Electronic Supplementary Information (ESI) for:

Hydrogen Atom Transfer Reactions in Thiophenol: Photogeneration of Two New Thione Isomers

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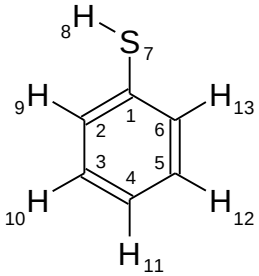
Table S1. Atom numbering and internal coordinates used in the normal mode analysis for thiophenol.



Internal coordinate definition	**Symbol**
$S_1 = (6^{-1/2})\ (r_{2,9}+2r_{3,10}+r_{4,11})$	ν_aCH
$S_2 = (10^{-1/2})\ (r_{2,9}+2r_{3,10}-2r_{5,12}-r_{6,13})$	ν_bCH
$S_3 = (3^{-1/2})\ (r_{2,9}-r_{4,11}+r_{6,13})$	ν_cCH
$S_4 = (10^{-1/2})\ (2r_{2,9}-r_{3,10}+r_{5,12}-2r_{6,13})$	ν_dCH
$S_5 = (11^{-1/2})\ (r_{2,9}-2r_{3,10}+r_{4,11}-2r_{5,12}+r_{6,13})$	ν_eCH
$S_6 = r_{7,8}$	νSH
$S_7 = (12^{-1/2})\ (r_{1,2}-2r_{2,3}+r_{3,4}+r_{4,5}-2r_{5,6}+r_{6,1})$	ν_aCC
$S_8 = (1/2)\ (r_{1,2}-r_{3,4}+r_{4,5}-r_{6,1})$	ν_bCC
$S_9 = (6^{-1/2})\ (r_{1,2}-r_{2,3}+r_{3,4}-r_{4,5}+r_{5,6}-r_{6,1})$	ν_cCC
$S_{10} = (2^{-1/2})\ (r_{1,2}+r_{6,1})$	ν_dCC
$S_{11} = (12^{-1/2})\ (r_{1,2}+2r_{2,3}+r_{3,4}-r_{4,5}-2r_{5,6}-r_{6,1})$	ν_eCC
$S_{12} = (2^{-1/2})\ (r_{3,4}+r_{4,5})$	ν_fCC
$S_{13} = r_{1,7}$	νCS
$S_{14} = (2^{-1/2})\ (\beta_{7,6,1}-\beta_{7,2,1})$	δCS
$S_{15} = \beta_{8,1,7}$	δSH
$S_{16} = (8^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}+\beta_{10,2,3}-\beta_{10,4,3}-\beta_{12,4,5}+\beta_{12,6,5}-\beta_{13,5,6}+\beta_{13,1,6})$	δ_aCH
$S_{17} = (12^{-1/2})\ (\beta_{10,2,3}-\beta_{10,4,3}+2\beta_{11,3,4}-2\beta_{11,5,4}+\beta_{12,4,5}-\beta_{12,6,5})$	δ_bCH
$S_{18} = (22^{-1/2})\ (2\beta_{9,1,2}-2\beta_{9,3,2}+\beta_{10,2,3}-\beta_{10,4,3}+\beta_{11,3,4}-\beta_{11,5,4}+\beta_{12,4,5}-\beta_{12,6,5}+2\beta_{13,5,6}-2\beta_{13,1,6})$	δ_cCH
$S_{19} = (8^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}-\beta_{10,2,3}+\beta_{10,4,3}+\beta_{12,4,5}-\beta_{12,6,5}-\beta_{13,5,6}+\beta_{13,1,6})$	δ_dCH
$S_{20} = (12^{-1/2})\ (\beta_{10,2,3}-\beta_{10,4,3}-2\beta_{11,3,4}+2\beta_{115,4}+\beta_{12,4,5}-\beta_{12,6,5})$	δ_eCH
$S_{21} = (6^{-1/2})\ (\beta_{6,2,1}-\beta_{1,3,2}+\beta_{2,4,3}-\beta_{3,5,4}+\beta_{4,6,5}-\beta_{5,1,6})$	δ_aR
$S_{22} = (12^{-1/2})\ (2\beta_{6,2,1}-\beta_{1,3,2}-\beta_{2,4,3}+2\beta_{3,5,4}-\beta_{4,6,5}-\beta_{5,1,6})$	δ_bR
$S_{23} = (1/2)\ (\beta_{1,3,2}-\beta_{2,4,3}+\beta_{4,6,5}-\beta_{5,1,6})$	δ_cR
$S_{24} = (6^{-1/2})\ (\tau_{4,3,2,1}-\tau_{5,4,3,2}+\tau_{6,5,4,3}-\tau_{1,6,5,4}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	τ_aR
$S_{25} = (1/2)\ (\tau_{5,4,3,2}-\tau_{6,5,4,3}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	τ_bR
$S_{26} = (12^{-1/2})\ (-\tau_{3,2,1,6}+2\tau_{4,3,2,1}-\tau_{5,4,3,2}-\tau_{6,5,4,3}+2\tau_{1,6,5,4}-\tau_{2,1,6,5})$	τ_cR
$S_{27} = (2^{-1/2})\ (\tau_{8,7,1,6}+\tau_{8,7,1,2})$	τSH
$S_{28} = \gamma_{7,6,1,2}$	γCS
$S_{29} = (3^{-1/2})\ (\gamma_{10,2,3,4}-\gamma_{11,3,4,5}+\gamma_{12,4,5,6})$	γ_aCH
$S_{30} = (1/2)\ (\gamma_{9,1,2,3}-\gamma_{10,2,3,4}+\gamma_{12,4,5,6}-\gamma_{13,5,6,1})$	γ_bCH
$S_{31} = (3^{-1/2})\ (\gamma_{9,1,2,3}-\gamma_{11,3,4,5}+\gamma_{13,5,6,1})$	γ_cCH
$S_{32} = (1/2)\ (\gamma_{9,1,2,3}+\gamma_{10,2,3,4}-\gamma_{12,4,5,6}-\gamma_{13,5,6,1})$	γ_dCH
$S_{33} = (5^{-1/2})\ (\gamma_{9,1,2,3}+\gamma_{10,2,3,4}+\gamma_{11,3,4,5}+\gamma_{12,4,5,6}+\gamma_{13,5,6,1})$	γ_eCH

Abbreviations:

$r_{i,j}$ – distance between atoms A_i and A_j ; $\beta_{i,j,k}$ – angle between the vectors A_kA_i and A_kA_j ;

$\tau_{i,j,k,l}$ – dihedral angle between the planes defined by A_i, A_j, A_k, and by A_j, A_k, A_l atoms;

$\gamma_{i,j,k,l}$ – angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.

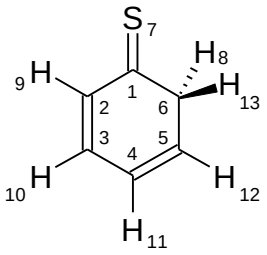
ν – stretching, δ – bending, γ – out-of-plane, τ – torsion.

Table S2. Experimental wavenumbers ($\tilde{\nu}$ / cm^{-1}) and relative integrated intensities (***I***) of the bands observed in the infrared spectrum of thiophenol (**PhSH**) monomers isolated in an Ar matrix compared with wavenumbers ($\tilde{\nu}$ / cm^{-1}), absolute infrared intensities (A^{th} / km mol^{-1}), and potential energy distribution (PED) calculated at the B3LYP/aug-cc-pVTZ level.[a]

Experiment Ar matrix		Calculation B3LYP/aug-cc-pVTZ				
$\tilde{\nu}$ [b]	***I***	sym [c]	mode No.	$\tilde{\nu}$ [d]	A^{th}	PED [e], %
3070	8	A'	Q1	3131	11	ν_aCH (96)
3056	6	A'	Q2	3119	22	ν_bCH (94)
3064	2	A'	Q3	3115	4	ν_cCH (93)
		A'	Q4	3104	0.04	ν_dCH (96)
3037	2	A'	Q5	3101	4	ν_eCH (99)
2610	0.6	A'	Q6	2634	0.4	νSH (100)
1599	3	A'				
1591	20	A'	Q7	1593	36	ν_aCC (69), δ_dCH (22)
1580	1	A'	Q8	1583	1	ν_bCC (69), δ_eCH (10)
1483	39	A'	Q9	1485	31	δ_aCH (67), ν_dCC (16), ν_fCC (15)
1446	11	A'	Q10	1449	7	δ_bCH (65), ν_eCC (34)
1330	vw [f]	A'	Q11	1332	1	δ_cCH (83)
1303,1298	vw [f]	A'	Q12	1289	2	ν_cCC (77), δ_eCH (11)
1185	1	A'	Q13	1183	2	δ_dCH (75), ν_aCC (26)
		A'	Q14	1158	0.3	δ_eCH (80), ν_cCC (13)
1121	11	A'	Q15	1091	30	ν_dCC (45), νCS (18), δ_aCH (17), δ_aR (15)
1097	12	A'	Q16	1083	4	ν_eCC (47), δ_bCH (32)
1072	1					
1027	7	A'	Q17	1027	10	ν_fCC (63), δ_aR (20), δ_aCH (15)
		A'	Q18	999	0.2	δ_aR (57), ν_dCC (23), ν_fCC (20)
		A"	Q19	987	0.02	γ_aCH (125)
		A"	Q20	967	0.004	γ_bCH (112)
915	7	A'	Q21	906	8	δSH (90)
891, 890	2	A"	Q22	898	1	γ_cCH (109)
		A"	Q23	832	0.02	γ_dCH (98)
735, 733	77	A"	Q24	740	50	γ_eCH (74), τ_aR (17), γCS (13)
701	11	A'	Q25	693	12	δ_bR (54), νCS (28), ν_dCC (11)
688, **687**	33	A"	Q26	689	22	τ_aR (95), γ_eCH (24)
		A'	Q27	619	0.1	δ_cR (88)
468	12	A"	Q28	471	11	τ_bR (57), γCS (40)
		A"	Q29	402	0.1	τ_cR (115)
		A'	Q30	402	0.4	νCS (50), δ_bR (37)
		A'	Q31	269	1	δCS (90)
		A"	Q32	182	3	τ_bR (53), γCS(34)
		A"	Q33	128	11	τSH (92)

