The ORD spectrum showed a positive Cotton effect with a maximum at 276 mμ (molecular rotation +28,500°), zero rotation at 260 mμ, and a minimum at 232 mμ (molecular rotation −40,500°). See Table I for the nmr spectrum.

Hydrolysis with 80% acetic acid at 100° for 30 min gave N_3-methyluridine (**19**) that was chromatographically identical with the major product from the action of diazomethane on uridine.

1-(2,5-Di-O-trityl-β-D-xylofuranosyl)-N_3-methyluracil. 1-(2,5-Di-O-trityl-β-D-xylofuranosyl)uracil (**11**, 57 mg) was treated overnight in a mixture of chloroform (1 ml), methanol (1 ml), and ether (2 ml) with an excess of diazomethane. Evaporation of the solvent left a solid residue (63 mg) which was homogeneous by thin layer chromatography using chloroform–ethyl acetate (20:1). Crystallization from ether gave 43 mg of 1-(2,5-di-O-trityl-β-D-xylofuranosyl)-N_3-methyluracil, mp 244–246°; λ_{max}^{MeOH} 260 mμ (ϵ 9900), unchanged in alkali, $[\alpha]^{22}D$ +51.9° (*c* 0.1, chloroform).

Anal. Calcd for $C_{43}H_{42}N_2O_6$: C, 77.60; H, 5.70; N, 3.77. Found: C, 77.39; H, 5.64; N, 3.73.

The ORD spectrum in methanol showed a positive Cotton effect with a maximum at 273 mμ (molecular rotation +14,900°), zero rotation at 256 mμ, and a minimum at 236 mμ (molecular rotation −17,200°). The mass spectrum (15 ev) showed an intense peak at *m/e* 126 corresponding to N-methyluracil.

Detritylation with 80% acetic acid at 100° for 30 min gave 1-(β-D-xylofuranosyl)-N_3-methyluracil which ran as a single spot on paper chromatograms and on borate electrophoresis but was not isolated in crystalline form.

An Electron Spin Resonance Study of the Radical Cations of Some *p*-Dialkoxybenzenes

W. F. Forbes, P. D. Sullivan, and H. M. Wang

Contribution from the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada. *Received October 31, 1966*

Abstract: The electron spin resonance spectra of some *p*-dialkoxybenzene cation radicals in aluminum chloride–nitromethane have been investigated. The spectra can be interpreted by assuming *cis–trans* isomerism. The temperature dependence of the β-proton splitting constants, observed for the larger alkoxy compounds (ethoxy upwards), is explained by assuming hindered rotation of the alkoxy side chain.

As a continuation of earlier work,[1,2] the cation radicals of some *p*-dialkoxybenzenes have been studied. The aim was to investigate how larger alkyl groups would affect properties such as *g* values, spin densities, conformations, and the free energy difference between conformations. These systems also illustrate some of the advantages of the aluminum chloride–nitromethane system for producing cation radicals.

Experimental Section

Hydroquinone, *p*-dimethoxybenzene, *p*-diethoxybenzene, and *p*-di-*n*-butoxybenzene were commercially available samples, which were recrystallized several times. The other *p*-dialkoxybenzenes were prepared by the Williamson reaction[3,4] and purified by standard methods.

The sulfuric acid was best grade commercially available 98% sulfuric acid. Dideuteriosulfuric acid was a commercially available sample (Fluka). Sulfuric acid spectra were determined in *ca.* 0.2 *M* solution, *ca.* 0.04 ml of which was placed in a glass capillary tube which was then inserted in the spectrometer cavity.

Nitromethane and aluminum chloride (anhydrous) were Fisher reagent grade. Nitromethane was dried (CaH_2) and deoxygenated by passing dried (H_2SO_4, Al_2O_3) nitrogen gas through the solution, followed by degassing under vacuum. Radical formation was carried out (*cf.* ref 5) in an inverted U tube (diameter *ca.* 8 mm), one arm of which was filled with aluminum chloride and the appropriate benzene (*ca.* 20 and 5 mg, respectively). The U tube was connected to a vacuum line (*ca.* 0.5 mm) and nitromethane (*ca* 1 ml) was distilled into the mixture. The reaction proceeded at room temperature, and the solution was subsequently transferred under vacuum to a capillary tube (diameter *ca.* 1 mm) which was sealed directly to one arm of the U tube. The capillary tube was then placed in the esr cavity. If necessary, concentrations were varied by distilling solvent from one arm to the other.

Esr spectra were determined on a JES-3BX spectrometer at 100-kc/sec modulation using a field-selector unit. *g* Values were obtained in a dual cavity with reference to Fremy's salt which was used as a secondary standard being first calibrated against the spectrum of anthracene (positive ion) for which an accurate *g* value (2.002565 ± 0.000006) is available.[6] The magnetic field was calibrated with both Fremy's salt (a_N = 13.07 gauss)[7] and an nmr probe, and values of the splitting constants are believed accurate to ±0.5% (for splitting constants >1 gauss). The magnetic field was swept in both directions, and the first derivative spectra of the energy absorption were recorded in the relevant figures. Radical concentrations were estimated by overmodulating the signal and comparing it, under similar conditions, with a standard diphenylpicrylhydrazyl (DPPH) sample.

Spectra were simulated on an IBM 7040 computer, with a modified program kindly supplied by Dr. Lawrence C. Snyder of the Bell Telephone Laboratories.[8] The output data from the IBM 7040, in the form of punched cards, were plotted *via* an IBM 1710 computer. Approximate splitting constants were obtained directly from the observed spectra, usually by careful inspection of the wings. Sometimes, however, such direct measurement is not possible, and it is necessary to estimate splitting constants by measuring the total width of the spectrum. It is these values which are then slightly altered, within the experimental error, until a good simulated spectrum is obtained. Molecular orbital calculations were carried out by the self-consistent-field method of McLachlan[9] on an IBM 7040 computer, with a program kindly supplied by Dr. J. M. Fritsch[10] of the University of Kansas.

