

Autoaccelerative Diazo Coupling with Calix[4]arene: Substituent Effects on the Unusual Co-operativity of the OH Groups†

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Diazo coupling between calix[4]arene and five substituted benzenediazonium ions in tetrahydrofuran at 5 °C in the presence of pyridine afforded the tetrasubstituted calix[4]arenes as main products and small amounts of mono-, di- and tri-substituted calix[4]arenes even in the presence of unchanged calix[4]arene: the unusual autoaccelerative substitution reaction is attributed to the specific hydrogen-bonding effect among the calix[4]arene OH groups. The products were applied as new 'chromophoric calix[4]arenes,' which selectively recognised Li⁺.

The chemistry of cyclodextrins and crown ethers has focussed interest in host-guest chemistry for the last two decades and many functionalised derivatives which can partly mimic the *in vivo* action of enzymes have been exploited.¹⁻⁴ More recently, Gutsche and co-workers⁵ have reported on a series of new cyclic oligomers called 'calixarenes'. We are currently interested in the functionalisation of calixarenes which may act as new host molecules in solution.⁶⁻⁸ It is now known that certain skilfully modified calixarenes are capable of including small molecules in their cavities.⁶⁻¹¹ It thus occurred to us that introduction of chromophoric groups into calixarenes would be of great value for the development of a new class of functionalised calixarenes. It is already known that a crown ether family, called 'chromophoric crown ethers',¹² has a crown ring and a chromophoric group within a molecule and changes the spectral properties upon binding of metal cations to the crown ring. The concept may be applicable to calixarene chemistry: when a chromophoric group is introduced into the appropriate position in calixarenes, one may expect novel association properties and spectral properties for this class of 'chromophoric calixarenes.' The object is readily accomplished by means of the diazo coupling reaction, one of the most well known substitution reactions in phenol derivatives. We carried out diazo coupling of calix[4]arene **1** and five substituted benzenediazonium tetrafluoroborates **2**.¹³ In the course of this synthetic study, we unexpectedly found that the diazo coupling reaction on calix[4]arene occurs in an autoaccelerative manner: in Scheme 1, compounds **3**; $x = 4$ resulted predominantly even in the presence of unchanged substrate **1**. This means that the reaction proceeds autoacceleratively: diazo coupling with one phenol unit facilitates further diazo coupling with remaining phenol units. In this paper we discuss why such an auto-acceleration effect is observed for calix[4]arene and how the reaction is affected by the substituent in diazonium salts **2**.

Experimental

Materials.—Tetrakis(phenylazo)-substituted calix[4]arenes **3**; $x = 4$ were synthesized according to the following method. Calix[4]arene **1** (0.50 g, 1.1 mmol) and the BF₄⁻ salt of *para*- or *meta*-substituted benzenediazoniums **2** (5.5 mmol) were dissolved in tetrahydrofuran (THF) (20 cm³). The reaction was initiated by the addition of pyridine (1.0 cm³) to the cooled THF solution (at 0 °C). After 3 h, the orange precipitates were recovered by filtration and washed successively with THF and methanol. The product was dissolved in pyridine and treated with activated charcoal. After filtration, the filtrate was

concentrated to dryness. The residual solid was dispersed in aq. HCl (5%) and the solution was stirred for 1.5 h at room temperature. Finally, the product was collected by filtration and dried at room temperature *in vacuo*. The yields and analytical data are recorded below.

p-Tetrakis-(4-nitrophenylazo)calix[4]arene **3a**; $x = 4$.—This was produced in 39% yield, m.p. 337 °C (decomp.); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1580 (N=N) and 1340 and 1520 (NO₂); $\delta[(\text{CD}_3)_2\text{SO}; 140^\circ\text{C}]$ 4.06 (8 H, s, ArCH₂Ar), 7.79 (8 H, s, ArH in the phenol moiety), and 7.87 and 8.27 (both 8 H, d, ArH in the 4-nitrophenyl moiety) [Found: C, 61.2; H, 3.7; N, 16.3. (C₁₃H₉N₃O₃)₄ requires C, 61.2; H, 3.6; N, 16.5%].

