probe temperature was constant, 10 min were allowed for temperature equilibration of the ion samples, and the temperature was rechecked following recording of the sample spectrum.

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Registry No. **1**, 71486-34-5; **8**, 110-02-1; **10**, 492-97-7; **11**, 71486-35-6; **12**, 3339-85-3; **13**, 71486-36-7; **14**, 18494-74-1; **15**, 3339-79-5; **16**, 18592-88-6; **17**, 3480-11-3; 5,5′-dimethyl-2,2′-bithienyl, 16303-58-5; 5′-iodo-2-(2′-thienyl)-5-thiophenium ion, 71486-37-8; 5′-bromo-2-(2′-thienyl)-5-thiophenium ion, 71486-38-9; 5′-chloro-2-(2′-thienyl)-5-thiophenium ion, 71486-39-0; 5′-fluoro-2-(2′-thienyl)-5-thiophenium ion, 71486-40-3; 5′-methyl-2-(2′-thienyl)-5-thiophenium ion, 71486-41-4.

Aromatic Nucleophilic Substitution. 12.[1] Electronic Structures of 1,1-Disubstituted 2-X-4-Y-Naphthalene Meisenheimer Complexes

Shizen Sekiguchi,* Tetsuo Hirose, Kinzo Tsutsumi, Toshiaki Aizawa, and Haruo Shizuka

Department of Synthetic Chemistry, Gunma University, Tenjincho, Kiryu, Gunma 376, Japan

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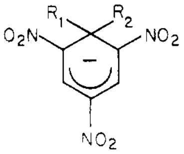
The electronic structures of 1,1-disubstituted 2-X-4-Y-naphthalene Meisenheimer complexes (**2b**$^-$, X = NO_2, Y = CN; **2c**$^-$, X = CN, Y = NO_2; **2d**$^-$, X = Y = CN) were studied by UV–visible and IR spectrophotometry and compared with the results calculated by a semiempirical SCF–MO–CI method. The electronic transitions in the complexes were assigned to those of π–π^*. Calculated transition energies and intensities agree well with the observed values. Calculations showed that ca. 48–78% of one negative charge donated by a nucleophile ($^-OCH_3$) in the formation of the complex is distributed on the X and Y groups in the S_0 state, while ca. 67–86% is distributed on them in the S_1 state. The more the one negative charge is distributed on the X and Y groups, the more stable an anionic σ complex is.

A number of Meisenheimer complexes (hereafter referred to as anionic σ complexes) such as 1^- (hereafter the minus sign represents an anionic σ complex; R_1 and R_2 are alkoxyl, hydroxyl, amino, cyano, and halogeno groups, etc.) have been prepared by nucleophilic attack on polynitroaromatic compounds.[2] Since such anionic σ complexes were found as intermediates in some aromatic nucleophilic substitution reactions, much attention has been paid to them from mechanistic and theoretical points of view. The electronic structure of anionic σ complexes such as 1^- was already reported by several workers.[3-5] However, no MO treatment has been performed for naphthalene anionic σ complexes except for our work[5] on **2a**$^-$. As a preliminary stage preceding a kinetic study on the formation and decomposition of **2a**$^-$, **2b**$^-$, **2c**$^-$, and **2d**$^-$, we have attempted the MO treatment of **2b**$^-$, **2c**$^-$, and **2d**$^-$.



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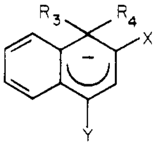
This paper reports the electronic structures of **2b**$^-$, **2c**$^-$, and **2d**$^-$ and the comparison of the observed spectral results with those of the MO treatment.



2a$^-$, X = Y = NO_2
b$^-$, X = NO_2; Y = CN
c$^-$, X = CN; Y = NO_2
d$^-$, X = Y = CN
R_3 = OCH_3; R_4 = piperidyl

Method of Calculation

Calculation was carried out on the basis of a semiempirical SCF–MO–CI method according to the procedure described in a previous work.[6]

The geometry of complex 2^- was assumed as follows (see Figure 1). The C–C bond lengths and all bond angles were assumed to be 1.39 Å and 120°, respectively. The C–N, C≡N, and N–O bond lengths were assumed to be 1.486, 1.160, and 1.210 Å, respectively. The computation was carried out with a HITAC 8800/8700 located at the Computer Center of the University of Tokyo.

Experimental Section

Melting points are uncorrected. Elemental analyses were performed at the Microanalytical Center of Gunma University. Visible absorption spectra were measured with a Hitachi-124 UV spectrophotometer. All reagents were purified by repeated recrystallizations or by distillations.

