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Substituent effects on the photolysis of methyl 2-carboxylate substituted aliphatic 2*H*-azirines

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Abstract

In this study, the UV induced photochemical reactions of two 2*H*-azirines – methyl 2-chloro-3-methyl-2*H*-azirine-2-carboxylate (MCMAC) and methyl 3-methyl-2*H*-azirine-2-carboxylate (MMAC) – isolated in argon matrices are compared. For both compounds, irradiation with $\lambda > 235$ nm led to observation of two primary photoprocesses: (a) C—C bond cleavage, with production of nitrile ylides (P1-type products), and (b) C—N bond cleavage, with production of methylated ketene imines (P2-type products). However, subsequent photoprocesses were found to be different in the two cases. In MCMAC, both primary photoproducts were shown to undergo further reactions: P1-type products decarboxylate, giving [(1-chloroethylidene)imino]ethanide, which bears a C=N$^+$=C$^-$ group (P3-type product); P2-type products decarbonylate, yielding a substituted ylidene methanamine (P4-type product). In MMAC, only P2-type primary photoproducts appeared to react, undergoing decarbonylation or decarboxylation (both reactions leading to P4-type products), whereas P1-type products were found to be non-reactive. The non-observation of any secondary photoproduct resulting from photolysis of P1-MMAC revealed the higher photostability of this species when compared with the corresponding photoproduct obtained from MCMAC.

The C—N photochemical cleavage is an unusual process in aliphatic 2*H*-azirines. In the studied compounds, its preference over the commonly observed C—C azirine-ring bond photocleavage is attributed to the presence of electron withdrawing substituents (methylcarboxy group in both azirines and also the chlorine atom in MCMAC), which accelerates intersystem crossing towards the triplet state from where the cleavage of the C—N bond takes place. The lack of the chlorine atom in MMAC may be partially compensated by the significantly higher stabilization of the P2-type photoproduct derived from this molecule (*ca.* -52 kJ mol^{-1}) relatively to the reactant, when compared to that obtained from MCMAC (*ca.* -26 kJ mol^{-1}). Nevertheless, the obtained results indicate that the methylcarboxy substituent plays the most important role in determining the photochemical behavior of these aliphatic 2*H*-azirines, in particular the preference they exhibit for the unusual C—N bond cleavage over the "classic" C—C bond cleavage.

Keywords: 2*H*-azirines; Photolysis; Matrix isolation FTIR spectroscopy; Substituent effects

1. Introduction

2*H*-azirines are three-membered heterocyclic compounds containing one nitrogen atom. Due to significant intrinsic strain of the 2*H*-azirine ring [estimated as 44.6 and 46.7 kJ mol^{-1} at the MP2/6-31G(d) and B3LYP/6-31G(d), respectively, for the unsubstituted 2*H*-azirine] [1], these compounds are highly reactive, undergoing easily cleavage of the ring upon thermal [2–5] or photochemical [3,5–7] excitation, as well as in result of reactions with both nucleo- [1,8,9] and electrophiles [1]. Therefore, 2*H*-azirines are recognized nowadays as important intermediates in the preparation of acyclic functionalized amino compounds and heterocycles [6,10,11], functionalized aziridines [12] and α and β amino acid derivatives [13].

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The thermal reactions of 2*H*-azirines result most of times in the C—N bond cleavage of the azirine ring [2,3,5], due to the unusual length of this bond [1,14,15], whereas thermally induced C—C bond cleavage appears to be rare [4].

On the other hand, the C—C bond cleavage of the azirine ring, leading to formation of the corresponding nitrile ylide, has been shown to be the preferred photochemical reaction channel [5–7,16–20]. Indeed, this reaction, followed by reaction of the photochemically produced nitrile ylide with an adequate 1,3-dipolarophile, has been widely explored in organic synthesis, allowing to obtain a variety of five-membered heterocycles [5–7,16–19]. The formation of nitrile ylides upon photochemical excitation of 2*H*-azirines has also been observed as the general dominant process in low-temperature inert matrices [21,22].

The theoretical predictions of Klessinger and Bornemann [23,24] allowed explanation of the above-mentioned results, as the authors concluded, in accordance with the observation of the ultrafast formation of phenylnitrile ylide from 2*H*-phenylazirine [17], that the C—C photochemical cleavage occurs from the $n\pi^*$ S_1 excited state *via* conical intersection between the S_1 and S_0 states, whereas the thermal breakage of this bond requires a high activation energy and is disfavored.

Nevertheless, recent findings by Inui and Murata [25–27] demonstrated that both C—C and C—N bonds can be cleaved upon photolysis of matrix-isolated 2*H*-azirines bearing an aromatic (naphthyl) substituent on C_2 and that the preference by one of these processes depends on the applied wavelength, host gas and substituents present in the azirine ring. The tendency toward the C—N bond cleavage increases with the electron-withdrawing ability of the ring substituents. For example, 3-methyl-2-(1-naphthyl)-2*H*-azirine irradiated with $300 < \lambda < 366$ nm light underwent exclusive C—C bond cleavage, while replacement of the naphthyl hydrogen in the *para* position relatively to the 2*H*-azirine ring by a halogen atom led to a mixture of the products arising from both the C—C and C—N bond cleavages, and its substitution by the strong electron-withdrawing NO_2 group led to the exclusive occurrence of the C—N bond cleavage, with production of the ketene imine derivative [25].

