40. ESR. Spectra of the Radical Anions of Cycloalkylbenzenes

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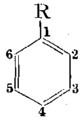
Summary. Radical anions of five cycloalkylbenzenes (alkyl = propyl, butyl, pentyl, hexyl, or heptyl) have been studied by ESR. spectroscopy at −90°C. In the case of cyclopropylbenzene, no reliable experimental data could be obtained, because of the instability of its radical anion. The spectra of the radical anions of the four higher homologues have been analysed by means of a computer program. The assignment of the coupling constants to the α-protons in the *para* position of the benzene ring and to the cycloalkyl β-protons has been based on the spectra of specifically deuterated derivatives.

The experimental data of the radical anion of cycloalkylbenzenes have been compared with those of the radical anions of five alkylbenzenes (alkyl = methyl, ethyl, *n*-propyl, isopropyl, or *t*-butyl), the spectra of the latter being reexamined at −90°C. In the cycloalkyl series the degeneracy of the two benzene-type lowest antibonding orbitals is the more effectively removed the larger the substituent, whereas the reverse relation holds for the non-cyclic series. The preferred conformation of the substituents is that in which the alkyl or cycloalkyl β-proton is near to the nodal plane of the benzene π-system, and this preference is accentuated with the increasing size of the substituent group.

Because of the near-degeneracy of orbitals in monosubstituted alkyl derivatives of benzene, the corresponding radical ions are of special interest for theoretical chemistry (see *e.g.* [1]). ESR. spectra of the radical anions I$^{\ominus}$ to V$^{\ominus}$ have been extensively investigated [1]–[11].



	R =		R =		R =
I	methyl	V	*t*-butyl	VIII	cyclopentyl
II	ethyl	VI	cyclopropyl	IX	cyclohexyl
III	*n*-propyl	VII	cyclobutyl	X	cycloheptyl
IV	isopropyl				

However, analogous studies of cycloalkyl derivatives have not yet been carried out in a systematic way. Only a few scattered reports exist in the literature, exlusively by Russian workers [3] [12] [13].

In the present paper we communicate the ESR. results for the radical anions of five cycloalkylbenzenes, VI$^{\ominus}$ to X$^{\ominus}$. These results partially disagree with those reported previously. Whereas the radical anions VII$^{\ominus}$ to X$^{\ominus}$ were sufficiently stable for ESR. studies at −90°C, the instability of VI$^{\ominus}$ precluded the observation of intense and reproducible spectra.

The investigations reported in the present paper were restricted to a single temperature cited above. Since the coupling constants of the protons in the radical

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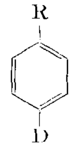
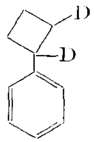
anions of monosubstituted alkylbenzenes are markedly temperature dependent [6] [10], a valid comparison between the data of $VII^{\ominus}$ to $X^{\ominus}$ with those of $I^{\ominus}$ to $V^{\ominus}$ required the same temperature for the recording of all spectra. The ESR. spectra of $I^{\ominus}$ to $V^{\ominus}$ were therefore reexamined at −90 °C.

In the case of $IV^{\ominus}$ and $VII^{\ominus}$ to $X^{\ominus}$, an ambiguity existed with respect to the assignment of coupling constants to the single alkyl β-proton and to the α-proton in the *para* position of the benzene ring[2]). This ambiguity was removed by the ESR. studies of the deuterio derivatives $XI^{\ominus}$ to $XV^{\ominus}$.



R =
XI isopropyl
XII cyclopentyl
XIII cyclohexyl
XIV cycloheptyl



XV

Experimental Section[3]). – *Source of compounds.* Toluene (I), ethylbenzene (II), *n*-propylbenzene (III), cumene (IV) and *t*-butylbenzene (V) were purchased from *Fluka AG*, Buchs.

Cyclopropylbenzene (VI) was produced by the ring closure of 1,3-dibromo-1-phenyl-propane with Zn-Cu powder.

Cyclobutylbenzene (VIII) was prepared from 1-hydroxy-1-phenyl-cyclobutane by abstraction of water (few drops of perchloric acid in a solution of VII in glacial acetic acid) followed by catalytic hydrogenation with Pd (10%) on charcoal. The hydroxy compound was obtained from the reaction of phenylmagnesium bromide with cyclobutanone.

