117. Molecular Orbital Studies of the Protonation of Diazomethane

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Summary. CNDO/2, MINDO/3 and *ab initio* molecular orbital calculations indicate that C-protonated diazomethane is more stable than N(end)-protonated diazomethane. Extrapolation of these results to solution chemistry as well as the kinetic preferences of protonation of diazomethane are discussed.

In the acid-catalysed hydrolysis of aliphatic diazo compounds [1] [2] the products formed arise *via* an intermediate protonated on the carbon atom; while it has been possible to prepare C-protonated trifluoromethyl derivatives of diazoalkanes in super-acid media at low temperatures [3], the intermediacy of N(end)-protonated species has been postulated in some instances [4]. Current interest in this department in the acid-catalysed hydrolysis of diazo compounds [5] has led us to investigate, from a theoretical viewpoint, the relative importance of C-protonated (II) and N-protonated (III) diazomethane.

Several molecular orbital studies of diazomethane (I) have appeared in the recent literature with emphasis of different aspects of its chemical and physical properties [6–10]. The present work deals mainly with the relative stabilities of its tautomeric conjugate acids.

$$CH_2=\overset{+}{N}=\overset{-}{N} \longleftrightarrow \overset{-}{C}H_2-\overset{+}{N}\equiv N$$

Ia **Ib**

$$CH_3-\overset{+}{N}\equiv N \qquad CH_2=\overset{+}{N}=NH$$

II **III**

Methods. – Two semiempirical molecular orbital methods have been employed in this study: CNDO/2 [11] and MINDO/3 [12]. While it appears that MINDO/3 is suitable for evaluating the energy of a system, electron distributions and the quantities which depend on them are not as reliable. On the other hand, CNDO/2 yields more reliable wavefunctions and electron distributions, but in many instances fails to give a proper description of the energy of a system. We have used both methods in order to benefit from their particular powers to a full extent.

The geometries of the protonated species are unknown. Therefore, although it has been shown that CNDO/2 yields better results when experimental geometries are used [13], the energies were minimized with respect to geometrical parameters in order to gain internal consistency; this also renders these results directly comparable with those of MINDO/3, which has been parametrized on the basis of optimized geometries. In the CNDO/2 approximation the procedure involved variation of each bond length and angle successively until a minimum in energy with respect to each variable was found. Each parameter was then reoptimized in the same order as previously, although the changes in them or in the energies were usually very small (less than 0.0002 u.a. in energy, 0.5 degrees in angles and 0.002 Å in bond lengths). The MINDO/3 approximation involves a procedure [14] based on the *Davidon-Fletcher-Powell* method of minimizing a function of several constrained variables [15].

The *ab initio* methods used were those of *Pople* et al. [16] using 2 different basis sets[1]), the minimum STO-3G and the extended 4-31G. These methods were employed as one-point checks on the results given by the semiempirical methods and used the optimized geometries of the CNDO/2 calculations. Supporting this choice is the fact that the optimum geometry determined for diazomethane with the *ab initio* STO-3G method [7] lies close to that determined in the CNDO/2 approximation.

Results and discussion. – *Geometrical parameters.* The geometries of the species studied are collected in Table 1. It has been suggested that a non-planar form of diazomethane with a pyramidal carbon atom would be only a few kcal/mol higher in energy than the equilibrium configuration [20]. We have not found an energy well corresponding to such structure. Nevertheless a distorsion of planar diazomethane to one having a tetrahedral carbon atom (the other geometrical parameters remaining unchanged) requires an energy of only 12.2 kcal/mol.

Bastide & Henri-Rousseau [8] have reported a CNDO/2 study of diazomethane in connection with its 1,3-dipolar reactivity in cycloadditions. They deduced that a bent form of diazomethane exists in equilibrium with planar diazomethane, the former being 8.3 kcal/mol lower in energy than the latter. These authors obtained bent diazomethane by successive optimization of CN and NN distances, CNN angle and again CN and NN distances. Neither the CH distance, the HCH angle nor the angle between the plane containing the CH_2 moiety and the bisector plane of the molecule were varied. The data in Table 1 and the fact that, as mentioned above, the optimization of a reasonably chosen initial geometry of diazomethane leads to the planar species, suggest that this bent diazomethane corresponds to a species that upon relaxation will fall into the potential well of diazirine which, in the CNDO/2 approximation, lies well below the minimum for diazomethane (*vide infra*).

