Substituent effects on stability of ketenimines

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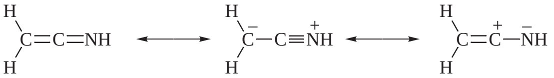
An isodesmic reaction was designed to study substituent effects on the stability of ketenimines. A good correlation ($\Delta E = -11.31\ \chi_{BE} + 31.07$) between substituent group electronegativity and the stability of ketenimines has been found. Electropositive substituents stabilize ketenimines while electronegative substituents destabilize ketenimines. Ketenimines gain extra stabilization when their substituents are π acceptors, such as AlH_2, BH_2, O=CH–, HO_2C–, CN, NO_2, and HSO_2, resulting in the existence of cyano-cation resonance structures. An ynamine resonance structure plays an important role in ketenimine with a lithium substituent.

Introduction

Ketenimines were first prepared by Staudinger and Hauser in the 1920s,[1] and have attracted considerable interest as substrates for the synthesis of heterocycles, largely through processes involving cycloaddition reactions.[2] The chemistry of ketenimines has been reviewed by Krow in 1971[3a] and by Barker and McHenry in 1980.[3b] Ketenimines are isoelectronic with allenes and ketenes, and they can be represented by resonance structures **1a**, **1b**, and **1c**. The resonance structure **1b** has a negative charge on C_β and the carbanion character of C_β is reflected in the reaction of ketenimines with electrophiles at C_β.[4] The ketenimine system is potentially axially dissymmetric in a similar manner to allenes. However, inversion of its configuration by rotation about the C=N bond or inversion of the nitrogen lone pair has a barrier less than 10 kcal mol^{-1}.[5] Therefore, ketenimines undergo configuration interconversion rapidly at room temperature.



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

Kinetic studies of hydration of ketenimines at a wide range of pH values have been reported by Hegarty *et al.*[4a,b] and Kresge *et al.*,[4c] showing that the hydration mechanism of ketenimines in acidic conditions is substituent-dependent.[4a] Ketenimines with CX(=O) substituents can be thermally interconverted with the corresponding imidoyl ketenes by a 1,3-X shift under mild FVT conditions.[6] Some stable linear ketenimines with special substituents have been prepared, where the linear structures were created and stabilized by electronic as well as steric effects.[7]

Ab initio calculations in conjunction with isodesmic reactions have been used to provide quite informative data for the understanding of substituent effects on the structure and stability of cumulene systems by Tidwell *et al.*,[8a,c,d] and Fuchs *et al.*[8b] These cumulene systems include ketenes,[8a] allenes,[8b,c] diazomethanes,[8c] and isocyanates.[8d] However, substituent effects on the stability of ketenimines have not been studied yet. Therefore, we use *ab initio* calculations, density function theory (DFT), and isodesmic reactions in this article to study how substituents have an influence on the stability of ketenimines.

Computational details

All the calculations reported here were performed with the GAUSSIAN94 program.[9] 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 the 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.[8,10]

Results

The Mulliken charge distribution of ketenimine **1a** calculated at the level of HF/6-31+G* shows that both the C_β and N atoms carry negative charges of −0.33 and −0.67, respectively, and C_α carries a positive charge of 0.13. This is consistent with previous theoretical calculations[11] and ^{13}C NMR studies of a series of ketenimines,[12] in which C_α exhibits signals between δ 186 and 195 ppm while C_β signals are between δ 34 and 78 ppm.

