



DFT study on IR spectral and structural changes caused by the conversion of substituted benzophenones into ketyl radicals



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ABSTRACT

The structural and spectral changes, arising from the conversion of a series of benzophenones into ketyls, are studied on the basis of standard DFT methods, employing different functionals and basis sets, without and with inclusion of solvent. Their relative predictive capabilities are evaluated by comparing the theoretically predicted and experimentally observed carbonyl frequencies. A very good agreement is achieved at combination between IEFPCM and ONIOM method with the basis functions 6-311+G(2df,p) for high layer and 6-311+G for low layer, showing the relevance of including high-order polarization functions in the basis set of high layer and solvent effect. The chosen level of theory ONIOM[B3LYP/6-311+G(2df,p)//6-311+G]-IEFPCM is applied to analyze the vibrational spectra, geometry and spin populations over the C=O groups of the title species. The spin populations over the C=O groups in ketyls correlate excellently with these decreases $\Delta\nu_{\text{CO}}$ and prove to be dominant factor determining the frequency variation in the IR spectra.

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1. Introduction

Organic radical-anions could be formed by addition of a single electron (one-electron reduction) to various organic molecules [1–4]. The generated species are negatively charged and in the same time possess radical properties due to the odd number of electrons. They are powerful synthons and their spectra and structure are of special interest for the physical organic chemistry [1–4]. Historically the benzophenone ketyl was the first recognized radical-anion [5,6]. Following its discovery, different other ketyls radicals were synthesized through one-electron reduction of benzophenones using reducing metals, such as sodium and potassium or generated electrochemically [7,8]. This class of compounds is widely used in many areas, as important intermediates in organic and organometallic reactions [9–11]. Therefore, a better knowledge of the structure is an essential goal in understanding of the reactivity. However, the highly reactive nature of ketyl radical species has limited the structural characterization of benzophenone ketyls to a few complexes [12–14]. Some information on the structure of radical-anions, including ketyls, can be obtained by means of ESR method [15–17]. The vibrational spectra are also informative regarding the changes in the force field resulting from the conversion of the neutral molecules into radical-anions. The IR

spectra of m- and p-substituted benzophenones ketyls were studied earlier [18–21] and revealed intriguing spectral features much different from those of the neutral parent compounds. Moreover the observed spectral behavior could not be explained based simply on the conventional concepts of inductive and resonance effects [20], so need of correlation to the some more sophisticated characteristics such as electron distribution over the molecule, was assumed based on Hueckel calculations [21]. Nowadays, quantum-chemical methods provided powerful means to study the spectra and electronic structure of organic molecules. Combined with the experimental data they could support and explain from theoretical point of view the changes occurring upon radicalization. A large series of organic molecules and their radical-anions, containing cyano and nitro groups have been successfully studied recently on the basis of IR spectra and DFT computations [22–25].

Hence we decide to study a series of substituted benzophenones by computational methods and to relate the theoretically calculated IR frequencies, molecular structure, and electronic charge distribution to the available experimental spectral data in order to find interpretation of the observed effects. For this purpose, a comprehensive evaluation of different DFT methods was carried out to select the most suitable level of theory for the study of benzophenone ketyl derivatives. The chosen method was then applied to describe the changes in the energies, IR spectra and structure, related to the chemical transformation of the benzophenones into ketyls. The comparison of the relative predictive capacity of the

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hybrid DFT functionals, basis sets and solvent models was used to recommend the most accurate and efficient approach for future studies of carbonyl radical-anions.

2. Computational details

Full geometry optimization and computation of vibrational frequencies of all studied species were done using Gaussian-09 program package [26]. Several various unrestricted hybrid functionals were used: UB3LYP [27–29] – three-parameter functional which combined 20% Hartree–Fock exchange and 72% Becke’s nonlocal exchange; UB1LYP [30] – one-parameter functional, which incorporated 25% Hartree–Fock exchange; UBHandHLYP [31] – “half and half” functional, which incorporated 50% Hartree–Fock exchange; CAM-UB3LYP [32] – long range corrected version of B3LYP which comprised of 19% Hartree–Fock and 61% Becke’s exchange interaction at short-range, and 65% Hartree–Fock and 35% Becke’s exchange at long-range. Pople type basis sets [33] 6-311+G(d,p) and 6-311+G(2df,p) were used for full geometry optimizations of the molecules and the corresponding radical-anions. Incorporation of solvent effect was performed by a combination, provided by the last version of Gaussian-09 [26], between ONIOM method, developed by Morokuma and coworkers [34], and Integral Equation Formalism of Polarizable Continuum Model (IEFPCM), proposed by Tomasi and coworkers [35,36]. The stationary points found on the potential energy hypersurface for each structure, were characterized using the standard harmonic vibrational analysis. The absence of imaginary frequencies confirmed that the stationary points corresponded to local minima on the potential hypersurfaces. A standard least-squares program was used to calculate single parameter regression indices.

3. Results and discussion

Subject of the present study was a series of 14 benzophenones – ketones and their radical-anions – ketyls, separated into three types as shown in Fig. 1. The ketyls which are arranged in one group possess topological and structural analogy, and also spectroscopic similarity as it was established by their IR spectra [18–21].

3.1. Correlation analysis

Careful evaluation of the method accuracy is a key step in the study of any group of organic radical-anions. On the other hand, the variability of method/basis set could improve considerably the agreement between theory and experiment, which is crucial as indication for reliable description of the computed structural parameters. For this purpose, a smaller test series, containing representatives from each type I, II and III, was selected to examine the performance of various combinations between method/basis sets in predicting the corresponding carbonyl IR frequencies in gas phase. The experimental spectra were measured in polar aprotic

solvent DMSO, but it is known that in this solvent the ions exist as free species and there are no strong anion/counter ion interactions [4,37]. The influence of the tetrabutylammonium counterions on the carbonyl frequencies is neglectful. This makes it possible to compare, in this work, the experimental infrared data for the radical anions with the theoretical data for free radicals.

