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# Linear Ketenimines. Variable Structures of *C,C*-Dicyanoketenimines and *C,C*-Bis-sulfonylketenimines

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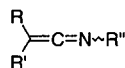
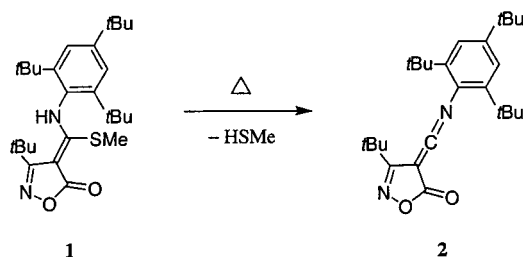
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Received April 17, 2001

*C,C*-Dicyanoketenimines **10a–c** were generated by flash vacuum thermolysis of ketene *N,S*-acetals **9a–c** or by thermal or photochemical decomposition of  $\alpha$ -azido- $\beta$ -cyanocinnamionitrile **11**. In the latter reaction, 3,3-dicyano-2-phenyl-1-azirine **12** is also formed. IR spectroscopy of the ketenimines isolated in Ar matrixes or as neat films, NMR spectroscopy of **10c**, and theoretical calculations (B3LYP/6-31G\*) demonstrate that these ketenimines have variable geometry, being essentially linear along the CCN–R framework in polar media (neat films and solution), but in the gas phase or Ar matrix they are bent, as is usual for ketenimines. Experiments and calculations agree that a single CN substituent as in **13** is not enough to enforce linearity, and sulfonyl groups are less effective than cyano groups in causing linearity. *C,C*-Bis(methylsulfonyl)ketenimines **4–5** and a *C*-cyano-*C*-(methylsulfonyl)ketenimine **15** are not linear. The compound  $p$ -O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=C=C(COOMe)<sub>2</sub> previously reported in the literature is probably somewhat linearized along the CCNR moiety. A computational survey (B3LYP/6-31G\*) of the inversion barrier at nitrogen indicates that electronegative *C*-substituents dramatically lower the barrier; this is also true of *N*-acyl substituents. Increasing polarity causes lower barriers. Although *N*-alkylbis(methylsulfonyl)ketenimines are not calculated to be linear, the barriers are so low that crystal lattice forces can induce planarity in *N*-methylbis(methylsulfonyl)ketenimine **3**.

## Introduction

Recently, we reported that ketenimine **2** was obtained as the primary product of thermolysis of the isoxazolone **1**.<sup>1,2</sup> Compound **2** has unusual properties for a ketenimine: a strong IR band at 2230 cm<sup>-1</sup> (most ketenimines absorb at 2000–2090 cm<sup>-1</sup> 2,3) and <sup>13</sup>C resonances at 52 and 119 ppm that look more like those of a nitrile (37–77 and ca. 190 ppm are typical for the  $\beta$  and  $\alpha$  carbons of ketenimines, respectively<sup>1,2</sup>). The X-ray structure of **2** revealed a short C=N bond (1.15 Å) and a linear CCNR moiety ( $\angle$ CNR = 179.6°).<sup>1</sup>



**3**: R = R' = CH<sub>3</sub>SO<sub>2</sub>, R'' = Me

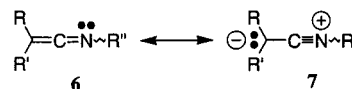
**4**: R = R' = CH<sub>3</sub>SO<sub>2</sub>, R'' = Et

**5**: R = PhSO<sub>2</sub>, R' = CH<sub>3</sub>SO<sub>2</sub>, R'' = Me

Only one other stable, linear ketenimine, *N*-methylbis(methylsulfonyl)ketenimine **3**, has been reported ( $\angle$ CNR

= 180°).<sup>4</sup> Surprisingly, the *N*-ethyl analogue **4** (144°)<sup>5</sup> as well as *N*-methyl(methylsulfonyl)(phenylsulfonyl)ketenimine **5** (171°)<sup>6</sup> are not strictly linear. Our own IR investigation of **3**, detailed below, indicates that it is not completely linear in solution, so perhaps crystal packing forces contribute to its linearity in the solid state.<sup>2</sup> A survey of the Cambridge Crystallographic Database reveals that the CNR angles in ketenimines usually fall within the range of 117–129° with a mean value of 126°.<sup>7–9</sup> Like in allenes, the N–R bond is perpendicular to the two C–R' bonds in a structure of the type R'<sub>2</sub>C=C=N–R.

Resonance structures **6–7** are the most important ones for ketenimines. While ketenimines are potentially axially asymmetric, the inversion barrier at nitrogen can be low.



Reported inversion barriers for ketenimines<sup>9</sup> are in the range 30–60 kJ mol<sup>-1</sup> (for imines<sup>10</sup> they are 57–64 kJ mol<sup>-1</sup>). A high degree of triple-bond character of the CN bond as in **7** could lead to a more linear structure along the CCNR system and may account for the low inversion

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Table 1. Computational Data for Ketenimines<sup>a</sup>

dielectric constant $\epsilon$	nitrogen inversion barrier/kJ mol <sup>-1</sup>			ground state					transition state					
				distances (Å)		angles (deg)		$\nu(\text{CCN})$ (cm <sup>-1</sup> )	distances (Å)		angles (deg)		$\nu(\text{CCN})$ (cm <sup>-1</sup> )	
	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$	C=C	C=N	CCN	CNR		C=C	C=N	CCN	CNR		
ketenimine														
1	50	-3.4	51.1	1.313	1.23	174.5	115.4	2057.9	1.326	1.192	180	180	2179.9	
40	48.9	-3.4	49.9	1.313	1.231	174.5	114.8	2044.9	1.329	1.189	180	180	2169.8	
<i>N</i> -methylketenimine														
1	40.6	8.3	38.2	1.316	1.224	176	123	2073.2	1.329	1.191	180	180	2258.2	
40	34.5	9.3	31.7	1.316	1.224	175.8	122.9	2062.1	1.334	1.187	180	180	2237.8	
<i>N</i> -ethylketenimine														
1	39.7	1.8	39.2	1.316	1.224	176.1	122.8	2067.1	1.329	1.192	180	180	2245.6	
40	36.7	1.7	36.2	1.316	1.224	175.9	122.8	2054.3	1.329	1.192	180	180	2231.7	
<i>N</i> -phenylketenimine														
1	25	-6.1	26.8	1.314	1.228	175.1	125.7	2044.8	1.326	1.194	180	180	2239.4	
40	25.3	-5.3	26.9	1.314	1.228	175	125.7	2037.5	1.326	1.194	180	180	2219.7	
cyano- <i>N</i> -phenylketenimine <b>13<sup>b</sup></b>														
1	13.9	-3.5	15	1.331	1.214	174.3	130.8	2060.6	1.345	1.182	180	180	2223	
4	8.8	-4.5	10.2	1.335	1.209	173.6	133.7	2064	1.352	1.182	180	180	2191	
10	3.3	-9.9	6.2	1.337	1.207	173.3	135.4	2066.4	1.355	1.806	180	180	2181.2	
40	-0.5	-11.9	3	1.339	1.205	173	136.6	2068.9	1.357	1.180	175.4	178.1	2174	
dicyano- <i>N</i> -methylketenimine <b>10a<sup>b</sup></b>														
1	9	1.6	8.5	1.35	1.196	174.4	134.9	2121.6	1.366	1.171	180	180	2305.8	
4	0.6	-3.1	1.6	1.363	1.182	174.1	147.1	2174.9	1.374	1.167	180	180	2307.3	
10	0.3	-13.5	4.3	1.373	1.172	175.6	159.1	2213.2	1.378	1.166	180	180	2307.8	
40	1.3	-21.3	7.7	1.38	1.66	178.2	172.4	2219.6	1.38	1.165	180	180	2221.6	
dicyano- <i>N</i> -ethylketenime <b>10b<sup>b</sup></b>														
1	9.3	-8	11.7	1.352	1.196	174.2	135.7	2113.7	1.366	1.172	180	180	2294.5	
4	-3.7	-14.6	0.7	1.365	1.182	173.9	147.7	2155.9	1.376	1.168	179.1	174.9	2293.7	
10	-	-	-	1.376	1.171	175.7	161.7	2208.2	-	-	-	-	-	
40	-	-	-	1.337	1.17	175.9	163.1	2306.5	-	-	-	-	-	
dicyano- <i>N</i> -phenylketenimine <b>10c<sup>b</sup></b>														
1	7.8	-4.3	9.1	1.349	1.201	174	137.7	2084.6	1.363	1.177	180	180	2219.3	
4	-2.5	-17.3	2.7	1.362	1.188	174.1	149.5	2131.3	1.372	1.174	180	180	2207.23	
10	0.3	-24.7	7.7	1.37	1.179	175.7	160.4	2173.6	1.374	1.174	180	180	2204.27	
40	-	-	-	1.381	1.174	180	180	2193.4	-	-	-	-	-	
bis(methylsulfonyl)- <i>N</i> -methylketenimine <b>3</b>														
1	9.9	5.6	8.2	1.326	1.21	173.7	121.7	2066	1.344	1.174	180	180	2202.6	
40	2	0.6	1.8	1.338	1.193	174.2	138.6	2125.5	1.356	1.169	179.8	179.8	2288.3	
bis(methylsulfonyl)- <i>N</i> -ethylketenimine <b>4</b>														
1	10.1	-7.1	12.2	1.334	1.199	174.5	134.2	2101	1.351	1.172	180	180	2279	
40	3	2.7	2.2	1.34	1.193	174.1	138.3	2113	1.357	1.170	179.5	177.3	2273.8	
bis(methylsulfonyl)- <i>N</i> -phenylketenimine														
1	5.4	-11.5	8.8	1.329	1.204	174.4	136.1	2068.4	1.347	1.176	180	180	2254	
40	-2.4	-17.2	2.7	1.337	1.197	174	142	2085.5	1.354	1.175	180	180	2222.2	

