# Substituent Effects on the Structures and Energies of Isocyanates and Imines by *Ab Initio* Molecular Orbital Calculations

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The energies and geometries of substituted isocyanates RN=C=O and imines $RN=CH_2$ have been obtained by *ab initio* MP2/6-31G*//MP2/6-31G* calculations. For imines the stabilization energies SE = $\Delta E$ for the isodesmic exchange reaction of the substituent with alkenes show there is a very large energetic preference for electropositive substituents to be substituted on the imine compared with the alkene, with a linear correlation of SE with group electronegativities $\chi_{BE}$. For isocyanates the SE values derived by comparison with either alkenes or imines give excellent correlations with $\chi_{BE}$ values. The geometries of both imines and isocyanates bearing strongly electropositive substituents are linear, and this is attributed to charge repulsions and a preference for sp hybridization at nitrogen when this atom is bonded to an electropositive group. The much higher dependence of substituent stabilization SE of isocyanates compared with other cumulenes is attributed to the greater polar character of the isocyanates, and a linear relationship between the HOMO coefficient at the substituted atom of the cumulene and the slope of the dependence of SE on $\chi_{BE}$ was found. Atomic charges calculated for these substrates by the natural bond orbital (NBO) method give distinctly better correlations with $\chi_{BE}$ values than do charges calculated by the Mulliken method. Calculated and experimental isocyanate IR asymmetric stretching frequencies are in reasonable agreement, but the effects of substituents on the isocyanate frequencies differ from those for ketenes.

The study of substituent effects on molecules containing the fundamental functional groups of organic chemistry by the use of *ab initio* molecular orbital calculations has been the subject of intense interest in recent years, both by our group [1] and many others.[2] Our attention has concentrated on the cumulenes, including ketenes,[1a-d] allenes,[1a,d] and diazomethanes,[1d,e] as well as cyclopropenes [1d] and diazirines,[1d,e] which are respectively isomeric with the latter two, and alkenes as reference compounds.[1a,d] Others have recently reported studies on alkanes,[2a,b] alkenes,[2b,c] alkynes,[2c] and carbonyl compounds,[2d] as well as α-substituted carbocations [2e] and carbanions.[2f]

The present manuscript deals with the isocyanates, an important class whose structures and energies have not previously been the subject of a systematic theoretical study, although various individual compounds have been examined by calculation [3] and experiment.[4] As we have done previously [1] the correlation [5a] of the substituent effects with group electronegativities [5b,c] was of particular interest, as this technique has proved to be very useful in predicting the properties of ketenes. For the better understanding of the effects of substituents bonded to nitrogen the corresponding *N*-substituted imines have been studied. There have been previous experimental [6] and theoretical [6c,7] studies of individual members of this important class, but no systematic study.

## Results

The *ab initio* molecular orbital calculations were carried out using the GAUSSIAN 90 and GAUSSIAN 92 series of programs [8a] on Hewlett Packard 9000-750 and IBM RS/6000-530 minicomputers. All geometries were gradient optimized using the standard split valence 6-31G* basis set at both the HF and MP2 levels of theory,[8b,c] with the Berny Optimizer with no geometrical constraints.[8b] The orders (number of negative diagonal elements of the Hessian matrix) of all critical points were determined at both the HF/6-31G* and MP2/6-31G* levels by analytical differentiation of the restricted Hartree–Fock wavefunction. This also provided the necessary thermodynamic data for the calculation of zero point vibrational energies (ZPVE) and infrared absorption frequencies and intensities. The ZPVE were scaled by 0.90 for the HF/6-31G* calculated values, and by 0.95 for the MP2 calculations. All of the MP2/6-31G* and MP2/6-311++G** calculations were done at the full level, that is, the frozen core approximation was not used.

At the suggestion of a referee we have calculated the energies and structures of the isocyanates and imines bearing the substituents Li, $BH_2$, $CH_3$ and Na at the MP2/6-311++G**//MP2/6-311++G** level to ascertain whether this higher level of calculation causes any significant differences, particularly regarding the linear structures. The data are included in Tables 1–3, and as can be seen there are no qualitative changes in the energies or in the structures.

Energies calculated for optimized geometries at both the MP2/6-31G*//MP2/6-31G* and HF/6-31G*//HF/6-31G* levels, and zero point vibrational energies (ZPVE) for substituted isocyanates RN=C=O, imines $RN=CH_2$, and alkenes [1a,d] are given in Table 1. These were used to calculate isodesmic stabilization energies according to eqns. (1)–(3), as also given in Table 1.

$$\mathrm{RN{=}CH_2} + \mathrm{CH_3CH{=}CH_2} \xrightarrow[\mathrm{SE(1)}]{\Delta E\,=} \mathrm{CH_3N{=}CH_2} + \mathrm{RCH{=}CH_2} \quad (1)$$

$$\mathrm{RN{=}C{=}O} + \mathrm{CH_3N{=}CH_2} \xrightarrow[\mathrm{SE(2)}]{\Delta E\,=} \mathrm{CH_3N{=}C{=}O} + \mathrm{RN{=}CH_2} \quad (2)$$

$$\mathrm{RN{=}C{=}O} + \mathrm{CH_3CH{=}CH_2} \xrightarrow[\mathrm{SE(3)}]{\Delta E\,=} \mathrm{CH_3N{=}C{=}O} + \mathrm{RCH{=}CH_2} \quad (3)$$

Bond distances and angles calculated for isocyanates and imines are given in Tables 2 and 3, respectively, and calculated infrared stretching frequencies and intensities for the N=C=O

**Table 1** Calculated energies and zero point vibrational energies (ZPVE) (Hartree) for substituted isocyanates, imines and alkenes, and values of SE (kcal mol$^{-1}$) for isodesmic reactions

