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Dimethoxycarbene: Conformational Analysis of a Reactive Intermediate

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Dedicated to Prof. R. W. Hoffmann

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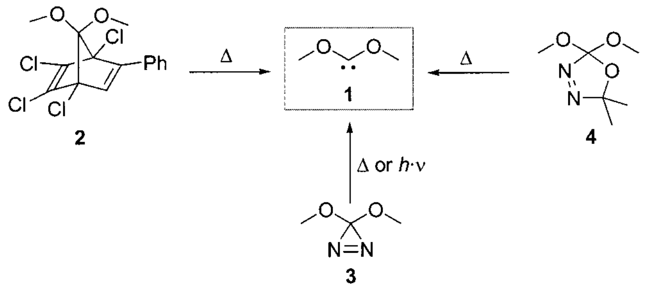
Dimethoxycarbene was prepared from an oxadiazoline precursor under high-vacuum flash pyrolysis (HVFP) conditions and was trapped at low temperatures by matrix isolation techniques (Ar, 10 K). The excellent agreement between the computed [CCSD(T)/cc-pVDZ] IR spectrum of the mixture of conformers of dimethoxycarbene and the experimentally measured IR absorptions allows a detailed analysis of the conformational preference of dimethoxycarbene. Its UV spectrum is in agreement with earlier studies and our TD-B3LYP/6-311+G(d,p) computations. The computed [CCSD(T)/cc-pVDZ] rotational profile is rather steep and separates the *s-trans*,*s-trans* and *s-cis*,*s-trans* conformers by a 16 kcal mol^{-1} barrier, whilst the *s-cis*,*s-cis* conformer is too high-lying to be observable (+17 kcal mol^{-1}). In marked contrast with the *gauche*,*gauche* minimum of dimethoxymethane, the *s-trans*,*s-trans* conformer of dimethoxycarbene is slightly preferred (0.5 kcal mol^{-1}). The *s-cis*,*s-trans* conformer equilibrates at the high temperatures required during HFVP generation and both conformers can be identified in the IR spectrum of the argon matrix at 10 K. The conformational preference is partly due to the minimization of the overall dipole moment in the *s-trans*,*s-trans* conformer.

Introduction

While Group 5 electronic ground state singlet heterocarbenes are structurally very well characterized, their chalcogen-heterosubstituted analogues have proven to be far more elusive, owing to their lower stabilities.[1] Free dithiocarbenes, for instance, have only just recently been generated and examined under conditions that allow their direct spectroscopic identification.[2] Although dimethoxycarbene (**1**, Scheme 1) can readily be generated and trapped with a variety of reagents, there are, for example, no infrared data that would allow a more detailed examination of the conformational preference of this prototypical species.

In the early 1970s, Hoffmann and co-workers were the first to generate **1** by heating the norbornadiene derivative **2** at 140 °C.[3] This results in the formation of tetrachlorobiphenyl and **1**, as is evident from its reactions with chemical traps.[3,4] In 1987, Moss et al. synthesized dimethoxydiazirine (**3**) as a thermal and photochemical precursor for the generation of **1**.[5] This elegant method suffers, however, from the low thermal stability of the diazirine, which decomposes in solution at room temperature.[6,7] Warkentin et al. prepared the far more stable precursor **4**, which produces **1** together with acetone and nitrogen upon heating.[8] This convenient carbene source was the key for a variety of interesting reactions between **1**, generated in situ, and electron-poor olefins and acetylene derivatives in reactions that could be compared with those of other precursors.[9] Direct evidence for **1** has been obtained from photoelectron spectroscopy and neutralization-reionization mass spectrometry through the gas-phase pyrolysis of **4**[10] and from UV/Vis studies of the photolysis of diazirine precursor **3** in organic glasses at 77 K, as well as from laser flash photolysis of **3** in pentane at room temperature.[6] To the best of our knowledge, though, **1** has not been characterized by IR



Scheme 1. Generation of dimethoxycarbene (**1**) from different precursors.

