Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Intramolecular charge transfer excitation induced by CH_3O substitution in 3-methoxy-1-propoxy radical

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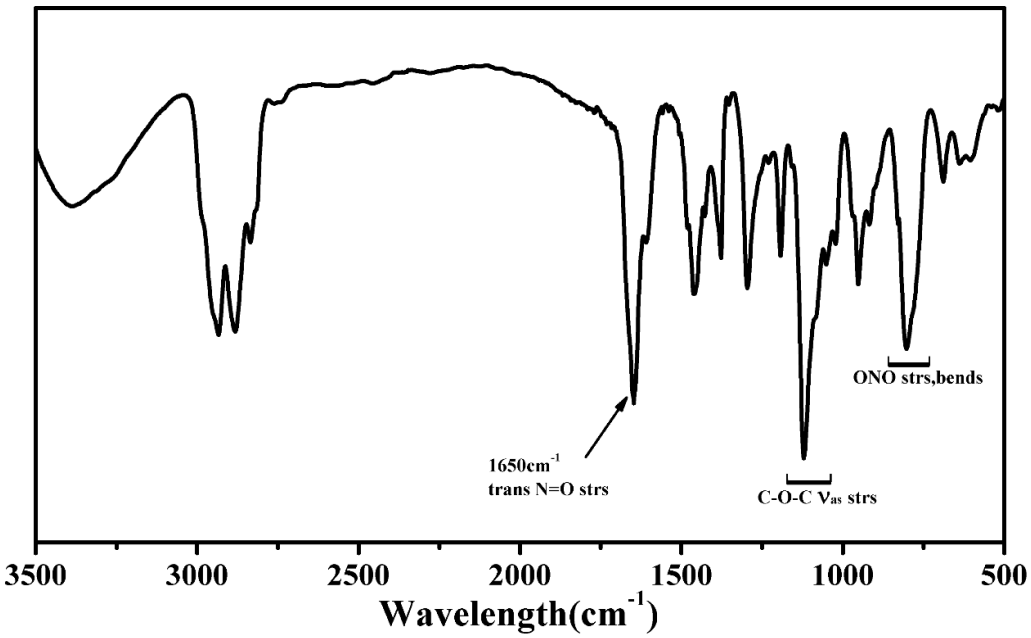


Fig. S1 IR spectrum of 3-methoxy-1-propyl nitrite.

