lower than the triplet state of isobutyroin. Hence, triplet–triplet energy transfer from the former to the latter would be extremely inefficient and may be neglected. The concentration of the isobutyril radical formed in the thiobenzophenone-sensitized reaction is an order of magnitude smaller than in the benzophenone-sensitized reaction. It is not clear yet whether this is due to the absence of the first mechanism in the thiobenzophenone case or to the weaker hydrogen-scavenging capacity of the excited triplet of thiobenzophenone when compared with that of benzophenone.

Acknowledgment. The author wishes to thank M. Collins for assisting with the preparation of thiobenzophenone, and Dr. P. H. Rieger for a helpful communication regarding the computer program used in the present work.

An Electron Spin Resonance Study of the Dihydroxy- and Dimethoxydurene Cation Radicals[1]

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Abstract: The duroquinol cation radical has been studied in aluminum chloride-nitromethane in the temperature range −90 to +10°. At low temperatures the spectrum was analyzed in terms of *cis* and *trans* isomers, in agreement with earlier predictions. A four-jump model gives good agreement with the experimental data throughout the temperature range and the effective potential barrier to rotation is estimated to be 4.2 ± 0.6 kcal/mole. The dimethoxydurene cation radical was shown, on the other hand, to exist as only one species throughout the temperature range, and possible conformations of this radical are discussed. The line-width asymmetries of the duroquinol spectrum indicate that the signs of the isotropic splitting constants of the hydroxyl and methyl protons are negative and positive, respectively.

Modulations of the isotropic splitting constants of esr spectra are known to occur in a variety of ways, such as by hindered rotations,[2] fluctuating complexes with "gegenions" or solvent molecules,[3,4] and conformational interconversions.[5,6] The effect of these modulations[7,8] on the shape of esr lines can be related to the lifetime (τ) of the contributing species. In the limit of long τ values, one observes a spectrum which is the sum of the individual spectra of the contributing species. When τ is short, a time-averaged spectrum of the individual species is observed. At intermediate values of τ, the phenomenon of line-width alternation often occurs and such spectra can be simulated provided an adequate model for the exchange process is available.

Since the lifetime (τ) of each species depends on the temperature, it should be possible to observe the spectra of the individual forms at low-temperature, line-width alternation on raising the temperature and eventually the time-averaged spectra. In the few instances, where this has been done,[9,10] the postulated model can then be tested, and the potential barrier between the individual forms can be estimated.

The duroquinol cation radical lends itself to this type of treatment and has been studied previously in H_2SO_4 by Bolton and Carrington[11] in the range +10 to +50°. The 13 lines from the four methyl group protons were found to be alternatively sharp and broad at lower temperatures, and the methyl group splittings were assumed to depend on the orientation of the hydroxyl groups with respect to the benzene ring plane. This suggests a model of rapid interconversion between four possible conformations (four-jump model), corresponding to two *cis* and two *trans* forms, and can account for the observed line-width alternation.[2,11] However, as pointed out by Fraenkel,[8] if one form (*cis* or *trans*) is present in excess, the problem reduces to a two-jump model, which can also account for the observed spectral changes. To decide between the two models, one should obtain a low-temperature spectrum, when the interconverting forms can be isolated and identified. This is not possible in H_2SO_4, because of the high viscosity of sulfuric acid solution at low temperatures.

However, a recent study of the related hydroquinone cation[10] radical in aluminum chloride–nitromethane[12] suggested that this system would similarly prove advantageous for the duroquinol and dimethoxydurene cation radicals. The latter radical is of interest because of the additional steric interactions.

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[1] Presented, in part, at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

[2] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 37, 1156 (1962).

[3] E. DeBoer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964).

[4] T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 269 (1966).

[5] E. DeBoer and A. P. Praat, *Mol. Phys.*, **8**, 291 (1964).

[6] M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Japan.*, **38**, 1547 (1965).

[7] A. Carrington, *Mol. Phys.*, **5**, 425 (1962).

[8] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

[9] J. R. Bolton, A. Carrington, and P. F. Todd, *Mol. Phys.*, **6**, 169 (1963).

[10] A. B. Barabas, W. F. Forbes, and P. D. Sullivan, *Can. J. Chem.*, **45**, 267 (1967).

[11] J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161 (1962).

[12] W. F. Forbes and P. D. Sullivan, *J. Am. Chem. Soc.*, **88**, 2862 (1966).

Experimental Section

Duroquinol was a commercially available sample. The author is indebted to Drs. H. G. Cassidy and M. Hashimoto for a generous sample of dimethoxydurene. The radicals were produced by reaction with aluminum chloride in nitromethane[12–14] or by dissolution in H_2SO_4, the spectra being determined as described previously.[15] The computer programs were also those described previously.[16]

Results and Discussion

Duroquinol. The experimental spectrum (Figure 1) shows pronounced changes with temperature. At +2°, the spectrum (Figure 1a) corresponds to rapid interconversion, and a time-average value for the splitting constants is obtained. The 12 methyl protons give 13 lines (splitting constant 2.051 gauss), each line being further split into triplets (2.615 gauss) because of the two hydroxyl protons. However, the lines do not obey the binomial intensity distribution, suggesting that even at this temperature some line-width alternation occurs on the methyl group lines.