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spectroscopy, nor is there a connected high-level computational study on the rotamer structures of this fundamental organic reactive intermediate. With the aid of a combination of high-vacuum flash pyrolysis (HVFP) of the easily accessible oxadiazoline precursor **4** with matrix isolation techniques and high-level computations, here we provide a thorough structural characterization of dimethoxycarbene (**1**).

Results and Discussion

Oxadiazoline **4**, prepared by the procedure of Warkentin et al.,[8] was evaporated from a precooled storage bulb (–45 °C, pressure ca. 10^{-4} bar) into a quartz pyrolysis tube (inner diameter: 8 mm, length of heating zone: 50 mm), connected to the vacuum shroud of a closed-cycle refrigerator system. Immediately after leaving the tube, after a distance of about 50 mm, the pyrolysis products were co-condensed with a large excess of argon on the surface of a cold (10 K) CsI or BaF_2 window. The thus formed argon matrices were investigated by FTIR and UV/Vis spectroscopy, with several pyrolysis experiments being performed at temperatures from 300 to 700 °C in order to determine the optimal reaction temperature (Scheme 2).

At ca. 400 °C the conversion was nearly total, whilst the extent of the secondary cleavage of dimethoxycarbene (**1**) into CO_2 and the CH_3 radical (broad, structured IR bands at 620–600 cm^{-1}) was low (Figure 1, A); these were the main products at pyrolysis temperatures around 700 °C. As has also been found in the case of the bis(thioalkoxy) analogue of **4**,[2] matrix photolysis does not yield even a trace of carbene **1**, with methyl carbonate (**6**) and 2-diazopropane (**7**) being formed instead. Astonishingly, the former product is generated exclusively in the thermodynamically less stable *s-cis* conformation, as deduced from comparisons of the DFT computated and experimentally measured IR spectra.

The IR spectrum of the matrix-isolated pyrolysis products shows a rather complex mixture of some unreacted precursor **4**, acetone (**5**), and an additional set of bands. Irradiation of the matrix at λ = 254 nm (low-pressure mercury lamp) resulted in the fast and complete disappearance not only of this set of IR absorptions (Figure 1, B) but also of the UV band (Figure 4), with all absorptions diminishing at the same rate and the only photolysis reaction product being methyl acetate (**8**). We infer from comparison of the

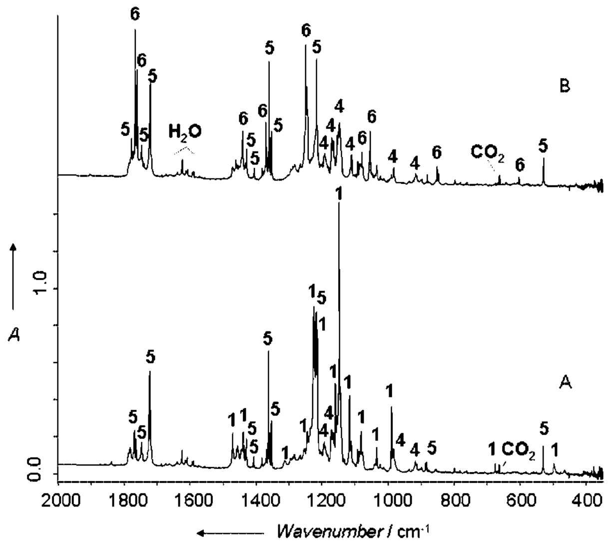


Figure 1. A: IR spectrum of the matrix-isolated (Ar, 10 K) pyrolysis products of the HVFP (400 °C) of oxadiazoline **4**. B: The same matrix after 15 min irradiation at λ = 254 nm with a low-pressure mercury lamp.