A comprehensive evaluation of DFT methods was carried out, in order to find a suitable and cost effective level of theory to be used in the study of benzophenone ketyl derivatives. By varying the hybrid functional, we found that the agreement between theoretical and experimental carbonyl frequencies increases in the order: O3LYP < mPW1PW91 \approx B1B95 \approx B3PW91 < PBE < B3LYP < B3P86 \approx CAM-B3LYP \approx B1LYP < BHandHLYP. We tested also three kinds of basis sets: Pople [33] 6-311+G(d,p), Dunning [38] (aug-cc-pVTZ), and Barone [39] (EPR-III); and found, that the Pople basis sets provide better accuracy at lower computational cost. Four of the best performing functionals (B3LYP, B1LYP, CAM-B3LYP, BHandHLYP), which are also the most similar in definition, combined with 6-311+G(d,p) basis set are the most appropriate for calculation of the carbonyl frequencies of the whole series of studied benzophenones.

The native theoretical carbonyl IR frequencies of the whole series were scaled according to the following equation:

$$\nu_{\text{exp}} = \rho \nu_{\text{theor}} + b \quad (1)$$

The values of slopes ρ and intercepts b calculated at different level of theory are listed in Table 1. The scaled theoretical carbonyl frequencies are compared to the experimental ones in Table 2. The mean absolute deviations ($MAD = n^{-1} \sum |(\rho \nu_i^{\text{theor. (native)}} + b) - \nu_i^{\text{exp.}}|$) were used as a measure for the deviation between theoretical and experimental values (Table 2). In contrast to the carbonyl frequencies of the ketones, the frequencies of the ketyls are poorly predicted in gas phase. Although the calculations included diffuse functions (which are required for open shell systems as ketyls) they failed to provide a good agreement. The MADs found ($20\text{--}30\text{ cm}^{-1}$) are larger than expected.

The advantages of B3LYP functional among other DFT methods and the reliability of Pople basis set for frequency calculations of organic systems were previously shown both in the harmonic and anharmonic approach [40,41]. Their good performance in terms of accuracy and computational cost were also demonstrated for various radical-anions [24,25,42–45] and anions [46–49]. Based on series of carbanions [46], azanions [47,48] and oxyanions [49] it was established that the mean absolute deviation between the IR experimental frequencies and that calculated by B3LYP typically falls within the interval $9\text{--}20\text{ cm}^{-1}$. The accuracy reported for nitrile radical-anions and anions is respectively $8\text{--}12\text{ cm}^{-1}$ [24]. In the present case however, the prediction of the carbonyl frequencies of the benzophenones and ketyl radicals by this method led to insufficient results as the MADs lie at the upper limit or outside the above-mentioned intervals [24,46–49]. These values make the theoretical method rather impracticable for further analysis.

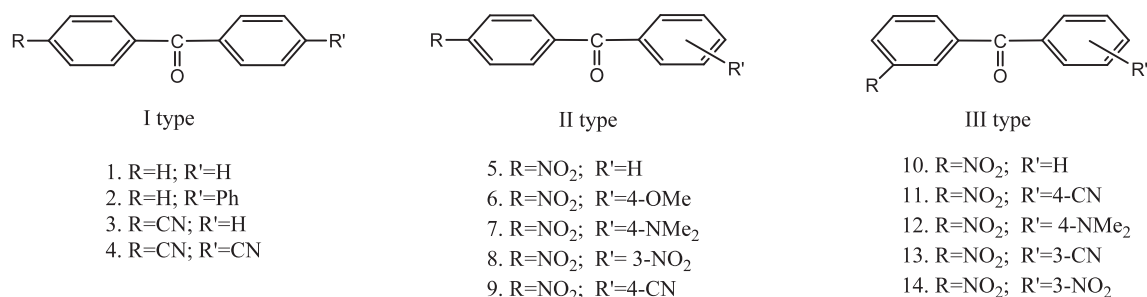


Fig. 1. Chemical structures of benzophenones separated into three types.

Table 1

Correlations between theoretical and experimental carbonyl stretching frequencies of the substituted benzophenone molecules and ketyls according to Eq. (1).

	Gas phase ^a				ONIOM-IEFPCM ^b			
	B3LYP	B1LYP	BHandHLYP	cam-B3LYP	B3LYP	B1LYP	BHandHLYP	cam-B3LYP
ρ	0.8783	0.8603	0.8712	0.8996	0.9597	0.9346	0.8250	0.8641
b	163.0	187.2	82.0	76.9	39.7	69.4	179.5	153.1
R^c	0.8472	0.8676	0.9492	0.9329	0.9974	0.9977	0.9939	0.9975
SD ^d	47.2	44.8	28.0	32.0	6.4	6.1	9.8	6.3

^a Basis set – 6-311+G(d,p).^b Basis set – 6-311+G(2df,p)//6-311+G.^c Correlation coefficient.^d Standard deviation.**Table 2**

Comparison of frequencies of the C=O stretching vibrations calculated at different level of theory (scaled according Eq. (1)) with experimental values.

