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ENDOR Investigation of Internal Dynamics in Cyclopropyl Galvinoxyl Radicals

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Abstract: The ESR and ENDOR spectra of cyclopropyl-substituted galvinoxyls exhibit temperature-dependent line positions and line widths. This behavior could be interpreted by assuming two different types of dynamic processes to be present, giving rise to temperature-dependent β-proton hyperfine couplings and to line-shape effects, respectively. The latter process could be described by a jump model for the hindered rotation of the aroxy rings within the galvinoxyl moiety. Barriers to internal rotation and activation parameters of the jump processes have been evaluated. The measured hyperfine coupling constants were assigned to molecular positions; the signs of the couplings could be determined by means of the electron-nuclear-nuclear TRIPLE resonance technique. Possible mechanisms of the dynamic processes and the equilibrium geometries of the radicals are briefly discussed.

Introduction

The magnetic resonance methods ESR and ENDOR have proved to be of unique value in the elucidation of the structure of organic free radicals. Besides the determination of electron spin distributions and equilibrium conformations, e.g., twist angles, they permit an insight into the internal dynamics of molecules.[1] Such dynamic processes can affect the widths of spectral lines provided the characteristic time of the interconversions is comparable to the ESR/ENDOR time scale (10^{-9}–10^{-4} s).[2] Quite different mechanisms can be responsible for the intramolecular dynamic behavior: hindered rotation,[3] ring inversion,[4] pyramidal atomic inversion,[5] intramolecular electron transfer,[6] ion pairing,[7] or torsional oscillations.[8] There are two distinct effects with respect to the temperature-dependent appearance of the spectra. Firstly, β-proton hyperfine coupling constants often show a marked temperature dependence due to torsional oscillations of sterically hindered alkyl groups.[9] Secondly, line shapes can be temperature dependent because the molecule is involved in a rate process modulating isotropic hyperfine couplings, the rates being temperature dependent.[10] Furthermore, intermolecular exchange effects, i.e., chemical and Heisenberg exchange, may be a cause of line broadening.

In the present paper we report on the syntheses and ESR/ENDOR studies of cyclopropyl and cycloprop[*a*]acenaphthylenyl galvinoxyls. Since we are currently interested in studying the internal dynamics in substituted galvinoxyl radicals,[11,12] we found it worthwhile to investigate in detail the different types of dynamic processes conceivable in cyclopropyl galvinoxyl, e.g., hindered rotation of the cyclopropyl group and the phenoxyl groups. Another aspect was to gather further information on the spin-transfer mechanism, i.e., spin polarization or hyperconjugation, into the cyclopropyl substituent. For that purpose, the possibility of relative sign determination of the hyperfine couplings by means of the electron-nuclear-nuclear TRIPLE resonance technique[13] appeared to be of special value. In order to increase the bulkiness of the substituent, we have extended our investigation to cycloprop[*a*]acenaphthylenyl galvinoxyl.

Experimental Section

Preparation of Compounds. The galvinoxyl precursors, i.e., the galvinols, were prepared from cyclopropanecarboxylic acid (to give **1b**), from 6b,7a-dihydro-7*H*-cycloprop[*a*]acenaphthylene-7-carboxylic acid (to give **2b**), and from the respective deuterated carboxylic acid[14] (to give **3b**) by using our organometallic synthetic pathway described elsewhere.[15] Corresponding to this procedure, the esterified carboxylic acids **1a**–**3a** were treated with (2,6-di-*tert*-butyl-4-lithium phenoxy)trimethylsilane, followed by elimination of the protecting trimethylsilyl group. The NMR spectra of all compounds are consistent with the structures given in Figure 1. In particular, the possibility of a rearrangement could be ruled out (protons of the three-membered ring, **1b**: δ_A 0.61 ppm, δ_B 1.01 ppm, δ_X 2.33 ppm, J_{cis} = 8 Hz, J_{trans} = 4.5 Hz; **2b**: A_2X spin system, δ_A 3.15 ppm, δ_X 2.32 ppm, J_{AX} = 3.5 Hz). The results for **2b** prove the exo configuration of the galvinol (trans position of the protons) in accordance with previous NMR studies of the carboxylic acid **2a** (methyl ester).[16] Moreover, the galvinoxyls **1c**–**3c** yielded the parent galvinols on reduction.[15] The elemental analyses differ slightly from the usual criterion of $\leq$0.3% deviation, since removal of residual solvent molecules calls for elevated temperatures causing decomposition of the galvinols.

