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

Oxidative addition of carbon dioxide into mesoionics

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Supplementary information

Table S1. Optimized geometrical parameters. [a]

system	label	sym.	formula	$d_{C\text{-}C}$	$d_{C\text{-}O}$	α_{OCO}	ω_{CCCO}	μ
pyrilium family								
ortho	**34**	C_1	$C_5H_4O\text{-}CO_2$	1.527	1.236	136.0	68.9	10.0
meta	**35**	C_s	$C_5H_4O\text{-}CO_2$	1.572	1.238	134.9	0.0	11.5
para	**1**	C_2	$C_5H_4O\text{-}CO_2$	1.517	1.238	134.2	60.0	9.4
o-diamino *ortho*	**36**	C_2	$C_5H_6ON_2\text{-}CO_2$	1.556	1.249	128.8	13.7	9.1
pyridinium family								
ortho	**37**	C_s	$C_5H_5N\text{-}CO_2$	1.566	1.240	134.8	0.0	10.3
meta	**38**	C_s	$C_5H_5N\text{-}CO_2$	1.570	1.240	134.4	0.0	13.2
para	**2**	C_{2v}	$C_5H_5N\text{-}CO_2$	1.569	1.241	134.3	0.0	14.0
N-amino *ortho*	**4**	C_1	$C_5H_6N_2\text{-}CO_2$	1.584	1.240	132.2	1.6	9.7
N-amino *meta*	**39**	C_s	$C_5H_6N_2\text{-}CO_2$	1.572	1.240	134.3	0.0	12.3
N-amino *para*	**40**	C_s	$C_5H_6N_2\text{-}CO_2$	1.568	1.240	134.3	0.0	14.4
N-methyl *ortho* (homarine)	**41**	C_1	$C_6H_7N\text{-}CO_2$	1.575	1.237	133.8	38.8	10.1
N-methyl *meta* (trigonelline)	**3**	C_s	$C_6H_7N\text{-}CO_2$	1.570	1.240	134.2	0.0	13.8
N-methyl *para*	**42**	C_s	$C_6H_7N\text{-}CO_2$	1.567	1.241	134.2	0.0	15.0
ectoine	**43**	C_1	$C_5H_{10}N_2\text{-}CO_2$	1.594	1.244	132.6	11.3	12.4
iso-ectoine (*para*)	**44**	C_s	$C_5H_{10}N_2\text{-}CO_2$	1.603	1.241	133.3	28.6	16.0
triazinium family								
$(CO_2)_1$	**5**	C_{2v}	$C_3H_3N_3\text{-}CO_2$	1.582	1.232	138.3	0.0	6.2
$(CO_2)_2$	**6**	C_{2v}	$C_3H_3N_3\text{-}(CO_2)_2$	1.603	1.227	140.2	0.0	5.3
$(CO_2)_1$ *p-N*-amino	**8**	C_s	$C_3H_4N_4\text{-}CO_2$	1.575	1.233	138.1	0.6	7.3
$(CO_2)_1$ *o-N,N*-diamino	**9**	C_2	$C_3H_5N_5\text{-}CO_2$	1.583	1.234	134.2	38.8	5.5
$(CO_2)_1$ *o,p-N,N*-diamino	**10**	C_1	$C_3H_5N_5\text{-}CO_2$	1.586	1.235	135.5	5.8	6.7
$(CO_2)_2$ *o-N,N*-diamino	**45**	C_1	$C_3H_4N_5\text{-}(CO_2)_2$	1.594	1.231	135.6	4.7	4.7
$(CO_2)_1$ *N,N,N*-triamino	**11**	C_1	$C_3H_6N_6\text{-}CO_2$	1.585	1.235	133.7	35.1	6.4
$(CO_2)_2$ *N,N,N*-triamino	**12**	C_s	$C_3H_6N_6\text{-}(CO_2)_2$	1.597	1.232	134.2	32.6	5.9
$(CO_2)_3$ *N,N,N*-triamino	**13**	C_s	$C_3H_6N_6\text{-}(CO_2)_3$	1.615	1.232	133.0	24.6	0.5
tropylium family								
tropylium	**16**	C_2	$C_7H_6\text{-}CO_2$	1.564	1.239	134.3	32.7	11.1
o-diamino tropylium	**17**	C_2	$C_7H_8N_2\text{-}CO_2$	1.571	1.254	124.8	8.5	9.0
m-diamino tropylium	**18**	C_{2v}	$C_7H_8N_2\text{-}CO_2$	1.599	1.241	132.8	0.0	14.1
tetraamino tropylium	**19**	C_s	$C_9H_{10}N_4\text{-}CO_2$	1.554	1.256	126.0	0.0	9.3
tetraamino *N,N*-dimethyl tropylium	**46**	C_s	$C_{11}H_{14}N_4\text{-}CO_2$	1.557	1.243	131.8	90.0	8.5
hexaamino tropylium	**20**	C_s	$C_{10}H_{12}N_6\text{-}CO_2$	1.550	1.257	125.9	0.0	11.4
azulene ammonium	**21**	C_1	$C_{10}H_9N\text{-}CO_2$	1.580	1.243	132.2	15.3	26.2
azulene ammonium tetraamino	**22**	C_s	$C_{12}H_{13}N_5\text{-}CO_2$	1.566	1.255	125.7	1.3	22.4
phenalene family								
P1 major	**14**	C_1	$C_{13}H_8\text{-}CO_2$	1.510	1.241	132.9	70.1	10.6
P1 minor	**15**	C_2	$C_{13}H_8\text{-}CO_2$	1.561	1.242	133.8	17.2	14.3
P3 major	**53**	C_1	$C_{31}H_{14}\text{-}CO_2$	1.525	1.243	131.4	54.8	16.7
P3 minor	**54**	C_1	$C_{31}H_{14}\text{-}CO_2$	1.555	1.244	132.4	9.4	20.6