Results and Discussion

***p*-Dihydroxybenzene.** The spectrum of the cation radical of hydroquinone in aluminum chloride–nitro-

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

(2) A. B. Barabas, W. F. Forbes, and P. D. Sullivan, *ibid.*, **45**, 267 (1967).

(3) G. S. Hartley, *J. Chem. Soc.*, 1828 (1939).

(4) J. B. Gallent, *J. Org. Chem.*, **23**, 75 (1958).

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

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(7) G. Vincow and P. M. Johnson, *ibid.*, **39**, 1143 (1963).

(8) S. H. Glarum and L. C. Snyder, *J. Chem. Phys.*, **36**, 2989 (1962).

(9) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(10) J. M. Fritsch, T. P. Layloff, and R. N. Adams, *J. Am. Chem. Soc.*, **87**, 1724 (1965).

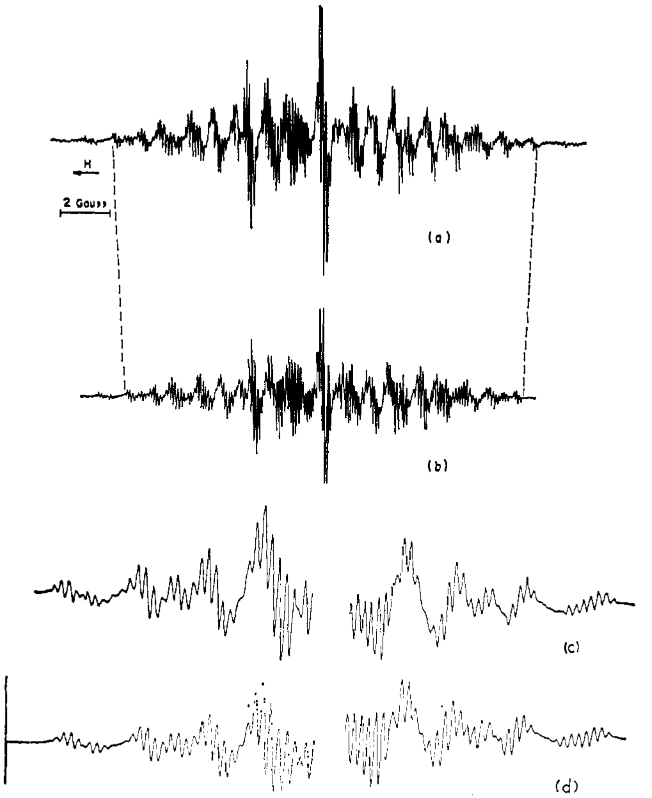

Figure 1. (a) The observed esr spectrum of the *p*-diethoxybenzene cation radical at −49°; (b) a computed spectrum using the parameters given in the text; (c) the experimental wing lines using increased amplification; and (d) the computed wing lines.

methane has previously been interpreted in terms of *cis–trans* isomerism.[2] Table I shows the temperature dependence of the splitting constants, indicating significant changes for the hydroxy splittings. A similar trend has been observed for other *p*-dihydroxy-substituted benzenes.[11]

Table I. Variation of Splitting Constants with Temperature for the Hydroquinone Cation Radical in Aluminum Chloride–Nitromethane

Temp, °C	Total width,[a] gauss	Sum of ring splittings,[b] gauss	Hydroxy splittings,[c] gauss
−103 (Semisolid)	15.72_6	9.04_0	3.34_3
−68	15.63_2	9.02_6	3.30_3
−55	15.59_6	8.99_8	3.29_9
−51	15.56_6	8.97_2	3.29_7
−32	15.56_7	9.00_0	3.28_3
−16.5	15.51_5	8.98_8	3.26_3
−5	15.46_4	8.98_8	3.23_8
+2.5	15.47_4	8.98_6	3.24_4
+14	15.47_9	8.99_0	3.24_5
+28	15.42_2	8.99_0	3.21_6

[a] Estimated experimental error = ±0.08; *i.e.*, significant trend.
[b] Estimated experimental error = ±0.05; *i.e.*, no significant trend.
[c] Estimated experimental error = ±0.02; *i.e.*, significant trend.

***p*-Dimethoxybenzene.** The spectrum of the cation radical of this compound, previously investigated in sulfuric acid,[1] has been further studied in aluminum chloride–nitromethane. Splitting constants under various conditions are shown in Table II; the data indicate no significant changes with temperature.

Table II. Variation of Splitting Constants with Temperature for the *p*-Dimethoxybenzene Cation Radical

Splitting constants, gauss		Aluminum chloride–nitromethane −60°	−34°	−10°	*Ca.* 50% CCl_4 added −9°	Concd H_2SO_4 +20°
$a_{H(2,5)}$	T[a]	1.59_9	1.59_8	1.59_9	1.58_8	1.49_9
$a_{H(3,6)}$	T	2.92_1	2.94_0	2.92_6	2.96_0	2.99_0
Sum of ring splittings	T	9.04_0	9.07_6	9.05_0	9.09_6	8.97_8
a_{CH_3}	T	3.44_3	3.43_2	3.43_7	3.47_2	3.45_0
Total width	T	29.70_0	29.66_7	29.67_1	29.93_1	29.68_0
$a_{H(5,6)}$	C	1.87_6	1.87_6	1.85_9	1.86_6	1.81_0
$a_{H(2,3)}$	C	2.64_3	2.66_4	2.63_5	2.63_4	2.68_0
Sum of ring splittings	C	9.03_8	9.06_0	8.99_0	9.00_5	8.98_0
a_{CH_3}	C	3.28_6	3.28_0	3.28_9	3.33_4	3.33_0
Total width	C	28.75_4	28.73_9	28.72_3	29.00_9	28.96_0
$\Delta_{CH_3} = a_{CH_3}(T) - a_{CH_3}(C)$		0.15_7	0.15_2	0.14_8	0.14_8	0.12_0

[a] For nomenclature used in this and subsequent tables, see ref 1; also T = *trans* and C = *cis*, throughout.