<sup>a</sup> Geometries and vibration frequencies (scaled by 0.9613) calculated at the B3LYP/6-31G\* level. <sup>b</sup> See Table 2 for details of the CN and CCN vibration frequencies.

barrier observed for ketenimines. The linear resonance structure **7** would be the transition state for nitrogen inversion in ordinary ketenimines. If the zwitterionic resonance structure **7** explains the linear structures of **2** (and perhaps **3**), one would predict that other electron withdrawing groups at the C-terminus could also stabilize this geometry. Thus, nitro, acyl, and cyano substituents are particularly promising candidates.

A consequence of linearity is the increased frequency of the CCN stretching vibration from the region of 2000–2090 to 2190–2250 cm<sup>-1</sup>. This is due to the shortening of the carbon–nitrogen bond as it adopts more triple-bond character, and it provides a convenient tool for the detection of potentially linear ketenimines. The present investigation of dicyanoketenimines **10a–c** resulted from our experimental observation that the IR spectra, and

hence the structures, of ketenimines were highly dependent on the medium. Since the interpretation of the experimental spectra is aided by comparison with calculated spectra, the theoretical section will be presented first.

## Results and Discussion

**Theoretical Calculations.** DFT calculations (B3LYP/6-31G\*) of the structures of ground and transition states, energies, nitrogen inversion barriers, IR spectra, and dipole moments were performed for a number of ketenimines with a large variety of substituents at C and N.<sup>11</sup> Data for a few of these compounds relevant to the present study are presented in Table 1 and in the Supporting Information. The calculated inversion barriers are usually lower by 3–17 kJ mol<sup>-1</sup> than those found experimentally.<sup>12–14</sup> For ketenimines H<sub>2</sub>C=C=N–R (R = alkyl or aryl) the inversion barriers follow the reported trends,<sup>9,13–14</sup> that is, a change in the alkyl group has only

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**Table 2.** Calculated (B3LYP 6-31G\*) Ketenimine and Nitrile Stretching Modes (cm<sup>-1</sup>) as a Function of Dielectric Constant  $\epsilon$  (Intensities in Parentheses)<sup>a</sup>

ground-state molecules									
<b>13</b>	$\epsilon = 1$	2061	(677)	CCN	2249	(51)	CN		
	$\epsilon = 4$	2064	(1077)	CCN	2240	(112)	CN		
	$\epsilon = 10$	2066	(1267)	CCN	2235	(151)	CN		
	$\epsilon = 40$	2069	(1404)	CCN	2231	(182)	CN		
<b>10a</b>	$\epsilon = 1$	2122	(795)	CCN	2249	(39)	CN	2264	(5) CN
	$\epsilon = 4$	2175	(1253)	CCN	2232	(118)	CN	2258	(3) CN
	$\epsilon = 10$	2213	(1105)	CCN + CN	2220	(190)	CN	2271	(314) CCN + CN
	$\epsilon = 40$	2211	(237)	CN	2220	(735)	CCN + CN	2302	(725) CCN
<b>10b</b>	$\epsilon = 1$	2114	(833)	CCN	2247	(43)	CN	2262	(7) CN
	$\epsilon = 4$	2165	(1394)	CCN	2230	(129)	CN	2256	(0) CN
	$\epsilon = 10$	2208	(1280)	CCN + CN	2217	(209)	CN	2269	(320) CCN + CN
	$\epsilon = 40$	2207	(267)	CN	2214	(951)	CN	2292	(696) CCN
<b>10c</b>	$\epsilon = 1$	2085	(701)	CCN	2247	(40)	CN	2261	(20) CN
	$\epsilon = 4$	2131	(1004)	CCN	2221	(113)	CN	2262	(47) CN
	$\epsilon = 10$	2174	(1069)	CCN	2231	(165)	CN	2250	(18) CN
	$\epsilon = 40$	2193	(954)	CCN + CN	2202	(256)	CN	2262	(3) CCN + CN
transition state for nitrogen inversion									
<b>13</b>	$\epsilon = 1$	2223	(1023)	CN	2271	(1023)	CCN		
	$\epsilon = 4$	2191	(1725)	CCN + CN	2247	(301)	CCN + CN		
	$\epsilon = 10$	2181	(1984)	CCN + CN	2243	(295)	CCN + CN		
	$\epsilon = 40$	2174	(2167)	CCN + CN	2241	(277)	CCN + CN		
<b>10a</b>	$\epsilon = 1$	2237	(86)	CN	2241	(403)	CN	2306	(710) CCN
	$\epsilon = 4$	2224	(166)	CN	2230	(575)	CN	2307	(776) CCN
	$\epsilon = 10$	2217	(13)	CN	2225	(13)	CN	2308	(13) CCN
	$\epsilon = 40$	2217	(13)	CN	2225	(13)	CN	2308	(13) CCN
<b>10b</b>	$\epsilon = 1$	2237	(548)	CCN + CN	2294	(668)	CCN		
<b>10c</b>	$\epsilon = 1$	2219	(930)	CCN	2237	(82)	CN	2269	(138) CCN + CN
	$\epsilon = 4$	2207	(1058)	CCN	2222	(159)	CN	2264	(69) CCN + CN
	$\epsilon = 10$	2204	(1053)	CCN + CN	2218	(181)	CN	2262	(43) CCN + CN

<sup>a</sup> Full details of the calculations from which these data are extracted is given in the Supporting Information. The major contributors, CCN and/or CN stretching modes, to each vibrational frequency are indicated.

a minor influence on the inversion barrier, while replacement of *N*-alkyl by *N*-phenyl reduces the barrier by ca. 10 kJ mol<sup>-1</sup>. Electron-withdrawing *C*-substituents cause a decrease in the calculated inversion barrier of ca. 12 kJ mol<sup>-1</sup> for one cyano group (from 27 to 15 in compound **13**), and of an additional 3–6 kJ mol<sup>-1</sup> for two (to 9–12 kJ mol<sup>-1</sup> in **10a–c**) (Table 1). Self-consistent reaction field (SCRF) calculations applying a dielectric constant  $\epsilon$  of up to 40 progressively lower the barrier to 3 kJ mol<sup>-1</sup> for **13**, and to zero for **10b** and **10c**. A similar effect on the barrier was calculated for methylsulfonyl substituents (8–12 kJ mol<sup>-1</sup> for  $\epsilon = 1$  and 2–3 kJ mol<sup>-1</sup> for  $\epsilon = 40$ ; see Table 1). Inclusion of polarity by means of SCRF calculations have little or no effect on the barriers for the ordinary *C*-unsubstituted ketenimines (Table 1).

