

## 150. Isomerism and Protonation of $\alpha$ -Diazocarbonyl Compounds. A Molecular Orbital Study

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### Summary

CNDO/2, MINDO/3 and *ab initio* molecular orbital calculations are used in a study of conformational isomerism, protonation site and mechanism of protonation of the title compounds.

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Several studies have recently appeared concerning the structure, site of protonation under equilibrium conditions, and mechanism of hydrolysis of  $\alpha$ -diazocarbonyl compounds.

The analysis of their IR. [1-5] and UV. [4] [6] spectra, the changes in the UV. spectra of their solutions in non-hydroxylic solvents upon addition of hydroxylic ones [1] [7], their dipole moments [8-10] and the temperature dependence of the NMR. spectra of their solutions [11] [12] has established the presence of *cis/trans* isomerism around the C(N)-C(O) bond. The UV. spectra of  $\alpha$ -diazoacetophenone and  $\alpha$ -diazoacetone have been interpreted in terms of the energy levels calculated with the Extended *Huckel* MO Method for each pair of conformers [13]. CNDO/2 calculations with standard geometries [14] satisfactorily reproduce the *cis/trans* ratios deduced from spectroscopic measurements and from experimental dipole moments of  $\text{CH}_2\text{ClCOCHN}_2$  and  $\text{CH}_3\text{COCCH}_3\text{N}_2$  [9]. The reactions of cyclic  $\alpha$ -diazoketones with *m*-chloroperoxybenzoic acid indicate similar nucleophilic character for both conformers [15].

Studies in super-acid media have shown that the oxygen atom of  $\alpha$ -diazocarbonyl compounds is the preferred site of protonation under equilibrium conditions [16] [17] although the hydrolysis products normally result from C-protonation of the reactant [18] [19].

This investigation deals with some of the afore-mentioned data from a quantum mechanical viewpoint and seeks to clarify some problems arising from inconclusive experimental studies.

**Methods.** - *MO methods.* The following two semiempirical MO methods were employed in this study: CNDO/2 [20] and MINDO/3 [21]. While it was claimed that the heats of formation given by the latter method provide, in most cases, a good approximation to the experimental ones [21], the former method was proven to lead to reasonable charge distributions [14] and, within certain limits, fair values for total energies (see, for example, [9] [10]).

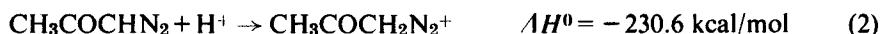
The CNDO/2 method yields better results when experimental geometries are used [22]. Nevertheless, as neither the geometries of the  $\alpha$ -diazocarbonyl compounds nor those of their conjugate acids are known, the results were standardized by calculating optimal geometries (those which give the lowest energies) for all the species studied; we have successfully used this approach in other instances [23–25]. The procedure involved the successive optimization of each geometrical parameter. Recently, however, more efficient optimization methods have become available [26].

The MINDO/3 method has been parametrized with the use of optimal geometries which are determined by a procedure based on the *Davidon-Fletcher-Powell* method of minimizing a function of several constrained variables [27]. This method was used in its original form.

Some of the results obtained were compared with *ab initio* results using the minimal STO-3G basis set [28]. This method produces reliable results in conformational equilibria around essentially single bonds [29]. The calculations using optimized CNDO/2 geometries are justified, since it has been shown for diazomethane that optimized geometries are similar for CNDO/2 [24] and *ab initio* with STO-3G basis set [30].

*Protonation studies.* A theoretical method has recently been developed for studying the protonation of neutral species [31]. The information about charge distribution contained in a set of molecular orbitals permits the calculation of an electrostatic potential map representing the environment experienced by a positively charged reagent.

Semiempirical calculations show that gas phase protonation reactions of  $\alpha$ -diazocarbonyl compounds are very exothermic, as exemplified in equations (1) and (2).