***p*-Diethoxybenzene.** Figures 1a and 1c show the spectrum of the cation radical of *p*-diethoxybenzene in aluminum chloride–nitromethane. The spectrum can be interpreted in terms of two species A and B with splitting constants (in gauss) as follows: species A, a_{4H} = 4.104, a_{2H} = 2.922, a_{2H} = 1.614, and a_{6H} = 0.152; species B, a_{4H} = 3.802, a_{2H} = 2.660, a_{2H} = 1.880, and a_{6H} = 0.152. Figures 1b and 1d show a simulated spectrum using these parameters and assuming a line width of 73 mgauss, a displacement of centers of 35 mgauss, and an intensity ratio A:B = 56:44.

The two species are assumed to correspond to *trans* and *cis* isomers. The assignment of the species to the isomers is made by analogy with previous calculations.[1,2] For the cation radicals of *p*-dimethoxybenzene[1] and hydroquinone,[2] empirical molecular orbital calculations following Stone and Maki[12] predicted that the species with the larger ratio of ring proton splitting constants is the *trans* isomer. On this basis, species A is the *trans* and B the *cis* isomer (see also later discussion). Assignments shown in Tables II–V are also based on these calculations.[12a]

In sulfuric acid, a similar but less intense signal was observed (see Table III for parameters). In D_2SO_4, a broad five-line spectrum (intensity ratio *ca.* 1:4:6:4:1) was obtained and, since rapid exchange of the ring protons is known to occur for compounds of this type,[1] the main splittings are ascribed to the four CH_2 protons (β-protons) of the alkoxy groups. The splitting constants are, moreover, *ca.* 3.7 gauss, corresponding to the splitting constants of the four equivalent protons used in computing the spectrum shown in Figure 1b.

The temperature dependence of the spectrum (Table III) is illustrated in Figures 2a, 2b. The data show that the ring splitting constants remain approximately constant, but that the β-proton splittings vary significantly.

***p*-Di-*n*-propoxy-, *p*-Di-*n*-butoxy-, *p*-Di-*n*-pentoxy-, *p*-Di-*n*-hexoxy-, *p*-Di-*n*-heptoxy-, and *p*-Di-*n*-octoxybenzene.** The spectra of all these cations proved to be

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(11) P. D. Sullivan, unpublished information.

(12) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(12a) NOTE ADDED IN PROOF. A recent study[11] of 2,3- and 2,5-dimethylhydroquinones which exist only in the *cis* and *trans* form, respectively, afforded results consistent with the present assignments.