1-Chloro-2-nitro-4-cyanonaphthalene (3b). 4-Hydroxy-1-naphthaldehyde (**4**) was prepared from α-naphthalenol according to the method of Gattermann and Horlacher;[7] mp 171–175 °C (lit.[7] mp 180 °C). 4-Hydroxy-1-naphthonitrile (**5**) was prepared

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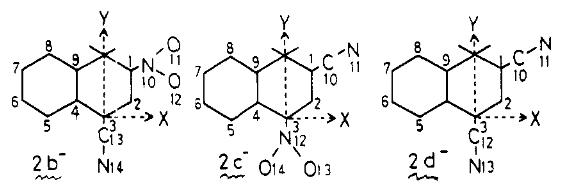


Figure 1. Geometry of the anionic σ complexes (positional number is available only for MO calculations).

from hydroxylamine and **4** according to the procedure of van Es;[8] mp 173.5–174.5 °C (lit.[9] 176–176.5 °C).

To a stirred solution of 0.7 g (0.0041 mol) of **5** in 20 mL of glacial acetic acid was added dropwise 0.5 mL of HNO_3 (d = 1.42) below 10 °C. After the mixture had been stirred for another 10 min, it was poured into 100 mL of ice–water. The crystals formed were filtered and recrystallized from ethanol or glacial acetic acid to give 0.4 g (52.9%) of 2-nitro-4-cyanonaphthalenol (**6**), mp 155.5–160.0 °C. Anal. Calcd for $C_{11}H_6N_2O_2$: C, 66.66; H, 3.05; N, 14.14. Found: C, 66.83; H, 3.04; N, 14.25.

After the mixture of 3.2 g (0.0149 mol) of **6**, 3.0 g (0.0157 mol) of p-toluenesulfonyl chloride, and 4.8 g (0.032 mol) of N,N-diethylaniline had been stirred at 80 °C for 2 h, 100 mL of 2 N HCl solution was added dropwise. The raw crystals formed were filtered, washed with a 0.5% Na_2CO_3 solution, and recrystallized from n-propyl alcohol, giving 1.2 g (34.5%) of **3b**, mp 158.5–159.0 °C. Anal. Calcd for $C_{11}H_5ClN_2O_2$: C, 56.80; H, 2.17; N, 12.04. Found: C, 56.82; H, 2.18; N, 12.04.

1-Chloro-2-cyano-4-nitronaphthalene (3c). To a saturated glacial acetic acid solution with 25.0 g (0.133 mol) of 1-hydroxy-2-naphthoic acid was added dropwise under stirring 8 mL of HNO_3 (d = 1.42) below 20 °C. After the mixture had been stirred for another 30 min at 20 °C, it was poured into 100 mL of ice–water, giving the raw crystals. The crystals were filtered, dissolved in an NaOH solution, and acidified with an HCl solution. The crystals filtered were recrystallized from glacial acetic acid, giving 14.7 g (47.7%) of 1-hydroxy-4-nitro-2-naphthoic acid (**7**), mp 214.0–215.0 °C (lit.[10] mp 214 °C).

The mixture of 22.0 g (0.0943 mol) of **7**, 18.2 g (0.106 mol) of p-toluenesulfonamide, and 64.7 g (0.311 mol) of PCl_5 was heated to 120 °C and then to 190 °C in another 2 h, with $POCl_3$ (by-product) beginning to distill out. After the mixture had been heated for another 2 h at 190 °C until no more $POCl_3$ distilled out, it was cooled to 100 °C, and 150 mL of pyridine was added carefully and dropwise. After the mixture had been cooled to below 50 °C and acidified with a cooled dilute HCl solution, the crystals formed and were filtered, washed with water, and submitted to column chromatography (benzene, silica gel). Recrystallization of the crude product from n-propyl alcohol yielded 1.0 g (2.7%) of **3c**, mp 179.5–180.5 °C. Anal. Calcd for $C_{11}H_5ClN_2O_2$: C, 56.80; H, 2.17; N, 12.04. Found: C, 56.44; H, 2.18; N, 11.79.

1-Chloro-2,4-dicyanonaphthalene (3d). 1,3-Dimethylnaphthalene (**8**) was prepared from benzylmagnesium chloride and acetylacetone according to the procedure of Balaban and Barabas;[11] bp 100.0–101.5 °C (3 mmHg) [lit.[11] bp 123 °C (0.9 mmHg)].