The agreement between calculated and experimental geometrical parameters is only fair: average discrepancies in bond angles are within 6–7 degrees and in bond lengths within 0.02–0.03 Å ,although some of the latter are as high as 0.07 Å. Nevertheless, within a particular level of approximation, the bond lengths are consistent with structures I, II and III. Thus, taking the CNDO/2 calculations as example, in III the length of the NN double bond is 1.200 Å, being longer than the NN triple bond in II (1.146 Å); the NN bond in I, being formally intermediate in character between double and triple bond, is also intermediate in length (1.192 Å). The same first order analysis can be applied to the CN and CH bonds. Furthermore, the bond lengths indicate that resonance structure Ia is more important than Ib since the bond lengths of diazomethane resemble more closely those of III than those of II.[2])

A similar analysis can be carried out by examining bond orders (Table 2). Following *Wiberg* [24] the bond order between atoms A and B is defined as the sum of the squares of all the elements in the CNDO/2 density matrix common to atoms A and B.

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[1]) We thank Dr. *Martin Jungen* at the University of Basel for performing these calculations.

[2]) This conclusion if further supported by the facts that in the 3-centered π-orbitals of diazomethane in the CNDO/2 approximation, the electron population is C(1.327e)-N(1.003e)-N(1.670e), and that the dipole moment in diazomethane points from the carbon atom to the nitrogen atoms [22]. The same conclusion has been reached by *Moore & Pimentel* [21] on the basis of dipole moment and microwave quadrupole measurements. However, the importance of resonance structure Ib cannot be disregarded on the basis of ^{13}C-NMR. experiments on diazoalkanes [23].

Table 1. *Geometrical parameters*[a][b]

Diazomethane (I)	NN: 1.191, 1.113 (1.139); CN: 1.297, 1.274 (1.300); CH: 1.108, 1.099 (1.075); HCH: 120.4, 115.1 (126)
C-protonated diazomethane (II)	NN: 1.146, 1.085; CN: 1.392, 1.383; CH: 1.120, 1.115; NCH: 108.5. 110.9
N-protonated diazomethane (III)	NN: 1.200, 1.159; CN: 1.281, 1.251; CH: 1.112, 1.110; NH: 1.060, 0.997; HCH: 120.6, 117.0; NNH: 180.0, 117.1[c]
Diazomethane[d] protonated over the NN bond (IV)	NN: 1.252, 1.190; CN: 1.288, 1.261; CH(1): 1.114, 1.107; CH(2): 1.112, 1.104; N(1)H: 1.132, 1.232; N(2)H: 1.135, 1.232; NCH(1): 118.1, 119.5; NCH(2): 121.8, 124.0
Transition[e] state for internal proton transfer (V)	NN: 1.222, 1.137; CN: 1.428, 1.544; NH(1): 1.287, 1.946; CH: 1.121, 1.117; CNN: 70.2, 76.2; NNH(1): 111.8, 98.1; HCH: 114.8, 104.0; α: 145.2, 116.0
Diazirine	NN: 1.248, 1.215 (1.228); CN: 1.410, 1.437 (1.482); CH: 1.119, 1.116 (1.09); HCH: 111.6, 107.8 (117)
H_2O	OH: 1.029, 0.949 (0.957); HOH: 104.2, 103.7 (104.5)
HO^-	OH: 1.068, 0.949

[a] Values given correspond to CNDO/2, MINDO/3 and, when available, (experimental value). These latter are taken from [17] (diazomethane), [18] (diazirine) and [19] (H_2O).

[b] Bond distance in Å, angles in degrees.

[c] The H bond to N is located on the plane bisecting the rest of the molecule.