The unusual photochemical process implying the cleavage of the C—N bond was rationalized by formation of a vibrationally excited biradical generated from the triplet excited state of the azirine that can be produced by intersystem crossing from the S_1 state having an electronic character of a local $\pi\pi^*$ excitation of the naphthyl moiety [27]. The biradical later undergoes a Curtius-like rearrangement to the experimentally observed ketene imine [27].

The relevance of azirine-ring electron withdrawing substituents to the photochemistry of 2*H*-azirines has also been recently evaluated in our laboratory for two aliphatic 2*H*-azirines: methyl 2-chloro-3-methyl-2*H*-azirine-2-carboxylate (MCMAC) [28] and methyl 3-methyl-2*H*-azirine-2-carboxylate (MMAC) [29]. Our studies have demonstrated that the C—N bond is also preferentially cleaved after UV ($\lambda > 235$ nm) irradiation of these two compounds [28,29], and this was explained considering that the presence in the azirine ring of the electron-withdrawing substituents (methylcarboxy group in both azirines and also the chlorine atom in MCMAC) accelerates intersystem crossing towards the triplet state from where the cleavage of the C—N bond takes place.

The methylcarboxy ester substituent is common for both MCMAC and MMAC. However, the chlorine substituent is only present in the first compound, being replaced by a hydrogen atom in the second. In the present study, a comparison between the photochemical reactivity of the two compounds has been explored taking into account this chemical difference. As shown in detail below, this comparison allowed us to shed light on the relative importance of the chlorine and methylcarboxy substituents in determining the observed preference for the C—N bond photocleavage exhibited by the two compounds. In addition, the secondary photoprocesses following the primary photochemical step in the two compounds, which were found to be distinct, were also rationalized.

2. Materials and methods

2.1. Infrared spectroscopy

The studied compounds were synthesized as described elsewhere [1,30]. The infrared spectra were obtained using a Mattson (Infinity 60AR Series) Fourier Transform infrared spectrometer, equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beamsplitter, with $0.5\,cm^{-1}$ spectral resolution.

The compounds were placed in a specially designed doubly thermostatable Knudsen cell, whose compartments (sample container and valve nozzle compartments) were kept at 298 K during deposition of the matrices. The matrices were prepared by co-deposition of the compounds' vapors coming out from the Knudsen cell together with large excess of the matrix gas (argon N60, obtained from Air Liquide) onto the CsI substrate of the cryostat cooled to 10 K. All experiments were performed using an APD Cryogenics closed-cycle helium refrigeration system with a DE-202A expander. Irradiation of the matrices were carried out with a 500 W Hg(Xe) lamp (Newport, Oriel Instruments) through the outer KBr window of the cryostat ($\lambda > 235$ nm).

2.2. Computational methodology

The DFT calculations were performed with the B3LYP density functional [31,32] and the 6-311++G(d,p) basis set, using Gaussian98/03 [33,34]. Geometries of MMAC, MCMAC and their photoproducts were optimized using the Geometry Direct Inversion of the Invariant Subspace (GDIIS) method [35,36]. For all molecules studied, vibrational frequencies were calculated at the same level of

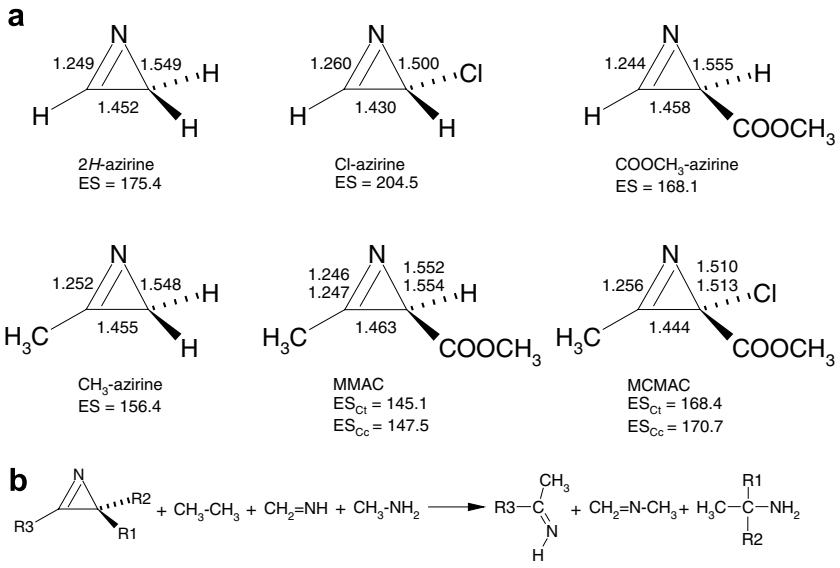

Fig. 1. (a) Comparison of calculated [B3LYP/6-311++G(d,p)] geometrical parameters of the 2*H*-azirine ring in: 2*H*-azirine, 2-chloro-2*H*-azirine (Cl–azirine), methyl 2*H*-azirine-2-carboxylate ($COOCH_3$-azirine), 3-methyl-2*H*-azirine (CH_3-azirine), MMAC and MCMAC. The bond lengths are in Å, strain energy values (ES) in kJ mol^{-1}. Strain energies are given for both the *Ct* and *Cc* conformers of MMAC and MCMAC. (b) Homodesmotic reaction used to calculate strain energies.

theory and scaled down by the factor 0.978, to account mainly for anharmonicity effects and limitations of the basis set.