A solution of 25.1 g (0.160 mol) of **8**, 25.5 g (0.189 mol) of sulfuryl chloride, and a catalytic amount of $FeCl_3$ (ca. 0.1 g) in 100 mL of carbon tetrachloride was refluxed for 6 h. After the mixture had been poured into cooled water, the carbon tetrachloride layer was washed with water and dried over calcium chloride. Evaporation of the carbon tetrachloride solution and distillation under reduced pressure gave 20.1 g (66.1%) of 1-chloro-2,4-dimethylnaphthalene [**9**, bp 123–128.5 °C (2.5 mmHg)] which was submitted to the following procedure without further purification.

To a solution of 20.1 g (0.105 mol) of **9** and 38.0 g (0.213 mol) of N-bromosuccinimide in 100 mL of carbon tetrachloride was added 0.1 g of benzoyl peroxide. After the mixture had been refluxed for 4 h, it was poured into cooled water, and the carbon tetrachloride layer was dried over calcium chloride.

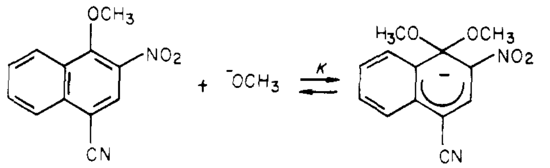
Evaporation of the carbon tetrachloride solution gave 9.2 g (25.1%) of crude 1-chloro-2,4-bis(bromomethyl)naphthalene (**10**), which was processed by the following procedure. The compound **10** underwent the Sommelet reaction, giving 1-chloro-2,4-diformylnaphthalene (**11**, mp 158.0–159.0 °C) in 73.5% yield.[12] Anal. Calcd for $C_{12}H_7O_2Cl$: C, 65.92; H, 3.23; Cl, 16.22. Found: C, 65.75; H, 3.20; Cl, 16.35.

The compound **3d** was prepared from **11** and hydroxylamine according to the procedure described in the literature;[8] mp 202.0–203.0 °C. Anal. Calcd for $C_{12}H_5N_2Cl$: C, 67.78; H, 2.37; N, 13.17. Found: C, 67.68; H, 2.48; N, 12.79.

1-Piperidino-2-nitro-4-cyano- (12b), 1-Piperidino-2-cyano-4-nitro- (12c), and 1-Piperidino-2,4-dicyanonaphthalenes (12d). A solution of 1.0 g of the proper compound (**3b–d**) in 1 mL of piperidine was stirred for 3 h at 50 °C and then poured into cooled water. The crystals formed were submitted to column chromatography (benzene, silica gel) and recrystallized from ethanol, giving 1-piperidino-2,4-disubstituted naphthalenes in ca. 80% yield: mp 145–146 (**12b**), 146–147 (**12c**), 140–141 °C (**12d**). Anal. Calcd for $C_{16}H_{15}N_3O_2$ (**12b** and **12c**): C, 68.31; H, 5.38; N, 14.94. Found: C, 68.51; H, 5.56; N, 14.73 for **12b**. Found: C, 68.24; H, 5.36; N, 15.03 for **12c**. Calcd for $C_{17}H_{15}N_2$ (**12d**): C, 78.13; H, 5.79; N, 16.08. Found: C, 77.83; H, 5.82; N, 16.09.

1-Methoxy-2-nitro-4-cyano- (13b) and 1-Methoxy-2-cyano-4-nitronaphthalenes (13c). A typical preparation was described in the case of **13c**. After 4.5 mL (0.0095 mol) of methanolic $NaOCH_3$ (2.1 N) had been added dropwise to a stirred 60-mL Me_2SO solution containing 1.5 g (0.0064 mol) of **3c** at room temperature, the mixture was further stirred for 2 h at the same temperature and then poured into an HCl-acidified 200-mL solution of ice–water. The precipitate formed was filtered and dried. The residue was submitted to chromatographic separation (silica gel, benzene) and recrystallized from benzene–ligroin, giving 1.3 g (87%) of **13c**: mp 154–155 °C; λ_{max} (CH_3OH) 343 nm (ϵ 5840). In the case of **13b** the yield was 50%: mp 161.5–162.5 °C; λ_{max} (CH_3OH) 303 nm (ϵ 7530), 348 (2490). Anal. Calcd for $C_{12}H_8O_3N_2$ (**13b** and **13c**): C, 63.13; H, 3.53; N, 12.28. Found: C, 63.37; H, 3.57; N, 12.48 for **13b**. Found: C, 63.37; H, 3.48; N, 12.59 for **13c**. The preparation of 1-methoxy-2,4-dicyanonaphthalene (**13d**) was unsuccessful probably owing to some interaction between $NaOCH_3$ and the cyano groups.