[a] A reduced version of this table is provided in the main article Table 1;
[b] most intense components of split bands are shown in bold;
[c] sym – symmetry of irreducible representations of the C_s point group.
[d] theoretical wavenumbers were scaled by a factor of 0.980.
[e] PED's lower than 10% are not included. Internal coordinates used in the normal mode analysis are defined in Table S1;
[f] vw – very weak band, tentative assignment.

Table S3. Atom numbering and internal coordinates used in the normal mode analysis for cyclohexa-2,4-diene-1-thione.



Internal coordinate definition	**Symbol**
$S_1 = (6^{-1/2})\ (r_{4,11}+r_{3,10}+2r_{2,9})$	ν_fCH
$S_2 = (6^{-1/2})\ (r_{5,12}+2r_{4,11}-r_{2,9})$	ν_gCH
$S_3 = (6^{-1/2})\ (-r_{5,12}+2r_{3,10}-r_{2,9})$	ν_hCH
$S_4 = (6^{-1/2})\ (2r_{5,12}-r_{4,11}+r_{3,10})$	ν_iCH
$S_5 = (2^{-1/2})\ (r_{6,8}-r_{6,13})$	ν_aC6H$_2$
$S_6 = (2^{-1/2})\ (r_{6,8}+r_{6,13})$	ν_bC6H$_2$
$S_7 = (2^{-1/2})\ (r_{4,5}-r_{2,3})$	ν_gCC
$S_8 = (2^{-1/2})\ (r_{4,5}+r_{2,3})$	ν_hCC
$S_9 = (2^{-1/2})\ (r_{1,2}+r_{6,1})$	ν_iCC
$S_{10} = (2^{-1/2})\ (r_{1,2}-r_{6,1})$	ν_jCC
$S_{11} = (2^{-1/2})\ (r_{3,4}+r_{5,6})$	ν_kCC
$S_{12} = (2^{-1/2})\ (r_{3,4}-r_{5,6})$	ν_lCC
$S_{13} = r_{1,7}$	νCS
$S_{14} = (2^{-1/2})\ (\beta_{7,2,1}-\beta_{7,6,1})$	δCS
$S_{15} = (8^{-1/2})\ (\beta_{12,6,5}-\beta_{12,4,5}+\beta_{11,5,4}-\beta_{11,3,4}-\beta_{10,4,3}+\beta_{10,2,3}-\beta_{9,3,2}+\beta_{9,1,2})$	δ_fCH
$S_{16} = (8^{-1/2})\ (\beta_{12,6,5}-\beta_{12,4,5}+\beta_{11,5,4}-\beta_{11,3,4}+\beta_{10,4,3}-\beta_{10,2,3}+\beta_{9,3,2}-\beta_{9,1,2})$	δ_gCH
$S_{17} = (8^{-1/2})\ (\beta_{12,6,5}-\beta_{12,4,5}-\beta_{11,5,4}+\beta_{11,3,4}-\beta_{10,4,3}+\beta_{10,2,3}+\beta_{9,3,2}-\beta_{9,1,2})$	δ_hCH
$S_{18} = (8^{-1/2})\ (\beta_{12,6,5}-\beta_{12,4,5}-\beta_{11,5,4}+\beta_{11,3,4}+\beta_{10,4,3}-\beta_{10,2,3}-\beta_{9,3,2}+\beta_{9,1,2})$	δ_iCH
$S_{19} = \beta_{8,13,6}$	δ_aC6H$_2$
$S_{20} = (1/2)\ (\beta_{8,1,6}-\beta_{8,5,6}+\beta_{13,1,6}-\beta_{13,5,6})$	δ_bC6H$_2$
$S_{21} = (1/2)\ (\beta_{8,1,6}-\beta_{8,5,6}-\beta_{13,1,6}+\beta_{13,5,6})$	δ_cC6H$_2$
$S_{22} = (1/2)\ (\beta_{8,1,6}+\beta_{8,5,6}-\beta_{13,1,6}-\beta_{13,5,6})$	δ_dC6H$_2$
$S_{23} = (6^{-1/2})\ (\beta_{6,2,1}-\beta_{1,3,2}+\beta_{2,4,3}-\beta_{3,5,4}+\beta_{4,6,5}-\beta_{5,1,6})$	δ_aR
$S_{24} = (12^{-1/2})\ (2\beta_{6,2,1}-\beta_{1,3,2}-\beta_{2,4,3}+2\beta_{3,5,4}-\beta_{4,6,5}-\beta_{5,1,6})$	δ_bR
$S_{25} = (1/2)\ (\beta_{1,3,2}-\beta_{2,4,3}+\beta_{4,6,5}-\beta_{5,1,6})$	δ_cR
$S_{26} = (6^{-1/2})\ (\tau_{4,3,2,1}-\tau_{5,4,3,2}+\tau_{6,5,4,3}-\tau_{1,6,5,4}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	τ_aR
$S_{27} = (1/2)\ (\tau_{5,4,3,2}-\tau_{6,5,4,3}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	τ_bR
$S_{28} = (12^{-1/2})\ (-\tau_{3,2,1,6}+2\tau_{4,3,2,1}-\tau_{5,4,3,2}-\tau_{6,5,4,3}+2\tau_{1,6,5,4}-\tau_{2,1,6,5})$	τ_cR
$S_{29} = \gamma_{7,6,1,2}$	γCS
$S_{30} = (2^{-1/2})\ (\gamma_{12,6,5,4}+\gamma_{11,5,4,3})$	γ_fCH
$S_{31} = (2^{-1/2})\ (\gamma_{12,6,5,4}-\gamma_{11,5,4,3})$	γ_gCH
$S_{32} = (2^{-1/2})\ (\gamma_{10,4,3,2}+\gamma_{9,3,2,1})$	γ_hCH
$S_{33} = (2^{-1/2})\ (\gamma_{10,4,3,2}-\gamma_{9,3,2,1})$	γ_iCH

Abbreviations:

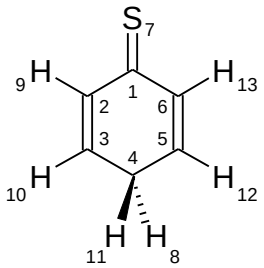
$r_{i,j}$ – distance between atoms A_i and A_j ; $\beta_{i,j,k}$ – angle between the vectors A_kA_i and A_kA_j ;
$\tau_{i,j,k,l}$ – dihedral angle between the planes defined by A_i, A_j, A_k, and by A_j, A_k, A_l atoms;
$\gamma_{i,j,k,l}$ – angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.
ν – stretching, δ – bending, γ – out-of-plane, τ – torsion.

