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Substituent effects on the stability of carbodiimides

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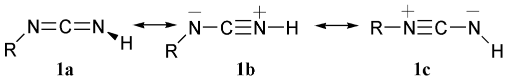
The geometries and energies of mono-substituted carbodiimides RN=C=NH and imines $RN=CH_2$ have been obtained by *ab initio* DFT calculations. The geometries of carbodiimides with strongly electropositive substituents are linear, which is attributed to charge repulsion and a preference for sp-hybridization at the nitrogen atom. An isodesmic reaction was designed to study substituent effects on the stability of carbodiimides. The correlation between substituent group electronegativity χ_{BE} and the stability of carbodiimides was reasonably good. Electronegative substituents destabilize carbodiimides, whereas electropositive substituents stabilize them.

Introduction

Carbodiimides are an important class of unsaturated compounds that contain two carbon–nitrogen double bonds in an orthogonal geometry. They have attracted considerable attention because of their importance as a versatile reagent in organic and biochemical synthesis.[1–4] Carbodiimides are isoelectronic with allenes, ketenes and ketenimines, and can be represented by the resonance structures **1a**, **1b** and **1c**. They have an asymmetric allene-like structure.



1a **1b** **1c**

Optical isomerism in such compounds is possible but resolution has not been achieved because of the low free energy barrier to racemization.[5–11]

Semiempirical quantum mechanical calculations (INDO) predict the intuitively favored asymmetric geometry with substituents in perpendicular planes that intersect along the N=C=N axis.[5] The calculated energy for thermal racemization of carbodiimides and difluorocarbodiimides are 8 and 22 kcal mol^{-1}, respectively.[5] The configurational flexibility of diisopropylcarbodiimide has been studied by ^1H-NMR measurements[6] and the free activation energy for racemization was found to be 6.7 kcal mol^{-1}. X-Ray diffraction results have been reported for diarylcarbodiimides.[9] These molecules exhibit an allene-type structure with the dihedral angle between the two aryl groups being 88° for di-*p*-tolylcarbodiimide.[9] Geometrical isomerisation involving carbodiimides can take place by two processes: planar nitrogen inversion and internal rotation about the C=N bond, which may lead to a *cis* or *trans* transition state. According to MP4/6-311G(d,p) calculations[7] for the parent carbodiimide, the corresponding barriers are 10.6, 8.0 and 7.9 kcal mol^{-1}, respectively. Recently, AM1 SCF MO calculations were carried out on the configurational mechanism of some substituted carbodiimides.[12]

Systematic studies of substituent effects on molecules containing different functional groups in organic compounds have been presented by many groups in recent years.[13–21] These compounds include ketenes,[13a–c] isocyanates,[13d] imines,[13d] allenes,[13c,14] ketenimines,[15a,b] oxiranes,[15c] nitriles,[15d] isocyanides,[15d] cyclopropanes,[16] diazirines,[13c,17a,b] diazomethanes,[13c,17c–e] alkanes,[16] alkenes,[16a,c,18b] alkynes,[16a,18b] 1,3-dienes,[19a] cyclopropenes,[13a] carbonyl compounds,[18a,19b] carbocations,[20] carbanions,[21a] and organolithium compounds.[21b]

In this work, we wish to report the use of *ab initio* calculations using density functional theory (DFT) and isodesmic reactions to study the influence of different substituents on the geometry and stability of carbodiimides.

Computational details

All the calculations reported here were performed with the Gaussian 98 program.[22] All geometries were gradient optimized at the HF/6-31+G(d) level without any symmetry restriction. The orders (number of negative diagonal elements of the Hessian matrix) of all critical points were evaluated at the same level to determine the nature of the located stationary points. Thus, all of the stationary points found were properly characterized by evaluation of the harmonic frequencies. This also provides the necessary thermodynamic data for the calculation of zero-point vibrational energies (ZPVE). The scaling factor of 0.8929 for zero-point vibrational energies is used in accordance with the literature.[13b–d,23]

Single point energies of the optimized structures were determined by density functional theory (DFT) at the B3LYP/6-311+G(2d,p) level using the optimized HF/6-31+G(d) geometries. The energies of all stationary points were calculated at the DFT level with scaled zero-point vibrational energies included.

Results

The optimized geometries and calculated structural parameters of carbodiimides **2–25** are given in Fig. 1 and Table 1. The calculated energies of substituted carbodiimides RN=C=NH and imines $RN=CH_2$ are shown in Table 2.

All of the carbodiimides have an NH group perpendicular to the carbodiimide plane. In addition, all of the calculated carbodiimides with different substituents show a bent structure around the N=C=N angle by about 5–8° (see Fig. 1 and Table 1). The calculated net atomic charges of the nitrogen atoms and central carbon atom of substituted carbodiimides **2–25** as well as dipole moments calculated at the HF/6-31+G(d) level of theory are shown in Table 3.