We have also calculated the structures of ketenimines with *N*-amino, *N*-hydroxy, *N*-fluoro, *N*-chloro, *N*-trifluoromethyl, *N*-cyano, *N*-formyl, and *N*-acetyl substituents (gas phase;  $\epsilon = 1$ ).<sup>11</sup> For electron-withdrawing atoms very high inversion barriers were calculated (*N*-amino = 70.1, *N*-hydroxy = 116.7, *N*-fluoro = 198.4, *N*-chloro = 105.3 kJ mol<sup>-1</sup>). The inversion barrier for the *N*-trifluoromethyl case is somewhat higher than for *N*-methyl (48.4 and 38.3 kJ mol<sup>-1</sup>, respectively), while for *N*-cyano it is slightly lower (27.1 kJ mol<sup>-1</sup>). *N*-Acyl substituents dramatically decrease the inversion barrier. For *N*-formylketenimine (no *C*-substituents), an inversion barrier of only 13.2 kJ mol<sup>-1</sup>, and for *N*-acetylketenimine a barrier of 15.4 kJ mol<sup>-1</sup> was calculated. Two *C*-cyano groups further reduce the inversion barrier by ca. 6 kJ mol<sup>-1</sup> (to 7.4 kJ mol<sup>-1</sup>

for *N*-formyldicyanoketenimine and to 9.2 kJ mol<sup>-1</sup> for *N*-acetyldicyanoketenimine) (see the Supporting Information).

The calculated infrared spectra are in good agreement with the reported spectra of ketenimine,<sup>15</sup> *N*-methylketenimine,<sup>16</sup> *N*-ethylketenimine,<sup>17</sup> and *N*-phenylketenimine<sup>18</sup> (Table 1). All *C*-unsubstituted ketenimines are found to have nonlinear C=N–R moieties experimentally as well as computationally. These calculations were performed for the gas-phase molecules ( $\epsilon = 1$ ), and the calculated structures, inversion barriers, and IR spectra did not change appreciably when a dielectric reaction field was applied ( $\epsilon = 40$ ; SCRF calculation). In contrast, for the dicyanoketenimines **10a–c** the application of the reaction field ( $\epsilon = 4, 10$ , or 40) caused these compounds to become nearly linear (**10a**) or completely linear (**10c**) (Table 1). The effect is less for **10b**, but nevertheless the CNR angle widens by 27.4°. As the CNR angles widen, the calculated ketenimine stretching vibrations ( $\nu_{\text{CNN}}$ ) move to progressively higher frequencies, by as much as

(15) HNCCH<sub>2</sub> Ar matrix IR spectrum 2042 cm<sup>-1</sup>: Jacox, M. E.; Milligan, D. E. *J. Am. Chem. Soc.* **1963**, *85*, 278. 2040 cm<sup>-1</sup>: M. E. Jacox, *Chem. Phys.* **1979**, *43*, 157. Neat IR spectrum (–196 °C) 2038 cm<sup>-1</sup>: Guillemin, J.-C.; Denis, J.-M.; Lasne, M.-C.; Ripoll, J.-L. *J. Tetrahedron* **1988**, *44*, 4447.

(16) (a) MeNCCH<sub>2</sub> neat IR spectrum 2040 cm<sup>-1</sup>: Ripoll, J.-L.; Thuillier, A. *Tetrahedron Lett.* **1978**, 463. (b) IR on NaCl 2035 cm<sup>-1</sup>; <sup>13</sup>C NMR 33.6, 188.9 ppm: De Corte, B.; Denis, J.-M.; De Kimpe, N. *J. Org. Chem.* **1987**, *52*, 1147. (c) Gas-phase IR spectrum 2060 cm<sup>-1</sup>: Amatatsu, Y.; Hamada, Y.; Tsuboi, M. *J. Mol. Spectrosc.* **1987**, *123*, 476. August, J.; Klemm, K.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1841.

(17) EtNCCH<sub>2</sub> IR spectrum on NaCl 2030 cm<sup>-1</sup>; <sup>13</sup>C NMR 35.0, 187.7 ppm. See ref 18b.

(18) PhNCCH<sub>2</sub> neat film IR spectrum 2040, 2020 cm<sup>-1</sup>: Winter, H.-W.; Wentrup, C. *Angew. Chem.* **1980**, *92*, 743; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 720. Ar matrix IR spectrum 2050, 2030 cm<sup>-1</sup>: Orton, E.; Collins, S. T.; Pimentel, G. C. *J. Phys. Chem.* **1986**, *90*, 6139.

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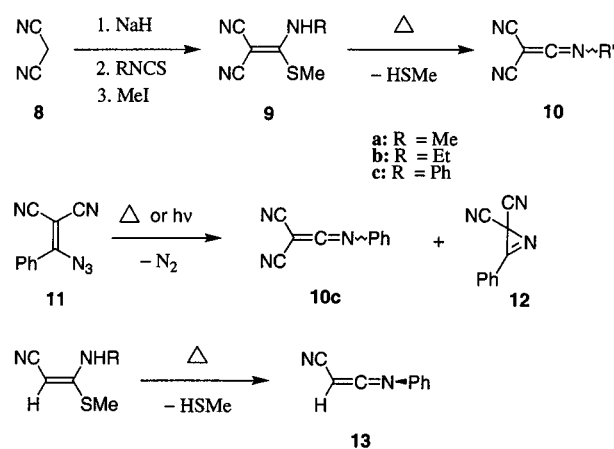


50  $\text{cm}^{-1}$  already at  $\epsilon = 4$  and by 100 or more  $\text{cm}^{-1}$  at  $\epsilon = 40$ . The characteristic wavenumbers and their assignments to CN and/or CCN groups are reported in Table 2. At high  $\epsilon$  values, one of the CN stretching bands tends to mix with a CCN stretch as the CCN band moves from the lowest wavenumber (ca. 2100  $\text{cm}^{-1}$ ) to the highest (2200–2300  $\text{cm}^{-1}$ ). The wavenumbers of the two bands for the cyano groups (symmetric and antisymmetric combinations) remain relatively unchanged or move to slightly lower wavenumbers during this polarity increase. Since the *C,C*-dicyanoketenimines tend toward linearity in the more polar media, a high value for  $\nu_{\text{CNN}}$  can be associated with linearity. The  $\nu_{\text{CNN}}$  bands can be recognized easily because they are usually far more intense than the  $\nu_{\text{CN}}$  bands. Since the transition states (TS) for nitrogen inversion in the ketenimines are linear, it is not surprising that the calculated IR spectra of the TSs also give very high values for  $\nu_{\text{CNN}}$ , and they are not strongly influenced by the solvent dielectric constant (Table 2). Thus, the calculated IR spectrum of the TS, even with  $\epsilon = 1$ , gives an indication of the position of  $\nu_{\text{CNN}}$  if the ketenimine were linear. As discussed below, the experimental IR spectra of the dicyanoketenimines in Ar matrixes agree rather well with the calculations for the classical, bent, compounds in the gas phase, whereas the very high values of  $\nu_{\text{CNN}}$  in the more polar neat films or solids agree with expectations for linear or almost linear structures.

The data in Tables 1 and 2 also reveal that a single cyano group is not sufficient to cause an appreciable shift in  $\nu_{\text{CNN}}$  or widening of the CNR angle (*N*-phenylcyano-ketenimine **13**). This too is in agreement with the experimental observations.

Similar calculations were performed for some *C,C*-bis-sulfonylketenimines (Table 1). The effect of polarity is much less pronounced in these cases. Even though **3** is known to have a linear CNR moiety in the solid state, the calculated angle is no more than 138.6° at  $\epsilon = 40$ , and  $\nu_{\text{CNN}}$  only increases by 60  $\text{cm}^{-1}$ . Small increases in the CNR angles and  $\nu_{\text{CNN}}$  are calculated for **4** and *N*-phenyl-bis(methylsulfonyl)ketenimine. Since these compounds have different structures in the solid state, viz  $\angle\text{CNR} = 180^\circ$  for **3**, 144° for **4**, and 171° for **5**, it is tempting to conclude that crystal packing forces are responsible for the linearity of **3** (see below). The low inversion barriers at nitrogen will allow these forces to dictate the structures.

**FVT and Photolysis Experiments.** The ketenimines **10** were generated by thermal elimination of methanethiol from methylthioenamines (ketene *N,S*-acetals) **9**.<sup>2,19</sup> The precursors **9** were prepared by coupling the carbanion of malononitrile (**8**) with the appropriate isothiocyanate. The resulting thiolates were methylated with iodomethane to give the methylthioenamines in yields of 23–60%. Flash vacuum thermolysis (FVT) of **9** afforded ketenimines **10**, which were isolated at low temperatures for IR spectroscopy (Ar matrix at 7–14 K or neat film at ca. 130 K). Ketenimine **10c** was also obtained from 2-cyano-3-azidocinnamionitrile (**11**). This pathway has been used previously,<sup>20</sup> but the highly unstable ketenimine was not isolated, and no spectroscopic data were reported.