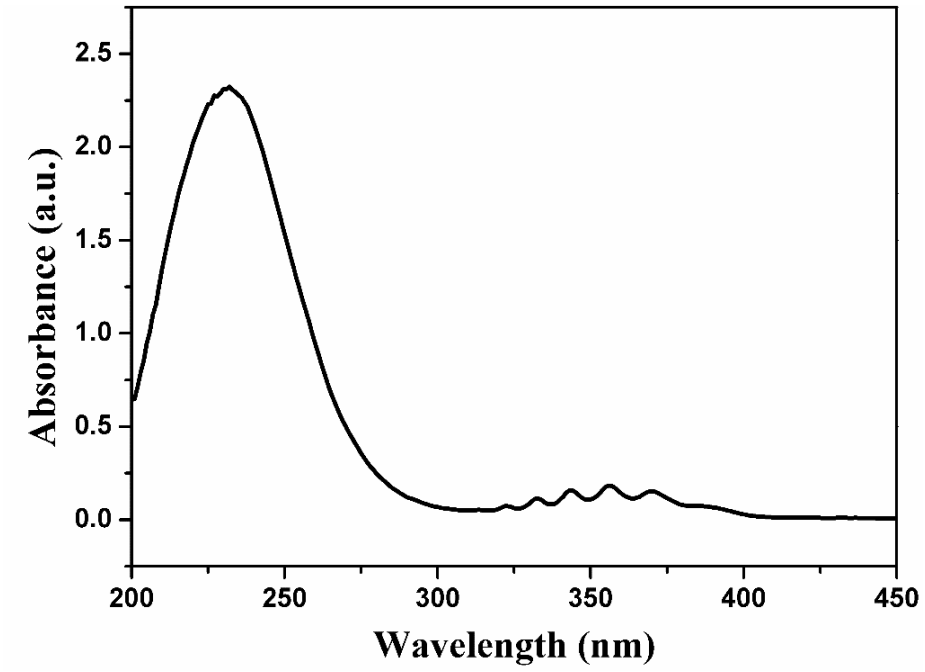


Fig. S2 UV absorption spectrum of 3-methoxy-1-propyl nitrite.

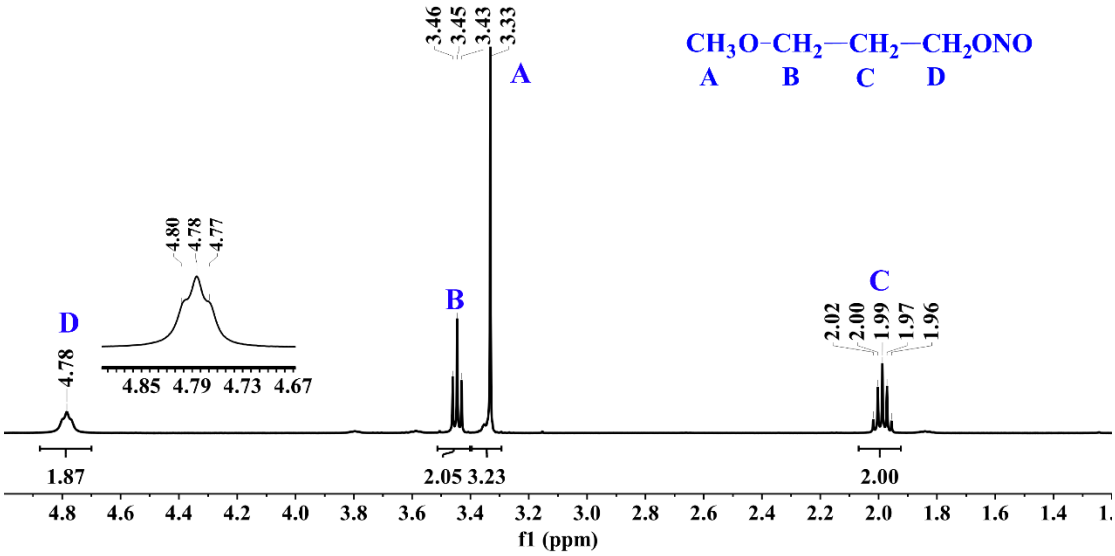


Fig. S3 NMR spectrum of 3-methoxy-1-propyl nitrite.

Table S1 Relative energies (in kcal mol^{-1}) of 12 unique conformers of 3-methoxy-1-propoxy radical calculated at the UB3LYP/6-311++G(d,p) Level. The corresponding Newman projections are also shown.