All the optimized structures and energies of ketenimines **1**–**24** are shown in Fig. 1 and Tables 1 and 2. All the ketenimines have an N–H bond perpendicular to the ketenimine plane and have C_α–N–H angles ranging from 113.4 to 120.3°, which are consistent with previous results.[11] Ketenimines with CH_3 (**5**), CF_3 (**6**), and SiH_3 (**13**) substituents have only one stationary point located, which has C_α–C_β–C(Si)–H(F) almost in the same plane. Ketenimine with an NH_2 substituent has three stationary points located with one (**7c**) 0.07 and 0.27 kcal mol^{-1} more stable than the other two (**7a**, **7b**). Ketenimines with AlH_2 (**12**) and BH_2 (**4**) substituents have only one stationary point located, which has H–Al–H and H–B–H located almost in the same plane as the ketenimine plane. Ketenimine with a PH_2 substituent has two stationary points located; one (**14b**) is 4.52 kcal mol^{-1} more stable than the other (**14a**). Ketenimine with an OH substituent has two stationary points located; one (**8a**) with O–H and N–H at *syn* and the other (**8b**) with O–H and N–H at *anti*. The latter is 0.23 kcal mol^{-1} more stable than the former. This also happens with the SH substituent, and one stationary point (**15b**) with S–H and N–H at *anti* is 0.10 kcal mol^{-1} more stable than the other (**15a**) with S–H and N–H *syn*. Ketenimines with a CH=O substituent have *trans* and *cis* stationary points, and the *trans* one (**19a**) is 1.19 kcal mol^{-1} more stable than the *cis* one (**19b**). Both *cis* and *trans* conformers have C=O and C=C=N almost in the same plane.

Table 1 Bond lengths, angles, and dihedral angles of ketenimines **1**–**24**

Compound	R	χ_{BE}	C1–C2	C2–N	N–H1	C1–H2	C1–X	X–H3	C2–C1–H2	C2–C1–X	C2–N–H1	C1–C2–N	C2–C1–X–H3
1	H	2.20	1.304	1.213	1.005	1.073	1.073		120.1	120.1	115.6	175.7	
2	Li	1.0	1.293	1.235	1.005	1.080	1.961		116.2	115.0	114.0	173.7	
3	BeH	1.47	1.309	1.211	1.004	1.081	1.669	1.334	115.0	121.4	117.4	175.1	
4	BH_2	1.93	1.323	1.199	1.003	1.077	1.530	1.191	116.2	119.5	120.0	175.4	0.1
5	CH_3	2.56	1.302	1.217	1.006	1.076	1.510	1.084	116.8	124.0	114.8	175.3	1.31
6	CF_3	2.68	1.307	1.203	1.005	1.073	1.488	1.324^{a}	120.1	122.0	117.3	175.5	0.8^{b}
7a	NH_2	3.10	1.303	1.220	1.007	1.074	1.424	1.000	118.1	125.4	114.3	177.2	10.3
7b	NH_2	3.10	1.307	1.213	1.006	1.077	1.426	1.000	117.6	120.5	115.2	175.1	123.9
7c	NH_2	3.10	1.306	1.220	1.007	1.074	1.422	1.000	118.0	125.1	114.3	172.2	19.8
8a	OH	3.64	1.306	1.216	1.007	1.074	1.371	0.948	119.9	121.6	114.8	173.9	113.2
8b	OH	3.64	1.305	1.215	1.007	1.073	1.373	0.949	120.1	121.6	114.7	175.4	102.6
9	F	4.00	1.301	1.215	1.007	1.068	1.339		124.0	120.9	114.7	174.6	
10	Na	1.0	1.245	1.288	1.003	1.064	2.620		138.9	63.1	113.4	162.5	
11	MgH	1.33	1.301	1.221	1.004	1.081	2.074	1.713	115.2	120.7	115.9	174.6	
12	AlH_2	1.62	1.311	1.209	1.003	1.080	1.934	1.582	115.5	121.4	118.0	175.7	2.7
13	SiH_3	1.91	1.306	1.210	1.004	1.078	1.867	1.474	116.3	122.5	116.8	175.5	1.3
14a	PH_2	2.17	1.305	1.210	1.005	1.075	1.833	1.401	117.4	124.4	116.6	174.9	27.6
14b	PH_2	2.17	1.307	1.209	1.005	1.076	1.826	1.403	117.2	120.4	116.7	175.5	130.2
15a	SH	2.63	1.307	1.028	1.005	1.073	1.774	1.329	119.0	121.2	116.6	175.1	103.7
15b	SH	2.63	1.037	1.208	1.005	1.073	1.774	1.329	119.1	121.2	116.6	175.8	99.1
16	Cl	3.05	1.302	1.210	1.006	1.069	1.735		121.8	121.8	115.7	175.3	
17a	Cyclopropyl	2.56	1.303	1.218	1.007	1.077	1.491	1.076	117.1	123.8	114.6	175.2	2.6
17b	Cyclopropyl	2.56	1.304	1.216	1.006	1.077	1.495	1.078	117.1	123.8	115.0	174.6	113.7
17c	Cyclopropyl	2.56	1.304	1.216	1.006	1.077	1.495	1.078	116.9	124.1	115.1	176.2	112.3
18	NO_2	3.22	1.317	1.192	1.004	1.067	1.427	1.199^{c}	124.2	119.0	120.3	174.8	1.4^{d}
19a	CHO	2.60	1.316	1.202	1.005	1.074	1.466	1.192^{e}	119.8	120.5	118.3	175.3	179.0^{f}
19b	CHO	2.60	1.320	1.196	1.004	1.074	1.467	1.194^{e}	118.9	120.4	119.7	175.3	2.8^{f}
20a	$CH{=}CH_2$	2.61	1.309	1.212	1.006	1.076	1.467	1.326^{g}	117.3	123.0	115.8	175.1	178.5^{h}
20b	$CH{=}CH_2$	2.61	1.309	1.211	1.006	1.075	1.476	1.325^{g}	116.7	124.4	115.9	175.8	20.9^{h}
21a	CO_2H	2.66	1.311	1.204	1.006	1.073	1.481	1.335^{i}	119.5	123.5	117.6	174.9	12.2^{j}
21b	CO_2H	2.66	1.316	1.199	1.004	1.072	1.464	1.333^{i}	119.6	122.4	118.7	175.3	1.1^{j}
21c	CO_2H	2.66	1.317	1.197	1.004	1.072	1.464	1.330^{i}	119.7	119.6	119.2	175.3	178.2^{j}
22	C≡CH	2.66	1.312	1.206	1.005	1.074	1.432	1.191^{g}	118.1	122.3	116.9	175.3	
23	CN	2.69	1.315	1.199	1.005	1.073	1.430	1.138^{k}	119.6	121.1	118.8	175.3	
24	SO_2H	2.53	1.314	1.195	1.004	1.072	1.738	1.432^{l}	121.9	119.9	119.7	175.6	13.8^{m}