[d] N(2) refers to the N attached to C, H(1) to the H on the side opposite to the protonating H. In the MINDO/3 calculation, this latter H was assumed to lie over the center of the NN bond.

[e] H(1) refers to the transferring H. α refers to the angle between the line bisecting the CH_2 group and the CN bond.

The results are in complete agreement with the formulae I, II and III, and confirm the larger contribution of resonance structure Ia.

Dipole moments and energies. The calculated dipole moments agree reasonably well with experiment in the cases of CNDO/2 and *ab initio* STO-3G calculations (see Table 2). The MINDO/3 results show a large discrepancy which is nevertheless within the range of errors reported in [12].

The total energies are schematised in the figure.

Large discrepancies have existed in the literature for a long time regarding the heats of formation of diazomethane and diazirine, values between 49 and 103 kcal/mol having been suggested for the ΔH_f^0 of diazomethane [25]. More recently, the ΔH_f^0 values have clustered around an intermediate figure. Thus, while *Laufer* & *Okabe* set the limits of 61–66 kcal/mol for diazirine [26] and 51–60 kcal/mol for diazomethane [27], determined by photon impact and photodissociation methods respectively, *Foster* & *Beauchamp* suggest a values of 64–73 kcal/mol for diazomethane [28] based on ion cyclotron resonance spectroscopy results, with 71 kcal/mol being a likely value.

The theoretical methods employed show also disagreement among each other. Comparing with the probably most trustworthy of them, the *ab initio* method, the large stability of diazirine with respect to diazomethane shown by the CNDO/2 results reflects the well known tendency of this method to underestimate the strain energies of small rings [29]. This defect seems to have been overcorrected for this type of compounds in the newly parametrized MINDO/3 version.

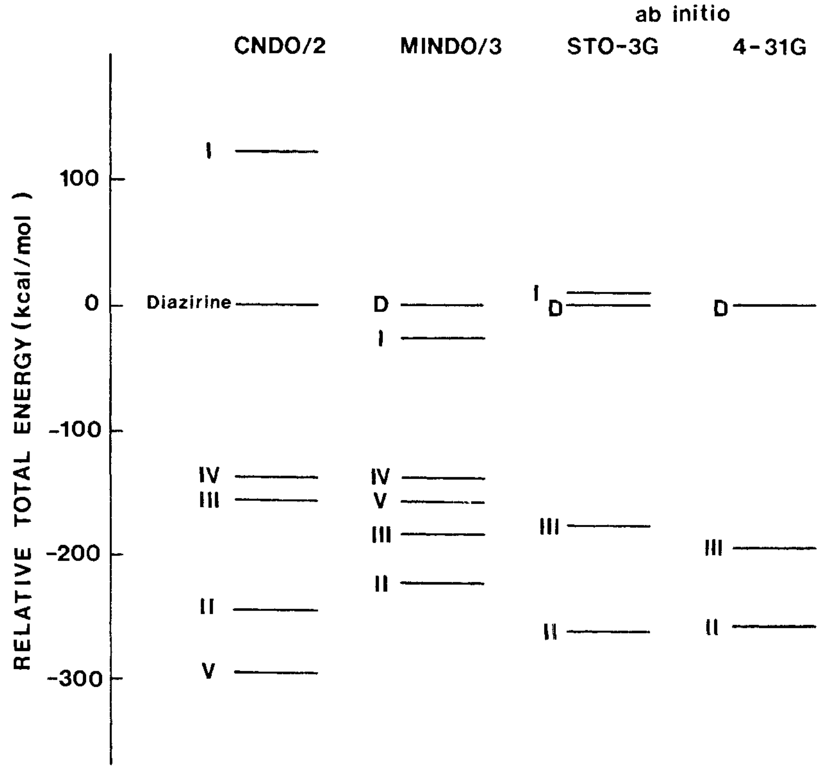
Table 2. *Electron population data*

	Bond orders[a]) N–N	Bond orders[a]) N–C	Charges[a]) [b])	Dipole moments[c])
Diazomethane	2.113	1.662	N(1): –0.149 N(2): 0.230 C: –0.151 H: 0.035	1.583, 0.935, 1.446 (1.50)
C-protonated diazomethane	0.983	2.839	N(1): 0.260 N(2): 0.316 C: 0.019 H: 0.135	
N-protonated diazomethane	1.839	1.994	N(1): –0.032 N(2): 0.333 C: 0.053 H(1): 0.350 H(2): 0.148	
Diazirine	0.986	1.896	N: –0.017 C: 0.090 H: –0.028	1.436, 0.505, 1.631 (1.59)

[a]) CNDO/2 values.

