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A MOLECULAR ORBITAL THEORY APPROACH TO THE WALLACH REARRANGEMENT[1]

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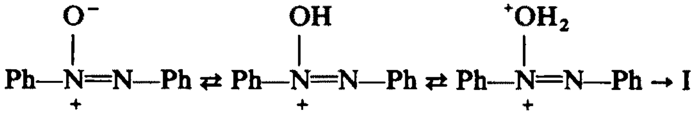
Abstract—Hückel MO theory is applied to the dicationic species proposed as an intermediate in the Wallach rearrangement of azoxybenzene. It is first shown that two distinct structures must be considered for this intermediate, a bent (sp^2 hybridized nitrogens) and a linear (sp nitrogens). Application of the simple HMO method yields electron densities which are in accord with product orientation but does not distinguish between the two structures. Calculations of π bonding energies per electron and of delocalization energies suggest that the bent structure with the positive charges distributed over the phenyls is the energetically favoured one.

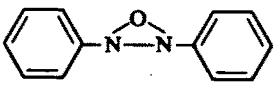
In contrast, application of an extended HMO method shows that of the two structures for the dicationic intermediate the linear is of lower energy. The disagreement with the result of the simple HMO method is discussed. Several reactivity criteria with respect to the dicationic intermediate are examined by the extended HMO method: electron densities, frontier electron orbitals, and the relative energies of hydrated reaction intermediates.

A RECENT kinetic study,[2] of the Wallach rearrangement, the conversion of azoxybenzene into *p*-hydroxyazobenzene in strongly acidic media, was interpreted on the basis of a delocalized dicationic intermediate I. The experimental observation of a two proton process and the kinetic analysis were in accord with either[3] two equilibrium protonations of azoxybenzene followed by rate-determining loss of H_2O (Eq. 1) or[2] with a single equilibrium protonation followed by a rate determining proton-transfer with simultaneous loss of H_2O and formation of I. Reaction of I with water of the medium at aromatic carbon followed by proton loss leads to product.



$$\mathrm{Ph{-}\underset{+}{\overset{\overset{\textstyle O^-}{|}}{N}}{=}N{-}Ph \rightleftarrows Ph{-}\underset{+}{\overset{\overset{\textstyle OH}{|}}{N}}{=}N{-}Ph \rightleftarrows Ph{-}\underset{+}{\overset{\overset{\textstyle {}^+OH_2}{|}}{N}}{=}N{-}Ph \rightarrow I} \qquad (1)$$

I



II

The above mechanism involving the dicationic intermediate* was proposed as an alternative to one by Shemyakin *et al.*[7] These workers had advanced the N,N-oxide intermediate (II) in order to account for the observed equalization of the nitrogen label in the reaction product when azoxybenzene labelled on one nitrogen with

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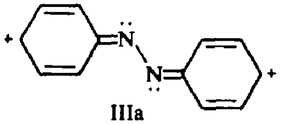
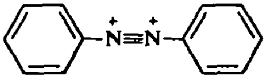
* See also Refs 4–6.

N^{15} was allowed to rearrange in sulfuric acid. Since a previous discussion[2] had pointed out some of the difficulties adherent to the N,N-oxide intermediate mechanism (e.g. in accounting for the presence and the form of acid catalysis) it was decided to subject to detailed scrutiny the hypothesis of the dicationic intermediate. The MO theory approach was chosen for this purpose. Hückel calculations for other cationic species have recently been presented.[8–10]

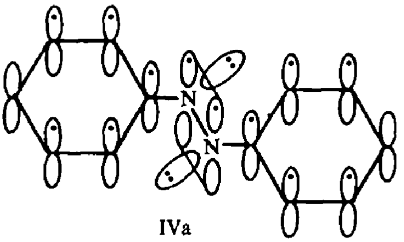
Consideration of the dicationic intermediate for the purpose of carrying out HMO calculations soon revealed the dilemma that the intermediate may *not* be represented by a single delocalized structure. Thus structure IIIa in which the positive charges reside on the phenyls cannot be considered as a canonical structure with IIIb in which the nitrogens bear the positive charges. While the plausiblity of the former structure is self evident, the latter structure must also be considered due to the stability associated with the nitrogen triple bond; it is also noted that IIIb is isoelectronic with diphenylacetylene. The presence of adjacent positive nitrogens in IIIb should not eliminate its consideration since other species with adjacent positive nitrogens exist, e.g. benzocinnoline N,N-dioxide, nitrosobenzene dimer, while diprotonated hydrazobenzene is an intermediate in the benzidine rearrangement.[11] Simple alkyl dicarbonium ions have recently been observed.[12]



