

The Origin of the Remarkable Stability of the 1*H*-3,5-Dimethylpyrazole-4-diazonium Cation: an X-Ray Crystallographic and MNDO Theoretical Investigation

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The unusual stability 1*H*-3,5-dimethylpyrazole-4-diazonium chloride has been investigated by a combination of X-ray crystallography and MNDO calculations. Crystals of the diazonium chloride are orthorhombic, space group *Pnma*, with four molecules in a unit cell of dimensions $a = 7.964(1)$, $b = 6.308(2)$, $c = 15.060(3)$ Å. The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R = 0.032$ for 539 reflections with $I > 3\sigma(I)$ measured by diffractometer. The cation lies on a crystallographic mirror plane and the diazonium moiety is essentially linear [C(4)–N(7)–N(8) 177.5(4)°]. While the diazonium N–N distance [N(7)–N(8) 1.096(4) Å] is typical of that in arenediazonium cations, the C(4)–N(7) distance is short [1.351(4) Å] suggesting that the stability of the cation is due to a contribution from a diazo resonance form in which this bond acquires p_π – p_π character. The MNDO-optimised geometry of the cation agrees well with the experimental data. Calculated energy profiles for the dissociation of the heterocyclic diazonium cation and the benzenediazonium cation to the corresponding carbonium ion and N₂ show that the strength of the *ipso*-C–N₂ bond is the major distinguishing feature. The difference in bond strength arises from greater availability of π -electron density on the *ipso* carbon of the pyrazolyl cation and hence greater *ipso*-C→N₂ π^* back-donation. Both carbonium ions have large π density on the *ipso*-carbon but in the phenyl cation this is predominantly located in the lowest energy π orbital while in the pyrazolyl cation it is located in the HOMOs and hence available for interaction with the diazonium function.

It is well known that the vast majority of arenediazonium halides are extremely reactive substances in solution. They are also shock-sensitive in the solid state, often detonating with extreme violence.¹ In the course of a study of the reactions of heterocyclic diazonium cations with transition metal carbonyl substrates² we became intrigued by the remarkable stability of the 1*H*-3,5-dimethylpyrazole-4-diazonium cation (1). This diazonium cation has been recovered unchanged after heating for 3 h at 100 °C in aqueous hydrochloric acid and is not completely decomposed after similar treatment for 48 h.³ Even more remarkable is the fact that the solid chloride salt of cation (1), [1]Cl, is not at all shock-sensitive and on heating it is reported to explode 'feebly' at 175 °C!⁴ The unusual lack of reactivity of (1) appeared to us to merit some further investigation and in the present paper we attempt to trace its origin *via* an X-ray crystallographic study combined with theoretical calculations employing the MNDO⁵ approach. To our knowledge this report represents the first application of either of these techniques to a heterocyclic diazonium cation.†

Results and Discussion

The Crystal and Molecular Structure of [1]Cl.—The structural features of a number of arenediazonium salts have been established by X-ray diffraction methods⁶ but no such information has been available for species in which the diazonium function is attached to a heteroaromatic nucleus. A

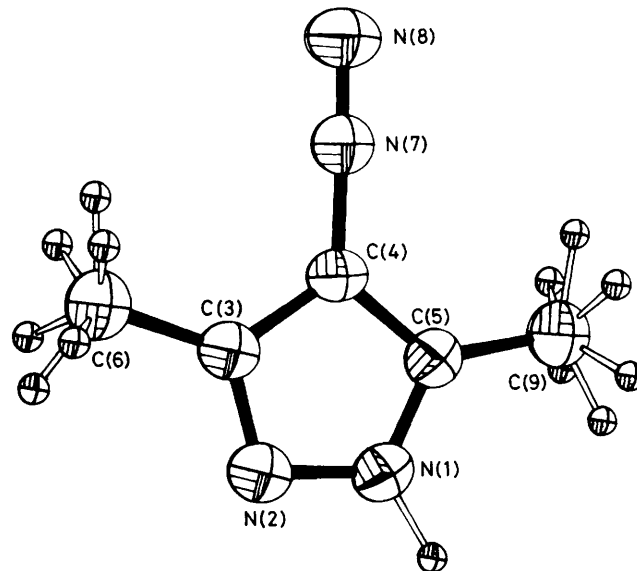


Figure 1. View of 1*H*-3,5-dimethylpyrazole-4-diazonium chloride with the crystallographic numbering scheme

view of [1]Cl showing the crystallographic numbering-scheme is given in Figure 1 and the contents of the unit cell are illustrated in Figure 2. Table 1 lists the final fractional coordinates for [1]Cl; interatomic distances and bond angles are in Table 2. Crystals of [1]Cl contain discrete cations which lie on crystallographic mirror-planes and which are hydrogen-bonded to the chloride counter-anions (Cl...H 1.96 Å, N...Cl 3.034 Å) lying on the same mirror-plane. The chloride

† By way of a historical footnote we would point out that it is curiously appropriate that this work should issue in part from University College Cork. The diazonium salt (1)Cl was first prepared by Joseph Reilly⁴ who from 1924 to 1957 was Professor of Chemistry in this Department where he carried out the first quantitative estimation of its remarkable stability.³