At −27°, line-width alternation is more pronounced (Figure 1b) and increases further at −42° (Figure 1c). At −58°, the alternation is almost complete (Figure 1d), and every alternate methyl group line is almost completely broadened out. Instead of 13 lines (relative intensities 1:12:66:220:495:792:924:792:...), seven main lines would be anticipated with intensity ratios (1:36:225:400:225:...) if a two-jump, or (1:18:99:164:99:...) if a four-jump process occurs.[7]

At −83°, further changes in the spectrum are observed (Figure 1f), but even then it is still possible to discern the lines due to some methyl group protons which remain sharp throughout, and splittings associated with the hydroxyl protons are also still observable. The spectrum can be analyzed as the sum of *cis* and *trans* spectra, as predicted by Bolton and Carrington.[11] A reasonable fit can be obtained with the following splitting constants (in gauss): *cis* isomer, $a_{2CH_3} = 2.151$, $a_{2CH_3} = 1.903$, $a_{OH} = 2.730$; *trans* isomer, $a_{2CH_3} = 2.483$, $a_{2CH_3} = 1.571$, $a_{OH} = 2.730$. The assignment of *cis* and *trans* isomers is made by comparison with previous examples of *cis–trans* isomerism, which indicated that the *trans* form has the larger ratio of ring proton splittings.

Since two effects have been neglected in computing the spectrum from the above parameters, the agreement with the experimental spectrum can be reported as good. The neglected effects are the anisotropic dipolar g tensor terms of the line-width equation, which become important at lower temperatures (see later discussion), and the possibility of a small "g" displacement between the isomers as has been found, for example, with the *p*-dialkoxybenzenes.[15,16]

Two other effects were also noted. (i) The hydroxyl proton splitting constant is temperature dependent, increasing from 2.615 gauss at +2° to 2.742 at −90°, whereas methyl group splitting constants remain approximately constant within experimental error (see Table I and Figure 2). (ii) There are significant differences in the a_{OH} and a_{CH_3} splitting constants between the aluminum chloride–nitromethane and H_2SO_4 systems. (See Table I and Figure 2.) Similar differences have been noted for other compounds[15] and are ascribed to solvent interactions.

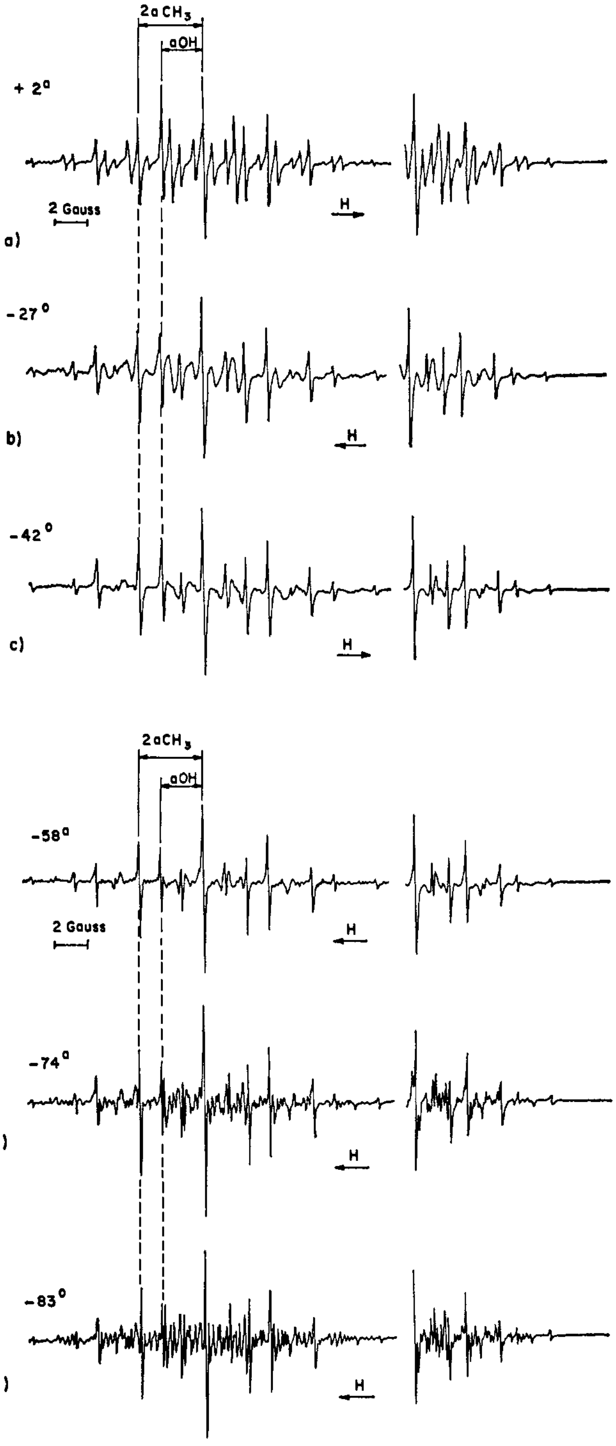

Figure 1. On the left, the experimental esr spectra of the duroquinol cation radical; on the right, the matched computed spectra from the four-jump model: a, +2°; b, −27°; c, −42°; d, −58°; e, −74°; f, −83°.