The strain energies of the 2*H*-azirine ring in MCMAC, MMAC and some model compounds were also computed at the B3LYP/6-311++G(d,p) level of theory, with the application of the homodesmotic reaction [37] given in Fig. 1. Previously it has been shown that the strain energies of oxiranes (three-membered heterocyclic compounds containing the oxygen atom) calculated at the B3LYP/6-311++G(d,p) level of theory with the application of several different homodesmotic reactions brought similar results, particularly when the simpler reactants have been employed [38]. Therefore, in this work we used the above-mentioned computational method with the homodesmotic reaction with the simplest possible suitable (having corresponding hybridization and number of hydrogen atoms connected) substrates and products. This reaction was previously applied to calculate the strain energy of the unsubstituted 2*H*-azirine at MP2/6-31G(d) and B3LYP/6-31G(d) [39].

3. Results and discussion

Both MCMAC and MMAC are characterized by two internal rotation axes, O═C—O—CH_3 and O═C—C—Cl(H), which can give rise to four conformational isomers. In order to identify the minimum energy conformations of both MCMAC and MMAC, a systematic investigation of the potential energy surface of the molecules was undertaken using the B3LYP/6-311++G(d,p) method. Two experimentally relevant conformers were found: the *Ct* and *Cc* forms (Fig. 2), which differ in the relative orientation of the azirine and methylcarboxy groups. The capital and lowercase letters denote the *cis* or *trans*

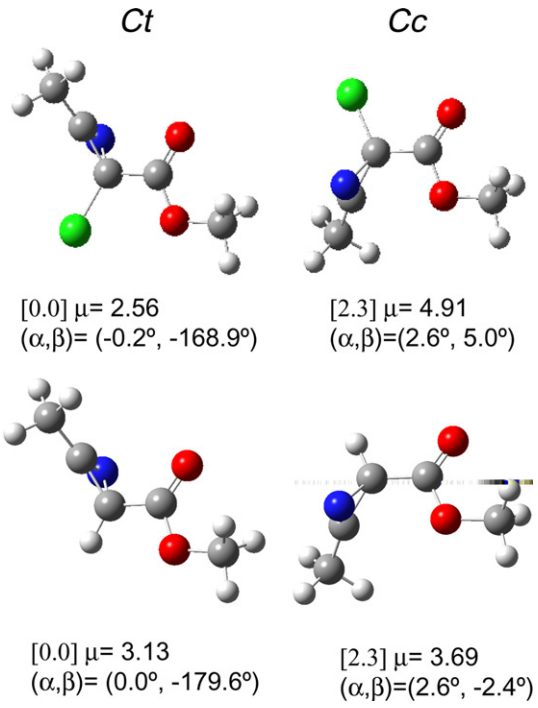

Fig. 2. Experimentally relevant conformers of MCMAC (upper line) and MMAC (bottom line). The numbers in parentheses denote zero-point corrected energy (in kJ mol^{-1}) relative to the most stable conformer of MCMAC and MMAC, respectively. The values of dipole moment (μ) are in debyes. The symbols α and β indicate the values of the O═C—O—C and O═C—C—R (R = Cl for MCMAC and H for MMAC) dihedral angles, respectively.

conformations in respect to the O═C—O—C and O═C—C—Cl(H) dihedral angles, respectively. For both compounds in the gaseous phase, the *Ct* conformer was predicted to be more stable than the *Cc* form by *ca.* 2 kJ mol^{-1} [28,29].

In order to investigate the influence of the substituents on the stability of the studied 2*H*-azirines, the strain energy (ES) has been calculated for the 2*H*-azirine ring in these structures and compared with the strain energy computed for the simplest, unsubstituted 2*H*-azirine and some single-substituted 2*H*-azirines (Fig. 1). The influence of a substituent on the stability of the strained ring depends mainly on its electro-donating or withdrawing properties and size [40]. For unsubstituted 2*H*-azirine, the calculated strain energy amounts to 175 kJ mol^{-1} in agreement with the previously calculated values (44.6 and 46.7 kcal mol^{-1} at MP2/6-31G(d) and B3LYP/6-31G(d) levels of theory, respectively) [39]. Interestingly, the substitution of all hydrogen atoms in MCMAC (methyl group at C_3; chlorine atom and methylcarboxy group at C_2) does not change significantly the strain energy of the system, which is *ca.* 168–171 kJ mol^{-1} (depending on the conformer). On the other hand, the calculated strain energy of MMAC (methyl group at C_3; methylcarboxy group at C_2) is considerably lower than for both MCMAC and unsubstituted azirine, amounting only to *ca.* 145–148 kJ mol^{-1} (depending on the conformer). These results suggest that both methyl and methylcarboxy groups (or at least one of them) stabilize the ring, while the presence of a chlorine atom at C_2 acts in the opposite way. This hypothesis was checked by calculations of the strain energy of three 2*H*-azirines bearing a single substitutent: –CH_3 at the C_3 atom (CH_3–Azirine), –Cl at the C_2 atom (Cl–Azirine) and –C(=O)OCH_3 at the C_2 atom ($COOCH_3$–Azirine). A significant destabilization of Cl–Azirine was found (ES = 204.5 kJ mol^{-1}), while a quite neutral (only slightly stabilizing) effect due to the methylcarboxy substituent at the C_2 atom (ES = 168.1 kJ mol^{-1}) and a considerably stabilizing influence of the methyl group at the C_3 carbon (ES = 156.4 kJ mol^{-1}) were theoretically predicted. This interpretation is supported by the significant differences found in the geometries of the azirine ring in MMAC and MCMAC. According to the calculations, the C—N and C—C bonds are considerably shorter for MCMAC than for MMAC (see Fig. 1), while the effect is even more striking when Cl–Azirine is considered, for which further shortening of both C—N and C—C bonds is predicted. The stabilizing properties of an electron releasing group at C_3 have been recently shown for methylene-2*H*-azirines [41] in line with our findings.