The parent carbodiimide **2** shows two identical N=C bond lengths of 1.205 Å. Carbodiimide **6** with a CH_3 substituent shows two unequal $N^3=C^2$ and $C^2=N^1$ bond lengths of 1.199 and 1.218 Å. Carbodiimide **3** with a Li substituent shows a long bond length for the Li–N bond (1.749 Å), which indicates its ionic character. The $N^3=C^2$ bond length is significantly shorter

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Table 1 Calculated structural parameters (bond lengths/Å; bond angles and dihedral angles/°) for carbodiimides **2–25** $X_{a,b}MN^3{=}C^2{=}N^1H$

	M	N^3C^2	C^2N^1	MN^3	X_aM	X_bM	$N^3C^2N^1$	MN^3C^2	X_aMN^3	X_bMN^3	$X_aMN^3C^2$	$X_bMN^3C^2$
2	H	1.205	1.205	0.999			173.6	118.0				
3	Li	1.181	1.246	1.749			174.9	175.6				
4	BeH	1.190	1.213	1.493	1.329		174.4	179.2	179.5		0.0	
5	BH_2	1.183	1.217	1.400	1.187	1.187	174.7	178.5	119.1	119.1	−115.7	64.5
6	CH_3	1.199	1.218	1.451	1.085	1.081, 1.081	173.5	127.4	112.6	108.9, 108.6	0.3	−120.0, 121.4
7	CF_3	1.216	1.196	1.400	1.327	1.316, 1.315	172.9	123.7	113.3	110.5, 110.3	3.3	−117.3, 123.6
8	NH_2	1.212	1.213	1.418	1.004	1.000	172.2	119.2	107.8	105.1	−78.8	167.6
9	OH	1.221	1.209	1.386	0.948		172.6	114.1	103.8		178.6	
10	F	1.236	1.200	1.379			172.4	109.1				
11	Na	1.178	1.256	2.103			175.0	173.4				
12	MgH	1.186	1.229	1.896	1.700		174.5	176.4	178.7		180.0	
13	AlH_2	1.187	1.218	1.776	1.574	1.572	174.5	180.0	118.3	117.6	−13.6	164.9
14	SiH_3	1.183	1.216	1.711	1.469	1.471, 1.470	174.4	174.7	110.1	109.0, 108.4	−1.4	−121.4, 118.7
15a	PH_2	1.195	1.216	1.716	1.405	1.398	174.3	137.9	99.9	97.0	56.8	152.9
15b	PH_2	1.195	1.216	1.718	1.404	1.397	173.4	136.9	99.7	97.0	59.9	156.1
16a	SH	1.206	1.213	1.705	1.322		173.3	124.8	94.6		177.9	
16b	SH	1.204	1.214	1.699	1.331		173.6	127.9	99.9		7.4	
17	Cl	1.223	1.203	1.713			172.8	115.6				
18a	Cyclopropyl	1.200	1.218	1.432	1.077[a]	1.494,[b] 1.495[b]	173.5	126.8	115.4[c]	117.3,[d] 117.1[d]	1.8[e]	−144.0,[f] 147.2[f]
18b	Cyclopropyl	1.200	1.217	1.436	1.073[a]	1.496,[b] 1.491[b]	173.1	128.0	111.2[c]	122.3,[d] 119.4[d]	−129.7[e]	17.3,[f] 89.1[f]
19	NO_2	1.244	1.180	1.386	1.198	1.179	171.3	114.7	118.5	114.9	−5.0	174.6
20a	CHO	1.226	1.190	1.398	1.186[g]	1.083[b]	172.2	121.2	125.6[h]	111.7[d]	−9.4[i]	171.4[f]
20b	CHO	1.217	1.198	1.401	1.179[g]	1.090[b]	173.5	123.2	122.7[h]	115.3[d]	−173.8[i]	6.7[f]
21a	$H_2C{=}CH$	1.205	1.211	1.407	1.321[a]	1.073[b]	173.7	128.3	125.9[c]	112.5[d]	30.5[e]	−151.0[f]
21b	$H_2C{=}CH$	1.206	1.212	1.405	1.319[a]	1.077[b]	173.4	126.5	121.7[c]	116.8[d]	−177.4[e]	3.1[f]
22a	CO_2H	1.222	1.192	1.386	1.182[g]	1.333[j]	172.1	123.7	123.7[h]	113.0[k]	174.2[i]	−6.3[lm]
22b	CO_2H	1.227	1.188	1.403	1.183[g]	1.318[j]	172.6	119.9	125.6[h]	111.6[k]	−6.4[i]	174.2[ln]
22c	CO_2H	1.225	1.190	1.387	1.191[g]	1.317[j]	172.1	120.1	126.1[h]	110.2[k]	−6.9[i]	173.7[lo]
23	HC≡C	1.212	1.201	1.343	1.187		172.3	127.7	176.7		177.1	
24	CN	1.223	1.188	1.334	1.137		172.2	125.1	176.5		175.5	
25a	HSO_2	1.225	1.188	1.650	1.321[p]	1.426,[q] 1.419[q]	173.1	121.9	97.1[r]	109.7,[s] 109.3[s]	−140[t]	−27.3,[u] 107.7[u]
25b	HSO_2	1.226	1.187	1.649	1.320[p]	1.426,[q] 1.419[q]	173.0	121.7	97.1[r]	108.7,[s] 108.4[s]	5.2[t]	−107.2,[u] 118.0[u]

