

SPECTRAL STUDIES OF AZOMETHINES AND AZINES

By
J. CSÁSZÁR

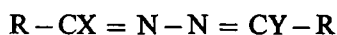
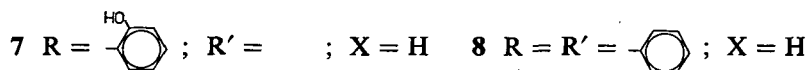
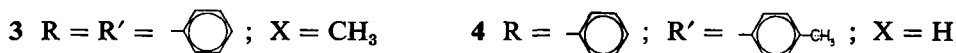
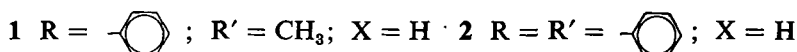
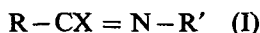
Institute of General and Physical Chemistry, Attila József University, Szeged, Hungary

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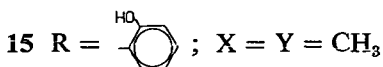
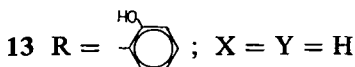
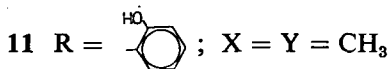
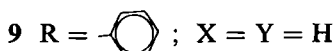
The u.v., i.r. and ^1H NMR spectra of several Schiff bases and azines are reported. The benzaldehydes, ethylenediamine derivatives and azines are compared with respect to spectral behaviour.

A great number of studies have already been made of the u.v. [1—5], ^1H NMR [5—8] and i.r. [6, 9—11] spectra of the salicylidene-aniline type Schiff bases, as well as their benzoid/quinoid tautomeric equilibrium [12—15] in polar solvents. However, the spectral behaviour of the aromatic azines has received relatively little attention. CURTIS and PFLUG [16] have described the preparation of several hydrazones and azines. HONEYBOURNE ET AL. [17] have investigated the structures of di-(*o*-aminobenzylidene)-hydrazine and di-(*o*-amino-1-methyl-benzylidene)-hydrazine and their complexes. ARCOVITO ET AL. [18] and BOSSA ET AL. [19] have determined the crystal structure and the u.v. spectrum of salicylaldehyde-azine.

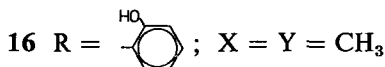
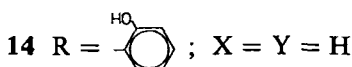
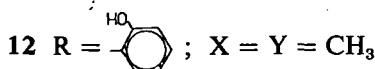
In this paper we report u.v., ^1H NMR and i.r. spectral studies of the Schiff bases of types I—III:



(II)



(III)



Experimental

The Schiff bases of types I and II were prepared by mixing alcoholic or benzene solutions of the appropriate aldehydes and amines in molar ratios of 1:1 or 1:2. **5** was prepared by passing gaseous ammonia into an ethanolic solution of salicylaldehyde, which had been purified by distillation under reduced pressure. The azines (type III) were prepared by the following procedure. 0.01 mole of the appropriate aldehydes were dissolved in 15 ml absolute methanol. To the solutions was added 0.003—0.004 mole of hydrazine hydrate, followed by 3—4 ml of glacial acetic acid. The mixtures were maintained at ca. 40 °C for 20—25 minutes. Yellow crystals separated.

All the compounds under study were recrystallized several times from methanol. Table I contains the analytical data on compounds **9—16**.

Table I

Analytical data on the Schiff bases of types II and III

Compound	m.p. ^{a)}	C%		H%	
		calcd.	found	calcd.	found
9	51.6	81.33	81.27	6.83	6.77
10	92.2	80.74	80.68	5.81	5.80
11	99.6	81.78	81.66	7.63	7.66
12	121.8	81.32	81.30	6.82	6.77
13	125.6	71.63	71.48	6.01	6.00
14	216.8	69.99	69.87	5.03	5.00
15	197.0	72.95	72.90	6.80	6.71
16	198.2	71.62	71.60	6.01	5.96

^{a)} uncorrected values

Solution electronic spectra were recorded on a SPECORD UV-VIS spectrometer; the solvents were purified according to the literature [20]. The ^1H NMR spectra* were measured in CDCl_3 solution at 25°C on a JEOL 60 MHz instrument, using TMS as internal standard. The infrared spectra were taken in KBr pellets on a UNICAM SP-100 spectrometer.

