Small Rings, 92[◇]

The Thermally and Photochemically Induced Ring Opening of *cis*-3,4-Dichlorocyclobutene and *trans*-3,4-Dichlorocyclobutene: New Insights from a Matrix-Spectroscopic Study

Günther Maier* and Axel Bothur

Institut für Organische Chemie der Justus-Liebig-Universität Gießen,
Heinrich-Buff-Ring 58, D-35392 Gießen, Germany
Fax: (internat.) +49(0)641/99-34309
E-mail: guenther.maier@org.chemie.uni-giessen.de

Received May 25, 1998

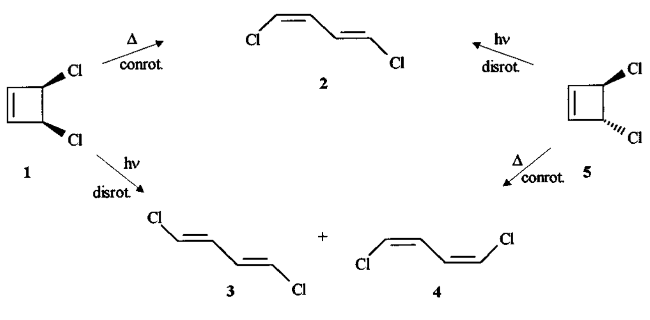
Keywords: Matrix isolation / Ring opening / Flash pyrolysis / Photochemistry / Cyclobutenes

The thermally induced ring opening of **1** and **5** proceeds with high stereospecifity in a conrotatory fashion in agreement with the Woodward–Hoffmann rules. Upon flash pyrolysis of **1** the matrix-isolated (Xe, 12 K) products **2a** and **2b** were found, whereas the corresponding reaction of **5** yielded **3a** and **3b**. The *s-cis* conformers **2b** and **3b** were identified for the first time by comparison of the experimental and calculated (BLYP/6-311G*) IR absorptions. A non-stereospecific photochemical reaction could be observed if matrix-isolated (Ar or Xe, 12 K) **1** was excited directly with λ = 193 nm. Products of the allowed disrotatory pathway as well as those of the forbidden conrotatory reaction were found, a behaviour that corresponds with the known photochemistry of cyclobutenes. A surprising reaction was found if **1** and **5** were irradiated in a xenon matrix with λ > 270 nm. The precursors, which were photostable in an argon matrix, opened the ring in a conrotatory fashion, the expected pathway for a thermal reaction. In this case the light is absorbed by the solid xenon in a cooperative process with the precursor molecules. A detailed discussion of the possible energy transfer mechanisms is given. Most probably, a hot ground-state reaction of vibrationally excited **1** and **5** occurs, although the reaction of the radical cations cannot be excluded.

1. Introduction

One of the classical textbook examples for pericyclic reactions is the electrocyclic ring opening of cyclobutene. The stereochemical outcome of this interconversion is dependent on whether the reaction is photochemically or thermally induced. Predictions can be made by the principle of *orbital symmetry conservation*, which is the basis for the Woodward−Hoffmann rules, and most widely applied by chemists.[1]

In the case of 3,4-disubstituted cyclobutenes like *cis*-3,4-dichlorocyclobutene, *cis*-DCCB (**1**), the thermally allowed ring opening proceeds according to orbital-symmetry considerations in a conrotatory fashion. One expects only one product, namely *cis,trans*-1,4-dichlorobutadiene (**2**). Both chlorine atoms should rotate in the same direction. The photochemically allowed ring opening follows a disrotatory pathway by rotating the chlorine atoms in different directions, and the expected products are *trans,trans*-1,4-dichlorobutadiene (**3**) and/or *cis,cis*-1,4-dichlorobutadiene (**4**). For the electrocyclic opening of *trans*-3,4-dichlorocyclobutene, *trans*-DCCB (**5**), the stereospecificity of the thermal and the photochemical reaction is reversed. Although the cyclobutenes open their ring in the first step to the *s-cis* conformers of the corresponding butadienes, which isomerize to the *s-trans* conformers immediately, only the *s-trans* conformers − these are the stable and observable conformers at ambient temperature − are discussed in the literature. Therefore, the question arose whether it is possible to observe the *s-cis* conformers − the primary products of the reaction − under matrix-isolation conditions at 12 K.



In most cases the ring opening of cyclobutenes can be induced easily with temperatures between 100 and 200 °C[2a], and therefore the literature reports hundreds of examples[2b], all of them demonstrate that the thermal reaction indeed proceeds in a conrotatory fashion, the stereospecifity often exceeding 99%.[2c] The number of photochemically induced reactions is much smaller.[3] Since cyclobutenes absorb at lower wavelengths (λ < 230 nm), a ring

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[◇] Part 91: G. Maier, S. Senger, *Liebigs Ann.* **1996**, 45−47.

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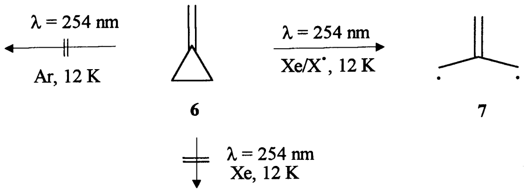
opening is only conceivable with vacuum-UV techniques, whereas the photoinduced ring closure of butadienes is the usually observed reaction due to the strong UV absorption of the butadienes and thermodynamic aspects. In contrast to the predicted disrotatory pathway, for the ring opening – with few exceptions – no stereospecifity is found, and conrotatory as well as disrotatory modes can be observed. According to earlier calculations[4] the photochemical ring opening of cyclobutene starts in the first excited electronic state S_1, but crosses onto the second state S_2 and follows this surface to a well, which lies above a maximum of the ground-state potential-energy surface. Through a reaction funnel internal conversion to the ground-state surface occurs. Spectroscopical experiments with cyclobutene as well as simple polyenes confirmed[5], that the excited state S_1 is reached by irradition initially, but crosses immediately within 10 to 30 fs onto the S_2 state. Recent ab initio calculations of Bernardi, Robb and coworkers[6] suggest, that the transition from the excited-state surface S_2 to the ground-state surface S_0 proceeds via a *conical intersection* at which both surfaces cross directly. On the S_2 state the disrotatory ring opening is still the dominant pathway, but at the conical intersection different ground-state pathways are accessible. In addition to the disrotatory reaction a *cis-trans* isomerization of a double bond is possible. Following this competitive path the reaction loses its stereospecificity.

Recently, we found reactions in halogen-doped xenon matrices at 12 K, which could be induced photochemically although the precursors had no UV absorption in the range of the used photolysis wavelengths and were photostable in argon matrices.[7] Surprisingly, the products of these experiments were formally those of "thermal" reactions. For example methylenecyclopropane (**6**) was transformed photochemically into trimethylenemethane (**7**).[7a][7b]



In a working hypothesis we suggested that the photoinduced excitation of the matrix material xenon forms xenon-halogen exciplexes with a delocalized hole in the valence band of the solid and an electron localized on the halogen anion. The neutralization of the separated charges sets the stored irradiation energy free, which leads to the vibrational excitation of the precursor and enforces its thermal reaction. One of the central questions in the mechanistic discussion was, if the energy transfer really leads to the vibrational excited precursor. We therefore chose the electrocyclic ring opening of 3,4-disubstituted cyclobutenes as a system to test our hypothesis, since the products of this reaction allow a clear distinction between a thermal and a photochemical reaction.

A comprehensive matrix-spectroscopic study of *cis*-DCCB (**1**) and *trans*-DCCB (**5**) was initiated to obtain new insights into the thermally – with regard to the primary products – and photochemically induced reactions of these compounds as well as into the energy-transfer mechanism in xenon matrices.