[a] C–C. [b] C–H. [c] C–C–N. [d] H–C–N. [e] C–C–N=C. [f] H–C–N=C. [g] O=C. [h] O=C–N. [i] O=C–N=C. [j] O–C. [k] O–C–N. [l] O–C–N=C. [m] −0.9 (H–O–C=O). [n] −179.7 (H–O–C=O). [o] 0.3 (H–O–C=O). [p] H–S. [q] O=S. [r] H–S–N. [s] O=S–N. [t] H–S–N=C. [u] O=S–N=C.

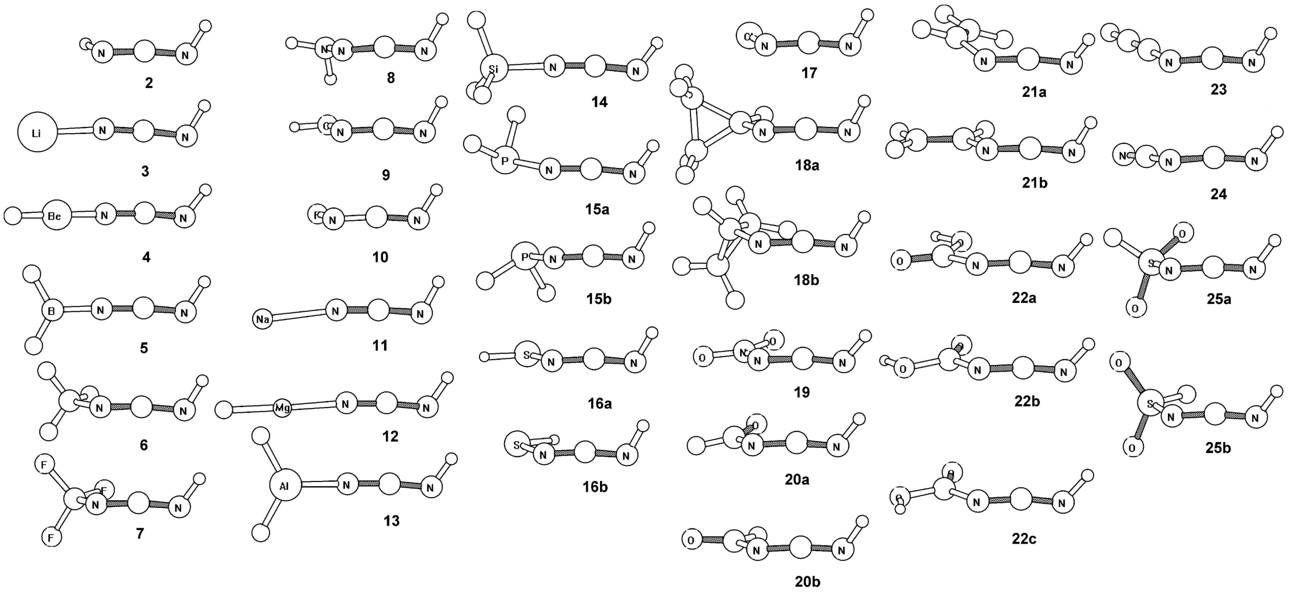


Fig. 1 Optimized structures of carbodiimides at the HF/6-31+G(d) level.

(1.181 Å) than the $C^2{=}N^1$ bond length (1.246 Å). Carbodiimide **11** with an Na substituent shows a similar pattern. The long Na–N bond length (2.103 Å) and two different C=N bond lengths (1.178 and 1.256 Å) suggest an ionic nitrilamine structure for these substituents.