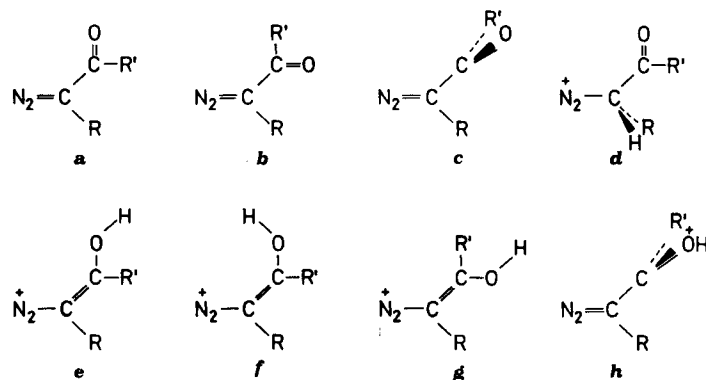


According to *Hammond's* postulate [32] the transition state should closely resemble the reactants in energy, geometry and electron distribution. Hence, perturbations such as deformations, charge transfer and polarization caused by the proximity of the electrophilic reagent, which are not taken into account by the electrostatic potential method, should not be of great consequence, and electrostatic potential maps should result in a reliable measure of reactivity towards protonation. Furthermore, correlations have been reported between protonation energies, calculated as differences between the energies of the protonated and neutral species, and electrostatic potential minima [33].

In the present study we have used an approximate treatment [34] which makes a complete use of the zero-differential-overlap approach in semiempirical methods and greatly reduces the computation time required. Reasonable agreement has been obtained between electrostatic potential maps calculated by this method using CNDO/2 and INDO wave functions and full treatments based on *ab initio* calculations [34]. The calculations covered the volume around the molecule with a grid of 0.5 Å. In the region around the minima a finer grid of 0.1 Å was used<sup>1)</sup>.

<sup>1)</sup> We thank Dr. *Rosa Caballol* at the Instituto Químico de Sarriá, Barcelona, for performing these calculations.

**Results and discussion.** – The following parent compounds were considered: diazoacetaldehyde (I), diazoacetone (II), 3-diazo-2-butanone (III), 1-diazo-2-butanone (IV), 3-diazo-4-methyl-2-pentanone (V) and methyl diazoacetate (VI). For each parent compound, one or more of the following species were studied: *cis* conformation (a), *trans* conformation (b), transition state for rotation around the C(N)–C(O) bond (c), carbon-protonated species (d), *cis* conformation of the *O*-protonated species with an *anti* OH bond (e), *cis* *O*-protonated species with *syn* OH bond (f), *trans* conformation corresponding to e (g), and transition state for rotation around the C(N)–C(O) bond in e (h). These species are illustrated in *Figure 1*.



	I	II	III	IV	V	VI
R :	H	H	Me	H	i-Pr	H
R' :	H	Me	Me	Et	Me	OMe

Fig. 1. Species studied

**Geometrical parameters.** The geometrical parameters calculated<sup>2)</sup> are consistent with the interaction between the carbonyl and the diazo moieties predicted on the basis of the resonance structures depicted in *Figure 2*. Using the CNDO/2 values for the N,N bond distances, the methylene carbon atom in **d** effectively isolates the diazonium and carbonyl groups and the N,N bond distances are clustered around 1.146 Å, close to the bond distance of N<sub>2</sub> (1.140 Å). In **e**, **f** and **g** the triply-charged structures hardly contribute to the hybrid and consequently the N,N-distances lie close to the previous value, 1.149 Å. Whereas crystallographic evidence on (+)-3-diazo-camphor points to a modest contribution of the diazonium enolate form in **a** [35], IR. data on various aliphatic and aromatic diazoketones argue in favour of a substantial one [10]. At any rate, the N,N-bond distance in **a** is predicted to be intermediate between diazoalkanes<sup>3)</sup> and the structures just discussed. The values are in

<sup>2)</sup> Optimal parameters for all the species studied are available upon request.

<sup>3)</sup> For diazomethane for example, the CNDO/2 optimized N,N-distance is 1.191 Å [24]. The contribution of structures  $\bar{\text{C}}\text{H}_2-\text{N}^+\equiv\text{N}$  and  $\text{CH}_2=\bar{\text{N}}=\text{N}^+$  to the hybrid has been estimated as 30% and 70% respectively [36].

