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CARBON-13 NMR AND CNDO/2 STUDIES OF PHENOXACHALCOGENINS

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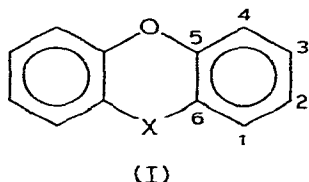
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Summary

The ^{13}C chemical shifts of the carbon atoms in dibenzodioxin, phenoxathiin, phenoxaselenin and phenoxatellurin were determined in CDCl_3 solutions and assigned. The total (σ and π) charge densities on the carbon atoms calculated by the CNDO/2 method without consideration of d -orbitals correlated well with the experimentally determined shifts. Rather good agreement was also found between experimental shifts and shifts calculated from ^{13}C data for phenyl methyl chalcogenides on the assumption that a phenoxachalcogenin molecule can be assembled from $\text{C}_6\text{H}_5\text{O}$ and $\text{C}_6\text{H}_5\text{X}$ groups. Only the shifts of the carbon atoms bonded to the heavier chalcogen atoms show an upfield trend in the sequence O, S, Se, Te. All other shifts exhibit a downfield trend. These trends are rationalized in terms of the electronegativities, abilities to participate in π -interactions, and anisotropy effects of the chalcogen atoms.

Introduction

The conformational and electronic effects exerted by the chalcogen atoms X in the phenoxachalcogenins I ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) were studied earlier [1] by means of dipole moment studies and ultraviolet and photoelectron spectroscopic methods. Additional information about the electron distributions in these molecules can be obtained from the ^{13}C chemical shifts, which are, in general, reliable indicators of the ground-state electronic environments of the carbon atoms. While the ^1H NMR spectra of the phenoxachalcogenins I were



studied in detail by other workers [2], the ^{13}C spectra have not been systematically investigated. Kende and his coworkers [3] reported ^{13}C chemical shifts for dibenzo-*p*-dioxin I ($X = \text{O}$). Isbrandt, Jensen and Petrakis [4] calculated the ^{13}C chemical shifts for phenoxathiin I ($X = \text{S}$) based on shifts for 9,10-dihydroanthracene, xanthene and thioxanthene, and found quite good agreement between predicted and observed resonances. ^{13}C NMR data for phenoxaselenin I ($X = \text{Se}$) and phenoxatellurin I ($X = \text{Te}$) were not available. Therefore, an investigation of the ^{13}C NMR spectra of the series of four phenoxachalcogenins I ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$) under the same conditions was carried out. In addition, the electronic structures of these compounds were determined by means of CNDO/2 MO calculations, to assist in assigning the ^{13}C resonances and in interpreting the variations observed in the experimental ^{13}C shifts.

Experimental

^{13}C Chemical shifts were measured on a JEOL PFT-100 Nicolet Fourier transform NMR spectrometer operating at 25.034 MHz using 2000 transients with an internal CDCl_3 lock. The proton noise decoupled spectra were obtained employing freshly prepared, 1.0 M solutions of the phenoxachalcogenins in chloroform- d_6 . The chemical shifts were measured relative to chloroform- d_6 and then converted to the TMS standard. All samples were examined in 10 mm tubes at a temperature of $28^\circ\text{C} \pm 1^\circ$. Spectral widths of 5600 Hz and pulse widths of 20 μs were used. The uncertainty in the δ values is 0.1 ppm.

Dibenzo-*p*-dioxin and phenoxathiin were obtained from commercial sources and used without further purification. Phenoxaselenin [5] and phenoxatellurin [6] were prepared as described in the literature.

