Conformations, Chemical Reactivities and Spectroscopic Characteristics of Some Di-substituted Ketenes: An *ab initio* Study

V. P. Gupta,* Archna Sharma, and S. G. Agrawal†

*Department of Physics, University of Jammu, Jammu-Tawi 180 006, India. *E-mail: vpgpt1@yahoo.co.in*
†Regional Research Laboratory, Jammu-Tawi 180 004, India

Received May 17, 2006

A systematic study of the structure, energetics and spectral characteristics of substituted aminoketenes $R(NH_2)C{=}C{=}O$ (R = H, CH_3, NH_2, OH, OCH_3, $CH{=}CH_2$, $C{\equiv}CH$, CN, CHO, NO, NO_2) which are highly reactive and transient intermediates in synthesis has been conducted by *ab initio* calculations at the MP2/6-31G*//MP2/6-31G* level. Twenty four stable isomers of the eleven substituted aminoketenes having dihedral angles ϕ_{NH2}~120° and 60° have been identified and their optimized geometries and energies obtained. Electrostatic and steric effects on the molecular geometries have been analyzed. While the π-acceptor groups lead to planar conformations, the electron-donor groups give rise to non-planar conformations. Isodesmic substituent stabilization energies relative to alkenes have been calculated and correlation with group electronegativities established. Role of induction effect by the substituent groups and resonance effects in charge distribution in the molecules has been analyzed. An analysis of the asymmetric stretching frequencies and intensities of the C=C=O group shows that affect of non-π acceptor substituents on the frequency is determined by the field effect (F) and resonance effect (R) parameters, the calculated intensities I (km/mol.) are correlated to group electronegativities χ of the substituents by the relationship $I = 640.2 - 100.1\,\chi$ ($r = 0.92$). The π-acceptor substituents increase the intensity which may be explained in terms of their delocalizing effect on the negative charge at the C_β atom.

Key Words : Conformations, Chemical reactivities, Spectroscopic characteristics, Disubstituted ketenes, *ab initio* study

Introduction

Considerable interest has been shown in the recent past in the determination of the reactivity and structure of ketenes.[1] It has been demonstrated that these compounds are intermediates in a variety of reactions.[2] The interstellar identification of several members of cyanopolyene series and their possible generation from carbyne opens the question of possible existence of other interstellar series of high-carbon-content chain molecules such as ketenes.[3] The spectral data are potentially important as a basis for future astrophysical studies of these high-carbon-content molecules. *Ab initio* calculations have been quite informative for the understanding of substituent effects, structures and reactivities of ketenes.[4-9] Badawi *et al.*[10] have investigated the structural stability and vibrational spectra of some mono-substituted ketenes using MP2 and DFT theories. McAllister *et al.*[4] have utilized isodesmic reactions to compare the effects of substituents on ketenes and obtained correlation between the group electronegativities[11] and stabilization energies for many substituents.Gong *et al.*[5] have used *ab initio* molecular orbital calculations to make a broad survey of the effect of representative substituents on the ground states of ketenes and used this information to understand ketene structures and reactivities in terms of the electronic properties of the substituents. McAllister *et al.*[12] and Gano and Jacob[13] addressed the question of substituent effects on ketene stretching frequencies and proposed the correlations with the Hammett-type substituent parameters specifically the field effect parameter F and the resonance effect parameter R of Swain and Lupton.[14] The studies so far have mainly been devoted to mono-substituted ketenes except for reference[13] which also considers some symmetrically di-substituted ketenes ($R_2C{=}C{=}O$; R = H, Cl, CN and NH_2). Electropositive substituents such as NH_2, OH, PH_2, SH are known to adopt twisted conformations in ketenes. Several explanations have been advanced for this behaviour, the most plausible of which is that π-donation by substituents is destabilizing in ketenes.[4] π-acceptor substituents like CHO, NO and NO_2, on the other hand, are known to lead to a planar structure of the ketenes. No systematic study related to the structure, energetics or spectral characteristics is available for di-substituted ketenes where the two substituents are of the same or opposite nature. An attempt is presently being made to fill this void on the basis of *ab initio* calculations for substituted aminoketenes which are highly reactive but important intermediates in synthesis.[15] Effect of group electronegativity and field effect and resonance parameters of the substituents on the position and intensity of vibrational frequencies, atomic charges and stabilization energies has also been analyzed.

Computational Methods

Ab initio molecular orbital calculations were carried out for a series of substituted amino-ketenes using Gaussian98W software.[16] Geometrical parameters were fully optimized using HF theory with second order Moller-Plesset (MP2) corrections and 6-31G* basis sets, which were also used to compute electronic energies, harmonic vibrational frequencies and zero-point vibrational energies (ZPVE). Geometry optimizations were carried out to better than 0.001 Å for bond lengths and 0.1° for bond angles with a self-consistent convergence of at least 10^{-9} on the density matrix and with a residual r.m.s force of less than 10^{-4}. Following the procedure adopted by McAllister *et al.*,[4] isodesmic reactions as in eq. (1) have been utilized to compare the effect of substituents on aminoketene to those on alkenes, with CH_3 as a reference substituent.

$$R(NH_2)C{=}C{=}O + CH_3CH{=}CH_2 \xrightarrow[\Delta E]{SE} CH_3(NH_2)C{=}C{=}O + RCH{=}CH_2 \quad (1)$$

In general,

$$M_2(M_1)C{=}C{=}O + CH_3CH{=}CH_2 \xrightarrow[\Delta E]{SE} CH_3(M_1)C{=}C{=}O + M_2CH{=}CH_2 \quad (2)$$

where, M_1 and M_2 are the substituent groups. In the present case $M_1 = NH_2$.

This approach has been widely used[17] and offers the advantage that the effect of the substituent on the property in question is isolated and systematic errors are minimized.

