# A Remarkably Stable Linear Ketenimine

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Substituted isoxazol-5(4*H*)-ones (**1**) have been thoroughly investigated in our laboratory as potential precursors of highly reactive cumulenes.[1] Under flash vacuum pyrolysis (FVP) conditions, isoxazolones **1** (X = $CH_3S$ or $(CH_3)_2N$) eliminate $CH_3SH$ or $(CH_3)_2NH$ at relatively low temperatures (ca. 300 °C), leading to the formation of ketenimine intermediates **2** (Scheme 1). At higher temperatures, $CO_2$ is expelled to form keteniminoazirine **4** or cyanoketenimine **5** via a diradical or nitrene **3** (Scheme 1). A 1,2-aryl shift gives bisketenimine **6** as the final product. In special cases, **2**, **4**, **5**, and **6** can be observed under cryogenic conditions or in the mass spectrometer, but they are not normally isolable.[2]

In order to stabilize **2**, we have synthesized precursors with sterically demanding substituents and report here the behavior of the 2,4,6-tri-*tert*-butylphenyl derivative **7** (the synthesis is described in the supplementary material). Upon heating to the melting point (180 °C), **7** underwent elimination of methanethiol with formation of a new compound (mp 220 °C), which could be purified by sublimation under $N_2$ but in the presence of moisture hydrolyzed quantitatively under the sublimation conditions (200 °C) to 2,4,6-tri-*tert*-butylaniline (**9**) and isoxazolone **10** (Scheme 2). The reaction of the thermolysis product of **7** with ethanol led to the formation of **11** (Scheme 2), which corresponds to trapping of ketenimine **8**. However, the IR and NMR data for the thermolysis product of **7** are most unusual for a ketenimine. A very strong CN stretching vibration is detected at 2226 and 2223 $cm^{-1}$ in Ar matrix, 2229 $cm^{-1}$ in $CCl_4$, and 2231 $cm^{-1}$ in the solid state. Ketenimines typically have IR absorptions at 2000−2050 $cm^{-1}$.[3] In the $^{13}C$ NMR spectrum of the thermolysis product, signals at $\delta = 52.2$ and 119.1 can be assigned to the quaternary carbon ($C_4$) and the exocyclic C=N carbon, respectively. The $^{13}C$ NMR signals of ketenimines are normally found at ~50 and >190 ppm for the $\beta$- and $\alpha$-C, respectively.[4] The data would be more reasonable if a nitrile (e.g., **12**) rather than the ketenimine **8** had been formed.

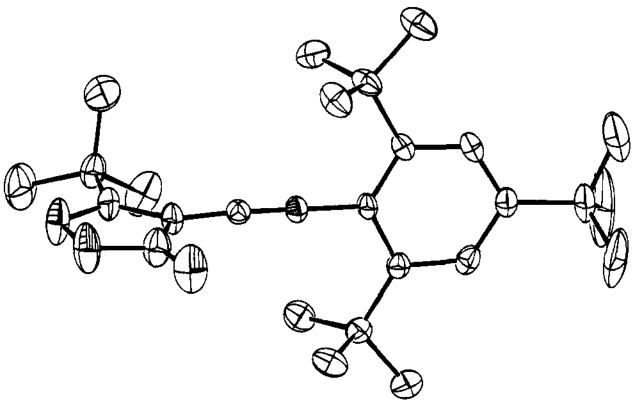
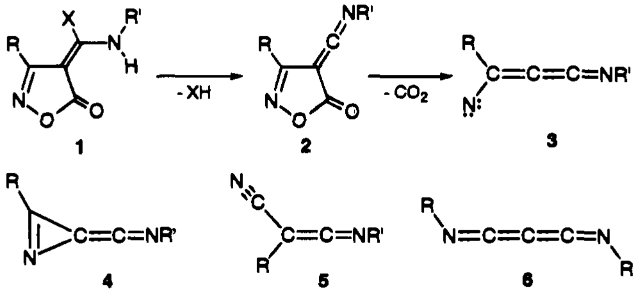
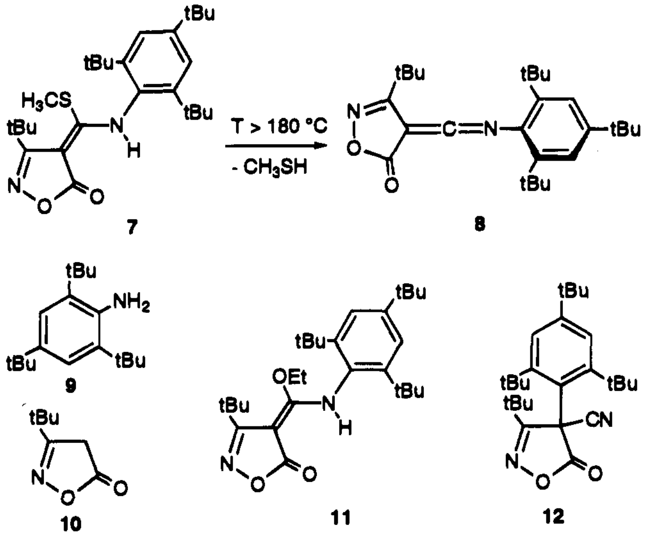


