^{13}C NMR and Azomethine ^{1}H NMR Spectra of Substituted *N*-Benzylideneanilines and Hammett Correlations

Aurea Echevarria
Departamento de Química, Universidade Federal Rural do Rio de Janeiro, 23460, Itaguai, RJ, Brazil

Joseph Miller*
Universidade de São Paulo, Faculdade de Filosofia, Ciências e Letras, Departamento de Química, 14100, Ribeirão Preto, SP, Brazil

M. Graça Nascimento
Departamento de Química, Universidade Federal de Santa Catarina, Trindade, 88000, Florianópolis, SC, Brazil

Twenty-four *N*-benzylideneanilines (four being new compounds) have been prepared, which are divided conveniently into three series: (I) with 4-substituents, plus one compound with 3- and 4-substituents; (II) with 4′-substituents, plus one compound with 3′- and 4′-substituents; and (III) with 4- and 4′-substituents. Their ^{13}C NMR spectra and the ^{1}H NMR absorption of the hydrogen attached to the imidoyl carbon atom have been studied and their Hammett correlations were tested.

INTRODUCTION

As part of a study of addition reactions of *N*-benzylideneanilines we have synthesized a considerable range of such compounds, mostly with 4- and/or 4′-substituents. It was appropriate to determine their ^{13}C NMR spectra since some of the compounds are new, while the ^{13}C NMR spectra of many of the others have not been recorded.

We present in this paper the ^{13}C NMR spectra of 24 *N*-benzylideneanilines and the chemical shifts of the methine proton in their ^{1}H NMR spectra. Of these, four are new compounds, while the spectra of 15 of the 24 have not previously been recorded (see Table 1).

RESULTS AND DISCUSSION

The *N*-benzylidenanilines are divided into three series: (I) with 4-substituents, plus one compound with 3- and 4-substituents; (II) with 4′-substituents, plus one compound with 3′- and 4′-substituents; and (III) with 4- and 4′-substituents.

The ^{1}H chemical shifts for the azomethine protons and the ^{13}C chemical shifts for C-α, C-1, C-4, C-1′ and C-4′ in series I–III were determined in $CDCl_3$ or DMSO-d_6. These data and the Hammett substituent constants, σ_p, are presented in Table 1. The Hammett reaction constants, ρ, are discussed in the text. Some compounds of series I and II have previously been studied by Inamoto and co-workers[1–3] and Olah and Donovan.[4]

Significant shifts are evident at C-1 (series I), C-1′ (series II) and C-1, C-1′ (series III) as a result of deshielding or shielding due to the resonance effect of electron acceptors or electron donors, respectively.

The changes are substantial at the *ipso* carbons, but since there is little change at the 2-, 3-, 2′- and 3′-positions their ^{13}C resonances have not been included in Table 1.

The lack of direct transmission between the rings is shown by analysis of the data for series III, which demonstrates that there is no real effect of a 4-substituent on the 4′-carbon, and vice versa. This is consistent with the non-planarity of the two rings in *N*-benzylideneanilidnes.[5,7]

Figure 1 shows that the ^{1}H NMR shifts of the azomethine proton, H-α, correlate reasonably well with the σ_p values of 4-substituents (series I). The points for 4-OH and for 4-Cl-3-NO_2 as a combined substituent are off the plot, however. [This deviation for the 4-Cl-3-NO_2 compound is not unexpected, bearing in mind that the two substituents are *ortho* to one another. This possibility is supported by the deviations shown by this and the 4′-Cl-3′-NO_2 compound in plotting the ^{13}C NMR spectra of the imidoyl carbon (Figs 2 and 3).] In contrast, there is no correlation between the ^{1}H NMR shifts and the σ_p values of the 4′-substituents (series II). Thus, there appears to be no clear direct effect of the aniline ring substituents on the proton attached to C-α.

We now direct attention to the ^{13}C NMR shifts of the imidoyl carbon, C-α (Figs 2 and 3).

It is clearly evident that there is only a small effect from the 4-substituents on the electron density of C-α, as shown by the ^{13}C chemical shifts. This is in itself surprising. Still more surprising, however, is that these small effects are in the opposite sense to what one

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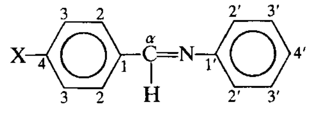
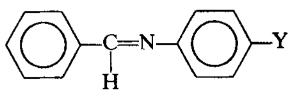
* Author to whom correspondence should be addressed.