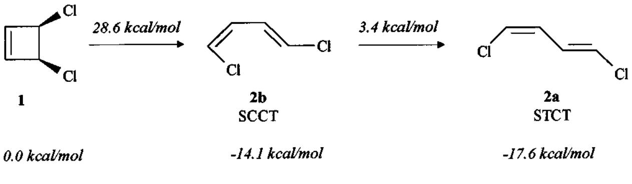
2. Thermally Induced Reactions

The knowledge about the thermal reactions of *cis*-DCCB (**1**) and *trans*-DCCB (**5**) is mostly focussed on their activation parameters. In 1965 Criegee, Seebach et al. determined an activation energy of 35.6 kcal/mol for the ring opening of **1**.[2a] The corresponding value for **5** is remarkably lower with 25.7 kcal/mol.[8] Studies, in which **1** was excited with an IR laser, showed that the vibrationally excited molecule obeys the Woodward–Hoffmann rules and yields the product of a conrotatory pathway under the premise, that the vibrational activation was not too high.[9]

DFT Calculations

As shown by Ziegler and Deng, DFT methods turned out to be appropiate for the description of the ring opening of cyclobutene.[10] We therefore performed DFT calculations for the electrocyclic reactions of *cis*-DCCB (**1**) and *trans*-DCCB (**5**) on the BLYP/6-311G* level. For **1** only one reaction path, the conrotatory opening to *s-cis-cis,trans*-1,4-dichlorobutadiene, SCCT (**2b**, SCCT stands for *s-cis-cis,-trans*), was found (Scheme 1). The transition state for this exothermic reaction was calculated to lie 28.6 kcal/mol above **1**, which is in fairly good agreement with the experimental value of 35.6 kcal/mol. IRC (intrinsic reaction coordinate) calculations showed that this activated complex indeed connects **1** with **2b**. On the other hand it turned out that the reaction is concerted, since all changes in energy, bond lengths, angles and dihedral angles were continuous.

Scheme 1. Calculated (BLYP/6-311G*; including zero-point correction) energy profile for the conrotatory ring opening of *cis*-DCCB (**1**) and subsequent isomerization of the primary product SCCT (**2b**) to STCT (**2a**)

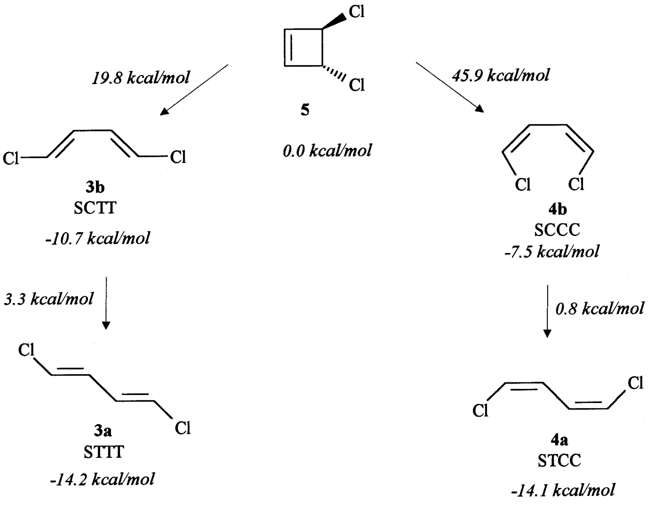


In contrast to the well-characterized *s-trans* conformer STCT (**2a**) the *s-cis* conformer SCCT (**2b**) could not be observed in experiments.[11a] Astonishingly, the calculated structure of **2b** is nearly planar with a dihedral angle of the carbon skeleton of 0.01°. Presumably a bonding interaction of the chlorine atom in the *cis* position and a *cis* hydrogen atom is stronger than the steric repulsion in this molecule.

The activation energy of 3.4 kcal/mol for the rotation of the *s-cis* to the *s-trans* conformer is low with respect to the ring opening, and the primary product of the reaction, SCCT (**2b**), should be transformed quickly into STCT (**2a**), which dominates the equilibrium at ambient temperatures.[11a] Nevertheless, the barrier seems to be high enough for being able to isolate the *s-cis* conformer **2b** in a matrix at 12 K.

For *trans*-DCCB (**5**) two concerted conrotatory pathways were found (Scheme 2). Over a comparably high barrier of 45.9 kcal/mol **5** opens exothermically to *s-cis-cis,cis*-1,4-dichlorobutadiene, SCCC (**4b**), both chlorine atoms rotating inwards. The steric hindrance of this molecule leads to a dihedral angle of the carbon skeleton of 53.4°, which correlates nicely with the value of 60° from gas-phase electron-diffraction (GPED) experiments.[11b] Another effect of the steric repulsion is the low rotational barrier of 0.8 kcal/mol to the unhindered *s-trans* conformer STCC (**4a**). An activation energy of 19.6 kcal/mol, which is comparable with the experimental value, is found for the ring opening, in which both chlorine atoms rotate outwards producing *s-cis-trans,trans*-1,4-dichlorobutadiene, SCTT (**3b**). Repulsion of the central hydrogen atoms twists the carbon skeleton of **3b** up to a dihedral angle of 35.6°, a value that deviates significantly from the experimentally deduced angle of 52°.[11a] For the rotation around the single bond a value of 3.3 kcal/mol is calculated. A detection of SCTT (**3b**) under matrix-isolation conditions is therefore conceivable. Altogether the thermal electrocyclic reaction of *trans*-DCCB (**5**) should produce with high stereospecifity SCTT (**3b**) and STTT (**3a**), whereas SCCC (**4b**) and STCC (**4a**) can be excluded due to the high activation energy for this reaction path.

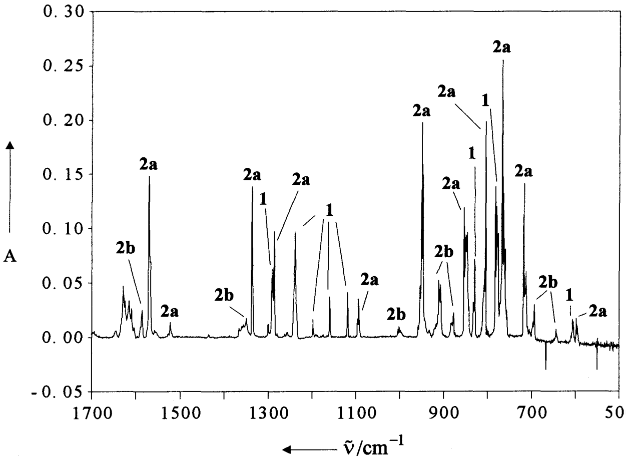
Scheme 2. Calculated (BLYP/6-311G*; including zero-point correction) reaction pathways for the conrotatory ring opening of *trans*-DCCB (**5**) and subsequent isomerization of the primary products SCTT (**3b**) and SCCC (**4b**) to STTT (**3a**) and STCC (**4a**), respectively



Flash Pyrolysis of *cis*-DCCB (1)

1 was pyrolyzed at 750°C and trapped with an excess of xenon at 12 K. Besides the unreacted precursor – the reaction was not complete – the most dominant product in the IR spectrum was STCT (**2a**), which was identified by a comparison with the known gas-phase absorptions[12] and the calculated (BLYP/6-311G*) IR bands (Figure 1, Table 1).

Figure 1. Matrix IR spectrum (Xe, 12 K) of the pyrolysis (750°C) of *cis*-DCCB (**31**)



The remaining IR absorptions were attributed to the *s-cis* conformer SCCT (**2b**). An assignment of this unknown species was made by a comparison of the experimental with the calculated (BLYP/6-311G*) IR spectrum. A good correlation (Table 2) was found. That means **1** opens in a thermal reaction exclusively to the products of the allowed conrotatory pathway.

