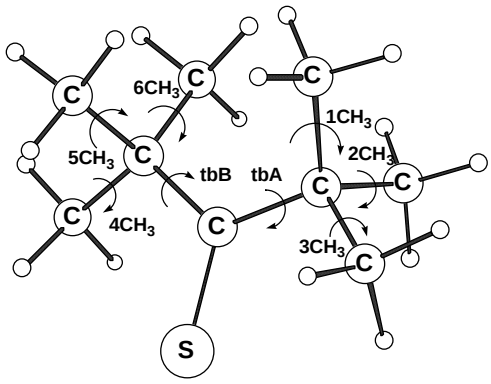
•**$C(CH_3)_3$**



Rotational barriers for the CH_3-group rotations

	$1CH_3$	**$2CH_3$**	**$3CH_3$**
Barrier, Hartree	0.00150	0.00150	0.00150
Assigned Frequency, cm^{-1}	126.0	128.7	135.2

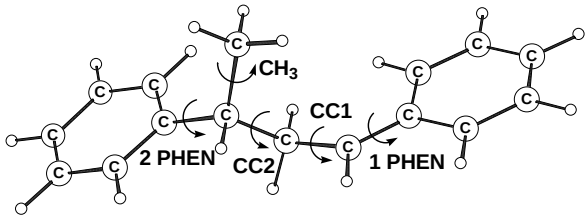
$S=C(C(CH_3)_3)_2$



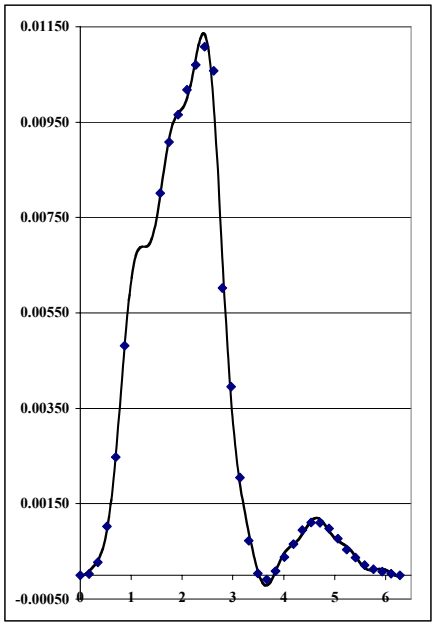
Rotational barriers of the rotations

	tbA	tbB	$1CH_3$	$2CH_3$	$3CH_3$	$4CH_3$	$5CH_3$	$6CH_3$
Barrier, Hartree	0.00204	0.00204	0.00403	0.00403	0.00403	0.00403	0.00403	0.00403
Assigned Frequency, cm^{-1}	25.1	106.8	196.3	224.0	229.4	243.1	270.3	275.2

