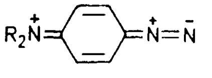
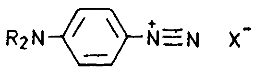
Ring Asymmetry in 4-Morpholinobenzenediazonium Tetrafluoroborate: Crystallographic and SCF Studies

By **Nathaniel W. Alcock, Trevor J. Greenhough, David M. Hirst, Terence J. Kemp,*** and **David R. Payne,** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Contrary to previous reports, we find the aromatic ring in the 4-morpholinobenzenediazonium cation in (II) to be considerably distorted compared with that in the benzenediazonium ion (I), very much in the manner in which substitution of a 4-dialkylamino-group distorts the ring in nitrobenzene. These new data are used in a critique of the frequently expressed view that the electronic ground-state of a 4-dialkylaminobenzenediazonium cation is quinoidal in nature rather than aromatic: SCF calculations by several methods, while predicting a shortening of the C-2 to C-3 bond of (II), fail to reproduce the observed bond distances. Crystals of (II) are monoclinic, space group $P2_1/c$, a = 13.675(4), b = 10.686(4), c = 8.982(2) Å, β = 106.72(2)°, Z = 4. The structure was refined to R 0.065 for 1 674 observed reflections. Mean bond distances are: C(1)–C(2) (systematic numbering) 1.395(1), C(2)–C(3) 1.371(1), C(3)–C(4) 1.424(1), C(1)–N(diazonium) 1.381(1), C(4)–N(morpholino) 1.352(1), and N–N 1.100(1) Å.

BOTH the spectroscopy and photochemistry of 4-amino- and 4-*NN*-dialkylamino-benzenediazonium salts are sufficiently well differentiated from those of their simpler analogues to have provoked suggestions that their electronic ground-state should be more correctly represented as (Q) (*i.e.* a quinoidal form) than the conventional aromatic form (A) [although it is clear that (A) will make some contribution to a structure based essentially on (Q) and *vice versa*]. For example, the absorption spectrum in the 200—400 nm region closely resembles that of diphenylquinomethane, $Ph_2C{:}C_6H_4{:}O$, and is rather similar to that of 4-phenylenediazoimine, $HN{:}C_6H_4{:}N_2$, whilst it is quite unlike that of 4-phenylenediamine (or its protonated form).[1] An analogous situation was found in a comparison of the spectra of several 4-acylaminobenzenediazonium cations with those of two 4-acylaminobenzenediazoimides, $RCON{:}C_6H_4{:}N_2$, prompting the formulation [2] of the diazonium cations as $RCO\overset{+}{N}H{:}C_6H_4{:}N_2$. The effect of substitution by successively larger alkyl groups at the 3-position of the 4-*NN*-dimethylaminobenzenediazonium cation (III) is to systematically shift $\lambda_{max.}$ to the red (*e.g.* from 378 nm in the parent compound to 406 nm for the 3-t-butyl analogue and 425 nm for the 3,5-dimethyl analogue).[3] This shift is attributed to steric destabilisation of the ground-state (Q) [as compared with the excited state, regarded as (A)] with a consequent decrease of the energy gap (Q)→(A)*. In parallel with the red-shift on substitution there is an increase in the N–N stretching frequency from 2 171 (parent compound) to 2 220 cm^{-1} (3-t-butyl analogue).[3] Further support for a ground-state assignment to (Q) has come from other measurements of ν(N–N)[4,5] and of the thermal stabilities of arenediazonium salts.[4]


(Q)


(A)

The widespread use of the 4-dialkylamino-substituted compounds in the so-called diazo-reprographic method [6] makes it desirable to establish by a more direct approach the relative roles of (Q) and (A) in the ground-state electronic configuration, and, following the approach of Mak and Trotter [7] in determining a degree of quinoidal character in 4-*NN*-dimethylnitrobenzene by *X*-ray crystallography, we have determined accurate bond distances and angles in the tetrafluoroborate of (II). Both preliminary and more refined structural studies of the tetrachlorozincate of (III) have been reported [8,9] (see below), and a refined structure of (I) is available [10] for comparison. A more extended summary of the evidence concerning the roles of (Q) and (A) in the electronic structure of arenediazonium salts has appeared recently.[11]

EXPERIMENTAL

4-Morpholinobenzenediazonium tetrafluoroborate was prepared by diazotisation of the parent amine by the so-called direct method, and block-shaped crystals were grown from a solution in aqueous ethanol.

