

## THE CONFIGURATION AND CONFORMATION OF ARYL DIAZOTATES AND DIAZOCYANIDES

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**Abstract**  $^{15}\text{N}$  and  $^{13}\text{C}$  NMR parameters and 4-substituent effects reflect the configuration and conformation in solution of  $^{15}\text{N}$ -labelled *syn*-(Z)- and *anti*-(E)- aryl diazotates  $\text{ArN}=\text{NO}^{\ominus}$  and aryl diazocyanides  $\text{ArN}=\text{N}-\text{CN}$ , as for other aryl diazo compounds.

### Introduction

Following our investigation of solutions of benzenediazonium salts<sup>1</sup> and *syn* and *anti* diazocyanides<sup>2</sup> by  $^{15}\text{N}$  and  $^{13}\text{C}$  NMR and other physical methods, we report comparable results on *syn* and *anti* aryl diazotate ions  $\text{ArN}_{\alpha}=\text{N}_{\beta}\text{O}^{\ominus}$ , the constitution of which has been much discussed,<sup>3,4</sup> and further comments on the diazocyanides.<sup>2</sup>  $^{15}\text{N}$  (with  $^{13}\text{C}$ ) NMR spectroscopy<sup>5</sup> gives unique information on these molecules, since the shifts and coupling constants are sensitive to the geometry, which may differ from the solution to the solid, and some conformers (such as *syn*-diazocyanides) can only be studied in solution.<sup>4</sup> Strong deshielding on bending<sup>5</sup> is a useful criterion of structure of diazenido ligands,<sup>6</sup> triazines,<sup>7</sup> etc., since the presence of a lone pair on nitrogen ( $n_{\text{N}}$ ) in a  $\pi$ -system allows low-energy paramagnetic (deshielding) currents, increasingly with reduction in the excitation energy  $\Delta E(n_{\text{N}} \rightarrow \pi^*)$ .<sup>5</sup> In organic aryl diazo compounds  $\text{ArNNX}$  the nitrogen shifts cover a range of 250 ppm,<sup>5</sup> or 400 ppm with the inclusion of diazonium compounds,<sup>1</sup> in which CNN is linear; in diazenido complexes of transition metals ( $\text{X} = \text{ML}_n$ ), in which MNN may be bent or linear, the range is 500 ppm.<sup>6</sup>

In aryl diazo molecules ( $\text{ArN}_{\alpha}\text{N}_{\beta}\text{X}$ ) there are variations in twist (the dihedral angle between the ring plane and the azo plane) to reduce ortho-repulsions, and in the geometry of the CNNX group, depending on ( $\sigma + \pi$ ) influences of the X group and ring substituents, and steric factors. Twisting reduces NN, ring  $\pi$ -interactions and increases  $n_{\text{N}}$ ,  $\pi$ -ring interactions, raising the  $n_{\text{N}}$  orbital of the distant nitrogen: thus ortho-substitution by alkyl groups in *cis* and *trans* azobenzenes substantially red-shifts the  $n_{\text{N}} \rightarrow \pi^*$  absorption.<sup>8</sup> Twisting, therefore, deshields the nitrogen, as observed for *cis* compared with *trans* azobenzene (by 20 ppm).<sup>9</sup> A 53° twist is observed for crystalline *cis*-azobenzene,<sup>10</sup> while *trans*-azobenzene, though near-planar in the solid<sup>11</sup> (for economy in crystal packing) has a 30° twist in the gas phase<sup>12</sup> which probably persists to some degree in solution. Azobenzene twists in the gas phase are greater than in corresponding stilbenes, in which ortho repulsions are somewhat larger, so there seems to be some advantage in  $n_{\text{N}}$ ,  $\pi$ -ring interaction<sup>12</sup> (indeed, CNDO/2 calculations have given dihedral angles of 90° for *trans*-azobenzene<sup>13</sup>).  $\Delta G^{\ddagger}$  values of 7.2-9.6 kcal mol<sup>-1</sup> are given by  $^{13}\text{C}$  NMR studies of internal rotation in 4-substituted azobenzenes.<sup>14</sup> Twisting is monitored also by effects of 4-substituents in the ring, e.g. with change from a  $\pi$ -donor such as  $\text{NMe}_2$  or OMe to a  $\pi$ -acceptor such as  $\text{NO}_2$  or CN. Changes in the 4-substituent produce large changes in  $\text{N}_{\beta}$  shift in aryl diazocyanides,<sup>2</sup> so they are likely to be planar in solution as in the solid. The range for 4-substituted *trans*-azobenzenes ( $\text{C}_6\text{H}_4\text{X}-4$ ) $\text{N}_{\alpha}=\text{N}_{\beta}\text{Ph}$  is 13 ppm for  $\text{N}_{\alpha}$  and 44 ppm for  $\text{N}_{\beta}$ .<sup>9</sup>

