

Yutaka Tsunashima and Masatane Kuroki*

Department of Chemistry, Shibaura Institute of Technology, Fukasaku, Ohmiya-shi, Saitama 330 Japan
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Electronic spectra of a number of methylcarbazoles were measured. Spectral shifts of the longest wavelength absorption bands were evaluated by the HMO-perturbation method. The calculated shifts of 1-substituted (group II) and 4,5-disubstituted carbazoles (group III) did not agree with the observed values. The effect of the methyl group on the direction and magnitude of the shift is closely additive except for 4,5-disubstituted carbazoles. The additivity principle is a useful tool for determination of methylcarbazoles.

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The electronic spectra of methylcarbazoles have received attention in connection with the determination of carbazole derivatives isolated from plant degraded products, coal tar and petroleum. Basu (1) predicted spectral shifts of the longest wavelength absorption bands for mono- and dimethylcarbazoles by means of the second-order perturbation method in the framework of the Hückel molecular orbital theory.

In the present paper, we will test the applicability of Basu's prediction, and demonstrate existence of additivity of the spectral shifts. Spectral data for 42 methylcarbazoles and their additivity will serve to determine the naturally occurring carbazoles.

The longest wavelength absorption band of carbazole at 332 nm had been assigned to 1L_b (2) (3), and it corresponds to the electron transition from the highest occupied molecular orbital (a) to the lowest vacant molecular orbital (b) (4). Spectral shift caused by methyl group can be given by equation 1, as demonstrated by Longuet-Higgins and Sowden (5).

$$\Delta\epsilon_{ab} = (\Delta\epsilon_{ab})_{\text{induct}} + (\Delta\epsilon_{ab})_{\text{hyperconj}} \quad (1)$$

The first term, $(\Delta\epsilon_{ab})_{\text{induct}}$, depends on inductive effect of methyl group, and the net change is given by equation 2;

$$(\Delta\epsilon_{ab})_{\text{induct}} = (C_{br}^2 - C_{ar}^2)\delta\alpha_r + \left(\sum_{j(\neq b)} \frac{C_{br}^2 C_{jr}^2}{\epsilon_b - \epsilon_j} - \sum_{j(\neq a)} \frac{C_{ar}^2 C_{jr}^2}{\epsilon_a - \epsilon_j} \right) (\delta\alpha_r)^2 \quad (2)$$

where C_{jr} refers to atomic orbital coefficient of the r carbon in the j molecular orbital. The term $\delta\alpha_r$ is the change of the Coulomb integral for carbon by the introduction of a methyl group. The term, $(\Delta\epsilon_{ab})_{\text{hyperconj}}$ is the hyperconjugation effect, and it is expressed by

$$(\Delta\epsilon_{ab})_{\text{hyperconj}} = \beta_{rs}^2 \left\{ C_{br}^2 \left(\frac{C_{1s}^2}{\epsilon_b - \epsilon_1} + \frac{C_{2s}^2}{\epsilon_b - \epsilon_2} \right) - C_{ar}^2 \left(\frac{C_{1s}^2}{\epsilon_a - \epsilon_1} - \frac{C_{2s}^2}{\epsilon_a - \epsilon_2} \right) \right\} \quad (3)$$

where β_{rs} is the resonance integral of the bond between the r carbon atom of carbazole and s carbon atom of substituent, and C_{1s} and C_{2s} are atomic orbital coefficients in molecular orbital functions ψ_1 and ψ_2 for methyl group, respectively.

Basu (1) calculated the extent and directions of spectral shifts for all isomers of mono- and dimethylcarbazoles by equations 1-3. We were interested in testing his prediction. In Table I experimental data are compiled for complete series of mono- and dimethylcarbazoles and also eleven trimethylcarbazoles, ten tetramethylcarbazoles and one pentamethylcarbazole in cyclohexane. Table II shows spectral shifts for the peaks corresponding to the 331.9 nm band of carbazole. This table contains several data taken from the literature. As these spectra were measured for ethanolic solutions, the shifts were based on the 337.0 nm band of carbazole in ethanol. Solvent shift involves various factors, and therefore, correspondence of the shifts in ethanolic solution to those in cyclohexane solution may be somewhat ambiguous.