Table S4. Experimental wavenumbers ($\tilde{\nu}$ / cm^{-1}) and relative integrated intensities (***I***) of the bands observed in the infrared spectrum of cyclohexa-2,4-diene-1-thione (form **24**) monomers isolated in an Ar matrix compared with wavenumbers ($\tilde{\nu}$ / cm^{-1}), absolute infrared intensities (A^{th} / km mol^{-1}), and potential energy distribution (PED) calculated at the B3LYP/aug-cc-pVTZ level.[a]

Experiment Ar matrix		Calculation B3LYP/aug-cc-pVTZ				
$\tilde{\nu}$ [b]	***I***	sym [c]	mode No.	$\tilde{\nu}$ [d]	A^{th}	PED [e], %
3088, 3075	44	A'	Q1	3131	7	ν_fCH (97)
3057		A'	Q2	3124	14	ν_gCH (98)
3039		A'	Q3	3104	11	ν_hCH (95)
		A'	Q4	3098	0.01	ν_iCH (95)
		A"	Q5	2963	0.01	ν_aC6H$_2$ (100)
		A'	Q6	2954	1	ν_bC6H$_2$ (100)
1635	10	A'	Q7	1649	13	ν_gCC (63), δ_hCH (18)
1534	50	A'	Q8	1539	76	ν_hCC (64)
1430	31	A'	Q9	1434	32	δ_fCH (68), ν_lCC (12)
1385, **1378**	15	A'	Q10	1388	23	δ_gCH (68)
1363	28	A'	Q11	1370	23	δ_aC6H$_2$ (91)
1328	6	A'	Q12	1326	5	δbC6H$_2$ (53), ν_jCC (12)
1233	5	A'	Q13	1236	10	ν_jCC (36), δ_iCH (16), δ_bC6H$_2$ (15)
1184	18	A'	Q14	1179	11	δ_hCH (58), ν_gCC (21)
		A"	Q15	1178	0.4	δ_cC6H$_2$ (94)
1156	36	A'	Q16	1155	34	δ_iCH (46), ν_jCC (14), νCS (10)
1136, 1128	89	A'	Q17	1123	103	νCS (31), δ_aR (23), δ_iCH (17)
		A"	Q18	1006	0.4	γ_iCH (107), γ_gCH (12)
		A"	Q19	987	0.2	γ_gCH (103), γ_iCH (10)
981	8	A'	Q20	980	8	ν_lCC (49), δ_fCH (11), δ_aR (11)
959	4	A'	Q21	955	4	ν_kCC (38), δ_aR (20), ν_iCC (13)
912	17	A'	Q22	902	18	ν_kCC (33), δ_aR (32), ν_lCC (11)
		A"	Q23	902	0.5	δ_dC6H$_2$ (39), γ_fCH (23), γ_hCH (18), γCS (13), τ_aR (10)
802	12	A"	Q24	818	8	γ_hCH (62), τ_aR (23), δ_dC6H$_2$ (16)
700	66	A"	Q25	709	40	γ_fCH (63), γ_hCH (13), γCS (11)
692	13	A'	Q26	688	6	ν_iCC (50), δ_bR (24), νCS (17)
577	3	A'	Q27	579	2	δ_cR (82), ν_jCC (11)
506	17	A"	Q28	511	14	δ_dC6H$_2$ (28), τ_cR (27), γCS (25), τ_aR (22)
		A"	Q29	434	2	τ_bR (48), γCS (28), τ_aR (27)
		A'	Q30	414	14	δ_bR (60), νCS (22)
		A'	Q31	309	1	δCS (87)
		A"	Q32	250	1	τ_cR (72), γCS (23), δ_dC6H$_2$ (10)
		A"	Q33	25	3	τ_bR (57), τ_aR (30)

[a] A reduced version of this table is provided in the main article Table 2;
[b] most intense components of split bands are shown in bold;
[c] sym – symmetry of irreducible representations of the C_s point group.
[d] theoretical wavenumbers were scaled by a factor of 0.980.
[e] PED's lower than 10% are not included. Internal coordinates used in the normal mode analysis are defined in Table S3.

Table S5. Atom numbering and internal symmetry coordinates used in the normal mode analysis for cyclohexa-2,5-diene-1-thione.



Symmetry coordinate definition		**Symbol**
$S_1 = (10^{-1/2})\ (2r_{2,9}+r_{3,10}+r_{5,12}+2r_{6,13})$	A_1	ν_iCH
$S_2 = (10^{-1/2})\ (2r_{2,9}+r_{3,10}-r_{5,12}-2r_{6,13})$	B_2	ν_kCH
$S_3 = (10^{-1/2})\ (-r_{2,9}+2r_{3,10}+2r_{5,12}-r_{6,13})$	A_1	ν_lCH
$S_4 = (10^{-1/2})\ (r_{2,9}-2r_{3,10}+2r_{5,12}-r_{6,13})$	B_2	ν_mCH
$S_5 = (2^{-1/2})\ (r_{4,8}-r_{4,11})$	B_1	ν_aC4H$_2$
$S_6 = (2^{-1/2})\ (r_{4,8}+r_{4,11})$	A_1	ν_bC4H$_2$
$S_7 = (2^{-1/2})\ (r_{2,3}+r_{5,6})$	A_1	ν_mCC
$S_8 = (2^{-1/2})\ (r_{2,3}-r_{5,6})$	B_2	ν_nCC
$S_9 = (2^{-1/2})\ (r_{1,2}+r_{6,1})$	A_1	ν_oCC
$S_{10} = (2^{-1/2})\ (r_{1,2}-r_{6,1})$	B_2	ν_pCC
$S_{11} = (2^{-1/2})\ (r_{3,4}+r_{4,5})$	A_1	ν_qCC
$S_{12} = (2^{-1/2})\ (r_{3,4}-r_{4,5})$	B_2	ν_rCC
$S_{13} = r_{1,7}$	A_1	νCS
$S_{14} = (2^{-1/2})\ (\beta_{7,6,1}-\beta_{7,2,1})$	B_2	δCS
$S_{15} = \beta_{8,11,4}$	A_1	δ_aC4H$_2$
$S_{16} = (8^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}+\beta_{10,2,3}-\beta_{10,4,3}-\beta_{12,4,5}+\beta_{12,6,5}-\beta_{13,5,6}+\beta_{13,1,6})$	A_1	δ_iCH
$S_{17} = (8^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}+\beta_{10,2,3}-\beta_{10,4,3}+\beta_{12,4,5}-\beta_{12,6,5}+\beta_{13,5,6}-\beta_{13,1,6})$	B_2	δ_kCH
$S_{18} = (20^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}-2\beta_{10,2,3}+2\beta_{10,4,3}+2\beta_{12,4,5}-2\beta_{12,6,5}-\beta_{13,5,6}+\beta_{13,1,6})$	A_1	δ_lCH
$S_{19} = (20^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}-2\beta_{10,2,3}+2\beta_{10,4,3}-2\beta_{12,4,5}+2\beta_{12,6,5}+\beta_{13,5,6}-\beta_{13,1,6})$	B_2	δ_mCH
$S_{20} = (1/2)\ (\beta_{8,3,4}-\beta_{8,5,4}+\beta_{11,3,4}-\beta_{11,5,4})$	B_2	δ_bC4H$_2$
$S_{21} = (1/2)\ (\beta_{8,3,4}-\beta_{8,5,4}-\beta_{11,3,4}+\beta_{11,5,4})$	A_2	δ_cC4H$_2$
$S_{22} = (1/2)\ (\beta_{8,3,4}+\beta_{8,5,4}-\beta_{11,3,4}-\beta_{11,5,4})$	B_1	δ_dC4H$_2$
$S_{23} = (6^{-1/2})\ (\beta_{6,2,1}-\beta_{1,3,2}+\beta_{2,4,3}-\beta_{3,5,4}+\beta_{4,6,5}-\beta_{5,1,6})$	A_1	δ_aR
$S_{24} = (12^{-1/2})\ (2\beta_{6,2,1}-\beta_{1,3,2}-\beta_{2,4,3}+2\beta_{3,5,4}-\beta_{4,6,5}-\beta_{5,1,6})$	A_1	δ_bR
$S_{25} = (1/2)\ (\beta_{1,3,2}-\beta_{2,4,3}+\beta_{4,6,5}-\beta_{5,1,6})$	B_2	δ_cR
$S_{26} = (6^{-1/2})\ (\tau_{4,3,2,1}-\tau_{5,4,3,2}+\tau_{6,5,4,3}-\tau_{1,6,5,4}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	B_1	τ_aR
$S_{27} = (1/2)\ (\tau_{5,4,3,2}-\tau_{6,5,4,3}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	B_1	τ_bR
$S_{28} = (12^{-1/2})\ (-\tau_{3,2,1,6}+2\tau_{4,3,2,1}-\tau_{5,4,3,2}-\tau_{6,5,4,3}+2\tau_{1,6,5,4}-\tau_{2,1,6,5})$	A_2	τ_cR
$S_{29} = \gamma_{7,6,1,2}$	B_1	γCS
$S_{30} = (1/2)\ (\gamma_{9,1,2,3}-\gamma_{10,2,3,4}-\gamma_{12,4,5,6}+\gamma_{13,5,6,1})$	B_1	γ_iCH
$S_{31} = (1/2)\ (\gamma_{9,1,2,3}-\gamma_{10,2,3,4}+\gamma_{12,4,5,6}-\gamma_{13,5,6,1})$	A_2	γ_kCH
$S_{32} = (1/2)\ (\gamma_{9,1,2,3}+\gamma_{10,2,3,4}-\gamma_{12,4,5,6}-\gamma_{13,5,6,1})$	A_2	γ_lCH
$S_{33} = (1/2)\ (\gamma_{9,1,2,3}+\gamma_{10,2,3,4}+\gamma_{12,4,5,6}+\gamma_{13,5,6,1})$	B_1	γ_mCH

Abbreviations:

$r_{i,j}$ – distance between atoms A_i and A_j ; $\beta_{i,j,k}$ – angle between the vectors A_kA_i and A_kA_j ;

$\tau_{i,j,k,l}$ – dihedral angle between the planes defined by A_i, A_j, A_k, and by A_j, A_k, A_l atoms;

$\gamma_{i,j,k,l}$ – angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.