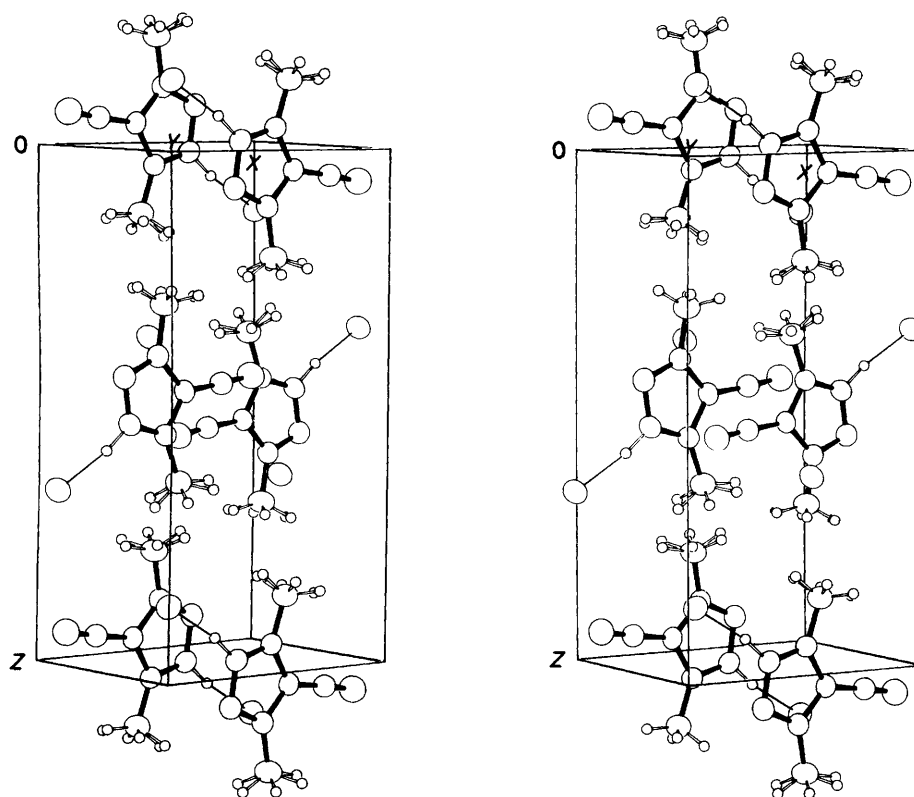


Figure 2. Stereoview of the contents of the unit cell of 1*H*-3,5-dimethylpyrazole-4-diazonium chloride

Table 1. Final fractional co-ordinates $\times 10^4$ for 1*H*-3,5-dimethylpyrazole-4-diazonium chloride with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cl	8 437(1)	2 500	1 303(1)
N(1)	5 365(3)	2 500	149(2)
N(2)	5 622(4)	2 500	-757(2)
C(3)	4 124(4)	2 500	-1 122(2)
C(4)	2 913(4)	2 500	-427(2)
C(5)	3 763(4)	2 500	390(2)
C(6)	3 832(5)	2 500	-2 097(2)
C(9)	3 152(5)	2 500	1 315(2)
N(7)	1 230(4)	2 500	-540(2)
N(8)	-126(4)	2 500	-663(2)

counterion also makes short contacts with the nitrogen atoms of the diazonium function of symmetry-related cations. Similar interactions between the diazonium functional group and the counterion have also been observed in crystalline arenediazonium salts and in the majority of these cases the shortest such contact is with the terminal nitrogen atom of the diazonium function.⁶ A similar pattern obtains for (1), the distance between chloride anion and N(8ⁱ) is 3.160 Å while that between chloride and N(7ⁱ) is 3.364 Å. The attachment of the acidic ring proton to N(1) [rather than to N(2)] was established from a difference map but this could also be inferred from the endocyclic N-N-C bond angles which are 114.4(3) and 106.3(3)° for N(1) and N(2), respectively. In the parent pyrazole ring system the protonated ring nitrogen is also associated with the larger N-N-C angle (112.3°, as compared with 103.6°).⁷

Figure 3 illustrates the resonance forms which might be expected to make a significant contribution to the ground state

Table 2. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for 1*H*-3,5-dimethylpyrazole-4-diazonium chloride

(a) Bond lengths

N(1)-N(2)	1.378(4)	C(4)-C(5)	1.404(4)
N(1)-C(5)	1.327(4)	C(4)-N(7)	1.351(4)
N(2)-C(3)	1.314(4)	C(5)-C(9)	1.476(4)
C(3)-C(4)	1.423(4)	N(7)-N(8)	1.096(4)
C(3)-C(6)	1.486(5)		

