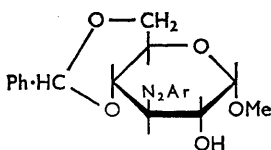


202. *Nitrogen-containing Carbohydrate Derivatives. Part V.\* Ultra-violet, Proton Magnetic Resonance, and Infrared Spectra of Some Arylazoglucosides.*

By G. J. F. CHITTENDEN and R. D. GUTHRIE.

The ultraviolet spectra of ethanol solutions of a number of methyl 3-aryl-azo-4,6-*O*-benzylidene-3-deoxy- $\alpha$ -D-glucosides have been measured and compared with those of the corresponding arylazoarenes. The infrared and proton magnetic resonance spectra of the arylazoglucosides are discussed.

ALTHOUGH the spectral properties of aromatic azo-compounds (arylaazoarenes) have been widely studied, little work has been carried out on mixed azo-compounds (arylaazoalkanes).<sup>1</sup> Since a number of arylazo-glucosides are now available<sup>2,3</sup> their spectral properties have been investigated. The compounds studied were (I)—(IX), and their 2-acetates which will be referred to as (Ia)—(IXa).



- |   |   |
|---|---|
| (I) Ar = Ph   | (VI) Ar = <i>p</i> -Cl·C <sub>6</sub> H <sub>4</sub>                                  |
| (II) Ar = <i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> | (VII) Ar = <i>p</i> -Br·C <sub>6</sub> H <sub>4</sub>                                 |
| (III) Ar = <i>p</i> -Me·C <sub>6</sub> H <sub>4</sub> | (VIII) Ar = <i>p</i> -NH <sub>2</sub> ·SO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> |
| (IV) Ar = <i>o</i> -Me·C <sub>6</sub> H <sub>4</sub>  | (IX) Ar = <i>p</i> -HO <sub>2</sub> C·C <sub>6</sub> H <sub>4</sub>                   |
| (V) Ar = <i>p</i> -F·C <sub>6</sub> H <sub>4</sub>    |   |

*Ultraviolet Spectra.*—All the compounds (I)—(IX) and (Ia)—(IXa) were prepared under normal laboratory conditions, that is without the exclusion of light. By analogy<sup>4</sup> with the phenylazo-compound (I) they are therefore expected to be about 92% pure *trans*.

\* Part IV, Guthrie and Murphy, *J.*, 1963, 5288.

<sup>1</sup> Zollinger, "Azo and Diazo Chemistry," trans. Nursten, Interscience, London, 1961.

<sup>2</sup> Guthrie and Johnson, *J.*, 1961, 4166.

<sup>3</sup> Chittenden and Guthrie, *J.*, 1963, 3658.

<sup>4</sup> Chittenden and Guthrie, *J.*, 1963, 2358.

Since it has been shown<sup>4</sup> that the "normal" and *trans*-forms have essentially the same spectral characteristics, particularly with respect to band position, it is assumed that the values quoted for the above compounds will differ little, if at all, from those of the *trans*-compounds.

The ultraviolet spectra of simple arylazoalkanes, such as phenylazomethane, consists of two bands,<sup>1,5-7</sup> one with a maximum at about 266 m $\mu$  ( $\epsilon$  8000—10,000) assigned to a  $\pi \longrightarrow \pi^*$  transition, and a second at 390—410 m $\mu$  ( $\epsilon$  100—250) assigned to an  $n \longrightarrow \pi^*$  transition. It is reported that the length of the alkyl chain, or branching within it, has very little or no effect on the spectra of phenylazoalkanes, which are wholly determined by the Ph·N:N group.<sup>5</sup> It has been noted that substitution of a *p*-methyl group in 2-phenylazobutane caused a shift of the  $\pi \longrightarrow \pi^*$  band to longer wavelengths (267  $\longrightarrow$  273 m $\mu$ );<sup>6</sup> this appears to be the only substituent effect noted for arylazoalkanes, but the effect of substituents on the spectra of arylazoarenes has been much studied.<sup>1</sup>

The spectra of compounds (I)—(IX) and their 2-acetates (Table 1) are in agreement

TABLE 1.

Ultraviolet maxima (for ethanol solutions) of methyl 3-arylazo-4,6-*O*-benzylidene-3-deoxy- $\alpha$ -D-glucosides and their 2-acetates.