Computations: Previous CNDO/2 calculations on furan, thiophene, selenophene and tellurophene provided good correlations between calculated total charge densities and ^{13}C chemical shifts [7]. It was considered worthwhile to examine similar correlations for the phenoxachalcogenins. Therefore, the electron distributions in these molecules were calculated employing the CNDO/2 method together with the parametrization given by Sichel and Whitehead [8] (VOIP's and one-center/two-electron Coulomb integrals) and Clementi and Raimondi [9] (orbital exponents for all orbitals but the 1s orbital of hydrogen for which a value of 1.2 was used). The β -integrals were calculated according to the standard Wolfsberg-Helmholtz formula [9] with a K value of one. The two-center/two-electron integrals were evaluated using the Ohno relation [10]. The d orbitals were not considered in these calculations. The bond length and bond angles derived from X-ray diffraction studies of the solid compounds I [11,12, 13] were employed in the computations. The structure of phenoxaselenin has not yet been determined. Its geometry was assumed to be similar to that of the analogous sulfur and tellurium compounds.

Results and discussion

The experimental and calculated ^{13}C chemical shifts for the phenoxacalco-
genins I are listed in Table 1. The signals arising from the quaternary carbon
atoms C(5) and C(6) were identified by means of off-resonance ^1H resonance
data [2] and qualitative agreements.

The assignments for dibenzodioxin I ($X = \text{O}$) and phenoxathiin I ($X = \text{S}$)
agree with those reported in the literature [3,4]. Solutions kept in the NMR
tubes at room temperature for several days gave the expected number of ^{13}C
signals, which were shifted downfield by 4–10 ppm with respect to the signals
obtained with fresh solutions. The ^{13}C chemical shifts of fresh solutions of
phenoxathiin were temperature-independent in the range 28–52°C.

The total ($\sigma + \pi$) charge densities calculated by means of the CNDO/2 meth-
od correlate fairly well with the observed shifts. The calculated chemical shifts
listed in Table 1 were obtained from linear least squares plots of the calculated
total charge densities versus the experimental chemical shifts for each one of

TABLE 1

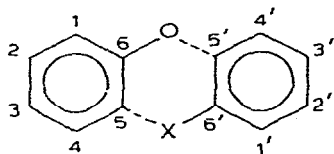
^{13}C CHEMICAL SHIFTS AND CALCULATED CHARGE DENSITIES FOR PHENOXACHALCOGEN-
INS I

X	C atom	δ (ppm from TMS)		Q_C	Q_X	Q_O	δ (ppm from TMS) calc. from PhXCH_3^a
		exp.	calc. from Q_C				
O	1	116.2	116.9	-0.0780	-0.4562	-0.4562	121.8
	2	123.6	123.9	-0.0429			125.2
	3	123.6	125.4	-0.0429			125.2
	4	116.2	117.8	-0.0780			121.8
	5	142.1	142.0	0.2558			137.0
	6	142.1	142.7	0.2558			137.0
S	1	127.4	125.4	-0.0552	-0.0843	-0.4724	128.2
	2	124.3	124.0	-0.0439			124.7
	3	126.5	124.9	-0.0458			127.2
	4	117.5	116.8	-0.0724			121.4
	5	151.9	151.7	0.2902			143.4
	6	119.9	112.8	0.0287			126.3
Se	1	129.2	132.1	-0.0372	-0.1587	-0.4618	130.0
	2	124.8	125.0	-0.0535			124.8
	3	128.0	128.2	-0.0282			127.8
	4	118.5	118.4	-0.0811			121.5
	5	152.8	153.7	0.2963			145.2
	6	116.1	113.6	0.0349			123.0
Te	1	134.8	133.1	-0.0347	-0.1144	-0.4645	133.1
	2	125.4	125.2	-0.0555			124.9
	3	128.9	128.4	-0.0271			128.3
	4	119.5	118.6	-0.0821			121.5
	5	155.6	154.7	0.2997			148.3
	6	102.0	110.9	0.0147			113.3

^a ^{13}C Chemical shifts from ref. 14 for $\text{C}_6\text{H}_5\text{X}$ [carbon atom numbers (see structure II), ^{13}C shift]: X = O: 1', 5', 114.1; 2', 4', 129.5; 3', 120.8; 6', 159.9. X = S: 1', 5', 126.9; 2', 4', 128.7; 3', 125.0; 6', 132.6. X = Se: 1', 5', 130.6; 2', 4', 128.9; 3', 126.1; 6', 132.0. X = Te: 1', 5', 136.7; 2', 4', 129.0; 3', 127.1; 6', 112.5.