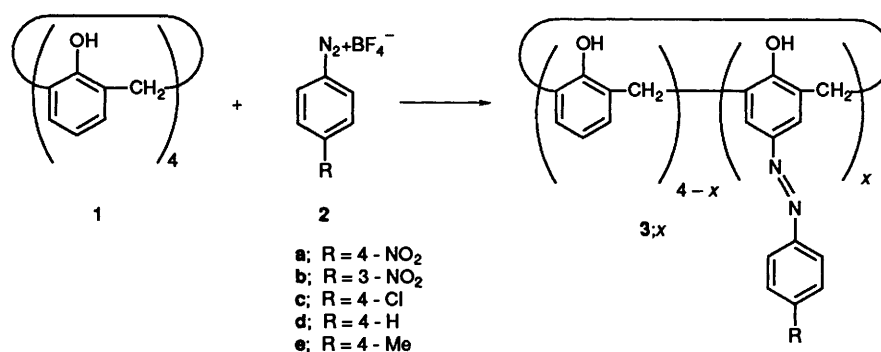
p-Tetrakis-(3-nitrophenylazo)calix[4]arene **3b**; $x = 4$.—71% Yield, m.p. 262 °C (decomp.); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1570 (N=N) and 1320 and 1500 (NO₂); $\delta[(\text{CD}_3)_2\text{SO}; 60^\circ\text{C}]$ 3.86 (8 H, s, ArCH₂Ar), 7.85 (8 H, s, ArH in the phenol moiety), and 7.73, 8.14, 8.19 and 8.40 (each 4 H, t, d, d and s, ArH in the 3-nitrophenyl moiety) [Found: C, 61.1; H, 3.8; N, 16.3. (C₁₃H₉N₃O₃)₄ requires C, 61.2; H, 3.6; N, 16.5%].

p-Tetrakis-(4-chlorophenylazo)calix[4]arene **3c**; $x = 4$.—53% Yield, m.p. 310 °C (decomp.); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1580 (N=N); $\delta[(\text{CD}_3)_2\text{SO}; 60^\circ\text{C}]$ 4.06 (8 H, s, ArCH₂Ar), 7.73 (8 H, s, ArH in the phenol moiety), and 7.51 and 7.74 (both 8 H, d, ArH in the 4-chlorophenyl moiety) [Found: C, 63.3; H, 3.9; N, 11.0; Cl, 14.2. (C₁₃H₉ClN₂)₄·0.6H₂O requires C, 63.1; H, 3.8; N, 11.3; Cl, 14.3%].

p-Tetrakis(phenylazo)calix[4]arene **3d**; $x = 4$.—43% Yield, m.p. 280 °C (decomp.); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1580 (N=N); $\delta[(\text{CD}_3)_2\text{SO}; 60^\circ\text{C}]$ 4.09 (8 H, s, ArCH₂Ar), 7.76 (8 H, s, ArH in the phenol moiety), and 7.40, 7.47 and 7.73 (4 H, 8 H and 8 H, t, t and d, ArH in the phenyl moiety) [Found: C, 74.0; H, 4.9; N, 12.9. (C₁₃H₁₀N₂O)₄·0.3H₂O requires C, 73.8; H, 4.8; N, 13.2%].

p-Tetrakis-(4-methylphenylazo)calix[4]arene **3e**; $x = 4$.—45% Yield, m.p. 305 °C (decomp.); ν_{\max} 1600 (N=N) cm⁻¹; $\delta[(\text{CD}_3)_2\text{SO}; 60^\circ\text{C}]$ 2.34 (12 H, s, Me), 4.07 (8 H, s, ArCH₂Ar), 7.72 (8 H, s, ArH in the phenol moiety), and 7.28 and 7.63 (both

† Preliminary communication: S. Shinkai, K. Araki, J. Shibata and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, 1989, 195.