Coupling constants to nitrogen are sensitive to the presence of a lone pair with s character, since non-bonding and bonding electrons give oppositely-signed contributions to the Fermi contact term which dominates the coupling:<sup>15-17</sup>  $|J|$  is thus reduced by twisting or decrease in the nitrogen angle. When two such lone pairs are adjacent, as in the azo group, their combination at a dihedral angle of 180° (*trans*) gives a large positive Fermi contact contribution, whereas a dihedral angle of 0° (*cis*) gives a large negative one.<sup>17</sup>

In the solid state disodium *syn*-4-sulphonatobenzene diazotate shows a remarkable degree of twisting,<sup>18</sup> a dihedral angle of 69°, while potassium *syn*-methyl diazotate is planar,<sup>19</sup> as are *anti*-diazocyanides (with 4-Cl, 4-Br, or 2,4-Br<sub>2</sub> substituents).<sup>20-22</sup> The NNX

angle (in ArNNX) is maximal in transition metal diazenides ArNNML<sub>n</sub> with linear MNN groups, the diazenido group acting as a 1-electron donor ArNN<sup>+</sup> (cf. the linear nitrosyl ligand NO<sup>+</sup>). The 120°-bent ligand is a 1-electron acceptor ArNN<sup>-</sup> (cf. the bent NO<sup>-</sup> ligand). In the doubly-bent relative to the singly-bent ligand (the NNAr group is always bent), MN coupling constants are reduced, and both nitrogens strongly deshielded, sometimes by 400 ppm or more.<sup>6</sup> (Interaction of lone pairs on N<sub>α</sub> and N<sub>β</sub> gives n<sub>+</sub> and n<sub>-</sub> levels, the higher level giving the greater contribution to the deshielding).

In aryldiazo compounds the CNN angle is normally less than 120°: solid state values are around 110° in azoalkanes, 112-115° in aryldiazo compounds including triazenes,<sup>23</sup> and 113-117° in the (*anti*)-diazocyanides with 4-Cl, 4-Br, or 2,4-Br<sub>2</sub> substituents.<sup>20-22</sup> In the *syn*-diazotates the CNN angle is 116° in the alkyl compound, but 119° in the aryl compound. A significant increase is observed for *cis*-azobenzene, in which CNN is 122°, compared to 114° for *trans*-azobenzene, larger increases being observed with ortho-substitution.<sup>8</sup> Aryldiazotate bond lengths show some evidence of π-delocalisation: the NO bond is short (1.32 Å) and the NN bond slightly lengthened (1.30 Å),<sup>4</sup> cf. 1.25-1.26 in azobenzenes, and 1.25 Å in the 4-Cl diazocyanide (though 1.28 and 1.32 Å in the diazocyanides with ortho bromo substituents). There is no evidence for delocalisation in the (*anti*)-diazocyanide side-chain: the NNX angle is 108-114°, and the NCN angle near 180° (170-174°), the carbon being linear in principle in N-C=N or N=C=N.<sup>20-22</sup>

#### <sup>15</sup>N and <sup>13</sup>C nmr parameters in aryl diazotates and diazocyanides

Tables 1 and 2 show <sup>15</sup>N and <sup>13</sup>C nmr shifts and coupling constants in *syn*- and *anti*-aryldiazotates with 4-substituents ranging from the π-donor OMe to the π-acceptor CN, with values of their Hammett constants σ<sub>p</sub>. (All substituent constants are taken from ref. 24.) In contrast to the diazocyanides, the influence of the substituents on the *syn*-diazotate nmr parameters is relatively small, so the twist observed in the solid state is expected to persist in solution. The shielding of <sup>15</sup>N<sub>β,anti</sub> shows the greatest variation with the 4-substituent, decreasing over a range of 20 ppm with increase in π-acceptor ability of the 4-substituent; the shielding of N<sub>β,syn</sub> varies less (by 8 ppm), in the same sense. The shielding of the *ipso* carbon, also, tends to decrease with increase in σ<sub>p</sub>, slightly more for the *syn* compounds (13 ppm) than the *anti* (11 ppm). The variation of δ<sup>15</sup>N<sub>α</sub> is small, about 5 ppm, for both *syn* and *anti* diazotates.

Table 1. <sup>15</sup>N and <sup>13</sup>C nmr shifts (ppm) of sodium *syn*- (*Z*) and *anti*-(*E*)-benzenediazotates ArN<sub>α</sub>N<sub>β</sub>O<sup>-</sup> (aq).

The reference for the <sup>15</sup>N shifts is neat liquid nitromethane.