Compounds			Gas phase ^a				ONIOM/PCM ^b				Experimental ^c
			B3LYP	B1LYP	BHandHLYP	CAM-B3LYP	B3LYP	B1LYP	BHandHLYP	CAM-B3LYP	
M1	H	H	1667	1672	1670	1668	1656	1655	1653	1655	1658
M2	4-Ph	H	1664	1670	1668	1666	1653	1653	1664	1653	1659
M3	4-CN	H	1675	1676	1675	1673	1664	1663	1674	1664	1662
M4	4-CN	4-CN	1676	1682	1681	1678	1673	1673	1667	1672	1668
M5	4-NO ₂	H	1673	1682	1677	1666	1667	1666	1659	1666	1665
M6	4-NO ₂	4-OMe	1664	1670	1668	1674	1657	1657	1641	1658	1658
M7	4-NO ₂	4-DMA	1639	1659	1657	1681	1641	1640	1677	1640	1644
M8	4-NO ₂	4-CN	1683	1683	1684	1680	1677	1676	1679	1676	1673
M9	4-NO ₂	3-NO ₂	1681	1684	1683	1681	1680	1680	1666	1677	1673
M10	3-NO ₂	H	1674	1677	1675	1673	1667	1667	1641	1665	1665
M11	3-NO ₂	4-DMA	1653	1659	1634	1655	1649	1640	1675	1641	1642
M12	3-NO ₂	4-CN	1678	1682	1681	1678	1676	1676	1674	1674	1670
M13	3-NO ₂	3-CN	1678	1683	1681	1679	1677	1676	1677	1674	1671
M14	3-NO ₂	3-NO ₂	1630	1684	1682	1680	1680	1679	1677	1677	1672
K1	H	H	1469	1474	1438	1442	1406	1407	1417	1410	1396
K2	4-Ph	H	1474	1479	1437	1479	1409	1409	1422	1407	1397
K3	4-CN	H	1498	1502	1471	1478	1429	1426	1422	1427	1430
K4	4-CN	4-CN	1465	1469	1492	1443	1450	1450	1446	1449	1457
K5	4-NO ₂	H	1544	1550	1536	1539	1564	1565	1558	1563	1570
K6	4-NO ₂	4-OMe	1545	1549	1536	1538	1561	1562	1559	1564	1565
K7	4-NO ₂	4-DMA	1646	1546	1553	1559	1567	1568	1561	1568	1564
K8	4-NO ₂	4-CN	1603	1551	1511	1517	1569	1569	1558	1565	1575
K9	4-NO ₂	3-NO ₂	1522	1552	1521	1524	1563	1564	1557	1562	1580
K10	3-NO ₂	H	1609	1612	1637	1631	1642	1651	1654	1653	1654
K11	3-NO ₂	4-DMA	1624	1621	1634	1631	1634	1633	1635	1635	1632
K12	3-NO ₂	4-CN	1516	1536	1630	1619	1655	1657	1662	1661	1659
K13	3-NO ₂	3-CN	1627	1574	1634	1623	1656	1658	1661	1660	1661
K14	3-NO ₂	3-NO ₂	1599	1602	1634	1625	1660	1661	1664	1663	1660
MAD ^d			31.4	30.5	20.6	23.3	5.0	4.6	6.3	4.2	

^a Basis set – 6-311+G**.^b Base functions 6-311+G(2df,p) for high layer and 6-311+G for low layer.^c From [20].^d Mean absolute deviation. M – molecule. K – ketyl.

On the other hand, benzophenone derivatives differ significantly in structure from other aromatic compounds, able to form stable radical-anions. They are non-planar, they possess low level of symmetry, and the carbonyl group lies outside the planes of the phenyl rings. This fact in combination with the high polarizability of the carbonyl group might be responsible for the larger deviation, observed at computations.

For improvement of the model, inclusion of the solvent effect was tested by polarized continuum model (IEFPCM). Rendering an account of the medium influence and adding of subsidiary d and f functions into the atoms of the functional groups (ONIOM model) vastly improved the agreement between theory and experiment. ONIOM model, with high level 6-311+G(2df,p) for the functional groups, and low level 6-311+G for the hydrocarbon residues, proved to be a very good compromise between accuracy and computational cost. Taking into account the solvent medium, the differences between the functionals become minor. As seen in Table 2, the agreement between the scaled theoretical frequencies obtained at ONIOM-IEFPCM computations and the experimental

ones is excellent for all DFT functionals used. The MADs (4.2–6.3 cm⁻¹) are about 5 times lower, than those calculated in gas phase without extended basis set (Table 2). In this way, the accuracy obtained by this approach is much higher than in the studies discussed above [24,42–49]. The most popular B3LYP functional will be used in the following study of the energy, IR spectra and structure.

3.2. Spectral analysis

The chosen level of theory (ONIOM[B3LYP/6-311+G(2df,p)]/6-311+G]-IEFPCM) predicts very well the vibrational spectra of the molecules and radical-anions (Table 2). The mean absolute deviation between theoretical and experimental $\nu_{\text{C=O}}$ frequencies is 5 cm⁻¹. The graphical representation of the relationship between the calculated ν^{theor} and measured ν^{exp} frequencies of the studied ketones and ketyls can be seen on Fig. 2.

The presence of carbonyl group in all compounds and its bonding in central position make it very sensitive about the structure of

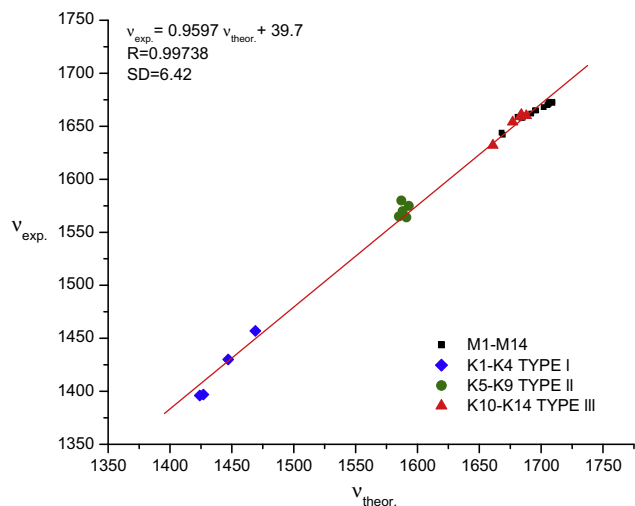


Fig. 2. Correlation between theoretical carbonyl stretching frequencies $\nu_{\text{C=O}}$ of molecules (M1–M14) and ketyls (K1–K14) and experimental ones.

ketones and ketyles. In agreement between theory and experiment, the IR carbonyl stretching frequencies of neutral benzophenones M1–M14 appear in a narrow interval (1680–1650 cm^{-1}). In contrary, the $\nu_{\text{C=O}}$ of ketyls K1–K14 are spread over an interval of more than 250 cm^{-1} (1660–1400 cm^{-1}). The spectral behavior of the neutral compounds is in accordance with the simple concepts for the inductive and resonance effects, while the effects on $\nu_{\text{C=O}}$ of ketyls are 7–8 times stronger and require a different explanation.