Photolysis of the pyrolysate (containing **1**, **2a** and **2b**) with λ > 270 nm led to the partial formation of SCTT (**3b**), STTT (**3a**) and STCC (**4a**) (IR absorptions of **2a**, **3a**, and **4a** are given in Table 1; for **3b** see below). Since the IR bands of still present *cis*-DCCB (**1**) lost intensity, whereas the IR absorptions of **2a** and **2b** grew, **2a** and **2b** appeared

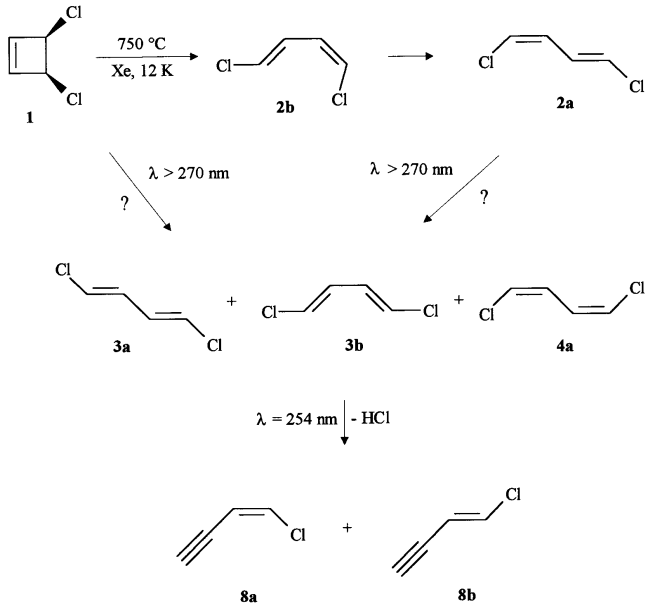


Table 1. Experimental IR absorptions ([cm^{-1}], Xe, 12 K) of the dichlorobutadienes STCT (**2a**), STTT (**3a**) and STCC (**4a**); relative intensities (exp. peak areas) are given in parentheses

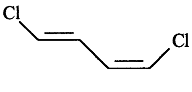
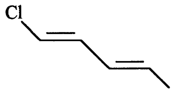
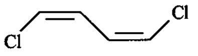
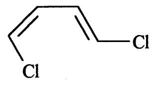
 STCT (**2a**)		 STTT (**3a**)		 STCC (**4a**)	
approx. descr.	$\tilde{\nu}_{\mathrm{exp.}}$	approx. descr.	$\tilde{\nu}_{\mathrm{exp.}}$	approx. descr.	$\tilde{\nu}_{\mathrm{exp.}}$
$\nu_{\mathrm{CH,terminal},cis}$	3086.1 (0.06)	$\nu_{\mathrm{s,CH,terminal}}$	3069.8 (0.19), 3060.6		
$\nu_{\mathrm{CH,terminal},trans}$	3072.2 (0.07)				
	1753.4 (0.08)		1770.4 (0.04)		
$\nu_{\mathrm{s,C=C}}$	1616.4 (0.07)			$\nu_{\mathrm{s,C=C}}$	1629.6 (0.10)
$\nu_{\mathrm{a,C=C}}$	1571.6 (0.68)	$\nu_{\mathrm{a,C=C}}$	1571.2 (0.44), 1566.6	$\nu_{\mathrm{a,C=C}}$	1576.0 (0.03), 1562.6 (0.05)
$\delta_{\mathrm{ip,CH}}$	1337.3 (0.36)	$\delta_{\mathrm{a,ip,CH}}$	1295.0 (0.02)	$\delta_{\mathrm{ip,s,CH,terminal}}$	1300.9 (0.34)
$\delta_{\mathrm{ip,CH},trans}$	1287.2 (0.14)	$\delta_{\mathrm{s,ip,CH}}$	1187.7 (0.04)	$\delta_{\mathrm{ip,CH,central}}$	1180.8 (0.04)
$\nu_{\mathrm{C\text{-}C}}$	1094.9 (0.11)				
$\chi_{\mathrm{a,=CHC}}$	951.2 (0.90), 948.4	$\chi_{\mathrm{=CHC}}$	958.6 (0.89), 956.5	$\chi_{\mathrm{=CHC}}$	955.2 (0.30)
$\nu_{\mathrm{C\text{-}Cl},trans}$	854.0 (1.00), 850.5	$\nu_{\mathrm{C-Cl}}$	810.5 (1.00)		804.1 (0.03)
$\chi_{\mathrm{s,=CHCl},trans}$	807.4 (0.50), 805.2	$\chi_{\mathrm{=CHCl}}$	758.4 (0.10)		
$\nu_{\mathrm{C-Cl,cis}}$	768.0 (1.00), 764.2			$\nu_{\mathrm{C-Cl}}$	771.1 (1.00)
$\chi_{\mathrm{a,=CHCl},cis}$	718.4 (0.53), 713.6			$\chi_{\mathrm{=CHCl}}$	704.7 (0.39)
$\delta_{\mathrm{s,C=C-C}}$	598.9 (0.08)	δ_{CCl}	496.7 (0.15)		

Table 2. Calculated (BLYP/6-311G*) and experimental (Xe, 12 K) IR absorptions [cm^{-1}] of SCCT (**2b**)

	 SCCT (**2b**)	
approx. descr.	$\tilde{\nu}_{\mathrm{calc.}}$	$\tilde{\nu}_{\mathrm{exp.}}$
$\nu_{\mathrm{CH,terminal},trans}$	3178.9 (0.03)	
$\nu_{\mathrm{CH,terminal},cis}$	3140.6 (0.06)	
$\nu_{\mathrm{s,CH,central}}$	3983.6 (0.07)	
$\nu_{\mathrm{a,CH,central}}$	3054.4 (0.10)	
$\nu_{\mathrm{C=C},cis}$	1607.2 (0.37)	1610.8 (0.92)
$\nu_{\mathrm{C=C},trans}$	1569.3 (0.51)	1586.2 (0.79)
$\delta_{\mathrm{ip,CH},cis}$	1350.6 (0.24)	1350.0 (0.35)
$\delta_{\mathrm{ip,CH},trans}$	1310.6 (0.04)	
δ_{CH}	1263.3 (0.03)	1258.9 (0.13)
	1225.5 (<0.01)	
$\nu_{\mathrm{C\text{-}C}}$	984.7 (0.09)	999.5 (0.19)
$\chi_{\mathrm{=CHC},trans}$	938.4 (0.34)	944.0 (0.59)
$\chi_{\mathrm{=CHC},cis}$	887.9 (0.07)	911.9 (0.10)
$\nu_{\mathrm{C-Cl},trans}$	855.5 (0.29)	883.5 (0.55), 881.8
$\chi_{\mathrm{=CHC},trans}$	784.7 (0.24)	809.5 (0.38)
$\nu_{\mathrm{C-Cl}}$	725.2 (1.00)[a]	771.9 (1.00)
$\chi_{\mathrm{=CHC}}$	674.1 (0.36)	694.0 (0.99)
$\chi_{\mathrm{=CHCl}}$	611.3 (0.21)	647.5 (0.31)
	468.5 (0.02)	
	361.4 (0.06)	
	241.9 (0.03)	
	170.5 (0.01)	
	119.8 (< 0.01)	
	78.1 (0.02)	

[a] Absolute intensity: 108.3 km/mol.

