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Characterization of a distonic isomer $C_6H_5C^+(OH)OCH_2^\bullet$ of methyl benzoate radical cation by associative ion–molecule reactions

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Dedicated to the memory of Chava Lifshitz.

Abstract

The $C_6H_5C^+(OH)OCH_2^\bullet$ radical cation, formally a distonic isomer of ionized methyl benzoate, has been prepared by dissociative ionization of neopentyl benzoate, as earlier suggested by Audier et al. [H.E. Audier, A. Milliet, G. Sozzi, S. Hammerum, Org. Mass. Spectrom. 25 (1990) 44]. Its distonic character has now been firmly established by its high reactivity towards neutral methyl isocyanide (ionized methylene transfer) producing *N*-methyl ketenimine ions. Other mass spectrometric experiments and ab initio quantum chemical calculations also concur with each other pointing toward the existence of a stable distonic radical cation.

Keywords: Methyl benzoate; Distonic radical cations; Collisional activation; Neutralisation–reionization; Ion–molecule reactions; Quantum chemical calculations

1. Introduction

The structure assignment of an organic ion in the gas phase is commonly based on information derived from either its dissociation chemistry, or its reactivity in selected ion–molecule reactions. The methodology used in the former approach probes the collision induced (CID) and spontaneous dissociation of the ions and, when combined with energetic information derived from experiment and/or theoretical calculations, often leads to a definitive structure assignment [1,2]. In the second approach, the reactivity of the ion under consideration is probed by its interactions with selected neutral molecules. Apart from charge exchange and protonation reactions, highly structure specific associative ion–molecule reactions may occur and can be served to conveniently distinguish the ion from its structurally related isomers [3].

We have previously reported that the methyl formate radical cation has a distonic isomer formed upon a hydrogen transfer from the methyl group to the carbonyl oxygen, $H–C^+(–OH)OCH_2^\bullet$ [4]. The distonic isomer is actually more stable than the conventional formate ion. This isomer was prepared by dissociative ionization of isobutyl formate (by loss of propene), and it was expected that an hydrogen migration from the δ-position relative to the carbonyl group initiated the whole process as indicated in Scheme 1.

In the same time, Audier et al. [5] proposed a similar sequence for the possible generation of a distonic isomer **D**(distonic)$^{\bullet+}$ of ionized methyl benzoate **1**$^{\bullet+}$. In this particular case, a neopentyl ester was supposed to be necessary in order to obtain a satisfactorily yield of distonic ions upon isobutene loss (Scheme 1). Deuterium labeling experiments (neopentyl benzoate-1,1-d_2) have confirmed that the isobutene loss occurs by specific migration of a methyl hydrogen atom. Nevertheless, no firm evidence has been obtained to prove the existence of the latter isomer. In view of the fact that a distonic structure **D**$^{\bullet+}$ apparently plays the role of key-intermediate in the overall decarboxylation process of metastable methyl benzoate ions **1**$^{\bullet+}$, we have set out to carry out novel experiments with the aim of demonstrating its actual generation in the gas phase [6]. We wish to report here the results derived from

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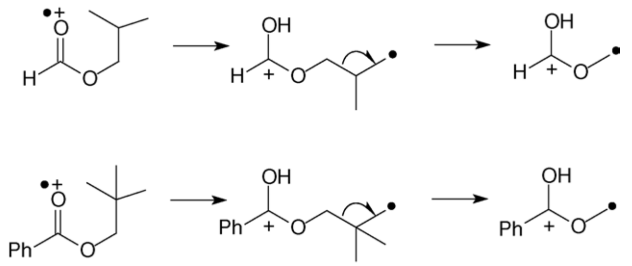


Scheme 1.

different complementing mass spectrometric experiments including mass-analyzed ion kinetic energy (MIKE), collisional activation (CA), neutralization–reionization mass spectrometry (NRMS) and associative ion–molecule reactions. In addition, some ab initio quantum chemical calculations have also been performed to obtain more quantitative information.

2. Experimental setup

The spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of cE_1B_1cE_2qcE_3B_2cE_4 geometry (E_i stands for electric sector, B_i for magnetic sector, q for a quadrupole collision cell and c for conventional collision cells). Typical conditions have been reported elsewhere [7]. The installation of the RF-only quadrupole collision cell (Q cell) inside the instrument between E_2 and E_3 has also been reported [8]. This modification allows the study of associative ion–molecule reactions and the study of low energy (ca. 20–30 eV) collision induced dissociations of decelerated ions. Briefly, the experiments utilizing the quadrupole consist of the selection of a beam of fast ions (8 keV) with the three first sectors ($E_1B_1E_2$), the deceleration of these ions to approximately 5 eV. The interaction between the ions and the reagent gas is thereafter realized in the Q cell and, after re-acceleration at 8 keV, all the ions generated in the quadrupole are separated and mass measured by scanning the field of the second magnet. The high-energy collisional activation (CA) spectra of mass-selected ions generated in the Q cell can be recorded by scanning the field E_4 after selection of the ions with E_3 and B_2. The products of dissociation of metastable ions within the quadrupole (without collision gas) can also be recorded by scanning the field of the second magnet; this kind of spectra will be referred in the text to “resolved” MIKE spectra.

