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ESR Studies of the Conformation and Restricted Rotation of 4-Phenyl-1,3-dioxane Anion

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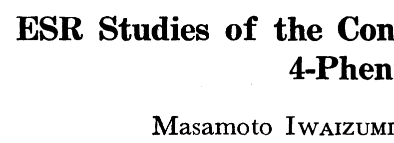
The ESR of the 4-phenyl-1,3-dioxane anion shows a line-width alternation effect which can be attributed to the restricted rotation between the 1,3-dioxane and benzene rings. From the temperature dependence of the line-width alternation effect, the activation energy was determined to be 180 ± 110 cal·mol^{-1}. The preferential conformation between the two rings was estimated from the hyperfine splitting constant of the proton at the 4 position in the 1,3-dioxane ring, to be that where the two rings have some angle close to 90° rather than the structure where they are parallel. It was also found that an odd electron, which mainly occupies a vacant π orbital in the benzene ring, delocalizes appreciably into a part of the 1,3-dioxane ring.

Studies of hindered intramolecular motion have attracted much interest. In some cases, ESR has been a very effective technique for this kind of study. In this paper we wish to report an investigation of the restricted rotation and the preferential conformation between the benzene and 1,3-dioxane rings in the anion of 4-phenyl-1,3-dioxane (I) by means of ESR.



[I]

The ESR of this anion shows a line-width alternation effect, which can be connected to the restricted rotation between the benzene and 1,3-dioxane rings. Since β-proton hyperfine splitting constants are sensitive functions of molecular geometry,[1] the hyperfine splitting constants of the proton at the 4 position of the 1,3-dioxane ring are also an effective source of information about the conformation and restricted rotation between the two rings. Although the conformational analysis of saturated heterocyclic rings is one of the most interesting problems in organic stereochemistry, no information about the structure of the 1,3-dioxane ring of this anion can be obtained by ESR. It can be seen, however, from a NMR study of the neutral molecule of 4-phenyl-1,3-dioxane that the phenyl group is in an equatorial position of the 1,3-dioxane ring. The details of the NMR study of this material, however, will not be discussed here.

Experimental

The anion of 4-phenyl-1,3-dioxane was prepared by the reduction of 4-phenyl-1,3-dioxane with sodium-potassium alloy using a mixed solvent of tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) in a 1 : 1 volume ratio. The 4-pheyl-1,3-dioxane used was obtained commercially (Tokyo Kasei's product) and was purified by distillation. The distilled 4-phenyl-1,3-dioxane was stored over a potassium metal in a bottle connected to a vacuum line. For the preparation of the anion, the compound was taken by distillation from the bottle through the vacuum line into a reaction vessel. The reduction reaction did not proceed in THF or when sodium or potassium was used separately.

The ESR spectra were obtained on a Hitachi Model 771 X-band ESR spectrometer. Variable temperature experiments were performed using a Hitachi gas-flow-temperature control unit. The calculation for the simulation of the spectra was carried out using the NEAC 700 computer at the Tohoku University Computer Center.

Results and Discussion

Reaction of 4-phenyl-1,3-dioxane with Sodium-potassium Alloy. A colorless solution of 4-phenyl-1,3-dioxane turns orange upon contact with sodium-potassium alloy and then changes to green in a few hours. This reaction rate is prompted by an increase

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[1] a) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960). b) E. W. Stone and A. H. Maki, *ibid.*, **37**, 1326 (1962).

