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^{17}O NMR chemical shifts of 3-(substituted methylene)-(*Z*)-1(3*H*)-isobenzofuranones: correlations with IR stretching wavenumbers and AM1 charges

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ABSTRACT: ^{17}O NMR chemical shifts were determined for 1(3*H*)-isobenzofuranone, its 3-methylene- and 3-(*Z*)-(methylmethylene) derivatives and a series of 3-aryl-, 3-aryloxy- and 3-arylthiomethylene-(*Z*)-1(3*H*)-isobenzofuranones. The observed $\delta(^{17}O)$ values of the C=O-group of the furanone moiety in the arylidene series show significant linear dependences on the wavenumber of the IR stretching vibration, ν(CO), the AM1 charge density at the double bond oxygen, q(O), and the Hammett σ^+ constant of the substituent in the phenyl ring. These findings suggest that the substituent effects are efficiently transmitted from the phenyl ring to the C=O group via the conjugated double bond system of the 3-arylidene-(*Z*)-1(3*H*)-isobenzofuranone. In the case of aryloxy and arylthio derivatives these correlations were less significant than in arylidene compounds, reflecting the diverse effects of the heteroatoms (O or S) on the transmission mechanism. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{17}O NMR; chemical shifts; substituent effects; IR; AM1 charge densities; empirical correlations; 3-(arylidene)-(*Z*)-1(3*H*)-isobenzofuranones

INTRODUCTION

Steric effects on the ^{17}O NMR chemical shifts of the phthaloyl moiety in isobenzofuranones have been reviewed by Baumstark and Boykin.[1] These studies revealed that ^{17}O NMR chemical shifts of carbonyl oxygens in these conformationally rigid structures correlate significantly with the bond angle deformations, reactivity constants and charge densities (double bond character) of the C=O groups. In spite of these findings, the identification of the origin of the steric factors that affect ^{17}O NMR data is still partly unclear but need to be understood in order to give increased insight into molecular structure using ^{17}O NMR methodology.[1]

As with phthalides, the transmission of electronic effects in arylidene phthalides is of continuing interest.[2–5] This is due to the fact that in these structures the carbonyl group is cross-conjugated with a dicoordinated oxygen. It has been shown previously that the wavenumbers of unperturbed fundamental C=O stretching vibrations exhibit excellent linear correlations with Hammett's constants and ^{13}C NMR chemical shifts of the C=O group.[5] Further, IR[6] and ^{13}C NMR[7] spectroscopic measurements for phenylidenephthalides and related compounds reveal that the electronic effects are transmitted from the arylidene subsystem to the C=O group. Consequently, substitution at the phenylidene moiety should also reflect some variation in the ^{13}C and ^{17}O NMR chemical shifts of the carbonyl group. However, as far as we know there has been no systematic ^{17}O NMR investigation of these structures. Taking also into account the above-mentioned necessity for further studies in this area, we now report the ^{17}O NMR chemical shifts of 3-(substituted methylene)-(*Z*)-1(3*H*)-isobenzofuranones (**1**–**20**) and 1(3*H*)-isobenzofuranone (**21**) itself. Further, these data are related to the IR stretching vibrations of carbonyl groups, AM1 charge densities at the oxygen of the C=O-group in 1(3*H*)-isobenzofuranone and the Hammett σ^+ constants of the substituent in the phenylidene moiety.

RESULTS AND DISCUSSION

The general structures of the compounds studied are shown in Scheme 1. The ^{17}O NMR chemical shifts of **1**–**21**, the wavenumbers of the IR stretching vibrations, (C=O), and AM1 charge densities, q(O), are given in Table 1.

Considering the ^{17}O NMR data in Table 1, two general observations can be made. First, the ^{17}O NMR chemical shifts of alkylidene derivatives **19** and **20** are strongly deshielded compared with those of the parent

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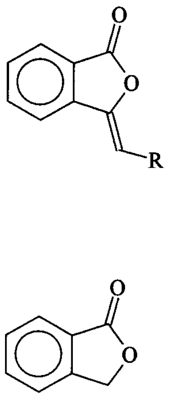

1 - 20

21

Scheme 1. Structures of compounds **1–21**. For R, see Table 1.

compound **21**. Such a behavior can be explained as a consequence of a competitive cross-conjugation between lone-pair electrons of the bridging oxygen and the π-electron systems of the two unsaturated parts of the molecule. This deshielding effect is transmitted efficiently via the conjugated system in the isobenzofuranone ring to the oxygen of the carbonyl group. Second, introduction of an arylmethylene, aryloxymethylene or arylthiomethylene moiety into position 3 of the 1(3*H*)-isobenzofuranone system in **1–18** causes a marked shielding of the both oxygens of the phthalide moiety in comparison with the alkylidene derivatives **19** and **20**. Qualitatively, the latter finding can be explained by further delocalization of the electron density between the phthalide moiety and the aromatic π-system.

