

A femtosecond stimulated Raman spectroscopic study on the oxazine ring opening dynamics of structurally-modified indolobenzoxazines

Supplementary material

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A. Information on the spontaneous Raman scattering experiments

Spontaneous Raman spectra of samples **IB1** and **IB4** were recorded using an Echelle type spectrometer *RamanFlex 400* (*PerkinElmer, Inc.*), equipped with a thermoelectrically cooled (up to $-50\text{ }^{\circ}\text{C}$) CCD camera and a fiber optic cable for excitation and collection of the Raman spectra in a 180° scattering geometry. The excitation of the IB samples was performed with a $\lambda=785\text{ nm}$, $P=30\text{ mW}$ diode laser radiation, focused to a $200\text{ }\mu\text{m}$ diameter spot. The resolution of the experiments was ca. 1 cm^{-1} .

Spontaneous Raman spectra of samples **IB0**, **IB2**, and **IB3** were recorded using a FT-Raman spectrometer *Multiram* (*Brucker Optik GmbH*). The excitation was performed with a $\lambda=1064\text{ nm}$, $P=300\text{ mW}$ Nd:YAG laser, and the spectra were recorded with liquid N_2 cooled Ge diode. The resolution of the experiments was ca. 4 cm^{-1} .

All of the above-described spontaneous Raman scattering measurements were performed on crystalline **IB** samples at room temperature.