sydnone family								
sydnone	**23**	C_s	$C_2H_2N_2O$-CO_2	1.637	1.222	139.8	0.0	11.2
N-phenyl sydnone	**24**	C_1	$C_8H_6N_2O$-CO_2	1.610	1.227	138.5	0.0	14.3
C-phenyl sydnone	**26**	C_1	$C_8H_6N_2O$-CO_2	1.575	1.230	136.6	58.2	10.8
C-amino sydnone	**27**	C_1	$C_2H_3N_3O$-CO_2	1.566	1.238	135.7	0.0	11.0
C-amino *N*-phenyl sydnone	**28**	C_1	$C_8H_7N_3O$-CO_2	1.562	1.238	135.1	0.0	13.4
sydnone (alternative isomer)	**29**	C_s	$C_2H_2N_2O$-CO_2	1.610	1.229	137.9	0.0	7.2
3,5,8-membered rings								
cyclopropene diamino	**25**	C_{2v}	$C_3H_4N_2$-CO_2	1.606	1.229	137.8	0.0	12.5
cyclopentadiene *o*-diamino	**47**	C_{2v}	$C_5H_6N_2$-CO_2	1.499	1.258	129.8	0.0	10.0
diazole	**48**	C_{2v}	$C_3H_4N_2$-CO_2	1.561	1.235	137.1	0.0	9.8
diazole (unsymmetrical)	**49**	C_s	$C_3H_4N_2$-CO_2	1.562	1.239	135.3	0.0	12.6
diazole *o*-diamino	**50**	C_2	$C_3H_6N_4$-CO_2	1.550	1.241	133.1	9.8	7.4
COT allene diamino	**51**	C_2	$C_8H_8N_2$-CO_2	1.630	1.238	132.8	17.6	12.9
COT $(CO_2)_2$ tetraamino	**52**	D_2	$C_8H_{10}N_4$- $(CO_2)_2$	1.593	1.242	130.7	38.3	0.0
linear polyene family								
nona-tetraenyl		C_2	C_9H_{10}-CO_2	1.519	1.240	132.3	71.6	6.8
undeca-pentaenyl		C_2	$C_{11}H_{12}$-CO_2	1.593	1.236	134.2	46.0	8.3
trideca-hexaenyl		C_2	$C_{13}H_{14}$-CO_2	1.527	1.241	131.9	66.8	7.1
pentadeca-heptaenyl		C_2	$C_{15}H_{16}$-CO_2	1.584	1.239	133.4	43.8	8.8
heptadeca-octaenyl		C_2	$C_{17}H_{18}$-CO_2	1.532	1.242	131.8	64.2	7.2
nonadeca-nonaenyl		C_2	$C_{19}H_{20}$-CO_2	1.581	1.240	133.0	42.7	9.3
uncosa-decaenyl		C_2	$C_{21}H_{22}$-CO_2	1.534	1.242	131.6	62.6	7.3
α,ω-diamino allyl		C_{2v}	$C_3H_6N_2$-CO_2	1.539	1.255	127.6	0.0	8.5
α,ω-diamino penta-dienyl		C_2	$C_5H_8N_2$-CO_2	1.587	1.243	130.8	36.4	9.1
α,ω-diamino hepta-trienyl		C_2	$C_7H_{10}N_2$-CO_2	1.580	1.245	130.0	18.4	10.4
α,ω-diamino nona-tetraenyl		C_2	$C_9H_{12}N_2$-CO_2	1.554	1.244	131.3	53.7	8.2
α,ω-diamino undeca-pentaenyl		C_2	$C_{11}H_{14}N_2$-CO_2	1.577	1.244	131.2	33.7	10.9
α,ω-diamino trideca-hexaenyl		C_2	$C_{13}H_{16}N_2$-CO_2	1.545	1.243	131.4	58.1	7.6
α,ω-diamino pentadeca-heptaenyl		C_2	$C_{15}H_{18}N_2$-CO_2	1.576	1.243	131.6	37.0	11.7
α,ω-diamino heptadeca-octaenyl		C_2	$C_{17}H_{20}N_2$-CO_2	1.543	1.243	131.4	58.7	7.4
α,ω-diamino nonadeca-nonaenyl		C_2	$C_{19}H_{22}N_2$-CO_2	1.576	1.243	131.8	38.2	12.0
α,ω-diamino uncosa-decaenyl		C_2	$C_{21}H_{24}N_2$-CO_2	1.542	1.243	131.4	58.6	7.2