The carbodiimide with a BeH substituent (**4**) shows bond lengths of 1.190 and 1.213 Å for the $N^3{=}C^2$ and $C^2{=}N^1$ bonds, respectively, the former is 1.5 pm shorter and the latter is 0.8 pm longer than the corresponding bonds in carbodiimide **2**. The carbodiimide with an MgH substituent (**12**) shows a long bond length (1.896 Å) for the Mg–N bond, while the $N^3{=}C^2$ bond length (1.186 Å) is 1.9 pm shorter and the $C^2{=}N^1$ bond length (1.229 Å) is 2.4 pm longer than the corresponding bonds in the carbodiimide with an H substituent (**2**). Both carbodiimides **4** and **12** have a linear arrangement about the X–N=C moiety, in which X corresponds to the BeH and MgH groups. Carbodiimides with BH_2 (**5**) and AlH_2 (**13**) substituents have BH_2 and AlH_2 groups located almost in the same plane as the carbodiimide fragment. The B–N and Al–N bond lengths are 1.400 and 1.776 Å, respectively. The $N^3{=}C^2$ bond lengths for carbodiimides **5** and **13** are 2.2 and 1.8 pm shorter than the corresponding bond in carbodiimide **2**, respectively, while

Table 2 Calculated energies [B3LYP/6-311+G(2d,p)//HF/6-31+G(d)] (hartrees) for carbodiimides R–N=C=NH and imines R–N=CH$_2$ and ΔE (kcal mol^{-1}) for the isodesmic reaction shown in eqn. (1)

R	χ_{BE}	E (RN=C=NH)	E (RN=CH$_2$)	ΔE
Na	1.00	−310.547918	−256.326566	29.84
Li	1.00	−155.785521	−101.569259	26.65
MgH	1.33	−348.941720		23.31
BeH	1.47	−163.609373	−109.405324	18.99
AlH$_2$	1.62	−391.895918	−337.696530	15.31
SiH$_3$	1.91	−439.542776	−385.349113	12.47
BH$_2$	1.93	−174.277041	−120.108413	−3.24
PH$_2$[a]	2.17	−490.776124	−436.594358	5.01
H	2.20	−148.806189	−94.625765	4.16
HSO$_2$[a]	2.53	−697.449395	−643.183504	−0.26
CH$_3$	2.56	−188.095122	−133.921334	0
Cyclopropyl[a]	2.56	−265.467448	−211.296547	−1.81
CHO[a]	2.60	−262.153238	−207.974664	3
CH=CH$_2$[a]	2.61	−226.187443	−172.013676	−0.01
SH[a]	2.63	−547.000025	−492.833304	−4.44
C≡CH	2.66	−224.944432	−170.773049	−1.51
CO$_2$H[a]	2.66	−337.422217	−283.244710	2.33
CF$_3$	2.68	−485.947509	−431.774850	−0.71
CN	2.69	−241.053132	−186.881148	−1.13
Cl	3.05	−608.389969	−554.229818	−10.44
NH$_2$[a]	3.10	−204.114087	−149.960241	−12.51
NO$_2$	3.22	−353.325417	−299.163639	−7.54
OH	3.64	−223.976565	−169.831070	−17.75
F	4.00	−247.988954	−193.848959	−21.2

[a] The most stable conformer.

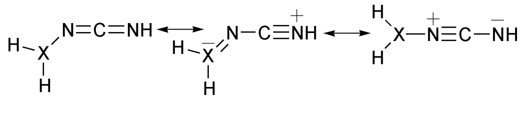
Table 3 Calculated net atomic charges and dipole moments of carbodiimides RN=C=NH [HF/6-31+G(d)]

R	C^2	N^1	N^3	R[b]	μ/D
Na	0.35	−0.89	−0.69	0.87	11.20
Li	0.33	−0.84	−0.38	0.53	8.68
MgH	0.29	−0.78	−0.56	0.61	1.70
BeH	0.72	−0.75	−0.93	0.61	1.70
AlH$_2$	0.36	−0.71	−0.17	−0.43	2.01
SiH$_3$	0.59	−0.77	−0.68	0.87	1.94
BH$_2$	0.64	−0.73	−0.59	0.42	1.78
PH$_2$[a]	0.55	−0.75	−0.59	0.42	1.55
H	0.63	−0.73	−0.73	0.41	2.50
HSO$_2$[a]	0.60	−0.66	−0.65	1.53	3.32
CH$_3$	0.57	−0.57	−0.41	−0.43	2.63
Cyclopropyl[a]	0.47	−0.72	−0.36	−0.15	2.52
CHO[a]	0.69	−0.70	−0.48	0.33	2.12
CH=CH$_2$[a]	0.53	−0.72	−0.44	−0.07	2.21
SH[a]	0.59	−0.71	−0.56	0.15	1.95
C≡CH	0.61	−0.71	−0.46	−0.25	2.20
CO$_2$H[a]	0.70	−0.68	−0.57	0.84	1.59
CF$_3$	0.59	−0.68	−0.54	1.43	3.01
CN	0.64	−0.69	−0.46	0.44	5.09
Cl	0.63	−0.67	−0.48	0.09	2.48
NH$_2$[a]	0.61	−0.71	−0.34	−0.80	1.32
NO$_2$	0.71	−0.64	−0.42	0.40	4.93
OH	0.64	−0.66	−0.39	−0.52	1.78
F	0.63	−0.62	−0.22	−0.22	3.15

[a] The most stable conformer. [b] Atom connected to N^3.

the C^2=N^1 bond lengths for these carbodiimides are 1.2 and 1.3 pm longer than the C^2=N^1 bond length of carbodiimide **2**, respectively.