A good indication of the structural changes caused by the conversion of the ketones into ketyles is the lowering of carbonyl frequency ($\Delta\nu_{\text{C=O}} = \nu_{\text{C=O}}(\text{ketone}) - \nu_{\text{C=O}}(\text{ketyl})$) and its magnitude. Sometimes the value of $\Delta\nu_{\text{C=O}}$ is around 250 cm^{-1} , and in other cases only 10 cm^{-1} .

When the C=O group is the strongest electron-withdrawer in the system (compounds 1–4, type I in Fig. 2) the decrease in $\nu_{\text{C=O}}$ frequency is the most significant. In the case of the unsubstituted benzophenone the shifting of $\nu_{\text{C=O}}$ is the strongest (calc. 250 cm^{-1} , obs. 262 cm^{-1}). The presence of a large conjugated system as in 4-Ph-benzophenone is not influencing the frequency decrease (calc. 247 cm^{-1} , obs. 262 cm^{-1}). The shifting is slightly reduced when one (calc. 235 cm^{-1} , obs. 232 cm^{-1}) or both phenyl rings (calc. 223 cm^{-1} , obs. 211 cm^{-1}) contain an acceptor weaker than the C=O group e.g. CN (Table 2).

In the presence of stronger electron-withdrawers e.g. NO_2 in p-position conjugated with the carbonyl group (compounds 5–9, Table 2), $\nu_{\text{C=O}}$ decreases are smaller compared to those of compounds of type I, but still significant (calc. and obs. near 100 cm^{-1}). The electronic effects of the second substituent (regardless electron withdrawing or releasing by nature) have no essential effect on $\nu_{\text{C=O}}$.

When the stronger acceptor is in m-position (compounds 10–14, Table 2), and not conjugated with the carbonyl group, the frequency decrease is small. In this case, the influence of m- NO_2 on $\nu_{\text{C=O}}$ is comparable to the inductive substituents in the neutral molecules.

This very broad frequency region of the ketyl stretching bands can be explained by very different contribution of the electron density, and that will be discussed in more detail in the next section.

3.3. Energy analysis

Experimental data about energy of formation of ketyles are scarce in the literature due to the experimental difficulties in the isolation and investigation of such species. They are highly reactive in solid

Table 3

Calculated enthalpies of formation (kJ mol^{-1}) of studied benzophenone ketyles.^a

Ketyles type I		Ketyles type II		Ketyles type III	
K1	165.9	K5	263.1	K10	247.5
K2	172.9	K6	260.0	K11	243.6
K3	206.1	K7	254.4	K12	250.6
K4	227.7	K8	269.1	K13	250.3
		K9	264.7	K14	247.7

^a For numbering see Fig. 1.

state, room temperature and oxygen atmosphere. This problem is not limited to the benzophenone ketyles, but concerns the whole radical chemistry. That forces us to trust entirely to theory, when discussing energies of formation. Despite the lack of experimental data to compare, useful information could be obtained by comparing the theoretical values for the different compounds to each other. It is of interest to show whether the energies of formation of the different types of ketyles differ significantly.

Taking into account Eq. (2), the enthalpy of formation of the ketyles could be defined with the following expression:

$$\Delta H = H(\text{kethyl}) - [H(\text{ketone}) + H(\text{sol.v.e}^-)] \quad (2)$$

In order to account for the experimental conditions, the values of ketone and ketyl energies were calculated in DMSO solution. The enthalpy of solvated electron (DMSO) was taken from the literature [50]. The results listed in Table 3 show that the enthalpies of formation are the lowest for the first type. The highest enthalpies are computed for the second type, which are a little bit higher than those, calculated for the third type.

These results can be related to the nature of the electron acceptor in each ketone. The attachment of solvated electron and formation of a ketyl would be energetically the most favored when no other acceptor then the carbonyl group is present. It is due to delocalization of the odd electron over larger part of the conjugated system. The analysis of electronic distribution is presented in detail in the next section. The highest enthalpies are calculated for the nitro compounds, where the electron density is concentrated mainly into the acceptor group. The influence of the electron donors like methoxy- and dimethylamino-groups is weaker: they lead to lowering of the enthalpy only by several kJ mol^{-1} . In general the enthalpies of 4-nitro species are slightly higher than those of 3-nitro ones. The differences should be attributed to the different electronic conjugation with the carbonyl group.

3.4. Structural analysis

The already mentioned experimental difficulties in the preparation and isolation of radical-anions lead to only limited number of structural studies on benzophenone ketyles. The crystal structure of the unsubstituted benzophenone ketyl was determined in complexes with metal ions including solvent molecules as ligands [12] and free of solvent [14]. The structure of the free radical-anions as present in the DMSO solution, cannot be directly observed, but could be characterized by theoretical calculations by taking into account the solvent within the model ONIOM[B3LYP/6-311+G(2df,p)//6-311+G]–IEFPCM. The calculated C–Ph and C=O bond lengths and dihedral angles between CO and phenyl rings of the species studied are compared in Table 4. The conversion of the unsubstituted benzophenone in ketyl caused a significant elongation of the C–O bond and shortening of the C–Ph bonds. It is accompanied also by decrease of the dihedral angles between the CO group and the phenyl rings stabilizing the radical through delocalization of the odd electron over the whole conjugated system. The reported X-ray studies of the unsubstituted benzophenone [51] and its ketyl in K [12] and Ca [14] complexes show similar changes in the geometrical parameters. None

Table 4Calculated C=O and C–Ph bond lengths (Å) and dihedral angles(°) in the molecules and ketyls of studied benzophenone.^a