**Table 1.** TLC separation of azocalix[4]arenes **3**

Calixarene	Solvent v/v) CHCl ₃ :MeOH:pyridine:Pr ⁱ OH	R _f			
		x = 1	x = 2	x = 3	x = 4
3a ; x	10:1:1:0	1.00	0.71	0.23	0.07
3b ; x	10:1:1:0	0.99	0.30	0.21	0.08
3c ; x	10:1:0:4	0.95	{ 0.58 0.71	0.27	0.15
3d ; x	10:1:0:6	0.96	{ 0.74 0.84	0.40	0.23
3e ; x	10:1:0:4	0.98	{ 0.87 0.94	0.58	0.36

Table 2. Product distribution for diazo coupling of the tetrafluoroborates **2a** with calix[4]arene **1**

Molar quotient in feed 2a /1	Unchanged 1 recovered (mol %)	Product yield (mol %)			
		3a ; x = 1	3a ; x = 2	3a ; x = 3	3a ; x = 4
1.00	70.0	5.3	1.2	1.5	22.0
2.00	44.2	5.6	3.4	1.7	45.1
3.00	20.1	6.0	1.6	2.3	70.0
4.00	0	0	0	1.0	99.0

Table 3. Product distribution for diazo coupling of the tetrafluoroborates **2b** with calix[4]arene **1**

Molar quotient in feed 2b /1	Unchanged 1 recovered (mol %)	Product yield (mol %)			
		3b ; x = 1	3b ; x = 2	3b ; x = 3	3b ; x = 4
1.00	67.8	8.4	1.0	1.6	21.3
2.00	44.9	5.5	0	1.7	47.4
3.00	20.8	5.5	0	0	73.7
4.00	0	0	0	0	100

Table 4. Product distribution for diazo coupling of the tetrafluoroborates **2c** with calix[4]arene **1**

Molar quotient in feed 2c /1	Unchanged 1 recovered (mol %)	Product yield (mol %)			
		3c ; x = 1	3c ; x = 2	3c ; x = 3	3c ; x = 4
1.00	60.2	14.7	6.0	4.8	14.7
2.00	36.7	12.7	6.3	5.1	39.9
3.00	15.5	8.5	5.1	2.5	68.4

8 H, d, ArH in the 4-methylphenyl moiety) [Found: C, 74.5; H, 5.5; N, 12.2. (C₁₄H₁₂N₂O)₄·0.3H₂O requires C, 74.5; H, 5.4; N, 12.4%].

Product Distribution.—Compounds **1** (0.46 g, 1.09 mmol) and

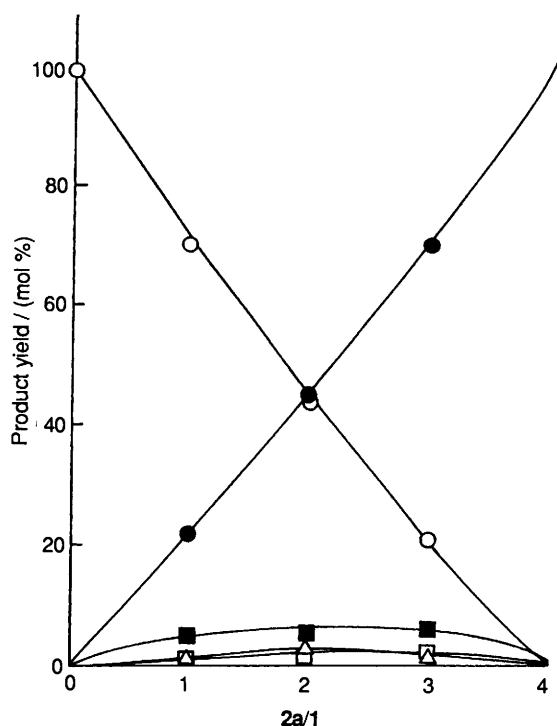
2 (see Tables 2–6 for the concentration) were dissolved in THF (30 cm³) at 5 °C and the diazo coupling reaction was initiated by the addition of pyridine (1 cm³). The reaction was completed in 15 min (confirmed by the reaction with disodium 3-hydroxy-naphthalene-2,7-disulphonate). The solution was concentrated

