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N-Substituent effects on the stability of ketenimines

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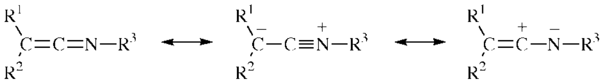
A homodesmotic reaction was designed to study *N*-substituent effects on the stability of ketenimines. A good correlation (SE1 = $-12.27\chi_{BE} + 29.81$) between *N*-substituted ketenimine stabilization energies (SE1) and substituent group electronegativity has been found. Both *N*-substituted and C_β-substituted ketenimine stabilization energies (SE1 and SE2) have good correlations with Taft's dual-substituent-parameters and modified Swain–Lupton constants. As to *N*-substituent and C_β-substituent effects on the stability of ketenimines, σ-donors stabilize ketenimines while σ-acceptors destabilize them; π-acceptors stabilize ketenimines while π-donors destabilize them.

Introduction

Substituent effects on the structures and stability of a variety of organic compounds have been extensively studied by *ab initio* calculations in recent years.[1] These compounds include ketenes,[1a–c] isocyanates,[1d] imines,[1d] allenes,[1c,2] cyclopropanes,[3] diazirines,[1c,4a,b] diazomethanes,[1c,4c–e] alkanes,[3c] alkenes,[3a,c,5] alkynes,[3a,5b] 1,3-dienes,[6a] cyclopropenes,[1c] carbonyl compounds,[5a,6b] and carbocations.[7] Recently we have studied C_β-substituent effects on the stablity of ketenimines, and found that electronegative C_β-substituents destabilize ketenimines while electropositive C_β-substituents stabilize them.[8] However, the stability was correlated with group electronegativity only. It has been suggested that the stability can be correlated with Taft's dual-substituent parameters (DSP) in order to consider both σ and π effects separately. Therefore, in this article we not only explore the *N*-substituent effects on stability of ketenimines by separately considering the σ and π effects of the substituents, but we also reinforce our previous results[8] on the C_β-substituent effects on the stablity of ketenimines by considering the separate σ and π effects of the substituents.

Ketenimines are isoelectronic with allenes and ketenes, and they can be represented by resonance structures **1a**, **1b**, and **1c**,



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

resulting in electron deficiency on C_α and electron sufficiency on C_β and N. The electron population on the cumulene is experimentally and theoretically reflected in the acid-catalyzed hydration reactions and the nucleophilic addition reactions of ketenimines.[9,10] The mechanism of the acid-catalyzed hydration reactions depends on the ketenimine structure, and it may involve either general acid protonation of C_β of the ketenimine in a rate determining step, or reversible protonation of N of the ketenimine by specific acid, H_3O.[9] Nucleophilic addition to ketenimines has nucleophiles undergo in-plane attack on the electron-deficient C_α of the ketenimine.[10]

A *syn–anti* isomerization of the imine system has been investigated since the 1960s.[11] It has been confirmed that the isomerization involves a lateral shift mechanism (inversion mechanism) rather than a torsional rotation mechanism, because the former has a lower barrier than the latter.[11] Substituent effects on the lateral shift mechanism of the imine system have been studied theoretically[11b] and experimentally.[11a,c] The conclusion is that σ-accepting and π-donating *N*-substituents disfavor the isomerization, while π-accepting *N*-substituents favor it.[11] Ketenimines possess the imine functional group and may undergo the *Z–E* isomerization by the lateral shift mechanism. The barrier to the lateral shift mechanism for the ketenimines is *ca.* 10 kcal mol^{-1}, that is, ketenimines undergo the configuration interconversion rapidly at room temperature.[12]