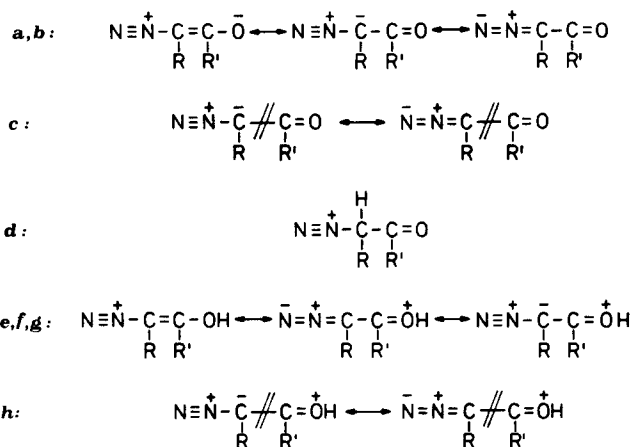


Fig. 2. Principal valence-bond structures for the species studied

fact grouped around 1.171 Å. On the other hand, in **c** the diazo function is isolated from the carbonyl group and shows values similar to diazoalkanes, 1.187 Å. Finally, in **h** the two functions are again conjugatively independent but the positive charge on the oxygen atom renders the structure with the negative end of the diazo dipole closest to it more important: the N,N-distances are now 1.175 Å.

The same analysis can be applied to other bonds in the molecules; it can also be carried out with the MINDO/3 parameters and in terms of bond orders rather than bond lengths. These two quantities have been found to be related for each type of bond at best in a linear fashion or at worst through a monotonic function<sup>4</sup>).

*Isomerism in the unprotonated compounds.* The isomerism in  $\alpha$ -diazocarbonyl compounds is believed to arise from the restricted rotation around the C(N)-C(O) bond caused by delocalization of electrons forming a diazonium enolate. Usually it is the *cis* form that predominates, presumably due to electrostatic interaction between the positively charged diazonium and the negatively charged enolate moieties (see however [12]). NMR. measurements have provided the relative populations of the two isomers in a number of cases [11] [12]. Furthermore, the rate of interconversion of the isomers can be followed by dynamic NMR. techniques and the barriers to rotation around the C,C-bond have been determined in some cases [11] [12].

It has been found previously that the position of a conformational equilibrium around an essentially single bond or/and the rotation barrier associated with it as calculated by CNDO/2 and MINDO/3 methods are in poor agreement with experimental determinations [38] [39]. The discrepancy probably arises partly from a distortion in the relative energies of  $\pi$  and  $\sigma$  orbitals that allows a favourable interaction between the unsaturated groups in the transition state, and partly from an underestimation of conjugation energies. Thus, it is necessary when applying these semiempirical methods to new molecules, to assess their reliability by comparing results with known experimental quantities. In the present case, the CNDO/2 results compare reasonably well with experimental results. The values for rotational barriers

<sup>4</sup>) The definition of *Wiberg* has been used for calculating the bond orders [37].

