

Paramagnetic species in the reactions of organometallic reagents
XVI.* Ketyl radicals and the variation of their unpaired spin density by substituents and counter ions

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Dedicated to Professor Ing. RNDr. A. Tkáč, DrSc., in honour of his 60th birthday

The push and pull effect of oxido anion group of the experimentally investigated aryl aryl and aryl alkyl ketyl radicals is interpreted by INDO calculations. From the counter ions in questions (H^+ , $MgCl^+$, Ni^0 , Ni^{2+}) the best agreement between the experiment and the calculations was obtained for Ni^{2+} . The observed nonequivalence of β protons attached to ketyl group is explained by hindered rotation of CH_2 group assuming its proton is in the plane of aromatic ring.

При помощи INDO метода был объяснен толкательный и притягивающий эффекты оксидо-анионной группы арил-арил и арил-алкил кетильных радикалов до этого исследованных экспериментально. В системе противоионов (H^+ , $MgCl^+$, Ni^0 , Ni^{2+}) самое хорошее согласие расчета с экспериментом было достигнуто для Ni^{2+} . Наблюдаемая неравноценность β протонов кетильной группы была объяснена заторможенным вращением метильной группы в случае, когда протон находится в плоскости ароматического круга.

According to the structure and to the influence of substituents on the distribution of unpaired electron density, the radicals described in our series of papers [1] can be divided into the following groups (Scheme 1).

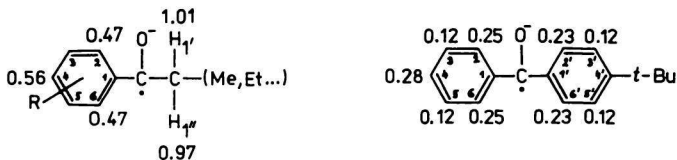
The indices marked at various positions of radical structures represent the proton splitting constants expressed in mT. In the first couple of aryl alkyl ketyl radicals *1.a* differs from *1.b* by the substitution of oxido anion group in position 2 of

*For Part XV see Ref. [1].

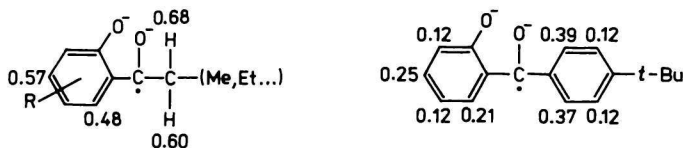
1. aryl alkyl ketyl radicals

2. aryl aryl ketyl radicals

a) without oxido anion



b) with 2-oxido anion



Scheme 1

benzene ring. Typical for such couple is the decrease of splitting constants of CH_2 protons attached to the ketyl group if the proton of benzene ring in position 2 is substituted by oxido anion group ($a_{H'} = 1.01$ mT and $a_{H''} = 0.97$ mT by 1.a decreases to $a_{H'} = 0.68$ mT and $a_{H''} = 0.60$ mT by 1.b). Another remarkable observation is the nonequivalence of β protons with the ratio of splitting constants 1.01 : 0.97 by 1.a and 0.68 : 0.60 by 1.b.

Another similar couple are aryl aryl ketyl radicals 2.a and 2.b differing from each other by the oxido anion group. This group doubles the splitting constants on the unsubstituted benzene ring ($a_{H'} = 0.23$ mT by 2.a increases to 0.39 and 0.37 mT by 2.b).

The nonequivalence of the β protons (structures 1.a, b) is probably caused by the hindered rotation round the bond between the ketyl and methylene group. This is a consequence *e.g.* of conjugation widening to the carbon of methylene group (mechanism of hyperconjugation) or eventually a consequence of hydrogen bridge formation between the protons of methylene and ketyl group.

The change of the spin density on the protons attached to the ketyl group in structures 1.a, b accompanied with the substitution of anion group is obviously connected with the shift of π electrons and not only in the highest singly occupied orbital but also in the lower orbitals with π symmetry. As in all investigated systems we dealt with the anion radicals, the distribution of the unpaired spin density can depend on the counter ion or eventually a donor acceptor bond between ketyl group and the transition metal can be formed. Therefore, in the first part of our work we investigated model systems with various counter ions (H^+ , MgCl^+ , Ni^0 ,

NiCl_2 resp. NiCl_3^-) and calculated their distribution of unpaired electron. The INDO method in UHF version adapted for the study of transition metal compounds was exploited [2–5]. As in this way the wave functions were obtained which are not eigenfunctions of operator S^2 , the components of the higher spin multiplet states were removed by partial annihilation [6]. By all systems standard geometry [7] was used as our computer capacity is limited to optimize such large systems.

