for a rigorous definition of sterically crowded molecules. Such a definition does not involve any empirical quantities. In addition, the concept of the van der Waals radii can be replaced by that of contact interatomic separations (CISs). In this manner, not only the bonding patterns but also the pairs of sterically interacting atoms can be pinpointed solely from the knowledge of the electron density. To paraphrase the well-known statement of Levy,[24] one deals with "electron densities in search of steric interactions in molecules".

The computed values of CIS are only weakly dependent on the quality of basis sets used in computation of the electron density. In addition, they appear to be transferable between similar (meaning with analogous atomic connectivities) molecules.

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Registry No. Biphenyl, 92-52-4; 2,6-difluorobiphenyl, 2285-29-2; 2,2-difluorobiphenyl, 388-82-9; 2,2′,6,6′-tetrafluorobiphenyl, 781-16-8.

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An ab Initio Study of a Retro-Wolff Rearrangement: From Diazafulvenone to Cyanovinyl Isocyanate without a Singlet α-Oxocarbene Intermediate

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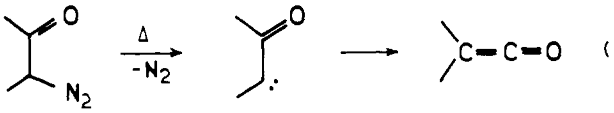
Abstract: Ab initio molecular orbital calculations have been used to study the unimolecular rearrangement of diazafulvenone leading to cyanovinyl isocyanate. The geometries of stationary points were optimized at HF/6-31G** while relative energies were obtained from multireference configuration interaction (MRCISDQ) calculations with the 6-31G** basis set. A singlet oxocarbene structure was not found to be a local minimum but rather a transition structure connecting diazafulvenone to isocyanovinyl isocyanate, the latter molecule being a distinct intermediate during the rearrangement to cyanovinyl isocyanate. Diazafulvenone is calculated to lie 14 and 32 kcal/mol, respectively, above isocyano- and cyanovinyl isocyanate (*Z* conformers) and to be separated from the isocyanide form by an energy barrier of 44 kcal/mol. The diazafulvenone → isocyanovinyl isocyanate interconversion, which can be regarded as a retro-Wolff rearrangement, is thus a concerted reaction without a discrete singlet oxocarbene intermediate. It also constitutes the rate-determining step of the entire rearrangement process, in agreement with experimental observation. As shown by an analysis of localized orbitals, the diazafulvenone → isocyanovinyl isocyanate interconversion involves six electron pairs that circulate following a cyclic motion.



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In organic synthesis, the Wolff rearrangement is conveniently employed to convert α-diazo ketones **1** and related compounds to ketenes **3** (eq 1).[1] Although singlet α-oxocarbenes **2** are commonly assumed to be transient intermediates, there is until now neither kinetic nor spectroscopic evidence for their existence.[2] According to the principle of microscopic reversibility, such evidence could also be found by investigating the reverse transformation, namely, the rearrangement of ketenes. MO calculations[3] showed however, that α-oxocarbene lies much higher in energy than ketene, thus rendering the **3** → **2** reaction extremely difficult. In fact, a retro-Wolff rearrangement is rare. Burton and Groh[4] studied the decomposition of hydridosilylketenes and claimed to have the first example of a retro-Wolff rearrangement. However, the evidence is not unequivocal; the formation of the reaction products can be interpreted by involving other reaction mechanisms. Hochstrasser and Wirz[5] reported the reversible formation of ethynol (HC≡C—OH) by photolysis of ketene ($H_2C{=}C{=}O$) in an argon matrix. They suggested that the reaction occurs via decarbonylation of ketene followed by insertion of CO into a C–H bond of methylene and hydrogen transfer to oxygen. More importantly, no evidence for the formation of formylmethylene has been found by these authors.[5] Recently, Bender, Meutermans, and Wentrup[6] investigated the rearrangement of different heterocyclic ketenes using the flash vacuum pyrolysis (FVP) technique and have found that the outcome of the reactions can be formally rationalized in terms of a retro-Wolff rearrangement.