Dimethoxydurene. In H_2SO_4, the esr spectrum corresponding to the duroquinol cation was obtained. However, in aluminum chloride–nitromethane, a completely different spectrum is obtained (Figure 3), which is assigned to the dimethoxydurene cation radical. At −75°, the spectrum can be analyzed in terms of 12

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[13] H. M. Buck, W. Bloemhoff, and L. J. Oosterhoff, *Tetrahedron Letters*, No. 9, 5 (1961).

[14] D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, **1**, 319 (1965).

[15] W. F. Forbes, P. D. Sullivan, and H. M. Wang, *J. Am. Chem. Soc.*, **89**, 2705 (1967).

[16] W. F. Forbes and P. D. Sullivan, *Can. J. Chem.*, **44**, 1501 (1966).

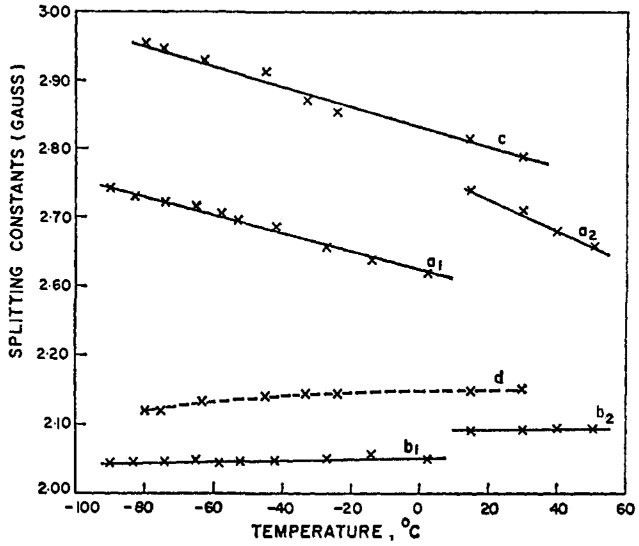

Figure 2. The temperature dependence of the esr splitting constants: a_1 and a_2, b_1 and b_2, the hydroxy and methyl splitting constants of duroquinol in (1) aluminum chloride-nitromethane and (2) H_2SO_4; c and d, the methoxy and methyl splitting constants of dimethoxydurene.

methyl proton splittings (2.079 gauss) and six methoxy proton splittings (2.889 gauss). The latter splitting constant is temperature dependent (see Table II and Figure 2), varying from 2.955 at −80° to 2.790 at +30°. No line-width alternation was observed under the conditions of the experiment, nor did the lines differ appreciably from the predicted binomial intensity distribution.

Table I. Splitting Constants (in gauss) of the Duroquinol Cation Radical

Aluminum chloride-nitromethane			H_2SO_4		
Temp, °C	$2a_{\mathrm{CH_3}}$[a]	a_{OH}[b]	Temp, °C	$2a_{\mathrm{CH_3}}$[a]	a_{OH}[b]
−90	4.089	2.742	+15	4.188	2.741
−83	4.090	2.730	+30	4.182	2.710
−74	4.090	2.723	+40	4.188	2.680
−65	4.095	2.717	+51	4.182	2.660
−58	4.090	2.705			
−53	4.091	2.694			
−42	4.095	2.673			
−27	4.105	2.656			
−14	4.113	2.639			
+2	4.102	2.615			

[a] Measured on lines which remain sharp throughout; reproducibility ±0.012 gauss. [b] Reproducibility ±0.006 gauss.

Table II. Splitting Constants (in gauss) of Dimethoxydurene Cation Radical in Aluminum Chloride-Nitromethane

Temp, °C	$a_{\mathrm{CH_3}}$[a]	$a_{\mathrm{OCH_3}}$[a]
−80	2.119	2.955
−75	2.120	2.946
−63	2.134	2.928
−45	2.141	2.913
−33	2.144	2.872
−24	2.144	2.853
+15	2.148	2.814
+30	2.153	2.790

[a] Reproducibility ±0.01 gauss.

