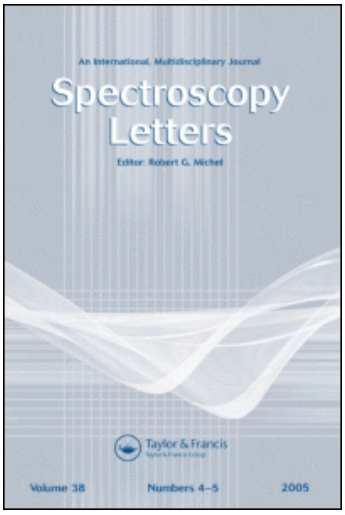


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared Spectra and Structure of the Anion-Radicals of Substituted Benzophenones

I. N. Juchnovski[a]; Ts. M. Kolev[a]
[a] Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

To cite this Article Juchnovski, I. N. and Kolev, Ts. M.(1985) 'Infrared Spectra and Structure of the Anion-Radicals of Substituted Benzophenones', Spectroscopy Letters, 18: 7, 481 — 490
To link to this Article: DOI: 10.1080/00387018508062248
URL: http://dx.doi.org/10.1080/00387018508062248

SPECTROSCOPY LETTERS, 18(7), 481-490 (1985)

INFRARED SPECTRA AND STRUCTURE OF THE ANION-RADICALS OF SUBSTITUTED BENZOPHENONES

KEY WORDS: IR spectra; anion-radicals; isotope labelling; correlation of anion-radical carbonyl frequencies with substituent constants; substituted benzophenones

I. N. Juchnovski and Ts. M. Kolev

Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

ABSTRACT

$\nu_{C\cdots O}$ bands of 23 anion-radicals of meta- and para-substituted benzophenones have been assigned and compared to $\nu_{C=O}$ of the parent neutral compounds. Carbonyl frequencies of the anion-radicals (assigned on the basis of data for isotope-labelling compounds) have been found to appear in a 7-8 times wider frequency interval as compared to the frequency range of corresponding neutral compounds, i.e. the structural effects on $\nu_{C\cdots O}$ on the anion-radicals are 7-8 times stronger, compared to those on $\nu_{C=O}$ of the neutral benzophenones.

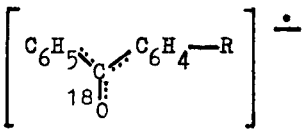
 0038-7010/85/1807-0481$3.50/0

Comparison of ketyl $\nu_{C=O}$ with the sum of the substituent constants has shown three separate correlations for: i) ketyls free of nitro groups; ii) ketyls with nitro groups in para-position; iii) ketyls with nitro groups in meta-position. The absence of general correlation has been explaned by the different types of the odd-electron distribution.

These results do reject a series of literature conclusions about the substituent effects on $\nu_{C=O}$ of the anion-radicals of substituted benzophenones.

INTRODUCTION

Detailed studies on the vibrational spectra of anion-radicals have been published for quinone anion-radicals only[1]. Spectra of the strongly reactive aromatic ketone anion-radicals (ketyls) have not been studied completely. We have recently described[2] the infrared spectra of several ketyls with the following general formula:



R are -H, -CN and $-NO_2$ para-substituents

We have found in the same study some essential errors in the literature assignment[3] of benzophenone-ketyl IR bands.

Unambigous band assignment of ketyl infrared spectra is quite difficult because of the strong variations in both band frequencies and intensities resulting from the conver-.

tion of neutral ketones into ketyls, low transparency of the usual solvents, the high reactivity of ketyls with respect to oxygen, moisture and most common solvents, etc., and nevertheless the reliable band assignment is an obligatory basis for drawing well-grounded conclusion about the odd-electron distribution over the conjugated system and structural factors which determins its variations.

We report in this paper $\nu_{C\cdots O}$ data for a representative series of substituted benzophenone anion-radicals and we discuss the substituent induced variations in the odd-electron distribution, reflecting in the $\nu_{C\cdots O}$ band behaviour. This approach would make it possible to check the validity of some literature conclusions[3] and to form a new concept about structural effects on $\nu_{C\cdots O}$ of substituted benzophenone anion-radicals.

