

# Radical cations from 4,4'-methylenediphenols Intermediary products of electron transfer indicated by the EPR method

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*Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday*

Differently substituted 4,4'-methylenediphenols *I* donate an electron to the  $\text{AlCl}_2^+$  electron acceptor in the  $\text{AlCl}_3\text{—CH}_3\text{NO}_2\text{—benzene}$  solution at laboratory temperature to give radical cations *II* of different stability. The symmetrical distribution of spin density in individual phenyl rings remains preserved. Nevertheless, an asymmetrical redistribution to equivalent positions (*ortho*, *meta*) in each of these rings takes place owing to steric distortion in the process of formation of the ion-radical complex. The effect of voluminous substituents in *ortho* positions on stability of the primary complex of ion-radical with the  $\text{AlCl}_4^-$  counterion is discussed. This complex is subjected to fragmentation and subsequently gives rise to radical cations from 4,4'-biphenyldiols.

The sterically hindered 4,4'-methylenediphenols belong among very efficacious inhibitors of oxidation processes. Their reaction with the  $\text{RO}_2^{\bullet}$  radicals involves hydrogen transfer from antioxidant and gives rise to the phenoxyl radicals which undergo a series of consecutive reactions and yield radicals of the galvinoxyl type [1]. The radical cations arising from 4,4'-methylenediphenols as products of electron transfer at laboratory temperature have not yet been described. *Pokhodenko et al.* obtained radical cations from the substituted 2,6-di-*tert*-butyl-4-*R*-phenols by oxidation with the  $\text{AlCl}_3\text{—CH}_3\text{NO}_2$  system at decreased temperature [2]. A detailed theoretical interpretation of EPR spectra of the mentioned radicals was presented by *Nemoto et al.* [3]. The radical cations from the substituted 4,4'-biphenyldiols were described by *Sullivan* [4]. The preparation of radical cations from the substituted hydroquinones as well as the interpretation of their EPR spectra is also a topic of several publications [5—8]. 4,4'-Diphenols with sulfur- or oxygen-bridge subjected to oxidation with the

$\text{AlCl}_3\text{—CH}_3\text{NO}_2$  system afford stable radical cations with spin distribution involving both phenyl rings [9, 10]. The aim of this study is to appreciate the influence of methylene bridge in the substituted 4,4'-diphenols on stability of the generated radical cations in coherence with distribution of spin density.

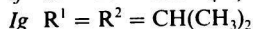
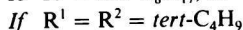
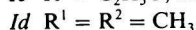
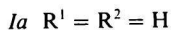
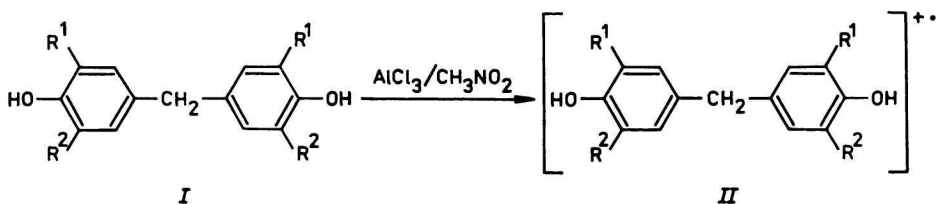
## Experimental

4,4'-Methylenediphenols *Ia—Ig* were synthesized at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences, Prague, according to the methods described in previous papers [1]. The generation of radical cations *II* was executed at laboratory temperature as follows: The solution containing  $\text{AlCl}_3$ ,  $\text{CH}_3\text{NO}_2$ , and benzene in proportion  $50 \text{ mg AlCl}_3 : 0.1 \text{ cm}^3 \text{ CH}_3\text{NO}_2 : 0.9 \text{ cm}^3 \text{ benzene}$  was prepared in inert atmosphere. Then it was added in the amount of  $0.2 \text{ cm}^3$  to about 5 mg of 4,4'-methylenediphenol *I* on the bottom of an EPR cell in inert atmosphere.

The EPR spectra were taken on a spectrometer Varian E-3 with 100 kHz modulation frequency in zone X. The simulations were performed by using a spectral computer Varian SS 100.