(b) Bond angles

N(2)-N(1)-C(5)	114.4(3)	C(3)-C(4)-N(7)	125.4(3)
N(1)-N(2)-C(3)	106.3(3)	C(5)-C(4)-N(7)	126.1(3)
N(2)-C(3)-C(4)	107.8(3)	N(1)-C(5)-C(4)	102.9(3)
N(2)-C(3)-C(6)	123.8(3)	N(1)-C(5)-C(9)	125.1(3)
C(4)-C(3)-C(6)	128.4(3)	C(4)-C(5)-C(9)	132.0(3)
C(3)-C(4)-C(5)	108.6(3)	C(4)-N(7)-N(8)	177.5(4)

(c) Inter-ion contacts

Cl...H(N1)	1.96	Cl...N(7 ⁱ)	3.364
Cl...N(1)	3.034	Cl...N(8 ⁱ)	3.160

The superscripts refer to the following equivalent positions: I, $1 - x, -y, -z$; II, $1 + x, y, z$.

of (1). Since the pyrazole ring is a π -excessive system our intuitive expectation was that the enhanced stability of (1) was due to conjugative transfer of π -electron density from the five-membered ring to the diazonium function. In terms of resonance structures this would imply that the diazo canonical form (1f) should be an important contributor to the ground state of the cation. Corroborative evidence in favour of this

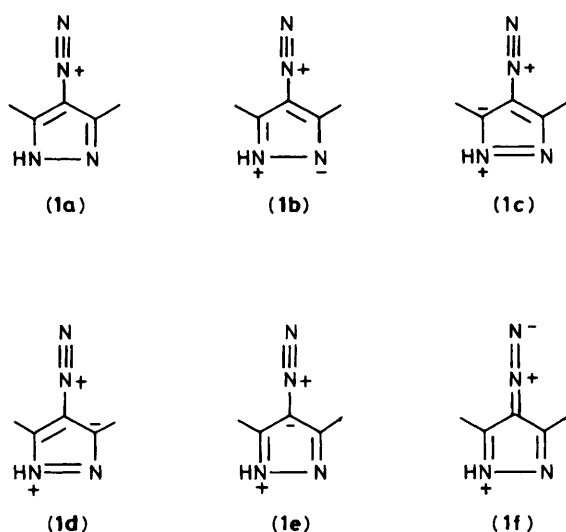


Figure 3. Resonance canonicals for 1H-3,5-dimethylpyrazole-4-diazonium cation (1)

suggestion is available from a number of sources. First it may be noted that the majority of those few arenediazonium cations which form stable chloride salts involve ring substituents which are capable of conjugative electron release towards the diazonium group.¹ Secondly the N–N stretching frequency of (1) ($2\,235\text{ cm}^{-1}$) is significantly lower than the corresponding frequency for the benzenediazonium cation ($2\,285\text{ cm}^{-1}$).⁸ Thirdly we have recorded the ^{13}C n.m.r. spectrum of [1]Cl and find that the resonance of the *ipso*-carbon atom C(4) (to which the diazonium function is attached) occurs at $\delta\,56.98\text{ p.p.m.}$ in D_2O . This carbon atom is therefore significantly more shielded than the analogous *ipso*-carbon in benzenediazonium cations ($\delta\,^{13}\text{C} > 100\text{ p.p.m.}$) but similar to that found in a range of authentic neutral diazo compounds ($\delta\,^{13}\text{C}$ ca. 67 p.p.m.).^{9,10} An important contribution from the diazo resonance canonical (1f) implies that the net N(7)–N(8) bond order should be less than three while the C(4)–N(7) bond simultaneously acquires some p_π – p_π character, the anticipated structural consequences of which would be a relative lengthening of N(7)–N(8) and a contraction of C(4)–N(7). At first glance the experimental evidence on this point appears to be somewhat contradictory. The N(7)–N(8) bond distance in (1) [$1.096(4)\text{ \AA}$] is virtually identical to the analogous bond length found in a range of authentic diazonium cations⁶ and may be compared *inter alia* with the N–N bond distance of $1.091(3)\text{ \AA}$ found in the 4-sulphobenzenediazonium inner salt $4\text{-SO}_3^-\text{-C}_6\text{H}_4\text{-N}_2^+$ where no significant participation of diazo resonance structures is to be anticipated.¹¹ Furthermore the N(7)–N(8) distance in (1) is significantly shorter than the N–N bond lengths in authentic neutral diazo compounds [e.g. benzoylphenyldiazomethane, $1.132(5)\text{ \AA}$;¹² dibenzoyldiazomethane, $1.113(2)\text{ \AA}$;¹³ and very much shorter than the N–N double bond in 1,1'-azobiscarbamide (1.238 \AA).¹⁴ On the other hand the C(4)–N(7) bond distance [$1.351(4)\text{ \AA}$] is also distinctly short when compared with the corresponding $sp^2\text{C}$ –N(diazonium) bond length in $4\text{-SO}_3^-\text{-C}_6\text{H}_4\text{-N}_2^+$ (1.412 \AA)¹¹ and falls well within the range of short $sp^2\text{C}$ –N(diazo) bond lengths [$1.308(7)$ – $1.37(2)\text{ \AA}$] of bond order ca. 1.5 which has been established for neutral diazo compounds.¹³ This apparent contradiction may be resolved in one of two ways. The data may be regarded as evidence for significant participation of resonance form (1e) [rather than (1f)] in the overall structure of (1). In this case N(7)–N(8) would maintain its essentially triply bonded character while C(4)–N(8) would be contracted by coulombic