**Figure 1.** ORTEP drawing of the X-ray structure of ketenimine **8** (30% probability).

**Scheme 1**



**Scheme 2**



To elucidate the structure of the thermolysis product of **7**, we prepared crystals suitable for X-ray structure determination by slow sublimation ($10^{-5}$ mbar, 200 °C).[5,6] The compound turned out to be the ketenimine **8** in accordance with the collected chemical evidence. As is to be expected from the IR and NMR results for **8**, the structural data reveals highly unusual properties. Ketenimines ($R_1R_2C{=}C{=}NR_3$) normally possess CNC angles close to 120°, and the average C=N double bond length is 1.27 Å.[7] The isomerization barrier around the C=N double bond lies between 30 and 80 kJ $mol^{-1}$ so that in certain cases two distinct bent isomers can be detected.[7c,8] In sharp contrast to the "normal" ketenimines, the CNC angle in **8** is 179.6(4)° and the C=N distance is very short (1.151(5) Å). Of

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(5) The X-ray crystal structure was determined on an Enraf-Nonius CAD4 four-circle diffractometer[5b] with molybdenum X-radiation (graphite monochromator). The structure was solved with the use of direct methods (TREF 2000) in SHELXS 86.[5c] Full-matrix least-squares refinement[5d] was on $F^2$s; C, H, O scattering factors[5e] were used; hydrogen positions were calculated. The *tert*-butyl group at C411 (phenyl-*para*) was rotationally disordered over two sites, approximately 60° apart, with occupancies 0.66 and 0.33. The full data is given in the supplementary material (Tables 2−7). (b) Frenz, B. A. *Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1985. (c) Direct methods: Sheldrick, G. M. *SHELXS 86. Program for Solution of Crystal Structures*; University of Göttingen: 1986. (d) Refinement: Sheldrick, G. M. *SHELXL-93. Program for Refinement of Crystal Structures*, University of Göttingen: 1993. (e) Scattering factors: *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, 1974; Vol. 4.

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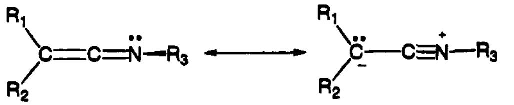
**Table 1.** Calculated Structural Parameters,[a,b] CCN Stretching Frequencies[a,c] (cm$^{-1}$), Dipole Moments[a] ($\mu$, D), and Inversion Barriers[d] (kJ mol$^{-1}$) for Substituted Ketenimines ($R_1R_2C{=}C{=}NR_3$)

| species | $R_1$ | $R_2$ | $R_3$ | *r*(C=C) | *r*(C=N) | ∠CCN | ∠CNR$_3$ | CCN freq | $\mu$ | barrier |
|---|---|---|---|---|---|---|---|---|---|---|
| **15** | H | H | H | 1.301 | 1.213 | 176.5 | 115.1 | 2029 | 1.84 | 53.5 |
| **16** | H | H | $CH_3$ | 1.304 | 1.206 | 177.8 | 122.2 | 2047 | 1.66 | 43.2 |
| **17** | CHO | H | H | 1.314 | 1.202 | 176.1 | 117.8 | 2018 | 3.89 | 35.3 |
| **18** | CN | H | H | 1.314 | 1.199 | 175.9 | 118.4 | 2038 | 4.69 | 37.2 |
| **19** | CN | CN | H | 1.329 | 1.186 | 175.5 | 122.8 | 2046 | 5.65 | 24.8 |
| **20** | CN | CN | $CH_3$ | 1.334 | 1.171 | 176.4 | 136.4 | 2095 | 7.56 | 14.8 |
| **21** | *e* | *e* | $C_6H_5$ | 1.328 | 1.177 | 176.2 | 137.8 | 2072 | 8.75 | 10.8 |
| **22** | *e* | *e* | DTTP[f] | 1.351 | 1.147 | 179.1 | 178.4 | 2249[g] | 10.53 | |

[a] HF/6-31G* values. [b] Bond lengths in Å and angles in deg. [c] Scaled by a factor of 0.8929 (ref 13). [d] MP2/6-311+G**//HF/6-31G* values. [e] $R_1$ and $R_2$ = isoxazol-5(4*H*)-one substituent. [f] 2,5-Di-*tert*-butylphenyl (DTTP) group. [g] HF/3-21G value.