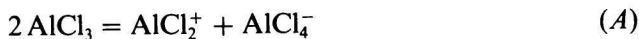
## Results and discussion

The electron transfer from 4,4'-methylenediphenols to the  $\text{AlCl}_3\text{—CH}_3\text{NO}_2$  oxidation system giving rise to radical cations may be described by the general scheme



Scheme 1

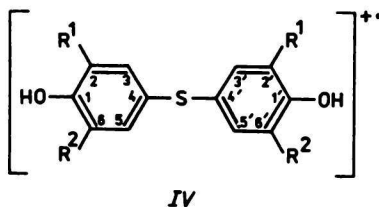
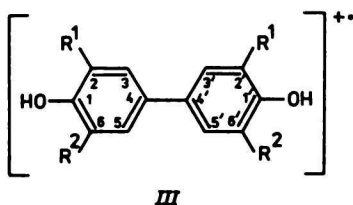
We can assume that the oxidizing component is the  $\text{AlCl}_2^+$  cation [11] originating in dissociation of  $\text{AlCl}_3$  according to the following equation



The  $\text{AlCl}_4^-$  anion is counterion of the generated radical cations. On adopting an electron, the electron acceptor  $\text{AlCl}_2^+$  forms the unsaturated particle  $^*\text{AlCl}_2$  which is probably stabilized by dimerization.



The *para*-methylene bridge in the molecule of diphenol *I* represents a different structural factor when compared with sulfidic or etheric bridge. The lone electron pairs on sulfur or oxygen atoms of the corresponding 4,4'-diphenols (analogous to structure *I*) forward the potentiality of spin delocalization in both phenyl rings of the neutral or ionic radicals which derive from those. As to neutral phenoxy radicals, numerous EPR studies show that the spin density, irrespective of type of the bridge ( $-\text{CH}_2-$ ,  $-\text{S}-$ ,  $-\text{O}-$ ) remains localized only in one phenyl ring [1, 12–14]. The delocalization of spin density in the whole aromatic system comes into existence by direct binding of two phenyl rings (phenoxy radicals from 4,4'-biphenyldiols or 4-phenylphenols [12, 15]). On the other hand, it is known that the presence of sulfur- or oxygen-bridge in radical cations in *para* position of diphenols does not prevent the delocalization of spin density [9, 10]. A comparison of the EPR parameters of radical cations of type *III* and *IV* with each other



shows that the alternation of spin density in the corresponding positions with respect to the OH group remains preserved and the values of splitting constants themselves do not significantly change (e.g. in the case  $\text{R}^1 = \text{R}^2 = \text{H}$  it is valid for type *III*:  $a_{\text{H}}^{\text{OH}} = 0.164 \text{ mT}$ ,  $a_{\text{H}}^{3,5,3',5'} = 0.195 \text{ mT}$ ,  $a_{\text{H}}^{2,6,2',6'} = 0.073 \text{ mT}$ ; and for

type *IV*:  $a_{\text{H}}^{\text{OH}} = 0.106 \text{ mT}$ ,  $a_{\text{H}}^{3,5,3',5'} = 0.161 \text{ mT}$ ,  $a_{\text{H}}^{2,6,2',6'} = 0.091 \text{ mT}$ ). The introduction of methylene group into the molecule of diphenol (type *I*) results in significant change in distribution of spin density in the pertinent radical cation *II*. The EPR spectrum of radical cation *IIb* is represented in Fig. 1 and the splitting constants obtained by simulation are given in Table 1. In all EPR spectra of radical cations *II* a triplet splitting  $a_{\text{H}} = 0.51\text{--}0.64 \text{ mT}$  which also remains preserved for radical *V* can be observed. For this reason, the above