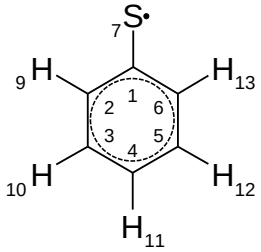
ν – stretching, δ – bending, γ – out-of-plane, τ – torsion.

Table S6. Experimental wavenumbers ($\tilde{\nu}$ / cm^{-1}) and relative integrated intensities (***I***) of the bands observed in the infrared spectrum of cyclohexa-2,5-diene-1-thione (form **25**) monomers isolated in an Ar matrix compared with wavenumbers ($\tilde{\nu}$ / cm^{-1}), absolute infrared intensities (A^{th} / km mol^{-1}), and potential energy distribution (PED) calculated at the B3LYP/aug-cc-pVTZ level.[a]

Experiment Ar matrix		Calculation B3LYP/aug-cc-pVTZ				
$\tilde{\nu}$ [b]	***I***	sym [c]	mode No.	$\tilde{\nu}$ [d]	A^{th}	PED [e], %
		A_1	Q1	3128	2	ν_jCH (99)
		B_2	Q2	3125	10	ν_kCH (97)
		A_1	Q3	3096	5	ν_lCH (98)
		B_2	Q4	3096	10	ν_mCH (98)
		B_1	Q5	2916	4	ν_aC4H_2 (100)
		A_1	Q6	2915	10	ν_bC4H_2 (100)
1640, **1632**	82	A_1	Q7	1650	87	ν_mCC (68), δ_lCH (15)
1582	8	B_2	Q8	1588	11	ν_nCC (80), δ_mCH (11)
1417	30	A_1	Q9	1422	26	δ_jCH (82), ν_oCC (10)
1389	45	A_1	Q10	1393	40	δ_aC4H_2 (100)
1393	16	B_2	Q11	1392	13	δ_kCH (52), ν_pCC (18), ν_rCC (14), δ_cR (12)
		B_2	Q12	1349	0.4	δ_bC4H_2 (53), ν_rCC (19), δ_mCH (15)
1258	3	B_2	Q13	1261	2	ν_pCC (39), δ_kCH (37), δ_mCH (13)
1213	15	A_1	Q14	1211	11	δ_lCH (64), ν_mCC (19), νCS (13)
		A_2	Q15	1175	0	δ_cC4H_2 (91)
1145	90	A_1	Q16	1136	116	νCS (38), δ_aR (20), δ_lCH (18), ν_oCC (16)
		B_2	Q17	1125	1	δ_mCH (59), δ_bC4H_2 (18), ν_pCC (16)
		B_1	Q18	1014	0.03	γ_jCH (116)
		A_2	Q19	1002	0	γ_kCH (113)
980	4	B_2	Q20	973	5	ν_rCC (56), δ_bC4H_2 (20), ν_nCC (11)
961	3	A_1	Q21	958	4	δ_aR (61), ν_oCC (29)
917	18	B_1	Q22	925	17	δ_dC4H_2 (49), γ_mCH (38), τ_aR (14)
878	28	A_1	Q23	869	30	ν_qCC (83)
784, 783	27	B_1	Q24	795	17	γ_mCH (38), τ_aR (31), γCS (29), δ_dC4H_2 (12)
		A_2	Q25	753	0	γ_lCH (93)
		A_1	Q26	695	3	ν_oCC (38), δ_bR (25), νCS (22)
593	10	B_2	Q27	580	3	δ_cR (81), ν_pCC (12)
550	40	B_1	Q28	553	29	γCS (27), δ_dC4H_2 (24), γ_mCH (24), τ_aR (20)
		A_1	Q29	424	2	δ_bR (65), νCS (22)
		A_2	Q30	369	0	τ_cR (117)
		B_2	Q31	308	1	δCS (87)
		B_1	Q32	302	0.1	τ_aR (53), γCS (30), τ_bR (13), δ_dC4H_2 (10)
		B_1	Q33	104	0.01	τ_bR (84), γCS (12)

[a] A reduced version of this table is provided in the main article Table 3;
[b] most intense components of split bands are shown in bold;
[c] sym – symmetry of irreducible representations of the C_{2v} point group.
[d] theoretical wavenumbers were scaled by a factor of 0.980.
[e] PED's lower than 10% are not included. Internal coordinates used in the normal mode analysis are defined in Table S5.

Table S7. Atom numbering [a] and internal symmetry coordinates used in the normal mode analysis for phenylthiyl radical.



Symmetry coordinate definition		**Symbol**
$S_1 = (5^{-1/2})\ (r_{2,9}+r_{3,10}+r_{4,11}+r_{5,12}+r_{6,13})$	A_1	ν_nCH
$S_2 = (10^{-1/2})\ (2r_{2,9}+r_{3,10}-r_{5,12}-2r_{6,13})$	B_2	ν_oCH
$S_3 = (14^{-1/2})\ (-2r_{2,9}+r_{3,10}+2r_{4,11}+r_{5,12}-2r_{6,13})$	A_1	ν_pCH
$S_4 = (10^{-1/2})\ (r_{2,9}-2r_{3,10}+2r_{5,12}-r_{6,13})$	B_2	ν_qCH
$S_5 = (14^{-1/2})\ (r_{2,9}-2r_{3,10}+2r_{4,11}-2r_{5,12}+r_{6,13})$	A_1	ν_rCH
$S_6 = (12^{-1/2})\ (-r_{1,2}+2r_{2,3}-r_{3,4}-r_{4,5}+2r_{5,6}-r_{6,1})$	A_1	ν_sCC
$S_7 = (1/2)\ (r_{1,2}-r_{3,4}+r_{4,5}-r_{6,1})$	B_2	ν_tCC
$S_8 = (6^{-1/2})\ (r_{1,2}-r_{2,3}+r_{3,4}-r_{4,5}+r_{5,6}-r_{6,1})$	B_2	ν_uCC
$S_9 = (6^{-1/2})\ (r_{1,2}+r_{2,3}+r_{3,4}-r_{4,5}-r_{5,6}-r_{6,1})$	B_2	ν_vCC
$S_{10} = (1/2)\ (r_{1,2}-r_{3,4}-r_{4,5}+r_{6,1})$	A_1	ν_wCC
$S_{11} = (6^{-1/2})\ (r_{1,2}+r_{2,3}+r_{3,4}+r_{4,5}+r_{5,6}+r_{6,1})$	A_1	ν_xCC
$S_{12} = r_{1,7}$	A_1	νCS
$S_{13} = (2^{-1/2})\ (\beta_{7,6,1}-\beta_{7,2,1})$	B_2	δCS
$S_{14} = (8^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}+\beta_{10,2,3}-\beta_{10,4,3}-\beta_{12,4,5}+\beta_{12,6,5}-\beta_{8,5,6}+\beta_{13,1,6})$	A_1	δ_nCH
$S_{15} = (6^{-1/2})\ (\beta_{10,2,3}-\beta_{10,4,3}+\beta_{11,3,4}-\beta_{11,5,4}+\beta_{12,4,5}-\beta_{12,6,5})$	B_2	δ_oCH
$S_{16} = (10^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}+\beta_{10,2,3}-\beta_{10,4,3}+\beta_{11,3,4}-\beta_{11,5,4}+\beta_{12,4,5}-\beta_{12,6,5}+\beta_{13,5,6}-\beta_{13,1,6})$	B_2	δ_pCH
$S_{17} = (8^{-1/2})\ (\beta_{9,1,2}-\beta_{9,3,2}-\beta_{10,2,3}+\beta_{10,4,3}+\beta_{12,4,5}-\beta_{12,6,5}-\beta_{13,5,6}+\beta_{13,1,6})$	A_1	δ_qCH
$S_{18} = (28^{-1/2})(\beta_{9,1,2}-\beta_{9,3,2}-2\beta_{10,2,3}+2\beta_{10,4,3}+2\beta_{11,3,4}-2\beta_{11,5,4}-2\beta_{12,4,5}+2\beta_{12,6,5}+\beta_{13,5,6}-\beta_{13,1,6})$	B_2	δ_rCH
$S_{19} = (6^{-1/2})\ (\beta_{6,2,1}-\beta_{1,3,2}+\beta_{2,4,3}-\beta_{3,5,4}+\beta_{4,6,5}-\beta_{5,1,6})$	A_1	δ_aR
$S_{20} = (12^{-1/2})\ (2\beta_{6,2,1}-\beta_{1,3,2}-\beta_{2,4,3}+2\beta_{3,5,4}-\beta_{4,6,5}-\beta_{5,1,6})$	A_1	δ_bR
$S_{21} = (1/2)\ (\beta_{1,3,2}-\beta_{2,4,3}+\beta_{4,6,5}-\beta_{5,1,6})$	B_2	δ_cR
$S_{22} = (6^{-1/2})\ (\tau_{4,3,2,1}-\tau_{5,4,3,2}+\tau_{6,5,4,3}-\tau_{1,6,5,4}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	B_1	τ_aR
$S_{23} = (1/2)\ (\tau_{5,4,3,2}-\tau_{6,5,4,3}+\tau_{2,1,6,5}-\tau_{3,2,1,6})$	B_1	τ_bR
$S_{24} = (12^{-1/2})\ (-\tau_{3,2,1,6}+2\tau_{4,3,2,1}-\tau_{5,4,3,2}-\tau_{6,5,4,3}+2\tau_{1,6,5,4}-\tau_{2,1,6,5})$	A_2	τ_cR
$S_{25} = \gamma_{7,6,1,2}$	B_1	γCS
$S_{26} = (5^{-1/2})\ (\gamma_{9,1,2,3}-\gamma_{10,2,3,4}+\gamma_{11,3,4,5}-\gamma_{12,4,5,6}+\gamma_{13,5,6,1})$	B_1	γ_nCH
$S_{27} = (1/2)\ (\gamma_{9,1,2,3}-\gamma_{10,2,3,4}+\gamma_{12,4,5,6}-\gamma_{13,5,6,1})$	A_2	γ_oCH
$S_{28} = (3^{-1/2})\ (\gamma_{9,1,2,3}-\gamma_{11,3,4,5}+\gamma_{13,5,6,1})$	B_1	γ_pCH
$S_{29} = (1/2)\ (\gamma_{9,1,2,3}+\gamma_{10,2,3,4}-\gamma_{12,4,5,6}-\gamma_{13,5,6,1})$	A_2	γ_qCH
$S_{30} = (5^{-1/2})\ (\gamma_{9,1,2,3}+\gamma_{10,2,3,4}+\gamma_{11,3,4,5}+\gamma_{12,4,5,6}+\gamma_{13,5,6,1})$	B_1	γ_rCH