[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]cyclopropane (1b). Cyclopropanecarboxylic acid ethyl ester (0.64 g) was treated with a mixture of 5.0

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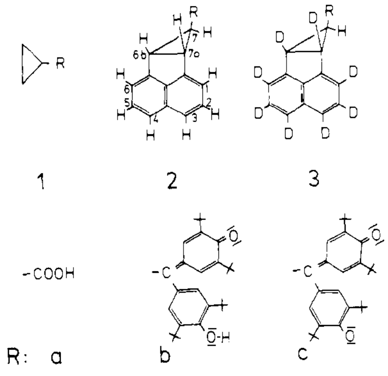

Figure 1. Numbering scheme of compounds: **a**, carboxylic acids; **b**, galvinols; **c**, galvinoxyls.

g of (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane, 9.5 mL of *n*-butyllithium in *n*-hexane (20%), and 2.1 mL of tetramethyldiaminoethane. Subsequent elimination of the trimethylsilyl group with KOH/CH$_3$OH (5%, 10 min, 50 °C) and careful acidification with diluted acetic acid (1:1) yielded 0.65 g of **1b**, mp 159–160 °C. Anal. Calcd: C, 83.06; H, 10.44. Found: C, 83.13; H, 10.02. Mass spectrum (70 eV) *m/e* 462 (M$^+$).

7-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]-6b,7a-dihydro-7*H*-cycloprop[*a*]acenaphthylene (2b) and -d_8 (3b). The respective carboxylic acid **2a** or **3a** (1.35 g) was converted to the trimethylsilyl ester by reaction with 0.96 mL of triethylamine and 0.88 mL of chlorotrimethylsilane for 3 h at 50 °C. After separation from triethylamine hydrochloride, the solution of the ester was treated with a mixture of 5.0 g of (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane, 9.5 mL of *n*-butyllithium in *n*-hexane (20%), and 2.1 mL of tetramethyldiaminoethane. Subsequent elimination of the trimethylsilyl groups under conditions identical with those described for **1b** yielded 2.2 g of the respective galvinol **2b** or **3b**, mp 185–186 °C. Anal. Calcd for **2b**: C, 85.96; H, 8.59. Found: C, 85.61; H, 8.62. Mass spectrum (70 eV) *m/e* 856 (M$^+$), for **3b** *m/e* 864 (M$^+$).

The galvinoxyl radicals were prepared on a vacuum line following our procedure recently described,[17] i.e., treating carefully degassed toluene solutions of the galvinols with lead dioxide in the ESR/ENDOR sample tube, allowing distillation of the solvent under high vacuum conditions for concentrating or diluting.

Instrumentation. To record the ESR spectra a commercial AEG 12-X (125 kHz) spectrometer was used. The spectrometer used for ENDOR and TRIPLE resonance consists basically of an AEG-20-X ESR spectrometer; the additional NMR equipment was built in this laboratory. A detailed description of our cw ENDOR spectrometer will be presented elsewhere.[18] The temperature of the sample was varied with an AEG temperature control unit and measured with a copper-constantan thermocouple; temperature data are accurate within ±1 K over the length of the sample in the sample tube within the cavity. Simulations of ESR spectra were performed with a CDC Cyber 72 computer system with STATOS plotter 3313.

Theory

Influence of Jump Processes on Line Shapes. The treatment of line-shape effects in ESR and ENDOR is largely the same as in dynamic NMR.[19] The line-broadening effects of modulating an isotropic hyperfine coupling constant can be investigated by using the modified Bloch equations,[20] the density matrix treatment,[21] or the relaxation matrix treatment.[22] The theory and applications to the study of chemical rate processes by means of ESR are covered by a number of reviews.[23] In the following it will be assumed that the phenomena can be described by jump models.[19]