EXPERIMENTAL

Anion-radicals have been generated electrochemically in a special CaF_2 electrolysis cell of 0,26 mm path lenght, supplied with a central platinum cathode and two platinum anodes build in its spaser[4]. Purified dimethyl sulfoxide-d_6 (DMSO-d_6), containing 0,1 mol/l tetraethylammonium perchlorate has been used as a solvent. Concentrations: in the range of 0.05 - 0,1 mol/l. A similar cell, containing the same solvent has been used as a reference. After 2 - 10 minutes after applying a voltage of 1 - 2,5 V, the solution

in cathode space through which the measuring beam passes gets the colour characteristic for corresponding anion-radical.

RESULTS AND DISCUSSION

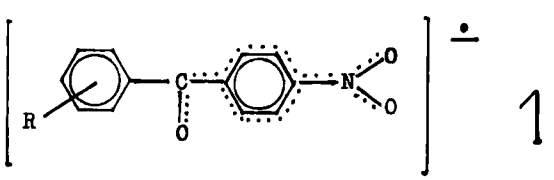
The final results for $\nu_{C\cdots O}$ band assignment of 23 anion-radicals studied of meta- and para-substituted benzophenones are presented in Table 1.

Attempts to correlate $\nu_{C=O}$ of the parent ketones with $\nu_{C\cdots O}$ of the corresponding anion-radicals lead to the formation of three separate correlation for: i) ketyls without nitro groups; ii) ketyls with nitro groups in para position and iii) ketyls with meta-nitro groups.

The comparison of $\nu_{C\cdots O}$ of substituted benzophenones anion-radicals with the sum of substituent constants has given also three separate correlations (Fig. 1).

Anion-radicals of benzophenones with electron-withdrawing substituents (weaker than the carbonyl group) show lowest frequencies (correlation I on Fig. 1) and this can be related to the expected high odd electron density within the the carbonyl group[5].

$\nu_{C\cdots O}$ of benzophenone anion-radicals with para-nitro groups (Formula 1)



1

Table 1. Comparison between $\nu_{C=O}$ of meta- and para-substituted benzophenones and $\nu_{C=O}$ of corresponding anion-radicals.

No	R_1	R_2	$\nu_{C=O}(cm^{-1})$	$\nu_{C=O}(cm^{-1})$	$\Delta\nu(cm^{-1})$
1.	H	H	1658	1396	262
2.	D[a]	D[a]	1657	(1396)	(261)
3.	H[b]	D[b]	1657	1386	261
4.	H*	H*	1629	1386	243
5.	4-CN	H	1662	1430	232
6.	4-CN*	H*	1634	1420	214
7.	4-C_6H_5	H	1659	1397	262
8.	4-CF_3	H	1662	1437	225
9.	4-CN	4-CN	1668	1457	211
10.	4-COPh	H	1659	1421	238
11.	4-NO_2	H	1665	1570	95
12.	4-NO_2*	H*	1638	1560	78
13.	4-NO_2	4-$N(Me)_2$	1644	1667	77
14.	4-NO_2	4-OMe	1658	1565	93
15.	4-NO_2	4-CN	1673	1575	98
16.	4-NO_2	3-NO_2	1673	1580	93
17.	3-NO_2	H	1665	1654	11
18.	3-NO_2	4-$N(Me)_2$	1642	1632	10
19.	3-NO_2	4-CN	1670	1659	11
20.	3-NO_2	3-CN	1671	1661	10
21.	3-NO_2	3-Br	1672	1660	12
22.	3-NO_2	4-Br	1668	1657	11
23.	3-NO_2	3-NO_2	1672	1660	12

[a],$C_6D_5COC_6D_5$; [b],$C_6H_5COC_6D_5$; *,^{18}O labelled compounds.