Crystal Data.—$[C_{11}H_{10}N_3O]^+[BF_4]^-$. Monoclinic, $P2_1/c$, a = 13.675(4), b = 10.686(4), c = 8.982(2) Å, β = 106.72(2)°, U = 1 257.0(9) Å^3, D_c = 1.52, Z = 4. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 1.29 cm^{-1}.

Data were collected with a Syntex $P2_1$ four-circle diffractometer, with a graphite monochromator; the crystal was held at −100 °C with the LT-1 attachment, to minimise the chance of radiation-induced decomposition. Accurate cell constants were obtained by least-squares fit to the reflecting positions of 15 high-angle reflections. In the θ—2θ scan mode, reflections were scanned at rates between 1 and 29.5° min^{-1} depending on the intensity of a 2-s pre-scan, over the range $2\theta_{\alpha_1} - 0.9$ to $2\theta_{\alpha_2} + 0.9°$, to $2\theta_{max.}$ 50°. Background counts were taken for one-quarter of the scan time at each end of the range. The intensities of three standard reflections monitored every 100 reflections, showed no significant variation. In all, 2 466 reflections were collected, including 10 intense ones taken at low power; for refinement the 1 674 unique reflections with $I/\sigma(I) > 3.0$ were used.

Systematic absences $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ indicated space group $P2_1/c$. Data were corrected for Lorentz and polarisation effects, but not absorption.

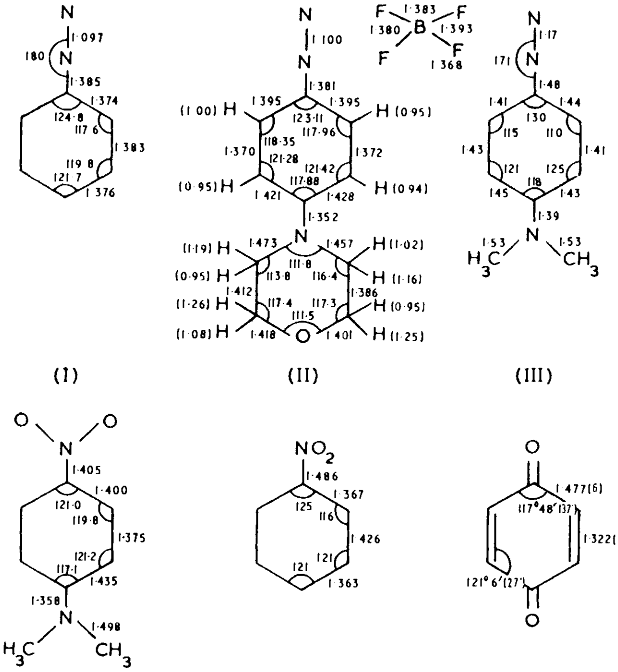
The structure was solved by direct methods, with the program MULTAN [12] from the '*X*-Ray '76' system,[13] which was also used for the remaining calculations, implemented

TABLE 1

Atom co-ordinates ($\times 10^5$) with standard deviations in parentheses (crystallographic numbering; see Figure 2)