Basu's calculations are not necessarily sufficient to predict the magnitude and direction of the shifts, especially for 4- or 5-substituted carbazoles. He used $\alpha_N = \alpha_C + 1.5\beta_C$ as a Coulomb integral for the nitrogen atom of carbazole. However, this conventional value has been proved to be inadequate in many respects by one of the authors (6).

Calculations by using the Coulomb integrals, $\alpha_N = \alpha_C + 0.9\beta_C$ and $\alpha_C' = \alpha_C + 0.1\beta_C$ proposed by us led to fair agreement with the experimental data for the carbazoles in group I. As other parameters, $\alpha_{Me} = \alpha_C - 0.1\beta_C'$, $\beta_{Me} = 2.5\beta$ and $\alpha_{H_3} = \alpha_0 - 0.5\beta_C$ were used. Present calculations showed that the spectral shift of 4-methylcarbazole is expected to be slightly hypsochromic (-0.4 nm), in contrast to the largest bathochromic shift (+5.0 nm) predicted by Basu. In accordance with the present calculation, the slight hypsochromic shift (-0.2 nm) was observed in the spectrum of 4-methylcarbazole, and same tendency was reported for 4-methoxycarbazole (7).

Table I

Electronic Absorption Spectra of Methylcarbazoles in Cyclohexane [λ max, nm (log ϵ)]				
Carbazole	210.8 (4.38)	233.2 (4.63)	281.0 (4.04)	307.8 (3.45)
	221 s (4.49)	246.0 (4.36)	285.7 (4.12)	319.0 (3.58)
	230 s (4.60)	255.6 (4.11)	291.3 (4.31)	331.9 (3.56)
1-methyl- carbazole	215 s (4.46)	237.5 (4.66)	280.5s (4.06)	307.5 (3.57)
	222.5 s (4.50)	247.6 (4.42)	286 s (4.14)	318.7 (3.69)
	233.0 s (4.64)	256.4 (4.09)	290.5 (4.33)	331.5 (3.68)
2-	212.5 (4.48)	234.5 (4.77)	285 s (4.15)	
		247.5 (4.45)	290.0 s (4.23)	317.5 (3.70)
	230 s (4.69)	257.3 (4.16)	295.0 (4.37)	330.3 (3.67)
3-	216 s (4.46)	235.0 (4.78)	283.6 (4.07)	312.8 (3.50)
	224.5 s (4.54)	248.5 (4.35)	288.5 (4.15)	324.0 (3.60)
	231.6 (4.61)	258.0 (4.08)	294.5 (4.34)	337.9 (3.58)
4-		238.3 (4.69)	278.5 (4.03)	308.0 (3.43)
		247.0 s (4.37)	283.0 (4.10)	319.0 (3.61)
		258.4 (4.12)	288.0 (4.35)	331.7 (3.67)