all the ketenimines reported in the literature, there is only one type, the bis-sulfonyl substituted ketenimines $RO_2SC(SO_2R'){=}C{=}NR''$ (**13**), possessing spectral and crystallographical data similar to those of **8**.[9] In order to compare with **8**, we prepared **13a** (R = R′ = R″ = $CH_3$) and recorded its IR and $^{13}$C NMR spectra. The IR spectrum shows absorptions at 2135 cm$^{-1}$ in Ar matrix, 2170 cm$^{-1}$ in $CHCl_3$, and 2280 cm$^{-1}$ in the solid state. It has $^{13}$C NMR signals at $\delta$ 79 and 134 ppm. The CNC angle is 180°.[9a] **13b** (R = R′ = $CH_3$; R″ = $C_2H_5$) and **13c** (R = R″ = $CH_3$; R′ = $C_6H_5$) reportedly deviate significantly from linearity (CNC angles 144° and 172° for **13b** and **13c**, respectively).[9b,c] Some of the spectroscopic data indicate that **8** and **13** are indeed very similar compounds. On the other hand, the large shifts of the ketenimine IR absorption in **13a** on going from the isolated state to condensed phases do not correspond to our observations in the case of **8**. The spectroscopic and structural data for compounds **8** and **13** differ drastically from those of other "normal" ketenimines.[3,4,7]

To shed light on the unusual spectroscopic and structural properties of **8**, we have carried out *ab initio* calculations[10,11] on several C- and N-substituted ketenimines. As one might have expected from the resonance structures (**14a,b**) of ketenimine, the linear CNC structure (**14b**) is stabilized both by electron-withdrawing C-substituents (e.g., CN and CHO) and by electron-donating N-substituents (e.g., $CH_3$). Geometry optimization (HF/6-31G*)[10] of substituted ketenimines confirms the substituent effect (Table 1). In particular, successive C- and N-substitutions (**15** → **18** → **19** → **20**) lead to progressively shorter C=N bond lengths, larger CNC angles, and higher dipole moments. The shortening of the C=N bond length is associated with an increasing value for the CCN stretching frequency (Table 1). It is important to note that the linear CNC zwitterionic structure (**14b**) corresponds to the transition structure for the inversion of two possible bent conformers of ketenimine. Hence, C- and N-substituents which favor structure **14b** would result in a smaller isomerization barrier. This is readily demonstrated by the calculated rotational barriers (MP2/6-311+G**+ZPVE)[10,12] of compounds **15**−**21**. Model calculations for ketenimine **8** (**21**) predict a short C=N bond length of 1.177 Å. However, the CNC moiety is still far from linearity (136°) and the CCN stretching frequency is slightly higher than the norm[3] for ketenimines. Experimentally, we find values of 2091 and 2071 cm$^{-1}$ for ketenimine **21** (**2**; R = tBu, R′ = Ph) in Ar matrix. **21** is estimated to have a small isomerization barrier (11 kJ mol$^{-1}$). 2,6-Di-*tert*-butyl substitution of the phenyl group in **21** (i.e., **22**) leads to a remarkable change in the optimized geometry. **22** is predicted to have a *linear* CNC moiety, an even shorter C=N bond length of 1.147 Å, and a significantly higher CCN stretching frequency of 2249 cm$^{-1}$, in excellent accord with the experimental findings for **8**. In contrast to compounds **15**−**21**, which have planar isomerization transition structures, the isoxazolone group in the equilibrium structure **22** is perpendicular to the phenyl ring. This suggests that there is significant steric interaction caused by the *tert*-butyl groups. Hence, we may conclude that the combination of electronegative substituents on carbon and in particular steric hindrance by the *tert*-butyl groups in ketenimine **8** is sufficient to induce a single minimum potential with a linear CNC structure.



**14a** **14b**

In summary, an extremely unusual ketenimine **8**, where the linear structure is stabilized by electronic as well as steric effects, has been synthesized. *Ab initio* calculations provide rationalization for the unusual spectroscopic and crystallographical properties.

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**Supplementary Material Available:** Preparation and spectroscopic data for compounds **7**, **8**, **11**, and 4-[bis(methylthio)methylene]-3-*tert*-butylisoxazol-5(4*H*)-one and tables of X-ray crystallographic data for compound **8** (9 pages); observed and calculated structure factors for **8** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(6) Selected bond lengths (Å) and bond angles (deg) in ketenimine **8**: r(C=N) = 1.151(5), *r*(N−C(Ar)) = 1.412(4), *r*(C=CN) = 1.352(5), ∠CCN = 173.1(4), and ∠CNC = 179.6(4). The angle between the two ring planes is 86.5(4)°.

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