[a] Distances in angströms, angles in degrees, dipole moments (μ) in Debyes; in systems carrying more than one CO_2, average is taken for the geometrical parameters.

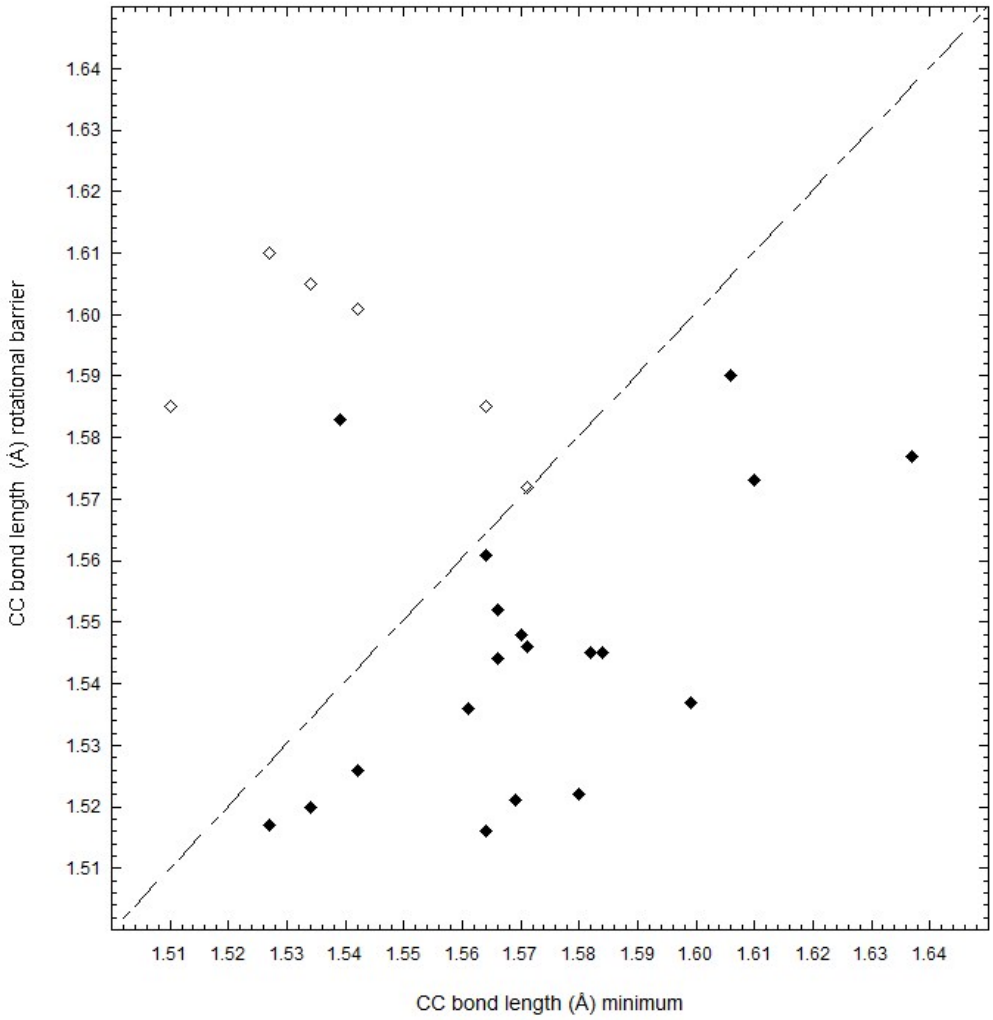

Figure S1. Visualization of C-C bond shortening when going from equilibrium minima to orthogonal rotational transition states. Empty dots refer to cases where