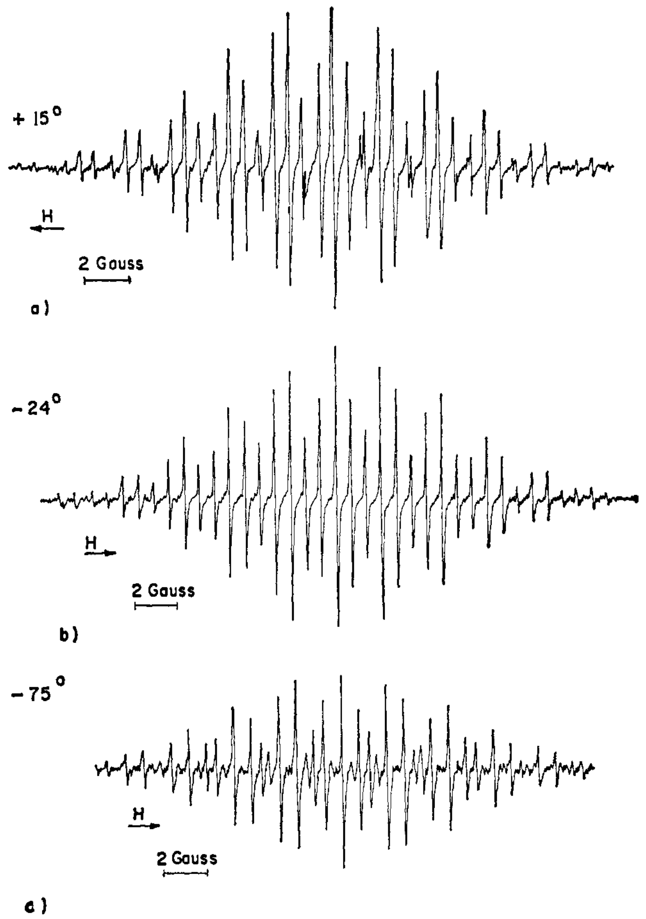

Figure 3. The esr spectrum of the dimethoxydurene cation radical at a, +15°; b, −24°; c, −75°.

Four-Jump Model and Potential Barrier to Rotation

The effects of the modulation of the isotropic splitting constants can be predicted from the complete relaxation matrix theory of line widths,[8] or by solution of the modified Bloch equations.[7] In the present case, it is required to simulate the spectra for long, short, and intermediate values of τ. Since the relaxation matrix theory only holds in the limit of fast exchange, the Bloch equations were used.

The relevant Bloch equations for the four-jump model have been solved by Carrington,[7] assuming (i) the two hydroxyl protons are equivalent and have the same splitting constant in all four conformations, (ii) conformational changes take place without change in the proton spin orientations, and (iii) each conformation has the same average lifetime.

Using these equations,[8] one calculates the first derivative of the imaginary part of the net average magnetization, $\langle G \rangle$, with respect to ω for each proton spin arrangement. The complete spectrum is obtained by incorporating the 1:2:1 triplet from the hydroxyl protons. This calculation was then repeated for varying values of τ. τ values were then assigned to the various experimental spectra within narrow limits by comparing the simulated and experimental spectra with respect to the rate of change of amplitude for certain lines relative to the center line. In this way error