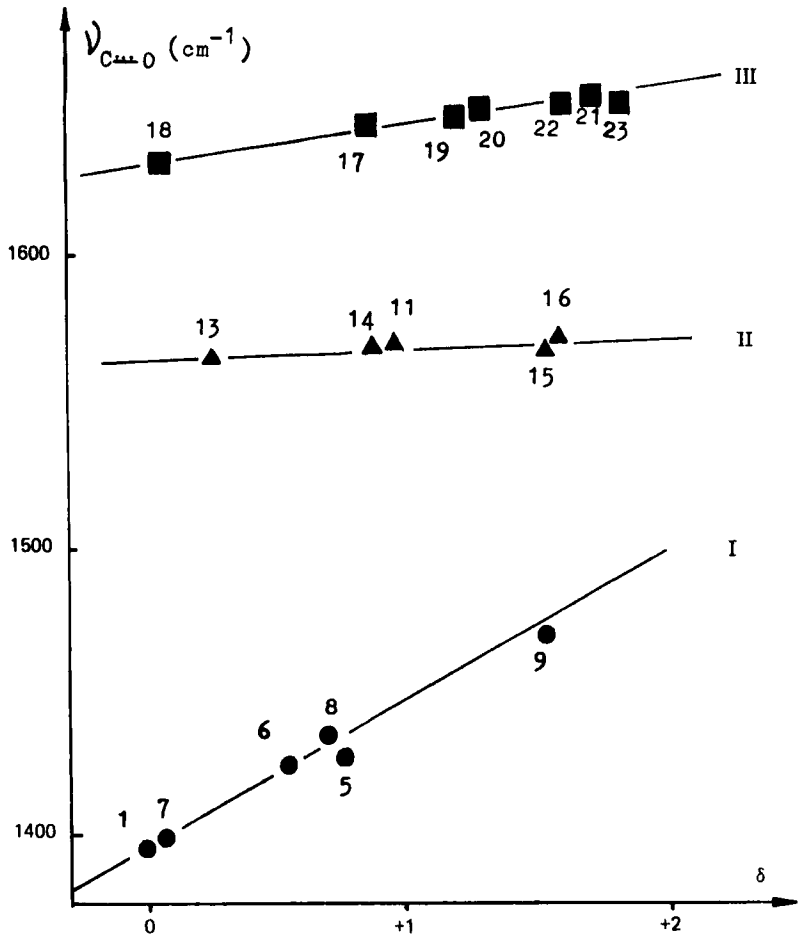
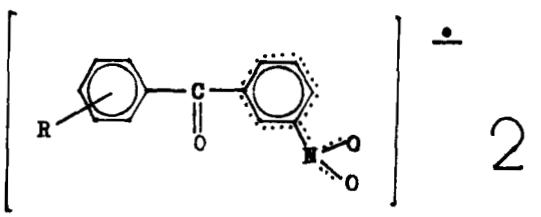


Fig. 1

Correlation between $\nu_{C\cdots O}$ of anion-radicals of substituted benzophenones (solvent DMSO-d_6) and the sum of σ substituent constants.

form the correlation II (Fig. 1) due to the high electron-withdrawing ability of the nitro group. $\nu_{C=O}$ lowering on convertion of para-nitrobenzophenones into corresponding anion-radicals is ca. 100 cm^{-1}.

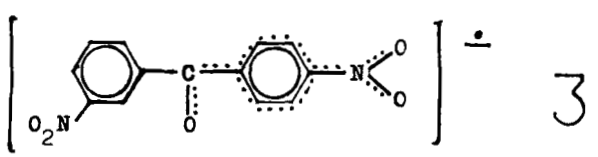
$\nu_{C\cdots O}$ of anion-radicals with meta-nitro groups (Formula 2)



2

are only of 10-11 cm^{-1} lower than those of the parent ketones. This result can be ascribed to a definite localization of the odd-electron density within the nitro group (the strongest electron-withdrawer), for there are no possibilities of CO/NO_2 competitive conjugation in these cases.

$\nu_{C\cdots O}$ data for the case of 3,4′-dinitrobenzophenone-ketyl (Formula 3)



3

point to the pronounced localization of the odd-electron density within the 4-nitrobenzoyl fragment, while the 3-nitro group is practically out of the antibonding orbital influence.