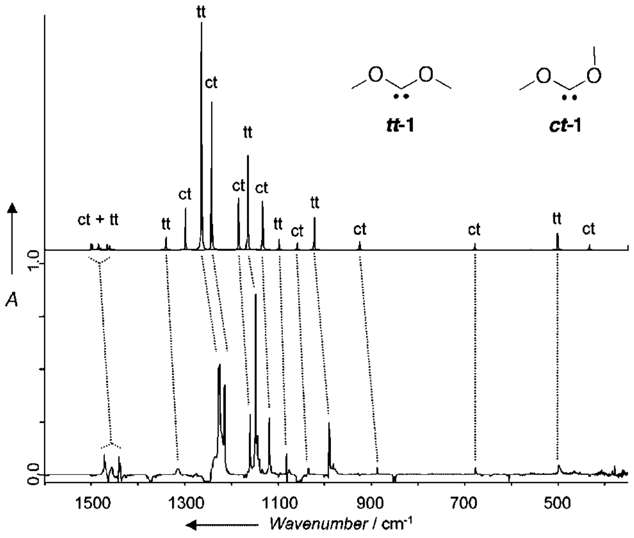
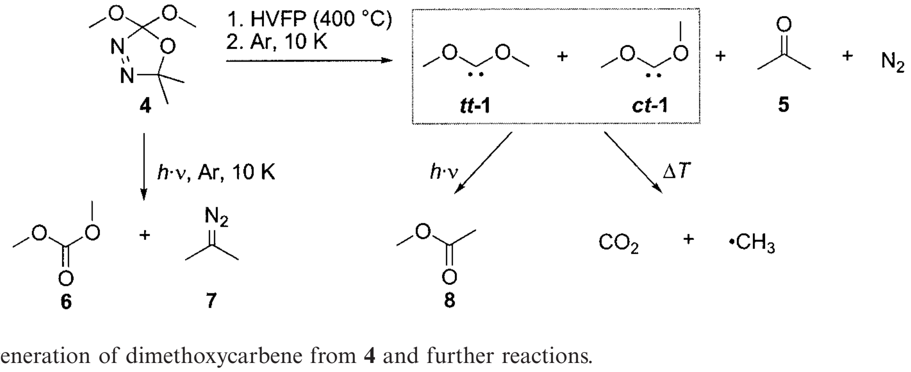


Figure 2. IR difference spectrum (pyrolysate minus irradiated pyrolysate) monitoring the photorearrangement of dimethoxycarbene (*tt*)-**1** and (*ct*)-**1** (positive bands) into methyl acetate (**8**) (negative bands, truncated). *Top*: Computed [CCSD(T)/cc-pVDZ] IR spectrum of a 1:1 mixture of dimethoxycarbene (*tt*)-**1** and (*ct*)-**1**.



Scheme 2. Thermal generation of dimethoxycarbene from **4** and further reactions.

difference IR spectra (Figure 2) of the irradiated and non-irradiated matrices with the computed vibrational spectra (Table 1) that only the *s-trans*,*s-trans* (*tt*) and *s-cis*,*s-trans* (*ct*) conformers of dimethoxycarbene (**1**) were formed in the pyrolysis (cf. Figure 3); no other conformers were present within our detection limits. Apart from the CH stretch-

Table 1. Comparison of computed (unscaled) and experimentally measured IR absorption frequencies of dimethoxycarbene (*ct*)-**1**.