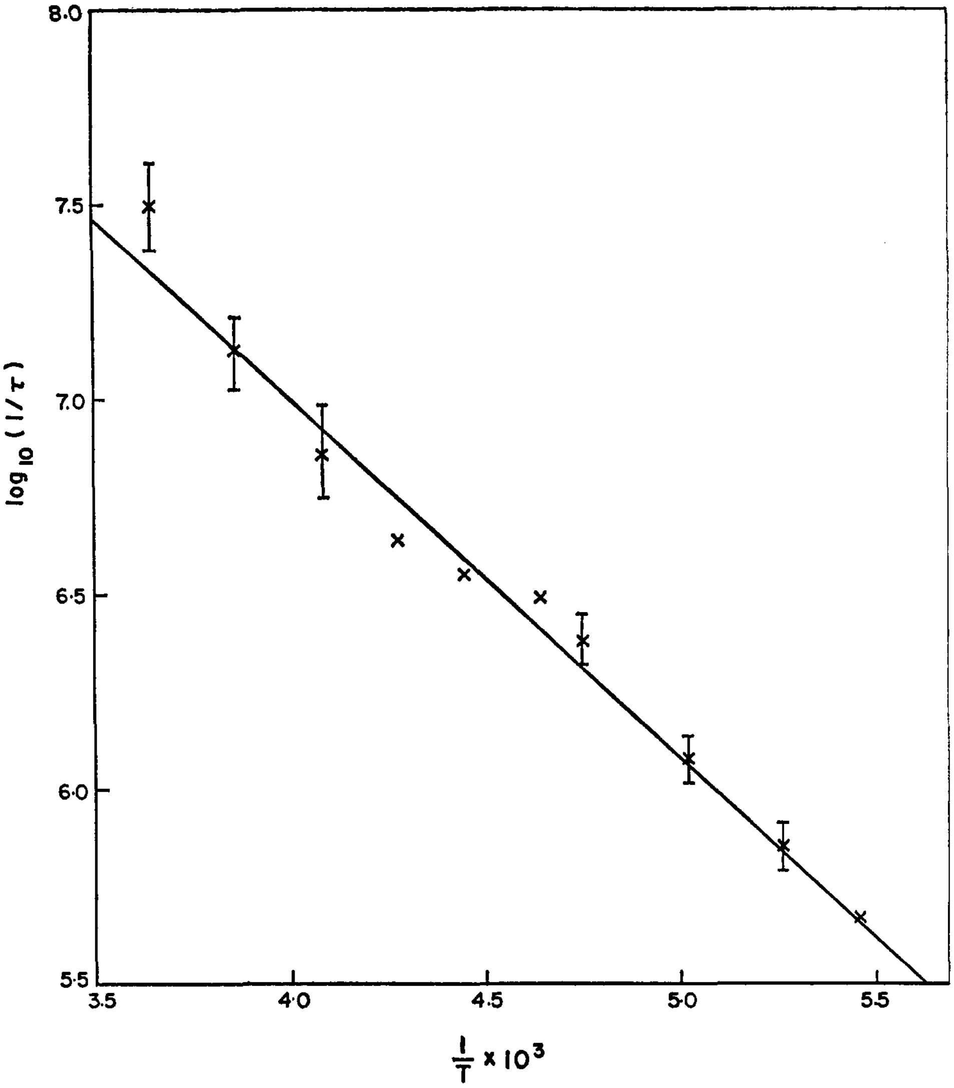

Figure 4. A plot of log $1/\tau$ against $1/T \times 10^3$.

limits were obtained for the τ's. When the line-width alternation was close to its maximum, amplitude changes were small, and the spectra were then compared visually (no error limits were placed on these readings; see Table III).

Table III. Assignment of Lifetime (τ) at Various Temperatures for Duroquinol

Temp, °C	τ, sec	Temp, °C	τ, sec
−90	2.19×10^{-6}	−53	2.9×10^{-7}
−83	$1.44 \pm 0.10 \times 10^{-6}$	−42	2.35×10^{-7}
−74	$8.4 \pm 0.9 \times 10^{-7}$	−27.5	$1.38 \pm 0.32 \times 10^{-7}$
−62.5	$4.2 \pm 0.6 \times 10^{-7}$	−14	$7.50 \pm 1.2 \times 10^{-8}$
−58	3.4×10^{-7}	+1	$3.16 \pm 0.18 \times 10^{-8}$

Assuming the rate of isomerization to be a function of temperature,[9] $k = 1/\tau = k_0 \exp(-E_A/RT)$, where k_0 = the frequency factor and E_A = potential barrier to rotation, a plot of log $(1/\tau)$ against $1/T$ should and, in fact, gives a straight line (Figure 4). This leads to a effective potential barrier to rotation, $E_A = 4.2 \pm 0.6$ kcal/mole and $\log k_0 = 10.9 \pm 0.6$.

This value for the potential barrier may be compared with that of the hydroquinone cation[10] (10 ± 3 kcal/mole). In hydroquinone, steric interactions are relatively smaller, and the energy of the planar conformation may be lowered through conjugation, leading to a large potential barrier. For duroquinol, steric interactions may make the planar conformation less favorable, hence decreasing the energy well and barrier height. If the steric forces are of sufficient magnitude, the position of minimum energy may be displaced from the planar arrangement, thus leading to a greater decrease in the barrier height due to loss of conjugation. These results may, however, be equally well rationalized in terms of complex formation with solvent molecules.

Anisotropic Dipolar Line-Width Effects and the Signs of the Isotropic Splitting Constants

As a first approximation, the effects of the modulations of the isotropic splitting and the anisotropic intramolecular interactions can be considered additive and noninteracting. In this section, these latter effects are considered.

Table IV. Duroquinol Line-Width Parameters[a] for Degeneracies Associated with Long, Short, and Intermediate Lifetimes of the Conformations

Temp, °C	Degeneracy	B_{CH_3}	B_{OH}	C_{CH_3}	C_{OH}	E_{CH_3OH}
−90	Long	−0.033	0.156	0.002	0.133	−0.061
	Int	−0.036	0.162	0.017	0.138	−0.065
	Short	−0.034	0.156	0.009	0.133	−0.063
−74	Long	−0.018	0.093	0.005	0.114	−0.041
	Int	−0.019	0.095	0.012	0.119	−0.042
	Short	−0.018	0.091	−0.002	0.114	−0.040
−58	Long	−0.007	0.056	−0.001	0.072	−0.026
	Int	−0.007	0.058	0.006	0.075	−0.027
	Short	−0.006	0.055	−0.008	0.085	−0.026
−42	Long	−0.003	0.028	−0.001	0.035	−0.014
	Int	−0.003	0.029	0.006	0.039	−0.014
	Short	−0.004	0.028	−0.007	0.035	−0.013
−14	Long	−0.005	0.001	−0.001	0.016	−0.008
	Int	−0.005	0.001	0.006	0.020	−0.008
	Short	−0.005	0.002	−0.008	0.017	−0.008

[a] Values less than 0.01 are probably not significant. The signs of the parameters are more important than the magnitudes which are only of secondary importance to the discussion.