The diazofulvenone **4**, generated in situ following thermal decomposition of methyl imidazole-2-carboxylate, was found[6] to

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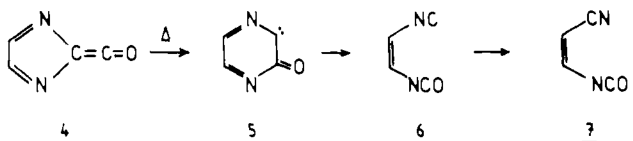
undergo unimolecular rearrangements leading finally to the formation of cyanovinyl isocyanate **7**.[6] The latter can be isolated



4 5 6 7

at low temperatures and unambigously identified by IR spectroscopy. In going from the ketene **4** to the isocyanate **7**, four atoms have thus changed their original positions. This fact clearly indicates a multistep transformation for the **4** → **7** reaction. As an interpreation for the formation of **7**, Bender and co-workers[6] proposed a mechanism involving the oxocarbene **5** and isocyanate **6** as intermediates. The intermediacy of isocyanovinyl isocyanate **6** in the process seems to be realistic; its isomerization into the more stable isomer **7** under high temperature conditions (>850 °C) should be rapid, thus rendering its detection quite difficult. With regard to the carbene **5**, experimental results[6] do not disprove, neither do they prove, its formation. If formed, the **4** → **5** conversion corresponds phenomenologically to a retro-Wolff rearrangement by involving migration of the C═O group to one of the two nitrogen atoms in **4** followed by ring expansion.[6] In this context, the question of particular interest is whether or not the α-oxocarbene **5** exists as a distinct intermediate during transformation of ketene **4**. In the present work, we attempt to tackle this question using ab initio molecular orbital calculations. We have explored extensively the portions of the potential energy surface containing the reaction pathway **4** → **7** and found no local minimum corresponding formally to an α-oxocarbene structure **5**.

Details of Calculations

Geometries of five stationary points were optimized at the single determinantal Hartree–Fock level of MO theory using the split-valence 3-21G and dp-polarization 6-31G** basis sets.[7] Harmonic vibrational wavenumbers were computed at the HF/3-21G level in order to characterize stationary points (as minima and transition structures) and to estimate the zero-point energy contributions to the relative energies between stationary points. The latter quantities were computed at the HF/6-31G**-optimized geometries and with the 6-31G** basis set using different types of correlated wave functions that include the Møller–Plesset perturbation theory (MPn)[8] and single-reference, and multireference configuration interaction methods. In the MPn calculations, the seven core orbitals are kept frozen. A single-reference configuration interaction calculation with dimension of 5000 was first carried out for the five stationary points within the single and double excitation scheme (CISD) employing the HF molecular orbitals as reference sets. This preliminary CISD calculation was necessary to identify important configurations which should be used in the following multireference configuration interaction (MRCI) calculations.[9] An extended MRCI calculation was thus performed accordingly using 10 reference configurations in each structure which give rise to $\sum_i C_i^2 \simeq 0.9$, where C_i (i = 1–10) are the coefficients of the reference configurations. The coefficients of the first and second CI terms amount approximately to 0.92 and 0.12, respectively. As orbitals of the active space, the lower-lying 75 MO's of each structure considered have been employed whereby the core orbitals were not kept frozen. A separate CISD calculation with a larger dimension of about 40.000 was also performed in order to have a direct comparison with the MPn results. Finally, the correction which accounts for the quadruple excitations was also considered (CISD(Q) and MRCISD(Q)). While all the HF and MPn calculations were carried out using the GAUSSIAN 88 program[8] implemented on an IBM 3090 computer (K.U. Leuven), the CI calculations were performed with the MELD program package[9] implemented on a CRAY X-MP/28 computer (ETH-Zürich). Unless otherwise noted, our relative energies mentioned hereafter are obtained from MRCISD(Q)/6-31G** calculations corrected for zero-point energies. In order to interprete the reaction mechanism, the localized orbitals were computed using HF/6-31G** wave functions and the Boys[10] method. Throughout this paper, bond lengths are given in angström, bond angles in degrees, total energies in hartrees, and zero-point and relative energies in kcal/mol.