| | −E(RN=C=O) | ZPVE | −E(RN=CH$_2$) | ZPVE | −(RCH=CH$_2$) | ZPVE | SE(1)[a] | SE(2)[b] | SE(3)[c] | $\chi_{BE}$[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| H[e] | 167.7614 | 0.0205 | 94.0285 | 0.0390 | 78.0317 | 0.0493 | 3.5 | 2.8 | 6.3 | 2.20 |
| H[f] | 168.2324 | 0.0203 | 94.3231 | 0.0387 | 78.2943 | 0.0495 | 4.1 | 3.7 | 7.8 | |
| Li[e] | 174.6869 | 0.0130 | 100.8959 | 0.0275 | 84.8614 | 0.0386 | 28.2 | 36.8 | 65.0 | 1.00 |
| Li[f] | 175.1656 | 0.0125 | 101.2042 | 0.0275 | 85.1356 | 0.0389 | 29.4 | 34.3 | 63.7 | |
| Li[g] | 175.3092 | 0.0125 | 101.3065 | 0.0269 | | | | 35.2 | | |
| BeH[e] | 182.4637 | 0.0210 | 108.6922 | 0.0359 | 92.6587 | 0.0473 | 27.8 | 24.8 | 52.6 | 1.47 |
| BeH[f] | 182.9671 | 0.0210 | 109.0240 | 0.0362 | 92.9572 | 0.0477 | 28.4 | 23.0 | 51.3 | |
| BH$_2$[e] | 193.0594 | 0.0325 | 119.3186 | 0.0495 | 103.2897 | 0.0603 | 24.6 | 6.8 | 31.4 | 1.92 |
| BH$_2$[f] | 193.6026 | 0.0329 | 119.6945[h] | 0.0501 | 103.6262[i] | 0.0610 | 28.9 | 2.2 | 31.1 | |
| BH$_2$[g] | 193.7602 | 0.0326 | 119.8097 | 0.0531 | | | | 6.2 | | |
| CH$_3$[e] | 206.7912 | 0.0491 | 133.0615 | 0.0663 | 117.0715 | 0.0769 | 0.0 | 0.0 | 0.0 | 2.55 |
| CH$_3$[f] | 207.3963 | 0.0493 | 133.4917 | 0.0665 | 117.4697 | 0.0776 | 0.0 | 0.0 | 0.0 | |
| CH$_3$[g] | 207.5719 | 0.0488 | 133.6275 | 0.0655 | | | | 0.0 | | |
| NH$_2$[e] | 222.7368 | 0.0386 | 149.0293 | 0.0561 | 133.0620 | 0.0669 | −14.2 | −13.7 | −27.9 | 3.12 |
| NH$_2$[f] | 223.3736[j] | 0.0378 | 149.4933[k] | 0.0554 | 133.4913[l] | 0.0668 | −12.4 | −14.9 | −27.3 | |
| OH[e] | 242.5308 | 0.0257 | 168.8410 | 0.0437 | 152.8889 | 0.0550 | −23.4 | −24.5 | −47.9 | 3.55 |
| OH[f] | 243.1842 | 0.0246 | 169.3208 | 0.0427 | 153.3322 | 0.0545 | −20.5 | −25.3 | −45.7 | |
| F[e] | 266.4989 | 0.0135 | 192.8184 | 0.0313 | 176.8820 | 0.0429 | −33.0 | −30.5 | −63.5 | 4.00 |
| F[f] | 267.1442 | 0.0127 | 193.2893 | 0.0306 | 177.3152 | 0.0426 | −29.5 | −30.7 | −60.1 | |
| Na[e] | 329.0709 | 0.0119 | 255.2728 | 0.0262 | 239.2456 | 0.0377 | 23.9 | 41.1 | 65.0 | 1.00 |
| Na[f] | 329.5507 | 0.0115 | 255.5815 | 0.0261 | 239.5226 | 0.0381 | 23.7 | 38.9 | 62.7 | |
| Na[g] | 329.8143 | 0.0114 | 255.8046 | 0.0256 | | | | 39.5 | | |
| MgH[e] | 367.4054 | 0.0176 | 293.6234 | 0.0324 | 277.5969 | 0.0439 | 23.5 | 31.3 | 54.8 | 1.30 |
| MgH[f] | 367.9063 | 0.0174 | 293.9531 | 0.0324 | 277.8954 | 0.0442 | 22.8 | 29.2 | 52.0 | |
| AlH$_2$[e] | 410.3002 | 0.0258 | 336.5329 | 0.0417 | 320.5076 | 0.0527 | 22.4 | 22.8 | 45.2 | 1.60 |
| AlH$_2$[f] | 410.8245 | 0.0259 | 336.8870[m] | 0.0407 | 320.8285[i] | 0.0532 | 23.8 | 19.3 | 43.0 | |
| SiH$_3$[e] | 457.8842 | 0.0377 | 384.1245 | 0.0539 | 368.1125 | 0.0648 | 14.0 | 18.2 | 32.2 | 1.90 |
| SiH$_3$[f] | 458.4380 | 0.0377 | 384.5062 | 0.0542 | 368.4631 | 0.0653 | 13.2 | 16.6 | 29.9 | |
| PH$_2$[e] | 509.0667 | 0.0306 | 435.3238 | 0.0473 | 419.3259 | 0.0582 | 5.1 | 8.0 | 13.1 | 2.17 |
| PH$_2$[f] | 509.6465 | 0.0302 | 435.7313[j] | 0.0470 | 419.7011 | 0.0583 | 5.3 | 6.4 | 11.8 | |
| SH[e] | 565.2432 | 0.0215 | 491.5225 | 0.0387 | 475.5419 | 0.0499 | −5.6 | −5.6 | −11.2 | 2.65 |
| SH[f] | 565.8436 | 0.0211 | 491.9507 | 0.0404 | 475.9359 | 0.0498 | −5.6 | −6.0 | −11.6 | |
| Cl[e] | 626.5993 | 0.0129 | 552.8944 | 0.0302 | 536.9337 | 0.0415 | −17.9 | −15.5 | −33.4 | 3.05 |
| Cl[f] | 627.2111 | 0.0129 | 553.3328 | 0.0297 | 537.3361 | 0.0415 | −15.4 | −16.8 | −32.1 | |
| CF$_3$[e] | 503.3795 | 0.0279 | 429.6562 | 0.0455 | 413.6568 | 0.0563 | 6.1 | −3.8 | 2.3 | 2.71 |
| CF$_3$[f] | 504.4925 | 0.0270 | 430.5930 | 0.0447 | 414.5634 | 0.0557 | 4.7 | −2.8 | 1.9 | |
| CH=CH$_2$[e] | 244.6386 | 0.0540 | 170.9111 | 0.0714 | 154.9197 | 0.0824 | 1.2 | −1.3 | −0.1 | 2.58 |
| CH=CH$_2$[f] | 245.3685[n] | 0.0535 | 171.4648[o] | 0.0706 | 155.4417 | 0.0821 | 0.9 | −0.5 | 0.4 | |
| CH=O[e] | 280.4933 | 0.0321 | 206.7602 | 0.0488 | 190.7624 | 0.0599 | 5.2 | 1.8 | 7.0 | 2.60 |
| CH=O[f] | 281.2673[p] | 0.0312 | 207.3562[q] | 0.0480 | 191.3286[r] | 0.0592 | 3.6 | 3.9 | 7.5 | |
| C≡CH[e] | 243.4164 | 0.0313 | 169.6923 | 0.0484 | 153.7079 | 0.0596 | −3.1 | −3.6 | −6.7 | 2.66 |
| C≡CH[f] | 244.1410 | 0.0294 | 170.2403 | 0.0465 | 154.2249 | 0.0580 | −3.9 | −2.5 | −6.4 | |
| CN[e] | 259.4716 | 0.0212 | 185.7511 | 0.0384 | 169.7680 | 0.0495 | −7.5 | −5.8 | −13.3 | 2.69 |
| CN[f] | 260.2285 | 0.0200 | 186.3302 | 0.0372 | 170.3161 | 0.0485 | −4.8 | −3.9 | −8.7 | |
| NO[e] | 296.3754 | 0.0190 | 222.6603 | 0.0368 | 206.6774 | 0.0481 | −4.0 | −8.8 | −12.8 | 3.12 |
| NO[f] | 297.1946[s] | 0.0170 | 223.2983[t] | 0.0348 | 207.2808[r] | 0.0465 | −2.4 | −4.8 | −7.2 | |
| NO$_2$[e] | 371.1818 | 0.0255 | 297.4755 | 0.0429 | 281.5041 | 0.0542 | −11.2 | −14.6 | −25.8 | 3.22 |
| NO$_2$[f] | 372.2001 | 0.0237 | 298.3164 | 0.0412 | 282.3113 | 0.0532 | −10.0 | −12.9 | −23.0 | |

[a] Isodesmic stabilization energy (kcal mol$^{-1}$, including ZPVE) of imines relative to alkenes by eqn. (1). [b] Isodesmic stabilization energy (kcal mol$^{-1}$, including ZPVE) of isocyanates relative to imines according to eqn. (2). [c] Isodesmic stabilization energy (kcal mol$^{-1}$, including ZPVE) of isocyanates relative to alkenes according to eqn. (3). [d] Group electronegativity. [e] HF/6-31G*//HF/6-31G*. [f] MP2/6-31G*//MP2/6-31G*. [g] MP2/6-311++G**//MP2/6-311++G**. [h] Perpendicular; 119.6300 (planar). [i] Planar. [j] Twisted; 223.3575 (planar). [k] Pyramidal; 149.4884 (planar). [l] Pyramidal. [m] Perpendicular; 336.8677 (planar). [n] *anti*; 245.3678 (*syn*). [o] *anti*; 171.4563 (*syn*). [p] *syn*; 281.2643 (*anti*). [q] *syn*; 207.3552 (*anti*). [r] *anti*. [s] *anti*; 297.1893 (*syn*). [t] *syn*; 223.2911 (*anti*).

group are given in Table 4. Atomic charges for the isocyanates and imines were also calculated by the Mulliken method,[9a] as well as the natural bond orbital (NBO) method of Reed and Weinhold,[9b,c] and the results are given in Tables 5 and 6.

*Structures of Isocyanates and Imines.*—Comparison of the calculated geometries of isocyanates and imines with experimentally determined values are given in Table 7. These include calculations at the HF/6-31G* level reported by others for isocyanates substituted with *c*-Pr,[3e] $CH_3CO$,[3a] and ClCO[3b] substituents. For $SiH_3N{=}C{=}O$ there are two experimentally determined structures[4c,d] and it would appear that the structure determined more recently by electron diffraction,[4d] is more accurate than the microwave structure determined earlier,[4c] as the $N^1C^1$ and $C^1O^1$ bond lengths in the electron diffraction structure[4d] are much closer to those for the other compounds in the group, and the former bond is longer than the latter in agreement with all the other experimentally determined values. Only this latter geometry is considered in the following paragraph.

Comparison of the geometries calculated at the HF/6-31G* and MP2/6-31G* levels show that the latter bond distances are consistently longer, and there are also significant differences in the bond angles calculated by the two methods, with the N–C–O angles usually being smaller at the MP2 level, while the M–N–C angles are usually larger, with some exceptions. The geometry of $CH_3N{=}C{=}O$ has also been reported at the MP2/6-311++G** level,[3g] and these results are almost identical with