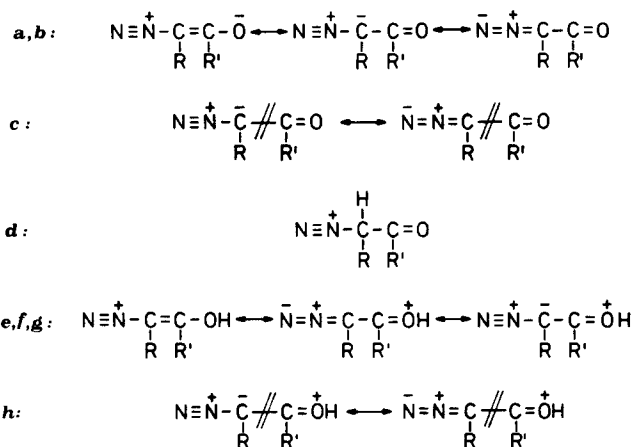


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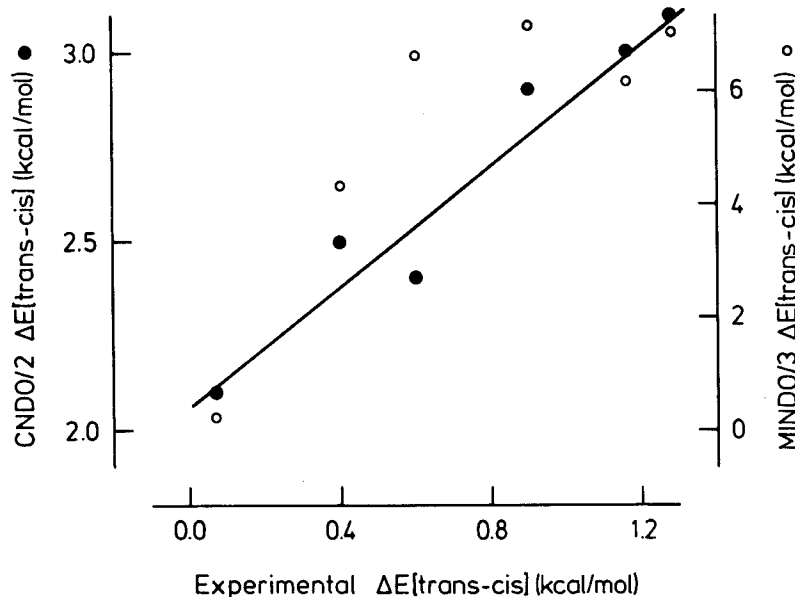


Fig. 3. Correlation of experimental and calculated trans-cis energy differences.

● = CNDO/2, ○ = MINDO/3. The line drawn applies to the CNDO/2 results

are reproducible within 20% (Experimental: 15.4 and 12.8 kcal/mol for II and VI; CNDO/2: 16.9 and 16.0 kcal/mol). The calculated *trans-cis* energy differences, although comparing disfavouredly with experimental data on an absolute basis, provide a linear correlation with it (correlation coefficient = 0.970), amenable for predictive purposes (Fig. 3). The *trans-cis* energy difference calculated for II with the *ab initio* method, 1.09 kcal/mol, agrees well with the experimental result, 1.16 kcal/mol [11] (see however [16]). The MINDO/3 method, on the other hand, fails to provide even a qualitative picture of the experimental trends both in the *cis/trans* energy differences (Fig. 3) and in the rotational barriers (MINDO/3: 8.5 and 3.1 kcal/mol for II and VI).

The available NMR. data [16] left uncertain the assignment of *cis* and *trans* isomers in compounds III and V. Our results indicate that in all cases the *cis* isomer is the more stable. Apparently the increased steric hindrance in II and V is compensated by additional electrostatic interaction between the enolate and diazonium moieties in preference to rotation around the C(N)-C(O) bond.

The electrostatic potential maps show deep minima identifiable with lone pairs on the oxygen atoms and a weakly repulsive zone around the diazo moiety (see Fig. 4) in agreement with its electropositive character. The dominant effect of the interaction between the diazo moiety and the carbonyl oxygen is indicated by the more negative potential shown by the lone pair *syn* to the former (*ca.* -60 kcal/mol) as compared with the one *anti* to it (*ca.* -50 kcal/mol).

*Site of protonation.* The energy differences between neutral species and their conjugate acids are not reliably given by the semiempirical methods because correlation