Compounds			Molecules					Ketyl					$\Delta R_{C=O}^c$
No.	R	R'	C=O	C–Ph	C–Ph'	α^b	β^b	C=O	C–Ph	C–Ph'	α^b	β^b	
1	H	H	1.224	1.498	1.498	30.1	30.1	1.287	1.471	1.471	19.2	19.2	0.063
2	4-Ph	H	1.224	1.496	1.499	28.3	30.8	1.281	1.458	1.484	14.8	25.8	0.057
3	4-CN	H	1.222	1.505	1.494	33.8	26.5	1.271	1.447	1.498	10.9	35.7	0.049
4	4-CN	4-CN	1.220	1.501	1.501	30.5	30.5	1.272	1.470	1.470	20.0	20.0	0.052
5	4-NO ₂	H	1.221	1.507	1.493	35.4	25.1	1.235	1.474	1.504	17.3	38.3	0.014
6	4-NO ₂	4-OMe	1.224	1.508	1.484	38.9	20.8	1.236	1.478	1.498	20.4	32.9	0.012
7	4-NO ₂	4-DMA	1.230	1.511	1.470	43.5	14.4	1.238	1.484	1.488	24.5	27.3	0.008
8	4-NO ₂	4-CN	1.219	1.503	1.499	32.8	28.3	1.236	1.469	1.508	15.1	40.2	0.017
9	4-NO ₂	3-NO ₂	1.218	1.503	1.500	33.5	27.2	1.235	1.469	1.509	15.8	39.2	0.016
10	3-NO ₂	H	1.221	1.504	1.494	31.0	28.7	1.225	1.497	1.499	28.3	31.5	0.004
11	3-NO ₂	4-DMA	1.230	1.510	1.472	38.9	17.2	1.232	1.503	1.480	36.3	20.8	0.002
12	3-NO ₂	4-CN	1.219	1.501	1.501	29.3	30.8	1.223	1.492	1.505	25.1	34.3	0.004
13	3-NO ₂	3-CN	1.219	1.501	1.500	30.3	30.3	1.223	1.493	1.505	25.3	33.8	0.004
14	3-NO ₂	3-NO ₂	1.219	1.501	1.501	30.0	30.1	1.222	1.492	1.505	26.6	34.4	0.004

^a For numbering see Fig. 1.^b α and β represent dihedral angles toward the phenyl ring bearing substituent R and R', respectively.^c $\Delta R_{C=O} = R_{ketyl} - R_{molecule}$.

of the other ketyls 2–14 was characterized by experimental structural methods. Full coincidence between the theoretical data for the free ketyl structure and X-ray data of ketyl complexes cannot be expected because of the counter ion influence in solid state. Allinger and Fan [52] have stated that finding good theoretical descriptions of the spectroscopic features guarantees obtaining of so good or better structural predictions within the same theoretical methods and basis set. Having in mind the good ONIOM–IEFPCM spectral descriptions obtained in this work and the relevance to the X-ray structural data of the unsubstituted ketyl only available in the literature, we consider that the predictions of the structural variations caused by the conversion of benzophenones into ketyls are reliable.

The largest bond length changes, $\Delta R_{C=O} = R(ketyl) - R(ketones)$ (Table 4), correspond to compounds 1–4 of type I where the substituents are acceptors weaker than the C=O group, smaller in presence of stronger electron-withdrawers, which are conjugated with the carbonyl group (compounds 5–9, type II) and very small when the carbonyl group is not conjugated with the stronger acceptor (compounds 10–14, type III).

The dihedral angles formed between the carbonyl group and the phenyl rings (α toward the phenyl ring bearing substituent R; and by β – toward the one with R') are also altered by the conversion. The variations could be classified in three groups corresponding to the three types of ketyls. Within type I, both α and β are reduced upon conversion. With identical substituents (K1 and K4), the reduction of α and β is the same. In the other two cases the change is bigger for α and the bond lengths C–Ph and C–Ph' follow the same trend. Within type II, the benzophenones are characterized by β smaller than α showing that in neutral form the conjugation is spread over Ph' rather than Ph. Upon conversion both angles change, but in the opposite direction, resulting in ketyl groups effectively conjugated with the 4-nitro substituted phenyl rings. The C–Ph bond lengths are correspondingly shortened, while C–Ph' become longer. Within type III, the neutral benzophenones have comparable α and β (except for M11 where R' is a strong electron releasing group). Similarly to type II, upon conversion α is reduced and β becomes larger, but the change is less dramatic. The difference between C–Ph and C–Ph' in the ketyls is considerably smaller as well. Among the whole series of ketyls, the reduction of α is the smallest for type III, another evidence that in this case the conversion of benzophenones into ketyls is accompanied by the least significant structural changes.

Similarly to the radicals and other open shell systems, the structure of radical-anions is determined in general by the distribution

of the odd electron. Having in mind the strong dependence of the IR spectroscopic band positions on the electronic structure, it is worthwhile to study the correlation between the spectral characteristics and the electronic structure in order to explain the observed particularities. For this purpose the spin density populations over different fragments on the basis of Mulliken population analysis (denoted as Mulliken spin densities) and NBO analysis (natural spin densities) were calculated. The spin densities over the C=O groups in the ketyls were correlated with the corresponding experimental frequency decreases ($\Delta\nu_{C=O}$). The data are presented in Table 5. As can be seen there the correlation coefficients are better, when natural spin densities are used.

Computed spin densities ONIOM–IEFPCM over various atomic groups together with the frequency lowering ($\Delta\nu_{C=O}$) are listed in Table 6. Spin densities over atoms for representative ketyls of each group are presented in Fig. 3. The spin densities over the carbonyl group vary significantly but their values are close within the framework of a given type. These results are in agreement with the spectroscopic data. The ability of different groups to accept electron decreases in the row: nitro-, carbonyl-, cyano groups. The spin density over the methoxy- and dimethylamino groups practically could be neglected.

In the case of the unsubstituted benzophenone ketyl a considerable part of the odd electron ($0.473 e^-$) is localized over the carbonyl group. It leads to the strongest decrease of carbonyl stretching frequency ($\Delta\nu_{C=O} = 262 \text{ cm}^{-1}$). The localization of spin density within the carbonyl group is a little bit smaller ($0.412\text{--}0.387 e^-$) for the other compounds of type I. The lowering of carbonyl stretching bands is almost the same as in the previous case ($\Delta\nu_{C=O}$ is $262\text{--}211 \text{ cm}^{-1}$).