Within the series of substituted phenylideneisobenzofuranones **1–10**, the $\delta(^{17}O)$ chemical shifts of the carbonyl oxygens exhibit a range of 9.0 ppm, the 4-NH_2 and 2,4-Cl_2 derivatives showing the minimum and maximum values of 332.2 and 341.2 ppm, respectively. This range for the dicoordinated oxygen within the series **1–10** is only 3.2 ppm. Further, because the accuracy of the ^{17}O NMR chemical shifts is limited owing to the broadness of the resonance lines (350 Hz $< w_{1/2}(O{=}C) <$ 500 Hz and 350 Hz $< w_{1/2}(—O—) <$ 400 Hz), the linear regression analysis is done only for the ^{17}O chemical shifts of the carbonyl oxygen.

The quantitive correlations $\delta(^{17}O = C)$ *vs* (C=O) and *q*(O) at the carbonyl oxygen are given by Eqns (1) and (2), respectively, for **1–10** (arylidene derivatives):

Table 1. ^{17}O NMR chemical shifts, $\delta(^{17}O)$, IR stretching wavenumbers, $\nu(CO)$, and AM1 charge densities at carbonyl oxygen, $-q(O)$, for 3-(substituted methylene)-(*Z*)-1(3*H*)-isobenzofuranones (**1–20**) and for the parent 1(3*H*)-isobenzofuranone (**21**)

Compound	R	$\delta(^{17}O)$ (ppm)[a] C=O	—O—	$\nu(CO)$ (cm^{-1})[b]	$-q(O)$[c]
1	C_6H_5	336.1	216.1	1776.8	0.2670
2	4-$NH_2C_6H_4$	332.2	212.9	1769.4	0.2725
3	4-$CH_3C_6H_4$	335.8	215.4	1775.5	0.2680
4	3-$CH_3C_6H_4$	336.3	215.3	1777.6	0.2674
5	4-FC_6H_4	335.6	214.1	1779.1	0.2643
6	4-ClC_6H_4	337.5	215.7	1780.3	0.2636
7	3-FC_6H_4	338.4	215.0	1782.1	0.2631
8	3-ClC_6H_4	339.0	215.1	1782.5	0.2638
9	3-$CF_3C_6H_4$	340.4	215.2	1784.0	0.2609
10	2,4-$Cl_2C_6H_3$	341.2	214.6	1784.4	0.2617
11	C_6H_5O[d]	328.2	204.4	1776.0	0.2674
12	3-$CH_3C_6H_4O$	328.5	204.8	1777.1	0.2682
13	4-$CH_3C_6H_4O$	328.8	204.9	1776.6	0.2683
14	4-$CH_3OC_6H_4O$	326.5	206.6	1775.2	0.2691
15	C_6H_5S	334.1	216.5	1781.6	0.2665
16	3-ClC_6H_4S	337.4	217.3	1795.6	0.2637
17	4-$CH_3C_6H_4S$	334.4	217.8	1792.0	0.2673
18	4-ClC_6H_4S	337.1	217.2	1783.3	0.2636
19	H	374.6	263.9	1774.5	0.2666
20	CH_3	370.8	261.8	1775.9	0.2698
21	—	317.3[e]	168.9[e]	1766.4	0.2793

[a] ppm from external H_2O; measured for saturated CD_3CN solutions at 75 °C

[b] Wavenumbers of unperturbed C=O stretching vibrations for $CHCl_3$ solutions; taken from Ref. 5 for **1–10**, **19** and **20** and from Ref. 4, for **11–18**.

[c] Atomic charge density at the oxygen of the C=O group calculated by the AM1 method.[12]

[d] $\delta(^{17}OC_6H_5) = 107.45$ ppm.

[e] Literature values: $\delta(^{17}O{=}C) = 320$ ppm and $\delta(—^{17}O—) = 170$ ppm taken from Ref. 1a, p. 78.

$$\delta(^{17}\mathrm{O}) = -(650 \pm 100) + (0.55 \pm 0.06)\nu(\mathrm{CO}) \qquad n = 10, r = 0.96 \quad (1)$$

$$\delta(^{17}\mathrm{O}) = (520 \pm 30) + (-700 \pm 100)q(\mathrm{O}) \qquad n = 10, r = 0.92 \quad (2)$$

Both correlations are very significant, which is understandable because all three parameters, $\delta(^{17}\mathrm{O})$, $\nu(\mathrm{C{=}O})$ and $q(\mathrm{O})$, are direct descriptors of the same functionality of the molecule. A corresponding linear correlation in substituted acetophenones has been reported by St Amour *et al.*[8] and in furan-2,3-diones possessing the same structural unit as phthalides by Hnach *et al*,[9] where

$$\nu(\mathrm{CO}) = 1052.3 + 2.02\delta(^{17}\mathrm{O}), \qquad n = 7, r = 0.79 \quad (3)$$

Recently, a linear correlation between the $\delta(^{17}\mathrm{O}_2\mathrm{N})$ and the symmetric IR stretching, (NO_2), has also been reported for *ortho*-substituted nitrobenzenes and 2,4-dinitrobenzenes.[10]