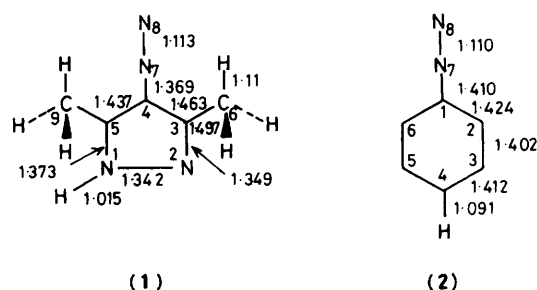


Figure 4. MNDO-optimised bond lengths (\AA) for 1H-3,5-dimethylpyrazole-4-diazonium cation (1) and for benzenediazonium cation (2)

forces rather than by an increase in bond order. Alternatively it is entirely possible that the diazo resonance form (1f) is involved but that the N(7)–N(8) bond distance in (1) may be relatively insensitive to moderate changes of bond order in the three to two region. This appears to be the case for the diazonium functions in the inner salt $1,10\text{-B}_{10}\text{H}_8(\text{N}_2)_2$ ¹⁵ and a similar insensitivity to bond order changes has been noted for the carbon–oxygen triple bond in co-ordinated CO ¹⁶ and, in some cases, for the carbon–nitrogen triple bond in co-ordinated isocyanides.¹⁷ We cannot decide between these two possibilities on the basis of the structural evidence alone.

Within the pyrazole ring the N(2)–C(3), C(3)–C(4), C(4)–C(5), and C(5)–N(1) bond distances show a short–long–short–long pattern of alternation in the sense expected for resonance form (1a) (Figure 1) suggesting that the latter may make a significant contribution to the ground state of the cation. While the difference in length between related pairs of 'short' and 'long' bonds [N(2)–C(3) $1.314(4)$, N(1)–C(5) $1.327(4)\text{ \AA}$; C(4)–C(5) $1.404(4)$, C(3)–C(4) $1.423(4)\text{ \AA}$] is close to the range of experimental error we nonetheless believe the effect to be real since the MNDO-optimised geometry of (1) (see below) produces a qualitatively similar pattern of alternation and it has also been observed in the structure of pyrazole itself.⁷ The endocyclic N–N bond [N(1)–N(2), $1.378(4)\text{ \AA}$] is quite long and not significantly shorter than the analogous bond distance in 1,2-bis(methoxycarbonylamino)-3,5-dimethylpyrazolium cation where no p_π – p_π character was attributed to the N–N bond.¹⁸ In contrast, noticeably shorter endocyclic N–N distances are found in related heterocycles where N–N π -bonded forms are likely to contribute significantly to the ground state, e.g. pyrazole [$1.342(2)\text{ \AA}$]⁷ and pyridazine hydrochloride [$1.334(4)\text{ \AA}$].¹⁹ While the long N(1)–N(2) bond length might be taken as evidence that resonance forms (1c) and (1d) (which require this bond to have some p_π – p_π character) do not make a significant contribution to the ground state of (1), such a conclusion is not supported by the results of our theoretical studies.

MNDO Calculations.—The MNDO-optimised geometries of the 1H-3,5-dimethylpyrazole-4-diazonium cation (1) and of benzenediazonium cation (2) are shown in Figure 4 and are in very good agreement with our own crystallographic results for (1) and with the data reported by Romming for the benzenediazonium cation.²⁰ Our calculated geometry for the latter cation is also very similar to that recently calculated by Vincent and Radom using *ab initio* methods,²¹ being slightly less accurate for the bond lengths within the benzene ring but considerably more accurate for the dimensions of the exocyclic C–N₂ structure. The calculated geometry of (1) also produces slightly long intra-ring bonds except for N(1)–N(2) which is shorter than experiment (see below). Again the calculated C–N₂ bond lengths agree well with our crystallographic data.

The most significant difference between the calculated

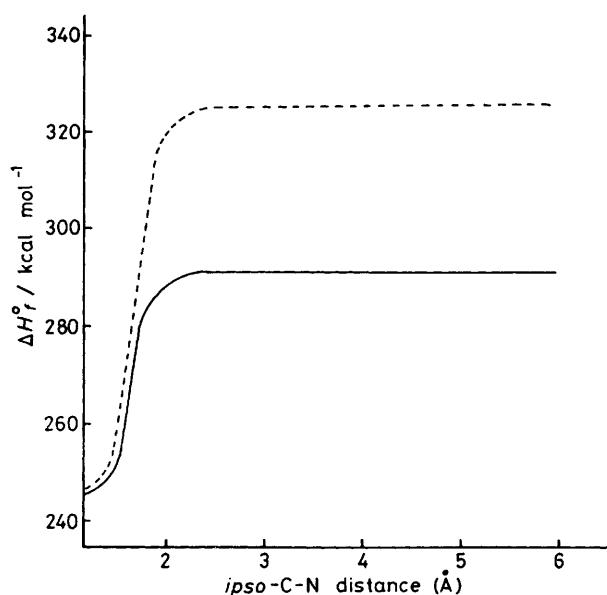
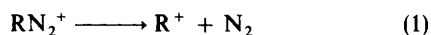