1,2-dimethyl- carbazole	215.0 (4.46)	237.9 (4.68)	284.5 s (4.08)	
		248.3 (4.45)	289.5 s (4.17)	318.0 (3.71)
		257.5 (4.09)	294.0 (4.33)	331.0 (3.64)
1,3-		239.5 (4.45)	284.0 s (3.93)	312.3 (3.43)
	226.5 s (4.37)	250.0 s (4.18)	289.5 s (3.99)	324.3 (3.48)
	233.9 (4.44)	259.1 (3.95)	293.8 (4.15)	338.0 (3.41)
1,4-		240.7 (4.71)	278.0 (3.98)	309.5 s (3.40)
	225.9 (4.50)	250.0 s (4.37)	283 s (4.04)	319.6 (3.60)
	235 s (4.63)	259.0 (4.09)	287.7 (4.29)	332.5 (3.66)
1,5-		240.5 (4.74)	278.0 (4.01)	308.5 s (3.43)
		249.5 (4.43)	283 s (4.08)	318.5 (3.63)
	235.5 s (4.68)	258.4 (4.12)	287.0 (4.32)	331.5 (3.68)
1,6-		240.0 (4.58)	283.3 (4.02)	313.0 (3.40)
	227 s (4.51)	250.2 (4.37)	288.7 (4.09)	324.0 (3.55)
	233.5 (4.58)	258.7 (4.03)	293.7 (4.31)	337.4 (3.55)
1,7-	213.0 (4.48)	237.4 (4.67)	284 s (4.05)	
		249.3 (4.41)	289 s (4.13)	317.2 (3.62)
		258.2 (4.10)	294.2 (4.26)	330.2 (3.47)
1,8-	215.5 (4.42)	239.9 (4.68)	280.0 (3.98)	307.5 (3.45)
	220.8 (4.42)	248.9 (4.47)		318.5 (3.62)
	235 s (4.64)	256 s (4.06)	289.5 (4.26)	331.0 (3.62)
2,3-	214.3 (4.21)	235.5 (4.39)	287 s (4.11)	
		248.3 (4.36)	292 s (4.19)	321.5 (3.62)
	232 s (4.36)	259.0 (4.07)	297.1 (4.36)	335.3 (3.54)
2,4-	214.5 (4.35)	238.0 (4.71)	282.3 (4.07)	
		248.5 s (4.43)	287.5 s (4.15)	317.5 (3.60)
		260.1 (4.13)	292.1 (4.35)	330.3 (3.53)
2,5-	214.8 (4.32)	237.7 (4.72)	282.4 (4.06)	305 s (3.47)
		248.5 s (4.40)	287.5 s (4.14)	317.8 (3.60)
		260.4 (4.12)	291.8 (4.31)	330.7 (3.56)
2,6-	216.5 (4.45)	236.7 (4.68)	288.0 s (4.09)	
		249.8 (4.36)	293.5 s (4.18)	322.3 (3.62)
		260.0 (4.07)	298.5 (4.34)	336.0 (3.48)
2,7-	215.0 (4.39)	236.5 (4.74)		
		250.2 (4.36)	293 s (4.15)	315.0 (3.72)
		254 s (4.27)	298.6 (4.27)	329.0 (3.41)
		259.5 (4.12)		
3,4-		240.5 (4.64)	280.9 (4.04)	
	227 s (4.51)	250.2 (4.34)	286.0 (4.11)	324.9 (3.55)
	234.5 (4.61)	262.0 (4.10)	291.2 (4.37)	338.8 (3.59)
3,5-		241.0 (4.64)	281.1 (4.04)	314.5 (3.36)
		250.5 (3.74)	286.2 (4.10)	324.4 (3.56)
	235.0 (4.63)	261.7 (4.08)	291.1 (4.37)	338.2 (3.61)