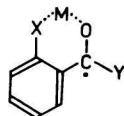
Results and discussion

Counter ions of ketyl radicals

The formation of ketyl radicals proceeds in the system of carboxylic acids, Grignard reagents, and nickel salts. Consequently in our calculations we assumed following alternative of counter ions of ketyl radicals: A. without, B. H^+ , C.

Table 1

Summary of the structures investigated by INDO calculations



Structure	Substituent		M				
	X	Y	A	B	C	D	E
1.a	H		—	H^+	MgCl^+	Ni^0	NiCl_3^-
1.b	O^-		—	H^+	MgCl^+	Ni^0	NiCl_2
2.a	H		—	H^+	MgCl^+	Ni^0	NiCl_3^-
2.b	O^-		—	H^+	MgCl^+	Ni^0	NiCl_2

MgCl⁺, D. Ni⁰, and E. Ni²⁺ counter ions. Ni⁺ was not considered as no indication of Ni⁺ was observed in e.s.r. spectra. The investigated structures are summarized in Table 1 and the experimental and calculated splitting constants are given in Table 2. Investigating the aryl alkyl ketyl radicals, *i.e.* group 1.a, b by INDO calculations, the optimal dihedral angle of the rotating methylene group described

Table 2

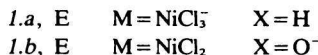
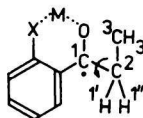
Proton splitting constants of structures 1.(a, b), E and 2.(a, b), E calculated by INDO method assuming various counter ions M

Structure	Position of proton	Proton splitting constants expressed in 0.1 mT for various counter ions M					Experiment
		A	B	C	D	E	
1.a	2	-3.03	1.84	-3.02	-2.27	4.75	4.0
	3	2.15	-1.08	-0.59	0.49	0.65	—
	4	-4.11	1.57	2.27	1.70	4.97	5.0
	5	2.22	-0.22	-0.32	0.11	-0.76	—
	6	-3.19	1.73	2.27	0.55	4.59	4.0
	1'	9.51	-9.29	-7.18	16.07	-9.50	10.0
	1''	9.10	-8.91	-6.53	15.61	-8.64	9.0
	2'	0.22	0.27	0.46	-0.55	0.97	—
1.b	3	-0.97	0.76	0.86	0.76	-0.54	1.2
	4	-2.70	-2.16	3.67	2.00	4.86	5.71
	5	1.89	1.51	1.13	0.32	-0.59	1.6
	6	-4.43	-3.46	-2.65	-1.57	3.13	4.69
	1'	16.57	2.60	-4.16	-5.34	-5.13	6.76
	1''	14.90	2.27	-3.29	-4.70	-4.97	5.98
	2'	-0.49	-0.97	0.70	0.49	0.76	—
2.a	2	-1.46	2.27	0.01	1.10	3.03	2.5
	3	1.08	-1.40	-0.76	-1.01	-0.92	1.2
	4	-1.46	1.94	1.24	1.65	3.30	2.8
	5	1.30	-0.49	-0.43	-0.97	-0.89	1.2
	6	-5.56	3.19	1.89	2.17	2.79	2.5
	2'	-4.43	3.51	4.43	1.94	4.32	3.95
2.b	3	-1.72	2.16	0.01	0.13	0.60	1.0
	4	1.51	-1.57	-0.65	-0.71	1.73	2.5
	5	-1.83	2.81	1.67	-0.46	-0.61	1.0
	6	0.49	-0.43	-0.13	-0.69	-1.48	2.1
	2'	-4.43	3.51	4.43	1.94	4.32	3.95
	3'	0.15	0.10	0.06	0.53	0.65	1.2
	4'	2.19	1.67	1.39	3.89	5.23	—
	5'	-0.23	-0.17	-0.09	-0.16	-0.69	1.2
	6'	-3.83	-3.66	-2.67	-4.63	-3.82	3.7

below was considered. The best agreement between the calculated and experimental proton splitting constants was found for structures of type E, *i.e.* if anion radical forms a donor acceptor bond with nickel(II) compounds. For other models, there is a considerable difference between calculations and experiment. The transfer of unpaired electron spin density to the orbital of transition metal was also calculated. Since π radicals are involved, this transfer is negligibly small. In agreement with this conclusion is the experiment, where cobalt, having nonzero nuclear spin moment, was employed as transition metal and where no interaction with cobalt nucleus was found in e.s.r. spectra.