Figure 5. Energy profile of the reaction $\text{RN}_2^+ \rightarrow \text{R}^+ + \text{N}_2$ for 1H-3,5-dimethylpyrazole-4-diazonium cation (1) (---) and for benzenediazonium cation (2) (—)

geometries of the two diazonium cations is the distinct shortening of the exocyclic C–N₂ bond in (1) *vis-à-vis* (2). The calculation shows this contraction to be reflected in a significant increase in C–N bond order: 0.997 in (1) compared with 0.888 in (2). The calculated heats of formation for (1) and (2) are almost identical, 246.45 and 245.02 kcal mol^{−1}, respectively. Hence the difference in thermal stability of the two cations does not arise from differences in the thermodynamic stability of the two species and must instead be related to the energy changes involved in the decomposition process. If we consider the most probable thermal decomposition process to be (1), then the



relative strengthening of the exocyclic C–N bond of (1) *vis-à-vis* (2) implicit in the bond-order data seems likely to be the most important effect in determining their relative stabilities.

The energy profile for reaction (1) was investigated by gradually extending the *ipso*-C–N₂ bond lengths of (1) and (2) from the ground-state ion value to 6 Å and calculating the energy of the fully optimised geometry at points along this reaction co-ordinate. The results of this calculation are shown in Figure 5 and clearly reflect the experimental evidence on the relative stabilities of the two diazonium cations. The energy required to dissociate the pyrazolediazonium cation (1) is nearly twice that required for the benzenediazonium cation (2); 78.64 as compared with 46.33 kcal mol^{−1}. An *ab initio* calculation of reaction (1) applied to the benzenediazonium cation (2) yielded a very similar dissociation energy, 44.3 kcal mol^{−1}, despite producing a slightly lower heat of formation, 209.94 kcal mol^{−1} for the cation.²¹ The lack of an activation energy for the dissociation process is not surprising. As the reaction involves a single bond-breaking step, the process depicted in Figure 5 is merely the long bond length section of the Morse potential corresponding to the C(4)–N(7) bond stretch and no transition state is involved in such processes.

The contrasting stabilities of the two diazonium cations can now be located definitely in their different exocyclic C–N₂ bonding. This bond has been shown to be stronger in the more stable compound and formation of the bond stabilises the carbonium cation R⁺ far more in the pyrazole than in the

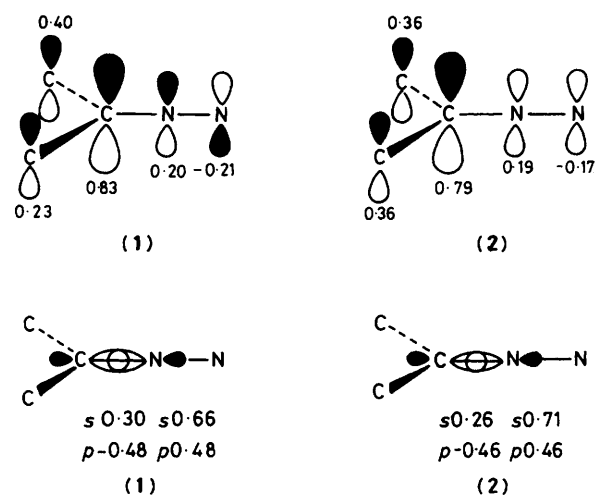


Figure 6. Localised orbitals contributing to *ipso*-C–N₂ bonding in 1H-3,5-dimethylpyrazole-4-diazonium cation (1) and benzenediazonium cation (2), with orbital coefficients

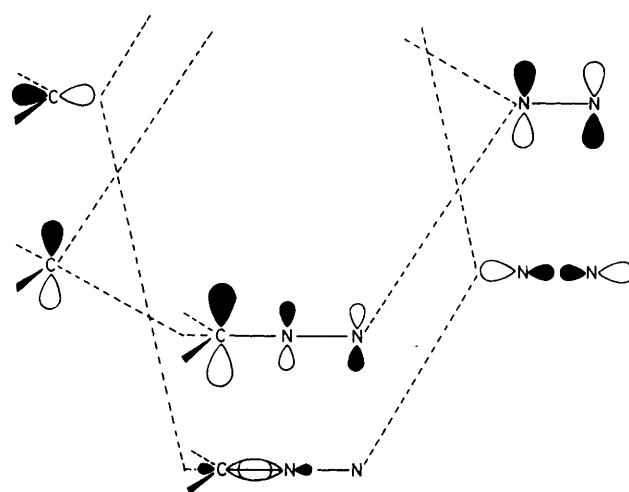


Figure 7. Generalised orbital interaction diagram for the formation of RN_2^+ from R^+ and N_2

benzene system. Inspection of the SCF molecular orbitals for information on the C–N bonding provides no useful data as the bonding is spread over several molecular orbitals and these are not directly comparable. We therefore localised the molecular orbitals using the method of Perkins and Stewart.²² The C–N₂ bonding was found to be located in only two of the localised orbitals (Figure 6), one of which is strictly two-centre σ-bonding and the other more delocalised onto adjacent atoms but still predominantly C–N π-bonding.