[a] C–F. [b] C2–C1–C–F. [c] N–O. [d] C2–C1–N–O. [e] C–O. [f] C2–C1–C–O. [g] C–C. [h] C2–C1–C–C. [i] C–OH. [j] C2–C1–C–OH. [k] C–N. [l] S–O. [m] C2–C1–S–O.

Table 2 Calculated energies (B3LYP/6-311 + G(2d,p)//HF/6-31+G*) (Hartrees) for ketenimines RCH=C=NH and alkenes $RCH{=}CH_2$ and ΔE (kcal mol^{-1}) for the isodesmic reaction of eqn. (1)

R	χ_{BE}	*E* (RCH=C=NH)	*E* ($RCH{=}CH_2$)	ΔE/kcal mol^{-1}
Na	1.00	−294.42549	−240.24362	22.89
Li	1.00	−139.65184	−85.47275	21.15
MgH	1.33	−322.81701	−278.64564	16.30
BeH	1.47	−147.47953	−93.31138	14.28
AlH_2	1.62	−375.77782	−321.60996	14.10
SiH_3	1.91	−423.43612	−369.27789	8.06
BH_2	1.93	−158.17093	−104.00361	13.76
PH_2	2.17	−474.68762	−420.53497	4.56
H	2.20	−132.71900	−78.56860	3.14
HSO_2	2.53	−681.36895	−627.21834	3.28
CH_3	2.56	−172.01762	−117.87223	0.00
Cyclopropyl	2.56	−249.38729	−195.24349	−1.00
C(O)H	2.60	−246.07015	−191.91883	3.72
$CH{=}CH_2$	2.61	−210.10974	−155.96301	0.84
SH	2.63	−530.93288	−476.78871	−0.77
Ethynyl	2.66	−208.87363	−154.72742	0.51
CO_2H	2.66	−321.34514	−267.19303	4.22
CF_3	2.68	−469.86710	−415.72032	0.87
CN	2.69	−224.98434	−170.83705	1.19
Cl	3.05	−592.34024	−538.20266	−4.90
NH_2	3.10	−188.06253	−133.93134	−8.91
NO_2	3.22	−377.27569	−283.13069	−0.24
OH	3.64	−207.94196	−153.81423	−11.08
F	4.00	−231.97369	−177.84591	−11.05