The following equations[3] relating the rate constant k or the mean lifetime τ of an individual site ($k = 1/\tau$) to the line width, $\delta\omega$ (full width at half-height, ω in angular frequency units), or to the line separation, $\Delta\omega$, refer to a two-jump model with equivalent sites. In the slow-jump region ($\tau\Delta\omega_0 \gg 1$), the additional line broadening is given by:

$$\delta\omega = 2/\tau \tag{1}$$

and the separation of two correlated lines is diminished according to:

$$\Delta\omega = (\Delta\omega_0{}^2 - 8/\tau^2)^{1/2} \tag{2}$$

In the fast-jump region ($\tau\Delta\omega_0 \ll 1$) the additional line broadening is given by:

$$\delta\omega = \frac{1}{4}(\Delta\omega_0)^2\tau \tag{3}$$

and at the coalescence point $\tau\Delta\omega_0 = 2\sqrt{2}$. The line-separation parameter, $\Delta\omega_0$, can be expressed in terms of hyperfine coupling constants (in frequency units):

$$\text{ESR:} \qquad \Delta\omega_0 = 2\pi|(a_1 - a_2)(M_1 - M_2)| \tag{4}$$

$$\text{ENDOR:} \qquad \Delta\omega_0 = \pi|a_1 - a_2| \tag{5}$$

where M_1 and M_2 are the spin quantum numbers of the nuclei or groups of equivalent nuclei involved in the jump process. The applicability of eq 1 to 3 is restricted to the limiting cases; more complicated formulas with a wider range of validity are given in ref 24 and 25. In the intermediate region or in the case of overlapping or inhomogeneously broadened lines, a complete line-shape analysis has to be performed. An explicit expression for a simple two-jump model is given in ref 26, an equation for the complex magnetization for a four-jump model in ref 27.

In view of the complexity usually encountered in the ESR spectra, it is often advantageous to make use of the higher resolution of ENDOR in the study of dynamic processes.[3,28] However, ENDOR spectra with a good signal-to-noise ratio are only observable in a much smaller temperature region and special care has to be taken in the extrapolation of the ENDOR line widths to vanishingly small NMR fields.[3] Furthermore, the unperturbed line width is less well defined because of the complicated relaxation mechanisms which determine the ENDOR line widths.[29]

Temperature Dependence of β-Proton Hyperfine Coupling Constants. Couplings of β protons, i.e., protons which are one carbon removed from a trigonal carbon bearing π spin density, are generally ascribed to hyperconjugative interactions. This mechanism is characterized by two main features because of the implied direct overlap with the 2p$_z$ orbital on the α carbon atom. Firstly, in contrast to α protons, the β-proton hyperfine coupling should have the same sign as the carbon π spin population ρ_α and, secondly, β-proton splittings show a pronounced orientation dependence, usually of the form:[30]

$$a_\beta = (B_0 + B_2\cos^2\theta)\rho_\alpha \tag{6}$$

where θ is the dihedral angle between the C–H$_\beta$ bond and the 2p$_z$ orbital on the α carbon. This orientation dependence in general gives rise to a strong temperature dependence of β-proton hyperfine couplings due to a different average torsional angle. Depending on the height of the potential barrier and the temperature, the internal rotation can be "frozen out", restricted to torsional oscillations about a preferred dihedral angle θ_0, or ideally free ($\langle\cos^2\theta\rangle = \frac{1}{2}$, e.g., rapidly rotating methyl groups). For the intermediate case, the conventional model assumes that the temperature dependence of β-proton hyperfine coupling constants arises from the fact that the observed coupling is the average of the expectation values of a_β for all torsional states weighted by their populations according to Boltzmann statistics.[31] In the classical approach one obtains:[32]

$$\bar{a}_\beta = \frac{\int_{-\pi}^{\pi} a_\beta(\theta)\exp[-V(\theta)/k_BT]\mathrm{d}\theta}{\int_{-\pi}^{\pi}\exp[-V(\theta)/k_BT]\mathrm{d}\theta} \tag{7}$$

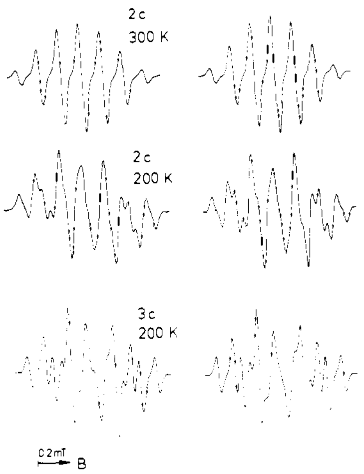

Figure 2. Experimental (left) and computer-simulated (right) ESR spectra of **2c** at 300 K (top), **2c** at 200 K (center), and **3c** at 200 K (bottom) (solvent, toluene).