Whenever carbonyl group is not dominant but competing with the other electron acceptors (comps. 5–9, type II in Fig. 2), spin

Table 5Correlation coefficients(R) and standard deviations (SD) received at correlation analysis between $\Delta\nu_{C=O}$ and spin density upon carbonyl group on different theory levels.

	B3LYPb	B1LYPb	BHandHLYPb	cam-B3LYPb
<i>Mulliken spin densities</i>				
R	0.9735	0.9603	0.9083	0.9300
SD	0.043	0.057	0.103	0.088
<i>Natural spin densities</i>				
R	0.9773	0.9693	0.9399	0.9443
SD	0.039	0.047	0.073	0.070

Table 6
NBO atomic spin populations over fragments of benzophenone ketyls.

No.	R	R'	CO	CN	CN'	NO ₂	NO ₂ '	$\Delta\nu_{\text{CO}}^a$
K1	H	H	0.473					262
K2	4-Ph	H	0.412					262
K3	4-CN	H	0.348	0.096				232
K4	4-CN	4-CN	0.387	0.047	0.047			211
K5	4-NO ₂	H	0.083			0.608		95
K6	4-NO ₂	4-OMe	0.073			0.623		93
K7	4-NO ₂	4-DMA	0.055			0.645		80
K8	4-NO ₂	4-CN	0.106		0.003	0.573		98
K9	4-NO ₂	3-NO ₂	0.098			0.591	0.000	93
K10	3-NO ₂	H	0.009			0.722		11
K11	3-NO ₂	4-DMA	0.000			0.734		10
K12	3-NO ₂	4-CN	0.005		0.000	0.713		11
K13	3-NO ₂	3-CN	0.005		0.006	0.715		10
K14	3-NO ₂	3-NO ₂	0.009			0.716	0.004	12

^a $\Delta\nu_{\text{CO}} = \nu_{\text{CO}}(\text{molecule}) - \nu_{\text{CO}}(\text{ketyl})$ from [20].

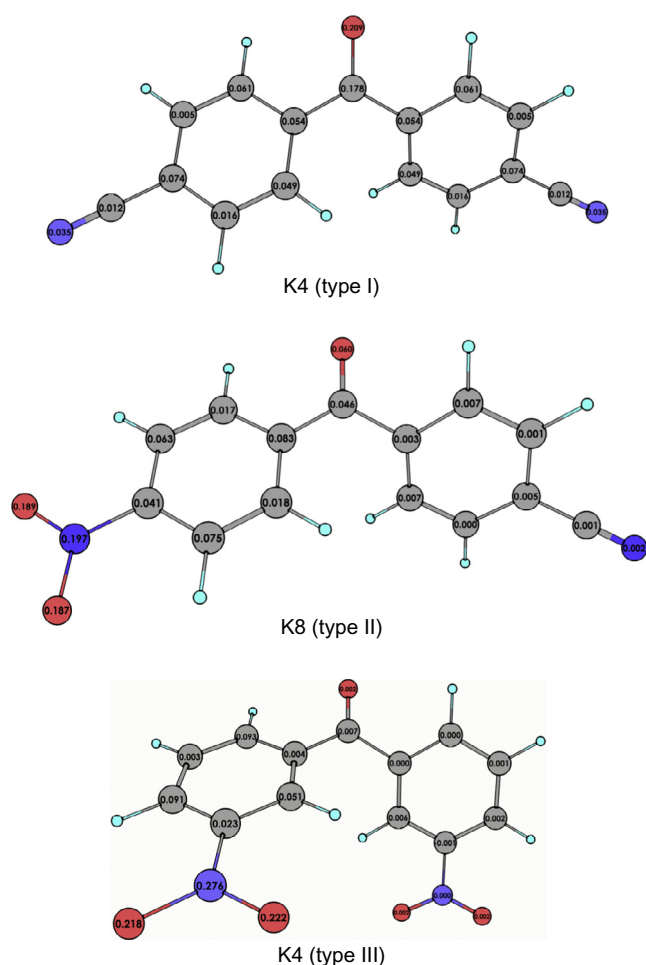


Fig. 3. Spin densities over atoms for representative ketyls of type I, II and III. C-atoms in grey; O-atoms in red; N-atoms in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

population is 0.11–0.08 e^- . The $\nu_{\text{C=O}}$ decrease is smaller with respect to compounds type I, but still significant (95–77 cm^{-1}).

In the third case, the odd electron is localized over the stronger acceptor (compounds 10–14, type III in Fig. 2) and the spin population over the carbonyl group is less than 0.01 e^- thus resulting in very small frequency decrease by only 10–12 cm^{-1} .

The benzophenones have low symmetry as it was discussed above. However, considering the data in Table 4 and Fig. 3 it could be concluded that the neutral benzophenones M1, M4 and M14

possess a little bit higher order of symmetry C_2 . It is interesting to note that according to the calculations, the symmetry is preserved for ketyls K1 and K4, while for K14 it is lowered to C_1 . The data in Table 6 support these conclusions showing that the spin density is distributed equally over the two cyano groups of ketyl K4, in contrast to K14. This is explained by the fact that in the first case the dominant carbonyl group is situated in a central position and it is conjugated with competing cyano groups, while in the second case the dominant nitro group is out of the center and not conjugated with its competitors. The lack of conjugation results in unequal distribution of the odd electron.

The good correlation between the experimental frequency decreases ($\Delta\nu_{\text{C=O}}$) and the calculated spin populations over the C=O fragments proves that the distribution of the odd electron over the functional groups of the radical-anions is the dominant factor determining the frequency variation in their IR spectra.