Measurement of Equilibrium Constants. The reaction of **13b** with $NaOCH_3$ in methanol is shown in eq 1.



(1)

13b **13b⁻**

If the molecular extinction coefficient (ϵ) of an anionic σ complex is determined, the equilibrium constant (K) can be obtained at various $^-OCH_3$ concentrations according to eq 2 where

$$K = [\mathbf{13b}^-]/[\mathbf{13b}][^-OCH_3] \qquad (2)$$

$[\mathbf{13b}] = [\mathbf{13b}]_0 - [\mathbf{13b}^-]$.

Furthermore, the coefficient (ϵ) can be obtained by use of the Benesi–Hildebrand equation.[13] The physical properties of **13b⁻** and **13c⁻** (corresponding to **2b⁻** and **2c⁻**, respectively) are as follows: **13b⁻**, λ_{max} (CH_3OH) 446 nm (ϵ 22 500); **13c⁻**, λ_{max} (CH_3OH) 407 nm (ϵ 22 400). The results on **13b** are shown in Table I.

IR Spectra of the Reaction System of 12b, 12c, or 12d with $NaOCH_3$ in Me_2SO. To a Me_2SO solution (0.15 mL, 1.48×10^{-4} mol) of **12b** (or **12c** or **12d**) was added 0.035 mL of methanolic $NaOCH_3$ (4.18 N), in which the molar ratio of **12b** (or **12c** or **12d**)

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Table I. Equilibrium Constant (K) for the Reaction of 1-Methoxy-2-nitro-4-cyanonaphthalene (**13b**) with Sodium Methoxide in Methanol[a] at 25 °C

[NaOCH$_3$],[b] M	optical density[c]	K, M^{-1}	[NaOCH$_3$],[b] M	optical density[c]	K, M^{-1}
0.0060[d]	0.254	13.4	0.0241	0.182	14.4
0.0096	0.403	13.8	0.0386	0.262	15.1
0.0120	0.109	15.0	0.0482	0.298	15.0
					av 14.4

[a] Ionic strength (μ) 0.05 M (NaClO$_4$). [b] [**13b**]$_0$ = 3.15 × 10^{-5} M. [c] Optical density of **13b**$^-$ at 446 nm. [d] [**13b**]$_0$ = 1.53 × 10^{-4} M.

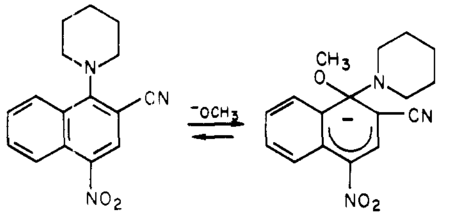
Table II. Calculated and Observed Transition Energies, Transition Moments, and Oscillator Strengths of Meisenheimer Complexes

	transition energy, eV			transition moment			oscillator strength	
complex	$S_i \leftarrow S_0$	E_{calcd}	E_{obsd}	X	Y	total	f_{calcd}	f_{obsd}
12b$^-$	S_1	2.940	2.64	−1.563	−1.144	2.303	1.107	0.370
	S_2	3.718		−0.251	−0.292	0.319	0.034	
	S_3	3.833	3.84	0.384	−1.126	1.22	0.511	
12c$^-$	S_1	3.105	2.92	1.176	1.364	1.971	1.103	0.394
	S_2	3.611	3.66	−0.716	1.033	1.252	0.507	0.198
	S_3	3.810		0.202	0.348	0.380	0.505	
12d$^-$	S_1	2.906	3.20	−1.503	1.375	2.037	1.104	0.258
	S_2	3.378		0.391	−0.264	0.472	0.068	
	S_3	3.585	4.24	−0.509	1.226	1.387	0.560	

to NaOCH$_3$ was unity, and the IR spectrum of the mixture was recorded on a JASCO IRA-2 spectrophotometer.

Results and Discussion

Absorption Spectra of the Reaction System of 1-Piperidino-2-nitro-4-cyano- (12b), 1-Piperidino-2-cyano-4-nitro- (12c), or 1-Piperidino-2,4-dicyanonaphthalene (12d) with NaOCH$_3$ in Me$_2$SO. Addition of excess NaOCH$_3$ to a Me$_2$SO solution of **12c** [λ_{max} 404 nm (ϵ 9.5 × 10^3)] at room temperature yielded a red solution after 1.5 h ([**12c**] = 1.11 × 10^{-5} M, [NaOCH$_3$] = 1.11 × 10^{-1} M), indicating the formation of an anionic σ complex (eq 3).



