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Supporting Information

Competitivity and cooperativity of hydrogen-bonding and tetrel-bonding interactions involving triethylene diamines (DABCO), H_2O and CO_2 in air

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Table S1 The bond angles (θ, in º) of CO_2 in the dimers (**D2**, **D3**, **D5**) and trimers (**T2**, **T3**, **T5**, **T6**, **T7**, **T8**, **T9**) at the M06-2X/aug-cc-pVDZ level of theory without (non-CP) and with the CP methods, and the corresponding parameters of CO_2.

	Method	Bond angle
D2	Non-CP	θ(O2-C1-O3)=177.9
	CP	θ(O2-C1-O3)=178.0
D3	Non-CP	θ(O2-C1-O3)=180.0; θ(O2′-C1′-O3′)=179.5
	CP	θ(O2-C1-O3)=180.0; θ(O2′-C1′-O3′)=179.5
D5	Non-CP	θ(O2-C1-O3)=175.7
	CP	θ(O2-C1-O3)=176.0
T2	Non-CP	θ(O2-C1-O3)=175.9
	CP	θ(O2-C1-O3)=176.1
T3	Non-CP	θ(O2-C1-O3)=175.8; θ(O2′-C1′-O3′)=175.8
	CP	θ(O2-C1-O3)=176.0; θ(O2′-C1′-O3′)=176.0
T5	Non-CP	θ(O2-C1-O3)=175.1; θ(O2′-C1′-O3′)=178.9
	CP	θ(O2-C1-O3)=175.3; θ(O2′-C1′-O3′)=179.0
T6	Non-CP	θ(O2-C1-O3)=176.6
	CP	θ(O2-C1-O3)=176.7
T7	Non-CP	θ(O2-C1-O3)=177.4
	CP	θ(O2-C1-O3)=177.5
T8	Non-CP	θ(O2-C1-O3)=177.5
	CP	θ(O2-C1-O3)=177.4
T9	Non-CP	θ(O2-C1-O3)=174.3
	CP	θ(O2-C1-O3)=174.6
CO_2	Non-CP	θ(O2-C1-O3)=180.0

Table S2 The bond lengths (R, in Å) and stretching vibrational frequencies (v, in cm^{-1}) for the dimers **D1**-**D5** at the M06-2X/aug-cc-pVDZ level of theory without (non-CP) and with the CP methods, and the corresponding parameters for DABCO, H_2O and CO_2.

	Method	R	v
D1	Non-CP	$R_{O1\text{-}H1}$=0.969	$v_{O1\text{-}H1}$=3770
	CP	$R_{O1\text{-}H1}$=0.969	$v_{O1\text{-}H1}$=3775
D2	Non-CP	$R_{O1\text{-}H1}$=0.962	$v_{O1\text{-}H1}$=3866
		$R_{C1\text{-}O2}$=1.162	$v_{C1\text{-}O2}$=1403
	CP	$R_{O1\text{-}H1}$=0.962	$v_{O1\text{-}H1}$=3864
		$R_{C1\text{-}O2}$=1.162	$v_{C1\text{-}O2}$=1403
D3	Non-CP	$R_{C1\text{-}O2}$=1.162	$v_{C1\text{-}O2}$=1409
	CP	$R_{C1\text{-}O2}$=1.162	$v_{C1\text{-}O2}$=1409
D4	Non-CP	$R_{O1\text{-}H1}$=0.979	$v_{O1\text{-}H1}$=3527
	CP	$R_{O1\text{-}H1}$=0.979	$v_{O1\text{-}H1}$=3511
D5	Non-CP	$R_{C1\text{-}O2}$=1.163	$v_{C1\text{-}O2}$=1396
	CP	$R_{C1\text{-}O2}$=1.163	$v_{C1\text{-}O2}$=1397
DABCO	Non-CP	$R_{C2\text{-}H3}$=1.098	$v_{C2\text{-}H3}$=3131
		$R_{C2\text{-}H4}$=1.098	$v_{C2\text{-}H4}$=3131
		$R_{C3\text{-}H5}$=1.098	$v_{C3\text{-}H5}$=3131
		$R_{C3\text{-}H6}$=1.098	$v_{C3\text{-}H6}$=3131
		$R_{C4\text{-}H7}$=1.098	$v_{C4\text{-}H7}$=3131
CO_2	Non-CP	$R_{C1\text{-}O2}$=1.161	$v_{C1\text{-}O2}$=1407
H_2O	Non-CP	$R_{O1\text{-}H1}$=0.962	$v_{O1\text{-}H1}$=3867

