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SCF-PERTURBATIONAL ANALYSIS OF SUBSTITUENT EFFECTS IN THE DEDIAZONIATION OF ARYLDIAZONIUM IONS[†]

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Abstract—A M.O. rationalization of the substituent effects on the rate constants for the dediazoniation of substituted aryldiazonium ions has been performed using SCF-perturbation theory. The total perturbation energies arising from a distortion of the Ar–N bonds reflect the substituent effects on the rate constants. The substituent effects are analysed by means of energy components characterising the role of the unperturbed electron density distribution, its relaxation via mixing of orbitals and the nuclear repulsion energy. The influences of the substituents are separated into σ and π contributions using energy increments for localised orbitals. These energy components of the perturbation energy correlate reasonably with the σ_I and σ_R^+ constants for the inductive and resonance effects, respectively, of the substituents.

Within recent decades the thermal dediazoniation of aryldiazonium ions has been studied extensively. The dissociation of the Ar–N bond is found to occur homolytically or heterolytically depending on the solvent.[1,2] A heterolytic bond fission into aryl cations and molecular nitrogen has been found for the dediazoniation in trifluoroethanol.[3] Indirect evidence for the occurrence of aryl cations has been derived from kinetic studies of the dediazoniation in acidic solutions. These investigations support a S_N1 mechanism, where the breaking of the Ar–N bond is the rate determining step.[4-6] In addition primary[7] and secondary[8] isotope effects have been employed to prove aryl cations in the dediazoniation of aryldiazonium ions. Thus, the decomposition in acidic solutions proceeds heterolytically producing aryl cations and molecular nitrogen.

Another aspect of the dediazoniation reaction in acidic aqueous solution is the dependence of the rate constants k_R on the substituents R of the benzene ring as evaluated by Crossley *et al.*[5]

$$\text{R–}\phi\text{–N}_2 \xrightarrow[0.1\,n\,\text{HCl}]{k_R} \text{R–}\phi\text{–OH} + \text{N}_2.$$

This observation has been reinvestigated by Schulte-Frohlinde and Blume using twenty two *para* and *meta* substituted benzenediazonium ions.[6] Most substituents in *para* position decrease the rate constants compared to benzenediazonium ion independently of the electron donating or accepting character of the substituents. A significant enhancement of the reaction is observed for the *m*-Me, *m*-MeO and *m*-phenyl derivatives.[6] For the discussion of the substituent effects an analysis based on dual substituent constants has been performed.[4] A correlation of the rate constants obtained by Schulte-Frohlinde and Blume with Hammett's σ constants turned out to be unsatisfactory.[6]

Several theoretical investigations deal with the geometry,[9,10] multiplicity,[9-11] spectroscopic properties,[10] and substituent effects[12] in aryl cations which are the final products of the rate determining step of the S_N1 reaction. Vincent and Radom investigated the geometry of the benzenediazonium ion and the potential energy surface of the $N_\alpha N_\beta$-rearrangement by means of the *ab initio* STO-3G method.[13] Moreover, electronic spectra of substituted benzenediazonium ions have been calculated by the PPP-method.[14] Only few attempts with a view to a MO-theoretical rationalisation of the substituent effects in the dediazoniation reaction have been performed. The substituent effects on the rate constants have been studied by Klasinc and Schulte-Frohlinde[15] using the Hückel method. A fair correlation between the rate constants for the *para* derivatives and the Ar–N bond order is achieved.[15] Recently, Dill *et al.* argued that a correlation between the substituent effects on the rate constants and the stability of the corresponding aryl cations implies that the stabilisation of the diazonium ions is unaffected by the properties of the substituents.[16] However, this implication is not valid, since a similar pattern for the stabilisation of aryl cations and the diazonium ions is evaluated.[16]

In the following sections an SCF-perturbational analysis of the substituent effects in the dediazoniation reaction based on the data of Schulte-Frohlinde and Blume[6] is attempted. Their kinetic data are used since for the kinetic measurements the diazonium salts were isolated and the Arrhenius plots include at least three temperatures.[6] Our primary intention is to explain why electron donating and accepting substituents in *para* position decrease the rate constants. Moreover, the influence of the substituents transferred via σ and π electrons is discussed.

Intramolecular SCF-perturbation theory

General assumptions and perturbation energies. The kinetic measurements on the dediazoniation of substituted benzenediazonium ions in acidic aqueous solutions support a S_N1 mechanism, where the rate determining step is a heterolytic decomposition into aryl cations and molecular nitrogen.[6] Consequently, as a

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[†] Dedicated to Prof. O. E. POLANSKY on the occasion of his 60th birthday.

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model for the reaction coordinate we employ the CNDO/2 potential energy curve for the elongation of the Ar–N bond. For this bond breaking process leading to two closed shell molecules a one determinantal wave function is suitable to describe the heterolytic bond fission.