B. FSRS spectra of supplementary phenyl-substituted IB compounds

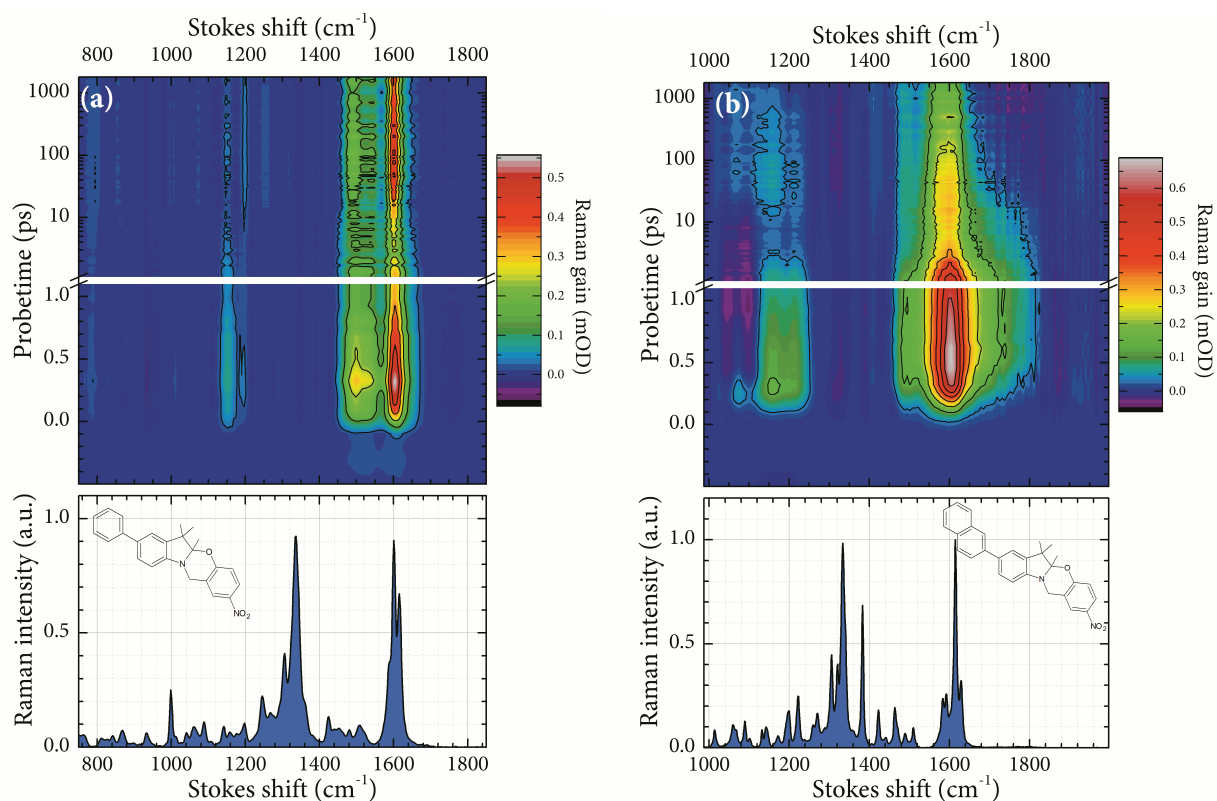


Figure B1. Experimentally-resolved background-corrected FSRS datamaps (top panels) of several additional *para*-substituted **IB** compounds (structural formulae, along with their spontaneous Raman scattering spectra, are presented in the bottom panels). Optical excitation was performed with $\lambda_{\text{AP}}=325$ nm, $E_{\text{AP}}=1$ μJ , $\tau_{\text{AP}}=70$ fs actinic pulses; the Raman pumps, acknowledging the results of ref. [1], were set to (a) **IB3**: $\lambda_{\text{RP}}=610$ nm, $E_{\text{RP}}=4$ μJ , $\tau_{\text{RP}}=4$ ps, and (b) **IB4**: $\lambda_{\text{RP}}=795$ nm, $E_{\text{RP}}=5$ μJ , $\tau_{\text{RP}}=3.5$ ps.