Atom	*X*	*Y*	*Z*
C(1)	25 514(5)	19 867(7)	13 125(9)
C(2)	19 404(5)	12 083(7)	2 190(9)
C(3)	22 047(5)	−720(7)	947(8)
C(4)	31 258(5)	−5 202(7)	11 410(8)
C(5)	37 423(5)	2 473(7)	22 387(8)
C(6)	34 505(5)	14 934(7)	22 968(8)
C(7)	19 296(7)	−20 683(8)	−13 584(12)
C(8)	11 234(8)	−28 939(10)	−20 629(13)
C(9)	−340(7)	−12 552(10)	−28 618(13)
C(10)	7 067(8)	−3 790(10)	−21 783(15)
O	3 010(4)	−24 090(5)	−32 723(6)
N(1)	45 770(5)	28 977(7)	42 526(8)
N(2)	40 770(5)	22 741(6)	33 870(7)
N(3)	15 857(5)	−8 383(6)	−9 635(8)
B	33 703(7)	51 293(9)	11 646(11)
F(1)	40 224(3)	42 194(4)	8 758(5)
F(2)	37 887(4)	62 916(4)	11 634(7)
F(3)	24 359(3)	50 567(5)	444(7)
F(4)	32 193(5)	48 592(5)	25 845(6)
H(1)	23 701(45)	28 392(58)	14 110(67)
H(2)	13 479(45)	15 718(58)	−4 407(68)
H(4)	33 537(42)	−13 594(54)	11 202(64)
H(5)	43 659(44)	−1 020(57)	29 949(67)
H(71)	22 293(54)	−19 798(70)	−24 788(83)
H(72)	24 291(54)	−24 077(71)	−4 945(83)
H(81)	8 384(56)	−29 881(74)	−8 527(86)
H(82)	13 712(57)	−37 216(73)	−25 378(86)
H(91)	−5 771(58)	−9 358(75)	−36 973(88)
H(92)	−3 185(58)	−13 300(73)	−16 665(88)
H(101)	4 149(60)	3 535(79)	−17 129(91)
H(102)	8 394(59)	−815 (77)	−33 462(92)

on a Burroughs B6700 computer. Refinement by full-matrix least-squares, with anisotropic temperature factors, proceeded satisfactorily to *R* 0.084. At this point, hydrogen atoms were inserted at calculated positions and allowed to refine isotropically (but with fixed *U* for those on the morpholino-ring). This gave a final *R* of 0.065 with the final refinement being performed in separate cycles on carbon and hydrogen atom parameters. Unit weights were found satisfactory and were used. Scattering factors were taken from ref. 14, in the analytical form. Final atom-co-ordinates are listed in Table 1, bond lengths and angles in Table 2 and Figure 1, and equations of least-squares planes in Table 3. Final temperature factors and structure factors are in Supplementary Publication No. SUP 22593 (14 pp.).*



(I) (II) (III)

(IV) (V) (VI)

FIGURE 1 Structural parameters for 4-morpholinobenzenediazonium tetrafluoroborate (II) and related molecules. Estimated standard deviations: (I) 0.008 Å, 0.6°; (III) 0.04 Å

TABLE 2

Bond lengths (Å) and angles (°), with standard deviations in parentheses (crystallographic atom numbering; see Figure 2)