Although the differences in the atomic orbital coefficients contributing to the localised orbitals are not large they do, of course, account for the bond-order differences. In the pyrazolediazonium cation (1) the σ bond order is greater by 0.048 and the π bond order by 0.067 than in benzenediazonium cation (2). The localised orbitals also show how a general interaction diagram for the orbitals of RN_2^+ can be constructed from the orbitals of R^+ and N_2 , respectively (Figure 7). The σ bond is formed by the LUMO of R^+ (an empty *p* orbital on the *ipso* carbon atom) accepting electrons from the HOMO of N_2 (the 3σ lone pair orbital). The π-bond is formed by back-donation from the HOMO-1 of the ring system (a π-orbital with a large contribution on the *ipso* carbon) to the

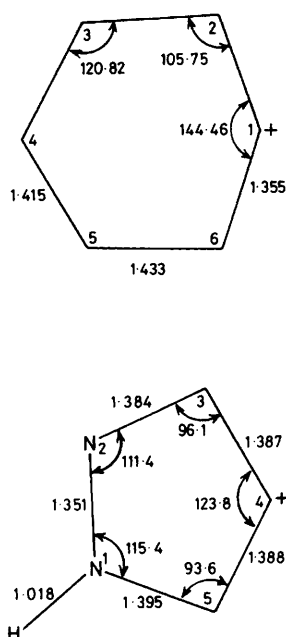


Figure 8. MNDO-optimised bond lengths (Å) and bond angles (°) for the phenyl and 1H-3,5-dimethylpyrazol-4-yl cations. For clarity the C-H bonds of the phenyl cation (1.085–1.093 Å) and the methyl groups of the pyrazolyl cation [C(ring)–C(methyl) 1.490 Å; C–H 1.109 Å] have been omitted

$1\pi^*$ orbital of N_2 . The HOMOs of both R^+ ions have no composition on the *ipso* carbon atoms.

The source of the difference in the π back-bonding contribution to the C– N_2 bonding can now be identified from the SCF orbitals of the two R^+ cations. The relevant ring orbital in the phenyl cation is 25% localised on the *ipso* carbon [C(1)] whereas it is 50% localised on the corresponding carbon atom [C(4)] in the pyrazolyl cation. The two cation LUMOs are identical and themselves provide no direct reason for the larger σ bond order in the pyrazole diazonium cation (1). The σ bond order is a more rapidly increasing function of the C– N_2 bond length than the π bond order simply because the bonding overlap is directed along the bond axis. Hence any shortening of the C– N_2 bond produced by increased π bonding will increase the σ bond order without requiring any difference in the R^+ LUMOs.

The problem of the different stabilities of the diazonium cations (1) and (2) has now been reduced to explaining the origin of the different *ipso* carbon contributions to the HOMO-1 of the two cations. The MNDO-optimised geometries of the two cations are summarised in Figure 8 and the geometry of the phenyl cation is again in very good agreement with the results of an *ab initio* calculation.²¹ Both cations show a large increase in the ring angle at the *ipso* carbon atoms (compared with the corresponding diazonium cations) due to the tendency of the now approximately *sp*-hybridised *ipso* carbon to adopt a linear geometry. We can best explain the differences in the electron density on the *ipso* carbon atoms of the phenyl and 1H-3,5-dimethylpyrazol-4-yl cations by considering the formation of these ions from the corresponding hydrocarbons. The geometry changes produced by breaking the C–H σ -bonds indirectly affect the π -electron distributions by changing the energies and bonding capacities of the individual π atomic orbitals. This is equivalent to changing the individual atomic α and β parameters in the Hückel formalism. According to our calculations, generation of $C_6H_5^+$ from C_6H_6 causes the π -electron density associated with C(1) to increase from 1.00 to