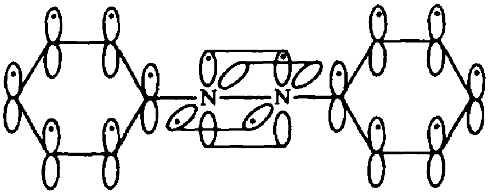
IIIa



IIIb



IVa



IVb

The different geometries and the non-equivalent π-electron systems of IIIa and IIIb are further illustrated in IVa and IVb, representing the orbital diagrams corresponding to IIIa and IIIb. In IVa the nitrogens are sp^2 hybridized, with one of the sp^2 orbitals on each nitrogen containing the unshared pair of electrons and one of the p orbitals on each aromatic ring being vacant. Thus we have a system of 14 π orbitals occupied by 12 π electrons. In IVb the hybridization of the nitrogens is sp, with two p-π orbitals parallel to the π system of the phenyls and two p-π orbitals perpendicular to the aromatic system, leading to a situation of 14 π electrons distributed among 14 π orbitals. It appeared necessary to carry out HMO calculations for both species.

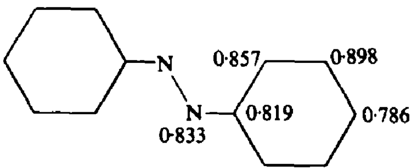
Application of simple HMO theory

The simple HMO (LCAO-MO) method is readily applicable to the 12 π electron-14 π orbital system of IVa. The nitrogens may be treated as pyridine-like in that they contribute a single positive charge to the core potential. According to the usual treatment for heteroatoms,[10a] the Coulomb integral α_N is given by $\alpha_N = \alpha_0 + h_N\beta_0$ and the CN resonance integral by $\beta_{CN} = k_{CN}\beta_0$, where α_0 and β_0 are the standard values for benzene. The values chosen initially for the parameters h_N and k_{CN} correspond to those previously used[13] for azo derivatives, that is $h_N = 0{\cdot}5$ and $k_{CN} = 1{\cdot}0$. It is assumed that $\beta_{CN} = \beta_{NN}$ and that the phenyl rings are coplanar. The electron densities ($q_r = \Sigma n_j c_{jr}^2$) were obtained by solution of the appropriate secular determinant with an IBM System/360-Model 50 computer.[14] Improved values of the electron densities were obtained by use of the iterative ω-method.[15–18] The results recorded below (Va, Vb) represent the charge (q) values obtained in the initial HMO calculation and in the first iteration with the ω technique.[*]

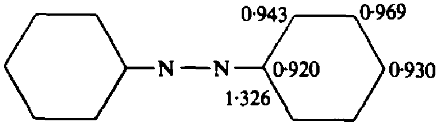
The case of the linear dication may be treated by a particular application of the ω-method equation, $\alpha_r = \alpha_0 + (1 - q_r)\omega\beta_0$. Since this equation relates the value of α_r associated with a particular atom to the charge q_r on this atom, an effective unit positive charge is imposed on each nitrogen in the present case, so that $q_r = 0$. The ω parameter is given the standard value [10b] of 1·4. Now the value of α_N obtained above for neutral nitrogen was $\alpha_N = \alpha_0 + 0{\cdot}5\,\beta_0$; hence in the case of the positively charged nitrogens, and using the ω-method, we have

$$\alpha_N = \alpha_0 + 0{\cdot}5\,\beta_0 + (1 - q_r)\omega\beta_0 = \alpha_0 + 1{\cdot}9\,\beta_0 \tag{2}$$

In MO calculations on substitution in the quinolinium ion a value of $h = 2$ was used by Brown and Harcourt,[19] which is very similar to the result of Eq. 2.