(3)

12c 12c$^-$

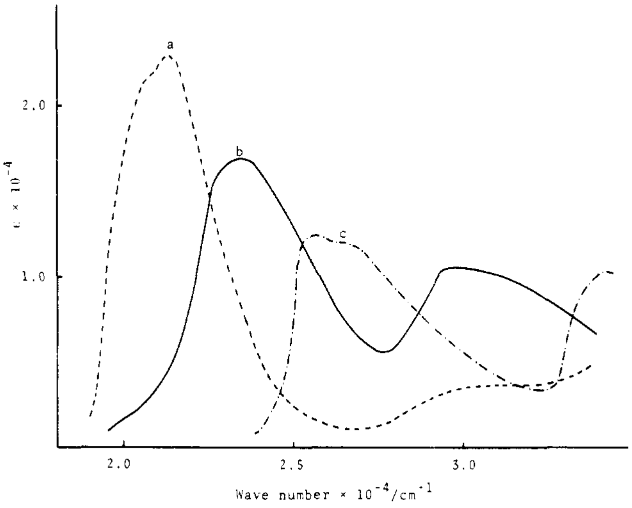


Figure 2. Absorption spectra of the complexes **12b**$^-$, **12c**$^-$, and **12d**$^-$: a, **12b**$^-$ ([**12b**] = 1.11 × 10^{-4} M, [CH$_3$ONa] = 1.16 × 10^{-2} M); b, **12c**$^-$ ([**12c**] = 1.11 × 10^{-4} M, [CH$_3$ONa] = 1.11 × 10^{-1} M); c, **12d**$^-$ ([**12d**] = 3.03 × 10^{-5} M, [CH$_3$ONa] = 1.11 × 10^{-4} M).

Table III. Negative Charge Distributions in the S_0 State of Anionic σ Complexes and Free Energy Changes and Equilibrium Constants for the Reactions of 1-Methoxy-2-X-4-Y-naphthalenes with Sodium Methoxide in Methanol at 25 °C

complex	substituent	charge distribution, %	total, %	K, M^{-1}	ΔG_{298},[a] kcal·mol
12a$^-$ [6]	2-NO$_2$	30.57		230[14]	−3.2$_4$
2a$^-$	4-NO$_2$	30.05	60.62		
12b$^-$	2-NO$_2$	35.68		14.4	−1.5$_9$
2b	4-CN	18.35	54.03		
12c$^-$	2-CN	17.88		3.3	−0.71$_9$
2c$^-$	4-NO$_2$	35.39	53.27		
12d$^-$	2-CN	23.54			
2d$^-$	4-CN	24.02	47.56		

[a] $\Delta G = -RT \ln K$.

The absorption spectra of the complexes **12b**$^-$, **12c**$^-$, and **12d**$^-$ (corresponding to **2b**$^-$, **2c**$^-$, and **2d**$^-$, respectively) are shown in Figure 2. Table II shows calculated and observed transition energies, transition moments, and oscillator strengths of the anionic σ complexes. The absorption spectra (Figure 2) are attributable to the $\pi^* \leftarrow \pi$ transitions, judging from the data in Table II. The first absorption band (band I) can be assigned to that of the $S_1 \leftarrow S_0$ transition in the complexes. The second absorption band (band II) in **12c**$^-$ corresponds to that of the $S_2 \leftarrow S_0$ transition, while those in **12b**$^-$ and **12d**$^-$ are assigned to the bands of the $S_3 \leftarrow S_0$ transition. It is of interest that the $S_1 \leftarrow S_0$ transition energies are in the order of **12b**$^-$, **12c**$^-$, and **12d**$^-$, indicating that the presence of a nitro group on the naphthalene ring, especially in the 2-position, results in a red shift in band I.