Table I. Proton Hyperfine Coupling Constants[a]

	a, MHz			
	1c (170 K)[b]	**1c** (210 K)[b]	**2c** (190 K)[b]	**2c** (300 K)[c]
galvinoxyl	+4.03 (2)		+4.26 (2)	
moiety	+3.27 (1)	+3.63 (4)	+2.94 (1)	+3.72 (4)
	+3.01 (1)		+2.80 (1)	
	+0.13 (36)	+0.15 (36)	+0.13 (36)	+0.19 (36)
substituent	−8.05 (1)	−8.00 (1)	−7.86 (1)	−7.37 (1)
		+0.52	+0.90 (1)	

[a] All hyperfine coupling constants are measured by ENDOR, accurate within ±0.01 MHz; the number of equivalent protons is given in parentheses. [b] Solvent toluene. [c] Solvent mineral oil.

where a_β is given by eq 6 and $V(\theta)$ is the potential function which in first order can be represented by:

$$V(\theta) = \frac{V_2}{2}\left[1 - \cos 2\,(\theta - \theta_0)\right] \qquad (8)$$

if the rotating group has C_2 symmetry.

Results and Discussion

Measurement and Assignment of Hyperfine Coupling Constants. Figure 2 (top left) shows the room temperature ESR spectrum of galvinoxyl **2c**, which is virtually identical with those of **1c** and **3c**. The seven-line pattern can readily be interpreted and simulated (right part of Figure 2) on the basis of a set of four equivalent protons (3.7 MHz) and one proton with twice as large a coupling (7.4 MHz), taking account of inhomogeneous line broadening from unresolved hyperfine structure of the *tert*-butyl protons. The appearance of the ESR spectrum of **1c** does not change significantly on lowering the temperature, but there is a striking change in those of **2c** and **3c**; see Figure 2. More detailed information was obtained from the corresponding ENDOR spectra. Figure 3 reveals a splitting of the ENDOR lines belonging to the second largest hyperfine coupling of **1c** when the temperature is decreased to 170 K, indicating an inequivalence of the ring protons in the galvinoxyl moiety. Such a splitting is even more pronounced and already evident at a somewhat higher temperature in the ENDOR spectra of **2c**; see Figure 4. The possibility that the smaller of the splittings might be due to a coherence effect[33] could be ruled out because the splitting remained observable even at reduced rf power. From the general TRIPLE spectra also reproduced in Figures 3 and 4, the signs of all hyperfine couplings could be determined (see Table I), knowing the ring proton couplings of the galvinoxyl moiety to be positive from NMR measurements.[34]

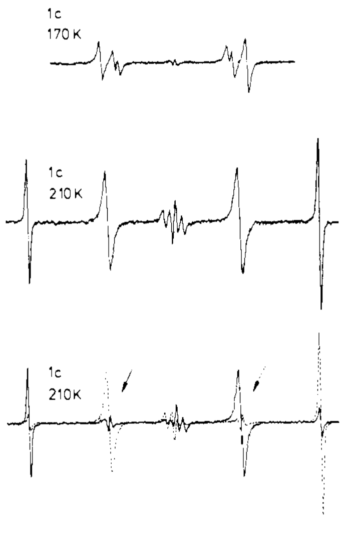

Figure 3. Top: ENDOR spectrum of **1c** at 210 K and part of the spectrum obtained at 170 K (insert), B_{NMR} = 0.46 mT (rotating frame). Bottom: General TRIPLE spectra of **1c** (toluene, 210 K); the arrows indicate the setting of the pump frequency in the two experiments (solid and broken lines, respectively), B_{NMR}(pump) = 0.71 mT, B_{NMR}(scan) = 0.45 mT.