The analysis is based on energies E^P arising from an elongation of the Ar–N equilibrium distance by 0.1 A. The primary assumption of the applied model is, that differences in the activation energies of various derivatives are reflected by differences in the energies E^P. Experimental support for the substituent effects on the Ar–N bond is a significant dependence of the Ar–N vibrational frequencies on the electronic properties of substituents in *para* position.[17]

The energy increase E^P is calculated using intramolecular SCF-perturbation theory up to third order:[18]

$$E^P = E^1 + E^2 + E^3. \tag{1}$$

The main advantage of this procedure is to break up the total E^P into energy components which facilitate the analysis of the substituent effects in the dediazoniation reaction. Only a brief summary of the SCF-perturbation theory is given here; for a more comprehensive account of the method the reader is referred to Ref. 18. The first order energy correction E^1 can be separated into different components:

$$E^1 = E^1_{res} + E^1_{ex} + E^1_{el} + E^1_{ND}. \tag{2}$$

Generally, E^1 contains energy contributions arising from the distortion of the molecular geometry in the charge distribution calculated for the equilibrium nuclear arrangement. The first term of eqn (2), E^1_{res}, depends on the corrections of the CNDO/2 resonance integrals. Consequently, E^1_{res} is related to the capability of the equilibrium charge distribution to prevent an elongation of the Ar–N bond. The contribution E^1_{ex} arises from a change of the exchange operator, whereas E^1_{el} is due to the electrostatic interaction of the net charges of atoms. The last term E^1_{ND} contains changes in the nuclear repulsion energy and is referred to as nuclear distortion term. The second order energy E^2 is separated into:[18]

$$E^2 = E^2_{res} + E^2_{ex} + E^2_{pol}. \tag{3}$$

These energy contributions arise from the relaxation of the equilibrium charge distribution to the elongated Ar–N bond; they are energy components which diminish the total energy E^P. The third order correction is found to be small compared to E^1 and E^2. Consequently, the analysis of the substituent effects is restricted to a discussion of E^1 and E^2.

Energy increments for localised orbitals. For a rationalisation of the substituent effects we are interested in examining how the substituents influence the strengths of the breaking Ar–N bonds of the diazonium ions. Therefore, a partitioning into energy components referring to definite bonds is desirable. Such a resolution is facilitated by a decomposition of E^1_{res} into energy increments E^1_{ii} for the localised orbital $\lambda_i{}^{\circ}$ derived for the equilibrium geometry:

$$E^1_{res} = 2\sum_i^{occ} \lambda_i{}^{\circ t} H^1 \lambda_i{}^{\circ} = \sum_i^{occ} E^1_{ii}. \tag{4}$$

H^1 contains the first order changes of the CNDO/2 resonance integrals arising from the elongation of the Ar–N bonds. The quantities E^1_{ii} measure the capability of the charge distribution referring to the localised orbital $\lambda_i{}^{\circ}$ to prevent the elongation of the Ar–N bond. The second order contribution E^2_{res} is decomposed into energy increments E^2_{ij}:

$$E^2_{res} = \sum_i^{occ} \sum_j^{unocc} l^1_{ij}(\lambda_i{}^{\circ t} H^1 \lambda_j{}^{\circ} + \lambda_j{}^{\circ t} H^1 \lambda_i{}^{\circ}) = \sum_i^{occ} \sum_j^{unocc} E^2_{ij}. \tag{5}$$

The l^1_{ij} is the first order coefficient for a linear combination of the localised occupied $\lambda_i{}^{\circ}$ and the unoccupied orbital $\lambda_j{}^{\circ}$; the linear combinations adjust the equilibrium charge distribution to the elongated Ar–N bond and result in a negative E^2_{res} value. The sum over E^2_{ij} for all j represents an energy decrease arising from the relaxation of the occupied orbital $\lambda_i{}^{\circ}$. The resolution of E^2_{res} will be used to determine an orbital interaction scheme for the breaking of the Ar–N bond in terms of localised orbitals. For all pairs the contributions E^2_{ij} are calculated and the important pairs are characterised by large E^2_{ij} values. In this way a relationship between an orbital interaction scheme and the form of the CNDO/2 potential curve is established.

For the analysis of substituent effects occupied and unoccupied CNDO/2 orbitals were localised by the method of Edmiston and Ruedenberg.[19] From this localization procedure, implemented in the CNDO/2 scheme, pure σ and π localised orbitals are derived and were used to discuss the σ and π electronic effects of the substituents.

Geometries and computational details

For the study of the substituent effects the benzene ring was assumed to transfer the influence of the substituents to the breaking Ar–N bond. Therefore, a standard geometry for the benzene ring in all diazonium ions was used with r(CC) = 1.38 A and r(CH) = 1.11 A. Moreover, all angles were fixed at 120°. In contrast to the ring geometry, the bond lengths and the bond angles of the substituents and the Ar–N bond lengths were optimised. Preliminary calculations indicated that the N–N bond length is almost independent of the substitution of the ring. Consequently, the value of 1.1473 A found for the benzenediazonium ion was used in all substituted derivatives. This N–N bond length is close to the value of 1.143 A derived by Vincent and Radom[13] using the STO-3G *ab initio* procedure.