	$\pi \longrightarrow \pi^*$		$n \longrightarrow \pi^*$			$\pi \longrightarrow \pi^*$		$n \longrightarrow \pi^*$	
	$\lambda_{\max.}$ (m $\mu$ )	( $\epsilon_{\max.}$ )	$\lambda_{\max.}$ (m $\mu$ )	( $\epsilon_{\max.}$ )		$\lambda_{\max.}$ (m $\mu$ )	( $\epsilon_{\max.}$ )	$\lambda_{\max.}$ (m $\mu$ )	( $\epsilon_{\max.}$ )
(I) <sup>4</sup> .....	266(10,280)		390(227)		(Ia) <sup>4</sup> .....	267(10,590)		400(248)	
(II) .....	298(10,690)		392(440)		(IIa) .....	305(13,760)		396(396)	
(III) .....	274(12,110)		394(257)		(IIIa) .....	276(16,500)		390(226)	
(IV) .....	270(8456)		395(278)		(IVa) .....	272(10,740)		398(284)	
(V) .....	266(9800)		388(192)						
(VI) .....	273 (†)		388 (†)		(VIa) .....	273 (†)		392 (†)	
(VII) .....	283(14,930)		398(173)		(VIIa) .....	281(12,960)		392(291)	
(VIII) .....	266(16,000)		388(330)		(VIIIa) .....	268(11,900)		406(338)	
(IX) (Na-salt) ‡	269(16,040)		376(7037)		(IXa) .....	269(19,200)		347(388)	

† Too insoluble for determination of accurate values. ‡ Also  $\lambda_{\max.}$  317 m $\mu$  ( $\epsilon$  14,480).

with the assigned structures, and with the values for the corresponding arylazoarenes (Table 2). The *p*-methoxyphenylazo-compounds (II) and (IIa) showed the greatest shift of the  $\pi \longrightarrow \pi^*$  band to longer wavelengths, in agreement with compound (XI). The halogenated compounds showed the expected shifts in this transition, the order being Br > Cl > F, with the latter's band in the same position as the phenylazo-glucoside (I) [cf. (XIII)—(XV)]. The tolylazo-compounds (III) and (IV) also exhibited a shift to longer wavelength for this band, the values being similar to those obtained for 2-*p*-tolyl-

TABLE 2.

Ultraviolet maxima (for ethanol solutions) of *trans*-arylazobenzenes.†

Aryl group	$\pi \longrightarrow \pi^*$		$n \longrightarrow \pi^*$	
	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon_{\max.}$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon_{\max.}$
Phenyl (X) .....	320	21,300	444	510
<i>p</i> -Ethoxyphenyl (XI) .....	348	26,100	433(?)	—
<i>p</i> -Tolyl (XII) .....	333	23,500	451	680
<i>p</i> -Fluorophenyl (XIII) .....	323	20,300	441	512
<i>p</i> -Chlorophenyl (XIV) .....	328	23,600	443	606
<i>p</i> -Bromophenyl (XV) .....	329	27,000	445	635

† Birnbaum, Linford, and Style, *Trans. Faraday Soc.*, 1954, **49**, 735.

azobutane.<sup>6</sup> In all compounds there was a smaller variation in the position of the  $n \longrightarrow \pi^*$  transition. The  $\pi \longrightarrow \pi^*$  band-shift in the acetates was generally slightly larger than for the non-acetylated compounds, and the extinction coefficient was often increased; in

<sup>5</sup> Uemura and Inemura, *Bull. Chem. Soc. Japan*, 1935, **10**, 169.

<sup>6</sup> O'Connor and Rosenbrook, *J. Org. Chem.*, 1961, **26**, 5208.

<sup>7</sup> Iffland, Salisbury, and Schafer, *J. Amer. Chem. Soc.*, 1961, **83**, 747.

some compounds acetylation caused a slight decrease in the wavelength of the  $n \rightarrow \pi^*$  band. These changes are presumed to be due to loss of hydrogen-bonding between the 2-hydroxyl group and the azo-group on acetylation.

