Oxygen-17 and Selenium-77 Nuclear Magnetic Resonance of Carbonyl and Selenocarbonyl Compounds. Correlation of Oxygen-17 and Selenium-77 Chemical Shifts

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The ^{77}Se, ^{17}O, and ^{13}C n.m.r. spectra of some carbonyl and selenocarbonyl compounds were studied. The ^{77}Se chemical shifts are found to be dominated by the local paramagnetic screening term. $\delta(^{17}O)$, $\delta(^{77}Se)$, and $^{1}J(^{77}Se-^{13}C)$ are shown to be affected by the ring size of the molecules. $\delta(^{77}Se)$ and $\delta(^{17}O)$ of corresponding compounds show excellent correlation and a comparison of them indicates that the bond order terms of C=Se and C=O, as well as their trends of variation, are practically identical.

In our previous investigations (hereafter referred to as papers I and II),[1,2] we reported the selenium-77 chemical shifts and $^{13}C-^{77}Se$ coupling constants for a series of molecules containing a carbon–selenium double bond. Excellent correlation was observed between $\delta(^{77}Se)$, $^{1}J(^{13}C-^{77}Se)$, the $\lambda_{max.}$ $n \longrightarrow \pi^*$, and the CC(Se)C angle variation due to ring formation. The local paramagnetic screening term was shown to dominate $\delta(^{77}Se)$.[1,3] To extend this study, we have investigated several more selones (selenoketones) with different ring sizes. In paper I, we also observed that a deshielding of $\delta(^{77}Se)$ is always accompanied by a shielding of $\delta(^{13}C{=}Se)$,[1,2] a trend similar to that of the change of $\delta(^{17}O)$ *versus* $\delta(^{13}C{=}O)$ reported for a series of ketones.[4,5] Therefore, it appears that $\delta(^{77}Se)$ may parallel $\delta(^{17}O)$ for the corresponding compounds. A comparison of these shifts should provide some information on the relative bond orders and polarities of C=Se bonds *versus* the corresponding C=O bonds. We have therefore also measured the $\delta(^{17}O)$ of the corresponding carbonyl molecules for the compounds reported in refs. 1 and 2.

Experimental

The selenium compounds were synthesized according to procedures published elsewhere.[6] Di-tert-butyl ketone was purchased from ICN Pharmaceuticals, Plainville, NY; 2,2,4,4-tetramethylcyclobutanedione was purchased from Alpha Products, Danvers, MA. Other tetramethylated ketones were prepared by modifying the method of Rathke.[6]

All spectra were obtained at 21 °C on a Nicolet NT-300 spectrometer (^{13}C at 75.4 MHz, ^{77}Se at 57.2 MHz, and ^{17}O at 40.7 MHz) with 20 mm probes. For ^{17}O n.m.r., samples were made in a 2 : 1 (v/v) mixture of $CDCl_3$ and dimethylsulphoxide (DMSO), the latter serving also as the internal standard. The chemical shift $\delta(^{17}O)$ of DMSO is 13 p.p.m. downfield from water.[7] Typical conditions are: spectral width 20 KHz, 4—8 K points, and 10 000—20 000 scans with 50—100 ms repetition rate (1—3 h). For ^{13}C and ^{77}Se n.m.r., samples were prepared in $CDCl_3$, which also serves as the internal standard for ^{13}C. For ^{77}Se spectra, triphenylphosphine selenide, which give a doublet of 729 Hz splitting, centering at -263 p.p.m. from Me_2Se in $CDCl_3$, was used as the internal standard.[1] Typical conditions are: 16—32 K data points, broadband decoupled, 40° nutation angle (25 μs), and 1—4 h of accumulation time.

The coupling constant $^{1}J(^{77}Se-^{13}C)$ was usually measured from the selenium satellites (7.6%) of the ^{13}C spectrum. During the course of this investigation, we have found that the ^{77}Se T_1 of these compounds is very short (<1 s) at high magnetic fields, owing to the chemical-shift anisotropy mechanism,[8] therefore it would be advantageous to obtain $^{1}J(^{77}Se-^{13}C)$ from the ^{13}C satellites of the ^{77}Se spectrum. Thus, for 4-Se (see Table 2), of which we initially had only a small amount, $^{1}J(^{77}Se-^{13}C)$ was obtained with the latter method. It was not possible to obtain this coupling constant from the ^{13}C spectrum owing to low sensitivity and the long relaxation time of the carbonyl carbon. The drawback of obtaining the ^{13}C satellites from the ^{77}Se spectrum is that ^{77}Se resonance is very temperature dependent (see Results section); long-term averaging usually leads to excessive broadening of the main resonance and can ' wash out ' the satellites if the sample temperature is not carefully controlled.