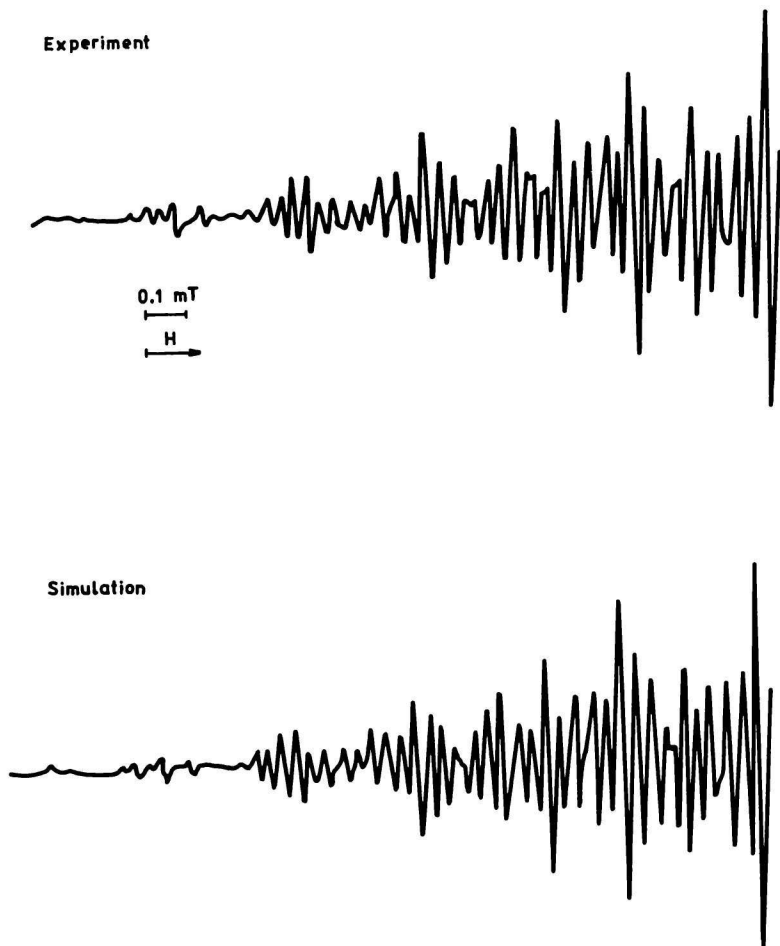
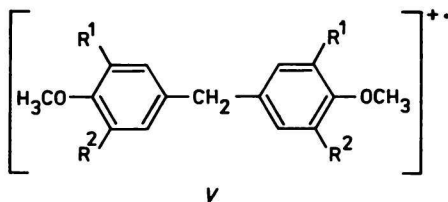


Fig. 1. Experimental and simulated EPR spectrum of radical cation *IIb* (a half of the total width of spectrum).



values are to be ascribed to protons of the  $-\text{CH}_2-$  bridge. A triplet splitting  $a_{\text{H}}^{\text{OH}} = 0.06\text{--}0.07$  mT which turns into septet  $a_{\text{H}}^{\text{CH}_3\text{O}} = 0.03$  mT by replacing the OH group by the  $\text{CH}_3\text{O}$  group (type *V*) also appears for all radical cations *II*.

Table 1

EPR parameters of radical cations

Radical	$a_{\text{H}}^{\text{CH}_2}$	$a_{\text{H}}^{\text{OH}}$	Splitting constant/mT			
			$a_{\text{H}}^{6,6'}$	$a_{\text{H}}^{2,2'}$	$a_{\text{H}}^{5,5'}$	$a_{\text{H}}^{3,3'}$
<i>Ila</i>	0.640	—	0.306	0.306	0.135	0.135
<i>Ilb</i>	0.514	0.068	0.330	—	0.295	—
<i>Ilc</i>	0.570	0.060	0.341	—	0.332	—
<i>Ild</i>	0.528	0.070	0.343	0.017	0.310	—
<i>Ile</i>	0.514	0.068	0.330	—	0.295	—
<i>V</i>	0.538	0.030 <sup>a</sup>	0.331	—	0.308	—

a) Splitting caused by protons of the  $\text{CH}_3\text{O}$  groups in position 1,1'

The symmetrical distribution of spin density in positions 2,2',6,6' and 3,3',5,5' can be observed only for radical *Ila* which is derived from the nonsubstituted 4,4'-methylenebisphenol. As to other radical cations of this group, the asymmetrical distribution of spin density in those positions can be observed. *Nemoto et al.* [3] stated the existence of this fact in the EPR spectra of the radical cations arising from 2,6-di-*tert*-butyl-4-R-phenols (nonequivalence of *meta*-protons) and interpreted it by the idea of hindered rotation of the OH group at the temperature of generation of these radicals ( $-40^\circ\text{C}$ ). On the other hand, the values of splitting constants for positions 2,2',6,6' and 3,3',5,5' (type *III*) in the case of radical cations arising from 4,4'-biphenyldiols [4] are equal in the temperature interval  $0\text{--}-50^\circ\text{C}$ . Quite symmetrical distribution of spin density was also observed in the case of radical cations arising from the substituted 4,4'-thiodiphenols (type *IV*) at laboratory temperature [9].