Reduction of the phenylazo-compound (I) with hydrazine hydrate gave the corresponding phenylhydrazino-derivative<sup>4</sup> with a completely different type of spectrum ( $\lambda_{\max}$ , 240, 287, and 394;  $\epsilon$  10,700, 1850, and 128).

*Proton Magnetic Resonance Spectra.*—Some of the arylazo-glucosides and their 2-acetates have been examined (Table 3). Excellent band correlation was found throughout, and the values obtained were consistent with those obtained for the phenylazo-compounds (I) and (Ia).<sup>2</sup> For all compounds the doublet due to the anomeric proton

TABLE 3.  
Proton magnetic resonance spectra ( $\tau$  values) for chloroform solutions of methyl 3-arylaazo-4,6-*O*-benzylidene-3-deoxy- $\alpha$ -D-glucosides.

	2-OAc	1-OCH <sub>3</sub>	1-H *	Ph·CH	Ar-CH <sub>3</sub>	1-H doublet splitting (c.p.s.)
3- <i>p</i> -Tolylazo (III) .....	—	6.54	5.14	4.47	7.64	3.0
3- <i>p</i> -Tolylazo 2-acetate (IIIa) .....	8.10	6.56	4.99	4.46	7.63	3.6
3- <i>o</i> -Tolylazo- (IV) .....	—	6.56	5.14	4.46	7.48	3.6
3- <i>o</i> -Tolylazo 2-acetate (IVa) .....	8.06	6.53	4.96	4.47	7.48	3.6
3- <i>p</i> -Chlorophenylazo 2-acetate (VIa) ...	8.10	6.54	4.99	4.47	—	3.6
3- <i>p</i> -Carboxyphenylazo 2-acetate (IXa)	8.06	6.52	4.95	4.44	—	3.0
3-Phenylazo (I) <sup>2</sup> .....	—	6.58	5.15	4.45	—	3.7
3-Phenylazo 2-acetate (Ia) <sup>2</sup> .....	8.08	6.55	4.97	4.45	—	3.8

\* Doublet-mean quoted.

had a splitting of 3—4 c.p.s., characteristic of the *ax,eq* arrangement of the C<sub>(1)</sub> and C<sub>(2)</sub> protons.<sup>8</sup> In all cases where both the arylazo-glucoside and its 2-acetate were studied, a downfield shift of the C<sub>(1)</sub> proton signal was observed of 0.15—0.18 p.p.m., presumably due to decrease in shielding of this proton by the acetate group. The 1-OCH<sub>3</sub> signal occurred at  $\tau$  6.52—6.58, somewhat downfield from the position found by Barker and his co-workers for this signal in  $\alpha$ -anomers.<sup>9</sup> The signals from the protons of the 2-acetate group at  $\tau$  8.06—8.10 agree well with the position found by Barker.<sup>9</sup> for equatorial groups. The signal due to the CH<sub>3</sub> protons of the tolyl group were found at  $\tau$  7.63 for the *p*-isomer, as expected;<sup>10</sup> it was shifted downfield by 0.15 p.p.m. in the *o*-isomer.

*Infrared Spectra.*—It has so far proved difficult to assign a characteristic infrared frequency to the stretching of the azo-group. A great deal of work has been carried out on arylazoarenes,<sup>11-16</sup> and it has been suggested<sup>15</sup> that for these compounds the -N=N- band is in the 1400—1450 cm.<sup>-1</sup> range. Ueno<sup>16</sup> tentatively assigned two bands to this group, at 1400 and 1455 cm.<sup>-1</sup>, for a series of polyazobenzenes. In unconjugated systems such as azomethane, the Raman band noted by West and Killingsworth<sup>17</sup> at 1576 cm.<sup>-1</sup> has been assigned by Herzberg<sup>18</sup> to the -N=N- stretching mode. Le Fèvre and his co-workers have studied the infrared spectra of other alkylazoalkanes and concluded that the azo-group frequency occurs between 1565 and 1576 cm.<sup>-1</sup>.

<sup>8</sup> Lemieux, Kullnig, Bernstein, and Sneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.

<sup>9</sup> Barker, Homer, Keith, and Thomas, *J.*, 1963, 1538.

<sup>10</sup> Jackman, "Application of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon, London, 1959.

<sup>11</sup> Le Fèvre, O'Dwyer, and Werner, *Chem. and Ind.*, 1953, 378.