the six sets of different carbon atoms in this series of four phenoxachalcogenins. The following correlation coefficients were obtained: C(1), 0.995; C(2), 0.925; C(3), 0.783; C(4), 0.575; C(5), 0.992; and C(6), 0.913. The calculated total charge densities for the C(3) and C(4) atoms of phenoxathiin do not follow the pattern established by the other phenoxachalcogenins and, therefore, cause the correlation coefficients to be low. Without inclusion of the sulfur derivative correlation coefficients of 0.995 and 0.997 were obtained for the C(3) and C(4) plots, respectively. These deviations are probably caused by the neglect of *d* orbitals in the calculation, which are expected to influence the charge distribution in the phenoxachalcogenins most profoundly in the sulfur derivative. Of course, in addition to simple charge effects the anisotropies of the chalcogen atoms as well as the conformational effects associated with the ring strains in the heterocyclic frameworks and concomitant changes in the hybridization will play some role in determining the ^{13}C chemical shifts of the phenoxachalcogenins. These influences cannot easily be recognized and sorted out at the present time. The question of the conformational motions and the consequent changes in hybridization is now being investigated through analysis of ^{13}C relaxation times.

The ^{13}C chemical shifts of the phenoxachalcogenins can be predicted also by using the experimental data for the phenyl methyl chalcogenides, $\text{C}_6\text{H}_5\text{-X-CH}_3$ ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$), which have just become available [14]. The phenoxachalcogenin molecule is assumed to be a combination of the $\text{C}_6\text{H}_5\text{-O}$ group from anisole and the $\text{C}_6\text{H}_5\text{-X}$ fragment from the phenyl methyl chalcogenide. The expected ^{13}C shifts of the phenoxachalcogenins I were calculated as the averages of the chemical shifts of corresponding carbon atoms (e.g., 4,1'; 3,2' etc.) in the fragments II required to build a phenoxachalcogenin molecule I (Table 1).



(II)

The difference between experimental and calculated shifts for the carbon atoms 1, 2 and 3 in the sulfur, selenium and tellurium derivatives of I and for the C(2) and C(3) atoms in dibenzodioxin are less than 1.7 ppm. The differences are larger for the C(4) shifts ranging from 5.6 ppm to 2.0 ppm for the oxygen and tellurium derivative, respectively, with the calculated shifts downfield from the experimental shifts. The corresponding differences for the quaternary carbon atoms C(5) and C(6) are larger than those for the hydrogen-bearing carbon atoms with the exception of the C(1) and C(4) atoms of dibenzodioxin. The shift differences for the C(6) carbon atoms are 5.2 ppm upfield for $\text{X} = \text{O}$, and 6.4, 6.9 and 11.3 ppm downfield for $\text{X} = \text{S}, \text{Se},$ and Te , respectively, from the experimental shifts. This trend is probably caused by the anisotropy effects of the chalcogen atoms with the greatest deshielding effect exerted by the tellurium atom in the condensed heterocycles I. An inverse

trend is observed for the C(5) atoms for which the calculated shifts are upfield from the experimental shifts. The difference is smallest for the oxygen derivative (5.2 ppm) and largest for phenoxathiin (8.5 ppm). The differences for the selenium and tellurium derivatives are 7.6 and 7.3 ppm, respectively. These results are consistent with an effective interaction of the oxygen atom with the adjacent carbon atoms. Finally, chemical shifts calculated for the phenoxachalcogenins employing data from phenyl methyl chalcogenides are useful for checking resonance assignments on a correlative basis.