Rotation of methylene group

The nonequivalence of methylene protons was investigated. The dependence of splitting constants on the total energy, Wiberg indexes, and on the dihedral angle given by atoms $OC^1C^2C^3$ (see formulae) was analyzed by INDO method.



In the first stage we assumed that energetically the most favourable conformation is with $\varphi = 120^\circ$, where the interaction between the oxygen of ketyl and hydrogens of methylene group occurs. By this conformation we found that the most suitable counter ion is Ni²⁺, also structures 1.(a, b), E. Then for these structures the angle dependence of splitting constants was calculated and the obtained results are summarized in Table 3. The splitting constants $a_{1'}$ and $a_{1''}$ of methylene protons depend on rotation angle, whereas splitting constants a_{2-6} of aromatic protons are practically angle independent. In all investigated cases a free rotation of methyl attached to the methylene group was assumed.

The dependence of the total energy on the rotation angle is illustrated in Fig. 1. It shows two expressive minima at the equivalent positions with $\varphi = 120$ and 240° , separated by a local minimum at 180° . The energetical barrier for passing between the minima is $E_{2(1.a, E)} = 4.53 \text{ kJ mol}^{-1}$ and $E_{2(1.b, E)} = 7.14 \text{ kJ mol}^{-1}$. For the transition from configuration with $\varphi = 120^\circ$ to $\varphi = 0^\circ$ the barrier is $E_{2(1.a, E)} = 40.81 \text{ kJ mol}^{-1}$ and $E_{2(1.b, E)} = 50.17 \text{ kJ mol}^{-1}$. These data confirm a relatively strong hindered rotation caused by the hydrogen bridge formation (structure i),

Table 3

Proton splitting constants of structures 1.(a, b), E calculated by INDO method for various angles φ and the experimentally observed values

Structure	Position of proton	Proton splitting constants expressed in 0.1 mT for various angles φ				
		0°	60°	120°	180°	Experiment
1.a, E	2	4.82	4.80	4.75	4.80	4.0
	3	-0.65	-0.65	-0.65	-0.65	—
	4	5.0	4.99	4.97	4.96	5.0
	5	-0.76	-0.76	-0.76	-0.76	—
	6	4.75	4.64	4.59	4.53	4.0
	1'	-9.50	-8.85	-9.50	-9.77	10.0
	1''	-9.50	-9.61	-8.64	-9.77	9.0
	2'	1.08	1.03	0.97	0.92	—
1.b, E	3	-0.59	-0.59	-0.54	-0.59	1.2
	4	4.90	4.89	4.86	4.85	5.71
	5	-0.65	-0.65	-0.65	-0.65	1.6
	6	3.35	3.24	3.13	3.08	4.69
	1'	-5.07	-4.64	-5.13	-5.29	6.76
	1''	-5.07	-5.18	-4.97	-5.29	5.98
	2'	0.81	0.76	0.76	0.70	—

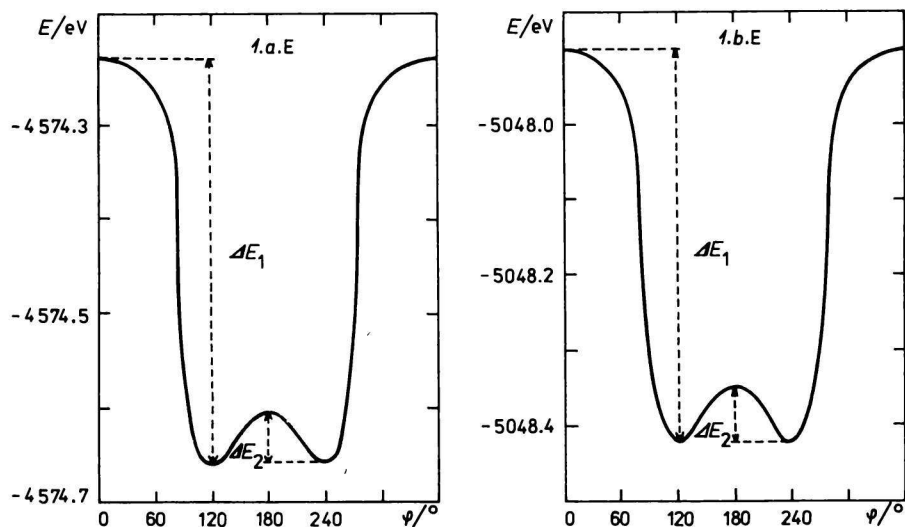
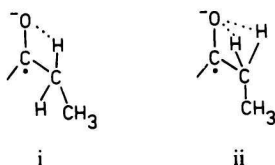