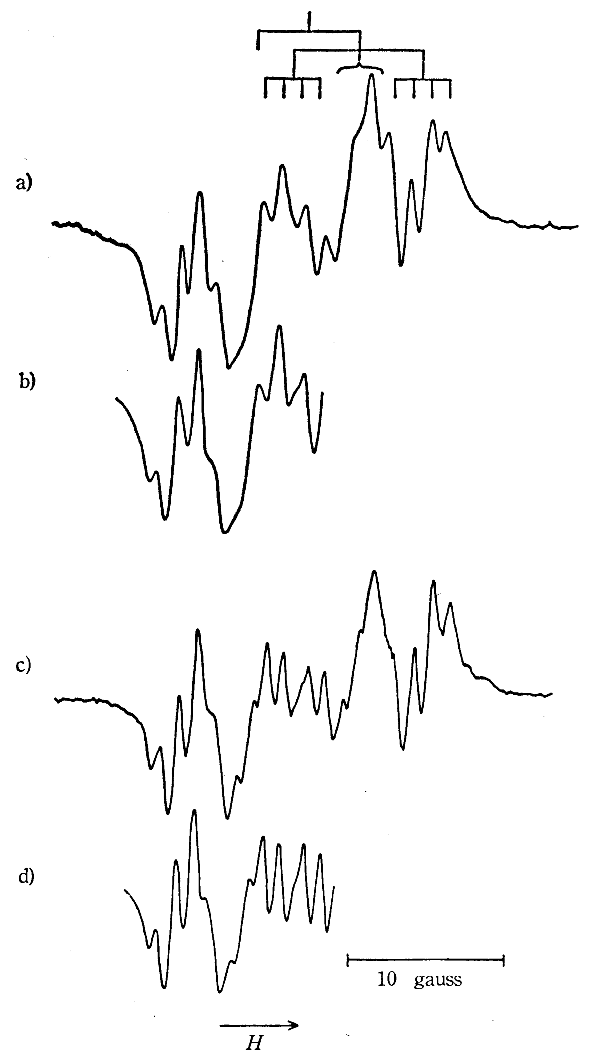


Fig. 1. ESR spectra of the 4-phenyl-1,3-dioxane anion.
a) Spectrum at −8°C. b) Computer-simulated spectrum for (a) using the hyperfine splitting constants listed in Table 1 and the parameters, $\Delta a = 1.30$ gauss, $\tau = 1.6 \times 10^{-7}$ sec, and $T_2^{-1} = 2.43$ MHz. c) Spectrum at −100°C. d) Computer-simulated spectrum for (c) using the hyperfine splitting constants listed in Table 1 and the parameters, $\Delta a = 1.30$ gauss, $\tau = 2.0 \times 10^{-7}$ sec, and $T_2^{-1} = 1.80$ MHz.

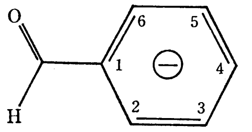
in the quantity of DME in the mixed solvent. Both the orange and green solutions show ESR spectra. Figure 1 shows the spectra which were taken from the orange solution. This spectra can be attributed to the 4-phenyl-1,3-dioxane anion, while the spectrum taken from the green solution consists of 25(=5×5) hyperfine lines and fits perfectly with the hyperfine pattern of the naphthalene anion.[2] The change in color from orange to green, therefore, may be attributed to the formation of the naphthalene anion from the 4-phenyl-1,3-dioxane anion. The reaction mechanism will be discussed elsewhere.

The Line-width Alternation Effect in ESR and the Restricted Rotation between the Benzene and 1,3-dioxane Rings. Figure 1 shows that the spectra of the 4-phenyl-1,3-dioxane anion are temperature-dependent, although the change with the temperature is not very drastic. The spectra at room temperature can be analyzed in terms of two sets of doublet splittings due to hyperfine interaction with single protons, a triplet splitting which is due to two protons and which shows a line-width alternation effect, and a quartet splitting due to the interaction with three protons. It is seen, through the computer simulation of the spectra, that the quartet splitting splits to a doublet and a triplet splitting at lower temperatures. The hyperfine splitting constants, as determined by the computer simulation of the spectra, are listed in Table 1. The assignment of the hyperfine splitting constants to the proton positions was reasonably made by comparison with the hyperfine splitting constants for the acetophenone or benzaldehyde anion previously reported by Steinberger and Fraenkel.[3] The hyperfine splitting constants for the 4-phenyl-1,3-dioxane and benzaldehyde anions are compared in Table 1. Apparently the protons which show the line-width alternation effect can be assigned to the protons at the 2′ and 6′ positions of the benzene ring. In the cases of the acetophenone and benzaldehyde anions, the carbonyl groups are locked into the plane of the aromatic ring, and the two ortho protons as well as the two meta protons show different hyperfine splitting constants. It seems likely that, as in the case of the acetophenone or benzaldehyde anion, the hyperfine splitting constants of two protons at the 2′ and 6′ positions of the 4-phenyl-1,3-dioxane anion have different splitting constants because of the presence of the oxygen atom at the 3 position in the