For the geometry optimisation an iterative Newton type method[20] with numerical evaluation of the first and second derivatives was used.[21] The numerical derivatives were calculated by the difference formulas given by Payne.[22] The CNDO/2 iterations were found in some cases to be divergent. Convergence was achieved in all cases by the level shifting method of Saunders and Hillier.[23] The geometry iterations were continued until the norm of the energy gradient with respect to the parameters was less than 10^{-3}. In all calculations the last corrections to the geometrical parameters were of the order of 10^{-4} to 10^{-5} A or radians.

The parameters selected and the results of the geometry optimisations are recorded in Table 1. Generally, the C–X bond lengths are found to be smaller than the values in substituted benzenes. The other parameters of the substituents are in reasonable

Table 1. Results of the geometry optimisation of the substituents and the ϕ–N distance in Y_nX–ϕ–N_2^+. Values in brackets were not optimised

-XYn	r(ϕ-N)	r(ϕ-X)	r(X-Y)	∡(ϕXY)
H	1.3990	-	-	-
p-CH_3	1.3971	1.4651	(1.11)	(109.47)
p-F	1.3979	1.3430	-	-
p-OCH_3	1.3963	1.3649	1.3764	115.22
p-$N(CH_3)_2$	1.3933	1.3899	1.4173	126.51
p-NO_2	1.3999	1.4275	1.2244	118.38
m-CH_3	1.3992	1.4681	(1.11)	(109.47)
m-F	1.3996	1.3457	-	-
m-OCH_3	1.3993	1.3699	1.3754	114.97
m-NO_2	1.4000	1.4273	1.2243	118.36

agreement with the data of the literature.[24] The bond distance between the aromatic ring and the diazonium group in the unsubstituted compound is shorter than the value derived from STO-3G calculations by Vincent and Radom.[13] However, our value of 1.3990 A is close to 1.385 A derived from the X-ray structure of benzenediazonium tetrafluoroborate.[25] To ensure that the bond lengths and bond angles recorded in Table 1 are unique, optimisations have been performed using different starting geometries. In all cases the results of Table 1 were reproduced. The numerical accuracy of the geometrical parameters guarantees the perturbation energies E^P to be reliable within 0.01 kcal/mol.

Localised orbitals and the dediazoniation of benzenediazonium ion

In this section the partitioning of E^1_{rel} and E^2_{rel} into energy parts for localised orbitals is used to determine important orbitals and to derive an orbital interaction scheme for the dediazoniation of the benzenediazonium ion. In Table 2 the perturbation energy E^P for benzenediazonium ion and the resolution into the components of eqns (2) and (3) are recorded in the third line. A large value of 72.5 kcal/mol is calculated for E^1_{rel} being the largest positive energy component compared to all other perturbational terms (Table 2). This finding illustrates the capability of the equilibrium charge distribution to inhibit the elongation of the Ar–N bond. The partitioning of the total E^1_{rel} into localised energy parts (eqn 4) indicates that 96% of E^1_{rel} is determined by the three orbitals shown in Fig. 1. Almost 60 kcal/mol arise from an orbital localised in the Ar–N σ bond region. A smaller value of 8.4 kcal/mol is calculated for the four centre π orbital localised in the ring and to a smaller extent on the leaving N_2 group. The π orbital localised in the diazonium group and partially in the benzene ring contributes with 1.5 kcal/mol to the total E^1_{rel}. According to this partitioning a distortion of the Ar–N bond is inhibited more by the σ than by the π molecular orbitals. This finding characterises the Ar–N bond primarily as a σ bond as represented by the Ar–N single bond of the mesomeric structure for benzenediazonium ion.[26]

The interactions of occupied and unoccupied orbitals lead to a negative E^2_{rel} contribution of −3.6 kcal/mol (Table 2). The resolution of E^2_{rel} into energy parts for pairwise orbital interactions is performed using eqn (5); the significant pairs and their relaxational contributions E^2_{ij} are recorded in Fig. 2. The σ and π orbitals localised in the region of the breaking Ar–N bond relax via an interaction with unoccupied orbitals possessing a nodal surface which promotes the Ar–N bond breaking process.

In contrast to the partitioning of E^1_{rel} the ring orbitals adjacent to the breaking Ar–N bond contribute significantly to E^2_{rel}. These interactions with unoccupied orbitals (Fig. 2) weaken the σ bond since the linear combination results in a bent σ orbital. The interaction indicates a flexibility of the ring geometry near the Ar–N bond breaking region and accords with a pronounced difference in the geometries of the benzene rings of benzene diazonium ion[13] and the phenyl cation.[13] Thus, a change of the molecular geometry determined for a final product is already indicated by orbital interactions at the beginning of the reaction coordinate.

Analysis of the substituent effects

For the discussion of substituent effects representative derivatives with electron donating and electron accepting substituents, namely the *p,m*-Me, *p,m*-MeO, *p,m*-F, *p,m*-NO_2 and *p*-$N(Me_2)$ diazonium ions were investigated. After establishing the correlation between the total per-

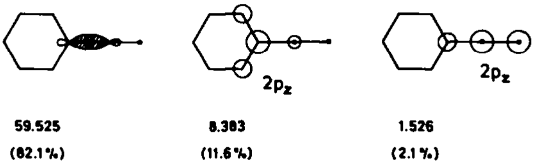

Fig. 1. The form of localised orbitals determining the total E^1_{rel} in the dediazoniation of benzenediazonium ion. All values are recorded in kcal/mol; the percentage values with respect to the total E^1_{rel} are also given.