U.v.-visible spectra were run on a Perkin-Elmer 320 spectrophotometer using cyclohexane as a solvent. I.r. spectra were run on neat samples using a Perkin-Elmer 283B i.r. spectrometer interfaced with a Perkin-Elmer computer-data station. All values were read from peak tables generated by the computer (± 2 cm^{-1}, polystyrene reference).

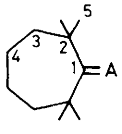
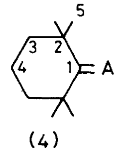
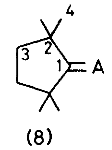
Results

^{13}C *N.m.r.*—The ^{13}C n.m.r. results of 3-O, 4-O, 4-Se, 8-O, and 8-Se are given in Table 1. The spectral characteristics of these compounds are very similar to those reported in paper II, *i.e.* $\delta(^{13}C{=}Se)$ lies at *ca.* 290 p.p.m., with $\delta(^{13}C{=}O)$ at 220 p.p.m.[2] The chemical shift of the carbon α to the C=Se group is about 20 p.p.m. downfield from the corresponding carbon chemical shifts of the carbonyl compounds. The chemical shifts of the methyl groups of the selenium compounds are also about 5 p.p.m. downfield from those of the carbonyl compounds. As was pointed out by Mason,[5] the variation of the $\delta(^{13}C{=}O)$ [and in this case $\delta(^{13}C{=}Se)$ also] is sometimes hard to predict. For example, the direction of the variation of $\delta(^{13}C{=}O)$ *versus* $\delta(^{17}O)$ within a certain functional group category of molecules (*e.g.*, ketones) may be opposite to the general direction of variation between different categories of molecules (*e.g.*, between ketones and amides). However, the variation of $\delta(^{13}C{=}Se)$ with $\delta(^{13}C{=}O)$ closely follows a linear relationship as derived in paper II. The additional data obtained in this study changed the slope and the intercept slightly and thus yield a modified equation, equation (1). The correlation coefficient, R, is 0.980. The

$$\delta(^{13}C{=}Se) = 1.536\ \delta(^{13}C{=}O) - 47.0\ (\text{p.p.m.}) \qquad (1)$$

difference between this equation and the one previously described [2] is relatively insignificant.

Table 1. ^{13}C Chemical shifts of some selones and corresponding ketones [a]

Compound	Carbon	A = O	A = Se
 (3)	1	219·7	b
	2	48·8	
	3	38·9	
	4	25·5	
	5	27·7	
 (4)	1	217·1	294·7
	2	42·1	58·9
	3	37·9	38·4
	4	15·9	18·3
	5	25·6	33·5
 (8)	1	223·8	297·8
	2	43·0	64·2
	3	32·6	37·4
	4	23·0	29·3

[a] Chemical shifts in p.p.m. downfield from Me_4Si. [b] This selone cannot be prepared using standard procedures.[6]