CCC-0749–1581/85/0023–0809$02.50

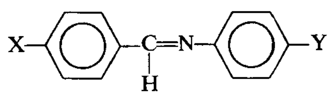
Table 1. Chemical shifts (δH, δC in $CDCl_3$ or DMSO-d_6[a]) and Hammett substituent constants[b] (σ_p) for substituted *N*-benzylideneanilines



I



II



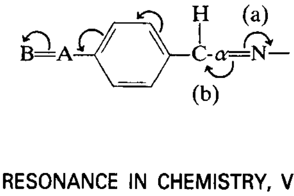
III

No.	X	δH	δC-α	δC-1	δC-4	δC-1′	δC-4′	σ_p[4,5]
1[c]	Cl (and 3-NO_2)	8.38	155.57	131.24	136.09	150.37	124.92	1.01
2[d]	NO_2	8.54	157.38	141.78	149.40	151.06	127.27	0.78
3[d]	Cl	8.36	158.28	134.88	137.20	151.65	126.14	0.23
4	Br	8.36	158.25	125.60	135.01	151.46	126.06	0.23
5	H	8.40	159.62	136.36	131.04	152.05	125.77	0.00
6[d]	CH_3	8.34	157.87	134.12	141.64	152.45	125.73	−0.17
7[d]	OCH_3	8.35	159.41	129.52	162.39	152.58	125.60	−0.27
8	OH	8.22	160.16	128.12	161.26	152.48	121.30	−0.46
9[d]	$N(CH_3)_2$	8.27	160.00	124.74	153.24	152.65	125.07	−0.83
	Y							
10[c]	Cl (and 3′-NO_2)	8.50	162.59	146.00	—	151.12	135.01	1.01
11[d]	NO_2	—	162.79	135.57	132.56	158.08	145.69	0.78
12	COOH	8.60	162.26	136.11	129.82	167.67	155.87	0.27
13[c]	$COOCH_3$	8.55	162.44	137.11	132.09	155.96	140.53	0.45
14	$COCH_3$	8.60	161.38	130.54	120.59	156.08	135.63	0.52
15[d]	Cl	8.39	160.40	136.21	131.57	150.59	121.57	0.23
16	Br	8.40	160.21	135.74	131.89	150.69	119.03	0.23
17	I	8.36	160.21	135.67	137.81	151.29	90.14	0.28
18[d]	CH_3	8.39	158.81	136.61	130.91	149.53	135.41	−0.17
19[d]	OCH_3	8.45	157.95	136.81	131.04	144.96	158.55	−0.27
20	OH	8.55	157.21	136.78	131.04	143.01	156.75	−0.46
	X, Y							
21[c]	OCH_3, Cl		159.11	130.54	162.06	150.44	130.25	
22	Cl, Cl		158.57	137.35	161.78	149.82	131.51	
23	OCH_3, OCH_3		157.51	129.36	131.51	145.06	157.60	
24[c]	Cl, OCH_3		156.11	136.59	134.81	144.17	158.31	

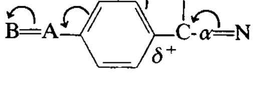
[a] Compounds **8, 12, 13** and **20** were recorded in DMSO-d_6 and the others in $CDCl_3$.
[b] For the 4-Cl-3-NO_2 and 4′-Cl-3′-NO_2 compounds the σ_p and σ_m values of the chloro and nitro groups, respectively, are added together.
[c] New compounds.
[d] Ref. 6.

might expect but, at the same time, demonstrating an acceptable Hammett correlation with $\rho = -2.25$ (correlation coefficient = 0.887). A better correlation is obtained on omitting the points for 4-Cl-3-NO_2 and for 4-CH_3, with $\rho = -1.84$ (correlation coefficient = 0.926). In this series, the effect of the 4-NO_2 group, for example, is to change the chemical shift from 159.62 to 157.38. Groups such as 4-OH and 4-NMe_2 cause only small changes, from 159.62 to 160.16 and to 160.00, respectively.