FVT of **9a** at 500 °C afforded a pyrolysate, which after deposition in an argon matrix at 8 K delivered the IR spectrum shown in Figure 1D. Absorptions similar to those in the calculated ground-state spectrum ( $\epsilon = 1$ ) of dicyano-*N*-methylketenimine (**10a**) (Figure 1E) appeared in the region 2140–2120  $\text{cm}^{-1}$  (three bands with about equal intensities at 2138, 2133, and 2122  $\text{cm}^{-1}$ ), together with absorptions attributed to the cyano groups at 2259 and 2235  $\text{cm}^{-1}$  (Figure 1D; the multiple peaks for  $\nu_{\text{CNN}}$  may be due to a matrix site effect). A neat film of the pyrolysate from **9a** at 130 K showed a very different spectrum with a strong absorption at 2213  $\text{cm}^{-1}$  and weaker ones at 2282, 2256, 2100, and 2086  $\text{cm}^{-1}$  (Figure 1B). The presence of a small band at 1565  $\text{cm}^{-1}$  indicates incomplete conversion of starting material (cf. Figure 1A), but while this may account for some of the peaks in the 2300–2000  $\text{cm}^{-1}$  range, the peak at 2213  $\text{cm}^{-1}$  is much too strong to be due to the cyano groups of the starting material. The calculated values for  $\nu_{\text{CNN}}$  in the bent ground state in the gas phase ( $\epsilon = 1$ ; Figure 1E) and the almost linear structure in a solvent field ( $\epsilon = 10$ ; Figure 1C) are 2122 and 2213  $\text{cm}^{-1}$ , respectively. The calculated value for the linear TS in the gas phase is 2306  $\text{cm}^{-1}$  (Tables 1 and 2 and Figure 1F).

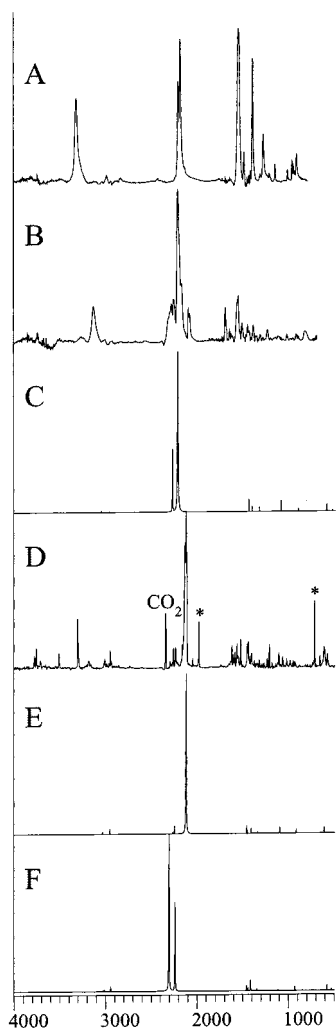
The differences between the IR spectra of the neat film, the argon matrix, and the calculated spectra, together with the low calculated inversion barrier of  $\Delta G^\ddagger = 8.3$  kJ  $\text{mol}^{-1}$  indicate a structural flexibility resulting in different equilibrium geometries in different environments, bent in the gas phase and in Ar matrix, but linear in a polar medium.

Although to a smaller extent, a similar trend is observed for the ethyl analogue **10b**. Again, the calculated barrier for nitrogen inversion is remarkably low ( $\Delta G^\ddagger = 0.7$ –11.7 kJ  $\text{mol}^{-1}$ ; Table 1). The ketenimine stretch  $\nu_{\text{CNN}}$  occurs at a relatively high value (2173  $\text{cm}^{-1}$  at 130 K) in the neat film spectrum. The Ar matrix isolated **10b** has the most prominent band at 2142  $\text{cm}^{-1}$ . The calculated values are 2208, 2156, and 2114  $\text{cm}^{-1}$  for the ground state at  $\epsilon = 10$ , 4, and 1, respectively (Tables 1 and 2). Note that the ground state is calculated to remain bent in this case ( $\angle\text{CNR} = 137$ –163° for  $\epsilon = 1 \rightarrow 40$ ); therefore, wavenumber shifts as large as for **10a** and **10c** are not expected. So, although the wavenumber shifts are not so spectacular in this case, the qualitative agreement with calculations is remarkable.

Dicyano-*N*-phenylketenimine (**10c**), prepared by FVT of ketene-*N,S*-acetal **9c** at 650 °C, showed absorptions at 2234 (CN) and 2090 (CCN)  $\text{cm}^{-1}$  (Ar matrix, 12 K;

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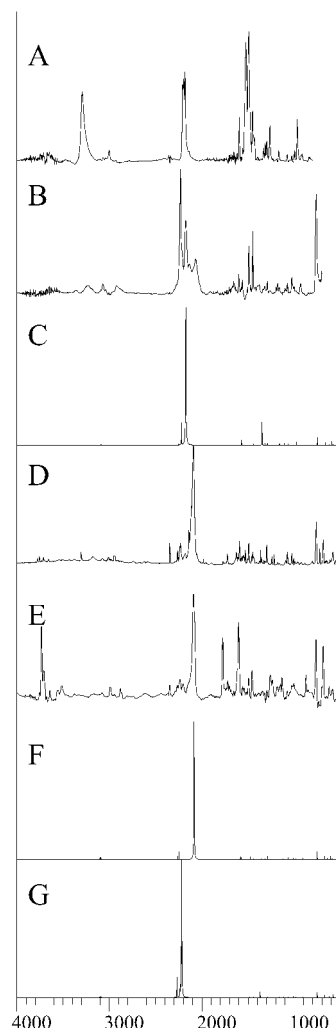
(20) Friedrich, K. *Angew. Chem.* **1967**, 79, 980; *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 959.



**Figure 1.** Infrared spectra of *C,C*-dicyano-*N*-methyl-ketenimine **10a**. (A) Ketene-*N,S*-acetal **9a** in KBr. (B) Neat film spectrum of **10a** at 130 K. (C) Calculated spectrum of **10a** in a polar medium (B3LYP/6-31G\*-SCRF;  $\epsilon = 10$ ). (D) Ar matrix isolated **10a** at 10 K (the peak at 2340  $\text{cm}^{-1}$  is due to  $\text{CO}_2$ ; \* impurity at ca. 2000 and 700  $\text{cm}^{-1}$ ;  $\text{CO}_2$  at 2340  $\text{cm}^{-1}$ ). (E) Calculated spectrum for the ground state of **10a** in the gas phase (B3LYP/6-31G\*;  $\epsilon = 1$ ). (F) Calculated spectrum for the transition state for nitrogen inversion in **10a** (B3LYP/6-31G\*;  $\epsilon = 1$ ). All calculated wavenumbers are scaled by 0.9613. Abscissae: wavenumbers ( $\text{cm}^{-1}$ ); ordinates: arbitrary absorbance units.

Figure 2D). The calculated ground-state spectrum ( $\epsilon = 1$ ) agrees well with the observed spectrum for matrix-isolated **10c**. The neat film spectrum obtained from FVT of **9c** above 700 °C had major absorptions at 2229 and 2173  $\text{cm}^{-1}$  (Figure 2B) in agreement with the calculated spectrum (2193  $\text{cm}^{-1}$ ) and structure ( $\angle\text{CNR} = 180^\circ$ ) for  $\epsilon = 40$  (Tables 1 and 2 and Figure 2).