Figure 3 shows the π formal charges of the complexes in the S_0 and S_1 states. As shown in Table III, in the case of **12b**$^-$ the negative charge donated by a nucleophile to the π system is distributed on the nitro group (ca. 36%) and the cyano group (ca. 18%) in the S_0 state. In the S_1 state, however, ca. 77% of one negative charge is distributed on the former (ca. 56%) and latter groups (ca. 21%). In the case of **12c**$^-$ and **12d**$^-$, the similar tendency is also shown in Figure 3. These results indicate that band I ($S_1 \leftarrow S_0$ transition) corresponds to an intramolecular CT

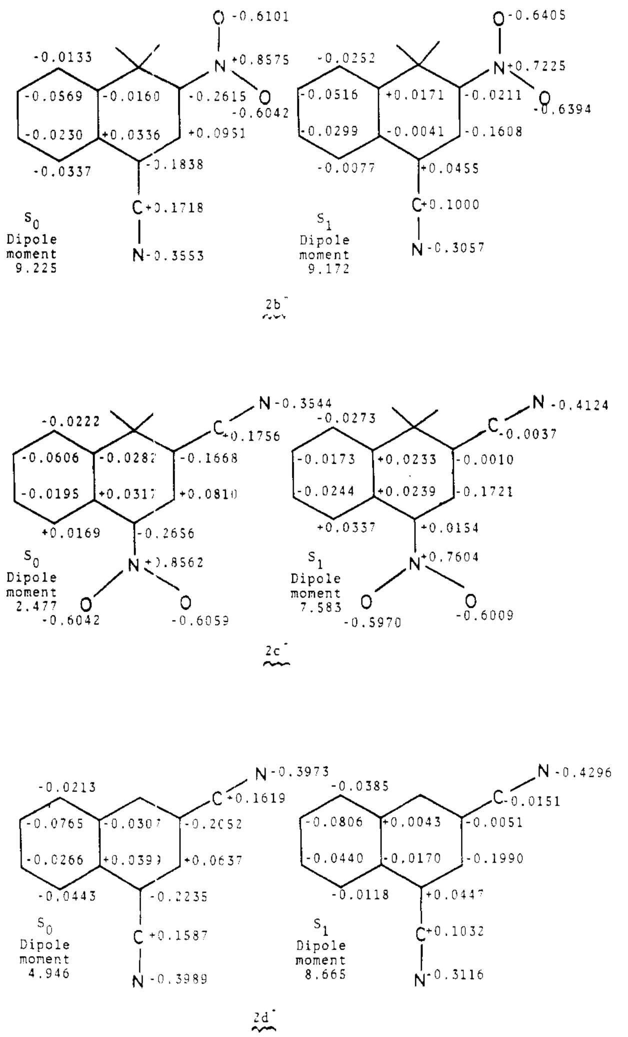


Figure 3. π formal charges of the complexes in the S_0 and S_1 states.

band. Furthermore, the fact that the absorption spectra of **12b⁻**, **12c⁻**, and **12d⁻** agree well with the results of SCF-MO-CI calculations of the complexes on the basis of the assumption of the 16π-electron and 14π-electron closed systems indicates that **12b⁻**, **12c⁻**, and **12d⁻** are not anion radicals but anionic σ complexes.

Negative Charge Distributions and Stabilities of Anionic σ Complexes. Table III shows the negative charge distribution of π formal charge on the X and Y groups in the S_0 state and the equilibrium constants (K) of the reactions of **13a–c** with $NaOCH_3$ in methanol at 25 °C (eq 1). The K values are often referred to as a good measure for the stabilities of anionic σ complexes.[2g] Although a number of 1,1-disubstituted benzene anionic σ complexes have been studied,[2g] little information on naphthalene ones has been reported. Table III suggests that the more the one negative charge donated by a nucleophile ($^-OCH_3$) is distributed on the X and Y groups, the more stable a complex is; that is, the larger the equilibrium constant is. It can be said that the negative charge distribution on the X and Y groups in the S_0 state may seriously affect the stability of anionic σ complexes and that more negative charge distribution on the X and Y groups, corresponding to resonance stabilization, is more responsible for formation of a stable anionic σ complex than that on the carbon atoms in the naphthalene ring. Therefore, an unstable anionic σ complex may be expected by introduction of cyano groups into the 2- and 4-positions (see Table III). It is of interest that the total charge distribution ratio of nitro to cyano groups (60.62/47.56 = 1.27) is close to that of their Hammett σ values (0.778/0.628 = 1.24).

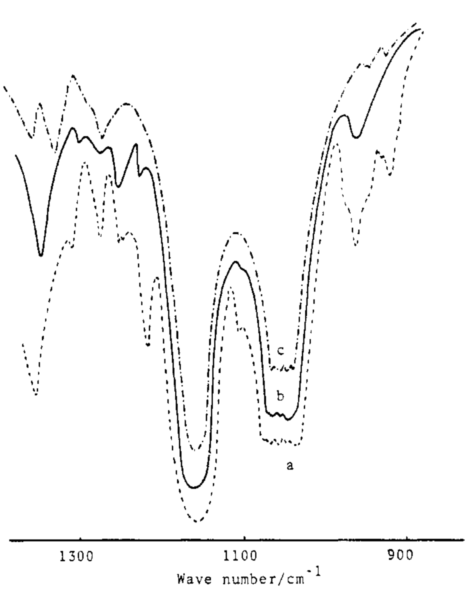
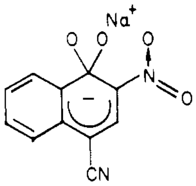
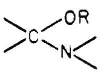


Figure 4. Infrared spectra of the anionic σ complexes: a, **12b⁻**; b, **12c⁻**; c, **12d⁻**.