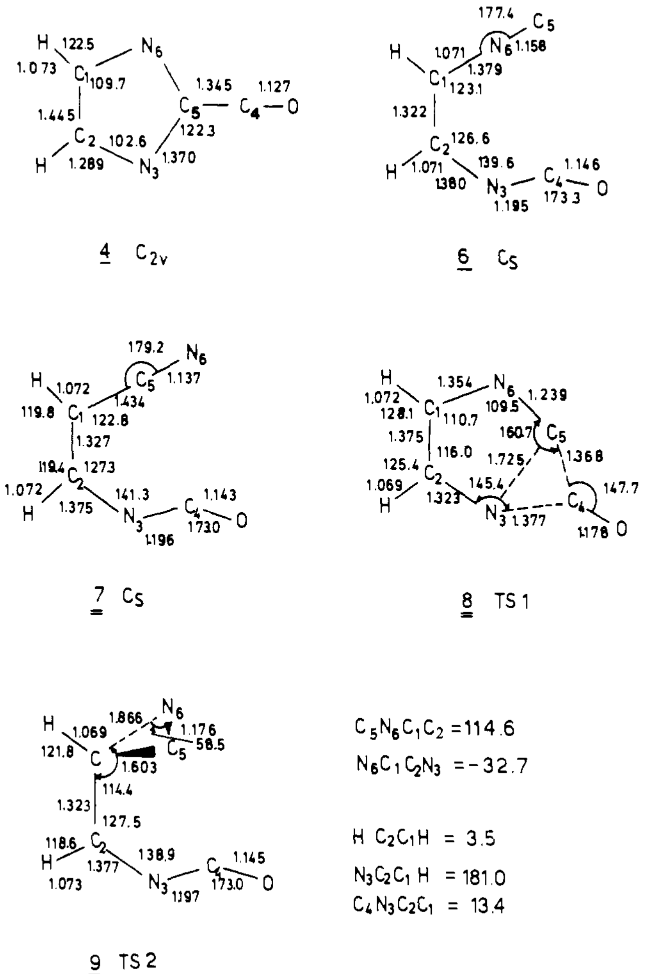
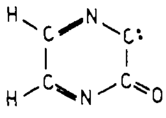


Figure 1. HF/6-31G**-optimized geometries for five points on the diazafulvenone potential energy surface.

Results and Discussion

We have located five stationary points on the singlet potential energy surface of interest. The relevant HF/6-31G** optimized geometrical parameters are displayed in Figure 1. The diazafulvenone **4**, isocyanovinyl isocyanate **6**, and cyanovinyl isocyanate **7** are found to be energy minima having all vibrational wavenumbers real. Structures **8** (TS1) and **9** (TS2) are both characterized as transition structures with one imaginary wavenumber.

For both isocyanates, we have considered only the *Z* conformers that are the primary products of the rearrangement. Of course, the *E* isomers also exist, but if formed they apparently are not involved in the chemical process under consideration. Extensive attempts were made to locate a local energy minimum having an oxocarbene structure **5**, but such a minimum has not been found at the HF/6-31G** level; all optimizations starting with that form



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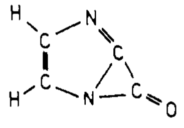

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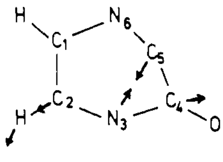
Table I. Calculated Total (hartrees), Zero-Point Vibrational (kcal/mol), and Relative (kcal/mol) Energies for Five Stationary Points Considered at Different Levels Using the 6-31G** Basis Set

level[a]	**4** (ketene)	**6** (isocyanide)	**7** (cyanide)	**8** (TS1)	**9** (TS2)
Total Energies					
HF	−336.340 64	−336.345 65	−336.375 38	−336.247 06	−336.274 02
MP2	−337.343 06	−337.324 02	−337.364 79	−337.282 04	−337.265 21
MP3	−337.343 36	−337.328 21	−337.363 85	−337.264 84	−337.267 17
MP4	−337.411 13	−337.398 34	−337.435 22	−337.349 26	−337.340 78
CISDQ[c]	−337.053 32	−337.074 36	−337.105 75	−336.970 29	−336.988 62
MRCISDQ[c]	−337.064 35	−337.085 39	−337.113 91	−336.990 72	−337.033 43
C_0(MRCISD)[d]	0.920	0.923	0.922	0.922	0.885
ZPE[b]	34.7	33.5	34.0	32.8	31.5
Relative Energies					
HF	0.0	−3.1	−21.8	58.7	41.8
MP2	0.0	11.9	−13.6	38.3	48.9
MP3	0.0	9.5	−12.9	49.3	47.8
MP4	0.0	8.0	−15.1	38.8	44.1
CISDQ	0.0	−13.2	−32.9	52.1	40.6
MRCISDQ	0.0	−13.2	−31.1	46.2	19.4
MRCISDQ+ZPE[e]	0.0	−14.4	−31.8	44.3	16.2

[a] Using HF/6-31G** geometries given in Figure 1. [b] Zero-point energies computed at HF/3-21G and scaled by 0.9 to account for typical overestimation. [c] Quadruple contributions using the Davidson's correction. [d] Coefficients of the reference configurations in MRCISD wave functions. [e] Including MRCISDQ relative energies and ZPE's.

eventually converged either to ketene **4** or to isocyanide **6**. Starting geometries having the bicyclic form **10** were also considered, but again the supersystem always collapses to isocyanide **6** following energy minimization. We should stress that the search was carried out with much care. The Hessian mode following algorithm[11] was employed, and the full Hessian matrix was computed analytically at the HF/6-31G** level after each iteration of the optimization procedure with the hope of obtaining an appropriate curvature on the potential surface leading to an α-oxocarbene minimum.