Table 5. Product distribution for diazo coupling of the tetrafluoroborates **2d** with calix[4]arene **1**

Molar quotient in feed 2d /1	Unchanged 1 recovered (mol %)	Product yield (mol %)			
		3d ; $x = 1$	3d ; $x = 2$	3d ; $x = 3$	3d ; $x = 4$
1.00	45.1	30.2	11.5	8.2	5.5
2.00	23.7	22.1	12.2	14.5	27.5
3.00	12.0	9.7	5.2	12.3	60.7
4.00	0	7.0	0	4.0	89.0

Table 6. Product distribution for diazo coupling of the tetrafluoroborates **2e** with calix[4]arene **1**

Molar quotient in feed 2e /1	Unchanged 1 recovered (mol %)	Product yield (mol %)			
		3e ; $x = 1$	3e ; $x = 2$	3e ; $x = 3$	3e ; $x = 4$
1.00	37.1	37.7	15.1	6.9	3.1
2.00	11.9	31.7	18.5	16.7	20.3
3.00	0	21.0	14.0	17.0	48.0

**Fig. 1** Plots of the product yield vs. the molar quotient in feed for the diazo-coupling reactions of calix[4]arene **1** and compounds **2a**: \circ **1**, \blacksquare **2a**; $x = 1$, \triangle **2a**; $x = 2$, \square **2a**; $x = 3$, \bullet **2a**; $x = 4$

under reduced pressure and the residual orange powder was analysed by TLC (Merck Kieselgel 60F 254). We could observe four orange spots for compounds **3a**; x and **3b**; x and five orange spots for compounds **3c**; x , **3d**; x and **3e**; x in addition to one colourless spot for calix[4]arene **1**. The R_f values are summarised in Table 1. From the C:N ratio in elemental analysis, the four orange spots for nitro compounds **3a**; x and **3b**; x were identified (in the order of increasing R_f) to be for $x = 1, 2, 3$ and 4 , respectively. Interestingly, we found on the basis of elemental analysis data that compound **3c**; x , **3d**; x and **3e**; x afford two orange spots for $x = 2$. These two spots are attributed to the *proximal* (5,11-disubstituted) and *distal* (5,17-disubstituted) isomers. It is not yet clear why these compounds give two isomers whereas the nitro compounds **3a**; x and **3b**; x give only one isomer.

The yields of products **3**; $x = 1-3$; $x = 4$ were determined by use of a high-speed TLC scanner (Shimadzu CS-920). Here, compounds **3**; $x = 4$ were used as standard samples in order to prepare the calibration curves. In all cases, we assumed that the absorption coefficient for each azobenzene unit is the same: for compound **3a**; x , for example, ϵ for **3a**; $x = 1 = 0.25 \cdot \epsilon$ for **3a**; $x = 4$. The results are summarised in Tables 2-6.

Miscellaneous.—The IR and ^1H NMR spectra were recorded with Shimadzu IR-470 and JEOL GX-400 instruments respectively.

Results and Discussion

Substituent Effects on Autoacceleration.—Examination of Tables 2-6 reveals that in every case the recovery of unchanged calix[4]arene **1** decreases with increasing molar ratio **2**:**1**. When the salts **2a** and **2b** were used, with increasing molar ratio only the concentrations of tetrasubstituted products **3**; x (*i.e.*, **3a**; $x = 4$ and **3b**; $x = 4$) increased and those for mono-, di- and tri-substituted products **3**; x were always low and almost constant (except for the molar ratio 4:1: see Fig. 1). They exist only in the level of the steady-state concentration. These findings led us to the conclusion that the diazo-coupling reaction of salts **2a** and **2b** with calix[4]arene **1** occurs autoacceleratively. In contrast, this tendency was not so obviously seen for the salt **2e** having an electron-donating methyl group in the *para*-position (Fig. 2).