(*a*) Distances		(*b*) Angles	
N(1)–N(2)	1.100 1(9)	N(1)–N(2)–C(6)	179.82(8)
N(2)–C(6)	1.380 6(9)	N(2)–C(6)–C(1)	118.37(7)
C(6)–C(1)	1.395 0(10)	N(2)–C(6)–C(5)	118.52(6)
C(1)–C(2)	1.372 0(10)	C(1)–C(6)–C(5)	123.11(6)
C(2)–C(3)	1.427 6(11)	C(6)–C(1)–C(2)	117.96(7)
C(3)–C(4)	1.420 6(10)	C(1)–C(2)–C(3)	121.42(6)
C(4)–C(5)	1.370 0(10)	C(2)–C(3)–C(4)	117.88(6)
C(5)–C(6)	1.395 3(11)	C(2)–C(3)–N(3)	120.94(6)
C(1)–H(1)	0.955(6)	C(4)–C(3)–N(3)	121.17(7)
C(2)–H(2)	0.939(6)	C(3)–C(4)–C(5)	121.28(7)
C(4)–H(4)	0.951(6)	C(4)–C(5)–C(6)	118.35(6)
C(5)–H(5)	0.997(5)	H(1)–C(1)–C(6)	120.4(3)
C(3)–N(3)	1.351 9(9)	H(1)–C(1)–C(2)	121.6(3)
N(3)–C(7)	1.473 3(12)	H(2)–C(2)–C(1)	116.0(4)
C(7)–C(8)	1.411 6(13)	H(2)–C(2)–C(3)	122.6(4)
C(8)–O	1.417 9(11)	H(4)–C(4)–C(3)	122.5(3)
O–C(9)	1.401 1(13)	H(4)–C(4)–C(5)	116.2(3)
C(9)–C(10)	1.386 4(15)	H(5)–C(5)–C(4)	119.6(4)
C(10)–N(3)	1.456 6(12)	H(5)–C(5)–C(6)	122.0(4)
C(7)–H(71)	1.194(8)	C(3)–N(3)–C(7)	122.08(6)
C(7)–H(72)	0.946(7)	C(3)–N(3)–C(10)	122.50(6)
C(8)–H(81)	1.260(9)	C(7)–N(3)–C(10)	111.85(7)
C(8)–H(82)	1.078(8)	N(3)–C(7)–C(8)	113.78(8)
C(9)–H(91)	0.954(7)	C(7)–C(8)–O	117.39(9)
C(9)–H(92)	1.245(9)	C(8)–O–C(9)	111.55(7)
C(10)–H(101)	1.021(9)	O–C(9)–C(10)	117.28(9)
C(10)–H(102)	1.159(9)	C(9)–C(10)–N(3)	116.39(9)
B–F(1)	1.393(1)	H(71)–C(7)–N(3)	110.0(4)
B–F(2)	1.368(1)	H(71)–C(7)–C(8)	94.9(3)
B–F(3)	1.383(1)	H(71)–C(7)–H(72)	112.3(6)
B–F(4)	1.380(1)	H(72)–C(7)–N(3)	110.5(5)
		H(72)–C(7)–C(8)	114.5(5)
		H(81)–C(8)–C(7)	93.4(3)
		H(81)–C(8)–O	108.4(3)
		H(81)–C(8)–H(82)	119.1(6)
		H(82)–C(8)–C(7)	113.3(4)
		H(82)–C(8)–O	105.5(4)
		H(91)–C(9)–O	110.3(5)
		H(91)–C(9)–C(10)	114.3(5)
		H(91)–C(9)–H(92)	109.6(6)
		H(92)–C(9)–O	112.2(4)
		H(92)–C(9)–C(10)	91.8(3)
		H(101)–C(10)–C(9)	112.2(5)
		H(101)–C(10)–N(3)	106.7(4)
		H(101)–C(10)–H(102)	110.0(6)
		H(102)–C(10)–C(9)	94.0(4)
		H(102)–C(10)–N(3)	117.4(4)
		F(1)–B–F(2)	110.09(8)
		F(1)–B–F(3)	109.42(7)
		F(1)–B–F(4)	107.47(7)
		F(2)–B–F(3)	110.47(7)
		F(2)–B–F(4)	111.38(7)
		F(3)–B–F(4)	107.94(8)

In the final refinement, the benzenoid hydrogen atoms refined satisfactorily, but the axial C–H distances for the

---

* See Notice to Authors, No. 7, in *J.C.S. Perkin II*, 1978, Index issue.