^{77}Se *N.m.r.*—The chemical shifts $\delta(^{77}Se)$ and coupling constants $^1J(^{77}Se-^{13}C)$ obtained for (4-Se) and (8-Se) (Table 2) fall within the expected range for selones (1 600—2 150 p.p.m. for chemical shifts and 210—220 Hz for the *J* coupling constants) reported in paper I and ref. 3. The chemical shifts $\delta(^{77}Se)$ of the selones occur at a lower field than any other type of selenium compound, and the magnitude of $^1J(^{77}Se-^{13}C)$ is about twice that for C–Se single bonds. For (4-Se), the values can be predicted from paper I based on the simple ring-size and ring-strain argument. It is less clear from the above argument why $\delta(^{77}Se)$ and $^1J(^{77}Se-^{13}C)$ of (8-Se) should lie between those of (6-Se) and (7-Se) and that of (9-Se); however, the values of both $\delta(^{77}Se)$ and $^1J(^{77}Se-^{13}C)$ follow this order. Furthermore, the chemical shift $\delta(^{17}O)$ of (8-O), which will be discussed later, also lies between those of (6-O) and (7-O), and that of (9-O). The $\lambda_{max.}$ $n \longrightarrow \pi^*$ of those compounds is also consistent with this order. Apparently, the failure of the simple ring-size argument arises from the interaction of the aromatic and olefinic π-electron systems in (6) and (7) with that of the C=X (X = O, Se) group. This reduces the mean excitation energy, Δ*E*, which strongly affects the local paramagnetic screening term, σ_p. The linear correlation between $\delta(^{77}Se)$ and $\lambda_{max.}$ $n \longrightarrow \pi^*$ clearly shows that the ^{77}Se chemical shift is dominated by the local paramagnetic screening term. With the additional data on $\delta(^{77}Se)$ and $\lambda_{max.}$ $n \longrightarrow \pi^*$ and ignoring that of (13-Se), which appears to be anomalous, a linear equation based on the values presented in Table 2 is derived [equation (2)], where $\delta(^{77}Se)$ is in p.p.m. and $\lambda_{max.}$ $n \longrightarrow \pi^*$ in

$$\delta(^{77}Se) = 5.806\ \lambda_{max.}\ n \longrightarrow \pi^* - 1\,983 \qquad (2)$$

nm. The correlation coefficient *R* is 0.990. The origin of the anomalous behaviour of (13-Se) is unclear. It may either be due to the additional resonance stabilization involving both amide groups, or to the solvent effect [C_6D_6 was used as the solvent for (13-Se) in ref. 3 and $CDCl_3$ for other compounds in Table 2].

The one-bond spin–spin coupling constant, $^1J(^{77}Se-^{13}C)$, is believed to be negative.[1] Its magnitude varies monotonically with the ^{77}Se chemical shift. It was argued [1] that the change of the CC(Se)C bond angle owing to the formation of rings of varying size causes a change in the *s* character of the carbon orbitals used to form the exocyclic C–Se bond. The smaller the CC(Se)C angle, the larger is the *s* contribution [9] and thus the larger the $^1J(^{77}Se-^{13}C)$. The larger *s* character of the C=Se bond should be reflected also in a higher bond strength and a higher C–Se stretching frequency $\nu_{C=Se}$. The $\nu_{C=Se}$ for this series of compounds is not available. However, it can be shown that the variation of the bond strengths of the C=O bond parallels that of the C=Se bond in analogous molecules (see Discussion section). Therefore a comparison of the $^1J(^{77}Se-^{13}C)$ and the $\nu_{C=O}$ of the corresponding carbonyl compounds has been made. As shown in Table 3, the increase of the magnitudes of $^1J(^{77}Se-^{13}C)$ parallels that of $\nu_{C=O}$.

There are several problems associated with a direct comparison of ^{77}Se chemical shifts obtained from different laboratories or under different conditions. One is the solvent dependence of $\delta(^{77}Se)$,[10] which can vary by hundreds of p.p.m. depending on the solvents in extreme cases. The other is the temperature dependence of $\delta(^{77}Se)$. Because of the small mean excitation energy, Δ*E*, which is important in the paramagnetic screening term, $\delta(^{77}Se)$ of these compounds is expected to be rather temperature dependent. We have carefully measured the temperature dependence of $\delta(^{77}Se)$ of (4-Se) and (8-Se) and found that they are 0.34 and 0.48 p.p.m. K^{-1}, respectively. Over the temperature range of 14—40 °C, the variation of $\delta(^{77}Se)$ with temperature is perfectly linear. As expected, the resonance appears further downfield as the temperature increases. The temperature dependence of $\delta(^{77}Se)$ for other selenium compounds, as far as we know, has seldom been reported.[11] In one such investigation, Lardon reported that the $\delta(^{77}Se)$ in aromatic diselenides increases *ca.* 0.4 p.p.m. K^{-1}.[12] It should be noted that both diselenides and the selenocarbonyl compounds are highly coloured. Also as a comparison, in ^{123}Te and ^{125}Te n.m.r., the chemical shift of Te in $TeMe_2$ and $TeCl_4$ varies with temperature at the rate of 0.128 and 0.167 p.p.m. K^{-1}, respectively.[13]