We have no explanation which we can put forward with confidence. We speculate that it may involve what is essentially an inversion of the normal conjugative interaction of the C=N function, i.e. (b) instead of (a) in the following representation, in which A=B represents an electron-withdrawing group acting through the conjugative effect:



or, in a more limited form, as follows:



We lean more towards the second form of this possible effect; this receives support from the observed values of the chemical shifts of C-1, which correspond to the expected values. The possibility of the first version of these effects has already been suggested by Tabei and Saitou[6] in relation to the ^1H NMR shifts of some *N*-benzylideneanilines.

The effects of 4′-substituents on the electron density of C-α are larger. Further, in this case, the direction of the effects is as expected. An acceptable Hammett plot is obtained with $\rho = 4.06$ (correlation coefficient = 0.922). A better correlation is obtained on leaving out the points for 4′-Cl-3′-NO_2 and for 4′-CO_2H, with the value of $\rho = 4.88$ (correlation coefficient = 0.973). We can exemplify the effect in the

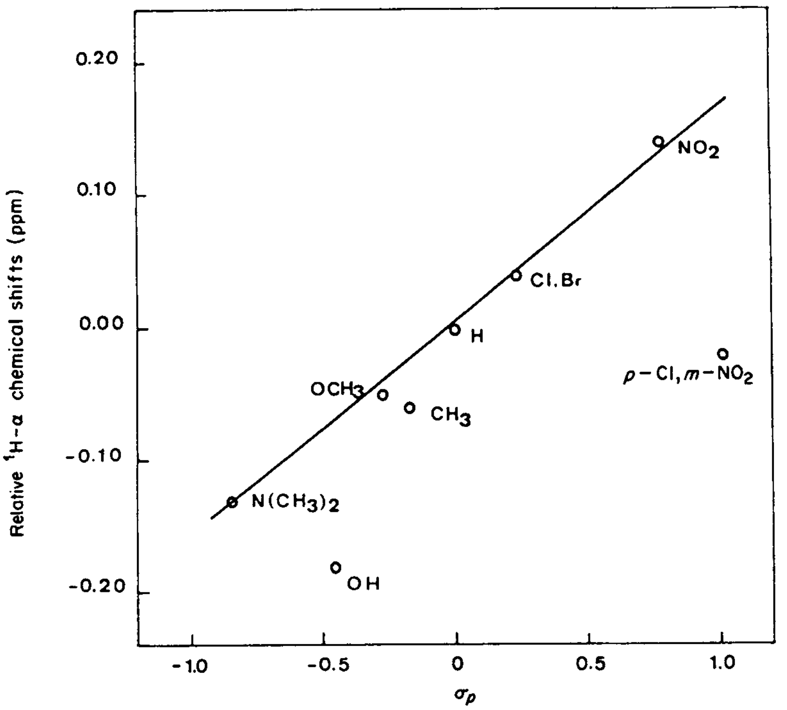
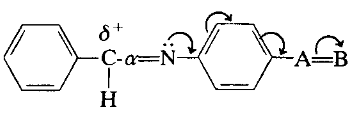


Figure 1. Relative ^{1}H NMR shifts of the proton attached to the imidoyl carbon (H-α) plotted against the Hammett substituent constants (σ_p) (series I). For compounds with two substituents in one ring, the relevant σ_p and σ_m values were added together.

following representation:



There is one common feature of our comments on the effects of benzal and aniline substituents, viz. that the ^{13}C NMR shifts of C-α are largely dependent on perturbation of the C-α—N π-bond.[8]

On examining series III, with 4- and 4′-substituents, one cannot discern any really significant pattern. In all cases the ^{13}C NMR chemical shifts correspond to an increase in electron density. The result showing the clearest relationship to values obtained in series I and