Results and Discussion

Conformational studies. In a quantum chemical study on amino ketene, McAllister *et al.*[4] have indicated that the amino group can have two possible orientations, both non-planar, in which the amino group may have a dihedral angle (ϕ) of about 60° or 120° relative to the C=C=O group. The latter isomeric form is found to be more stable than the former by about 2 kcal/mol. and is indicative of the absence of any stabilizing interaction between the lone pair on nitrogen and the in-plane electron-deficient p-orbital at C_α, which was proposed by Brady *et al.*[18] It was, therefore, considered appropriate to carry out structural analysis on aminoketenes substituted at the C_β position by electron-donor groups CH_3, NH_2, OH and OCH_3, π-electron acceptor groups CHO, NO and NO_2 and conjugated substituents $HC{=}CH_2$, C≡CH and C≡N to understand the effect of substituents on molecular structure and to determine the types of stable conformers and their structural characteristics. Results of calculations based on optimized geometries using MP2/6-31G* method are given in Table 1 for substituted aminoketenes with $\phi_{NH_2} \sim 120°$.

This table contains total energies, zero-point vibrational energies (ZPVE) and stabilization energies calculated by eq. (2) for substituted aminoketenes and alkenes.[4] The stability of the optimized structure was verified by frequency calculations which give positive values of frequencies for stable structures and atleast one negative frequency for an unstable structure. The electronic energies, zero-point vibrational energies and total energies of all the aminoketene derivatives and the enthalpy difference between the rotational isomers, where existing, are given in Table 2.

It follows from Tables 1 and 2 that with H, CH_3, C≡CH, $HC{=}CH_2$, CN and NH_2 substituents the rotational isomerism is possible only about the NH_2 group resulting in two conformers each with $\phi_{NH_2} \sim 60°$ or 120°. However, with CHO and NO substituents, in addition to the above conformations, *cis* and *trans* conformers relative to the C=C=O group are also possible. However, with strong π-acceptor group NO_2 and electron-donor group OH only one conformation with $\phi_{NH_2} \sim 120°$ is possible. As in the case of mono-substituted ketenes[4] the OH group adopts a perpendicular configuration with dihedral angle $HOC_1C_2 = 103.0$ [Table 3]. Another electron-donor group OCH_3 gives rise to two

Table 1. Total energies, zero-point vibrational energies and stabilization energies (SE) for Isodesmic Reactions for substituted aminoketenes ($\phi_{NH2} \sim 120°$) and alkenes and group electronegativities (χ)

S.No	M_1	M_2	Energy (a.u) -E($M_2(M_1)C{=}C{=}O$)	ZPVE (a.u)	Energy (a.u) -E($M_2CH{=}CH_2$)[a]	ZPVE[a] (a.u.)	SE (kcal/mol)	Relative SE (kcal/mol)	X
1	NH_2	H	−207.3222549	0.051137	78.2983	0.0495	−7.26	0.0	3.10
2	NH_2	CH_3	−246.4923871	0.080177	117.4697	0.0775	0.0	7.26	2.56
3	NH_2	C≡CH	−283.2438222	0.059559	154.2249	0.0596	−0.66	6.6	2.66
4	NH_2	$HC{=}CH_2$	−284.4619602	0.084949	155.4226	0.0864	12.99	5.73	2.58
5	NH_2	NO (t)	−336.3116671	0.047958	207.2655	0.0494	17.30	10.04	3.12
6	NH_2	NO (c)	−336.3162770	0.048160					3.12
7	NH_2	CN	−299.3359892	0.049872	170.3161	0.0495	−0.31	6.95	2.69
8	NH_2	NH_2	−262.5097603	0.068902	133.4913	0.0668	−2.29	4.97	3.12
9	NH_2	CHO (t)	−320.3595112	0.061004	191.3116	0.0623	6.15	13.41	2.60
10	NH_2	CHO (c)	−320.3571222	0.060975	191.3093	0.0623	18.29	11.03	2.60
11	NH_2	NO_2	−411.3382322	0.054343	282.3113	0.0542	4.25	11.51	3.22
12	NH_2	OCH_3 (c)	−321.4990160	0.084627	–	–	–	–	3.53
13	NH_2	OCH_3 (g)	−321.5015142	0.084824	–	–	–	–	3.53
14	NH_2	OH	−282.3455589	0.055511	153.3322	0.0545	−4.81	2.45	3.64

[a] Ref. [3]

Table 2. Energies, zero-point vibrational energies, total energies and enthalpy difference for di-substituted ketenes

S.No	M_1	M_2	Energy (a.u)	ZPVE (a.u)	Total energy (a.u.)	H (kcal/mol)
1	NH_2 (1)	H	−207.3222549	0.051137	−207.2711179	
2	NH_2 (2)	H	−207.3206132	0.050863	−207.2697502	0.858
3	NH_2 (1)	CH_3	−246.4923871	0.080177	−246.4122101	
4	NH_2 (2)	CH_3	−246.4909169	0.079769	−246.4111479	0.667
5	NH_2 (1)	C≡CH	−283.2438222	0.059559	−283.1842632	
6	NH_2 (2)	C≡CH	−283.2395275	0.059033	−283.1804945	2.366
7	NH_2 (1)	$HC{=}CH_2$(t)	−284.4619602	0.084949	−284.3770112	
8	NH_2 (2)	$HC{=}CH_2$(t)	−284.459221	0.084545	−284.3746760	1.466
9	NH_2 (1)	NO (t)	−336.3116671	0.047958	−336.2637091	
10	NH_2 (2)	NO (t)	−336.3074012	0.047343	−336.2600582	2.292
11	NH_2 (1)	NO (c)	−336.3162770	0.048160	−336.2681170	
12	NH_2 (2)	NO (c)	−336.3072301	0.047539	−336.2596911	5.289
13	NH_2 (1)	CN	−299.3359892	0.049872	−299.2861172	
14	NH_2 (2)	CN	−299.3321715	0.049418	−299.2827535	2.111
15	NH_2 (1)	NH_2 (1)	−262.5097603	0.068902	−262.4408583	
16	NH_2 (2)	NH_2 (1)	−262.5083608	0.068608	−262.4397528	0.694
17	NH_2 (1)	CHO (t)	−320.3595112	0.061004	−320.2985072	
18	NH_2 (2)	CHO (t)	−320.3519716	0.060415	−320.2915566	4.363
19	NH_2 (1)	CHO (c)	−320.3571222	0.060975	−320.2961472	0.03
20	NH_2 (2)	CHO (c)	−320.3571900	0.060995	−320.2961950	
21	NH_2 (1)	NO_2	−411.3382322	0.054343	−411.2838892	–
22	NH_2 (1)	OCH_3(c)	−321.4990160	0.084627	−321.4143890	–
23	NH_2 (1)	OCH_3(g)	−321.5015142	0.084824	−321.4166902	–
24	NH_2 (1)	OH	−282.3455589	0.055511	−282.2900479	–