**Table 2** Bond distances (Å) and bond angles (°) calculated for isocyanates $H_{a,b}MN^1C^1{=}O^1$

| M | $N^1C^1$ | $O^1C^1$ | $MN^1$ | $H_{a,b}M$ | $N^1C^1O^1$ | $MN^1C^1$ | $H_{a,b}MN^1$ | $H_aMN^1C^1$ | $H_bMN^1C^1$ |
|---|---|---|---|---|---|---|---|---|---|
| H[a] | 1.200 | 1.148 | 0.994 | | 174.2 | 125.2 | | | |
| H[b] | 1.224 | 1.184 | 1.008 | | 171.7 | 125.9 | | | |
| Li[a] | 1.180 | 1.172 | 1.755 | | 180.0 | 180.0 | | | |
| Li[b] | 1.214 | 1.202 | 1.756 | | 180.0 | 180.0 | | | |
| Li[c] | 1.210 | 1.195 | 1.748 | | 180.0 | 180.0 | | | |
| BeH[a] | 1.185 | 1.152 | 1.495 | 1.327 | 180.0 | 180.0 | 180.0 | | |
| BeH[b] | 1.213 | 1.185 | 1.495 | 1.327 | 180.0 | 180.0 | 180.0 | | |
| $BH_2$[a] | 1.178 | 1.153 | 1.412 | 1.187 | 180.0 | 180.0 | 119.2 | | |
| $BH_2$[b] | 1.218 | 1.183 | 1.419 | 1.193, 1.190 | 174.2 | 149.9 | 119.7, 118.2 | 0.0 | 180.0 |
| $BH_2$[c] | 1.220 | 1.171 | 1.427 | 1.191, 1.188 | 174.0 | 141.3 | 119.4, 118.2 | 0.0 | 180.0 |
| $CH_3$[a] | 1.180 | 1.158 | 1.437 | 1.083, 1.081 | 175.1 | 143.1 | 111.5, 109.2 | 0.0 | 120.7 |
| $CH_3$[b] | 1.214 | 1.191 | 1.442 | 1.093, 1.089 | 172.3 | 138.0 | 110.8, 108.4 | 180.0 | 60.7 |
| $CH_3$[c] | 1.213 | 1.180 | 1.445 | 1.092, 1.089 | 172.7 | 135.6 | 110.8, 108.6 | 180.0 | 60.7 |
| $NH_2$[a] | 1.208 | 1.147 | 1.424 | 1.002 | 172.8 | 122.4 | 105.1 | 124.1 | 124.1 |
| $NH_2$[b] | 1.230 | 1.186 | 1.430 | 1.021 | 168.3 | 127.2 | 104.4 | 124.9 | 124.9 |
| OH[a] | 1.217 | 1.144 | 1.389 | 0.948 | 173.1 | 116.7 | 102.7 | 180.0 | |
| OH[b] | 1.242 | 1.184 | 1.422 | 0.974 | 169.0 | 118.1 | 100.6 | 180.0 | |
| F[a] | 1.239 | 1.135 | 1.374 | | 173.2 | 109.9 | | | |
| F[b] | 1.262 | 1.177 | 1.418 | | 168.8 | 110.8 | | | |
| Na[a] | 1.178 | 1.180 | 2.088 | | 180.0 | 180.0 | | | |
| Na[b] | 1.213 | 1.208 | 2.086 | | 180.0 | 180.0 | | | |
| Na[c] | 1.209 | 1.201 | 2.111 | | 180.0 | 180.0 | | | |
| MgH[a] | 1.184 | 1.161 | 1.891 | 1.700 | 180.0 | 180.0 | 180.0 | | |
| MgH[b] | 1.213 | 1.193 | 1.903 | 1.704 | 180.0 | 180.0 | 180.0 | | |
| $AlH_2$[a] | 1.184 | 1.154 | 1.780 | 1.573 | 180.0 | 180.0 | 117.9 | | |
| $AlH_2$[b] | 1.211 | 1.187 | 1.790 | 1.579 | 180.0 | 180.0 | 117.5 | | |
| $SiH_3$[a] | 1.178 | 1.154 | 1.715 | 1.469 | 180.0 | 180.0 | 109.9 | | |
| $SiH_3$[b] | 1.205 | 1.188 | 1.721 | 1.479 | 180.0 | 180.0 | 108.8 | | |
| $PH_2$[a] | 1.183 | 1.154 | 1.709 | 1.399 | 176.5 | 148.6 | 97.8 | 132.2 | 132.2 |
| $PH_2$[b] | 1.215 | 1.188 | 1.725 | 1.415 | 174.1 | 141.3 | 97.0 | 132.7 | 132.7 |
| SH[a] | 1.193 | 1.151 | 1.695 | 1.321 | 175.1 | 133.3 | 94.9 | 180.0 | |
| SH[b] | 1.223 | 1.187 | 1.708 | 1.338 | 172.4 | 130.8 | 93.8 | 180.0 | |
| Cl[a] | 1.217 | 1.141 | 1.694 | | 173.8 | 120.2 | | | |
| Cl[b] | 1.241 | 1.181 | 1.709 | | 169.7 | 121.9 | | | |
| $CF_3$[a] | 1.204 | 1.139 | 1.398 | 1.311, 1.322[d] | 174.6 | 129.6 | 112.1,[e] 110.4[e] | | |
| $CF_3$[b] | 1.228 | 1.177 | 1.406 | 1.350, 1.339[d] | 172.7 | 128.4 | 112.3,[e] 110.2[e] | 0.0 | 120.3 |
| CH=$CH_2$[a,f] | 1.188 | 1.153 | 1.397 | 1.075[g] | 174.8 | 139.3 | 115.9[h] | 0.0 | |
| CH=$CH_2$[b,f] | 1.218 | 1.188 | 1.397 | 1.087[g] | 172.4 | 138.0 | 116.3[i] | 0.0 | |
| CH=O[a,j] | 1.213 | 1.137 | 1.397 | 1.081[k] | 174.1 | 126.8 | 111.4[l] | | |
| CH=O[b,j] | 1.234 | 1.177 | 1.412 | 1.096[m] | 172.6 | 127.9 | 111.0[n] | | |
| C≡CH[a] | 1.192 | 1.146 | 1.331 | 1.184[o] | 173.9 | 141.0 | 177.5[p] | | |
| C≡CH[b] | 1.218 | 1.184 | 1.331 | 1.218[q] | 171.7 | 142.6 | 174.7[p] | | |
| CN[a] | 1.206 | 1.136 | 1.325 | 1.136[r] | 173.7 | 133.7 | 177.1[s] | | |
| CN[b] | 1.227 | 1.176 | 1.330 | 1.184[r] | 171.6 | 135.8 | 176.9[s] | | |
| NO[a,f] | 1.222 | 1.136 | 1.409 | 1.155[t] | 174.3 | 118.6 | 111.8[u] | | |
| NO[b,f] | 1.243 | 1.179 | 1.517 | 1.191[t] | 173.4 | 117.3 | 110.9[u] | | |
| $NO_2$[a] | 1.238 | 1.126 | 1.382 | 1.197, 1.175[t] | 172.8 | 115.8 | 117.7, 115.0[u] | | |
| $NO_2$[b] | 1.251 | 1.172 | 1.448 | 1.232, 1.222[t] | 171.9 | 115.6 | 117.8, 113.7[u] | | |

[a] HF/6-31G*. [b] MP2/6-31G*. [c] MP2/6-311 + +G**. [d] C–F. [e] FCN. [f] *anti*. [g] 1.316 (C=C). [h] 122.3 (C=C–N). [i] 121.5 (C=C–N). [j] *syn*. [k] 1.182 (C=O). [l] 125.0 (O=C–N). [m] 1.214 (C=O). [n] 125.2 (OCN). [o] C≡C, 1.056 (C–H). [p] C≡C–N. [q] C≡C, 1.065 (C–H). [r] C≡N. [s] NC–N. [t] N–O. [u] O–N–N.

ours, obtained at the same level without the frozen core approximation. This structure shows closer agreement with the experimental structure compared with the MP2/6-31G* geometry (Table 7), and it was suggested[3g] that these calculations give the best structural data available for methyl isocyanate.

For the nine isocyanate structures where comparisons of the calculated and experimental structures are possible, the differences in the *N*-substituent bond lengths are rather small, ranging from 0.0 to 0.018 Å, except for the cyano derivative, where the difference is 0.047 Å. For the $N^1C^1$ and $C^1O^1$ bond lengths the HF/6-31G* calculated values are consistently shorter by an average of 0.017 Å, with a largest variation of 0.038 Å, for the $SiH_3$ substituent, while the MP2/6-31G* distances are usually longer, with an average deviation of 0.015 Å. This same trend was also noted for ketenes, with the experimental values almost halfway between the HF/6-31G* and MP2/6-31G* values.[1d] For the M–$N^1$–$C^1$ and $N^1$–$C^1$–$O^1$ bond angles the deviations at the HF/6-31G* level average 2.2°, with the largest difference of 6.3° for the CN derivative. The MP2/6-31G* calculated values are closer to the experimental values, with an average deviation of 1.6°. Thus with the possible exception of the CN substituted case the agreement with the calculated and experimental geometries is rather good, and this lends confidence to the utility and accuracy of the calculations. It may also be noted that in three cases the $N^1C^1O^1$ bonds were assumed to be linear in deriving the experimental structures, although this is contrary to the results calculated and found experimentally for all the other compounds in Table 7, with the exception of $SiH_3N{=}C{=}O$. These results agree with previous findings that whereas the geometry of HNCO calculated without polarization functions is linear the inclusion of these functions gives a bent HNC bond, in agreement with experiment.[3c]

There have been many theoretical calculations of the structures of substituted imines,[7] and a comparison of the