Abbreviations:

$r_{i,j}$ – distance between atoms A_i and A_j ; $\beta_{i,j,k}$ – angle between the vectors A_kA_i and A_kA_j ;
$\tau_{i,j,k,l}$ – dihedral angle between the planes defined by A_i, A_j, A_k, and by A_j, A_k, A_l atoms;
$\gamma_{i,j,k,l}$ – angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.
ν – stretching, δ – bending, γ – out-of-plane, τ – torsion.

[a] Atom with number 8 is missing on purpose. This symbolizes the H8 atom removed from the SH group (compare with numbering of thiophenol, Table S1).

Table S8. Wavenumbers ($\tilde{\nu}$ / cm^{-1}), absolute infrared intensities (A^{th} / km mol^{-1}) and potential energy distribution (PED) of thiyl radical (**PhS•**) calculated at the B3LYP/aug-cc-pVTZ level.

Calculation B3LYP/aug-cc-pVTZ				
sym [a]	mode No.	$\tilde{\nu}$ [b]	A^{th}	PED [c], %
A_1	Q1	3137	6	ν_nCH (94)
B_2	Q2	3133	7	ν_oCH (99)
A_1	Q3	3125	9	ν_pCH (96)
B_2	Q4	3115	7	ν_qCH (100)
A_1	Q5	3106	0.01	ν_rCH (102)
A_1	Q6	**1565**	**32** [d]	ν_sCC (64), δ_qCH (23)
B_2	Q7	1547	0.5	ν_tCC (55), δ_oCH (15)
A_1	Q8	1457	0.7	δ_nCH (70), ν_wCC (26)
B_2	Q9	1434	12 [e]	δ_oCH (66), ν_vCC (22), ν_tCC (10)
B_2	Q10	**1318**	**7** [d]	δ_pCH (72), ν_uCC (33)
B_2	Q11	1276	0.1	ν_uCC (53), δ_pCH (32), ν_vCC (10)
A_1	Q12	1176	2	δ_qCH (72), ν_sCC (26)
B_2	Q13	1155	1	δ_rCH (83), ν_tCC (11), ν_uCC (11)
B_2	Q14	1075	3	ν_vCC (56), δ_oCH (47)
A_1	Q15	**1061**	**14** [d]	δ_aR (32), νCS (26), ν_wCC (21)
A_1	Q16	1021	1	ν_wCC (44), δ_nCH (18), δ_aR (23), ν_xCC (14)
B_1	Q17	996	0.01	γ_nCH (125)
A_1	Q18	989	3	ν_xCC (61), δ_aR (35)
A_2	Q19	983	0	γ_oCH (115)
B_1	Q20	934	1	γ_pCH (108)
A_2	Q21	836	0	γ_qCH (100)
B_1	Q22	**759**	**38** [d]	γ_rCH (69), τ_aR (30), γCS (14)
A_1	Q23	717	0.3	δ_bR (44), νCS (29), ν_xCC (10)
B_1	Q24	**675**	**36** [d]	τ_aR (77), γ_rCH (31)
B_2	Q25	610	0.002	δ_cR (86), ν_tCC (10)
B_1	Q26	455	4	τ_bR (63), γCS (34)
A_1	Q27	419	1	δ_bR (46), νCS (41)
A_2	Q28	377	0	τ_cR (115)
B_2	Q29	292	0.002	δCS (90)
B_1	Q30	158	0.008	τ_bR (48), γCS (47)

[a] sym – symmetry of irreducible representations of the C_{2v} point group.
[b] theoretical wavenumbers were scaled by a factor of 0.980.
[c] PED's lower than 10% are not included. Internal coordinates used in the normal mode analysis are defined in Table S7;
[d] bold formatting designates the five modes, with the strongest intensities in infrared, whose counterparts were identified in the experimental spectra, see Figures S1-S4.
[e] Q9 mode of the radical, despite relatively intense in infrared, could not be identified in experiment, because it overlaps with a stronger absorption of cyclohexa-2,4-diene-1-thione (form **24**), predicted at the same frequency (see Table S4, mode Q9).

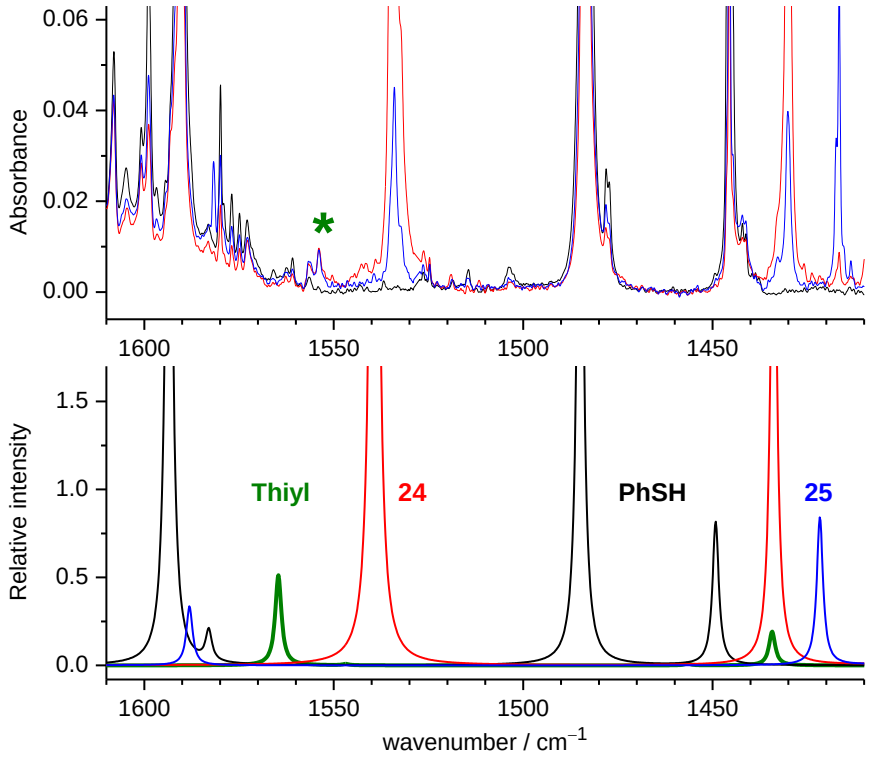


Figure S1. See caption of Figure S2 for details.