The origin of the remarkable effect on the azirine ring bond lengths induced by the chlorine substituent at the C_2 atom (shortening of both the C—N and C—C bond lengths and lengthening of the C=N bond; see Fig. 1) was investigated by analysis of the charge distribution in the two molecules. The calculated Mulliken charges provide a simple picture of the electronic distribution in the azirine ring of MMAC and MCMAC that enables to easily understand the structural trends. Indeed, due to the presence of the chlorine atom in MCMAC, in this molecule the charge of C_2 became considerably more positive than in MMAC (0.567 *vs.* 0.255 *e*), whereas the charges of C_3 and N are calculated as being (−0.275, −0.088 *e*) in MCMAC and (0.063, −0.146 *e*) in MMAC. Hence, the C—N and C—C bonds are stronger (shorter) in MCMAC because the charge interactions between C_2 and both C_3 and N are attractive and relatively strong, while in MMAC the C_2…C_3 charge interaction is repulsive and the C_2…N interaction in spite of being attractive is weaker than in MCMAC (essentially because the charge on C_2 in MMAC is about half of that of the same atom in MCMAC). In its turn, the C=N bond is weaker (longer) in MCMAC than in MMAC because in MCMAC the charges on C_3 and N are both negative, while they have opposite signs in MMAC.

The IR spectra of the studied compounds isolated in argon matrices were obtained and fully assigned based on the comparison between the experimental data and the B3LYP/6-311++G(d,p) calculated spectra for their *Ct* and *Cc* conformers, which fit nicely the observed spectra (Fig. 3). Upon broadband UV irradiation ($\lambda > 235$ nm) both compounds react to form new species, as noticed by the observed decrease in the intensity of the IR bands attributed to MCMAC or MMAC and appearance of new features in the spectra of the irradiated matrices. According to the observed rate of growing of the emerging bands, [28,29] two primary photoproducts were formed, which could be identified on the basis of the comparison of the experimental data and the predicted infrared spectra of the possible photoproducts: a nitrile ylide (photoproduct P1), corresponding to the expected product resulting from the usual azirine-ring C—C bond cleavage, and a methylated ketene imine (photoproduct P2), which resulted from the unusual C—N bond cleavage (Figs. 4 and 5).

Both P1 and P2-type products can exist in two different low energy conformers, which can be correlated with the two low energy forms of the original compounds. The most

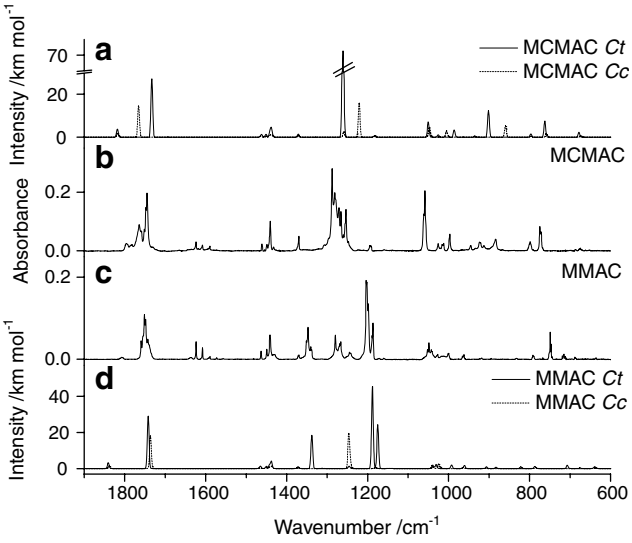

Fig. 3. Infrared spectra of MCMAC (b) and MMAC (c) isolated in solid argon at 10 K and DFT(B3LYP)/6-311++G(d,p) calculated spectra for the experimentally relevant conformers of these compounds (a and d, respectively) scaled by their relative populations at 298 K (*Ct*, 72%; *Cc*, 28%, for both compounds), estimated from the calculated relative energies and assuming the Boltzmann distribution.