How are the diazo-coupling products produced if the reaction were to occur according to probability theory? We calculated the product distribution for reactant quotient **2**/**1** 1.00. The mole fractions of mono-, di-, tri- and tetra-substituted products are expressed as 4α , $12\alpha^2 (= 4\alpha \cdot 3\alpha)$, $24\alpha^3 (= 12\alpha^2 \cdot 2\alpha)$ and $24\alpha^4 (= 24\alpha^3 \cdot \alpha)$, respectively, and that of unchanged calix[4]arene **1** as $1 - 4\alpha$ where α is the reaction probability. Based on the relationship (1) we obtained $\alpha = 0.154$. Thus, the

$$4\alpha + 12\alpha^2 + 24\alpha^3 + 24\alpha^4 = 1 \quad (1)$$

molar proportions of the species are estimated to be **1**:**3**; $x = 1$:**3**; $x = 2$:**3**; $x = 3$:**3**; $x = 4 = 0.389:0.335:0.199:0.075:0.002$. Comparison of these proportions with those in Tables 2-6 establishes that distinct autoacceleration takes place in the reaction with salts **2a**-**2d**, and almost no autoacceleration with salt **2e**.

What is the origin of the novel autoacceleration effect observed for calix[4]arene? It is known that the OH groups in calix[4]arene interact intramolecularly through hydrogen

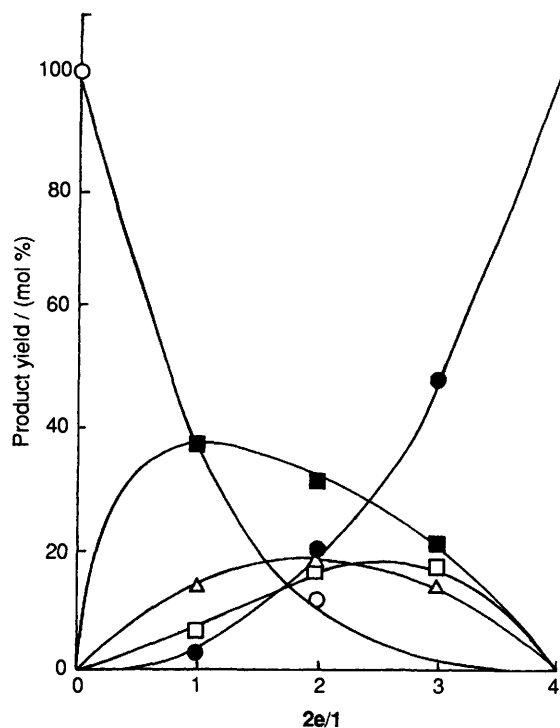
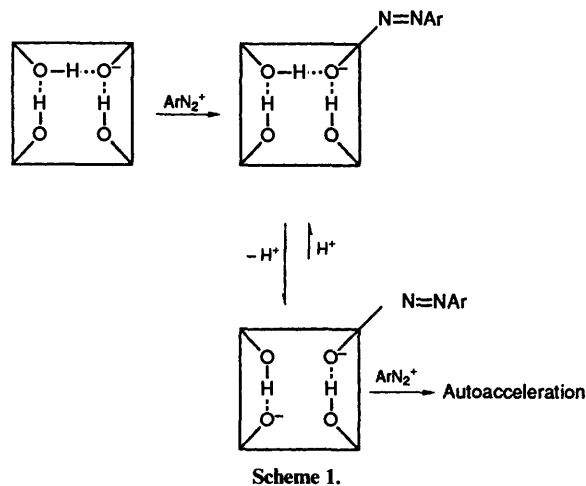


Fig. 2 Plots of the product yield vs. the molar quotient in feed for the diazo-coupling reaction of calix[4]arene **1** and compounds **2e**: ○ **1**, ■ **2e**; $x = 1$, △ **2e**; $x = 2$, □ **2e**; $x = 3$, ● **2e**; $x = 4$



bonding.^{5,6,14-17} The interaction is so strong that the first dissociation of the OH groups (K_{a1}) occurs at a very acidic pH-value while the last (fourth) dissociation (K_{a4}) occurs at a very basic pH-value.^{14,17} Owing to the hydrogen-bonding interactions, introduction of electron-withdrawing groups into calix[4]arene would lower the pK_a of the OH groups not only in the substituted phenol unit but also in the neighbouring phenol units. The azophenyl group is an electron-withdrawing substituent (Hammett's $\sigma + 0.64$). The first electrophilic attack of the salt **2** occurs towards the phenolate unit dissociated by pyridine. This reaction lowers the pK_a and facilitates the dissociation of the OH groups in the neighbouring phenol units. Thus, the subsequent electrophilic attack of the salt **2** can take