The carbodiimide **6** with a CH$_3$ substituent shows a C–N=C angle about 127°, while carbodiimide **14** with an SiH$_3$ substituent shows co-planarity of the SiH$_3$ substituent with the carbodiimide moiety, which is caused by a π-donation mechanism as found for **4**, **5**, **12** and **13**. The N^3=C^2 bond length of **14** is 1.6 pm shorter than the corresponding bond of the carbodiimide with a CH$_3$ substituent (**6**), while the C^2=N^1 bond length of **14** is only 0.2 pm shorter than the same bond of **6**. Carbodiimide **7** with a CF$_3$ substituent also shows a bent arrangement around the C–N=C moiety. The N^3=C^2 bond length of **7** is 1.7 pm longer than the N^3=C^2 bond length of a carbodiimide with a CH$_3$ substituent, while the C^2=N^1 bond length of **7** is 2.2 pm shorter than the similar bond length of **6**.



For the elements of group V, the carbodiimide with an NH$_2$ substituent (**8**) has only one stationary point, while the carbodiimide with a PH$_2$ substituent (**15**) has two stationary points, in which structure **15b** is less than 0.1 kcal mol^{-1} more stable than **15a**. The N^3=C^2 and C^2=N^1 bond lengths of carbodiimide **8** are 0.7 and 0.8 pm longer than the N^3=C^2 and C^2=N^1 bond lengths of carbodiimide **2**. The N^3=C^2 bond length of carbodiimide with a PH$_2$ substituent (**15**) is 1.0 pm shorter than the N^3=C^2 bond length of **2**, while the C^2=N^1 bond length of **15** is 1.1 pm longer than the similar bonds in carbodiimide **2**. The larger X–N=C angle in **15** (X = PH$_2$, 137°) in comparison with **8** (X = NH$_2$, 119°) is caused by the higher electron-donating character of the PH$_2$ group compared to the NH$_2$ group. This pattern is also observed for the group VI ligands. Carbodiimide **9** with an OH substituent has only one stationary point, while the carbodiimide with an SH substituent (**16**) has two stationary points, in which **16a** is 1.4 kcal mol^{-1} more stable than **16b**. The X–N=C angle in **9** is about 114° while this angle in **16** is larger (about 125 and 128° for the two different rotamers). The N^3=C^2 bond length of **9** is 1.6 pm longer than the corresponding bond length of **2**, while the C^2=N^1 bond length of **9** is only 0.4 pm longer than the corresponding bond of **2**. Carbodiimide **10** with an F substituent has a short F–N bond length (1.379 Å). This molecule has a longer N^3=C^2 bond length of 3.1 pm with respect to the corresponding bond length in **2**. On the other hand, the C^2=N^1 bond length of **10** is 0.5 pm shorter than that of carbodiimide **2**. The carbodiimide with a Cl substituent (**17**) has longer N^3=C^2 (1.8 pm) and shorter C^2=N^1 (0.2 pm) bond lengths with respect to the corresponding bond lengths of carbodiimide **2**. The X–N=C angle of carbodiimide **10** is about 6° smaller than that of carbodiimide **17** with a Cl substituent.

These results suggest that the more electronegative substituents allow smaller X–N=C angles, while more electropositive substituents produce a co-planar arrangement of substituents with the carbodiimide moiety and the X–N=C angle increases to about 180°.

Carbodiimide **18** with a cyclopropyl substituent has two stationary points, in which the H–C–N=C dihedral angles of **18a** and **18b** are 1.8 and −129.7°, respectively, and **18a** is 1.3 kcal mol^{-1} more stable than **18b**. Carbodiimide **19** has only one stationary point, in which the NO$_2$ group is almost in the same plane as the N=C=N fragment. The N^3=C^2 bond length of **19** is 3.9 pm longer than the N^3=C^2 length of **2**, while the C^2=N^1 bond length of **19** is 2.5 pm shorter than that of **2**. The carbodiimide with a CH=O substituent has s-*trans* and s-*cis* stationary points, and the s-*cis* conformer (**20a**) is 0.7 kcal mol^{-1} more stable than the s-*trans* conformer (**20b**). Both the s-*cis* and the s-*trans* conformers contain C=O and N=C=N almost in the same plane, and have longer N^3=C^2 bond lengths (2.1 and 1.2 pm) and shorter C^2=N^1 bond lengths (1.5 and 0.7 pm) than the corresponding bonds of **2**.