Duroquinol. Following Fraenkel, *et al.*,[8,17] an expression for the line widths can be written in the form

$$W_{av}(\tilde{M}_{CH_3},\tilde{M}_{OH}) = 1 + B_{OH}(\tilde{M}_{OH}) + B_{CH_3}(\tilde{M}_{CH_3}) + C_{OH}(\tilde{M}_{OH})^2 + C_{CH_3}(\tilde{M}_{CH_3})^2 + E_{OH,CH_3}(\tilde{M}_{OH},\tilde{M}_{CH_3}) \quad (1)$$

W_{av} is calculated from the spectra by the relation

$$W_{av} = \sqrt{\frac{D_i/A_i}{D_c/A_c}}$$

where D_c and D_i are the degeneracies of the center and ith line, respectively, and A_c and A_i are the corresponding amplitudes. For duroquinol, the degeneracies of the lines change when the isotropic splitting constants are modulated. For example, the calculated ratio $(\tilde{M}_{CH_3} = 0)/(\tilde{M}_{CH_3} = \pm 2)$ changes from 1.867 for free rotation (short lifetimes) to 1.657 for intermediate lifetimes and 1.778 for long lifetimes of the *cis* and *trans* species. This change affects the determination of C_{CH_3} (see Table IV) but does not affect the other parameters within the experimental error. From the experimental W_{av} values eq 1 can be solved for the various parameters.

A counterpart of eq 1 can be obtained from the relaxation matrix theory[8] in the form

$$T_2^{-1}(\tilde{M}_{OH},\tilde{M}_{CH_3}) = \frac{8}{3}j_{OH}^{(D)}(\tilde{M}_{OH})^2 + \frac{16}{3}B_0 j_{OH}^{(DG)}(\tilde{M}_{OH}) + \frac{8}{3}j_{CH_3}^{(D)}\Gamma(\tilde{M}_{CH_3})^2 + \frac{16}{3}B_0 j_{CH_3}^{(DG)}\tilde{M}_{CH_3} + \frac{16}{3}j_{CH_3OH}\tilde{M}_{OH}\tilde{M}_{CH_3} + X \quad (2)$$

where only the anisotropic dipolar and anisotropic dipolar g tensor terms are considered and X represents the contribution from all other forms of broadening. Γ takes into account that the methyl groups are not all completely equivalent. From (1) and (2)

$$B_{OH}X = \pm\frac{16}{3}j_{OH}^{(DG)}B_0 \quad (3)$$

$$C_{OH}X = \frac{8}{3}j_{OH}^{(D)} \quad (4)$$

$$B_{CH_3}X = \pm\frac{16}{3}j_{CH_3}^{(DG)}B_0 \quad (5)$$

$$C_{CH_3}X = \frac{8}{3}j_{CH_3}^{(D)}\Gamma \quad (6)$$

$$E_{OH,CH_3}X = \pm\frac{16}{3}j_{CH_3OH}^{(D)} \quad (7)$$

where the so-called spectral densities are given by[8]

$$j_{ij}^{(D)} = 7.896\tau_R \sum_{m=-2}^{2} \tilde{D}_i^{(m)}\tilde{D}_j^{(-m)} \quad (8)$$

$$j_i = (2.256 \times 10^6)\tau_R \sum_{m=-2}^{2} D_i^{(m)}\tilde{g}^{(-m)} \quad (9)$$

$\tilde{D}_i^{(m)}$ are the coefficients of the anisotropic dipolar interaction, $\tilde{g}^{(-m)}$ represents the spherical tensor components of the g tensor $[g^{(0)} = 2g_3 - g_1 - g_2, g^{(\pm 2)} = 1.225(g_1 - g_2)]$, and τ_R is the correlation time for molecular tumbling.

In (3) and (5), the upper sign applies when the hyperfine splitting a_i is negative and *vice versa*. For (7), the upper sign applies if a_{OH} and a_{CH_3} are of the same sign, and the lower sign, when they are of opposite sign.

The absolute determination of the signs in eq 3, 5, and 7 requires the evaluation of all the $\tilde{D}_i^{(m)}$'s; these can be estimated from the formulas of McConnell and Strathdee,[18] provided the molecular geometry and spin density distribution are known. Since both of these sets of parameters are only known approximately, accurate calculations are not possible.

$\tilde{D}_i^{(m)}$ values have been estimated for the OH protons ($\tilde{D}_{OH}^{(0)} \cong -3.5 \times 10^6$ sec^{-1} and $\tilde{D}_{OH}^{(\pm 2)} \cong [-1.8 + 5.6i] \times 10^6$ sec^{-1}). It is found that $j_{OH}^{(DG)}$ is positive provided that $g^{(0)}$ is negative and greater than $g^{(2)}$. This latter assumption is supported by theoretical arguments[19] and also other line-width studies.[17,20]

Since B_{OH} is found experimentally to be positive, the upper sign in eq 3 is appropriate, suggesting a negative

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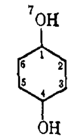
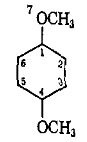
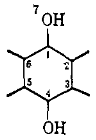
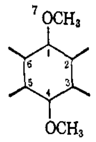
(17) B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 695 (1964).

(18) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

(19) A. J. Stone, *Proc. Roy. Soc.* (London), **A271**, 424 (1963).