In general, the symmetrical distribution of spin density in both aromatic rings in the case of radical cations *II* gives the evidence that the methylene group in

4,4'-position does not prevent delocalization. This fact hitherto observed only with radical anions [16] indicates a high frequency value of intramolecular electron transfer between two phenyl rings (for radical anion from diphenylmethane  $\nu_{\text{deloc}} = 10^7 \text{ s}^{-1}$ ). The interpretation of asymmetrical distribution of spin density in individual phenyl rings requires to take into consideration not only the conformational effects (hindered rotation of the OH group) but also the structure of the ion pair containing the radical cation and the  $\text{AlCl}_4^-$  counterion. As the asymmetrization of spin density in individual phenyl rings of the radical cations originating from 4,4'-biphenyldiols and 4,4'-thiodiphenols does not exist at laboratory temperature, the influence of hindered rotation of the OH group on shape of the EPR spectra of the radical cations originating from 4,4'-methylene-diphenols appears to be little probable. Though the  $\text{AlCl}_3\text{—CH}_3\text{NO}_2$  oxidation system has been used for generation of the radical cations originating from phenols, biphenyldiols or thiodiphenols of all the discussed types, the influence of structure of the ion pair containing the radical cation and the  $\text{AlCl}_4^-$  counterion on stability and spectral properties of radicals has not yet been discussed. While the origination of a "sandwich" radical cation—counterion complex may be expected for the radical cations arising from 4,4'-biphenyldiols [4], we must assume other orientation of phenyl rings with respect to counterion owing to bent structure of the methylene bridge of radical cation *II*. Such arrangement can be a cause of asymmetrical distribution of spin density (Fig. 2).

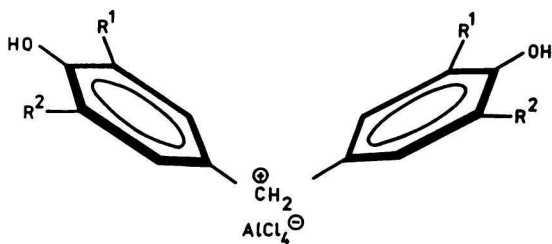


Fig. 2. Scheme of the complex containing radical cation *II* and  $\text{AlCl}_4^-$  counterion.

The structure of the alkylidene bridge is an important factor influencing stability of the ion pair. By replacing the  $\text{—CH}_2\text{—}$  group by sterically more voluminous bridges of the type  $\text{—C(CH}_3)_2\text{—}$ ,  $\text{—CH(CH}_3)\text{—}$  or  $\text{—CH(C}_3\text{H}_7)\text{—}$  at laboratory temperature we did not succeed in preparing the radical cations from the corresponding 4,4'-alkylidenediphenols. The steric properties of *ortho* substituents are also operative in origination of the complex consisting of radical cation and counterion. If the *ortho* position is fully occupied by voluminous substituents (*If*, *Ig*), a stable ion pair cannot arise and the primary radical