The Hammett equation and its extensions [eqn. (1)] correlate

$$m\log(K/K_0) = m\,\Delta\Delta G = \log(k/k_0) = \Delta\Delta G^{\ddagger} = \rho\sigma = \rho_I\sigma_I + \rho_R\sigma_R \quad (1)$$

substituent effects on reaction rates (*k*) or equilibrium constants (*K*),[13] and have been applied to substituent effects on isodesmic and homodesmotic stabilization energies of cyclopropanes, ethylenes, acetylenes, benzenes, allenes, and ketenimines.[2a,3a,8] Since entropy changes of isodesmic and homodesmotic reactions are so small as to be negligible, it is reasonable that isodesmic and homodesmotic stabilization energies are directly correlated with substituent constants (σ) [eqn. (2)]. Both the sign and the magnitude of σ for a substituent

$$\Delta E\ (\text{for isodesmic and homodesmotic reactions}) = \rho\sigma = \rho_I\sigma_I + \rho_R\sigma_R \quad (2)$$

are a measure of its capacity to perturb its environment electronically. Substituent constants σ_p and σ_m may involve both inductive and resonance contributions of substituents, but Taft's dual-substituent parameters (DSP) and modified Swain–Lupton constants provide a good way to divide the substituent constant (σ) into σ_I or *F* for inductive contribution only and σ_R or *R* for resonance contribution only.[13,14] Therefore, in this article we study substituent effects on the stability of ketenimines by correlating substituted ketenimine stabilization energies with substituent group electronegativity, Taft's DSP and modified Swain–Lupton constants, in order to study how substituents affect the stability of ketenimines *via* inductive and resonance effects.

A isodesmic reaction is one in which the total number of each type of bond is identical in the reactants and products, but there may be changes in the relationship of one bond to another.[15a] A homodesmotic reaction is defined as a reaction in which not only is the number of bonds of each type conserved, but the number of carbon atoms with zero, one, two, or three hydrogen atoms is also conserved.[15b] Isodesmic and

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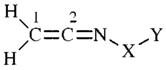
Table 1 Calculated bond lengths (Å) and angles (degrees) of *N*-substituted ketenimines



	Bond lengths/Å					Bond angle/degrees			
N-Substituent	C1–C2	C2–N	C1–H1	N–X	X–Y	C2–C1–H1	C1–C2–N	C2–N–X	N–X–Y
Li	1.339	1.180	1.073	1.755		120.0	180.0	180.0	
BeH	1.315	1.188	1.072	1.497	1.328	119.8	180.0	180.0	180.0
BH_2	1.310	1.186	1.073	1.390	1.187	120.0	180.0	180.0	118.7
MgH	1.326	1.185	1.072	1.903	1.700	119.9	180.0	180.0	180.0
AlH_2	1.317	1.187	1.072	1.778	1.572	119.9	180.0	180.0	117.4
CH_3	1.307	1.205	1.073	1.455	1.085	120.2	177.4	122.8	112.6
CF_3	1.296	1.215	1.073	1.412	1.323	120.0	175.8	121.6	114.3
SiH_3	1.311	1.197	1.073	1.745	1.475	119.9	178.2	135.6	111.4
NH_2	1.303	1.212	1.074	1.391	1.003	120.6	176.7	121.1	111.7
PH_2	1.308	1.202	1.073	1.733	1.406	120.1	178.0	128.6	100.5
OH	1.297	1.220	1.074	1.380	0.948	120.4	175.1	114.1	103.9
SH	1.303	1.210	1.073	1.715	1.323	120.2	176.7	121.2	94.6
F	1.293	1.226	1.074	1.382		120.3	174.3	110.2	
Cl	1.298	1.218	1.073	1.731		120.1	175.2	115.1	
Ethynyl	1.298	1.216	1.073	1.350	1.187	120.1	175.5	124.1	176.0
Vinyl	1.304	1.211	1.074	1.412	1.319	120.2	177.1	122.2	121.0
CHO	1.299	1.213	1.073	1.407	1.182	120.2	176.8	123.0	124.6
CN	1.293	1.222	1.074	1.346	1.137	120.0	175.4	122.0	175.7
CO_2H	1.297	1.215	1.073	1.400	1.186	119.7	176.3	120.9	125.6
NO_2	1.290	1.228	1.074	1.416	1.190	120.0	174.9	114.6	118.3
SO_2H	1.298	1.215	1.073	1.673	1.418	119.9	178.5	119.7	107.5

homodesmotic reactions are widely used in theoretical studies because errors in the energies of reactants and products are more likely to cancel, thereby allowing simple computational approaches to give accurate estimates of heats of reactions.[15c] Generally speaking, a substituted reactant is more stable than a substituted product if the isodesmic or homodesmotic reaction is endothermic; a substituted product is more stable than a substituted reactant if the reaction is exothermic.