Table 2. The total perturbation energies E^P and their decomposition into energy components. All energy quantities are given in kcal/mol

R	E^1_{res}	E^1_{ex}	E^1_{el}	E^1_{ND}	E^2_{res}	E^2_{ex}	E^2_{pol}	E^3	E^P	E_{var}
m-me	72.3939	6.1066	-0.7911	-63.5130	-3.6603	-0.3583	-0.0208	-0.0794	10.0776	10.0851
m-meO	72.3917	6.0987	-0.8272	-63.4733	-3.6403	-0.3547	-0.0206	-0.0779	10.0964	10.1032
H	72.4788	6.1231	-0.8332	-63.5692	-3.6341	-0.3550	-0.0198	-0.0781	10.1125	10.1198
p-me	72.8841	6.1938	-0.7401	-64.0318	-3.6879	-0.3700	-0.0226	-0.0830	10.1425	10.1501
m-F	72.4325	6.1060	-0.9255	-63.4144	-3.5895	-0.3456	-0.0185	-0.0751	10.1699	10.1762
p-NO_2	72.4109	6.1124	-0.9998	-63.3321	-3.5748	-0.3414	-0.0175	-0.0731	10.1846	10.1910
p-F	72.8072	6.1848	-0.8529	-63.8475	-3.6264	-0.3571	-0.0201	-0.0786	10.2094	10.2171
p-N$(me)_2$	73.7669	6.3546	-0.6238	-64.9980	-3.7703	-0.3960	-0.0254	-0.0902	10.2178	10.2268
p-meO	73.1058	6.2360	-0.7351	-64.2517	-3.6882	-0.3728	-0.0229	-0.0835	10.1876	10.1955
m-NO_2	72.3969	6.1153	-1.0025	-63.3168	-3.5636	-0.3409	-0.0164	-0.0738	10.1982	10.2052

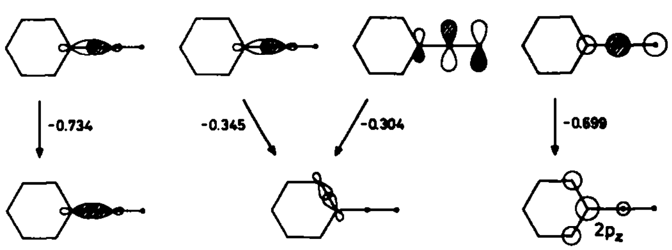

Fig. 2. Important pairs of interacting localised orbitals predominating the total E^2_{res} in the dediazoniation of benzenediazonium ion. All E^2_{ij} quantities are given in kcal/mol.

turbation energies and the experimental rate constants an analysis is performed to determine how the substituents affect the breaking of the Ar–N bonds via changes of the total density distributions, its relaxation, and by influencing the nuclear repulsion. In addition the substituent effects transferred via σ and π electrons are discussed by means of energy increments for localised orbitals.

Total perturbation energies and the rate constants. The total E^P values for all derivatives considered are recorded in Table 2. All E^P are close to the E_{var} values calculated as the difference between the CNDO/2 total energies for the distorted and undistorted geometries. This agreement between E^P and E_{var} illustrates the good convergence of the perturbation series.

In Fig. 3 the perturbation energies are compared with the rate constants obtained by Schulte-Frohlinde and Blume.[6] Since we are interested in the substituent effects, ΔE^P values are considered which are differences between the E^P for the derivatives and E^P for the benzene-diazonium ion; k_H designates the rate constant for the unsubstituted compound. The plot of ΔE^P against log (k_R/k_H) indicates a reasonable linear correlation for electron donating and electron accepting substituents in *para* and *meta* positions. The ΔE^P values reproduce correctly the rate enhancing influence of the Me and MeO groups when they are in the *meta* position of the benzenediazonium ion. The ordering of the rate decreasing properties p-Me $<$ m-F $<$ p-NO_2 $<$ p-$N(Me_2)$ of the electron donating and electron withdrawing substituents is also satisfactory reproduced. Exceptions are the p-MeO and p-F derivatives deviating from the linear correlation. An explanation for this behaviour is difficult to arrive at within the crude assumptions of the perturbational model. However, the experimental frequency factors for the p-MeO and p-F derivatives support a side reaction or a different reaction mechanism compared to the other derivatives as pointed out by Schulte-Frohlinde and Blume.[6]

Influence of the substituents on the resonance contributions. In this section the influence of the substituents on the total electron density distribution and its relaxation is investigated by means of the energy components E^1_{res} and E^2_{res}. In this way a relationship between the substituent effects on the electron density and the reaction coordinate near the equilibrium geometry is obtained.