•**CH(Ph)CH2CH(CH3)Ph**

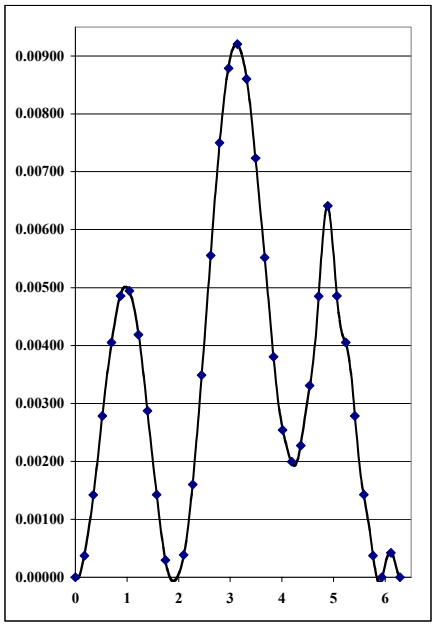


Rotation around CC1



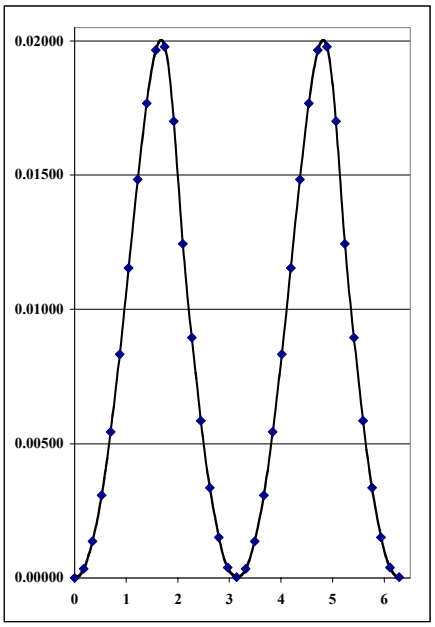
Assigned ω = 12.3 cm^{-1}

Rotation around CC2



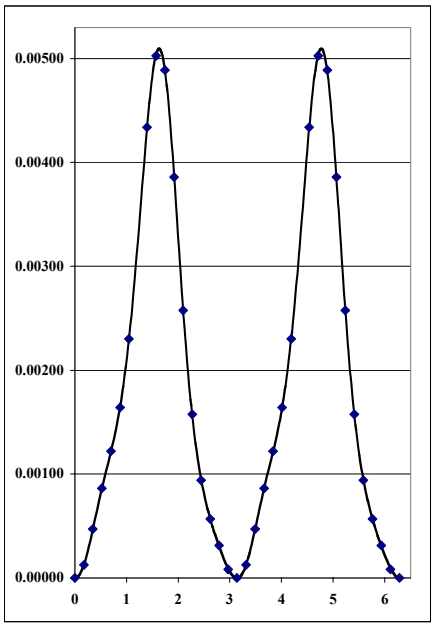
Assigned ω = 28.9 cm^{-1}

Rotation around 1 PHEN



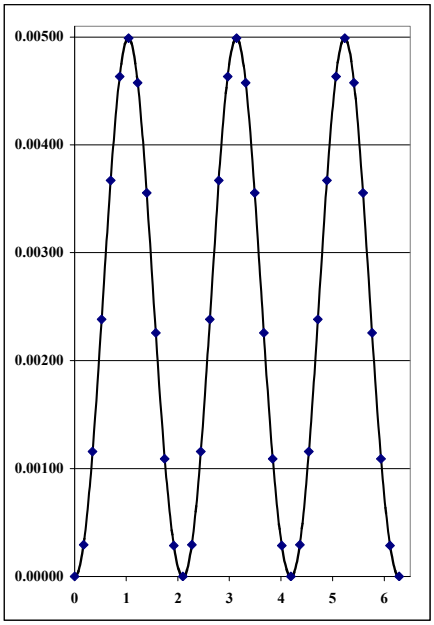
Assigned ω = 46.9 cm^{-1}

Rotation around 2 PHEN



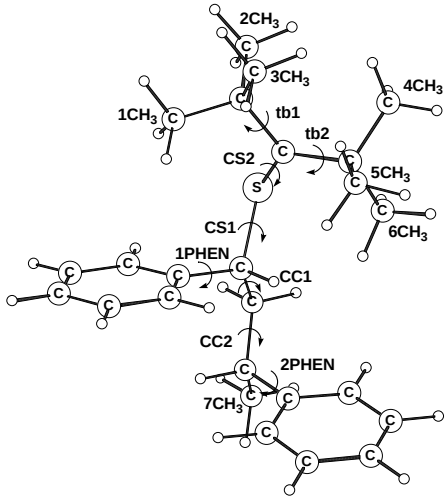
Assigned ω = 34.0 cm^{-1}

Rotation around CH_3

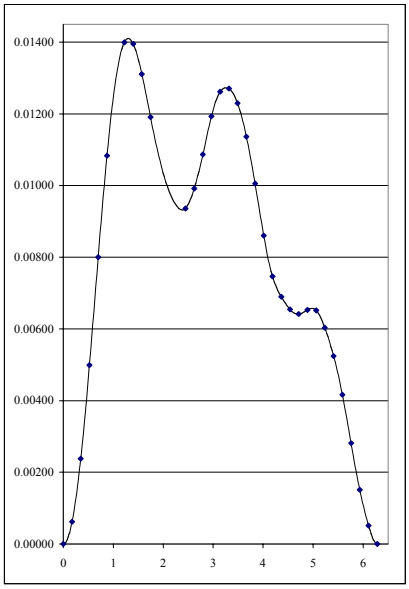


Assigned ω = 232.8 cm^{-1}

PhCH(CH3)CH2CH(PH)–SC•(C(CH$_3$)$_3$)$_2$

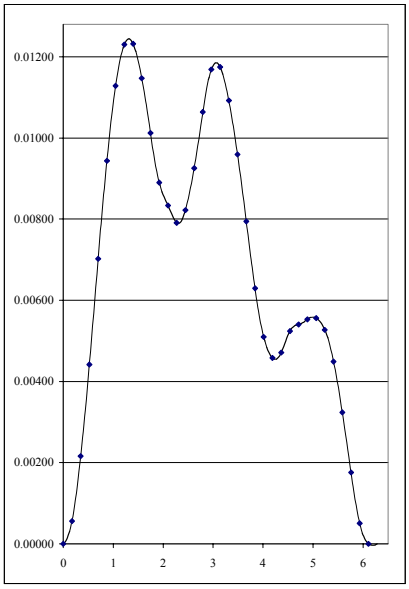


Rotation around the CC1 bond



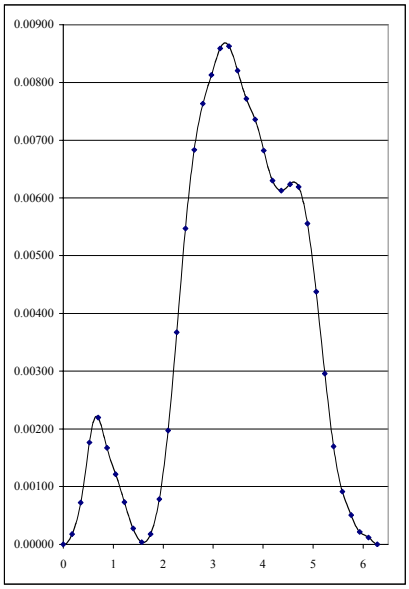