TABLE 1. HYPERFINE SPLITTING CONSTANTS OF THE 4-PHENYL-1,3-DIOXANE AND BENZALDEHYDE ANIONS (IN GAUSS)

4-Phenyl-1,3-dioxane anion			Benzaldehyde anion[b]	
Positions	Splitting constants −100°C	Splitting constants −8°C	Positions[c]	Splitting constants
2′, 6′	4.186[a]	4.285[a]	2	4.685
			6	3.393
3′, 5′	1.035	1.209	3	1.307
			5	0.750
4′	6.712	6.703	4	6.471
4	1.166	1.209	CHO	8.507

a) These protons show the line-width alternation effect and the hyperfine splitting constant listed is the average value for the two potons.
b) Taken from reference 3.
c) Numbering for the proton positions is as follows.



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[2] a) B. H. J. Bielski and J. M. Gebicki," Atlas of Electron Spin Resonance", Academic Press, New York, N. Y. (1967), p. 351.
b) M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, This Bulletin, **41**, 732 (1968).

[3] N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

1,3-dioxane ring. The line-width alternation effect, therefore, can be attributed to the modulation effect of the 2′ and 6′ proton hyperfine splittings caused by the restricted rotation between the benzene and 1,3-dioxane rings, the modulation of the hyperfine splittings having an out-of-phase correlation for the two protons.

By using Bloch's two-jump model,[4)] the spectra at various temperatures were analyzed in order to estimate the activation energy for the rotation. According to the theory of the line-width alternation effect,[4d,5)] the line-width broadening is proportional to the square of the magnitude of fluctuation in the hyperfine splitting, Δa, and to the correlation time for the fluctuation, τ, *i. e.*, proportional to $\Delta a^2 \cdot \tau$. Since the hyperfine splitting constants for the static conformation of the molecule were not available, we assumed the magnitude of the fluctuation for the 2′ and 6′ proton hyperfine splittings to be 1.30 gauss by reference to the case for the hyperfine splitting constants of the benzaldehyde anion. By neglecting the temperature dependence of the value for Δa, the τ values were evaluated for the spectra at various temperatures by computer simulation of the spectra. Of course, the absolute magnitude for the τ thus obtained contains some error, because of the use of an assumed value for Δa. However, the error in the τ will not lead to a large error in the calculation of the activaiton energy for the rotation, since a large part of the error in τ can be compensated for the procedure for obatining the activation energy by the Arrhenius relation. In Fig. 2, the plot of $\log_{10}(1/\tau)$ *vs.* $1/T$ is shown. The activation energy is obtained as $180 \pm 110\ \mathrm{cal \cdot mol^{-1}}$ from the slope by the Arrhenius relation. Here the $1/\tau = k$ relation was assumed, where k is a rate constant for rotation.

In the cases of the acetophenone and benzaldehyde anions, the meta protons also have different hyperfine splitting constants, just as they have different ortho proton hyperfine splittings. In the present case, however, it was not obvious from the computer simulation of the spectra whether or not the hyperfine splitting of the 3′ and 5′ protons also shows a line-width alternation effect.

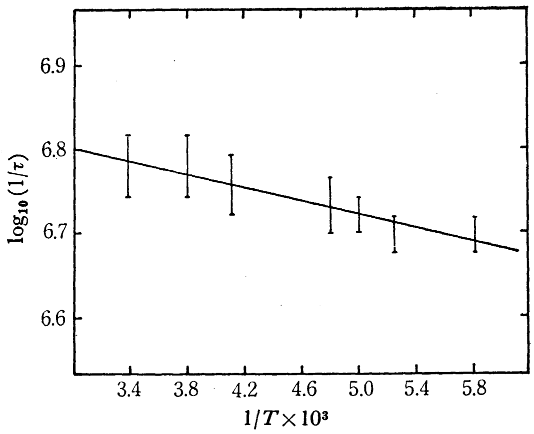

Fig. 2. Plot of $\log_{10}(1/\tau)$ against $1/T \times 10^3$.

It should be noticed here that the evaluated activation energy is small compared to kT. In such a situation, the two-jump model, which assumes a "jump" between the two conformations, may not be strictly correct for treating the system. However, it may not be unreasonable to consider that the activation energy thus estimated still has meaning as an approximate value.