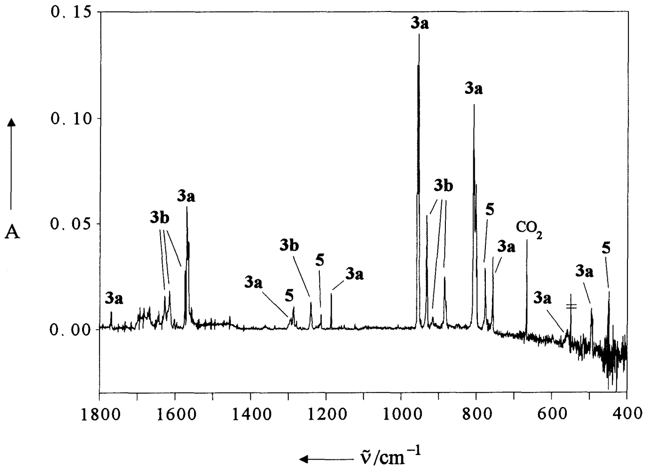
to be photoproducts of **1**, but it was not possible to determine whether the butadienes STCT (**2a**) and SCCT (**2b**) were isomerized upon photolysis or whether the unreacted precursor opened the ring photochemically to **3a**, **3b** and **4a**.

Upon subsequent irradiation with λ = 254 nm elimination of HCl could be observed. As products of this elimination *cis*-1-chlorobuten-3-yne (**8a**) and *trans*-1-chlorobuten-3-yne (**8b**) were found, but due to the complex IR spectrum this assignment remains tentative. The IR spectra of **8a** and **8b** are reported in the literature[13], but the postulated structural elucidation appears to be questionable if one compares the experimental IR spectra with calculated IR absorptions.

Flash Pyrolysis of *trans*-DCCB (5)

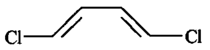
At a pyrolysis temperature of 650 °C the thermal reaction of **5** was nearly complete (Figure 2). This reflects the lower activation energy for the ring opening of **5** with respect to **1**. The main product of this reaction was STTT (**3a**).[12] All remaining IR absorptions could be assigned to the *s-cis* conformer SCTT (**3b**) by comparison with the theoretical IR spectrum (Table 3). This is the first experimental identification of SCTT (**3b**), whose existence was deduced from

Figure 2. Matrix IR spectrum (Xe, 12 K) of the pyrolysis (650 °C) of *trans*-DCCB (**5**)



GPED experiments earlier,[11a] but could not be proved unequivocally.

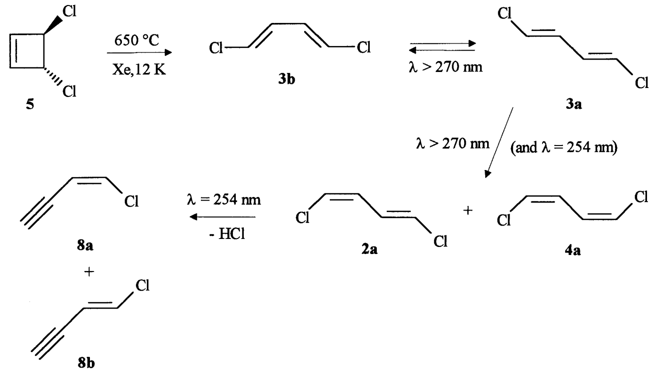
Table 3. Theoretical (BLYP/6-311G*) and observed (Xe, 12 K) IR absorptions [cm^{-1}] of SCTT (**3b**)



SCTT (3b)

approx. descr.	$\tilde{\nu}_{calc.}$[a]	$\tilde{\nu}_{exp.}$
$\nu_{s,CH,terminal}$	3133.1 (0.01)	
$\nu_{a,CH,terminal}$	3129.1 (0.19)	
$\nu_{s,CH,central}$	3079.2 (0.07)	
$\nu_{a,CH,central}$	3069.0 (0.09)	
$\nu_{a,C=C}$	1610.7 (0.78)	1629.1 (0.21), 1616.1 (0.54)
$\nu_{s,C=C}$	1571.4 (0.04)	1575.7 (0.26)
δ_{CH}	1308.9 (<0.01)	
δ_{CH}	1279.2 (0.01)	
$\delta_{s,CH}$	1249.7 (0.33)	1242.5 (0.32)
$\delta_{a,CH}$	1225.7 (0.06)	
ν_{C-C}	1030.4 (< 0.01)	
$\delta_{a,CH}$	923.6 (0.92)	934.0 (1.00)
$\delta_{s,CH}$	913.0 (0.10)	918.1 (0.09)
ν_{aC-Cl}	851.8 (1.00)[b]	886.8 (0.63)
$\nu_{s,C-Cl}$	810.4 (< 0.01)	
$\chi_{a,=CHC}$	746.4 (0.04)	756.9 (0.12)
$\chi_{s,=CHC}$	730.9 (0.28)	
$\chi_{a,=CHCl}$	532.7 (0.59)	560.4 (0.15)
	328.4 (0.01)	
	319.4 (0.02)	
	265.5 (0.01)	
	167.6 (< 0.01)	
	115.3 (0.01)	
	90.8 (0.01)	

[a] **3b** was calculated in C_2 symmetry. – [b] Absolute intensity: 107.9 km/mol.



Similar to the case of *cis*-DCCB (**1**), the thermally induced electrocyclic reaction of **5** proceeds with high stereospecifity in a conrotatory fashion in good agreement with the Woodward–Hoffmann rules, both chlorine atoms rotating outwards only as expected from theoretical calculations. Upon photolysis with λ > 270 nm STTT (**3a**) was isomerized to SCTT (**3b**), STCT (**2a**) and STCC (**4a**). Again the irradiation with λ = 254 nm led to the products of a HCl elimination.

In all experiments the observation could be made that upon photoexcitation the preferred isomerization product of the dichlorobutadienes was STCC (**4a**). A possible explanation for this observation is the UV absorption of this species.[14] STTT (**3a**, λ_{max} = 240 nm, ε = 32500), STCT (**2a**, λ_{max} = 243 nm, ε = 28600) and STCC (**4a**, λ_{max} = 246 nm, ε = 26100) possess similar UV absorptions, but the absorption coefficient for STCC (**4a**) is weaker than for the other isomers. The photochemical equilibria between these isomers are in consequence shifted to the isomer with the weakest absorption.

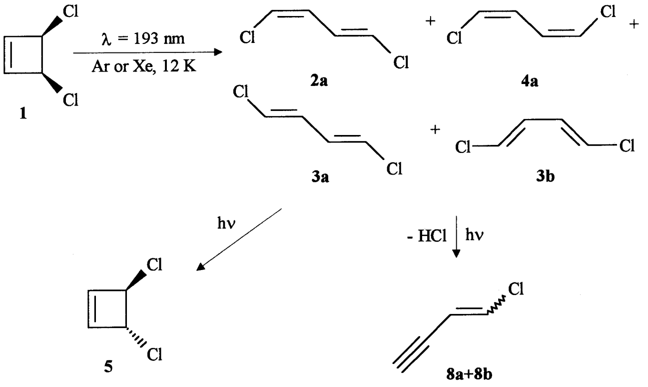
3. Photochemically Induced Reactions

The UV/Vis spectra of *cis*-DCCB (**1**) and *trans*-DCCB (**5**, solution in cyclohexane) show a weak end absorption below 230 nm. A direct excitation of these species should only be possible with wavelengths λ < 230 nm.

Laser Photolysis with λ = 193 nm

If matrix-isolated **1** (Ar, 12 K) was exposed to the emission of an ArF excimer laser (λ = 193 nm) a complex product mixture could be observed. The most intense IR absorptions came from STTT (**3a**), the product of a disrotatory pathway. Besides other disrotatory products like SCTT (**3b**) and STCC (**4a**) rather intense IR absorptions of STCT (**2a**), the product of a conrotatory mode, were found. Since the band-growth behaviour of these butadienes was nearly identical, isomerization reactions could be neglected, and the observed product cocktail represents the primary photoreaction. In addition the products of a HCl elimination as well as the product of a ring-closure – *trans*-DCCB (**5**), probably formed via **2b** – were found.

