# 2,6-DI-TERT-BUTYLPHENYLVINYL ETHER: EFFECT OF THE UNSHARED OXYGEN ELECTRON PAIR ON THE $^{13}C-^{13}C$ SPIN-SPIN INTERACTION CONSTANT

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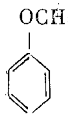
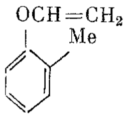
We previously showed [1] that the presence of an unshared electron pair in the nitrogen atom in the syn position to the neighboring carbon–carbon bond can result in an additional positive contribution to the direct $^{13}C-^{13}C$ spin–spin interaction constant (SSIC) of the corresponding carbon nuclei which attain values of up to 20% of the value of the constant itself. The discovery of this effect opened up new possibilities for solving structural problems in the chemistry of nitrogenous compounds: a new universal method of establishing the configuration of oximes [2, 3] and their derivatives [4] was developed; methods for the unambiguous identification of isomeric forms of disubstituted tetrazoles were proposed [5], etc. The appearance of this effect should also be anticipated in the case of other heteroatoms with unshared electron pairs, primarily oxygen. This is especially important for developing new methods in the stereochemistry of oxygen-containing compounds.

Compounds (I)-(V), which exist in an equilibrium mixture of two planar (A), (C) and one orthogonal (B) conformers due to rotation of the $OCH=CH_2$ group around the C1–O bond, are examined below as model systems for studying the effect of the orientation of the unshared electron pairs of the oxygen atom on the $^{13}C-^{13}C$ SSIC of the neighboring carbon–carbon bond. The Newman projections of the three conformers discussed are represented on the assumption that the oxygen atom has $sp^2$ hybridization (i.e., one of the unshared pairs has a pure $p_z$ character and is in conjugation with the $\pi$ system of the benzene ring). The effect of the unshared pairs in the oxygen on the $^{13}C-^{13}C$ SSIC of the olefin nuclei of the carbon in the vinyl group was studied previously [6] and is not discussed in the present article



(I)



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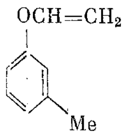

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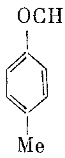

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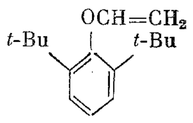

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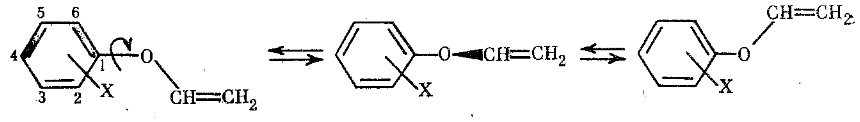
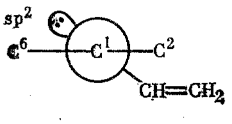
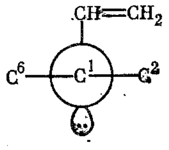
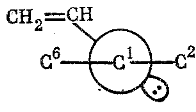




(A)



(B)



(C)

It is necessary to consider the fact that 2,6-di-tert-butylphenylvinyl ether (V), in contrast to compounds (I)-(IV), exists totally in the orthogonal conformer (B) due to destabilization of the planar forms by the teric interaction of the $OCH=CH_2$ group with the bulky tert-butyl group in the ortho position of the benzene ring. In the $^{13}C$ NMR spectra, this is manifested by pronounced unshielding of the p-carbon atom in the ring and even greater shielding of the β-carbon atom in the vinyl group in comparison to compounds (I)-(IV), caused by steric

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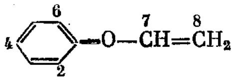
TABLE 1. $^{13}C$ NMR Chemical Shifts ($\delta$, ppm) and $^{13}C-^{13}C$ SSIC (J, Hz) of Arylvinyl Ethers (I)-(V)



| Compound | $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_7$ | $\delta_8$ |
|---|---|---|---|---|---|---|---|---|
| (I) | 156,89 | 116,92 | 129,67 | 123,07 | 129,67 | 116,92 | 148,83 | 95,50 |
| (II) | 154,68 | 128,06 | 131,11 | 123,42 | 127,03 | 116,80 | 149,00 | 93,27 |
| (III) | 156,90 | 117,60 | 139,54 | 123,84 | 129,35 | 113,86 | 148,30 | 94,35 |
| (IV) | 155,71 | 117,84 | 130,97 | 133,08 | 130,97 | 117,84 | 149,58 | 94,90 |
| (V) | 155,60 | 143,91 | 126,79 | 125,24 | 126,79 | 143,91 | 155.77 | 89,67 |