Results

The u.v. spectral data on methanolic solutions of **1**–**8** are listed in Table II.

Table II

U.V. absorption data on the Schiff bases of type I in methanol

Compound	nm (log ϵ)				
1	205 (4.32)		245 (4.10)	290 (2.90)	
2	218 (4.25)	236 (4.01)	263 (4.25)	310 (3.95)	
3	216 (4.18)		242 (4.11)	320 (3.26)	
4	224 (4.12)	241 (4.04)	263 (4.48)	317 (4.01)	
5			258 (3.80)	321 (3.34)	405 (3.00)
6		253 (4.10)	280 (3.36)	312 (3.66)	405 (3.04)
7	~224		269 (4.11)	340 (4.00)	435 (2.26)
8	~230		269 (4.00)	347 (4.08)	442 (3.28)

The spectra of the benzaldehyde derivatives **1**–**4** are very similar; there are two main bands of high intensity ($\epsilon \sim 10,000$) around 200–230 and 240–260 nm. The lower energy bands are associated with a sharp inflexion at about 310–330 nm (**2**–**4**). In benzene, chloroform and acetonitrile the spectra remain almost unchanged. In concentrated sulphuric acid **2**–**4** give a new, very intense band around 340–360 nm. (To slow down and minimize hydrolysis; concentrated sulphuric acid was used as medium and the spectra were measured immediately after making the solution.)

The spectra of **5**–**8** are completely different. At 250–280 and 310–350 nm we found two bands of high intensity; the solvent effect is not important in this region. In polar, hydrogen-bonding solvents a new band appears above 400 nm; the intensity of this depends strongly on the dipole moment of the solvent. In sulphuric acid **7** and **8** yield bands at 368 and 392 nm, respectively.

The spectral data on **9**–**16**, measured in different solvents, are presented in Table III. It can be seen (see Figs. 1–8) that these spectra differ completely from those of the aldehyde components.

The spectrum of **9** (Fig. 1) was measured in methanol and is characterized by two intense bands at 205 and 249 nm, with a shoulder at 300 nm. This spectrum is similar to that of benzaldehyde. The spectrum of **10** (Fig. 2) differs markedly from the former; the main band appears at 300 nm, with shoulders at 285 and 312 nm. The spectral behaviour of **11** (Fig. 3) is similar to that of **9**. The characters of the spectra of **9**–**12** (see Fig. 4 also) remain unchanged in various solvents.

* The author wishes to thank Dr. GY. Dombi for the NMR spectral measurements.

Table III
U.V. absorption data on compounds of type II and III in various solvents

Compound no.	Sol-vent**	nm (log ϵ)		
9	a	~205	249 (4.44)	~300
	b	214 (4.26)		296 (4.56)
	c		247 (4.50)	~280
10	a	206 (4.30)	~220	300* (4.56)
	b	217 (4.30)		298 (4.22)
	c			300* (4.58)
11	a		240 (4.34)	~280
	b	~215		277 (4.45)
	c		240 (4.31)	~280
12	a	206 (4.39)	264 (4.38)	~290
	b	~215		
	c		266 (4.40)	~295
13	a	213 (4.48)	257 (4.38)	319 (3.88)
	b	203 (4.30)	226 (4.24)	292 (4.56)
	c	216 (4.62)	257 (4.30)	318 (3.81)
14	a	220 (4.34)	~240	293 (4.38)
	b	~220		338 (4.44)
	c	~220		296 (4.28)
15	a	217 (4.59)	256 (4.19)	~275
	b	206 (4.34)	226 (4.37)	280 (4.49)
	c	217 (4.65)	253 (4.23)	~280
16	a	221 (4.37)	~245	294 (4.31)
	b	~220		312 (4.52)
	c	~220		293 (4.22)

* composed of three bands

** a: in methanol

b: in concentrated sulphuric acid

c: in basic methanol (0.02 M in NaOH)

Table IV
 ^1H NMR data on compounds 9—16 in CDCl_3
(in ppm)

Compound No.	δCH_3	δCH_2	δCHN	δOH
9		3.94	8.30	
10			8.68	
11	2.30	3.87		
12	2.30			
13		3.97	8.45	13.23
14			8.68	11.45
15	2.38	3.92		16.10
16	2.56			13.35

The spectral behaviour is more complicated in the cases of 13 and 14 (Figs. 5—6). It is significant that in methanol 13 displays a medium intensity band at 408 nm, which disappears in indifferent solvents. This band is absent from the spectrum of 14. An analogous difference is observed between 15 and 16 (Figs. 7—8).