In the neutralization–reionization experiments, the Q cell and its ion optics are extracted from their housing and an additional neutralization collision cell is inserted before the reionization cell which precedes E_3. Un-reacted ions are eliminated by floating at 9000 V the intermediate calibration ion source.

All the samples were commercially available and used in this work without any further purification except for neopentyl benzoate **2** prepared by reaction of benzoyl chloride with neopentyl alcohol, and the partially labeled neopentyl benzoate PhC(=O)CHDC$(CH_3)_3$, prepared by reaction of benzoyl chloride with neopentyl alcohol-1-d_1 (prepared by reduction of pivalaldehyde with D_4LiAl in dry ether).

3. Results and discussion

3.1. Metastable ion characteristics

The major dissociation channel observed in the 70 eV electron ionization mass spectrum (EIMS) of methyl benzoate **1** mainly consists, as expected for aromatic carbonyl compounds [9], of the loss of a methoxyl radical (*m/z* 105) followed by decarbonylation of the so-formed benzoyl cations (*m/z* 77). Surprisingly, this chemistry is strongly modified when metastable molecular ions are considered as shown in Fig. 1a by the mass-analyzed ion kinetic spectrum of the *m/z* 136 molecular ions. In this particular energy window, decarboxylation (*m/z* 92) is the main dissociation process, beside a loss of hydrogen (*m/z* 135) and a minor loss of water (*m/z* 118). The peak seen at *m/z* 105 is probably already due to collisional activation (CA) even at the low pressure used as its relative intensity depends strongly on the field-free region concerned (see below) and as it represents the base peak upon real CA conditions as described in Fig. 1b.

As shortly mentioned in Section 1, methyl formate radical cation possesses a distonic isomer H–C^+(–OH)$OCH_2^\bullet$, which was prepared by dissociative ionization (propene loss) of isobutyl formate. A similar sequence was also proposed for the possible generation of a distonic isomer of methyl benzoate starting with neopentyl benzoate **2** (see Scheme 1). Indeed, the MIKE spectrum of the *m/z* 192 ions of neopentyl benzoate features two peaks corresponding to a loss of benzoic acid with charge retention on the C_5H_{10} alkene (*m/z* 70), and a loss of isobutene (*m/z* 136). These two reactions probably start with hydrogen migration from one methyl group to the carbonyl oxygen as the corresponding peaks are cleanly shifted at *m/z* 71 and 137 in the case of the Ph–C(=O)OCHDC$(CH_3)_3$ isotopomer (vide infra).

The MIKE spectrum of the $\mathbf{D}^{\bullet+}$ ions is found to be quite similar to the corresponding one of methyl benzoate ions $\mathbf{1}^{\bullet+}$, with however, a significant intensity decrease of the *m/z* 105 peak (see Table 1).

3.2. High energy collisional activation

Upon helium collisional activation conditions, as seen from a comparison of Fig. 1b and c, the distonic species is readily

Table 1
“Resolved” MIKE spectra of *m/z* 136 ions (see Section 2)

Precursor	*m/z*					
	135	119	118	105	92	91
Methyl benzoate **1**	32	–	3	2	61	2
Neopentyl benzoate **2**	33	–	3	–	63	1
Phenylacetic acid **3**	1	–	2	–	96	1
CI (oxirane) of benzoic acid	2	1	42	<1	52	2

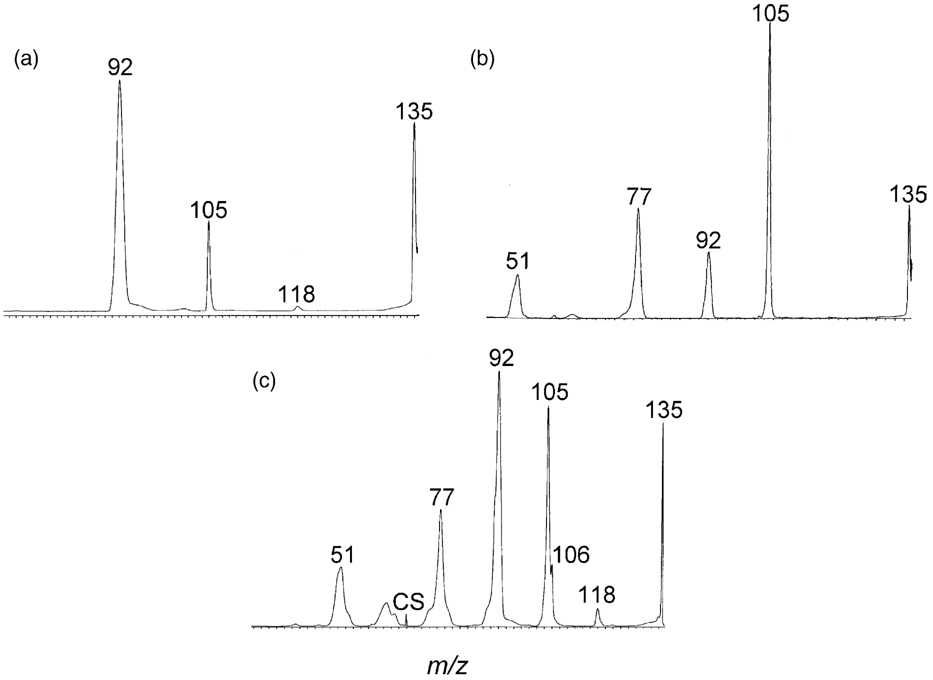


Fig. 1. (a) MIKE and (b) CA (E scan, helium collision gas) spectra of the *m*/*z* 136 molecular ions of methyl benzoate. (c) CA spectrum of the *m*/*z* 136 ions obtained by dissociative ionization of neopentyl benzoate. CS refers to charge stripping.

differentiated from the conventional ion by a base peak at *m*/*z* 92, and peaks at *m*/*z* 118 (loss of water) and *m*/*z* 106 (loss of formaldehyde). The *m*/*z* 105/77/51 sequence could be ascribed to the presence of some methyl benzoate ions. The occurrence of charge stripping (CS) is also worthy of note and indicated by the peak at *m*/*z* 68; such a process is usually found to be more favorable for the distonic ions than for the corresponding conventional counterparts [10].