In a xenon matrix *cis*-DCCB (**1**) showed an absolutely similar behaviour upon laser photolysis.

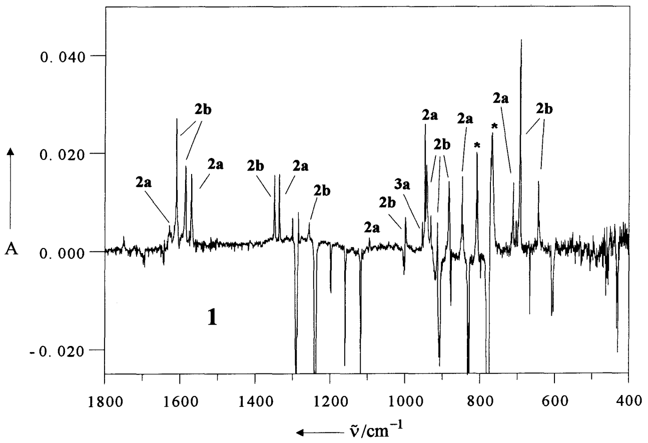


The photochemically induced ring opening of **1** with λ = 193 nm is – in agreement with the known photochemistry of cyclobutenes[3] – not stereospecific and produces a complex product mixture independent from the used matrix material argon or xenon. It can be assumed that the precursor is directly excited by the irradition. The experimental result is in accordance with the theoretical considerations of Bernardi, Robb et al.[4]

Photolysis of *cis*-DCCB (1) with λ > 270 nm

In an *argon* matrix **1** is *photostable* against irradiation with λ ≥ 254 nm. This situation changes dramatically if the irradiation (λ > 270 nm) is performed in a *xenon* matrix. Within a few hours **1** vanishes completely. The observed products were STCT (**2a**), SCCT (**2b**), STTT (**3a**), SCTT (**3b**, in traces) and STCC (**4a**, Figure 3).

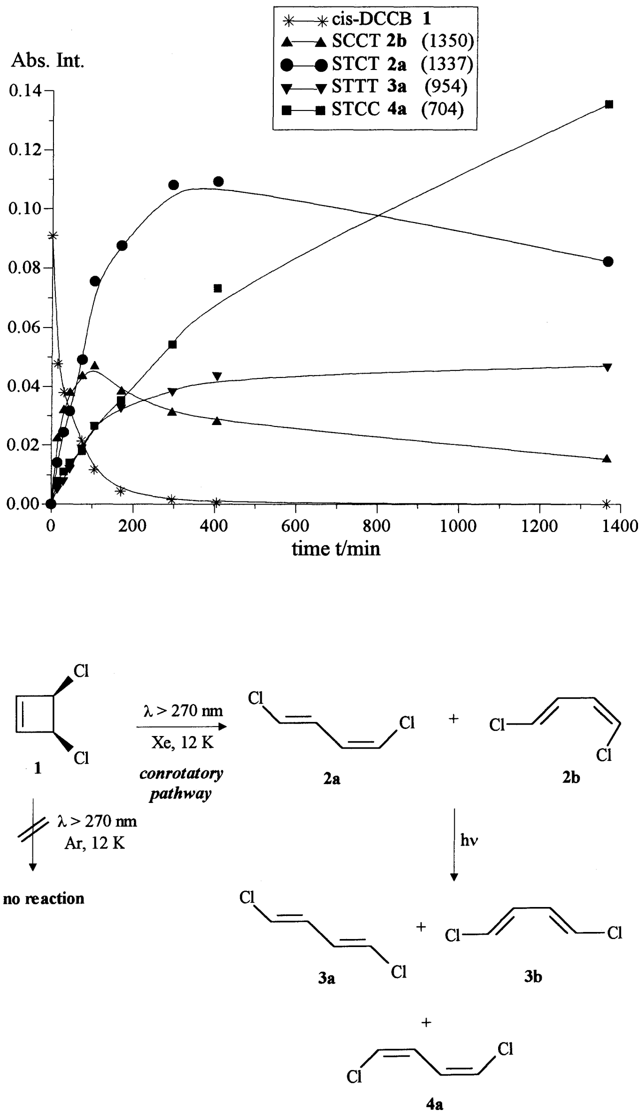
Figure 3. Matrix IR spectrum (Xe, 12 K) of the photolysis of *cis*-DCCB (**1**) with λ > 270 nm (30 min; negative absorptions: **1**; positive absorptions: products); bands marked with * are due to overlapping absorptions of different dichlorobutadienes



This valence isomerization showed a very different band-growth pattern (Scheme 3) compared to the irradiation with λ = 193 nm. At the beginning the strongest increase was detected for SCCT (**2b**), whose IR absorptions decreased slowly afterwards. A similar photolysis behaviour was found for STCT (**2a**), which reached its maximum later. On the other hand the IR absorptions of STTT (**3a**) and STCC (**4a**) grew much slower at the beginning and increased continuously afterwards parallel to the decreasing absorptions of SCCT (**2b**) and STCT (**2a**).

A band-growth pattern of this kind is expected for a reaction A → B → C, in which precursor A reacts to a primary product B.[15] The primary product is transformed to a secondary product C. From this point of view, the photochemically induced ring opening of *cis*-DCCB (**1**) in a xenon matrix with λ > 270 nm proceeds via the primary products SCCT (**2b**) and STCT (**2a**) in a *"thermally allowed" conrotatory* fashion. SCCT (**2b**) and STCT (**2a**) are subsequently isomerized to STTT (**3a**) and STCC (**4a**). To determine the stereospecifity of this reaction, the composition of the product mixture was deduced from a correlation of the experimentally observed IR intensities with the calculated intensities. In an early stage of this reaction more than 90% of the products are due to a conrotatory path, a remarkably high stereospecificity.

Scheme 3. Growth pattern of the most significant product IR absorptions upon photolysis (λ > 270 nm) of *cis*-DCCB (**1**) in a xenon matrix at 12 K; the corresponding wavenumbers for SCCT (**2b**), STCT (**2a**) STTT (**3a**) and STCC (**4a**) are given in parentheses

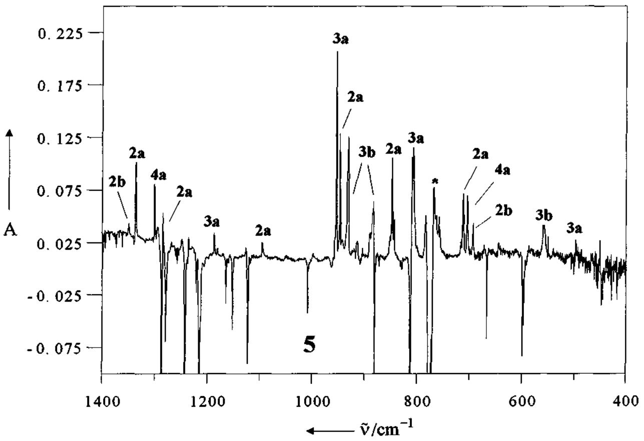


Photolysis (λ > 270 nm) of *trans*-DCCB (5)