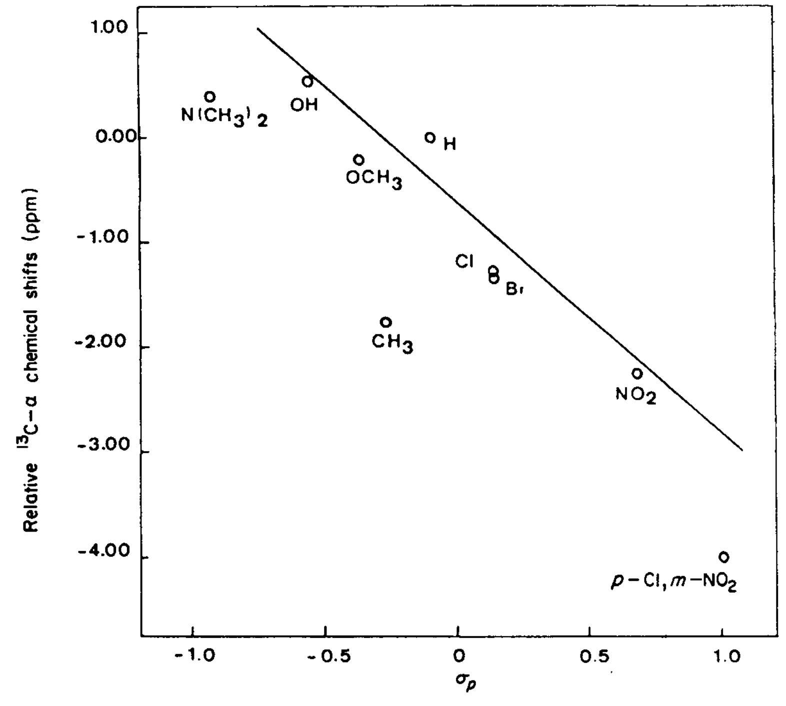


Figure 2. Relative ^{13}C NMR shifts of the imidoyl carbon, C-α, plotted against the Hammett substituent constants (σ_p) of the 4-substituents. For compounds with two substituents in one ring, the relevant σ_p and σ_m values were added together.

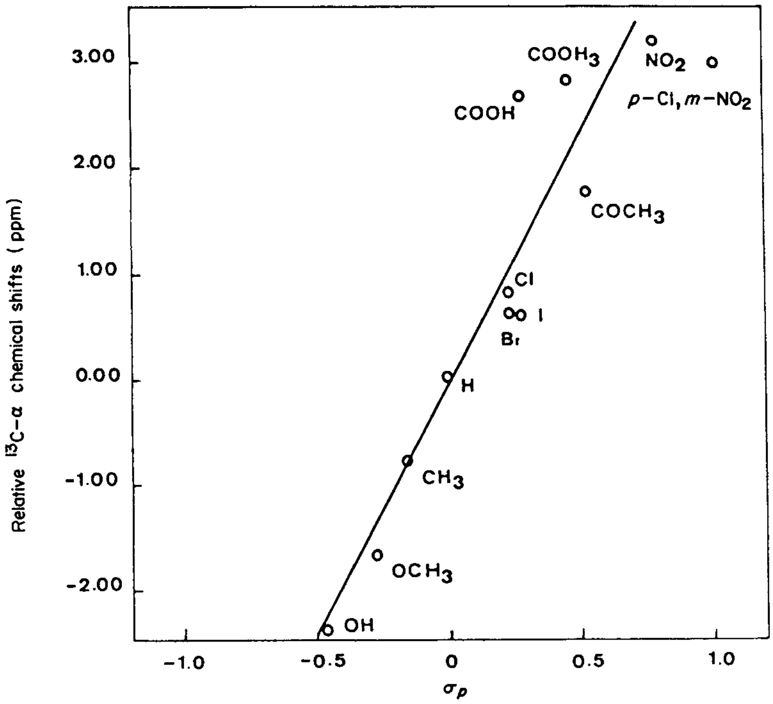


Figure 3. Relative ^{13}C NMR shifts of C-α plotted against the Hammett substituent constants (σ_p) of the 4′-substituents. For compounds with two substituents in one ring, the relevant σ_p and σ_m values were added together.

II is for the 4-Cl-4′-OMe derivative, for which the chemical shift changed from 159.62 to 156.11 for C-α.

We have examined the ^{13}C NMR shifts at other carbon atoms in less detail, and without Hammett plots.

We note the following:

(i) At C-1, the direction of the effects of 4-substituents is as expected, except for a slight anomaly with the halogen atoms which we relate to the high polarizability of their valence electrons.

(ii) At C-1 there is virtually no effect from the 4′-substituents, as one might expect. However there is a marked shift in the 4′-Cl-3′-NO_2 derivative in the expected direction, and a significant shift in the 4′-$COCH_3$ derivative in the inverse direction. We have no explanation for these divergences.