Table S3 The bond lengths (R, in Å) and stretching vibrational frequencies (v, in cm^{-1}) for the trimers **T1**-**T9** at the M06-2X/aug-cc-pVDZ level of theory without (non-CP) and with the CP methods.

	Method	R	v
T1	Non-CP	$R_{O1\text{-}H1}$=0.978	$v_{O1\text{-}H1}$=3547
		$R_{O1'\text{-}H1'}$=0.978	$v_{O1'\text{-}H1'}$=3547
	CP	$R_{O1\text{-}H1}$=0.978	$v_{O1\text{-}H1}$=3545
		$R_{O1'\text{-}H1'}$=0.978	$v_{O1'\text{-}H1'}$=3545
T2	Non-CP	$R_{O1\text{-}H1}$=0.978	$v_{O1\text{-}H1}$=3521
		$R_{C1\text{-}O2}$=1.162	$v_{C1\text{-}O2}$=1397
	CP	$R_{O1\text{-}H1}$=0.978	$v_{O1\text{-}H1}$=3535
		$R_{C1\text{-}O2}$=1.162	$v_{C1\text{-}O2}$=1398
T3	Non-CP	$R_{C1\text{-}O2}$=1.163	$v_{C1\text{-}O2}$=1396
		$R_{C1'\text{-}O2'}$=1.163	$v_{C1'\text{-}O2'}$=1396
	CP	$R_{C1\text{-}O2}$=1.163	$v_{C1\text{-}O2}$=1397
		$R_{C1'\text{-}O2'}$=1.163	$v_{C1'\text{-}O2'}$=1397
T4	Non-CP	$R_{O1\text{-}H1}$=0.997	$v_{O1\text{-}H1}$=3138
		$R_{O1'\text{-}H1'}$=0.977	$v_{O1'\text{-}H1'}$=3616
		$R_{C3\text{-}H5}$=1.096	$v_{C3\text{-}H5}$=3140
		$R_{C4\text{-}H7}$=1.096	$v_{C4\text{-}H7}$=3152
	CP	$R_{O1\text{-}H1}$=0.996	$v_{O1\text{-}H1}$=3139
		$R_{O1'\text{-}H1'}$=0.976	$v_{O1'\text{-}H1'}$=3630
		$R_{C3\text{-}H5}$=1.097	$v_{C3\text{-}H5}$=3139
		$R_{C4\text{-}H7}$=1.096	$v_{C4\text{-}H7}$=3152
T5	Non-CP	$R_{C1\text{-}O2}$=1.164	$v_{C1\text{-}O2}$=1399
		$R_{C1'\text{-}O3'}$=1.163	$v_{C1'\text{-}O3'}$=1404
		$R_{C3\text{-}H5}$=1.097	$v_{C3\text{-}H5}$=3141
		$R_{C4\text{-}H7}$=1.097	$v_{C4\text{-}H7}$=3132
	CP	$R_{C1\text{-}O2}$=1.164	$v_{C1\text{-}O2}$=1395
		$R_{C1'\text{-}O3'}$=1.063	$v_{C1'\text{-}O3'}$=1405
		$R_{C3\text{-}H5}$=1.097	$v_{C3\text{-}H5}$=3139
		$R_{C4\text{-}H7}$=1.097	$v_{C4\text{-}H7}$=3130
T6	Non-CP	$R_{O1\text{-}H1}$=0.985	$v_{O1\text{-}H1}$=3379
		$R_{C1\text{-}O3}$=1.163	$v_{C1\text{-}O3}$=1400
		$R_{C3\text{-}H5}$=1.096	$v_{C3\text{-}H5}$=3145
		$R_{C4\text{-}H7}$=1.096	$v_{C4\text{-}H7}$=3140
	CP	$R_{O1\text{-}H1}$=0.985	$v_{O1\text{-}H1}$=3392
		$R_{C1\text{-}O3}$=1.163	$v_{C1\text{-}O3}$=1401
		$R_{C3\text{-}H5}$=1.097	$v_{C3\text{-}H5}$=3144
		$R_{C4\text{-}H7}$=1.097	$v_{C4\text{-}H7}$=3141
T7	Non-CP	$R_{O1\text{-}H1}$=0.963	$v_{O1\text{-}H1}$=3865
		$R_{C1\text{-}O3}$=1.165	$v_{C1\text{-}O3}$=1395
	CP	$R_{O1\text{-}H1}$=0.963	$v_{O1\text{-}H1}$=3866
		$R_{C1\text{-}O3}$=1.165	$v_{C1\text{-}O3}$=1360