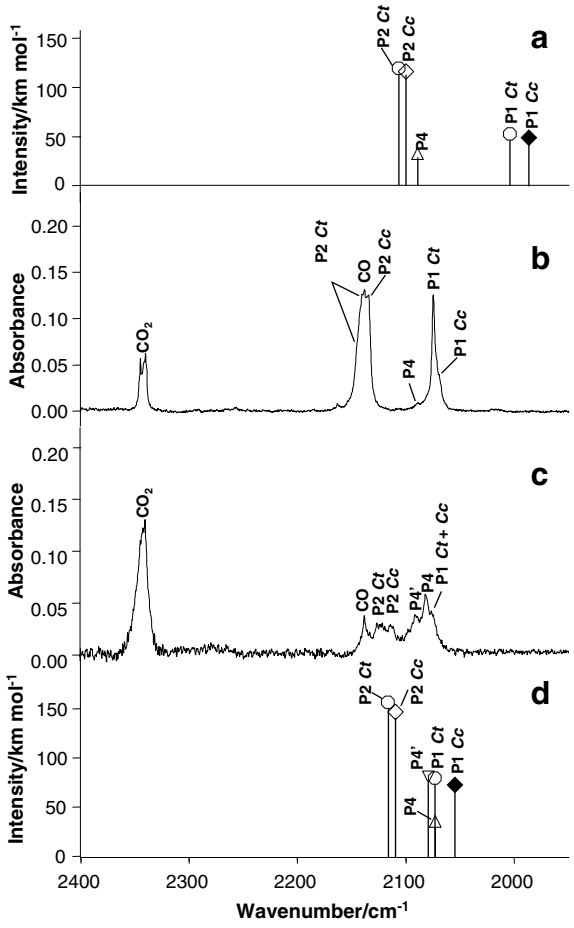

Fig. 4. The comparison of the normalized to the same initial concentration of reactant spectra of matrix-isolated MCMAC (b) and MMAC (c) in the 2400–1950 cm^{-1} range after 10 min of irradiation with $\lambda > 235$ nm, and B3LYP/6-311++G(d,p) calculated spectra of the observed photoproducts of MCMAC (a) and MMAC (d) in the same spectral region.

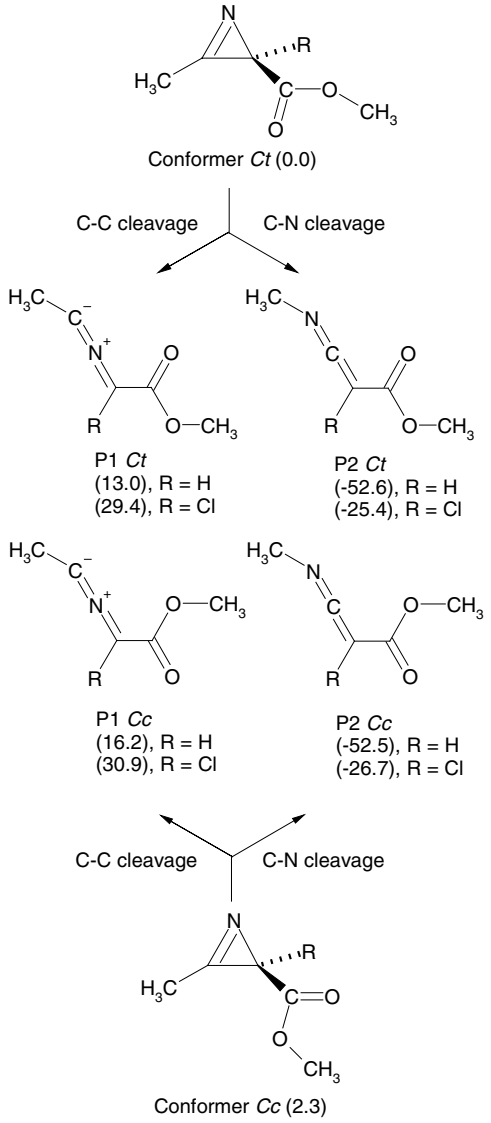

Fig. 5. Primary reaction pathways resulting from irradiation ($\lambda > 235$ nm) of matrix-isolated MCMAC and MMAC. The numbers in parenthesis correspond to energy differences (kJ mol^{-1}) of products of reaction and reactants. The energy difference between the *Cc* and *Ct* conformers is, for both MMAC and MCMAC equal to *ca.* 2.3 kJ mol^{-1}.

intense bands of the MCMAC photoproducts appear at 2145/2141 and 2135 cm^{-1} (Fig. 4b), and could be assigned to the ν(C═C═N) asymmetric stretching mode in the two conformers of P2, P2-*Ct* (2145/2141 cm^{-1}) and P2-*Cc* (2135 cm^{-1}), which result from the C—N bond cleavage of the azirine ring of *Ct* and *Cc* conformers of MCMAC, respectively (see Fig. 5). The bands are overlapped with the characteristic absorption of CO isolated in argon, at *ca.* 2138 cm^{-1}. As described in detail below, CO is a secondary product of the photolysis of matrix-isolated MCMAC. The noticeably less intense absorptions at 2069 (shoulder) and 2073 cm^{-1} were attributed to the ν(C^{-}═N^{+}═C) asymmetric stretching vibration of the P1-type photoproducts resulting from cleavage of the C—C bond of MCMAC. The corresponding bands in MMAC occur in the region 2126–2112 cm^{-1} (P2) and at 2077 cm^{-1} (P1), appearing considerably overlapped with absorptions associated to secondary photoproducts (P4, P4′ and CO) (Fig. 4c).

As mentioned in Section 1, the unusual photochemical C—N bond cleavage was observed for the first time for aliphatic 2*H*-azirines in the case of MCMAC and MMAC, where it was in fact found to be the preferred process in the case of the matrix-isolated compounds [28,29]. Such behavior was attributed to the presence in these molecules of the electron-withdrawing substituents on the azirine ring (methylcarboxy group in both azirines and also the chlorine atom in MCMAC), which accelerates the intersystem crossing toward the triplet state from where the cleavage of the C—N bond takes place and, in this way, the observed C—N bond breakage [23,24,28,29].

