E. S. R. Spectra of the Terphenyl-Anions

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We have observed the E.S.R.-spectra of the anions of ortho-, meta- and para-terphenyl produced by reaction with alkali metals. In each case several hundred hyperfine structure components could be resolved, but only in the case of p-terphenyl a theoretical interpretation of the spectrum in terms of 4 coupling constants was obtained.

It is well known that aromatic hydrocarbons react with alkali metals in non protonic solvents to form mono- or divalent anions [1]. The addition of one or two electrons is the easier and the anions obtained are the more stable the lower the reduction potential of the hydrocarbon is; a correlation between the reduction potential and the energy of the lowest vacant molecular orbital has been demonstrated by Hoijtink [2]. In dilute solutions the addition of one single electron to the lowest vacant molecular orbital of the hydrocarbon results in monovalent radical-ions which can be studied by E.S.R. While the more stable ions formed by the condensed hydrocarbons have been investigated in some detail [3], an E.S.R.-spectrum of the biphenyl-anion has been observed in medium resolution by de Boer [4] and recently a completely resolved spectrum has been given by Carrington [5] and others. It may be noted for comparison with the terphenyl-ion that in the case of the biphenyl the experimental values of the hyperfine structure coupling constants are in fair agreement with the spin densities calculated with the simple Hückel-method for the ortho- and para-positions, but not for the meta position.

The E.S.R.-spectrum of the p-terphenyl-anion obtained by Weissman and de Boer [3] did not exhibit any resolved HFS. More recently Solodovnikov [6] has observed a splitting into 8 components, but since an even number of lines is in disagreement with the structure of the radical, the author himself expresses some doubts concerning his results.

Experimental Results

We have obtained the E.S.R.-spectra of the o-, m- and p-terphenyls resolved into several hundreds of hyperfine structure components. The experimental spectrum of the p-terphenyl is given in Fig. 1 together with the theoretical reconstruction. The latter is based on 4 coupling constants with one group of 2 equivalent protons (a_1) and 3 groups of 4 equivalent protons each ($a_2 - a_4$). The values are $a_1 = 3.30$ G, $a_2 = 2.07$ G, $a_3 = 0.95$ G, $a_4 = 0.56$ G. The theoretical number of lines is 375, but due to superpositions of lines and to the weak intensities of some HFS-components, only 105 could be identified in the experimental spectrum.

The theoretical number of lines for the ortho- and meta-terphenyl-ions are 675 and 900 resp.; so far we have not been able to evaluate the coupling constants of these anions.

The experimental spectra of the ortho-terphenyl are given in Fig. 2 and 3. The spectrum in Fig. 2 with an even number of lines is very unstable and transforms itself into the spectrum of Fig. 3 with an uneven number of lines.

Fig. 4 shows the spectrum of the m-terphenyl exhibiting an even number of lines in agreement with the structure of the molecule.

Discussion

We could not observe any difference between the spectra of p-terphenyl obtained by reduction with

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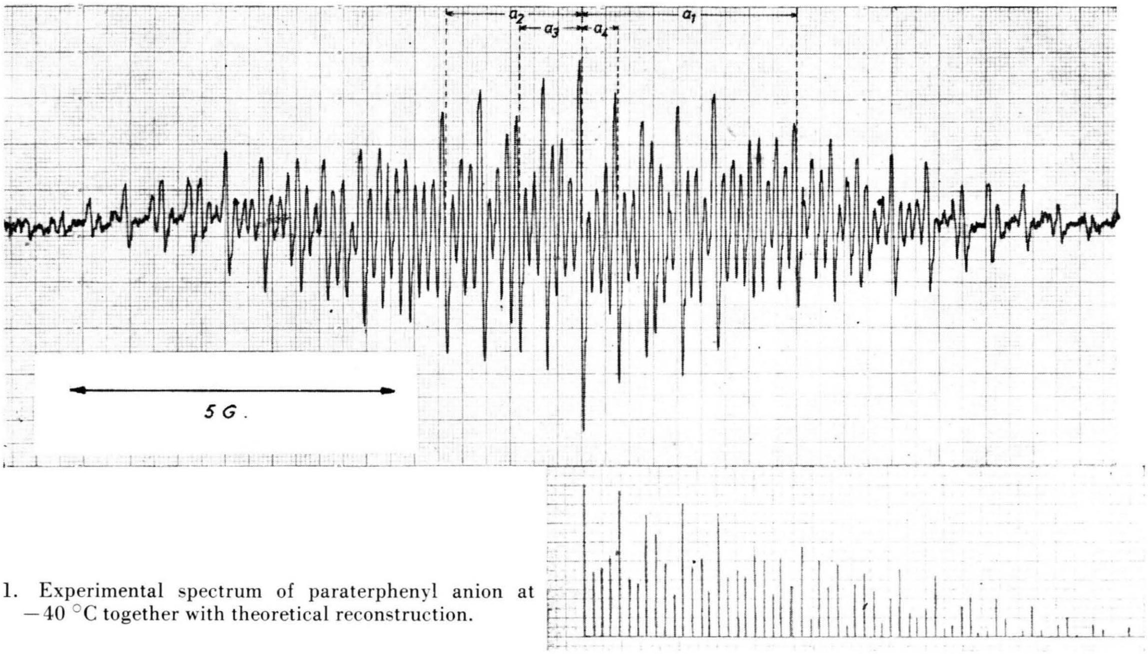