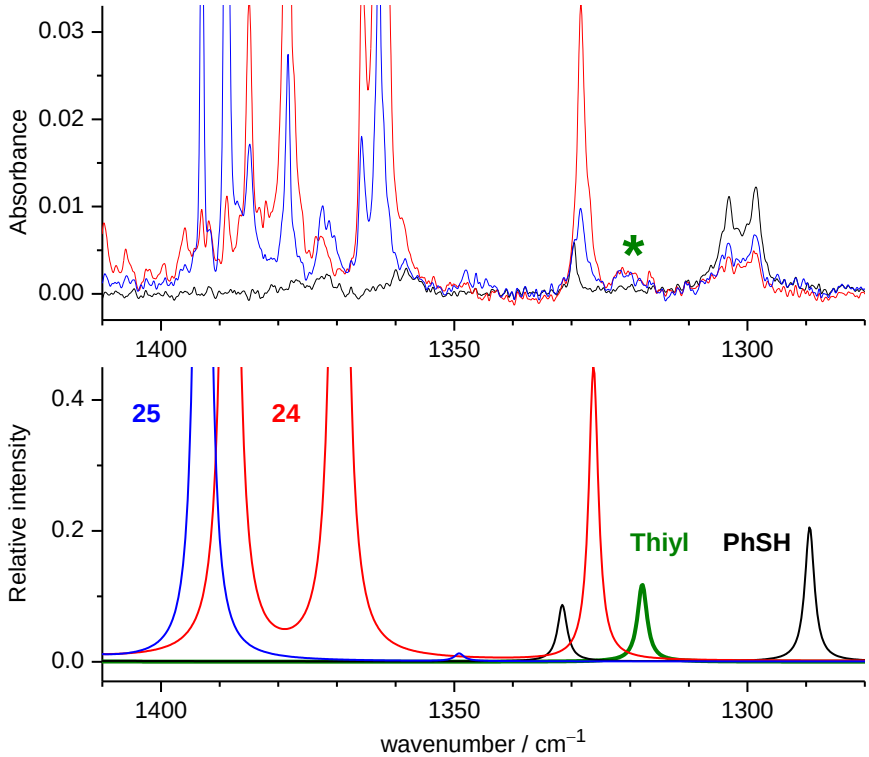


Figure S2. Spectral indication of the phenylthiyl radical. Top panel: black – spectrum of the freshly deposited matrix; red – spectrum recorded after subsequent 10 min of UV irradiation at 285 nm; blue - spectrum recorded after subsequent 80 min of UV irradiations at 425 - 400 nm; green asterisks – bands assigned to the phenylthiyl radical. Bottom panel: black, red, blue, green – simulated spectra of **PhSH**, **24**, **25**, and **PhS• (Thiyl)** species, respectively. See section 5.4 of the main article for the details of simulation.

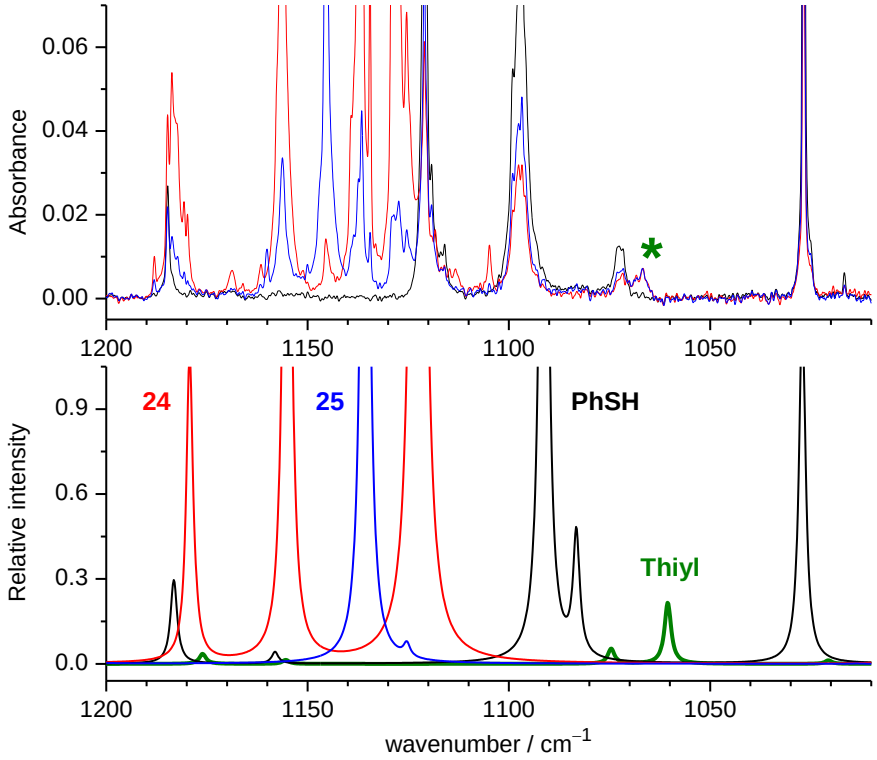


Figure S3. See caption of Figure S4 for details.

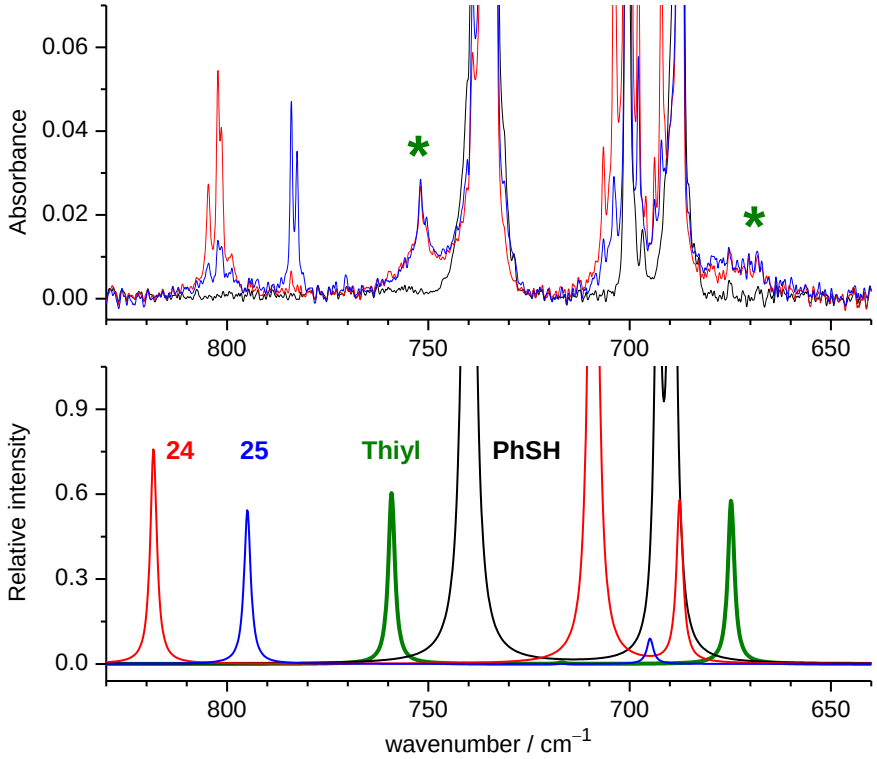
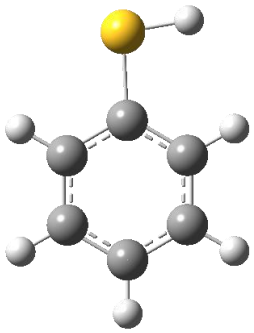


Figure S4. Spectral indication of the phenylthiyl radical. Top panel: black – spectrum of the freshly deposited matrix; red – spectrum recorded after subsequent 10 min of UV irradiation at 285 nm; blue - spectrum recorded after subsequent 80 min of UV irradiations at 425 - 400 nm; green asterisks – bands assigned to the phenylthiyl radical. Bottom panel: black, red, blue, green – simulated spectra of **PhSH**, **24**, **25**, and **PhS• (Thiyl)** species, respectively. See section 5.4 of the main article for the details of simulation.

Table S9. Cartesian coordinates for the optimized geometries of **PhSH**, **24**, **25**, and **PhS•** species calculated at the B3LYP/aug-cc-pVTZ level.