Va



Vb

The π electron densities calculated by the methods indicated above are shown under Va and Vb, corresponding to structures IIIa and IIIb.[†] It is seen that in each case it is the *para* positions that have the lowest π electron density. These data predict, therefore, that nucleophilic attack on the dication should occur preferentially at the *para* position, as is in fact observed experimentally. The results, however, do not distinguish between the two structures of the dicationic species.

It appeared worthwhile to explore the applicability of the simple HMO method to distinguish, on the basis of π-bonding energies and delocalization energies, between the two dicationic species. As a first step it was decided to test whether the commonly used[10b] ω value of 1·4 is appropriate for this system, that is whether it would lead to a convergence of electron densities. A number of iterations for the bent structure using this ω value showed (Table 1) that convergence was not in fact reached. Hence additional calculations were performed at other values of ω. With $\omega = 1{\cdot}2$ convergence was not obtained but use of $\omega = 1{\cdot}0$ led to convergence for

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[*] cf. Ref. 16 for a similar procedure.

[†] The electron density data in Vb correspond only to the main 14 π-electron system and exclude the perpendicular 2 π-electron system (*vide infra*).

TABLE 1. ELECTRON DENSITIES FOR BENT AND LINEAR DICATIONS AS FUNCTION OF ω AND OF ITERATION

No. of iterations	q_N	q_1	q_2	q_3	q_4
Bent dication: ω = 1·4					
0	0·829	0·817	0·834	0·974	0·739
1	0·841	0·821	0·880	0·883	0·833
2	0·841	0·826	0·828	0·962	0·736
3	0·822	0·822	0·885	0·887	0·820
4	0·839	0·826	0·823	0·963	0·766
5	0·823	0·816	0·889	0·885	0·812
Bent dication: ω = 1·2					
0	0·829	0·817	0·834	0·974	0·739
1	0·825	0·819	0·877	0·894	0·816
2	0·834	0·826	0·831	0·957	0·763
3	0·825	0·818	0·873	0·904	0·800
4	0·832	0·825	0·833	0·951	0·773
Bent dication: ω = 1·0					
0	0·829	0·817	0·834	0·974	0·739
1	0·824	0·818	0·864	0·908	0·803
2	0·834	0·822	0·838	0·949	0·768
3	0·827	0·818	0·861	0·922	0·787
4	0·839	0·804	0·848	0·942	0·777
5	0·821	0·829	0·854	0·930	0·782
6	0·833	0·816	0·852	0·934	0·779
Linear dication: ω = 1·0					
0	1·460	0·860	0·920	0·987	0·866
1	1·153	0·985	0·973	0·963	0·990
2	1·394	0·886	0·924	0·997	0·876
3	1·282	0·935	0·957	0·958	0·953
4	1·334	0·919	0·929	0·992	0·904
5	1·314	0·923	0·951	0·973	0·916
6	1·320	0·919	0·937	0·982	0·923
7	1·315	0·922	0·943	0·975	0·926

both the bent and the linear structures (Table 1); this value of ω was used in the calculations described below. In previous work[17, 18] "best" values of ω ranged between 1·0 and 2·0.

Convergent π-energies were calculated for various values of the Coulomb parameter h. For the linear structure h was varied from 0·5 to 3·0 but for the bent structure data were obtained only for the range 0·2 to 2·0 owing to a change in degeneracy of molecular orbitals. Whereas for h = 0·5–3·0 for the linear case and h = 0·2–2·0 for the bent species molecular orbitals 5 and 6 were degenerate, with $h > 2$ for the bent structure molecular orbitals 6 and 7 became degenerate. Since these degenerate orbitals are singly occupied in the 12 π electron system of the bent dication the resulting open shell system becomes intractable by the simple HMO method. In practice for $h > 2$ in the bent case unsymmetrical electron densities were obtained for corresponding positions of the two phenyl rings, as a direct result of the coefficients of various atomic orbitals in these degenerate orbitals being now antisymmetric.

Table 2 records the results of the energy calculations for the bent dication and Table 3 for the linear. In the latter case account was taken of the two perpendicular systems, 14 π electrons in one plane (E_π^z) and 2 π electrons in a plane perpendicular to the aromatic system (E_π^Y). The criteria of stability considered to be relevant to these systems are the π-bonding energies per electron and the delocalization energies per electron. The data of Tables 2 and 3 show that although the stability of the linear structure increases with increasing *h* values and that of the bent structure correspondingly decreases, the stability of the bent structure exceeds that of the linear over the entire range of h values. Some exploratory calculations in which the parameter k was varied were likewise in accord with this result.