C. Global analysis fitting of the FSRs experimental data

Table C1. Reciprocal transition rates (in ps) between the intermediate states of compounds **IB1** and **IB2**. The model for the global fit [2] (presented on the left) was for simplicity purposes adapted from previous studies on substituted IBs [3,4] and used as is. Result of the global fit are depicted as continuous curves in Fig. 3 in the main text.

	IB1	IB2
$\tau_{1 \rightarrow 2}$	0.75	0.95
$\tau_{2 \rightarrow 3}$	7	18
$\tau_{3 \rightarrow 3}$	25000	13300
$\tau_{1 \rightarrow 0}$	0.9	0.7
$\tau_{0 \rightarrow 0}$	0.4	0.4

D. Optimized molecular structures of the IB compounds

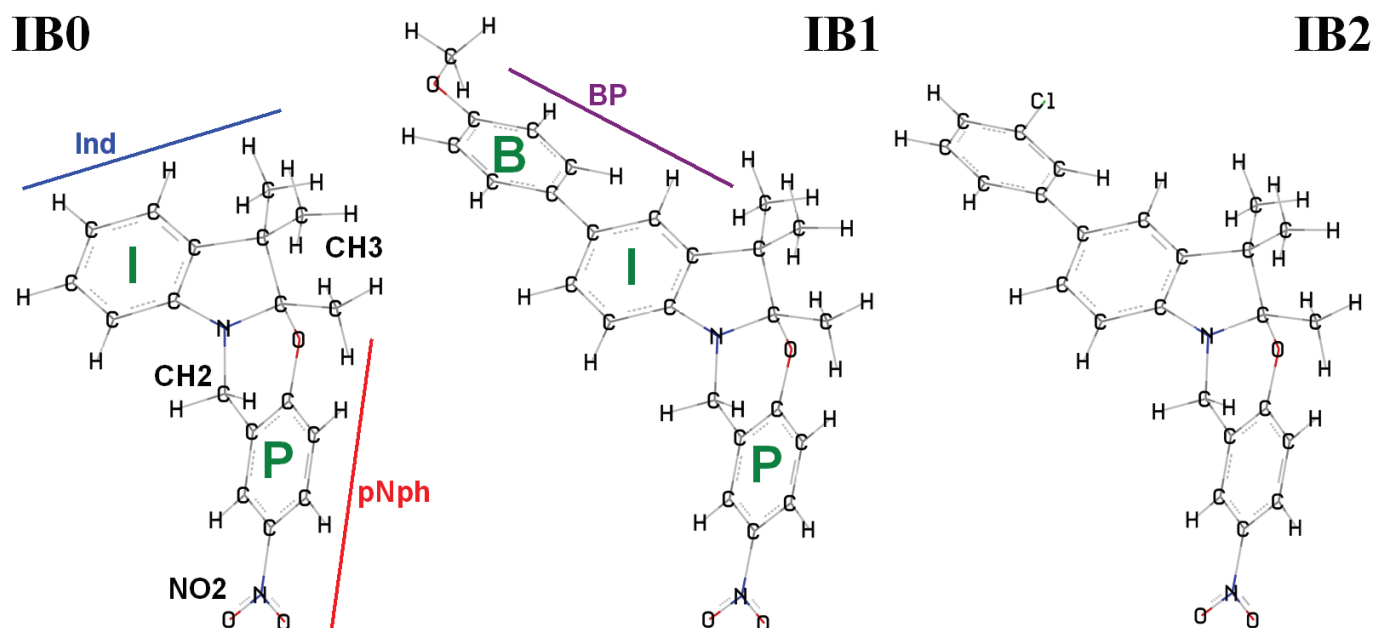


Figure D1. Molecular structure and markings of **IB** compounds.