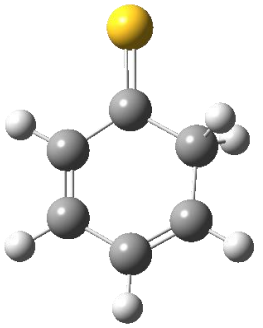
Thiophenol, **PhSH**
Symmetry C_s

C	0.000000	0.505242	0.000000
C	1.206585	-0.194170	0.000000
C	1.204725	-1.583553	0.000000
C	0.007086	-2.289119	0.000000
C	-1.194957	-1.590258	0.000000
C	-1.203314	-0.201716	0.000000
S	-0.086480	2.284005	0.000000
H	1.237329	2.514663	0.000000
H	2.146514	0.340964	0.000000
H	2.147475	-2.114245	0.000000
H	0.010423	-3.370142	0.000000
H	-2.134598	-2.126242	0.000000
H	-2.144219	0.332365	0.000000



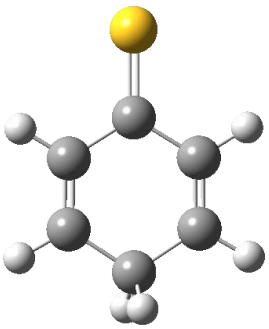
Cyclohexa-2,4-diene-1-thione (form **24**)
Symmetry C_s

C	0.000000	0.639903	0.000000
C	-1.259919	-0.201673	0.000000
C	-1.081129	-1.684614	0.000000
C	0.132925	-2.248560	0.000000
C	1.316258	-1.417653	0.000000
C	1.254206	-0.063850	0.000000
S	-0.071353	2.291426	0.000000
H	-1.871862	0.091590	0.859796
H	-1.871862	0.091590	-0.859796
H	-1.976697	-2.293118	0.000000
H	0.247545	-3.323754	0.000000
H	2.284462	-1.902323	0.000000
H	2.156013	0.531885	0.000000



Cyclohexa-2,4-diene-1-thione (form **24**)
Symmetry C_{2v}

C	0.000000	0.000000	0.661309
C	0.000000	1.237678	-0.103678
C	0.000000	1.246949	-1.443957
C	0.000000	0.000000	-2.257065
C	0.000000	-1.246949	-1.443957
C	0.000000	-1.237678	-0.103678
S	0.000000	0.000000	2.316069
H	-0.863255	0.000000	-2.937514
H	0.000000	2.160338	0.459799
H	0.000000	2.189550	-1.977763
H	0.863255	0.000000	-2.937514
H	0.000000	-2.189550	-1.977763
H	0.000000	-2.160338	0.459799



Phenylthiyl radical, **PhS•**
Symmetry C_{2v}

C	0.000000	0.000000	0.574267
C	0.000000	1.214509	-0.149758
C	0.000000	1.209548	-1.532167
C	0.000000	0.000000	-2.227731
C	0.000000	-1.209548	-1.532167
C	0.000000	-1.214509	-0.149758
S	0.000000	0.000000	2.297600
H	0.000000	2.144117	0.401162
H	0.000000	2.144793	-2.075353
H	0.000000	0.000000	-3.309330
H	0.000000	-2.144793	-2.075353
H	0.000000	-2.144117	0.401162

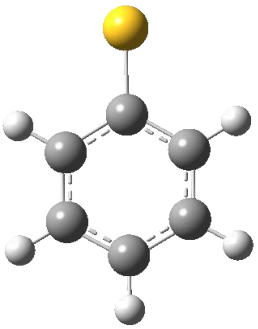
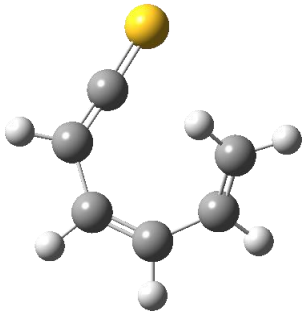


Table S10. Cartesian coordinates for the optimized geometries of the eight open-ring thioketene (**TK**) isomers of thiophenol (named by capital letters from **A** to **H**, in no particular order) calculated at the B3LYP/aug-cc-pVTZ level.

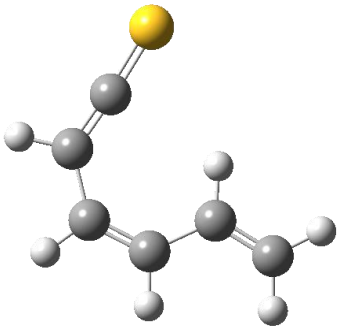
Open ring thioketene isomer (form **TK-A**)
Symmetry C_1

C	-1.132653	-0.604072	0.065760
C	1.013714	1.745338	0.542013
C	1.794032	1.050669	-0.289255
C	2.050567	-0.384706	-0.276671
C	1.243491	-1.421952	0.020441
C	-0.181723	-1.479925	0.309692
S	-2.293940	0.396282	-0.199118
H	0.934401	2.820298	0.457601
H	0.454385	1.277006	1.339337
H	2.369611	1.605906	-1.024303
H	3.062931	-0.656079	-0.558027
H	1.707223	-2.400953	0.022907
H	-0.550088	-2.418813	0.716488



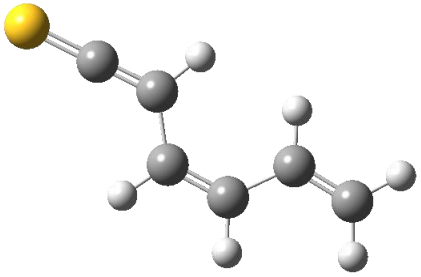
Open ring thioketene isomer (form **TK-B**)
Symmetry C_s

C	1.036925	-1.048819	0.000000
C	-1.568462	2.677319	0.000000
C	-1.075159	1.433374	0.000000
C	-1.894944	0.245378	0.000000
C	-1.489460	-1.042187	0.000000
C	-0.153382	-1.611555	0.000000
S	2.484913	-0.471906	0.000000
H	-2.635741	2.861930	0.000000
H	-0.921092	3.542568	0.000000
H	0.000000	1.305467	0.000000
H	-2.966546	0.413360	0.000000
H	-2.266483	-1.795500	0.000000
H	-0.101862	-2.698396	0.000000



Open ring thioketene isomer (form **TK-C**)
Symmetry C_s

C	-0.816851	1.579359	0.000000
C	2.553960	-3.052245	0.000000
C	1.815393	-1.937061	0.000000
C	0.370500	-1.922132	0.000000
C	-0.430558	-0.835425	0.000000
C	0.000000	0.546440	0.000000
S	-1.778637	2.803688	0.000000
H	2.096089	-4.033660	0.000000
H	3.633896	-3.015317	0.000000
H	2.330593	-0.982615	0.000000
H	-0.114512	-2.891875	0.000000
H	-1.501394	-0.993391	0.000000
H	1.058851	0.784239	0.000000



Open ring thioketene isomer (form **TK-D**)
Symmetry C_1

C	1.563780	-0.140685	0.094692
C	-2.765746	-1.291744	-0.191103
C	-2.872587	-0.009478	0.169918
C	-1.925050	1.070096	-0.077038
C	-0.577517	1.025714	-0.095044
C	0.252179	-0.122766	0.200728
S	3.115344	-0.173342	-0.036910
H	-1.928063	-1.665359	-0.763733
H	-3.547068	-2.000204	0.046654
H	-3.785436	0.295722	0.673788
H	-2.372187	2.046735	-0.225352
H	-0.047797	1.944955	-0.311436
H	-0.215304	-1.035207	0.557721

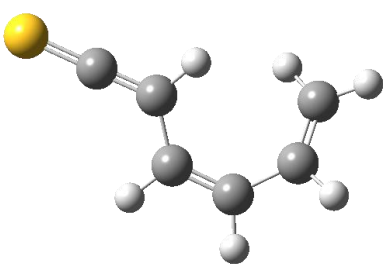
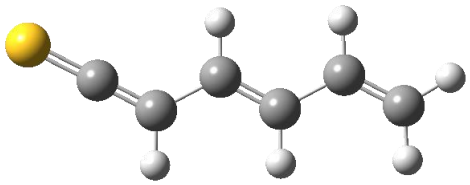


Table S10 (continued). Cartesian coordinates for the optimized geometries of the eight open-ring thioketene (**TK**) isomers of thiophenol (named by capital letters from **A** to **H**, in no particular order) calculated at the B3LYP/aug-cc-pVTZ level.

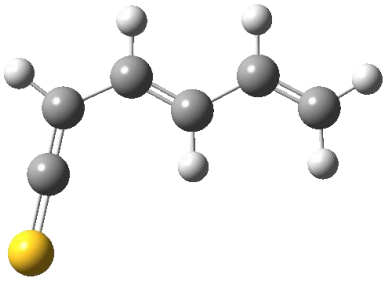
Open ring thioketene isomer (form **TK-E**)
Symmetry C_s

C	-0.278343	-1.924333	0.000000
C	1.083645	4.044391	0.000000
C	0.307613	2.954758	0.000000
C	0.797837	1.597067	0.000000
C	0.000000	0.511289	0.000000
C	0.483622	-0.849685	0.000000
S	-1.173533	-3.198376	0.000000
H	2.163999	3.969681	0.000000
H	0.661227	5.038877	0.000000
H	-0.771368	3.077498	0.000000
H	1.875471	1.462576	0.000000
H	-1.075725	0.646456	0.000000
H	1.556685	-1.022000	0.000000



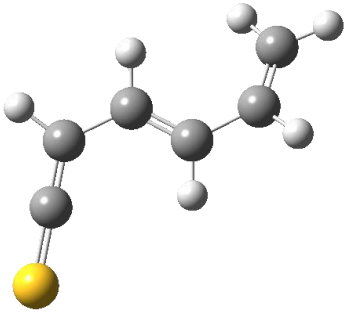
Open ring thioketene isomer (form **TK-F**)
Symmetry C_s