Table I continued

3,6-		238 s (4.57)	287.3 (4.08)	319.5 (3.42)
	227.0 s (4.57)	251.0 (4.30)	292.3 (4.17)	329.4 (3.54)
	232.9 (4.60)	260.3 (4.01)	298.4 (4.36)	343.8 (3.47)
4,5-	218.2 (4.44)	246.0 (4.66)	274.0 s (3.72)	315 s (3.49)
		253.2 (4.42)	282.4 (4.07)	326.3 (3.70)
	239.9 (4.59)	258.s (4.59)	292.2 (4.34)	333.0 (3.55)
				339.7 (3.82)
1,3,4-trimethyl- carbazole		242.0 (4.67)	280.5 (4.02)	315 s (3.36)
	226.5 (4.51)	251.5 s (4.36)	286 s (4.07)	325.2 (3.57)
	235.5 s (4.61)	263.2 (4.11)	290.5 (4.32)	339.2 (3.60)
1,4,8-		242.3 (4.58)	277.0 (3.94)	308.5 s (3.39)
		251.6 (3.90)		318.7 (3.62)
	236 s (4.40)	258.5 s (4.07)	286.6 (4.25)	331.7 (3.67)
1,5,7-	217.5 s (4.31)	241.3 (4.74)	282.0 s (4.03)	305.3 (3.45)
		250.0 s (4.47)		316.8 (3.59)
		260.2 (4.11)	290.8 (4.30)	329.8 (3.56)
2,3,5-	215.2 (4.40)	238.1 (4.70)	283.5 (4.08)	310.0 (3.39)
		250.0 s (4.38)	288.5 s (4.15)	321.7 (3.59)
		262.2 (4.09)	293.4 (4.36)	335.0 (3.57)
2,3,6-	217.7 (4.52)	238.0 (4.64)	289.5 s (4.12)	
		251.0 (4.33)	294.9 (4.21)	326.5 (3.64)
	233.5 s (4.63)	261.3 (4.02)	300.6 (4.38)	339.8 (3.50)
2,4,5-	218.9 (4.42)	246.8 (4.68)	286.0 (4.08)	311.9 (3.48)
		254.1 (4.48)		324.0 (3.62)
	240.5 (4.63)	262 s (4.04)	295.6 (4.31)	337.8 (3.62)
2,4,6-	216.6 (4.41)	240.0 (4.70)	285.0 (4.08)	311.7 (3.45)
		251.7 (4.42)	290 s (4.17)	322.8 (3.58)
		263.0 (4.11)	295.0 (4.36)	336.0 (3.54)
2,4,7-	214.2 (4.38)	239.1 (4.81)	286 s (4.12)	
		250 s (4.45)		316.2 (3.67)
		262.0 (4.15)	295.3 (4.34)	328.8 (3.51)
3,4,6-		243.0 (4.63)	283.9 (4.07)	
	230 s (4.56)	252.0 (4.32)	289.0 (4.13)	329.8 (3.55)
	236.1 (4.62)	264.3 (4.06)	294.3 (4.40)	343.9 (3.57)
1,2,5,7-tetra- methyl- carbazole	215.3 (4.35)	240.5 (4.75)	285 s (4.04)	
		251.5 s (4.46)		317.2 (3.55)
		262.0 (4.09)	294.4 (4.30)	329.6 (3.42)
1,2,6,7-	216.8 (4.49)	239.0 (4.30)	289 s (4.11)	
		251.5 (4.43)		320.5 (3.72)
		260.5 s (4.08)	299.4 (4.35)	333.7 (3.56)
1,3,4,6-		244.5 (4.65)	283.5 (4.05)	
	230.0 (4.56)	253 s (4.35)		329.8 (3.59)
	237.8 (4.62)	265.3 (4.08)	296.5 (4.32)	343.8 (3.58)
1,4,5,8-	221.0 (4.38)	248.4 (4.39)	281.0 (3.98)	314.5 s (3.44)
		255 s (4.45)		325.2 (3.71)
	243.5 s (4.36)	269.4 (3.76)	290.6 (4.26)	338.9 (3.79)
2,3,5,7-	215.6 (4.40)	240.0 (4.49)	287.0 s (4.12)	
		252.0 (4.42)		320.0 (3.64)
		263.5 (4.13)	296.8 (4.37)	333.0 (3.54)
2,3,6,7-	216.8 (4.54)	238.0 (4.69)	293 s (4.16)	
		251.0 (4.35)	298 s (4.25)	324.0 (3.72)
	233.0 s (4.65)	262.0 (4.04)	302.5 (4.38)	337.1 (3.45)
2,4,5,6-	222.0 (4.40)	248.2 (4.64)		319.0 s (3.39)
		256.5 s (4.43)	288.5 (4.06)	329.7 (3.57)
	242.3 (4.59)	265.5 s (4.04)	297.8 (4.29)	344.0 (3.55)

For 1-substituted carbazoles (group II), both calculations failed to agree with experimental results, although some improvement was recognized for the present calcula-