**Table 3** Bond distances (Å) and bond angles (°) calculated for imines $H_{a,b}MN^1{=}CH^1$

| $MH_{a,b}$ | $N^1C^1$ | $MN^1$ | $C^1H^1$ | $C^1H^2$ | $MH_a$ | $MH_b$ | $MN^1C^1$ | $N^1C^1H^1$ | $N^1C^1H^2$ | $H_{a,b}MN^1$ | $H_{a,b}MN^1C^1$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H[a] | 1.250 | 1.006 | 1.084 | 1.080 | | | 111.5 | 124.7 | 119.3 | | |
| H[b] | 1.281 | 1.026 | 1.094 | 1.089 | | | 109.7 | 125.5 | 118.4 | | |
| Li[a] | 1.237 | 1.731 | 1.099 | 1.099 | | | 180.0 | 123.9 | 123.9 | | |
| Li[b] | 1.263 | 1.763 | 1.110 | 1.110 | | | 180.0 | 123.9 | 123.9 | | |
| Li[c] | 1.262 | 1.727 | 1.111 | 1.111 | | | | | | | |
| BeH[a] | 1.234 | 1.477 | 1.089 | 1.089 | 1.334 | | 180.0 | 122.8 | 122.8 | 180.0 | |
| BeH[b] | 1.259 | 1.482 | 1.100 | 1.100 | 1.332 | | 180.0 | 122.7 | 122.7 | 180.0 | |
| $BH_2$[a] | 1.230 | 1.362 | 1.084 | 1.084 | 1.191 | 1.191 | 180.0 | 121.9 | 121.9 | 119.0 | 90.0 |
| $BH_2$[b] | 1.256 | 1.363 | 1.093 | 1.093 | 1.194 | 1.194 | 180.0 | 121.5 | 121.5 | 118.4 | 90.0 |
| $BH_2$[c] | 1.256 | 1.366 | 1.093 | 1.093 | 1.192 | 1.192 | 180.0 | 121.3 | 121.3 | 118.3 | 90.0 |
| $CH_3$[a] | 1.247 | 1.444 | 1.086 | 1.079 | 1.089 | 1.084 | 118.6 | 123.7 | 119.6 | 113.6, 109.0 | 0.0, 121.6 |
| $CH_3$[b] | 1.277 | 1.456 | 1.098 | 1.088 | 1.100 | 1.093 | 116.3 | 123.9 | 119.0 | 113.6, 108.6 | 0.0, 121.7 |
| $CH_3$[c] | 1.276 | 1.455 | 1.098 | 1.089 | 1.100 | 1.093 | 116.2 | 123.3 | 119.2 | 113.1, 108.8 | 0.0, 121.6 |
| $NH_2$[a] | 1.251 | 1.371 | 1.084 | 1.074 | 1.003 | 0.998 | 118.4 | 123.4 | 118.4 | 113.5, 108.9 | 30.9, 154.3 |
| $NH_2$[b] | 1.285 | 1.386 | 1.095 | 1.083 | 1.023 | 1.014 | 116.7 | 123.7 | 117.7 | 113.5, 108.5 | 29.2, 152.2 |
| OH[a] | 1.249 | 1.369 | 1.077 | 1.073 | 0.947 | | 112.0 | 122.6 | 117.3 | 104.5 | 180.0 |
| OH[b] | 1.283 | 1.409 | 1.088 | 1.083 | 0.973 | | 110.0 | 122.8 | 116.4 | 102.0 | 180.0 |
| F[a] | 1.248 | 1.369 | 1.075 | 1.073 | | | 109.7 | 122.8 | 116.3 | | |
| F[b] | 1.279 | 1.417 | 1.085 | 1.083 | | | 108.1 | 123.1 | 115.4 | | |
| Na[a] | 1.236 | 2.065 | 1.104 | 1.104 | | | 180.0 | 124.4 | 124.4 | | |
| Na[b] | 1.261 | 2.066 | 1.116 | 1.116 | | | 180.0 | 124.5 | 124.5 | | |
| Na[c] | 1.261 | 2.097 | 1.116 | 1.116 | | | 180.0 | 124.2 | 124.2 | | |
| MgH[a] | 1.237 | 1.872 | 1.094 | 1.094 | 1.709 | | 180.0 | 123.4 | 123.4 | 180.0 | |
| MgH[b] | 1.262 | 1.888 | 1.105 | 1.105 | 1.712 | | 180.0 | 123.4 | 123.4 | 180.0 | |
| $AlH_2$[a] | 1.234 | 1.751 | 1.089 | 1.089 | 1.579 | 1.579 | 180.0 | 122.8 | 122.8 | 118.2 | 90.0 |
| $AlH_2$[b] | 1.259 | 1.766 | 1.099 | 1.099 | 1.583 | 1.583 | 180.0 | 122.6 | 122.6 | 117.2 | 90.0 |
| $SiH_3$[a] | 1.248 | 1.746 | 1.089 | 1.084 | 1.482 | 1.472 | 124.7 | 124.5 | 120.6 | 111.5, 108.8 | 0.0, 120.5 |
| $SiH_3$[b] | 1.278 | 1.764 | 1.101 | 1.094 | 1.492 | 1.481 | 120.9 | 124.9 | 120.0 | 111.6, 108.3 | 0.0, 120.7 |
| $PH_2$[a] | 1.248 | 1.723 | 1.087 | 1.081 | 1.411 | 1.399 | 123.5 | 124.4 | 119.6 | 101.8, 97.5 | 26.8, 124.0 |
| $PH_2$[b] | 1.279 | 1.742 | 1.098 | 1.091 | 1.427 | 1.412 | 120.5 | 124.9 | 118.9 | 101.6, 96.6 | 28.3, 125.1 |
| SH[a] | 1.251 | 1.709 | 1.083 | 1.078 | 1.322 | | 117.7 | 124.8 | 118.0 | 95.6 | 180.0 |
| SH[b] | 1.285 | 1.730 | 1.094 | 1.087 | 1.338 | | 115.5 | 125.5 | 116.8 | 94.3 | 180.0 |
| Cl[a] | 1.250 | 1.725 | 1.078 | 1.077 | | | 114.4 | 125.0 | 116.2 | | |
| Cl[b] | 1.283 | 1.750 | 1.089 | 1.087 | | | 112.8 | 125.5 | 115.0 | | |
| $CF_3$[a] | 1.249 | 1.410 | 1.079 | 1.077 | 1.315[d] | 1.327[d] | 119.4 | 124.2 | 118.4 | 115.0,[e] 109.7[e] | |
| $CF_3$[b] | 1.278 | 1.423 | 1.090 | 1.087 | 1.342[d] | 1.357[d] | 117.5 | 124.3 | 117.7 | 115.7,[e] 109.1[e] | |
| $CH{=}CH_2$[a,f] | 1.252 | 1.404 | 1.085 | 1.078 | 1.082 | 1.319[g] | 118.1 | 123.6 | 119.5 | 117.6[h] | |
| $CH{=}CH_2$[b,f] | 1.284 | 1.408 | 1.098 | 1.088 | 1.095 | 1.338[g] | 116.5 | 123.8 | 119.1 | 120.2 | |
| CH=O[a,i] | 1.257 | 1.420 | 1.080 | 1.078 | 1.086 | 1.185[j] | 115.8 | 123.3 | 118.8 | 111.9[k] | |
| CH=O[b,i] | 1.284 | 1.444 | 1.093 | 1.088 | 1.099 | 1.217[j] | 114.1 | 123.1 | 118.5 | 111.6 | |
| C≡CH[a] | 1.256 | 1.353 | 1.081 | 1.076 | 1.187[l] | 1.056[m] | 119.0 | 123.6 | 118.5 | 177.2[n] | |
| C≡CH[b] | 1.288 | 1.356 | 1.093 | 1.087 | 1.221[l] | 1.065[m] | 118.2 | 123.8 | 117.9 | 177.4[n] | |
| CN[a] | 1.257 | 1.350 | 1.080 | 1.076 | 1.137[o] | | 118.1 | 123.9 | 118.1 | 176.8[p] | |
| CN[b] | 1.287 | 1.357 | 1.091 | 1.086 | 1.184[o] | | 117.4 | 124.0 | 117.5 | 174.6[p] | |
| NO[a,i] | 1.256 | 1.412 | 1.080 | 1.075 | 1.163[q] | | 109.0 | 122.4 | 118.8 | 111.9[r] | |
| NO[b,i] | 1.279 | 1.568 | 1.095 | 1.086 | 1.202[q] | | 111.8 | 123.0 | 118.2 | 114.8[r] | |
| $NO_2$[a] | 1.255 | 1.422 | 1.075 | 1.074 | 1.179[q] | 1.194[q] | 113.9 | 123.9 | 116.3 | 113.5, 120.1[r] | |
| $NO_2$[b] | 1.280 | 1.468 | 1.089 | 1.085 | 1.228[q] | 1.231[q] | 111.1 | 123.8 | 116.6 | 113.4, 118.3[r] | |

[a] HF/6-31G*. [b] MP2/6-31G*. [c] MP2/6-311++G**. [d] C–F. [e] FCN. [f] *anti*. [g] C=C. [h] 121.3 (C=C–N). [i] *syn*. [j] C=O. [k] 126.1 (O=C–N). [l] C≡C. [m] C–H. [n] C≡C–N. [o] C≡N. [p] N≡C–N. [q] N–O. [r] ONN.

experimental geometry of $CH_2{=}NH$ to those calculated with various basis sets has been presented.[7j] Closer agreement was obtained using the MP2/6-31G* level as compared with HF/6-31G*, and some further improvement was observed for some of the geometrical parameters at still higher levels.[7j] Despite the abundance of theoretical studies there are few experimental studies of the geometries of simple imines $RN{=}CH_2$. In particular for $ClN{=}CH_2$ and $CH_2{=}CHN{=}CH_2$ the microwave spectra were measured,[6c] but calculated geometries were used in assigning these spectra.[6c] Similarly for $CH_3N{=}CH_2$ some of the geometrical parameters were assumed,[6b] and so apparently only for $HN{=}CH_2$[6a] and $HON{=}CH_2$[6h] are complete experimental structures available. For this latter compound the agreement between the experimental and the MP2/6-31G* geometries is excellent (Table 7).

The calculated linearity of isocyanates and imines with electropositive substituents (Li, BeH, Na, MgH, and $AlH_2$, plus $SiH_3N{=}C{=}O$ and $BH_2N{=}CH_2$) is a striking structural feature. At the HF/6-31G* level $BH_2N{=}C{=}O$ is also linear, but at the MP2/6-31G* level the structure is bent. Experimentally the structures of $SiH_3N{=}C{=}O$[4c,d,m] and $SiMe_3N{=}C{=}O$[4e] have been interpreted as being linear,[4c,e,11e] or bent with a very small barrier to linearity.[4d,m] This linearity is consistent with a more effective σ-withdrawal by the nitrogen from the electropositive substituents when the nitrogen is sp hybridized in a linear geometry. The possibility of π-delocalization between nitrogen and lithium was considered for lithioimine and ruled out[7h] as a contributing factor in determining the linear geometry, as it was found this geometry is still maintained when the π orbitals are removed from the basis set for the calculated structure.[7h] For the Li-, BeH- and $BH_2$-substituted imines it has also been proposed that the 180° MNC bond angle arises from nuclear repulsion terms involving the electropositive group M, presumably with the $CH_2$ group, whereas for electronegative substituents M the electronic repulsion between M and the lone pair on nitrogen N results in a decreased angle.[7h,i] Lithium