The only oxocarbene structure that we have been able to locate is the transition structure **8** (TS1). The normal coordinates of its imaginary vibrational mode are given in **11**. The largest components of the transition vector **11** are situated on the N_3, C_4, and C_5 atoms. At first sight, this reaction mode resembles well an intramolecular insertion of the isocyanide carbon C_5 into the C_4=N_3 double bond in isocyanovinyl isocyanate **6**. In order to ascertain the identity of **8**, we have performed optimizations with small distortions on the geometry of **8** toward both sides of the transition vector. With a N_3C_5 distance smaller than that of **8** (1.725 Å), the supermolecule minimized to ketene **4**, whereas, with larger values for both N_3C_5 and C_4C_5 distances (or smaller values for N_3C_4 distance), the supermolecule went down to isocyanide **6**. This is similar to the observation mentioned above during the search for an oxocarbene minimum. Although this search for reaction path does not employ the intrinsic reaction coordinate, it does show unambiguously that **8** is the transition structure interconverting diazafulvenone **4** and isocyanovinyl isocyanate **6**. There is thus no distinct intermediate between both equilibrium structures **4** and **6** on the HF/6-31G** potential energy surface. Similarly, the saddle point **9** (TS2) was confirmed as the transition structure linking both isocyanate **6** and cyanide **7** molecules.



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Diazafulvenone **4** is calculated to have a C_{2v} symmetry. The rather large C=N bond distance (1.289 Å versus 1.250 Å in H_2C=NH) indicates a certain electronic delocalization within the five-membered ring. Within the ketene moiety, the C_5=C_4 distance is also stretched (1.345 Å with respect to 1.306 Å in H_2C=C=O), while the C_4=O distance (1.127 Å) is now closer to that in free monoxide carbon (1.145 Å in H_2C=C=O and 1.114 Å in CO at the same level). For both isocyanates **6** and **7**, a noticeable point concerns the apparently large $C_2N_3C_4$ bond angles. However, the values of 139.6° in **6** and 141.3° in **7** are both smaller than that of 142.3° calculated for vinyl isocyanate (H_2C=CHNCO) at the same level. With regard to the transition structure **8**, it is worthwhile to note that (i) the value for each of the C_1–C_2, C_2–N_3, C_1–N_6, and C_5–N_6 distances is close to the average of the corresponding values in ketene **4** and isocyanate **6**; (ii) both the C_4–C_5 (1.368 Å) and the N_3–C_4 (1.377 Å) distance are relatively short, while the N_3–C_5 distance is rather long (1.725 Å). This indicates that, as the C_4O group in ketene **4** migrates into the middle region of the N_3–C_5 bond, the latter is broken followed by the formation of a new N_3–C_4 bond. For its part, the saddle point **9** (TS2) resembles closely the transition structure previously reported for the (hydroxyvinyl)isocyanide–cyanide (HOCH=CHCN) rearrangement[12] in that the C_1–N_6 distance was also found to be longer (by 0.211 Å at HF/3-21G) than the C_1–C_5 distance.

Table I lists total and relative energies of five stationary points calculated at different levels. At all levels considered, cyanide **7** is found to be the most stable form. As compared with the MRCI value of 31.1 kcal/mol, the MPn values for the energy difference between **4** and **7** are significantly reduced. Similarly, MPn calculations predict a higher stability of ketene **4** with respect to isocyanide **6**, in contrast with configuration interaction results. Of the two transition structures **8** and **9**, **9** (TS2) is computed by MPn calculations to be higher in energy than **8** (TS1), whereas CI calculations yield a reversed energy ordering. These results point toward a slow convergence of the MP perturbation expansions for the structures under consideration that all contain multiple bonds. As a matter of fact, the erratic behavior of the MP perturbation theory in describing the structures and energies of closed-shell species containing multiple bonds is now well documented.[13] The values of the C_0 coefficients seen in Table I also indicate a particular need of a multiconfigurational treatment for the transition structure **9**. Apart from this, the similarity between both CISDQ and MRCISDQ results points out that the remaining structures can be well represented by wave functions based on single determinant HF references. Thus, it is likely that a singlet α-oxocarbene minimum will not be found