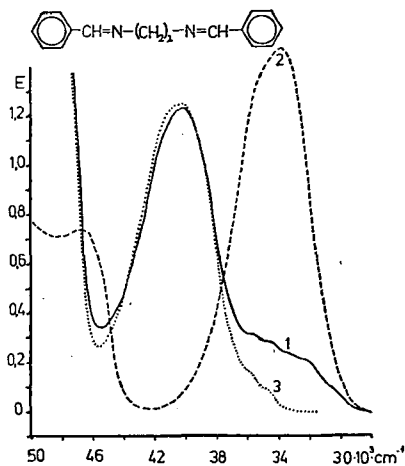


Fig. 1. Spectrum of 9 in 1: methanol, $c=4.44 \cdot 10^{-4}$ M; 2: conc. H₂SO₄, $c=4 \cdot 10^{-4}$ M; 3: NaOH/methanol, $c=3.99 \cdot 10^{-4}$ M. $d=0.1$ cm.

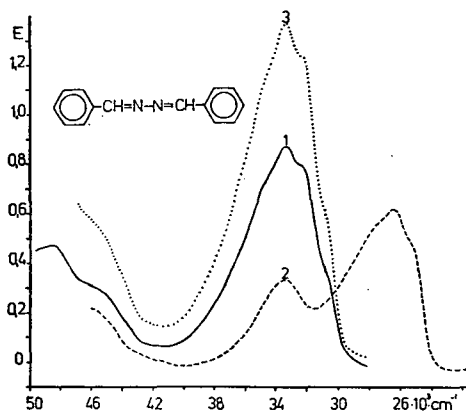


Fig. 2. Spectrum of 10 in 1: methanol, $c=2.36 \cdot 10^{-4}$ M; 2: conc. H₂SO₄, $c=2.07 \cdot 10^{-4}$ M; 3: NaOH/methanol, $c=3.63 \cdot 10^{-4}$ M. $d=0.1$ cm.

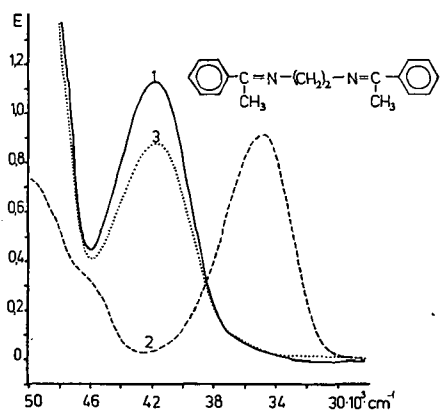


Fig. 3. Spectrum of 11 in 1: methanol, $c=5.11 \cdot 10^{-4}$ M; 2: conc. H₂SO₄, $c=3.24 \cdot 10^{-4}$ M; 3: NaOH/methanol, $c=4.36 \cdot 10^{-4}$ M. $d=0.1$ cm.

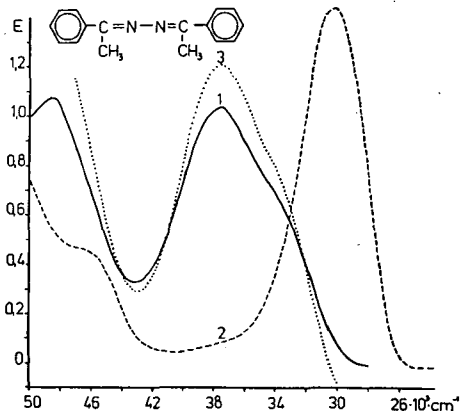


Fig. 4. Spectrum of 12 in 1: methanol, $c=4.36 \cdot 10^{-4}$ M; 2: conc. H₂SO₄, $c=4.30 \cdot 10^{-4}$ M; 3: NaOH/methanol, $c=4.88 \cdot 10^{-4}$ M. $d=0.1$ cm.