For MCMAC, the P2/P1 photoproducts' ratio was estimated to be *ca.* 2/1 under irradiation with a Xe lamp ($\lambda > 235$ nm) [28]. As mentioned above, the same photochemical preference is observed for MMAC and MCMAC irradiated with the Xe(Hg) 500 W lamp ($\lambda > 235$ nm), although a quantitative analysis cannot be done in these

cases due to overlap of bands due to the primary and secondary photoproducts. These results indicate that the methylcarboxy group plays the most important role in determining the photochemical behaviour of these aliphatic 2*H*-azirines, in particular the preference for the unusual C—N bond cleavage over the "classic" C—C bond cleavage they exhibit.

The yields of the photochemical reactions of MMAC and MCMAC have been compared after 10 min of irradiation under the same experimental conditions. It was found that in the case of MMAC *ca.* 37% and 60% of the initial population of the *Ct* and *Cc* conformers reacted after that period of irradiation (these values were extracted from the intensities of bands at 1370–1330 and 1280–1260 cm^{-1}, which were given rise by *Ct* and *Cc* forms, respectively). Unfortunately, in MCMAC spectrum, the most intense bands due to individual conformers are significantly overlapped and, therefore, the comparison of reactivity of both forms has to be treated as very approximate. From the relative intensities of the low-intensity bands at 923–913 cm^{-1} (*Ct*) and 888–884 cm^{-1} (*Cc*), the yields of reaction could be estimated as being *ca.* 18% and 52%, for *Ct* and *Cc*, respectively. Additionally, the more intense groups of bands (at 1061–1058, 999–997, 804–796 and 775–771 cm^{-1}), assigned to both conformers of MCMAC, were also used to estimate the reaction yields. As expected, the calculated reaction yield was found to be considerably lower when obtained from those absorptions to which, according to the calculated relative infrared intensities, *Ct* has the dominating contribution (*ca.* 37, 24, 12 and 17% for groups of bands at 1061–1058, 999–997, 804–796 and 775–771 cm^{-1}, respectively; with the *Ct*:*Cc* calculated contribution to intensities being considerably higher for the two latter cases, *ca.* 3–4, *vs.* approximately 1, for the first two groups of bands). These results unequivocally attest the higher photostability of conformer *Ct*, when compared with *Cc*, in both studied compounds.

Globally, the photoreactivity of MMAC is higher than that of MCMAC. Indeed, after the same time of irradiation, a more pronounced decrease in the total intensity of the bands due to the reactant was observed in the case of MMAC [in addition, the fact that a significantly higher total intensity of bands due to CO (around 2138 cm^{-1}) and CO_2 (in the range 2345–2341 cm^{-1}) was also observed provides further indication of the greater facility of MMAC to undergo photolysis under the present experimental conditions]. Since the irradiation conditions used were the same and the integrated absorptions of the two compounds in the relevant spectral range ($\lambda > 235$ nm) are nearly equal (see Figure S1, provided as Supplementary Information), the higher photoreactivity of MMAC compared to MCMAC can in fact be ascribed to a higher quantum yield for the MMAC reaction, which in turn can be correlated with the different geometry of both compounds. It can be rationalized by comparing the relevant bond lengths in the two compounds. In the more strained MCMAC ring, *both* the C—C and C—N bonds are considerably shorter than for MMAC in the ground electronic state (see Fig. 1). If the assumption is made that the bond lengths do not change significantly in the excited state from which the reaction takes place (or undergo similar relative changes), then the cleavage of *both* the C—C and C—N bonds should be facilitated for MMAC. The lack of relation of strain and chemical reactivity, particularly for molecules in which activated complex resembles the reactant, has been previously emphasized [42].

The primary products of photoreaction (P1 and P2) are stabilized for MMAC relative to MCMAC. Products of P2 type are lower in energy for both compounds. However, a significantly higher stabilization of P2 relatively to MMAC (*ca.* -52 kJ mol^{-1}) in comparison with the corresponding photoproduct obtained from MCMAC (*ca.* -26 kJ mol^{-1}) is theoretically predicted (see Fig. 5). Similarly, although all P1 products are higher in energy than the corresponding reactant species, the P1 photoproduct resulting from MMAC is less destabilized relatively to the reactant (13 and *ca.* 16 kJ mol^{-1}, for *Ct* and *Cc* forms, respectively) than the P1 photoproduct resulting from MCMAC (*ca.* 30 kJ mol^{-1}, for both conformers).

Since in principle both electron withdrawing Cl and methylcarboxy groups should increase the reactivity of the compounds, in particular their trend to undergo the unusual C—N bond cleavage, the lack of the chlorine atom in MMAC must be, at least partially, compensated by the above-mentioned significantly higher stabilization of P2 relatively to MMAC in comparison with the corresponding photoproduct obtained from MCMAC. These results indicate that the methylcarboxy group plays the most important role in determining the photochemical behaviour of these aliphatic 2*H*-azirines, in particular the preference for the unusual C—N bond cleavage over the "classic" C—C bond cleavage they exhibit.