Fig. 1. Dependence of the total energy E on the rotation angle φ in radicals 1.(a, b), E.

whereas the configuration with $\varphi = 180^\circ$, with two equivalent hydrogen bridges (structures ii) is less favourable.



The most populated are the configurations with $\varphi = 120$ and 240° . Consequently the protons of methylene group appear as nonequivalent. Assuming these configurations a good agreement between the experimental and calculated splitting constants was obtained.

The formation of hydrogen bridge results also from the calculated angle dependence of Wiberg indexes (Fig. 2) which reflect the bond multiplicity. The index value is maximal at $\varphi = 120^\circ$. At this angle also an index increase for the bonds C—C₁ and C₁—C₂ was found. This confirms the maximal stability of the system for the conformation with $\varphi = 120^\circ$ and its equivalent conformation with $\varphi = 240^\circ$.

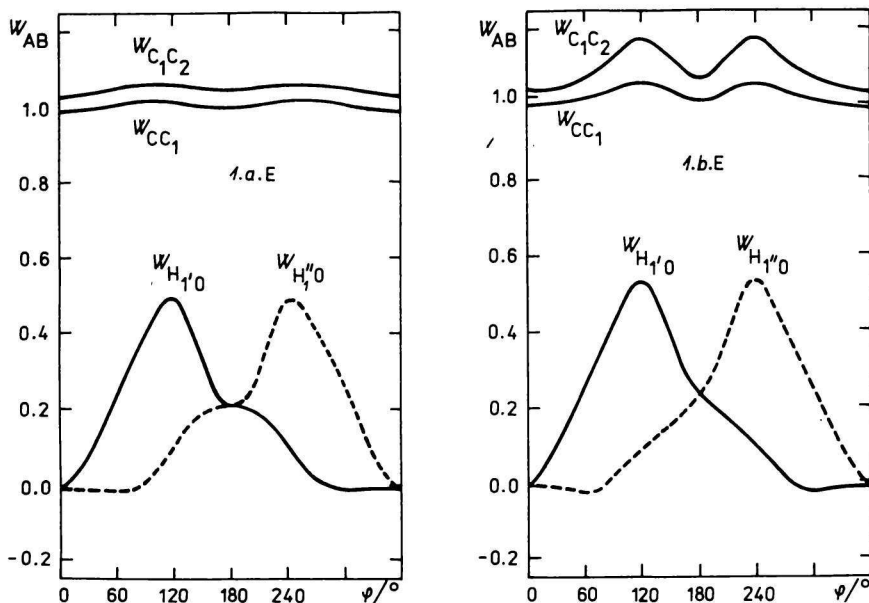


Fig. 2. Dependence of the Wiberg indexes W on the rotation angle φ of CH₂ protons in radicals 1.(a, b), E.

The dependence of spin density on the rotation angle is shown in Fig. 3. According to several authors [8—10] it is caused by the following four effects:

1. Spin polarization. This results from the population of spin density on p atom orbitals of carbon C^2 as a consequence of $\sigma-\pi$ interaction. This effect is practically independent of the rotation angle φ .

2. Hyperconjugation between the protons of CH_2 group and spin density on C^1 carbon orbital. This interaction is maximal for $H_{1'}$ proton at $\varphi = 30^\circ$, then decreases to zero, and at 120° increases again with the maximal value at 210° . For proton $H_{1''}$ this behaviour is shifted by 120° .

3. A direct interaction of CH_2 protons with the unpaired electron spin density on oxygen of ketyl group. This is maximal for proton $H_{1'}$ in the region $\varphi = 30$ and 210° and minimal in the region $\varphi = 120$ and 300° .