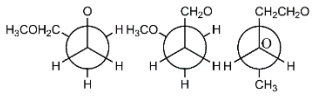
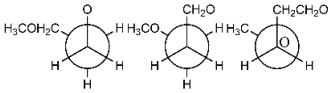
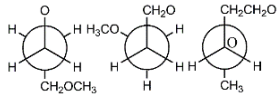
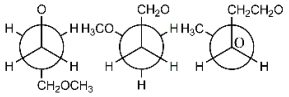
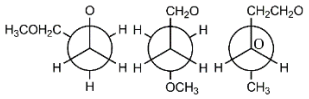
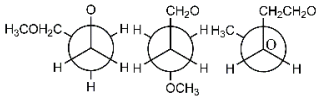
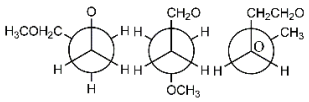
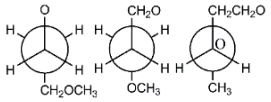
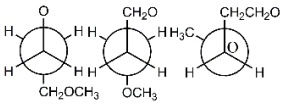
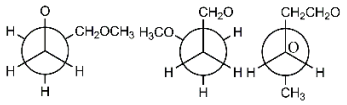
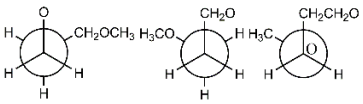
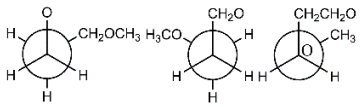
Conformer	$E_{\mathrm{rel}}^{\tilde{\mathrm{X}}}$+ΔZPE	Newman projection	Mirror image
$G_1G_2t_3$	0.00		$G_1'G_2't_3$
$G_1G_2g_3$	2.07		$G_1'G_2'g_3'$
$T_1G_2t_3$	0.44		$T_1G_2't_3$
$T_1G_2g_3$	2.08		$T_1G_2'g_3'$
$G_1T_2t_3$	0.93		$G_1`T_2t_3$
$G_1T_2g_3$	2.59		$G_1'T_2g_3'$
$G_1T_2g_3'$	2.80		$G_1'T_2g_3$
$T_1T_2t_3$	1.28		
$T_1T_2g_3$	4.37		$T_1T_2g_3'$
$G_1'G_2t_3$	2.71		$G_1G_2't_3$
$G_1'G_2g_3$	3.14		$G_1G_2'g_3'$
$G_1'G_2g_3'$	4.90		$G_1G_2'g_3$

Table S2 Calculated 48 vibrational frequencies (cm^{-1}) of the GTG′t conformer of 4-methoxy-1-butoxy radical in its ground state and CO $\sigma \rightarrow$ O p excited state. [a]

assignment	CASSCF(9,7)[b] $\tilde{B}$	CASSCF(9,7)[b] $\tilde{X}$	B3LYP[c] $\tilde{X}$
ν_{48}	47	49	49
ν_{47}	85	84	80
ν_{46}	105	105	99
ν_{45}	150	152	140
ν_{44}	218	219	215
ν_{43}	257	254	241
ν_{42}	277	274	267
ν_{41}	327	329	318
ν_{40}	428	421	355
ν_{39}	567	467	466
ν_{38}	598	577	561
ν_{37}	759	772	745
ν_{36}	851	858	834
ν_{35}	899	903	873
ν_{34}	984	953	927
ν_{33}	1000	1029	997
ν_{32}	1015	1055	1019
ν_{31}	1075	1078	1049
ν_{30}	1116	1121	1074
ν_{29}	1192	1201	1119
ν_{28}	1207	1212	1142
ν_{27}	1222	1230	1160
ν_{26}	1226	1243	1174
ν_{25}	1286	1295	1218
ν_{24}	1307	1319	1244
ν_{23}	1321	1362	1298
ν_{22}	1355	1381	1305
ν_{21}	1385	1416	1314
ν_{20}	1455	1463	1345
ν_{19}	1475	1468	1378
ν_{18}	1488	1481	1389
ν_{17}	1526	1520	1445
ν_{16}	1527	1527	1447
ν_{15}	1533	1532	1456
ν_{14}	1535	1533	1462
ν_{13}	1544	1544	1471

ν_{12}	1568	1568	1491
ν_{11}	2962	2959	2806
ν_{10}	2965	2977	2845
ν_{9}	2980	2986	2890
ν_{8}	2996	2988	2910
ν_{7}	3021	3000	2919
ν_{6}	3021	3010	2950
ν_{5}	3058	3016	2956
ν_{4}	3083	3030	2966
ν_{3}	3097	3037	2993
ν_{2}	3124	3058	3014
ν_{1}	3215	3094	3049

[a] All calculations employed the 6-311++G(d,p) basis set. [b] A uniform scale factor of 0.95 was used for CASSCF(9,7). [c] The calculated B3LYP frequencies were scaled by 0.98.