Table D1. Atomic coordinates and total energies of the optimized molecular structures of **IB** compounds.

Calculation parameters:

```
#p b3lyp cc-pVTZ opt fchk
```

IB0:

E(RB3LYP) = -1032.20686460 a. u.

O	-0.34084	-1.33994	-0.60149
C	0.91313	-0.87221	-0.42265
C	1.85118	-1.19531	-1.41089
C	3.15267	-0.75139	-1.30767
C	3.51628	0.02217	-0.20961
C	2.59583	0.35869	0.77129
C	1.28462	-0.08062	0.67623
H	1.53271	-1.79984	-2.24792
H	3.89045	-0.99222	-2.05669
N	4.89616	0.49883	-0.08975
O	5.68555	0.18996	-0.97298
O	5.18458	1.17888	0.88753
H	2.91595	0.97234	1.60102
C	-1.30498	-1.21283	0.51105
C	-2.71549	-1.04993	-0.1528
C	-2.75089	0.45724	-0.34179
C	-3.58292	1.2466	-1.11034
C	-3.44833	2.63641	-1.05772
C	-2.48972	3.2096	-0.23269
C	-1.6452	2.42155	0.55045

C	-1.7893	1.04314	0.48476
N	-1.09945	0.04432	1.19936
C	0.24234	0.26725	1.7122
H	0.38403	-0.33047	2.61667
H	0.33725	1.30678	2.01831
C	-1.10344	-2.43161	1.39623
H	-0.06326	-2.51216	1.70927
H	-1.72692	-2.37545	2.28529
H	-1.34997	-3.3372	0.8444
C	-2.87668	-1.84934	-1.44827
H	-2.16794	-1.53449	-2.20866
H	-2.73954	-2.91753	-1.27186
H	-3.88556	-1.71174	-1.83856
C	-3.82891	-1.4519	0.83855
H	-4.79683	-1.18375	0.41639
H	-3.83157	-2.52687	1.02327
H	-3.72586	-0.93401	1.79151
H	-4.32869	0.79889	-1.75481
H	-0.90263	2.88845	1.18212
H	-2.3865	4.28596	-0.19765
H	-4.08774	3.26493	-1.66185

IB1:

E (RB3LYP) = -1377.90568485 a. u.

O	2.22451	1.34934	1.08724
C	3.08158	0.34824	0.7938
C	3.67038	-0.31291	1.87888
C	4.55164	-1.35219	1.66671
C	4.84375	-1.73279	0.36047
C	4.26063	-1.09408	-0.72336
C	3.37237	-0.04943	-0.52117
H	3.42077	0.01131	2.87892
H	5.01713	-1.87227	2.489
N	5.77841	-2.83524	0.1231
O	6.2765	-3.38162	1.09883
O	6.01135	-3.14887	-1.038
H	4.50393	-1.42933	-1.72133
C	1.73798	2.20834	-0.01224
C	0.28738	2.64635	0.38967
C	-0.50955	1.48127	-0.1738
C	-1.81282	1.09645	0.05611
C	-2.36875	0.01344	-0.64805
C	-1.56317	-0.643	-1.58283
C	-0.24583	-0.26036	-1.82757
C	0.27298	0.80882	-1.11361
N	1.54114	1.41524	-1.20781
C	2.70269	0.67135	-1.66659
H	3.40134	1.35987	-2.14965
H	2.39194	-0.03361	-2.43472
C	2.76275	3.31818	-0.17951
H	3.75655	2.90416	-0.345
H	2.50961	3.9559	-1.02299

H	2.80668	3.92332	0.72462
C	0.10869	2.86197	1.89431
H	0.29969	1.95433	2.45937
H	0.77622	3.64306	2.26214
H	-0.91266	3.18596	2.09676
C	-0.11673	3.93232	-0.36336
H	-1.17495	4.12822	-0.19414
H	0.44423	4.7976	-0.00804
H	0.03679	3.83351	-1.43743
H	-2.42366	1.6363	0.76806
H	0.34484	-0.80533	-2.55057
H	-1.96106	-1.4966	-2.11456
C	-3.76218	-0.42034	-0.40052
C	-4.59155	-0.84716	-1.44836
C	-5.89233	-1.25509	-1.2227
C	-6.41801	-1.24992	0.07138
C	-5.61484	-0.8292	1.12921
C	-4.30686	-0.42306	0.8841
H	-4.21586	-0.8358	-2.46281
H	-6.52693	-1.57281	-2.03842
O	-7.70885	-1.66786	0.1947
H	-5.98691	-0.82352	2.14245
H	-3.6921	-0.127	1.72386
C	-8.29664	-1.67558	1.48458
H	-8.32221	-0.67285	1.91971
H	-9.31382	-2.03319	1.3489
H	-7.76601	-2.34869	2.16337

IB2:

E(RB3LYP) = -1722.97192412 a. u.