(iii) At C-4 there are large effects from the 4-substituents, correlating best, however, with the electronegativity of the atom linked to C-4.

(iv) At C-4 there is virtually no effect from the 4-substituents, as expected.

(v) At C-1′ there is virtually no effect from the 4-substituents, as expected.

(vi) At C-1′ there are significant effects from the 4′-substituents, which are in the expected direction except for a slight anomaly with the halogens (see above).

(vii) At C-4′ there is virtually no effect from the 4-substituents, as expected.

(viii) At C-4′, except for the halogens (see above), the ^{13}C NMR chemical shifts due to the 4′-substituents correspond to a reduction in electronic density for electron acceptors and an increase in electron density for electron donors.

EXPERIMENTAL

^{1}H NMR chemical shifts were determined at ambient temperature on a Varian T-60 spectrometer (60 MHz), for *ca* 0.3 M solutions in $CDCl_3$ or DMSO-d_6, with internal TMS as reference. The ^{13}C NMR spectra were determined at ambient temperature on a Varian FT-80A (20 MHz) spectrometer, for saturated solutions in $CDCl_3$ or DMSO-d_6, with TMS as internal reference. Instrumental conditions were as follows: spectral width, 5000 Hz; flip angle, 24–45°; pulse width, 5–13 μs; 8K data points.

Preparation of *N*-benzylideneanilines: general procedure

Equimolar amounts of the appropriate aniline and aldehyde were refluxed in ethanol or toluene, collecting the water formed in a Dean–Stark tube. The *N*-benzylideneanilines separated on cooling, and were recrystallized from ethanol.

Twenty of the *N*-benzylideneanilines studied have been described in the literature, as follows (all m.p.s in °C): *N*-benzylideneaniline, m.p. 51.0–52.0, lit.[9] m.p. 52.0; *N*-benzylidene-4′-carboxyaniline, m.p. 195.0–195.3, lit.[10] m.p. 194.0–196.0; 4-chloro-3-nitro-*N*-benzylideneaniline, m.p. 68.0–68.5, lit.[11] m.p. 69.5–70; 4-methoxy-*N*-benzylideneaniline, m.p. 63.0–63.8, lit.[12] m.p. 63.0–64.0; *N*-benzylidene-4′-methoxyaniline, m.p. 69.2–70.6, lit.[6] m.p. 71.0–71.5; 4-chloro-*N*-benzylideneaniline, m.p. 60.7–62.2, lit.[6] m.p. 63.5–64.5; *N*-benzylidene-4′-hydroxyaniline, m.p. 184.0–184.8, lit.[6] m.p. 182.0–183.0; *N*-benzylidene-4′-chloroaniline, m.p. 61.0–63.0, lit.[12] m.p. 63.0–63.5; *N*-benzylidene-4′-bromoaniline, m.p. 61.8–63.4, lit.[12] m.p. 65.0–66.0; 4-methyl-*N*-benzylideneaniline, m.p. 45.5–47.0, lit.[13] m.p. 47.0; *N*-benzylidene-4′-methylamiline, b.p. 158.0–159.0 (3 mmHg), lit.[12] b.p. 154 (8 mmHg); *N*-benzylidene-4′-iodoaniline, m.p. 85.0–86.0. lit.[12] m.p. 84.2–84.9; 4-methoxy-*N*-benzylidene-4′-methoxyaniline, m.p. 143.0–143.5, lit.[14] m.p. 142.0; 4-chloro-*N*-benzylidene-4′-chloroaniline, m.p. 109.0–111.6, lit.[14] m.p. 109.0–111.0; 4-hydroxy-*N*-benzylideneaniline, m.p. 189.5–191, lit.[12] m.p. 191.0–193.0; 4-nitro-*N*-benzylideneaniline, m.p. 91.0–92.0, lit.[12] m.p. 92.0–93.0; 4-bromo-*N*-benzylideneaniline, m.p. 72.5–73.5, lit.[12] m.p. 73.0–74.0; *N*-benzylidene-4′-nitroaniline, m.p. 119.7–121.2, lit.[15,16] m.p. 93 and 117.0–118.0; *N*-benzylidene-4′-acetylaniline, m.p. 98.6–99.8, lit.[10] m.p. 99.0–100.0; and 4-(*N*,*N*-dimethylamino)-*N*-benzylideneaniline, m.p. 97.0–98.6; lit.[12] m.p. 99.5–100.0.