^{17}O *N.m.r.*—The chemical shifts $\delta(^{17}O)$ for (1-O)—(13-O) are listed in Table 2. The ^{17}O chemical shifts generally agree with those of similar types of compounds reported previously.[4,5] That is, the chemical shifts $\delta(^{17}O)$ for saturated ketones range from 500 to 580 p.p.m. (measured from water), and from 300 to 400 p.p.m. for both esters and amides.[14] For the ketones we have studied in the present investigation, ring formation and the methyl substitution at the position γ to the oxygen atom cause $\delta(^{17}O)$ to become more shielded. For example, the $\delta(^{17}O)$ of fenchone (9-O) at 489.8 p.p.m. is the highest field $\delta(^{17}O)$ ever reported for ketones. The closest examples reported in the literature are that of camphor at 514 p.p.m.,[15] and that of (8-O) at 508.1 p.p.m. in the present study.

The trend of the variation of $\delta(^{17}O)$ among the ketones does not depend entirely on ring size. In addition to (8-O), mentioned in the previous section, the chemical shift $\delta(^{17}O)$ of (5-O) also does not follow this order. This apparent inconsistency can be attributed either to the interaction of the π-electrons of the two C=O bonds [16] or to the unusual behaviour frequently observed in four-membered rings. An example of the latter is the unusual ^{13}C and ^{17}O chemical shifts in four-membered ring sulphonyl compounds.[17]

Delseth and Kintzinger [4] reported the β^{π} and γ^{π} shielding effects * for aldehydes and ketones. The γ^{π} shielding effect was

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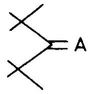
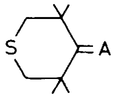
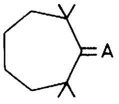
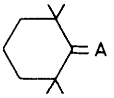
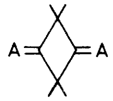
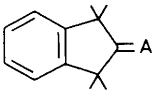
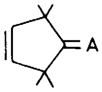
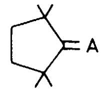
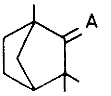
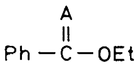
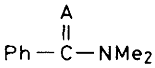
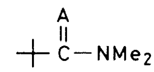
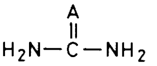
* The notation in this paragraph follows that of ref. 4, where α β *etc.* refer to positions relative to the oxygen atom.

Table 2. $\delta(^{77}Se)$, $^1J(^{77}Se-^{13}C)$, $\lambda_{max.}$ $n \longrightarrow \pi^*$, and $\delta(^{17}O)$ of selenocarbonyl and the corresponding carbonyl compounds

Molecule (A = O, Se)		$\delta(^{17}Se)$[a]	$^1J(^{77}Se-^{13}C)$(Hz)	$\lambda_{max}^{n\to\pi^*}$ (A = Se)(nm)	$\delta(^{17}O)$[a]
	(1)	2131[b]	213·6[b] 211·2[c]	710[b]	554·8
	(2)	2135[b]		689[b]	
	(3)				552·9
	(4)	2034	214·8	685	545·6
	(5)				519·1
	(6)	1844[b]	215·1[b]	625,658[b]	518·4
	(7)	1803[b]	216·0[b]	623,656[b]	517·3
	(8)	1737	217·0	665	508·1
	(9)	1613[b]	220·8[b]	616[b]	489·8
 $Ph-\overset{A}{\overset{\|}{C}}-OEt$	(10)	915[b,d]	211·1[b]	512[b]	338·1
 $Ph-\overset{A}{\overset{\|}{C}}-NMe_2$	(11)	733[b]	209·4[b]	455[b]	344·5
 $+\overset{A}{\overset{\|}{C}}-NMe_2$	(12)	640[b]		453[b]	338·3
 $H_2N-\overset{A}{\overset{\|}{C}}-NH_2$	(13)	195[c]	203·0[c]	260[c]	205[e]

[a] $\delta(^{77}Se)$ in p.p.m. downfield from Me_2Se, $\delta(^{17}O)$ in p.p.m. downfield from water. Uncertainties for the chemical shift measurement are about ±0.5 p.p.m. [b] From ref. 1. [c] From ref. 3, in C_6D_6. [d] The $\delta(^{17}O)$ for the alkoxy oxygen atom is 160.6 p.p.m. [e] From ref. 8.