In spite of the fact that both compounds undergo essentially identical primary photoreactions, subsequent photoprocesses were found to be different in the two cases, as result of the different photostability of the primary photoproducts (Fig. 6). In MCMAC, both primary photoproducts were shown to undergo further reactions: P1-type products decarboxylate, giving [(1-chloroethylidene)imino]ethanide, which bears a $C{=}N^{+}{=}C^{-}$ group (P3-type product); P2-type products decarbonylate, yielding a substituted ylidene methanamine (P4-type product). On the other hand, in MMAC, only P2-type primary photoproducts appeared to react, undergoing decarbonylation or decarboxylation [both reactions leading to P4-type products, namely *N*-(2-methoxyethenylidene) methanamine (P4) and *N*-prop-1-en-1-ylidemethamine (P4′)], whereas P1-type products were found to be non-reactive.

The lack of any secondary photoproduct resulting from decomposition of P1-MMAC reveals the higher photostability of this species when compared with the corresponding photoproduct obtained from MCMAC, though the reasons for such behavior are still open to investigation. On the other hand, the preference of P2-MMAC to decarboxylate

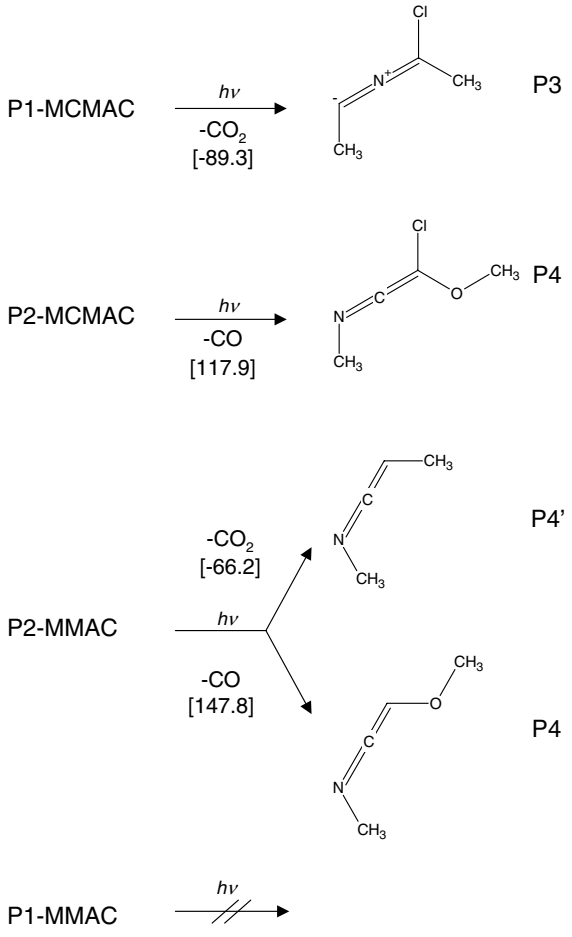

Fig. 6. Structures of secondary photoproducts resulting from irradiation ($\lambda > 235$ nm) of matrix-isolated MCMAC and MMAC. Reaction energies (kJ mol^{-1}) are provided in brackets.

(as revealed by the relative observed intensities of the CO_2 and CO bands normalized-to-calculated intensities; see Fig. 4) are in consonance with the relative energies of the reactions leading to P4′ (*ca.* −66 kJ mol^{-1}; decarboxylation) and P4 (*ca.* 148 kJ mol^{-1}; decarbonylation) secondary photoproducts.

4. Conclusions

Two substituted 2*H*-azirines, methyl 2-chloro-3-methyl-2*H*-azirine-2-carboxylate (MCMAC) and methyl 3-methyl-2*H*-azirine-2-carboxylate (MMAC), were synthesized and their reactivity in low-temperature argon matrices after UV excitation with $\lambda > 235$ nm was investigated.

Previously, it has been shown that irradiation of aromatic 2*H*-azirines may result in unusual C—N cleavage, which was, however, found to be particularly sensitive to chemical substitution [25]. As we have recently demonstrated that aliphatic substituted 2*H*-azirines possessing electron-withdrawing substituents at the azirine ring might also undergo the C—N bond breakage after UV excitation [28,29], the comparison of the photochemical behavior of compounds of this type bearing different substituents appeared the natural continuation of our study on the photoreactivity of this family of substances. Therefore, the results of the photoexcitation of the above-mentioned 2*H*-azirines (which differ by one substituent at C_2) isolated in argon matrices at 10 K have now been analyzed in detail.

The global photoreaction yield was found to be higher for MMAC relative to MCMAC. This could be correlated with the different azirine-ring geometries in the two molecules, as both the C—C and C—N bonds (which are cleaved in the reaction) are longer for MMAC than in MCMAC (assumption is made here that geometry of the ground state and the excited states from which the reaction takes place, are not very different).

The obtained results strongly suggest that methylcarboxy group, but *not* the chlorine atom, is the key factor enabling the unusual photochemical C—N bond cleavage observed for the two compounds examined. Secondary photoprocesses following primary C—N and C—C azirine ring bond cleavages were also investigated and found to be significantly different in the two studied 2*H*-azirines. The secondary products are obtained both from P1 and P2 type of products in the case of MCMAC, while only the P2 product reacts in the case of MMAC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.12.027.

References

[1] T.M.V.D. Pinho e Melo, A. Gonsalves, Current Organic Synthesis 1 (2004) 275–292.
[2] T.M.V.D. Pinho e Melo, C.S.J. Lopes, A. Gonsalves, R.C. Storr, Synthesis-Stuttgart (2002) 605–608.
[3] A. Padwa, J. Smolanoff, A. Tremper, Journal of Organic Chemistry 41 (1976) 543–549.
[4] L.A. Wendling, R.G. Bergman, Journal of Organic Chemistry 41 (1976) 831–836.
[5] A. Padwa, J. Smolanoff, A. Tremper, Journal of the American Chemical Society 97 (1975) 4682–4691.
[6] A. Padwa, M. Dharan, J. Smolanof, S.I. Wetmore, Journal of the American Chemical Society 95 (1973) 1945–1954.