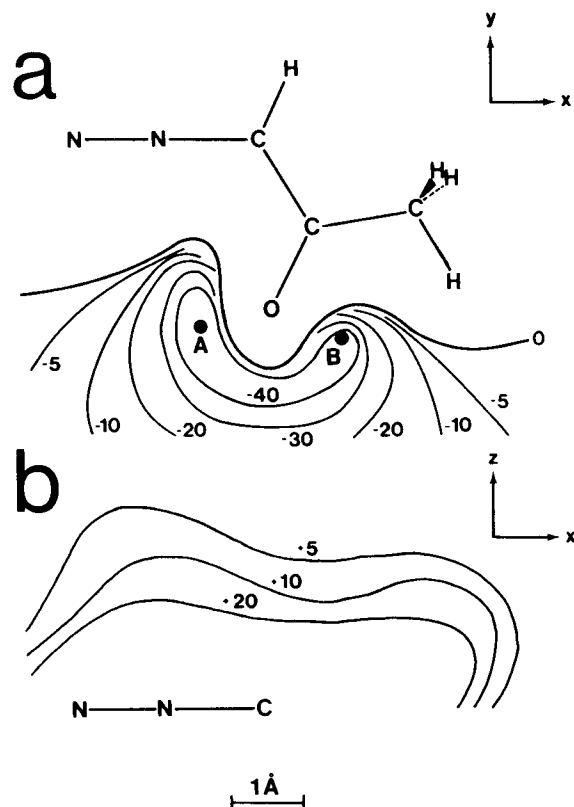


Fig. 4. Electrostatic potential maps for diazoacetone in the plane of the molecule (a) and in a plane perpendicular to the plane of the molecule and containing the  $NNC$  moiety (b). The contour lines are given in kcal/mol. Minima are  $-62.7$  kcal/mol (A) and  $-49.5$  kcal/mol (B)

energies [14] and the energies of inner shells [40] may exhibit substantial variations. However, the comparison between two isomeric conjugate acids has been shown to be trustworthy [24]. The results from the three MO methods employed coincide in showing oxygen-protonation to be the thermodynamically favoured process in the gas phase (see Fig. 5). The presence of a solvent causes stabilization of the ions, in particular those which possess a highly localized charge such as  $H^+$  (see equations 1 and 2). The stabilization of the  $C$ -protonated and  $O$ -protonated ions however is likely to be similar since, as shown above, both ions carry a charge substantially localized at the diazonium moiety and hence the order of stability found for the conjugated acids in the gas phase applies also to solution.

Electrostatic potential maps indicate that  $O$ -protonation is also kinetically favoured in the gas phase. However, the reduction by solvent of the exothermicity of the protonation reactions renders this method inapplicable to solutions. The kinetically preferred  $C$ -protonation found experimentally undoubtedly reflects the preferred solvation of the carbonyl-oxygen atom and hence the hindrance to its protonation due to electrostatic and steric effects.

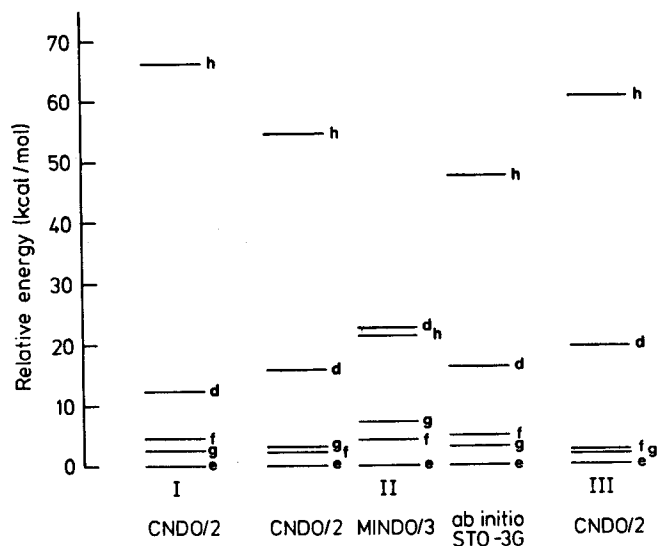


Fig. 5. Relative energies of protonated diazoketones. Figures 1 and 2 contain the definition of symbols

*Isomerism in O-protonated species.* Olah *et al.* have found that in *O*-protonated ketones the OH proton couples with the substituent *cis* to it, in analogy with olefinic systems [41]. On the basis of this assignment and the pattern of coupling in the *O*-protonated diazocarbonyl compounds, Wentrup & Dahn suggested that the stable form of the latter compounds were those which possessed a *syn* OH bond (I–VI f) [16].

On the other hand, other workers have found that long range coupling between H atoms is optimized when the skeleton between them adopts a W shape [42]. On this basis and the observed coupling pattern in *O*-protonated diazoketones, Levisalles *et al.* concluded that the stable form is the one with an *anti* OH bond (I–VI e) [17].

The results from semiempirical calculations, confirmed by *ab initio* calculations, point to the species with an *anti* OH bond as the most stable one. Furthermore, we have obtained reasonably linear correlations between <sup>1</sup>H-NMR. chemical shifts and charge on the H atoms [43], calculated both by CND0/2 and MIND0/3. The charges calculated for species e fit better into the linear plots than those for species f. However, the differences are not large enough to warrant a firm conclusion on this basis alone.