[b]) N(2) refers to the N bond to C; H(1) to the H bond to N.

[c]) The values given are in Debye units and correspond to CNDO/2, MINDO/3, *ab initio* STO-3G, (experimental value). The later are taken from [17] (diazomethane) and [18] (diazirine).



The inclusion of inner shells in the calculation of proton affinities has recently been pointed out to be of importance [30], since upon protonation not only the outer shells but also the inner shells of the neutral species are observed to be stabilized in *ab initio* all-electron calculations. Thus, semiempirical methods that take into account only valence electrons may not give quantitatively reliable energy differences between neutral and protonated species, but the comparison of the energies of the two protonated species should at least show the correct trend.

We have found that the MINDO/3 method gives a value of 144 kcal/mol for this difference, while a value of 152 kcal/mol has been determined experimentally for the difference in ΔH_f^0 between II and I [28]. Further, the trends shown by the semiempirical methods employed concerning the relative stabilities of II and III are fully corroborated by the results of the *ab initio* methods (see figure).

C-protonation vs *N-protonation*. The recently developed molecular electrostatic potential method [31] can be used to study relative basicities. From the information about charge distribution contained in a set of molecular orbitals, an electrostatic potential for the molecule is constructed that represents the environment experienced by an attacking reagent, thus furnishing an indication of the tendency of this latter species to attack the molecule at different sites. Since perturbations such as deformations, charge transfer, and polarization caused by the attacking reagent are not taken into account, the potential diagram gives in principle a measure of reactivity only at early stages of the reaction.

The reaction of diazomethane with a proton in the gas-phase is an exothermic process, as shown for reactions (1) and (2)³). According to

$$CH_2N_2 + H^+ \rightarrow CH_3N_2^+ \; \Delta H^\circ \text{ (MINDO/3)} = -221.8 \text{ kcal/mol} \qquad (1)$$

$$CH_2N_2 + H^+ \rightarrow CH_2NNH^+ \; \Delta H^\circ \text{ (MINDO/3)} = -182.9 \text{ kcal/mol} \qquad (2)$$

Hammond's postulate [32] the transition state resembles closely the reactants in energy, geometry and electron distribution and the electrostatic potential diagram would thus be a good indication of the kinetic reactivity of diazomethane towards positively charged species in the gas-phase.

This method has been applied to diazomethane by two authors. *Hart* [9], using an *ab initio* self-consistent-field molecular orbital method with LW [5.33;3] Gaussian lobe basis set to generate the wave functions, found a deeper potential well near nitrogen (–34.4 kcal/mol) than near carbon (–13.5 kcal/mol)⁴). Recent calculations by *Caballol* et al. [10] using INDO wave functions have yielded a potential well of –14.9 kcal/mol around carbon and –13.2 kcal/mol around nitrogen⁵). The nature of the molecular orbital methods employed in these calculations as well as the small preference shown by INDO as compared with *ab initio* results, allows the suggestion that N-protonation of diazomethane is kinetically favoured in the gas-phase. On the

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³) For this calculation a thermodynamic cycle was used which includes the heats of formation of diazomethane and those of the protonated species, available from MINDO/3, the ionisation potential of the H atom, and the dissociation energy of H_2.

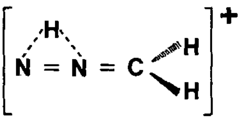
⁴) It should be pointed out that *Hart*, on the basis of these results, wrongly concluded that N-protonation was *thermodynamically* favoured over C-protonation.