Electron-spin Delocalization in the Molecule. It is well known that the hyperfine splitting constant of the aromatic ring proton, a_i^{H}, can be related to the spin density, ρ_i^{H}, on the carbon atom to which the proton is attached by McConnell's relation, $a_i^{\mathrm{H}} = Q^{\mathrm{H}} \rho_i^{\mathrm{H}}$, or a modification of it.[6)] Here, Q is an empirical constant and has a value of $-22.5 \sim -30$ gauss. In Table 2 the spin densities evaluated by McConnell's relation using $Q = -22.5$ guass are listed. From a comparison with the calculated spin densities for the acetophenone or benzaldehyed anion,[3)] a negative sign was assigned to that for the 3′ and 5′ positions. As Table 1 shows, the hyperfine splitting constant for the protons at the 3′ and 5′ positions has a positive temperature coefficient, showing a contrast to the other ring-proton hyperfine splittings. On a basis of a consideration of the vibrational effects on the proton hyperfine splitting constants,[7)] the assignment of the negative sign to the spin density at the 3′ and 5′ positions may also be justified by this positive temperature coefficient of the hyperfine splitting constant.

Table 2. Spin densities for the 4-phenyl-1,3-dioxane and benzaldehyde anions

4-Phenyl-1,3-dioxane anion		Benzaldehyde anion	
Positions	Spin densities[a)]	Positions	Spin densities[b)]
2′, 6′	0.186	2	0.1748
		6	0.1196
3′, 5′	(−)0.046[c)]	3	−0.0567
		5	−0.0226
4′	0.299	4	0.2492

a) Calculated by the relation, $|\rho_i| = |a_i^{\mathrm{H}}|/22.5$ using the hyperfine splitting constants obtained at −100°C.
b) Taken from reference 3. Calculated values.
c) See text.

Interstingly, it is shown that the spin density on the benzene ring is far less from unity. That is, the algebraic sum of the spin densities for the carbon positions from 2′ to 6′ is only 0.6; in order for the sum of the spin densities on the benzene ring to be unity, one must consider the spin density of the 1′ position

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4) a) H. S. Gutowski and C. H. Holm, *J. Chem. Phys.*, **25**, 1288 (1956). b) H. S. Gutowski, D. W. McCall and C. P. Slichter, *ibid.*, **21**, 279 (1953). c) H. M. McConnell, *ibid.*, **28**, 430 (1958). d) P. Sullivan and J. R. Bolton," Advances in Magnetic Resonance" Vol. 4 ed J. S. Waugh, Academic Press, New York, N. Y., (1970) p. 39.

5) a) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963). b) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).

6) a) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958). b) J. P. Colpa and J. R. Bolotn, *Mol. Phys.*, **6**, 273 (1963). c) G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theoret. Chim. Acta* (Berlin) **1**, 404 (1963).

7) a) M. Iwaizumi and G. K. Fraenkel, unpublished data. b) A. H. Reddoch, C. L. Dodson and D. H. Paskovich, *J. Chem. Phys.*, **52**, 2318 (1970).

to be 0.4. One can see from the comparison with the spin densities for the acetophenone or benzaldehyde anion that this estimated spin density for the 1 position is unreasonably large; about 0.1 seems to be suitable for this position. The spin density on the benzene ring is, therefore, apparently far from a full unit. This decrease in the spin densities on the benzene ring from unity indicates that the electron spin delocalizes into a part of the 1,3-dioxane ring.

In studies of the conformation of organic π radicals with a cyclopropyl substituent, it has been shown that the cyclopropyl ring preferentially adopts a bisected conformation to the aromatic ring except in sterically-crowded environments, and that the electron-donative hyperconjugation effect of the cyclopropyl ring has an important role in the adoption of the conformation.[8] This hyperconjugation effect of the cyclopropyl ring has been explained by Walsh's model,[9] which considerd the sp^2 hybridization for the carbon valency to hydrogen and the $2p$ atomic orbital for carbon valencies to carbon. Walsh points out, in his theoretical study of cyclopropane and related compounds, that even cyclohexane appears to have a greater tendency towards a $2p$ character in the carbon valencies to carbon. In view of the fact that the 1,3-dioxane ring prefers a conformation at right angles to rather than planar with the benzene ring, as will be discussed later, the electron-spin delocalization may take place by means of the hyperconjugation effect of the 1,3-dioxane ring. On the other hand, the charge-transfer effect of a lone-pair electron on the oxygen atom at the 3 position may be considered as another possible mechanism for the electron-spin delocalization into the 1,3-dioxane part. In both cases, an electron with a β spin will transfer from the 1,3-dioxane ring or the lone-pair electron of the oxygen into the vacant π orbital of the benzene ring, leaving a α spin on the 1,3-dioxane part. However, there is not definite experimental proof on which mechanism is dominant.