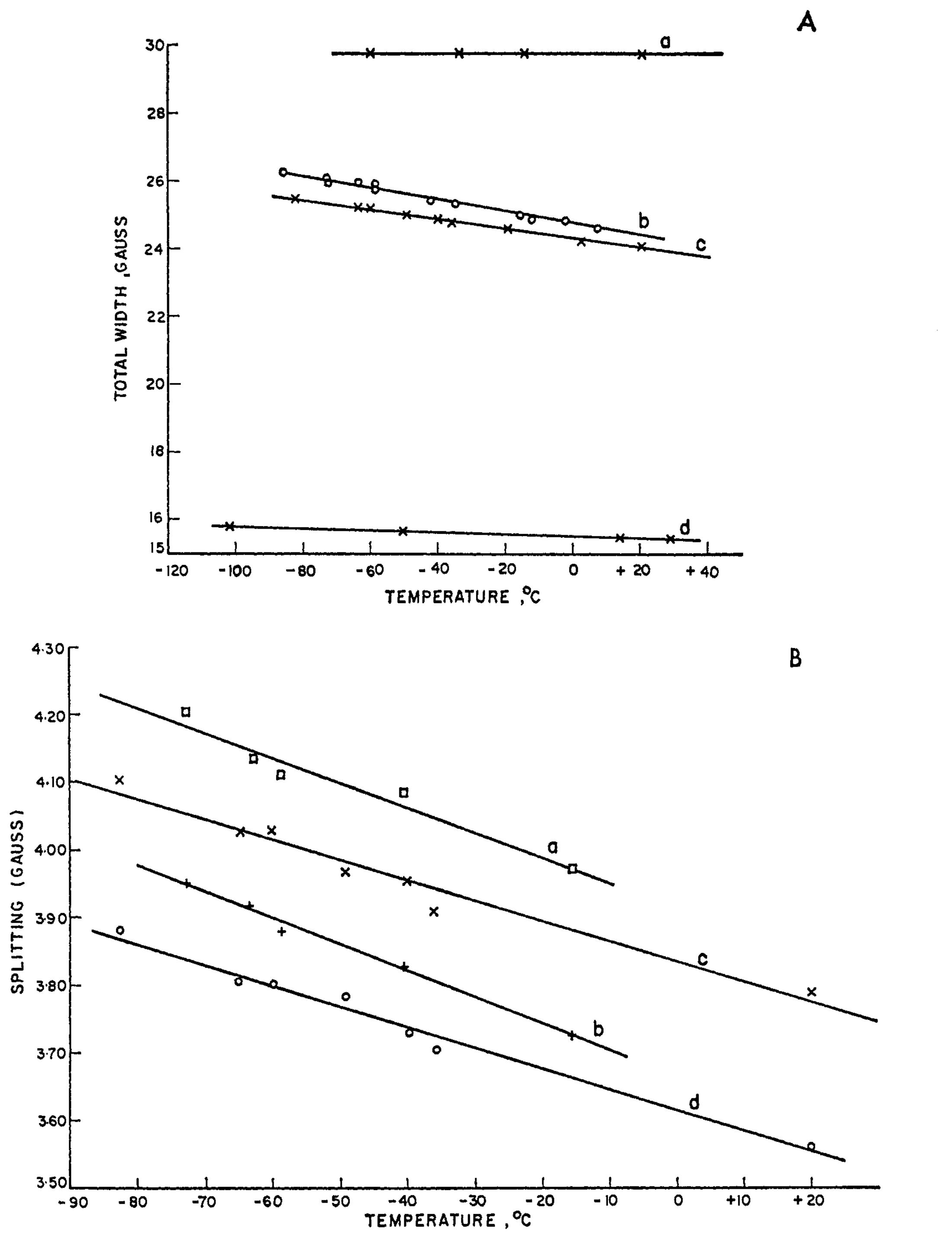

Figure 2. (A) Plots of the total width of the spectra against temperature for the cation radicals of (a) *p*-dimethoxybenzene, (b) *p*-di-*n*-butoxybenzene, (c) *p*-diethoxybenzene, (d) *p*-dihydroxybenzene. (B) Plots of the β-proton splitting constants against temperature for (a) *trans*- and (b) *cis*-*p*-di-*n*-butoxybenzene, and (c) *trans*- and (d) *cis*-*p*-diethoxybenzene, respectively.

similar under our conditions. Splitting constants are listed in Table IV. The spectrum of the *p*-di-*n*-octoxybenzene cation is shown in Figures 3a and 3c and a simulated spectrum with the following parameters is shown in Figures 3b and 3d. For species A (in gauss), $a_{4H} = 4.168$, $a_{2H} = 2.930$, $a_{2H} = 1.622$, $a_{4H} = 0.118$; for species B, $a_{4H} = 3.968$, $a_{2H} = 2.660$, $a_{2H} = 1.880$, $a_{4H} = 0.118$; a line width of 85 mgauss, a displacement of centers of 35 mgauss, and an intensity ratio A:B = 61:39 were assumed.

The temperature dependence of the splitting constants are shown in Table V and Figure 2, and again a change in the β-proton splitting constant is noted. In sulfuric acid a weak signal is obtained, but the broadness of the lines precludes any accurate measurement of splitting constants. In D_2SO_4, a five-line spectrum (intensity ratio *ca.* 1:4:6:4:1) with a splitting constant of *ca.* 3.7 gauss was again obtained.

***p*-Diisopropoxybenzene.** The spectrum of the cation radical of *p*-diisopropoxybenzene in sulfuric acid is shown in Figure 4b. It is not well resolved and a complete analysis has not been carried out, although the spectrum appears to consist of more than one component, consistent with the occurrence of *cis* and *trans* isomers. In D_2SO_4, only three broad lines, with a splitting constant of 2.74 ± 0.05 gauss, are observed

Table III. Temperature Dependence of Splitting Constants for the *p*-Diethoxybenzene Cation Radical

Splitting constants, gauss	Aluminum chloride–nitromethane −82.5°	−64°	−60°	−49°	−40°	−36°	−19°	+2°	H_2SO_4 +20°
$a_{\mathrm{H}(2,5)}$ T	1.614	1.616	1.613	1.606	1.602	1.612	x[a]	x	1.587
$a_{\mathrm{H}(3,6)}$ T	2.925	2.928	2.921	2.921	2.911	2.929	x	x	2.885
Total ring splittings T	9.078	9.088	9.068	9.042	9.026	9.082	x	x	8.944
$a_{\beta\text{-CH}_2}$ T	4.103	4.023	4.027	3.969	3.951	3.908	x	x	3.789
Total width T	25.491	25.182	25.177	24.927	24.832	24.714	24.514	24.201	24.100
$a_{\mathrm{H}(5,6)}$ C	1.883	1.886	1.879	1.875	1.901	1.887	x	x	1.812
$a_{\mathrm{H}(2,3)}$ C	2.639	2.649	2.659	2.640	2.637	2.661	x	x	2.661
Total ring splittings C	9.044	9.070	9.076	9.030	9.076	9.096	x	x	8.946
$a_{\beta\text{-CH}_2}$ C	3.883	3.807	3.801	3.786	3.730	3.704	x	x	3.561
Total width C	24.618	24.337	24.337	24.176	23.995	23.913	23.688	23.391	23.190
$\Delta_{\mathrm{CH}_2} = a_{\beta\text{-CH}_2}(\mathrm{T}) - a_{\beta\text{-CH}_2}(\mathrm{C})$	0.220	0.216	0.226	0.183	0.221	0.204	0.206	0.202	0.228
γ_{CH_3}	0.154	0.153	0.148	0.146	x	0.144	x	x	0.131

[a] x = Not measured.

and corresponding lines are also observed in sulfuric acid (*cf.* Figures 4a and b). By analogy with previous spectra, this splitting is assigned to the two β-protons of the alkoxy groups.