For all derivatives considered, a positive E^1_{res} value is calculated (Table 2) which shows that the equilibrium electron density distribution hinders an elongation of the Ar–N bond. The influence of the substituents is illustrated in Fig. 4, where the differences ΔE^1_{res} between E^1_{res} for the substituted derivatives and benzenediazonium ion are recorded. Since all E^1_{res} are positive quantities, a positive ΔE^1_{res} indicates a larger E^1_{res} for the substituted derivative compared to benzenediazonium ion. Inspection of Fig. 4 shows that for the *para* substituents p-Me, p-MeO, p-F and p-$N(Me)_2$ positive ΔE^1_{res} values are calculated. This finding illustrates the property of these substituents to donate electron density which inhibits the

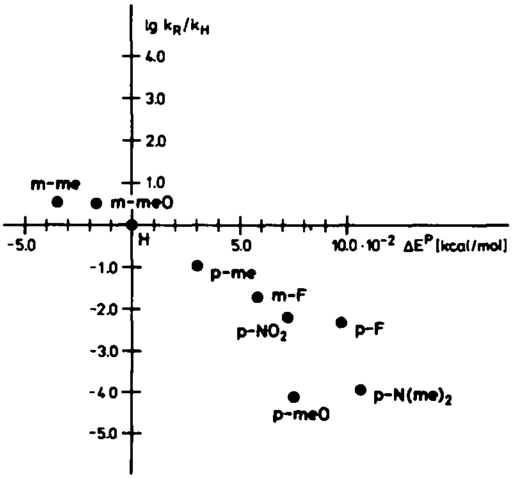

Fig. 3. Correlation between the perturbation energies and the rate constants. The ΔE^P represents the difference between the perturbation energies E^P for the substituted derivative and the benzenediazonium ion; k_H is the rate constant for the unsubstituted compound. The ΔE^P values are recorded in kcal/mol.

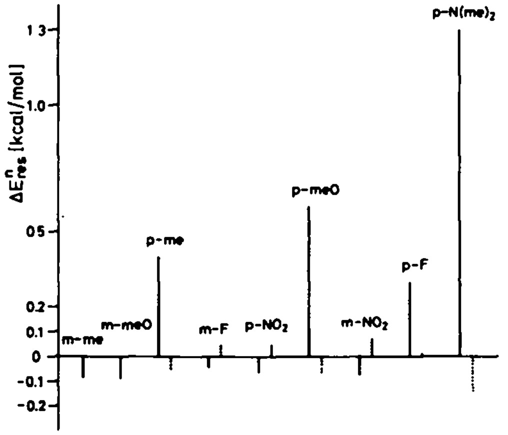

Fig. 4. Comparison of the substituent effects on E^1_{res} and E^2_{res}. A positive ΔE^1_{res} (——) indicates a larger positive E^1_{res} compared to the benzenediazonium ion. A negative ΔE^2_{res} (·········) corresponds to a larger negative E^2_{res} compared to benzenediazonium ion. All values are given in kcal/mol.

elongation of the Ar–N bond more effectively than in the benzenediazonium ion. For the nitro group in *para* position and all *meta* derivatives negative ΔE^1_{res} quantities are calculated corresponding to a decrease of electron density which facilitates slightly the Ar–N bond distortion.

The pattern of substituent effects on E^1_{res} derived for the *para* derivatives accords remarkably well with the substituent effects on π charge densities in *para* substituted benzenes.[27] The substituents Me, F, MeO and NH_2 increase the electron density in the ring, whereas the NO_2 group diminishes the π electron density.[27] This analogy supports the idea of similar mechanisms for the substituent effects in the derivatives of benzene and benzenediazonium ion.

The negative signs of all E^2_{res} (Table 2) illustrate that the relaxation of the electron density facilitates the Ar–N bond distortion. The dependence of E^2_{res} on the substituents is discussed by means of the ΔE^2_{res} values represented in Fig. 4. Negative ΔE^2_{res} are calculated for the *p*-Me, *p*-MeO and *p*-N(Me$_2$) derivatives whereas a positive ΔE^2_{res} is evaluated for the *p*-nitro compound. The substituent effects on E^1_{res} and E^2_{res} establish a correspondence between the electronic charge distribution and its relaxation. Substituents which increase the electron density induce also a larger energy gain due to the relaxation of the electron density, whereas substituents with electron accepting properties diminish the energy gain. However, this correspondence is violated for the *m*-Me, *m*-MeO and *p*-F compounds.

Substituent effects via σ and π molecular orbitals. A generally accepted concept for the analysis of substituent effects is the partitioning into influences transferred via the σ and π electronic system. In the case of substituted benzenes these effects have been investigated by a σ and π separation of the total electron densities.[27,28] Moreover, a correlation of the σ and π electron densities with empirical substituent contants for the inductive or resonance effect has been established.[28,29]

In this section the energy increments of E^1_{res} and E^2_{res} for localised orbitals are employed to investigate the inductive and resonance effects of the *para* substituents. This discussion is based on the proposition that inductive effects are predominantly transferred via σ orbitals, whereas resonance effects operate via π orbitals. As a measure for the inductive effect on the Ar–N bond we define a quantity I which is the sum of the components of E^1_{res} and E^2_{res} pertaining to the Ar–N σ bond orbital. Similarly, the quantity R refers to the resonance effect and contains components of E^1_{res} and E^2_{res} belonging to π orbitals corresponding to those depicted in Fig. 1. The conceptual advantage of the quantities I and R compared to the electron densities at the atoms is that the former are energy terms referring to the σ and π electron densities localised in the breaking Ar–N bond.