T8	Non-CP	$R_{O1\text{-}H1}$=0.981	$v_{O1\text{-}H1}$=3447
		$R_{C1\text{-}O2}$=1.161	$v_{C1\text{-}O2}$=1401
		$R_{C2\text{-}H3}$=1.097	$v_{C2\text{-}H3}$=3135
		$R_{C3\text{-}H6}$=1.096	$v_{C3\text{-}H6}$=3138
	CP	$R_{O1\text{-}H1}$=0.982	$v_{O1\text{-}H1}$=3463
		$R_{C1\text{-}O2}$=1.161	$v_{C1\text{-}O2}$=1401
		$R_{C2\text{-}H3}$=1.098	$v_{C2\text{-}H3}$=3137
		$R_{C3\text{-}H6}$=1.097	$v_{C3\text{-}H6}$=3138
T9	Non-CP	$R_{O1\text{-}H1}$=0.966	$v_{O1\text{-}H1}$=3827
		$R_{C1\text{-}O3}$=1.166	$v_{C1\text{-}O3}$=1392
		$R_{C2\text{-}H4}$=1.096	$v_{C2\text{-}H4}$=3137
		$R_{C4\text{-}H8}$=1.096	$v_{C4\text{-}H8}$=3141
	CP	$R_{O1\text{-}H1}$=0.966	$v_{O1\text{-}H1}$=3830
		$R_{C1\text{-}O3}$=1.166	$v_{C1\text{-}O3}$=1393
		$R_{C2\text{-}H4}$=1.097	$v_{C2\text{-}H4}$=3136
		$R_{C4\text{-}H8}$=1.096	$v_{C4\text{-}H8}$=3139

Table S4 The difference (Δd_1, in Å) between the intermolecular distance (d_i, in Å) in the dimer and the sum of the van der Waals radii (d_r, in Å) involved in the intermolecular interaction.[a]

	d_i	d_r	Δd_1
D1	$d_{i(O1'\cdots H1)}$=1.939	$d_{r(O1', H1)}$=2.60	0.661
D2	$d_{i(O1\cdots C1)}$=2.667	$d_{r(O1, C1)}$=3.10	0.433
D3	$d_{i(O2\cdots C1')}$=2.885	$d_{r(O2, C1')}$=3.10	0.215
D4	$d_{i(H1\cdots N1)}$=1.883	$d_{r(H1, N1)}$=2.70	0.817
D5	$d_{i(C1\cdots N1)}$=2.671	$d_{r(C1, N1)}$=3.20	0.529

[a] $\Delta d_1 = d_r - d_i$.

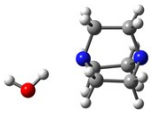
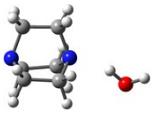
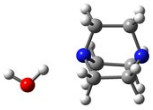
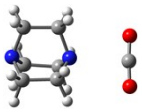
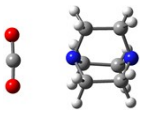
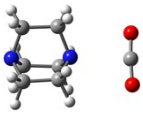
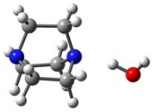
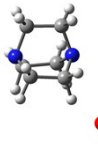
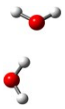
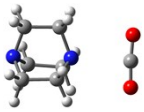
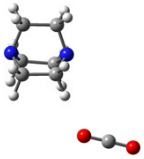
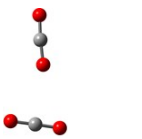
Table S5 The difference (Δd_2, in Å) between the intermolecular distance (d_i, in Å) in the trimer and the sum of the van der Waals radii (d_r, in Å) involved in the intermolecular interaction, and the cooperativity factor (B_d).