In comparison of **12b⁻** with **12c⁻** the K value of the former is larger by a factor of ca. 4 than that of the latter, although the difference between the total charge distribution is comparatively small. This stabilization may be partly attributed to the interaction between a sodium cation and the three oxygen atoms of two methoxyl groups and one 2-nitro group (formation of an ion pair;[15] the methyl groups are omitted for clarity).



IR Spectra of the Reaction of 1-Piperidino-2-nitro-4-cyano- (12b), 1-Piperidino-2-cyano-4-nitro- (12c), or 1-Piperidino-2,4-dicyanonaphthalene (12d) with Methanolic $NaOCH_3$ in Me_2SO. We already found that 1-dimethylamino-2,4-dinitronaphthalene (**14a**) reacts with $NaOCH_3$ in Me_2SO at room temperature to form the complex **14a⁻** (corresponding to **2a⁻**) which is stable for a long enough time to be observed by IR measurement.[16] Similarly, stable complexes **12b⁻**, **12c⁻**, and **12d⁻** were produced in the reactions of **12b**, **12c**, and **12d** with $NaOCH_3$ in Me_2SO, respectively (eq 2). The IR spectra of the anionic σ complexes produced show the strong and broad bands near 1020–1040 cm⁻¹ as shown in Figure 4 (in the case of **12a⁻**, see ref 6). The band is clearly attributable to the structure



as has been stated by Ohsawa.[17] This evidence supports the idea that the hybrid orbital of the proper carbon atom, to which a piperidyl group is attached, changes from sp^2

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[15] (a) M. R. Crampton and H. A. Khan, *J. Chem. Soc., Perkin Trans. 2*, 1173, 2286 (1972).

[16] S. Sekiguchi, K. Shinozaki, T. Hirose, K. Matsui, and K. Sekine, *Bull. Chem. Soc. Jpn.*, 47, 2264 (1974).

[17] S. Ohsawa, *Nippon Kagaku Kaishi*, 8, 1486 (1973).

into sp^3. On the basis of the results it can be concluded that **12b**$^-$, **12c**$^-$, and **12d**$^-$ are anionic σ complexes.

^{1}H NMR Spectroscopic Evidence for Anionic σ Complexes. It is well-known that ^{1}H NMR spectroscopy is a useful tool for elucidating the structures of anionic σ complexes.[2] We already reported the time-dependent ^{1}H NMR spectra of the reaction of 1-piperidino-2,4-dinitronaphthalene (**12a**; 1.83×10^{-4} mol) with $NaOCH_3$ (1.83×10^{-4} mol) in 0.62 mL of Me_2SO–CH_3OH (4.2/1, v/v),[16] in which the changes in chemical shifts of aromatic protons from **12a** to **2a**$^-$ were typical for formation of an anionic σ complex.

The results of relevant chemical shifts (**12b,c**, **2b**$^-$,**c**$^-$, **13b,c**, and **12b**$^-$,**c**$^-$) are listed in Table IV[18] [for information about the spectra of **13a** (1-methoxy-2,4-dinitronaphthalene) and **13a**$^-$ (anionic σ complex), see ref 2g]. The changes in chemical shifts of aromatic protons from **12b** and **12c** to **2b**$^-$ and **2c**$^-$ are similar to those from **13b** and **13c** to **13b**$^-$ and **13c**$^-$, respectively.

In addition, in the course of the reactions of **13b** → **13b**$^-$ and **13c** → **13c**$^-$ the signal of the methoxyl protons shifted upfield as a sharp singlet [δ 4.18 (3 H) → 2.78 (6 H) and 4.45 (3 H) → 2.87 (6 H)], indicating the change in hybridization of the C_1 atom of a naphthalene ring ($sp^2 \rightarrow sp^3$). These results clearly indicate that the anionic σ complexes are formed in the reactions of **12a–c** or **13a–c** with $^-OCH_3$ in Me_2SO.