In Fig. 5 the differences ΔI between the I values for the substituted *para* derivatives and benzenediazonium ion are correlated with the σ_I constants[30] for the inductive effect of the substituents. This correlation holds in spite of σ_I being determined by means of kinetic and thermodynamic data, whereas the I values are derived within a quantum mechanical model. The nitro group having the largest positive σ_I constant induces a significant increase of the I values (Fig. 5). This finding implies an increase of the σ electron density in the Ar–N bond of the *p*-NO$_2$ derivative compared to benzenediazonium ion. This result contrasts to the overall σ electron withdrawing properties of the NO_2 group indicated by the positive σ_I. The capability of increasing the σ electron density in the Ar–N bond decreases in the sequence *p*-NO$_2$ > *p*-F > *p*-MeO > *p*-N(Me$_2$), whereas the Me group in *para* position turns out to be weakly electron withdrawing.

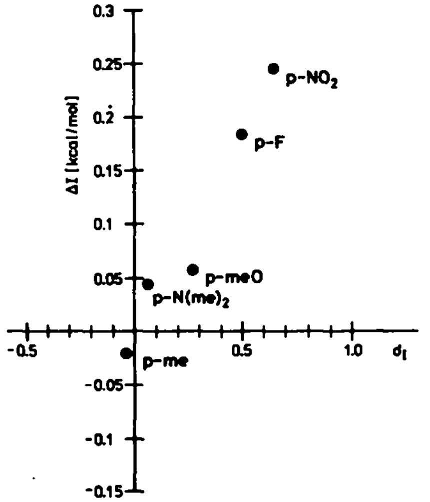

Fig. 5. Correlation of the ΔI values with Taft's σ_I constants. The quantities ΔI measure the substituent effects on the Ar–N bond region transferred via the σ-electrons. The ΔI values are given in kcal/mol.

The substituent effects transferred via the π electron system are analysed by investigating the ΔR values. In Fig. 6 the ΔR quantities are correlated with the $\sigma_R{}^+$ constants[30] associated with the resonance effects of the substituents. This scale of constants is more appropriate than the σ_R values,[30] since the substituents are attached to a positively charged system. Figure 6 indicates a correlation between the ΔR quantities and the $\sigma_R{}^+$ constants which is acceptable for all *para* substituents except for the Me group. Substituents with a large π electron donating power increase the R value compared

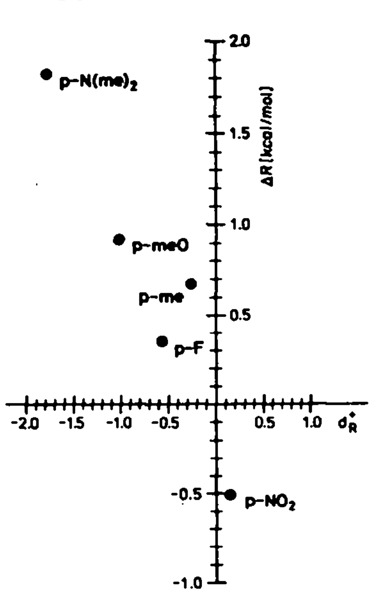

Fig. 6. Correlation of ΔR with Taft's $\sigma_R{}^+$ constants. The quantites ΔR measure the substituent effects on the Ar–N bond region transferred via π-electrons. The ΔR values are given in kcal/mol.

to the benzenediazonium ion; the largest increase is found for the p-N(Me$_2$) substituent. The magnitudes of the ΔI and ΔR values (Figs. 5 and 6) designate the π electronic effects to be more pronounced than the σ electronic effects. Thus, the *para* substituents operate predominantly via their π electron donating or withdrawing properties.

The strength of the σ and π electronic effects varies in a reversed order except for the Me group as established by the ΔI and ΔR values. The σ electronic effects increase in the sequence N(Me$_2$) < MeO < F < NO$_2$, whereas for the π electronic effects the order NO$_2$ < F < MeO < N(Me$_2$) is observed. This result accords qualitatively with the inverse changes of the σ and π charge densities in the *para* position of substituted benzenes.[31] This inverse behaviour is a further support for the similarity between the substituent effects in the derivatives of benzene and benzenediazonium ion.

In the *meta* substituted derivatives the effects transferred via the π electron system are smaller compared to the *para* derivatives. However, the σ electronic effects are almost of the same magnitude. This result agrees with the observation that inductive effects for substituents in *meta* and *para* position are similar,[30] whereas the resonance effect is diminished compared to substituents in *para* position.[30] The σ electronic influence of the substituents is transferred into the Ar–N bond and the adjacent ring σ bonds. Therefore, the substituent effects in the *meta* derivatives are not as localised as for the *para* substituted compounds.

Substituent effects on the nuclear distortion term. The nuclear distortion terms E^{1}_{ND} recorded in Table 2 are the largest negative energy components of the total perturbation energy E^{P}. A numerical separation of E^{1}_{ND} into contributions referring to the change in the nuclear repulsion energy and the correction term (eqn 17 of Ref. 18) shows that E^{1}_{ND} is dominated by changes in the nuclear repulsion energy. Consequently, the negative signs of E^{1}_{ND} indicate that the Ar–N bond fission is enhanced by changes in the nuclear repulsion energies.