<sup>12</sup> Le Fèvre, O'Dwyer, and Werner, *Austral. J. Chem.*, 1953, **6**, 341.

<sup>13</sup> Le Fèvre and Werner, *Austral. J. Chem.*, 1957, **10**, 26.

<sup>14</sup> Kubler, Lüttke, and Weckherlin, *Z. Elektrochem.*, 1960, **64**, 650.

<sup>15</sup> Le Fèvre, O'Dwyer, and Werner, *Austral. J. Chem.*, 1961, **4**, 315.

<sup>16</sup> Ueno, *J. Amer. Chem. Soc.*, 1957, **79**, 3205.

<sup>17</sup> West and Killingsworth, *J. Chem. Phys.*, 1938, **6**, 1.

<sup>18</sup> Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

In the compounds discussed in the present Paper there is conjugation of the azo-group with an aryl ring and it would be expected, therefore, that the  $\text{-N=N-}$  stretching frequency would be between the values suggested for arylazoarenes and those for alkylazoalkanes. The only compounds of this class that have been studied are a series of phenylazoalkanes, for which O'Connor<sup>19</sup> noted a number of bands around  $1450\text{ cm.}^{-1}$ , the strongest occurring at  $1460\text{ cm.}^{-1}$ .

TABLE 4.

Infrared spectra (for chloroform solutions) of methyl 3-substituted 4,6-*O*-benzylidene-3-deoxy- $\alpha$ -D-glucosides.

<i>3-Arylazo-compounds</i>	
Ph (I) .....	1412ms, 1458s, 1475m, 1485m, 1505vw, 1530w
<i>p</i> -OMe (II) ...	1410m, 1457s(1450sh), 1473m, 1490w, 1504w, 1520m
<i>p</i> -Me (III) ...	1410s, 1456s(1460sh), 1470s, 1500w, 1526s
<i>o</i> -Me (IV).....	1408s, 1455s(1448sh and 1460sh), 1470s, 1485s, 1505vw, 1525w
<i>p</i> -F (V) .....	1410m, 1416m, 1455m(1448sh and 1460sh), 1470m, 1497vs, 1528s
<i>p</i> -Cl (VI) .....	1406m, 1456m(1448sh), 1471m, 1483ms, 1502w, 1523m
<i>p</i> -Br (VII) ...	1402w, 1410s, 1455ms(1450sh), 1460ms, 1472ms, 1482s(1489sh), 1510m, 1520ms
<i>3-Arylazo-compounds (acetates)</i>	
Ph (Ia) .....	1410w, 1456s(1448sh), 1470m, 1483m, 1500w, 1530m
<i>p</i> -Me (IIIa) ...	1412m, 1456s(1448sh and 1459sh), 1470m, 1500w, 1525s
<i>o</i> -Me (IVa) ...	1410w, 1448w, 1456m(1460sh), 1470m, 1485m, 1500vw, 1528w
<i>p</i> -Me (VIIa) ...	1402m, 1450w, 1456m, 1460m, 1470m, 1480m, 1500vw, 1523m
<i>3-Arylhydrazino-compounds</i>	
Ph .....	1410m, 1465m, 1472m, 1502s
<i>p</i> -OMe .....	1410w, 1425vw, 1445m, 1460m, 1470m, 1517vs

The infrared spectra of a number of 3-arylazo-glucosides have now been studied in the  $1400\text{--}1550\text{ cm.}^{-1}$  region (Table 4). As in the studies on arylazoarenes, the interpretation is complicated by the bands due to the vibrations of the aryl rings. The much studied aryl bands in this region are those found<sup>20</sup> around  $1450$  and  $1500\text{ cm.}^{-1}$ . It was the former band that made the assignments of Le Fèvre *et al.* and of Ueno tentative. All the arylazo-glucosides studied had a medium to strong band at or very near  $1455\text{ cm.}^{-1}$ , with generally two bands on either side of it; this band was not present in the arylhydrazine derivatives. Nevertheless, it is not assigned to the azo-link of the  $\text{Ar}\cdot\text{N}=\text{N}$  group, because it is at too low a frequency and because substituents in the aryl nucleus have no effect on the band position. A weak band at the other frequency mentioned above occurred for five of the arylazo-glucosides, and for all of the acetates.