$\nu_{C=O}$ of neutral benzophenones appear in a quite narrow frequency region (33 cm^{-1}); in cases of the corresponding anion-radicals this region is much larger (ca. 270 cm^{-1}, Table 1) so the structural effects on $\nu_{C\cdots O}$ of anion-radicals are 7-8 times stronger than in the cases of the neutral ketones.

There is a close analogy between structural effects on odd-electron density distribution (and on $\nu_{C\equiv N}$) in anion-radicals of aromatic nitriles[6] and aromatic ketyls.

The above reported data on the relation between the structure and frequencies of the $\nu_{C\cdots O}$ band of benzophenone anion-radicals can be qualitatively described in the following way:

The presence of the odd electron an antibonding π-orbital results in a weakening of the π-bonds of pronounced double character in the conjugated system, including those of the carbonyl group. The latter group is an electron-acceptor and therefore a considerable part of the odd electron density is localized over it, which leads to a strong decrease in $\nu_{C=O}$ (e.g. anion-radical of benzophenone). The presence of a large conjugated system gives the possibility of a strong delocalization of the odd electron; in this case the $\nu_{C=O}$ is little bit smaller (e.g. 4-phenyl benzophenone-ketyl). If beside the carbonyl group another strong acceptor is present in the anion-radical, the odd electron distribution is determined by the competition

between the two acceptors; smaller frequency decrease of the $\nu_{C=O}$ bands were found in the cases where carbonyl group is the weaker acceptor (e.g. 4-nitrobenzophenone ketyl). If the two acceptors are not mutually conjugated, the possibilities of a competition decrease and the odd electron proves to be practically completely localized over the strongest acceptor. When the carbonyl group is the weaker acceptor, only small variations in the frequency of the $\nu_{C=O}$ bands were found (e.g. anion-radical of 3-nitrobenzophenone).

Electron-releasing substituents (even dimethylamino group) have not essential effect on $\nu_{C=O}$ of anion-radicals (Table 1.). The low sensitivity of $\nu_{C\cdots O}$ of anion-radicals to electron-releasing substituent effects is evidently due to the presence of considerable amounts of negative charge on the carbonyl group. Their influence on $\nu_{C\cdots O}$ of the neutral ketones is, on the contrary, very strong.

As it is seen the structural effects on $\nu_{C=O}$ of neutral ketones and on $\nu_{C\cdots O}$ of the corresponding anion-radicals are very different. Carbonyl frequencies in ketyls are determined mainly by the odd electron distribution over the conjugated system, which on its part depends very strongly on the position and the type of the electron-withdrawing substituents but very weakly by electron-releasing ones.

REFERENCES

1. Y. Iida, Bull. Chem. Soc. Jap., 43, 345 (1970); 44, 1271 (1971); 45, 105 (1972); 51, 2523 (1978);

G. Varsanyi and M. Kubinyi, J. Mol. Struct., 45, 107 (1978);
A. Girlando, I. Zanon, R. Bozio and C. Pecile, J. Chem. Phys., 68, 22 (1978).

2. I. N. Juchnovski, Ts. M. Kolev and I. G. Binev, Compt. rend. Acad. Bulg. Sci., 30, 1017 (1977).

3. D. H. Eargle and R. Cox, Alkali Metals, Chem. Soc. London Spec. Publ. No 22, 1967, 116; D. H. Eargle and R. Emrich, J. Org. Chem., 35, 3774 (1970).

4. I. N. Juchnovski, I. G. Binev, Compt. rend. Acad. Bulg. Sci., 24, 483 (1971).

5. V. M. Khazakova, B. I. Shapiro, I. D. Morozova and E. A. Polenov, J. Struct. Khim., 12, 19 (1971).

6. I. N. Juchnovski, I. G. Binev and J. Kaneti, Izv. Khim., 10, 554 (1977).

Received: 03/05/85
Accepted: 04/10/85