Computation

All the calculations reported here were performed with Gaussian94 program.[16] Geometry optimizations were carried out at the level of HF/6-31+G* without any symmetry restriction. After geometry optimizations were performed, analytically vibrational frequencies were calculated at the same level to determine the nature of the located stationary points. Thus all the stationary points found were properly characterized by evaluation of the harmonic frequencies. Single point energies of the optimized structures were carried out by density functional theory (DFT) at level of B3LYP/6-311+G(2d,p)//HF/6-31+G*, and energies of all the stationary points were calculated at the same level with scaled zero-point vibrational energies included. The scaled factor of 0.8929 for zero-point vibrational energies is used according to the literature.[1b,c,13]

A method of B3LYP/6-311+G(2d,p)//HF/3-21G* was reported to have 3.2 kcal mol^{-1} of mean absolute deviation and 3.0 kcal mol^{-1} of standard deviation in prediction of thermochemical quantities.[15a] In this article we used a better basis set (6-31+G*) to optimize all the compounds, so the mean absolute deviation and standard deviation would be expected to be smaller for our results.

Results

All the C_β-substituted and *N*-substituted ketenimines were optimized at level of 6-31+G* and the most stable conformation for each of them was chosen. Structural information of the C_β-substituted ketenimines was shown in our previous paper,[8] and geometric data and figures of the *N*-substituted ketenimines are shown in Table 1 and Fig. 1.

The *N*-substituent effects on the stability of ketenimines were studied with the homodesmotic reaction eqn. (3), which

$$H_2C{=}C{=}NR + H_2C{=}NH \xrightarrow{\Delta E = \mathrm{SE1}} H_2C{=}C{=}NH + H_2C{=}NR \quad (3)$$

measures the stabilizing effect of the *N*-substituent, *R*, on the ketenimine relative to its effect on the imine. The *N*-substituted ketenimine stabilization energies (SE1) obtained from the homodesmotic reaction were correlated with substituent group electronegativity. A good linear relationship ($\mathrm{SE1} = -12.27\chi_{\mathrm{BE}} + 29.81$) was found between them with a correlation coefficient of 0.91 (Fig. 2).

In addition, the stabilization energies (SE1) were correlated with Taft's DSP and modified Swain–Lupton constants to study the inductive and resonance contribution to the *N*-substituent effects on ketenimines (Table 2). Two independent parameters (σ_I and σ_R) of Taft's DSP were taken from Charton's compendium,[14d] and two parameters (*F* and *R*) of modified Swain–Lupton constants were taken from Taft's review article.[14c] Since both π-donors and π-acceptors can cause stabilization, one must treat them separately. Therefore, substituents were divided into two categories, π-donating and π-accepting substituents. In each category, the values of σ_I (or *F*) and σ_R (or *R*) of the substituents were correlated with the stabilization energies (SE1) by eqn. (4). In the category of

$$\rho_\mathrm{I}F + \rho_\mathrm{R}R + \text{constant} = \mathrm{SE} = \rho_\mathrm{I}\sigma_\mathrm{I} + \rho_\mathrm{R}\sigma_\mathrm{R} + \text{constant} \quad (4)$$

π-donating substituents, the stabilization energies (SE1) correlate well with Taft's DSP ($r^2 = 0.91$, sey = 1.86) and modified Swain–Lupton constants ($r^2 = 0.93$, sey = 1.63) [eqns. (5) and

π Donors (F, Cl, OH, NH_2, vinyl, ethynyl, CH_3, H):

$$\mathrm{SE1} = (-14.51)\sigma_\mathrm{I} + (10.87)\sigma_\mathrm{R} - 0.15 \quad (5)$$
$$(r^2 = 0.91, \text{sey} = 1.86)$$