In basic methanol the spectra of 9–12, and 16 scarcely change. The 408 nm band of 13 disappears; the spectrum of 15 remains unchanged and the visible band can also be found. In concentrated sulphuric acid the spectra are completely different: the bands of 9–12 shift by 47, 78, 37 and 66 nm, respectively, to the red.

The data in Table IV show that the CH₃, CH₂ and CH=N signals are generally observed at 2.20–2.60, 3.80–4.20 and 8.40–9.20 ppm, respectively. The OH sig-

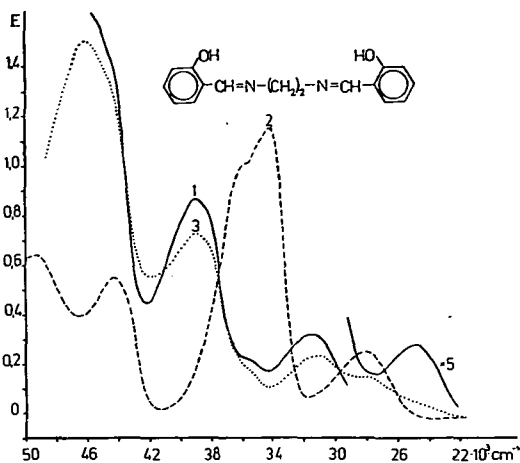


Fig. 5. Spectrum of 13 in 1: methanol, $c=3.64 \cdot 10^{-4}$ M;
2: conc. H_2SO_4 , $c=3.19 \cdot 10^{-4}$ M;
3: NaOH/methanol, $c=3.64 \cdot 10^{-4}$ M. $d=0.1$ cm.

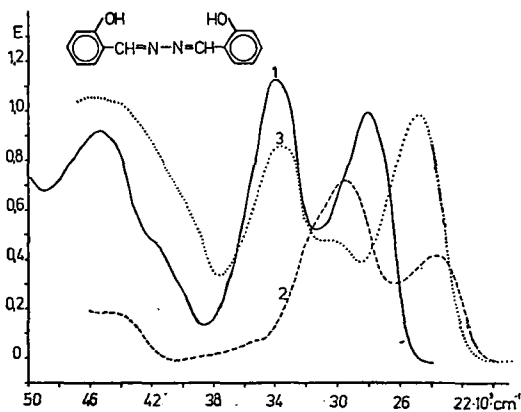


Fig. 6. Spectrum of 14 in 1: methanol, $c=4.20 \cdot 10^{-4}$ M;
2: conc. H_2SO_4 , $c=2.62 \cdot 10^{-4}$ M;
3: NaOH/methanol, $c=4.50 \cdot 10^{-4}$ M. $d=0.1$ cm.

nals appear above 11 ppm, with the neighbouring $-C(CH_3)N-$ group above 13 ppm.

The i.r. spectra of 9–16 are complicated, and the assignments of bands is very difficult. The main frequencies of these compounds are reported in Table V.

Table V
The main frequencies of Schiff bases 9—16
(in cm^{-1})

Compound No.	$\nu\text{C}=\text{N}$	βOH	νCC			γCH	γCC
9	1646s		1582m,	1450m,	1376m	754s	695s
10	1626s		1575s,	1494s,	1447s	754s	693s
11	1633s		1580m,	1494m,	1447m,	1373m	757s
12	1606s		1568m,	1494m,	1445m		762s
13	1631s	1280s	1602m,	1573s,	1480m		744s
14	1626s	1279s	1574m,	1488m,	1452m		751s
15	1615s	1297m	1580m,	1512m,	1448s		762s
16	1609s	1254s	1592s,	1567s,	1492m,	1441m	758s

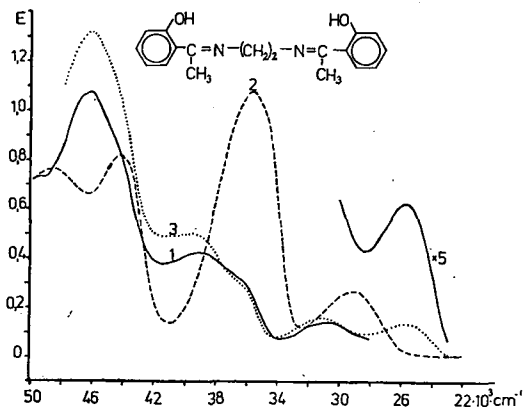


Fig. 7. Spectrum of 15 in 1: methanol, $c=2.75 \cdot 10^{-4}$ M; 2: conc. H_2SO_4 , $c=3.51 \cdot 10^{-4}$ M; 3: NaOH/methanol, $c=2.94 \cdot 10^{-4}$ M; $d=0.1$ cm.