Symmetry	Approx. description	B3LYP/6-311+G**	CCSD(T)/cc-pVDZ	Experiment (Ar matrix, 10 K)
a″	CH$_3$-twist.	90.2 (0.8)	95.6 (0.7)	–
a″	CH$_3$-twist.	154.0 (2.2)	171.8 (3.4)	–
a″	COCOC-o.o.p.def.	197.5 (2.4)	226.0 (0.4)	–
a′	COC-def.	241.8 (9.6)	260.6 (8.6)	–
a″	COCOC-o.o.p.def.	390.4 (0.2)	387.9 (0.2)	–
a′	COC-def.	415.2 (11.7)	433.3 (9.5)	–
a′	CO-str.+OCO-def.	679.8 (15.3)	679.0 (11.9)	675.4 (w)
a′	CO-str.	876.3 (13.9)	925.8 (16.4)	885.5 (w)
a′	CO-str.+CH$_3$-def.	1039.2 (19.2)	1058.9 (14.2)	1033.8 (w)
a′	CH$_3$-def.+CO-str.	1124.7 (164.9)	1133.2 (131.3)	1116.9 (m)
a″	CH$_3$-def.+CO-str.	1139.8 (1.3)	1146.9 (2.1)	–
a″	CH$_3$-def.	1179.4 (0.6)	1179.3 (1.2)	–
a′	OCO-str.+CH$_3$-def.	1171.4 (132.6)	1184.4 (106.3)	1158.3 (m)
a′	OCO-str.+CH$_3$-def.	1234.4 (256.3)	1242.5 (305.6)	1213.4 (s)
a′	OCO-str.	1287.9 (60.7)	1298.4 (74.7)	1243.9 (w)
a′	CH$_3$-def.	1455.2 (0.8)	1451.4 (0.7)	1436.6 (w)[a]
a′	CH$_3$-def.	1466.7 (21.0)	1466.2 (4.2)	1439.1 (w)[a]
a″	CH$_3$-def.	1485.9 (8.4)	1480.5 (4.6)	1453.2 (w)[a]
a′	CH$_3$-def.	1490.2 (22.7)	1484.7 (14.1)	1454.8 (w)[a]
a″	CH$_3$-def.	1492.3 (8.6)	1487.0 (4.4)	1467.4 (w)[a]
a′	CH$_3$-def.	1501.1 (15.1)	1497.5 (7.6)	1470.6 (w)[a]
a′	CH-str.	3048.3 (47.9)	3064.4 (52.5)	2900.0 (w)[b]
a′	CH-str.	3059.0 (21.0)	3073.8 (24.2)	2925.2 (w)[b]
a″	CH-str.	3130.6 (18.2)	3159.6 (24.6)	2966.5 (w)[b]
a″	CH-str.	3138.9 (20.0)	3169.4 (25.2)	3017.9 (w)[b]
a′	CH-str.	3143.4 (7.0)	3178.8 (8.5)	3020.9 (w)[b]
a′	CH-str.	3164.3 (14.7)	3193.8 (19.0)	3048.2 (w)[b]

[a] 1430–1470 cm^{-1}: strongly overlapping bands of (*tt*)-**1** and (*ct*)-**t**, individual assignments not possible. [b] 2900–3050 cm^{-1}: strongly overlapping bands of (*tt*)-**1** and (*ct*)-**t**, individual assignments not possible.

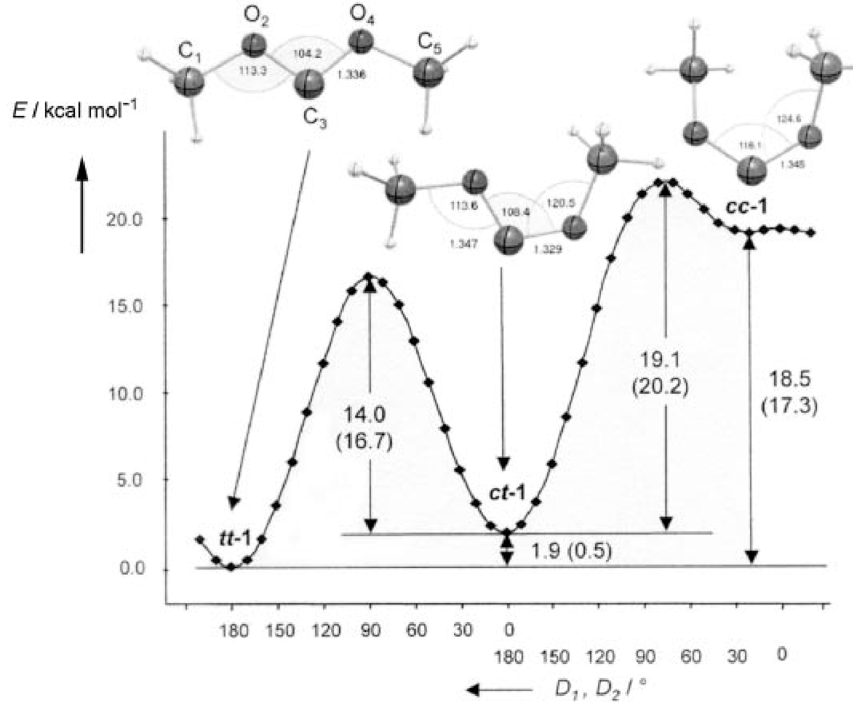


Figure 3. Computed energy profile [B3LYP/6-311+G(d,p)] of the internal rotations around the dihedral angles D_1 ($C^1O^2C^3O^4$) and D_2 ($C^5O^4C^3O^2$) in dimethoxycarbene **1**; fully optimized CCSD(T)/cc-pVDZ + ZVPE (values in parentheses).