As discussed earlier, the *O*-protonated species has a predominant enolic character. This extensive conjugation is completely lost in the transition state for rotation around the C(N)–C(O) bond. The barriers for rotation in the *O*-protonated species calculated both by the CND0/2 and *ab initio* methods are of the order of 4 times the barriers for the unprotonated species. Judging from the ability of the CND0/2 method to reproduce the experimental barriers of rotation for the unprotonated species (see above), one can deduce that no rotation takes place in the *O*-protonated species at the temperature the experiments are performed (around 210 K). Since protonation of the parent compound is much faster than rotation around the C(N)–C(O) bond, it is expected that when *O*-protonation of a  $\alpha$ -diazocarbonyl compound occurs, the ratio of *cis* to *trans* *O*-protonated isomers will be a direct reflection of the ratio



shown by the parent compound. This is indeed the experimental result: in all cases measured, the *cis/trans* ratio was found to be identical in *O*-protonated and unprotonated compounds [16].

From the data presented above the following mechanism can describe *O*-protonation: in the *cis* diazocarbonyl compound, protonation occurs initially at the lone pair close to the diazo group. As the OH bond is formed and charge transfer and polarization effects come into play, a repulsive interaction arises between the OH and the diazo group. The weakening of the C-O-bond now permits free rotation exposing the other lone pair to the favourable attraction of the diazo moiety. The *cis* relationship between carbonyl and diazo functions is maintained throughout the reaction.

**Conclusions.** – Three MO methods have been employed in this work, of which only CNDO/2 and *ab initio* with STO-3G basis set give a reasonable account of the experimental trends and may thus be used in the prediction of unknown properties. CNDO/2 results have been used to clarify questions concerning the structure, *cis/trans* isomerism and mechanism of formation of *O*-protonated  $\alpha$ -diazocarbonyl compounds.

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#### REFERENCES

- [1] C. Pecile, A. Foffani & S. Ghersetti, *Tetrahedron* 20, 823 (1964).
- [2] S. Sorriso & A. Foffani, *J. chem. Soc. Perkin II* 1973, 2142.
- [3] A. B. Remizov, R. D. Gareev & A. N. Pudovik, *Ž. Obšč. Chim.* 43, 1381 (1973).
- [4] R. Bassani, F. DiFuria & R. Curci, *Spectroscopy Letters* 7, 531 (1974).
- [5] C. Pecile, A. Foffani & S. Ghersetti, *Tetrahedron* 11, 285 (1960).
- [6] L. L. Leveson & C. W. Thomas, *Tetrahedron* 22, 209 (1966).
- [7] E. Fahr, *Chem. Ber.* 92, 398 (1959).
- [8] G. Piazza, S. Sorriso & A. Foffani, *Tetrahedron* 24, 4751 (1968).
- [9] S. Sorriso, F. Stefani, A. Flamini & E. Semprini, *J. chem. Soc. Faraday I* 71, 682 (1975).
- [10] S. Sorriso, G. Piazza & A. Foffani, *J. chem. Soc. B* 1971, 805.
- [11] F. Kaplan & G. K. Maloy, *Tetrahedron Letters* 1964, 2427; F. Kaplan & G. K. Maloy, *J. Amer. chem. Soc.* 88, 950 (1966).
- [12] R. Curci, F. DiFuria & V. Lucchini, *Spectroscopy Letters* 7, 211 (1974).
- [13] J. G. Csizmadia, S. A. Houlden, O. Merez & P. Yates, *Tetrahedron* 25, 2121 (1969).
- [14] J. A. Pople & D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York 1970.
- [15] R. Curci, F. DiFuria, J. Ciabattini & P. W. Concannon, *J. org. Chemistry* 39, 3295 (1974).
- [16] C. Wentrup & H. Dahn, *Helv.* 53, 1637 (1970).
- [17] M. Allard, J. Levisalles & J. M. Sommer, *Chem. Commun.* 1969, 1515.
- [18] R. A. More O'Ferral, *Adv. phys. org. Chemistry* 5, 331 (1967); J. D. Roberts, C. M. Regan & I. Allen, *J. Amer. chem. Soc.* 74, 3679 (1952); W. J. Albery & R. P. Bell, *Trans. Farad. Soc.* 57, 1942 (1961); H. Dahn & H. Gold, *Helv.* 46, 983 (1963).
- [19] H. Dahn, H. Gold, M. Ballenegger, J. Lenoir, G. Diderich & R. Malherbe, *Helv.* 51, 2065 (1968); H. Dahn & M. Ballenegger, *ibid.* 52, 2417 (1969); W. J. Albery, A. N. Campbell-Crawford & J. S. Curran, *J. chem. Soc. Perkin II* 1972, 2206 and preceding papers in the series.
- [20] 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); P. A. Dobosh, CNINDO, QCPE Program No 141.