Cyclopentylbenzene (VII), cyclohexylbenzene (IX) and cycloheptylbenzene (X) were synthesized by addition of the corresponding cycloalkene to benzene in presence of conc. sulfuric acid.

The *p*-deuterio derivatives XI to XIV of cumene (IV) and of the cycloalkylbenzenes VIII, IX and X were prepared from the corresponding *p*-bromo compounds by reaction with

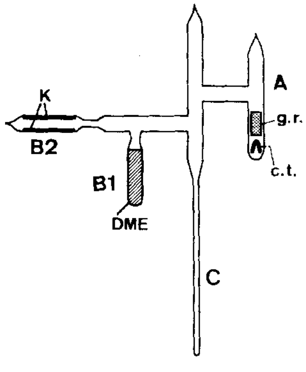


Fig. 1. *Apparatus for preparation of radical anions*

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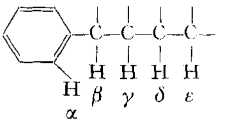
[2]) In ESR. spectroscopy the protons of alkyl-substituted π-electron systems are denoted as α, β, γ, δ, ε... according to whether they are separated by 0, 1, 2, 3, 4... sp^3-hybridized carbon atoms from the π-center.



[3]) See [14] for a more detailed description of the synthetic work reported in this Section.

n-butyllithium and subsequent addition of heavy water. The isotopic impurities, consisting of the undeuterated hydrocarbons IV, VIII, IX or X, were negligible in all cases (1–5%).

1,2-Dideuterio-1-phenyl-cyclobutane (XV) was synthesized in the same way as the parent cyclobutylbenzene (VII), the last step involving catalytic deuteration instead of hydrogenation (see above). The dideuterio derivative XV resulted as the major product (ca. 60%); the next largest isotopic component was 1-deuterio-1-phenyl-cyclobutane (ca 30%).

All samples of the compounds I to XV were purified by preparative gas chromatography prior to their conversion into radical anions.

Preparation of radical anions. The compounds I to XV were converted into their radical anions $I^{\ominus}$ to $XV^{\ominus}$ by reaction with a potassium mirror in 1,2-dimethoxyethane (DME) at the temperature of dry ice-alcohol bath (ca −80°C).

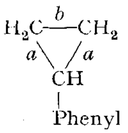
Beside this standard procedure, the following modification was applied for the reduction of cyclopropylbenzene (VI) in order to avoid direct contact of the compound with the metal suface (*cf.* Fig. 1).

Into the arm A of the sample tube, a sealed capillary tube (c.t.) containing 3–4 mg of degassed VI was introduced, together with a glass rod (g.r.). The second arm, B, included two compartments: B1, with freshly distilled DME, and B2, coated with a clean K mirror. A solution of $e^{\ominus}_{\text{solv.}}$ (solvated electrons) was generated in the evacuated sample tube by pouring cold DME from B1 to B2. After 15 to 30 min, the contact of DME with K resulted in a clear, deep blue solution which was separated from the metal by decanting into B1. Subsequently the compartment B2 was removed by sealing. In a few experiments DME contained several drops of dried and degassed hexamethylphosphoramide (HMPA) which were injected into B1 prior to the vacuum distillation of DME. By the addition of HMPA to DME (ratio 1:10) a larger concentration of $e^{\ominus}_{\text{solv.}}$ was attained.

Gentle shaking of the sample tube in the dry ice-alcohol bath resulted in breaking of the capillary tube by the glass rod. The contents of the arms A and B were then rapidly mixed and immediately transferred into the ESR. tube C for the recording of the spectrum.

Results. – *Cyclopropylbenzene (VI).* Numerous experiments were carried out with the aim to obtain the ESR. spectrum of $VI^{\ominus}$. The modified procedure which has been depicted in the 'Experimental Section' was preferentially applied. None of the spectra observed, however, could be ascribed with certainty to $VI^{\ominus}$.

One experiment resulted in a weak spectrum which was analysed in terms of two coupling constants of 4.9 ± 0.1 and 1.7 ± 0.1 gauss for four and two nearly equivalent protons, respectively. Unfortunately, attempts to reproduce this spectrum, which might in fact be due to $VI^{\ominus}$, failed so far. Another poorly resolved spectrum, also acceptable for $VI^{\ominus}$, was observed in a few experiments. Its analysis yielded one coupling constant of 4.95 ± 0.1 gauss for four nearly equivalent protons, and two coupling constants of 1.2 ± 0.1 and 0.55 ± 0.05 gauss, each for one single proton. These values are close to those found for $IV^{\ominus}$, the radical anion of cumene [5] [10][4]. Thus in the absence of further evidence, the possibility that the spectrum arises from $IV^{\ominus}$ cannot be excluded.