* We have found that the autoacceleration for **2e** and **2e** is observed more clearly by use of a stronger base (e.g., 1,8-diazabicyclo[5.4.0]undec-7-ene).

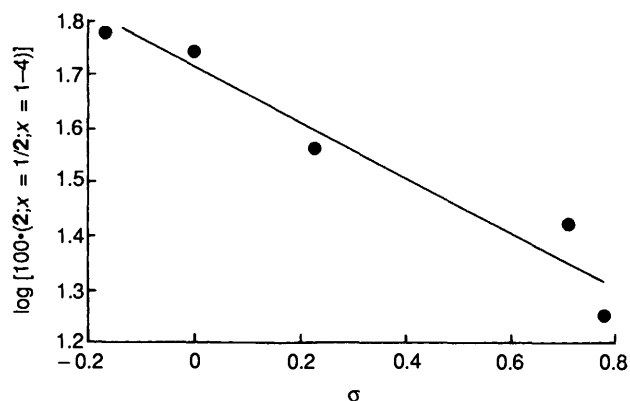


Fig. 3 Plots of $\log [100 \cdot (2; x = 1/2; x = 1-4)]$ (as a measure of the autoaccelerativity) vs. Hammett's σ -value

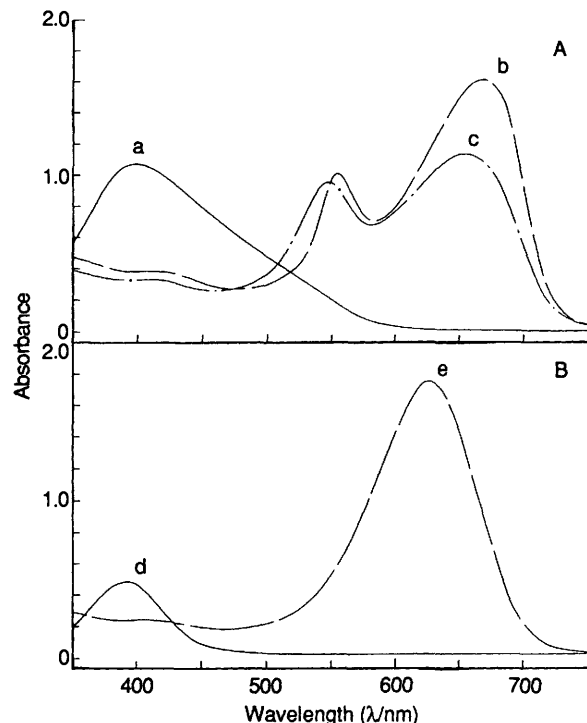


Fig. 4 Absorption spectra of compound **3a**; $x = 4$ and 2,6-dimethyl-4-(4-nitrophenylazo)phenol in THF (1.8 vol % MeOH) at 30 °C: (A) [**3a**; $x = 4$] $6.67 \times 10^{-6} \text{ mol dm}^{-3}$, (a) no additive, (b) [Me_4NOH] $3.0 \times 10^{-3} \text{ mol dm}^{-3}$, (c) [Me_4NOH] $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ and [LiClO_4] $6.67 \times 10^{-6} \text{ mol dm}^{-3}$; (B) [2,6-dimethyl-4-(4-nitrophenylazo)phenol] $1.34 \times 10^{-5} \text{ mol dm}^{-3}$, (d) no additive, (e) [Me_4NOH] $1.6 \times 10^{-3} \text{ mol dm}^{-3}$. The spectrum (e) was scarcely changed by the addition of any alkali perchlorate

place even in the presence of the same amount of pyridine. As a result, the diazo-coupling reaction proceeds autoacceleratively (Scheme 1).