The $\nu(\mathrm{CO})$ values of the present compounds[4,5] have been previously related to the Hammett σ^+ constants.[11] Consequently, the latter values can be further related to the present $\delta(^{17}\mathrm{O})$ values based on these previous data. Nevertheless, for the sake of clarity, the Eqn (4) now describes the $\delta(^{17}\mathrm{O})$ *vs.* σ^+ constants for compounds **1**–**9**:

$$\delta(^{17}\mathrm{O}) = (340 \pm 10) + (4.2 \pm 0.5)\sigma^+ \qquad n = 9, r = 0.95 \quad (4)$$

For the carbonyl oxygen-2 in furan-2,3-diones,[9] the corresponding equation was reported to be as follows:

$$\delta(^{17}\mathrm{O}) = 379.6 + 4.64\sigma^+ \qquad n = 7, r = 0.93 \quad (5)$$

The correlations $\delta(^{17}\mathrm{O})$ *vs* $\nu(\mathrm{CO})$ demonstrated here and $\delta(^{13}\mathrm{C})$ *vs* $\nu(\mathrm{CO})$ shown earlier[5] suggest that there should be some dependence between $\delta(^{17}\mathrm{O})$ and $\delta(^{13}\mathrm{C})$ of the C=O group. A direct comparison of the previous ^{13}C NMR data[7] and the ^{17}O chemical shifts obtained here shows that there is a reverse correlation between these parameters. Unfortunately, there are only few derivatives for which both values are available owing to difficulties in obtaining reliable ^{17}O NMR chemical shifts. Therefore, a regression analysis cannot produce any significant quantitative result for these parameters, especially because the variation range of the available ^{13}C NMR chemical shifts is relatively small.[7]

There are clear differences between the series arylidene **1**–**10** and heteroatom bridging, aryloxy **11**–**14**/arylthiomethylene **15**–**18**. Introducing a phenoxy group instead of phenyl on the methylene moiety causes a clear shielding effect on both furanone oxygens, whereas with a phenylthio substituent these effects are not very clear in comparison with aryl derivatives. Further, the influence of substituents in the aryloxy and arylthio groups (**11**–**19**) upon $\delta(^{17}\mathrm{O})$ of the C=O group is small, yielding no significant correlations with the other above-mentioned parameters.

CONCLUSIONS

This work has verified that ^{17}O NMR chemical shifts are consistent with and complementary to a wide range of spectroscopic and other data. Consequently, the potential of ^{17}O NMR spectroscopy for monitoring electronic effects in conjugated π-systems is significant. Especially the ^{17}O NMR chemical shifts of the arylidene phthalides studied in this work show dependences on IR stretching wavenumbers, Hammett σ^+ constants and AM1 charge densities as in substituted furan-2,3-diones reported earlier. The carbonyl oxygen of the 1(3*H*)-isobenzofuranone system is strongly deshielded owing to cross-conjugation with the dicoordinated oxygen bound to a C = C moiety in position 3. Further, substitution at a phenyl ring which is bound to this double bond system is clearly reflected in the ^{17}O NMR chemical shifts of the furanone moiety. Inclusion of a heteroatom (O or S) in this transmission route causes some diverse effects depending on the nature of the heteroatom. Nevertheless, substituent effects from an aryloxy or arylthio system are still transmitted to the furanone moiety as detected by ^{17}O NMR.

EXPERIMENTAL

Spectroscopy

^{17}O NMR spectra were measured for saturated $\mathrm{CD_3CN}$ solutions of **1**–**21** at 75 °C using a Bruker Avance DRX500 FT NMR spectrometer equipped with a 5 mm diameter multinuclear probehead. An aring pulse sequence was used to remove baseline artefacts caused due to the acoustic ringing. The spectral width was 610 ppm and the number of data points in the time domain was 8K, which was zero-filled to 16K and exponentially windowed by 50 Hz prior to Fourier transformation. The acquisition time was 100 ms and a pulse delay of 100 ms was also included in the pulse sequence. The total experimental time varied from 16 h (300 000 scans) to 40 h (750 000 scans), depending on the concentration (solubility) of the sample. In every case the accumulation was continued until the signal-to-noise ratio was better than 10. A 1 mm diameter capillary tube of $\mathrm{H_2O}$ inserted coaxially inside the NMR tube was used as a reference signal ($\delta = 0.0$ ppm). The accumulations were performed without sample spinning and with the field locked to the deuterium resonance of the solvent. The structures of the compounds were ascertained from their ^{1}H and ^{13}C NMR spectra and ^{1}H, ^{13}C HMQC correlation maps. The synthetic details, IR spectroscopic parameters and description of kinetic measurements were reported previously.[2,3]

Computational details

All computations were performed using the semi-empirical AM1[12] Hamiltonian as implemented in the

VAMP[13] program package. Geometries were completely optimized (keyword PRECISE) using an eigenvector following routine.[14] Charges were obtained from a Mulliken population analysis. Starting structures for all compounds were created by the SYBYL[15] molecular modeling package.

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