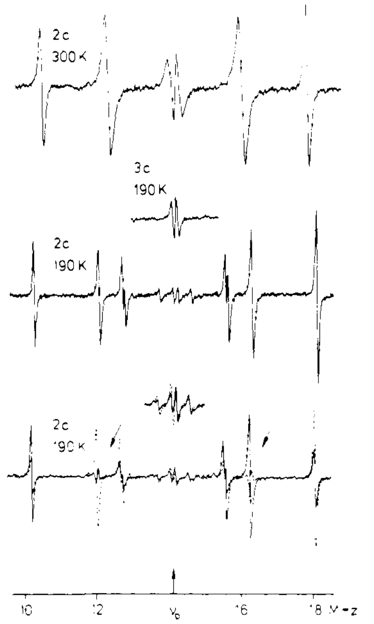

Figure 4. Top: ENDOR spectrum of **2c** at 300 K (solvent, mineral oil). Center: ENDOR spectra of **2c** and **3c** (central part, see insert) at 190 K in toluene, B_{NMR} = 0.42 mT (rotating frame), 10-kHz frequency modulation ± 16 kHz amplitude. Bottom: General TRIPLE spectra of **2c** (toluene, 190 K; insert, gain × 2.5); for experimental conditions see caption of Figure 3.

The assignment of hyperfine coupling constants to the ring and *tert*-butyl protons within the galvinoxyl fragment is based on a comparison with other galvinoxyl systems. The largest coupling (ca. 8 MHz) could unequivocally be assigned to the β proton at the top of the three-membered ring, i.e., the substituted position, by means of the partially deuterated compound **3c**. Accordingly, the coupling of about 0.5 MHz in **1c** must stem from the remaining cyclopropyl protons (γ protons), but the number of contributing protons is not known. However, the respective small coupling (ca. 0.9 MHz) showing up in the

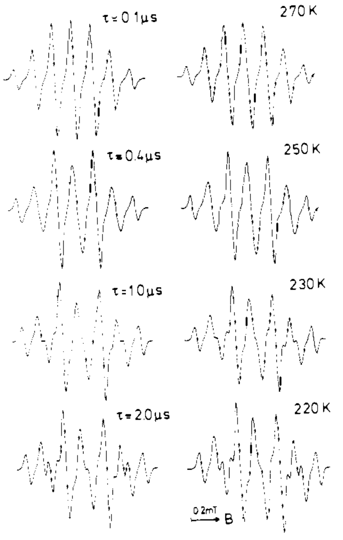

Figure 5. Experimental (right) and computer-simulated (left) ESR spectra of **3c** for a series of temperatures and roughly corresponding mean lifetimes.

Table II. Activation Parameters

	1c[a]	**2c**[b]	**2c**[c]	estimated error
E_a, kJ mol^{-1}	18	33	32	±2
k_0, 10^{11} s^{-1}	0.44	78	16	factor of 2
$\Delta H^{\ddagger}$, kJ mol^{-1}	16	31	30	±2
$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	−47	−6	−20	±6

[a] Determined by ENDOR in the fast-jump region; solvent toluene. [b] Determined by ESR in the fast-jump region and by ENDOR in the slow-jump region; solvent toluene. [c] Determined by ENDOR in the fast-jump region; solvent mineral oil.

low-temperature ENDOR spectrum of **2c** belongs undoubtedly to just *one* γ proton as could be established by computer simulations of the corresponding ESR spectrum (see Figure 2). Obviously, the two protons in the fused positions (6b and 7a) of the cyclopropane ring are inequivalent, indicating a skew conformation of the galvinoxyl moiety with respect to the cycloprop[*a*]acenaphthylene part.

Line-Shape Analysis and Determination of Activation Parameters. The line-shape effects showing up in the ESR and ENDOR spectra of **1c**–**3c** are clearly caused by an intramolecular dynamic process. The four galvinoxyl ring protons yield *three* different hyperfine coupling constants in the low-temperature ENDOR spectra and become apparently equivalent on increasing the temperature. The rate process can adequately be described by a (restricted) four-jump model.[3,27] Two of the four sites are magnetically equivalent within the ENDOR line width, and neglect of the minor inequivalence (**2c**/**3c**: Δa = 0.14 MHz compared to the major splitting of Δa = 1.39 MHz) would allow the application of a two-jump model, vide infra. The inequivalence of the galvinoxyl ring protons must be due to an inequivalence of the two aroxy rings because of different twist angles and/or interactions with the substituent (i.e., the cyclopropyl or cyclopropacenaphthenyl fragment), and furthermore, the two protons of one aroxy ring are not equivalent. The dynamic process, a hindered rotation, can be pictured as a series of interconversions between four energetically equivalent conformations by concerted movements of the two aroxy rings. It has to be noted that an alternative possibility involving pyramidal atomic inversion or a change in hybridization at the central carbon atom could be ruled out by our recent ^{13}C ENDOR study on some substituted galvinoxyl radicals which proved the temperature dependence of the ^{13}C hyperfine coupling constant to be negligible.[12]