π Donors (F, Cl, OH, NH_2, vinyl, PH_2, SH, CH_3, H):

$$\mathrm{SE1} = (-18.20)F + (13.32)R + 1.66 \quad (6)$$
$$(r^2 = 0.93, \text{sey} = 1.63)$$

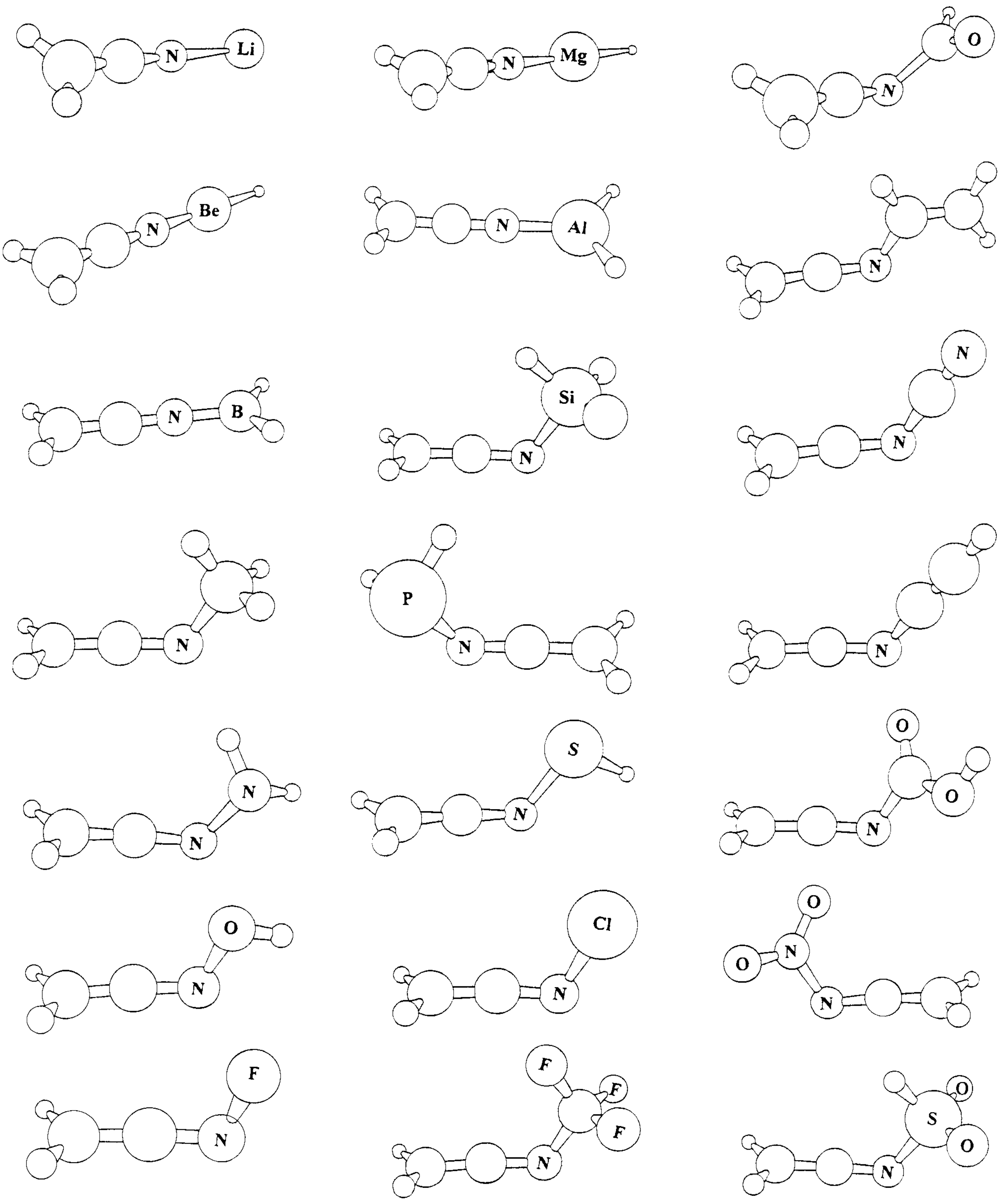


Fig. 1 Optimized structures of *N*-substituted ketenimines at the level of HF/6-31+G*.

