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NMR Spectra of Tropolone Derivatives*

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Synopsis

NMR spectra of bromotropolones and of 5-substituted tropolones have been measured and the effect of those substituents on the tropolone system are discussed compared with the benzene system.

I. Introduction

It is well known that NMR spectroscopy is a powerful method for solving the problem on aromatic character by ring current estimation⁽¹⁾, as well as estimating electron density on the aromatic system⁽²⁾.

In order to establish the relationship between electron densities and reactivities of the troponoid systems, NMR study on these welldefined aromatic system was undertaken using deuterio-derivatives to conclude the decrease of aromatic character⁽³⁾. The study has been extended to the effect of substituents, the result of which is described in this paper. Bromo-derivatives are for the effect of substituted position, and 5-substituted ones are for the effect of various functional groups.

II. Experimental

All materials used in this study are known and derived by reported methods. 3-Bromo (II)⁽⁴⁾, 4-bromo (III)⁽⁵⁾, 5-bromo (IV)⁽⁴⁾, 3,5-dibromo (V)⁽⁴⁾, 3,6-dibromo

* This paper is a part of author's D. Sc. thesis, Tohoku Univ. (1963).

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(VI)⁽⁶⁾, 3,7-dibromo (VII)⁽⁴⁾, 3,5,7-tribromo (VIII)⁽⁴⁾, 5-isopropenyl (IX)⁽⁷⁾, 5-chloro (X)⁽⁸⁾, 5-iodo (XI)⁽⁸⁾, 5-methoxy (XII)⁽⁹⁾, 5-hydroxy (XIII)⁽⁹⁾, 5-amino (XIV)⁽⁸⁾, 5-nitro (XV)⁽¹⁰⁾, 5-cyano (XVI)⁽¹¹⁾, 5-methoxycarbonyl (XVII)⁽¹¹⁾, and 5-acetyltropolone (XVIII)⁽⁷⁾. Measurements were carried out at 60 Mcps using a Varian A-60 spectrometer in deuteriochloroform for bromotropolones and in trifluoroacetic acid for 5-substituted tropolones with TMS as internal standard. The concentration is less than 10 M %. since the concentration shift is not observed for 4-bromotropolone between 2.9 to 11.4 M %. Because of low solubility of (IV), its chemical shifts are determined in deuteriochloroform and the fine structure of its spectrum is observed in dioxane.

III. Results and Discussion

The analysis of spectra of these compounds, except (II) and (III), was made relatively easily⁽⁴⁾. For compound (II) Swalen's program was used with IBM 7090 computer (fig. 1)⁽¹²⁾. The spectrum of compound (III) does not show well resolved fine structure, so that the analysis could not be made and might be done in near future with a 100 Mcps spectrometer or by double resonance method. Obtained results are listed in Table I.

On the spin-spin coupling constants of (II) between adjacent hydrogens, J_{45}

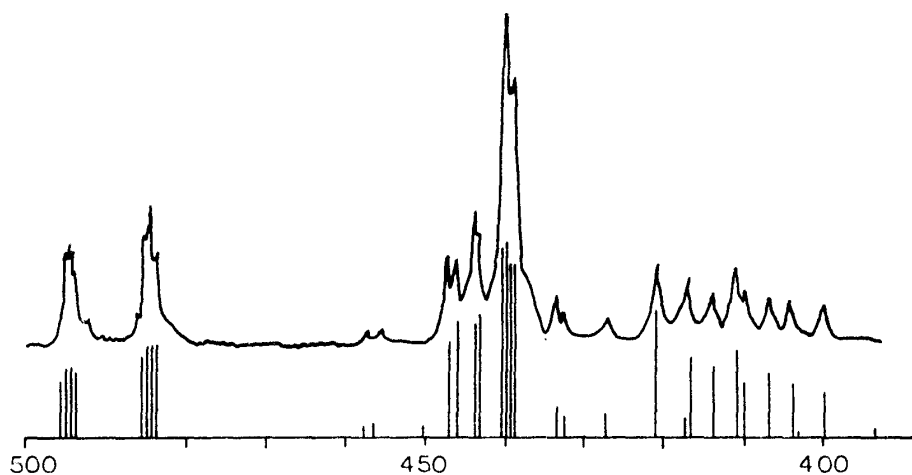


Fig. 1. Observed (top) and calculated (bottom) NMR spectra of 3-bromotropolone.

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Table I. a. Chemical shifts and spin-spin coupling constants of bromotropolones. All chemical shifts are presented by cps from internal standard TMS in CDCl_3 at 60 Mcps.