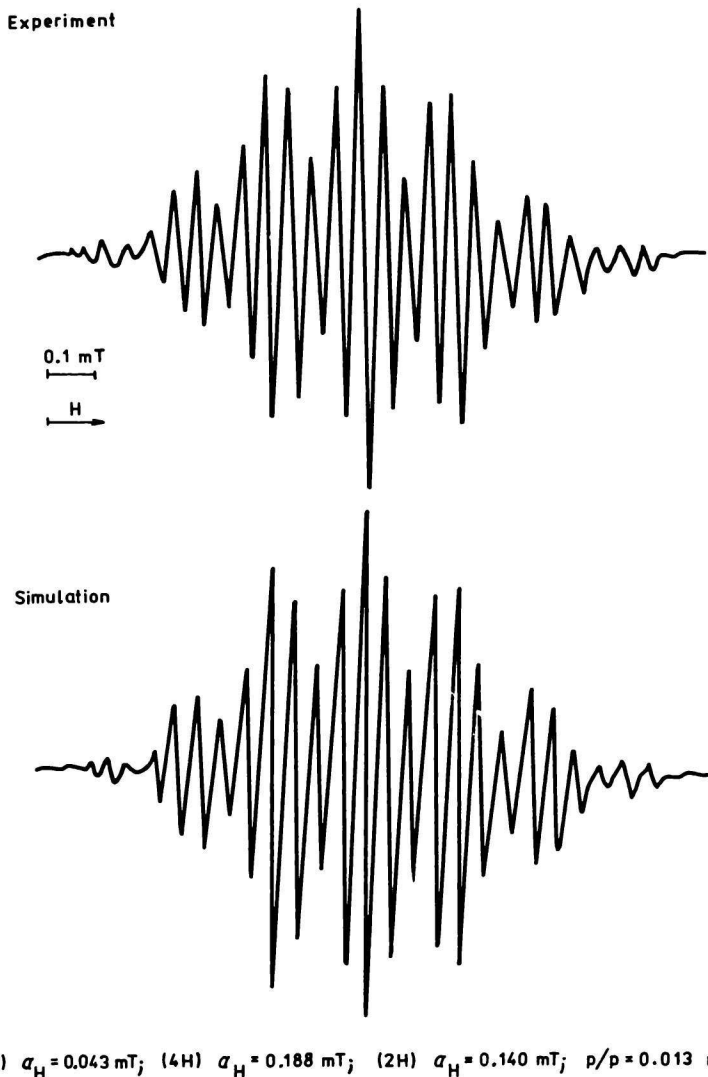
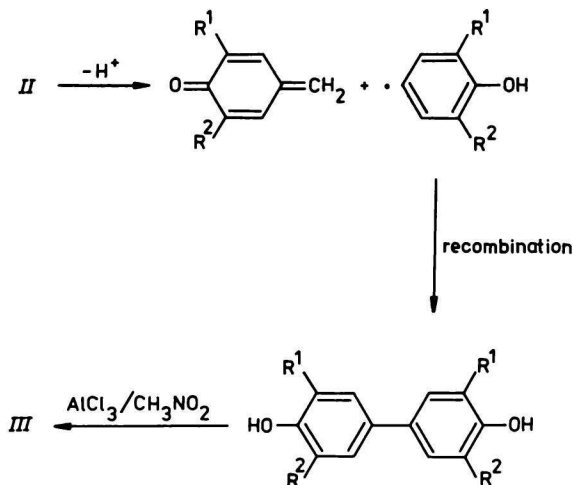


Fig. 3. Experimental and simulated EPR spectrum of radical cation *III* ( $R^1 = R^2 = \text{CH}(\text{CH}_3)_2$ ) prepared by oxidation of 4,4'-methylenediphenol *Ig* with the  $\text{AlCl}_3\text{—CH}_3\text{NO}_2$  system in benzene.

cation is subjected to fragmentation. Owing to this fact, only the EPR spectra of consecutively arising radicals can be observed during oxidation of 4,4'-methylenediphenols of this structure (Fig. 3). The simulation has unambiguously evidenced that the radical cations of 4,4'-biphenyldiol type *III* [4] arising according to Scheme 2 are involved. Thus in principle, two mechanisms of electron transfer from 4,4'-methylenediphenols to  $\text{AlCl}_2^+$  in the medium



Scheme 2

$\text{CH}_3\text{NO}_2$ —benzene can be observed. They are dependent on spin distribution of radical cation *II* which is controlled by substituents and steric factors. In the absence of voluminous substituents in *ortho* position a stable ion-radical complex comes into existence, while in the presence of *tert*-butyl or isopropyl groups the methylene bridge splits, the fragments leave ionic complex and the  $\text{H}^+$  ion liberated from radical cation is neutralized by the  $\text{AlCl}_4^-$  counterion. The neutral radical fragments undergo dimerization to give 4,4'-biphenyldiols. Provided the oxidation system is present in excess, the formed 4,4'-biphenyldiols function again as electron donors to yield radical cations *III*.

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