(6)]. (Sey means standard deviation of estimated stabilization energies.) The coefficients of (σ_I, σ_R) and (F, R) are (−14.51, +10.87) and (−18.20, +13.32), respectively. In the category of π-accepting substituents, the stabilization energies (SE1) correlate well with Taft's DSP ($r^2 = 0.97$, sey = 0.69) and modified Swain–Lupton constants ($r^2 = 0.84$, sey = 2.19) [eqns. (7) and (8)]. The coefficients of (σ_I, σ_R) and (F, R) are (−11.95, +2.52) and (−20.72, +11.16), respectively.

π Acceptors (CO_2H, CN, C(O)H, NO_2, CF_3, H):

$$\mathrm{SE1} = (-11.95)\sigma_I + (2.52)\sigma_R + 0.22 \qquad (7)$$

$$(r^2 = 0.97, \mathrm{sey} = 0.69)$$

π Acceptors (SiH_3, CO_2H, CN, C(O)H, NO_2, CF_3, H):

$$\mathrm{SE1} = (-20.72)F + (11.16)R + 3.19 \qquad (8)$$

$$(r^2 = 0.84, \mathrm{sey} = 2.19)$$

The C_β-substituent effects on the stability of ketenimines have been studied by correlating C_β-substituted ketenimine stabilization energies with substituent group electronegativity.[8] To study how both inductive and resonance effects of the C_β-

Table 2 Calculated energies (B3LYP/6-311+G(2d,p)//HF/6-31+G* (hartrees) for ketenimines $H_2C{=}C{=}NR$ and imines $H_2C{=}NR$ and SE1 (kcal mol^{-1}) for the homodesmotic reaction [eqn. (3)]

R	χ_{BE}	σ_I	σ_R	F	R	$E(H_2C{=}C{=}NR)$	$E(H_2C{=}NR)$	SE1
Na	1.00					−294.46160	−256.32670	26.17
Li	1.00					−139.69240	−101.56924	18.80
MgH	1.33					−332.84752	−294.73079	14.77
BeH	1.47					−147.51440	−109.40532	9.96
AlH_2	1.62					−375.80464	−337.69667	9.27
SiH_3	1.91			0.06	0.04	−423.45130	−385.34909	5.65
BH_2	1.93					−158.19442	−120.10055	0.42
PH_2	2.17			0.09	−0.04	−474.68924	−436.59433	1.07
H	2.20	0	0	0.03	0	−132.71900	−94.62580	0.00
HSO_2	2.53					−681.36344	−643.27613	3.70
CH_3	2.56	−0.01	−0.16	0.01	−0.18	−172.01109	−133.92135	−2.17
C(O)H	2.60	0.25	0.20	0.33	0.09	−246.06416	−207.97470	−2.35
$CH{=}CH_2$	2.61	0.11	−0.15	0.13	−0.17	−210.10210	−172.01381	−3.08
SH	2.63			0.30	−0.15	−530.91967	−492.83330	−4.29
Ethynyl	2.66	0.29	−0.04	0.22	0.01	−208.85789	−170.77307	−5.26
CO_2H	2.66	0.30	0.11	0.34	0.11	−321.33331	−283.24475	−2.91
CF_3	2.68	0.40	0.11	0.38	0.16	−469.86145	−431.77490	−4.17
CN	2.69	0.57	0.08	0.51	0.15	−224.96548	−186.88118	−5.58
Cl	3.05	0.47	−0.25	0.42	−0.19	−592.31091	−554.22980	−7.59
NH_2	3.10	0.17	−0.80	0.08	−0.74	−188.03877	−149.96027	−9.22
NO_2	3.22	0.67	0.10	0.65	0.13	−337.24360	−299.16370	−8.35
OH	3.64	0.24	−0.62	0.33	−0.70	−207.90363	−169.83109	−12.96
F	4.00	0.54	−0.48	0.45	−0.39	−231.91932	−193.84899	−14.35