(20) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

Table V. Summary of Molecular Orbital Calculations

Compound	Position	ρ_i calcd	a_i[a] calcd	a_i exptl	Q_{OR}[b]
	1	0.1528			
	2	0.0947	2.273	2.253	
	7	0.1580		3.294	20.8
	1	0.1242			
	2	0.0957	2.296	2.261	
	7	0.1758		3.360	19.1
	1	0.1741			
	2	0.0833	2.249	2.050	
	7	0.1513	3.15[c]	2.70	
	1	0.1533			
	2	0.0820	2.214	2.14	
	7	0.1675	3.20[d]	2.85	

[a] Calculated from $a_i = Q_i\rho_i$, where $Q_{CH} = 24$, $Q_{CCH_3} = 27$. [b] Calculated from $a_{OR} = Q_{OR}\rho_O$, for hydroquinone and dimethoxybenzene. [c] $Q_{OH} = 20.8$. [d] $Q_{OCH_3} = 19.1$.

isotropic splitting constant for a_{OH}, as predicted.[21] $\tilde{D}_i^{(m)}$ values for the methyl protons are not easily calculated but will be small. The experimental results (see Table IV) can be rationalized in the following manner. E_{OH,CH_3} is calculated experimentally to be negative; $j_{CH_3OH}^{(D)}$ will therefore be positive, if the $\tilde{D}_{CH_3}^{(m)}$ values carry an over-all negative sign. The negative sign would then be appropriate in eq 7, suggesting opposite signs for a_{CH_3} and a_{OH}. Assuming $\tilde{D}_{CH_3}^{(m)}$ is negative, $j_{CH_3}^{(DG)}$ should be positive; since B_{CH_3} is negative, the negative sign in eq 5 is correct, indicating a positive isotropic splitting constant for a_{CH_3}. This would be expected if the method of coupling is hyperconjugative.[22] If, however, $\tilde{D}_{CH_3}^{(m)}$ was positive, the opposite signs would be predicted. It is therefore concluded that $\tilde{D}_{CH_3}^{(m)}$ is negative in order to obtain results, consistent with earlier predictions.

As pointed out previously, the magnitude of the line-width parameters depends on the degeneracies used and evaluation of the constants for the three limiting cases of the degeneracies are shown in Table IV.

C_{CH_3} should always be positive, but this condition is only met over the whole temperature range by using degeneracies associated with intermediate τ values.

Line-width parameters are directly proportional to the correlation time for molecular tumbling, which is proportional to viscosity. At lower temperatures, the viscosity increases and line-width parameters would therefore be expected to and do, in fact, increase at lower temperatures (Figure 5).

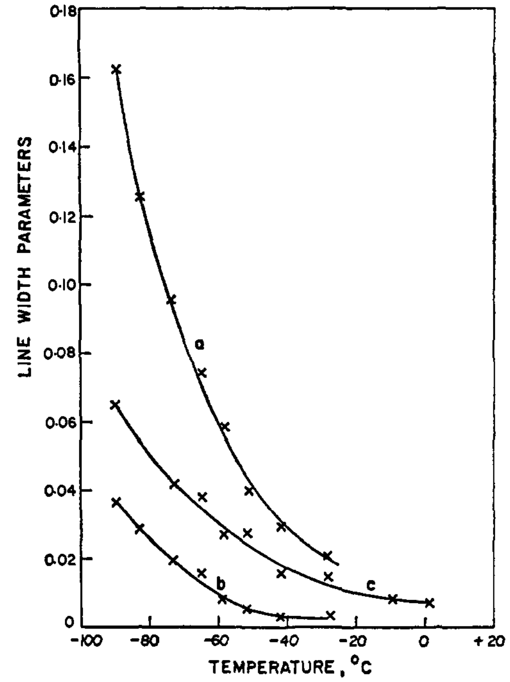


Figure 5. A plot of the esr line-width parameters against temperature: a, B_{OH}; b, B_{CH_3}; c, $E_{OH.CH_3}$.

Dimethoxydurene. Line-width variations are small and hence line-width parameters could not be determined accurately. This is somewhat surprising, but may be due to the rotation of the methoxy groups which might effectively average the dipolar interactions to small values.

Molecular orbital calculations were carried out using parameters ($h_{OO} = 1.60$, $k_{OC} = 1.37$, $h_{CH_3-CH_3} = 3.0$, $h_{O-CH_3} = 0.70$, and $h_{C-CH_3} = 0.76$) which gave reasonable results for related compounds.[10,16,23] The Q_{OH} and Q_{OCH_3} values used were those obtained from calculations on hydroquinone and *p*-dimethoxybenzene (Table V).[24]

Experimentally a decrease in the ring splitting constants is observed on methylating the ring positions; for the hydroxyl group the decrease is *ca.* 18% while for the methoxy group it is *ca.* 15%. MO calculations also predict a decrease, but only of 4.4 and 4.8%, respectively (see next section).

Conformations

The four-jump model satisfactorily explains the temperature dependence of the duroquinol spectrum. The low-temperature spectrum therefore consists of two species (*cis* and *trans*) and hence the hydroxyl group is predominantly in the plane of the benzene ring.