Four *N*-benzylideneanilines are new compounds. Some details of their preparation and physical properties are given below.

***N*-Benzylidene-4′-methoxycarbonylaniline.** Benzaldehyde (1.02 ml, 10 mmol) and methyl *p*-aminobenzoate (1.49 g, 10 mmol) in 25 ml of ethanol gave 0.78 g (32.9%) of *N*-benzylidene-4′-methoxycarbonylaniline; following recrystallization from methanol it had m.p. 91.2–92.6 °C. IR (cm^{-1}): 1178 (Ar—N), 1285 (C—O—C), 1620 (C═N), 1700 (C═O), 2950 (C—H of CH_3), 2950, 3040, 3060 (—CH of CH_3). UV (MeOH): $\lambda_{max.}$ 220 nm ($\varepsilon = 11300$); 268 nm ($\varepsilon = 19600$); 310 nm ($\varepsilon = 3000$). Elemental analysis: calculated for $C_{15}H_{13}NO_2$, C 75.35, H 5.44, N 5.86; found, C 75.97, H 5.81, N 5.86%.

***N*-Benzylidene-4′-chloro-3′-nitroaniline.** Benzaldehyde (10.2 ml, 100 mmol) and 4-chloro-3-nitroaniline (17.2 g, 100 mmol) in 50 ml of toluene were refluxed for 24 h, collecting the water formed in a Dean–Stark tube; 16.4 g (62.6%) of *N*-benzylidene-4′-chloro-3′-nitroaniline were obtained. Following recrystallization from ethanol it had m.p. 53.3–54.1 °C IR (cm^{-1}): 690 and 760 (C—H out of plane, monosubstituted aromatic), 900 (C—H out of plane, 1,2,4-trisubstituted aromatic), 1360 and 1530 (Ar—NO_2) 1630 (C═N). UV (MeOH); $\lambda_{max.}$ 260 nm ($\varepsilon = 16300$), 320 nm ($\varepsilon = 7500$). Elemental analysis: calculated for $C_{13}H_9N_2O_2Cl$, C 59.88, H 3.45, N 10.47; found, C 59.85, H 3.30, N 10.55%.

4-Chloro-*N*-benzylidene-4′-methoxyaniline. *p*-Chlorobenzaldehyde (7.02 g, 50 mmol) and *p*-anisidine (6.15 g, 50 mmol) in 25 ml of ethanol gave 11.7 g (91.7%) of 4-chloro-*N*-benzylidene-4′-methoxyaniline. Following recrystallisation from ethanol it had m.p. 123.3–124.2 °C. IR (cm^{-1}): 840 (C—H out of plane, disubstituted aromatic), 1500 (C—C aromatic), 1620 (C═N), 2940 (C—H out of CH_3). UV (MeOH): $\lambda_{max.}$ 270 nm ($\varepsilon = 13400$), 335 ($\varepsilon = 7700$). Elemental analysis: calcd. for $C_{14}H_{12}NOCl$. C 68.43, H 4.90, N 5.71; found, C 68.51, H 4.91, N 5.27%.

4-Methoxy-*N*-benzylidene-4′-chloroaniline. *p*-Anisaldehyde (6.37 g, 50 mmol) and *p*-chloraniline (6.37 g, 50 mmol) in 25 ml of ethanol gave 10.6 g. (86.3%) of 4-methoxy-*N*-benzylidene-4′-chloroaniline. Following recrystallisation from methanol it had m.p. 93.3–94.8 °C. IR (cm^{-1}): 840 (C—H out of plane), 1620 (C═N), 2820 and 2940 (C—H of CH_3). UV (MeOH): λ_{max}. 227 nm ($\varepsilon = 17500$), 320 nm ($\varepsilon = 20200$). Elemental analysis: calculated for $C_{14}H_{12}NOCl$, C 68.57, H 4.90, N 5.71; found, C 68.38, H 4.93, N 5.23%.

Acknowledgements

The authors thank Mr Luiz Carlos Roque for the NMR spectral measurements and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for a doctoral level scholarship (M.G.N.).

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Received 3 September 1984; accepted (revised) 12 March 1985