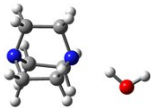
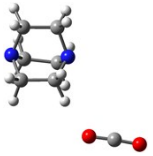
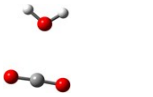
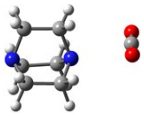
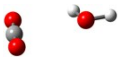
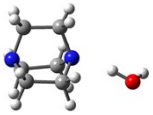
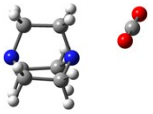
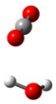
	d_i	d_r	Δd_2[a]	B_d[b]
T1	$d_{i(H1\cdots N1)}$=1.892	$d_{r(H1, N1)}$=2.70	0.808	0.989
	$d_{i(H1'\cdots N2)}$=1.892	$d_{r(H1', N2)}$=2.70	0.808	0.989
T2	$d_{i(H1\cdots N1)}$=1.890	$d_{r(H1, N1)}$=2.70	0.810	0.991
	$d_{i(C1\cdots N2)}$=2.677	$d_{r(C1, N2)}$=3.20	0.523	0.989
T3	$d_{i(C1\cdots N1)}$=2.676	$d_{r(C1, N1)}$=3.20	0.524	0.991
	$d_{i(C1'\cdots N2)}$=2.676	$d_{r(C1', N2)}$=3.20	0.524	0.991
T4	$d_{i(H1\cdots N1)}$=1.744	$d_{r(H1, N1)}$=2.70	0.956	1.170
	$d_{i(H1'\cdots O1)}$=1.834	$d_{r(H1', O1)}$=2.60	0.766	1.159
T5	$d_{i(C1\cdots N1)}$=2.648	$d_{r(C1, N1)}$=3.20	0.552	1.043
	$d_{i(C1'\cdots O2)}$=2.772	$d_{r(C1', O2)}$=3.10	0.328	1.526
T6	$d_{i(H1\cdots N1)}$=1.827	$d_{r(H1, N1)}$=2.70	0.873	1.069
	$d_{i(C1\cdots O1)}$=2.613	$d_{r(C1, O1)}$=3.10	0.487	1.125
T7	$d_{i(C1\cdots N1)}$=2.711	$d_{r(C1, N1)}$=3.20	0.489	0.924
T8	$d_{i(H1\cdots N1)}$=1.850	$d_{r(H1, N1)}$=2.70	0.850	1.040
	$d_{i(O1\cdots C1)}$=2.789	$d_{r(O1, C1)}$=3.10	0.311	0.718

[a] $\Delta d_2 = d_r - d_i$.

[b] $B_d = \Delta d_2/\Delta d_1$. Note that the intermolecular distance in the trimer has correspondence with that in the dimer.

Table S6 The geometries and interaction energies (ΔE_{int}, in kcal/mol) of the ingredients in trimers **T1**-**T8** at the M06-2X/aug-cc-pVDZ level of theory without the CP methods, and the sum of the interaction energies (ΔE_{sum}, in kcal/mol) of the ingredients.

	Geometry	ΔE_{int}	ΔE_{sum}
T1		-8.66	-17.32
		-8.66	
T2		-8.77	-14.77
		-6.00	
T3		-5.98	-11.96
		-5.98	
T4		-8.99	-17.13
		-3.14	
		-5.00	
T5		-6.06	-8.28
		-1.01	
		-1.21	