minima are skewed and rotational barriers occur for planar arrangements. The upper-left orphan full dot corresponds to the diaminoallyl adduct.

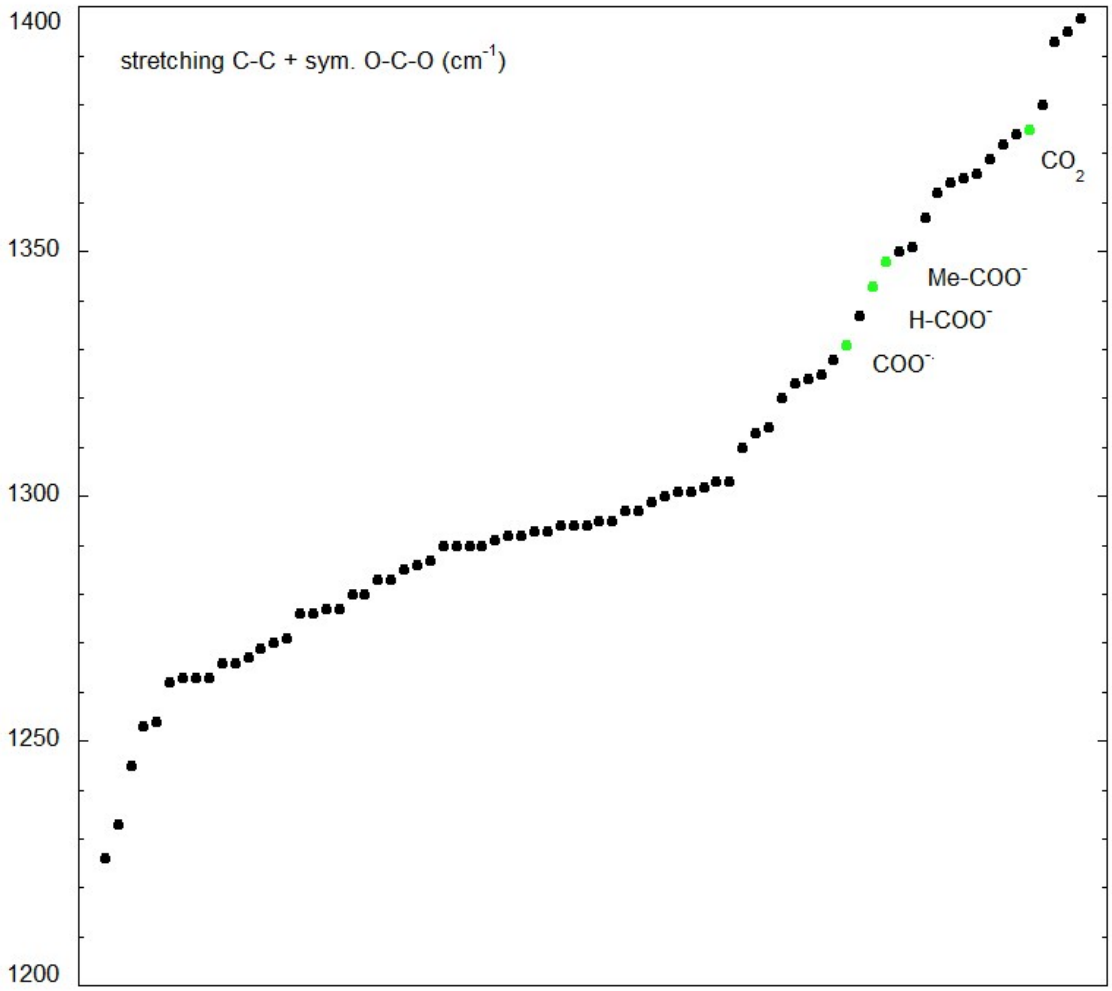

Figure S2. Range of calculated harmonic vibrational frequencies for the symmetric O-C-O stretching mode (with various mixing); green dots refer to simple parent carboxylates.