Table 2. Comparison of computed (unscaled) and experimentally measured IR absorption frequencies of dimethoxycarbene (*tt*)-**1**.

Symmetry	Approx. description	B3LYP/6-311+G**	CCSD(T)/cc-pVDZ	Experiment (Ar matrix, 10 K)
a_2	CH_3-twist.	82.9 (0.0)	96.9 (0.0)	–
b_1	CH_3-twist.	93.9 (2.4)	102.4 (1.9)	–
a_2	COCOC-twist.	232.1 (0.0)	227.0 (0.0)	–
b_1	COCOC-def.	227.5 (11.0)	231.8 (8.37)	–
a_1	COC-def.	242.2 (9.7)	247.5 (6.8)	–
b_2	COC-def.	482.8 (46.1)	501.4 (44.4)	497.3 (w)
a_1	OCO-def.	554.7 (1.4)	559.7 (1.0)	–
b_2	CO-str.	990.4 (70.2)	1022.7 (57.9)	988.5 (m)
a_1	CO-str.+CH_3-def.	1087.1 (35.1)	1098.1 (21.0)	1080.6 (w)
b_2	CH_3-def.+CO-str.	1166.4 (202.1)	1164.7 (171.6)	1146.8 (s)
a_1	CH_3-def.+CO-str.	1160.7 (4.9)	1168.3 (12.2)	–
a_2	CH_3-def.	1175.9 (0.0)	1175.5 (0.0)	–
b_1	CH_3-def.	1182.7 (1.1)	1183.7 (2.6)	–
b_2	OCO-str.	1256.6 (579.4)	1264.0 (621.8)	1225.6/1233.9 (vs)[a]
a_1	OCO-str.	1333.2 (26.7)	1339.9 (24.3)	1312.2 (w)
a_1	CH_3-def.	1467.5 (2.3)	1460.8 (0.8)	1436.6 (w)[b]
b_2	CH_3-def.	1468.3 (21.2)	1460.8 (9.9)	1439.1 (w)[b]
a_2	CH_3-def.	1490.9 (0.0)	1485.9 (0.0)	1453.2 (w)[b]
b_1	CH_3-def.	1491.4 (11.2)	1486.3 (4.5)	1454.8 (w)[b]
a_1	CH_3-def.	1503.2 (15.8)	1498.9 (9.4)	1467.4 (w)[b]
b_2	CH_3-def.	1503.7 (20.9)	1500.5 (10.7)	1470.6 (w)[b]
b_2	CH-str.	3045.1 (98.4)	3060.7 (111.5)	2900.0 (w)[c]
a_1	CH-str.	3046.4(1.8)	3062.5(0.8)	2925.2 (w)[c]
a_2	CH-str.	3126.6(0.0)	3156.1(0.0)	2966.5 (w)[c]
b_1	CH-str.	3126.7(40.2)	3156.2(54.5)	3017.9 (w)[c]
a_1	CH-str.	3138.3(16.6)	3172.5(20.6)	3020.9 (w)[c]
b_2	CH-str.	3138.5(3.0)	3172.8(5.5)	3048.2 (w)[c]

[a] Broad band, split by matrix effects. [b] 1430–1470 cm^{-1}: strongly overlapping bands of (*tt*)-**1** and (*ct*)-**t**, individual assignments not possible. [c] 2900–3050 cm^{-1}: strongly overlapping bands of (*tt*)-**1** and (*ct*)-**1**, individual assignments not possible.

ing (3050–2900 cm^{-1}) and deformation (1470–1430 cm^{-1}) regions, the IR bands of the two conformers are well separated (Table 1 and Table 2). The most intense bands, around 1250–1000 cm^{-1}, arise from the strongly coupled C–O stretching vibrations.