Abbreviations: NH_2(1) – ϕ_{NH_2} ~ 120°, NH_2(2) – ϕ_{NH_2} ~ 60°, c-*cis*, t-*trans*

stable conformers s-*cis* and gauche relative to C=C=O group with ϕ_{NH_2} ~ 120°. In general, the conformers with ϕ_{NH_2} ~ 120° are found to be more stable than those with ϕ_{NH_2} ~ 60° by energies ranging from 0.67 kcal/mol. to 5.29 kcal/mol. (Table 2) depending upon the nature of the substituent. The enthalpy difference between the two types of conformers follows the following sequence :

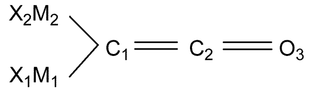
NO(c) (5.29) > CHO(t) (4.36) > C≡CH (2.37) > C≡N (2.11) > $HC{=}CH_2$ (1.47) > NH_2 (0.69) > CH_3 (0.67)

The terms in parentheses represent enthalpy difference between the ϕ_{NH_2} ~ 120° and ϕ_{NH_2} ~ 60° conformers in kcal/mol (Table 2). This series broadly follows the sequence of field effect parameters (F) of the substituents groups as suggested by Hansch *et al.*[19] and the group electronegativities C suggested by Boyd *et al.*[11] It, therefore, appears that the relative stabilities of the conformers arising out of isomerism of the NH_2 group are mainly influenced by the field effects though other factors cannot be excluded. Substituents such as NO, CHO and $HC{=}CH_2$ can also adopt *cis* and *trans* conformations relative to the C=C=O group. *Ab initio* calculations suggest the existence of 4,4 and 2 conformers of the aminoketene with NO, CHO and $HC{=}CH_2$ substituents, respectively. When ϕ_{NH_2} ~ 120° CHO (*trans*) conformer is more stable than the CHO (*cis*) conformer. The reverse is the case with ϕ_{NH_2} ~ 60°. In contrast, in the case of NO substituent the NO (*cis*) conformer with ϕ_{NH_2} ~ 120° is more stable than the NO (*trans*) conformer.

Two important factors seem to determine the stability of the *cis* and *trans* conformers in the above cases: (a) Electrostatic interaction between the atomic charges on the substituent and the ketene group and (b) steric effects in the case of larger groups. Thus, the absence of stable conformers for $HC{=}CH_2$ (*cis*) substituents with ϕ_{NH_2} ~ 120° or ~60° can be explained in terms of electrostatic interaction as no steric interaction with the amino group can be expected in these cases. Similarly, the greater stability of NO (*cis*) conformer over the NO (*trans*) conformer with ϕ_{NH_2} ~ 120° can be explained by attraction between the oxygen atom of the NO group and the ketene (C_α) group and the absence of steric effects. The greater stability of the OCH_3 (gauche) conformer with $\phi(COC_1C_2) = -107.28°$ relative to the OCH_3 (*cis*) conformer can be explained in terms of the destabilizing effect of a π-donating group on ketenes on the same pattern as the twisted conformation of the NH_2 group in aminoketenes.[4]

Based on *ab initio* calculations, McAllister *et al.*[4] and Gong *et al.*[5] reported the effect of electropositive and electronegative substituents on the structure of ketenes and observed a systematic trend with longer C=C and shorter C=O bond lengths for electronegative substituents and the reverse for electropositive substituents. These trends in mono-substituted ketenes were explained by them in terms of resonance structures. Birney[6] reported similar results for acetylketene and its 2-methyl and 2-cholro derivatives and concluded that the structures of the Z- and E- conformers

Table 3. Optimized geometries of di-substituted ketenes and their stable conformers