[7] A. Padwa, M. Dharan, J. Smolanof, S.I. Wetmore, Journal of the American Chemical Society 95 (1973) 1954–1961.
[8] M.J. Alves, T.L. Gilchrist, J.H. Sousa, Journal of the Chemical Society–Perkin Transactions 1 (1999) 1305–1310.
[9] Y.S.P. Alvares, M.J. Alves, N.G. Azoia, J.F. Bickley, T.L. Gilchrist, Journal of the Chemical Society–Perkin Transactions 1 (2002) 1911–1919.
[10] T.M.V.D. Pinho e Melo, C.S.J. Lopes, A. Gonsalves, A.M. Beja, J.A. Paixao, M.R. Silva, L.A. da Veiga, Journal of Organic Chemistry 67 (2002) 66–71.
[11] F. Palacios, D. Aparicio, A.M.O. de Retana, J.M. de los Santos, J.I. Gil, J.M. Alonso, Journal of Organic Chemistry 67 (2002) 7283–7288.
[12] F. Palacios, A.M.O. de Retana, E.M. de Marigorta, J.M. de los Santos, Organic Preparations and Procedures International 34 (2002) 219–269.
[13] C.B. Bucher, H. Heimgartner, Helvetica Chimica Acta 79 (1996) 1903–1915.
[14] L.L. Lohr, M. Hanamura, K. Morokuma, Journal of the American Chemical Society 105 (1983) 5541–5547.
[15] A. Doughty, G.B. Bacskay, J.C. Mackie, Journal of Physical Chemistry 98 (1994) 13546–13555.
[16] A. Padwa, J.K. Rasmussen, A. Tremper, Journal of the American Chemical Society 98 (1976) 2605–2614.
[17] E. Albrecht, J. Mattay, S. Steenken, Journal of the American Chemical Society 119 (1997) 11605–11610.
[18] K.H. Pfoertner, K. Bernauer, F. Kaufmann, E. Lorch, Helvetica Chimica Acta 68 (1985) 584–591.
[19] K.H. Pfoertner, F. Montavon, K. Bernauer, Helvetica Chimica Acta 68 (1985) 600–605.
[20] R.L. Barcus, L.M. Hadel, L.J. Johnston, M.S. Platz, T.G. Savino, J.C. Scaiano, Journal of the American Chemical Society 108 (1986) 3928–3937.
[21] H. Frei, G.C. Pimentel, in: L. Andrews, M. Moskovits (Eds.), Chemistry and Physics of Matrix-isolated Species, Elsevier Science Publisher B.V., 1989, pp. 139–166.
[22] E. Orton, S.T. Collins, G.C. Pimentel, Journal of Physical Chemistry 90 (1986) 6139–6143.
[23] M. Klessinger, C. Bornemann, Journal of Physical Organic Chemistry 15 (2002) 514–518.
[24] C. Bornemann, M. Klessinger, Chemical Physics 259 (2000) 263–271.
[25] H. Inui, S. Murata, Journal of the American Chemical Society 127 (2005) 2628–2636.
[26] H. Inui, S. Murata, Chemical Physics Letters 359 (2002) 267–272.
[27] H. Inui, S. Murata, Chemistry Letters (2001) 832–833.
[28] A. Gomez-Zavaglia, A. Kaczor, A.L. Cardoso, T.M.V.D. Pinho e Melo, R. Fausto, Journal of Physical Chemistry A 110 (2006) 8081–8092.
[29] A. Kaczor, A. Gomez-Zavaglia, T.M.V.D. Pinho e Melo, A.L. Cardoso, R. Fausto, Journal of Physical Chemistry A 110 (2006) 10742–10749.
[30] T.M.V.D. Pinho e Melo, C.S.J. Lopes, A.L. Cardoso, A. Gonsalves, Tetrahedron 57 (2001) 6203–6208.
[31] A.D. Becke, Physical Review A 38 (1988) 3098–3100.
[32] C.T. Lee, W.T. Yang, R.G. Parr, Physical Review B 37 (1988) 785–789.
[33] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J.W. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 2001.
[34] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, Gill, P. M. W.; B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Wallingford, CT, 2004.
[35] P. Csaszar, P. Pulay, Journal of Molecular Structure 114 (1984) 31–34.
[36] O. Farkas, H.B. Schlegel, Journal of Chemical Physics 111 (1999) 10806–10814.
[37] P. George, M. Trachtman, C.W. Bock, A.M. Brett, Tetrahedron 32 (1976) 317–323.
[38] A. Vila, R.A. Mosquera, Chemical Physics 287 (2003) 125–135.
[39] S. Calvo-Losada, J.J. Quirante, D. Suarez, T.L. Sordo, J. Comput. Chem. 19 (1998) 912–922.
[40] J.F. Liebman, A. Greenberg, Chemical Reviews 76 (1976) 311–365.
[41] J.R. Fotsing, K. Banert, European Journal of Organic Chemistry (2006) 3617–3625.
[42] K.B. Wiberg, Angewandte Chemie-International Edition in English 25 (1986) 312–322.