All the compounds studied had one band in the  $1402\text{--}1412\text{ cm.}^{-1}$  range, and another at or very near  $1470\text{ cm.}^{-1}$ , and so presumably neither is due to the azo-linkage. The remaining band present in all the arylazo-glucosides and absent in the arylhydrazine compounds is the band near  $1525\text{ cm.}^{-1}$ . This band showed varying shifts to lower frequencies for the various substituents from the value of  $1530\text{ cm.}^{-1}$  for the phenylazo-compound (I); the largest shift, as expected, being for the bromo- (VII) and methoxy-compounds (II), to  $1520\text{ cm.}^{-1}$ . There was remarkably little change in the spectra on acetylation of the 2-hydroxyl group, although this would prevent hydrogen bonding with the azo-group. However, Bellamy<sup>21</sup> states: "the effects [of hydrogen bonding] on the proton acceptor group are usually small unless resonance stabilisation is involved." The same slight shifts were again found for these acetates.

This tentative assignment of a band at  $1520\text{--}1530\text{ cm.}^{-1}$  to the azo-linkage of the  $\text{Ar}\cdot\text{N}=\text{N}\cdot\text{R}$  molecule agrees well with the higher and lower values suggested for the  $\text{R}\cdot\text{N}=\text{N}\cdot\text{R}$  and  $\text{Ar}\cdot\text{N}=\text{N}\cdot\text{Ar}$  molecules, respectively.

<sup>19</sup> O'Connor, *J. Org. Chem.*, 1961, **26**, 4375.

<sup>20</sup> Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

<sup>21</sup> Ref. 20, p. 383.

Preliminary optical rotatory dispersion measurements (kindly determined by Professor W. Klyne) on some of the 3-aryloxy-4,6-*O*-benzylidene-glucosides, and on some related compounds, show that these compounds exhibit a Cotton effect.

## EXPERIMENTAL

Ultraviolet spectra were determined on a Unicam S.P. 700 spectrophotometer, for ethanol solutions in 1-cm. quartz cells. Proton magnetic resonance spectra were kindly determined by Drs. S. Trippett and J. M. Pryce on Varian A-60 spectrometers, for chloroform solutions (5—10%). Infrared spectra were determined on a Unicam S.P. 100 spectrophotometer, for chloroform solutions (~5%).

*Methyl 4,6-O-Benzylidene-3-p-bromophenylazo-3-deoxy- $\alpha$ -D-glucoside* (VII).—Reaction of periodate-oxidised methyl 4,6-*O*-benzylidene- $\alpha$ -D-glucoside (1 mol.) with *p*-bromophenylhydrazine hydrochloride (1.2 mol.) in aqueous sodium acetate solution as described for phenylhydrazine<sup>3</sup> gave, on rapid cooling and shaking, a yellow solid (78%). Recrystallisation from propan-1-ol gave the *product* (VII) (60%), m. p. 190—192° (decomp.),  $[\alpha]_D^{20} + 115^\circ$  (*c* 1.0 in 1 : 1 chloroform-dimethylformamide) (Found: C, 53.7; H, 4.7.  $C_{20}H_{21}BrN_2O_5$  requires C, 53.5; H, 4.7%).

Acetylation with acetic anhydride-pyridine gave, after four recrystallisations from propan-1-ol, the 2-*acetate* (VIIa), m. p. 179—180°,  $[\alpha]_D^{22} + 51^\circ$  (*c* 0.96 in dimethylformamide) (Found: C, 54.1; H, 4.8.  $C_{22}H_{23}BrN_2O_6$  requires C, 53.8; H, 4.7%).

Catalytic hydrogenation of the 3-*p*-bromophenylazo-glucoside (VII), under the conditions previously described,<sup>2</sup> gave methyl 3-amino-4,6-*O*-benzylidene- $\alpha$ -D-glucoside (64%), m. p. 182°,  $[\alpha]_D^{21} + 101^\circ$  (*c* 0.57 in chloroform) (lit.,<sup>2</sup> m. p. 184.5—186°,  $[\alpha]_D^{20} + 102^\circ$ ), further characterised as the 3-acetamido-derivative, m. p. 292°.

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