Table II

Spectral Shifts of the Longest Wavelength Absorption Bands

Carbazole	Found	Spectral Shift, nm		
		Additivity	Basu (1)	This Work
[Group I]				
2-methyl-	-1.6 (-2.1)(a)		-1 (0.6)	-2.6 (-1.0)
3-	6.0 (6.2)(a)		3 (-3.0)	5.6 (-0.4)
4-	-0.2 (-0.5)(a)		5 (5.2)	-0.4 (-0.2)
2,3-dimethyl-	3.4	4.4 (1.0)	2 (-1.4)	3.0 (-0.4)
2,4-	-1.6	-1.8 (-0.2)	4 (5.6)	-3.0 (-1.4)
2,5-	-1.2	-1.8 (-0.6)	4 (5.2)	-3.0 (-1.8)
2,6-	4.1	4.4 (0.3)	2 (-2.1)	3.0 (-1.1)
2,7-	-2.9	-3.2 (-0.3)	-2 (0.9)	-5.1 (-2.2)
3,4-	6.9	5.8 (-1.1)	4 (-2.9)	5.2 (-1.7)
3,5-	6.3	5.8 (-0.5)	4 (-2.3)	5.2 (-1.1)
3,6-	11.9	12.0 (0.1)	6 (-5.9)	11.5 (-0.4)
2,3,5-tri-methyl-	3.1	4.2 (1.1)		2.6 (-0.5)
2,3,6-	7.9	10.4 (2.5)		8.7 (0.8)
2,4,6-	4.1	4.2 (0.1)		2.6 (-1.5)
2,4,7-	-3.1	-3.4 (-0.3)		-5.5 (-2.4)
3,4,6-	12.0	11.8 (-0.2)		11.1 (-0.9)
2,3,5,7-tetramethyl-	1.1	2.6 (1.5)		0.0 (-1.1)
2,3,6,7-	5.2	8.8 (3.6)		6.0 (0.8)
[Group II]				
1-methyl-	-0.4 (-0.3)(a)		4 (4.4)	4.7 (5.1)
1,2-dimethyl-	-0.9	-2.0 (-1.1)	4 (4.9)	2.0 (2.9)
1,3-	6.1	5.6 (-0.5)	8 (1.9)	10.5 (4.4)
1,4-	0.6	-0.6 (-1.2)	9 (8.4)	4.3 (3.7)
1,5-	-0.4	-0.6 (-0.2)	9 (9.4)	4.3 (4.7)
1,6-	5.5	5.6 (0.1)	8 (2.5)	10.5 (5.0)
1,7-	-1.7	-2.0 (-0.3)	4 (5.7)	2.0 (3.7)
1,8-	-0.9	-0.8 (0.1)	8 (8.9)	9.5 (10.4)
1,2,3-tri-methyl- (22)	5.1	4.0 (-1.2)		7.8 (2.6)
1,2,5- (19)	3.0 (a)	-2.9 (-5.9)(a)		1.7 (-1.3)
1,3,4-	7.3	5.4 (-1.9)		10.1 (2.8)
1,4,8-	-0.2	-1.0 (-0.8)		9.1 (9.3)
1,5,7-	-2.1	-2.2 (-0.1)		1.7 (3.8)
1,2,5,7-tetra-methyl-	-2.4	-3.8 (-1.4)		-0.8 (1.6)
1,2,6,7-	1.8	2.4 (0.6)		5.1 (3.3)
1,2,7,8- (19)	1.0 (a)	-4.8 (-5.8)(a)		4.1 (3.1)
1,3,4,6-	11.9	11.4 (-0.5)		16.1 (4.2)
1,3,6,8- (19)	15.0 (a)	11.8 (-3.2)(a)		21.7 (6.7)
1,2,3,5,7-pentamethyl- (19)	5.0 (a)	1.2 (-3.8)(a)		7.4 (2.4)
[Group III]				
4,5-dimethyl-	7.8	-0.4 (-8.2)	10 (2.2)	-0.8 (-8.6)
2,4,5-tri-methyl-	5.9	-2.0 (-7.9)		-6.0 (-11.9)
1,4,5,8-tetra-methyl-	7.0	-1.2 (-8.2)		9.1 (2.1)
2,4,5,6-	12.1	3.2 (-8.9)		2.2 (-9.9)
2,4,5,7- (21)	2.0 (a)	-5.2 (-7.2)(a)		-6.0 (-8.0)

(a) Reported data in ethanol; the shift from the 337.0 nm band of carbazole in ethanol.