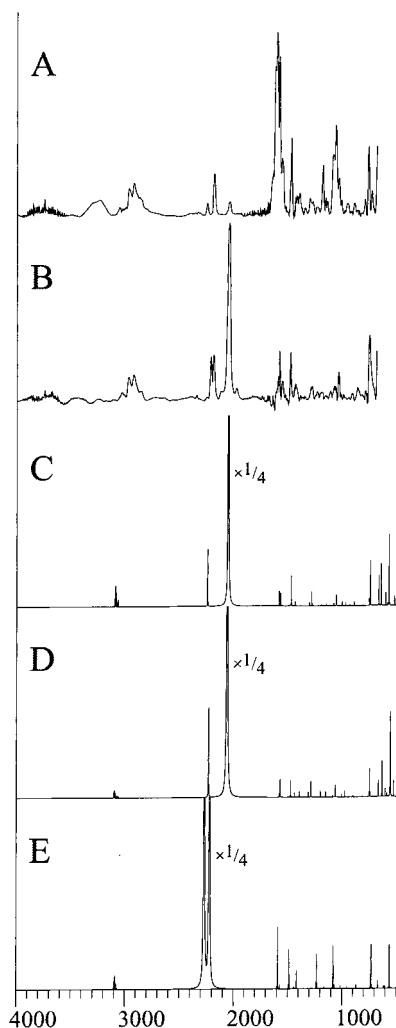
Further evidence for linearity of **10c** was obtained by NMR and IR experiments on the thermal and photochemical decomposition of 2-cyano-3-azidocinnamionitrile **11** in solution. Its thermal decomposition proceeds slowly at ambient temperature and rapidly at 60 °C leading to ketenimine **10c** as the primary decomposition product. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **10c** were recorded at  $-50^\circ\text{C}$  in  $\text{CDCl}_3$  solution ( $^{13}\text{C}$  NMR: 127 ppm ( $\text{C}=\text{C}=\text{N}$ ) and 21 ppm ( $\text{C}=\text{C}=\text{N}$ )). The NMR spectra revealed that besides ketenimine **10c**, a small amount of azirine **12** was formed (ratio  $\sim 8:1$  in favor of ketenimine **10c**).



**Figure 2.** Infrared spectra of *C,C*-dicyano-*N*-phenylketenimine **10c**. (A) Ketene-*N,S*-acetal **9c** in KBr. (B) Neat film of **10c** at 130 K. (C) B3LYP/6-31G\*-SCRF ( $\epsilon = 10$ ) calculated spectrum of **10c**. (D) Ar matrix isolated **10c** (10 K) after FVP of **10a** at 650 °C. (E) Ar matrix isolated (8 K) **10c** from photochemical decomposition of **11** (peaks at ca. 1600 and 3700  $\text{cm}^{-1}$  are attributed to water, and the one at 1773  $\text{cm}^{-1}$  to azirine **12**). (F) Calculated spectrum for the ground-state gas phase (B3LYP/6-31G\*;  $\epsilon = 1$ ). (G) Calculated spectrum for the transition state for nitrogen inversion in **10c** (B3LYP/6-31G\*;  $\epsilon = 1$ ). All calculated wavenumbers are scaled by 0.9613. Abscissae: wavenumbers ( $\text{cm}^{-1}$ ). Ordinates: arbitrary absorbance units.

The signals of ketenimine **10c** disappeared on warming, and at ambient temperature a bright red precipitate formed rapidly. The low-temperature spectra of **10c** contained impurities due to the presence of either azirine **12** or the polymerization products. Similar decomposition of **11** at 60 °C in  $\text{CHCl}_3$  solution allowed the observation of a part of the IR spectrum of **10c** (IR ( $\text{CHCl}_3$ )  $\nu$  2221 s, 2202 m, 2131 m, 2108 br  $\text{cm}^{-1}$ ).

In contrast to thermal decomposition, photolysis of **11** at 0 °C in  $\text{CHCl}_3$  solution resulted in the exclusive formation of azirine **12**, which was identified by its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, as well as by DEPT, HSQC and HMBC  $^1\text{H}/^{13}\text{C}$ -COSY spectra. The IR spectrum of **12** in  $\text{CHCl}_3$  is in good agreement with the calculated spectrum. Although **12** also polymerizes to a bright red precipitate, its solutions in chloroform are much more stable than those of ketenimine **10c**. Presumably, the azirine poly-

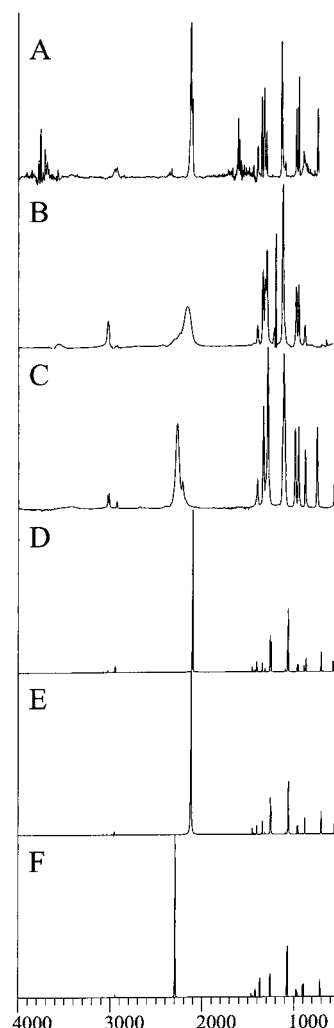


**Figure 3.** Infrared spectra of *C*-cyano-*N*-phenylketenimine **13**. (A) Precursor, 3-methylthio-3-phenylaminoacrylonitrile (neat film, 130 K; the CN stretch is at 2194  $\text{cm}^{-1}$ ). (B) Ketenimine **13** obtained by FVT of the precursor at 700 °C (neat film, 130 K;  $\nu_{\text{CNN}}$  2055–2060  $\text{cm}^{-1}$ ;  $\nu_{\text{CN}}$  2221  $\text{cm}^{-1}$ ; a residual precursor band is present at 2194  $\text{cm}^{-1}$ ) (for Ar matrix, see ref 2). (C) Calculated spectrum (B3LYP/6-31G\*;  $\epsilon = 1$ ). (D) Calculated spectrum (B3LYP/6-31G\*;  $\epsilon = 10$ ). (E) Calculated spectrum for the linear TS (B3LYP/6-312G\*;  $\epsilon = 1$ ). All calculated wavenumbers are scaled by 0.9613. Abscissae: wavenumbers ( $\text{cm}^{-1}$ ); ordinates: arbitrary absorbance units. The  $\nu_{\text{CNN}}$  peaks in C–E have been attenuated by a factor of 4.

merizes via ring opening to the vinylnitrene which rearranges to the ketenimine. The latter polymerizes at ambient temperature, thus making it spectroscopically unobservable.

Photolysis of **11** in an Ar matrix produced both ketenimine **10c** and azirine **12**. The IR absorptions of **10c** produced by FVT of **9c** and by photolysis of **11** were identical (compare parts D and E of Figure 2).

The highly shielded  $^{13}\text{C}$  NMR resonance of the carbon atom of **10c** that bears the cyano substituents (21 ppm) as well as the extraordinary position of the signal for the imine carbon in the triple bond region (127 ppm) together with the high IR frequency  $\nu_{\text{CNN}}$  (2173  $\text{cm}^{-1}$ ; neat film) are reminiscent of the data for **2** and suggest that **10c** is linear in chloroform solution and in the neat film, whereas the more normal value of the IR band in Ar matrix (2092  $\text{cm}^{-1}$ ) suggests a normal, bent geometry in



**Figure 4.** Infrared spectra of *N*-methyl-bis(methylsulfonyl)-ketenimine **3**. (A) Ar matrix, 14 K;  $\nu_{\text{CNN}} = 2135 \text{ cm}^{-1}$ . (B)  $\text{CHCl}_3$  solution, rt;  $\nu_{\text{CNN}} = 2170 \text{ cm}^{-1}$ . (C) KBr pellet, rt;  $\nu_{\text{CNN}} = 2288 \text{ cm}^{-1}$ . (D) Calculated spectrum for the ground state (B3LYP/6-31G\*;  $\epsilon = 1$ );  $\nu_{\text{CNN}} = 2109 \text{ cm}^{-1}$ . (E) Calculated spectrum for the ground state (B3LYP/6-31G\*;  $\epsilon = 40$ );  $\nu_{\text{CNN}} = 2125.5 \text{ cm}^{-1}$ . (F) Calculated spectrum for the TS for nitrogen inversion ( $\epsilon = \infty$ );  $\nu_{\text{CNN}} = 2288 \text{ cm}^{-1}$ . All calculated wavenumbers are scaled by 0.9613. Abscissae: wavenumbers ( $\text{cm}^{-1}$ ). Ordinates: arbitrary absorbance units.

this environment. The linear structure and the consequently polar character in solution could also explain the high reactivity and polymerizability of the ketenimine (the calculated dipole moment is 8.5 D).