Carbodiimide **21** with a CH=CH$_2$ substituent has s-*cis* (**21a**) and s-*trans* (**21b**) stationary points, in which the s-*trans* is 1.9 kcal mol^{-1} more stable than the s-*cis* conformer. The s-*trans* conformer has C=C and N=C=N almost in the same plane, while the s-*cis* conformer has a twisted structure with a dihedral angle of 30.5° between C=C and N=C=N. The carbodiimide with a CO$_2$H substituent (**22**) has three stationary points, of which **22b** is the most stable conformer. All three conformers have CO$_2$H and N=C=N almost in the same plane. Each of carbodiimides **23** and **24** has only one stationary point. The carbodiimide with an HSO$_2$ substituent (**25**) has two stationary points, of which conformer **25b** is less than 0.1 kcal mol^{-1}

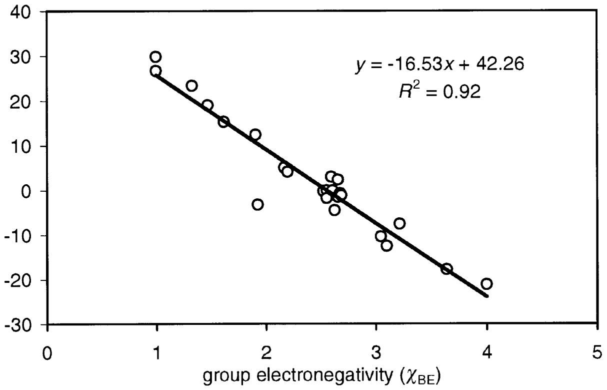
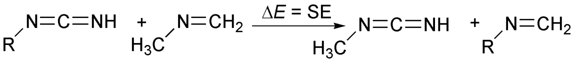


Fig. 2 A plot of ΔE of the isodesmic reaction [eqn. (1)] against substituent group electronegativity (χ_{BE}).

more stable than **25a**. All of the carbodiimides **22**, **24** and **25** have significantly longer $N^3{=}C^2$ and shorter $C^2{=}N^1$ bond lengths relative to carbodiimides with H or CH_3 substituents.

Isodesmic and homodesmic reactions are widely used to predict the stability of compounds, because errors in the energies of reactants and products are more likely to cancel out, thereby allowing simple computational approaches to give accurate estimates of heats of reaction.[23,24] Generally, a substituted reactant of one type is more stable than the substituted product of another type if the isodesmic or homodesmic reaction is endothermic, and a substituted product of one type is more stable than the substituted reactant of another type if the reaction is exothermic. The isodesmic methyl exchange reaction [eqn. (1)] was used to study the stabilizing effect of a substituent R on a carbodiimide relative to the effect of R on an imine. In this reaction not only are the numbers of N=C, N–H, C–R and C–H bonds unchanged, but also R is transferred from one secondary nitrogen atom to another and so the energy change resulting from factors other than electronic stabilization are minimized. The calculated energies at the B3LYP/6-311+G(2d,p)//HF/6-31+G(d) level were used to calculate the isodesmic stabilization energies according to eqn. (1).



$$R{-}N{=}C{=}NH + H_3C{-}N{=}CH_2 \xrightarrow{\Delta E\,=\,SE} H_3C{-}N{=}C{=}NH + R{-}N{=}CH_2 \qquad (1)$$

There has been a recent spirited discussion about the definition of electronegativity[25] and there are several different electronegativity scales. It has been shown that for cumulene systems like ketenes, ketenimines, allenes, isocyanates and diazomethanes the Boyd and Edgecombe scale[25b] gives the best correlation of substituent effects. The χ_{BE} values have another advantage in that they are available for most of the substituents studied, but not for hydrogen, for which the Pauling value of 2.20 is used. A plot (Fig. 2) of the ΔE values for the isodesmic reactions against substituent group electronegativity (χ_{BE}) gives a linear correlation ($r^2 = 0.92$). The linear correlation can be represented by eqn. (2).

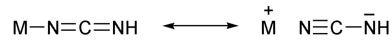
$$\Delta E = -16.53\,\chi_{BE} + 42.26 \qquad (2)$$

The negative slope of eqn. (2) indicates that the stabilization energy of the isodesmic reaction [eqn. (1)] decreases as the electronegativity of the substituent increases. Electronegative substituents like F, Cl, OH and NH_2 show significant negative stabilization energies, while electropositive substituents like Li, Na, BH, MgH, AlH_2 and SiH_3 show significant positive stabilization energies.