T6		-8.89	
		-1.15	-13.69
		-3.65	
T7		-5.73	-8.75
		-3.02	
T8		-8.33	
		-3.97	-13.47
		-1.17	

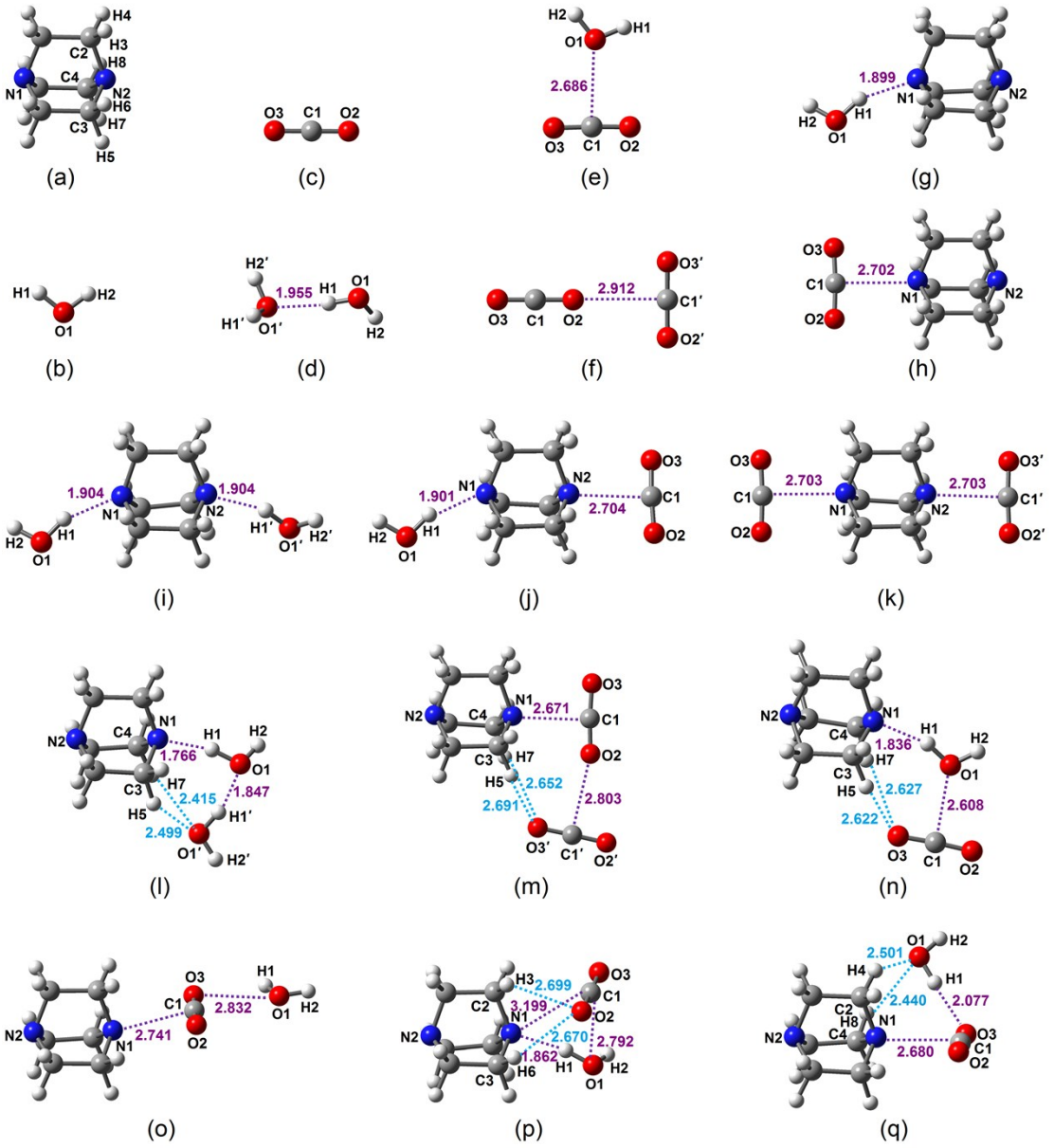


Fig. S1 The optimized geometries of the monomers (a) DABCO; (b) H_2O; (c) CO_2; and the dimers (d) **D1**; (e) **D2**; (f) **D3**; (g) **D4**; (h) **D5**; and the trimers (i) **T1**; (j) **T2**; (k) **T3**; (l) **T4**; (m) **T5**; (n) **T6**; (o) **T7**; (p) **T8**; (q) **T9** and the intermolecular distances (Å) for these complexes at the M06-2X/aug-cc-pVDZ level of theory with CP optimization.