3.3. Neutralization–reionization experiments

Neutralization–reionization (NR) mass spectrometry has proved to be a valuable method for identifying elusive, short-lived, neutral molecules in the gas phase. As far as ions are concerned, such methodology has also been useful for isomer differentiation when collisional activation results failed, or were poorly conclusive [11]. This was generally attributed to a higher degree of energy deposition in NR than in CA. Fig. 2 collects the NR data.

The NR spectrum of ionized methyl benzoate displayed in Fig. 2a features a recovery signal (RS) at *m*/*z* 136, but of very low amplitude. This results probably, at least in part, from slightly different geometries between ionized and neutral benzoates. As it will be shown in the theoretical section, the ester functionality deviates from the plane of the benzenic ring by ∼50° in the ionized state. The difference between both vertical and adiabatic ionization energies amounts to about 0.3–0.4 eV, which is rather significant. The *m*/*z* 44 ions, not present in the CA spectrum, result from the reionization of neutral carbon dioxide lost in the spontaneous unimolecular dissociation. Most of the peaks are those observed in the high-energy collisional activation regime, mainly *m*/*z* 105 and 77.

The NR spectrum of the distonic isomer of methyl benzoate (Fig. 2b) is not really different from the previous spectrum, but some relative intensities are nevertheless worthy of note:

(i) a reduced intensity of the recovery signal at *m*/*z* 136;
(ii) the occurrence of a small but significant signal at *m*/*z* 122 (loss of CH_2), which could be explained by the neutralization–dissociation of the distonic species;
(iii) the intensity increase of unresolved peaks at *m*/*z* 92, 62, 44, 37 (compared to the *m*/*z* 105, 77, 51 ions) which could be accounted for by neutralization of an ionized complex linking ionized toluene (or/and isotoluene) to carbon dioxide (vide infra). In such event, one should assist to a severe broadening of the corresponding peaks as observed for instance in the NRMS of nitrosated arenes [12].

3.4. Other potential distonic ions

We have also attempted to generate the distonic intermediate by electron ionization of a mixture of benzoic acid and oxirane in a chemical ionization source. Ionized oxirane has been reported to transfer an ionized methylene to benzoic acid in reasonably good yield [13]. In contrast with the results of the latter work, these ions have been found to give rise, under our experiment conditions, to a new MIKE spectrum, which is very different from the MIKE spectrum of the *m*/*z* 136 ions formed by the isobutene loss from ionized neopentyl benzoate and considered as a distonic species. Such differences can be figured out from the data listed in Table 1. The major differences are in fact the smaller intensity of peaks at *m*/*z* 135, 105, and 92, an enhanced signal at *m*/*z* 118 (water loss) and the presence of a small peak at *m*/*z* 119 (loss of $OH^{\bullet}$). Moreover, the NR spectrum of these