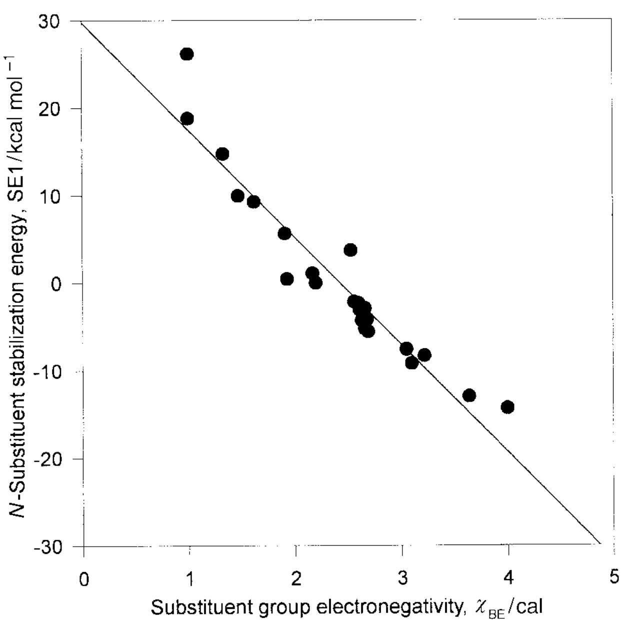


Fig. 2 A plot ($SE1 = -12.27\chi_{BE} + 29.81$) of eqn. (3)-based *N*-substituted ketenimine stabilization energies (SE1) against substituent group electronegativity (χ_{BE}).

substituents influence the stability of ketenimines, Taft's DSP and modified Swain–Lupton constants were applied and correlated with the C_β-substituted ketenimine stabilization energies (SE2) using eqn. (4). The C_β-substituted ketenimine stabilization energies (SE2) were obtained from the homodesmic reaction eqn. (9) (Table 3). In the category of π-donating substituents, the stabilization energies (SE2) correlate with Taft's DSP ($r^2 = 0.94$, sey = 1.64) and modified Swain–Lupton constants ($r^2 = 0.94$, sey = 1.68) [eqns. (10) and (11)].

$$RHC{=}C{=}NH + H_2C{=}CH_2 \xrightarrow{\Delta E = SE2} H_2C{=}C{=}NH + RHC{=}CH_2 \quad (9)$$

π Donors (F, Cl, OH, NH_2, vinyl, ethynyl, CH_3, H):

$$SE2 = (-11.08)\sigma_I + (15.71)\sigma_R + 0.34 \quad (10)$$
$$(r^2 = 0.94, \text{sey} = 1.64)$$

π Donors (F, Cl, OH, NH_2, vinyl, SH, PH_2, CH_3, H):

$$SE2 = (-15.61)F + (16.97)R + 1.74 \quad (11)$$
$$(r^2 = 0.94, \text{sey} = 1.68)$$

Coefficients of (σ_I, σ_R) and (F, R) are (−11.08, +15.71) and (−15.61, +16.97), respectively. In the category of π-accepting substituents, the stabilization energies (SE2) correlate with Taft's DSP ($r^2 = 0.73$, sey = 1.21) and modified Swain–Lupton constants ($r^2 = 0.60$, sey = 2.14) [eqns. (12) and (13)].

π Acceptors (CO_2H, CN, C(O)H, NO_2, CF_3, H):

$$SE2 = (-6.51)\sigma_I + (10.64)\sigma_R + 0.32 \quad (12)$$
$$(r^2 = 0.73, \text{sey} = 1.21)$$

π Acceptors (SiH_3, CO_2H, CN, C(O)H, NO_2, CF_3, H):

$$SE2 = (-10.37)F + (3.63)R + 2.90 \quad (13)$$
$$(r^2 = 0.60, \text{sey} = 2.14)$$

Coefficients of (σ_I, σ_R) and (F, R) are (−6.51, +10.64) and (−10.37, +3.63), respectively.