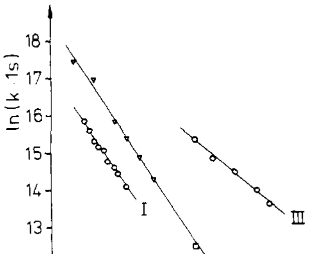

Figure 6. Arrhenius plots of ln k vs. T^{-1} for **2c** in mineral oil (I), **2c** in toluene (II), and **1c** in toluene (III): (○) ENDOR measurements in the fast-jump region; (□) ENDOR measurements in the slow-jump region; (▼) ESR measurements.

Rate data have been obtained from line-width analyses of the ENDOR spectra, for compounds **1c** and **2c** in the fast-jump region and for **2c** also in the slow-jump region, selecting the line which does not show the minor splitting. The ENDOR line at about 18 MHz was assumed to give a reasonably good approximation to the intrinsic line width in the absence of exchange. For signal-to-noise reasons, some overmodulation had to be applied, and the modulation broadening (about 10%) was corrected for subsequently.[35] The measured widths of the exchange-broadened and of the reference line were extrapolated to vanishingly small NMR fields by means of a plot of $\delta\omega^2$ against the radiofrequency power; the error of the extrapolated line widths was about ±5 kHz.[36] Saturation broadening from the microwave field was not detected when the microwave power was chosen about 3 dB lower than necessary to produce the maximum ENDOR signal amplitude. For the evaluation of rate data, the four-jump model was taken account of by using $k = 1/(2\tau)^3$ and replacing eq 3 by the appropriate equation[37] (altering the proportionality constant by 1% for **2c** and by 8% for **1c** as compared to the two-jump model).

For the determination of rate data from ESR spectra, only those of **3c** appeared to be suitable since the low resolution in the case of **1c** and **2c** prevented an unambiguous analysis. Even for **3c**, the additional broadening due to the dynamic process is small as compared to the inhomogeneous line width. Therefore complete line-shape analyses by means of computer simulations were performed. The minor inequivalence of the galvinoxyl ring protons (Δa = 0.005 mT) which is much smaller than the inhomogeneous ESR line width (~0.035 mT) was neglected and a two-jump model was adopted for the analysis. For this purpose, the explicit formula given in ref 26 has been programmed, taking account of all hyperfine splittings including those of the *tert*-butyl protons by means of a superposition procedure. The hyperfine couplings were taken from the ENDOR spectrum. Figure 5 shows the experimental and simulated ESR spectra for a series of temperatures and roughly corresponding mean lifetimes. The precise determination of the rate constants was achieved by a comparison of experimental and calculated line intensities by means of a plot of the calculated amplitude ratio vs. the mean lifetime; for details see ref 37.

The activation parameters were obtained from the Arrhenius plots by standard least-squares procedures; see Figure 6 and Table II. The thermodynamic constants for the activated complex result from application of the Eyring equation.[38] The results obtained for **2c** clearly show a solvent dependence, the rates measured in toluene solutions being three–four times larger than in mineral oil at the same temperature. This fact is further demonstrated by the different coalescence temperatures which have been found in the ENDOR spectra, i.e., (246

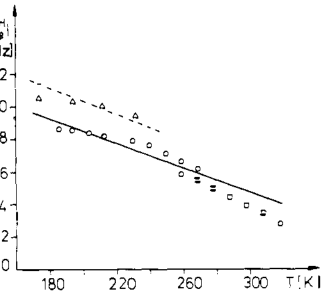

Figure 7. Temperature dependences of the β-proton coupling constants: (△) **1c** in toluene; (○) **2c** in toluene; (□) **2c** in mineral oil. The solid and broken lines represent the calculated values; see text.