O	1.96668	1.32582	1.10748
C	2.90289	0.39525	0.81894
C	3.49164	-0.26169	1.90625
C	4.45154	-1.22988	1.6984
C	4.82201	-1.54304	0.39421
C	4.23991	-0.90862	-0.69231
C	3.27262	0.06457	-0.49443
H	3.17991	0.0094	2.90464
H	4.91912	-1.74497	2.52266
N	5.84148	-2.56947	0.16109
O	6.33649	-3.11417	1.13891
O	6.14238	-2.82421	-0.99862
H	4.54686	-1.19072	-1.68918
C	1.48676	2.1994	0.01987
C	-0.00131	2.55158	0.36791
C	-0.71325	1.3747	-0.27844
C	-2.00481	0.92026	-0.12725
C	-2.4722	-0.15662	-0.90163
C	-1.5941	-0.73896	-1.81921
C	-0.28614	-0.28867	-1.9808
C	0.14549	0.77549	-1.20266
N	1.38372	1.43918	-1.20994

C	2.60155	0.77534	-1.64558
H	3.27503	1.51399	-2.08836
H	2.35776	0.07291	-2.43953
C	2.46171	3.36202	-0.06699
H	3.47988	3.00082	-0.20614
H	2.212	4.01741	-0.89775
H	2.44198	3.93503	0.85849
C	-0.25936	2.69455	1.86997
H	-0.04811	1.77439	2.40679
H	0.35032	3.49124	2.29932
H	-1.30384	2.95975	2.03669
C	-0.43404	3.84704	-0.35159
H	-1.50698	3.98597	-0.22366
H	0.06752	4.72146	0.06425
H	-0.22852	3.8021	-1.4206
H	-2.67307	1.40173	0.57493
H	0.36435	-0.77793	-2.69197
H	-1.92539	-1.58744	-2.40211
C	-3.85564	-0.66034	-0.74574
C	-4.60344	-1.08336	-1.85096
C	-5.90037	-1.55172	-1.69641
C	-6.49148	-1.60869	-0.44008
C	-5.75057	-1.18768	0.65452
C	-4.45247	-0.72201	0.51885
H	-4.17385	-1.01976	-2.84097
H	-6.46508	-1.86683	-2.56368
H	-7.50103	-1.96891	-0.31025
Cl	-6.46781	-1.25874	2.25515
H	-3.8986	-0.43211	1.39941

E. Vibrational modes of IB compounds

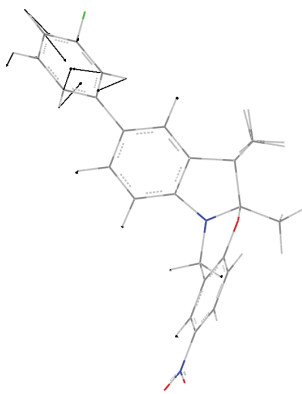
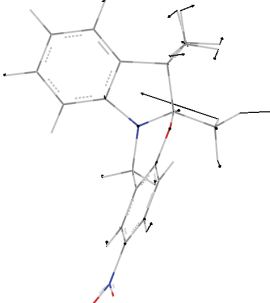
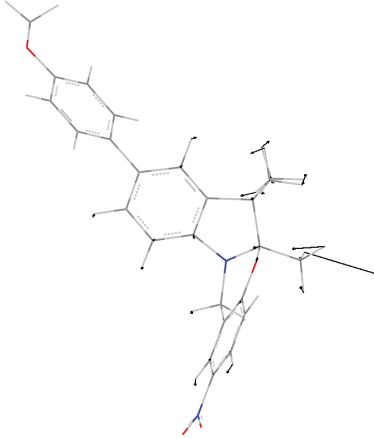
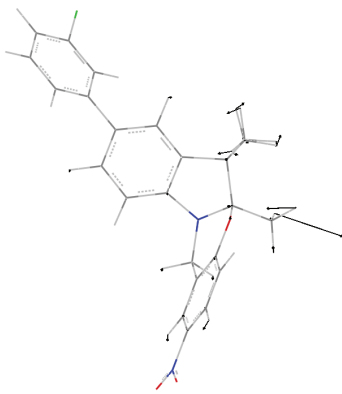
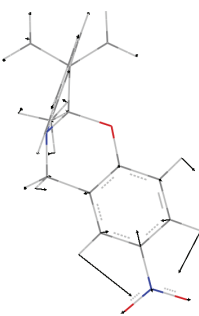
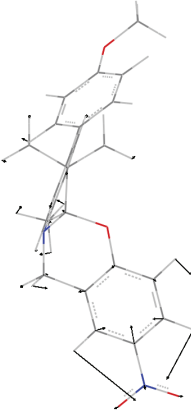
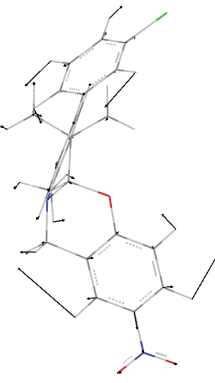
Table E1. Properties of selected vibrational modes of IB compounds. See Fig. D1 for notation. Raman shift values (cm^{-1} , columns 1 and 2) correspond to the listed compounds in the following order (if present): **IB0**, **IB1**, and **IB2**.