Conformation Preference of the 1,3-*dioxane Ring in Relation to the Benzene Ring.* The β proton hyperfine splitting constants are sensitive to the conformation of the C–H$_\beta$ bond. When the alkyl group is undergoing torsional oscillation about a particular equilibrium conformation of a restricted rotation, the β proton hyperfine splitting constants are temperature-dependent and are generally expressed by the equation;[1a]

$$a_\beta{}^{\mathrm{H}} = B\langle\cos^2\theta\rangle_{\mathrm{av}}\rho_i \tag{1}$$

Here, B is an empirical constant and in the range of of 45±6 gauss, ρ_i, is the spin density at the trigonal carbon (i) of the attachment, and θ is the dihedral angle between the C–H$_\beta$ bond and the $2p$ orbital on the i-th carbon. The average $\langle\mathrm{con}^2\theta\rangle$ depends upon the nature of the rotation and is expressed by the following equation:

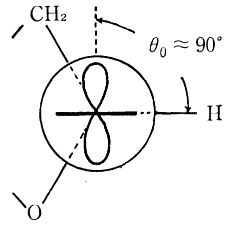
$$\langle\cos^2\theta\rangle_{\mathrm{av}} = \frac{\sum_{j=0}^{\infty} g_j\langle\cos^2\theta\rangle_j \exp\,(-E_j/kT)}{\sum_{j=0}^{\infty} g_j \exp(-E_j/kT)} \tag{2}$$

with:

$$\langle\cos^2\theta\rangle_j = \langle\psi_j(\alpha)\,|\cos^2(\alpha+\theta_0)|\,\psi_j(\alpha)\rangle \tag{3}$$

in which ψ_j and E_j designate the wave function and the energy eigenvalue respectively for the torsional quantum state or rotational state j, in which g shows the degeneracies of the state, and in which θ_0 is the equilibrium angle of the θ. The ψ_j and E_j values used for these equations are obtained by solving the Schrödinger equation for the torsional oscillation or restricted rotation of the system. In the present case, as Table 1 shows, the proton at the 4 position shows a temperature-dependent hyperfine splitting with a positive temperature coefficient. However, it is not quantitatively treated here, and only the equilibrium conformation of the 1,3-dioxane ring against the benzene ring is qualitativaly considered.

Stone and Maki[1] calculated the values of $\langle\cos^2\theta\rangle$ for some typical cases as a function of the activation energy for four possible values of θ_0 and T=298°K. We refer to his calculation for estimating θ_0 for the case of the 4-phenyl-1,3-dioxane anion. In the present case, if it is assumed that the spin density at the 1′ position is 0.1, and if we use B=45 guass, $\langle\cos^2\theta\rangle$ is obtained as 0.25, corresponding to $\langle\theta\rangle=60°$. The value of $\langle\theta\rangle$ for the free rotation is 45°, and as the potential barrier for rotation increases, the value of $\langle\theta\rangle$ approaches the value for the equilibrium conformation. Taking into consideration the fact that the activation energy for the rotation of the 4-phenyl-1,3-dioxane anion is 180 cal·mol^{-1}, the equilibrium angle of the C–H bond must be larger than 60°, and rather close to 90° (II). The positive temperature coefficient of the hyperfine splitting constant for this proton will support such a bisected conformation of the 1,3-dioxane ring against the benzene, ring. Such a conformation seems plausible from the point of view of the steric effect between the two rings, and also in view of the conjugative electronic interaction discussed above, although the contribution of both interactions are small, as is shown by the small activation energy obtained.



[II]

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[8] a) G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, **89**, 160 (1967). b) N. L. Bauld, R. Gordon and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967). C) N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon and J. S. Hyde, *ibid.*, **91**, 6666 (1969).

[9] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).