The two cyano groups strongly influence the rearrangement path of the vinyl azide. Normally, thermolysis of vinyl azides furnishes azirines rather than ketenimines.<sup>21</sup> A compound similar to **11** in which one of the cyano groups is replaced by a methyl group reportedly afforded the corresponding azirine with no evidence of ketenimine formation.<sup>22</sup> On the other hand, a vinyl azide substituted with two electron withdrawing methoxycarbonyl groups at C2 and *p*-nitrophenyl at C1 yielded only the ketenimine *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N=C=C(COOMe)<sub>2</sub> and no azirine.<sup>23</sup> The high value of  $\nu_{\text{CNN}}$  and the low values of the  $^{13}\text{C}$  NMR chemical shifts reported<sup>23</sup> for this compound

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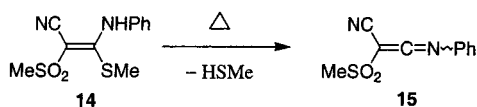
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(IR (2100–2150  $\text{cm}^{-1}$  in  $\text{CHCl}_3$ ;  $^{13}\text{C}$  NMR 125, 131 ppm) suggest that it may be (nearly) linear (cf. refs 1 and 2).

That two electron-withdrawing groups at the *C*-terminus are required in order to push the ketenimine structure toward linearity is demonstrated by the results for monocyano-*N*-phenylketenimine **13**, which has a perfectly normal IR spectrum. The Ar matrix spectrum is shown in ref 2. Although the calculated inversion barrier for this compound is low (15  $\text{kJ mol}^{-1}$ ), the experimental data indicate nonlinearity in both the neat film ( $\nu_{\text{CNN}}$  2055–2060  $\text{cm}^{-1}$ ;  $\nu_{\text{CN}}$  2221  $\text{cm}^{-1}$ ) and Ar matrix ( $\nu_{\text{CNN}}$  2054, 2062  $\text{cm}^{-1}$ ;  $\nu_{\text{CN}}$  2230, 2270  $\text{cm}^{-1}$ ). These IR frequencies are in excellent agreement with the calculated ground-state spectrum (2061  $\text{cm}^{-1}$ ;  $\epsilon = 1$ ). The calculated value of  $\nu_{\text{CNN}}$  does not change much as a function of  $\epsilon$ , and the CNR moiety remains bent. In contrast, the linear TS has a calculated  $\nu_{\text{CNN}}$  at 2270  $\text{cm}^{-1}$  and an equally strong  $\nu_{\text{CN}}$  at 223  $\text{cm}^{-1}$  ( $\epsilon = 1$ ) (see Table 2 and Figure 3).

**Sulfonylketenimines.** Some *C*-sulfonylketenimines were investigated in a similar manner. Compound **3**, known to have a linear CNR moiety in the crystal,<sup>4</sup> shows a ketenimine band in Ar matrix at 2135  $\text{cm}^{-1}$ . This is just a little higher than the expectation for the bent gas-phase molecule (2109  $\text{cm}^{-1}$ ;  $\angle\text{CNR} = 121.7^\circ$ ;  $\epsilon = 1$ ), but far from the linear TS (2292  $\text{cm}^{-1}$ ). The calculated geometries of the sulfonylketenimines are not very sensitive to the dielectric constant  $\epsilon$ , and the  $\nu_{\text{CNN}}$  values also do not increase greatly (Table 1). An experimental value of 2170  $\text{cm}^{-1}$  was obtained in chloroform solution ( $\epsilon = 4.9$ ). The value for the crystalline solid in KBr is 2280  $\text{cm}^{-1}$ , in agreement with calculations for the linear TS (2288  $\text{cm}^{-1}$  and  $\angle\text{CNR} = 180^\circ$  at  $\epsilon = 40$ ; 2202  $\text{cm}^{-1}$  and  $\angle\text{CNR} = 180^\circ$  at  $\epsilon = 1$ ) (Table 1 and Figure 4). These calculations indicate that compounds **3**–**5** are *not* intrinsically linear, although they may have somewhat widened CNR angles in highly polar media. Compound **4** is far from linear experimentally.<sup>5</sup> It is very likely, therefore, that the observed linearity of crystalline **3** is enforced by the lattice. The low calculated inversion barrier between 1.8 and 8.2  $\text{kJ mol}^{-1}$  would allow crystal lattice forces to dictate the structure. Consequently, the IR spectrum of crystalline **3** resembles that of the linear TS for nitrogen inversion.

As mentioned above, one cyano group is not enough to cause intrinsic linearity of a ketenimine in a polar medium. A cyano group plus a sulfonyl group are also not enough to enforce linearity, as indicated by the IR spectra of *N*-phenyl-*C*-cyano-*C*-(methylsulfonyl)ketenimine **15**. This compound was generated by FVT of ketene-*N,S*-acetal **14** at 440  $^\circ\text{C}$ . The spectrum of the neat film indicates an ordinary, bent, structure, with  $\nu_{\text{CNN}} = 2050 \text{ cm}^{-1}$  in good agreement with calculations for  $\epsilon = 1$  (2072  $\text{cm}^{-1}$ ) and far from predictions for the linear TS (2272  $\text{cm}^{-1}$ ). The spectra are shown in the Supporting Information.



### Conclusions

In the Ar matrix IR spectra, the cumulenic absorptions of dicyanoketenimines ( $\nu_{\text{CNN}}$ ) appear in the characteristic

range for bent ketenimines (2000–2090  $\text{cm}^{-1}$ ;  $\angle\text{CNR} \ll 180^\circ$ ). In contrast, neat film and some solution spectra show significant shifts of the CCN vibration to wavenumbers around 2200  $\text{cm}^{-1}$ , thereby indicating more linearized geometries ( $\angle\text{CNR} \sim 180^\circ$ ). This was confirmed by  $^{13}\text{C}$  NMR spectroscopy of **10c**, which suggests a strong contribution of resonance structure **7** with a linear array of atoms along the CCNR chain.

There is good agreement between the observed infrared spectra of the ketenimines isolated in Ar matrixes and the calculated spectra for the gas phase. There is little or no agreement between the neat film spectra and the Ar matrix. The higher wavenumbers observed in the neat film spectra resemble the calculated IR spectra of the linear transition states for nitrogen inversion. These high wavenumbers, and the linearized geometries, were reproduced by SCRF calculations, in which a reaction solvent field with a dielectric constant  $\epsilon$  of up to 40 was added. The variability of the observed ketenimine bands  $\nu_{\text{CNN}}$  in the IR spectra indicate that the structures of ketenimines are sensitive to effects of the media. Two cyano groups are required for this effect to materialize: for *C*-cyano-*N*-phenylketenimine **13** the neat film and Ar matrix spectra both agree with the calculated bent gas phase structure. Sulfonyl groups are less effective than cyano groups in enforcing linearity: there is only one example of a linear *C,C*-bis(methylsulfonyl)ketenimines (**3**), and then only in the crystalline solid. It is likely that this linearity is due to crystal lattice forces.

### Computational Method

Molecular orbital calculations<sup>24</sup> were carried out with the Gaussian 94<sup>25</sup> and Gaussian 98<sup>26</sup> systems of programs. All geometry optimizations were performed with the polarized split-valence 6-31G\* basis set<sup>24</sup> at the B3LYP level.<sup>27</sup> Wave function stability and harmonic vibrations (shown as wavenumbers, scaled by 0.9613<sup>28</sup>) were calculated at this level in order to characterize the stationary points as minima or saddle points and to evaluate zero-point vibrational energies (ZPVEs). Relative energies were also obtained using the expanded basis set 6-311+G(3df,2p) and the B3LYP method on the previously optimized 6-31G\* geometries, the aggregate

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method being B3LYP/6-311+G(3df,2p)//B3LYP/6-31G\*. The chosen method can be presumed to have an accuracy between B3LYP/6-311+G(2d,p)//B3LYP/6-31G\* and B3LYP/6-311+G(3df,2df,2p)//B3LYP/6-31G\*. When compared with the experimental data from the Gaussian G2 molecule set, these two methods had mean absolute deviations (standard deviations) of less than 13(12.5) and less than 11(11) kJ mol<sup>-1</sup> and largest errors of 57/-84 and 53/-39 kJ mol<sup>-1</sup>, respectively.<sup>29</sup> While the overall mean absolute deviation of the energies calculated with the chosen method is estimated at <13 kJ mol<sup>-1</sup>, the mean absolute deviation for closely related compounds would be expected to be smaller. Enthalpies were calculated using energy values from the higher level and an unscaled correction from the vibration calculation at the lower level. Entropies were taken directly from the vibration calculation at the lower level. The free energies were then calculated from these two values. The temperature used in the vibration calculations and hence the free energy values was 298.15 K. All transition state structures were characterized by having one imaginary vibration. These vibrations are listed in the Supporting Information. Self-consistent reaction field (SCRF) calculations<sup>29</sup> were performed in two steps. The volume of the structure was calculated and then used with the appropriate value in a Gaussian 98 SCRF dipole calculation to optimize geometry and obtain frequency data. If the geometry changed markedly, these two steps were repeated. A single point energy calculation using the expanded basis set was then performed within the SCRF.