Application of extended Hückel theory

The desirability of examining the present problem with a more advanced MO method is seen by the following considerations. Whereas electron densities calculated by the simple HMO method are expected to be at least qualitatively correct, derived delocalization energies may be subject to greater uncertainty,[20] particularly due to the necessary use of different parameters for the two species. However, the validity of delocalization energies as a criterion of stability in this system must, in any case, be further scrutinized. The linear structure contains two more π electrons than the bent and the two extra electrons are derived from the σ electron network in the bent structure. This non-equivalence of the two electronic systems casts doubt on the validity of a direct comparison of delocalization energies. There are other grounds for questioning the result of the simple HMO method that the bent structure is the energetically preferred one. Experience with other systems indicates that loss of one or more electrons from a species results in a positive ion having the highest possible symmetry. Examples of this are: formation of linear NH_2^+ from bent NH_2 and of linear H_2O^+ from bent H_2O;[21] formation of planar CH_3^+ from tetrahedral CH_3^-.[22] Perhaps the strongest factor favouring the linear structure for the dication is that it is isoelectronic with diphenylacetylene. It is difficult to find major exception to the principle that isoelectronic species tend to assume the same geometries. Further discussion of the electronic character of the linear species is reserved for later in this article.

The extended Hückel theory (EHT) as developed by Hoffmann, Lipscomb and Lohr[23] appeared to be particularly suited to the problem at hand, for the following reasons: (1) the different geometries of the dicationic species can be specifically allowed for; (2) a direct comparison of the two structures, through the sum of the orbital energies of the two systems, becomes feasible; (3) σ-electron networks are treated as well as π; (4) the hydrated reaction intermediates in the Wallach rearrangement, following reaction of the dication with the medium, can be examined from the point of view of energetics, thus allowing a further test of the proposed mechanism. Recently the EHT method has been applied to other carbonium ion problems[24] and also to orientation in aromatic substitution.[25] It should perhaps be emphasized that at present the EHT method is the only one that can be used to compute both σ and π electronic structure for molecules of the size considered in this problem.

In the EHT method[23] the MO functions are expressed as a linear combination of Slater AO functions and the basis set includes all the valence shell atomic orbitals, in the present case the 1s orbital for hydrogen and the 2s and three 2p orbitals for

TABLE 2. CONVERGENT ENERGY DATA FOR BENT DICATION

	$h = 0·20$ $k = 1·00$	$h = 0·50$ $k = 1·00$	$h = 1·00$ $k = 1·00$	$h = 1·50$ $k = 1·00$	$h = 2·00$ $k = 1·00$
Total π-energy	$12\,\alpha_0 + 19·7772\,\beta_0$	$12\,\alpha_0 + 20·2784\,\beta_0$	$12\,\alpha_0 + 21·1332\,\beta_0$	$12\,\alpha_0 + 22·0946\,\beta_0$	$12\,\alpha_0 + 23·1558\,\beta_0$
Atomic orbital energy	$12\,\alpha_0 + 0·40\,\beta_0$	$12\,\alpha_0 + 1·0\,\beta_0$	$12\,\alpha_0 + 2·0\,\beta_0$	$12\,\alpha_0 + 3·0\,\beta_0$	$12\,\beta_0 + 4·0\,\beta_0$
π-Bonding energy	$19·3772\,\beta_0$	$19·2784\,\beta_0$	$19·1332\,\beta_0$	$19·0946\,\beta_0$	$19·1558\,\beta_0$
π-*Bonding energy*/π el.	$1·6148\,\beta_0$	$1·6065\,\beta_0$	$1·5944\,\beta_0$	$1·5912\,\beta_0$	$1·5963\,\beta_0$
$E_{C=N}$	$2\,\alpha_0 + 2·210\,\beta_0$	$2\,\alpha_0 + 2·56\,\beta_0$	$2\,\alpha_0 + 3·24\,\beta_0$	$2\,\alpha_0 + 4·0\,\beta_0$	$2\,\alpha_0 + 4·83\,\beta_0$
Delocalization energy	$7·3572\,\beta_0$	$7·1584\,\beta_0$	$6·6532\,\beta_0$	$6·0946\,\beta_0$	$5·4958\,\beta_0$
D E/π el	$0·6131\,\beta_0$	$0·5965\,\beta_0$	$0·5538\,\beta_0$	$0·5079\,\beta_0$	$0·4580\,\beta_0$