Discussion

Highly electropositive *N*-substituents like Li, BeH, BH_2, MgH, and AlH_2 make the ketenimines linear. The linear ketenimines should have the greatest contribution from resonance structure **1b**, which has an sp-hybridized N carrying positive charge and a C_β carrying negative charge. Therefore, electron-donating *N*-substituents and electron-withdrawing C_β-substituents may help to stabilize **1b** and make the ketenimines linear. This is consistent with a previous result.[17]

Based on the correlations between the *N*-substituted ketenimine stabilization energies (SE1) and substituent group electronegativity, electronegative *N*-substituents destabilize ketenimines while electropositive *N*-substituents stabilize them. This result agrees with that which we found for C_β-substituent effects on the stability of ketenimines ($SE = -11.31\chi_{BE} + 31.07$),[8] but the stability of the ketenimines is a little bit more sensitive to the electronegativity of the *N*-substituents than to that of the C_β-substituents.

As to ketenimines with π-donating *N*-substituents, SE1 correlates well with Taft's DSP ($r^2 = 0.91$) and modified Swain–Lupton constants ($r^2 = 0.93$). The σ_I and F coefficients (−14.51 and −18.20) imply that σ-donating *N*-substituents stabilize

Table 3 Calculated energies (B3LYP/6-311+G(2d,p)//HF/6-31+G*) (hartrees) for ketenimines RCH=C=NH and alkenes $RCH{=}CH_2$ and SE2 (kcal mol^{-1}) for the homodesmic reaction [eqn. (9)]

R	χ_{BE}	σ_I	σ_R	F	R	E(RCH=C=NH)	$E(RCH{=}CH_2)$	SE2
SiH_3	1.91			0.06	0.04	−423.43612	−369.27789	4.91
PH_2	2.17			0.09	−0.04	−474.68762	−420.53497	1.41
H	2.20	0	0	0.03	0	−132.71900	−78.56860	0.00
CH_3	2.56	−0.01	−0.16	0.01	−0.18	−172.01762	−117.87223	−3.14
C(O)H	2.60	0.25	0.20	0.33	0.09	−246.07015	−191.91883	0.58
$CH{=}CH_2$	2.61	0.11	−0.15	0.13	−0.17	−210.10974	−155.96301	−2.30
SH	2.63			0.30	−0.15	−530.93288	−476.78871	−3.91
Ethynyl	2.66	0.29	−0.04	0.22	0.01	−208.87363	−154.72742	−2.63
CO_2H	2.66	0.30	0.11	0.34	0.11	−321.34514	−267.19303	1.07
CF_3	2.68	0.40	0.11	0.38	0.16	−469.86710	−415.72032	−2.27
CN	2.69	0.57	0.08	0.51	0.15	−224.98434	−170.83705	−1.95
Cl	3.05	0.47	−0.25	0.42	−0.19	−592.34024	−538.20266	−8.04
NH_2	3.10	0.17	−0.80	0.08	−0.74	−188.06253	−133.93134	−12.05
NO_2	3.22	0.67	0.10	0.65	0.13	−337.27569	−283.13069	−3.39
OH	3.64	0.24	−0.62	0.33	−0.70	−207.94196	−153.81423	−14.23
F	4.00	0.54	−0.48	0.45	−0.39	−231.97369	−177.84591	−14.19

ketenimines while σ-accepting *N*-substituents destabilize them. This result is consistent with the result we found by correlating SE1 with substituent group electronegativity. The σ_R and R coefficients (+10.87 and +13.32) imply that π-donating *N*-substituents destabilize ketenimines while π-accepting *N*-substituents stabilize them. For the ketenimines with π-donating *N*-substituents, the ketenimine stability is more sensitive to the electronegativity of the substituents than to their resonance effects.