Assigned frequency 49.4 cm^{-1}

Rotation around the CC2 bond



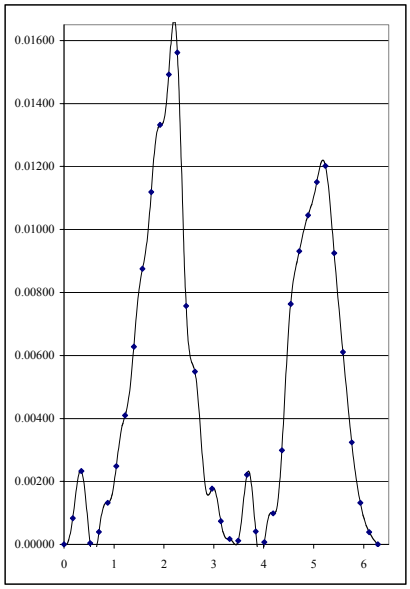
Assigned frequency 73.5 cm^{-1}

Rotation around the CS1 bond



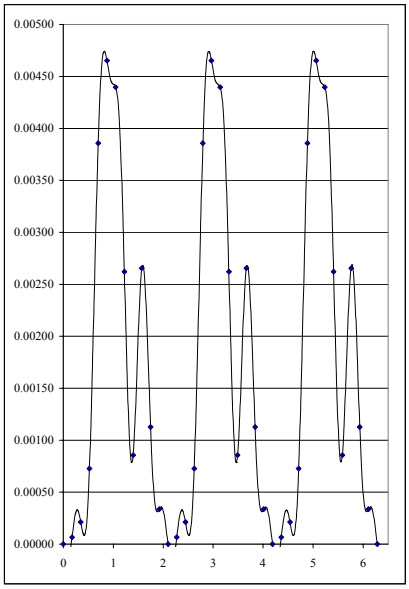
Assigned frequency 10.5 cm^{-1}

Rotation around the CS2 bond



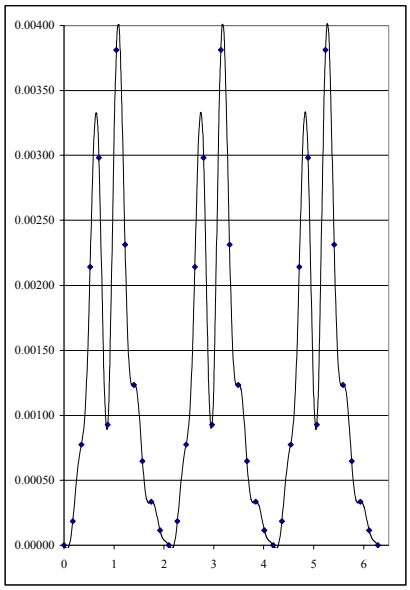
Assigned frequency 39.4 cm^{-1}

Rotation around the tb1 bond



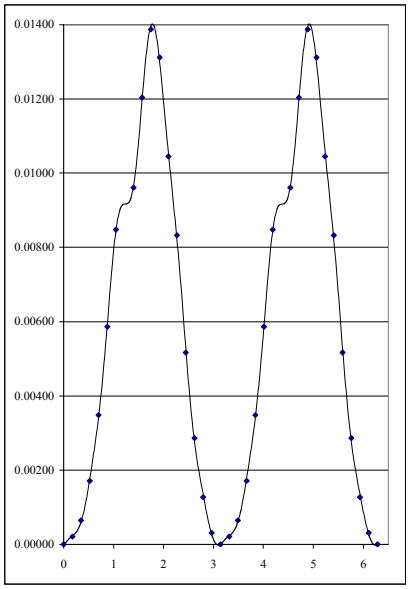
Assigned frequency 17.8 cm^{-1}

Rotation around the tb2 bond



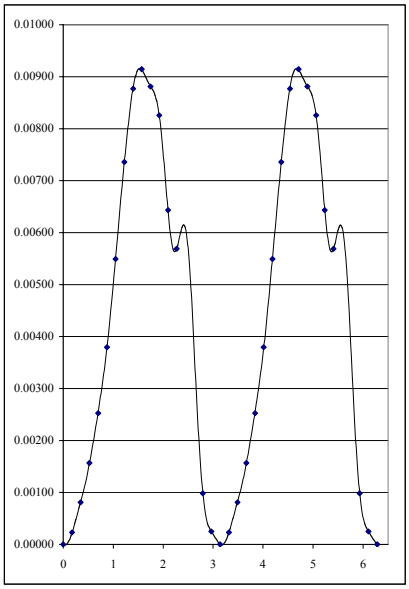
Assigned frequency 23.1 cm^{-1}

Rotation around the 1PHEN bond



Assigned frequency 52.9 cm^{-1}

Rotation around the 2PHEN bond



Assigned frequency 40.9 cm^{-1}

Rotational barriers of the CH_3 rotations

	1CH_3	**2CH_3**	**3CH_3**	**4CH_3**	**5CH_3**	**6CH_3**	**7CH_3**
Barrier, Hartree	0.00631	0.00409	0.00599	0.00523	0.00409	0.00409	0.00409
Assigned Frequency, cm^{-1}	204.7	238.7	231.7	267.7	162.9	320.4	225.9

Table S3. The absolute energies at the various levels of theory (ROMP2, G3(MP2)-RAD and W1), enthalpy (H_0 with no ZPE in Hatree), zero-point vibrational energy (ZPVE in kJ mol^{-1}), temperature correction (TC in kJ mol^{-1}), entropy (S in J mol^{-1}) and free energy of Gibbs (G in kJ mol^{-1}) for the attacking radicals, thioketone agent and the forming radicals.