Ketenimines with a $CH{=}CH_2$ substituent have *trans* (**20a**) and *cis* (**20b**) stationary points with the former 2.36 kcal mol^{-1} more stable than the latter. The *trans* conformer has C=C and C=C=N almost in the same plane while the *cis* conformer has a twisted structure with a dihedral angle of 20.9° between C=C and C=C=N. Ketenimines with NO_2 (**18**) and SO_2 (**24**) substituents have C_α–C_β–N(S)–O almost in the same plane with a dihedral angle of 1.4° for the NO_2 substituent and 13.8° for the SO_2 substituent.

Ketenimines with substituents of AlH_2, BH_2, CN, CH=O, ethynyl, NO_2, HSO_2 have a significantly longer C=C bond length and a shorter C=N bond length than those found in ketenimines with H and CH_3 substituents. For the ketenimine with a BH_2 substituent (**4**), the C=C bond length (1.323 Å) is 21

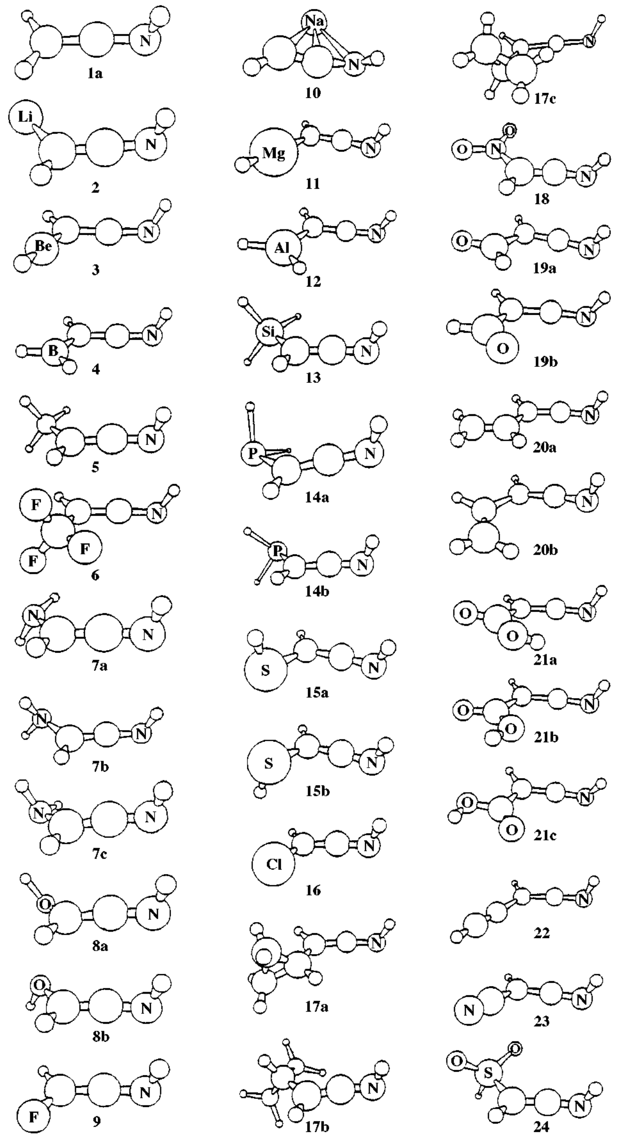


Fig. 1 Optimized structures of compounds **1**–**24** at the HF/6-31+G* level.