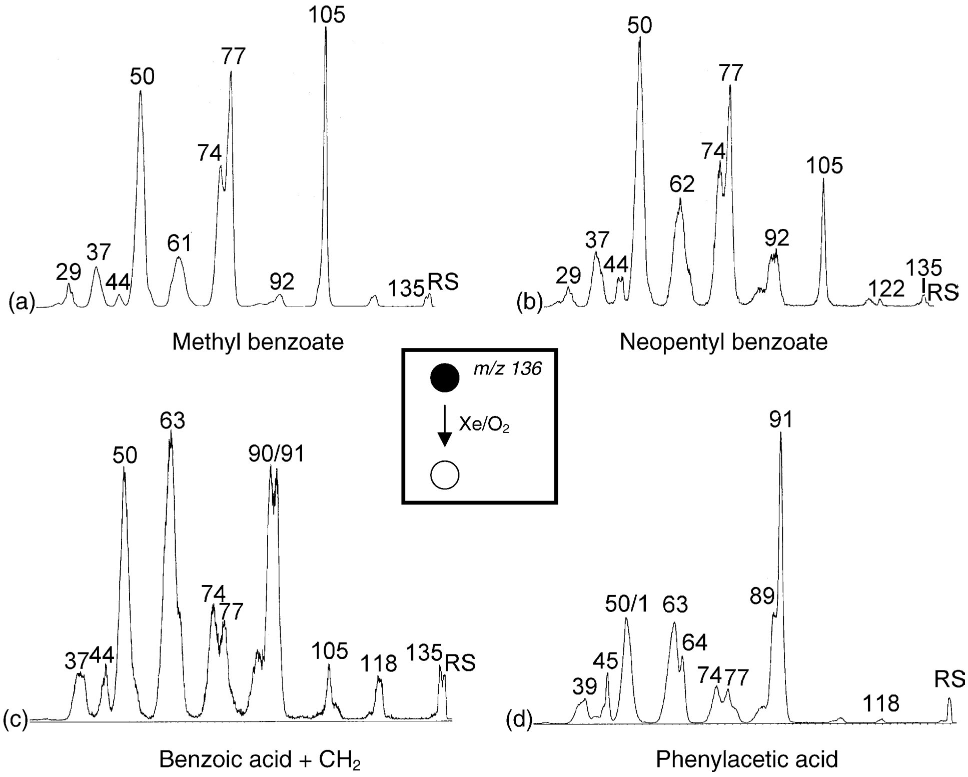


Fig. 2. Neutralization–reionization spectra (Xe and O_2 collision gases) (a) of the molecular ions of methyl benzoate, (b) of the m/z 136 ions (M–isobutene)$^{\bullet+}$ generated from neopentyl benzoate, (c) of the m/z 136 (CI (oxirane) of benzoic acid) ions and (d) of the molecular ions of phenylacetic acid.

m/z 136 ions features an intense recovery signal (Fig. 2c), in clear contrast with the benzoate distonic isomer. Such an intense recovery signal indicates that the structure of this ion is not a complex linking benzoic acid ion and a methylene, but rather a structure having covalent bonding.

Given the fact that these m/z 136 [CI (oxirane) of benzoic acid] ions are not ionized methyl benzoate or the distonic isomer, we compared these ions with other m/z 136 species as follow: the phenylacetic acid **3** and toluic acid molecular ions. Phenylacetic acid **3** behaves in a similar way as methyl benzoate **1** upon 70 eV electron ionization conditions: unstable molecular ions suffer the single bond CH_2–CO_2 cleavage (m/z 91, 100%), but the corresponding metastable ions mainly rearrange into C_7H_8 radical cations (m/z 92) upon loss of carbon dioxide (see Table 1).

On the one hand, the NR spectrum of phenylacetic acid **3** features (Fig. 2d), as in the case of methyl benzoate, a very low intensity RS, and the overall spectrum differs markedly from the one recorded for m/z 136 ions resulting from the methylene transfer. On the other hand, MIKE, CA and NRMS experiments performed on the *o*-, *m*-, *p*-toluic acid isomers indicate that, although some similarities are observed between the spectra of all these m/z 136 ions, the m/z 136 ions resulting from a methylene transfer cannot be attributed to one or even a mixture of the three toluic acids.

3.5. Ion–molecule reactions with methyl isocyanide

Methyl isocyanide (MeNC) has proved to be an efficient neutral reagent for the identification of some distonic ions. As the result of its relatively high ionization energy (11.24 eV) [14], charge exchange is usually not allowed, and therefore structurally significant reactions can take place.

Products of the reactions of MeNC with methyl benzoate ions can be identified from Fig. 3. The main product (Fig. 3a) is observed at m/z 118. Such a loss of 18 amu was at first sight unexpected because dehydration was not detected as a prominent process in low collisional energy conditions using argon collision gas. It is therefore more probable that these ions arise from a fast interaction of methyl benzoate radical cations with methyl isocyanide; substitution of ester group (CO_2CH_3) by MeNC should therefore produce *N*-methyl benzonitrilium, Ph–C≡N^+–Me, ions. Other minor reactions are observed at m/z 162 and 176 and their actual structure is presently under study. Protonated methyl isocyanide is also detected at m/z 42.

The situation becomes dramatically different for [M–isobutene]$^{\bullet+}$ ions of neopentyl benzoate **2**. Among the ions produced within the quadrupole reaction cell, the m/z 55 ions are of great interest. They formally correspond to an ionized methylene transfer to methyl isocyanide generating MeN=C=CH_2 (*N*-methylketene imine) radical cations. Such a connectivity, which is not the isomeric $MeCNCH_2$ connectivity, is readily demonstrated by a consecutive high energy collisional activation step giving a CA spectrum, in excellent agreement with reported literature data (Fig. 4). In a previous work, we have indeed reported the CA spectra of $MeNCCH_2^{\bullet+}$ and isomeric $MeCNCH_2^{\bullet+}$ radical cations [15]. These spectra were virtually