Fig. 1. Experimental spectrum of paraterphenyl anion at −40 °C together with theoretical reconstruction.

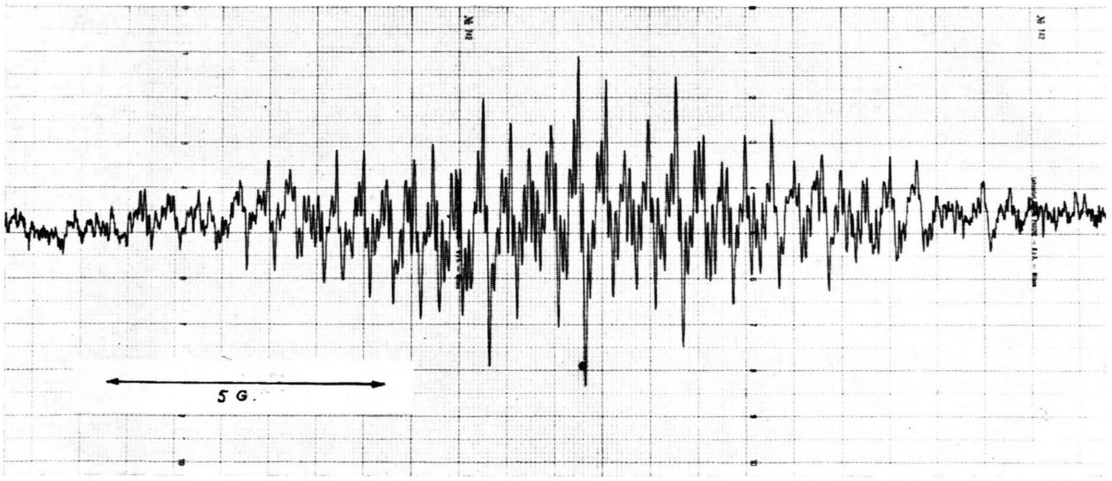

Fig. 2. Spectrum of orthoterphenyl at room temperature (a).

Li or Na in dimethoxyethane (DME). In contrast to the results of ATHERTON and WEISSMAN[7] with the naphthalene-ion we have not observed any structure due to the alkali metal when using tetrahydrofuran as a solvent.

We have also tried to reduce the terphenyls with K, but were never able to resolve any HFS, we found only one single absorption line with a line width of the order of 10 Gauss. This behaviour of the terphenyls in contrast to other aromatic ions like diphenyl could not be explained so far.