pm longer and the C=N bond length (1.199 Å) is 18 pm shorter than those of ketenimine with a CH_3 substituent. The C=C and C=N bond lengths in the ketenimine with an AlH_2 substituent (**12**) are 1.311 and 1.209 Å; the former is 9 pm longer and the latter is 8 pm shorter than those of ketenimine with a CH_3 substituent. The C=C and C=N bond lengths in the ketenimine with a CH=O substituent (**19a**) are 1.316 and 1.202 Å, which are 14 pm longer for the C=C bond and 15 pm shorter for the C=N bond than those of ketenimine with a CH_3 substituent. The C=C and C=N bond lengths of the ketenimine with a CN substituent (**23**) are 1.315 and 1.199 Å, which are 15 pm longer for the C=C bond and 18 pm shorter for the C=N bond than those of ketenimine with a CH_3 substituent. The C=C and C=N bond lengths in the ketenimine with an ethynyl substituent (**22**) are 1.312 and 1.206 Å, which are 10 pm longer for the C=C bond and 11 pm shorter for the C=N bond than those of ketenimine with a CH_3 substituent. The ketenimine with an NO_2 substituent (**18**) has a C=C bond length of 1.317 Å and a C=N bond length of 1.192 Å; the former is 15 pm longer and the latter is 25 pm shorter than those of ketenimine with a CH_3 substituent. The ketenimine with an SO_2 substituent (**24**) has a C=C bond length of 1.314 Å and a C=N bond length of 1.195 Å; the former is 12 pm longer and the latter is 22 pm shorter than those of ketenimine with a CH_3 substituent.

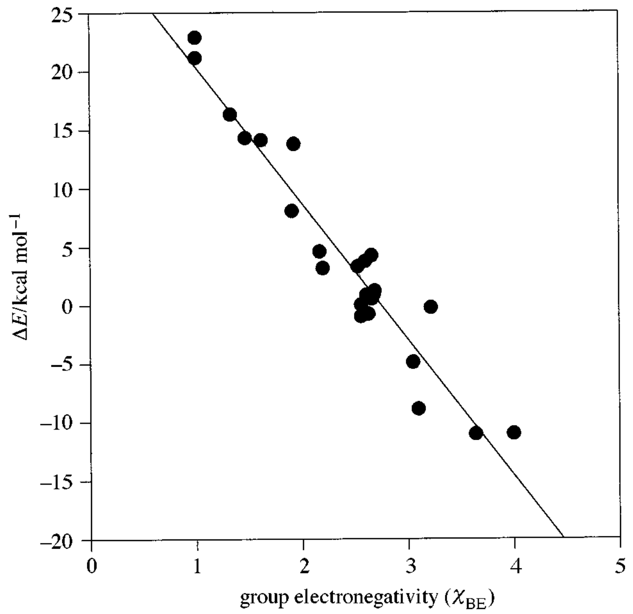
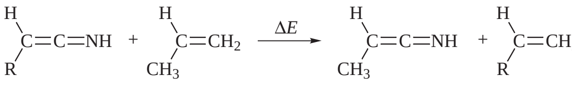


Fig. 2 A plot ($\Delta E = -11.31\chi_{BE} + 31.07$) of ΔE of the isodesmic reaction [eqn. (1)] against substituent group electronegativity (χ_{BE}).

The ketenimine with an F substituent (**9**) has a C=C bond length of 1.301 Å and a C=N bond length of 1.215 Å, which are very little different from those of ketenimines with CH_3 and H substituents. Ketenimines with substituents of Li (**2**) and MgH (**11**) have a shorter C=C bond length and a longer C=N bond length than those found in ketenimines with CH_3 and H substituents. The ketenimine with an Li substituent has a C=C bond length of 1.293 Å and a C=N bond length of 1.235 Å, which are 11 pm shorter for C=C bond and 22 pm longer for the C=N bond than those of ketenimine with an H substituent. The C=C and C=N bond lengths of the ketenimine with an MgH substituent are 1.301 and 1.221 Å, which are 3 pm shorter for the C=C bond and 8 pm longer for the C=N bond than those of ketenimine with a CH_3 substituent. The ketenimine with an Na substituent (**10**) has Na coordinated to C_α, C_β and N of the ketenimine.