M_1	M_2	M_1C_1	M_2C_1	C_1C_2	C_2O_3	M_1X_1	M_2X_2	$M_1C_1C_2$	$M_1C_1M_2$	$C_1C_2O_3$	$X_1M_1C_1C_2$	$X_2M_2C_1C_2$
NH_2 (1)	H	1.4344	1.0874	1.3302	1.1808	1.0169	–	116.8	125.3	179.5	120.1	–
NH_2 (2)	H	1.4379	1.0836	1.3297	1.1835	1.0161	–	121.6	119.7	181.7	61.4	–
NH_2 (1)	CH_3	1.4361	1.5042	1.3311	1.1833	1.0188	1.0945	114.6	123.7	179.4	120.6	−0.3
NH_2 (2)	CH_3	1.4426	1.5020	1.3292	1.1868	1.0169	1.0945	119.1	118.5	181.9	60.6	−0.6
NH_2 (1)	C≡CH	1.4373	1.4243	1.3409	1.1774	1.0183	1.2242	115.0	125.5	180.1	120.7	180.0
NH_2 (2)	C≡CH	1.4392	1.4233	1.3403	1.1808	1.0164	1.2232	118.9	121.5	182.5	61.9	180.0
NH_2 (1)	$HC=CH_2$	1.4349	1.4570	1.3406	1.1792	1.0191	1.3453	113.9	125.4	179.7	120.7	180.0
NH_2 (2)	$HC=CH_2$	1.4405	1.4598	1.3379	1.1835	1.0165	1.3430	118.2	120.7	182.3	61.9	180.0
NH_2 (1)	NO (t)	1.4119	1.3988	1.3623	1.1673	1.0167	1.2590	117.8	124.6	179.8	118.9	0.0
NH_2 (2)	NO (t)	1.4044	1.4129	1.3569	1.1716	1.0132	1.2481	121.9	126.7	182.8	67.1	180.0
NH_2 (1)	NO (c)	1.4138	1.3983	1.3576	1.1680	1.0201	1.2573	118.1	128.8	180.1	122.0	180.0
NH_2 (2)	NO (c)	1.4051	1.4065	1.3614	1.1703	1.0136	1.2566	122.8	120.6	182.4	66.1	0.0
NH_2 (1)	CN	1.4304	1.4266	1.3430	1.1737	1.0174	1.1856	115.9	125.2	180.7	119.5	179.8
NH_2 (2)	CN	1.4304	1.4263	1.3426	1.1767	1.0154	1.1848	120.6	120.8	180.0	63.2	179.7
NH_2 (1)	NH_2 (1)	1.4258	1.4258	1.3365	1.1807	1.0180	1.0180	115.7	128.6	180.0	119.0	119.0
NH_2 (2)	NH_2 (2)	1.4252	1.4305	1.3346	1.1838	1.0189	1.0164	115.8	123.4	182.2	121.0	−63.0
NH_2 (1)	CHO (t)	1.4309	1.4560	1.3461	1.1731	1.0193	1.2314	116.6	124.3	178.6	122.3	−180.0
NH_2 (2)	CHO (t)	1.4270	1.4645	1.3464	1.1765	1.0150	1.2255	119.9	122.2	181.6	63.4	−180.0
NH_2 (1)	CHO (c)	1.4274	1.4580	1.3505	1.1700	1.0161	1.2319	116.5	127.4	179.5	118.4	0.0
NH_2 (2)	CHO (c)	1.4290	1.4611	1.3473	1.1734	1.0158	1.2308	122.3	121.2	181.1	62.7	0.0
NH_2 (1)	NO_2	1.3937	1.4436	1.3467	1.1710	1.0172	1.2470	121.3	125.0	182.9	118.4	180.0
NH_2 (1)	OCH_3 (c)	1.4030	1.3932	1.3339	1.1898	1.0178	1.4249	117.2	118.7	181.5	119.4	−1.2
NH_2 (1)	OCH_3 (g)	1.4073	1.3952	1.3343	1.1835	1.0177	1.4332	118.1	124.5	179.8	117.6	−107.2
NH_2 (1)	OH	1.4074	1.4027	1.3370	1.1833	1.0178	0.9746	117.6	124.1	180.1	115.7	103.0

were influenced both by the electrostatic and steric effects. Present study devoted to di-substituted ketenes leads to similar findings. Thus, the lengths of C=C and C=O bonds in aminoketene with an electronegative substituent NO at the C_β position are 1.3576 and 1.1680 Å, respectively, as against the values 1.3311 and 1.1833 Å with an electropositive substituent CH_3 [Table 3]. Similar trend is observed with other substituents in accordance with the findings of McAllister *et al.*[4]

In a study on α-oxoketenes, Birney[6] has demonstrated the effect of steric congestion on conformational preferences, notably on the angle between the substituent groups at the C_β position. A similar effect has been observed in the present series of molecules. It may be seen from Table 3 that the angle $M_1C_1M_2$ is wider in the case of ϕ_{NH_2} ~120° than in ϕ_{NH_2} ~60° by upto 5° and may be explained in terms of greater steric interaction between the two substituents. Similarly, the angle $M_1C_1C_2$ in isomers with ϕ_{NH_2} ~60° is found to be larger by about 3-5° than in those with ϕ_{NH_2} ~120°.

Energetics. It is reported[4,5] that ketenes are stabilized by π-acceptor groups like CHO, NO, NO_2 etc. which adopt coplanar geometries and are destabilized by electron-donor groups such as NH_2 and OH which adopt twisted geometries. In order to understand the effect of a substituent group on stabilization energies of aminoketenes where NH_2 adopts a twisted conformations with ϕ_{NH_2} ~60° or 120°, stabilization energies (SE) were calculated using isodesmic reaction given by eq. (1). The results are given in Table 1 which also contains stabilization energies relative to aminoketene.

It follows from Table 1 that with electropositive groups like H, CH_3, NH_2 and OH the stabilization energy has negative values ranging from –7.26 to –2.29 kcal/mol. These groups, therefore, have destabilizing effect on ketenes. A number of conjugating substituents like C≡CH, C≡N and $HC=CH_2$ have the ability to act both as electron-donors and electron-acceptors.[20] While the SE energies for the first two substituents are found to be –0.66 and –0.31 kcal/mol showing that they too have a very mild destabilizing affect, the SE energy for $HC=CH_2$ is 12.99 kcal/mol and points towards a strong stabilizing influence of this group. In contrast, electron-acceptor groups like NO, NO_2, CHO have positive values of SE ranging from 4.25 to 18.29 kcal/mol. and hence show strong stabilizing influence. The stabilization energies are found to depend both upon the conformation of the amino group as well as the *cis* and *trans* orientations of the substituents.