Regarding ketenimines with π-accepting *N*-substituents, SE1 correlates well with Taft's DSP ($r^2 = 0.97$) and modified Swain–Lupton constants ($r^2 = 0.84$). The σ_I and F coefficients are −11.95 and −20.72, indicating that σ-donating *N*-substituents stabilize ketenimines while σ-accepting *N*-substituents destabilize them. This result agrees with the result we found by correlating SE1 with substituent group electronegativity. The σ_R and R coefficients are +2.52 and +11.16, indicating that π-donating *N*-substituents destabilize ketenimines while π-accepting *N*-substituents stabilize them. The sensitivity of the ketenimine stability to the resonance effect of π-accepting *N*-substituents is small, compared to the inductive effect of the substituents.

As to ketenimines with π-donating C_β-substituents, SE2 correlates well with Taft's DSP ($r^2 = 0.94$) and modified Swain–Lupton constants ($r^2 = 0.94$). The σ_I and F coefficients (−11.08 and −15.61) imply that σ-donating C_β-substituents stabilize ketenimines while σ-accepting C_β-substituents destabilize them. This result is consistent with the result we found by correlating SE2 with substituent group electronegativity.[8] The σ_R and R coefficients (+15.71 and +16.97) imply that π-donating C_β-substituents destabilize ketenimines while π-accepting C_β-substituents stabilize them.

Regarding ketenimines with π-accepting C_β-substituents, SE2 has fair correlations with Taft's DSP ($r^2 = 0.73$) and modified Swain–Lupton constants ($r^2 = 0.60$). The σ_I and F coefficients are −6.51 and −10.37, indicating that σ-donating C_β-substituents stabilize ketenimines while σ-accepting C_β-substituents destabilize them. This result is the same as the result we found by correlating SE2 with substituent group electronegativity.[8] The σ_R and R coefficients are +10.64 and +3.63, indicating that π-donating C_β-substituents destabilize ketenimines while π-accepting C_β-substituents stabilize them.

The sp-hybridized C_α of the ketenimines is strongly electronegative and this causes the observed stabilization by σ-donating substituents at either of the termini. This phenomena also occurs in ketenes[1b] and allenes.[2a] Regarding the π-effects of substituents on the stability of ketenimines, π-acceptors on C_β may significantly stabilize the resonance structure **1b** by resonance but π-donors on C_β may significantly destabilize it. Similarly, π-acceptors on N may significantly stabilize the resonance structure **1c** by resonance but π-donors on N may significantly destabilize both **1b** and **1c**. Therefore, these effects may cause the observed stabilization by π-accepting substituents and destabilization by π-donating substituents at either of the termini of the cumulene.

A highly σ-accepting and median π-donating Cl substituent ($\chi_{BE} = 3.05$, $\sigma_I = 0.47$, $F = 0.42$, $\sigma_R = -0.25$, $R = -0.19$) on C_β of the ketenimine has a destabilizing effect (SE2 = −8.04 kcal mol^{-1}) on it. This is consistent with previous experimental results,[18a,b] which described chloroketenimines as unstable intermediates. Ketoketenimines have a mild σ-accepting and highly π-accepting CH=O substituent ($\chi_{BE} = 2.60$, $\sigma_I = 0.25$, $F = 0.33$, $\sigma_R = 0.20$, $R = 0.09$) on C_β, and so they are slightly stabilized (SE2 = 0.58 kcal mol^{-1}) because the stabilizing π-accepting effect compensates the destabilizing σ-accepting effect on the ketoketenimine. This is consistent with experimental results,[18a,c–e] where ketoketenimines were reported to be stable at 0 °C. A silyl substituent ($\chi_{BE} = 1.91$) is classed as an electropositive group and both a C_β-silyl substituent (SE2 = 4.91 kcal mol^{-1}) and an *N*-silyl substituent (SE1 = 5.65 kcal mol^{-1}) give a stabilizing effect on a ketenimine, which is consistent with experimental results.[18a,f]

Conclusions

Electropositive (σ-donating) and π-accepting *N*-substituents stabilize ketenimines, while electronegative (σ-accepting) and π-donating *N*-substituents destabilize them. Similarly, just as we found previously for C_β-substituted ketenimines,[8] electropositive (σ-donating) and π-accepting C_β-substituents stabilize ketenimines, while electronegative (σ-accepting) and π-donating C_β-substituents destabilize them.

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