VI

Formation of $IV^{\ominus}$ from $VI^{\ominus}$ requires an opening of the bond *b* of the cyclopropyl ring and an abstraction of two hydrogen atoms from the solvent. On the other hand, if one of the bonds *a* is broken, $III^{\ominus}$, the radical anion of *n*-propylbenzene [5][4] should be obtained. The spectrum of the latter was indeed observed in some experiments in which DME contained a small amount of HMPA (see 'Experimental Section').

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[4] See also Table 1 of the present paper.

Besides the ESR. spectra of III$^{\ominus}$ and IV$^{\ominus}$, those of other secondary radicals or mixtures of radicals were recorded, but the relevant species could not be identified.

Cycloalkylbenzenes with alkyl = butyl, pentyl, hexyl or heptyl (VII to X). Figure 2 shows the ESR. spectra of the radical anions of cyclobutylbenzene (VII$^{\ominus}$; top); cyclopentylbenzene (VIII$^{\ominus}$; middle) and cyclohexylbenzene (IX$^{\ominus}$; bottom). The spectrum of the radical anion of cycloheptylbenzene (X$^{\ominus}$) is not shown in Fig. 2, because its splitting pattern closely resembles that observed for IX$^{\ominus}$. All spectra exhibit five nearly equidistant groups of lines; the relative intensities of the groups have an approximate ratio of 1:4:6:4:1. In the case of VII$^{\ominus}$, there are four resolved lines of equal intensity within each group. This number is reduced to two in the spectra of IX$^{\ominus}$ and X$^{\ominus}$. In the intermediate case represented by VIII$^{\ominus}$, each group consists of

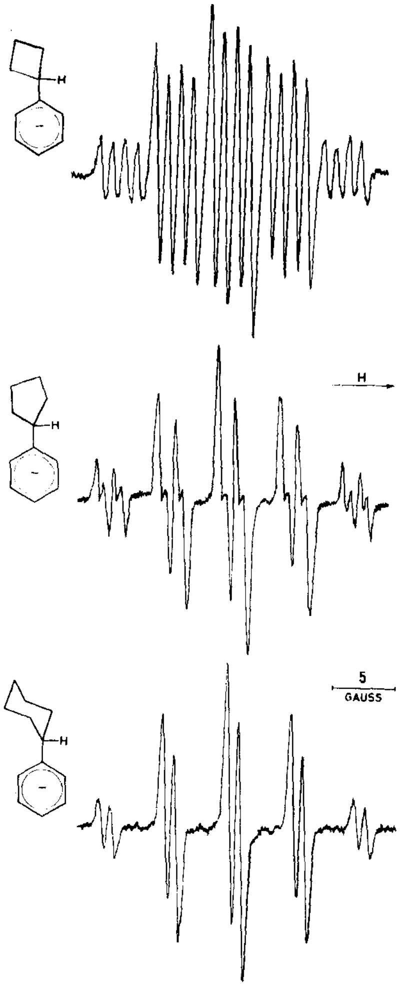

Fig. 2. *ESR. spectra of the radical anions of cyclobutyl-, cyclopentyl-, and cyclohexyl-benzene*
Solvent: 1,2-dimethoxyethane; 'gegenion': K$^{\oplus}$; temperature: –90°C

a pair of well separated lines which are in turn split into two partially resolved components.