The theoretical spin densities of the p-terphenyl have been given by WEISSMAN and are shown in Fig. 5. In agreement with this calculation we have found the highest value for the coupling constant a_1 with the two para protons. If we attribute the constant a_2 to the ortho-protons, the ratio $a_1/a_2 \approx 3/2$ agrees also fairly well with the calculation. The agreement is much worse for the m-protons, but the

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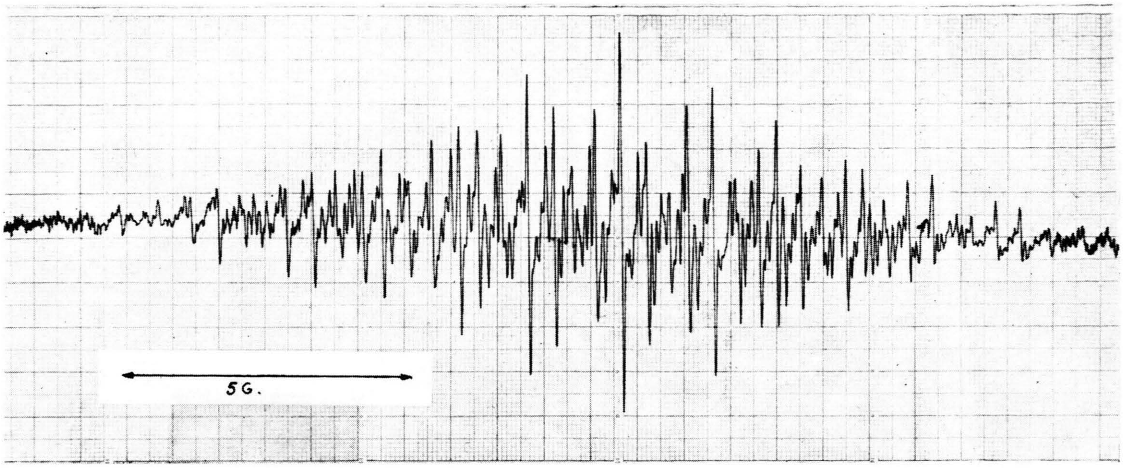


Fig. 3. Spectrum of orthoterphenyl at room temperature (b).

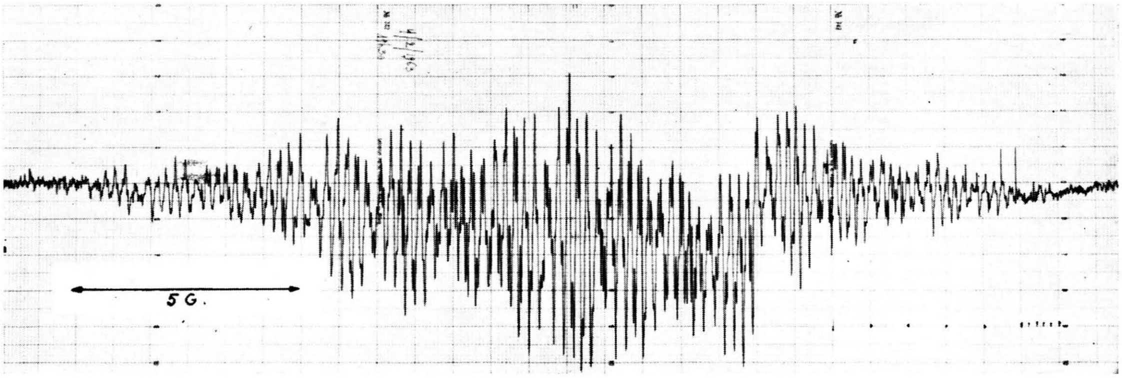
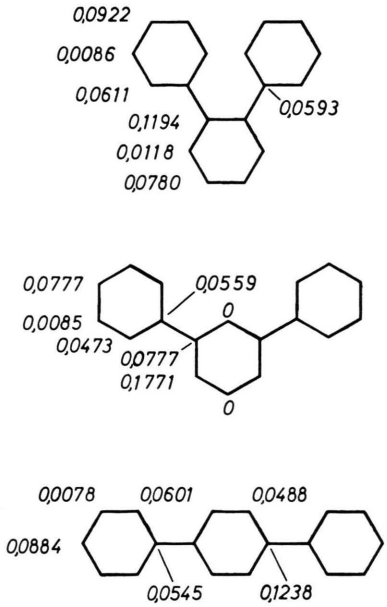


Fig. 4. Spectrum of metaterphenyl at room temperature.



← Fig. 5. Hückel-unpaired electron densities of the terphenyl anions.

deviation is similar to that found for the biphenyl-anion.