**Table 4** Calculated infrared stretching frequencies ($\nu$) and intensities ($I$) for isocyanates RN=C=O (experimental values in parentheses)

| | $\nu$/cm$^{-1}$ | | $I$/km mol$^{-1}$ [a] | |
|---|---|---|---|---|
| R | HF/6-31G* [a] | MP2/6-31G* [b] | HF/6-31G* | MP2/6-31G* |
| H | 2235.2 (2289, 2260)[c] | 2259.1 | 1047.0 | 506.9 |
| Li | 2196.6 | 2214.5 | 1734.7 | 1082.8 |
| BeH | 2262.7 | 2301.0 | 2048.1 | 1304.2 |
| $BH_2$ | 2312.2 (2285)[d] | 2295.8 | 2383.3 | 1223.2 |
| $CH_3$ | 2286.2 (2288)[e,f] | 2292.8 | 1622.4 | 778.4 |
| $NH_2$ | 2199.8 | 2221.6 | 1430.6 | 685.5 |
| OH | 2211.4 | 2192.0 | 1127.2 | 478.8 |
| F | 2197.4 | 2144.2 | 877.9 | 344.2 |
| Na | 2190.3 | 2198.8 | 1537.6 | 946.1 |
| MgH | 2223.1 | 2256.6 | 1889.5 | 1138.2 |
| $AlH_2$ | 2258.5 | 2296.3 | 2058.9 | 1237.0 |
| $SiH_3$ | 2301.5 (2323)[g] | 2341.8 | 1890.1 | 1116.4 |
| $PH_2$ | 2272.4 (2285)[h] | 2288.4 | 2234.4 | 1165.2 |
| SH | 2247.8 | 2261.0 | 1819.3 | 852.0 |
| Cl | 2203.2 | 2196.0 | 1446.1 | 636.3 |
| $CF_3$ | 2263.0 (2309, 2273)[i] | 2278.2 | 1443.0 | 798.6 |
| HC≡C | 2293.7 | 2322.2 | 2254.3 | 1168.3 |
| HC=O (*syn*) | 2240.5 (2246)[j] | 2233.8 | 1682.0 | 939.1 |
| N=O (*anti*) | 2201.3 | 2174.2 | 1501.8 | 949.8 |
| $NO_2$ | 2231.0 | 2178.1 | 1171.0 | 698.2 |
| $CH_2CH$ (*anti*) | 2258.6 (2220)[k] | 2284.8 | 2224.8 | 1100.2 |
| CN | 2275.5 (2270)[l] | 2305.1 | 1716.8 | 1080.9 |

[a] Scaled by 0.9. [b] Scaled by 0.95. [c] Ref. 11(*a*). [d] Ref. 11(*b*). [e] Ref. 11(*c*). [f] Ref. 11(*a*), (*d*), for octadecyl and isopropyl isocyanate, respectively. [g] Ref. 11(*e*). [h] $PF_2$, refs. 11(*f*), (*g*). [i] Refs. 11(*h*), (*i*). [j] Ref. 11(*j*). [k] PhCH=C(CN), ref. 11(*k*). [l] Ref. 11(*l*).

**Table 5** Mulliken and natural bond orbital (NBO) (parentheses) charges for atoms in isocyanates $H_{a,b}MN$=C–O, and dipole moments $\mu$/D

| M | N$^1$ | C$^1$ | O$^1$ | M | $H_{a,b}$ (ave) | $\mu$[k] | $X$[l] | $Z$[l] |
|---|---|---|---|---|---|---|---|---|
| H | −0.69 (−0.89) | 0.81 (1.05) | −0.46 (−0.60) | 0.34 (0.45) | | 2.35[m] | 1.83 | 1.48 |
| Li | −0.79 (−1.20) | 0.70 (0.95) | −0.58 (−0.71) | 0.67 (0.95) | | 9.01 | 0.0 | 9.01 |
| BeH | −0.49 (−1.31) | 0.78 (1.07) | −0.48 (−0.62) | 0.28 (1.43) | −0.10 (−0.57) | 1.51 | 0.0 | 1.51 |
| $BH_2$ | −0.57 (−0.93) | 0.80 (1.09) | −0.47 (−0.61) | 0.40 (0.67) | −0.08 (−0.11) | 1.66 | 0.0 | 1.66 |
| $CH_3$ | −0.61 (−0.68) | 0.79 (1.05) | −0.50 (−0.64) | −0.12 (−0.41) | 0.14 (0.22) | 3.29[n] | 1.60 | 2.88 |
| $NH_2$ | −0.52 (−0.57) | 0.86 (1.07) | −0.46 (−0.59) | −0.49 (−0.69) | 0.30 (0.39) | 2.69 | 0.64 | 2.62 |
| OH | −0.35 (−0.41) | 0.85 (1.03) | −0.43 (−0.56) | −0.46 (−0.58) | 0.38 (0.52) | 1.91 | 0.24 | 1.90 |
| F | −0.18 (−0.27) | 0.84 (1.03) | −0.38 (−0.52) | −0.28 (−0.24) | | 0.93 | −0.02 | −0.93 |
| Na | −0.80 (−1.13) | 0.63 (0.91) | −0.61 (−0.74) | 0.78 (0.96) | | 11.35 | 0.00 | 11.35 |
| MgH | −0.79 (−1.26) | 0.68 (1.01) | −0.52 (−0.66) | 0.75 (1.57) | −0.11 (−0.66) | 2.92 | 0.00 | 2.92 |
| $AlH_2$ | −0.71 (−1.17) | 0.77 (1.07) | −0.49 (−0.63) | 0.80 (1.59) | −0.18 (−0.43) | 2.39 | 0.00 | 2.39 |
| $SiH_3$ | −0.69 (−1.09) | 0.78 (1.09) | −0.49 (−0.63) | 0.40 (1.33) | 0.17 (−0.23) | 2.39 | 0.00 | 2.39 |
| $PH_2$ | −0.72 (−0.99) | 0.79 (1.07) | −0.48 (−0.62) | 0.54 (0.67) | −0.06 (−0.06) | 2.66 | 0.29 | 2.65 |
| SH | −0.70 (−0.85) | 0.81 (1.06) | −0.46 (−0.60) | 0.28 (0.27) | 0.08 (0.13) | 2.40 | 0.57 | 2.33 |
| Cl | −0.64 (−0.71) | 0.85 (1.06) | −0.42 (−0.55) | 0.21 (0.20) | | 0.92 | 0.91 | 0.07 |
| $CF_3$ | −0.69 (−0.78) | 0.84 (1.11) | −0.42 (−0.56) | 1.29 (1.44) | −0.34[a] (−0.41)[a] | 0.37 | 0.01 | −0.37 |
| $CH=CH_2$ | −0.60 (−0.69) | 0.80 (1.07) | −0.48 (−0.62) | 0.12[b] (−0.01)[c] | 0.16 (0.22) | 2.52[o,p] | 1.39 | 2.11 |
| CH=O | −0.67 (−0.80) | 0.88 (1.13) | −0.41 (−0.55) | 0.53[e] (0.67)[f] | 0.15 (0.17) | 1.95[q] | −1.45 | 1.30 |
| C≡CH | −0.68 (−0.68) | 0.79 (1.11) | −0.45 (−0.58) | 0.25[g] (0.17)[h] | 0.26[d] (0.25)[d] | 1.45 | 0.97 | 1.08 |
| CN | −0.61 (−0.72) | 0.86 (1.13) | −0.40 (−0.54) | 0.57 (0.50) | −0.42[i] (−0.38)[i] | 2.65[r] | −1.39 | −2.26 |
| NO | −0.49 (−0.62) | 0.88 (1.09) | −0.40 (−0.54) | 0.26 (0.35) | −0.25[j] (−0.28)[j] | 1.04[s] | 0.21 | −1.02 |
| $NO_2$ | −0.45 (−0.57) | 0.93 (1.12) | −0.35 (−0.49) | 0.75 (0.80) | −0.44 (−0.43)[j] | 2.42 | −1.59 | −1.82 |

[a] F. [b] −0.29 ($C_\beta$). [c] −0.43 ($C_\beta$). [d] H-alkyne. [e] −0.47 (O). [f] −0.63 (O). [g] −0.18 ($C_\beta$). [h] −0.27 ($C_\beta$). [i] N. [j] O. [k] Debye. [l] Dipole vectors, see the text. [m] 2.07: ref. 11(*m*). [n] 2.81: ref. 11(*n*). [o] *anti*. [p] 2.12: ref. 4(*g*). [q] *syn*; *anti* ($X$, 1.74; $Z$, −1.70; net, 2.43). [r] 2.53: ref. 4(*f*). [s] *anti*; *syn* ($X$, −0.44; $Z$, −0.59; net, 0.74).

amides are suggested to exist as ion pairs,[7o] and for lithium isocyanate (**1**) and lithium methyleneamide (**2**) the ionic structures are **1a** and **2a**, respectively. Particularly for $CH_2$=$NBH_2$ substantial dative $\pi$ bonding between the lone pair of electrons on nitrogen and the p orbital on boron was suggested to contribute to the linear geometry.[7i] The charges on Li calculated for lithium isocyanate by the Mulliken and natural bond orbital (NBO) methods are 0.67 and 0.95, respectively (Table 5), and these highly positive values also indicate that the $\sigma$-withdrawal effect represented by structure **1a** is the most important for this molecule. A recent study[3h] of four-membered ring bridged structures of LiNCO and NaNCO agrees with our results that the linear structures are more stable. For NaCH=C=O the bridged structure is more stable.[1d]

$$\underset{\mathbf{1}}{\text{Li–N=C=O}} \longleftrightarrow \underset{\mathbf{1a}}{\text{Li}^{+}\bar{\text{N}}\text{=C=O}}$$

$$\underset{\mathbf{2}}{\text{Li–N=CH}_2} \longleftrightarrow \underset{\mathbf{2a}}{\text{Li}^{+}\bar{\text{N}}\text{=CH}_2}$$