Table IV. Splitting Constants for the Radical Cations of *p*-Di-*n*-propoxy-, *p*-Di-*n*-butoxy-, *p*-Di-*n*-heptoxy-, and *p*-Di-*n*-octoxybenzenes in Aluminum Chloride–Nitromethane

Splitting constants, gauss	Benzene radical cations *p*-Di-*n*-propoxy −58°	*p*-Di-*n*-butoxy −58°	*p*-Di-*n*-heptoxy −73°	*p*-Di-*n*-octoxy −63°
$a_{\mathrm{H}(2,5)}$ T	1.645	1.630	1.664	1.675
$a_{\mathrm{H}(3,6)}$ T	2.965	3.000	3.000	3.031
Total ring splittings T	9.220	9.260	9.320	9.410
$a_{\beta\text{-CH}_2}$ T	4.114	4.102	4.188	4.135
Total width T	25.675	25.670	26.074	25.950
$a_{\mathrm{H}(5,6)}$ C	1.820	1.864	1.886	1.899
$a_{\mathrm{H}(2,3)}$ C	2.590	2.651	2.706	2.764
Total ring splittings C	8.820	9.030	9.184	9.326
$a_{\beta\text{-CH}_2}$ C	3.873	3.874	3.952	3.918
Total width C	24.709	24.560	25.092	x
$\Delta_{\mathrm{CH}_2} = a_{\beta\text{-CH}_2}(\mathrm{T}) - a_{\beta\text{-CH}_2}(\mathrm{C})$	0.241	0.228	0.238	0.216
γ_{CH_2}	0.101	0.113	0.122	x

Table V. Temperature Dependance of Total Width and of the β-CH_2 Splittings for the Cation Radical of Some Di-*n*-alkoxybenzenes

Temp, °C	Substituents	Total width, gauss *trans*	*cis*	$a_{\beta\text{-CH}_2}$, gauss *trans*	*cis*	$[a_{\beta\text{-CH}^2}(\mathrm{T}) - a_{\beta\text{-CH}_2}(\mathrm{C})] = [(\text{total width(T)} - \text{total width (C)}]/4$
−86	*n*-Butoxy	26.178	25.191	x	x	0.244
−73	*n*-Butoxy	25.986	25.006	4.219	3.947	0.278
−73	*n*-Heptoxy	26.074	25.092	4.188	3.952	0.238
−66	*n*-Propoxy	25.927	24.961	x	x	0.241
−63	*n*-Octoxy	25.950	x	4.134	3.918	0.216
−58	*n*-Butoxy	25.670	24.560	4.102	3.874	0.228
−58	*n*-Heptoxy	25.902	24.878	x	x	0.256
−58	*n*-Propoxy	25.675	24.709	4.114	3.873	0.241
−42	*n*-Butoxy	25.359	24.436	4.082	3.826	0.236
−35	*n*-Butoxy	25.321	24.345	x	x	0.244
−16	*n*-Butoxy	24.960	24.022	3.971	3.723	0.248
−3.5	*n*-Butoxy	24.822	23.981	x	x	0.210
+7	*n*-Butoxy	24.568	x	x	x	x

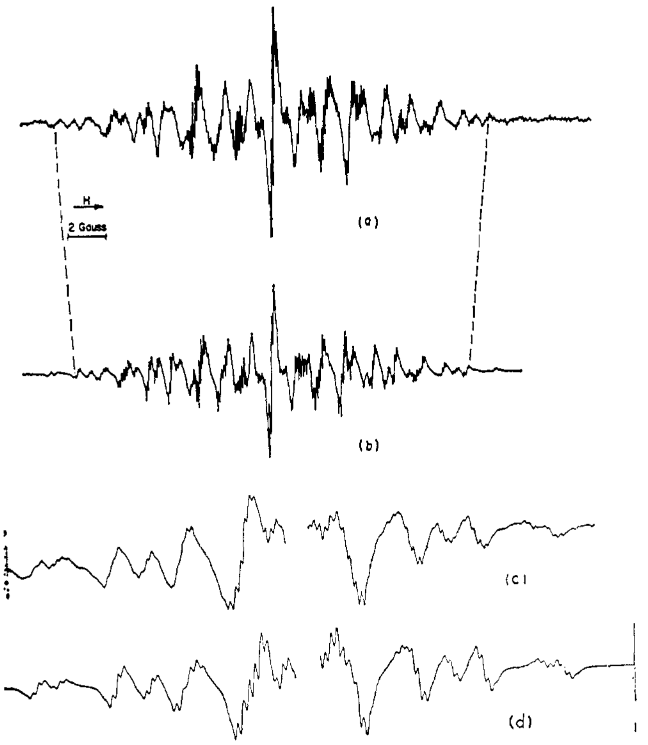

Figure 3. (a) An experimental esr spectrum of the *p*-di-*n*-octoxybenzene cation radical at −63°; (b) a computed spectrum using the parameters given in the text; (c) the experimental wing lines using increased modulation and amplification; and (d) the computed wing lines.

The temperature dependence of the splitting shows a reverse trend to that observed for the other *p*-dialkoxybenzenes; it decreases from 2.70 ± 0.05 gauss at 0° to 2.50 ± 0.05 gauss at −50° (*cf.* Tables III and V).

The Formation of Cation Radicals in Sulfuric Acid and Aluminum Chloride–Nitromethane. For the compounds studied, the same radicals were obtained in both systems. However, the radical concentrations in $AlCl_3$–CH_3NO_2 approximated 100%, whereas in sulfuric acid less than 1% of the compounds was converted to the radical (*cf.* ref 5). This low radical yield

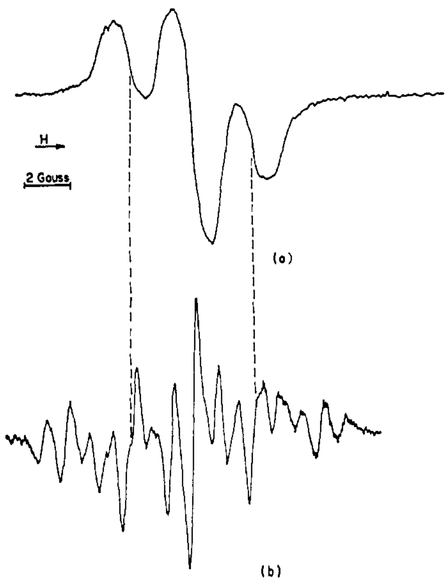

Figure 4. An esr spectrum of *p*-diisopropoxybenzene in (a) D_2SO_4 and (b) H_2SO_4.

may be due to a competing sulfonation reaction (unpublished data from this laboratory).