It is found that in the case of most stable conformers of substituted aminoketenes with ϕ_{NH_2} ~120° a correlation exists between the stabilization energies and group electro-

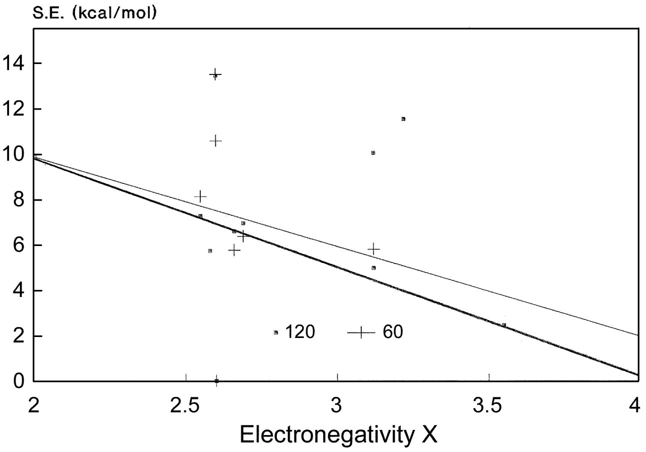


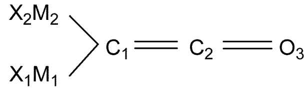
Figure 1. Isodesmic stabilization energy (SE, kcal/mol) of aminoketenes by substituents versus group electronegativies.

negativities χ of the substituents. A plot between the stabilization energies of substituted aminoketenes relative to aminoketene and the group electronegativity χ^{11} of substituents is given in Figure 1 which shows a linear relationship for electron-donating groups. Large positive deviations are, however, observed for π-acceptor substituents HC=CH_2, CHO, NO and NO_2 which may be attributed to the strong stabilizing influence of these groups that results in their coplanar geometries. If the points corresponding to these substituents are omitted, a fairly good correlation of the type SE = –4.8 C + 19.45 (r = 0.99) is found. Similar results have been reported for allenes,[4] diazirines[5] and mono-substituted ketenes.[4] In the case of ϕ_{NH_2} ~60° conformers a poorer correlation SE = –3.9 C + 17.92 (r = 0.70) is obtained.

Atomic charges. An evaluation of atomic charges obtained by Mulliken, NBO and Bader methods have been done by McAllister *et al.*[4] in mono-substituted ketenes by correlating the charge on the substituted atom with the substituent electronegativity. It was concluded that the trend of charges obtained by all the three methods are similar but Mulliken and NBO methods give comparable results. A similar observation has been made by Birney.[6] As such, the method of Mulliken population analysis was used for the present study. Atomic charges calculated from a Mulliken population analysis and calculated dipole moments are included in Table 4.

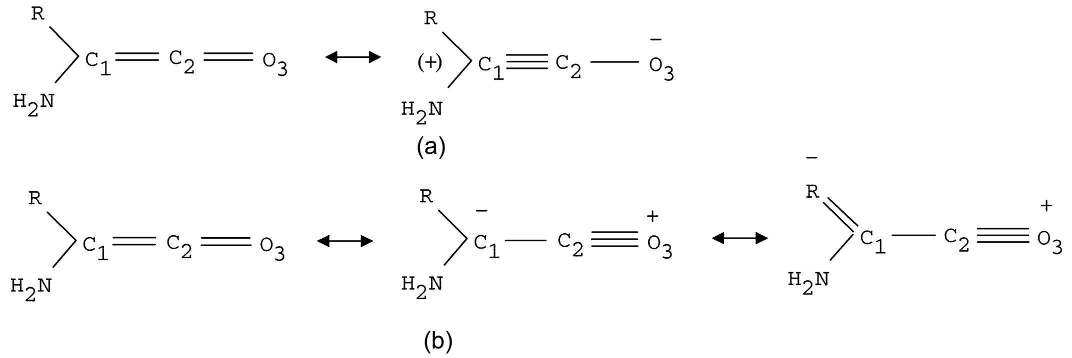
There have been major reservations about the validity of the calculated atomic charges[5,21] and these should be interpreted with caution. The greatest changes in the atomic charges in disubstituted ketenes has been found in atoms C_1, the substituent bearing carbon and O_3. As against mono-substituted ketenes where atom C_1 has negative charge, in

Table 4. Net atomic charges and dipole moments for di-substituted ketenes



$$(X_2M_2)(X_1M_1)C_1{=}C_2{=}O_3$$

M_1	M_2	C_1	C_2	O_3	M_1	X_1	M_2	X_2	(μ)
NH_2 (1)	H	−0.223	0.592	−0.470	−0.823	0.353	0.218	–	
NH_2 (2)	H	−0.192	0.545	−0.472	−0.832	0.359	0.234	–	1.030
NH_2 (1)	CH_3	0.030	0.546	−0.477	−0.833	0.348	−0.488	0.171	3.515
NH_2 (2)	CH_3	0.057	0.500	−0.482	−0.853	0.358	0.471	0.181	1.235
NH_2 (1)	C≡CH	−0.057	0.596	−0.443	−0.831	0.360	0.175	−0.465	2.627
NH_2 (2)	C≡CH	−0.047	0.567	−0.449	−0.828	0.364	0.176	−0.453	1.099
NH_2 (1)	HC=CH_2	0.032	0.553	−0.456	−0.845	0.356	−0.115	−0.439	2.626
NH_2 (2)	HC=CH_2	0.079	0.503	−0.465	−0.866	0.363	−0.141	−0.417	1.085
NH_2 (1)	NO (t)	0.201	0.637	−0.400	−0.829	0.375	0.050	−0.410	1.920
NH_2 (2)	NO (t)	0.248	0.601	−0.413	−0.862	0.379	0.035	−0.367	4.145
NH_2 (1)	NO (c)	0.167	0.674	−0.393	−0.839	0.373	0.071	−0.428	3.301
NH_2 (2)	NO (c)	0.200	0.641	−0.400	−0.863	0.376	0.098	−0.429	4.508
NH_2 (1)	CN	−0.007	0.633	−0.414	−0.826	0.373	0.331	−0.463	2.942
NH_2 (2)	CN	0.011	0.603	−0.419	−0.827	0.375	0.344	−0.463	4.822
NH_2 (1)	NH_2 (1)	0.154	0.613	−0.473	−0.839	0.346	−0.839	0.346	4.391
NH_2 (2)	NH_2 (1)	0.180	0.569	−0.477	−0.826	0.349	−0.867	0.361	
NH_2 (1)	CHO (t)	−0.054	0.593	−0.422	−0.827	0.369	0.332	−0.542	0.963
NH_2 (2)	CHO (t)	−0.009	0.554	−0.429	−0.838	0.368	0.328	−0.511	3.636
NH_2 (1)	CHO (c)	−0.105	0.668	−0.414	−0.851	0.365	0.362	−0.553	4.294
NH_2 (2)	CHO (c)	−0.077	0.628	−0.420	−0.862	0.368	0.362	−0.555	4.468
NH_2 (1)	NO_2	0.216	0.663	−0.395	−0.830	0.385	0.522	−0.458	3.517
NH_2 (1)	OCH_3(c)	0.409	0.472	−0.477	−0.843	0.363	−0.623	−0.208	2.585
NH_2 (1)	OCH_3(g)	0.332	0.560	−0.469	−0.852	0.364	−0.618	−0.172	3.783
NH_2 (1)	OH	0.292	0.571	−0.468	−0.840	0.364	−0.723	0.451	3.551