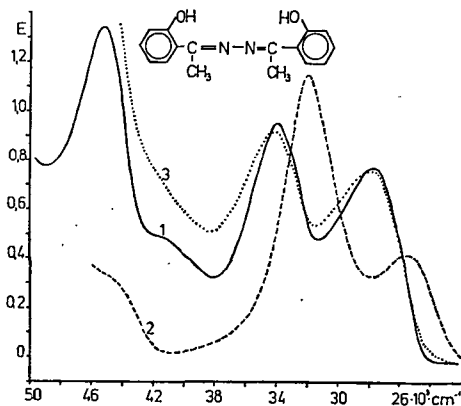
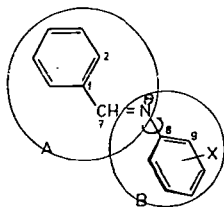


Fig. 8. Spectrum of 16 in 1: methanol, $c=4.56 \cdot 10^{-4}$ M; 2: conc. H_2SO_4 , $c=3.48 \cdot 10^{-4}$ M; 3: NaOH/methanol, $c=5.55 \cdot 10^{-4}$ M. $d=0.1$ cm.

Discussion

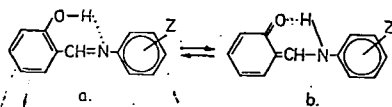
The u.v. spectrum of benzilideneaniline **2** differs markedly from those of the isoelectronic *trans*-stilbene and *trans*-azobenzene [21]. The difference is interpreted in terms of the rotation of the N-phenyl ring of **2** [21—23] out of the plane defined by the rest of the molecule. If the molecule were planar, the π -system would extend over both phenyl rings and the azomethine group, and the spectrum would be expected to be similar to that of stilbene. However, if the molecule is nonplanar, the π -electron delocalisation decreases and the spectrum should be more or less a superposition of the spectra of the two, weakly-interacting benzal and aniline parts of the molecules (Structure i) [e.g. 28]. If the nitrogen doublet is partially loca-



lized by protonation, the unshared pair of electrons on the nitrogen atoms can not conjugate with the terminal N-phenyl group and a considerable increase will be observed in the intensity of the ~ 340 nm band.

On the basis of the spectrum of **2** in concentrated sulphuric acid (protonated form), a twist angle of $\theta_N \approx 50^\circ$ can be calculated [24]. This value is very close to the θ_N values published by MINKIN ET AL. [25], GILL and SARAIVA [26] and Japanese authors [27]. BÜRGI and DUNITZ [29] also assume that the benzylidene ring is twisted, but in the opposite sense and by a much smaller amount ($\sim 10^\circ$). Our calculations suggest that the twist angles for **3** and **4** are $\theta_N \approx 60^\circ$ and $\theta_N \approx 48^\circ$, respectively.

The spectra of salicylidene derivatives **5**—**8** are more complicated. Rotation of the N-phenyl ring of **7** and **8** can also be supposed; the calculated θ_N values are 83° and 68° , respectively. The solvent-sensitive, medium intensity band above 400 nm for **5**—**8** can be interpreted by the formation of a benzoid/quinoid tautomeric equilibrium (Structure ii) [7, 14, 15], similarly to the photochromic and thermochromic behaviours [30].



It is interesting to compare the spectra of the benzylidene, salicylidene and azine derivatives.

2 and **10** differ only by a $-\text{CH}=\text{N}-$ group. The $\pi^* \leftarrow n$ transition of the unconjugated azomethine group occurs [31] at 236 nm, with an extinction coefficient around 100. In spite of this fact, the spectra of **2** and **10** are completely different, the main band lying at 263 and 300 nm, respectively. If the two azomethine groups

are separated by an ethylene group (9), the band occurs at 249 nm, similarly as for the corresponding aldehydes.