Table III

Spectral Shifts of the 255.6 nm Band

Carbazole	Found	Calculated by Additivity	Difference
1-methyl-	0.8 (0.5) (a)		
2-	1.7 (2.2) (a)		
3-	2.4 (2.5) (a)		
4-	2.8 (2.6) (a)		
1,2-dimethyl-	1.9	2.5	0.6
1,3-	3.5	3.2	-0.3
1,4-	3.4	3.6	0.2
1,5-	2.8	3.6	0.8
1,6-	3.1	3.2	0.1
1,7-	2.6	2.5	-0.1
1,8-	0.9	1.6	0.7
2,3-	3.4	4.1	0.7
2,4-	4.5	4.5	0
2,5-	4.8	4.5	-0.3
2,6-	4.4	4.1	-0.3
2,7-	3.9	3.4	-0.5
3,4-	6.4	5.2	-1.2
3,5-	6.1	5.2	-0.9
3,6-	4.7	4.8	0.1
1,2,3-trimethyl- (22)	3.4	4.9	1.5
1,2,5- (19)	6.7 (a)	5.3 (a)	-1.4
1,3,4-	7.6	6.0	-1.6
1,4,8-	2.9	4.4	1.5
1,5,7-	4.6	5.3	0.7
2,3,5-	6.6	6.9	0.3
2,3,6-	5.7	5.6	-0.1
2,4,6-	7.4	6.9	-0.5
2,4,7-	6.4	6.2	-0.2
3,4,6-	8.7	7.6	-1.1
1,2,5,7-tetramethyl-	6.4	7.0	0.6
1,2,6,7-	4.9	6.6	1.7
1,2,7,8- (19)	2.7 (a)	5.4 (a)	2.7
1,3,4,6-	9.7	8.4	-1.3
1,3,6,8- (19)	6.7 (a)	6.0 (a)	-0.7
2,3,5,7-	7.9	8.6	0.7
2,3,6,7-	6.4	8.2	1.8
1,2,3,5,7-penta-methyl- (19)	8.7 (a)	10.0 (a)	1.3

(a) Reported data in ethanol; the shift from the 257.3 nm band of carbazole in ethanol.

tions. As a possibility, these discrepancies might be attributed to the fact that the 1-methyl group perturbs the electronic state of carbazole in a different manner due to interaction with a polar imino group. However, this explanation was not supported by the nmr spectra of monomethylcarbazoles. Chemical shifts of the methyl protons (1-CH₃, τ 7.47; 2-CH₃, 7.55; 3-CH₃, 7.53 and 4-CH₃, 7.16 in deuteroacetone) are proportionately related to the shifts of ring protons of carbazole [1-H, τ 2.51; 2-H, 2.64; 3-H, 2.84 and 4-H, 1.92 in acetone (8)], and no specific behavior of the 1-methyl group was appreciable. As another explanation, strain effect may be taken into account. Taylor

(9) showed that deactivation at the 1-position of carbazole in electrophilic substitutions is accounted for a fused strain ring (Mills-Nixon effect). In fact, Kurahashi, *et al.* (10), reported that the C-C-C bond angle at the 1-position (115.6°) is smaller than that of benzene. The strain, as was pointed out by Streitwieser (11), should increase the electronegativity of the 1-carbon atom so that a smaller spectral shift is produced. Unless such an effect is regarded, the MO method would not give good results in the interpretation of properties of carbazole. Actually, several simple (12) and advanced MO methods (13) reported earlier have been shown to give a notable disagreement with experimental results indicating that the carbazole 3-position is more reactive than the 1-position in electrophilic substitutions.

As shown in Table II, the shifts are additive for the carbazoles in groups I and II. The carbazoles in group III, which bear two methyl groups at the 4- and 5-positions, showed an unusual red shift. Similar anomalies have been observed in the spectra of 4,5-dimethylphenanthrene (14) and 1,10-disubstituted benzo[c]cinnolines (15), and these can be understood as the crowding effect.