⁵) *Caballol* et al. appeal to experimental results [2] to settle the contradiction between their results and those of *Hart*. However the data available refer to the product-forming step in the acid-catalysed reactions of diazoalkanes and do not indicate preference towards N- or C-protonation.

other hand, the present calculations indicate that the product of a thermodynamically-controlled protonation reaction in the gas-phase is the C-protonated diazomethane.

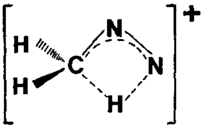
The role of the solvent is difficult to predict but the following speculations can be made. The solvent will preferentially stabilise those ions which possess a highly localized charge. In reactions (1) and (2) the stabilization of H^+ will predominate and the reaction will be less exothermic than in the gas-phase. The stabilization due to unspecific solvation effects is likely to be similar in II and III, since the size and polarisabilities of these ions are similar and the charge is roughly distributed over the entire molecule (see Table 2). Furthermore, although III would be in a position to benefit more from H-bonding due to the presence of a highly positive H atom, this effect will not be large enough to overcome the initial gas-phase energy separation between the two species. Thus, it appears that in solution C-protonation would still be favoured thermodynamically.

Other protonated species. We have studied the possibility of protonation at the two-center π-system of the NN bond in diazomethane, with formation of a π-complex IV (see Table 1). Both semiempirical methods agree in showing that this species is of considerably higher energy than any of the other protonated species studied (see figure).



IV

It is possible in principle to interconvert II and III intramolecularly rather than by an intermolecular process going through I. A plausible mechanism for this transformation starting from III would be the following: the terminal N and its attached H coil in such a way that the latter can attack the p orbital on C in the direction of maximum overlap, pushing backwards the two hydrogen atoms attached to it. As carbon atom becomes tetrahedral, the nitrogen atom moves back again reestablishing linearity. The transition state for such a process might have the structure V, and the energy barrier for the process could in principle be assessed by calculating the energy of V. The CNDO/2 energy of this species (Figure) undoubtedly reflects the overestimation of small ring stabilities by this method. In the MINDO/3 approximation, which is expected to be more realistic, the energy of V is seen to be substantially higher than those of II and III. Nevertheless, the interconversion of II and III via V could in principle take place especially since the initial protonated species contain excess energy, at least in the gas-phase (see equations (1) and (2)).



V

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REFERENCES

[1] *R. A. More O'Ferral*, Adv. phys. org. Chemistry *5*, 331 (1967).

[2] *G. W. Cowell & A. Ledwith*, Quart. Rev. chem. Soc. *24*, 119 (1970).

[3] *J. R. Mohrig & K. Keegstra*, J. Amer. chem. Soc. *89*, 5492 (1967); *G. Diderich*, Helv. *55*, 2103 (1972); *J. R. Mohrig, K. Keegstra, A. Maverick, R. Roberts & S. Wells*, Chem. Commun. *1974*, 780.

[4] *G. L. Closs, R. A. Moss & S. H. Goh*, J. Amer. chem. Soc. *88*, 364 (1966); *K. B. Wiberg & J. M. Lavanish*, J. Amer. chem. Soc. *88*, 365 (1966).

[5] *R. Malherbe & H. Dahn*, Helv. *57*, 2492 (1974) and preceeding papers in the series.

[6] *R. Hoffmann*, Tetrahedron *22*, 539 (1966); *J. del Bene & H. H. Jaffé*, J. chem. Physics *50*, 1126 (1969); *J.-M. André, M. Cl. André, G. Leroy & J. Wieler*, Int. J. Quant. Chemistry *3*, 1013 (1969); *J. P. Jacobsen, K. Schaumburg & J. T. Nielsen*, J. Magnetic Resonance *13*, 372 (1974); *S. P. Walch & W. A. Goddard, III*, J. Amer. chem. Soc. *97*, 5319 (1975).

[7] *G. Leroy & M. Sana*, Theoret. chim. Acta *33*, 329 (1974).

[8] *J. Bastide & O. Henri-Rousseau*, Tetrahedron Letters *1972*, 2879.