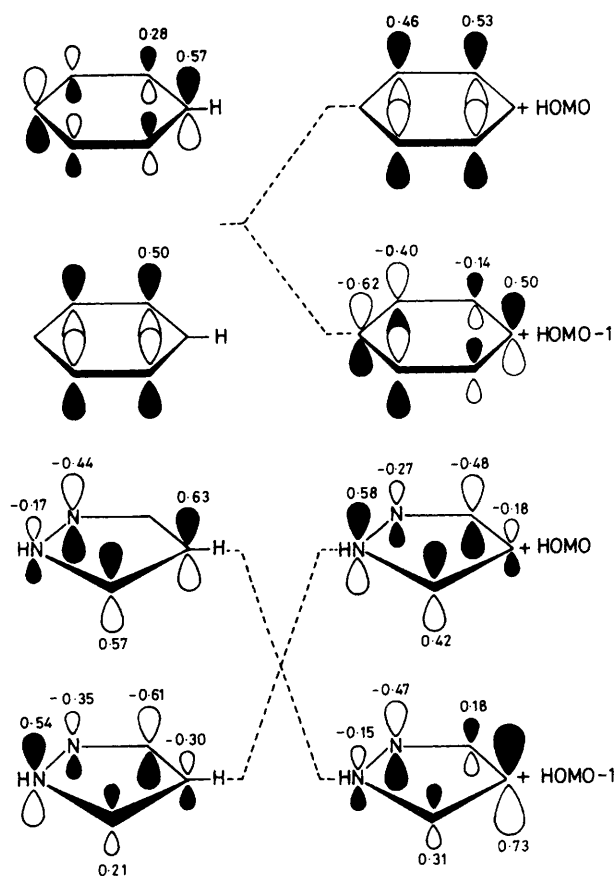


Figure 9. HOMO and HOMO-1 of RH and R^+ with orbital coefficients (electron density in text = $2 \times \text{coeff.}^2$)

1.20. This change in π -electron density is the result of an increase in the contribution of C(1) to the lowest lying (HOMO-3) π -orbital (0.33 in C_6H_6 , 0.68 in $[C_6H_5]^+$) and a decrease in the contribution to the HOMO-1 (0.65 in C_6H_6 , 0.50 in $[C_6H_5]^+$). As C(1) has the most stable atomic orbital in $[C_6H_5]^+$ the above contributions are exactly those that would be expected to result from its decreased α -parameter (Figure 9). The increased involvement of C(1) in the lowest energy π -orbital reduces its ability to donate π -electron density to the N_2 -group since the energy of this π atomic orbital is too low to take effective part in the interaction described by Figure 7.

The same basic effects also occur for the 1H-3,5-dimethylpyrazole-1H-3,5-dimethylpyrazol-4-yl cation pair but with very different results. The low symmetry of the pyrazole ring *vis-à-vis* benzene causes the molecular orbitals to be less conveniently localised on groups of related atoms, but the relationship between the hydrocarbon and cation orbitals and their correspondence to the orbitals of benzene and phenyl cation is clear from Figure 9. The most significant distinction between the two ring systems is that the α -parameters of the nitrogen atoms are much lower than those of the carbon atoms. Thus the lowest lying π -orbital in the pyrazole system (HOMO-4) is predominantly localised on nitrogen and is 6.0 eV lower in energy than the HOMOs compared with 2.5 eV in the benzene-phenyl cation case. Although formation of the cation stabilises the *ipso* carbon [*i.e.* C(4)] π atomic orbital compared with the other carbon atoms, the decrease in energy is here insufficient to produce a significant increase in the involvement of the *ipso* carbon in the lowest lying π -orbital. The calculated increase in π -electron density on C(4) (1.11 in 1H-3,5-dimethylpyrazole, 1.35 in the corresponding 4-cation) is therefore almost entirely

due to its involvement with the higher lying HOMOs, most specifically with the HOMO-1. Thus, unlike the situation in the phenyl cation, the increased π -density on C(4) of the pyrazolyl cation is largely available for C(4)-N₂ bonding. Our calculations therefore demonstrate (in agreement with the evidence from i.r. and ¹³C n.m.r. spectroscopy) that the increased stability of the 1*H*-3,5-dimethylpyrazole-4-diazonium cation (1) compared with the benzenediazonium cation (2) is a result of increased conjugative transfer of electron density from the ring to the diazonium function *via ipso* carbon to N₂ π^* - π bonding. The implication in valence-bond terms is that the diazo resonance from (1*f*) (Figure 3) *does* make a significant contribution to the ground state of the cation, despite the fact that the X-ray results show that this is not reflected in an increased N(7)-N(8) bond length. While some contribution from the resonance form (1*e*) cannot be entirely eliminated it is clearly not necessary to involve its participation in order to explain the stability of cation (1).

The calculated intra-ring bond lengths admit of no simple interpretation in terms of the remaining resonance forms (1*a*—*d*) (Figure 1), nor is this to be expected since the latter are idealised valence bond structures and their relative weighting is uncertain. The most significant discrepancy between theory and experiment concerns the N(1)-N(2) bond which is predicted by our calculations to be short (1.342 Å) and similar in length to the corresponding bond in pyrazole itself (1.342(2) Å)⁷ due to considerable N(1)-N(2) π -bonding in the HOMO-4. Our X-ray crystallographic results, however, yield a long N(1)-N(2) bond distance [1.378(4) Å] and suggest minimal π -contribution to this bond. It may be noted that it is the X-ray structural data rather than the theoretical results which are unexpected since aromatic delocalisation in the pyrazole ring requires some contribution from N(1)-N(2) π -bonded structures [resonance forms (1*c*, *d*), Figure 1] and there is no obvious reason why substitution on any of the carbon atoms should affect this π -bonding since the HOMO-4 is very low in energy. The origin of this discrepancy between theory and experiment is receiving further study.