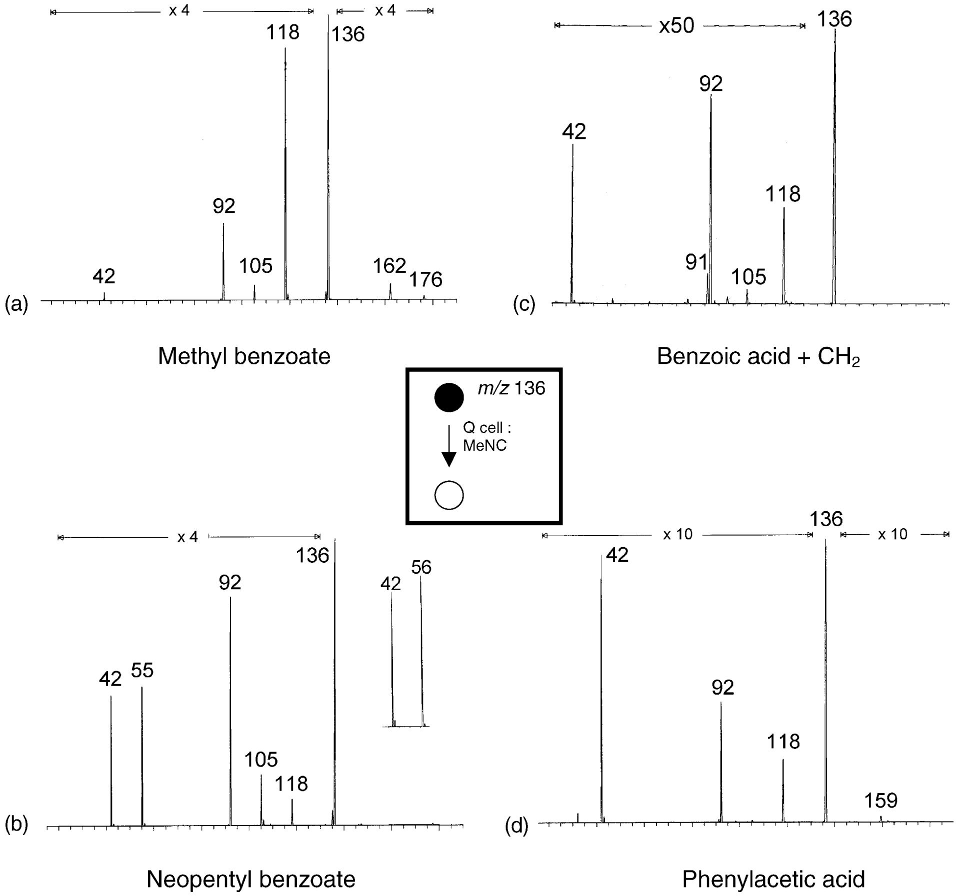
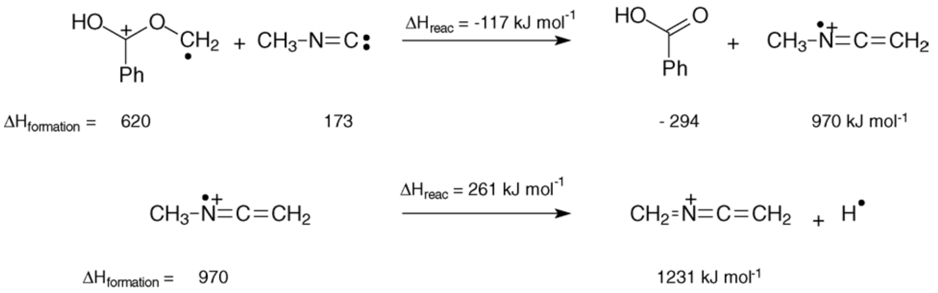


Fig. 3. Ion–molecule reactions of (a) ionized methyl benzoate (*m*/*z* 136), (b) ionized neopentyl benzoate ([M–isobutene]$^{\bullet+}$ ions) (*m*/*z* 136), (c) *m*/*z* 136 (CI (oxirane) of benzoic acid) and (d) ionized phenylacetic acid (*m*/*z* 136) with neutral methyl isocyanide (MW 41) in the quadrupole collision cell. The inset in (b) shows the *m*/*z* 40–60 region for a partially labeled neopentyl benzoate, $PhC(=O)OCHDC(CH_3)_3$: ion–molecule reactions between $[M–CH_2=C(CH_3)_2]^{\bullet+}$ ions (*m*/*z* 137) and methyl isocyanide.

identical, but with nevertheless two significant differences: a more intense *m*/*z* 15 peak for the ketenimine ions, together with a more abundant *m*/*z* 26.5 ions ($C_3H_3N^{2+}$ ions). This second feature is particularly evident if the spectra are recorded in a synchronous *B*/*E* mode (not shown here). Moreover, a partially labeled neopentyl benzoate, $Ph–C(=O)CHDC(CH_3)_3$, was used to confirm the specific ionized methylene transfer. Indeed, only the signal at *m*/*z* 56, corresponding to the $CHD=C=N^{\bullet+}–CH_3$ radical cation, was observed (see the inset of Fig. 3b). The fact that such a reaction was occurring, can indeed be predicted on the basis of available thermochemical data [15,16] depicted in Scheme 2:

The heat of reaction is thus calculated to be exothermic by 117 kJ mol^{-1}, and as this value is by far smaller than the energy required to decompose the keteneimine ion (loss of a hydrogen atom, 261 kJ mol^{-1}, cf. reference [15]), the *m*/*z* 55 ions should be an observable species, even in the absence of complete thermalization.

It can be noted that ionized phenylacetic acid **3**$^{\bullet+}$ mainly reacts with methyl isocyanide by proton transfer (*m*/*z* 42,



Scheme 2.

Fig. 3d), a process also of importance in the previous case. The signal observed at *m/z* 159 could thus correspond to an adduct formation between the *m/z* 118 ions and methyl isocyanide. The *m/z* 136 ions generated by CI (oxirane) of benzoic acid do not react with methyl isocyanide by methylene transfer but exclusively by proton transfer. The latter observation is thus in disagreement with a previous study [13], which was asserting that a methylene was transferred to the carbonyl oxygen atom of benzoic acid (Fig. 3c).