4. Conclusions

Quantum-chemical DFT methods have been applied to model the geometry and the infrared spectra of a series of benzophenones and their ketyls. The calculations were done employing different functionals (B1LYP, B3LYP, BHandLYP, and cam-B3LYP) and basis sets, without and with inclusion of solvent using the IEF-PCM model. The results of the calculations were evaluated based on their relative capability to predict correctly the IR spectral changes, arising from the conversion of the benzophenones into ketyls. An extensive set of polarization functions is necessary to correctly reproduce the frequencies the carbonyl group of both the neutral benzophenones and the ketyls. However, rendering an account of the medium influence is also crucial in order to obtain a good general agreement with the experimental data. An excellent correlation has been achieved at combination between IEFPCM and ONIOM method with the basis functions 6-311+G(2df,p) for high layer and 6-311+G for low layer. The latter level of theory was applied to analyze the vibrational spectra and geometry of the title species. In agreement with the experiment, the theory predicts that the decrease $\Delta\nu_{\text{CO}}$ is very strong when the substituent is an acceptor weaker than C=O group, smaller in presence of stronger electron-withdrawers, which is conjugated with carbonyl group, and very small when the carbonyl group is not conjugated with the stronger acceptor. The spin populations over the C=O groups in ketyls correlate excellently with these decreases $\Delta\nu_{\text{CO}}$ and prove to be dominant factor determining the frequency variation in the IR spectra. Having in mind the good agreement obtained between theoretical and experimental data we hope that calculations can successfully be used to predict spectral and structural changes, caused by conversions of other types of molecules into radical-anions. The great importance of the spin populations over the functional groups for the corresponding IR changes could also be confirmed.

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References

- [1] D.J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York, 1965.
- [2] M. Schwarc, *Carbanions, Living Polymers and Electron Transfer Processes*, Wiley-Interscience, New York, 1968.
- [3] J. Corset, in: E. Bunzel, T. Durst (Eds.), *Comprehensive Carbanion Chemistry, Part A*, Elsevier, Amsterdam, 1980.