The most striking feature of the ^{13}C shifts of the phenoxachalcogenins is the spread of 40 ppm and the variations shown by the chemical shifts of the C(6) atoms directly linked to the chalcogen atom X. The substitution of one oxygen atom in dibenzodioxin by a sulfur atom to give phenoxathiin results in a strong shielding effect at C(6) with a concomitant upfield shift of 22.2 ppm mainly caused by the inductive effect associated with the lower electronegativity of the sulfur atom (2.5 on Pauling's scale) as compared to that of the oxygen atom (3.5). On passing from the sulfur derivative to phenoxaselenin the C(6) atom shows a smaller upfield shift of 3.8 ppm congruent with a smaller electronegativity difference between sulfur (2.5) and selenium (2.4). In phenoxatellurin the C(6) shift is 102.0 ppm, 14.1 ppm upfield from the corresponding resonance in phenoxaselenin. This same upfield trend of the resonances of the carbon atoms bonded to a chalcogen atom was observed in the diphenyl dichalcogenides, $(\text{C}_6\text{H}_5)_2\text{X}_2$ [15], i.e., 137.0 ppm (S), 130.9 ppm (Se) and 108.0 ppm (Te). The overall monotonic shielding effect in the phenoxachalcogenin series is only partially accounted for by the increase in the total charge density as a calculated by the CNDO/2 method and, as a consequence, magnetic anisotropy effects seem to play a role also. The replacement of an oxygen atom in dibenzodioxin by a heavier chalcogen atom shifts the ^{13}C resonances of the C(5) atoms linked to the oxygen atom downfield by approximately 10–14 ppm with respect to the corresponding resonance in the dioxin. This effect can be accounted for by assuming that the σ electron withdrawal toward the oxygen atom outweighs the π electron donation from the sulfur, selenium or tellurium atom, which is expected to decrease with increasing atomic number of the chalcogen atom. The computed total charges Q_C (Table 1) agree well with this trend.

The carbon atoms 1,4 (116.2 ppm) and 2,3 (125.6 ppm) in dibenzodioxin are more shielded than in benzene (128.7 ppm) because of increase in electron density at these atoms due to resonance with the oxygen atoms. The C(1) atoms in the phenoxachalcogenins become more and more deshielded in the sequence O (116.2 ppm), S (127.4 ppm), Se (129.2 ppm) and Te (134.8 ppm), a trend also evident in the calculated total charge densities (Table 1). The largest C(1) shift difference (11.2 ppm) is found between dibenzodioxin and phenoxathiin. The presence of the sulfur atom in the cyclic system leads to diminished effectiveness of the charge distribution through resonance and allows σ electron withdrawal to predominate, and thus decrease the charge densities on the C(1) carbon atoms. The C(4), C(3) and C(2) carbon atom shifts show only a small downfield trend (<5 ppm between X = O and X = Te) indicating that the inductive, anisotropy and any mesomeric influences on these carbon atoms operate in the same direction and are of comparable magnitude.

This similarity of resonances may also be regarded as evidence for a similar conformation of the sulfur, selenium and tellurium derivatives, in agreement with previous conclusions derived from dipole moment and photoelectron spectroscopic data [1]. The observed downfield trend of the ^{13}C shifts of all hydrogen-bearing carbon atoms in the phenoxachalcogenins I in the sequence $\text{X} = \text{O}$ to $\text{X} = \text{Te}$ is in agreement with the trend in the ^1H resonances [2] and in line with the magnitude of the +M effects of the heteroatoms which diminishes in the series $\text{O} > \text{S} > \text{Se} > \text{Te}$.

Assuming that the C(1) to C(4) ^{13}C shifts reflect the electronic effects of the central heterocycles, the ^{13}C data provide information about the relative capabilities of the chalcogen atoms to transmit electronic effects in molecules in which they act as a bridge between two aromatic moieties. Thus, conjugative interactions decrease in the order $\text{O} > \text{S} > \text{Se} > \text{Te}$. This can also be interpreted as an indication that the replacement of an oxygen atom in dibenzodioxin by a heavier chalcogen atom lowers the activity of the fused phenyl rings of the phenoxachalcogenin molecule toward electrophilic substitution.

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