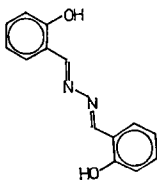
The substitution of one or both of the C=C bonds, *e.g.* in diphenylbutadiene, with a C=N bond shifts the absorption maxima to shorter wavelengths [32]. In the spectra of *trans-trans*-1,4-diphenylbutadiene and *trans*-stilbene the main bands around 320–350 and 280–320 nm show vibrational structure with three separate maxima. The band of **10** shows these vibrational components at 288, 300 and 312 nm. When the compounds contain OH groups, several studies have shown the clear presence of intramolecular hydrogen bonds, since the u.v. absorption is shifted towards shorter wavelengths [36, 37].

Essentially similar findings emerge from a comparison of the spectra of **3**, **11** and **12**; the latter yields a band without fine structure. In indifferent solvents or in basic medium the spectra remain almost unchanged. In sulphuric acid the bands shift to the red. Protonation of the *N* atoms of the azines gives rise to a greater change in the conjugated system of the molecule than for **9** and **12**, which contain separated azomethine groups. For **9** and **11**, θ_N is 68° and 80°, respectively.

When the molecule contains OH group(s), completely different spectral characteristics are observed (13–16).

A well-known example of this type is salicylaldehydeazine **14**, the spectrum of which contains three well-defined bands, at 220, 293 and 358 nm. In basic medium a change can be observed only in the region of the third band, which shifts to 402 nm. In acidic solution the two long wavelength bands appear at 338 ($\epsilon=27,500$) and 421 ($\epsilon=16,200$) nm. A very important difference from **8** is that for **14** the 440 nm band is absent. This fact is in contradiction with the finding of ARCOVITO ET AL. [18] that in **14** a strong internal hydrogen bond binds the phenolic OH group to the nearest nitrogen atom in the azine chain, giving rise to a nearly planar six-membered chelate ring. It must be noted, however, that observation in connection with the crystalline state are not generally valid for the dissolved state, and vice versa (*e.g.* [36]).

Similarly as concluded by HONEYBOURNE ET AL. [17], we can assume that **14** has a coplanar structure (Structure iii) with an extensive resonance system; the



dipole moment of **14** is zero. This is supported by the fact that the “monomeric” compounds **5** or **6**, of which **14** can be considered a perturbed “dimer”, have quite different spectra from the ones shown in Fig. 6. The shifts observed for the anionic or the protonated forms correspond to the general tendency. The analogous **13** gives a medium intensity band above 400 nm; this band disappears in indifferent solvents, in basic and in acidic media.

The *o*-oxyacetophenone derivatives **15** and **16** behave similarly to the former two compounds.

In view of the extensive vibrational coupling, there is considerable difficulty in making reliable empirical assignments regarding the i.r. spectra of Schiff bases. In this paper we report only the more significant vibrations (Table V).

For the salicylideneanilines PERCY and THORNTON [6] found three bands in the 1570—1630 cm^{-1} region. Since only the central band is insensitive to ^{15}N -substitution, the two outer bands are assigned to coupled $\nu\text{C}=\text{N}$ vibrations. In the i.r. spectra of the compounds studied we have measured only one intense frequency between 1600 and 1650 cm^{-1} , which corresponds to the $\nu\text{C}=\text{N}$ vibration. It is important to note that the acetophenone derivatives give lower frequencies than the salicylaldehydes.

The proton magnetic resonance spectra show that 13—16 similarly to the simple salicylaldehydes exist in the phenolimine form at room temperature in CDCl_3 . From Table IV it can be seen that the OH signals appear at high ppm values; these values are higher for the ethylenediamines 13 and 15 than for the azines 14 and 16. Comparison of the salicylaldehydes 13 and 14 with the acetophenones 15 and 16 reveals that the OH signals of the former are at lower ppm values, similarly as for the free aldehydes (10.90 and 12.07 ppm, respectively) [38].

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СПЕКТРАЛЬНОЕ ИЗУЧЕНИЕ АЗОМЕТИНОВ И АЗИНОВ

Й. Часап

Приведены УФ, ИК и ¹НЯМР спектры ряда Шиффовых оснований и азинов. Проведено сравнение спектральных свойств бензальдегидных, этилендиаминных производных и соответствующих азинов.