Discussion

As seen from eqn. (2), the correlation between the stabilization energy [eqn. (1), $\Delta E = SE$] with group electronegativity of different substituents is quite good. This correlation indicates that electropositive substituents stabilize carbodiimides while electronegative substituents destabilize them. Similar results have been found for some other cumulenes like ketenes,[13a–c] ketenimines,[15] allenes,[13c,14] diazomethanes[13c,17c–e] and isocyanates.[13d] The slopes of the correlation curves are −11.3 for ketenimines, −15.6 for ketenes, −10.6 for diazomethanes, −5.8 for allenes, −23.6 for isocyanates and −16.5 for carbodiimides. These numbers show that among the cumulenes, the isocyanates are most sensitive to substituent group electronegativity. The order of sensitivities of cumulenes with substituent group electronegativity is isocyanates > carbodiimides > ketenes > ketenimines > diazomethanes > allenes. It implies that the electronegative heteroatoms located at the two ends of cumulenes may produce higher sensitivity of the cumulene stabilities to substituents *via* an electronic effect.

The calculated linearity of carbodiimides with highly electropositive substituents (Li, Na and Mg) is a striking structural feature. This linearity is consistent with a more effective σ-withdrawal by the nitrogen atom from the electropositive substituents when the nitrogen is sp-hybridized in a linear geometry. The carbodiimides with Li and Na and MgH show long M–N bond lengths and significantly shorter $N^3{=}C^2$ and longer $C^2{=}N^1$ bond lengths with respect to carbodiimide with an H substituent. These results suggest an ion-pair structure for these carbodiimides.

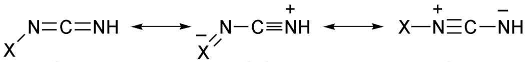


$$M{-}N{=}C{=}NH \longleftrightarrow \overset{+}{M}\;\; N{\equiv}C{-}\overset{-}{N}H$$

26a **26b**

M = Li, Na, MgH

The linear structure of carbodiimides with electropositive substituents like BeH, BH_2, AlH_2 and SiH_3 suggests that the resonance form **27c** has the greatest contribution to their structure. In this resonance form N^3 has sp-hybridization and carries positive charge, and N^1 carries negative charge. Therefore electron-donating N-substituents may help to stabilize **27c** and make the carbodiimide linear. Similar observations were reported previously for ketenimines.[15]



$$X{-}N{=}C{=}NH \longleftrightarrow X{-}\overset{-}{N}{-}C{\equiv}\overset{+}{N}H \longleftrightarrow X{-}\overset{+}{N}{\equiv}C{-}\overset{-}{N}H$$

27a **27b** **27c**

X = BeH, BH_2, AlH_2, SiH_3

Highly electronegative substituents (F, Cl, OH and NH_2) result in a bent carbodiimide structure and significant destabilization in comparison to a CH_3 substituent. Comparison of OH and SH shows that the more electronegative substituent caused greater bending of the X–N=C angle. The same pattern was observed when comparing NH_2 and PH_2 substituents. Similar π-acceptor effects were noted for BH_2 and BeH in RCH=CH_2 and ketenes.[13b]

Substituents like CN, CHO, CO_2H, SO_2H, C≡CH, and NO_2, which have unsaturated bonds conjugated with carbodiimides and serve as π-acceptors, are able to delocalize the π-electrons of carbodiimides. Although all of these substituents are electronegative [especially the nitro group which has a large electronegativity ($\chi_{BE} = 3.22$) and must destabilize carbodiimides], but because of their π-accepting properties, they have only a small destabilizing effect. For example, although NO_2 is more electronegative than the NH_2 substituent, it gives extra stabilization to the carbodiimide through π-acceptance. Even CHO and CO_2H substituents stabilize carbodiimides more than a CH_3 substituent.

Conclusions

The stability of carbodiimides is highly dependent both on the nature of the substituents and on their group electronegativity. Generally, electropositive substituents stabilize carbodiimides, while electronegative substituents destabilize them. In comparison to other studied cumulenes, carbodiimides are less sensitive to substituent group electronegativity than isocyanates, but they are more sensitive than ketenes, ketenimines, diazomethanes and allenes. Highly electropositive substituents like Li, Na and MgH provide an extra stabilization effect through an ion-pair nitrilamine resonance structure. The BeH, BH_2, AlH_2 and SiH_3 substituents delocalize π-electrons through their empty orbitals and so confer extra stability. The highly electronegative substituents F, Cl, OH and NH_2 have a destabilizing effect but the electronegative NO_2 substituent stabilizes carbodiimides by a π-acceptor effect through the bonds conjugated with the carbodiimide system.

References

1 A. Williams and I. T. Ibrahim, *Chem. Rev.*, 1981, **81**, 589.

2 M. Mikolajczyk and P. Kielbasinski, *Tetrahedron*, 1981, **37**, 233.

3 F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, 1967, **67**, 107.

4 W. Runge, in *The Chemistry of Ketenes, Allenes and Related Compounds*, ed. S. Patai, Part 1, ch. 2, Wiley, New York, 1980.

5 M. S. Gordon and H. Fischer, *J. Am. Chem. Soc.*, 1968, **90**, 2471.

6 F. A. L. Anet, J. C. Jochims and C. H. Bradley, *J. Am. Chem. Soc.*, 1970, **92**, 2557.

7 M. T. Nguyen, N. V. Riggs, L. Radom, M. Winnerwisser, B. P. Winnerwisser and M. Birk, *Chem. Phys.*, 1988, **122**, 305.