4. A direct interaction of CH_2 protons with spin density on benzene ring. This is maximal for $H_{1'}$ proton in the region $\varphi = 30$ and 210° and practically zero for $\varphi = 120$ and 270° .

Combination of these four effects results in a complex angle dependence of spin density for CH_2 protons as shown in Fig. 3.

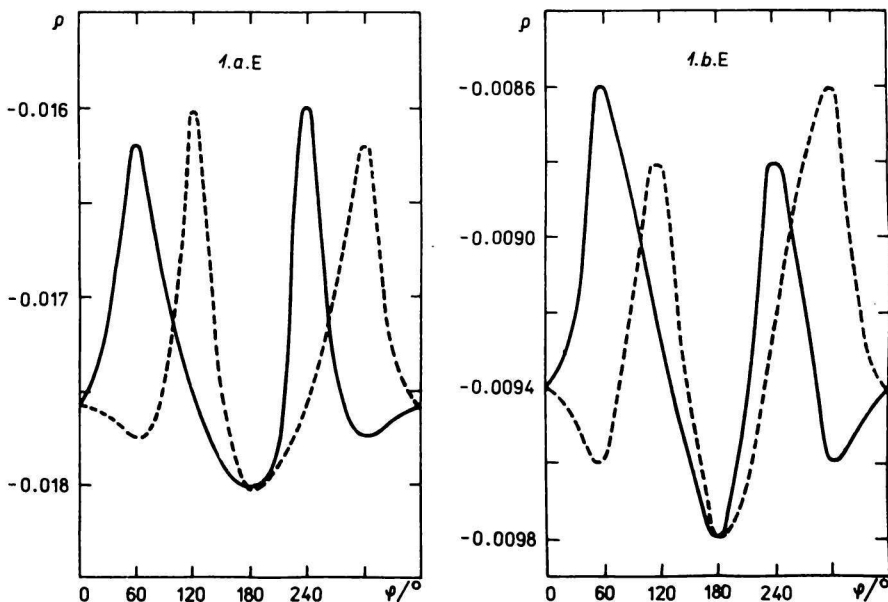


Fig. 3. Spin density dependence ρ of unpaired electron on the rotation angle φ of CH_2 protons in radicals 1.(a, b), E.

— $\rho_{H_{1'}}$; - - - $\rho_{H_{1''}}$.

Influence of oxido anion group on the distribution of spin density

As described in the introduction text we found experimentally an expressive influence of oxido anion group on the distribution of unpaired electron spin density. In the case of aryl alkyl ketyl radicals the substitution with the oxido anion group leads to the decrease of splitting constants of β protons attached to the ketyl group ($a_{H_1} = 1.01$ mT and $a_{H_1} = 0.97$ mT in the case of unsubstituted structure 1.a decrease to $a_{H_1} = 0.68$ mT and $a_{H_1} = 0.60$ mT by substituted structure 1.b). Otherwise, in the case of aryl aryl ketyl radicals an expressive push effect of oxido anion group was observed and the splitting constants of unsubstituted benzene ring increase nearly by factor two ($a_{H_{2,6}} = 0.23$ mT increase to $a_{H_2} = 0.39$ mT and $a_{H_6} = 0.37$ mT). The experimental facts reflect the by the calculations obtained shape of molecular orbitals containing one electron (at least in the first approximation). In the case of radical type 1.a, b the oxido anion group substituted in position 2 of aromatic ring enables an increase of the delocalization of unpaired electron to the substituted oxygen atom. So, the $\sigma-\pi$ polarization and herewith the spin density on the alkyl attached to the ketyl group decreases. In agreement with such explanation a decrease of splitting constants of CH_2 protons of ethyl group was observed as obvious from the comparison of structure 1.a to 1.b.

Substitution of oxido anion group in position 2 of aromatic ring (type 2.a, b) results in the alternation decrease of spin density on the substituted benzene ring. A considerable transfer of electron density to the oxygen, caused by the polarization of the lower with two electrons occupied molecular orbitals, is then mainly compensated by the transfer of spin density to another aromatic ring. So by the structure 2.b an increase of splitting constants nearly by factor two for the protons in positions 2' and 6' was observed if the structures 2.a and 2.b are compared.

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