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ISOMERIZATION OF 2,3',5',6-TETRA-*t*-BUTYLINDOPHENOL BY PROTON MAGNETIC RESONANCE SPECTROSCOPY

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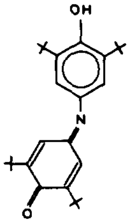
Recently Coppinger and Jungnickel[1] observed by PMR that 2,3',5',6-tetra-*t*-butylindophenol (I) was asymmetrical (three *t*-butyl H lines) in carbon tetrachloride but completely symmetrical (one *t*-butyl H line) in both acids and bases. We have determined the temperature dependence of the equilibration of asymmetrical forms and, moreover, have defined at least one other isomerization process.

The most definitive PMR spectrum[2] of the indophenol (I), prepared by the three step procedure of Coppinger[3], was obtained from a 6.8% carbon tetrachloride solution containing 0.4% glacial acetic acid (Fig. 1). The spectrum consists of an AB quartet - τ_A at 2.96 ppm, τ_B at 3.03 ppm and J_{AB} = 3.5 cps - (quinone H), and single lines at 3.25τ (aromatic H), 8.55τ (aromatic-*t*-butyl H), 8.66τ (*trans*-quinone-*t*-butyl H) and 8.76τ (*cis*-quinone-*t*-butyl H). Without added acid the hydroxyl proton appears at 4.80τ and the quinone protons appear as a broad line at 3.00τ. The assignments for the quinone-*t*-butyl protons are made from observations on the Fisher-Hirschfelder-Taylor molecular



I

FIG. 1

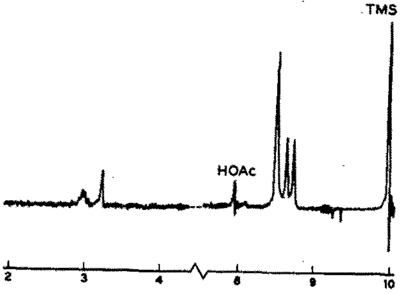


FIG. 2

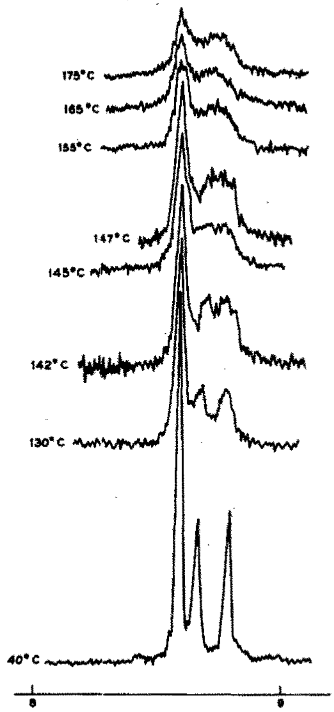
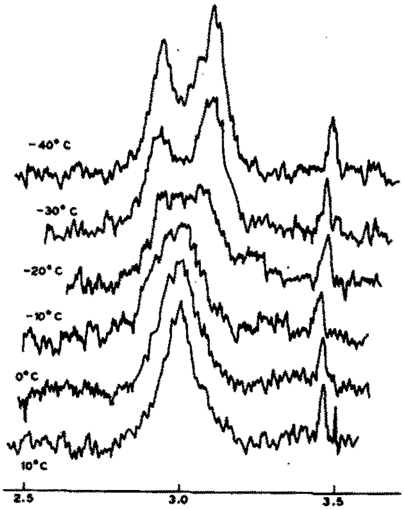


FIG. 3



model. Because of ring hydrogen interactions the aromatic and quinone rings are preferably orthogonal. The _cis_-quinone-_t_-butyl protons then are shielded by the aromatic ring current while the _trans_-quinone-_t_-butyl protons are deshielded.[4] The AB quartet for the quinone protons and two lines for the quinone-_t_-butyl protons are an obvious consequence of the asymmetry about the carbon-nitrogen double bond.[5]

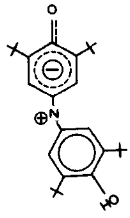
The temperature dependence of the peak linewidths for the _t_-butyl protons was measured in o-dichlorobenzene (Fig. 2). Various parameters calculated from these spectra are listed in Table I.

TABLE I

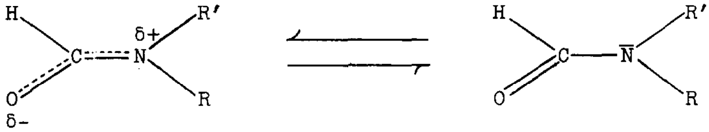
Observed Aromatic (W_A) and Quinone (W_B)-_t_-Butyl Linewidths[6] and Calculated Parameters[7] From the PMR Spectra of I at Various Temperatures

T °K	W_A cps	W_B cps	k_B sec^{-1}	$\Delta F_T^{\ddagger}$ kcal./mole
313	0.0	0.0	-	-
353	0.0	0.3	0.9	20.3_7
358	0.0	0.3	0.9	20.6_7
368	0.1	0.6	1.9	20.7_2
373	0.2	0.7	2.2	20.9_0
378	0.0	1.0	3.1	20.9_4
388	0.0	1.8	5.7	21.0_4
393	0.0	2.4	7.5	21.1_1
418	0.8	-	-	-
423	1.5	-	-	-

From the slope of the ln k_B versus 1/T line, E_a was found to be 17±4 kcal./mole. The increase of $\Delta F_T^{\ddagger}$ with increase in temperature points to a large negative $\Delta S^{\ddagger}$. This probably indicates that the nonpolar solvent allows very little charge separation in the activated complex (II) during passage over the barrier. This restriction is somewhat analogous to that for amides, in which the partially charged ground state (IIIA) is stabilized by polar solvents:

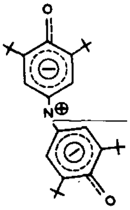


II



IIIA IIIB

The broadening of the quinone-t-butyl proton lines up to 120°C is attributed to isomerization about the carbon-nitrogen double bond. The broadening of the aromatic-t-butyl proton line above 120°C is evidence for a second process which we believe is a ring equilibration in which both rings become identical by intra- or intermolecular proton transfer (IV).



IV

The PMR spectra at different temperatures (Fig. 3) of the indophenol in 4.5% hexadeuteroacetone solution containing approximately 0.1% water confirm the ring equilibration process. Without water coalescence is not observed below 60°C. At room temperature all the aromatic and quinone protons appear as one line (3.00τ), both equilibration and isomerization processes being rapid. A substantial decrease in the rate for the ring equilibration process is observed below -20°C (appearance of two maxima for the aromatic and quinone protons), while the isomerization about the carbon-nitrogen double bond remains appreciable (only one line for the quinone-t-butyl protons) even at -55°C, the lower limit of the temperature probe.

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