The analysis of the substituent effects on the nuclear distortion term shows that the influence is primarily localised in the region of the breaking Ar–N bond. The observed dependence of E^{1}_{ND} on the electronic properties of the substituents is difficult to specify, since the diatomic increments are not explicit functions of the electron density. However, the diatomic increments contain the minimised Ar–N distances which are implicit functions of the electronic properties of the substituents.

In the following discussion a dependence of E^{1}_{ND} on the π electronic charge localised in the Ar–N bond is assumed. Such a dependence is suggested by the pronounced substituent effects on the π charge density of the Ar–N bond. As a measure for this π electron density we employ the overlap population[32] for the Ar–N π bond at the equilibrium distance. However, the overlap population is not rigorously defined in the CNDO/2 procedure, since the zero differential overlap approximation is applied.[33] Nevertheless, a numerical correlation between CNDO/2 and *ab initio* overlap populations has been established.[33] In addition, the total overlap population in a molecule seems to be a sensitive quantity for changes of the molecular geometry.[34] These observations designate the CNDO/2 overlap population to be a measure for the charge density in the Ar–N bond.

In Fig. 7 the ΔE^{1}_{ND} values for the various substituents are correlated with the π overlap populations for the Ar–N bonds. The observed linear correlation holds for all *para* and *meta* derivatives considered. Referring to this linear dependence, the effect of the substituents on the nuclear distortion term is rationalised as follows. Substituents donating π electrons into the Ar–N bond region decrease the CNDO/2 Ar–N bond distance compared to the benzenediazonium ion (Table 1). This effect is reflected by a more negative nuclear distortion term with respect to the unsubstituted compound; this substituent influence increases in the sequence p-F < p-Me < p-MeO < p-N(Me$_2$). If the substituents withdraw π electron density from the Ar–N bond, the CNDO/2 Ar–N bond distance is increased. Consequently, the nuclear distortion term is less negative compared to the benzenediazonium ion. This effect is observed in the p-nitro derivative and all *meta* substituted compounds.

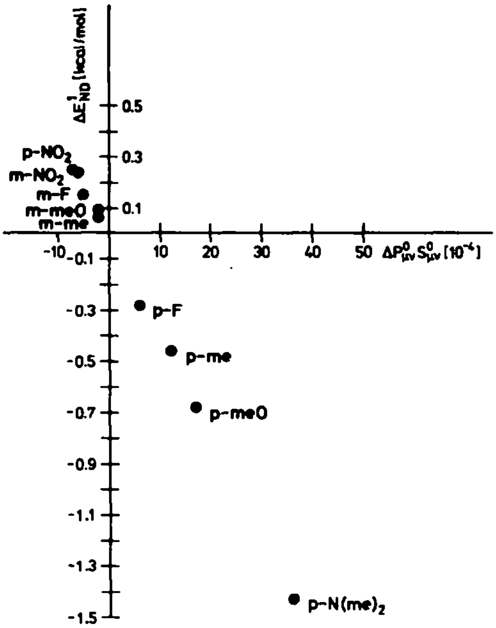

Fig. 7. Correlation between ΔE^{1}_{ND} and $\Delta P^{0}_{\mu\nu}S^{0}_{\mu\nu}$. The $\Delta P^{0}_{\mu\nu}S^{0}_{\mu\nu}$ values represent the difference between the overlap populations of the Ar–N π-bond for the benzenediazonium ion and the corresponding substituted derivatives.

DISCUSSION

In the previous sections the substituent effects on E^{1}_{res}, E^{2}_{res} and E^{1}_{ND} were investigated. However, within the scope of the perturbational model an explanation for the substituent effects on the rate constants has to be based on the total E^{P}. Such a discussion is facilitated by grouping all perturbational terms up to second order into E^{P}_{bond} and E^{P}_{coul},

$$E^{P}_{bond} = E^{1}_{res} + E^{1}_{ex} + E^{2}_{res} + E^{2}_{ex} \qquad (6)$$

$$E^{P}_{coul} = E^{1}_{el} + E^{1}_{ND} + E^{2}_{pol}. \qquad (7)$$

The analytic form[18] of the different energy components in eqns (6) and (7) shows that E^{P}_{bond} contains energy increments for bonds, whereas E^{P}_{coul} refers to changes in the electrostatic interaction of the atoms of the diazonium ions.