Exceptionally large discrepancy from the additivity principle was observed in spectrum of 2,3,6,7-tetramethylcarbazole. The 332 nm band is related to the transition carried along the short molecular axis (2,4,16). Thus, this discrepancy is interpreted by the effect of four methyl groups directed to the long axis of carbazole.

No additivity was observed for the bands near 291 nm (1L_a) and 211 nm (1B_a). On the contrary, the shift of the peaks near 253 nm (1B_b) is additive (Table III). As to the carbazoles in the group III, the corresponding peak is absent or not obvious.

The spectral additivities should be useful for determination of unknown carbazoles, in combination with nmr spectral data (18). Carruthers (19) isolated a pentamethylcarbazole from Kuwait petroleum. From the reported spectral data, we deduced substitution at the 1,2,4,6- and 8-positions, and this was confirmed by synthesis (20).

EXPERIMENTAL

All methylcarbazoles in Table I were prepared by the methods described in previous papers (17,18). Uv spectra were recorded on a Hitachi EPS-3T spectrophotometer at room temperature.

REFERENCES AND NOTES

- (1) R. Basu, *J. Indian Chem. Soc.*, **44**, 580 (1967).
- (2) S. Siegel and H. S. Judeikis, *J. Phys. Chem.*, **70**, 2205 (1966).
- (3) C. A. Pinkham and S. C. Wait, Jr., *J. Mol. Spectrosc.*, **27**, 326 (1968).
- (4) J. R. Huber and J. E. Adams, *Ber. Bunsenges, Phys. Chem.*, **78**, 217 (1974).
- (5) H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.*, 1404 (1952).
- (6) M. Kuroki, *Nippon Kagaku Zasshi*, **89**, 681 (1968); *ibid.*, **90**, 421 (1969).
- (7) D. P. Chakraborty, J. Dutta and A. Ghosh, *Sci. Cult.*, **31**, 529 (1965).
- (8) P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 353 (1965).
- (9) R. Taylor, *J. Chem. Soc. B*, 1559 (1968).
- (10) M. Kurahashi, M. Fukuyo, A. Shimada, A. Furusaki and I. Nitta, *Bull. Chem. Soc. Jpn.*, **42**, 2174 (1969).
- (11) A. Streitwieser, G. R. Ziegler, P. C. Mowery, A. Lewis and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).
- (12) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954); R. D. Brown and B. A. W. Collier, *Aust. J. Chem.*, **12**, 152 (1959).
- (13) P. J. Black, R. D. Brown and M. L. Heffernan, *ibid.*, **20**, 1325 (1967); I. Fischer-Hjalmal and M. Sundbom, *Acta Chem. Scand.*, **22**, 607 (1968); N. Mataga, Y. Torihashi and K. Ezumi, *Theor. Chim. Acta*, **2**, 158 (1964).
- (14) E. Ochiai, T. Okamoto, S. Sakai and M. Natsume, *Chem. Pharm. Bull.*, **5**, 113 (1957); A. W. Johnson, *J. Org. Chem.*, **24**, 833 (1959).
- (15) J. F. Corbett, P. F. Holt, A. N. Hughes and M. Vickery, *J. Chem. Soc.*, 1812 (1962).
- (16) S. C. Chakravorty and S. C. Ganculy, *J. Chem. Phys.*, **52**, 2760 (1970).
- (17) Y. Tsunashima and M. Kuroki, *J. Heterocyclic Chem.*, **18**, 315 (1981).
- (18) M. Kuroki and Y. Tsunashima, *ibid.*, **18**, 709 (1981).
- (19) W. Carruthers, *J. Chem. Soc. C*, 2244 (1968).
- (20) To be published elsewhere.
- (21) R. B. Carlin and W. O. Forshey, Jr., *J. Am. Chem. Soc.*, **72**, 793 (1950).
- (22) R. B. Carlin and M. S. Moores, *ibid.*, **84**, 4107 (1962).