substituted aminoketenes this atom is found to have both negative and positive charges in the range –0.192 to +0.409 depending upon the nature of the substituent; it is negative only in case of C≡N, C≡CH and CHO substituents and is positive in all other cases. Atom C_2 in all cases has a positive charge whereas the oxygen atom O_3 has a negative charge. Further, atom O_3 has a larger negative charge for ϕ_{NH_2} ~60° isomer rather than for ϕ_{NH_2} ~120° isomer. The reverse is the case with the positive charge on atom C_2. It is also noted that atom O_3 has larger negative charge in the case of electropositive substituents than in the case of electronegative substituents. This observation can be explained in terms of the resonance structures of the type (a) for electron-donors and (b) π-acceptors

It may also be noted that out of all the substituted ketenes presently studied, the atom C_1 has the largest negative charge in aminoketene. All substituents at C_β-position tend to reduce this charge and make it electron deficient. This trend can be explained on the basis of induction effect of the substituent group on the C_1 atom of ketene should be directly related to its electronegativity. A linear relationship between the atomic charge on C_1 atom relative to aminoketene and the group electronegativity χ both for ϕ_{NH_2} ~120° and ϕ_{NH_2} ~60° conformers [Fig. 2] tends to support this explanation.

Charge distribution with substitution at C_β-position also influences the dipole moments (Table 4). The more stable conformers with electron-donor substituents are found to have larger dipole moments than the less stable ones. Thus ϕ_{NH_2} ~120° conformers have larger dipole moment than the ϕ_{NH_2} ~60° conformers. The reverse is the case with π-acceptor groups. Also in the case of electron-donor groups, the dipole moments of ϕ_{NH_2} ~120° conformers are greater than those of the π-acceptor groups. Following Brown *et al.*[22] and McAllister and Tidwell,[4] the lower value of the dipole moment in the electronegative groups can be explained in terms of electron delocalization of negative charge at the C_β position leading to the resonance structure at (b) above.

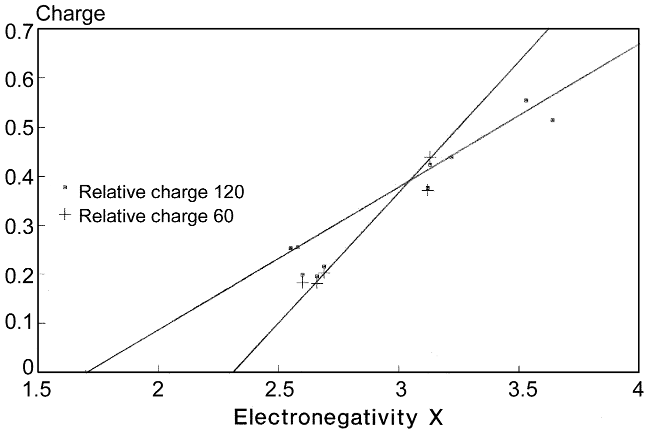


Figure 2. Correlation of charge on C_1 atoms of substituted aminoketenes relative to aminoketene and group electronegativies of substituents for ϕ_{NH_2} ~120° and ϕ_{NH_2} ~60° conformers.

Vibrational frequencies and intensities. In view of high reactivity and instability of substituted ketenes, matrix isolation and infrared spectroscopy methods have been used to trap and identify them to study their conformational preferences which are sensitive to substitution. The characteristic C=C=O stretching frequency near 2100 cm^{-1} is often used for this purpose. McAllister *et al.*[2a,4] and Birney[6] have used *ab initio* methods to calculate antisymmetric stretching frequencies and intensities of some mono and symmetrically disubstituted ketenes and have correlated them with the group electronegativities, field effect and resonance parameters of the substituent groups. In a similar attempt, we have attempted *ab initio* calculations using MP2/6-31G*// MP2/6-31G* method for substituted aminoketenes. The calculated vibrational frequencies and intensities of stretching and bending modes of the ketene group (C=C=O) for 11 substituted aminoketenes and their 26 possible conformers scaled by a factor 0.96 are given in Table 5.

Calculations predict bands of weak to medium intensity in spectral range 600-700 cm^{-1} and 450-550 cm^{-1} for the CCO in-plane and out of plane bending modes, respectively. In all cases, the frequencies of both these modes are higher in the ϕ_{NH_2} ~60° than in the ϕ_{NH_2} ~120° conformers. The CCO symmetric stretching modes are expected to appear as bands of weak to medium intensity in the spectral region 1210-1400 cm^{-1} and may be treated as non-characteristic due to a large interaction with other vibrational modes. The CCO asymmetric stretching modes may appear as strong to very strong bands in a narrow range of 2080-2140 cm^{-1}. In contrast to the bending modes, the frequencies of the stretching modes of ϕ_{NH_2} ~120° conformers in all cases are greater

Table 5. Frequencies and intensities of the ketene stretching and bending vibrational modes of substituted aminoketenes and the Field and Resonance effect parameters of the substituents