## Experimental Section

**Materials.** Compound **3** was prepared according to the literature procedure.<sup>30</sup> Cyano-*N*-phenylketenimine **13** and its precursor, 3-methylthio-3-(phenylamino)acrylonitrile, were prepared according to ref 2.

**Matrix Isolation.** Argon matrixes were prepared by vacuum deposition of samples with argon (99.999%) onto a KBr window at ca. 25 K using a closed-cycle liquid helium cryostat (Air Products DE202 with a Lakeshore 330 temperature controller). In FVT experiments,<sup>31</sup> a mixture of argon and sample was led through a quartz tube (10 cm length, 0.8 cm inner diameter, equipped with heating wire and a thermocouple), and the product was isolated on the cold window at ca. 25 K. Photolyses were carried out using a 1000 W Hanovia Xe/Hg lamp equipped with a water filter. IR spectra were recorded at 7–17 K.

**Neat Isolation of Flash Vacuum Thermolysis Products.** The sample was sublimed in a high vacuum ( $1.0 \times 10^{-5}$  mbar) into the same quartz thermolysis tube as described above, and the thermolysates were isolated on a KBr window at ca. 130 K. IR spectra were recorded at 130–143 K.

**2-Cyano-3-methylthio-3-methylaminoacrylonitrile 9a.**<sup>32</sup> To a stirred solution of malononitrile (198 mg, 3.00 mmol) in dry THF (3 mL) at -78 °C was added butyllithium (2.5 M in hexane, 1.10 mL, 2.75 mmol) over 10 min. After the mixture was stirred for a further 0.5 h at -78 °C, methyl isothiocyanate (219 mg, 3.00 mmol in 2 mL of THF) was added over 15 min.

After being stirred at 0 °C for 0.5 h, the mixture was extracted with water and the extracts were washed with toluene. The aqueous extracts were stirred with methyl iodide (426 mg, 0.19 mL, 3.00 mmol) for 14 h at 4 °C. The precipitate was collected and recrystallized from ethanol to give colorless prisms of **9a** (146 mg, 39%): mp 117–118 °C; IR (KBr)  $\nu$  3322 s, 2209 s, 2187 vs, 1555 vs, 1496 w, 1402 s, 1287 m, 1157 vw, 972 vw, 923 w cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  6.53 (bs, 1 H), 3.20 (d, *J* = 5.1 Hz, 3 H), 2.67 (s, 3 H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  175.3, 115.60, 115.42, 51.8, 33.1, 17.2. Anal. Calcd for C<sub>6</sub>H<sub>7</sub>N<sub>3</sub>S: C, 47.04; H, 4.61; N, 27.43; S, 20.93. Found: C, 47.06; H, 4.62; N, 27.52; S, 20.78.

**Dicyano-*N*-methylketenimine 10a.** FVT of **9a** at 500 °C followed by deposition of the thermolysate as a neat film, or by co-deposition with argon onto a KBr window, gave rise to the following spectra: IR (film, 135 K)  $\nu$  2282 m, 2256 m, 2213 s, 2175 sh/m, 2100 m, 2086 m, 1441 w, 1396 w, 1370 w, 1321 w, 1241 w, 1030 vw, 907 vw cm<sup>-1</sup>; IR (Ar matrix, 13 K)  $\nu$  2948 w, 2259 m, 2235 m, 2138 vs, 2133 vs, 2122 vs, 2117 vs, 1570 m, 1528 m, 1457 m, 1411 m, 1218 m, 1111 m, 617 m, 486 m cm<sup>-1</sup>; additional peaks at  $\nu$  = 2939 w, 1446 m, 1436 w, 1070 w cm<sup>-1</sup> belong to MeSH.<sup>19</sup>

**2-Cyano-3-methylthio-3-ethylaminoacrylonitrile 9b** was prepared as described for **9a** from malononitrile (203 mg, 3.07 mmol), butyllithium solution (2.5 M, 1.10 mL, 2.75 mmol), ethyl isothiocyanate (260 mg, 0.25 mL, 2.98 mmol), and iodomethane (426 mg, 0.19 mL, 3.00 mmol) to give crystals after standing for 14 h at 4 °C. The precipitate was collected and recrystallized from ethanol/water yielding colorless crystals of **9b** (300 mg, 60%): mp 82–83.5 °C; IR (KBr)  $\nu$  3292 m, 2987 w, 2942 w, 2208 s, 2195 s, 1547 s, 1516 m, 1464 m, 1280 m cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  6.40 (bs, 1 H), 3.62 (dq, *J* = 7.2 and 5.9 Hz, 2 H), 2.67 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  174.3, 115.53, 115.26, 52.3, 41.7, 17.5, 15.2. Anal. Calcd for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>S: C, 50.28; H, 5.42; N, 25.13; S, 19.17. Found: C, 50.25; H, 5.44; N, 25.14; S, 19.20.

**Dicyano-*N*-ethylketenimine 10b.** FVT of **9a** above 500 °C followed by co-deposition of the thermolysates with argon onto KBr or FVT at 700 °C with isolation of the product as a neat film on KBr gave rise to the following spectra: IR (film, 134 K)  $\nu$  2255 m, 2172 vs, 2055 sh/w, 1415 m, 1375 m, 1330 m, 1280 m, 1240 m, 1173 w, 1086 m cm<sup>-1</sup>; IR (Ar matrix, 17 K)  $\nu$  3008 w, 2985 w, 2948 w, 2265 m, 2235 m, 2142 s, 2103 m, 2089 m, 1540 m, 1440 s, 1389 m, 1327 w, 1177 w, 1147 w, 1023 m, 949 s, 852 w, 798 w, 666 w, 578 w, 460 w cm<sup>-1</sup>.

**2-Cyano-3-methylthio-3-phenylaminoacrylonitrile 9c** was prepared as described for **9a** from malononitrile (1.54 g, 23.3 mmol), butyllithium solution (2.5 M, 8.70 mL, 21.8 mmol), phenyl isothiocyanate (3.10 g, 2.74 mL, 22.9 mmol), and iodomethane (3.20 g, 1.41 mL, 22.5 mmol). The precipitate was collected and recrystallized from ethanol yielding colorless crystals of **9c** (2.40 g, 48%): mp 174–178 °C; IR (KBr)  $\nu$  3292 vs, 2207 vs, 2197 vs, 2182 vs, 1595 m, 1520 s, 1493 s, 1451 m, 1264 m, 967 m cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 25 °C)  $\delta$  7.25–7.50 (m, 5 H), 3.10 (bs, 1 H), 2.51 (s, 3 H); <sup>13</sup>C NMR (50 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 25 °C)  $\delta$  172.5, 139.3, 130.1, 127.5, 124.8, 115.0 (two CN groups with identical shift), 56.1, 16.2. Anal. Calcd for C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>S: C, 61.37; H, 4.21; N, 19.52; S, 14.89. Found: C, 61.50; H, 4.26; N, 19.47; S, 14.70.

**Dicyano-*N*-phenylketenimine 10c.** FVT at 650 °C followed by co-deposition of the thermolysate with argon onto KBr or FVT above 700 °C with isolation of a neat film of the thermolysate on KBr gave rise to the following spectra: IR (film, 134 K)  $\nu$  2229 vs, 2173 s, 1491 m, 1442 m, 762 s cm<sup>-1</sup>; additional signals prevalent at lower pyrolysis temperatures at  $\nu$  2284 w, 2213 s, 2134 br/m, 2097 sh/m, 2084 sh/m, 2066 sh/m, 1464 m, 1424 m cm<sup>-1</sup> are possibly due to the imine tautomer of **9c**; IR (Ar matrix, 17 K)  $\nu$  3008 w, 2948 w, 2234 m, 2090 vs, 2077 sh/m, 1492 m, 1295 m, 1073 m, 760 s, 685 s, 580 m, 524 m cm<sup>-1</sup>.