[9] *B. T. Hart*, Austral. J. Chemistry *26*, 461, 477 (1973).

[10] *R. Caballol, R. Carbo & M. Martin*, Chem. Physics Letters *28*, 422 (1973).

[11] *J. A. Pople, D. P. Santry & G. A. Segal*, J. chem. Physics *54*, 508 (1971); *J. A. Pople & G. A. Segal*, ibid. *44*, 3289 (1966); *J. A. Pople & D. L. Beveridge*, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York 1970; *P. A. Dobosh*, CNINDO, QCPE Program No 141.

[12] *R. C. Bingham, M. J. S. Dewar & D. H. Lo*, J. Amer. chem. Soc. *97*, 1285, 1294, 1302 (1975). The MINDO/3 program was obtained through Dr. J.-C. Perlberger at the University of Geneva.

[13] *L. B. Kier*, 'Molecular Orbital Studies in Chemical Pharmacology', Symposium held at Battelle Seattle Research Center, Oct. 20–22, 1969, Springer-Verlag, Berlin 1970.

[14] *M. J. S. Dewar, H. W. Kollner, D. H. Lo, H. Metiu, P. J. Student & P. K. Weiner*, to be published (cited in [12]).

[15] *W. C. Davidon*, Comput, J., *10*, 406 (1968); *R. Fletcher*, ibid. *8*, 33 (1965); *R. Fletcher & M. J. D. Powell*, ibid. *6*, 163 (1963).

[16] *W. J. Hehre, R. F. Stewart & J. A. Pople*, J. chem. Physics *51*, 2657 (1969); *R. Ditchfield, W. J. Hehre & J. A. Pople*, ibid. *54*, 724 (1971); *W. J. Hehre, W. A. Latham, R. Ditchfield, M. D. Newton & J. A. Pople*, GAUSSIAN-70, QCPE Program No 236.

[17] *A. P. Cox, L. F. Thomas & J. Sheridan*, Nature *181*, 1000 (1958); *A. P. Cox, L. F. Thomas & J. Sheridan*, Spectrochim. Acta *14*, 542 (1959).

[18] *L. Pierce & V. Dobyns*, J. Amer. chem. Soc. *84*, 2651 (1962).

[19] Tables of Interatomic Distances, The Chemical Society, London 1958.

[20] *C. B. Moore & G. C. Pimentel*, J. chem. Physics *40*, 342 (1964).

[21] *C. B. Moore & G. C. Pimentel*, ibid. *40*, 1529 (1964).

[22] *G. Piazza, S. Sorriso & A. Foffani*, Tetrahedron *24*, 4751 (1968).

[23] *J. Firl, W. Runge & W. Hartmann*, Angew. Chem. *86*, 274 (1974).

[24] *K. B. Wiberg*, Tetrahedron *24*, 1083 (1968).

[25] *W. Kirmse*, 'Carbene Chemistry', 2nd. ed., Academic Press, London, p. 25 (1971).

[26] *A. H. Laufer & H. Okabe*, J. phys. Chemistry *76*, 3504 (1972).

[27] *A. H. Laufer & H. Okabe*, J. Amer. chem. Soc. *93*, 4140 (1971).

[28] *M. S. Foster & J. L. Beauchamp*, J. Amer. chem. Soc. *94*, 2425 (1972); cf. *S. W. Benson & H. E. O'Neal*, NSRDS-NBS 21, U.S. Dept. of Commerce, Washington, 1970, p. 481.

[29] *E. I. Snyder*, J. Amer. chem. Soc. *92*, 7529 (1970).

[30] *A. C. Hopkinson & I. G. Csizmadia*, Theoret. chim. Acta *34*, 93 (1974).

[31] *R. Bonnaccorsi, E. Scrocco & J. Tomasi*, J. chem. Physics *52*, 5270 (1970); *E. Scrocco & J. Tomasi*, Fortschr. chem. Forsch. *42*, 95 (1973).

[32] *G. S. Hammond*, J. Amer. chem. Soc. *77*, 334 (1955).