Species	E(ROMP2)	E(G3(MP2)-RAD)[a]	E(W1)[b]	H_0 (no ZPE)	ZPVE	T = 298.15 K			T = 333.15 K		
						TC	S	-G	TC	S	-G
CH_3•	–	-39.78517	-39.84349	–	–	–	–	–	–	–	–
S=CH_2	–	-436.97759	-438.37761	–	–	–	–	–	–	–	–
CH_3-S-C•(H_2)	–	-476.81289	-478.27574	–	–	–	–	–	–	–	–
•C(CH_3)$_3$[c]	-157.39814	-157.58084	-157.63916	-157.63916	301.9	22.5	338.8	413670.1	19.3	328.7	413658.4
S=C(C(CH_3)$_3$)$_2$	-750.65745	-751.08606	-752.48608	-752.48608	653.8	46.4	501.8	1975119.2	36.7	466.7	1975100.9
(CH_3)$_3$C–SC•(C(CH_3)$_3$)$_2$	-908.08966	-908.69959	-910.16244	-910.16244	968.0	69.4	638.2	2388806.7	57.1	599.4	2388785.0
•CH(CH_3)Ph	-309.51471	-309.80231	–	–	–	–	–	–	–	–	–
S=C(CH(CH_3)$_2$)$_2$	-672.22573	-672.57141	–	–	–	–	–	–	–	–	–
PhCH(CH_3)-S-C•(CH(CH_3)$_2$)$_2$	-981.76520	-982.39260	–	–	–	–	–	–	–	–	–
•CH(Ph)CH_2CH(CH3)Ph[c]	-618.50188	-618.78947	-618.84779	-618.84779	726.2	40.5	524.8	1624174.6	49.6	553.5	1624193.5
S=C(C(CH_3)$_3$)$_2$[c]	-750.65745	-751.00313	-752.40315	-752.40315	653.8	36.7	466.7	1974883.1	46.4	501.8	1974901.4
PhCH(CH3)CH2CH(PH)–SC•(C(CH_3)$_3$)$_2$[c]	-1369.19545	-1369.82285	-1371.28570	-1371.28570	1387.4	79.1	816.3	3599087.5	96.5	870.4	3599116.6

[a] G3(MP2)-RAD numbers were calculated for all species explicitly, except for PhCH(CH_3)CH_2CH(PH)–SC•(C(CH_3)$_3$)$_2$. For the latter the G3(MP2)-RAD energy was calculated using the ONIOM approach with PhCH(CH_3)-S-C•(CH(CH_3)$_2$)$_2$ in core.

[b] W1 values were calculated explicitly for CH_3•, S=CH_2 and CH_3-S-C•(H_2). The rest of the energies were those of G3(MP2)-RAD corrected for W1 using the core species CH_3•, S=CH_2 and CH_3-S-C•(H_2) for the attacking radical, the RAFT agent and the forming radical, respectively.

c The G3(MP2)-RAD energies of S=C(C(CH_3)$_3$)$_2$, •CH(Ph)CH_2CH(CH_3)Ph and PhCH(CH_3)CH_2CH(PH)–SC•(C(CH_3)$_3$)$_2$ were calculated via the ONIOM approach using as core S=C(CH(CH_3)$_2$)$_2$, CH(CH_3)$_2$Ph and PhCH(CH_3)-S-C•(CH(CH_3)$_2$)$_2$, respectively. S=C-(*t*-Bu)$_2$ was calculated in the same manner in order to approximate the enthalpy of the reaction S=C(C(CH_3)$_3$)$_2$ + •CH(Ph)CH_2CH(CH_3)Ph = PhCH(CH_3)CH_2CH(PH)–SC•(C(CH_3)$_3$)$_2$, as the G3(MP2)-RAD calculation was not feasible for PhCH(CH_3)CH_2CH(PH)–SC•(C(CH_3)$_3$)$_2$.