As shown in Scheme 1, the pK_a of the OH groups in the neighbouring phenol units is efficiently lowered through the hydrogen-bonding interactions with the O^- entity in the azophenyl-substituted phenol unit. This effect is particularly strengthened in the azophenyl group having an electron-withdrawing substituent. This explains why the distinct autoacceleration effect is observed for nitro compounds **2a** and **2b**. In compound **2e**, on the other hand, the pK_a of the OH groups in the neighbouring phenol units is not lowered enough to allow dissociation by pyridine.* As a measure of the autoaccelerativity we selected the ratio of **2**; $x = 1$ vs. the total

yield of the azophenyl-substituted products (*i.e.*, **2**; $x = 1-4$), because among three intermediates the maximum yield was observed for this compound. A plot of $\log(\mathbf{2}; x = 1/2; x = 1-4)$ vs. σ is shown in Fig. 3. The linear relation with the negative slope supports the idea that the autoacceleration effect is correlated with the electron-withdrawing nature of the substituent: the more electron-withdrawing, the more auto-accelerative.

Applications as Chromophoric Calixarenes.—The metal affinity of *p*-*t*-butylcalix[*n*]arenes ($n = 4, 6$ and 8) was studied by Izatt *et al.* in a liquid-membrane transport system.^{18,19} Among alkali metal cations the greatest selectivity for Cs^+ was found for all *p*-*t*-butylcalix[*n*]arenes. Among alkaline earth metal cations Ba^{2+} was transported selectively. The results suggest that in the liquid-membrane transport system large metal cations are favourably extracted by *p*-*t*-butylcalix[*n*]arenes irrespective of the size-fit recognition pattern.

Compound **3a**; $x = 4$ gave an absorption maximum at 398 nm (ϵ 55 200 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) in THF at 30 °C (Fig. 4A). In the presence of excess of Me_4NOH , compound **3a**; $x = 4$ gave bimodal absorption maxima at 553 and 665 nm.* On the other hand, 2,6-dimethyl-4-(4-nitrophenylazo)phenol, a noncyclic analogue, gave an absorption maximum at 627 nm in the presence of excess of Me_4NOH (Fig. 4B). The difference suggests that tetra-anionic compound **3a**; $x = 4$ has two different electric transition moments. Presumably, the calix[4]arene ring of tetra-anionic **3a**; $x = 4$ is somewhat distorted from C_{4v} symmetry.

Addition of alkali perchlorates (MClO_4 where $\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+) scarcely changed the absorption spectrum of the tetra-anionic species **3a**; $x = 4$. In contrast, a significant spectral change was induced by the addition of LiClO_4 (Fig. 4a). In the anionic species of 2,6-dimethyl-4-(4-nitrophenylazo)phenol, the spectral change was not induced by the addition of any alkali perchlorates. The results indicate that among alkali metal cations only Li^+ can be bound to the oxyanionic cavity formed by the calix[4]arene lower rim. The Li^+ selectivity of calix[4]arene anions was also observed by Böhmer *et al.*¹⁵ Hence, the metal selectivity in the homogeneous solution system is quite different from that of the two-phase extraction system.†

* Compound **3a**; $x = 4$ gave bimodal absorption peaks even in the presence of excess of *n*-BuLi. Hence, this spectrum is assigned to the fully dissociated species of **3a**; $x = 4$.

† We added alkaline earth metal cations [$\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$] and heavy-metal cations [AgClO_4 , $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Zu}(\text{NO}_3)_2$], but they were all ineffective under the conditions recorded in the caption to Fig. 4.

Conclusions.—The autoacceleration effect, unexpectedly discovered for the diazo-coupling reaction with calix[4]arene, is closely related to the strong hydrogen-bonding interaction among the OH groups. Since this interaction is quite essential in calixarene chemistry, the similar autoacceleration effect may be generally observed for electrophilic substitution reactions at the calixarene *para*-position.

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