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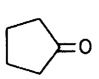
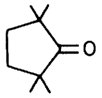
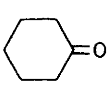
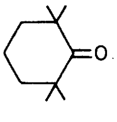
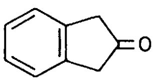
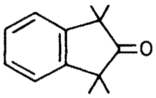
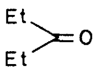
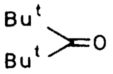
observed in several of the compounds in this study. As shown in Table 4, four additional methyl groups at the γ-positions lead to shielding of the oxygen atom by 36 p.p.m. in cyclopentanone, 34 p.p.m. in indan-2-one, and 13.4 p.p.m. in cyclohexanone. But in diethyl ketone, such a change (leading to di-tert-butyl ketone) results in deshielding by 6—17 p.p.m. Again, this apparent irregularity can be explained in terms of the CC(O)C bond-angle variations. In the three ring compounds listed in Table 4, methyl groups at the γ-position do not significantly change the CC(O)C angle owing to the constraint of the ring. The effect on $\delta(^{17}O)$ is thus purely inductive. On the other hand, going from diethyl ketone to (1-O), the

Table 3. The C=O vibrational frequencies of ketones and $^1J(^{77}Se-^{13}C)$ of the corresponding selones

Compound	$\nu_{C=O}/cm^{-1}$ [a]	$^1J(^{77}Se-^{13}C)$ Hz [b]
(1)	1 689	213.6, 211.2
(2)	1 688	
(4)	1 699	214.8
(5)	1 725, 1 755 [c]	
(6)	1 746	215.1
(7)	1 730, 1 750 [c]	216.0
(8)	1 739	217.0
(9)	1 740	220.8

[a] Numbering according to Table 2. [b] Of corresponding selones. [c] Two peaks were observed due to Fermi resonance.

Table 4. Effect of methyl substitution at the γ-position on the $\delta(^{71}O)$ of some ketones

Compound	$\delta(^{17}O)$	Compound	$\delta(^{17}O)$
	543[a]		508·1[b]
	558[a]		545·6[b]
	552·2[a]		518·4[b]
	547[a]		564·5,[a] 554·8[b]

[a] From ref. 4. [b] Present study.

bulky t-butyl groups cause an appreciable increase in the CC(O)C angle, leading to the deshielding of $\delta(^{17}O)$. This argument is consistent with that used to interpret the variation of $\delta(^{17}O)$, $\delta(^{77}Se)$, and $^1J(^{77}Se-^{13}C)$ in compounds (1)—(9).[1,2]

Discussion

Both the $\delta(^{17}O)$ and $\delta(^{77}Se)$ are found to vary in the opposite direction with $\delta(^{13}C{=}X)$ (X = O, Se). Furthermore, the correlation of $\delta(^{77}Se)$ of selones and $\delta(^{17}O)$ of the corresponding ketones is excellent. A linear relationship can thus be derived (Figure), equation (3). The correlation coefficient R is

$$\delta(^{77}Se) = 7.93\delta(^{17}O) - 2\,275 \text{ (p.p.m.)} \qquad (3)$$

0.997. All chemical shifts $\delta(^{77}Se)$ can be predicted by this equation from the $\delta(^{17}O)$ of the corresponding ketones to within 20 p.p.m. This is quite satisfactory considering the large range of ^{77}Se chemical shifts (>2 500 p.p.m.). The linear relationship derived for selones and ketones cannot be applied to amides, esters, and their selenium analogues (Figure). It is probably not reasonable to expect that a single equation such as (3) can adequately describe the correlation of $\delta(^{77}Se)$ and $\delta(^{17}O)$ for different categories of compounds. For example, in plotting $\delta(^{17}O)$ *versus* $\delta(^{13}C)$ of the carbon atom bonded to oxygen in many organic molecules, Mason[5] has observed that each category (*e.g.*, ketones, amides, and esters) of molecules behaves differently. Unfortunately, the number of esters and amides and their selenium analogues studied is as yet too small to provide the necessary information for deriving the correlation of $\delta(^{77}Se)$ and $\delta(^{17}O)$ for these functional groups.