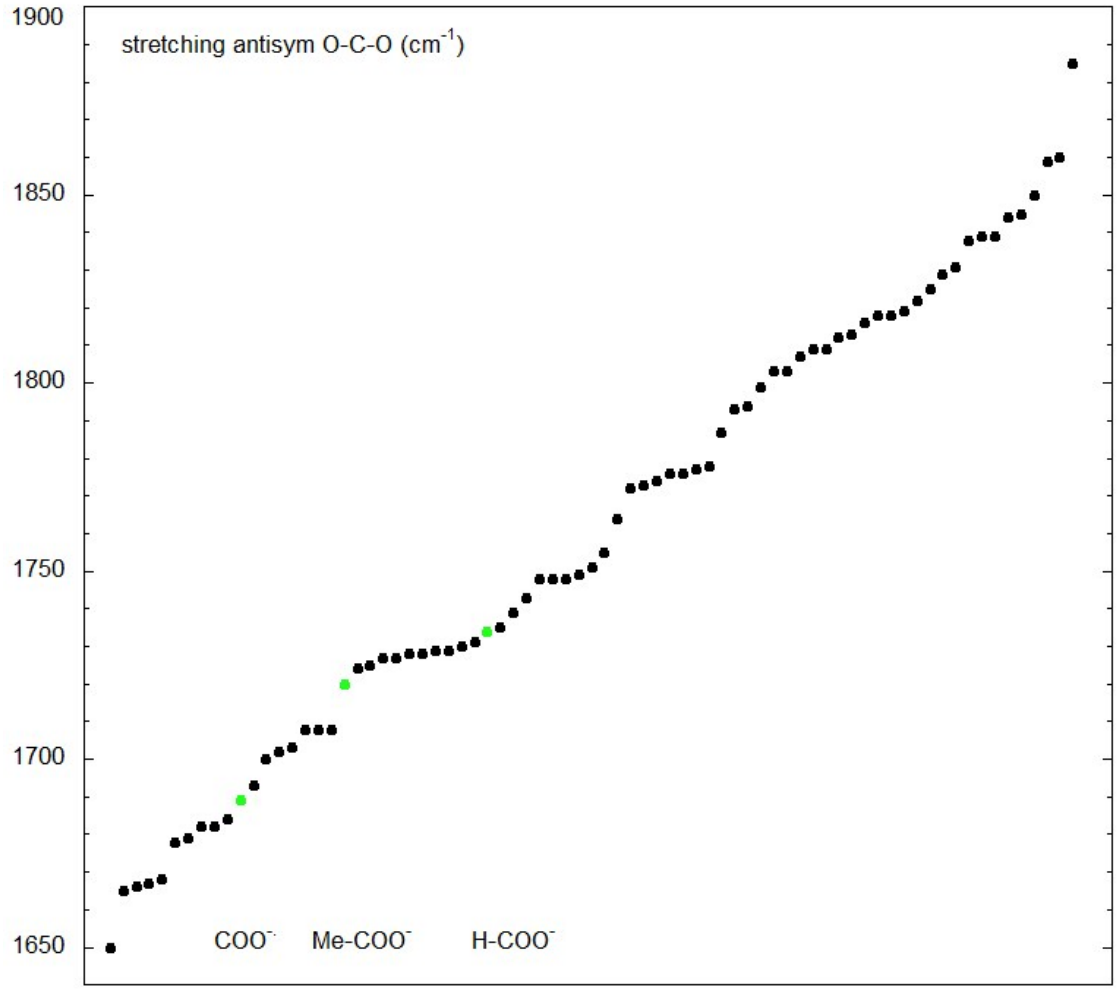

Figure S3. Range of calculated harmonic vibrational frequencies for the antisymmetric O-C-O stretching mode; green dots refer to simple parent carboxylates.