**Table 6** Mulliken and natural bond orbital (NBO) (parentheses) charges for atoms in imines $H_{a,b}MN{=}CH^1H^2$, and dipole moments $\mu$/D

| M | $N^1$ | $C^1$ | $H^1H^2$ (ave) | M | $H_{a,b}$ (ave) | $\mu^l$ | $X^m$ | $Z^m$ |
|---|---|---|---|---|---|---|---|---|
| H | −0.51 (−0.66) | 0.01 (−0.04) | 0.12 (0.17) | 0.26 (0.36) | | 2.24 | 1.56 | 1.62 |
| Li | −0.66 (−1.10) | 0.02 (−0.06) | 0.09 (0.12) | 0.55 (0.92) | | 5.21 | 0.00 | −5.21 |
| BeH | −0.37 (−1.22) | 0.08 (0.07) | 0.11 (0.16) | 0.19 (1.41) | −0.12 (−0.58) | 2.07 | 0.00 | 2.07 |
| $BH_2$ | −0.37 (−0.70) | 0.04 (0.03) | 0.13 (0.18) | 0.27 (0.50) | −0.10 (−0.09) | 2.10 | 0.00 | 2.10 |
| $CH_3$ | −0.42 (−0.47) | −0.01 (−0.06) | 0.12 (0.17) | −0.15 (−0.44) | 0.11 (0.20) | 1.74[n] | 1.39 | 1.05 |
| $NH_2$ | −0.24 (−0.26) | −0.06 (−0.15) | 0.12 (0.18) | −0.50 (−0.71) | 0.28 (0.38) | 2.18 | 1.39 | 0.87[o] |
| OH | −0.12 (−0.14) | −0.03 (−0.13) | 0.14 (0.20) | −0.50 (−0.64) | 0.36 (0.51) | 0.42 | −0.14 | 0.39 |
| F | 0.03 (0.00) | −0.03 (−0.12) | 0.16 (0.22) | −0.33 (−0.31) | | 2.98 | −0.55 | 2.93 |
| Na | −0.71 (−1.04) | 0.01 (−0.10) | 0.01 (0.11) | 0.68 (0.92) | | 7.59 | 0.00 | −7.59 |
| MgH | −0.71 (−1.17) | 0.03 (0.01) | 0.07 (0.14) | 0.67 (1.55) | −0.13 (0.67) | 0.80 | 0.00 | 0.80 |
| $AlH_2$ | −0.59 (−1.03) | 0.07 (0.06) | 0.11 (0.16) | 0.72 (1.50) | −0.20 (−0.43) | 1.48 | 0.00 | 1.48 |
| $SiH_3$ | −0.60 (−0.92) | 0.05 (0.03) | 0.11 (0.16) | 0.87 (1.29) | −0.18 (−0.24) | 1.75 | 0.84 | 1.56 |
| $PH_2$ | −0.56 (−0.79) | 0.01 (−0.02) | 0.12 (0.18) | 0.48 (0.62) | −0.08 (−0.08) | 2.10 | 0.87 | 1.75[p] |
| SH | −0.50 (−0.62) | −0.01 (−0.06) | 0.14 (0.18) | 0.17 (0.18) | 0.07 (0.12) | 0.98 | 0.15 | 0.96 |
| Cl | −0.42 (−0.44) | 0.02 (−0.04) | 0.16 (0.20) | 0.08 (0.07) | | 2.86[q] | −0.15 | 2.86 |
| $CF_3$ | −0.52 (−0.59) | 0.02 (0.03) | 0.16 (0.20) | 1.24 (1.41) | −0.35[a] (−0.42)[a] | 3.15 | −0.52 | 3.11 |
| $CH{=}CH_2$ | −0.43 (−0.49) | −0.01 (−0.04) | 0.12 (0.18) | 0.09[b] (−0.04)[c] | 0.13[d] (0.21)[d] | 1.72[r] | 1.20 | 1.23 |
| CH=O | −0.52 (−0.63) | 0.05 (0.07) | 0.16 (0.20) | 0.50[e] (0.65)[f] | 0.13 (0.15) | 1.81[s] | −1.45 | 1.07 |
| C≡CH | −0.53 (−0.51) | 0.01 (0.03) | 0.14 (0.19) | 0.24[g] (0.15)[h] | 0.25 (0.25)[i] | 2.23 | 0.77 | 2.09 |
| CN | −0.47 (−0.55) | 0.04 (0.07) | 0.16 (0.20) | 0.53 (0.47) | −0.44[j] (−0.39)[j] | 4.84 | −2.18 | 4.32 |
| NO | −0.29 (−0.40) | 0.02 (0.01) | 0.16 (0.20) | 0.21 (0.28) | −0.28[k] (−0.29)[k] | 3.63[t] | −0.56 | 3.59 |
| $NO_2$ | −0.28 (−0.38) | 0.04 (0.04) | 0.20 (0.22) | 0.72 (0.77) | −0.44[k] (−0.44)[k] | 4.56 | −2.06 | 4.07 |

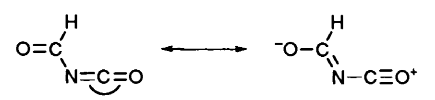
[a] F. [b] −0.29 ($C_\beta$). [c] −0.41 ($C_\beta$). [d] $H_{\alpha,\beta}$. [e] −0.49 (O). [f] −0.63 (O). [g] −0.25 ($C_\beta$). [h] −0.29 ($C_\beta$). [i] $H_\beta$. [j] N. [k] O. [l] Debye. [m] Dipole vectors, see the text. [n] 1.53: ref. 6(*d*). [o] *Y*: −1.52. [p] *Y*: −0.78. [q] 2.36: ref. 6(*c*). [r] 1.95: ref. 6(*c*). [s] *syn*; *anti* (*X*, 0.42; *Z*, 4.74; net, 4.76). [t] *anti*; *syn* (*X*, −0.82; *Z*, 2.89; net, 3.00).

Comparison of the atomic charges for isocyanates relative to imines shows that without exception for either Mulliken or NBO charges that the nitrogen of the isocyanate has more negative charge than that of the imine. This effect is contrary to what would be expected based on the greater inductive electron-withdrawing effect of the C=O in the isocyanato group compared with the $CH_2$ of the imine, but is consistent with the π-donor effect from the isocyanato C=O group as shown (**1b**, **c**), comparable to that for the carbonyl or diazo groups noted in ketenes and diazomethanes, respectively,[1a,d,e] and this would be enhanced by the electronegative nitrogen. The importance of π-donation from the carbonyl group to nitrogen in isocyanates has been noted,[4k] as particularly seen in their $^{14}N$ and $^{15}N$ NMR chemical shifts, which occur at remarkably high fields, overlapping the amine region.[4n–p]

$$\mathrm{RN{=}C{=}O} \longleftrightarrow \underset{\mathbf{1b}}{\mathrm{R\bar{N}{-}C{\equiv}O^+}} \longleftrightarrow \underset{\mathbf{1c}}{\mathrm{R\bar{N}{-}\overset{+}{C}{=}O}}$$

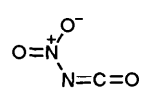
Isocyanates with the potential π-acceptor substituents $CH{=}CH_2$, CH=O, and NO, all adopt coplanar conformations in which such conjugation is possible, as illustrated for the case of formyl isocyanate (**3**). This interaction was originally proposed to account for the dipole moment of vinylketene, and has been used to explain several properties of ketenes and diazomethanes.[1a,d,e] For the CH=O, CN, NO, and $NO_2$ substituted isocyanates evidence for conjugation as in **3** is provided by the observation that the MP2/6-31G* isocyanato C–O bonds for these derivatives of 1.172–1.179 Å are the shortest (along with $CF_3N{=}C{=}O$ and FN=C=O) observed for the isocyanates. Studies of aryl isocyanates using IR and $^{19}F$ NMR spectroscopy also support the occurrence of π donation by the isocyanato group to suitable acceptors.[4l] Resonance stabilization of the imine $O_2NH{=}CH_2$ has been cited as the cause for the ready formation of this molecule in the mass spectral fragmentation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX).[6e] The imines $BH_2N{=}CH_2$ and $AlH_2N{=}CH_2$ adopt allene-like geometries with the hydrogens in perpendicular planes, permitting conjugation of the type $H_2\bar{M}{=}\overset{+}{N}{=}CH_2$, as previously noted for the $BH_2$ derivatives.[7h]

For the non-linear isocyanates the MP2/6-31G* bond angle indicated in **3a** is always less than 180° (168.3–174.2°) so the isocyanato oxygen bends away from the substituent, and there is a large variation in the M–N=C angle from low values of 110.8° for fluorine isocyanate and 115.6° for nitryl isocyanate



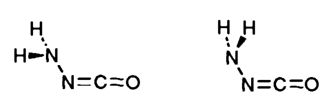
**3a** **3b**

$O_2NN{=}C{=}O$ to 142.6° for ethynyl isocyanate HC≡CN=C=O. This is the behaviour predicted if the fluorine and the oxygens of the nitro group are repelled by the lone pair on the isocyanato nitrogen and attracted to the carbonyl carbon in **4**. For the imines there are particularly small MNC angles of 108.1° for fluorine and 111.8° for nitroso. The approach to linearity of ethynyl isocyanate may represent a contributing π-acceptor effect for the alkynyl group.