8 P. Molina, M. Alajarin, P. Sanchez-Andrada, J. S. Carrio, M. Martinez-Ripoll, J. E. Anderson, M. L. Jimeno and J. Elguero, *J. Org. Chem.*, 1996, **61**, 4289.

9 A. T. Vincent and P. J. Wheatley, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1567.

10 F. A. L. Anet and I. Yavari, *Org. Magn. Reson.*, 1976, **8**, 327.

11 I. Yavari and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 4689.

12 I. Yavari, D. Nori-Shargh, M. Dadgar and A. Taherpour, *THEOCHEM*, 1998, **427**, 185.

13 (*a*) T. T. Tidwell, *Ketenes*, Wiley, New York, 1996; (*b*) L. Gong, M. A. McAllister and T. T. Tidwell, *J. Am. Chem. Soc.*, 1991, **113**, 6021; (*c*) M. A. McAllister and T. T. Tidwell, *J. Org. Chem.*, 1994, **59**, 4506; (*d*) M. McAllister and T. T. Tidwell, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2239.

14 (*a*) P. Furet, R. L. Matcha and R. Fuchs, *J. Phys. Chem.*, 1986, **90**, 5571; (*b*) C. Lambert, P. v. R. Schleyer and E.-U. Wurthwein, *J. Org. Chem.*, 1993, **58**, 6377.

15 (*a*) K. Sung, *J. Chem. Soc., Perkin Trans 2.*, 1999, 1169; (*b*) K. Sung, *J. Chem. Soc., Perkin Trans. 2*, 2000, 847; (*c*) K. Sung, *Can. J. Chem.*, 2000, **78**, 562; (*d*) K. Sung, *J. Org. Chem.*, 1999, **64**, 8984.

16 (*a*) A. Greenberg and T. A. Stevenson, *J. Am. Chem. Soc.*, 1985, **107**, 3488; (*b*) T. Clark, G. W. Spitznagel, R. Klose and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1984, **106**, 4412; (*c*) K. B. Wiberg and K. E. Laidig, *J. Org. Chem.*, 1992, **57**, 5092; (*d*) D. Cremer and E. Kraka, *J. Am. Chem. Soc.*, 1985, **107**, 3811.

17 (*a*) C. Liang and L. C. Allen, *J. Am. Chem. Soc.*, 1991, **113**, 1878; (*b*) P. L. Muller-Remmers and K. Jug, *J. Am. Chem. Soc.*, 1985, **107**, 7275; (*c*) J. M. Goodman, J. J. James and A. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1994, 109; (*d*) F. Wang, M. A. Winnik, M. P. Peterson and I. G. Csizmadia, *THEOCHEM*, 1991, **232**, 203; (*e*) S. D. Kahan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, 1987, **109**, 1871.

18 (*a*) N. Heinrich, W. Koch, G. Frenking and H. Schwarz, *J. Am. Chem. Soc.*, 1986, **108**, 593; (*b*) J. D. Dill, A. Greenberg and J. F. Liebman, *J. Am. Chem. Soc.*, 1979, **101**, 6814.

19 (*a*) K. B. Wiberg and R. E. Rosenberg, *J. Am. Chem. Soc.*, 1990, **112**, 1509; (*b*) K. B. Wiberg, C. M. Hadad, P. R. Rablen and J. Cioslowski, *J. Am. Chem. Soc.*, 1992, **114**, 8644.

20 J. C. White, R. J. Cave and E. R. Davidson, *J. Am. Chem. Soc.*, 1988, **110**, 6308.

21 (*a*) F. Bernardi, A. Bottoni, G. S. Valli and A. Venturini, *Gazz. Chim. Ital.*, 1990, **120**, 301; (*b*) J. P. Ritchie and S. M. Bachrach, *J. Am. Chem. Soc.*, 1987, **109**, 5909.

22 *Gaussian 98, Revision A.6*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

23 J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd edn., Gaussian Inc., PA, 1996, p. 152.

24 (*a*) W. J. Hehre, L. Radom, P. v. R. Scheleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986; (*b*) P. George, M. Trachtman, C. W. Bock and A. M. Brett, *Tetrahedron*, 1976, **32**, 317.

25 (*a*) L. C. Allen, *J. Am. Chem. Soc.*, 1989, **111**, 9003; (*b*) R. J. Boyd and K. E. Edgecombe, *J. Am. Chem. Soc.*, 1988, **110**, 4182; (*c*) R. J. Boyd and S. L. Boyd, *J. Am. Chem. Soc.*, 1992, **114**, 1652; (*d*) R. G. Pearson, *Acc. Chem. Res.*, 1990, **23**, 175.