± 5) K for toluene and (268 ± 5) K for mineral oil. The lower activation energy of **1c** also manifests itself in a lower coalescence temperature, (192 ± 5) K (toluene).

Discussion of the β-Proton Hyperfine Couplings. Since the sign of the spin population at the central carbon atom of the galvinoxyl moiety can safely be assumed to be negative,[39] the experimentally found negative sign of the β-proton hyperfine coupling constant (top of the three-membered ring) is in accordance with the hyperconjugative model. Accepting the validity of this model, it should be possible to deduce information about the preferred conformation, and, from the temperature dependence of the coupling, about the rotational barrier. A simple approach consists of a comparison with the β-proton hyperfine coupling constant of the corresponding radical in which cyclopropyl is replaced by methyl.[40] Of course, bond angles and lengths in the cyclopropyl group are not identical with those in a methyl group which might somewhat affect the values of the parameters B_0 and B_2 in eq 6. The β-proton hyperfine coupling of methyl galvinoxyl is reported to have the value $|a_{CH_3}{}^H| = 2.3$ G $\triangleq 6.44$ MHz,[41] to be compared with $a_\beta{}^H = -8.05$ MHz in **1c** and $a_\beta{}^H = -7.86$ MHz in **2c**. The larger hyperfine coupling $|a_\beta{}^H|$ in **1c** and **2c** indicates that the rotation of the cyclopropyl with respect to the galvinoxyl moiety is not completely free, conformations with $\theta < 45°$ being preferred.

Figure 7 shows that the absolute values of the β-proton hyperfine couplings decrease on increasing the temperature, approaching the value of the respective coupling in methyl galvinoxyl, i.e., the limit of free rotation. In order to obtain the rotational barrier, eq 7 was tentatively applied to calculate the temperature dependence of $a_\beta{}^H$. Unfortunately, the required parameters are neither exactly known a priori, nor accessible by a fit procedure if all parameters are allowed to vary.[31] Thus, for the parameters B_0 and B_2, standard values have been used ($B_0 = 2.8$ MHz, $B_2 = 138$ MHz),[42] and $\rho_\alpha = -0.0748$ was taken from an HMO-McLachlan calculation for Coppinger's radical.[39] (The spin density distributions in the galvinoxyl moiety, judging from the ring proton couplings in the fast-jump limit, are practically identical in all of these systems.) Approximately twofold symmetry was assumed for the galvinoxyl moiety and accordingly the potential function given by eq 8 was used. The parameters V_2 (potential barrier to internal rotation) and θ_0 (dihedral angle in the equilibrium conformation) were determined by a least-squares fit procedure, yielding $V_2 = 9$ kJ/mol and $\theta_0 = 26.3°$ for **2c**, and using the same value for V_2, $\theta_0 = 24.6°$ for **1c**. However, a closer inspection of Figure 7 reveals that the calculated graph is approximately linear, whereas experimentally an increasingly larger decrease of $|a_\beta{}^H|$ with increasing temperature is found. This might be due to small changes in the equilibrium geometries of the radicals, i.e., θ_0 or even ρ_α. Finally, it should be noted that the magnitude of V_2 fits in with the range of values reported for comparable radicals.[40]

Conclusions

In the present study we have investigated two different types of dynamic processes occurring simultaneously in cyclopropyl-substituted galvinoxyls by means of ESR and ENDOR techniques. (i) Hindered rotation of the substituent group, i.e., cyclopropyl or cycloprop[*a*]acenaphthenyl, with respect to the galvinoxyl moiety gave rise to temperature-dependent β-proton hyperfine couplings, and (ii) hindered rotation of the aroxy rings within the galvinoxyl moiety, being described by a jump model, gave rise to striking line-width and line-shape effects. The respective potential barriers and activation parameters could be evaluated. The activation energies are comparable in magnitude to those previously published for processes involving hindered rotations of phenyl groups in anion radicals (E_a = 18–38 kJ mol^{-1} for *o*- and *m*-terphenyls,[28c] 10–23 kJ mol^{-1} for 1- and 2-phenylnaphthalenes,[28b] and 9–30 kJ mol^{-1} for 2,5-diphenylsiloles[3]). The experimental results establish that the equilibrium geometry is represented by an unsymmetrical, skew conformation of the galvinoxyl part with respect to the three-membered ring of the substituent. It is noteworthy that an increase of the bulkiness of the substituent apparently has a much stronger influence on the jump process ii within the galvinoxyl part than on the potential barrier of process i.