**4**

π-Donor substituents $NH_2$ and $PH_2$, all favour twisted conformations in isocyanates in which π-donor effects are minimized. Thus **5a** is 10.1 kcal $mol^{-1}$ more stable than the conformation with a coplanar $NH_2$ group (MP2/6-31G*, Table 1). The conformation **5b** is 4.3 kcal $mol^{-1}$ less stable than **5a** at the MP2/6-31G*//MP2/6-31G* level and the mutual repulsion of the lone pairs in **5b** evidently contributes to this preference. This same preference for twisted $NH_2$ groups has been observed for ketenes and diazomethanes,[1a,d,e] and was explained as resulting from a repulsive interaction between the lone-pair on the substituent and the electron rich π system on the bonded



**5a** **5b**

Table 7 Comparison of experimental and calculated HF/6-31G* (parentheses) and MP2/6-31G* [brackets] bond distances (Å) and bond angles (°) of isocyanates $H_nMN^1{=}C^1{=}O^1$ and imines $H_nMN^1{=}C^1H^2$

| M | $MN^1$ | $N^1C^1$ | $C^1O^1$ | $MN^1C^1$ | $N^1C^1O^1$ | Ref. |
|---|---|---|---|---|---|---|
| Isocyanates | | | | | | |
| H | 0.995 (0.994) [1.008] | 1.214 (1.200) [1.224] | 1.166 (1.148) [1.184] | 123.9 (125.2) [125.9] | 172.6 (174.2) [171.7] | 4(*a*) |
| $CH_3$ | 1.451 (1.437) [1.442] [1.445][a] | 1.214 (1.180) [1.214] [1.213][a] | 1.166 (1.158) [1.191] [1.180][a] | 135.6 (143.1) [138.0] [135.6][a] | 172.6 (175.1) [172.3] [172.7][a] | 4(*b*) |
| $SiH_3$ | 1.699 (1.715) | 1.150 (1.178) | 1.179 (1.154) | — (180.0) | — (180.0) | 4(*c*) |
| $SiH_3$ | 1.703 [1.721] | 1.216 [1.205] | 1.164 [1.188] | 180.0 [180.0] | 180.0 [180.0] | 4(*d*) |
| $SiMe_3$ | 1.609 | 1.150 | 1.179 | 180.0 | 180.0 | 4(*e*) |
| Cl | 1.705 (1.694) [1.709] | 1.226 (1.217) [1.241] | 1.162 (1.141) [1.181] | 118.8 (120.2) [121.9] | 170.9 (173.8) [169.7] | 4(*a*) |
| CN | 1.283 (1.325) [1.330] | 1.218 (1.206) [1.227] | 1.141 (1.136) [1.176] | 140.0 (133.7) [135.8] | — (173.7) [171.6] | 4(*f*) |
| $CH{=}CH_2$ | 1.382 (1.397) [1.397] | 1.207 (1.188) [1.218] | 1.171 (1.153) [1.188] | 138.4 (139.3) [138.0] | — (174.8) [172.4] | 4(*g*) |
| *c*-Pr | 1.382 (1.421) | 1.210 (1.215) | 1.170 (1.190) | 136.9 (137.4) | 172.6 (172.7) | 3(*e*), 4(*h*) |
| $CH_3CO$ | 1.413 (1.411) | 1.199 (1.211) | 1.159 (1.139) | 128.2 (126.5) | 173.0 (174.3) | 3(*a*) |
| ClCO | 1.391 (1.382) | 1.227 (1.218) | 1.137 (1.133) | 119.2 (124.6) | 173.1 (173.9) | 3(*b*) |

| M | $MN^1$ | $N^1C^1$ | CH | $MN^1C^1$ | $N^1C^1H^1$ | $N^1C^1H^2$ | Ref. |
|---|---|---|---|---|---|---|---|
| Imines | | | | | | | |
| H | 1.021 (1.006) [1.026] | 1.273 (1.250) [1.281] | 1.09 (1.082) [1.094] | 110.5 (111.5) [109.7] | 123.3 (124.7) [125.5] | 119.7 (119.3) [118.4] | 6(*a*) |
| $CH_3$ | 1.440 (1.444) [1.456] | 1.30 (1.247) [1.277] | 1.08 (1.082) [1.098] | 116.9 (118.6) [116.3] | — (123.7) [123.9] | — (119.6) [119.0] | 6(*b*) |
| HO | 1.408 (1.369) [1.409] | 1.276 (1.249) [1.283] | 1.086 (1.084) [1.088] | 110.2 (112.0) [110.0] | 121.8 (122.6) [122.8] | 115.6 (117.3) [116.4] | 6(*h*) |

[a] MP2/6-311++G**.

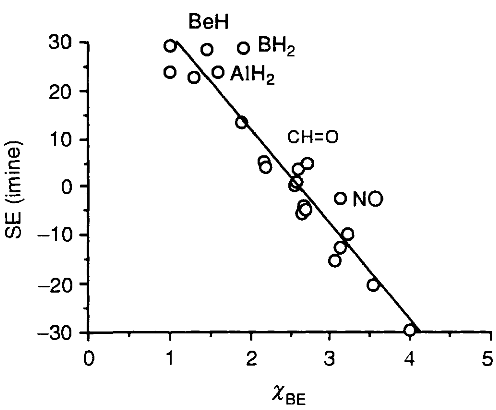



**Fig. 1** Correlation of imine isodesmic MP2/6-31G* stabilization energies [eqn. (1)] with substituent electronegativity $\chi_{BE}$

atom of the cumulene, which is nitrogen for isocyanates. For $CH_2{=}NNH_2$ the planar structure is 3.1 kcal $mol^{-1}$ less stable than the structure where pyramidalisation of the $NH_2$ group occurs (Table 3).

The repulsive π–π interaction for coplanar $H_2NCH{=}C{=}O$ has been confirmed by Cossio *et al.*[9d] These authors also suggested there is a stabilizing interaction between the lone pair of the nitrogen and the LUMO of the ketene in the ketene conformation corresponding to **5a**, but the ketene with the conformation corresponding to **5b** is only 1.5 kcal $mol^{-1}$ less stable.[1d] Thus any stabilization due to the lone pair–LUMO interaction in **5a** and in the corresponding ketene is evidently relatively small, and is not the major cause that these substituents adopt non-planar conformations.

*Energetics.*—The isodesmic reaction for the comparative substituent effect on imines and ethenes [eqn. (1)] is correlated with electronegativity by eqns. (4) and (5) for the HF and MP2 level calculations, respectively, and the latter correlation is shown in Fig. 1. These rather good correlations, with no essential difference between the HF and MP2 calculations, show a very strong preference of electropositive substituents for imines, and for electronegative substituents on alkenes, with a net difference in the MP2 SE between Li and F of 59.1 kcal $mol^{-1}$. In addition there is some evidence that π-acceptor substituents may favour imines in that the groups BeH, $BH_2$, $AlH_2$, CH=O, and NO deviate above the correlation of eqn. (4) by 6.2, 15.9, 4.1, 3.8 and 5.8 kcal $mol^{-1}$, respectively. These substituents have been identified on Fig. 1. This same effect for π-acceptor substituents has been noted for ketenes[1a,d] and diazomethanes.[1b,d] Exceptional behaviour is noted for $CF_3$, which favours the imine despite its electron-withdrawing (σ acceptor) character, and CN, which is a good π-acceptor but favours the alkene. As noted above the high stability of

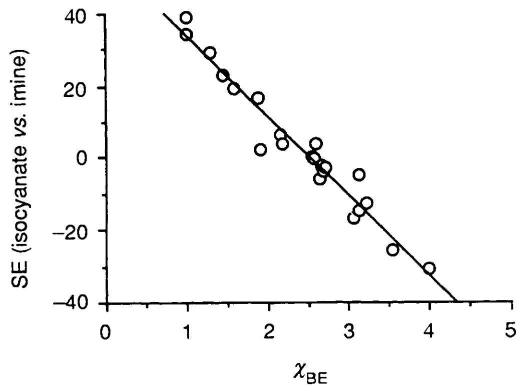



**Fig. 2** Correlation of isocyanate MP2/6-31G* isodesmic stabilization energies relative to imines [eqn. (2)] with substituent electronegativity $\chi_{BE}$

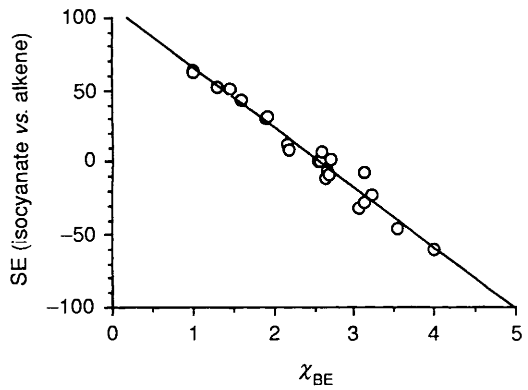



**Fig. 3** Correlation of isocyanate isodesmic MP2/6-31G* stabilization energies relative to alkenes [eqn. (3)] with substituent electronegativity $\chi_{BE}$

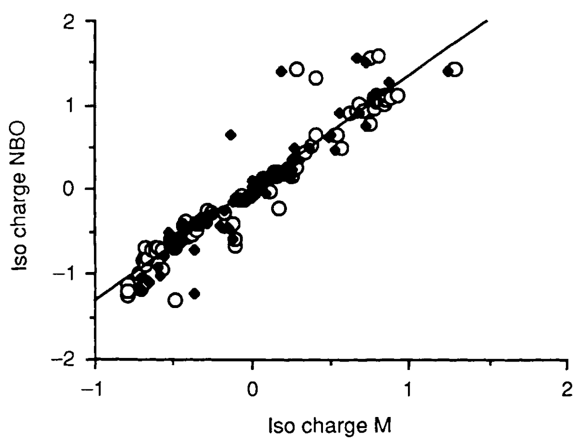



**Fig. 4** Comparison of natural bond orbital (NBO) atomic charges with Mulliken atomic charges for isocyanates (○) and imines (■)