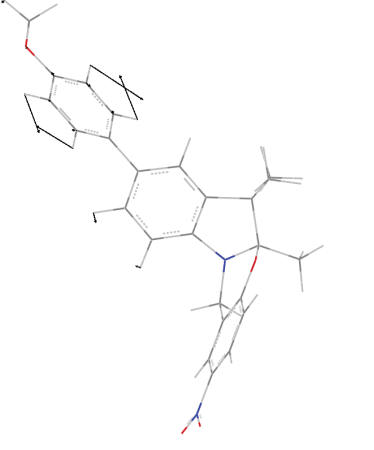
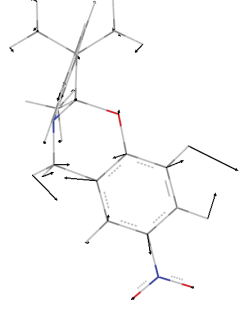
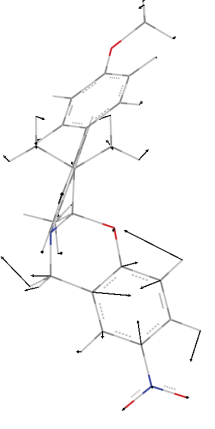
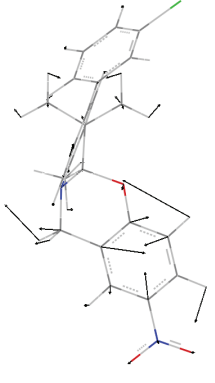
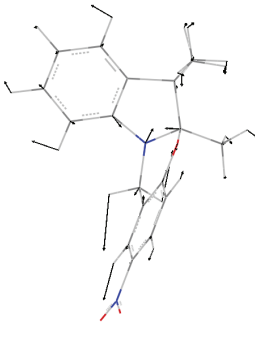
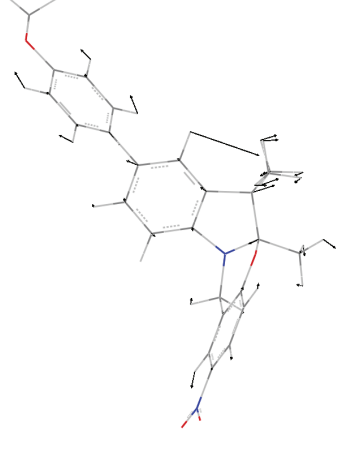
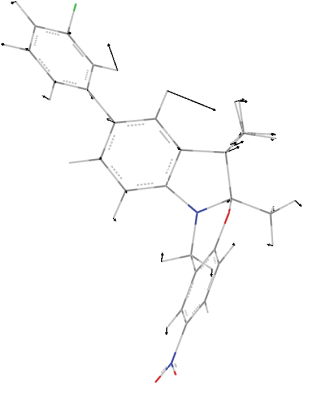
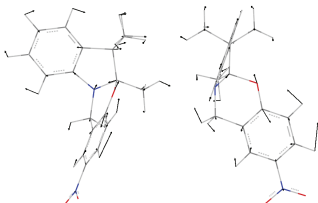
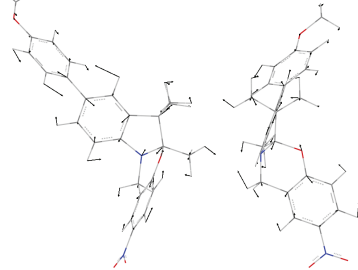
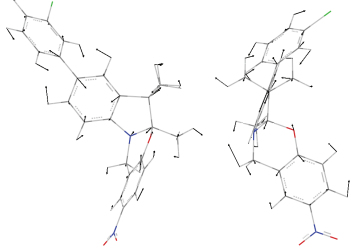
ν_{harm}	ν_{anh}	Compound	Location	Type	Description, notes
1017	996	IB2	B ring	CCC bend	3-fold
1081	1060	All	CH ₃	CH bend	Out-of plane <i>Strongly asymmetric</i>
1084	1060				
1084	1061				
1104	1081	All	P ring	CCH bend	2-fold rocking
1105	1081				
1105	1081				
		IB2	B ring	CCH bend	2-fold rocking
1203	1176	IB1	B ring	CCH bend	2-fold scissoring
1211	1183	All	P ring	CCC bend	3-fold beat
1211	1184				
1211	1184				
1261	1233	All	Collective	CH bend	Various movements
1267	1237				
1266	1237				
1303	1269	All	P ring	CCH bend	2-fold rocking
1314	1282				
1313	1282				
			CH ₂	CH bend	Out-of-plane twisting
		IB0	I ring	CCH bend	Twisting
		IB1, 2	B ring	CCH bend	2-fold rocking
			I ring	CCC bend	3-fold beat
1338	1306	IB1, 2	I, B rings	CCH bend	Twisting/ rocking
1321	1290				
1352	1321	All	P ring	CC stretch	3-fold
1350	1318				
1350	1318				
			CH ₂	CH bend	Out-of-plane wagging
		IB1, 2	B ring	CCH bend	Twisting
1365	1334	All	NO ₂	ON stretch	Symmetric
1365	1331				
1365	1332				
				CN stretch	
			CH ₂	CH bend	Out-of-plane wagging