- [21] 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.
- [22] L. B. Kier, 'Molecular Orbital Studies in Chemical Pharmacology', Symposium held at Battelle Seattle Research Center, Oct. 20–22, 1969, Springer-Verlag, Berlin 1970.
- [23] H. M. Niemeyer & P. Ahlberg, *Chem. Commun.* **1974**, 799; H. M. Niemeyer, O. Goscinski & P. Ahlberg, *Tetrahedron* **31**, 1699 (1975).
- [24] H. M. Niemeyer, *Helv.* **59**, 1133 (1976).
- [25] H. M. Niemeyer, *Tetrahedron* **33**, 775 (1977).
- [26] D. Rinaldi, GEOMO, QCPE program No. 290; K. F. Purcell & J. Zapata, GEOMIN, QCPE program No. 312.
- [27] W. C. Davidon, *Comput. J.* **10**, 406 (1968); R. Fletcher, *ibid.* **8**, 33 (1965); R. Fletcher & M. J. D. Powell, *ibid.* **6**, 163 (1963).
- [28] 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.
- [29] J. A. Pople, *Accounts chem. Research* **3**, 217 (1970); W. J. Hehre, R. Ditchfield, L. Radom & J. A. Pople, *J. Amer. chem. Soc.* **92**, 4796 (1970); L. Radom & J. A. Pople, *ibid.* **93**, 289 (1971).
- [30] G. Leroy & M. Sana, *Theoret. chim. Acta* **33**, 329 (1974).
- [31] R. Bonnacorsi, 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).
- [33] C. Ghio & J. Tomasi, *Theoret. chim. Acta* **30**, 151 (1973).
- [34] R. Caballol, R. Gallifa, M. Martín & R. Carbó, *Chem. Physics Letters* **25**, 89 (1974); R. Carbó & M. Martín, *Int. J. Quantum Chemistry* **9**, 193 (1975).
- [35] A. F. Cameron, N. J. Hair & D. G. Morris, *J. chem. Soc. Perkin II* **1972**, 1331.
- [36] C. B. Moore & G. C. Pimentel, *J. chem. Physics* **40**, 1529 (1964).
- [37] K. B. Wiberg, *Tetrahedron* **24**, 1083 (1968).
- [38] A. S. N. Murphy & C. N. R. Rao, *J. Mol. Structure* **6**, 253 (1970); G. Robinet, J.-F. Labarre & C. Leibovici, *Chem. Physics Letters* **22**, 356 (1973); C. Giessner-Prettre & A. Pullman, *Theoret. chim. Acta* **25**, 83 (1972).
- [39] E. I. Snyder, *J. Amer. chem. Soc.* **92**, 7529 (1970); O. Gropen & H. M. Seip, *Chem. Physics Letters* **11**, 445 (1971); D. Perahia & A. Pullman, *ibid.* **19**, 73 (1973); Å. Støgard, *Theoret. chim. Acta* **33**, 339 (1974).
- [40] A. C. Hopkinson & I. G. Csizmadia, *Theoret. chim. Acta* **34**, 93 (1974).
- [41] G. A. Olah, M. Calin & D. A. O'Brien, *J. Amer. chem. Soc.* **89**, 3586 (1967).
- [42] J. Meinwald & A. Lewis, *ibid.* **83**, 2769 (1961); K. B. Wiberg, B. R. Lowry & B. J. Nist, *ibid.* **84**, 1594 (1962); A. Rassat, C. W. Jefford, J. M. Lehn & B. Waegell, *Tetrahedron Letters* **1964**, 233.
- [43] D. G. Farnum, *Adv. phys. org. Chemistry* **11**, 123 (1975).