However, the hydroxyl splitting constant is approximately 14% less than that predicted from the MO calculations. Bearing in mind the semiquantitative nature of these calculations, the data can be rationalized in terms of steric interactions which displace the position of minimum energy from the planar conformation. But even if the hydroxyl group is twisted (±θ°) out of plane, this will not affect the general conclusions derived from the four-jump model. Two effects will,

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(21) A. Carrington and H. C. Longuet-Higgins, *Mol. Phys.*, **5**, 447 (1962).

(22) A. D. McLachlan, *ibid.*, **1**, 233 (1958).

(23) P. D. Sullivan, unpublished results.

(24) These values for Q_{OH} and Q_{OCH_3} of 21 and 19, respectively, are not consistent with the value of $Q_{OCH_3} \cong 7$ recently reported by Piette, *et al.* [G. P. Rabold, R. T. Ogata, M. Okamura, L. H. Piette, R. E. Moore, and P. J. Scheuer, *J. Chem. Phys.*, **46**, 1161 (1967)]. Use of the lower Q_{OCH_3} value with our splitting constants, however, leads to inordinately high values of spin density on the oxygen atoms.

however, be expected to occur; first, the hydroxyl splitting constant will decrease as the $p-\pi$ overlap between the oxygen and the ring decreases and second, hyperconjugative coupling to the ring will increase.[25] As the mechanism of coupling changes from spin polarization to hyperconjugation, the splitting constant is expected to change from a negative to a positive quantity. These two effects will each be approximately proportional to $\cos^2 \theta$, leading to an estimate for $\theta \cong 15°$. The observed temperature dependence of the hydroxyl splitting constant (*ca.* 5% in 100°) for duroquinol may be explained in terms of a change of θ with temperature. At low temperature, the mean value of θ might be expected to decrease, leading to an increased splitting constant. However, the hydroxyl splitting constant in hydroquinone is also temperature dependent[15] (*ca.* 2.7% in 100°). Since the steric effects are smaller, the temperature dependence may be caused by other effects such as a temperature-dependent Q_{OH} (compare also the temperature dependence of Q_{CH}, 1-2%/100° [26,27]). Moreover, the assumption implicit in the four-jump model, that the hydroxyl group spends a negligible amount of time out of plane, may only be approximately correct.

The conformation of dimethoxydurene can be considered in a related manner. The splitting of a methoxy group is expected to vary as $\cos^2 \theta$ and a comparison of the found (2.85) and predicted (3.20 gauss) values indicates that $\theta \cong 20°$. However, there is no evidence for *cis* and *trans* isomers as defined for duroquinol, nor for any line-width alternation. This may be due to the greater steric interactions which cause the potential barrier to rotation to be sufficiently small so that the lifetime of the conformations becomes relatively short thus giving a time-averaged spectrum. Alternatively, the methoxy group may be constrained to one side of the benzene ring plane and may oscillate rapidly between the two equilibrium positions with $\theta \cong 20°$. The temperature dependence of the methoxy splitting constant can be explained in a similar manner to that of the hydroxyl protons of duroquinol.

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(25) T. E. Gough, *Trans. Faraday Soc.*, **62**, 2321 (1966).

(26) I. A. Zlochower, W. R. Miller, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 3339 (1965).

(27) R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964).

Comparison of Chemical Exchange Rates Determined by Nuclear Magnetic Resonance Line-Shape and Equilibration Methods. Internal Rotation of N-Methyl-N-benzylformamide[1]

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Abstract: The rate of internal rotation about the C-N amide bond has been studied in N-methyl-N-benzylformamide between 170 and 90° by an nmr complete line-shape analysis method and between 20 and −2.5° by an equilibration technique. Exchange rates were calculated from the nmr spectra of the benzyl and formyl protons in the two rotational isomers by treating them as two separate, uncoupled, exchanging AB systems with unequal populations. The calculations for the formyl protons required inclusion of temperature dependence in the chemical shift. The equilibration studies were performed on samples in which the isomer with the methyl *cis* to the formyl proton was concentrated by complexing the equilibrium mixture with uranyl ion and stripping it off at low temperatures. The activation parameters obtained from the nmr studies agree well with those obtained by the classical equilibration method.

The various nmr techniques which may be employed to determine the nature and rate of fast exchange processes in liquids have been reviewed in several recent papers,[4-6] but there is one aspect which has received relatively little attention. This is the comparison of rates and/or activation parameters determined by nmr methods with those from more conventional approaches. Such comparisons are difficult because the 1 to 10^6 sec^{-1} exchange rates measured by nmr are too fast for most other methods applicable to liquids; moreover, many of the processes studied by nmr are con-

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(2) University of Illinois.

(3) E. I. du Pont de Nemours and Co.

(4) A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).

(5) C. S. Johnson, Jr., in "Advances in Magnetic Resonance," Vol. I, Academic Press Inc., New York, N. Y., 1965, Chapter 2.

(6) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).