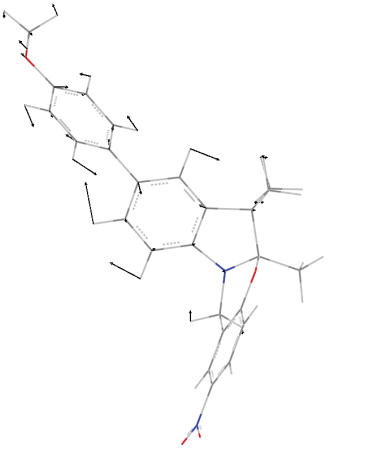
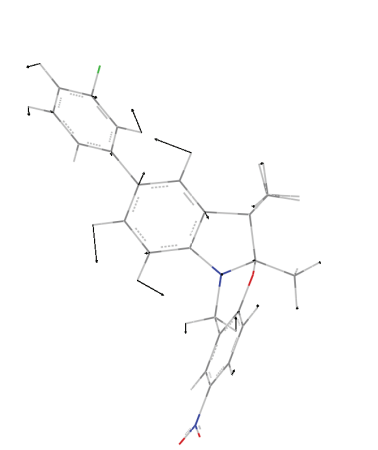
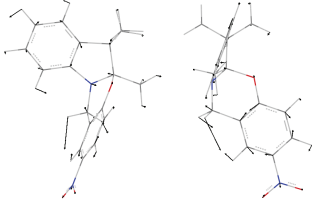
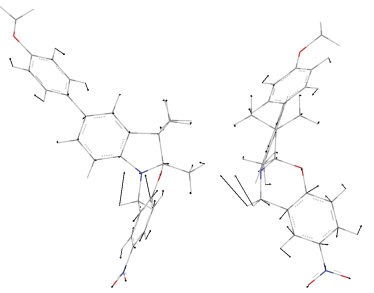
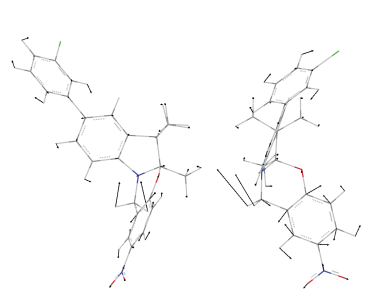
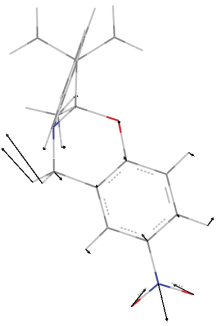
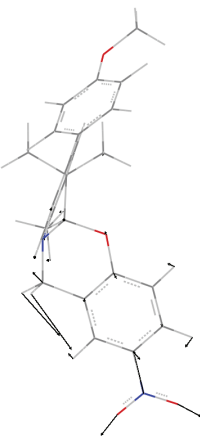
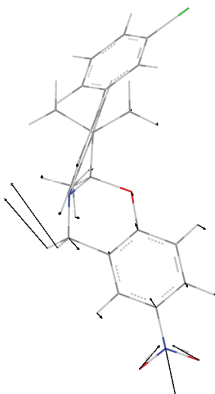
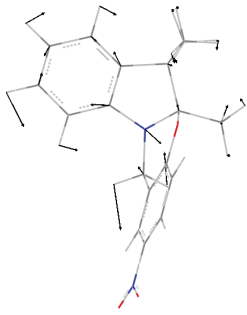
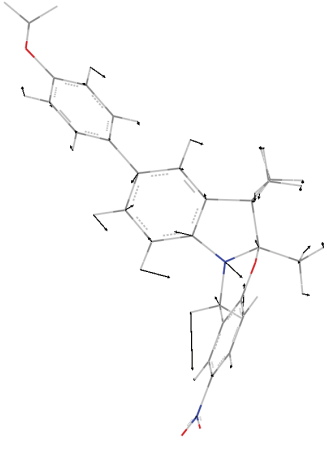
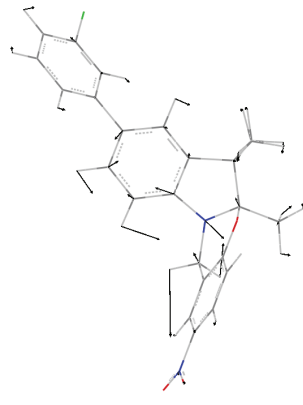
ν_{harm}	ν_{anh}	Compound	Location	Type	Description, notes
1393 1386 1387	1361 1352 1353	All	I ring	CC stretch	3-fold
			CH ₂	CH bend	Out-of-plane twisting
1553 1531	1512 1491	IB1, 2	I, B rings	CCH bend	2-fold rocking <i>CC stretching along BP axis</i>
1626 1627 1626	1585 1582 1583	All	P ring	CC stretch	2-fold, antisymmetric <i>Off pNph axis</i>
			NO ₂	ON stretch	Antisymmetric
1633	1588	IB2	B ring	CC stretch	2-fold, symmetric
1647	1606	IB0	I ring	CC stretch	2-fold, antisymmetric
1650	1604	IB1	I, B rings	CC stretch	2-fold, symmetric
1654 1654	1615 1609	IB0, 2	P ring	CC stretch	2-fold, symmetric <i>Off pNph axis</i>
			NO ₂	ON stretch	Antisymmetric
		IB2	I ring	CC stretch	2-fold, symmetric