morpholino-group became rather long. The ring angles there are wider than expected, and the carbon atoms have thermal ellipsoids elongated normal to the ring. Further, the only significant peaks on a final difference—Fourier synthesis (of *ca.* 0.5 e Å^{-3} height) are in the vicinity of these carbon atoms. This indicates some disorder in this ring, in which the predominant conformation is as found, but the inverse conformation is partly occupied. Attempts to locate and refine atoms corresponding to the inverse structure were not successful, no doubt because of the closeness to the original positions; it follows that apparent distances and angles around this ring will deviate from the true values, but those in the rest of the structure should not be affected. Positional standard deviations, derived in the usual way from the least-squares calculation, are unusually small for all atoms. We believe, however, that they do give realistic estimates of the errors, although they should perhaps be multiplied by a factor of about two (as is often suggested for crystallographic results). Confirmation of their validity comes in particular from comparison of equivalent pairs of bond lengths and angles around the benzene ring, whose agreement is very satisfactory. The worst discrepancy is C(5)–H(5) which is 6.0σ from the mean of all four C(benzene)–H distances, but may well be affected by an interaction with the anion. The H(5) · · · F(1) distance is 2.26 Å, considerably shorter than any other H · · · F distance. The two anomalous H–C–C angles [H(2)–C(2)–C(1) and H(4)–C(4)–C(5)] are very similar [116.0(4) and 116.2(3)]. For the morpholino-ring, of course, the standard deviations cannot be taken literally. They show that the maxima of the time- (or position-) averaged electron density has been well determined, but the disorder means that distances from these maxima cannot be interpreted as distances between atoms in the ring. The discrepancies between nominally equivalent distances are therefore not surprising.

TABLE 3

Least squares planes (in orthogonal Å space, $X_{\parallel}a$, $Y_{\perp}a$ in *ac* plane, *Z* orthogonal), with deviations (Å) of relevant atoms in square brackets

Plane (1): C(1)—(6) *

$$0.715X + 0.255Y - 0.651Z = 2.063$$

[C(1) −0.004, C(2) 0.0, C(3) 0.002, C(4) 0.001, C(5) −0.005, C(6) 0.007, N(1) 0.035, N(2) 0.020, N(3) −0.025, O 0.010, H(1) −0.02, H(2) 0.01, H(4) 0.01, H(5) −0.05, C(7) 0.27 C(8) −0.22, C(9) −0.31, C(10) 0.15]

Plane (2): N(3), O, C(7)—(10) *

$$0.643X + 0.228Y - 0.731Z = 2.106$$

[N(3) −0.148, O 0.174, C(7) 0.168, C(8) −0.182, C(9) −0.166, C(10) 0.155, H(71) 1.34, H(72) −0.16, H(81) −1.42, H(82) 0.21, H(91) 0.10, H(92) −1.38, H(101) −0.29, H(102) 1.27, C(3) −0.25, C(6) −0.53]

Dihedral angle: (1)–(2) 6.3°

* Crystallographic atom numbering; see Figure 2.

RESULTS AND DISCUSSION *

The crystal contains the expected diazonium cations (Figure 2) and fluoroborate anions, and the packing (Figure 3) is such that the cations lie in parallel planes, with the anions in gaps in the planes. The principal interaction is presumably of π-type between adjacent ions. The anion dimensions are standard, though it is noticeable that the individual distances and angles depart from the means (1.318 Å, 109.46°) by much more than the standard deviations; this is presumably due to packing effects.

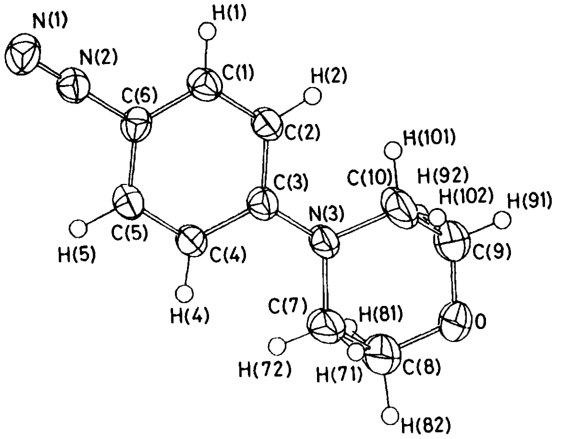


FIGURE 2 View of the 4-morpholinobenzenediazonium cation (II), showing the crystallographic atom numbering. For the chemical descriptions, systematic numbering is used: C(1) = C(6) C(2) = C(1) and C(5); C(3) = C(2) and C(4); C(4) = C(3)

In the cation, the planes of the two rings are virtually parallel (Table 3). Some of the morpholino-group dimensions are abnormal [C–C 1.40, C–H(axial) 1.16—1.26 Å] but this is due to the 'ring-flip' disorder mentioned earlier.