An isodesmic reaction [eqn. (1)] was designed to determine substituent effects on ketenimine stability. A plot (Fig. 2) of ΔE of the isodesmic reactions against substituent group electronegativity (χ_{BE}) gives a linear curve with a correlation coefficient of 0.93. The linear curve can be represented as eqn. (2), and the ΔE of the isodesmic reaction decreases as the electronegativity of the corresponding substituent group increases. The ΔE of isodesmic reactions (given in kcal mol^{-1}) are significantly positive with electropositive substituents such as Li ($\Delta E = 21.15$), MgH ($\Delta E = 16.30$), BeH ($\Delta E = 14.28$), AlH_2 ($\Delta E = 14.10$), BH_2 ($\Delta E = 13.76$), and SiH_3 ($\Delta E = 8.06$). The ΔE of isodesmic reactions are significantly negative with electronegative substituents such as Cl ($\Delta E = -4.9$), NH_2 ($\Delta E = -8.91$), OH ($\Delta E = -11.08$), and F ($\Delta E = -11.05$). The ΔE of isodesmic reactions are slightly positive with substituents which are conjugated with the ketenimine, and these substituents are SO_2 ($\Delta E = 3.28$ kcal mol^{-1}), $CH{=}CH_2$ ($\Delta E = 0.84$ kcal mol^{-1}), CH=O ($\Delta E = 3.72$ kcal mol^{-1}), ethynyl ($\Delta E = 0.51$ kcal mol^{-1}), CO_2H ($\Delta E = 4.22$ kcal mol^{-1}), and CN ($\Delta E = 1.19$ kcal mol^{-1}), while the ΔE of the isodesmic reaction is slightly negative with a substituent of NO_2 ($\Delta E = -0.24$ kcal mol^{-1}).



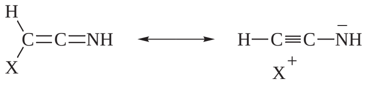
$$\mathrm{H(R)C{=}C{=}NH} + \mathrm{H(CH_3)C{=}CH_2} \xrightarrow{\Delta E} \mathrm{H(CH_3)C{=}C{=}NH} + \mathrm{H(R)C{=}CH_2} \quad (1)$$

$$\Delta E = -11.31\,\chi_{BE} + 31.07 \quad (2)$$

Discussion

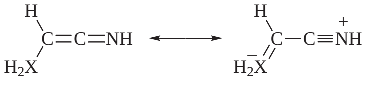
The stability of substituted ketenimines has a good linear correlation with substituent group electronegativity. Essentially, electropositive substituents stabilize the ketenimines while electronegative substituents destabilize the ketenimines. The substituent-stability effect on ketenimines is similar to that on ketenes ($\Delta E = -15.6\ \chi_{BE} + 42.3$),[8a] allenes ($\Delta E = -5.8\ \chi_{BE} + 15.3$),[8c] diazomethanes ($\Delta E = -10.6\ \chi_{BE} + 30.2$),[8c] and isocyanates ($\Delta E = -23.6\ \chi_{BE} + 60$).[8d] Slopes of the correlation curves for the cumulene systems are −11.31 for the ketenimine system, −15.6 for the ketene system, −10.6 for diazomethane system, −5.8 for the allene system, and −23.6 for the isocyanate system. This indicates that the stability of the isocyanate system is the most sensitive to substituent group electronegativity, while the stability of the allene system is the least sensitive to substituent group electronegativity. A sequence for the sensitivity of cumulene stability to substituent group electronegativity is isocyanate system > ketene system > ketenimine system > diazomethane system > allene system. It implies that the electronegative heteroatoms located at the two ends of the cumulene systems increase charge dispersion of the systems, resulting in higher sensitivity of the cumulene stability to substituents *via* an electronic effect.

Ketenimine with the highly electropositive substituent of Li is 11 pm shorter in the C=C bond and 22 pm longer in the C=N bond than the ketenimine with an H substituent, indicating that the ketenimine with an Li substituent has an ynamine resonance structure. The ynamine resonance structure provides the ketenimine with extra stability. The ketenimine with an MgH substituent has the ynamine resonance structure too, but it is much less significant. The ketenimine with an Na substituent has an unusual structure with the ketenimine serving as a π ligand to Na, providing the ketenimine with extra stability.