The best resolution has been obtained in DME at $-40\,^{\circ}$C. It may be possible that the linewidth is caused by unresolved HFS originating from interaction with the Na nucleus. Since Atherton and Weissman [7] have observed a decreasing interaction between the naphthalene-ion and the Na nucleus at decreasing temperature, a similar interaction could be the explanation for the observed behaviour. However, we feel that other mechanismes such as spin orbit and dipolar interaction cannot be excluded.

The spin densities for the ortho- and meta-terphenyl as calculated by simple Hückel-approximation are shown in Fig. 5. Because of the symmetry of the ortho-terphenyl one would expect a spectrum with an uneven number of components as given in Fig. 3. However, the primary product seems to possess an even number of lines. A possible explanation could be that the unpaired electron cannot move freely within the whole molecule since it is not planar, but for reasons of steric hindrance at least one phenyl-group must be more or less perpendicular to the rest of the molecule. If the unpaired electron is restricted to two phenyl groups for a time long compared with the reciprocal coupling constants, a spectrum with an even number of lines does not seem impossible.

In the case of the m-terphenyl the resolution obtainable with our spectrometer using 100 Kc. modulation was not sufficient; only about 250 of the 900 theoreticall lines could be partially resolved. It may be mentioned that the even number of lines observed agrees with the symmetry of the molecule. The total extent of the spectrum (25 Gauss) is about 30% larger than for the para- and ortho-terphenyl indicating appreciable negative spin densities at some positions.

Influence of Atomic Masses on the Coriolis Coupling Coefficients in some Symmetrical Molecules. Part II Tetrahedral XY_4 Molecules and Ions

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An investigation of Coriolis coupling of rotation-vibration in 35 tetrahedral XY_4 ions and 5 molecules of the same type is reported. The theoretical limits for $|\zeta_{24}|$ and ζ_{44} are quoted. The results for ζ_{24} are represented graphically and discussed in relation to the methane-curve for mass dependence of the same quantity.

In the first paper of this series [1] we communicated our studies on Coriolis coupling coefficients (ζ-values) for 36 tetrahedral XY_4 molecules. The main subject of the present work is a corresponding study of tetrahedral XY_4 ions. Also supplementary results are given for 5 molecules, which have not been included in the cited paper [1].

1. Brief Survey of the Theory

The Coriolis coupling of the presently considered molecule model (XY_4 of T_d symmetry) is described in terms of two ζ values, viz. ζ_{24} and ζ_{44}. These are of the types $E \times F_2$ and $F_2 \times F_2$, respectively, where E and F_2 refers to the species of the appropriate symmetry group (T_d). Theoretical limits for $|\zeta_{24}|$ and ζ_{44} have been found when the mass ratio,

$$\varrho = m_Y / m_X ,$$

approaches infinity or zero. The limiting values are as follows:

$$\varrho \to \infty ; \quad |\zeta_{24}| \to \tfrac{1}{2} , \quad \zeta_{44} \to \tfrac{1}{2} \text{ (upper limitis).}$$

$$\varrho \to 0 ; \quad |\zeta_{24}| \to 8^{-1/2} (1 - \tfrac{1}{3}\varkappa)^{1/2} , \quad \zeta_{44} \to -\tfrac{1}{4}(1+\varkappa) \text{ (lower limits).}$$

Here $\varkappa$ is a function of the force constants belonging to the triply degenerate species, viz.,

$$\varkappa = (\tfrac{1}{2} F_3 - F_4 + 4 F_{34}) [(\tfrac{1}{2} F_3 - F_4)^2 + 2 F_{34}^2]^{-1/2} .$$

For exact explanation of the symbols, and further details, the previous article of this series [1] should be consulted.

2. Five Tetrahedral XY_4 Molecules

The presently considered molecules are specified in Table 1, along with the corresponding mass ratios (ϱ) and values of $\varkappa$. The vibrational frequencies were taken from Nagarajan [2, 3], and an Urey-Brad-

Molecule	$\varrho = m_Y/m_X$	$\varkappa$	Reference
SnH_4	0.008	1.126	2
ZrF_4	0.208	1.187	2
TiF_4	0.397	1.252	2
TiI_4	2.649	2.471	2
SiI_4	4.518	1.491	3

Table 1. Mass ratios and $\varkappa$ of 5 tetrahedral XY_4 molecules.

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[2] G. Nagarajan (to be published).

[3] G. Nagarajan (to be published).