(Continued)

| Compound | $^1J_{1,2}$ | $^1J_{1,6}$ | $^1J_{2,3}$ | $^1J_{3,4}$ | $^1J_{4,5}$ | $^1J_{5,6}$ |
|---|---|---|---|---|---|---|
| (I) | 67,8 | 67,8 | 57,0 | 56,1 | 56,1 | 57,0 |
| (II) | 68,0(−0,9) | 68,0(−0,4) | 58,7(0,6) | 56,8(0,1) | 55,8(−0,6) | 57,0(−0,3) |
| (III) | 68.8(0.4) | 67.8(−0,3) | 58,5(0,4) | 58,0(0,8) | 57,1(0,4) | 57.2(−0,1) |
| (IV) | 68,3(0.2) | 68,3(0.2) | 58,0(0,4) | 57,6(0,4) | 57,6(0,4) | 58,0(0,4) |
| (V) | 66,2(−4,2) | 66.2(−4,2) | 57,9(−0.9) | 56,4(−0,3) | 56,4(−0,3) | 57.9(−0.9) |

inhibition of conjugation of the $2p_z$ electrons of the oxygen atom with the π system of the aromatic fragment and an increase in the competitive 2p—π interaction in the hydroxyvinyl fragment (Table 1). The use of an equation for calculating the effective dihedral angle with the CS of the p-carbon atom in the ArO fragment [7] for compound (V) results in a value of $\varphi \approx 90°$.

The measured values of the direct $^{13}C-^{13}C$ SSIC between the aromatic nuclei of the carbon in (I)-(V) are also reported in Table 1, and the deviations of these constants from the corresponding values calculated with an additive scheme are shown in parentheses. The question of the additivity of the $^{13}C-^{13}C$ SSIC in the benzene ring is an independent problem, but the data in Table 1 for the three isomeric arylvinyl ethers (II)-(IV) show that in this species of compounds, calculation of the $^{13}C-^{13}C$ SSIC by the additive scheme results in a difference from the measured values which does not exceed 1 Hz.

The experimental value of $^1J_{1,2} = {}^1J_{1,6}$ in ether (V) is 4.2 Hz less than the calculated value. The specific features of the conformational structure of (V) in comparison to ethers (I)-(IV), which primarily exist in planar conformers, is the cause of this difference.

In the planar forms of arylvinyl ethers, the $sp^2$-hybridized unshared pair of the oxygen atom is located in the plane of the benzene ring in the syn position to the $C^1-C^2$ bond (A) or the $C^1-C^6$ bond (C), which causes its contribution to each of constants $^1J_{1,2}$ and $^1J_{1,6}$. On the contrary, in conformer (B), the plane of the hydroxyvinyl fragment, i.e., the examined unshared pair in the oxygen, is orthogonal to both bonds, and an additional contribution to the corresponding constants is absent for this reason.

As a consequence, the deviation of constant $^1J_{1,2}$ in (V) from additivity toward a less positive value can be considered the result of the absence of the effect of the unshared pair in the oxygen on the constant discussed, since phenylvinyl ether (I), which has an almost planar structure, was used as the starting compound for the additive scheme of calculation. If the presence of the two planar forms (A) and (C) is taken into consideration, then the total effect of the $sp^2$-hybridized unshared pair in the oxygen atom on the direct $^{13}C-^{13}C$ SSIC between the carbon nuclei in the aromatic ring should attain ∿8 Hz.

This effect can be used for solving problems of the stereochemistry of oxygen-containing organic compounds related to the spatial orientation of the unshared pairs in the oxygen atom.

## Experimental

The $^{13}C$ NMR spectra were recorded on a Bruker WP-200SY spectrometer with an operating frequency for $^{13}C$ nuclei of 50.33 MHz. The $^{13}C-^{13}C$ SSIC were measured in the INADEQUATE pulsed sequence mode [8] using samples with a native concentration of isotopes. The resonance conditions of the spectrometer were stabilized with the signal from deuterated acetone-$d_6$. The free induction signal drop reading time was 0.5 sec, relaxation delay was 1.5 sec, the spectrum width was 1-2 kHz, the digital resolution in the transformed spectrum was 0.1-0.2 Hz/point, and the total accumulation time for one spectrum was 6-8 h.