- [4] I.N. Juchnovski, I.G. Binev, in: S. Patai, Z. Rappoport (Eds.), *Chemistry of Functional Groups*, Suppl. C, Wiley, New York, 1983, pp. 107–135. Chapter 4.
- [5] F. Bechman, T. Paul, Verhalten von ketonen und aldehyden gegen natrium bei gegenwart indifferenten lösungsmitteln, *Justus Liebigs Ann. Chem.* 266 (1891) 1–28.
- [6] W. Schlenk, T. Weickel, Ueber die Metallverbindungen der Diarylketone, *Ber. Dtsch. Chem. Ges.* 44 (1911) 1182–1189.
- [7] A. Miller, P.H. Solomon, *Writing Reaction Mechanisms in Organic Chemistry*, second ed., Academic Press, London, 2000. 283.
- [8] A.F. Parsons, *An Introduction to Free Radical Chemistry*, Blackwell Science, New York, 2000. 188.
- [9] G.A. Molander, C.R. Harris, Sequencing reactions with Samarium(II) Iodide, *Chem. Rev.* 96 (1996) 307–338.
- [10] M.I. Bruce, D.C. Kehoe, J.G. Matison, B.K. Nicholson, P.H. Rieger, M.L. Williams, Cluster chemistry. reactions between metal carbonyl clusters and Lewis bases initiated by radical ions: improved syntheses of substituted derivatives of M3 and M4 clusters, *J. Chem. Soc., Chem. Commun.* 8 (1982) 442–444.
- [11] N.G. Connelly, W.E. Geiger, Chemical redox agents for organometallic chemistry, *Chem. Rev.* 96 (1996) 877–910.
- [12] Z. Hou, X. Jia, M. Hoshino, Y. Wakatsuki, First structural characterization of a benzophenone ketyl complex, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1292–1294.
- [13] O.P. Lam, C. Anthon, F.W. Heinemann, J.M. O'Connor, K.J. Meyer, Structural and spectroscopic characterization of a charge-separated uranium benzophenone ketyl radical complex, *J. Am. Chem. Soc.* 130 (2008) 6567–6576.
- [14] T.A. Scott, B.A. Ooro, D.J. Collins, M. Shatruk, A. Yakovenko, K.R. Dunbar, H. Zhou, After 118 years, the isolation of two common radical anion reductants as simple, stable solids, *Chem. Commun.* 2009 (2009) 65–87.
- [15] N. Hirota, S.I. Weissman, Rates of oxidation–reduction reactions between ketyls and ketones, *J. Am. Chem. Soc.* 86 (1964) 2537–2538.
- [16] P.B. Ayscough, *Electron Spin Resonance in Chemistry*, Methuen & Co., London, 1967. 274.
- [17] N.J. Hirota, Electron paramagnetic resonance studies of ion pairs metal ketyls, *J. Am. Chem. Soc.* 89 (1967) 32–41.
- [18] I. Juchnovski, Ts. Kolev, I. Binev, Frequencies of the C=O stretching vibration in aromatic ketyl radicals, *Comp. rend. de l'Acad. Bulg. Sci.* 30 (1977) 1017–1020.
- [19] I. Juchnovski, Ts. Kolev, I. Rashkov, Infrared spectra of the anion-radicals of benzophenone and some of its isotopic isomers, *Spectrosc. Lett.* 18 (1985) 171–178.
- [20] I. Juchnovski, Ts. Kolev, Infrared spectra of the anion-radicals of benzophenone and some of its isotopic isomers, *Spectrosc. Lett.* 18 (1985) 481–490.
- [21] I.N. Juchnovski, Ts.M. Kolev, B.A. Stamboliyska, Infrared spectra of benzophenone-ketyls. Effects of meta and para-substituents on frequencies, *Spectrosc. Lett.* 26 (1993) 67–78.
- [22] B. Stamboliyska, A computational study on the changes in energies, IR spectra and structures of aromatic nitriles caused by their conversions into radical-anions, *Bulgarian Chem. Commun.* 37 (2005) 289–294.
- [23] S. Stoyanov, Scaling of B3LYP cyano stretching frequencies, *Comp. rend. de l'Acad. Bulg. Sci.* 62 (2009) 445–452.
- [24] S. Stoyanov, Scaling of computed cyano-stretching frequencies and IR intensities of nitriles, their anions, and radicals, *J. Phys. Chem.* 114 (2010) 5149–5161.
- [25] D.Y. Yancheva, Characterization of the structure, electronic conjugation and vibrational spectra of the radical anions of p- and m-dinitrobenzene: a quantum chemical study, *Bulgarian Chem. Commun.* 45 (2012) 24–31.
- [26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, D.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09, Revision A1*, Gaussian Inc., Wallingford CT, 2009.
- [27] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098–3100.
- [28] C. Lee, W. Yang, G.R. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789.
- [29] A.D.J. Becke, Densityfunctional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [30] C. Adamo, V. Barone, Toward reliable adiabatic connection models free from adjustable parameters, *Chem. Phys. Lett.* 274 (1997) 242–250.
- [31] A.D.J. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* 98 (1993) 1372–1377.
- [32] T. Yanai, D. Tew, N. Handy, A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chem. Phys. Lett.* 393 (2004) 51–57.
- [33] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, D.J. DeFrees, J.A. Pople, M.S.J. Gordon, Self-consistent molecular orbital methods. XXIII. A polarization type basis set for second row elements, *Chem. Phys.* 77 (1982) 3654–3665 (and references therein).
- [34] S. Dapprich, I. Komáromi, K.S. Byun, K. Morokuma, M.J. Frisch, A new ONIOM implementation in Gaussian98. Part I. The calculation of energies, gradients, vibrational frequencies and electric field derivatives, *J. Mol. Struct. (THEOCHEM)* 462 (1999) 1–21.
- [35] J. Tomasi, M. Perisco, Molecular interactions in solution: an overview of methods based on continuous distributions of the solvent, *Chem. Rev.* 94 (1994) 2027–2094.
- [36] J. Tomasi, B. Mennucci, E.J. Cancès, The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level, *J. Mol. Struct. (THEOCHEM)* 464 (1999) 211–226.
- [37] M. Szwarc, *Ions and Ion Pairs in Organic Reactions*, Wiley-Interscience, New York, 1972.
- [38] D.E. Woon, T.H.J. Dunning, Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon, *J. Chem. Phys.* 98 (1993) 1358–1371 (and references therein).
- [39] V. Barone, in: D.P. Chong (Ed.), *Recent Advances in Density Functional Methods, Part I*, World Scientific Publ. Co., Singapore, 1996.
- [40] P. Carbonniere, T. Lucca, C. Pouchan, N. Rega, V. Barone, Vibrational computations beyond the harmonic approximation: performances of the B3LYP density functional for semirigid molecules, *J. Comput. Chem.* 26 (2005) 384–388.
- [41] P. Carbonniere, V. Barone, Performances of different density functionals in the computation of vibrational spectra beyond the harmonic approximation, *Chem. Phys. Lett.* 399 (2004) 226–229.
- [42] S.L. Howell, K.C. Gorgon, Spectroscopic and density functional theory studies of 1,10-phenanthroline, its radical anion, *J. Phys. Chem. A* 108 (2004) 2536–2544.
- [43] H. Torii, Y. Ueno, A. Sakamoto, M. Tasimi, Vibrational spectra and electron vibration interactions of the naphthalene radical anion. Experimental and theoretical study, *Can. J. Chem.* 82 (2004) 951–963.
- [44] M.K. Georgieva, E.A. Velcheva, Computational and experimental studies on the IR spectra and structure of the simplest nitriles (C1 and C2), their anions, and radicals, *Int. J. Quant. Chem.* 106 (2006) 1316–1322.
- [45] H.A. Tachikawa, H. Kawabata, Structures and electronic states of permethyloligosilane radical ions with all-trans form $\text{Si}(\text{CH}_3)_{2n+2}^\bullet$ ($n = 2-6$): a density functional theory study, *J. Chem. Theory Comp.* 3 (2007) 184–193.
- [46] Y.I. Binev, M.K. Georgieva, S.I. Novkova, The conversion of phenylpropanedinitrile (phenylmalononitrile) into the carbanion, followed by IR spectra, ab initio and DFT force field calculations, *Spectroch. Acta A* 59 (2003) 3041–3052.
- [47] A.D. Popova, M.K. Georgieva, O.I. Petrov, K.V. Petrova, E.A. Velcheva, IR spectral and structural studies of 4-aminobenzenesulfonamide (sulfanilamide)-d0, -d4, and -15N, as well as their azanions: combined DFT B3LYP/experimental approach, *Int. J. Quant. Chem.* 107 (2007) 1752–1764.
- [48] L.I. Daskalova, E.A. Velcheva, I.G. Binev, Changes in the IR spectra and structures of pyridine-3-carboxamides-d0 and -d2 caused by their conversion into azanions-d0 and -d1: experimental and computational studies, *J. Mol. Struct.* 826 (2007) 198–204.
- [49] Y.I. Binev, M.K. Georgieva, L.I. Daskalova, Spectrochemical, ab initio and density functional studies on the conversion of 2-hydroxybenzonitrile (o-cyanophenol) into the oxyanion, *Spectrochim. Acta – Part A: Mol. Biomol. Spectrosc.* 60 (2004) 2601–2610.
- [50] J. Rimarčík, V. Lukeš, E. Klein, M.J. Ilčin, Study of the solvent effect on the enthalpies of homolytic and heterolytic N–H bond cleavage in p-phenylenediamine and tetracyano-p-phenylenediamine, *J. Mol. Struct. (THEOCHEM)* 952 (2010) 25–30.
- [51] E.B. Fleischer, N. Sung, S. Hawkinson, Crystal structure of benzophenone, *J. Phys. Chem.* 72 (1968) 4311–4312.
- [52] N.L. Allinger, Y.J. Fan, Force field calculations on glyoxal, quinones, and related compound, *J. Comput. Chem.* 15 (1994) 251–268.