Small, but significant, changes in the splitting constants of the ring protons for the cation radicals of *p*-dimethoxy- and *p*-diethoxybenzene were noted between the two systems (see Tables II and III), presumably due to a solvent effect. Because of the small radical concentration in sulfuric acid, comparisons were not made for the other compounds.

***g* Values.** *g* Values were determined, as described in the experimental section, and are listed in Table VI.

Table VI. *g* Values of *p*-Dialkoxybenzene Cation Radicals

Dialkoxybenzene *para* substituents	Solvent	Temp, °C	*g* values
(Hydroquinone)	$AlCl_3$–CH_3NO_2	−60	$2.0035_0 \pm 0.00002$
Methoxy	Concd H_2SO_4	+20	$2.0036_8 \pm 0.00002$
Methoxy	$AlCl_3$–CH_3NO_2	−60	$2.0036_8 \pm 0.00002$
Ethoxy	$AlCl_3$–CH_3NO_2	−60	$2.0037_1 \pm 0.00002$
n-Propoxy	$AlCl_3$–CH_3NO_2	−60	$2.0037_2 \pm 0.00002$
n-Butoxy	$AlCl_3$–CH_3NO_2	−60	$2.0037_0 \pm 0.00001$
n-Pentoxy	$AlCl_3$–CH_3NO_2	−60	$2.0036_8 \pm 0.00003$
n-Hexoxy	$AlCl_3$–CH_3NO_2	−60	$2.0037_2 \pm 0.00002$
n-Heptoxy	$AlCl_3$–CH_3NO_2	−60	$2.0037_1 \pm 0.00005$
n-Octoxy	$AlCl_3$–CH_3NO_2	−60	$2.0037_2 \pm 0.00003$
Isopropoxy	$AlCl_3$–CH_3NO_2	−60	$2.0036_9 \pm 0.00003$

The values for the dialkoxybenzenes all fall within the range 2.0037 ± 0.00006, consistent with the previously noted generalization[13] that delocalization onto an oxygen atom of an alkoxy group increases the *g* value by about 0.001 over the free spin value (2.0023). The slightly larger value, relative to the hydroquinone cation radical, is ascribed to the electronic effects of the alkyl substituents.

Differences between *cis* and *trans* Isomers. Assigning *cis* and *trans* isomers as indicated previously (see also Table VII), it is found that the percentage of the *trans* form increases with the size of the alkyl group in the order 50, 55, 56, 61 for the radicals of hydroquinone, *p*-dimethoxy-, *p*-diethoxy-, and *p*-di-*n*-propoxybenzenes, respectively. These percentages correspond to a free energy difference between the isomers of 0–250 cal/mole. Such an energy difference corresponds to a change in isomer ratio of only 3 or 4% over an 80° range and hence is not readily detected experimentally.

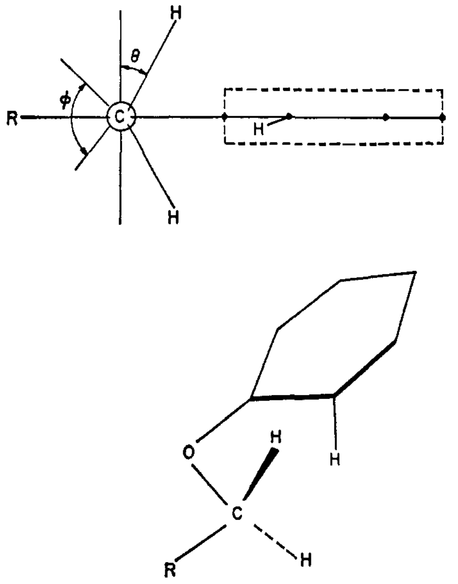

Figure 5. Schematic representation of the equilibrium conformation of *p*-di-*n*-alkoxybenzene.

Tables II, III, IV, and VII also show that differences in *β*-proton splitting constants between the two isomers increase from *ca.* 0.15 gauss (for *p*-dimethoxybenzene) to *ca.* 0.22 gauss (for di-*n*-propoxybenzene). This may be related to the slightly greater displacement, observed between the centers of the two isomer spectra, for *p*-diethoxybenzene (0.035 gauss) than for *p*-dimethoxybenzene (0.029 gauss).[1] Possibly, increased steric interactions in the *cis* form cause some out-of-plane movement in the CH_2–O bond, leading to a relatively lower *β*-proton splitting constant and *g* value for the *cis* isomer. Such steric interactions might also be expected to make the *trans* isomer thermodynamically more stable, consistent with the previous assignment of *cis* and *trans* isomers (see earlier discussion). The above results are consistent with those obtained for other related examples of *cis–trans* isomerism.[12,14]

Conformation of the Alkoxy Groups. To explain the temperature dependence of the *β*-proton splitting constants, various torsional oscillations of the alkoxy side chain are considered. Since the methoxy proton splitting constants of the *p*-dimethoxybenzene cation radical show no temperature dependence, and the hydroxy protons of hydroquinone show only a small dependence, it is probable that torsional motion about the nuclear C–O bond can be neglected.

The discussion is therefore confined to the oscillations of the alkyl groups. Molecular models indicate that for the alkyl groups, steric interactions between the *ortho* ring proton and the alkyl protons may cause hindered rotation (see Figures 5 and 6). For a methoxy group (Figure 5; R = H), there will be a threefold potential barrier to rotation about the O–C (alkyl) bond. Experimentally, all three methoxy protons are equiva-

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(13) R. O. C. Norman and R. J. Pritchett, *Chem. Ind.* (London), 2040 (1965).