Position	3	4	5	6	7
Tropolone (I)	442.0	442.0	423.0	442.0	442.0
	$J_{45}=J_{56}=10.2$:				
3-Bromo (II)		491.4	413.8	446.8	441.7
	$J_{45}=10.2$; $J_{56}=8.9$; $J_{67}=11.3$; $J_{46}=1.0$; $J_{57}=2.5$:				
4-Bromo (III)	463.8				
	$J_{35}=1.3$:				
5-Bromo (IV)	429.3	457.5		457.5	429.3
	$J_{34}=12.0$; $J_{46}=1.6$:				
3,5-Dibromo (V)		510.3		461.6	428.4
	$J_{67}=11.3$; $J_{46}=1.9$:				
3,6 dibromo (VI)		471.4	430.6		460.6
	$J_{45}=11.3$; $J_{57}=1.8$:				
3,7-Dibromo (VII)		482.0	398.9	482.0	
	$J_{45}=J_{56}=10.9$:				
3,5,7-Tribromo (VIII)		500.5		500.5	

Table I. b. Chemical shifts and spin-spin coupling constants of 5-substituted tropolones. All chemical shifts are presented by cps from internal TMS in trifluoroacetic acid at 60 Mcps.

Functional group	Chemical shift				Coupling constant J_{34}
	Ring proton		Other than ring proton		
Isopropenyl (IX)	488.6	498.0	331.6	137.0	11.6
Chloro (X)	474.8	486.8			11.6
Bromo (IV)	491.5	519.1			11.7
Iodo (XI)	456.6	513.4			11.7
Methoxy (XII)	467.0	489.2			12.0
Hydroxy (XIII)	466.8	485.2			11.9
Amino (XIV)	430.7	463.7			11.0
Nitro (XV)	455.2	518.8			11.9
Cyano (XVI)	453.8	471.4			11.3
Methoxycarbonyl(XVII)	468.5	517.5		242.9	11.7
Acetyl (XVIII)	464.9	507.1		169.0	11.5

and J_{67} are bigger than J_{56} as shown in Table I. In the tropolone system the high mobile tautomerism was suggested by Dewar to rationalize its remarkable stability and symmetric character⁽¹³⁾. In tropolone itself the tautomers, having the identical structure A and B (R=H, fig. 2), contribute equally to the equilibrium.

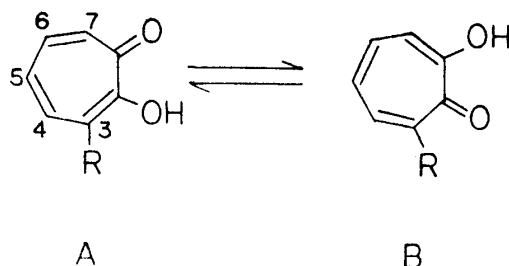


Fig. 2.

Asymmetrically substituted tropolone, however, may shift the equilibrium in favor of one tautomer. Recently, the existence of these tautomers, A and B (R=Alkyl, fig. 2) in 3-alkyltropolones, as well as of those in 4-alkyltropolones, has been suggested by Ikegami on the bases of IR and Raman spectroscopies⁽¹⁴⁾.

According to McConnell's theory, the spin-spin coupling constant (J) between hydrogens attached to adjacent carbons can be expressed as following,

$$J = J^{\sigma} + J^{\pi}.$$

J^{σ} is the contribution through σ -bonding electrons. J^{π} from π -electrons can be given as following,

$$J^{\pi} = (\beta Q \eta) / h \Delta E.$$

β ; electron Bohr magneton, η ; π -bond order, Q ; effective hyperfine interaction constant, ΔE ; energy difference between the ground singlet state and the excited triplet state, and h ; Planck constant⁽¹⁵⁾. Experimentally, this theory is supported in the benzenoid system⁽¹⁶⁾.

Direct application of this theory to the coupling constants of compound (II) suggests that the equilibrium in (II) (R=Br, fig. 2) is shifted towards A rather than to B, providing that the magnitudes of J^{σ} stay at the same value in all carbon-carbon bonds concerned⁽¹⁷⁾.

In order to find the effect of bromine position, the differences of chemical shifts of bromine derivatives are shown in Table II. At the α -position to bromine atoms, hydrogen chemical shifts shift 0.22–0.39 ppm to lower field by 4- or 5-substituted bromine atom, 0.59–0.88 ppm to lower field by 3- or 7-substituted

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Table II. The differences of hydrogen chemical shifts on bromotropolones (Minus sign shows lower field shift).