Experimental

A published procedure was employed to prepare 1*H*-3,5-dimethyl-4-aminopyrazole²³ and other reagents and solvents were commercial samples and used without further purification. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer and ¹H and ¹³C n.m.r. spectra were obtained using a JEOL FX60 spectrometer. Microanalyses were determined by the staff of the Microanalysis Laboratory of University College, Cork.

The MNDO program was used as supplied by the Quantum Chemistry Program Exchange without alteration. All MNDO calculations were run with completely free variation of all geometry parameters (*ca.* 40 parameters).

Preparation of 1*H*-3,5-Dimethylpyrazole-4-diazonium Chloride [1]Cl.—The compound was prepared essentially as described by Morgan and Reilly⁴ but employing pentyl nitrite in the place of ethyl nitrite. The crude product was dissolved in the minimum volume of cold water, treated with activated charcoal, and the solution was filtered through Celite. Slow addition of acetone to the filtrate precipitated the pure product (Found: C, 37.9; H, 4.4; Cl, 22.0; N, 35.4. Calc. for C₅H₇ClN₄ requires C, 37.9; H, 4.45; Cl, 22.35; N, 35.3%; ν (NN) (KBr) 2235 s cm⁻¹; δ_{H} [D₂O; Me₃Si(CH₂)₃SO₃Na reference] 2.70 (s, 3,5-Me₂); δ_{C} [D₂O; Me₃Si(CH₂)₃SO₃Na reference] 157.76 [C(3), C(5)], 56.98 [C(4)], and 13.84 (3,5-Me₂) p.p.m.

Very pale yellow crystals of [1]Cl suitable for X-ray crystallographic study were grown by slow evaporation of a

concentrated solution in aqueous acetone. Weissenberg and precession photographs gave preliminary unit cell dimensions; more accurate values were obtained from a least-squares treatment of the setting angles of twelve independent reflections [with $\theta(\text{Mo-K}\alpha)$ in the range 10–20°] measured on a diffractometer.

Crystal Data for [1]Cl.—C₅H₇ClN₄, *M* = 158.6. Orthorhombic, *a* = 7.964(1), *b* = 6.308(2), *c* = 15.060(3) Å, *U* = 756.6 Å³, *D_c* = 1.39 g cm⁻³, *F*(000) = 328, $\lambda(\text{Mo-K}\alpha)$ = 0.710 69 Å, $\mu(\text{Mo-K}\alpha)$ = 3.81 cm⁻¹, space group *Pn*2₁*a*(*C*_{2v}⁹, No. 33) or *Pnma*(*D*_{2h}¹⁶, No. 62) from systematic absences: *Ok**l* if *k* + *l* = 2*n* + 1, *hk*0, *h* = 2*n* + 1, *Pnma* from analysis.

Three-dimensional data were collected in our usual way²⁴ on a PDP81-controlled Hilger and Watts four-circle diffractometer. The intensity data were corrected for Lorentz, polarisation, and absorption factors. The 831 reflections measured with 1 < θ < 20° yielded 734 unique reflections, of which 539 were considered observed with *I* > 3 σ (*I*).

Structure Solution and Refinement.—The structure was solved and refined in space group *Pnma* using the direct-methods segment of SHELX²⁵ crystallographic system. The cation and chloride counteranion both lie on crystallographic mirror planes. Refinement by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters, proceeded smoothly. Difference maps computed at various stages of the refinement revealed all hydrogen atoms in positions close to those expected. The hydrogens of each methyl group adopt two different orientations about the mirror plane. In subsequent refinement cycles, the hydrogens were positioned geometrically (C–H 1.08 Å) and only their occupancy factors and isotropic temperature factor parameters were included in the refinement process, along with the non-hydrogen atoms. Refinement converged with *R* = 0.0316 and *R_w* = 0.0369. The occupancy parameters (with due allowance for the imposed mirror symmetry made in calculations) for the disordered methyl hydrogens were 0.57(4)/0.43(4) for methyl C(6) and 0.59(4)/0.41(4) for methyl C(9). The hydrogen isotropic thermal parameters (Å²) were 0.079(13), 0.084(12), and 0.066(10) for the N–H, C(6), and C(9) protons respectively. In the final difference map no peak was greater than 0.19 e Å⁻³ and the peaks which were present between 0.15 and 0.19 e Å⁻³ all lay at the centres of the bonds of the five-membered ring and in the position anticipated for the lone-pair of electrons at N(2). In the last cycle of calculations, the shift/e.s.d. ratios were all between 0.000 and 0.004. As a final check, refinement was attempted in space group *Pn*2₁*a* (with the mirror symmetry required by space group *Pnma* removed); there were no significant changes in any molecular parameter, and this was disregarded.* Scattering factors used in the refinement for chlorine, nitrogen, and carbon atoms²⁶ and for hydrogen²⁷ were taken from the literature. Allowance was made for anomalous dispersion of chlorine.²⁸ Listing of observed and calculated structure factors, calculated hydrogen co-ordinates, and thermal parameters have been deposited as supplementary material, No. SUP 56098 (7 pp.).†

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† For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

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