M_1	M_2	CCO o.p. bend	Int.	CCO i.p. bend	Int.	CCO sym str.	Int.	CCO asym str.	Int.	F	R
NH_2 (1)	H	492.8	53.1	635.1	40.4	1401.6	15.4	2135.6	349.6	0.08	
NH_2 (2)	H	498.3	43.4	652.9	2.6	1350.3	0.2	2112.2	359.1	0.08	−0.74
NH_2 (1)	CH_3	486.0	27.4	648.6	16.3	1372.6	34.4	2131.8	500.3	0.01	−0.18
NH_2 (2)	CH_3	490.3	3.7	656.3	3.9	1336.9	19.6	2107.0	392.0	0.01	−0.18
NH_2 (1)	C≡CH	488.6	25.9	630.4	2.6	1322.9	28.2	2133.2	503.3	0.22	0.01
NH_2 (2)	C≡CH	507.6	0.3	631.7	1.4	1269.8	8.9	2109.2	481.4	0.22	0.01
NH_2 (1)	$HC=CH_2$	472.7	27.6	630.0	13.3	1235.0	1.3	2119.5	624.2	0.13	−0.17
NH_2 (2)	$HC=CH_2$	478.2	2.2	636.9	3.7	1240.2	1.1	2094.9	546.8	0.13	−0.17
NH_2 (1)	NO (t)	506.8	30.7	599.8	14.7	1383.7	27.6	2128.5	652.7	0.49	0.42
NH_2 (2)	NO (t)	528.5	5.4	600.4	10.4	1353.5	37.9	2102.7	608.6	0.49	0.42
NH_2 (1)	NO (c)	532.7	30.4	692.6	15.9	1357.4	68.4	2105.3	523.6	0.49	0.42
NH_2 (2)	NO (c)	550.0	7.4	709.8	4.0	1349.6	28.0	2083.9	516.9	0.49	0.42
NH_2 (1)	CN	506.7	30.4	625.6	4.2	1328.6	19.6	2142.5	486.2	0.51	0.15
NH_2 (2)	CN	519.9	5.0	626.0	12.3	1279.9	5.3	2111.0	260.4	0.51	0.15
NH_2 (1)	NH_2(1)	530.2	61.8	640.7	91.6	1364.7	77.4	2140.2	339.0	0.08	−0.74
NH_2 (2)	NH_2(1)	518.3	13.6	651.3	20.9	1348.4	59.8	2117.5	345.1	0.08	−0.74
NH_2 (1)	CHO (t)	511.5	26.0	622.2	5.1	1234.6	53.7	2120.2	585.2	0.33	0.09
NH_2 (2)	CHO (t)	533.4	4.7	624.2	13.8	1217.3	28.9	2092.6	563.6	0.33	0.09
NH_2 (1)	CHO (c)	547.5	38.2	679.8	45.7	1320.0	60.5	2123.9	524.8	0.33	0.09
NH_2 (2)	CHO (c)	557.5	9.7	689.7	23.0	1289.1	110.8	2104.9	521.9	0.33	0.09
NH_2 (1)	NO_2	492.1	43.3	658.2	8.7	1429.5	40.9	2138.0	500.8	0.65	0.13
NH_2 (1)	OCH_3(c)	455.4	27.3	642.3	20.8	1380.6	79.5	2131.2	301.4	0.26	−0.56
NH_2 (1)	OCH_3(g)	426.7	43.8	658.7	17.8	1403.4	82.3	2116.0	192.9	0.26	−0.56
NH_2 (1)	OH	504.8	63.4	648.0	25.0	1387.6	66.2	2135.9	281.7	0.33	−0.70

than those of ϕ_{NH_2} ~60° conformers.

Gano and Jacob[13] have correlated the ketene stretching frequencies in some mono-substituted and symmetric disubstituted ketenes with Hammett type parameters, specifically the field effect parameters F and the resonance effect parameters R as originally derived by Swain and Lupton[14], and gave the relationship: $\nu(\mathrm{cm}^{-1}) = 2142 + 24\,F + 30\,R$. Similar studies were reported by McAllister *et al.*[3] by using modified F and R parameters of Hansch *et al.*[19] They have provided an empirical relationship $\nu(\mathrm{cm}^{-1}) = 2119 \pm 91(\pm 13)\,F - 6\,(\pm 9)\,R$ ($r = 0.86$) between the frequencies and the field effect (F) and resonance (R) parameters and have shown that in the case of monosubstituted ketenes, the field effect alone is sufficient to give an equally good correlation. Poor correlation has, however, been achieved by them for electron acceptor substituents.

A correlation of the calculated C=C=O asymmetric stretching frequencies (Table 5) with the field effect and resonance parameters[19] shows that unlike monosubstituted ketenes, where only the field effect parameter F is important in determining the frequency, in non-symmetrically disubstituted ketenes both the field effect (F) and resonance (R) parameters play some role. The effects of F and R parameters are different for different substituents. While in electron-donor substituents the frequency is primarily determined by the F parameter, in non-electron donor groups such as $CH=CH_2$, NO_2, NO and CN and C≡CH the resonance parameter R plays a more effective role. The correlation of frequencies calculated at the MP2/6-31G*//MP2/6-31G* level with these parameters may be given by the expression:

$$\nu(\mathrm{cm}^{-1}) = 2132 + 4.35\,F - 2.15\,R$$

having a correlation coefficient r = 0.64. As in the case of monosubstituted ketenes,[4,5] no useful linear relationship could be established between the vibrational frequencies and group electronegativities of the substituents.