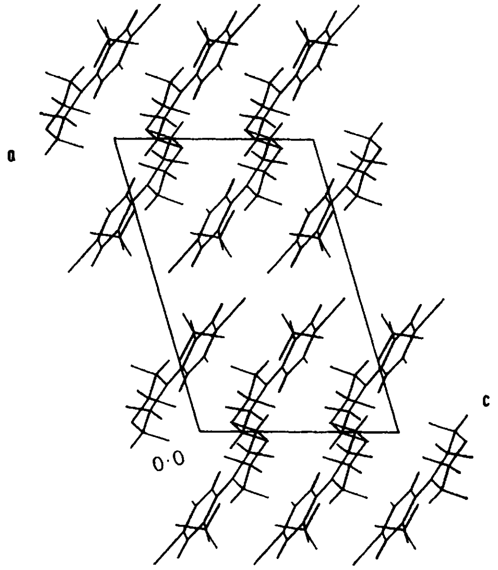


FIGURE 3 Packing diagram, viewed down *b*

Figure 1 contains the significant structural parameters of relevant molecules as follows: (I) benzenediazonium chloride,[10] (II) 4-morpholinobenzenediazonium tetrafluoroborate (our data), (III) 4-dimethylaminobenzenediazonium tetrachlorozincate[9] (IV) 4-dimethylamino-

---

* Tables 1—3 use the crystallographic atom numbering system depicted in Figure 2. In the subsequent discussion systematic atom numbering is used.

nitrobenzene,[7] (V) nitrobenzene,[15] and (VI) *p*-benzoquinone.[16] It can be seen that a considerable discrepancy exists between our data for (II) and those of Nesterova and Porai-Koshits for (III),[9] particularly as regards the bond lengths and angles in the ring. It is quite clear, in view of the quoted standard deviations for (III), that no significance whatever can be attached to the distortions in the ring. This structure is therefore not further considered. There is a close overall similarity between our data for the 4-amino-substituted benzenediazonium salt (II) and those of Mak and Trotter [7] for 4-dimethylaminonitrobenzene (IV), both as regards the ring (which is considerably distorted from hexagonal) and the amino-substituent. Comparison of data for (I) and (II) shows that while the presence of the 4-amino-substituent lengthens C(1)–C(2) by 0.02 Å, and reduces C(2)–C(3) by 0.01 Å, the major effects are an increase in C(3)–C(4) by *ca.* 0.05 Å and decrease in C(3)–C(4)–C(5) from 121.7 to 117.9°. These changes closely parallel those found when (V) [15] is substituted by a 4-dimethylamino-group (IV),[7] and these latter have been explained [17] in terms of differences in hybridisation of the carbon σ orbitals resulting from changes in the bond angles. However, no convincing reason was given as to the origin of the latter effects.

Both the similarity between the bond angles and distances in (II) and (IV), and the closely paralleled changes in these parameters on going from the parent compounds [(I) and (V) respectively] to their 4-dialkylamino-analogues [(II) and (IV)] suggest the operation of a common influence. We have carried out calculations by several well-established procedures in an attempt to quantify the simultaneous effects of the two substituents (N_2^+ and NH_2) on total energies, orbital populations, total atomic populations, and optimised geometries, as follows.

TABLE 4

Overlap populations for various bonds

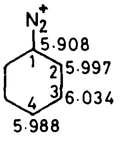
Compound	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)
4-Aminobenzenediazonium cation	0.970	1.050	0.971
Benzenediazonium cation	0.983	1.027	0.998
4-Aminonitrobenzene	1.008	1.029	0.997
Nitrobenzene	1.012	1.017	1.013