TABLE 3. CONVERGENT ENERGY DATA FOR LINEAR DICATION

	$h = 0{\cdot}5$ $k = 1{\cdot}00$	$h = 1{\cdot}20$ $k = 1{\cdot}00$	$h = 1{\cdot}50$ $k = 1{\cdot}00$	$h = 1{\cdot}90$ $k = 1{\cdot}00$	$h = 2{\cdot}00$ $k = 1{\cdot}00$	$h = 2{\cdot}50$ $k = 1{\cdot}00$	$h = 3{\cdot}00$ $k = 1{\cdot}00$
$E^{Y}\pi$	$2\alpha_0 + 3{\cdot}0\,\beta_0$	$2\alpha_0 + 4{\cdot}4\,\beta_0$	$2\alpha_0 + 5{\cdot}0\,\beta_0$	$2\alpha_0 + 5{\cdot}8\,\beta_0$	$2\alpha_0 + 6{\cdot}0\,\beta_0$	$2\alpha_0 + 7{\cdot}0\,\beta_0$	$2\alpha_0 + 8{\cdot}0\,\beta_0$
$E^{Z}\pi$	$14\alpha_0 + 19{\cdot}9022\,\beta_0$	$14\alpha_0 + 21{\cdot}4286\,\beta_0$	$14\alpha_0 + 22{\cdot}1202\,\beta_0$	$14\alpha_0 + 23{\cdot}0730\,\beta_0$	$14\alpha_0 + 23{\cdot}3248\,\beta_0$	$14\alpha_0 + 24{\cdot}6042\,\beta_0$	$14\alpha_0 + 25{\cdot}9858\,\beta_0$
Total π-energy	$16\alpha_0 + 22{\cdot}9022\,\beta_0$	$16\alpha_0 + 25{\cdot}8286\,\beta_0$	$16\alpha_0 + 27{\cdot}1202\,\beta_0$	$16\alpha_0 + 28{\cdot}8730\,\beta_0$	$16\alpha_0 + 29{\cdot}3248\,\beta_0$	$16\alpha_0 + 31{\cdot}6042\,\beta_0$	$16\alpha_0 + 33{\cdot}9858\,\beta_0$
Atomic orbital energy	$16\alpha_0 + 2{\cdot}0\,\beta_0$	$16\alpha_0 + 4{\cdot}8\,\beta_0$	$16\alpha_0 + 6{\cdot}0\,\beta_0$	$16\alpha_0 + 7{\cdot}6\,\beta_0$	$16\alpha_0 + 8{\cdot}0\,\beta_0$	$16\alpha_0 + 10{\cdot}0\,\beta_0$	$16\alpha_0 + 12{\cdot}0\,\beta_0$
π-Bonding energy	$18{\cdot}9022\,\beta_0$	$21{\cdot}0286\,\beta_0$	$21{\cdot}1202\,\beta_0$	$21{\cdot}2730\,\beta_0$	$21{\cdot}3248\,\beta_0$	$21{\cdot}6042\,\beta_0$	$21{\cdot}9858\,\beta_0$
π-Bonding energy/π el.	$1{\cdot}1814\,\beta_0$	$1{\cdot}3143\,\beta_0$	$1{\cdot}3188\,\beta_0$	$1{\cdot}3296\,\beta_0$	$1{\cdot}3328\,\beta_0$	$1{\cdot}3503\,\beta_0$	$1{\cdot}3741\,\beta_0$
Delocalization energy	$4{\cdot}9022\,\beta_0$	$5{\cdot}0282\,\beta_0$	$5{\cdot}1202\,\beta_0$	$5{\cdot}2730\,\beta_0$	$5{\cdot}3248\,\beta_0$	$5{\cdot}6042\,\beta_0$	$5{\cdot}9858\,\beta_0$
D.E./π el.	$0{\cdot}3064\,\beta_0$	$0{\cdot}3144\,\beta_0$	$0{\cdot}3200\,\beta_0$	$0{\cdot}3296\,\beta_0$	$0{\cdot}3328\,\beta_0$	$0{\cdot}3503\,\beta_0$	$0{\cdot}3741\,\beta_0$