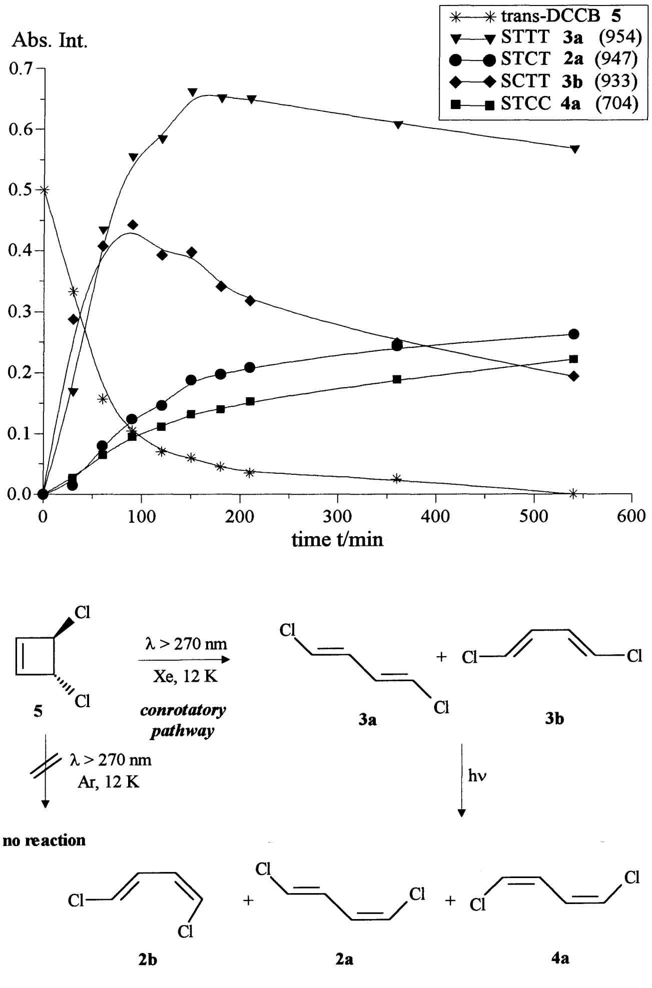
If the precursor was photolyzed in an *argon* matrix with λ ≥ 254 nm, *no photoreaction* occurred. Again a quick reaction could be observed upon irradiation (λ > 270 nm) in a *xenon* matrix. For the four observed products STTT (**3a**), SCTT (**3b**), STCT (**2a**) and STCC (**4a**) once more a different band-growth behaviour was found (Figure 4 and Scheme 4), compared to the 193 nm photoreaction.

STTT (**3a**) and SCTT (**3b**) grew quickly and then decreased slowly, with SCCT (**3b**) reaching its maximum at first. STCT (**2a**) and STCC (**4a**) showed a slow increase at the beginning of the photolysis, went through a turning point, and grew continuously afterwards. This band-growth pattern is in agreement with the observed behaviour in the case of *cis*-DCCB (**1a**) and is again typical for a consecutive reaction A → B → C.[15] STTT (**3a**) and SCTT (**3b**) are primary products of this reaction, which obviously follows therefore a *conrotatory* pathway, the *"thermally allowed"* reaction. The stereospecifity of this reaction is high, since

Figure 4. Matrix IR spectrum (Xe, 12 K) of the photolysis of *trans*-DCCB (**5**) with λ > 270 nm (120 min; negative absorptions: **5**; positive absorptions: products); bands marked with * are due to overlapping absorptions of different dichlorobutadienes



Scheme 4. Growth pattern of the most significant product IR absorptions upon photolysis (λ > 270 nm) of *trans*-DCCB (**5**) in a xenon matrix at 12 K; the corresponding wavenumbers for STTT (**3a**), SCTT (**3b**), STCT (**2a**) and STCC (**4a**) are given in parentheses



after 30 min irradiation 90% of the products originate from a conrotatory path.

Irradiation in a Halogen-Doped Xenon Matrix

In a pure xenon matrix *cis*-DCCB (**1**) was photostable against irradiation with λ = 313 nm. To test the outcome of this reaction in a halogen-doped matrix, a gaseous mixture **1**/Xe (3:1000) was cocondensed with a gaseous mixture Br_2/Xe (3:1000). The composition of the matrix **1**/Br_2/Xe was about 1.5:1.5:1000. Upon irradiation with λ = 313 nm a delayed photoreaction could be observed. After an initial period of 60 min the blue emission of an Xe/Br exciplex appeared[7b][16], and the IR absorptions of **1** began slowly to lose intensity. In a very early stage of this photochemically induced reaction only STCT (**2a**) and SCCT (**2b**) were found as products. The situation changed upon further irradiation. SCCT (**2b**) and STCT (**2a**) were the most dominant products, but in addition rather intense IR absorptions of STCC (**4a**) grew. Weak IR absorptions of STTT (**3a**) and SCTT (**3b**) were found, too. From the known photochemical behaviour of dichlorobutadienes in xenon matrix, it can be assumed that STCC (**4a**) is an isomerization product of STCT (**2a**) and SCCT (**2b**). The reaction therefore follows with high stereospecificity a *conrotatory* pathway, the *"thermal"* mode. The agreement with the corresponding reaction of **1** in an undoped xenon matrix is obvious and both reactions should have a similar mechanism.

4. The Mechanism of Photoinduced Reactions in Xenon Matrices

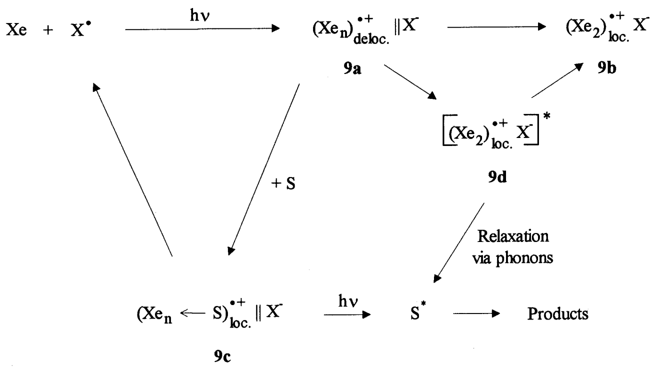
As shown before the photochemically induced ring opening of *cis*-DCCB (**1**) and *trans*-DCCB (**5**) in a xenon matrix with λ > 270 nm is not due to the direct photolytic excitation of the substrates. We assume that the photon energy is absorbed by the matrix material in a cooperative process with **1** or **5**. In a second step the absorbed photon energy is transferrred on the substrate and leads to a chemical reaction. The mechanistic discussion on this subject is still in progress and will be explained in detail in the forthcoming publications.

4.1. Photoinduced Reactions in Halogen-Doped Xenon Matrices

The photophysics of halogen-doped xenon matrices was studied extensively before[16] (for a detailed discussion of photoinduced reactions in undoped xenon matrices see ref.[7d]). On irradiation of halogen-doped xenon matrices, exciplexes $(Xe_n)_{deloc.}^{\bullet+}\ X^-$ (**9a**) are formed (Scheme 5). These exciplexes can be described as electron-hole pairs with a delocalized hole in the valence band of the solid xenon and a localized halogen anion. Polarization effects in the solid xenon and the electron affinity of the halogen strongly support this excitation. The irradiation energy is stored as coulombic energy of the separated charges. By self-trapping the delocalized hole relaxes to the more stable exciplex $(Xe_2)_{loc.}^{\bullet+}X^-$ (**9b**). Exciplexes of this kind are identified by their characteristic emissions.[7b][16] Another possibility to localize the hole is found for ternary systems with a substrate S.[17] The hole is trapped at this lattice defect, most probably via a charge-transfer complex $(Xe_n \leftarrow S)_{loc.}^{\bullet+}$ (**9c**). Upon irradiation with a second photon or by annealing of the matrix the separated charges are neutralized, since electron transfers in solids are possible over long distances.[18] The stored coulombic energy is set free and leads to the vibrational excitation of the substrate. The final result is a so-called *hot ground-state* reaction.