Ab Initio (*SCF*) *Calculations*.—The total energies of various ring geometries for the 4-aminobenzenediazonium cation were calculated, using a STO 3G basic set.[18] For structure (II) an energy of −388.170 0 a.u. was obtained, which was 0.061 2 a.u. higher than that for a regular hexagon with r_{C-C} 1.397 Å and 0.058 2 a.u. higher than for structure (I). Evidently this type of calculation has poor predictive value for the geometry of a molecule of such complexity; indeed, in its application to first-row hydrides, it consistently overestimates r_{M-H} by 0.12—0.03 Å.[19] On twisting the NH_2 group from being coplanar with the ring to being at 90° to the ring plane, the HOMO–LUMO separation increases from 0.359 to 0.408 a.u., *i.e.* predicting a blue-shift to the longest wavelength transition of 0.049 a.u. in contradiction to the observed effect of placing bulky alkyl groups at the 3-position.[3]

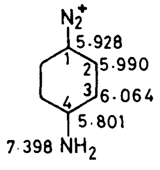
Overlap Populations from STO 3G *Calculations*.[20]—For a series of relevant compounds, the overlap populations for the various bonds (taken as having r_{C-C} 1.397 Å) are listed in Table 4.

A higher overlap population is predicted for C(2)–C(3), in all cases, with a particularly high order appearing in the 4-aminobenzenediazonium cation. However, the disparity between the bond orders in C(1)–C(2) and C(3)–C(4) evident in our crystallographic data for structure (II) is not apparent.

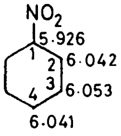
Total Atomic Populations (*by ATMOL*/3).[20]—Introduction of a 4-amino-group reduces that on C(4) for (I) [Structure (a)] from 5.988 to 5.801, whilst the atomic populations at the other carbon atoms are much less affected. Nitrobenzene is affected similarly by this substitution.



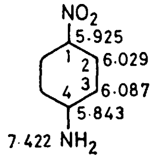
(a)



(b)

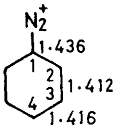


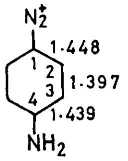
(c)



(d)

Optimised Geometries by MINDO/3 *Calculations*.[21]—These yielded the following results:

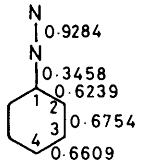




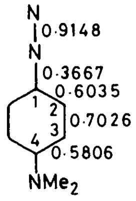
The only useful prediction here is that of the shortened C(2)–C(3) bond in the 4-aminobenzenediazonium cation: neither the shortening of C(1)–C(2) nor the lengthening of C(3)–C(4) is apparent from the calculations.

To summarise, most of the bond-length changes in going from (I) to (II) are too subtle to be predicted by any of the methods we have used, although treatments of (II) predict a considerably higher bond order in C(2)–C(3) than in C(1)–C(2) or C(3)–C(4). The greatest deficiencies have been the failure to predict the low bond-order in C(3)–C(4) and the near-aromatic bond-order in C(1)–C(2).

Previous theoretical results on the bonding in ArN_2^+ also failed to predict the experimental geometry. Schuster and Polansky [22] used Hückel calculations involving selected heteroatom parameters to compute π-bond orders in (I) and (III) *inter alia, viz*:



(e)



(f)

The effect of substitution by NMe$_2$ is to reduce the bond orders in C(1)–C(2), C(3)–C(4) (especially) and N–N and to increase those in C(2)–C(3) and C–N in accordance with an increased contribution from structure (Q). Klasinc and Schulte-Frohlinde [23] find the C(1)–N π-bond order in (III) [*i.e.* (f)] to be 0.351 0, whilst Sukigara and Kikuchi [24] obtained an N–N π-bond order of 0.816 for (III) [*i.e.* (f)] (compared with a value of 0.857 for the 4-fluorobenzenediazonium cation), which they consider to reflect a large influence of structure (Q).

Some indication of the true extent of quinoidal participation in the ground-state structure of (II) is given by comparison of (II) with (VI). The C(1)–C(2) and C(2)–C(3) distances may be taken as fair indications of C(sp^2)–C(sp^2) single and double bonds respectively, and clearly the C(3)–C(4) and C(2)–C(3) distances in (II) do not reflect 'pure' single and double bonds, but rather intermediate situations between these and the 'aromatic' position.