(14) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2811 (1962).

Table VII. Assignment of Splitting Constants for *cis* and *trans* Isomers

Subst	*cis* isomer: Splitting constants, gauss	*cis* isomer: Ratio of ring splittings	*cis* isomer: Sum of ring splittings	*trans* isomer: Splitting constants, gauss	*trans* isomer: Ratio of ring splittings	*trans* isomer: Sum of ring splittings
H	$a_{H(2,3)}$ 2.35_1	1.10	4.48_0	$a_{H(3,6)}$ 2.43_4	1.19	4.47_4
	$a_{H(5,6)}$ 2.12_9			$a_{H(2,5)}$ 2.04_0		
	a_{OH} 3.26_3			a_{OH} 3.26_3		
CH_3	$a_{H(2,3)}$ 2.64_4	1.41	4.51_3	$a_{H(3,6)}$ 2.93_7	1.84	4.53_3
	$a_{H(5,6)}$ 1.86_9			$a_{H(2,5)}$ 1.59_6		
	a_{CH_3} 3.29_7			a_{CH_3} 3.44_6		
CH_2CH_3	$a_{H(2,3)}$ 2.64_7	1.40	4.53_2	$a_{H(3,6)}$ 2.92_3	1.81	4.53_3
(−62°)	$a_{H(5,6)}$ 1.88_5			$a_{H(2,5)}$ 1.61_0		
	$a_{\beta\text{-}CH_2}$ 3.80_4			$a_{\beta\text{-}CH_2}$ 4.02_5		
	$a_{\gamma\text{-}CH_3}$ 0.15_1			$a_{\gamma\text{-}CH_3}$ 0.15_1		
n-Propoxy	$a_{H(2,3)}$ 2.69_4	1.46	4.53_4	$a_{H(3,6)}$ 2.96_1	1.80	4.60_8
↓	$a_{H(5,6)}$ 1.84_0			$a_{H(2,5)}$ 1.64_7		
n-Octoxy	$a_{\beta\text{-}CH_2}$ 3.88_6			$a_{\beta\text{-}CH_2}$ 4.11_8		
(−58°)	$a_{\gamma\text{-}CH_2}$ 0.11_3			$a_{\gamma\text{-}CH_2}$ 0.11_3		

lent, and, therefore, the barrier to rotation must be small. Since the CH_3 splittings are caused by a hyperconjugative mechanism, the maximum splitting will occur when the angle (θ) between the CH bond and the $p\pi$ orbitals is 0° (see Figures 5 and 6). The actual

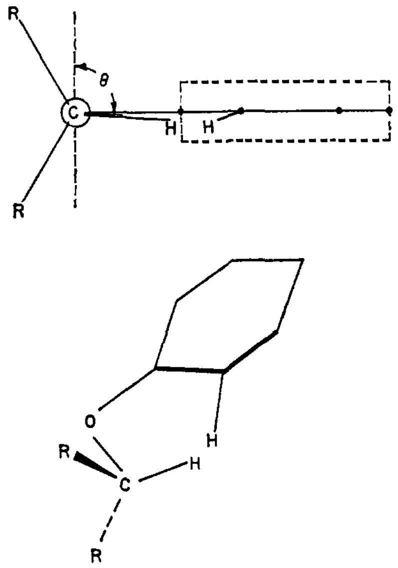

Figure 6. Schematic representation of the equilibrium conformation of *p*-diisopropoxybenzene.

form of the dependence of the splitting constant ($a_{\beta H}$) on θ may be postulated as (*cf.* ref 15),

$$a_{\beta H} = (B_0 + B_2 \cos^2 \theta)\rho_0\pi$$

where $\rho_0\pi$ = spin density on the oxygen atom, B_0 is a small constant, and B_2 has been found to be of the order 30–45 gauss for a number of radicals. For the freely rotating methyl group, the average value of $\theta = 45°$ gives $\langle\cos^2 \theta\rangle = {}^1/_2$. Using a value of $\rho_0\pi = 0.1758$, taken from MO calculations,[1,16] $B_0 + B_2 = 38.5$ gauss, in reasonable agreement with earlier work. This, together with the observed sharp lines and with the absence of line-width effects expected from a non-freely rotating methyl group,[17] suggests that the rotation is reasonably unhindered.

For the *p*-diethoxybenzene cation radical, increased steric interactions between the β-ethyl group and the *ortho* ring protons are expected. This should lead to a potential energy diagram of the form schematically shown in Figure 7. The minimum energy conformation will be that shown in Figure 5 ($R = CH_3$). If this is the actual conformation, then $2a_{\beta\text{-}CH_2}$(diethoxy) = $3a_{\beta\text{-}CH_3}$(dimethoxy), but experimentally $2a_{\beta\text{-}CH_2} = 8.05$ gauss and $3a_{\beta\text{-}CH_3} = 10.17$ gauss. Stone and Maki,[18] in their treatment of the systems RRCHAr· and RCH_2Ar·, have pictured the physical situation as one in which there is torsional oscillation about the equilibrium conformation. The form of this motion is assumed to be sinusoidal, leading to an equation for $a_{\beta\text{-}H}$ of the form[18]

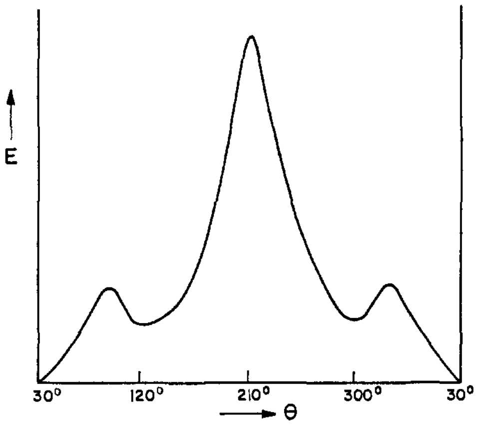

Figure 7. Schematic energy diagram for rotation about the O–C (alkyl) bond of *p*-diethoxybenzene.

$$a_{\beta\text{-}H} = [B_0 + B_2 \cos^2 (\theta_0 + \phi \sin 2t/\tau)]\rho_0\pi$$

where θ = the equilibrium angle, ϕ = torsional amplitude, and τ is the period of oscillation. Provided that τ is rapid compared to the hyperfine interaction, the equation may be averaged over time. If τ is of the same order as the hyperfine interaction (*ca.* 7×10^{-8} sec), the lines will be broadened (see also discussion for *p*-diisopropoxybenzene).