As in the spectra of $I^{\ominus}$ to $V^{\ominus}$ with non-cyclic alkyl substituents [5] [10], the grouping of lines arises from coupling with two pairs of equivalent α-protons2) in the *ortho*(2,6) and *meta*(3,5) positions of the benzene ring. On the other hand, the splitting within a group is due to the α-proton2) in the *para*(4) position and/or to the β-proton2) of the cycloalkyl substituent. Comparison of the spectrum of $VII^{\ominus}$, the radical anion of cyclobutylbenzene, with that of $XV^{\ominus}$, in which the alkyl β-proton was replaced by a deuteron (p. 362), permits the assignment of the two coupling constants responsible for the splittings within a group. The smaller one must be assigned to the β-proton, leaving the larger one for the α-proton in the *para* position. The assignment of the corresponding constants in the spectra of the three higher homologues $VIII^{\ominus}$, $IX^{\ominus}$ and $X^{\ominus}$ is based on comparison with the spectra of the *p*-deuterio derivatives, $XII^{\ominus}$, $XIII^{\ominus}$ and $XIV^{\ominus}$, respectively (p. 362). In all three cases, the larger and fully resolved splitting within a group of lines must be identified with the coupling constant of the α-proton in the *para* position. This assignment means that the cycloalkyl β-proton is responsible for the smaller, partially resolved (in the spectrum of $VIII^{\ominus}$) or unresolved splitting (in the spectra of $IX^{\ominus}$ and $X^{\ominus}$).

Hyperfine structure due to γ-, δ- and ε-protons, *i.e.* cycloalkyl protons separated by more than one sp^3-hybridized carbon atom from the π-electron system2), has not been resolved in any of the spectra.

Since the width of the hyperfine lines in the spectra of $VII^{\ominus}$ to $X^{\ominus}$ precluded a direct measurement of splittings smaller than 0.4 gauss, a computational analysis of the hyperfine structure was carried out by means of a program developed in this laboratory [15]. This program starts with tentative values for the coupling constants and modifies them by an iterative procedure until the computed and experimental spectra agree as closely as possible (least-square criterium). Table 1 gives the values

Table 1. *Coupling constants (in gauss) of the α- and β-protons in the radical anions of monosubstituted alkylbenzenes* a)

Radical anion of	Alkyl substituent	α-protons			β-protons	
		$a_{H(2)} = a_{H(6)}$	$a_{H(3)} = a_{H(5)}$	$a_{H(4)}$	$a_H^{CH_n}$	
		(*ortho*) b)	(*meta*) b)	(*para*)	(substit.)	
I	methyl	(–) 5.15	(–) 5.44	(–) 0.51	+ 0.77 d)	(n = 3)
II	ethyl	(–) 4.99	(–) 5.19	– 0.85 d)	+ 0.79 d)	(n = 2)
III	*n*-propyl	(–) 5.02	(–) 5.20	(–) 0.83	(+) 0.67	(n = 2)
IV	isopropyl	(–) 4.97	(–) 5.08	(–) 1.07 c)	+ 0.51 c) d)	(n = 1)
V	*t*-butyl	(–) 4.67	(–) 4.71	(–) 1.77	–	
VII	cyclobutyl	(–) 4.41	(–) 4.49	(–) 2.02 c)	(+) 1.00 c)	(n = 1)
VIII	cyclopentyl	(–) 4.79	(–) 4.95	(–) 1.28 c)	(+) 0.54 c)	(n = 1)
IX	cyclohexyl	(–) 4.99	(–) 5.17	(–) 0.84 c)	(+) 0.20 c)	(n = 1)
X	cycloheptyl	(–) 5.11	(–) 5.38	(–) 0.65 c)	(+) 0.15 c)	(n = 1)

a) Experimental error: ±0.04 gauss for $a_{H(2)} = a_{H(6)}$ and $a_{H(3)} = a_{H(5)}$, and ±0.01 to ±0.02 gauss for $a_{H(4)}$ and $a_H^{CH_n}$.

b) Assignment required by all theoretical models: $a_{H(2)} = a_{H(6)} < a_{H(3)} = a_{H(5)}$ [5] [8] [10].

c) Assignment of $a_{H(4)}$ and $a_H^{CH_n}$ based on the spectra of deuterio derivatives (see text).

d) Sign determined experimentally [9] [10].

resulting for the α- and β-protons in $\mathrm{VII}^{\ominus}$ to $\mathrm{X}^{\ominus}$. The corresponding coupling constants, obtained by the same procedure for $\mathrm{I}^{\ominus}$ to $\mathrm{V}^{\ominus}$, are also listed in this Table. All data refer to spectra taken in DME with $\mathrm{K}^{\oplus}$ as 'gegenion', at −90°C. In the case of $\mathrm{IV}^{\ominus}$, the assignment made previously for the α-proton in the *para*(4) position and the β-proton of the isopropyl substituent was confirmed by the ESR. study of $\mathrm{XI}^{\ominus}$, the *p*-deuterio derivative of $\mathrm{IV}^{\ominus}$.