3.6. *Quantum chemical calculations*

In order to obtain some quantitative information on the energetic of the systems considered, quantum chemical calculations were carried out with the Gaussian 98 suite of programs [17]. Structures were fully optimized using density functional theory with the hybrid B3LYP functional and the 6-311++G(d,p) basis set. The optimal shapes of the structures considered are displayed in Fig. 5, along with their relative energies. These include (a) neutral methyl benzoate **1**; (b) methyl benzoate radical cation $\mathbf{1}^{\bullet+}$; (c–e) the distonic ion $\mathbf{D}^{\bullet+}$ in different conformations; and also (f–l) various isomers of the radical cation. Some selected geometrical parameters are tabulated in Table 2.

In contrast to neutral methyl benzoate **1** which is calculated to be planar, the geometry of the corresponding radical cation $\mathbf{1}^{\bullet+}$ deviates significantly from planarity with a dihedral angle of 46° between the benzenic ring and the ester functionality. Vertical and adiabatic ionization energies of methyl benzoate were calculated at 9.4 and 9.1 eV, respectively. These values are in good agreement with the available experimental values of $\mathrm{IE_v} = 9.5$ eV and $\mathrm{IE_a} = 9.32$ eV (values taken from reference [18]). Note that the vertical ionization energy was evaluated by energy calculations using the neutral methyl benzoate geometry. Thus calculations suggest a larger energy gain of 0.3 eV following geometry relaxation. The geometrical changes are also consistent with the low intensity recovery signal noted above in the NR mass spectrum (Fig. 2a).

For the distonic ion $\mathbf{D}^{\bullet+}$, the $\mathbf{Da}^{\bullet+}$ form is calculated to be the most stable conformation showing again a near planarity. While the other *s-cis* conformation is only slightly less stable by about 13 kJ mol^{-1}, the *s-trans* conformation is found, as expected, to be less stable by about 21 kJ mol^{-1}, as a result of the steric hindrance between the methylene group and a hydrogen atom in the *ortho*-position. Overall, the distonic radical cation $\mathbf{Da}^{\bullet+}$ is marginally less stable than the conventional counterpart $\mathbf{1}^{\bullet+}$. The calculated energy difference of 8 kJ mol^{-1} (Fig. 5) lies however within the error bar of the level of theory employed. Note that in the case of methyl formate, the distonic radical cation has been found to be much lower in energy than the classical form [19].

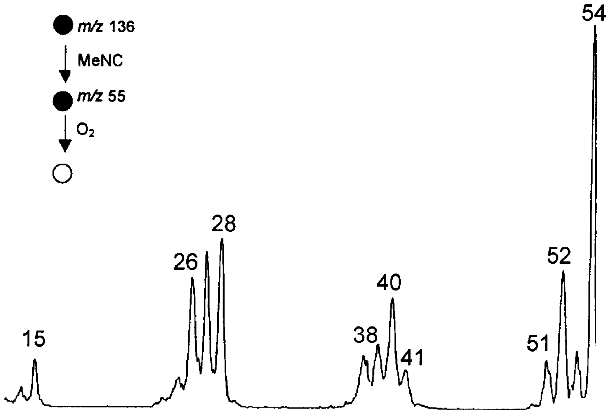


Fig. 4. CA spectrum of the *m/z* 55 ions formed by ion–molecule reaction between *m/z* 136 ions (neopentyl benzoate$^{\bullet+}$–isobutene) and neutral methyl isocyanide.

The transition structure connecting $\mathbf{1}^{\bullet+}$ to $\mathbf{Da}^{\bullet+}$ is calculated to be 98 kJ mol^{-1} higher in energy than $\mathbf{1}^{\bullet+}$. This 1,4-hydrogen shift having a rather moderate energy barrier, constitutes the first step of a complex reaction sequence leading *in fine* to the ultimate products of decarboxylation of metastable $\mathbf{1}^{\bullet+}$ ions [6].

Calculated charge and spin densities using the Mulliken population analysis with the HF/6-31G(d,p) method tend to confirm the distonic nature of the radical cation $\mathbf{Da}^{\bullet+}$. Accordingly, the positive charge is mainly located on the carbon (C_2) of the hemiacetal function (0.89e). Carbon atoms of the benzenic ring are also positively charged, except for the carbon C_1 bonded to the hemiacetal group (−0.13e). The two oxygen atoms are negatively charged (−0.12e for O_1 and −0.53e for O_2, cf. Fig. 5 for atoms numbering).

The methylene carbon C_3 is actually the radical center where the unpaired electron is located. The excess of α-electrons on this C_3 atom amounts to 1.17e. The remaining atoms are characterized by small excess spin, amounting to either −0.09 or 0.08e. Note also the markedly different carbon–oxygen bond lengths in $\mathbf{1}^{\bullet+}$, that correspond to classical single and double CO bonds. The latter become almost equivalent in $\mathbf{Da}^{\bullet+}$ (1.30–1.35 Å, see Table 2) Overall, both the electron distribution and geometrical parameters of $\mathbf{Da}^{\bullet+}$ are consistent with a distonic radical cation having a clear separation of charge and radical centers.

In agreement with the experimental results (oxirane chemical ionization, vide supra), we have been successful in optimizing the geometry of an isomeric covalent structure, which is supposed to be generated by cycloaddition reaction of an ionized methylene to one double bond of the benzene ring. The energies of such norcaradiene-like structures displayed in Fig. 5 as (f–h), are nevertheless higher, namely about 24 kJ mol^{-1} relative to $\mathbf{1}^{\bullet+}$.