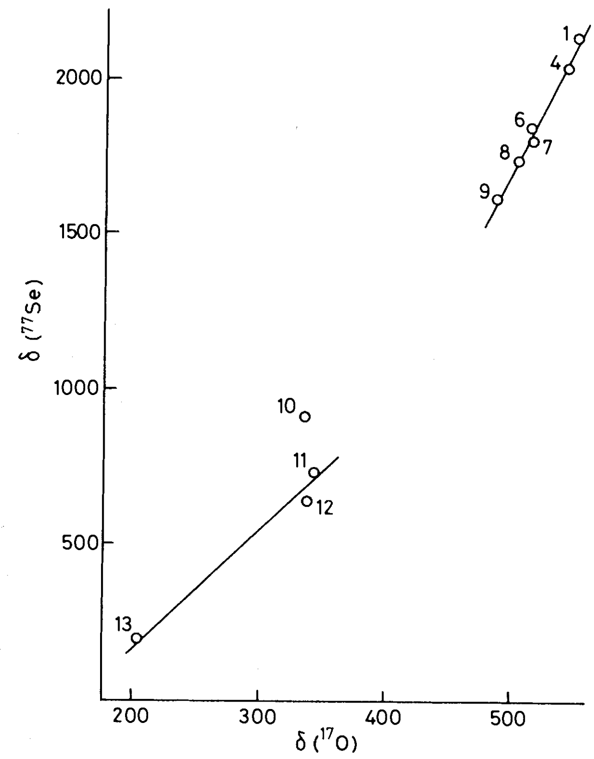


Figure. $\delta(^{77}Se)$ of selenocarbonyl compounds *versus* $\delta(^{17}O)$ of the corresponding carbonyl compounds. $\delta(^{77}Se)$ is in p.p.m. referred to Me_2Se and $\delta(^{17}O)$ in p.p.m. referred to water

It has been shown convincingly that both ^{77}Se [1] and ^{17}O [4,18] chemical shifts are dominated by the local paramagnetic screening term. Therefore, the slope of the plot of $\delta(^{77}Se)$ *versus* $\delta(^{17}O)$, *e.g.*, for the ketones and selones, is given in the Karplus–Pople approximation[19] by equation (4), where

$$\begin{aligned}\text{Slope} &= \frac{\Delta\sigma(^{77}Se)}{\Delta\sigma(^{17}O)} = \frac{\Delta\sigma_p(^{77}Se)}{\Delta\sigma_p(^{17}O)}\\ &= \frac{\langle r^{-3}\rangle_{Se,4p}\,(\Delta E)_O(Q_{AA} + \Sigma_B\, Q_{AB})_{C=Se}}{\langle r^{-3}\rangle_{O,2p}\,(\Delta E)_{Se}(Q_{AA} + \Sigma_B\, Q_{AB})_{C=O}} \qquad (4)\\ &= 7.93\end{aligned}$$

Q_{AA} and Q_{AB} are the charge-density and bond-order terms.

The ratio of $(\Delta E)_O/(\Delta E)_{Se}$ can be approximated by the inverse ratio of their $\lambda_{max.}$ $n \longrightarrow \pi^*$, the average value of which is 2.27. The $\langle r^{-3}\rangle$ term for the $4p$ orbitals of Se and $2p$ orbitals of O in these molecules was calculated approximately by using the Slater orbitals.[20] Thus $\langle r^{-3}\rangle_{Se,4p} = 1.12/a_0^3$ and $\langle r^{-3}\rangle_{O,2p} = 3.92/a_0^3$. Putting these into equation (4), we obtained equation (5). Although this cal-

$$\frac{(Q_{AA} + \Sigma_B\, Q_{AB})_{C=Se}}{(Q_{AA} + \Sigma_B\, Q_{AB})_{C=O}} = 0.998, \textit{ ca. } 1 \qquad (5)$$

culation is unavoidably approximate, and such excellent agreement is probably fortuitous, it is quite clear that the bond order terms of the C=Se bond in selones are not much different from those of the C=O bond of the corresponding ketones. The trends of their variation with structural changes are parallel to one another.

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