4-substituent		OCH <sub>3</sub>	H	Cl	CN
Hammett σ <sub>p</sub>		-0.27	0.0	0.24	0.7
N <sub>α</sub>	<i>syn</i>	-21.7	-17.1	-19.6	-18.8
	<i>anti</i>	0.2	2.1	-2.4	-2.8
N <sub>β</sub>	<i>syn</i>	102.5	106.3	108.4	110.5
	<i>anti</i>	133.3	137.5	145.4	153.4
C(1)	<i>syn</i>	141.7	149.2	147.0	154.4
	<i>anti</i>	144.0	150.0	147.3	154.7
C(2,6)	<i>syn</i>	123.9	122.2	123.7	123.6
	<i>anti</i>	123.0	121.8	121.7	122.6
C(3,5)	<i>syn</i>	114.8	129.7	129.2	134.1
	<i>anti</i>	115.8	130.4	128.9	135.2
C(4)	<i>syn</i>	157.1	126.3	130.5(?)	120.6
	<i>anti</i>	158.7	127.6	131.2	122(?)

δ<sup>13</sup>C in -OCH<sub>3</sub>, 56.3 (*syn*), 57.1 (*anti*); in -CN, 108.2 (*syn*), 109.1 (*anti*).

In the diazocyanides,<sup>2</sup> however, the shieldings decrease greatly from the  $\pi$ -donor OMe as 4-substituent to the  $\pi$ -acceptor NO<sub>2</sub>; by 8 ppm (*syn*) and 6 ppm (*anti*) for C(1), but 61 ppm (*syn*) and 51 ppm (*anti*) for N<sub>β</sub>, and 25 (*syn*) and 19 ppm (*anti*) for N<sub>α</sub>. This contrast arises because -CN is a ( $\sigma+\pi$ ) electron-acceptor, whereas O<sup>-</sup> is a ( $\sigma+\pi$ ) electron donor. In each case the carbon or nitrogen shielding is not very different in the two isomers, but somewhat higher in the *syn* than the *anti* compound, consistent with greater  $\pi$ -delocalisation and smaller twist in the latter (*cf.* the higher shielding<sup>25</sup> for comparable nitrogens in *Z* than *E* iminoazo triazenes ArN=N-N=CR<sub>2</sub>). The differences tend to increase with decrease in the shielding, since small variations in a small excitation energy bulk large.

Relative shieldings of N<sub>α</sub> and N<sub>β</sub> in the aryldiazo compounds depend on the ( $\sigma+\pi$ )-inductive properties of the X group. The  $\sigma$ -influence of X (measured by the inductive parameter  $\sigma_I$ ) is much greater on the adjacent nitrogen N<sub>β</sub>, than N<sub>α</sub>: in the aryldiazotates (*syn* or *anti*) N<sub>β</sub> is deshielded by 130-140 ppm relative to N<sub>α</sub> by the strong  $\sigma$ -donor ability of -O<sup>-</sup> ( $\sigma_I = -0.16$ ). This decreases  $\Delta E(n \rightarrow \pi^*)$  for N<sub>β</sub> by destabilizing the n<sub>N</sub> HOMO (part of the  $\sigma$  framework) relative to the  $\pi^*$ NN LUMO. In the diazocyanides, however, N<sub>β</sub> is shielded by about 140 ppm relative to N<sub>α</sub> by the strong  $\sigma$ -acceptor ability of -CN ( $\sigma_I = 0.57$ ), increasing  $\Delta E(n \rightarrow \pi^*)$  for N<sub>β</sub> by stabilising the n<sub>N</sub> HOMO, relative to the  $\pi^*$ NN LUMO. (The azobenzenes<sup>9</sup> and (iminoazo) triazenes<sup>25</sup> are intermediate.)

Similarly, N<sub>α</sub> shows more clearly than N<sub>β</sub> the  $\pi$ -influence of the X group. The N<sub>α</sub> shielding decreases with increase in the  $\pi$ -acceptor ability of the X group (measured by the mesomeric parameter  $\sigma_R^0$ ), which reduces  $\Delta E(n \rightarrow \pi^*)$  by lowering the  $\pi^*$ NN LUMO relative to the n<sub>N</sub> HOMO. The N<sub>α</sub> shielding decreases by nearly 200 ppm from the aryldiazotates, with  $\sigma_R^0 = -0.58$  for O<sup>-</sup>, to the diazocyanides, with  $\sigma_R^0 = 0.08$  for CN (again, the azobenzenes and iminoazo triazenes are intermediate). N<sub>β</sub> however shows the greater effect of twisting.