carbon, nitrogen and oxygen. The Slater exponent values[26] used are as follows: H(1s), 1·000; C(2s, 2p), 1·625; N(2s, 2p), 1·950; O(2s, 2p), 2·275. The effective Hamiltonian is expressed as the sum of one-electron terms and the total energy is taken to be the sum of the orbital energies for each electron, obtained from solution of the secular determinant $|H_{rs} - ES_{rs}| = 0$. The Coulomb integrals (H_{rr}) are taken as the valence state ionization energies, for which the following values[27] are used: H(1s), −13·60 eV; C(2s), −21·43 eV; C(2p), −11·42 eV; N(2s), −27·50 eV; N(2p), −14·49 eV; O(2s), −35·30 eV; O(2p), −17·28 eV. The overlap integrals (S_{rs}) are evaluated by the Mulliken method[28] and are used to calculate the resonance integrals (H_{rs}) by means of the Wolfsberg–Helmholtz relationship,[29] $H_{rs} = 0{\cdot}5\,K\,S_{rs}(H_{rr} + H_{ss})$. The constant K is taken as 1·75 in accord with previous practice.[23] The electron densities are obtained from a Mulliken population analysis.[30] The aromatic rings are described by normal bond lengths (C—C, 1·40 Å; C—H, 1·08 Å) and bond angles (120°). The C—N and N—N bond distances were initially taken as 1·41 Å and 1·24 Å, respectively, corresponding to the bond distances in *trans*-azobenzene.[31] In the case of the hydrated intermediates tetrahedral oxygen was assumed and the distances involving oxygen were the normal bond lengths (C—O = 1·47 Å, O—H = 1·00 Å).[31] An IBM 7094-II computer was used with a program described previously.[23, 32]

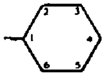
Electron densities and frontier orbitals. The π electron densities at the various atomic centres calculated by the method indicated above are given in Table 4. For comparison the data obtained by the simple HMO method are also shown. It is apparent that for the linear structure both methods give closely similar electron densities, but for the bent structure the results by the two methods differ significantly. For the bent structure the EHT method differentiates between the geometrically nonequivalent *ortho* and *meta* positions on each phenyl. The simple HMO method does not allow for geometry and hence treats the two types of *ortho* and *meta* positions in the bent structure as equivalent. One may conclude from the close agreement of data for the linear structure and the lack of agreement for the bent structure, that the EHT method by specifically allowing for geometry gives more reliable results than the simple HMO method. The EHT results are also in accord with product orientation, i.e. that nucleophilic attack on the dication occurs preferentially at the 4 (*para*) position.

Another criterion of reactivity is the frontier orbital electron approach.[33] An attacking nucleophilic reagent will tend to place its unshared pair of electrons in

TABLE 4. π-ELECTRON DENSITIES[a]

	q_N	q_1	q_2	q_3	q_4	q_5	q_6
			Linear dictation				
EHT data	1·283	0·915	0·944	0·996	0·921	0·996	0·944
HMO data	1·315	0·922	0·943	0·975	0·926	0·975	0·943
			Bent dication				
EHT data	1·261	0·912	0·954	0·992	0·929	0·998	0·949
HMO data	0·833	0·816	0·852	0·934	0·779	0·934	0·852

[a] The designation of the various atomic centres for the q values in the Table is as shown in the partial structure N



the lowest unoccupied MO (frontier orbital) in the ground state and the position of attack will be that atomic orbital which has the highest value of c_i^2. In the case of the linear structure the lowest unoccupied MO is found to be of π symmetry, with contributions from p_z orbitals only, and the carbon atom with the greatest c_i^2 is that corresponding to the *para* position. For the bent dication, the lowest unoccupied MO contains contributions from σ type orbitals *only*, which makes the frontier electron approach invalid. The next higher unoccupied MO, however, is again of π symmetry and the greatest c_i^2 corresponds again to the *para* carbon. The two relevant MO's are given below.