As well as being able to assign the conformers unambiguously in the IR spectra, we can also estimate their relative amounts as approximately 1:1 on the basis of the relative intensities of their associated absorption bands. Since the rotational barrier for the mutual interconversion of (*tt*)-**1** and (*ct*)-**1** is high (Figure 3), it is reasonable to assume that the equilibrium distribution at the pyrolysis temperature of around 400 °C is frozen out in the 10 K argon matrix. Hence, the free energy difference (ΔG_R) between (*tt*)-**1** and (*ct*)-**1** is almost zero at 400 °C. This experimental finding corresponds well with the computational results (ΔE_R) of 1.9 $kcal\,mol^{-1}$ (B3LYP) or 0.5 $kcal\,mol^{-1}$ [CCSD(T)] (Figure 3). The "missing" *cis,cis* conformer [(*cc*)-**1**] adopts a slightly twisted u-shape geometry and is 18.5 $kcal\,mol^{-1}$ (B3LYP) and 17.3 $kcal\,mol^{-1}$ [CCSD(T)] higher in energy, so it does not play a role in the conformational equilibrium mixture.

The UV/Vis spectrum of the matrix-isolated pyrolysis products (Figure 4) shows an absorption maximum at 257 nm for dimethoxycarbene (**1**); this value is very close to the one previously reported (255 nm).[6] It is also in good agreement with time-dependent (TD) density functional theory (DFT) computations of the three lowest-lying electronic transitions of **1** in its *s-trans,s-trans* (262 nm) and *s-cis,s-trans* (254 nm) conformations. A photolysis experiment carried out with light corresponding to the long-wavelength part of the absorption band (280 ± 10 nm) confirms the TD-DFT computations' prediction of a small bathochromic shift for (*tt*)-**1** relative to (*cc*)-**1**. Under these conditions the IR bands of (*tt*)-**1** vanished slightly more rapidly than those of (*ct*)-**1**; the computed spectrum of (*cc*)-**1** is substantially different (Table 3).

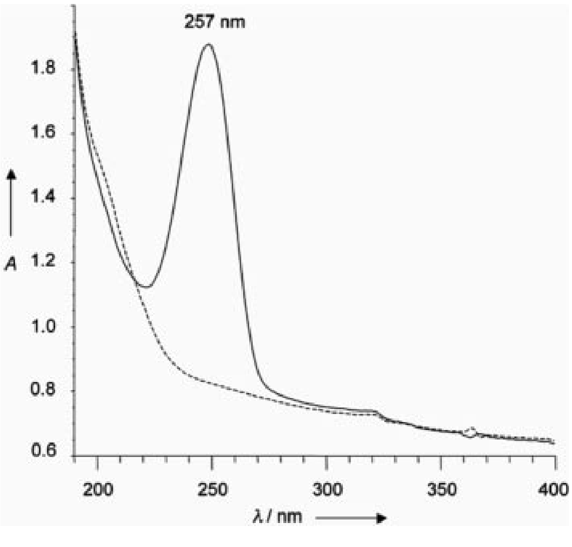


Figure 4. Solid line: UV/Vis spectrum of the matrix-isolated (Ar, 10 K) pyrolysis products of the high-vacuum flash pyrolysis (400 °C) of oxadiazoline **4**; dashed line: after 4 h irradiation with λ = 280 nm.

Table 3. Most intense UV absorptions of the conformers of **1**.

Species (point group)	Computations [TD-B3LYP/6-311+G(d,p)] excited state	wavelength/nm	oscillator strength	Experiment (argon, 10 K) λ_{max}/nm
(*tt*)-**1**	$^1B_1$	262	0.0297	257
(C_{2v})	$^1A_1$	205	0.0043	
	$^1B_2$	204	0.0387	
(*ct*)-**1**	$^1A''$	254	0.0342	257
(C_s)	$^1A'$	219	0.0235	
	$^1A'$	205	0.0070	
(*cc*)-**1**	^1B	280	0.0197	
(C_2)	^1A	245	0.0413	
	^1B	209	0.0279	