α Position to bromine atom.		Difference in ppm
4H on (I)	4H on (II)	- 0.832
4H on (IV)	4H on (V)	- 0.880
6H on (II)	4H on (VII)	- 0.587
6H on (V)	4H on (VIII)	- 0.468
3H on (I)	3H on (III)	- 0.363
5H on (II)	5H on (VI)	- 0.253
7H on (II)	7H on (VI)	- 0.320
4H on (I)	4H on (IV)	- 0.258
4H on (II)	4H on (V)	- 0.351
6H on (II)	6H on (V)	- 0.220
4H on (VII)	4H on (VIII)	- 0.308
β Position to bromine atom		
5H on (I)	5H on (II)	+ 0.160
5H on (II)	5H on (VII)	+ 0.248
4H on (II)	4H on (VI)	+ 0.333
3H on (I)	3H on (IV)	+ 0.212
7H on (II)	7H on (V)	+ 0.217
γ Position to bromine atom.		
4H on (I)	6H on (II)	- 0.080
4H on (IV)	6H on (V)	- 0.068
4H on (V)	4H on (VIII)	+ 0.163
4H on (II)	4H on (VII)	+ 0.158
δ Position to bromine atom.		
3H on (I)	7H on (II)	+ 0.005
3H on (IV)	7H on (V)	+ 0.015
3H on (III)	7H on (VI)	+ 0.053

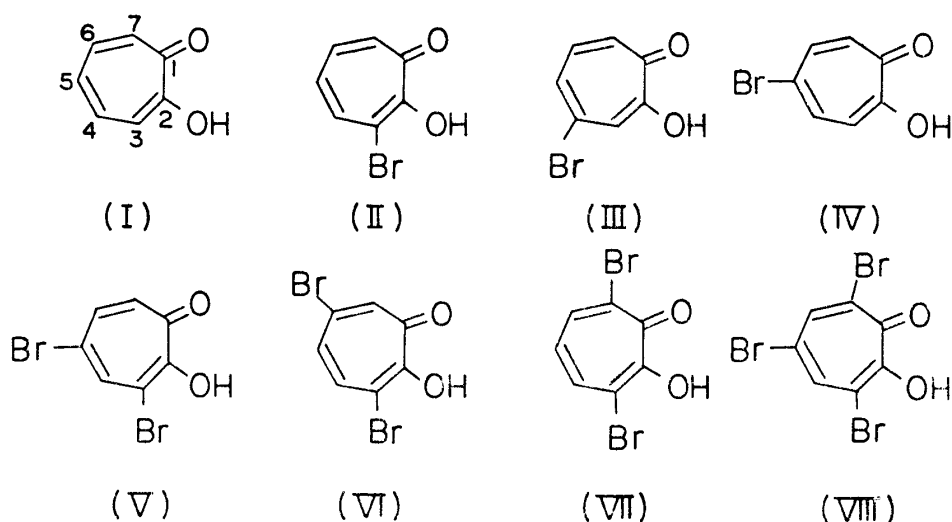


Fig. 3. Structures of bromotropolones used in this study.

bromine atom. These tendencies are very similar to the benzenoid system⁽¹⁸⁾, but the big difference is that the tropolone system makes much bigger shifts. Bromine atom on 3- or 7-position does not occupy the space within the van der Waals radius of oxygen atom on 1- or 2-position, but there should be the dipole-dipole repulsion between bromine and oxygen. As the result, bromine atom on 3- or 7-position should occupy much closer position to hydrogen atom on 4- or 6- position and this should make the chemical shift difference bigger. The comparison between α position and β position to bromine atoms shows the same tendency as the benzoid system^(18,19), but tropolone has bigger chemical shift differences.

Considering 3- and 7-bromine substituted derivatives, α position to bromine atom on asymmetrically substituted ones shows 0.62 ppm down field shift and on symmetrically substituted ones much bigger 0.83 ppm lower field shift. Moreover, γ position on symmetrical ones shows 0.16 ppm higher field shift and on asymmetrical ones 0.08 ppm lower field shift. Such relationship between symmetrical and asymmetrical derivatives can be closely related to the double bond fixation of (II) above mentioned.

The absorption frequencies of bromine pure quadrupole resonance of bromotropolones show the additivity⁽²⁰⁾, on this study, however, the additivity of chemical shift is not found.

Because of low solubility of 5-substituted tropolones, their spectra were taken in trifluoroacetic acid solution, which is only a solvent to make enough concentration for NMR measurement. Obtained spectra show not A_2B_2 type absorption but AB type one, so that only spin-spin coupling constants obtained are their J_{34} (J_{67})⁽¹⁾. There is the colinearity between 5-halotropolones' higher field chemical shifts and Hammett σ_m constants, but other derivatives do not show such correlation to ordinary Hammett constant, and unfortunately, Hammett σ constant in such strong acidic media can not be found. However, in the benzenoid system meta chemical shift does not show such regularity^(21,22), only the case, we can find, is the case of fluorine chemical shifts of fluorobenzene derivatives⁽²³⁾. Cox reported that there was correlation between spin-spin coupling constant and functional group's electronegativity⁽²⁴⁾, and Dischler⁽²⁵⁾ and Castellano⁽²²⁾ described the additivity for coupling constants, but in the tropolone system such additivity is not found because of the lack of experimental accuracy.

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