The sign of the coupling constants has been assumed to be negative for the α-protons and positive for the β-protons. This assumption was shown to be correct in the case of $\mathrm{I}^{\ominus}$, $\mathrm{II}^{\ominus}$ and $\mathrm{IV}^{\ominus}$, for which the signs of some of the coupling constants were determined by experiment [9] [10] (cf. Table 1).

Discussion. – *π-Spin populations and near-degeneracy of orbitals.* The coupling constants $a_{\mathrm{H}(\mu)}$ of α-protons can be converted into the π-spin populations at the adjacent centers μ by means of the well-known *McConnell* relation [16]:

$$a_{\mathrm{H}(\mu)} = Q \cdot \varrho_{\mu} \,. \tag{1}$$

The ϱ_{μ} values obtained in this way for the proton-bearing centers (μ = 2, 3, 4, 5 and 6) of $\mathrm{I}^{\ominus}$ to $\mathrm{V}^{\ominus}$ and $\mathrm{VII}^{\ominus}$ to $\mathrm{X}^{\ominus}$ are listed in Table 2. The conversion factor Q has been taken as −22.5 gauss, *i.e.* the total spread of the spectrum of benzene radical anion [2].

The spin populations ϱ_1 at the substituted center (μ = 1), also listed in Table 2, result from the condition

$$\sum_{\mu=1}^{6} \varrho_{\mu} = 1 \qquad \text{or} \qquad \varrho_1 = 1 - \sum_{\mu=2}^{6} \varrho_{\mu} \,. \tag{2}$$

The sign of all values ϱ_{μ} in Table 2 is positive, in accordance with theoretical expectation and experimental evidence [5] [7]–[10].

Table 2. *π-Spin populations ϱ_{μ} in the radical anions of monosubstituted alkylbenzenes*

Radical anion of	Alkyl substituent	$\varrho_2 = \varrho_6$ (*ortho*)	$\varrho_3 = \varrho_5$ (*meta*)	ϱ_4 (*para*)	ϱ_1 (substit.)
I	methyl	+0.229	+0.242	+0.023	+0.035
II	ethyl	+0.222	+0.231	+0.038	+0.056
III	*n*-propyl	+0.223	+0.231	+0.037	+0.055
IV	isopropyl	+0.221	+0.226	+0.048	+0.058
V	*t*-butyl	+0.208	+0.209	+0.079	+0.087
VII	cyclobutyl	+0.196	+0.200	+0.090	+0.118
VIII	cyclopentyl	+0.213	+0.220	+0.057	+0.077
IX	cyclohexyl	+0.222	+0.230	+0.037	+0.059
X	cycloheptyl	+0.227	+0.238	+0.029	+0.041

In the 3rd and 4th columns of Table 3, the averaged values $\frac{1}{2}(\varrho_{2,6} + \varrho_{3,5})$ and $\frac{1}{2}(\varrho_1 + \varrho_4)$ are compared with the corresponding spin populations $(\varrho_{\mu})_{+}$ and $(\varrho_{\mu})_{-}$ which have been computed by the CI (Configuration Interaction) method for the single occupancy of the orbitals ψ_{a+} and ψ_{a-}, respectively [8].

Table 3. *Some characteristic values derived from the experimental data of the radical anions of monosubstituted alkylbenzenes*

Radical anion of	Alkyl substituent	$\frac{\varrho_{2,6}+\varrho_{3,5}}{2}$	$\frac{\varrho_1+\varrho_4}{2}$	r	$\langle\cos^2\Theta\rangle$	Θ (degrees)
I	methyl	$+0.235_5$	$+0.029$	8.1	0.49	45
II	ethyl	$+0.226_5$	$+0.047$	4.8	0.31	56
III	*n*-propyl	$+0.227$	$+0.046$	4.9	0.27	59
IV	isopropyl	$+0.223_5$	$+0.053$	4.2	0.20	64
V	*t*-butyl	$+0.208_5$	$+0.083$	2.5	–	–
VII	cyclobutyl	$+0.198$	$+0.104$	1.9	0.19	64
VIII	cyclopentyl	$+0.216_5$	$+0.067$	3.2	0.16	66
IX	cyclohexyl	$+0.226$	$+0.048$	4.7	0.08	74
X	cycloheptyl	$+0.232_5$	$+0.035$	6.6	0.08	74
benzene	none	$+0.1667$	$+0.1667$	1.0	–	–
		$+0.0525$	$+0.3949$	←	$(\varrho_\mu)_+$	
		$+0.2808$	-0.0616	←	$(\varrho_\mu)_-$	