Our findings for dimethoxycarbene (**1**) are in marked contrast with those relating to its saturated analogue dimethoxymethane (DMM). Our own and previously reported matrix isolation infrared studies identified two low-lying conformers of DMM: namely the *gauche*,*gauche* (*gg*) and *gauche*,*trans* (*gt*) forms, with (*gg*)-DMM being the global minimum, ca. 2.3 kcal mol^{-1} [B3LYP/6-31++G(d,p)] below (*gt*)-DMM.[11] The *trans*,*trans* (*tt*) structure of DMM is the highest-lying conformer. These significant differences can be interpreted on the basis of two very different stabilizing interactions. The anomeric interactions in DMM require the C–O bonds to act as mutual acceptors of electron density of the oxygen lone pairs, resulting in an ideal *gg* conformation in which this stabilizing interaction is maximized. The donation of electron density of the oxygen lone pairs into the empty *p*-orbital on the carbene carbon in **1** favors overall *planar* arrangements of the heavy atoms. At the same time, (*tt*)-**1** also displays the lowest dipole moment at CCSD(T)/cc-pVDZ [in the *z*-direction: +0.54 D; (*ct*)-**1** (*xy*) = –2.73 D; (*cc*)-**1** (*z*) = –4.46 D], which may be one of the reasons for the observed conformational preference.[7,12]

Conclusions

Dimethoxycarbene (**1**) was prepared under HVFP conditions and trapped at low temperature by matrix isolation techniques. The excellent agreement between the computed [CCSD(T)/cc-pVDZ IR] spectrum of the mixture of conformers of **1** and the measured IR absorptions allows a detailed analysis of the conformational preference of **1**.

In marked contrast with the *gauche*,*gauche* minimum of dimethoxymethane, the *trans*,*trans* conformer of **1** is slightly preferred (0.5 kcal mol^{-1}). The *cis*,*trans* conformer equilibrates at the high temperatures required during HFVP generation and both conformers can be identified in the IR spectra of the argon matrix at 10 K. The conformational preference is due to the minimization of the overall dipole moment in the *trans*,*trans* conformer.

Experimental Section

Matrix-Isolation Studies: The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system with CsI windows for IR and BaF_2 windows for UV/Vis measurements. IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm^{-1}, resolution 0.7 cm^{-1}), UV/Vis spectra with an Agilent HP 8453 Diode-Array spectrometer (190–1100 nm, resolution ca. 1 nm). For the combination of high-vacuum flash pyrolysis with matrix isolation a small, home-built, water-cooled oven directly connected to the vacuum shroud of the cryostat was used. The pyrolysis zone consisted of a completely empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a coax heating wire. The temperature was controlled through a Ni/CrNi thermocouple. In a typical experiment, oxadiazoline **4** was evaporated from a pre-cooled storage bulb (–45 °C, pressure ca. 10^{-4} mbar) into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of ca. 50 mm, the pyrolysis products were co-condensed with a large excess of argon on the surface of the 10 K matrix window. Several experiments at temperatures from 300 to 700 °C were performed in order to determine the optimal reaction temperature. For irradiation, either a low-pressure mercury spiral lamp (Gräntzel) with a vycor filter or a high-pressure mercury lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used.

Computational Methods: Becke's gradient-corrected exchange functional[13] in conjunction with the Lee–Yang–Parr non-local correlation functional (B3LYP)[14] and a 6-311+G(d,p) basis set as implemented in Gaussian 03 were utilized for all initial optimizations.[15] These structures were further refined at the coupled cluster level of theory, including single, double, and perturbatively determined triple excitations [CCSD(T)][16] with the aid of a cc-pVDZ basis set[17] and with use of a full core (no deleted virtuals); we used the ACES II (Mainz–Austin–Budapest Version)[18] program suite for all coupled cluster computations. All structures were characterized as stationary points by determination of harmonic vibrational frequencies (with zero imaginary frequencies for minima and one imaginary frequency for transition structures). All reported energies refer to the CCSD(T)/cc-pVDZ + ZPVE (unscaled) level of theory, unless stated otherwise.

Supporting Information (see also the footnote on the first page of this article): Geometries and energies of all optimized species at CCSD(T)/cc-pVDZ (full core, no deleted virtuals).

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