According to lately conceived findings[19], an alternative way for the energy transfer is possible: If a vibrationally excited exciplex $[(Xe_2)_{loc.}^{\bullet+}X^-]^*$ (**9d**) relaxes, the excess energy is transferred onto the solid and dissipated via phonons (energy quanta of the lattice vibrations). The phonons are able to excite the substrate vibrationally, which reacts in a consecutive path to the thermal products.

Scheme 5. Possible energy-transfer reactions in a halogen-doped xenon matrix



A third alternative is the direct formation of a radical cation $S^{\bullet+}$, since the ionization energy of S might be reduced by the solid to such an extent, that an ionization with wavelengths in the UV range becomes possible.

Up to now we have not been able to decide definitely, which of the possible energy-transfer reactions is responsible for the photoinduced reactions in halogen-doped matrices.

4.2. Implications for the Ring-Opening of *cis*-DCCB (1) and *trans*-DCCB (5)

There are at least three different mechanistic explanations for the photoinduced ring-opening of **1** and **5** possible, which will be compared below.

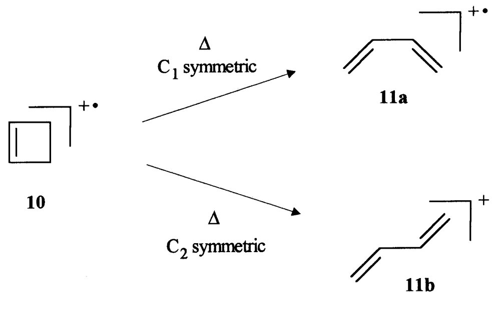
Ring-Opening via a Radical Anion

A photoinduced reaction of this kind can be described in similarity to the energy-transfer mechanism in halogen-doped xenon matrices. In the solid xenon an electron is excited from the valence band to the conduction band. The electron is trapped by the substrates **1** and **5**, respectively, which act as electron acceptors instead of a halogen atom. A reaction of this type should be possible, since the electron affinity of *cis*-DCCB (**1**, 4.5 eV)[20a] is even higher than the corresponding values of halogen atoms.[20b] In addition, halogen-containing compounds are known as suitable electron acceptors in low-temperature matrices.[21] The positively charged hole can either be delocalized in the solid or localized in the neighbourhood of the anion. Upon neutralization of the separated charges by a second photon the stored photoenergy is transferred onto the substrate and leads to the vibrational excitation of **1** and **5**. In a consecutive hot ground-state reaction thermal products are formed. Due to the high stereospecifity of the photoinduced ring opening of **1** and **5** this mechanims seems to be the most convincing explanation.

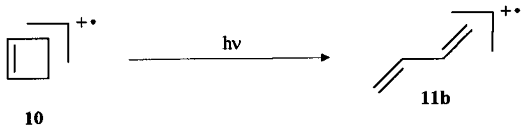
On the other hand the direct electrocyclic reaction of the cyclobutene radical anion and the neutralization of the products is possible. From experiments[22a] and theoretical considerations[22b] cyclobutene radical anions are known to open in a conrotatory fashion.

Ring-Opening via a Radical Cation

In a competitive reaction to the formation of a radical anion the substrates **1** or **5** might be ionized by the the positively charged hole in the solid xenon to the corresponding radical cations. The prediction for the electrocyclic ring opening of cyclobutene radical cations is complex, since orbital-correlation diagrams as well as state-correlations diagrams are not able to predict the stereochemical outcome of this reaction correctly.[23] In a recent ab initio study on the ground-state reactions of the cyclobutene radical cation $CB^{\bullet+}$ (**10**) two concerted pathways were found.[24] A C_1-symmetric path leads to the formation of the *s-cis* conformer of the butadiene radical cation $sBD^{\bullet+}$ (**11a**). In a C_2-symmetric pathway the *s-trans* conformer of the butadiene radical cation $tBD^{\bullet+}$ (**11b**) is formed directly. The activation energy for this reaction is − due to a pseudo Jahn−Teller distortion of the transition state − about 5 kcal/mol higher than for the C_1-symmetric reaction. Upon substitution of the cyclobutene the pseudo Jahn−Teller distortion is expected to disappear, and the C_2-symmetric pathway might become competitive with respect to the C_1-symmetric ring opening.



In an experimental study Bally et al. found that $CB^{\bullet+}$ (**10**) opens photochemically to $tBD^{\bullet+}$ (**11b**).[23d] The authors assumed that the excited radical cation relaxes to a vibrational excited ground state first and then reacts to the product.



In view of this complex reaction pattern of cyclobutene radical cations – either ground-state or excited-state reactions are possible – it is difficult to explain the highly stereospecific ring opening by the intermediate formation of a radical cation.

Ring-Opening via Xenon-Halogen Exciplexes

In a bromine-doped xenon matrix most probably the photoinduced ring opening of *cis*-DCCB (**1**) follows a mechanism, in which xenon-bromine exciplexes are involved (see chapter 4.1). The bromine atoms act as an electron acceptor, whereas **1** now stabilizes the hole in the solid xenon – in contrast to the reaction via a radical anion – as donor in a charge-transfer complex. Upon neutralization a hot ground-state reaction of vibrationally excited **1** occurs.

5. Conclusion

As predicted by the Woodward–Hoffman rules the thermal ring opening of **1** and **5** follows with high stereospecifity the conrotatory pathway only. The matrix-isolated (Xe, 12 K) pyrolysis products of **1** were the *s-trans* and the *s-cis* conformers **2a** and **2b**, whereas a thermally induced reaction of **5** yielded the *s-cis* and *s-trans* conformers **3a** and **3b**. In the latter case the other thermally allowed products **4a** and **4b** could not be observed in agreement with DFT calculations. The *s-cis* conformers **2b** and **3b** could be identified for the first time by comparison of the experimental and calculated IR absorptions.

Upon photolysis of **1** in a xenon or an argon matrix at 12 K with the emission of an ArF excimer laser ($\lambda = 193$ nm) products of the allowed disrotatory ring opening as well as those of the forbidden conrotatory reaction were observed. The reaction was complicated by a ring closure and the elimination of HCl. This non-stereospecific ring opening, in which **1** is directly excited by irradiation, is in agreement with the known photochemistry of cyclobutenes.

Since **1** and **5** exhibit no UV absorption at wavelengths > 230 nm, no photoreaction occurred if **1** and **5** were irradiated in an argon matrix with $\lambda > 270$ nm. The situation changed dramatically if both precursors were photolysed ($\lambda > 270$ nm) in a xenon matrix. A quick reaction could be observed in both cases, yielding in a primary process the products of a conrotatory mode, in contradiction to the expectation. In this case the photon does not lead to a direct excitation of the cyclobutenes, but to a cooperative absorption by the solid xenon and the precursors. The mechanism of this reaction, which is similar to photochemically induced reactions in halogen-doped xenon matrices, is still open. Most probably, the photon promotes an electron from the valence band of the solid to the conduction band, and the electron is trapped by precursors. The photon energy is stored as coulombic energy of an electron-hole pair, and is set free upon recombination of the separated charges resulting in the vibrational excitation of the precursor. A hot ground-state reaction, which now obeys the Woodward–Hoffmann rules, follows. Nevertheless, a reaction of radical cations cannot be completely excluded, since the formation of these charged radicals might be supported by the high polarization ability of the solid xenon.