$\Psi_{a+} = 0.577\ (\Phi_1+\Phi_4) - 0.289\ (\Phi_2+\Phi_3+\Phi_5+\Phi_6)$ and $\Psi_{a-} = 0.500\ (\Phi_1-\Phi_3+\Phi_5-\Phi_6)$ are the degenerate, lowest antibonding orbitals of unperturbed benzene; 'plus' signifies symmetric and 'minus' antisymmetric with respect to a mirror plane which passes through the centers 1 and 4 and is perpendicular to the nodal plane of the π-system. In the radical anion of benzene the probability of the odd electron occupying either Ψ_{a+} or Ψ_{a-} is equal, and hence $\varrho_\mu = \frac{1}{2}\ [(\varrho_\mu)_+ + (\varrho_\mu)_-]$. This is no longer the case in the radical anions of alkyl derivatives, since the perturbation due to the substituent effect lifts the degeneracy.

Comparison of $\frac{1}{2}\ (\varrho_{2,6} + \varrho_{3,5})$ and $\frac{1}{2}\ (\varrho_1 + \varrho_4)$ with $(\varrho_\mu)_+$ and $(\varrho_\mu)_-$ shows that the 'experimental' values resemble $(\varrho_\mu)_-$ rather than $(\varrho_\mu)_+$. Thus in all radical anions considered – in $\mathrm{I}^\ominus$ to $\mathrm{V}^\ominus$ as well as in $\mathrm{VII}^\ominus$ to $\mathrm{X}^\ominus$ – the odd electron preferentially occupies an antisymmetric benzene-type orbital ψ_{a-}, which is less destabilized by the electron-repelling effect of the alkyl substituents than its symmetric counterpart ψ_{a+}. However, in order to account more quantitatively for the experimental findings, a considerable contribution of $(\varrho_\mu)_+$ to $(\varrho_\mu)_-$ is required, which corresponds to an 'admixture' of ψ_{a+} with the more stable orbital ψ_{a-}.

Such an admixture is made possible by the 'near-degeneracy', *i.e.* the energetic proximity of Ψ_{a+} and Ψ_{a-} in monosubstituted alkyl derivatives of benzene (the relevant energy difference in toluene was estimated as 0.05 eV [8] [10] [11]). 'Thermal interaction' and 'vibronic coupling' are generally thought to be responsible for orbital mixing of this kind [1] [5] [8] [10] [11].

An increasing contribution of $(\varrho_\mu)_+$ to $(\varrho_\mu)_-$ changes the spin populations at the centers μ in the following way:

For $\mu = 2, 3, 5$ and 6 it decreases the positive values $(\varrho_\mu)_-$; for $\mu = 1$ and 4 it overcompensates the negative values $(\varrho_\mu)_-$ and leads to increasingly positive spin populations.

The ratio $r = (\varrho_{2,6} + \varrho_{3,5})/(\varrho_1 + \varrho_4)$ is therefore a sensitive function of this contribution; large (small) r values point to small (large) contributions of $(\varrho_\mu)_+$ to $(\varrho_\mu)_-$. It can be seen from the 5th column of Table 3 that r varies between 1.9 (for $\mathrm{VII}^\ominus$) and 8.1 (for $\mathrm{I}^\ominus$).

Since the contribution of $(\varrho_\mu)_+$ to $(\varrho_\mu)_-$ depends on the energy difference of ψ_{a+} and ψ_{a-}, the r values indicate how effective the substituents are in removing the degeneracy of the two orbitals. The following sequence based on the r values is suggested in this regard:

methyl > cycloheptyl > ethyl ≈ n-propyl ≈ cyclohexyl > isopropyl > cyclopentyl > t-butyl > cyclobutyl.

In the cycloalkyl series the degeneracy of ψ_{a+} and ψ_{a-} is thus the more effectively removed the larger the substituent, whereas the reverse relation holds for the non-cyclic series.