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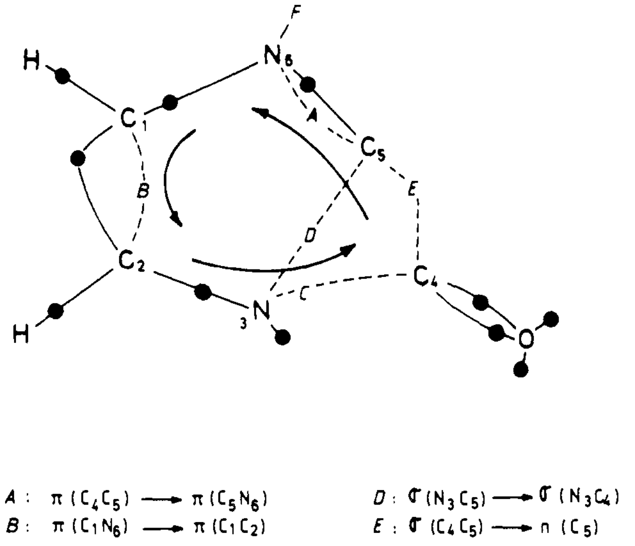

Figure 2. Centroids of charge of the Boys localized orbitals in the transition structure **8** projected in the molecular plane. A, B, C, D, E, and F are the electron pairs that participate in the bond redistribution while filled circles (●) are the pairs that remain unchanged during the rearrangement.

even if a full geometry optimization at a multiconfigurational level could be performed.

Our best estimates obtained from MRCISDQ/6-31G** calculations predict diazafulvenone **4** to lie 14.4 and 31.8 kcal/mol, respectively, above isocyanide **6** and cyanide **7**. Despite its high energy, ketene **4** is predicted to be separated from isocyanide **6** by a substantial energy barrier of 44.3 kcal/mol which is, however, well within reach in the FVP experiment.[6] The energy different between both isocyanide **6** and cyanide **7** amounts to 17.4 kcal/mol in favor of the latter. We note that, for the HNC–HCN pair, their energy difference has been calculated using various correlated wave functions to be between 13 and 16 kcal/mol[14] (the experimental value being 14.8 ± 2 kcal/mol[15]). The conversion of isocyanide **6** to its more stable isomer **7** has an energy barrier of 30.6 kcal/mol. This value should, however, be taken with caution because the geometry of **9** is, as discussed above, probably not well reproduced by HF wave functions. Nevertheless, the above value is comparable with experimental barriers for the isocyanide–cyanide rearrangment of aromatic isocyanides[16] (about 35 kcal/mol at 185 °C). In any case, the TS1 **8** is expected to lie higher in energy than the TS2 **9**. In other words, the conversion of diazafulvenone **4** to isocyanovinyl isocyanide **6** constitutes the rate-determining step of the entire process **4** → **7**. This is in agreement with experimental results reported by Bender and co-workers[6] in which no isocyanide has been detected in their low-pressure pyrolytic reaction.

Finally, we have also analyzed the movement of the Boys localized orbital centroids[10] in the structures **4**, **6**, and **8**. Figure 2 displays the positions of charge centroids calculated for the transition structure **8** and summarizes the bond reorganization along the **4** → **6** rearrangement. Six electron pairs in all are involved in the electron redistribution that occurs in a cyclic way. The C_4O group migrates, leaving both electron pairs of the C_4–C_5 bond of **4** behind (pairs A and E). The latter will be moving forward to form a multiple bond and a lone pair of the isocyanide C_5N_6 group. The consequence of a cyclic electronic migration leads to the formation of a $C_1{=}C_2$ double bond from an electron pair of the original $C_1{=}N_6$ double bond (pair B). The new $C_4{=}N_3$ double bond of the isocyanate moiety in **6** is apparently formed with the arrival of an electron pair from the initial $C_2{=}N_3$ bond (pair C) and another originally from the N_3–C_5 bond (pair D) which is already broken down at the transition structure **8**. When the transition state is passed on the reaction path, the lone pair of N_6 is moving to complete the formation of the $C_5{\equiv}N_6$ triple bond (pair F).

In conclusion, the most significant chemical result of the present molecular orbital study is a proposition that the singlet α-oxocarbene **5** does not exist as a distinct intermediate during a retro-Wolff-type rearrangement of diazafulvenone **4** leading to cyanovinyl isocyanate **7**. In this rearrangement, isocyanovinyl isocyanate **6** is a genuine intermediate and its formation from the initial ketene **4** occurs in a concerted way involving a singlet α-oxocarbene-type transition structure and constitutes, in addition, the rate-determining step for the whole chemical rearrangement **4** → **7**. The energy barrier of ca. 44 kcal/mol for the rearrangement **4** → **6** is easily reached in the FVP reactions which typically requires temperatures about 700 °C, thus making it difficult to observe both **4** and **6** directly.[6]

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Registry No. **4**, 99560-57-3; **6**, 140438-49-9; **7**, 140438-50-2.

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