Financial support by the *Fonds der Chemischen Industrie*, the *Deutsche Forschungsgemeinschaft*, and the *Volkswagen Stiftung* is gratefully acknowledged. We like to thank Prof. Dr. *Schwentner* (FU Berlin), Dr. *H. P. Reisenauer*, Dr. *S. Senger*, and Dipl.-Chem. *C. Lautz* for many helpful discussions.

Experimental Section

General: The equipment for matrix-isolation studies, photolyses, and pyrolyses is described in detail elsewhere.[25] Commercially available argon (Messer Griesheim; 99.996%), xenon (Messer Griesheim, 99.996%), bromine (Riedel-de Haën; 99%), and *cis*-3,4-dichlorocyclobutene (**1**, Fluka) were used without further purification. – *trans-3,4-Dichlorocyclobutene* (**5**) was synthesized according to a procedure of Hoberg et al.[26] – *Calculations:* The calculations were performed with the Gaussian package of programs.[27] In all cases the DFT method BLYP was used in combination with the basis set 6-311G*.

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[1] R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1970**.

[2] [2a] R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, H. Brune, *Chem. Ber.* **1965**, *98*, 2339–2352. – [2b] J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*, Academic Press, New York **1981**, pp. 45–58, and references cited therein. – [2c] J. I. Brauman, W. A. Archie, Jr., *J. Am. Chem. Soc.* **1972**, *94*, 4261–4265.

[3] W. J. Leigh, *Can. J. Chem.* **1993**, *71*, 147–155, and references cited therein.

[4] [4a] W. T. A. M. Van der Lugt, L. J. Oosterhoff, *J. Am. Chem. Soc.* **1969**, *91*, 6042–6049. – [4b] D. Grimbert, G. Segal, A. Devaquet, *J. Am. Chem. Soc.* **1975**, *97*, 6629–6632. – [4c] K. Morihashi, O. Kikuchi, *Theor. Chim. Acta* **1985**, *67*, 293–305.

[5] [5a] M. O. Trulson, R. A. Mathies, *J. Phys. Chem.* **1990**, *94*, 5741–5747. – [5b] M. K. Lawless, S. D. Wickham, R. A. Mathies, *Acc. Chem. Res.* **1995**, *28*, 493–502. – [5c] D. R. Cyr, C. C. Hayden, *J. Chem. Phys.* **1996**, *104*, 771–774.

[6] [6a] P. Celani, F. Bernardi, M Olivucci, M. A. Robb, *J. Chem. Phys.* **1995**, *102*, 5733–5742. – [6b] F. Bernardi, M. Olivucci, M. A. Robb, *Chem. Soc. Rev.* **1996**, *25*, 321–328.

[7] [7a] G. Maier, H. P. Reisenauer, K. Lanz, R. Troß, D. Jürgen, B. A. Hess, Jr., L. J. Schaad, *Angew. Chem.* **1993**, *105*, 119–121; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 74–76. – [7b] G. Maier, D. Jürgen, R. Troß, H. P. Reisenauer, B. A. Hess, Jr., L. J. Schaad, *Chem. Phys.* **1994**, *189*, 383–399. – [7c] G. Maier, S. Senger, *Angew. Chem.* **1994**, *106*, 605–606; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 558–559. – [7d] G. Maier, S. Senger, *Liebigs Ann.* **1996**, 45–47. – [7e] G. Maier, S. Senger, *J. Am. Chem. Soc.* **1997**, *119*, 5847–5861.

[8] W. Kirmse, N. G. Rondan, K. N. Houk, *J. Am. Chem. Soc.* **1984**, *106*, 7989–7991.

[9] [9a] W. C. Danen, D. F. Koster, R. N. Zitter, *J. Am. Chem. Soc.* **1979**, *101*, 4281–4283. – [8b] C. Mao, N. Presser, L. John, R. M. Moriarty, R. J. Gordon, *J. Am. Chem. Soc.* **1981**, *103*,

2105–2106. – [8c] N. Presser, C. Mao, R. M. Moriarty, R. J. Gordon, *J. Chem. Phys.* **1983**, *78*, 6021–6029.

[10] L. Deng, T. Ziegler, *J. Phys. Chem.* **1995**, *99*, 612–618.

[11] [11a] G. Gundersen, Z. Smith, H. Thomassen, *Acta. Chem. Scand.* **1988**, *42A*, 477–492. – [11b] G. Gundersen, F, Karlsson, Z. Smith, H. G. Thomassen, *Acta Chem Scand.* **1986**, *40A*, 522–532.

[12] [12a] E. Benedetti, M. Aglietto, P. Vergamini, R. A. Munoz, A. V. Rodin, Y. N. Panchenko, Y. A. Pentin, *J. Mol. Struct.* **1976**, *34*, 21–33. – [12b] G. Gundersen, P. Klaeboe, A. Borg, Z. Smith, *Spectrochim. Acta* **1980**, *36A*, 843–852.

[13] R. Vestin, A. Borg, T. Lindblom, *Acta Chem. Scand.* **1968**, *22*, 687–689.

[14] H.-G. Viehe, E. Franchimont, *Chem. Ber.* **1964**, *97*, 602–609.

[15] G. Wedler, *Lehrbuch der Physikalischen Chemie*, Verlag Chemie, Weinheim, **1982**, pp. 745–747.

[16] [16a] M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1986**, *85*, 5660–5681. – [16b] M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 4102–4123. – [16c] M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 4124–4136.

[17] R. Lenk, *Physik*, VEB Brockhaus Verlag, Leipzig, **1989**, pp. 273–275.

[18] [18a] J. R. Miller, J. A. Peeples, K. J. Schmitt, G. L. Closs, *J. Am. Chem. Soc.* **1982**, *104*, 6488–6493. – [18b] L. T. Calcaterra, G. L. Closs, J. R. Miller, *J. Am. Chem. Soc.* **1983**, *105*, 670–671.

[19] S. Senger, Dissertation, University of Giessen, **1997**.

[20] [20a] H. Hake, H. Landen, H.-D. Martin, B. Mayer, A. Steigel, G. Distefano, A. Modelli, *Tetrahedron Lett.* **1988**, *29*, 6601–6604. – [20b] T. M. Miller in *CRC Handbook of Chemistry and Physics* (Ed.: D. R. Lide), 72th ed., CRC Press, Boca Raton, **1991**.

[21] T. Bally in *Radical Ionic Systems* (Eds.: A. Lund, M. Shiotani), Kluwer Academic Publishers, Holland, **1991**, pp. 3–54.

[22] [22a] N. L. Bauld, C. Shang, F. R. Farr, *J. Am. Chem. Soc.* **1972**, *94*, 7164–7165. – [22b] N. L. Bauld, J. Cessac, *J. Am. Chem. Soc.* **1975**, *97*, 2284–2285.

[23] [23a] N. L. Bauld, J. Cessac, *J. Am. Chem. Soc.* **1977**, *99*, 23–26. – [23b] E. Haselbach, T. Bally, Z. Lanyiova, *Helv. Chim. Acta* **1979**, *62*, 577–582. – [23c] I. R. Dunkin, L. Andrews, *Tetrahedron* **1985**, *41*, 145–161. – [23d] J. N. Aebischer, T. Bally, K. Roth, E. Haselbach, F. Gerson, X.-Z. Qin, *J. Am. Chem. Soc.* **1989**, *111*, 7909–7914.

[24] O. Wiest, *J. Am. Chem. Soc.* **1997**, *119*, 5713–5719.

[25] G. Maier, J. Eckwert, A. Bothur, H. P. Reisenauer, C. Schmidt, *Liebigs Ann.* **1996**, 1041–1053.

[26] H. Hoberg, C. Fröhlich, *Synthesis* **1981**, 830–831.

[27] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94, Revision D.3*, Gaussian, Inc., Pittsburgh, PA, **1995**.

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