From Figure 5, $\theta = 30°$, and hence, by comparison with Figure 2 of ref 18, we can estimate that at a tem-

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(15) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 325 (1963), and references cited there.

(16) We have since improved the MO calculations in ref 1 by using a slightly different set of parameters.

(17) J. H. Freed and G. K. Fraenkel, *J. Am. Chem. Soc.*, **86**, 3477 (1964).

(18) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

perature of $-60°$, $\phi = 50°$ for the p-diethoxybenzene cation radical. As the temperature decreases, ϕ would be expected to decrease, leading to the observed increase in the β-proton splitting constant.

For the larger p-di-n-alkoxybenzene cation radicals, a similar temperature dependence would be expected, and is observed (see Table V). The torsional amplitude, ϕ, would be expected to decrease with increased size of the substituent, leading to an increased β-proton splitting constant, and this is observed for the n-propoxy compound (*cf.* Tables III and IV). Further lengthening of the side chain does not give rise to any significant changes, presumably because the effective size of the substituent is not altered on passing from n-propyl to n-octyl (*cf.* also ref 19).

Molecular models of the p-diisopropoxybenzene cation radical (see Figure 6; $R_1 = R_2 = CH_3$) indicate an equilibrium conformation in which $\theta \approx 90°$ for the lone CH proton, suggesting $a_{\beta\text{-H}} = 0$ in the absence of torsional oscillation. Increased torsional oscillation with temperature would be expected to lead to an increase in the value of $a_{\beta\text{-H}}$. Although the spectrum is not well resolved, because of line broadening, such an increase is indeed observed (see section on p-diisopropoxybenzene). The experimentally obtained value of $a_{\beta\text{-H}} = ca.\ 2.60$ is consistent with a torsional amplitude of about 57°.

The experimentally observed line-width increase of the p-diisopropoxybenzene cation compared with that of the other p-dialkoxybenzenes (*ca.* 250 mgauss to 70 mgauss) could be explained if the period of torsional oscillation, τ, in the isopropoxy compound was of the same order as the hyperfine splitting ($\sim 10^{-7}$ sec), thus leading to line broadening. Alternatively, it may be caused by small unresolved splittings of the β-CH_3 groups.

In the above discussion, changes because of the inductive effect of substituents have been ignored. The justification for this is based on the near-constancy of (i) the g values (see Table VI) and (ii) the ring proton splitting constants.

Acknowledgments. The authors are indebted to the National Research Council of Canada for a studentship (to P. D. S.) and continued financial assistance.

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(19) A. Carrington and P. F. Todd, *Mol. Phys.*, 7, 533 (1964).

Mass Spectrometry in Structural and Stereochemical Problems. CXXX.[1] A Study of Electron Impact Induced Migratory Aptitudes[2]

Peter Brown[3] and Carl Djerassi

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305.

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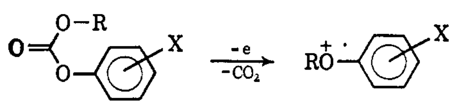
Abstract: The electron impact induced decarboxylation of aryl methyl and aryl phenyl carbonates has been investigated in some detail, using low-voltage and isotope-labeling techniques, and by studying substituent effects on the rate of loss of carbon dioxide. In the substituted-aryl methyl compounds, exclusive methyl group migration is observed, whereas in the aryl phenyl carbonates, competition between the two possible itinerant moieties is apparent, and aryl group relative migratory aptitudes can be assigned. In addition, the substituent dependence of the abundance of the CH_3OCO^+ ion from α cleavage in aryl methyl carbonates has been correlated with Hammett σ values.

Of the unimolecular processes energetically accessible to ions generated by electron impact, that of skeletal rearrangement[4] (in compounds other than hydrocarbons) has only recently been accorded recognition as a relatively common possibility. Despite the elegant application[5-7] of accepted physical organic techniques to simple mass spectral bond cleavages, no similar studies on systems undergoing alkyl or aryl group migrations have as yet been reported. We therefore elected to examine in some detail the necessary requirements for methyl migration in aryl methyl carbonates[8] (I → III) and aryl *vs.* phenyl migration in aryl phenyl carbonates[8] (II → IV), each with concomitant ejection of carbon dioxide as the neutral species.



I, $R=CH_3$
II, $R=C_6H_5$

III, $R=CH_3$
IV, $R=C_6H_5$

M - 44

The rearrangement reactions proved to be relatively facile, giving rise to intense peaks in the 70-ev spectra.[8] Reduction of the ionizing voltage to approxi-

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(1) Paper CXXIX: A. M. Duffield, W. Carpenter, and C. Djerassi, *Chem. Commun.*, 109 (1967).

(2) Financial support from the National Institutes of Health (Grant No. AM-04257) is gratefully acknowledged. The purchase of the Atlas CH-4 mass spectrometer was made possible through NASA Grant No. NsG 81-60.

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(5) (a) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966); (b) *ibid.*, **88**, 4484 (1966).

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