A completely different approach to the effect of substituents on benzene-ring geometry has recently been investigated by Vaciago and co-workers.[25] This involves the empirical correlation of the distortions in the ring with the nature of the substituents. So far, however, there is insufficient evidence on diazonium compounds for a clear pattern to appear.[26]

We thank the S.R.C. for a postdoctoral research assistantship (to T. J. G.) and a CASE studentship (to D. R. P.).

[8/1937 *Received*, *7th November*, 1978]

REFERENCES

[1] L. C. Anderson and J. W. Steedly, jun., *J. Amer. Chem. Soc.*, 1954, **76** 5144.

[2] L. C. Anderson and B. Manning, *J. Amer. Chem. Soc.*, 1955, **77**, 3018.

[3] R. J. Cox, P. Bushnell, and E. M. Evleth, *Tetrahedron Letters*, 1970, 207.

[4] A. F. Gremillion, H. B. Jonassen, and R. J. O'Connor, *J. Amer. Chem. Soc.*, 1959, **81**, 6134.

[5] K. Tabei and C. Ito, *Bull. Chem. Soc. Japan*, 1968, **41**, 514,

[6] M. F. Mizianty, E. A. Fitzgerald, and G. H. Kimber, jun., *Photo. Sci. Eng.*, 1971, **15**, 331; E. S. Baltazzi, E. E. Dailey, P. Datta, H. Printy, and W. J. Wagner, *Photo. Sci. Eng.*, 1974, **18**, 68.

[7] T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1965. **18**, 6.

[8] Ya. M. Nesterova, M. A. Porai-Koshits, A. V. Upadysheva, and L. A. Kazitsnya, *Zhur. strukt. Khim.*, 1966, **7**, 129.

[9] Ya. M. Nesterova and M. A. Porai-Koshits, *Zhur. strukt. Khim.*, 1971, **12**, 108.

[10] C. Römming, *Acta Chem. Scand.*, 1963, **17**, 1444.

[11] S. Sorriso in 'The Chemistry of Diazonium and Diazo Groups,' ed. S. Patai, Wiley, Chichester, 1978, chap. 3.

[12] M. M. Woolfson, in 'Crystallographic Computing Techniques,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1976.

[13] J. M. Stewart, Technical Report TR 446, Computer Science Centre, University of Maryland, 1976.

[14] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[15] J. Trotter, *Acta Cryst.*, 1959, **12**, 884.

[16] J. Trotter, *Acta Cryst.*, 1960, **13**, 86.

[17] J. Trotter, *Tetrahedron*, 1960, **8**, 13.

[18] W. J. Hehre, W. A. Latham, R. Ditchfield, M. D. Newton, and J. A. Pople, 'Gaussian 70,' Program 236, Quantum Chemistry Program Exchange, Indiana University, 1973.

[19] J. A. Pople in 'Modern Theoretical Chemistry,' ed. H. F. Schaefer, vol. 4, Plenum, New York, 1977, p. 1.

[20] V. R. Saunders and M. F. Guest, ATMOL/3 Reference Manual, Atlas Computing Division, Rutherford Laboratory, Chilton, Oxfordshire, 1976.

[21] M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. H. Lo, C. A. Ramsden, H. Kollmar, P. Weiner, and P. K. Bischof, MINDO/3, Program 279, Quantum Chemistry Program Exchange, Indiana University, 1975.

[22] P. Schuster and O. E. Polansky, *Monatsh. Chem.*, 1965, **96**, 396

[23] L. Klasinc and D. Schulte-Frohlinde, *Z. phys. Chem. (Frankfurt)*, 1968, **60**, 1.

[24] M. Sukigara and S. Kikuchi, *Bull. Chem. Soc. Japan*, 1967, **40**, 1077.

[25] A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 1630; M. Colapietro, A. Domenicano, and A. Vaciago, *Acta Cryst.*, 1970, **A34**, 594.

[26] A. Vaciago, personal communication.