Several correlationships between the intensities of carbonyl stretching modes and substituent constants have been reported in the literature.[2a,7,22] A linear relationship between the calculated intensity of C=C=O asymmetric stretching mode and group electronegativity[11] in monosubstituted ketenes has been reported by McAllister *et al.*[4] It has been suggested that substituents at the C_β position interact with the asymmetric vibrations and influence their intensities. In a similar exercise, in order to understand the affect of electron donor and electron acceptor substituents on the intensities of C=C=O symmetric and asymmetric stretch modes in asymmetric disubstituted ketenes, we have plotted curves (Fig. 3) between group electronegativities (χ)[11] and calculated intensities I (km/mol.) for these vibrational modes given in Table 5. It follows from Figure 3 that a linear correlation exists between these two parameters for non-π acceptor substituents. While in symmetric stretching modes

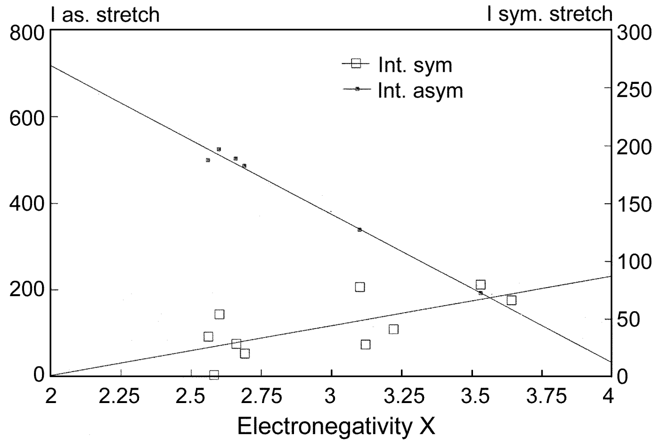


Figure 3. Plot of C=C=O calculated intensities (I, km/mol) of symmetric and asymmetric stretch modes versus group electronegativities of substituents for substituted aminoketenes (ϕ_{NH2} ~120°).

the intensity increases with electronegativity, in the asymmetric stretching modes it shows a reverse trend. In the latter case, the relationship may be expressed as :

$$\mathbf{I}\ (\text{kcal/mol}) = 640.2 - 100.1\ \chi$$

In the case of p-acceptor substituents NO_2, NO, CN, HC≡C, $CH=CH_2$ and CHO, however, a positive deviation of the calculated intensities from the defined correlation may be noted. The large intensity of these substituents may be explained by their strong interaction with the structure

which has enhanced C-C single bond character with a positive charge on oxygen and a negative charge on C_β. As earlier explained, a π-acceptor substituent could delocalize the negative charge causing an enhanced dipole moment change during the vibration and hence an increased intensity.

Acknowledgement. Grateful acknowledgement is made by one of the authors (VPG) to the financial assistance provided to this work by the Council of Scientific & Industrial Research (CSIR), Govt. of India, New Delhi in the form of a major research project.

References

1. (a) Pietri, N.; Chivassa, T.; Allouche, A.; Rajzmann, M.; Aycard, J.-P. *J. Phys. Chem.* **1996**, *100*, 7034. (b) Leung-Toung, R.; Wentrup, C. J. *J. Org. Chem.* **1992**, *57*, 4850. (c) Freiermuth, B.; Wentrup, C. J. *J. Org. Chem.* **1991**, *56*, 2286. (d) Kappe, C. O.; Wong, M. W.; Wentrup, C. J. *J. Org. Chem.* **1995**, *60*, 1686. (e) Bibas, H.; Wong, M. W.; Wentrup, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9582. (f) Fabian, W. M. F.; Kollenz, G. *J. Mol. Struct. (Theochem)* **1994**, *313*, 219.
2. (a) McAllister, M. A.; Tidwell, T. T. *Canadian J. Chem.* **1994**, *72*, 882. (b) Runge, W. *Prog. Phys. Org. Chem.* **1981**, *13*, 315.
3. Brown, R. D.; Godfrey, P. D.; Woodruff, M. *Aust. J. Chem.* **1979**, *32*, 2103.
4. McAllister, M. A.; Tidwell, T. T. *J. Org. Chem.* **1994**, *59*, 4506.
5. Gong, L.; McAllister, M. A.; Tidwell, T. *J. Am. Chem. Soc.* **1991**, *113*, 6021.
6. Birney, D. M. *J. Org. Chem.* **1994**, *59*, 2557.
7. Leszczynski, J.; Kwiatkowski, J. S. *Chem. Phys. Lett.* **1993**, *201*, 79.
8. Nguyen, M. T.; Ha, T.; More O'Ferral, R. A. *J. Org. Chem.* **1990**, *55*, 3251.
9. Allen, A. D.; Gong, L.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 6396.
10. (a) Badawi, H. M.; Forner, W.; Al-Saadi, A. *J. Mol. Struct. (THEOCHEM)* **2000**, *561*, 103. (b) Badawi, H. M.; Al-Saadi, A.; Forner, W. *Spectrochim. Acta* **2002**, *58A*, 33. (c) Badawi, H. M.; Forner, W.; Al-Saadi, A. *J. Mol. Struct. (THEOCHEM)* **2000**, *505*, 19.
11. Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652.
12. McAllister, M. A.; Tidwell, T. D. *Can. J. Chem.* **1994**, *72*, 882.
13. Gano, J. E.; Jacob, E. J. *Spectrochim Acta* **1987**, *43A*, 1023.
14. (a) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4326. (b) Swain, G. C.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.
15. Hegedus, L. S.; Imwinkelreid, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*,1109.
16. *Computer Program Gaussian 98W*; Gaussian Inc.: Pittsburg, P.A., 2001.
17. Schleyer, P. V. R. *Pure Appl. Chem.* **1987**, *59*, 1647.
18. Brady, W. T.; Dad, M. M. *J. Org. Chem.* **1991**, *56*, 6118.
19. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
20. Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885.
21. Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New-York, 1986.
22. Brown, R. D.; Godfrey, P. D.; Woodruff, M. *Aust. J. Chem.* **1979**, *32*, 2103.
23. (a) Deady, W.; Harrison, P. M.; Topsom, R. D. *Spectrochim. Acta* **1975**, *31A*, 1671. (b) Katritzky, A. R.; Topsom, R. D. *Linear Free Energy Relationships and Optical Spectroscopy* in *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972.