C	1.069778	-1.417470	0.000000
C	-1.882828	3.116794	0.000000
C	-2.074998	1.792720	0.000000
C	-1.018435	0.809659	0.000000
C	-1.239036	-0.519160	0.000000
C	-0.237985	-1.570796	0.000000
S	2.615018	-1.234044	0.000000
H	-0.887618	3.543578	0.000000
H	-2.713073	3.808304	0.000000
H	-3.090971	1.408717	0.000000
H	0.000000	1.186105	0.000000
H	-2.263711	-0.872478	0.000000
H	-0.583881	-2.599991	0.000000



Open ring thioketene isomer (form **TK-G**)
Symmetry C_1

C	1.711646	0.406967	-0.010509
C	-3.631517	-0.050085	0.342455
C	-2.631647	-0.766390	-0.179522
C	-1.217945	-0.416410	-0.189034
C	-0.724985	0.834537	-0.143692
C	0.677405	1.214528	-0.115781
S	2.932179	-0.550105	0.116670
H	-3.461160	0.883375	0.863323
H	-4.655190	-0.390031	0.274232
H	-2.873651	-1.722817	-0.632381
H	-0.525336	-1.248189	-0.267653
H	-1.415285	1.669383	-0.142874
H	0.918016	2.271086	-0.184864



Open ring thioketene isomer (form **TK-H**)
Symmetry C_1

C	-1.830096	0.247918	0.037614
C	3.416058	-1.111609	0.100706
C	3.113315	0.170035	-0.125464
C	1.806582	0.799562	0.006288
C	0.618142	0.170401	-0.053361
C	-0.653765	0.836763	0.107045
S	-3.223374	-0.443438	-0.038579
H	2.682135	-1.825789	0.451314
H	4.420832	-1.480620	-0.048184
H	3.916734	0.836388	-0.422996
H	1.809839	1.876449	0.141541
H	0.585176	-0.895509	-0.244944
H	-0.662136	1.905663	0.303556

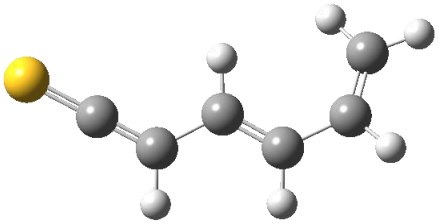


Table S11.
Harmonic wavenumbers (ν /cm^{-1}) and absolute intensities (A^{th} / km mol^{-1}) of the open-ring thioketene (**TK**) isomers **A-D** of thiophenol calculated at the B3LYP/aug-cc-pVTZ level.[a,b]

TK-A		TK-B		TK-C		TK-D	
ν	A^{th}	ν	A^{th}	ν	A^{th}	ν	A^{th}
69.7	0.2	31.0	0.2	64.0	0.0	75.3	0.4
99.4	0.2	98.0	0.1	97.1	0.4	103.8	1.4
129.4	1.6	133.8	0.9	134.4	0.3	148.0	4.2
186.4	0.5	199.0	0.9	197.7	0.6	195.0	0.2
342.9	1.0	371.3	3.1	342.1	0.5	323.5	0.2
379.0	10.1	371.6	9.1	357.3	7.7	391.9	1.8
420.6	1.6	413.8	0.5	404.6	3.8	421.7	4.1
570.8	7.8	521.0	15.4	522.3	29.2	526.0	17.1
586.1	54.6	619.7	44.9	640.5	4.8	613.6	33.8
709.6	8.7	703.4	28.9	645.2	38.4	714.2	14.0
735.1	13.6	723.2	2.0	746.8	5.5	751.9	19.7
808.4	7.5	830.3	3.3	822.5	6.5	807.0	7.9
851.3	1.4	840.3	2.2	890.6	27.5	886.5	9.8
910.3	8.1	926.1	5.2	934.3	15.2	932.8	46.5
955.0	39.1	940.0	46.8	937.1	52.4	951.5	34.3
994.5	4.3	985.7	0.2	982.4	1.6	994.8	3.0
1031.6	11.7	1035.0	11.2	1028.3	11.8	1035.3	11.2
1062.1	4.7	1059.1	4.7	1073.1	3.3	1095.2	3.3
1111.1	1.0	1173.8	0.0	1190.3	0.9	1110.0	4.7
1267.8	3.3	1277.9	11.1	1246.8	21.3	1240.4	16.1
1324.9	3.7	1318.5	5.4	1282.2	29.4	1278.7	16.5
1340.5	2.5	1334.3	2.3	1335.2	2.2	1337.3	0.3
1442.1	13.3	1410.2	3.7	1407.6	1.2	1442.8	4.5
1471.2	2.9	1481.2	11.0	1481.1	5.9	1471.9	3.2
1639.0	54.6	1624.7	22.3	1626.0	5.6	1634.6	59.0
1678.2	6.2	1669.7	45.2	1674.0	80.5	1676.2	8.8
1791.1	**418.1**	**1784.3**	**460.9**	**1787.9**	**716.2**	**1788.6**	**688.3**
3112.3	9.6	3108.4	11.0	3132.3	2.8	3117.3	19.2
3117.1	10.8	3134.5	2.2	3137.9	10.1	3131.2	22.3
3131.5	11.5	3138.4	5.5	3143.3	2.6	3140.5	7.7
3148.2	2.7	3167.8	0.0	3147.3	7.0	3146.4	0.7
3158.8	17.4	3171.6	18.0	3171.7	11.6	3167.0	12.5
3229.3	7.7	3224.1	9.6	3224.3	10.2	3225.2	12.7

[a] Calculated wavenumbers are not scaled;
[b] The frequency and intensity of the antisymmetric C=C=S vibration is shown in bold for each thioketene isomer. This strongest infrared mode of thioketene is depicted graphically in Figure 9a of the main article.

Table S11 (continued).
Harmonic wavenumbers (ν /cm^{-1}) and absolute intensities (A^{th} / km mol^{-1}) of the open-ring thioketene (**TK**) isomers **E-H** of thiophenol calculated at the B3LYP/aug-cc-pVTZ level.[a,b]

TK-E		TK-F		TK-G		TK-H	
ν	A^{th}	ν	A^{th}	ν	A^{th}	ν	A^{th}
74.5	0.1	72.7	0.0	44.7	0.1	79.5	0.3
85.8	1.1	88.5	0.0	83.8	0.2	84.0	0.2
192.6	0.4	156.6	2.2	180.4	0.4	132.0	2.3
214.6	1.9	210.6	4.1	195.0	1.2	225.1	0.3
269.9	2.3	299.0	0.9	249.4	3.9	249.6	2.5
388.8	2.4	385.0	9.5	361.1	2.1	342.8	2.0
396.5	5.0	403.6	5.6	387.2	8.8	398.2	5.4
448.8	0.3	465.5	1.1	534.6	33.5	505.8	31.0
597.1	29.6	638.4	0.4	629.8	5.6	601.7	2.4
650.1	0.5	673.0	36.3	689.7	21.1	660.3	4.4
734.5	22.5	704.3	28.9	707.9	19.1	728.2	21.4
879.0	29.6	820.4	6.0	815.4	6.4	876.5	29.5
891.7	2.5	889.3	2.5	882.5	1.7	882.0	1.6
929.8	31.0	926.7	33.5	934.9	39.4	935.5	37.6
968.6	0.2	965.7	0.1	983.2	22.8	984.4	35.0
974.0	23.6	973.2	14.7	1000.7	16.4	1000.6	14.6
1043.1	44.3	1041.1	39.8	1030.8	13.1	1030.7	13.1
1141.5	3.3	1090.7	6.1	1047.3	2.9	1068.4	3.4
1190.1	14.2	1199.9	13.4	1128.0	3.0	1169.8	7.0
1238.8	37.2	1278.9	1.2	1292.9	4.9	1225.9	6.2
1316.2	1.2	1314.2	3.1	1320.1	1.0	1316.0	4.2
1326.3	6.7	1332.3	10.0	1343.8	7.0	1351.3	6.4
1340.9	4.2	1343.4	7.2	1359.0	1.0	1362.9	23.3
1461.1	0.7	1458.8	0.9	1459.2	3.7	1460.4	13.9
1641.0	0.8	1637.0	29.2	1634.1	156.2	1639.4	114.2
1674.7	135.8	1670.9	98.1	1680.2	2.4	1680.4	2.9
1789.4	**664.4**	**1785.4**	**515.2**	**1785.7**	**550.7**	**1788.2**	**614.9**
3123.1	6.4	3123.4	6.3	3124.5	14.0	3122.9	5.2
3124.7	0.9	3130.9	2.1	3131.6	12.3	3124.6	17.2
3133.5	16.9	3135.5	25.7	3137.5	17.8	3137.5	22.4
3138.3	4.3	3138.6	4.2	3142.8	2.3	3143.1	3.6
3151.9	14.1	3155.4	15.1	3160.6	12.2	3158.6	9.8
3224.3	10.0	3224.4	9.3	3222.1	10.3	3223.1	9.8

[a] Calculated wavenumbers are not scaled;
[b] The frequency and intensity of the antisymmetric C=C=S vibration is shown in bold for each thioketene isomer. This strongest infrared mode of thioketene is depicted graphically in Figure 9a of the main article.