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Structural Effects in Solvolytic Reactions. 31. High Exo:Endo Rate and Product Ratios in the Solvolyses of the 2-Methyl-, 2-Phenyl-, and 2-(5′-Coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-Nitrobenzoates. Further Evidence for the Unimportance of σ-Participation as a Factor in the High Exo:Endo Rate and Product Ratios Realized in the Solvolysis of Tertiary 2-Norbornyl Derivatives[1]

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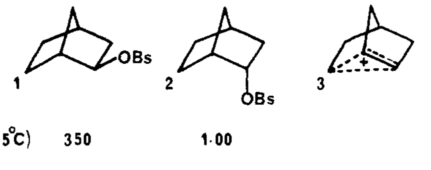
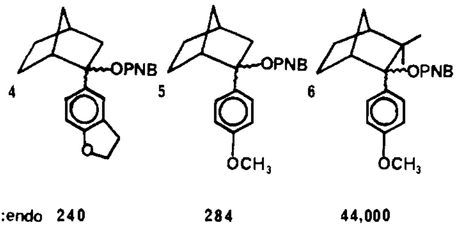
Abstract: Solvolyses of 2-methyl-, 2-phenyl-, and 2-(5′-coumaranyl)-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone reveal high exo:endo rate ratios of 420, 118, and 286, respectively. The solvolyses of these derivatives in the presence of sodium acetate afford exclusively the exo-substituted alcohol. The secondary *exo*-5,6-trimethylene-2-norbornyl system, with its low exo:endo rate ratio, 11.2, has been proposed as a model norbornyl system which solvolyzes through the intermediacy of classical carbocations, constrained into the classical structure by the 5,6-trimethylene bridge. Consequently, these stabilized tertiary derivatives should also undergo solvolyses through the intermediacy of classical carbocations. Yet they exhibit high exo:endo rate and product ratios, at one time considered essential criteria supporting σ-participation with the formation of a σ-bridged intermediate in the solvolysis of the exo derivative. It is clear that steric effects must make major contributions to the high exo:endo rate and product ratios observed in the solvolyses of these stabilized tertiary derivatives.

Winstein and Trifan observed[4] that *exo*-norbornyl *p*-bromobenzenesulfonate (**1**) solvolyzes 350 times faster than its endo epimer (**2**). They suggested that the C_1–C_6 bonding pair assists in the ionization of *exo*-brosylate; however, the geometry of the *endo*-brosylate prevents such anchimeric assistance. The norbornyl cation was formulated as the σ-bridged structure (**3**). Since then, various approaches have been made by physical organic chemists to confirm the existence of such a σ-bridged species in solvolytic media. The question was, is the high exo:endo rate and product ratio observed in the solvolysis of 2-norbornyl brosylate due to the driving force associated with the formation of a stabilized σ-bridged species (**3**) in the transition state? Or is some other factor responsible? The observation that highly stabilized tertiary norbornyl derivatives, such as 2-(5′-coumaranyl)-,[5] 2-*p*-anisyl-2-norbornyl[6] (**4, 5**), and 2-*p*-anisyl-2-camphenilyl[6] (**6**), are also capable of exhibiting such high exo:endo rate and product ratios failed to support the original conclusion. The high exo:endo rate ratios in these systems (**4, 5, 6**) were ascribed to the steric characteristics of the norbornyl system.[7]





High exo:endo rate ratios were also observed in the case of destabilized norbornyl derivatives carrying electron-withdrawing substituents in the 7 position.[8] It was proposed that such substituents resist σ-bridging. Consequently, it would appear that σ-participation cannot be a factor in the high exo:endo rate ratios observed in these derivatives.

On the other hand, the low exo:endo rate ratio, 11.2, observed in the acetolysis of *exo*-5,6-trimethylene-2-norbornyl tosylates (**7, 8**)[9] has been interpreted as indicating that σ-participation cannot be a major factor in this system. It is argued that the 5,6-trimethylene bridge prohibits σ-bridging

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