$BH_2N{=}CH_2$ has been attributed to a linear allene-like structure $H_2\bar{B}{=}\overset{+}{N}{=}CH_2$.[7h]

$$SE(1) = -20.5\,\chi_{BE} + 52.6 \quad r = 0.954\,(HF) \qquad (4)$$

$$SE(1) = -19.9\,\chi_{BE} + 51.5 \quad r = 0.947\,(MP2) \qquad (5)$$

For comparison of the effect of substituents on the stability of isocyanates, the isodesmic stabilization energies (SE) were calculated relative to both imines [eqn. (2)] and alkenes [eqn. (3)]. These SE values both gave excellent correlations *versus* the group electronegativities $\chi_{BE}$, for the imines [eqns. (6), (7)], and for the alkenes [eqns. (8), (9)], also with no essential difference between the correlations using the HF/6-31G* and the MP2/6-31G* energies. These are illustrated in Figs. 2 and 3 using the MP2/6-31G* energies for the imines and alkenes, respectively.

$$SE(2) = -23.6\,\chi_{BE} + 60.0 \quad r = 0.986\,(HF) \qquad (6)$$

$$SE(2) = -22.1\,\chi_{BE} + 55.8 \quad r = 0.975\,(MP2) \qquad (7)$$

$$SE(3) = -44.1\,\chi_{BE} + 112.5 \quad r = 0.996\,(HF) \qquad (8)$$

$$SE(3) = -41.9\,\chi_{BE} + 107.4 \quad r = 0.983\,(MP2) \qquad (9)$$

There is a remarkably large variation in the SE values as a function of substituent, with a range of 69.6 kcal $mol^{-1}$ relative to imines and 123.8 kcal $mol^{-1}$ relative to alkenes, and these ranges are much larger than for any other system studied.[1a,b,d] The isocyanates do not show substantial positive deviations from the correlations as was found for ketenes and diazomethanes for π-acceptor substituents.

There are no special energetic effects apparent for π-donor substituents, in particular $NH_2$ and $PH_2$, although these substituents adopt twisted geometries that preclude any π–π interactions of the substituent lone pairs and the cumulene π-systems, just as found for ketenes and diazomethanes.[1a,d,e] As noted above this geometrical feature is not primarily due to any attractive interactions between the lone pairs on the substituent and the electron deficient in-plane p orbital of the cumulene carbon, as the energetic difference between the *syn* and *anti* conformations **5a** and **5b** is significantly less than the difference in energy of the conformation with the planar substituent.

The high sensitivity of the isocyanate system to the electronegativity of the substituents may be related to the high coefficient of the highest occupied molecular orbital (HOMO) on the substituted nitrogen. For the various cumulene systems which have been studied, namely allenes,[1d] diazomethanes,[1e] ketenes[1a] and isocyanates, there is a linear correlation [eqn. (10)] between the respective HOMO coefficients of 0.395, 0.434, 0.436 and 0.474 of the substituent bonded atom of the cumulene, and the range of the calculated SE values relative to alkenes, for which the variation between the extreme substituents Na and F (ΔSE) is 16.3, 30.9, 45.8 and 130.6 kcal $mol^{-1}$, respectively, at the HF/6-31G* level.

$$E(\mathrm{HOMO}) = (5.68 \times 10^{-4})\,\Delta SE + 0.403 \quad r = 0.91 \qquad (10)$$

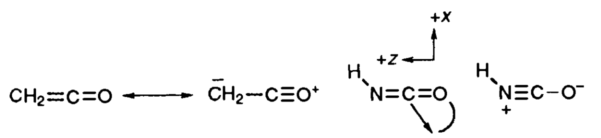
*Atomic Charges.*—Because of the major interest in the comparison of atomic charges calculated by different methods, including the Mulliken method[9a] and the natural bond orbital method of Weinhold,[9b] the charges for the isocyanates and imines have been calculated by these methods (Tables 5 and 6, respectively). These give reasonably good correlations by eqns. (11) and (12), which are comparable to those reported previously for ketenes, alkenes, diazomethanes, diazirines, allenes and cyclopropenes.[1d] Just as for these latter compounds the major deviations from the correlations occur for Be, Mg and Al, although the reason for the distinctive behaviour of these particular substituents has not yet been determined. An overlay plot of the NBO *vs.* Mulliken charges for isocyanates and imines is shown in Fig. 4.

$$\text{charge (NBO)}_{iso} = 1.34\,(\text{charge Mulliken}) + 7.50 \times 10^{-5}, \quad r = 0.97 \qquad (11)$$

$$\text{charge (NBO)}_{imine} = 1.41\,(\text{charge Mulliken}) + 7.06 \times 10^{-3}, \quad r = 0.93 \qquad (12)$$

Correlations of group electronegativities of M in MN=C=O and $MN=CH_2$ with the Mulliken charges of the N atom give correlation coefficients of 0.75 and 0.82, respectively, whereas the NBO charges give corresponding correlation coefficients of 0.96 for both systems. Thus while the Mulliken and NBO charges follow similar patterns, the latter seem better correlated with other important molecular properties. Similar trends and conclusions resulted from consideration of the calculated atomic charges in other cumulenes.[1a,b,d] An independent comparison of Mulliken and NBO charges in acylketenes also led to the conclusion that these give closely parallel trends.[9e]

*Dipole Moments.*—The calculated net dipole moments of the isocyanates are given in Table 5, along with the positive components of the dipole in the molecular plane defined as shown on structure **7**. The dipole moment of the parent isocyanate HN=C=O of 2.35 D (experimental 2.07 D[11m]) is more than those of diazomethane (1.53 D) and ketene (1.63 D).[1d] The latter two are directed along the molecular axis toward the electronegative nitrogens or oxygen, respectively, but are somewhat reduced by electron donation back to the $CH_2$ group, as shown in **6a**. The dipole moment[11m] of HN=C=O has been assigned to an orientation of 49.5° from the principal inertial axis of the molecule, as shown in **7**, and is affected by the lone pair on nitrogen, and the contributing structures **1c** and **7a**, although the latter is reported to be unimportant.[4k]



**6** **6a** **7** **7a**

*Infrared Frequencies.*—In Table 4 are listed both the HF and MP2 calculated IR frequencies (scaled by 0.9 and 0.95, respectively) and intensities for the isocyanate asymmetric stretch as a function of substituent. The MP2 frequencies have a maximum value of 2305 $cm^{-1}$ for N≡CN=C=O and a minimum value of 2144 $cm^{-1}$ for FN=C=O, and where experimental values are available[10,11] these agree with the calculated values with average deviations of $\pm 15$ $cm^{-1}$. The measured values have been found to vary depending on the physical state; thus for $CH_3N=C=O$ the reported frequencies are (2285, 2265),[3g] (2240, 2228),[3g] and 2288,[11c] for gas, solid and liquid phase measurements, respectively, and so close agreement is not expected.

We have recently carried out a fairly detailed analysis of the calculated IR frequencies and intensities for the C=C=O asymmetric stretch of ketenes,[1f] and find that for ketenes the calculated frequencies are also in reasonable agreement with experimentally determined values. It had been proposed[10c] that for ketenes there is a correlation of frequencies with the substituent field and resonance parameters $F$ and $R$, but we found the relationship: $\nu/\mathrm{cm}^{-1} = 2119 + 91\ (\pm 13)F - 6\,(\pm 9)\,R, r = 0.87$. Thus the correlation with the reasonance parameter $R$ is not significant. For the isocyanates the corresponding correlation at the HF/6-31G* level is $\nu/\mathrm{cm}^{-1} = 2281\ (\pm 23) - 106\ (\pm 39)\ F + 65\ (\pm 25)\ R, r = 0.68$. This is a very weak correlation, and while the isocyanates do show some dependence on the parameter $R$, the dependence on the field parameters $F$ is of the opposite sign to that for ketenes. The ketene frequencies span a range from 2186 $cm^{-1}$ for $O_2NCH=C=O$ to 2010 $cm^{-1}$ for NaCH=C=O, and a plot of isocyanate *vs.* ketene frequencies reveals no useful correlation, and there is only a very modest correlation of isocyanate and ketene intensities ($I_{isoc} = 1.12\ I_{ket} + 368, r = 0.70$). Allene and diazomethane cumulene group frequencies and intensities have also been studied, and show only poor correlations with the corresponding values for ketenes,[1d] and the same holds true for comparisons of the former groups to isocyanates. Thus the calculations indicate that the effect of substituents on the asymmetric stretching vibrations of different cumulenes show major differences, and that each group must be considered separately. As pointed out by a referee the polarities of isocyanates, with two strongly electronegative atoms, are intrinsically different from those of the other cumulenes. Thus the different behaviour of isocyanates is not unexpected.

Experimental studies of the substituent effect on the integrated intensities of the asymmetric stretch of isocyanates have been reported,[12] and it was proposed[12a] that correlations for $4\text{-}RC_6H_4NC=C=O$ gave a positive dependence on $\sigma_p^+$, so that the intensities increased for electron-withdrawing substituents. No evidence for this trend is found in the current study.

In summary *ab initio* calculations at the MP2/6-31G*//MP2/6-31G* and the HF/6-31G*//HF/6-31G* levels are quite useful in the understanding of the properties of substituted imines and isocyanates, and give structures which are in good agreement with available experimental values. The isodesmic stabilization energies of substituted imines compared with alkenes are correlated with substituent group electronegativity values. The corresponding isodesmic substituent effects on isocyanates give excellent correlations when compared with either imines or alkenes, and cover very large spans in isodesmic stabilization energies, particularly for the comparison with alkenes. These variations are much larger than those found for ketenes, diazomethanes, and allenes, and are attributed to the greater polar character of the isocyanates. The slopes of the SE *vs.* $\chi_{BE}$ plots are correlated with the HOMO coefficients of the atom of attachment of the cumulene to the substituent. Mulliken and natural bond orbital atomic charges for isocyanates and imines follow the same trends, but the latter are better correlated with other molecular properties, as found previously for other cumulenes and related species.

## Acknowledgements

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