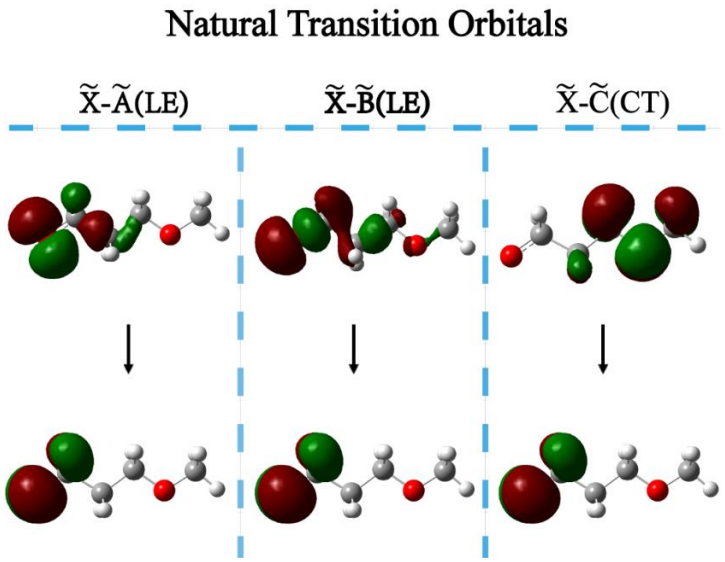
Table S3 Calculated 39 vibrational frequencies (cm^{-1}) of the TTt conformer of 3-methoxy-1-propoxy radical in its ground state and CO $\sigma \rightarrow$ O p excited state. [a]

assignment	CASSCF(9,7)[b] $\tilde{B}$	CASSCF(9,7)[b] $\tilde{X}$	B3LYP[c] $\tilde{X}$
ν_{39}	67	75	60
ν_{38}	90	104	77
ν_{37}	127	137	112
ν_{36}	141	145	140
ν_{35}	222	225	198
ν_{34}	312	327	222
ν_{33}	365	374	338
ν_{32}	493	429	363
ν_{31}	676	533	515
ν_{30}	799	801	769
ν_{29}	895	961	924
ν_{28}	1003	965	936
ν_{27}	1018	1029	1010
ν_{26}	1036	1068	1045
ν_{25}	1101	1100	1057
ν_{24}	1207	1211	1125
ν_{23}	1211	1215	1145
ν_{22}	1235	1247	1178

ν_{21}	1259	1274	1192
ν_{20}	1300	1323	1247
ν_{19}	1312	1328	1262
ν_{18}	1350	1354	1284
ν_{17}	1374	1433	1322
ν_{16}	1487	1473	1373
ν_{15}	1527	1493	1401
ν_{14}	1530	1529	1446
ν_{13}	1534	1533	1456
ν_{12}	1543	1538	1465
ν_{11}	1550	1544	1472
ν_{10}	1575	1571	1495
ν_{9}	2961	2953	2814
ν_{8}	2982	2975	2827
ν_{7}	2987	2977	2878
ν_{6}	3026	2987	2900
ν_{5}	3071	3018	2911
ν_{4}	3107	3018	2953
ν_{3}	3120	3031	2985
ν_{2}	3121	3074	3028
ν_{1}	3210	3099	3053

[a] All calculations employed the 6-311++G(d,p) basis set. [b] A uniform scale factor of 0.95 was used for CASSCF(9,7). [c] The calculated B3LYP frequencies were scaled by 0.98.

Scheme S1 Natural transition orbitals of the lowest three excited states of the TTt conformer of 3-methoxy-1-propoxy



Scheme S2 Change of Mülliken and NBO charge distribution due to intramolecular charge transfer excitation of 3-methoxy-1-propoxy radical (TTt conformer).