It is worth noting that the different derivatives of cycloheptatriene radical cation shown [structures (i–k)] turn out to be more stable than the norcaradiene structures. These covalent structures could explain the occurrence of the intense recovery signal observed in the neutralization–reionization mass spectrum (Fig. 2c).

On the contrary, we have not been able with the level of theory and basis used to optimize a distonic species resulting from the transfer of ionized methylene on the hydroxyl group of benzoic acid. All optimizations starting from the initial geometry $C_6H_5–C(=O)O^+(–H)CH_2^{\bullet}$ invariably lead to the cleavage of the carbonyl–oxygen bond yielding an ion–neutral complex connecting a benzoyl cation to an hydroxymethyl radical. This cleavage can be readily explained by the destabilizing interaction of the positively charged oxygen and the partially charged carbon of the carbonyl group.

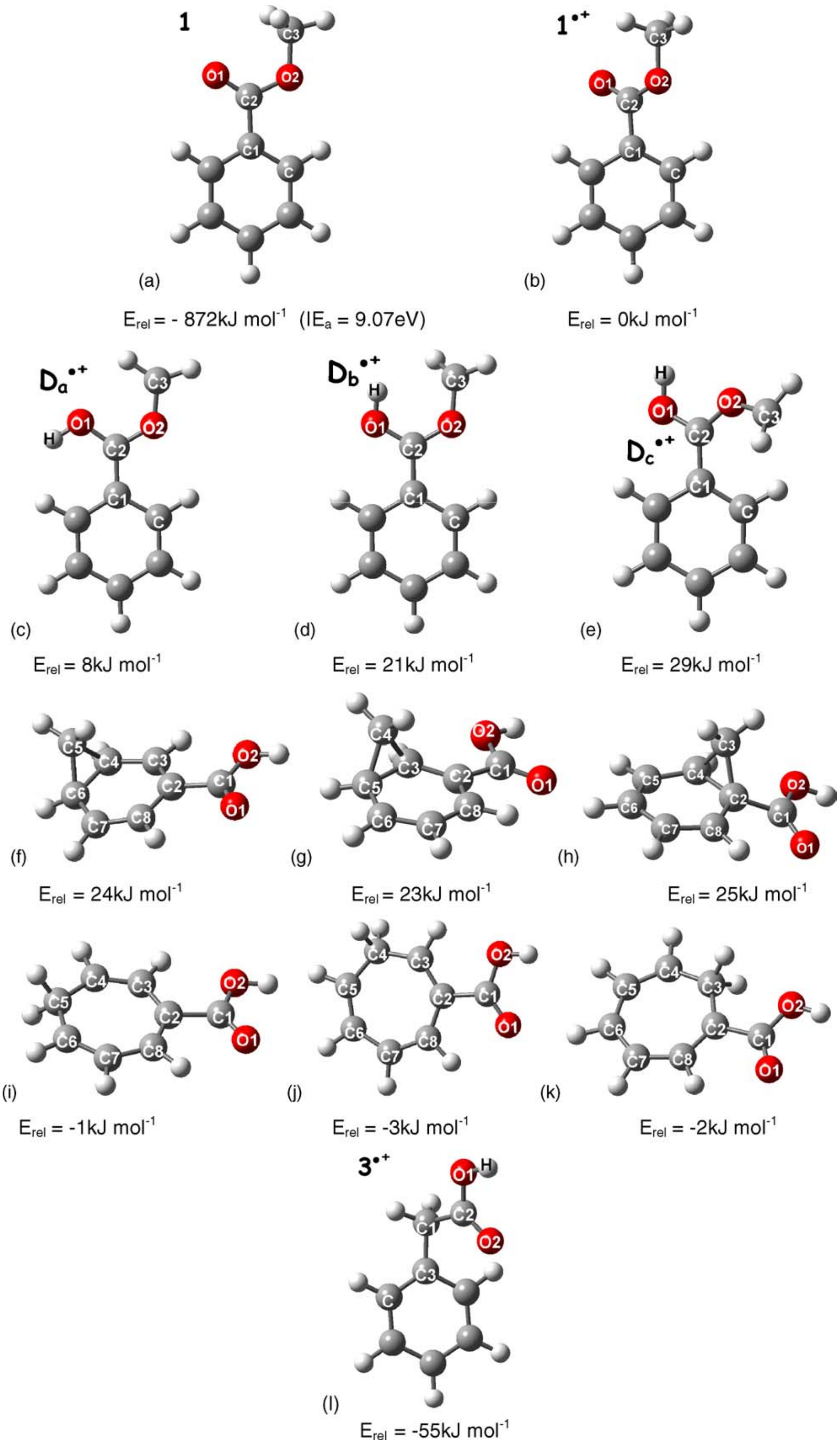


Fig. 5. Optimized geometries and relative energies (UB3LYP/6-311++G(d,p) + ZPE) of the following structures: (a) neutral methyl benzoate **1**, (b) methyl benzoate radical cation $\mathbf{1}^{\bullet +}$, (c) the most stable distonic isomer $\mathbf{Da}^{\bullet +}$, (d and e) two distonic rotamers $\mathbf{Db}^{\bullet +}$ and $\mathbf{Dc}^{\bullet +}$, (f–h) three bicyclic geometries of *m*/*z* 136 ions formed by CI (oxirane) of benzoic acid, (i–k) the three more stable carboxycycloheptatriene radical cations and (l) phenylacetic acid $\mathbf{3}^{\bullet +}$ radical cation.