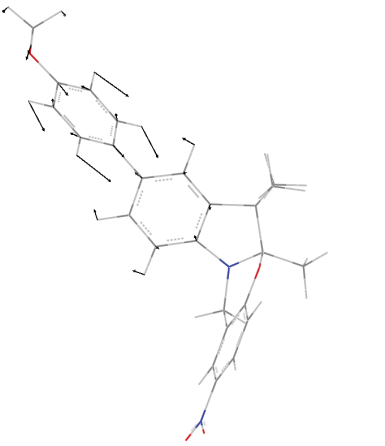
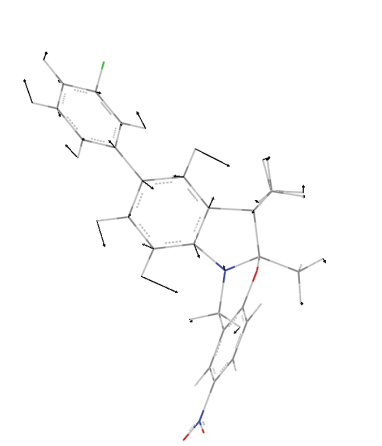
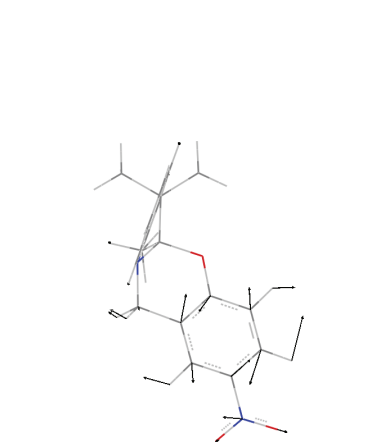
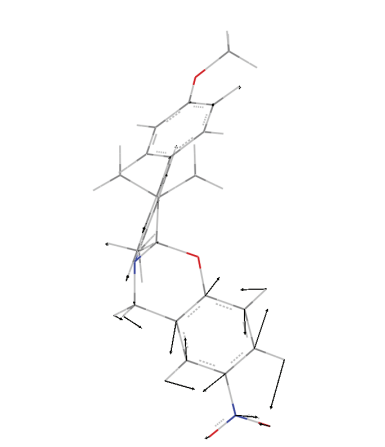
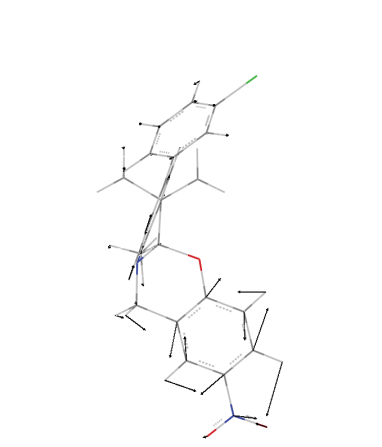
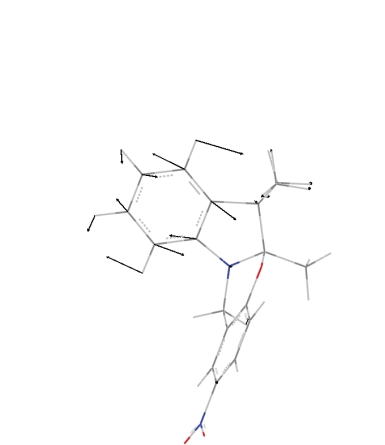
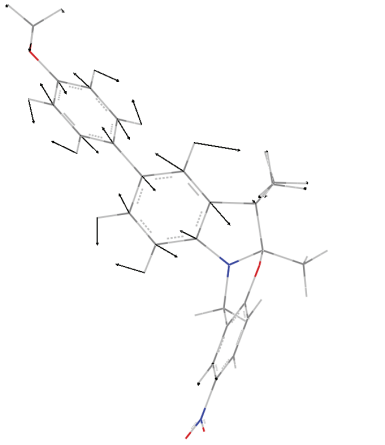
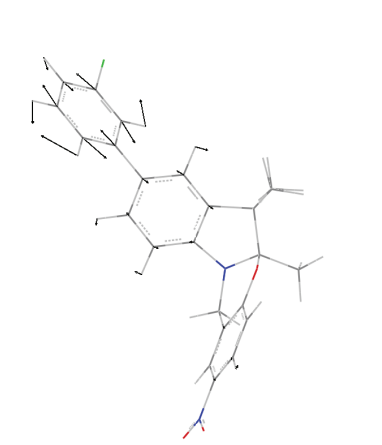
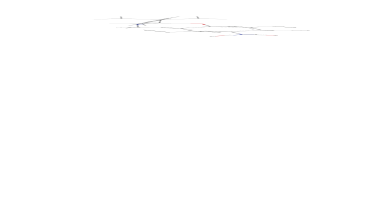
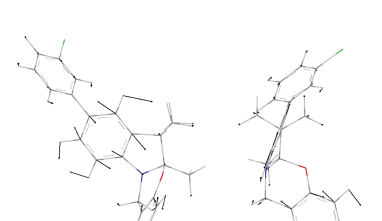
F. Displacement vectors of vibrational modes of IB compounds

Table F1. Images of displacement vectors corresponding to selected vibrational modes of IB compounds. Raman shifts (cm^{-1} , first column) correspond to the compounds in left-to-right order. Omitted data indicates missing/ inactive mode. Animated GIF files of the vibrations are provided separately.

ν	IB0	IB1	IB2
--- --- 1017			
1081 1084 1084			
1104 1105 1105			

ν	IB0	IB1	IB2
--- 1203 ---			
1211 1211 1211			
1261 1267 1266			
1303 1314 1313			

ν	IB0	IB1	IB2
--- 1338 1321			
1352 1350 1350			
1365 1365 1365			
1393 1386 1387			

ν	IB0	IB1	IB2
--- 1553 1531			
1626 1627 1626			
1647 1650 1633			
1654 --- 1654			

G.References

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