**2-Cyano-3-azidocinnamionitrile 11.** Since azide **11** decomposes slowly at ambient temperature (20 °C), all steps should be carried out in ice-cooled vessels. At -20 °C, sodium azide (414 mg, 6.36 mmol) in water (1 mL) was added to

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2-cyano-3-chlorocinnamionitrile<sup>33</sup> (**41**, 400 mg, 2.12 mmol) in acetone (2 mL) with stirring. The resulting mixture was stirred for 6 h at 0 °C. After addition of ice–water (4 mL), a colorless precipitate was filtered off and thoroughly washed with ice–water, ice–water/acetone 10:1, and diethyl ether to yield **11** (331 mg, 80%) as a colorless powder: mp 75 °C dec; IR (KBr)  $\nu$  2226 m, 2148 s, 1581w, 1551 s, 1492 m, 1446 m, 1343 s, 1247 s, 1190 m, 1017 w, 776 m, 734 w, 701 m, 681 w, 555 w, 526 w  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , –50 °C)  $\delta$  7.72–7.67 (m, 1 H), 7.65–7.60 (m, 2 H), 7.56–7.52 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , –50 °C)  $\delta$  171.1, 133.8 ( $\text{C}_{\text{para}}$ ), 129.9 ( $\text{C}_{\text{meta}}$  or  $\text{C}_{\text{ortho}}$ ), 127.81 ( $\text{C}_{\text{ipso}}$ ), 127.55 ( $\text{C}_{\text{meta}}$  or  $\text{C}_{\text{ortho}}$ ), 112.7, 111.1 (CN), 71.1 (C2); the assignments are supported by a DEPT spectrum. MS (EI);  $m/z$  195 [ $\text{M}^+$ ] (13), 168 (16), 167 [ $\text{M}^+ - 28$ ] (100), 140 (14), 115 (38), 103 (73), 77 (81), 76 (18). Anal. Calcd for  $\text{C}_{10}\text{H}_5\text{N}_5$ : C, 61.54; H, 2.58; N, 35.88. Found: C, 61.51; H, 2.46; N, 35.89.

**Dicyano-*N*-phenylketenimine 10c and 2-Phenyl-3,3-dicyano-1-azirine 12.** Photochemical decomposition of **11** in an argon matrix at 8 K gave dicyano-*N*-phenylketenimine **10c** accompanied by small amounts of 2-phenyl-3,3-dicyano-1-azirine **12**. Photochemical decomposition of **11** in  $\text{CHCl}_3$  solution at 0 °C afforded **12** as the primary photoproduct which slowly polymerized to yield a bright red precipitate. In contrast, thermal decomposition of **11** in  $\text{CHCl}_3$  solution at 60 °C gave only a small amount of **12** and mainly **10c** (ca. 1:8 by  $^1\text{H}$  NMR integration). Presumably due to the higher reactivity of the ketenimine this mixture polymerized within a few minutes to afford a bright red precipitate. **Dicyano-*N*-phenylketenimine 10c** had the following spectra: IR (Ar matrix, 8 K)  $\nu$  3008 w, 2948 w, 2234 m, 2090 vs, 2077 sh, 1492 m, 1295 m, 1073 m, 760 s, 685 s, 580 m, 524 m  $\text{cm}^{-1}$ ; IR ( $\text{CHCl}_3$ )  $\nu$  2221 s, 2202 m, 2131 m, 2108 br  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , –50 °C)  $\delta$  7.66–7.54 (m, 3 H,  $\text{H}_{\text{meta}}$  and  $\text{H}_{\text{para}}$ ), 7.53–7.47 (m, 2 H,  $\text{H}_{\text{ortho}}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , –50 °C)  $\delta$  144.5 ( $\text{C}_{\text{ipso}}$ ), 132.9 ( $\text{C}_{\text{para}}$ ), 130.4 ( $\text{C}_{\text{ortho}}$  or  $\text{C}_{\text{meta}}$ ), 127.8 ( $\text{C}_o$  or  $\text{C}_m$ ), 126.8 (NCC), 110.3 (two identical CN), 21.2 (NCC). The assignments are supported by a DEPT spectrum. **2-Phenyl-3,3-dicyano-1-azirine 12** had the following spectra: IR (Ar matrix, 8 K)  $\nu$  2263 w, 1773 s, 1455 m, 1130 m, 872 m, 698 w  $\text{cm}^{-1}$ ; IR ( $\text{CHCl}_3$ )  $\nu$  2221 w, 2202 w, 1769 vs, 1598 s, 1490 s, 1452 s, 1318 w, 1250 m, 1146 w, 870 w, 683 s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  8.02–7.97 (m, 2 H,  $\text{H}_{\text{ortho}}$ ), 7.87–7.82 (m, 1 H,  $\text{H}_{\text{para}}$ ), 7.75–7.69 (m, 2 H,  $\text{H}_{\text{meta}}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  154.9 ( $\text{C}_{\text{ipso}}$ ), 137.0 ( $\text{C}_{\text{para}}$ ), 131.7 ( $\text{C}_{\text{ortho}}$ ), 130.3 ( $\text{C}_{\text{meta}}$ ), 116.6 (C2), 113.6 (CN), 12.3 (C3). The assignments are supported by DEPT, HSQC, and HMBC  $^1\text{H}/^{13}\text{C}$  COSY spectra.

**2-Methylsulfonyl-3-methylthio-3-(phenylamino)acrylonitrile 14.** Butyllithium (2.8 mmol as a 2.5 M solution in hexanes) was added to a solution of methylsulfonylacetonitrile<sup>30a</sup> (364 mg; 3 mmol) in dry THF (3 mL) in the course of 10 min at –78 °C. After stirring for a further 0.5 h at this temperature, phenyl isothiocyanate (407 mg; 3 mmol) in 2 mL of THF was added in the course of 15 min. The resulting solution was stirred for 0.5 h at 0 °C and then extracted with water (3  $\times$  4 mL), and the extracts were washed with toluene (5 mL). To the aqueous extract was added iodomethane (456 mg; 3 mmol), and the mixture was stirred for 14 h at 4 °C. The precipitated material was collected and recrystallized from ethanol to give 263 mg (33%) of colorless prisms: mp 137–139 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.4–7.3 (m, 5 H), 3.2 (s, 3 H), 2.2 (s, 3 H), 1.7 (br s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  167, 130, 127, 124, 115, 86, 44, 17. Anal. Calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$ : C, 49.23; H, 4.51; N, 10.44. Found: C, 49.03; H, 4.44; N, 10.35.

**Cyano(methylsulfonyl)-*N*-phenylketenimine 15.** FVT of **14** at 300 °C gave unchanged starting material. FVT of **14** at 440 °C with deposition of the thermolysate as a neat film on KBr gave rise to the following spectrum: IR (film, 134 K)  $\nu$  2220 w, 2050 vs, 1590 m, 1568 m, 1490 m, 1453 w, 1152 m, 765 m  $\text{cm}^{-1}$ .

**Acknowledgment.** U.M. is a Feodor Lynen post-doctoral fellow and thanks the Alexander von Humboldt-Stiftung (Germany) for financial support. This work was also supported by the Australian Research Council.

**Supporting Information Available:** Expanded version of Table 1, showing absolute energies and dipole moments for the compounds in Table 1; table of inversion barriers, CCN vibrations, and absolute energies of ketenimines with *N*-amino, *N*-hydroxy, *N*-fluoro, *N*-chloro, *N*-trifluoromethyl, *N*-cyano, *N*-formyl, and *N*-acetyl substituents, the latter two also with *C,C*-dicyano substituents; expanded tables corresponding to Table 2 showing full calculated coordinates of the CCN and CN IR bands of **10a–c** and **13**; Cartesian coordinates, absolute energies, and full IR spectra of all calculated ketenimines in their ground states and transition states for *N*-inversion with appropriate imaginary frequencies; figures of the experimental IR spectrum of ketene *N,S*-acetal **14** and ketenimine **15** and the calculated IR spectra of **15** (ground and transition states);  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of ketenimine **10c** and azirine **12**, and HSQC and HMBC  $^1\text{H}/^{13}\text{C}$  2D NMR spectra of **12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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