$$\psi_1(\text{linear}) = 0{\cdot}1256\,\phi_N - 0{\cdot}4646\,\phi_1 - 0{\cdot}2512\,\phi_2 + 0{\cdot}2235\,\phi_3 + 0{\cdot}4663\,\phi_4 + 0{\cdot}2235\,\phi_5 - 0{\cdot}4646\,\phi_6 + \ldots$$

$$\psi_2(\text{bent}) = 0{\cdot}6024\,\phi_N - 0{\cdot}0506\,\phi_1 - 0{\cdot}2645\,\phi_2 + 0{\cdot}0397\,\phi_3 + 0{\cdot}2811\,\phi_4 + 0{\cdot}0102\,\phi_5 - 0{\cdot}2675\,\phi_6 + \ldots$$

Energies of reaction intermediates. The total energies of the two structures calculated by the EHT method are: bent dication, −1202·70 eV; linear dication, −1204·20 eV. According to these results the *linear* structure is the energetically favoured one, to the extent of 1·50 eV (34·6 kcal/mole). This result is opposite to that obtained by the simple HMO method. In order to test the EHT method the calculations were performed for azobenzene, linear and bent. The energy data are: linear, −1226·48 eV; bent, −1226·68 eV, so that the bent structure is found to be energetically preferred by 4·5 kcal/mole.* This particular test of the EHT method appears to be satisfactory. Now it could be argued that the EHT method correctly predicts the azobenzene geometry because the bond lengths used in this calculation are experimental values; in contrast the calculations on the dication use hypothetical bond lengths (assumed to be those corresponding to azobenzene). Hence the result of the dication calculations could simply be an artifact of the assumed bond lengths. In order to test this possibility a minimization procedure was adopted, that is the EHT calculations on the dication were repeated for a number of bond lengths. The data are shown in Tables 5 and 6. It is seen that for the linear structure an energy minimum (−1209·12 eV) is obtained corresponding to the bond distances C—N = 1·71 Å and N—N = 0·68 Å.† The bent structure does not appear to have a minimum energy but displays rather erratic behaviour: for C—N = 1·91 Å energy minima are obtained corresponding to N—N = 0·96 Å and 0·82 Å; then for C—N = 2·01 Å still lower energy values are obtained at N—N = 0·68 Å and 0·54 Å. It appears then that the energy decreases as the C—N distance increases and the N—N distance decreases, which is clearly an unrealistic situation. However it is noteworthy that even the lowest tabulated energy corresponding to the bent structure (−1206·80 eV) exceeds (by 53 kcal/mole) the minimized energy of the linear structure.

A further aspect of the structure of the dication has been examined: the degree of coplanarity of the two phenyls. The results of the calculations of energy of the system as a function of dihedral angle are shown in Table 7. It is seen that the fully coplanar

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* cf. Ref. 34.

† The low value (0·68 Å) of the N—N bond distance corresponding to the minimized energy compares with a calculated[23] C—C bond length of 0·85 Å for acetylene by the minimized procedure. Abnormally short bond lengths are generally obtained using the EHT method on multiple bonds, probably because the method does not include electron repulsion terms and derives its bonding from overlap terms alone.

TABLE 5. MINIMIZATION DATA FOR LINEAR DICATION. ENERGY (eV) AS FUNCTION OF BOND DISTANCES

C—N	N—N (Å)		
(Å)	0·82	0·68	0·54
1·41	−1208·165	−1208·514	−1207·307
1·51	−1208·295	−1208·938	—
1·61	−1208·339	−1209·119	−1208·690
1·71	−1208·222	−1209·124	−1208·975
1·81	−1208·033	−1209·006	−1209·082
1·91	—	—	−1209·059

TABLE 6. MINIMIZATION DATA FOR BENT DICATION. ENERGY (eV) AS FUNCTION OF BOND DISTANCES

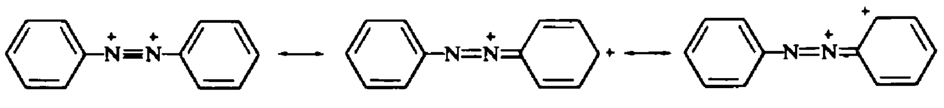
C—N	N—N (Å)			
(Å)	0·96	0·82	0·68	0·54
1·41	−1204·007	−1204·438	−1203·881	—
1·51	—	−1205·262	—	—
1·61	−1204·921	−1205·780	—	—
1·71	−1205·094	−1206·077	—	—
1·81	−1205·165	−1206·217	−1206·533	—
1·91	−1205·175	−1206·252	−1206·655	−1206·465
2·01	−1205·154	−1206·217	−1206·661	−1206·796