In Table 3 all quantities recorded are differences between the values for the *para* substituted derivatives and the unsubstituted compound. Inspection of Table 3 in-

Table 3. Partitioning of the perturbation energy for the para derivatives into bonding and coulombic components. The quantities recorded are differences between the values for the substituted and unsubstituted compounds. All energy components are given in kcal/mol

	ΔE^1_{res}	ΔE^1_{ex}	ΔE^2_{res}	ΔE^2_{ex}	ΔE^P_{bond}	ΔE^1_{el}	ΔE^1_{ND}	ΔE^2_{pol}	ΔE^P_{coul}	$\Delta(E^P_{bond} + E^P_{coul})$
p-me	0.4053	0.0707	-0.0538	-0.0150	0.4072	0.0931	-0.4626	-0.0028	-0.3723	0.0349
p-NO_2	-0.0679	-0.0107	0.0593	0.0136	-0.0057	-0.1666	0.2371	0.0023	0.0728	0.0671
p-F	0.3284	0.0617	0.0077	-0.0021	0.3957	-0.0197	-0.2783	-0.0003	-0.2983	0.0974
p-$N(me)_2$	1.2881	0.2315	-0.1362	-0.0410	1.3424	0.2094	-1.4288	-0.0056	-1.2250	0.1174
p-meO	0.6270	0.1129	-0.0541	-0.0178	0.6680	0.0981	-0.6825	-0.0031	-0.5875	0.0 805

Table 4. Partitioning of the perturbation energy for the meta derivatives into bonding and coulombic components. The quantities recorded are differences between the values for substituted and unsubstituted compounds. All energy components are given in kcal/mol.

	ΔE^1_{res}	ΔE^1_{ex}	ΔE^2_{res}	ΔE^2_{ex}	ΔE^P_{bond}	ΔE^1_{el}	ΔE^1_{ND}	ΔE^2_{pol}	ΔE^P_{coul}	$\Delta(E^P_{bond}+E^P_{coul})$
m-me	-0.0849	-0.0165	-0.0262	-0.0033	-0.1309	0.0421	0.0562	-0.0010	0.0973	-0.0336
m-meO	-0.0871	-0.0244	-0.0062	0.0003	-0.1174	0.0060	0.0959	-0.0008	0.1011	-0.0163
m-F	-0.0463	-0.0171	0.0446	0.0094	-0.0094	-0.0923	0.1548	0.0013	0.0638	0.0544
m-NO_2	-0.0819	-0.0078	0.0705	0.0141	-0.0051	-0.1693	0.2524	0.0034	0.0865	0.0814

dicates that the $\Delta(E^{p}_{bond} + E^{p}_{coul})$ values for the perturbation energies up to second order are positive and their increase correlates with the rate constants for the *para* derivatives. For the moment the *p*-NO_2 compound is omitted but is referred to later. The sign of $\Delta(E^{p}_{bond} + E^{p}_{coul})$ is determined by ΔE^{p}_{bond} which is closely approximated by the ΔE^{1}_{res} quantities. The positive ΔE^{1}_{res} values are induced by a transfer of electron density into the Ar–N bond. Therefore, we conclude that the decrease of the rate constants induced by the substituents *p*-Me, *p*-MeO, *p*-F and *p*-N(Me_2) arises from a strenghening of the Ar–N bond. The increase of bond strength is manifested by a larger electron density in the Ar–N bond. This rationalisation agrees qualitatively with the mesomeric structure proposed for the *para* derivatives with electron donating substituents, where the increase of electron density is symbolised by an Ar–N double bond.[35]

A different pattern emerges for the decrease of the rate constant as observed for the *p*-NO_2 derivative. Inspection of Table 3 suggests the positive sign of $\Delta(E^{p}_{bond} + E^{p}_{coul})$ to be determined by ΔE^{p}_{coul}. In contrast to the other *para* derivatives, ΔE^{p}_{bond} is found to be significantly smaller as indicated by the ΔE^{1}_{res} value. This negligible ΔE^{1}_{res} is easily interpreted using the analysis performed in the earlier section. Inspection of Figs. 5 and 6 designates *p*-NO_2 to be the only substituent where the π electron withdrawing properties predominate over the σ electron donating capabilities with respect to the Ar–N bond region. In this way the NO_2 group induces a decrease of electron density in the Ar–N bond compared to the unsubstituted compound. This reduction of electron density is reflected by the small negative ΔE^{1}_{res} value and by a positive ΔE^{2}_{res} almost cancelling ΔE^{1}_{res}. Moreover, the decrease of electron density corresponds to a lengthening of the Ar–N bond (Table 1) and a positive ΔE^{1}_{ND} determining the sign of $\Delta(E^{p}_{bond} + E^{p}_{coul})$. Therefore, the smaller rate constant for the *para*-NO_2 derivative arises from the less negative nuclear repulsion component of the perturbation energy induced by a decrease of electron density in the Ar–N bond region.

In Table 4 the ΔE^{p}_{bond} and ΔE^{p}_{coul} values for the *meta* derivatives and their partitioning into components are recorded. In contrast to the *para* derivatives energy increments for the localised orbitals reveal that the substituents do not operate predominantly in the Ar–N bond breaking region. Thus, a simple MO rationalisation as performed for the *para* derivatives seems to be difficult to arrive at. Nevertheless, Table 4 indicates that the increase of the rate constants for the *m*-Me and *m*-MeO derivatives is determined by ΔE^{p}_{bond}. These bonding contributions imply a rearrangement of the electron density within the bonds facilitating the decomposition compared to benzenediazonium ion. In contrast to *m*-Me and *m*-MeO, the decrease of the rate constants for the *m*-F derivative seems to be controlled by changes in the nuclear repulsion component.

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