Registry No. 3b, 61499-36-3; **3c**, 61499-37-4; **3d**, 61499-38-5; **5**, 35462-47-6; **6**, 71436-05-0; **7**, 71436-06-1; **8**, 575-41-7; **9**, 71436-07-2; **10**, 71436-08-3; **11**, 71436-09-4; **12b**, 71436-10-7; **12b**$^-$, 71462-69-6; **12c**, 71436-11-8; **12c**$^-$, 71462-70-9; **12d**, 71436-12-9; **12d**$^-$, 71462-71-0; **13b**, 71436-13-0; **13b**$^-$, 71462-72-1; **13c**, 67122-11-6; **13c**$^-$, 71462-73-2; 1-hydroxy-2-naphthoic acid, 86-48-6; $NaOCH_3$, 124-41-4.

Supplementary Material Available: Table IV, relevant NMR chemical shifts (1 page). Ordering information is given on any current masthead page.

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[18] Supplementary material.

Ipso Nitration. An Efficient Synthesis of Ipso Nitration Products of Aromatic Hydrocarbons

C. E. Barnes, K. S. Feldman, M. W. Johnson, H. W. H. Lee, and P. C. Myhre*

Department of Chemistry, Harvey Mudd College, Claremont, California 91711

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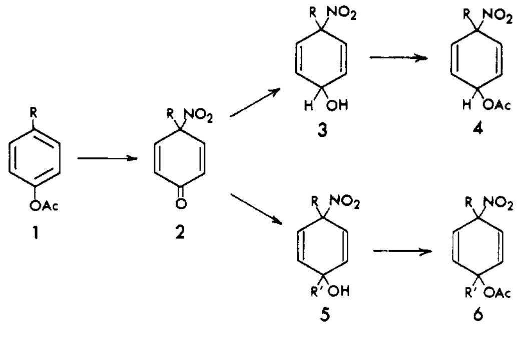
Ipso nitration products of aromatic hydrocarbons have been synthesized from phenols. Nitration of a number of 4-alkylphenyl acetates gave 4-alkyl-4-nitrocyclohexadienones. Reduction of these nitrodienones with sodium borohydride in methanol gave 4-alkyl-4-nitrocyclohexadienols. These labile nitrodienols were converted to the more easily handled 4-alkyl-4-nitrocyclohexadienyl acetates by low-temperature acylation with acetyl chloride and pyridine. Representative nitrodienyl acetates were synthesized by this three-step sequence in 60% yield from the starting phenyl acetate. The synthesis of 1,4-dimethyl-4-nitrocyclohexadienol from 4-methyl-4-nitrocyclohexadienone illustrates the use of organolithium reagents in 1,2-addition to the carbonyl center of nitrodienones.

In the course of studies of reaction pathways of ipso nitration products it became necessary to develop an indirect procedure for synthesis of certain specifically labeled ipso nitration products.[1,2] The procedure appeared to be an efficient one and one of quite general scope. Further, the method offered distinct advantages over direct methods, particularly for the preparation of ipso nitration products that contain only one alkyl group attached to the carbocyclic ring.[3] We report here a summary of some work directed toward development of this synthetic procedure.

The approach is based on the known reaction, nitration of 4-alkylphenyl acetates, which yields 4-alkyl-4-nitrocyclohexadienones.[4,5] We hoped that methods could be found to effect 1,2-addition at the carbonyl group by metal hydrides or alkyllithium reagents to yield nitrocyclohexadienols. These nitrodienols could be used directly or they could be converted to the more tractable acetate derivatives. This scheme is summarized in Chart I.

Chart I



The potential flexibility of the scheme deserves emphasis. The only formal requirement is the positioning of an alkyl group para to the oxygen substituent.[6] The five remaining positions are subject to considerable structural variation. It should also be noted that a characteristic reaction of 4-alkyl-4-nitrocyclohexadienols and their

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[1] C. E. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, **100**, 975 (1978).

[2] K. S. Feldman, A. McDermott, and P. C. Myhre, *J. Am. Chem. Soc.*, 101, 505 (1979).

[3] A. Fischer and J. N. Ramsay, *J. Chem. Soc., Perkin Trans. 2*, 237 (1973).

[4] D. J. Blackstock, J. R. Cretney, A. J. Lewis, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc. B*, 1212 (1971).

[5] A. H. Clemens, M. P. Hartshorn, K. E. Richards, and G. J. Wright, *Aust. J. Chem.*, **30**, 113 (1977).

[6] Possible use of *o*-alkylphenols and substituent groups other than alkyl would increase the flexibility of the scheme.

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