TABLE 7. DEPENDENCE OF ENERGY OF LINEAR DICATION (N—N = 1·24 Å, C—N = 1·41 Å) ON THE DIHEDRAL ANGLE BETWEEN PHENYL GROUPS

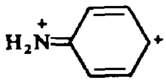
Dihedral angle	0°	30°	60°	90°
Energy (eV)	−1204·197	−1204·189	−1204·174	−1204·167

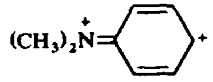
structure is of least energy, but the sensitivity to non-coplanarity is surprisingly small. These data are of interest with respect to studies on the interaction in perpendicular π systems.[35]

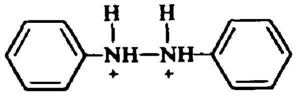
The conclusion of the EHT calculations, that the linear dicationic structure is more stable than the bent, requires careful evaluation. As was stated previously, several considerations are in accord with a preferred linear structure: bond energy, symmetry, and equivalent geometries of isoelectronic species. To these considerations we now add the following one. The linear dicationic species can be represented by a number of canonical structures:



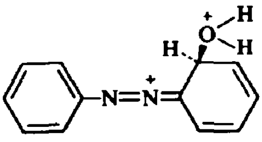
It is suggested that structures, such as those shown, in which one positive charge resides on nitrogen and the other on the adjacent phenyl are in fact heavy contributors and add to the stabilization of the linear form. It is noteworthy that the related structures VI,[36] VII[37] and VIII[11] were previously proposed as intermediates in other processes.

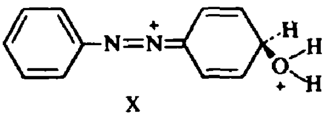

VI

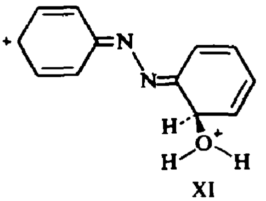

VII


VIII

The criteria for nucleophilic attack on the dication discussed previously were those based on π electron density and the frontier electron approach; both suggested *para* attack in favour of *ortho*. These criteria, while they usually correctly predict the reaction products, are however based on ground state considerations. It is desirable to extend the discussion to energies of the hydrated intermediates, which can also be calculated by the EHT method. Both linear (IX, X) and bent (XI, XII) hydrated intermediates were considered. The calculations were first performed using C—N and N—N bond lengths corresponding to those in azobenzene (1·41 Å and 1·24 Å, respectively). The results (Table 8) indicate that *the linear hydrated intermediates are more stable than the bent* (by ca. 10 kcal), but that the *ortho* isomers are slightly more stable than the *para*. However when the calculation was repeated using the bond distances corresponding to the minimized linear dication (C—N = 1·71 Å, N—N = 0·68 Å) the *para* hydrated intermediate becomes the more stable one (by 0·5 kcal).


IX


X


XI

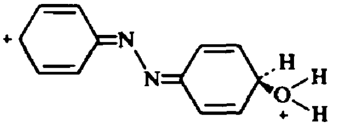

XII

TABLE 8. ENERGIES OF HYDRATED INTERMEDIATES

Structure	Energy (eV)
C—N = 1·41 Å, N—N = 1·24 Å	
linear, *ortho* (IX)	−1379·238
linear, *para* (X)	−1379·228
bent, *ortho* (XI)	−1378·756
bent, *para* (XII)	−1378·681
C—N = 1·71 Å, N—N = 0·68 Å	
linear (*ortho*)	−1382·136
linear (*para*)	−1382·158

The opposing results of the two sets of calculations for the hydrated structures and the small differences in energies between the *ortho* and *para* hydrated intermediates in both cases suggest that the relative energies of these intermediates should not be regarded as a definitive criterion of reactivity in this system. The possibility of a crossing in the potential energy surfaces before the transition state has been reached is also open. Nevertheless, the EHT results on the hydrated intermediates are in general accord with the proposed reaction mechanism. The simple HMO method can of course give no information on such σ-bonded species.

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