Unfortunately, no information is available for the cyclopropyl substituent, as the ESR. data of the radical anion VI$^\ominus$ have not been established with certainty. Guided by chemical evidence and by the results of investigations carried out in this laboratory[5], we can only anticipate that the overall effect of this substituent is also electron-repelling.

A contrary statement was previously made by some Russian authors [12]. These workers reduced VI with K in DME, at –30°C, and obtained an ESR. spectrum which was analysed in terms of one large coupling constant (9 gauss) of a single proton, and two smaller constants (4.2 and 2.1 gauss) of two pairs of equivalent protons. This spectrum was ascribed to VI$^\ominus$, the large value being assigned to the α-proton in the *para* position, and the two smaller ones to the two pairs of equivalent α-protons in the *ortho* and *meta* positions. A further partially resolved splitting (0.4 gauss) was thought to arise from cyclopropyl β- and γ-protons. Since the hyperfine structure due to the α-protons is consistent with the single occupancy of the benzene-type symmetric orbital Ψ_{a+}, the authors [12], were induced to postulate a stabilization of Ψ_{a+} relative to its antisymmetric couterpart Ψ_{a-}. The overall electron-attracting substituent effect required for such stabilization was accounted for by the assumption that the conjugation between the cyclopropyl σ-electrons and the benzene π-system overrides the inductive repulsion.

However, these arguments [12] are invalidated by the fact that – according to our experience – the spectrum ascribed to VI$^\ominus$ cannot be due to this radical anion, but must arise from an impurity or a secondary reduction product.

It is likewise doubtful whether the spectrum obtained from VI with K by another group of workers [13] can be ascribed to VI$^\ominus$. This spectrum, which consists of five broad and apparently overmodulated components (separation: ca 5 gauss; binomial distribution of intensities), may in fact be due to III$^\ominus$ or IV$^\ominus$ (see 'Results').

Conformation of the alkyl substituents. An approximate formula

$$a_{\mathrm{H}}^{\mathrm{CH}_n} = B \cdot \varrho_\mu \cdot \langle\cos^2\theta\rangle \qquad n = 1,2 \text{ or } 3 \tag{3}$$

relates the coupling constant $a_{\mathrm{H}}^{\mathrm{CH}_n}$ of the alkyl β-protons with the spin population ϱ_μ at the substituted π-center μ [17]. The averaged value $<\cos^2\theta>$ refers to an angle θ which is formed by the $2p_z$-axis of the substituted atom C(μ) and the projection of the C(alkyl)–H(β) bond on the plane passing through the $2p_z$-axis and perpendicular to the C(μ)–C(alkyl) linkage. The parameter B is usually estimated from the ESR. spectra of methyl-substituted radicals, since in this case $<\cos^2\theta> = 0.5$ and

$$a_{\mathrm{H}}^{\mathrm{CH}_3} = \tfrac{1}{2} B \cdot \varrho_\mu \,. \tag{4}$$

In the last two columns of Table 3 are listed the values $<\cos^2\theta>$ and θ which have been calculated by means of equation (3) from the coupling constants $a_{\mathrm{H}}^{\mathrm{CH}_n}$(Table 1), along with the spin populations ϱ_1 (Table 2). The parameter B was set equal to +44.8 gauss, *i.e.* twice the value $\frac{1}{2} B = +22.4$ gauss resulting from ESR. study of the radical anions of disubstituted methylnaphthalenes [18].

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[5] These results indicate that cyclopropylbenzene has a lower electron affinity than benzene.

It is true that for angles θ obtained by this procedure a high degree of accuracy cannot be claimed. The lack of precision is due not only to the approximate character of equation (3), but also to inaccuracy of the values used in the calculation. In particular, the spin populations ϱ_1 are subject to error, since they have been obtained by means of equation (2) as small differences of larger numbers. Nevertheless, an excellent argreement is achieved in the case of the methyl substituent ($I^{\ominus}$), for which a value $\theta = 45°$ is required (see above). The agreement suggests that the information deduced from the angles θ in Table 3 is at least qualitatively correct. Two conclusions can be drawn with regard to the preferred conformation of the alkyl substituents:

(1) The alkyl β-protons favour a position near the nodal plane of the benzene π-system ($55° < \theta < 75°$);

(2) The preference for this position is accentuated with the increasing size of the alkyl substituent.

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