Table 2
Bond lengths (in angstroms), angles and dihedral angles (in degrees) of different geometries

	1	**1**$^{\bullet+}$	**Da**$^{\bullet+}$	**Db**$^{\bullet+}$	**Dc**$^{\bullet+}$	**3**$^{\bullet+}$
Bond lengths						
C_1–C_2	1.49	1.49	1.43	1.42	1.43	1.51
C_2–O_1	1.21	1.21	1.30	1.30	1.30	1.32
C_2–O_2	1.35	1.35	1.30	1.31	1.30	1.22
O_2–C_3	1.43	1.43	1.35	1.37	1.37	–
O_1–H	–	–	0.96	0.97	0.97	0.97
C_1–C_3	–	–	–	–	–	1.5
Angles						
H–O_1–C_2	–	–	113	114	112	110
O_1–C_2–O_2	123	123	115	121	114	124
C_2–O_2–C_3	116	116	125	123	127	–
C_1–C_2–O_1	125	125	126	120	119	122
C_1–C_2–O_2	113	113	119	119	127	122
C_1–C_3–C	–	–	–	–	–	123
Dihedral angles						
H–O_1–C_2–C_1	–	–	−3	168	176	180
H–O_1–C_2–O_2	–	–	178	−12	−6	0
C_1–C_2–O_2–C_3	180	150	179	170	−20	–
O_1–C_2–O_2–C_3	0	0.5	−0.6	−10	162	–
C–C_1–C_2–O_2	0	139	−4	−5	−22	–
C–C_1–C_2–O_1	180	−46	176	175	156	–
O_1–C_2–C_1–C_3	–	–	–	–	–	−171
C_1–C_2–C_3–C	–	–	–	–	–	126

	(**i**) ($X = 5$)	(**j**) ($X = 4$)	(**k**) ($X = 3$)	(**f**) ($X = 5$)	(**g**) ($X = 4$)	(**h**) ($X = 3$)
Bond lengths						
C_1–O_1	1.20	1.20	1.20	1.19	1.20	1.20
C_1–O_2	1.33	1.33	1.34	1.33	1.33	1.33
O_2–H	0.97	0.97	0.97	0.97	0.97	0.97
C_1–C_2	1.52	1.52	1.51	1.50	1.50	1.51
C_2–C_3	1.42	1.36	1.49	1.39	1.45	1.55
C_3–C_4	1.37	1.48	1.48	1.44	1.53	1.52
C_4–C_5	1.48	1.48	1.36	1.54	1.55	1.44
C_5–C_6	1.48	1.36	1.41	1.54	1.43	1.39
C_6–C_7	1.36	1.41	1.39	1.44	1.39	1.40
C_7–C_8	1.42	1.39	1.41	1.39	1.40	1.39
C_8–C_2	1.39	1.42	1.37	1.41	1.39	1.44
C–H	1.08	1.08	1.08	1.08	1.08	1.08
$C_{(X-1)}$–$C_{(X+1)}$	–	–	–	1.52	1.52	1.54
C_X–H	1.1	1.1	($X = 3$) 1.1	1.08	1.08	1.08
Angles						
O_1–C_1–O_2	125	125	125	125	126	126
C_1–O_2–H	109	109	109	109	109	109
O_1–C_1–C_2	123	123	123	122	122	122
O_2–C_1–C_2	112	112	112	112	112	112
C_1–C_2–C_3	118	119	116	122	121	116
C_2–C_3–C_4	129	131	123	122	117	60
C_3–C_4–C_5	131	123	132	116	59	117
C_4–C_5–C_6	130	130	128	59	116	122
C_5–C_6–C_7	130	128	129	116	122	121
C_6–C_7–C_8	129	130	129	122	121	120
C_7–C_8–C_2	130	130	130	120	121	122
C_8–C_2–C_3	128	127	129	120	121	116
C_8–C_2–C_1	114	113	114	117	117	116
H–C_X–H	100	100	99	117	117	117
Dihedral angles						
O_1–C_1–O_2–H	0	0	0	0.5	0	0
O_1–C_1–C_2–C_3	180	180	180	180	−175	135
O_1–C_1–C_2–C_8	0	0	0	0	0	−7
C_2–C_3–C_4–C_5	0	0	0.25	61	−107	107
C_5–C_6–C_7–C_8	0	0	0	−61	−8	−1
H–C_X–$C_{(X+1)}$–$C_{(X+2)}$	127	127	127	0 −146	−0.6 −145	0 −147

4. Conclusions

Although CA, CS and NR mass spectrometric data consistently indicate that the (M–isobutene)$^{\bullet+}$ ions of ionized neopentyl benzoate **2** are structurally distinct from the methyl benzoate ions $\mathbf{1}^{\bullet+}$, the ion–molecule reactions with methyl isocyanide setup in the present work, strongly confirm that they contain a "free" methylene group and thereby point toward their distonic connectivity. Similar ion–molecule experiments also point out that these distonic ions are not produced in the chemical ionization (oxirane) of benzoic acid. Taken together, these experimental observations constitute the definitive evidence for the production of the distonic isomer $C_6H_5C^+(OH)OCH_2^\bullet$ of methyl benzoate radical cation.

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