Interestingly, changing the X-group from O<sup>-</sup> to CN has a much smaller effect on the shift range of N<sub>β</sub> (15-20 ppm) than N<sub>α</sub> (95-115 ppm). The  $\sigma$ -inductive influence of the X group affects the radial factor  $\langle r^{-3} \rangle_{2p}$  as well as the energy factor  $\Delta E(n \rightarrow \pi^*)$  in the paramagnetic term,  $r$  being the radius of the 2p electron: the deshielding is the greater the closer are the paramagnetic currents to the nucleus<sup>6</sup>). An electron acceptor X group like CN (relative to an electron donor such as O<sup>-</sup>) increases the radial term as well as the energy term for N<sub>β</sub>, so that the resultant effect on the shift is relatively small.

Table 2. <sup>15</sup>N, <sup>13</sup>C coupling constants |J| (Hz) in benzenediazotates

4-substituent	OCH <sub>3</sub>	H	Cl	CN
Hammett $\sigma_p$	-0.27	0.0	0.24	0.7
<sup>1</sup> J(N <sub>α</sub> N <sub>β</sub> )	<i>syn</i> 18.2	18	18.7	19.7
	<i>anti</i> 15.4	15.5	15.5	16
<sup>1</sup> J(C <sub>1</sub> N <sub>α</sub> )	<i>syn</i> 3.6	5.7		
	<i>anti</i> 4.8	0		
<sup>2</sup> J(C <sub>2</sub> N <sub>α</sub> )	<i>syn</i> 1.9	<1		
	<i>anti</i> 3.1	3		
<sup>2</sup> J(C <sub>1</sub> N <sub>β</sub> )	<i>syn</i> 1.8	<1	1.8	
	<i>anti</i> 5.5	4.9	4.0	
<sup>3</sup> J(C <sub>3</sub> N <sub>α</sub> )	<i>syn</i> 0	<1		
	<i>anti</i> 1.2	1		
<sup>3</sup> J(C <sub>2</sub> N <sub>β</sub> )	<i>syn</i> 1.2	<1	1.2	
	<i>anti</i> 3.7	3.0	3.6	
<sup>4</sup> J(C <sub>3</sub> N <sub>β</sub> )	<i>syn</i> 0	0	0	

Table 3. <sup>15</sup>N, <sup>13</sup>C spin-spin coupling constants |J| (Hz) in aryldiazo compounds

Linear	<sup>1</sup> J(NN)	<sup>1</sup> J(CN <sub>α</sub> )
benzenediazonium salts (CNN linear)	1.5-3.5	10-18
diazenido ligand, MNN linear (NNR bent):		
18e complexes	12-17	
16e complexes	7-8	
Doubly bent	<i>syn, cis, Z</i>	<i>anti, trans, E</i>
	<sup>1</sup> J(NN) <sup>1</sup> J(CN <sub>α</sub> )	<sup>1</sup> J(NN) <sup>1</sup> J(CN <sub>α</sub> )
aryldiazotates	18-20    3-6	15-16    0-5
aryldiazocyanides	23    8-9	15-16    0-3
azobenzenes	15    9	15-17    0-1
bent diazenido ligand		14-19

The coupling constants support the conclusions from the shifts.  $|^1J(^{15}N^{15}N)|$  is large in the *syn*-benzenediazotates, increasing with  $\pi$ -acceptor ability of the 4-substituent, and quite large in the *anti*-compounds.  $|^1J(^{13}C^{15}N)|$  is small in the *syn* compounds and smaller in the *anti* compounds. Azobenzene and aryldiazocyanide couplings are comparable, with somewhat larger  $^1J(^{15}N^{15}N)$  and  $^1J(^{13}C^{15}N)$  values in the latter; factors in these increases being the greater planarity and slightly smaller angles at the nitrogens (larger s character) in the diazocyanides than the diazotates, and the increase in  $|J|$  observed with an electronegative substituent such as CN.<sup>15</sup> (The coupling  $^1J(^{15}N\beta^{13}C)$  to the cyano group, 17-19 Hz, is large because of the near-sp (i.e. large s) character of the carbon.)

The <sup>15</sup>N-labelled molecules were prepared by literature methods<sup>26</sup> from 99% <sup>15</sup>N-enriched <sup>15</sup>NH<sub>4</sub>Cl, Na<sup>15</sup>NO<sub>2</sub> and aniline (MSD isotopes). <sup>15</sup>N-labelled anilines were prepared from the benzoyl chlorides by Lewis and Holliday's method and converted to <sup>15</sup>N<sub>α</sub>-diazonium sulphates by Hodgson and Mahudevan's method, <sup>15</sup>N<sub>β</sub>-diazonium sulphates being made from Na<sup>15</sup>NO<sub>2</sub>. Doubly-labelled diazonium salts were made similarly. *Syn*-diazotates were made by the method of Le Fevre and Sousa, *anti*-diazotates by that of Schraube and Schmidt. *Syn* and *anti*-diazocyanides were made from enriched diazonium salts as described by Le Fevre and Vine.

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