X = Li, MgH

Ketenimines with AlH_2 and BH_2 substituents have AlH_2 and BH_2 located almost in the same plane as the ketenimine plane. The C=C and C=N bond lengths of the ketenimine with an AlH_2 substituent are 9 pm longer for the C=C bond and 8 pm shorter for the C=N bond than those of ketenimine with a CH_3 substituent. The phenomenon is more pronounced with a BH_2 substituent. The C=C and C=N bond lengths of the ketenimine with a BH_2 substituent are 21 pm longer for the C=C bond and 18 pm shorter for the C=N bond than those of ketenimine with a CH_3 substituent. The π orbital of ketenimine is parallel with an empty p orbital of the Al and B atoms, and delocalization of the former into the latter produces a cyano-cation resonance structure, resulting in extra stabilization of the ketenimine systems.



X = Al, B

Ketenimines with substituents of cyano, O=CH–, nitro, HO_2C– and HSO_2– groups are 10–13 pm longer in the C=C bond and 11–21 pm shorter in the C=N bond in comparison with the ketenimine with an H substituent. This indicates that these substituents have unsaturated bonds conjugated with ketenimine and serve as π acceptors, resulting in a longer C=C bond and a shorter C=N bond in these ketenimines. Due to the π accepting effect, these substituents are able to delocalize π electrons on ketenimine, resulting in extra stabilization of these ketenimines. The argument is consistent with the results from the isodesmic reaction [eqn. (1)]. The ΔE of the isodesmic reactions for substituents of HO_2S–, HO_2C–, O=CH–, and cyano groups range from 1.19 to 4.22 kcal mol^{-1}, indicating a mild to medium stabilizing effect of these substituents on ketenimine in comparison to the CH_3 substituent. The electronegativity of the nitro group ($\chi_{BE} = 3.22$) is between that of the NH_2 ($\chi_{BE} = 3.10$) and OH ($\chi_{BE} = 3.64$) groups. However, ΔE of the isodesmic reaction for NH_2 and OH substituents are −8.91 and −11.08 kcal mol^{-1}, respectively, while the corresponding ΔE for the nitro substituent is only −0.24 kcal mol^{-1}, indicating that the high π accepting effect of the nitro group gives stabilization to the ketenimine and compensates for the instability induced by its high electronegativity.

A highly electronegative Cl substituent ($\chi_{BE} = 3.05$) has a destabilizing effect ($\Delta E = -4.9$ kcal mol^{-1}) on ketenimines, and this is consistent with previous experimental results,[3a,13] which described chloroketenimines as unstable intermediates. Ketoketenimines have a less electronegative CH=O substituent ($\chi_{BE} = 2.60$), and they gain mild stabilization from delocalization of the π electrons of the ketenimine into the carbonyl group, so the ketoketenimines ($\Delta E = 3.72$ kcal mol^{-1}) are more stable than chloroketenimines and this is consistent with experiment results,[3a,14] where ketoketenimines were reported to be stable at 0 °C. A silyl substituent ($\chi_{BE} = 1.91$) is classed as an electropositive group and gives a stabilizing effect ($\Delta E = 8.06$ kcal mol^{-1}) on ketenimines, which is consistent with experimental results.[3a,15]

Conclusions

The stability of ketenimines is substituent-dependent; electropositive substituents may stabilize ketenimines while ketenimines are destabilized by electronegative substituents. The stability of ketenimines is less sensitive to substituent group electronegativity than the stability of ketenes and isocyanates is, but it is more sensitive to substituent group electronegativity than the stability of diazomethanes and allenes is. An Li substituent provides the ketenimine with extra stabilization, which is from an ynamine resonance structure. The ketenimines with AlH_2 and BH_2 substituents have an empty p orbital on the Al and B atoms which delocalizes π electrons of the ketenimines, giving extra stability to the ketenimine systems. The ketenimines with π acceptors like cyano, O=CH–, HO_2C– and HSO_2– groups gain an extra stability from delocalization of the π electrons of the ketenimines through these π acceptors. A highly electronegative nitro substituent won't destabilize the ketenimine regularly because its π accepting character delocalizes the π electrons of the ketenimine and that produces a compensatory stabilizing effect.

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