The samples of the compounds studied were pure liquids with addition of 10-15 vol.% acetone-$d_6$ and 0.5-1% chromium Tris-acetylacetonate $Cr(acad)_3$, used as a relaxing agent.

Vinyl ethers (I)-(IV) were prepared by the well-known Favorskii—Shostakovskii method [9]. The purity of the compounds was controlled by GLC and by the PMR and $^{13}C$ NMR spectra.

Synthesis of 2,6-di-tert-butylphenylvinyl ether (V). A 0.5 liter rotating steel autoclave was filled with 5.15 g (0.025 mole) of 2,6-di-tert-butylphenol and 1 g (0.018 mole) of KOH in 50 ml of dioxane. Acetylene was fed in at ~20° to saturation. The reaction mixture was heated for 1.5 h at 225-230°C then repeatedly extracted with diethyl ether. The ether extract was washed with a 5% alkali solution and water and dried with $MgSO_4$. After distillation of the solvent, the residue was fractionated twice in a vacuum. Then 1.60 g (29%) of the final product was obtained; bp 95°C (5 mm), $n_D^{20}$ 1.5023. Found: C 82.85, H 10.40%. $C_{16}H_{24}O$. Calculated: C 82.76, H 10.34%. The $^{13}C$ chemical shifts are reported in Table 1.

We would like to thank V. D. Ryabov for kindly supplying the sample of 2,6-di-tert-butylphenol.

## Conclusions

The proximity of $sp^2$-hybridized unshared pair of oxygen atoms result in a secondary, positive contribution in the constant of spin—spin interaction between neighboring carbon nuclei in the aromatic ring.

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## STUDY OF INTRAMOLECULAR INTERACTIONS IN DIARYL SULFONES BY IR AND NMR SPECTROSCOPIC METHODS OF MOLECULAR COMPLEXES

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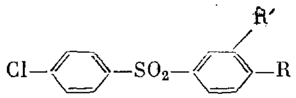
The electronic distribution and molecular structure of sulfones have been studied with the aid of various physicochemical methods [1-3].

Investigation of interactive effects in unsaturated sulfones [4, 5] has demonstrated the dominant role of the inductive effect of the sulfo-group (SG) when compared with its resonance interaction with the π-system. The SG acceptor character was confirmed with measurement of ionization potentials in dimethyl sulfone derivatives [2]. By NMR and electrochemical reduction methods it has been shown for p-chloro substituted diaryl sulfones that the SG experiences a significant substituent effect [6]. Transmission of the inductive effect of the substituent at the Cl atom is considerably weakened due to the disturbance to copolanarity of the aromatic nucleus [7]. This leads to a significant decrease in the sensitivity of the symmetric ($\nu_s$) and asymmetric ($\nu_{as}$) SG IR bands towards structural changes in diphenyl sulfones when compared with the $\nu_{C=O}$ frequencies of benzophenones (where there exists a direct polar interaction between the substituents in both rings and the CO bridge [8, 9]).

To examine further the intramolecular interactions in diaryl sulfones (DAS)



$Cl-C_6H_4-SO_2-C_6H_3(R')-R$ (I)—(X)

(Table 1) we have studied the effect of substituents R and R' on the spectral parameters for the ground state (GS) and for the charge-transfer state (CTS). Values for the $\nu_{as}$ and $\nu_s$ frequencies in the SG IR spectra (GS) for I, III-VII, IX and X (where R = H, see Table 1) were linearly dependent upon the $\sigma_p$ constants for the R substituent

$$\nu_{as} = (19 \pm 2)\,\sigma_p + (1331 \pm 1) \quad (r = 0.975) \tag{1}$$

$$\nu_s = (7 \pm 1)\,\sigma_p + (1161 \pm 1) \quad (r = 0.924) \tag{2}$$

The small values of the slope parameters in (1) and (2) were in agreement with literature data [8, 9] concerning the low sensitivity of $\nu_{as}$ and $\nu_s$ to the effect of a substituent in the ring.

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